Ligand-Based Reactions of Metal Bis- and Trisdithiolenes: Fresh Insights into Old Reactions and New Frontiers

by

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Metal dithiolenes \([\text{M}(\text{S}_2\text{C}_2\text{R}_2)_n]\) have been studied for decades because of their interesting chemical and spectroscopic properties, which are related to the unusual electronic properties of the dithiolen ligand. The ligand-based reactivity of metal bisdithiolenes \([\text{M}(\text{S}_2\text{C}_2\text{R}_2)_2]\) toward alkenes has been proposed for use in alkene purification schemes. According to the proposal, compounds \(\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2\) \((\text{R} = \text{CF}_3, \text{CN})\) react with simple alkenes to form stable S,S-interligand adducts and the alkene can be released from the adduct by reduction. We showed that \(\text{Ni}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2\) reacts with ethylene and 1-hexene to form, preferentially, S,S-intra-ligand adducts, which rapidly decompose to inactive metal-containing materials and dihydrodithiins. However, the product selectivity can be significantly modified so that stable S,S-interligand adducts are obtained as dominant products by adding \([\text{Ni}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2]^-\) to \(\text{Ni}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2/\text{alkene reaction mixtures}\). Mechanistic implications are discussed.
Next, the reactions of Pt(S$_2$C$_2$(CF$_3$)$_2$)$_2$ with 2,3-dimethyl-1,3-butadiene are addressed. Prior to our report, only symmetry-allowed S,S-interligand adducts had been observed as products in the reactions between conjugated dienes and metal bisdithiolenes. We discovered a novel mode of diene binding, where two dienes bind to one dithiolene ligand of Pt(S$_2$C$_2$(CF$_3$)$_2$)$_2$, in an C,S-\textit{intraligand} fashion, forming a new chiral bithioether ligand.

From bisdithiolenes, the focus shifts to new mixed-ligand molybdenum \textit{tris}dithiolenes [Mo(S$_2$C$_2$(CF$_3$)$_2$)$_2$(S$_2$C$_6$H$_4$) and Mo(S$_2$C$_6$H$_4$)$_2$(S$_2$C$_2$(CF$_3$)$_2$)]. These complexes rapidly and cleanly bind ethylene, in an S,S-\textit{intraligand} fashion, as predicted by MO arguments. The resulting intraligand adducts are sufficiently stable to be characterized, in contrast to the nickel bisdithiolene case. The metal-chelated dihydrobenzodithiin, formed upon ethylene addition, can be substituted with a variety of donor ligands, allowing access to new types of molybdenum dithiolenes. We have recently extended these studies to catalytic reactions: Mo(S$_2$C$_2$(CF$_3$)$_2$)$_2$(S$_2$C$_6$H$_4$) was used as a catalyst to form dihydrobenzodithiins from (S$_2$C$_6$H$_4$)$_2$ and a variety of alkenes, in the first example of dithiolene-based reactivity being exploited for carbon-heteroatom bond-forming catalysis.

Finally, the synthesis, characterization and redox reactivity of a new Fe$_2$Ni bis-double-decker complex is described, demonstrating for the first time a sandwich complex of a metal bisdithiolene with both NiS$_2$C$_2$ rings in an $\eta^5$ $\pi$-donating mode. For the radical cation, experimental and computation evidence indicates that the lone electron is delocalized over the entire molecule.
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<th>Full Form</th>
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<tr>
<td>Å</td>
<td>Angstroms</td>
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<td>Abs.</td>
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<td>AO</td>
<td>Atomic Orbital</td>
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<tr>
<td>atm</td>
<td>atmosphere</td>
</tr>
<tr>
<td>a.u.</td>
<td>atomic units</td>
</tr>
<tr>
<td>B.M.</td>
<td>Bohr Magneton, J⋅T⁻¹</td>
</tr>
<tr>
<td>BHT</td>
<td>2,6-di-tert-butyl-4-methylphenol</td>
</tr>
<tr>
<td>BTBB</td>
<td>3,5-Bis(Trifluoromethyl)BromoBenzene</td>
</tr>
<tr>
<td>BPTS</td>
<td>Bis-ο-Phenylene TetraSulfide [(S₂C₆H₄)₂]</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl (C₄H₉)</td>
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<tr>
<td>C</td>
<td>Celsius</td>
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<tr>
<td>ca.</td>
<td>Latin: circa (Translated: approximately)</td>
</tr>
<tr>
<td>cf.</td>
<td>Latin: confer (Translated: compare with)</td>
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<td>Cp</td>
<td>cyclopentadienyl (η⁵-C₅H₅)</td>
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<tr>
<td>Cp*</td>
<td>pentamethylcyclopentadienyl (η⁵-C₅(CH₃)₅)</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift</td>
</tr>
<tr>
<td>°</td>
<td>degrees (angular and temperature)</td>
</tr>
<tr>
<td>d</td>
<td>Doublet (NMR) or day (temporal)</td>
</tr>
<tr>
<td>DFT (TDDFT)</td>
<td>Density Functional Theory (Time-Dependent DFT)</td>
</tr>
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<td>DHD</td>
<td>DiHydroDithiin</td>
</tr>
<tr>
<td>DHBD</td>
<td>DiHydroBenzoDithiin</td>
</tr>
<tr>
<td>e.g.</td>
<td>Latin: exempli gratia (Translated: For example)</td>
</tr>
<tr>
<td>EI</td>
<td>Electron-Impact</td>
</tr>
<tr>
<td>equiv</td>
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<tr>
<td>Et</td>
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<tr>
<td>Etc.</td>
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<td>-------------</td>
</tr>
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<td>Hz (MHz)</td>
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<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<tr>
<td>i.e.</td>
<td>Latin: <em>Id est</em> (Translated: That is)</td>
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<td>InterValence Charge Transfer</td>
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<tr>
<td>J</td>
<td>coupling constant</td>
</tr>
<tr>
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</tr>
<tr>
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<td>Lowest Unoccupied Molecular Orbital</td>
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<tr>
<td>M</td>
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<tr>
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<tr>
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<td>Near-InfraRed</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<td>NOESY</td>
<td>Nuclear Overhauser Effect Spectroscopy</td>
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<tr>
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<td>overlapping</td>
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<td>o</td>
<td>ortho</td>
</tr>
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<td>pi</td>
</tr>
<tr>
<td>Ph</td>
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</tr>
<tr>
<td>ppm</td>
<td>Parts per Million</td>
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<td>quartet</td>
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<td>s</td>
<td>singlet</td>
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<tr>
<td>t</td>
<td>triplet</td>
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<td>Abbreviation</td>
<td>Definition</td>
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<td>----------------------------</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TOF</td>
<td>Time Of Flight or TurnOver Frequency</td>
</tr>
<tr>
<td>TP</td>
<td>Trigonal Prismatic</td>
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<td>UV-vis</td>
<td>UltraViolet-Visible</td>
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<td>wt.</td>
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Chapter 1

Introduction

1.1 Metal dithiolenes, dithiolene ligands and noninnocence

Metal dithiolenes (M(S₂C₂R₂)ₙ) have been studied for decades, with research focusing on, for example, their fascinating structural and spectroscopic properties, their redox and chemical reactivity, and their important roles in metalloenzymes. Dithiolene ligands (S₂C₂R₂; S,S-bidentate) can be reasonably formulated in 1,2-ene-dithiolate, radical anionic or dithioketone (isoelectronic with 1,2-dithiete) forms (Scheme 1.1), depending on their environment. In many dithiolene-transition metal complexes, the oxidation state of the metal cannot be confidently assigned because the charge state of the ligand is unclear. In such cases, the dithiolene groups are called “noninnocent”. A ligand is noninnocent if its charge state is ambiguous when it is coordinated to metal. Noninnocent (redox-active) ligands often have extended π systems and available π* orbitals, which can interact with metal-based orbitals of appropriate symmetry and energy, leading to delocalized frontier orbitals with substantial ligand character, as often encountered in dithiolene complexes.

Scheme 1.1

1.2 Bonding and structure in homoleptic metal dithiolenes

Many of the attractive properties associated with metal dithiolenes, such as their intense colors and remarkable ligand-based reactivity, are related to the noninnocence of the ligand(s) and the associated π-electronic delocalization. The following sections provide an introduction to structure and bonding in homoleptic metal bis- and trisdithiolenes, from
molecular orbital and valence bond theoretical standpoints, as these concepts will be useful for understanding the reactivity described in later chapters.

1.2.1 Metal bisdithiolenes

The first synthetic dithiolene complexes, made in the 1960s, were the bisdithiolenes of group 10 (Ni, Pd, Pt) metals (e.g., \([\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2]^n\); \(\text{R} = \text{Ph, CN}; n = 0, 1, 2\)),\(^{1a,16}\) which exhibit square planar geometries in all accessible charge states. The molecular orbitals (MOs) of metal bisdithiolenes have been calculated at different levels of theory, ranging from extended Hückel methods\(^7\) to density functional theory (DFT, correlated with sulfur K-edge spectroscopy).\(^8\) To illustrate the results of an early MO calculation, Figure 1.1 depicts the qualitative Hückel derivation of the MOs for a simple nickel bisdithiolene. This MO diagram reveals that a number of electronic transitions are possible for neutral bisdithiolenes, with the most intense transitions having primarily \(\pi \rightarrow \pi^*\) (e.g., \(2b_{1u} \rightarrow 3b_{2g}\), Figure 1.1) character,\(^{1c,7}\) as expected for strongly colored, highly conjugated molecules. From the various computational efforts, a consistent picture for the frontier orbitals of metal bisdithiolenes has emerged: For neutral group 10 bisdithiolenes (\(\text{M}(\text{S}_2\text{C}_2\text{R}_2)_2\)), calculated in \(D_{2h}\) symmetry, the highest occupied molecular orbital (HOMO, \(b_{1u}\)) and lowest unoccupied molecular orbital (LUMO, \(b_{2g}\)) are delocalized over the entire molecule and have primarily ligand-based character (>50% S character),\(^8\) with only small metal-based atomic orbital (AO) contributions (4p\(_z\) for HOMO, 3d\(_{xz}\) for LUMO) (Figure 1.1, inset). The symmetry properties of these orbitals, particularly the LUMO, will be important in the following discussions on ligand-based reactivity. Note that the LUMO has large coefficients (3p character) on the sulfur centers, which are in-phase across intraligand sulfur atoms, but out-of-phase for sulfur atoms on separate dithiolene ligands.
Figure 1.1 MO diagram for Ni(S₂C₂H₂)₂, adapted from reference 7b. Nonbonding ligand-based electrons are omitted. The inset at the lower right shows the frontier orbitals and the coordinate axis labelling system.
Valence bond theory is also useful for understanding some of the properties of metal dithiolenes.\textsuperscript{7b} Several resonance structures for neutral group 10 bisdithiolenes are shown in Figure 1.2. While structures with d\textsuperscript{10}/M(0) and d\textsuperscript{6}/M(IV) electronic configurations can be envisioned, spectroscopic and computational\textsuperscript{7,8} evidence indicates that the best resonance contributors (B and C in Figure 1.2) have d\textsuperscript{8}/M(II) configurations at the metal, as expected for square planar molecules. Thus, the ligands in neutral bisdithiolenes have significant thioketone (electronically unsaturated) character, as seen from structures B and C (Figure 1.2). Structure B, with one 1,2-ene-dithiolate and one 1,2-dithioketone ligand, is certainly an important resonance contributor, as will be seen in the reactivity studies presented below. Structures of type C, with antiferromagnetically coupled radicals, might also be important, either as ground-states or as low-lying excited states.\textsuperscript{8}

![Figure 1.2](image)

**Figure 1.2** Selected resonance structures for homoleptic neutral group 10 metal bisdithiolenes.

### 1.2.2 Metal trisdithiolenes

Metal trisdithiolenes (M(S\textsubscript{2}C\textsubscript{2}R\textsubscript{2})\textsubscript{3}) are fewer in number and have been studied in less detail than bisdithiolenes. Nonetheless, dozens of trisdithiolene complexes – most based on Mo, W or V – have been synthesized in a variety of charge states and many of these have been crystallographically characterized. Coordination geometries for trisdithiolenes range from trigonal-prismatic (TP) to octahedral, depending on the central metal and on the charge state of the complex.\textsuperscript{1b} The factors that affect the stability of TP versus octahedral geometries have been discussed in the literature.\textsuperscript{1b,9} For the simple case where the ligands are purely σ-donors, going from octahedral to TP geometry results in net stabilization of the t\textsubscript{1u} orbitals,
which transform as $e'$ and $a_2''$ in a TP ligand field. However, the $t_{2g}$ orbitals ($a_1'$ and $e'$ in a trigonal prismatic structure) are partially destabilized in TP geometry (Figure 1.3).\textsuperscript{1b,c,9} TP distortion is therefore generally unfavourable for low valent metal ions (with $d^n$, $n>2$), because the stabilization of the $t_{1u}$ orbitals is offset by the destabilization experienced by the electrons in the $t_{2g}$ orbitals. Furthermore, ligand-ligand repulsion is increased in TP geometry, relative to an octahedral structure. On the other hand, TP structures maximize ligand-metal and ligand-ligand $\pi$ bonding interactions,\textsuperscript{1c} which are clearly important for $\pi$-conjugated dithiolene ligands. For reduced (electron-rich) metal trisdithiolenes ($d^n$, $n>1$; e.g., $\text{[Mo}^{IV}(S_2C_2(CF_3)_2)_3]^2-$), with negative charge concentrated on the ligands and on the metal, orbital (electronic) and steric (ligand-ligand repulsion) effects favour structures with significant octahedral character; in their fully oxidized analogues ($d^n$, $n\leq 1$; e.g., $\text{Mo}(S_2C_2(CF_3)_2)_3$, formally $d^0$), with low $d$ electron counts and ligand $\pi^*$ orbitals available for bonding to the metal, TP geometries (or slight distortions thereof) are often observed.\textsuperscript{1b,10}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{orbital_changes.png}
\caption{MO correlation diagram showing the orbital changes in going from octahedral to TP geometry (adapted from ref. 9). This diagram considers only $\sigma$ interactions between the metal and ligands.}
\end{figure}
The MO situation for metal trisdithiolenes is complex relative to bisdithiolenes, owing to their increased structural complexity, but theoretical studies have nevertheless been fruitful for understanding their electronic structure. Different computational approaches have yielded slightly different results but, as with bisdithiolenes, a coherent picture has emerged. For example, extended Hückel\(^\text{11}\) and Fenske-Hall\(^\text{12}\) calculations (in \(D_{3h}\) symmetry) agree on the general ordering of the MOs and both methods predict the HOMO (\(a_2^\prime\), ligand \(\pi\) character\(^\text{13}\), \(L_{\pi}\) and LUMO (\(a_1^\prime\), metal \(d_{z^2}\) character\(^\text{13}\)) (Figure 1.4) to be close in energy. It will be shown in Chapter 4 that these orbitals can mix, by bending along the \(S---S\) intraligand axes, to form frontier orbitals with a mixture of \(L_{\pi}\) and \(d_{z^2}\) character. Note that the HOMO has nodal properties similar to the LUMO for bisdithiolenes (Figure 1, section 1.2.1).

![Figure 1.4](image)

**Figure 1.4** Frontier orbitals for Mo(\(S_2C_2H_2\))\(_3\) in \(D_{3h}\) symmetry. The ‘\(z\)’ axis coincides with the 3-fold rotational axis.

As for bisdithiolenes, valence bond analyses complement the insight provided by MO considerations. A large number of resonance structures can be envisioned when dealing with trisdithiolenes and several examples are shown in Figure 1.5, for neutral trisdithiolenes of group 6 (e.g., molybdenum) metals. Similar to the bisdithiolene situation, the limiting resonance contributors have either M(0) with three fully oxidized ligands (1,2-dithioketones), or M(VI) with all ligands fully reduced (1,2-ene-dithiolates). Computational and spectroscopic data\(^\text{11}\) once again rule out these extreme structures. The most valid contributors are intermediate between the two extremes, with metal oxidation states of (IV) or, possibly, (V) (B, C, Figure 1.5). Structures with M(V) must be diradicals\(^\text{13}\) (for neutral
group 6 trisdithiolenes) and, if these contributors are significant, the radicals must be antiferromagnetically coupled to explain the diamagnetic ground state. Our reactivity studies, discussed below, will show that structures of type B (Figure 1.5) are particularly important contributors for neutral trisdithiolenes of molybdenum.

![Figure 1.5](image)

**Figure 1.5** Selected resonance structures for homoleptic neutral group 6 metal trisdithiolenes.

### 1.3 Synthesis of metal dithiolenes

Methods for making dithiolenes are numerous and diverse and have been described in the literature. A few examples will be discussed here to illustrate the general approaches to dithiolene syntheses, especially those relevant to the following chapters.

#### 1.3.1 Metal dithiolenes from 1,2-ene-dithiolates and 1,2-ene-dithiols

Perhaps the most straightforward metal dithiolene syntheses start from the 1,2-ene-dithiolate (fully-reduced) form of the dithiolene ligand, when it is available as a simple salt (e.g., Na₂S₂(C₆H₄), Na₂S₂C₂(CN)₂, Equation 1.1). Simple salt metathesis reactions between the 1,2-ene-dithiolate and labile metal salts afford reduced dithiolene complexes (e.g., Equation 1.1). Reduced (dianionic) metal dithiolenes can be oxidized to monoanionic or neutral
analogues, by chemical oxidants or electrochemically, and, expectedly, the oxidation potentials are strongly dependent on the electronic nature of the dithiolene substituents (i.e., R group in R₂C₂S₂) (see section 1.4.3.1, below).¹
dithiolenes with the S₂(C₆H₄) ligand can also be made by condensation of commercially available 1,2-benzenedthiol [1,2-(HS)₂(C₆H₄)] with reactive metal oxo groups; the expulsion of water and the formation of a stable metal-dithiolene motif provide the driving force for these reactions (Equation 1.2).¹⁵

1.3.2 Metal dithiolenes from α-hydroxyketones or α-diketones (with P₂S₅)

A powerful route to metal dithiolenes with simple alkyl or aryl substituents involves converting α-hydroxyketones or α-diketones to an intermediate species, thought to be a thiophosphate ester, with P₄S₁₀. Hydrolysis of the thiophosphate ester in the presence of a metal ion affords a dithiolene complex (e.g., Equation 1.3).¹ᵃ,¹⁶ This approach is attractive because many α-hydroxyketones and α-diketones are commercially available.
1.3.3 Metal dithiolenes from 1,2-dithiethes or their equivalent

A rather specialized but useful route to metal dithiolenes utilizes oxidized forms of dithiolene ligands (i.e., 1,2-dithiethes, see Scheme 1.1). This method clearly requires that the 1,2-dithiete of the dithiolene ligand can be generated in free (or oligomeric, see below) form. Unfortunately, 1,2-dithiethes are generally very reactive, limiting the method to rare cases where the 1,2-dithiete is sufficiently stable to be isolated, or at least generated in situ. Among the few 1,2-dithiethes to be isolated is S₂C₂(CF₃)₂,¹⁷ which reacts as an oxidant with low-valent metals to form highly oxidizing dithiolene complexes with the electron-withdrawing S₂C₂(CF₃)₂ ligand (e.g., Equation 1.4).¹⁸

We have recently shown that the dithiete approach might also be useful for introducing the S₂C₆H₄ ligands to metals, as an alternative to using the dithiol or dithiolate (see section 1.3.1, above). While 1,2-benzodithiete (S₂C₆H₄) is not stable as a free monomer, oxidation of 1,2-benzenedithiol [1,2-(HS)₂(C₆H₄)] with iodine yields, along with intractable polymeric material, bis-ω-phenylene tetrasulfide (BPTS),¹⁹ the dimer of 1,2-benzodithiete. We found that BPTS reacts with a labile molybdenum bisdithiolene, ((F₃C)₂C₂S₂)₂Mo(2,3-dihydro-1,4-benzodithiin), to form the mixed-ligand trisdithiolene Mo(S₂C₂(CF₃)₂)₂(S₂C₆H₄) (Equation 1.5).²⁰ To our knowledge, this is the first example of BPTS being used for the preparation of a metal dithiolene.
1.4 Metal dithiolenes: Applications and reactions

While much of the early work on dithiolenes was motivated by the desire to understand fundamental bonding, structural/spectral relationships and reactivity in metal coordination compounds, the field is now driven, in large part, by the desire to harness the remarkable chemical and physical properties of dithiolenes for industrial/materials applications.

1.4.1 Dithiolenes in biology/implications for dithiolene catalysis

Nature unquestionably deserves credit for the first syntheses and applications of dithiolene ligands/complexes, considering that dithiolene-containing enzymes found in ancient archaea probably predate humans by billions of years.\(^{21,22}\) Interestingly, however, the discovery of dithiolene ligands in biological systems, in late 1980s/early 1990s, came long after the first synthetic dithiolene complexes were reported in the early 1960s. It has since been determined that nearly all Mo- and W-based enzymes incorporate one or two pterin groups, a complex dithiolene ligand (shown in its dithiolate form in Figure 1.6, center).\(^{1,21}\) These enzymes are found in many types of organisms (from mammals to fungi) and they catalyze a number of biological reactions, most of which involve oxygen-atom-transfer.\(^{1,1,21}\) For example, DMSO reductase (DMSOR), having dithiolene (pterin), alkoxide and oxo ligands, catalyzes the reversible reduction of dimethylsulfoxide (DMSO) to dimethylsulfide (Figure 1.6, oxidized form of DMSOR is shown), in a process that is important for the biological cycling of sulfur.\(^{1,23}\)
The discovery of dithiolene ligands in Nature has led to very productive biomimetic investigations,\textsuperscript{1,21} which have enhanced our understanding of dithiolene chemistry and the coordination chemistry of Mo and W. Considerable progress has been made in modeling structural aspects of dithiolene-containing oxygen-atom-transfer enzymes, but developing fully \textit{functional} synthetic models remains a challenge for biomimetic chemists. To date, natural enzymes, based on Mo- or W-pterin oxo cores, represent the state-of-the-art in dithiolene catalysis, and synthetic metal dithiolenes are implicated in surprisingly few catalytic cycles (a new example of dithiolene catalysis will be presented in Chapter 5). It is hoped that increasing knowledge of dithiolene-containing enzymes, coupled with biomimetic studies, will lead to new synthetic catalysts based on dithiolene ligands.

\textbf{1.4.2 Dithiolenes in materials science}

Dithiolenes are of interest as components in solid state devices, because of their intriguing electrical, magnetic and optical properties.\textsuperscript{1h} Bis(dithiolenes in partially reduced form are especially attractive candidates for conducting/superconducting applications due to their delocalized MOs (see section 1.2.1, above), associated redox reactivity, planar structures, and their tendency to stack in 1D arrays in the solid state.\textsuperscript{24} These traits enable significant intermolecular electronic interactions in the solid lattice, a prerequisite for molecular conductivity. A number of metal bis(dithiolenes with the S=CS\textsubscript{2}C\textsubscript{2}S\textsubscript{2} ligand (called ‘dmit’ in the literature,\textsuperscript{25} see Figure 1.7) exhibit metal-like conducting properties as a variety of salts

\textbf{Figure 1.6} Left: oxidized form of DMSOR catalytic site. Center: one representative form of the pterin ligand (congeners vary at the phosphate group). Right: reaction catalyzed by DMSOR.
in solid form. To obtain metallic-type conduction, a partially filled conduction band (i.e., LUMO in Figure 1, section 1.2.1) for the stacked molecules is needed, which can be accomplished, for example, by partial oxidation of monoanionic dithiolene salts to non-integer charge states (e.g., \([\text{Ni(dithiolene)}_2]^n\); \(n = 0.5\), as in Figure 1.7).\(^1\) In rare cases, related complexes with the dmit ligand, but with different metals and cations, are superconducting at low temperatures (\(T_c < 10\) K) in the solid state.\(^1\)

![Figure 1.7](image)

**Figure 1.7** Structure of the monomeric unit of a conducting (in solid state) nickel bisdithiolene salt with the ‘dmit’ \((S=CS_2C_2S_2)\) ligand.

Metal dithiolenes have also been considered as molecular magnetic materials. Although the unpaired electrons in radical dithiolene complexes (e.g., \([\text{Ni(dithiolene)}_2]\)) usually couple antiferromagnetically in the solid state,\(^1\) a small number of dithiolene-containing bulk ferromagnets have been identified. For example, microcrystalline samples of \((\text{NH}_4)[\text{Ni}(S_2C_2(CN)_2)_2]\cdot\text{H}_2\text{O}\)\(^2\) and \((\text{Cp}*\text{Mn})[\text{Ni}(S_2C_2S_2C=S)_2]\)\(^2\) behave as ferromagnets at very low temperatures (long-range ferromagnetic order observed below 5 K), and several more dithiolene-containing molecules exhibit short-range ferromagnetic behaviour. The prevalence of the \(S_2C_2S_2C=S\) ligand in materials applications – both electronic and magnetic – is related to its extended \(\pi\) system and its ability to facilitate intermolecular interactions in the solid state.\(^1\)

The optical properties of dithiolene complexes have been investigated in academic labs and have been exploited commercially. For instance, the ability of dithiolene complexes to strongly absorb near-infrared radiation\(^1\) makes them appealing for Q-switch laser dyes (for producing short, intense laser pulses).\(^1\)\(^2\) Additionally, dithiolenes have been examined as nonlinear optical (NLO) materials; some dithiolene-containing compounds, especially those with \(\text{Ni(dithiolene)(diimine)}\) motifs, show second-order NLO behaviour.\(^2\) Modest third-
order NLO effects have been observed for certain mono- or bisdithiolene complexes, but a better understanding of structure/function relationships is needed to maximize the potential of this field.

The IR-absorbing properties of metal dithiolenes have been exploited for commercial gain. Dithiolene complexes are used, for example, to prevent laser-induced fading of optical data storage media (e.g., compact discs) and the antioxidant properties of reduced dithiolenes are used to protect cyanine dyes in the recording layer.

1.4.3 Ligand-based reactions of dithiolenes and potential applications

As discussed above (sections 1.2.1 and 1.2.2), metal dithiolene complexes often have delocalized frontier orbitals with considerable ligand character, formed by mixing of metal d and ligand \( \pi^* \) orbitals (e.g., Figure 1). In contrast to standard metal reactivity, where substrates interact directly with the metal center, reactions of dithiolene complexes frequently occur at the dithiolene ligand(s), without the direct participation of the metal. The simplest examples of dithiolene ligand-based reactivity are their electron-transfer (redox) reactions, which involve orbitals with mainly ligand character. Metal dithiolenes can also react with electrophilic or nucleophilic substrates, depending on the electronic properties (e.g., charge state) of the complex, leading to the formation of covalent bond(s) between the substrate and the dithiolene ligand (usually the ligand S-atoms). General concepts, with examples from the literature, are included in the following sections to introduce the ligand reactivity described in forthcoming chapters.

1.4.3.1 Ligand-based reactions: dithiolene redox chemistry

The redox reactivity of metal dithiolenes has been studied in great detail. Rich redox chemistry is expected on the basis of their electronic delocalization (sections 1.2.1 and 1.2.2, above) and, indeed, dithiolene complexes are usually stable in multiple charge states. Neutral metal bisdithiolenes of group 10 metals, for example, generally undergo two reversible one-electron reductions at potentials that strongly depend on the dithiolene
substituents and, to a lesser extent, on the metal. Scheme 1.2 illustrates these reactions, with redox potentials (relative to Ag/AgCl)\(^{1e}\) for representative cases; the inset shows selected resonance forms of the mono-reduced radical anion. Carbon-based radical contributors are emphasized, but some thyl (S-) radical character is also possible.

![Scheme 1.2](image)

Reduction of a neutral (group 10 metal) bisdithiolene results in occupation of the LUMO shown in Figure 1 (section 1.2.1). Recall that the LUMO for neutral bisdithiolenes is bonding with respect to the C-C linkages (within the C\(_2\)S\(_2\) unit) and antibonding for the C-S linkages. Reduced bisdithiolenes, therefore, should exhibit shorter C-C bonds and longer C-S bonds compared to their oxidized congeners if the MO picture presented in Figure 1 is correct. Indeed, for bisdithiolenes that have been crystallographically characterized in different charge states, this expectation is usually met. To illustrate, Table 1.1 compares the selected bond distances for [Pt(S\(_2\)C\(_2\)(CF\(_3\))\(_2\)]\(^{n-}\) (n = 0 and 2).\(^{31}\) It is seen that the C-C bonds are indeed shortened and the C-S bonds are lengthened upon reduction to the dianionic form of the metal bisdithiolene. In other words, the oxidized form has more thioetone character, while in the reduced form the ligands are best described as 1,2-ene-dithiolates.
Metal trisdithiolenes are also redox active and, like bisdithiolenes, they can usually be isolated in three charge states (0, -1 and -2 for group 6 metal trisdithiolenes). For example, Mo(S₂C₂(CF₃))₃ is reduced to its monoanion at 0.58 V (versus SCE) and the monoanion is reduced to the dianion at 0.05 V.³² According to the MO analysis of trisdithiolenes presented in section 1.2.2, the electrons in the reduced forms should reside in an orbital with mainly metal dₓ² character (see Figure 1.4); it will be seen later, however, that the MO picture presented above is oversimplified and, in fact, this orbital has significant ligand character, with analogy to the bisdithiolene case.

In summary, metal bis- and tris-dithiolenes are redox active and can exist in multiple charge states. Expectedly, oxidized dithiolene complexes tend to react as electrophiles, while reduced (electron-rich) forms typically behave as nucleophiles. Unsurprisingly, the degree of electrophilicity or nucleophilicity is strongly dependent on the dithiolene substituents. Electron-releasing groups make neutral dithiolenes more difficult to reduce and favour nucleophilicity in the reduced forms. By the same rationale, oxidized (neutral, for group 10 bis- and group 6 trisdithiolenes) metal dithiolenes with electron-withdrawing groups are more inclined to react with nucleophilic substrates (see below) than analogous complexes with electron-releasing substituents on the dithiolene ligands.

### 1.4.3.2 Ligand-based reactions: dithiolenes as electrophiles

Ligand-centered reactivity, with metal bis- and trisdithiolenes reacting as electrophiles, is the central topic of chapters 2, 3, 4 and 5. Here, general classes of electrophilic dithiolene
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reactions (where covalent bonds are formed to the dithiolene ligand) are introduced, and more details will follow in subsequent chapters.

Among the very first ligand-based reactions to be discovered were those of the group 10 bisdithiolenes. Specifically, it was found that metal dithiolenes such as Ni(S₂C₂Ph₂)₂ and Ni(S₂C₂(CF₃)₂)₂ react with strained bicyclic alkenes (e.g., norbornadiene, reacting as a mono-alkene) at the ligand sulfur atoms. *Intraligand* alkene binding was initially proposed, on the basis of MO expectations (intraligand addition is symmetry-allowed, Scheme 1.3 and Figure 1). However, subsequent characterization of stable alkene adducts of metal bisdithiolenes revealed symmetry-forbidden *interligand* structures, contrary to MO predictions (Scheme 1.3), thus casting doubt on the ability of MO analysis to predict bisdithiolene reactivity. In later chapters, however, it is shown that MO approaches are indeed very useful for understanding the reactions of bisdithiolenes and trisdithiolenes.

![Scheme 1.3](image)

In 2001, it was suggested that the ligand-centered alkene reactivity of electron-deficient bisdithiolenes [Ni(S₂C₂R₂)₂; R = CF₃, CN] might be exploited to remove alkenes from crude petroleum streams, as a potential alternative to energetically-intensive cryogenic distillation processes. The same paper reported, for the first time, that highly oxidizing nickel bisdithiolenes react with not only strained bicyclic alkenes (e.g., norbornadiene) but also with simple (terminal, linear) alkenes such as ethylene and 1-hexene, and that the metal-bound alkene could be released by electrochemical reduction. Although conceptually very
appealing, the suggested electrocatalytic cycle (Scheme 1.4) is probably impractical for reasons that will be discussed later (chapter 2). Note that the proposal relies on symmetry-forbidden interligand alkene addition to the bisdithiolene.

Sufficiently electrophilic metal bisdithioleines can also react with conjugated 1,3-dienes and, as observed for the alkene reactions (above), the organic substrate attacks the S-atoms of the dithiolene ligands (Scheme 1.5).\textsuperscript{1e,36} In contrast to the alkene case, however, these reactions give symmetry-allowed interligand adducts, and products associated with symmetry-forbidden transition states are not observed. Chapter 3 shows that symmetry-allowed intraligand C,S-diene addition (instead of interligand S,S-diene addition) is also possible, which had not been observed prior to our work.
1.4.3.3 Ligand-based reactions: dithiolenes as nucleophiles

As mentioned in section 1.4.3.1, reduced metal dithiolenes often react as nucleophiles. For dianionic bisdithiolenes, simple electrophiles (e.g., alkyl cations) attack the S-atoms of the dithiolene ligand(s), as expected on the basis of large S-based coefficients for the HOMO (the LUMO for neutral bisdithiolenes, see above). An example involving the methylation of two dithiolene sulfur centers in a nickel bisdithiolene is shown in Equation 1.6. The nucleophilic behaviour of a reduced bisdithiolene is exploited in chapter 6 to form a multimetallic dithiolene derivative, using a metal-based electrophile (as opposed to an alkyl cation).

\[
\begin{array}{c}
\text{Ph} \equiv \text{S} \equiv \text{Ni} \equiv \text{S} \equiv \text{Ph} \quad 2 \text{MeI} \\
\text{Ph} \equiv \text{S} \equiv \text{Ni} \equiv \text{S} \equiv \text{Ph} \\
\end{array}
\]

Similar reactivity trends are seen for reduced metal trisdithiolenes. For instance, a dianionic tungsten trisdithiolene, \([W(S_2C_2Ph_2)_3]^{2-}\), also undergoes methylation when treated with MeI but, in this case, the two methyl groups add to the same dithiolene ligand.

1.5 Summary and thesis outline

The above sections have introduced dithiolene ligands and the concept of noninnocence. Specifically, MO and valence bond analyses were used to show that dithiolene ligands can interact in a $\pi$ fashion with metal orbitals to form frontier orbitals with primarily ligand character. Oxidized dithiolene complexes have appreciable thioketone character and are susceptible to nucleophilic attack, while the ligands in reduced analogues typically behave as nucleophilic 1,2-ene-dithiolates. The delocalization of $\pi$ electrons in the frontier orbitals of metal dithiolenes accounts for many of the interesting properties associated with these molecules, including their ligand-centered reactivity. The redox reactivity of metal bis- and trisdithiolenes illustrates the simplest cases of ligand-centered reactivity in dithiolene complexes. Bis- and trisdithiolenes can also participate in reactions that result in covalent
bond formation to the dithiolene ligands; depending on the charge state and the dithiolene substituents, metal dithiolenes can behave as electrophiles or nucleophiles. Chapters 2 and 3 focus on electron-deficient metal (Ni and Pt) bisdithiolenes reacting as electrophiles with alkenes and a diene. In chapter 4, the alkene reactivity of electrophilic mixed-ligand molybdenum trisdithiolenes is discussed. Chapter 5 shows how this reactivity was adapted for the catalytic production of 2,3-dihydro-1,4-benzodithiins (six-membered sulfur-containing heterocycles). Chapter 6 deals with novel trimetallic sandwich complexes with bisdithiolene cores, which were prepared by exploiting the nucleophilicity of reduced nickel bisdithiolenes. Finally, chapter 7 summarizes the results presented in the proceeding chapters and provides an outlook for ongoing research.

1.6 References


[2] Note that metal-free neutral 1,2-dithietes can be isolated in some cases (section 1.3.3) and certain 1,2-diene-dithiolates (section 1.3.1) are isolable as simple salts (e.g., Na+, Li+). Radical anionic character is only observed for dithiolene ligands attached to transition metals.


[4] Metal-ligand π interactions are often, but not necessarily, associated with noninnocent ligands. See reference 5(a), in which a potentially noninnocent, metal-containing ligand binds to metal centers in a strictly σ-fashion, presumably with a lack of direct electronic coupling between the metals.
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[5] (a) Ligands that incorporate a metal, such as bidentate bisphosphine ligands with redox-active ferrocenyl backbones (e.g., \((\eta^5-C_5H_4PPh)_2Fe\), ‘dpff’) can be noninnocent under certain circumstances. For an electrochemical study on group 6 metal carbynols bearing the dpff ligand in various coordination modes: Ohls, A. C.; Rheingold, A. L.; Shaw, M. J.; Nataro, C. *Organometallics* 2004, 23, 4655. (b) The sulfur ligands in certain metal sulfides, such as \((\text{Cp}^*\text{MoS}_2)_2\), can also be viewed as noninnocent, as it is not immediately clear whether the bridging sulfur atoms are mono- or disulfides (i.e., whether or not S-S bonds are present) and, consequently, the oxidation states of the metals are ambiguous. See: Tremel, W.; Hoffmann, R.; Jemmis, E. D. *Inorg. Chem.* 1989, 28, 1213.

[6] “Homoleptic” refers metal complexes in which all ligands are identical. Bonding models are necessarily more complex for less symmetrical heteroleptic complexes. Chapter 4 will introduce frontier MOs for heteroleptic (mixed-ligand) molybdenum trisdithiolene.


[17] This dithiete exists in equilibrium with its dimeric (tetrasulfide) form. For the synthesis of \(\text{S}_2\text{C}_2(\text{CF}_3)_2\), and its dimerization to a tetrasulfide, see: Krespan, C. G. *J. Am. Chem. Soc.* 1961, 83, 3434.


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[25] dmit$_2^2$ = 4,5-dimercapto-1,2-dithiole-3-thione-4,5-dithiolate.
Chapter 2

Alkene Reactivity of an Electrophilic Nickel Bisdithiolene [Ni(S₂C₂(CF₃)₂)₂]

2.1 Abstract

A reinvestigation of the reactivity of Ni(S₂C₂(CF₃)₂)₂ toward alkenes has revealed new mechanistic insights. While this nickel bisdithiolene was reported to undergo symmetry-forbidden interligand alkene addition to give stable adducts, we found that symmetry-allowed intraligand addition dominates, giving decomposition products (substituted dihydrodithiins and [Ni(S₂C₂(CF₃)₂)₂]ₙ), unless a sub-stoichiometric amount of the monoanionic form of the bisdithiolene ([Ni(S₂C₂(CF₃)₂)₂⁻]) is present. We have shown that the monoanion induces a change in product selectivity, such that stable interligand alkene adducts are obtained as the major products. The monoanion can be generated in situ from highly oxidizing Ni(S₂C₂(CF₃)₂)₂ using a variety of unusual reductants, including organic sulfides and water. A mechanism to describe the role of [Ni(S₂C₂(CF₃)₂)₂]⁻ in determining product selectivity is proposed and preliminary kinetic data is presented. Much of the work described here has been published.¹ Neilson Nguyen developed a safe synthesis of 1,2-bis(trifluoromethyl)dithiete [i.e., S₂C₂(CF₃)₂, used in the synthesis of Ni(S₂C₂(CF₃)₂)₂] and conducted the preliminary experiments for this project. In the present chapter and throughout the thesis, all X-ray crystal structures were solved by Dr. Alan J. Lough (staff crystallographer, University of Toronto, St. George campus).

2.2 Introduction

Chemical technology heavily relies on alkenes (olefins) as feedstocks and synthetic intermediates, and their utilization often involves transition metals.² In most metal-mediated reactions, the alkene coordinates to the metal in at least one step of the reaction sequence, rendering such systems easily poisoned by impurities (e.g., CO, H₂S, alkynes) in crude alkenes, which often bind more strongly to the metal than the alkene. Metal bisdithiolenes have delocalized frontier orbitals with primarily ligand character (see 1.2.1) and, therefore,
are expected to be considerably more resistant to typical catalyst poisons than complexes that rely on metal-centered reactivity, as emphasized by Wang and Stiefel in 2001.\textsuperscript{3} They reported that neutral nickel bisdithiolene complexes (\textit{Ni}(S_2C_2R_2)_2; R = CN, CF_3; compound 1 for \(R = \text{CF}_3\)) form adducts with linear alkenes, such as ethylene or 1-hexene, where the alkene binds through the ligand S-atoms, even in the presence of H_2S or CO. This tolerance of metal poisons (expected for noninnocent complexes) led the authors to suggest an olefin purification scheme in which the dithiolene-bound alkene is released by electrochemical reduction and the neutral bisdithiolene is regenerated by oxidation\textsuperscript{3} (see section 1.4.3.2). Their proposal has provided valuable impetus for researchers to consider approaches based on noninnocent metal complexes\textsuperscript{4} for olefin refining, as potential alternatives to energetically-demanding cryogenic distillation.

Understanding the mechanism of alkene binding to metal bisdithiolenes will be crucial for tuning the selectivity of such systems and for developing novel applications, but key mechanistic questions are unresolved. Orbital symmetry should prevent neutral bisdithiolene complexes, in their singlet ground state, from forming interligand alkene adducts in a concerted, synfacial manner.\textsuperscript{5,6} In fact, early structural proposals suggested symmetry-allowed intraligand alkene binding for stable adducts of bisdithiolenes.\textsuperscript{7} Crystallographic characterization of the adduct formed by reaction of norbornadiene with 1 [\textit{Ni}(S_2C_2(CF_3)_2)_2],\textsuperscript{8} however, showed interligand binding, in contrast to orbital symmetry predictions (see section 1.4.3.2). To address the orbital symmetry problem, a computational (DFT) contribution suggested a two-step mechanism for alkene addition, in which the alkene approaches the dithiolene complex in an antifacial fashion (symmetry-allowed), giving an intermediate with tetrahedral distortion at nickel, which rearranges to the familiar interligand adduct where the metal geometry is approximately square-planar (Scheme 2.1).\textsuperscript{9,10}
The reactions between alkenes and Ni(S$_2$C$_2$R$_2$)$_2$ were claimed to selectively afford interligand adducts (as shown in 1.4.3.2, Scheme 1.4) and competitive pathways leading to other products were not mentioned.\textsuperscript{3} However, it is relevant that group 10 metal bisdithiolenes with aryl substituents (e.g., Ni(S$_2$C$_2$R$_2$)$_2$; R = (C$_6$H$_4$)$_p$-F) react with norbornadiene to give mainly dihydridithiins and metal decomposition products, presumably via symmetry-allowed intraligand alkene addition (Scheme 2.2).\textsuperscript{5c} Scheme 2.2 shows the ring-numbering system for dihydridithiins (here, DHDs) for nomenclature purposes. The DHD shown is substituted in the 2, 3, 5 and 6 positions (note that dithiins have two double bonds within the S,S-heterocyclic ring). Various types of DHDs, formed by intraligand alkene addition to metal dithiolenes, will be frequently encountered here and in following chapters.

**Scheme 2.2**
2.3 Results and discussion

We found that neutral 1 [Ni(S₂C₂(CF₃)₂)₂] reacts with ethylene or 1-hexene to give primarily DHD/metal decomposition products and little or no interligand alkene adduct. Clearly, if 1 is to be useful in alkene purification schemes (see 1.4.3.2), this lack of selectivity for stable alkene adducts needs to be addressed. Importantly, we discovered that the product distribution can be impacted dramatically by adding monoanionic [1⁻] to 1/alkene reaction mixtures, such that interligand adducts are obtained as dominant products, rather than DHD and metal decomposition products. These results, and their mechanistic implications, are discussed in the following sections.

2.3.1 Reactions between 1 and ethylene (with and without [1⁻] present)

Reactions between compound 1 and alkenes (ethylene and 1-hexene) were followed by NMR spectroscopy (¹⁹F and ¹H). Oddly, NMR methods had not been used previously to probe the reactions of metal bisdithiolenes with simple (acyclic) alkenes. Our experiments were conducted under strictly water-free conditions (except where noted), since we found that trace water significantly affects the reactivity in these systems (see below).

Reacting compound 1 (8.8 mM) with excess ethylene (ca. 25 mM) for 2.5 h at ambient temperature in CDCl₃ formed DHD(H)¹¹ (Scheme 2.3B, R = H) in 70% yield.¹²,¹³ Upon overnight reaction, conversion to DHD(H) and metal decomposition products was near-quantitative (90%). These products are very likely formed via orbitally allowed 3(ethylene) (Scheme 2.3B). DHD derivatives were identified by comparison of their ¹⁹F and ¹H NMR data with those of independently prepared samples.¹⁴ No interligand adduct [2(ethylene)] was observed in the reaction between 1 and ethylene, contrary to previously reported results.³
We then investigated the effect of having anionic [1]– present. Compound 1 quantitatively oxidizes up to one equivalent of decamethylferrocene [(Me5C5)2Fe ≡ Fc*] to give the ion pair [Fc*]+[1]–. When we employed Fc* to reduce 22% of 1 (originally 9.7 mM), the resulting 1/[1]– (78:22) mixture reacted (25°C, 16 h, in CDCl3) with excess ethylene to afford 2(ethylene) (Scheme 2.3A) in 55% yield, and DHD(H) in 24% yield.12,13 Compound 2(ethylene) was identified by its AA’BB’ pattern in the 1H NMR spectrum and by its two sets of fluorine signals15 [approximate Cs symmetry is expected for 2(ethylene)] (Figure 2.1). Photolysis of 2(ethylene) released the alkene, regenerating 1,16 in accord with the expected photochemistry17 of such adducts.

![Scheme 2.3](image)

**Figure 2.1** 19F NMR spectrum (470 MHz, CDCl3, 343 K) of 2(ethylene).

Thus, obtaining 2(ethylene) preferentially over decomposition products requires a significant concentration of [1]– in the 1/ethylene reaction mixture.18 We prepared a 1:1 mixture of 1 and [Fc*]+[1]– (both species ca. 10 mM in CH2Cl2), and reaction (50°C, 1 h) with excess
ethylene formed 2(ethylene) in 71% yield (isolated). X-ray quality crystals of 2(ethylene) were grown under ethylene atmosphere from benzene. The structure\(^{19}\) (Figure 2.2) clearly shows interligand adduct, with the expected 1:1 alkene/bisdithiolene stoichiometry. Although a crystal structure of 2(norbornadiene) has been reported,\(^8\) the present structure is the first example involving a simple, acyclic alkene. Notable features include a bowl-type distortion (\(\text{centroid}_{\text{C1,C2}}-\text{Ni1}-\text{centroid}_{\text{C3,C4}} = 158^{\circ}\)), similar to 2(norbornadiene).\(^8\) Also, the \(\text{C}_2\text{H}_4\) bridge is twisted (torsion \(\text{S}_1\text{C}_5\text{C}_6\text{S}_3 = 19.7^{\circ}\)), leading to \(C_1\) molecular symmetry in the solid state.

![Figure 2.2 X-ray crystal structure (20% probability ellipsoids) for 2(ethylene). Selected distances and angles (Å, °): Ni1-S1, 2.163(1); Ni1-S2, 2.159(1); Ni1-S3, 2.165(1); Ni1-S4, 2.162(1); S1-C5, 1.842(3); S3-C6, 1.854(3); C1-C2 \(\approx\) C3-C4, 1.356(4); S1-Ni1-S2, 92.07(3); S3-Ni1-S4, 92.14(3).](image)

### 2.3.2 Reactions between 1 and 1-hexene (with and without [1]\(^+\) present)

1-Hexene also reacts with 1 to give mainly decomposition products in the absence of [1]\(^+\), similar to the ethylene reactions described above. Reaction between 1 (14 mM) and 1-hexene (0.14 M) (25°C, 1.9 h, in CDCl\(_3\)), afforded some (12% yield) interligand adduct, of type 2(1-hexene) (Scheme 2.3, \(R = \text{^nBu}\)), even if no reductant was added, but DHD(\(^n\text{Bu}\))\(^{11}\) was the main product (73% yield).\(^{12,13,20}\) When we reduced 5.8% of 1 (14 mM initially) with Fe\(^\ast\), the ca. 94:6 mixture of I/[Fe\(^\ast\)]\(^+\)[1]\(^-\) yielded, upon reaction with 1-hexene, stable adducts (61% yield) and some DHD(\(^n\text{Bu}\)) (27% yield) (25°C, 2.9 h, in CDCl\(_3\)). Thus, having [Fe\(^\ast\)]\(^+\)[1]\(^-\) present in 1/1-hexene reaction mixtures favours interligand adducts, as seen for the ethylene reactions. Reduction with sodium in THF-\(d_8\) released 1-hexene from the
equilibrium mixture of alkene adducts, in agreement with reports concerning the electrochemical reversibility (see also 1.4.3.2) of alkene binding to sulfur centers.\textsuperscript{3,21,22}

The 1-hexene reactions gave much more complex NMR spectra than the ethylene reactions, due to the $C_1$ symmetry of the resulting adducts and endo/exo isomerism. We observed three different types of 1-hexene adducts, in the approximate ratio 1:2:4, and propose that the two major species are interligand adducts $2(1$-hexene), as endo and exo isomers. The minor species is likely a binuclear complex formed by reaction between $1$ and $2(1$-hexene) (Scheme 2.4, $R = \text{nBu}$). As precedent for such a proposal, we have observed the analogous complex for the ethylene case, generated by combining $1$ and $2$(ethylene) (Scheme 2.4, $R = \text{H}$) and the product was crystallographically characterized (Scheme 2.4, inset, 30% probability ellipsoids, H and F atoms omitted for clarity).\textsuperscript{23} The process depicted in Scheme 2.4 probably involves metal-based oxidation of the alkene adduct $[2(\text{alkene})]$, from Ni(II) to Ni(III) or Ni(IV) (pseudo-octahedral, $d^7$ or $d^6$), with concomitant one- or two-electron reduction of the nickel bisdithiolene. This transformation is an interesting example of ligand-centered reactivity in which a nickel bisdithiolene acts as an electrophile (oxidant) and as a ligand (nucleophile), forming $\sigma$ bonds to another metal. The utility of reduced metal bisdithiolenes as ligands for electrophilic metals is highlighted in chapter 6. For the reaction involving $2$(ethylene), formation of the dinuclear complex is reversible ($K_{eq} = 0.1 \text{ mM}^{-1}$ at 20$^\circ\text{C}$).

\begin{Scheme}
\begin{center}
\includegraphics[width=\textwidth]{Scheme2.4.png}
\end{center}
\end{Scheme}
2.3.3 Effects of additives (water, acetone, SR₂, PR₃) on product distributions

It was shown above that Fe⁺ produces [Fe⁺][1⁻] in 1/alkene mixtures and causes interligand adducts [2(alkene)] to be formed preferentially. Interestingly, other additives such as water, acetone, organic sulfides and trialkylphosphines also favour larger 2(alkene):DHD(R) product ratios. Acetone, in large excess (as solvent), has been used to reduce 1 in the synthesis of [NEt₄⁺][1⁻].²⁴ Presumably, SR₂ and PR₃ also reduce 1 to [1⁻], to explain their impact on the product distribution in these alkene-binding reactions. It is, however, remarkable that water can effect the reduction of 1. We investigated the reaction between 1 and H₂O by UV-vis spectroscopy and found that 1 equiv of water reduces 1 to [1⁻] in tetrahydrofuran (THF). The spectrum of the product is virtually identical to that of independently prepared²⁴ [NEt₄⁺][1⁻] (Figure 2.3). Compound 1 is also reduced in a CH₂Cl₂ solution with excess water present (see experimental section). Although the spectra in Figure 2.3 clearly indicate the formation of [1⁻] upon treatment of 1 with water, the fate of the oxidized water and the nature of the counter cation are in question. Further experiments are needed, but one possible scenario involves the formation of hydrogen peroxide and H⁺, and then the proton (likely solvated) serves as the cation [1⁻] for (Equation 2.1).

![Overlaid UV-vis spectra of (a) 1, (b) [1⁻] as independently prepared [NEt₄⁺][1⁻] and (c) [1⁻] prepared by reduction with water. All analytes have ca. 0.25 mM concentrations in THF.](image)

*Figure 2.3* Overlaid UV-vis spectra of (a) 1, (b) [1⁻] as independently prepared [NEt₄⁺][1⁻] and (c) [1⁻] prepared by reduction with water. All analytes have ca. 0.25 mM concentrations in THF.
If the \(2(\text{alkene})/\text{DHD}(\text{R})\) selectivity reversal is due to \([1]^+\), then independently synthesized \([1]\) should induce the same effect. Indeed, \(1\) (19 mM) reacted with 1-hexene (0.15 M) to give \(2(1\text{-hexene})\) as the major product \([2(1\text{-hexene})/\text{DHD}(\text{aBu}) \approx 3:1\) when \([\text{NEt}_4]^+[1]^-\) (0.9 mM) was present. These observations confirm the importance of \([1]^+\) in determining product selectivity.

### 2.3.4 Mechanistic investigations into \(1/\text{alkene}\) systems

Our mechanistic studies on \(1/\text{alkene}\) systems have focused on discerning the nature of alkene addition to the bisdithiolene (e.g., concerted or stepwise?) and on discovering how the monoanionic species ([1]) might induce selectivity reversal in favour of interligand adducts.

#### 2.3.4.1 Alkene addition to \(1\) to form \(2(\text{alkene})\): Concerted or stepwise? Syn or anti?

Reactions involving a selectively deuterated alkene [(\(E\))-1-D-1-hexene] have shed light on the mode of alkene addition to the nickel bisdithiolene. When (\(E\))-1-D-1-hexene (ca. 10 equiv, excess) was reacted with 1, in the presence of dimethylsulfide,\(^{25}\) stereospecific alkene binding was observed and photolysis of the resulting adducts \([2(\text{E}-1-D-1\text{-hexene})]\) released unchanged (\(E\))-1-D-1-hexene. Compelling evidence for stereospecific binding of (\(E\))-1-D-1-hexene in stable adducts \(2((E)-1-D-1\text{-hexene})\) was obtained from \(^1\text{H}\) NMR data. Figure 2.4 juxtaposes the \(^1\text{H}\) NMR spectra (ABC portions, for protons on the alkyl bridge) for the main isomers (endo and exo) of \(2((E)-1-D-1\text{-hexene})\) and all-protio-\(2(1\text{-hexene})\). The downfield part of the ABC-spectrum seen for the all-protio compound vanishes if \(E\)-deuterated alkene is used, establishing that these resonances are associated with H\(^a\) (see Figure 2.4). If the alkene underwent syn- and anti-addition, the geminal hydrogens (H\(^a\) and H\(^b\) for all-protio case) would be scrambled in the product and proton signals would be expected downfield of 4 ppm in the \(2((E)-1-D-1\text{-hexene})\) reaction. However, the downfield signals seen in all-protio-\(2(1\text{-hexene})\) (Figure 2.4(b), ca. 4.02 – 4.09 ppm) are completely absent in the \(^1\text{H}\)
NMR spectrum for \( \mathbf{2}((E)-1-D-1\text{-hexene}) \) [Figure 2.4(a)]. Therefore, regardless of whether the main product is the endo- or the exo-isomer (for steric reasons, the exo-isomer is probably favoured), alkene addition is \textit{stereospecific} with respect to the relative positions of the substituents (\( ^{\text{\textsuperscript{6}}}\text{Bu} \) and \( D/H^a \)) on the alkyl bridge. Since we have not assigned the absolute stereochemistry of the protons on the alkyl bridge, we cannot state with certainty whether the addition is stereospecifically \textit{syn} or stereospecifically \textit{anti} (to give \( \text{trans-} \) or \( \text{cis-}D^{\text{\textsuperscript{6}}}\text{Bu} \) respectively), but it is clearly stereospecific. However, the alkene retains its (\( E \))-configuration (i.e., is \textit{not} isomerized to (\( Z \))-1-D-1-hexene) when it is \textit{photochemically} released from the bisdithiolene species, in a reaction that is expected to be symmetry-allowed, disrotatory, and thus the microscopic reverse of \textit{syn}-addition. Furthermore, the crystallographically characterized \( \mathbf{2} \)(norbornadiene) complex predictably exhibits \textit{cis} orientation of the substituents, indicating \textit{syn} attack of the bisdithiolene at the alkene. Indeed, \textit{anti}-addition, to give \textit{trans} substituents, is probably not feasible for sterically constrained bicyclic alkenes or dienes. The combined evidence therefore suggests that 1-hexene selectively undergoes \textit{syn}-addition, giving products with \( \text{trans-}^{\text{\textsuperscript{6}}}\text{Bu}/Y \) (\( Y = D \) or \( H^a \)) groups as depicted in the inset of Figure 2.4 (endo and exo isomers shown).

\[ \text{Figure 2.4} \] \text{Partial } ^1\text{H NMR (500 MHz, CDCl}_3) \text{ spectra of (a) } \mathbf{2}((E)-1-D-1\text{-hexene}) \text{ isomers and (b) all-protio-2(1-hexene) isomers, showing the } H^a, H^b, H^c \text{ regions. Our proposed assignment (inset) is based on } \text{syn-addition} \text{ of the nickel bisdithiolene to the alkene.} \]
The above observations strongly suggest that 1-hexene (D₁ and all-protio) adds to 1 in concerted fashion, and that carbocation (or carbon radicals) intermediates are probably not involved. If the alkene addition was stepwise (e.g., Scheme 2.5), a mixture of cis AND trans addition products (in endo and exo forms) would be expected due to scrambling of relative substituent positions on the alkyl bridge, via inversion at the prochiral carbon in the intermediates (either C⁺ or C●, Scheme 2.5). As shown above, we did not observe such scrambling in the products (only cis OR trans products were observed, not cis AND trans). A stepwise mechanism (cationic or radical) would require very rapidly collapsing intermediates to be consistent with the observed stereospecificity, and we regard it likely that the stereo-determining step is concerted.

Scheme 2.5

2.3.4.2 Kinetic studies: possible role of anion ([1]⁻)

Full understanding of the mechanism for reactions between 1 and alkenes, including the role of the anion, will require very detailed kinetic studies, but preliminary kinetics,²⁶ for 1-hexene, provide some insight. In the simplest mechanistic scenario, [1]⁻ catalyzes the production of 2(alkene). If [1]⁻ accelerates one of two parallel reactions, then \( k_{\text{obs}} \) for decay of 1 should increase with increasing [1]⁻ concentration. However, we observed the opposite: while higher anion concentrations favour alkene adducts over decomposition products, [1]⁻ actually slows the decay of 1 (by ca. 20%). Therefore, if [1]⁻ catalyzes formation of 2(alkene), it must simultaneously inhibit DHD(R) production to account for the decreased
rate. The pathway leading to decomposition products may be suppressed as shown in Scheme 2.6A. In this suggested mechanism, the symmetry-allowed adduct 3(alkene) quickly degrades to DHD(R) and metal decomposition products upon oxidation by 1. Higher [1]− concentrations shift the 3(alkene)/[3(alkene)]+ equilibrium to the left, slowing the decomposition pathway. Such a proposal may explain why small amounts of [1]− are produced in the reaction between norbornadiene and neutral 1, as observed by Geiger.22 It is possible that [1]− also reacts directly with alkenes to give the intermediate [2(alkene)]−,27 which is oxidized by 1 to yield 2(alkene) (Scheme 2.6B). This mechanistic proposal is novel, and transition states have not yet been computed. However, in the context of alkene release, the thermodynamics for [Ni(S₂C₂(CN)₂)(ethylene)]− (interligand adduct) versus [Ni(S₂C₂(CN)₂)₂]− and free ethylene were computed to be ΔH = 38 kJ/mol (not prohibitively uphill).9

Our proposed mechanism (Scheme 2.6A) involves oxidation of 3(alkene), leading to labilization and loss of the DHD ligand. The oxidation potentials of compounds 3(alkene) would be of great interest to assess the feasibility of this mechanism. Since adducts of type 3(alkene) have not been directly observed, related compounds have to serve as models.
Adducts of type 2(alkene) seem, at first inspection, to be attractive candidates. However, such adducts are very difficult to oxidize, as seen from Geiger’s work: 2(norbornadiene) was not oxidized at potentials as high as 1.3 V versus ferrocene (ca. 1.76 versus SCE).\textsuperscript{22} The potential for the reversible 1/[1]\textsuperscript{−} couple is 0.92 V versus SCE (in MeCN),\textsuperscript{28} and thus adducts 2(alkene) cannot be oxidized by 1 to any appreciable extent. However, adducts of type 3(alkene) should be much easier to oxidize. Ionic Lewis structures are shown for both types of ethylene adducts in Figure 2.5. Compound 2(alkene) contains two separate enethiolate units, whereas 3(alkene) contains a conjugated ene-1,2-dithiolate unit. The highly electron-rich ene-1,2-dithiolate unit is relatively easily oxidized. Compounds (“N\textsubscript{2}”\textsuperscript{2+})Ni(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3})\textsubscript{2}) (“N\textsubscript{2}” = nitrogen-based chelate ligand) (Figure 2.5) can serve as models. Compounds (“N\textsubscript{2}”)Ni(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3})\textsubscript{2}) undergo Ni-dithiolene-based one-electron oxidation at potentials between 0.74 and 1.08 V versus SCE, depending on the nature of the nitrogen-based chelate ligand and the solvent.\textsuperscript{29} We expect the potentials for the oxidation of compounds 3(alkene) to be close to 1.0 V versus SCE, and it thus appears very likely that intermediates 3(alkene) can be oxidized by 1 to an extent that is mechanistically important.

![Figure 2.5 Structures of isomeric ethylene adducts compared to (“N\textsubscript{2}”\textsuperscript{2+})Ni(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3})\textsubscript{2})](image)

Kinetic studies conducted by an undergraduate researcher (Aiman Alak) in our group, after the publication of the work described above,\textsuperscript{1} indicate that an alternative mechanism, involving isomerization of the intraligand adduct [3(alkene)] to the interligand adduct [2(alkene)], is also a possibility.\textsuperscript{30} More kinetic data are needed to determine which of these pathways is operating.
2.4 Conclusion

We conclude that 1 reacts with simple alkenes to give, preferentially, DHD and metal decomposition products, unless [1]⁻ is present. Our results suggest that the mechanism of stable adduct [2(alkene)] formation is more complicated than previously thought and might involve charged intermediates. Interestingly, additives such as water, organic sulfides or trialkyl phosphines favour larger 2(alkene):DHD(R) product ratios, very likely because these species are sufficiently reducing to produce [1]⁻. An electrochemical process, as originally envisioned by Wang and Stiefel,³ might be efficient for olefin purification: if the charge-neutral metal complex is generated in situ by oxidation from the monoanion, in the presence of the alkene, a sufficient amount of monoanion will be present to influence the reactivity towards interligand adducts.

2.5 Experimental section

2.5.1 General considerations

Experiments were conducted in an inert (N₂ or Ar) atmosphere using standard glovebox and Schlenk-type techniques unless otherwise noted. Reactions between Ni(S₂C₂(CF₃)₂)₂ (1) and alkenes were protected from light when possible, as alkene adducts [2(alkene)] are photosensitive. Benzene, hexanes, tetrahydrofuran-d₈ (THF-d₈), toluene and toluene-d₈ were dried over Na/benzophenone and vacuum-transferred prior to use. Chloroform-d (CDCl₃) and dichloromethane-d₂ (CD₂Cl₂) were dried over CaH₂ and vacuum-transferred prior to use. Acetone was dried by refluxing over MgSO₄ under a nitrogen atmosphere and vacuum-transferred prior to use. Nickel powder (100 mesh) (99%), bis(pentamethylcyclopentadienyl)iron (decamethylferrocene, Fc*) (97%), 3,5-bis(trifluoromethyl)bromobenzene (here, ‘BTBB’) (99%), 2-bromochlorobenzene (99%) and tributylphosphine (97%) were purchased from Aldrich and used as received. 1-Hexene (99+%) was purchased from Aldrich and dried over molecular sieves. Ethylene (99.5%) was
obtained from BOC Canada Ltd. and used as received. Silica gel (70-230 mesh, Alpha Aesar) was either used as received or dried/deoxygenated under high vacuum at 100°C for > 6 h, where noted. 1,2-Bis(trifluoromethyl)dithiete [S$_2$C$_2$(CF$_3$)$_2$]$_2$ [31] [NEt$_4$][Ni(S$_2$C$_2$(CF$_3$)$_2$)$_2$]" ([NEt$_4$][I])$^{24}$ and (E)-1-d-1-hexene (i.e., trans-DHC=CH$_n$Bu) were synthesized according to the reported methods. Ni(S$_2$C$_2$(CF$_3$)$_2$)$_2$ (1) and 2,3-dihydro-1,4-dithiins [DHD(H$_n$Bu)]$^{14}$ were made using modified literature procedures (see below). $^1$H NMR spectra were obtained on Varian Gemini 200 MHz or Unity/Inova Varian 500 MHz spectrometers. Residual proton peaks were used as reference: $^1$H (δ, ppm, chloroform-d, 7.26; THF-d$_8$, 1.73 and 3.58). $^{19}$F NMR data were recorded on a Unity/Inova Varian 500 MHz spectrometer at 470 MHz and referenced to external trifluoroacetic acid (δ, ppm, -76.55). UV-vis spectra were obtained on a Cary 14 spectrophotometer. Elemental analyses were conducted at Guelph Laboratories, Guelph, ON, Canada. The electronic crystallographic information file (cif) for 2(ethylene) is available as supporting information at http://pubs.acs.org.$^1$

### 2.5.2 Synthesis of Ni(S$_2$C$_2$(CF$_3$)$_2$)$_2$ (1)

1,2-Bis(trifluoromethyl)dithiete [S$_2$C$_2$(CF$_3$)$_2$] (9.97 g, 0.044 mol) was combined with nickel powder (1.60 g, 0.027 mol) in a 200 mL Pyrex reaction vessel, sealable with a Teflon® valve (“bomb”) (with stir bar). Toluene (30 mL) was added to give an orange solution, in which Ni remained insoluble. The vessel was heated (110°C) under nitrogen (sealed bomb) in an oil bath for 6 d, with stirring. During this time, the color of the solution became dark purple. The vessel was cooled to RT and the volatile materials were removed by vacuum, leaving behind black-purple solid residue. Hexane (60 mL) was added to the residue, giving a purple solution with suspended insoluble material (unreacted Ni). The soluble portion was passed through a silica gel column (12 g SiO$_2$, dried, inner diameter of column: 1.7 cm). The volume of the eluent was reduced by ca. 80%, causing purple crystalline material to precipitate. Further crystal growth was promoted by cooling the mixture overnight (-35°C). The purple solid material was recovered by decanting the supernatant and washing the solid portion with cold (ca. -35°C) hexane (1.5 mL x 3). The dark purple needles were dried in vacuo, then sublimed under high vacuum at 85°C (1.7 g, 15%). Anal. Calc. for C$_8$F$_{12}$S$_4$Ni: C 18.80, S 25.10; Found: C 18.69, S 25.24. $^{19}$F NMR (470 MHz, CDCl$_3$) δ -57.74 (s, 12F).
2.5.3 Synthesis of DHD(H)

S$_2$C$_2$(CF$_3$)$_2$ (100 mg, 0.44 mmol) was weighed into a 50 mL solvent bomb containing a stir bar and dissolved in benzene (5 mL). In air, the bomb was quickly opened and ethylene was bubbled through the S$_2$C$_2$(CF$_3$)$_2$/benzene mixture for ca. 1.5 min to saturate the solution. The bomb was sealed and heated under nitrogen in an oil bath (100°C), with stirring, for 4 d. Upon cooling the vessel to RT, the volatiles were removed under reduced pressure to reveal DHD(H) as orange-yellow oil. $^1$H NMR (200 MHz, CDCl$_3$) δ 3.29 (s, 4H). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -60.09 (s, 6F).

2.5.4 Synthesis of DHD(°Bu)

S$_2$C$_2$(CF$_3$)$_2$ (100.0 mg, 0.44 mmol) was weighed into a 25 mL solvent bomb containing a stir bar. 1-Hexene (55 mg, 83 μL, 0.66 mmol) was added. The vessel was heated under nitrogen (sealed bomb) at 120°C for 3 d, with stirring, in an oil bath. The bomb was allowed to cool to RT and the volatiles were removed under vacuum to give faintly yellow-orange oil [DHD(°Bu), Figure 2.6, inset]. $^1$H NMR (200 MHz, CDCl$_3$) (Figure 2.6) δ 0.95 (t, $^3$J$_{HH}$ = 7.2 Hz, 3H, CH$_3$R), 1.21-1.60 (ov m, 4H, CH$_2$CH$_2$Me), 1.75 (m, 2H, CH$_2$°Pr), 2.96 (m, $^2$J$_{HbHa}$ = -13.2 Hz, $^3$J$_{HcHa}$ = 7.8 Hz [spectrum was successfully simulated using Mestrec®], 1H, H$^a$), 3.21 (m, $^2$J$_{HaHb}$ = -13.2 Hz, $^3$J$_{HcHb}$ = 2.7 Hz , 1H, H$^b$), 3.46 (m, $^3$J$_{HaHc}$ = 7.8 Hz, $^3$J$_{HdHc}$ = $^3$J$_{HeHc}$ = 7.0 Hz, $^3$J$_{HbHc}$ = 2.7 Hz, 1H, H$^c$). $^{19}$F NMR (470 MHz, CDCl$_3$) δ -59.76 (complex m, 6F).
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Figure 2.6 ¹H NMR (200 MHz, CDCl₃) spectrum for DHD(ⁿBu) with aliphatic ring protons labeled. The inset shows the labeling scheme.

2.5.5 1 + excess ethylene (without [1]⁻)

1 (11.2 mg, 0.0219 mmol) was combined with BTBB³³ (internal NMR standard; 2.7 mg, 0.012 mmol) and dissolved in CDCl₃ (2.5 mL) in a 50 mL pyrex bomb. In air, the vessel was quickly opened and ethylene was bubbled through the purple 1/CDCl₃ solution for ca. 1 min to saturate the solution. The bomb was sealed and stirred at ambient temperature (ca. 23°C) for 2.5 h during which time the solution became dark brown in color. A portion (ca. 0.6 mL) of this solution was placed in a J. Young NMR tube for spectroscopic analysis. ¹H NMR (200 MHz, CDCl₃) (Figure 2.7, left) δ 3.30 (s, 4H, DHD(H), 70%¹²), 5.36 (s, unreacted ethylene), 7.83 (s, 1H, BTBB), 7.97 (s, 2H, BTBB). The sample was allowed to stand at RT overnight and then a ¹⁹F NMR spectrum was collected: ¹⁹F NMR (470 MHz, CDCl₃) (Figure 2.7, right) δ -60.11 (s, 6F, DHD(H), 90%), -60.0 to -51.0 (complex multiplets, [Ni(S₂C₂(CF₃)₂)]₃).

Comments: The exclusive products of reaction between 1 and ethylene, in the absence of [1]⁻, are DHD(H) and metal decomposition species, [Ni(S₂C₂(CF₃)₂)]₃ (Figure 2.7).
Chapter 2 – Alkene Reactivity of an Electrophilic Nickel Bisdithiolene [Ni(S₂C₂(CF₃)₂)₂]

Figure 2.7 NMR spectra for a 1 + ethylene reaction mixture. Left: ¹H NMR (200 MHz, CDCl₃). Right: ¹⁹F NMR (470 MHz, CDCl₃).

2.5.6 1 + excess ethylene (with 28 mol %³⁴ [1⁺])

1 (12.4 mg, 0.0243 mmol) was combined with BTBB (internal NMR standard; 7.3 mg, 0.025 mmol) and CDCl₃ (2.5 mL) in a 50 mL pyrex bomb, with a stir bar. Fc⁺ (75.0 μL of 0.0723 M Fc⁺/CDCl₃ solution, 0.0054 mmol) was added. Ethylene was passed through the resulting mixture for ca. 2 min to saturate the solution. The bomb was sealed and stirred overnight (ca. 16 h). The mixture was passed through a 2 cm plug of Celite® in a Pasteur pipet to remove [Fc⁺][1⁻]. A portion of the resulting brown solution was placed in a J. Young NMR tube for spectroscopic analysis. ¹⁹F NMR (470 MHz, CDCl₃) δ -64.00 (s, 6F, BTBB), -60.70 (m [q? Poorly resolved], 6F, 2(ethylene), 55% yield), -60.11 (s, 6F, DHD(H), 24% yield), -60.0 to -51.0 (complex multiplets, [Ni(S₂C₂(CF₃)₂)ₓ]), -55.40 to -53.50 (br m [shape is temperature dependent, see below], 6F, 2(ethylene)).

2.5.7 Synthesis of 2(ethylene) for characterization

1 (100 mg, 0.20 mmol) was combined with decamethylferrocene (Fc⁺) (30 mg, 0.092 mmol) in a 50 mL solvent bomb. Dichloromethane (10 mL) was added to give a purple-brown solution with some insoluble material visible ([Fc⁺][1⁺]). Ethylene was bubbled through the 1/[Fc⁺][1⁻]/dichloromethane solution for ca. 2 min to saturate the solution. The bomb was
sealed and heated (50°C) for 1 h, which afforded a brown-green, homogenous (i.e., all [Fc*][1]+ dissolved) solution. The solvent/volatiles were removed by purging the solution with a strong stream of ethylene while heating at 45°C to reveal brown-green solid residue. Chloroform (3 mL) was added to this crude product; some material remained insoluble in chloroform ([Fc*][1]+). The concentrated slurry was placed on a silica gel column (10 g SiO₂, dried, silica suspended in hexanes, inner column diameter = 1.7 cm). Hexanes (ca. 10 mL) were passed through the column to produce colorless eluent, which was discarded. The solvent system was then changed to 1:1 hexanes:chloroform and ca. 8 mL of this mixture was passed through the column until the eluent leaving the column was faintly brown. Then 20 mL of pure chloroform was passed through the column and the brown colored eluent was collected in a solvent bomb. Note that a dark brown band remained at the top of the column ([Fc*][1]+). The volatiles were removed from the brown coloured solution (eluent) by, again, passing a strong stream of ethylene gas through the mixture, while gently heating the vessel in an oil bath (45°C) to give yellow-brown, micro-crystalline material (40 mg, 71%, based on neutral 1 present after reduction). The product was stored under an ethylene atmosphere at -35°C. X-ray crystals were grown by slow evaporation of solvent from a 2(ethylene)/benzene solution, under a slow stream of ethylene. Anal. Calc. for C₁₀H₄F₁₂S₄Ni: C: 22.27%, H: 0.75%, S: 23.80%; Found: C: 22.13%, H: 0.61%, S: 24.21%. 

¹H NMR (200 MHz, CDCl₃) (Figure 2.8, left) δ 3.94 (m, 2H, Hᵃ or Hᵇ), 4.55 (m, 2H, Hᵃ or Hᵇ). ¹⁹F NMR (470 MHz, CDCl₃) (Figure 2.8, right) δ -60.71 (m [q?], 6F, Fᵃ or Fᵇ), -55.40 to -53.50 (br m [shape is temperature-dependent, see below], 6F, Fᵃ or Fᵇ). See Figure 2.10 for an alternative view of the crystal structure for 2(ethylene).
Figure 2.8  NMR spectra of 2(ethylene) (293 K).\textsuperscript{15}  Left: \textsuperscript{1}H NMR (200 MHz, CDCl\textsubscript{3}). Right: \textsuperscript{19}F NMR (470 MHz, CDCl\textsubscript{3}).

Comments: The NMR spectra of 2(ethylene) are temperature dependent. The effect is much more evident in the \textsuperscript{19}F NMR spectra (at 470 MHz field) than in the \textsuperscript{1}H NMR (200 MHz) spectra. This behaviour is likely a result of conformational changes in the strained 5-membered ring formed by alkene addition and/or slowed rotation of the C-CF\textsubscript{3} bonds closest to the C\textsubscript{2}H\textsubscript{4} bridge. The \textsuperscript{19}F NMR spectra of 2(ethylene) at various temperatures are shown in Figure 2.9. Note: since the downfield \textsuperscript{19}F resonance (-55.40 to -53.50 ppm) is perturbed to a greater extent than the upfield peak, we propose this signal should be attributed to fluorines in the CF\textsubscript{3}\textsuperscript{a} environment (see Figure 2.8, above), because it is closer to the C\textsubscript{2}H\textsubscript{4} bridge and thus experiences more steric strain.
Figure 2.9 \(^{19}\)F NMR (470 MHz, CDCl\(_3\)) spectra of 2(ethylene) at (a) 343 K, (b) 323 K, (c) 293 K and (d) 283 K.

Figure 2.10 X-ray crystal structure of 2(ethylene) showing the two benzene molecules in the unit cell. Thermal ellipsoids are shown at 50% probability.
2.5.8 Photolysis of 2(ethylene)

2(ethylene) (10 mg, 0.019 mmol) was dissolved in CDCl$_3$ (0.6 mL) and the resulting brown-yellow solution was placed in a J. Young NMR tube. The tube was affixed near (ca. 2 cm) a fluorescent light bulb overnight. During this time, the color of the solution changed from brown-yellow to light purple. $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 0.75-2.00 (ov m, polyethylene), 3.29 [s, DHD(H)], 5.40 (s, ethylene).

Comments: As expected, photolysis released the alkene from 2(ethylene) to regenerate 1, some of which reacted with free ethylene to form DHD(H) and metal decomposition products.

2.5.9 1 + excess 1-hexene (without [I$^-$]) in CDCl$_3$

A CDCl$_3$ solution (0.50 mL) containing 1 (0.0140 M, 0.0070 mmol) and BTBB (0.0124 M, 0.0062 mmol) was placed in a J. Young NMR tube. To this purple solution, 1-hexene (9.0 $\mu$L, 0.072 mmol) was added. After 1.9 h, the reaction was nearly complete by $^{19}$F NMR (i.e., >90% of 1 consumed). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -64.00 (s, 6F, BTBB), -61.1 to -60.2 [ov multiplets, 2(1-hexene)], -59.72 (m, 6F, DHD($^6$Bu), 73% yield), -57.72 (s, 12F, unreacted 1), -60.0 to -51.0 (complex multiplets, [Ni(S$_2$C$_2$(CF$_3$)$_2$)$_2$]$_x$), -55.0 to -53.4 [ov multiplets, 2(1-hexene)].

2.5.10 1 + excess 1-hexene (6.2 mol % [I$^-$]) in CDCl$_3$

A CDCl$_3$ solution (0.50 mL) containing 1 (0.0140 M, 0.0070 mmol) and BTBB (0.0124 M, 0.0062 mmol) was placed in a J. Young NMR tube. Fc*/CDCl$_3$ solution (0.0162 M, 25.0 $\mu$L, 4.0 $\times$ 10$^{-4}$ mmol) was added. 1-Hexene (9.0 $\mu$L, 0.072 mmol) was then added. The NMR tube was sealed and the mixture was allowed to react at 25.0°C for 2.9 h (94% of 1 was consumed during this time). $^{19}$F NMR (470 MHz, CDCl$_3$) (Figure 2.11) $\delta$ -63.89 (s, 6F, BTBB), -60.93 [br s, $\omega_{1/2} = 2.7$ Hz, 3F, 2(1-hexene)], -60.81 to -60.60 [ov m, 2(1-hexene)], -60.53 [q, $^5$J$_{FF} = 11.8$ Hz, 2(1-hexene)], -60.37 [m (q? Poorly resolved), 2(1-hexene)], -59.72
[complex m, DHD(\(^\text{Bu}\))] -57.72 (s, unreacted 1, 6% of initial concentration), -57.55 to -55.54 (complex multiplets, [Ni(S\(_2\)C\(_2\)(CF\(_3\))\(_2\)])\(_x\)), -55.43 [q, \(^5\)J\(_{\text{FF}}\) = 12.1 Hz, 2(1-hexene)], -53.97 [q, \(^5\)J\(_{\text{FF}}\) = 11.7 Hz, 2(1-hexene)], -53.82 [m (q? Poorly resolved), 2(1-hexene)], -53.64 [br s, \(\omega_{1/2} = 2.3\) Hz, 2(1-hexene)]. NMR yields (2.9 h, 25\(^\circ\)C): 2(1-hexene) (61%), DHD(\(^\text{Bu}\)) (27%). See section 2.5.20, below, for \(^1\)H NMR data for 2(1-hexene).

**Figure 2.11** A representative \(^{19}\)F NMR (470 MHz, CDCl\(_3\)) spectrum of the products from 1/[Fc*][\([1]\)] (ca. 94:6) + excess 1-hexene.

Comment: While the selectivity of alkene binding depended on the *relative amounts* of 1 and [\([1]\)] present, the *overall complex concentrations* had no pronounced effect on the selectivity, within the range 7 - 40 mM.

**2.5.11 1 + excess 1-hexene (without [\([1]\)]) in dichloromethane-\(d_2\)**

1 (0.014 M) was reacted with 1-hexene (0.053 M) for 2.9 h at 25\(^\circ\)C in CD\(_2\)Cl\(_2\). \(^{19}\)F NMR (470 MHz, CD\(_2\)Cl\(_2\)) yields (based on internal standard, BTBB): DHD(\(^\text{Bu}\)) (67%), 2(1-hexane) (29%). See sections 2.5.10 and 2.5.20 for \(^{19}\)F and \(^1\)H NMR data for 2(1-hexene).
2.5.12 \( \text{1} + \text{excess 1-hexene (8.7 mol \% [1]) in dichloromethane-d}_2 \)

A CD\(_2\)Cl\(_2\) solution with \( \text{1} \) (0.014 M), Fe\(^*\) (1.2 mM) (to give ca. 91:9 \( \text{1}/[\text{1}]^* \)) and 1-hexene (0.053 M) was allowed to react for 2.4 h at 25\(^\circ\)C. \(^{19}\)F NMR (470 MHz, CD\(_2\)Cl\(_2\)) yields (based on internal standard, BTBB): DHD\(^{n}\)Bu) (13\%), \(2\) (1-hexene) (55\%). See sections 2.5.10 and 2.5.20 for \(^{19}\)F and \(^1\)H NMR data for \(2\)(1-hexene).

Comments: The above experiments show that DHD\(^{n}\)Bu)/decomposition products are also favoured when \( \text{1} \) and 1-hexene are reacted in CD\(_2\)Cl\(_2\), in the absence of \([\text{1}]^*\). As seen for the analogous reactions in CDCl\(_3\), addition of anion perturbs the product distributions to give significantly more interligand alkene adducts \([2\text{(1-hexene)}] \).

2.5.13 \( \text{1} + \text{excess 1-hexene (10 mol \% } ^{\text{Bu}}_3\text{P}) \)

\( \text{1} \) (0.015 M) was reacted with 1-hexene (0.22 M) in the presence of tributylphosphine (1.5 mM) overnight (ca. 18 h) at 20\(^\circ\)C (solvent = CDCl\(_3\)). \(^1\)H NMR (500 MHz, CDCl\(_3\)) yields (based on internal standard, 2-bromochlorobenzene): DHD\(^{n}\)Bu) (31\%), \(2\) (1-hexene) (56\%).

2.5.14 \( \text{1} + \text{excess 1-hexene (with trace water)} \)

\( \text{1} \) (0.015 M) was reacted with 1-hexene (0.11 M) in CDCl\(_3\) (NOT DRIED, sample prepared in air) for 24 h at 20\(^\circ\)C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) yields (based on internal standard, 2-bromochlorobenzene): DHD\(^{n}\)Bu) (26\%), \(2\) (1-hexene) (68\%).

2.5.15 \( \text{1} + 1 \text{ equiv O=CMe}_2 + \text{excess 1-hexene} \)

\( \text{1} \) (10 mg, 0.020 mmol) was dissolved in CDCl\(_3\) (0.4 mL) to give a deep purple coloured solution. Dry acetone (1.4 \(\mu\)L, 1.1 mg, 0.019 mmol) was added, which caused no obvious color change. 1-Hexene (25 \(\mu\)L, 0.20 mmol) was added and the mixture was transferred to a J. Young NMR tube and allowed to react at ambient temperature (20-25\(^\circ\)C) for 1.5 h before analysis by \(^1\)H NMR spectroscopy. The \(^1\)H NMR spectrum indicates that adducts, of type
2(1-hexene), are the dominant products and DHD(n-Bu) is a minor product [2(1-hexene):DHD(n-Bu) ≈ 3:1]. See Figure 2.12, below, for the $^1$H NMR spectrum. See sections 2.5.10 and 2.5.20 for $^{19}$F/$^1$H NMR data for 2(1-hexene).

![Figure 2.12](image)

**Figure 2.12** $^1$H NMR (200 MHz, CDCl$_3$) spectrum of the products of a 1/1-hexene (excess) reaction conducted with acetone (1 equiv) present (2.5.15). 2(1-hexene) is the major product.

Comments: Experiments 2.5.13 and 2.5.14 show that small amounts of phosphine or water in 1/1-hexene systems influence the reactivity in favour of alkene adducts, rather than decomposition products. Note that the result is very similar to adding Fc* to form [1']*. We have shown that water is sufficiently reducing to produce [1']* from 1 (see section 2.3.3). Presumably, electron-rich phosphines also induce reduction of of 1 to [1']. Further, addition of acetone to a 1/1-hexene reaction mixture (2.5.15) causes alkene adducts to be produced as chief products, instead of DHD(n-Bu) and associated metal decomposition products. These observations further support the importance of [1']* in influencing reactivity towards alkene adducts, since acetone (in large excess relative to 1) to is known to reduce 1 to its monoanion.$^{24}$
2.5.16 \( \mathbf{1} + 10 \text{ equiv 1-hexene (no [1])} \) (kinetic experiment)

See 2.5.9 for experimental setup. After mixing the reagents, the NMR sample was quickly sealed, frozen in liquid N\(_2\) and thawed/warmed to RT to collect \(^{19}\)F NMR spectra (470 MHz, CDCl\(_3\), 25.0\(^\circ\)C over time (ca. 1 spectrum/3-4 min for 1.9 h). Concentrations were calculated by comparing starting material/product integrations (from \(^{19}\)F NMR data) to that of BTBB. A representative time trace (for decay of \(\mathbf{1}\)) is shown in Figure 2.13.

![Figure 2.13](image)

**Figure 2.13** A kinetic time trace from \(\mathbf{1} + \) excess 1-hexene (in CDCl\(_3\)) (experimental data points as black circles) overlaid with an exponential fit (grey line, least squares method, implemented by CurveExpert\(^\circledR\)). Experimental: \([\mathbf{1}]_o = 0.014 \text{ M}; [1\text{-hexene}]_o = 0.14 \text{ M}; T = 25.0^\circ\)C. Exponential fit (from least squares method): \([\mathbf{1}] = (0.0157 \text{ mol/L}) \cdot \exp(-5.74 \cdot 10^{-4} \text{ s}^{-1} \cdot t)\), indicating apparent pseudo-first-order decay of \(\mathbf{1}\) over ca. five half-lives.
2.5.17 1 + 10 equiv 1-hexene (6.2 mol % [1]−) (kinetic experiment)

See 2.5.10 for experimental setup. Figure 2.14 shows a representative time trace (for decay of 1). Note that the experimental data is not fit by a pseudo-first-order rate law when [1]− is present, in contrast to the situation where only neutral 1 (and no [1]−) is used. Also, the reaction, as measured by the decay of 1, is slower with the anion present. In the present experiment, consumption of one half of 1 required ca. 2400 s, whereas in the reaction without [1]− (otherwise same conditions, see 2.5.16), the concentration of 1 was reduced by half in ca. 1400 s.

![Figure 2.14 Kinetic time traces from 1 + 10 1-hexene (94:6 1/[1]−) (in CDCl3). [1]o = 0.013 M; [1]−o = 0.8 mM; [1-hexene]o = 0.14 M; T = 25.0°C.](image)

2.5.18 1 + 22 equiv 1-hexene (no [1]−) (kinetic experiment)

A toluene-d₈ solution (0.50 mL) containing 1 (0.0163 M, 0.00815 mmol) and BTBB (0.0154 M, 0.00770 mmol) was added to J. Young NMR tube. 1-Hexene (22.0 μL, 0.176 mmol) was added. The tube was quickly sealed and frozen in liquid N₂ until kinetic analysis (by ¹⁹F NMR, 470 MHz, toluene-d₈, 30.0°C) was commenced. See Figure 2.15 (left) for the time trace (decay of 1).
2.5.19 $1 + 11$ equiv 1-hexene (no $[1]$) (kinetic experiment)

Same experimental setup as 2.5.18, except alkene concentration was reduced by half. See Figure 2.15 (right) for the time trace (decay of 1).

![Figure 2.15](image_url)

**Figure 2.15** Kinetic time traces from $1 +$ excess 1-hexene (in toluene-d$_8$) (experimental data points as black circles), overlaid with exponential fits (grey lines, least squares method, implemented by CurveExpert®). Experimental: Left: $[1]_o = 0.0163$ M; [1-hexene]$_o = 0.352$ M; T = 30.0°C (ca. five half-lives). Right: $[1]_o = 0.0163$ M; [1-hexene]$_o = 0.176$ M; T = 30.0°C (ca. four half-lives). Exponential fit (from least squares method): Left: $[1] = (0.0180$ mol/L) $\cdot \exp(-8.04 \cdot 10^{-4}$ s$^{-1}$ $\cdot t)$. Right: $[1] = (0.0177$ mol/L) $\cdot \exp(-4.41 \cdot 10^{-4}$ s$^{-1}$ $\cdot t)$.

Comments: As reported by Stiefel et al.,$^3$ the decay of 1 follows pseudo-first order behaviour in the presence of excess 1-hexene (in toluene-d$_8$). When alkene is present in 22-fold excess (Figure 2.15, left), $k_{obs} = -8.04 \cdot 10^{-4}$ s$^{-1}$ (from a least squares fit using CurveExpert®). For the case were an 11-fold excess of alkene was used (Figure 2.15, right), $k_{obs} = -4.41 \cdot 10^{-4}$ s$^{-1}$ (from a least squares fit using CurveExpert®). However, these reactions also form a significant amount of DHD($^n$Bu) and metal decomposition products and 2(1-hexene) is formed in less than 50% yield when anion ($[1]^{-}$) is not present. NMR yields (by $^{19}$F NMR): 22-fold excess 1-hexene (1.3 h, 30°C): 2(1-hexene) (45%); DHD($^n$Bu) (50%); 11-fold excess 1-hexene (1.9 h, 30°C): 2(1-hexene) (36%); DHD($^n$Bu) (56%). That more DHD($^n$Bu) is not formed may be related to the $\pi$-basicity of toluene; that is, toluene is sufficiently reducing to produce some $[1]^{-}$. Davison et al. reported that *mesitylene* is capable of partially reducing...
Also, the reaction in toluene-d₈ appears to be slightly slower (as monitored by decay of 1) than the similar experiments in CDCl₃, in agreement with the observations of Stiefel et al. The analogous kinetic experiment (with no [1]) in CDCl₃ (see 2.5.16) was carried out with slightly lower 1/1-hexene concentrations, and at lower temperature, than experiment 2.5.19 (in toluene-d₈). Yet, the experiment in CDCl₃ gave a slightly larger pseudo-first-order rate constant [-5.74 ⋅ 10⁻⁴ s⁻¹ in CDCl₃ (25°C) versus 4.41 ⋅ 10⁻⁴ s⁻¹ in toluene-d₈ (30°C)]. The more rapid consumption of 1 in more polar CDCl₃ likely indicates the importance of charged intermediates leading to DHD(nBu) and/or 2(1-hexene).

2.5.20 1 + excess 1-hexene (15 mol % benzyl sulfide)

1 (12 mg, 0.023 mmol) was combined with CDCl₃ (2.8 mL) in a 25 mL solvent bomb containing a stir bar. A (PhCH₂)₂S/CDCl₃ solution (0.056 M, 60 μL, 0.0034 mmol) was added. 1-Hexene (25 μL, 0.20 mmol) was then added to the dark purple solution. The mixture was allowed to react for 23 h at 20°C. The volatiles, including unreacted alkene, were removed under vacuum. The residue was dissolved in CDCl₃ (ca. 0.7 mL) for spectroscopic analysis. The product is contaminated with (PhCH₂)₂S and a small amount of DHD(nBu). ¹H NMR (200 MHz, CDCl₃) (see Figure 2.16) δ 0.80-1.04 (ov m, RCH₃), 1.13-1.83 (ov m, RCH₂CH₂Me), 1.85-2.21 (br m, Hᵈ or Hᵉ, endo or exo), 2.31-2.59 (br m, Hᵈ or Hᵉ, endo or exo), 2.68-3.30 (ov m, 2/3 DHD(nBu) + ?), 3.34-4.28 [ov m, 2(1-hexene), Hᵃᵇᶜ + 1/3 DHD(nBu)], 3.70 (s, PhCH₂S x 2), 4.67-5.01 (br m, Hᵈ or Hᵉ, endo or exo), 6.87 (m, SCH₂Ph x 2), 7.02-7.41 (ov m, SCH₂Ph x 2).
Figure 2.16 $^1$H NMR (200 MHz, CDCl$_3$) spectrum of products (primarily 2(1-hexene) isomers) from 1 + excess 1-hexene (15 mol% (PhCH$_2$)$_2$S).

2.5.21  Reduction (with sodium) of 2(1-hexene) to release 1-hexene

Crude 2(1-hexene) (ca. 10 mg) produced in 2.5.20 was dissolved in THF-d$_8$ (0.8 mL). Excess metallic sodium (ca. 40 mg) was added to the brown solution and the mixture was left to react at ambient temperature for 40 h. A $^1$H NMR spectrum showed free 1-hexene.

$^1$H NMR (200 MHz, THF-d$_8$) (for alkenyl protons of 1-hexene) δ 4.89 (m, 2H, H$^a$H$^b$C=C), 5.74 (m, 1H, C=CH$^b$Bu). Alkene release under reducing conditions$^{3,22}$ (metallic sodium) confirms our assignment of the new species as 1-hexene interligand adducts [2(1-hexene)] (as a mixture of isomers, see 2.3.2).

2.5.22  Partial reduction of 1 to [1]$^+$ with excess water (in CH$_2$Cl$_2$)

1 (28.8 mg, 0.0564 mmol) was dissolved in CH$_2$Cl$_2$ (30.0 mL), giving a deep purple solution. In air, distilled water (5.0 mL, 0.28 mol) was added to the 1/CH$_2$Cl$_2$ solution. The bilayer mixture was stirred at ambient temperature (25-30$^\circ$C) for 10 min, during which time
the aqueous portion developed a green-brown color, while the organic phase remained purple. The phases were separated and the aqueous phase was diluted to ca. 1/3 its original concentration, by addition of more distilled water. The resulting solution was analyzed by UV-vis spectroscopy (Figure 2.17).

![UV-vis spectrum of [1CF3]- in water](image)

**Figure 2.17** UV-vis spectrum of 1 reduced to [1]⁻ using excess water (spectrum collected in water).

Comments: The above spectrum (Figure 17) indicates the presence of [1]⁻ by its characteristic absorbance signals (e.g., \( \lambda_{\text{max}} \approx 510 \text{ nm and } 810 \text{ nm}; \) cf. Figure 2.3(b and c), section 2.3.3). The reduction of 1 to [1]⁻ proceeds quantitatively when equimolar amounts of 1 and water are combined in THF (2.3.3). In CH₂Cl₂, however, reduction occurs primarily at the at the CH₂Cl₂/water interface. Presumably, the solvation energy for the ion pair is greater in THF, compared with CH₂Cl₂, which drives the reduction to completion in the THF case.

**2.5.23 1 + 1.5 equiv Fc* + 20 equiv 1-hexene (no reaction)**

1 (11.2 mg, 0.022 mmol) was combined with Fc* (10.8 mg, 0.033 mg) in a vial with a stir bar. CDCl₃ (2 mL) was added to give a brown-green coloured solution, with some precipitate visible. 1-Hexene (50 μL, 0.40 mmol) was added. The mixture was allowed to react at ambient temperature (25-30°C), with stirring, for ca. 18 h. The slurry was passed
through a 2 cm plug of silica gel (dry) in a Pasteur pipet. A NMR sample was prepared from the filtrate. A $^1$H NMR (200 MHz, CDCl$_3$) spectrum shows only unreacted 1-hexene. Alkene adducts [2(1-hexene)] and DHD($^\delta$Bu) were not observed.

Comments: The formation of 2(1-hexene) and/or DHD($^\delta$Bu) requires neutral 1, in accord with the mechanistic proposal outlined in section 2.3.4.2.

2.5.24  1 + excess 1-hexene (with [NEt$_4$]$^+$[1]$^-$, ca. 5 mol %)

1 (5.0 mg, 0.0098 mmol) was dissolved in CDCl$_3$ (0.4 mL). [NEt$_4$]$^+$[1]$^-$ was added as a CDCl$_3$ solution (120 μL, 0.004 M, 5×10$^{-4}$ mmol). The resulting solution was placed in a J. Young NMR tube and 1-hexene (10 μL, 0.080 mmol) was then added. The mixture was allowed to react at RT (ca. 25°C) for 1.5 hour before an NMR spectrum was obtained. $^1$H NMR shows the dominant product is 2(1-hexene) [2(1-hexene):DHD($^\delta$Bu) ≈ 3:1]. A control experiment without [NEt$_4$]$^+$[1]$^-$ (otherwise same conditions) gave DHD($^\delta$Bu) as the major product [DHD($^\delta$Bu):2(1-hexene) ≈ 3:1].

2.5.25  Synthesis of 2((E)-1-D-1-hexene)

1 (50 mg, 0.098 mmol) was combined with Fc* (4.8 mg, 0.015 mmol) and dissolved in CH$_2$Cl$_2$ (4 mL). (E)-1-D-1-hexene (110 μL, 0.88 mmol) was added to the purple solution. Note that the deuterated alkene was contaminated with a small amount of SME$_2$ (residue from synthesis) (ca. 5%). Organic sulfides influence reactivity in favor of interligand alkene adducts (see 2.5.20). The mixture was allowed to react at ambient temperature (25-30°C) for 1.75 h, with stirring, and the color changed from deep purple to dark brown. The resulting brown solution was passed through a 3 cm plug of dry silica gel in a Pasteur pipet. From the brown colored eluent, the volatiles were removed under vacuum to give dark brown-green residue. A portion of this material was dissolved in CDCl$_3$ for spectroscopic analysis. The spectrum shows primarily alkene adduct and a very small amount of DHD($^\delta$Bu)-d$_1$. Figure 2.18 shows the $^1$H NMR spectrum of the product mixture. See 2.5.20 for $^1$H NMR data for all-protio-DHD($^\delta$Bu).
In a separate experiment, but using similar reaction conditions to those described in 2.5.25, a high-resolution spectrum of $2((E)-1$-$D$-$1$-hexene) was obtained at 500 MHz field strength. The partial high-resolution spectrum is shown and compared with the spectrum of the all-protio analogue in Figure 2.4, section 2.3.4.1.

2.5.26 Photolysis of $2((E)-1$-$D$-$1$-hexene) to release alkene

Crude $2((E)-1$-$D$-$1$-hexene) (ca. 30 mg, 0.05 mmol) produced in 2.5.25 was dissolved in CDCl$_3$, (2.5 mL) giving a dark brown colored solution, which was placed in a bomb. The bomb was attached to a fluorescent light bulb (with aluminum foil backing to maximize light exposure) and was photolyzed at room temperature (25-30$^\circ$C) overnight (ca. 18 h). During this time, the solution changed color from dark brown to deep purple. A portion of the solution was passed through a 1 cm plug of silica gel (dry) in a Pasteur pipet and the eluent was collected in an NMR tube for spectroscopic analysis. The alkene region of the $^1$H NMR spectrum of the product is shown below, and compared with the spectrum of authentic $(E)-1$-$D$-$1$-hexene$^{25}$ (Figure 2.19).
Figure 2.19 $^1$H NMR (500 MHz, CDCl$_3$) spectra of (a) authentic $(E)$-1-$d$-1-hexene$^{25}$ and (b) the alkene product from photolysis of 2($(E)$-1-$d$-1-hexene).

Comments: The alkenyl resonances in the $^1$H NMR spectrum of the products of the photolysis of 2($(E)$-1-$d$-1-hexene) are identical to those of free $(E)$-1-$d$-1-hexene, indicating that the alkene retains its stereochemical configuration upon addition/release to/from 1. Also, some DHD($^a$Bu)-d$_1$ is formed in the photolysis of 2($(E)$-1-$d$-1-hexene) (free alkene:DHD($^a$Bu)-d$_1$ $\approx$ 3:2). Recall that photolysis of 2(ethylene) gives, in addition to free alkene, a significant amount of DHD(H) (see 2.5.8). These results are expected, since irradiation of alkene adducts is expected to form 1 and free alkene, which, we have shown, react by a preferred pathway to afford DHD derivatives.

2.5.27 1 + 2(ethylene) (1:1)

2(ethylene) (21 mg, 0.038 mmol), 1 (19 mg, 0.038 mmol) and BTBB (8.0 mg, 0.027 mmol) were combined in dry CDCl$_3$ (1.2 mL), giving a very dark purple-brown standard solution with 0.032 M in both adduct and dithiolene ([BTBB] = 0.023 M). One half of this solution was placed in a J. Young NMR tube for spectroscopic analysis. $^1$H NMR (200 MHz, CDCl$_3$) (Figure 2.20) (20°C) δ 2.50 – 3.38 (br s, $\omega_{1/2}$ = 36.3 Hz, H$^c$ or H$^d$), 3.43 - 4.30 (ov m, H$^c$ or
H<sup>d</sup> and H<sup>a</sup> or H<sup>b</sup>), 4.55 (m, H<sup>a</sup> or H<sup>b</sup>). Equation 2.2 shows the labeling of the relevant protons. X-ray quality crystals of 2(ethylene)-1 (see Scheme 2.4, above, for the structure) were obtained by slowly evaporating (to near-dryness, in air) a CH<sub>2</sub>Cl<sub>2</sub> solution containing a 1:1 mixture of 1 and 2(ethylene).

![Figure 2.20 1H NMR (200 MHz, CDCl<sub>3</sub>) spectrum of 1 + 2(ethylene) (1:1, both species 0.032 M).](image)

**Figure 2.20** 1H NMR (200 MHz, CDCl<sub>3</sub>) spectrum of 1 + 2(ethylene) (1:1, both species 0.032 M).
Comments: The new species $[2$(ethylene)$\cdot 1$] (Equation 2.2), formed by reaction between 1 and 2(ethylene) was discussed in section 2.3.2 and the product (in equilibrium with starting materials, see below) was crystallographically characterized (2.3.2, Scheme 2.4, inset). When $[1]_o = [2$(ethylene)$]_o = 32$ mM (at $20^\circ$C), the ratio of the binuclear compound to 1 and 2(ethylene) is ca. 1.5 (i.e., $[2$(ethylene)$\cdot 1]_{eq}/[1]_{eq}(=[2$(ethylene)$]_{eq}) \approx 1.5$). At lower concentration ($[1]_o = [2$(ethylene)$]_o = 8$ mM), this equilibrium is shifted to the left, away from the binuclear species ($[2$(ethylene)$\cdot 1]_{eq}/[1]_{eq}(=[2$(ethylene)$]_{eq}) \approx 0.5$). Note that $^1$H NMR spectra for 1 + 2(ethylene) (1:1) are invariant with time (>72 h, RT), once equilibrium is established (<15 min). The change of distribution of the species in equilibrium with change in absolute concentration is consistent with an $A + B \rightleftharpoons C$ equilibrium, with $K_{eq} = 0.1$ mM$^{-1}$.

2.5.28 $\text{1 + 2(ethylene) (ca. 1:1) + excess ethylene (5.3 mol % [1])}$

2(ethylene) (11 mg, 0.021 mmol) and 1 (10 mg, 0.020 mmol) were combined with CDCl$_3$ (0.8 mL), giving a very dark purple-brown (nearly black) coloured solution. This solution was placed in a NMR tube and allowed to sit at ambient temperature (protected from light) for ca. 20 min before a $^1$H NMR spectrum was obtained [Figure 2.21(a)]. BTBB (4.2 mg, 0.014 mmol) (internal standard) and Fe* (32 μL of 0.032 M solution in CDCl$_3$, 1.0x10$^{-3}$ mmol) were added to the mixture. In air, the NMR sample was quickly opened and ethylene was bubbled through the sample to saturate the solution. The NMR tube was quickly sealed and the resulting mixture was allowed to react at ambient temperature for 2.2 h and an NMR spectrum was obtained [Figure 2.21(b)].
Figure 2.21 $^1$H NMR (200 MHz, CDCl$_3$) spectra for (a) 1 + 2(ethylene) (1:1) (20 min, RT) and (b) products of 1 + 2(ethylene) + excess ethylene + Fc* (5.3 mol %) (2.2 h, RT).

Comments: The equilibrium mixture of 1, 2(ethylene) and 2(ethylene)-1 reacts with excess ethylene to afford mostly interligand adduct [2(ethylene)] and a small amount of DHD(H), in the presence of Fc* (5.3 mol %) (Figure 2.21). Therefore, the new species is not an important intermediate in the formation of DHD(H) and metal decomposition products. However, mechanistic/kinetic models will likely need to account for the decreased effective concentration of 1 caused by its equilibrium with alkene adducts 2(alkene).

2.6 References

Chapter 2 – Alkene Reactivity of an Electrophilic Nickel Bisdithiolene $[\text{Ni(S}_2\text{C}_2(\text{CF}_3)_2]^2]$  

[4] For example, noninnocent $[\text{Re(DPPBT)}]^{3+}$ ($[\text{DPPBT}]^- = 2$-diphenylphosphinobenzenedithiolate) binds ethylene (S,S- inter ligand adduct) for $n = 2$, and the alkene can be released by reduction: Grapperhaus, C. A.; Ouch, K.; Mashuta, M. S. *J. Am. Chem. Soc.*, 2009, 131, 64.


[6] Compound 1 might react in its triplet state. For $\text{Ni(S}_2\text{C}_2\text{Me}_2)^2$, the triplet state is computed (DFT) to be uphill by 60 kJ/mol in the ground state geometry: Szilagyi, R. K.; Lim, B. S.; Glaser, T.; Holm, R. H.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* 2003, 125, 9158.


[10] The representation of the metal bisdithiolene LUMO in Scheme 1 (and throughout chapter 2) omits, for clarity, the small metal-based AO contribution.

[11] DHD(H), in our nomenclature system, corresponds to 5,6-bis(trifluoromethyl)-2,3-dihydro-1,4-dithiin. DHD($^n$Bu): 2-butyl-5,6-bis(trifluoromethyl)-2,3-dihydro-1,4-dithiin (see ring number system in Scheme 2, section 2.2).

[12] Yields are based on 1, using product integration ($^1$H/$^19$F NMR) versus the internal standard 3,5-bis(trifluoromethyl)bromobenzene (BTBB). For reactions where a fraction of 1 was reduced with Fe*, yields are based on 1 present after reduction.

[13] In reactions where DHD(R) was formed, corresponding amounts of metal decomposition products were visible as a numerous overlapping $^19$F NMR resonances, for ill-defined $[\text{Ni(S}_2\text{C}_2(\text{CF}_3)_2]^n]_n$.

[14] DHD(H) and DHD($^n$Bu) were prepared by heating (ca. 80°C) ethylene or 1-hexene with the dithiete $\text{S}_2\text{C}_2(\text{CF}_3)_2$ (see 1.3.3 for structure), according to: Krespan, C. G.; McKusick, B. C. *J. Am. Chem. Soc.* 1961, 83, 3438. Detail in experimental section.

[15] Spectra are temperature-dependent due restricted C-CF$_3$ bond rotation and/or ring puckering. See the experimental section for details.

[16] Expectedly, some 1 reacted with the released alkene to produce DHD(H) and associated decomposition products.


[18] Note that $[1]^'$ does not react with 1-hexene in the absence of 1. As proposed in Scheme 2.6, it is possible that $[1]^'$ and free alkene are in equilibrium with $[2(\text{alkene})]^'$. If so, then neutral 1 is required to oxidize $[2(\text{alkene})]^'$, resulting in net conversion of alkene, 1 and $[1]^'$ to $[2(\text{alkene})]$ and $[1]$.

[19] For crystallographic details [including a Crystallographic Information File (cif format)] for $[2(\text{ethylene})]$, see the supporting information for ref. 1.
Similarly large DHD(\textsuperscript{	exttrademark}Bu):2(1-hexene) product ratios were observed in CD\textsubscript{2}Cl\textsubscript{2} and toluene-d\textsubscript{8} when [1] was not present.


Harrison, D. J.; Lough, A. J.; Fekl, U. Unpublished results. More details can be found in the experimental section.


Harrison, D. J.; Lough, A. J.; Fekl, U. Unpublished results. More details can be found in the experimental section.


Me\textsubscript{2}S was present as a contaminant (ca. 5 \%) in (E)-1-D-1-hexene (residue from the synthesis of the deuterated alkene). For the synthesis of (E)-1-D-1-hexene, see: Kabalka, G. W.; Newton, R. J., Jr.; Jacobus, J. J. Org. Chem. 1978, 43, 1567.

In CDCl\textsubscript{3} or toluene-d\textsubscript{8} in presence of excess 1-hexene. In the absence of [1], decay of 1 is pseudo-first order, as reported in ref. 3.

This proposal is novel, and transition states for this mechanism have not yet been computed. However, in the context of alkene release, the thermodynamics of [Ni(S\textsubscript{2}C\textsubscript{2}(CN))\textsubscript{2}(ethylene)]\textsuperscript{+} (interligand adduct) versus [Ni(S\textsubscript{2}C\textsubscript{2}(CN))\textsubscript{2}] + ethylene were computed (Ref. 9): \( \Delta H = 38 \text{ kJ/mol} \) (not prohibitively uphill).


Control experiments, without internal standard, establish that BTBB does not affect reactivity/product distributions in 1/alkene systems.

Because Fc* quantitatively reduces an equimolar portion of 1, mol % ([1]-1) is calculated by comparing the amounts of 1 and [1] that are present after reduction occurs. For example, adding Fc* (5.8 mol \%, relative to 1) to 1 gives a 5.8:94.2 mixture of ([1]-1), and anion is present in 6.2 mol \% relative to neutral 1.
Chapter 3

Unprecedented Reactivity of a Platinum Bisdithiolene with a Conjugated Diene

3.1 Abstract

The reaction of Pt(S$_2$C$_2$(CF$_3$)$_2$)$_2$ (1) with excess 2,3-dimethyl-1,3-butadiene initially yields the expected 1:1 adduct in which the diene has added across two sulfur atoms on separate S$_2$C$_2$(CF$_3$)$_2$ ligands. However, within 1 d at 50°C, this kinetic product quantitatively converts into a thermodynamic product where two dienes have added to one S$_2$C$_2$(CF$_3$)$_2$ ligand via unprecedented addition across the dithiolene CS bonds. The new reaction is highly selective for the C$_2$-symmetric diastereomer. A new chiral bisthioether chelate ligand has formed in the product, which has been characterized crystallographically. Most of the work described here has been published, with the exception of the phosphine-ligand substitution reactions. Initial experiments, including first the synthesis and characterization of the intraligand bisdiene adduct (complex 3, see below), were conducted by Mitchell J. Kerr (undergraduate researcher).

3.2 Introduction

As discussed in chapter 1, group 10 metal bisdithiolenes, M(S$_2$C$_2$R$_2$)$_2$ (M = Ni, Pd, Pt), were among the first metal complexes to demonstrate ligand-centered reactivity toward both monoolefins$^{2b-1}$ and 1,3-dienes.$^{2l,3}$ Although this reactivity was discovered decades ago, the field is far from being mature. Potential industrial applications for metal dithioleines were suggested comparatively recently (2001) (see section 1.4.3.2),$^{2e}$ in the context of alkene binding, but applications will require a better understanding of fundamental reactivity.

Theoretical studies$^4$ have shed some light on the reactions of unsaturated hydrocarbons (alkenes, dienes) with metal bisdithiolenes, although experimental findings continue to provide surprises. For reactions between alkenes and metal bisdithiolenes, intraligand alkene

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addition was initially proposed\textsuperscript{2k,1} [Scheme 3.1(a)]\textsuperscript{5} on the basis of frontier orbital analyses (see also chapters 1 and 2). Yet, despite expectations, the first characterized\textsuperscript{2h,1} alkene adducts of metal bisdithiolene revealed symmetry-forbidden \textit{interligand} binding [see Scheme 3.1(b)] of the organic substrates, thus casting doubt on the utility of frontier MO analysis for predicting metal bisdithiolene reactivity. More recent results, however, point to the validity of MO approaches for understanding the reactions of metal bisdithiolenes. Recall from chapter 2 that pure Ni(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3}))\textsubscript{2} reacts with alkenes (in rigorously purified/dried solvents) according to the Woodward-Hoffmann rules,\textsuperscript{6} giving symmetry-allowed intraligand addition [see Scheme 3.1(a)] preferentially. The symmetry-forbidden interligand addition pathway [Scheme 3.1(b)] is mediated, in impure samples, by the odd-electron species [Ni(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3}))\textsubscript{2}]\textsuperscript{-}.\textsuperscript{2b} Further, MO arguments were recently applied to the alkene reactivity of metal \textit{tris}dithiolenes, correctly predicting symmetry-allowed intraligand addition (see chapter 4).\textsuperscript{2a} Thus, frontier orbital arguments,\textsuperscript{2f,3a,b,4a} based on a spin-restricted (“closed shell”) picture, are extremely useful for predicting the reactivity of metal dithiolene complexes, despite the possibility of some singlet diradical (“open shell”) character for certain metal dithiolene complexes.\textsuperscript{4b,c,7}
3.3 Results and Discussion

The reactivity of square planar metal bisdithiolenes toward 1,3-dienes [e.g., 1,3-butadiene, Scheme 3.1(c-e)] has received less attention than their reactions with alkenes. Given the confusion surrounding the reactions of alkenes with metal bisdithiolenes (see chapter 2), the analogous diene reactions deserve to be revisited. In section 1.4.3.2, the reactions of conjugated 1,3-dienes with electrophilic metal bisdithiolenes were introduced. Prior to our work, only symmetry-allowed interligand addition products had been observed [Scheme 3.1(c); other conceivable reactions: Scheme 3.1(d,e)]\textsuperscript{21,3} We have investigated the reactions of the platinum bisdithiolene Pt(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3})\textsubscript{2})\textsubscript{2} (complex 1) with 2,3-dimethyl-1,3-butadiene. The platinum complex was chosen over the nickel bisdithiolene (i.e., Ni(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3})\textsubscript{2})\textsubscript{2}, see chapter 2) to enhance the stability of the products of diene addition; that is, based on hard/soft Lewis acid/base arguments, [Pt]-SR (metal-thiolate) and, particularly, [Pt]-SRR’ (metal-thioether) bonds are expected to be more robust than the corresponding bonds to nickel. Here, we describe our results, including the first example of intraligand C,S-addition of a 1,3-diene to a metal bisdithiolene.

3.3.1 NMR studies on Pt(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3})\textsubscript{2})\textsubscript{2} (1)/diene systems

The reactions of the platinum bisdithiolene with excess 2,3-dimethyl-1,3-butadiene were monitored by NMR spectroscopy. The reaction of 1 (ca. 10 mM in C\textsubscript{6}D\textsubscript{6}) with excess (4 equiv) diene is complete within less than 10 min at room temperature. S,S-Interligand addition is allowed by orbital symmetry [see Scheme 3.1(c)], and an interligand adduct (complex 2) is indeed observed, unambiguously assigned by \textsuperscript{19}F NMR (Figure 3.1, top) and \textsuperscript{1}H NMR spectroscopy (see experimental section). The \textsuperscript{1}H NMR spectrum is similar to the reported data\textsuperscript{3a} for the 2,3-dimethyl-1,3-butadiene adduct (interligand) of the analogous nickel complex, Ni(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3})\textsubscript{2})\textsubscript{2}, which has been crystallographically characterized.\textsuperscript{3b} A 1,3-diene (cyclohexa-1,3-diene) adduct of the palladium complex Pd(S\textsubscript{2}C\textsubscript{2}Ph\textsubscript{2})\textsubscript{2} also exhibits an interligand structure.\textsuperscript{3c} Using an internal standard with both hydrogens and fluorines (3,5-bis(trifluoromethyl)bromobenzene, BTBB), we confirmed 1:1 bisdithiolene/diene
stoichiometry for the initially formed adduct 2. However, a small amount of a new compound (3) can be seen (Figure 3.1, top), in addition to the interligand adduct 2. Conversion to complex 3 is complete in less than 20 h at 50 °C (Figure 3.1, bottom).

**Figure 3.1** $^{19}$F NMR spectra for a reaction mixture involving 1 (5 μmol) and excess 2,3-dimethyl-1,3-butadiene (20 μmol) in C₆D₆ (ca. 0.5 mL). Top: ca. 7 min after mixing (at RT): 2 is observed and trace 3 is already visible. Bottom: after heating to 50 °C for 20 h: complete conversion to 3.

NMR integration versus the internal standard BTBB shows that in 3, two dienes bind to one metal complex. Valuable structural information is obtained from $^{19}$F NMR spectroscopy: In diene adducts 2 and 3, the original high symmetry of 1 ($D_{2h}$) is lost, such that two sets of non-equivalent $^{19}$F NMR signals (each corresponding to two CF₃ groups) are observed for each complex. In compound 2, where the two CF₃ groups within a F₃C-CC-CF₃ subunit are non-equivalent, the fluorine signals occur as quartets ($^5J_{F-F} = 12.7$ Hz) (Figure 3.1, top). In contrast, for compound 3, the two CF₃ groups in each F₃C-CC-CF₃ substructure are equivalent, as seen from the fact that the $^{19}$F NMR spectrum for 3 shows two singlets; if the two CF₃ groups on each F₃C-CC-CF₃ unit were non-equivalent, quartets (as seen for 2) would be expected due their close van der Waals contacts, while F-F coupling is not observed between CF₃ groups on separate F₃C-CC-CF₃ units. It is therefore concluded that both dienes have added to one $S_2C_2(CF_3)_2$ ligand in 3. For complex 3, one set of fluorines is clearly coupled to $^{195}$Pt (12.6 Hz, expanded view in Figure 3.1, bottom), but the F-Pt
coupling is too small to be detected for the other resonance. The signal exhibiting F-Pt coupling can be reasonably assigned to the intact dithiolene ligand and the signal lacking Pt satellites should be attributed to the comparatively weakly bound bisthioether ligand formed by double diene addition.

### 3.3.2 Solid state structure of the bisdiene adduct (3) and mechanistic considerations

Crystals of 3 (as a benzene solvate) were grown from a concentrated solution in benzene at 12°C, and an X-ray crystallographic structure determination was carried out. The result (Figure 3.2) is fully consistent with solution NMR data and yields additional information: the symmetry element retained in complex 3 is not a mirror plane but a $C_2$ axis. That is, two dienes have added to one $S_2C_2(CF_3)_2$ ligand in C,S-intraligand [see Scheme 3.1(e)] fashion, but on opposite sides of the PtS$_4$ plane. This binding mode is unprecedented for metal dithiolenes, but it is in accord with frontier orbital expectations (Scheme 3.1).

![Figure 3.2](image)

**Figure 3.2** Molecular structure of 3, using 30% thermal ellipsoids. Hydrogen atoms are not shown, for clarity. Primed atoms are related to corresponding non-primed atoms by a crystallographic two-fold rotation axis. Selected distances and angles (Å, deg): Pt1-S1, 2.260(2); Pt1-S2, 2.302(1); S1-C1, 1.761(6); S2-C8, 1.814(5); S2-C3, 1.865(6); C1-C1’, 1.34(1); C3-C3’, 1.58(1); C3-C5, 1.564(6); C5-C6, 1.517(7); C6-C7 1.315(8); C7-C8, 1.493(7); S1-Pt1-S1’, 89.45(8); S2-Pt1-S2’, 88.81(7).
The reaction that gives 3 is high-yielding (quantitative conversion by NMR, 81 % isolated yield on a 0.1 g scale) and shows complete stereospecificity, yielding exclusively the $C_2$-symmetric isomer which features a new chiral bisthioether chelating ligand. The $C_2$-chiral ligand itself has two stereogenic centers (C3, C3’ in Figure 3.2) and complex 3 has two additional stereocenters due to chirality at the Pt-coordinated sulfur atoms (S2, S2’). The observed (Figure 3.2) configurations of the chiral sulfur atoms, relative to the adjacent chiral carbon atoms, is in line with a mechanism involving concerted syn-facial attack of the diene at the CS bond (Scheme 3.2, top). It is also conceivable that the diene addition occurs in a stepwise (nonconcerted) manner.\(^\text{10}\) If a stepwise mechanism was operating, the same stereospecificity for diene addition to the CS bonds would be expected, as the observed structure minimizes ring strain (Scheme 3.2, bottom). Future work could investigate solvent effects on the reaction rate to provide insight into the mechanism (e.g., concerted or stepwise) of diene addition.\(^\text{11}\) Regardless of the mechanism of CS diene addition, it should be syn-facial with respect to the CS bonds, giving the less strained syn addition product, as shown in Scheme 3.2.

Scheme 3.2

In complex 3, two C$_5$S$_1$ rings are formed by the addition of two dienes. Considering the diastereospecificity discussed above for the formation of a single C$_5$S$_1$ ring (affording the syn-facial addition product), two diastereomers are still possible for 3, depending on the
orientation of the newly formed C$_5$S$_1$ rings with respect to each other. Complex 3 could, in principle, adopt a C$_5$-symmetric meso structure, with both C$_5$S$_1$ rings on the same face of the PtS$_4$ plane, but only the C$_2$-chiral isomer, with the rings situated on opposite sides of the plane, is observed (Scheme 3.3).

A proposed mechanism for the formation of 3 is shown in Scheme 3.3. The initial binding of 2,3-dimethyl-1,3-butadiene to 1 to yield 2 is reversible, as we directly observed by NMR spectroscopy. Using a dilute (ca. 1 mM or less) solution of 2 with a small excess (ca. 2 equiv) of diene, complex 2 and a small amount of 1 were observed in equilibrium (at higher concentrations, 1 was not detectable by $^{19}$F NMR). Formation of 2 from 1 and 2,3-dimethyl-1,3-butadiene is associated with an equilibrium constant $K = 9(2) \times 10^3$ M$^{-1}$ (in C$_6$D$_6$ at 296 K).$^{12}$ It is reasonable to assume that the diene dissociates from 2 and then forms a monodiene-C,S-adduct (Scheme 3.3, structure in square brackets). The latter compound is expected to be highly reactive due to its pronounced thioketone character, but attack of the second diene should occur at the sterically more accessible side, forming C$_2$-symmetrical 3, rather than the C$_5$-isomer (Scheme 3.3). In contrast to compound 2, the formation of 3 is irreversible under the conditions we examined (no diene was lost in dilute solution or upon prolonged exposure to vacuum at RT).
3.3.3 Ligand substitution reactions of complex 3: toward catalysis?

Chiral chelating bisthioethers are useful for several enantioselective reactions, most prominently allylic substitutions.\(^\text{13}\) Achieving high yields of a $C_2$-chiral ligand instead of the $C_3$-symmetrical meso diastereomer is not trivial, and the newly discovered diastereospecific bisdiene-addition reaction described above thus appears promising for applications in ligand synthesis. Clearly, stoichiometric reactions involving platinum are not ideal for generating such ligands, considering the cost of the metal. However, the approach would be very attractive if the bisthioether could be formed by catalytic reactions between the 1,3-diene and the dithiete, $S_2C_2(CF_3)_2$, using a substoichiometric amount of the platinum bisdithiolene. Scheme 3.4 illustrates the suggested catalytic scenario. In the simplest case, the $C_2$-chiral ligand is displaced from the bisdiene adduct by $S_2C_2(CF_3)_2$, regenerating the neutral bisdithiolene, which then undergoes double diene addition (as described above) to regenerate the bisdiene adduct (Scheme 3.4).

![Scheme 3.4](image)

After verifying that $S_2C_2(CF_3)_2$ and 2,3-dimethyl-1,3-butadiene do not react in the absence of a catalyst,\(^\text{14}\) we attempted to implement such a cycle. Dithiete $S_2C_2(CF_3)_2$ and diene (2 equiv) were allowed to react in the presence of 1 (4 mol %) ($61^\circ\text{C}$, 20 h).\(^\text{15}\) The product
mixture contained a significant amount of starting materials (ca. 50% by $^1$H/$^{19}$F NMR), and $^1$H/$^{19}$F NMR data showed many products (oligomeric/polymeric), but no $C_2$-chiral ligand (based on comparison to authentic free ligand, see below). Thus, the catalytic cycle depicted in Scheme 3.3 is probably not feasible, possibly because the diethiete $S_2C_2(CF_3)_2$ is not sufficiently nucleophilic to displace the bisthioether ligand from complex 3, as suggested by the complete absence of the free bisthioether ligand in this product mixture.

We have recently shown that the bisthioether ligand can be cleanly substituted with 1,2-bis(diphenylphosphino)ethane (dppe) or with trialkyl/aryl monophosphines (PBu$_3$ or PPh$_3$, 2 equiv) under mild conditions. Specifically, the reaction between complex 3 and phosphine (dppe or PR$_3$; R = $^n$Bu or Ph) (RT in CDCl$_3$ or C$_6$D$_6$) liberated free bisthioether and formed the metal complexes (dppe)Pt($S_2C_2(CF_3)_2$) or (R$_3$P)$_2$Pt($S_2C_2(CF_3)_2$) (yields >90% by $^1$H/$^{19}$F/$^{31}$P NMR) (Scheme 3.5).

The above results highlight the possibility of using “stepwise” catalysis to form the bisthioether ligand, since the ‘Pt($S_2C_2(CF_3)_2$)’ fragment, when ligated with two phosphine donors, can be potentially converted to the bisdithiolene complex, 1, by treatment with excess $S_2C_2(CF_3)_2$. Indeed, the literature preparation of 1 involves the bisphosphine intermediate (Ph$_3$P)$_2$Pt($S_2C_2(CF_3)_2$), which is reacted with $S_2C_2(CF_3)_2$ (at least 3 equiv) to

![Scheme 3.5](image-url)
afford the bisdithiolene and SPPh$_3$ (2 equiv, and [SC$_2$(CF$_3$)$_2$]$_n$). Similariy, a mixed-ligand trisdithiolene, Mo(S$_2$C$_6$H$_4$)$_2$(S$_2$C$_2$(CF$_3$)$_2$)$_2$, has been synthesized by reacting (H$_6$C$_6$S$_2$)$_2$Mo(PPh$_3$Me)$_2$ with S$_2$C$_2$(CF$_3$)$_2$ (see chapter 4). Thus, a modified stepwise cycle can be envisioned, where phosphine (e.g., PPh$_3$, 2 equiv) is used to displace the Pt-bound bisthioether; the resulting platinum bisphosphine complex is converted to the neutral bisdithiolene by treatment with S$_2$C$_2$(CF$_3$)$_2$ (3 equiv) (Scheme 3.6). The formation of SPR$_3$ provides the driving force for the removal of the metal-bound phosphines, but also necessitates the use of sacrificial dithiete and phosphine equivalents. Accordingly, it will likely be possible to prepare the C$_2$-chiral bisthioether ligand, in free form, using a substoichiometric amount of platinum catalyst, through a process such as the one illustrated in Scheme 3.6.

![Scheme 3.6](image)

3.4 Conclusion

We have demonstrated the first example of intraligand 1,3-diene addition to a metal bisdithiolene. Specifically, 1 reacts with 2,3-dimethyl-1,3-butadiene to afford the expected monodiene interligand adduct (complex 2, above) as the kinetic product. The kinetic product reacts further to cleanly yield a double diene adduct (thermodynamic product), with
complete diastereospecificity for the $C_2$-chiral isomer (complex 3). The chiral bisthioether ligand in this complex is of interest for applications in enantioselective catalysis; we found that the ligand can be displaced from the metal with a variety of phosphine donors. Ongoing work will focus on finding conditions to make the bisthioether catalytically, either by employing a stepwise approach (see Scheme 3.6) or by screening other metal dithiolenes for catalytic activity.

3.5 Experimental Section

3.5.1 General Considerations

Samples were prepared in an inert (nitrogen) atmosphere using standard glovebox (MBraun Unilab) and Schlenk-type techniques. Reagents were purchased from Sigma-Aldrich if not specified otherwise. Benzene and benzene-$d_6$ ($C_6D_6$, from Cambridge Isotopes), were dried over sodium/benzophenone and vacuum-transferred prior to use. Chloroform-$d$ (CDCl$_3$) was dried over CaH$_2$ and vacuum-transferred before using. Compound Pt(S$_2$C$_2$(CF$_3$)$_2$)$_2$ (1) was prepared using the three-step procedure reported in the literature,$^{18}$ starting from commercially available (Strem) Pt(PPh$_3$)$_4$ and 1,2-bis(trifluoromethyl)dithietene, S$_2$C$_2$(CF$_3$)$_2$. The latter compound was prepared according to Krespan’s$^{20}$ procedure and freshly distilled before use. 1,2-Bis(diphenylphosphino)ethane (dppe) (Strem, 99%) and tributylphosphine (PBU$_3$) (99%) were obtained commercially. $^1$H and $^{19}$F NMR spectra were collected on a Bruker Avance III 400 MHz instrument. Residual proton peaks were used as reference: $^1$H ($\delta$, ppm, benzene-$d_6$, 7.16). $^{19}$F spectra were referenced against internal 3,5-bis(trifluoromethyl)bromobenzene (BTBB, 99%) set to $\delta$ -64.00; external reference trifluoroacetic acid appeared at $\delta$ -76.58 in $C_6D_6$ and $\delta$ -76.52 in CDCl$_3$. Elemental analysis was performed at ANALEST, University of Toronto. Mass spectrometry (ESI) was performed at Advanced Instrumentation for Molecular Structure (AIMS), Toronto, ON, Canada, using an AB/Sciex QStar mass spectrometer.
3.5.2 NMR data for compound 2 (interligand monodiene adduct)

Details for sample preparation are given above (section 3.3.1). $^1$H NMR (400.0 MHz, C$_6$D$_6$, 298 K), $\delta$ 1.18 (6 H, s, CH$_3$), 3.06 (2 H, m, CHH‘-CHH’), 3.32 (2 H, m, CHH’-CHH’); also present are free 2,3-dimethyl-1,3-butadiene [$\delta$ 1.84 (6 H, CH$_3$), 4.93 (2 H, m, alkenyl H), 5.05 (2 H, m, alkenyl H)] and BTBB (internal standard) [$\delta$ 7.36 (2 H, s), 7.40, (1 H, s)]. $^{19}$F NMR (376.5 MHz, C$_6$D$_6$, 298 K) $\delta$ -59.11 (6 F, q, $^5$J$_{F-F}$ = 12.7 Hz, CF$_3$), -53.21 (6 F, q, $^5$J$_{F-F}$ = 12.7 Hz, CF$_3$).

3.5.3 Synthesis of compound 3 (intraligand bisdiene adduct)

Compound 1 (90.6 mg, 0.139 mmol) was added to a 50 ml round bottom flask and dissolved in 12.5 ml of benzene. 1,2-Dimethyl-1,3-butadiene (0.626 mmol, 70.8 $\mu$L) (4 equiv) were added. The solution turned orange immediately upon mixing. The round bottom flask was connected to a vacuum adapter, sealed under N$_2$, and allowed to heat at 50°C in an oil bath for 20 h. The solution appeared a pale yellow color after heating. The solvent was removed and the yellow powder was allowed to dry under vacuum for about 1 h. 99.8 mg of 3·C$_6$H$_6$ (0.112 mmol) were collected (yield: 81 %). Compound 3 co-crystallizes with one equiv of C$_6$H$_6$, as observed in the X-ray structure (not shown in Figure 3.2). Partial loss of benzene occurs upon storage. See Figure 3.2 for the thermal ellipsoid drawing of the structure. Anal. Calc. for C$_{20}$H$_{21}$F$_{12}$Pt$_3$S$_4$·$\frac{2}{3}$C$_6$H$_6$: C: 33.37 %, H: 2.80 %; Found: C: 33.30 %, H: 2.71%. MS (ESI) data for 3-H$^+$ (C$_{20}$H$_{21}$F$_{12}$Pt$_3$S$_4^+$) correlates well with the predicted spectrum (Figure 3.3). $^1$H NMR (400.0 MHz, C$_6$D$_6$, 298 K), $\delta$ 1.20 (6 H, s, CH$_3$), 1.35 (6 H, s, CH$_3$), 1.86 (2H, m, CH$_2$), 2.56 (2H, m, CH$_2$), 3.09 (4H, m, CH$_2$ x 2). $^{19}$F NMR (376.5 MHz, C$_6$D$_6$, 298 K) $\delta$ -62.52 (6 F, s, CF$_3$), -56.55 (6 F, s with Pt satellites, $^4$J$_{Pt-F}$ = 12.6 Hz, CF$_3$).
Figure 3.3 Comparison of calculated/theoretical (black bars) isotopic intensities with experimental values [grey, with error (±σ)\textsuperscript{22} superimposed] for compound 3-H\textsuperscript{+} (C\textsubscript{20}H\textsubscript{21}F\textsubscript{12}Pt\textsubscript{4}S\textsubscript{4}\textsuperscript{+}), showing all isotope peaks with <1% calculated intensities. The experimental values were obtained MS (ESI) data (details in reference 22).

3.5.4 Equilibrium constant for 1 + 2,3-dimethyl-1,3-butadiene $\rightleftharpoons$ 2

1 (4.8 mg, 0.0074 mmol) was dissolved in C\textsubscript{6}D\textsubscript{6} (5.0 mL). BTBB (4.0 μL, 6.8 mg, 0.023 mmol) was added to the mixture, followed by 2,3-dimethyl-1,3-butadiene (1.5 μL, 1.1 mg, 0.013 mmol). The mixture was shaken vigorously for ca. 2 min to ensure complete mixing, to give a solution with the following initial concentrations:

\[ [1]_0 = 1.5 \text{ mM}; [\text{diene}]_0 = 2.6 \text{ mM}; [\text{BTBB}] = 4.6 \text{ mM} \]

Note: immediately upon addition of the diene, the color changed from purple to brown-yellow and the solution was homogenous by visual inspection. From this solution, 0.50 mL was taken and placed in a J. Young NMR tube, which was sealed under nitrogen. Within 20 min of adding the diene (sample kept at RT), \textsuperscript{1}H and \textsuperscript{19}F NMR spectra were collected to obtain equilibrium concentrations of diene (from \textsuperscript{1}H NMR) and compounds 1 and 2 (from
\[ K_{eq} = \frac{[2]_{eq}}{[1]_{eq}[\text{diene}]_{eq}} = \frac{(0.0012 \text{ M})}{(9.5 \times 10^{-5} \text{ M})(0.0014 \text{ M})} = 9.0 \times 10^3 \text{ M}^{-1} \]

Another NMR sample was prepared by diluting 0.25 mL of the stock solution prepared above with 0.25 mL of C\textsubscript{6}D\textsubscript{6} (to make a solution with \(\frac{1}{2}\) of the concentration of the solution used above to calculate \(K_{eq}\)). Again, an equilibrium constant was calculated, in the same fashion described above:

\[ K_{eq} = \frac{[2]_{eq}}{[1]_{eq}[\text{diene}]_{eq}} = \frac{(0.00058 \text{ M})}{(9.5 \times 10^{-5} \text{ M})(0.00070 \text{ M})} = 8.7 \times 10^3 \text{ M}^{-1} \]

The largest source of error resides in the addition of the small amounts of internal standard and diene and the determination of the equilibrium concentration by NMR integration (the \(^{19}\text{F} \text{NMR} \) signal for \(1\) was broad/weak). From the magnitude of these errors, the overall error is estimated to be ca. 23% and we report the equilibrium constant as \(9 (\pm 2) \times 10^3 \text{ M}^{-1}\).

### 3.5.5 Displacement of Pt-bound bisthioether ligand by substitution with phosphines

#### 3.5.5.1 With dppe

Complex 3 (12 mg, 0.015 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe) (11 mg, 0.028 mmol) were combined in CDCl\textsubscript{3} (0.6 mL) and the yellow solution was placed in a J. Young NMR tube. The mixture was protected from light and allowed to react at RT for 2 h (to give complete reaction/consumption of complex 3). The mixture was analyzed by \(^1\text{H}, ^{19}\text{F} \text{and} ^{31}\text{P} \text{spectroscopy.} \) \(^1\text{H} \text{NMR (400.0 MHz, CDCl}_3, 298 \text{ K}, \delta \ 1.76 \text{ (s, 3H, CH}_3, \text{free bisthioether), 1.80 \text{ (s, 3H, CH}_3, \text{free bisthioether), 2.10 \text{ (t, J_HH = 4.0 Hz, 4H, (CH}_2)_2, \text{free dppe), 2.51 \text{ (complex m, 4H, (CH}_2)_2, Pt-bound dppe), 2.65-2.90 \text{ (m, 4H, CH}_2, \text{free bisthioether), 2.96-3.09 \text{ (m, 2H, CH}_2, \text{free bisthioether), 3.12-3.53 \text{ (m, 2H, CH}_2, \text{free bisthioether), 7.27-7.36 \text{ (m, 20H, Ar, free dppe), 7.42-7.55 \text{ (m, 12H, Ar, Pt-bound dppe), 7.70-7.82 \text{ (m, 8H, Ar, Pt-bound dppe).} \) ^{19}\text{F} \text{NMR (376.5 MHz, CDCl}_3, 298 \text{ K), } \delta \ -68.86 \text{ to -66.89 (br m, 2F, 1/3 x [CF}_3 x 2, \text{free bisthioether), -65.41 to -63.84 (br m, 4F, 2/3 x [CF}_3 x 2, \text{free bisthioether).} \)}}} \]
2], free bisthioether), -55.08 [m, 6F, (dppe)Pt(S₂C₂(CF₃)₂)]. ³¹P NMR (162.0 MHz, CDCl₃, 298 K) δ -12.02 (s, 2P, free dppe), 44.51 [multiplet with Pt-satellites, Jₚₚₚₜ = 1388.6 Hz, Pt-bound dppe]. Conversion of 3 to the bisthioether and (dppe)Pt(S₂C₂(CF₃)₂) is quantitative by NMR.

### 3.5.5.2 With PBu₃

Complex 3 (10 mg, 0.012 mmol) and PBu₃ (6.2 μL, 5.1 mg, 0.025 mmol) were combined in CDCl₃ (0.6 mL) and the resulting mixture was placed in a J. Young NMR tube. The mixture was protected from light and left overnight (ca. 20.5 h). The mixture was analyzed by ¹H, ¹⁹F and ³¹P spectroscopy. ¹H NMR (400.0 MHz, CDCl₃, 298 K) δ 0.94 [t, J₁₉H = 7.0 Hz, 18H, CH₃ groups of (Bu₃P)₂Pt(S₂C₂(CF₃)₂)], 1.31-1.62 [m, 24H, CMe₂ of (Bu₃P)₂Pt(S₂C₂(CF₃)₂)]. ¹⁹F NMR (376.5 MHz, CDCl₃, 298 K) δ -55.67 [m, 6F, (Bu₃P)₂Pt(S₂C₂(CF₃)₂)]. Also visible by ¹H and ¹⁹F NMR: free bisthioether (see 3.6.5.1 for ¹H and ¹⁹F NMR data) in an amount commensurate with the amount of (Bu₃P)₂Pt(S₂C₂(CF₃)₂). ³¹P NMR (162.0 MHz, CDCl₃, 298 K) δ -4.0 [multiplet with Pt-satellites, Jₚₚₚₜ = 1369.0 Hz, Pt-bound PBu₃]. Yields of bisthioether and (Bu₃P)₂Pt(S₂C₂(CF₃)₂) were over 90% based on consumption of phosphine and the integration of product peaks, compared with integration unknown/contaminant peaks (minor).

### 3.5.5.3 With PPh₃

PPh₃ (5.5 mg, 0.021 mmol) was dissolved in C₆D₆ (0.7 mL) and the resulting mixture was placed in a J. Young NMR tube containing complex 3 (10 mg, 0.012 mmol). BTBB (7.0 μL, 12 mg, 0.041 mmol) was added as an internal standard. The tube was sealed and the mixture was allowed to react for 44 h at RT to obtain near-complete reaction (>95% of starting material consumed). Note: most of the product, (Ph₃P)₂Pt(S₂C₂(CF₃)₂),¹⁸ precipitated from the benzene-d₆ solution in the form of small yellow crystals; the material was barely soluble enough to observe weak ¹H, ¹⁹F and ³¹P NMR signals (see below). ¹H NMR (400.0 MHz, C₆D₆, 298 K) δ 1.20 (s, 3H, CH₃, Pt-bound bisthioether, <5% of original concentration), 1.35 (s, 3H, CH₃, Pt-bound bisthioether, <5%), 1.42 (s, 3H, CH₃, free bisthioether), 1.53 (s, 3H,
CH₃, free bisthioether), 2.23-3.42 (br ov multiplets, 8H, CH₂ groups of free bisthioether), 7.14-7.18 [m, 18H, (Ph₃P)₂Pt(S₂C₂(CF₃)₂), weak signal due to low solubility], 7.37-7.42 [m, 12H, (Ph₃P)₂Pt(S₂C₂(CF₃)₂), weak signal, overlapping with BTBB peaks {δ 7.36 (s, 2H), 7.40 (s, 1H)}]. ¹⁹F NMR (376.5 MHz, C₆D₆, 298 K) δ -68.36 to -66.53 (br m, 2F, 1/3 x [CF₃ x 2], free bisthioether), -64.67 to -63.16 (br m, 4F, 2/3 x [CF₃ x 2], free bisthioether, overlapping with BTBB peak (δ -64.00, s)], -55.38 [m, 6F, (Ph₃P)₂Pt(S₂C₂(CF₃)₂), weak signal due to low solubility]. ³¹P NMR (162.0 MHz, C₆D₆, 298 K) δ -4.77 (s, free PPh₃, very weak signal), 19.05 [s, cannot see Pt-satellites due to low solubility of (Ph₃P)₂Pt(S₂C₂(CF₃)₂), very weak signal].

3.6 References


[5] See ref. 4b for Kohn-Sham MOs of Ni(S₂C₂Me₂)₂. The depiction of the LUMO in Scheme 3.1 omits, for clarity, the small metal-based atomic orbital contribution.

Chapter 3 - Unprecedented Reactivity of Metal Bisdithiolene Toward a Conjugated Diene


[9] X-ray crystallographic data for 3 (mono-benzene solvate): data collection on Nonius-Kappa CCD diffractometer using Mo Kα (0.71073 Å) at 150(1) K, structure solution with direct methods, refinement on F² against all reflections. Crystal data and structure refinement: greenish-yellow needle, crystal size = 0.10 x 0.04 x 0.03 mm, C₂₆H₂₆F₁₂Pt₁S₄, M = 889.80, monoclinic, space group C 2/c, a = 13.2761(5) Å, b = 16.6218(9) Å, c = 14.4963(5) Å, β = 110.297(2)°, Z = 4, V = 3000.3(2) Å³. Dcalc = 1.970 gcm⁻³, 11556 reflections collected of which 3437 were independent, GOF = 1.038, R1 = 0.0429 (data with I >2σ(I)), wR2 = 0.0856 (all data). For Crystallographic Information Files (cif format) for this structure, see the supporting information for ref. 1.

[10] Considering that C-S bonds in Pt(S₂C₂R₂)₂ have some thioketone character, it is relevant that free diarylthioketones undergo hetero-Diels-Alder additions with 1,3-dienes (likely concerted for very reactive dienes but apparently stepwise for less reactive dienes): Wilker, S.; Erker, G. *J. Am. Chem. Soc.* 1995, 117, 10922.

[11] As suggested by the external reviewer of this thesis, Prof. P. Holland. Recall that solvent dependence on the rate was observed in reactions between Ni(S₂C₂(CF₃)₂)₂ and excess 1-hexene (Chapter 2, section 2.5.19), suggesting a mechanism with charge-separated intermediates.

[12] An extremely similar value was observed for the corresponding nickel system, where ref. 3a reports 1.1 ×10⁴ M⁻¹ at 298 K in hydrocarbon solvent.


[14] 2,3-Dimethyl-1,3-butadiene (0.56 M, excess) and S₂C₂(CF₃)₂ (0.14 M) did not react (only starting materials observed by ¹H and ¹⁹F NMR) upon heating the mixture for 19.5 h at 50°C (in C₆D₆). Harrison, D. J.; Fekl, U. Unpublished results.

[15] In refluxing CDCl₃ with CD₃CN present [CDCl₃/CD₃CN (v/v) = 25:1]. CD₃CN was added to facilitate the dissociation of the Pt-coordinated bisthioether ligand.


[17] As expected, the substitution reactions involving dppe or PBu₃ are considerably faster (complete in < 2 h) than the reaction with PPh₃ (not complete after 24 h at RT).


[22] From the experimental mass spectrum (expanded in the region of ca. 807-819 amu), the relative areas under the mass peaks were determined by approximating the shape of the peaks as isosceles triangles (setting the peak at 812.0 amu to 100%). The triangles were formulated to have two congruent sides of length 'a' and a third side of length 'b' (the base of the peak). The areas were calculated using $A = \frac{b}{4}(4a^2 - b^2)^{1/2}$. For each peak, the error associated with measuring a and b (estimated as ± 0.05 cm throughout) was propagated to obtain error for the area values (reported as ±σ(A), σ(A) = standard deviation in area). Using the partial derivative method and the errors associated with 'a' and 'b' (i.e., σ(a) = σ(b) = 0.05 cm), the standard deviation in area was obtained using $\sigma(A) = \left\{\left(\frac{\partial A}{\partial a}\right)^2[\sigma(a)]^2 + \left(\frac{\partial A}{\partial b}\right)^2[\sigma(b)]^2\right\}^{1/2}$. The experimental and calculated (theoretical) values agree within 2σ.
Chapter 4

Ethylene Reactivity of Electrophilic Mixed-Ligand Molybdenum Trisdithiolenes

4.1 Abstract

New molybdenum mixed-ligand trisdithiolenes \([\text{Mo}(\text{S}_2\text{C}_2\text{R}_2)\text{R}(\text{S}_2\text{C}_2\text{R'}_2)]\) have been synthesized. These complexes react with ethylene rapidly and cleanly to afford intraligand alkene adducts, which are stable/isolable, in contrast the intraligand adducts of \(\text{Ni}(\text{S}_2\text{C}_2(\text{CF}_3)_2)\) (chapter 2) and other metal bisdithiolenes. For the mixed-ligand complex \(\text{Mo}(\text{S}_2\text{C}_2(\text{CF}_3)_2)\text{R}(\text{S}_2\text{C}_6\text{H}_4)\), ethylene binding was shown to be reversible, such that alkene was released from the adduct, regenerating the trisdithiolene, in refluxing CDCl\(_3\) (under argon). We also present a crystal structure for the ethylene adduct of \(\text{Mo}(\text{S}_2\text{C}_2(\text{CF}_3)_2)\text{R}(\text{S}_2\text{C}_6\text{H}_4)\), which provides the first example of a 2,3-dihydro-1,4-dithiin acting as a chelate ligand for a transition metal. We discovered that the metal-bound dihydrodithiins formed by intraligand ethylene addition are easily substituted with other donor ligands, providing a novel approach to highly unsymmetrical bis- and trisdithiolenes of molybdenum. Most of the work described here has been published.\(^1\) Neilson Nguyen provided synthetic assistance for this study.

4.2 Introduction

As discussed in section 1.4.1, molybdenum dithiolenes are of interest as models for the active sites in a variety of oxygen-atom-transfer enzymes, all of which contain complex dithiolene ligands (pterin derivatives). Additionally, molybdenum sulfides are used on a large industrial scale in hydrodesulfurization (HDS) processes.\(^2\) Due to their industrial and biological relevance, molybdenum complexes with sulfur donors have received much attention. Sulfur-containing ligands are particularly prominent in noninnocent complexes\(^3\) and the sulfur atoms in such complexes are often implicated in ligand-centered reactivity (see, for instance, chapters 1, 2 and 3). For sulfur-ligated complexes of molybdenum and other transition metals, an increasing number of examples are surfacing where reactions with
organic substrates occur at the sulfur atoms, rather than at the metal. Sulfur-centered reactivity has been observed, for example, in complexes with bridging sulfides ([CpMo(μ-S)]2S2CH2),4 terminal sulfides (ReS4),5 P,S-chelates,6,6 and sulfur centers in metal-bound dithiolene ligands (M(S2C2R2)2; M = Ni, Pd, Pt) (see chapters 2 and 3).7,8,9,10,11 Surprisingly, however, the ligand-based reactivity of metal trisdithiolenes has received little attention, especially when compared with their exhaustively studied metal bisdithiolene counterparts.

4.3 Results and discussion

The foregoing two chapters have dealt with the ligand-centered reactions of group 10 metal bisdithiolenes with alkenes and 1,3-dienes. The present chapter details the reactions of new mixed-ligand molybdenum trisdithiolenes with ethylene.

As stated previously (1.4.3.2), alkene addition products of metal bisdithiolenes were initially proposed to be of the symmetry-allowed intra-ligand type.7 However, all characterized alkene adducts have shown inter-ligand binding.8,10 In fact, intraligand addition products, with a metal-bound dihydrodithiin, are generally unstable and had not been directly observed for any metal, although their existence was inferred in reactions that produce free dihydrodithiins (DHDs) (see chapter 2). We achieved rapid intraligand alkene binding by employing unsymmetrical trisdithiolenes with electronically disparate ligands attached to the central metal ion. Remarkably, the intraligand alkene adducts of our mixed-ligand trisdithiolenes are stable/isolable, in contrast to the analogous adducts of group 10 metal bisdithiolenes. These adducts are also useful inorganic “synthons”, allowing access to new types of bis- and trisdithiolene complexes.

We first investigated the reactions of previously reported Mo(S2C2(CF3)2)312 and Mo(S2C6H4)313 with ethylene and found slow14 reactions to give corresponding dihydrodithiins and decomposed metal species, presumably through intraligand alkene addition. We reasoned that “push-pull” trisdithiolenes, with a combination of electron-withdrawing and electron-donating dithiolene ligands [Mo(S2C2R2)2(S2C2R’2)], would react more readily with alkenes. For example, in a trisdithiolene complex with one relatively
electropositive dithiolene ligand, the more electron-withdrawing dithiolene groups are expected to “pull” electron density from the more electron-releasing ligand.\textsuperscript{15} Thus, we propose that the electron-releasing ligand is partially oxidized (with dithioketone character), relative to the electronegative ligands, and is poised for [4+2] cycloaddition reactions at the dithiolene sulfur centers (Figure 4.1).

**Figure 4.1** Left: preferred resonance structure for a mixed-ligand trisdithiolene (in box), compared with a decidedly less significant contributor (crossed out). Right: schematic for [4+2] cycloaddition reaction between an oxidized dithiolene ligand and an alkene.

### 4.3.1 Synthesis of new mixed-ligand trisdithiolenes

As mentioned in chapter 1 (1.2.2), homoleptic metal trisdithiolenes are have been known since the 1960s, with dozens of examples of such complexes in the literature. Heteroleptic (i.e., mixed-ligand) metal trisdithiolenes, on the other hand, are very rare and none of the previously reported complexes have been crystallographically characterized.\textsuperscript{15,16} We synthesized the new compounds Mo(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3})\textsubscript{2})\textsubscript{2}(S\textsubscript{2}C\textsubscript{6}H\textsubscript{4}) (complex 1) and Mo(S\textsubscript{2}C\textsubscript{6}H\textsubscript{4})\textsubscript{2}(S\textsubscript{2}C\textsubscript{2}(CF\textsubscript{3})\textsubscript{2}) (2), using the procedures shown in Scheme 4.1. For the preparation of 1, we started with the bisdithiolene oxo complex;\textsuperscript{17} the oxo is rendered amenable to condensation with benzene-1,2-dithiol (recall section 1.3.1) by one-electron oxidation with iodine. Condensation of the monoanionic [formally Mo(V)] oxo complex with the dithiol gave the monoanionic trisdithiolene, (NEt\textsubscript{4})\textsubscript{1}, which was oxidized to its
neutral form using Mo(S₂C₂(CF₃)₂)₃ [or Ni(S₂C₂(CF₃)₂)₂] (Scheme 4.1A). Compound 2 was synthesized in a single step, by treatment of a bisphosphine/bisdithiolene complex with dithiete (≥3 equiv) to install the S₂C₂(CF₃)₂ ligand on the metal, while generating SPPh₂Me and [SC₂(CF₃)₂]ₙ as by-products (Scheme 4.1B).

\[\text{Scheme 4.1}\]

### 4.3.2 Solid state structure of 2 and MO considerations

An X-ray crystal structure of 2 (Figure 4.2) revealed trigonal prismatic geometry at the metal, as has been observed in the solid state structures of a number of homoleptic trisdithiolenes. Also, the dithiolene S₂C₂ planes are canted away from the MoS₂ planes, along the intraligand S···S axes (“ligand bend”). This ligand bending has been attributed to second order Jahn-Teller effects; for homoleptic trisdithiolenes (e.g., Mo(S₂C₂H₂)₃), the distortion to lower symmetry (D₃h → C₃h) is likely driven by mixing of ligand π orbitals (Lπ) and the metal d₄z orbital [see below, Figure 4.3(a)]. See the experimental section (Figure 4.10) for another view of the X-ray structure for 2, clearly showing the ligand bending.
**Figure 4.2** Molecular structure of 2. One of two crystallographically independent molecules in the unit cell is shown, and thermal ellipsoids are 30% probability envelopes. A ‘ligand bend’ angle is defined as the angle between the ligand plane (least-squares plane through S-C-C-S unit) and the metal coordination plane (through S-Mo-S). Selected distances and angles (Å, deg): Mo1-S1, 2.367(1); Mo1-S2, 2.366(1); Mo1-S3, 2.371(1); Mo1-S4, 2.359(1); Mo1-S5, 2.363(1); Mo1-S6, 2.363(1); S1-Mo1-S2, 81.44(4); S3-Mo1-S4, 82.39(4); S5-Mo1-S6, 82.58(5); S2C6H4 C-C distances (averages of analogous but crystallographically independent bonds) are given in the insert, along with standard deviations and a limiting Lewis-structure for oxidized3a S2C6H4. Ligand bend: 17.9(1) for S2C2(CF3)2 ligand, 23.8(1) for both S2C6H4 ligands (values for the second molecule are 18.0(1) and 20.6(1), respectively ).

The reactions of the new mixed-ligand trisdithiolenes with ethylene are predicted to proceed in an intraligand manner. As a first-order approximation, the known MOs13a,21,22 of symmetrical (homoleptic) trisdithiolenes indicate that such a reaction should be allowed by symmetry to occur in a concerted, synfacial fashion. For homoleptic trisdithiolenes, such as Mo(S2C2H2)3, computed in D3h symmetry, extended Hückel,13a and Fenske-Hall21 computations predict the HOMO and LUMO [a2' (Lπ) and a1' (d2z), Figure 4.3(a,b)] to be close in energy (see also section 1.2.2). Further, by ligand bending along the S···S axes (D3h → C3h distortion, Figure 4.3), these orbitals can mix to form frontier orbitals with a mixture of metal d2z and ligand π (in-phase across intraligand sulfur atoms) character.21 For the mixed-ligand species, the symmetry will be further lowered compared to the C3h
(homoleptic) case. We expect that the $S_2C_2(CF_3)_2$ sulfur atoms contribute more to bonding MOs whereas the $S_2C_6H_4$ sulfur atoms should have larger coefficients for antibonding MOs.

**Figure 4.3** (a) Molecular orbital interactions that lead to ligand bending along $S\cdots S$ intraligand axes (distortion to lower symmetry) (see ref. 21). (b) Proposed LUMO for 1 and its symmetry-allowed interaction with ethylene.

It is likely that the sulfur atoms of the $S_2C_6H_4$ ligand significantly contribute to the LUMO, as shown schematically for 1 in Figure 4.3(b). Also, since structural data for compound 2 show larger ligand bending angles for the $S_2C_6H_4$ ligands compared to the $S_2C_2(CF_3)_2$ ligand, as well as evidence for a partially oxidized character of $S_2C_6H_4$ (Figure 4.2), the $S_2C_6H_4$ ligands appear to be more efficiently coupled to the $d_{z^2}$ orbital; we propose that electron density from an alkene can be very efficiently transferred to the metal and the $S_2C_2(CF_3)_2$ ligands through the $S_2C_6H_4$ ligand $\pi$ system.

After publishing our qualitative MO picture for mixed-ligand trisdithiolenes (see Figure 4.3), we calculated the MOs of 2 at the density functional theory (DFT, B3LYP) level. The result (Figure 4.4, LUMO) was fully consistent with the our proposed LUMO for 1 in terms of symmetry properties. Also, the DFT-calculated LUMO for 2 exhibits larger coefficients on sulfur atoms of the $S_2C_6H_4$ ligands, compared to the $S_2C_2(CF_3)_2$ ligand, and prominent
ligand bending, to allow overlap between the $d_{z^2}$ and $L_\pi$ group orbitals (in the HOMO; in the LUMO this interaction is expectedly antibonding), as predicted in our qualitative model (above). Note that the nodal properties of the dithiolene ligands in the trisdithiolene LUMO are analogous to those in the LUMO of metal bisdithiolenes (section 1.2.1): that is, the orbital contributions are in-phase across intraligand sulfur centers, which should correspond to intraligand alkene addition (see below).

**Figure 4.4** Calculated (DFT, B3LYP) LUMO for Mo(S$_2$C$_3$H$_4$)$_2$(S$_2$C$_2$(CF$_3$)$_2$). Note the ligand bending along S--S intraligand axes and larger coefficients for sulfur atoms on the S$_2$C$_3$H$_4$ ligands.

### 4.3.3 Reactions of mixed-ligand trisdithiolenes with ethylene

Both 1 and 2 react with ethylene in the fashion predicted (Scheme 4.2). The reactions are rapid,$^{14}$ take place exclusively at the sulfur atoms of the S$_2$C$_3$H$_4$ ligand, and selectively form intraligand adducts 3 and 4, where 2,3-dihydro-1,4-benzodithiin [here, DHBD(H,H)] acts as a chelate ligand, using the 1,4-sulfur atoms to bind to molybdenum. Both adducts can be formed in high yield (> 80 %) if the alkene addition reactions are conducted in weakly coordinating solvents (chlorinated or aliphatic hydrocarbons). In the presence of more
coordinating solvents (MeCN, THF), decomposition via loss of DHBD(H,H) is observed. Compound 3 is particularly stable, and it can be kept in CDCl$_3$ or CD$_2$Cl$_2$ at RT for days. We investigated 3 with respect to the reversibility of ethylene binding. Ethylene can be released from the metal-bonded dihydrodithiin to regenerate the dithiolene ligand, such that 1 is restored at mildly elevated temperature: Refluxing (21 h) a CDCl$_3$ solution of 3 under argon yielded a mixture of unchanged 3 (37%) and alkene release product 1 (41%), along with a small amount of DHBD(H,H) (12%) (accompanied by corresponding metal decomposition products). We expect that alkene dissociation from the alkene adduct of 1 is facilitated by back-donation$^{26}$ of an occupied d orbital (likely d$^z_2$) into the C-S $\sigma^*$ orbitals.

![Scheme 4.2]

X-ray quality crystals$^{19}$ of 3 were grown by allowing ethylene to slowly diffuse into a toluene solution of 1. Its structure (Figure 4.5) provides the first example of a dihydro-1,4-dithiin chelating to a transition metal using the sulfur atoms in 1,4-positions.
Figure 4.5  X-ray crystal structure of 3, shown using 30% probability ellipsoids. One orientation is shown for the rotationally disordered trifluoromethyl groups involving C7 and C8. Selected distances and angles (Å, deg): Mo1-S1, 2.329(3); Mo1- S2, 2.326(4); Mo1-S3, 2.328(3); Mo1-S4, 2.313(4); Mo1- S5, 2.523(3); Mo1- S6, 2.524(3); C9-C10, 1.508(19); S5-C9, 1.836(14); S6-C10, 1.848(14); S1-Mo1-S2, 82.3(1); S3-Mo1-S4, 82.3(1); S5-Mo1-S5, 72.4(1); C11-S5-C9, 96.3(6); C12-S6-C10, 97.9(1). Ligand bend angles (defined in Figure 4.2) are 0.4(4) deg [S2C6H4(CN)2 ligand having atoms S1, S2] and 4.5(4) deg [S2C6(CF3)2 having S3, S4]. ‘Ligand bend’ for Mo-S2C6H4 substructure (using Mo1, S5, S6, C11, C12), 52.1(4) deg.

4.3.4 Intraligand adducts as inorganic synthons

We have exploited the lability of the metal-coordinated dihydrodithiin to synthesize new compounds (NEt4)2[Mo(S2C6H4)(S2C2(CN)2)(S2C2(CF3)2)] (complex 5) and (NEt4)2[MoO(S2C6H4)(S2C2(CF3)2)] (6) in reasonable yields (67%), starting from compound 4 (Scheme 4.3). In both cases, the displacement of DHBD(H,H) is effected with appropriate nucleophiles ([S2C2(CN)2]2- or OH-). Dianionic [Mo(S2C6H4)(S2C2(CN)2)(S2C2(CF3)2)]2- is the first example of a metal trisdithiolene with three different dithiolene ligands. The mono-oxo bisdithiolene [MoO(S2C6H4)(S2C2(CF3)2)]2- is rare in that it contains two different dithiolene groups. Note that Holm et al.27a reported [MoO(S2C2H2)(S2C2(CN)2)]2-, prior to
our paper describing the synthesis of 6 and another method for making mixed-bisdithiolene Mo-oxo complexes (i.e., $[\text{MoO(dithiolene)(dithiolene')}]^{2-}$) has surfaced, since our paper was published.\textsuperscript{27b} Molybdenum oxo compounds with one or two dithiolene groups are of interest as models for the active sites in a variety of oxygen-atom transfer enzymes (see section 1.4.1).\textsuperscript{27} Both of the new compounds (5 and 6) were isolated in crystalline form as their NEt\textsubscript{4}\textsuperscript{+} salts. X-ray structure determinations\textsuperscript{19} confirmed the identity of the products (see insets in Scheme 4.3, NEt\textsubscript{4}\textsuperscript{+} cations not shown, more crystallographic details in the experimental section).

As will be shown in Chapter 5, complex 3 also reacts smoothly with nucleophiles to afford new derivatives upon loss of DHBD(H,H). In fact, a parallel research effort in our lab is
examining the intraligand adducts (of alkenes or alkynes) of compound 1 as precursors to the ‘Mo(S₂C₂(CF₃)₂)₂’ fragment, which is of interest as a model for the active sites in MoS₂-based hydrodesulfurization (HDS) catalysts (e.g., Scheme 4.4).²⁸ The active sites in such catalysts are thought to be the edges of MoS₂ sheets, featuring coordinatively unsaturated MoS₄ (four coordinate molybdenum) environments (Scheme 4.4, inset).²⁹ Our intraligand adducts should provide useful precursors to ‘MoS₄’ analogues for applications in HDS modelling. The DFT-calculated (B3LYP, SDD basis)²⁴ structure for the ‘Mo(S₂C₂(CF₃)₂)₂’ fragment (Scheme 4.4) exhibits marked metric similarities to the edge portion of molybdenite (selected bond lengths and angles are compared in Scheme 4.4), pointing to the suitability of ‘Mo(S₂C₂(CF₃)₂)₂’ as a homogenous HDS model.²⁸

4.4 Conclusion

We have prepared new molybdenum complexes with mixed dithiolene ligands. These compounds (1 and 2) rapidly and cleanly bind ethylene in a unconventional intraligand fashion, to form metal-chelating 2,3-dihydro-1,4-benzodithiin [DHBD(H,H)]. This alkene binding reaction was shown to be reversible for complex 1, consistent with the view that DHBD(H,H) can be regarded a protected form of ethylene. Dihydro-1,4-dithiins have been used previously as protected forms of cis-alkenes, and an excellent protocol for alkene release involves a heterogeneous reaction at the surface of Raney nickel.³⁰ Our demonstration of a dihydro-1,4-dithiin chelating to a transition metal might provide a homogeneous model for the alkene-release step in such reactions, and could also be of
relevance to the behavior of 1,4-disulfur-heterocycles in hydrodesulfurization reactions. Furthermore, we demonstrated that molybdenum-coordinated 2,3-dihydro-1,4-benzodithiin can be labilized if desired, which opens new synthetic routes to dithiolene complexes of molybdenum possessing highly unsymmetrical structures. We think that further development of this field can provide new insights into principles of reactivity as well as useful applications. For example, ongoing work in our lab focuses on utilizing the ‘Mo(S₂C₂(CF₃)₂)₂’ fragment, obtainable by displacement of DHBD(H,H) from 3, as a homogenous model for HDS catalysts. Also, we have recently shown that the reactivity described here can be extended to generate DHBDs catalytically (see chapter 5).

4.5 Experimental section

4.5.1 General considerations

Experiments were conducted under inert (N₂ or Ar) atmosphere using standard dry-box (M Braun UniLab) or Schlenk-type techniques except where noted. Compounds Mo(S₂C₂(CF₃)₂)₃,¹² Mo(S₂C₆H₄)₃,¹³b (NEt₄)₂[MoO(S₂C₂(CF₃)₂)₂],¹⁷ Mo(S₂C₆H₄)₂(PPh₂Me)₂,¹⁸ S₂C₂(CF₃)₂,¹⁹ and Na₂S₂C₂(CN)₂,²² were prepared by literature procedures. All other chemicals were purchased from Sigma Aldrich or Alpha Aesar and used as received. Dichloromethane, hexanes and tetrahydrofuran (THF) were dried/deoxygenated using an M Braun solvent purification system (MB-SPS). Acetonitrile-d₃ (CD₃CN), chloroform-d (CDCl₃) and dichloromethane-d₂ (CD₂Cl₂) were dried/degassed over CaH₂ and vacuum-transferred prior to use. Acetone-d₆ and chloroform were dried over activated molecular sieves and deoxygenated (with argon or N₂ purge) prior to use. Ethanol was dried/degassed over magnesium metal (with trace I₂) and vacuum-transferred before using (caution: EtOH over activated Mg evolves H₂). Silica gel (60-230 mesh) was used as received or dried/deoxygenated under vacuum (>3h, 80°C), where noted. UV-vis spectra were obtained on a Cary 14 spectrophotometer. ¹H NMR spectra were obtained on Varian Gemini 200 MHz or Unity/Inova Varian 500 MHz spectrometers. Residual proton peaks were used as reference: ¹H (δ, ppm, acetone-d₆, 2.05; acetonitrile-d₃, 1.94; chloroform-d, 7.26; dichloromethane-d₂, 5.32). ¹⁹F NMR data were recorded on a Unity/Inova Varian 500
MHz spectrometer at 470 MHz and referenced to external trifluoroacetic acid (δ, ppm, -76.55). In some NMR experiments, 3,5-bis(trifluoromethyl)bromobenzene (BTBB) was used as an internal standard (¹H/¹⁹F). Elemental analyses were conducted at Guelph (Chemisar) Laboratories, Guelph, ON, Canada.

4.5.2 Reaction of Mo(S₂C₂(CF₃)₂)₃ with excess ethylene (monitored by UV-vis)

Mo(S₂C₂(CF₃)₂)₃ (5.9 mg, 0.0076 mmol) was placed in a flask with 45.0 mL of CH₂Cl₂ and a stir bar. The flask was sealed and the mixture was stirred at RT for 20 min to completely dissolve the Mo(S₂C₂(CF₃)₂)₃, affording a violet colored solution [0.17 mM in Mo(S₂C₂(CF₃)₂)₃]. From the resulting solution, 4.0 mL was taken and placed in a sealable quartz cuvette (1.0 cm pathlength). Ethylene was introduced to the sample by allowing the gas to gently bubble through the solution for approximately 2 min to give a saturated solution. The cuvette was sealed under ethylene. UV-vis spectra (scan range: 250-850 nm) were collected over time after ethylene addition (T ≈ 25°C) (Figure 4.6):

![Figure 4.6](image-url)  

**Figure 4.6** UV-vis spectra (solvent = CH₂Cl₂) monitoring the reaction of Mo(S₂C₂(CF₃)₂)₃ (0.17 mM initially) with excess ethylene (saturated CH₂Cl₂ solution) (T ≈ 25°C).
Comments: The consumption of Mo(S₂C₂(CF₃)₂)₃ was monitored by decay of its characteristic absorption bands ($\lambda_{\text{max}} = 390$ nm, $\lambda_{\text{max}} = 582$ nm). A new peak grows in at $\lambda_{\text{max}} = 298$ nm. The half-life ($t_{1/2}$) for this reaction is approximately 11 h; after $>20$ h, the consumption of Mo(S₂C₂(CF₃)₂)₃ was not complete. Under the same conditions, I is completely consumed in the presence of ethylene in $<2$ min (see below).

4.5.3 Reaction of Mo(S₂C₂(CF₃)₂)₃ with excess ethylene (monitored by ¹H NMR)

Mo(S₂C₂(CF₃)₂)₃ (9.4 mg, 0.012 mmol) was weighed into a J. Young NMR tube. CD₂Cl₂ (0.6 mL) was added, which partially dissolved the dark colored solid, giving a faintly violet colored solution. Ethylene was added by allowing the gas to bubble through the solution for approximately 3 min and the tube was sealed under ethylene. The mixture was protected from light and left to react at RT for 48 h. A ¹H NMR spectrum was collected. The spectrum shows only unreacted ethylene and 2,3-dihydro-5,6-bis(trifluoromethyl)-1,4-dithiin (DHD(H,H), using the nomenclature of chapter 1). ¹H NMR (200 MHz, CD₂Cl₂) $\delta$ 3.30 [s, dihydrodithiin, (CH₂)$_2$], 5.40 (s, unreacted ethylene).

4.5.4 Reaction of Mo(S₂C₆H₄)₃ with excess ethylene (monitored by UV-vis)

Mo(S₂C₆H₄)₃ (10.5 mg, 0.0203 mmol) was placed in a flask with 25.0 mL of CH₂Cl₂ and a stir bar. The flask was sealed and the mixture was stirred, at RT, for 15 min to dissolve the Mo(S₂C₆H₄)₃, to afford a green solution with 0.812 mM in Mo(S₂C₆H₄)₃. Using a 1 mL syringe, 0.78 mL (6.3x10⁻⁴ mmol of Mo(S₂C₆H₄)₃) of this green solution was placed in a graduated cylinder and diluted to 4.0 mL. This faintly green solution [0.16 mM in Mo(S₂C₆H₄)₃] was placed in a sealable quartz cuvette (1.0 cm pathlength). Ethylene was added by allowing the gas to gently bubble through the green solution for approximately 2 min to give a saturated solution. The cuvette was sealed under ethylene and UV-vis data were collected over time (scan range: 250 nm – 850 nm) ($T \approx 25^\circ C$). See spectra below (Figure 4.7):
Chapter 4 - Ethylene Reactivity of Electrophilic Mixed-Ligand Molybdenum Trisdithiolenes

Figure 4.7  UV-vis spectra (solvent = CH₂Cl₂) monitoring the reaction of Mo(S₂C₆H₄)₃ (0.16 mM initially) with excess ethylene (saturated CH₂Cl₂ solution) (T ≈ 25°C).

Comments: The consumption of Mo(S₂C₆H₄)₃ was followed by decay of its characteristic absorbance signals (λ_max = 430 nm and 670 nm). As seen from Figure 4.7 (cf., Figure 4.6), this reaction is considerably faster (t₁/₂ ≈ 2 h) than the reaction of Mo(S₂C₂(CF₃)₂)₃ with ethylene under the same conditions (t₁/₂ ≈ 11 h). However, it is much slower than the reactions of the mixed-ligand complexes (1 or 2) with ethylene (see below).

4.5.5 Reaction of Mo(S₂C₆H₄)₃ with excess ethylene (monitored by ¹H NMR)

Mo(S₂C₆H₄)₃ (7.0 mg, 0.014 mmol) was weighed into a J. Young NMR tube. CD₂Cl₂ (0.6 mL) was added, which partially dissolved the dark colored solid, giving a green colored solution. Ethylene was added by allowing the gas to bubble through the solution for approximately 3 min and the tube was sealed under ethylene. The mixture was protected from light and left to react at RT for 48 h. A ¹H NMR spectrum was collected. The
spectrum shows unreacted Mo(S$_2$C$_6$H$_4$)$_3$ and ethylene, as well as 2,3-dihydro-1,4-benzodithiin [DHBD(H,H)] and metal decomposition products ([Mo(S$_2$C$_6$H$_4$)$_2$]$_n$). $^1$H NMR (200 MHz, CD$_2$Cl$_2$) $\delta$ 3.26 [s, dihydrodithiin (CH$_2$)$_2$], 5.40 (s, unreacted ethylene), 6.18-7.70 (ov m, [Mo(S$_2$C$_6$H$_4$)$_2$]$_n$), 7.00 [m, dihydrodithiin S$_2$(C$_6$H$_4$)], 7.14 [m, dihydrodithiin S$_2$(C$_6$H$_4$)], 7.43 [m, unreacted Mo(S$_2$C$_6$H$_4$)$_3$], 8.19 [m, unreacted Mo(S$_2$C$_6$H$_4$)$_3$].

4.5.6 Reaction of 1 with excess ethylene (monitored by UV-vis)

Complex 1 (10.3 mg, 0.0150 mmol) was weighed into a vial and dissolved in 2.0 mL of CH$_2$Cl$_2$, giving a solution with 0.00748 M in dithiolene. From this green-blue solution, 87 $\mu$L was taken and placed in a 10 mL graduated cylinder and diluted to 4.0 mL, giving a solution with 0.16 mM in dithiolene. This faint green-blue solution was put in a sealable quartz cuvette (1.0 cm pathlength). The cuvette was sealed and a UV-vis spectrum (250-850 nm) was collected. Ethylene was then added to the sample by allowing the gas to bubble through the solution for approximately 2 min to saturate the solution. The cuvette was sealed under ethylene. By the time ethylene addition was complete a color change was already evident; the mixture changed from green-blue to yellow-brown. UV-vis spectra (scan range: 250-850 nm) were collected over time after ethylene addition ($T \approx 25^\circ$C) (Figure 4.8):
Figure 4.8 UV-vis spectra (solvent = CH₂Cl₂) monitoring the reaction of 1 (0.16 mM initially) with excess ethylene (saturated CH₂Cl₂ solution) (T ≈ 25°C).

Comments: the consumption of 1 was followed by decay of the bands at λₓₘₐₓ = 630 nm and λₓₘₐₓ = 406 nm. As seen in Figure 4.8, the reaction between 1 and ethylene is very rapid (finished within 2 min), especially compared the reactions of Mo(S₂C₂(CF₃)₂)₃ or Mo(S₂C₆H₄)₃ with ethylene (see above). The product, 3, is characterized by a shoulder at 275 nm and a band at 386 nm (Figure 4.8).

4.5.7 Reaction of 2 with excess ethylene (monitored by UV-vis)

Compound 2 (9.8 mg, 0.0163 mmol) was weighed into a vial and dissolved in 2.0 mL of dichloromethane. From the resulting dark green solution (8.14 mM in 2), 79.0 μL (6.4x10⁻⁴ mmol) was taken and placed in a graduated cylinder and diluted to 4.0 mL, giving a solution with 0.16 mM in 2. The solution was placed in a sealable quartz cuvette (1.0 cm
pathlength). Ethylene was added by allowing the gas to gently bubble through the UV-vis sample for approximately 2 min. The cuvette was sealed under ethylene and UV-vis spectra were collected over time (scan range: 250-850 nm; T ≈ 25°C) (Figure 4.9):

![UV-vis spectra](image)

**Figure 4.9** UV-vis spectra (solvent = CH$_2$Cl$_2$) monitoring the reaction of 2 (0.16 mM initially) with excess ethylene (saturated CH$_2$Cl$_2$ solution) (T ≈ 25°C).

Comments: the consumption of 2 was followed by decay of the bands at $\lambda_{\text{max}} = 666$ nm and $\lambda_{\text{max}} = 418$ nm. Under these conditions, $t_{1/2}$ for 2 ≈ 11 min. Thus, reactions of mixed ligand complexes 1 and 2 with ethylene are more rapid than the analogous reactions involving homoleptic Mo(S$_2$C$_6$H$_4$)$_3$ and Mo(S$_2$C$_2$(CF$_3$)$_2$)$_3$. 
4.5.8 Synthesis of 1

(NEt₄)₂[MoO(S₂C₂(CF₃)₂)₂] (389 mg, 0.472 mmol) was combined with CH₂Cl₂ (5 mL) (orange solution/suspension). I₂ (60 mg, 0.24 mmol) was added, with an additional 3 mL of CH₂Cl₂ and the color of the solution changed to green-brown (with suspended solid material). The mixture was stirred at RT for 20 min. Benzene-1,2-dithiol (71 mg, 0.50 mmol) was added in CH₂Cl₂ (1.5 mL x 2) washings, causing the color to change from green-brown to a deeper green. The mixture was stirred at RT for 1.5 h under nitrogen. The volatiles were removed under vacuum to give dark green colored residue. In air: to this residue was added acetone/chloroform (1:1 v/v) (~4 mL) which dissolved most of the dark colored material. The resulting dark green colored solution was placed on a silica gel column (16 g SiO₂, suspended in chloroform, inner column diameter = 1.7 cm). Chloroform (75 mL) was passed through the column which produced (a) colorless eluent and (b) faintly green colored eluent (discarded). The solvent system was changed to acetone/chloroform (1:1 v/v); 30 mL of this solvent mixture produced (a) faintly green colored eluent (discarded). An additional 60 mL of acetone/chloroform (1:1 v/v) gave dark green colored eluent (kept). From the final green colored fraction, the volatiles were removed under vacuum to afford dark green colored residue. In air: this residue was redissolved in CH₂Cl₂ (approximately 3 mL). The solvent/volatiles were again removed under reduced pressure to give 210 mg of dark green colored residue [(NEt₄)[1], 0.26 mmol]. Under inert conditions: to this dark green residue was added chloroform (4 mL), which mostly dissolved the green product. Mo(S₂C₂(CF₃)₂)₃ (210 mg, 0.27 mmol) was added, with an additional 2 mL of chloroform, to the dark green solution. Note: Ni(S₂C₂(CF₃)₂)₂ can be used to oxidize (NEt₄)[1], in place of Mo(S₂C₂(CF₃)₂)₃. The mixture was stirred under N₂, at 55°C, for 3 h, during which time the color changed to very intense blue-green. Under reduced pressure, the volume of the dark blue-green solution was reduced by approximately half (to ~ 3 mL) and the concentrated solution/suspension was applied to a silica gel column (6-7 g SiO₂ (dried), suspended in hexanes/chloroform (1:1 v/v), inner column diameter = 1.7 cm). Hexanes/chloroform (1:1 v/v) (~ 15 mL) were passed through the column until the blue-green product reached the bottom of the column. The blue-green product was eluted from the column using hexanes/chloroform (1:1 v/v) (~ 20 mL). The solvent/volatiles were
removed under vacuum (>2 h under full vacuum, 70°C). The resulting dark blue-green solid was stored under an inert atmosphere (149 mg, 0.22 mmol, 46% based on (NEt₄)₂[MoO(S₂C₂(CF₃)₂)₂]). Anal. Calc. for C₁₄H₁₂F₁₂S₆Mo: C 24.42, H 0.59, S 27.95; Found: C 24.44, H 0.39, S 28.24.

1H NMR (500 MHz, CDCl₃) δ 7.64 [m, 2H, S₂(C₆H₄)], 8.33 [m, 2H, S₂(C₆H₄)]. 19F NMR (470 MHz, CDCl₃) δ -56.03 (s, 12F, (C₃F₃)₂ × 2).

UV-vis (dichloromethane): λ_max(ε) = 630 (11000), 580 (shoulder, 7000), 406 (9000). See Figure 4.8 for the UV-vis spectrum of 1.

4.5.9 Synthesis of 2

Mo(S₂C₆H₄)₂(PPh₂Me)₂ (300 mg, 0.39 mmol) was combined with CH₂Cl₂ (8 mL). 1,2-Bis(trifluoromethyl)dithiethene [S₂C₂(CF₃)₂] (290 mg, 1.3 mmol) was added to the red-orange solution/suspension in CH₂Cl₂ washings (3 × 1 mL). The mixture was stirred under static N₂ for 2.5 h, at RT (20-25°C) (the solution became deep green in color). The solvent/volatiles were removed under vacuum to afford very dark green colored amorphous residue. In air: This residue was dissolved in chloroform (approximately 4 mL) and the resulting deep green solution was placed on a silica gel column (16 g SiO₂, suspended in chloroform/hexanes (1:1 v/v), inner column diameter = 1.7 cm). Chloroform/hexanes (1:1 v/v, ~ 25 mL) were passed through the column until the eluent leaving the column was green in color (discarded). More chloroform/hexanes (1:1 v/v, ~ 45 mL) were passed through the column, producing deep green colored eluent (kept). From the green eluent, the solvent/volatiles were removed under reduced pressure (>2 h, 70°C) to give dark green microcrystalline solid [140 mg, 0.23 mmol, 60% based on Mo(S₂C₆H₄)₂(PPh₂Me)₂]. Anal. Calc. for C₁₆H₈F₆S₆Mo: C 31.89, H 1.34, S 31.93; Found: C 31.46, H 1.53, S 32.42. 1H NMR (500 MHz, CDCl₃) δ 7.50 (m, 4H, S₂(C₆H₄) x 2), 8.23 (m, 4H, S₂(C₆H₄) x 2). 19F NMR (470 MHz, CDCl₃) δ -55.92 [s, 6F, (CF₃)₂]. UV-vis (dichloromethane): λ_max(ε) = 666 (11000), 594 (shoulder) (8000), 418 (11000). See Figure 4.9 for UV-vis spectrum of 2.

X-ray quality crystals were grown by slow evaporation of toluene. See below (Figure 4.10) for an alternative view of one molecule from the unit cell (molecule ‘b’), showing the ligand bending of the dithiolene ligands along the intraligand S···S axes. Ligand bend angles (see
were calculated with PLATON \cite{33} using least-squares planes through the S-C-C-S units and the corresponding S-Mo-S units.

**Figure 4.10** Alternative view of the crystal structure for 2 (50\% probability ellipsoids) showing ligand bending along S···S intraligand axes. Toluene solvates not shown.

Comments: Both crystallographically independent molecules of 2 in the unit cell show ligand bending to be more pronounced for the \( \text{S}_2\text{C}_6\text{H}_4 \) ligand, compared to the \( \text{S}_2\text{C}_2(\text{CF}_3)_2 \) ligands. The average (for all four \( \text{S}_2\text{C}_6\text{H}_4 \) ligands in two molecules) ligand bend angle is 22.4\(^\circ\) for the \( \text{S}_2\text{C}_6\text{H}_4 \) ligands versus an average (for two \( \text{S}_2\text{C}_2(\text{CF}_3)_2 \) ligands in two molecules) ligand bend of 17.9\(^\circ\) for \( \text{S}_2\text{C}_2(\text{CF}_3)_2 \) ligands. This trend supports the assertion that electron-density is concentrated on the more electronegative \( \text{S}_2\text{C}_2(\text{CF}_3)_2 \) ligand in 2. The \( \text{S}_2\text{C}_2(\text{CF}_3)_2 \) ligand has partial ene-dithiolate character (i.e., fully reduced), while the \( \text{S}_2\text{C}_6\text{H}_4 \) ligands are partially oxidized (i.e., these ligands have significant thioketone character). Therefore, the ligand \( \pi \) system on the \( \text{S}_2\text{C}_6\text{H}_4 \) ligands is better suited to interacting with the occupied metal \( d_{\pi} \) orbital, compared the analogous orbitals on the \( \text{S}_2\text{C}_2(\text{CF}_3)_2 \) ligand, which have a higher degree of occupancy.
4.5.10 Synthesis of 3

Compound 1 (0.022 M) with 3,5-bis(trifluoromethyl)bromobenzene (BTBB) (internal standard, 0.041 M) in CD₂Cl₂ was treated with ethylene by allowing the gas to bubble through the NMR sample. ¹H and ¹⁹F NMR show the reaction to form 3 to be complete in <15 min. Comparison of product and internal standard integrations shows mass balance to be 83%. No other products were observed. The missing material is likely accounted for by a small amount of red-brown precipitate in the NMR tube (i.e., 3 is sparingly soluble in chlorinated solvents). ¹H NMR (500 MHz, CD₂Cl₂) δ 2.25 [m, 2H, (SCH⁻Hb)₂], 2.80 [m, 2H, (SCH⁻Hb)₂], 5.40 (s, unreacted ethylene), 7.34 [m, 2H, S₂(C₆H₄)], 7.59 [m, 2H, S₂(C₆H₄)], 7.87 (s, 1H, BTBB), 8.02 (s, 2H, BTBB). ¹⁹F NMR (470 MHz, CD₂Cl₂) δ -64.13 (BTBB), -55.34 [s, 6F, (CF₃)₂], -55.10 [s, 6F, (CF₃)₂]. In a separate experiment, crystals for X-ray analysis were grown by allowing ethylene (1 atm) to slowly diffuse (through a 25g5/8 gauge syringe needle) into a toluene solution of 1 (~0.01 M). Analysis of the data using PLATON revealed that the crystal was a non-merohedral twin, and a twin rotation matrix (1 0 0.005, 0 -1 0, 0 0 -1) was applied. The twin fraction refined to 0.664:0.336(3). The F atoms of two of the CF₃ groups are disordered over two sites with refined occupancies 0.58(3):0.42(3) and 0.65(2):0.38(2) for the major and minor components of the atoms F1/F2/F3 and F4/F4/F6, respectively. In addition, there are 1.5 molecules of toluene solvent in the asymmetric unit; one of these molecules lies on an inversion center and is hence disordered by virtue of the crystallographic symmetry.

4.5.11 Ethylene release from 3

A CDCl₃ solution of 1 (0.013 M) and BTBB (internal standard, 0.022 M) was treated with ethylene by allowing the gas to bubble through the blue-green solution for ~5 min. The mixture was stirred at RT, under ethylene, for 20 min, during which time the color changed from deep blue-green to dark red-brown (with some insoluble brown-red material visible). The mixture was heated to reflux, under active argon pressure (vented to a mineral oil bubbler) for 21 h. During this time, the mixture changed color from dark red-brown to deep blue-green. The mixture was cooled to RT and a portion of the blue-green solution was
placed in a J. Young NMR tube for spectroscopic analysis. Product concentrations were obtained by comparison of their $^1$H NMR integrations with those of BTBB (internal standard). $^1$H and $^{19}$F NMR show free 1 (5.1 mM, 41% of original concentration), unchanged 3 (4.6 mM), and 2,3-dihydro-1,4-benzodithiin [DHBD(H,H)] (1.5 mM). Mass balance was 87%. The missing material is probably explained by the low solubility of 3 or by the presence of paramagnetic products. DHBD(H,H) was identified by its $^1$H NMR spectrum. $^1$H NMR (500 MHz, CDCl$_3$) (for dihydrodithiin only; see above for spectral assignments for 1 and 3) δ 3.27 [s, 4H, (CH$_2$)$_2$], 7.00 [m, 2H, S$_2$(C$_6$H$_4$)], 7.16 [m, 2H, S$_2$(C$_6$H$_4$)].

4.5.12 Synthesis of 4 for characterization by elemental analysis

Complex 2 (100 mg, 0.17 mmol) was combined with hexanes (5-6 mL) in a 50 mL pyrex reaction vessel. To this green mixture, ethylene was added by allowing the gas to bubble through the hexanes/2 solution/suspension for ~5 min. The vessel was sealed under ethylene and the mixture was allowed to react at RT (protected from light) for 21 h. After overnight reaction, the green color associated with 2 had disappeared. The product, 4, was visible as brown-red precipitate in faintly red-brown supernatant solution. The brown-red solid was recovered by filtration and washed with hexanes (1 mL x 3) and dried in vacuo (86 mg, 80%). Anal. Calc. for C$_{18}$H$_{12}$F$_6$S$_6$Mo: C 34.28, H 1.92, S 30.51; Found: C 33.96, H 1.68, S 30.43.

4.5.13 Observation of 4 by NMR spectroscopy

A CD$_2$Cl$_2$ solution of 2 (0.020 M), with BTBB (internal standard, 0.028 M) was placed in a J. Young NMR tube and treated with ethylene by allowing the gas to gently bubble through the solution for ~2 min. The NMR tube was sealed under ethylene. The mixture was allowed to react at RT for ~30 min and an NMR spectrum was collected. Product concentrations were obtained by comparison of their $^1$H NMR integrations with those of BTBB: 2 (3.8 mM, 19% of original concentration), 4 (two diastereomers, 6.3 mM), 2,3-dihydro-1,4-benzodithiin [DHBD(H,H)], 2.2 mM] Mass balance is 62%; the missing
Chapter 4 - Ethylene Reactivity of Electrophilic Mixed-Ligand Molybdenum Trisdithiolenes

material is likely accounted for by the low solubility of the alkene adducts. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 2.17-2.28 (ov m, CH$^b$HCH$^b$H, two diastereomers), 2.62-2.80 (ov m, CHH$^b$CHH$^b$, two diastereomers), 3.25 [s, dihydrodithiin, (CH$_2$)$_2$] 5.39 (s, unreacted ethylene), 6.77 (m, [Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$), 6.92 (m, [Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$), 6.98 [m, dihydrodithiin, S$_2$(C$_6$H$_4$)], 7.01-7.07 (ov m, [Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$), 7.13 [m, dihydrodithiin, S$_2$(C$_6$H$_4$)], 7.16-7.46 (ov m, [Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$ and 4), 7.49-7.59 (ov m, [Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$/DHBD(H,H) and unreacted 2), 7.86 (s, BTBB), 8.01 (s, BTBB), 8.05-8.12 (ov m, [Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$), 8.17 (m, [Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$), 8.25 (m, unreacted 2). $^{19}$F NMR (470 MHz, CD$_2$Cl$_2$) -64.13 (s, BTBB), -57.4 to -56.1 (ov m, [Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$), -56.03 (s, unreacted 1, minor), -55.9 to -55.3 (ov m, [Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$), -55.02 (s, 4, one of two diastereomers), -54.82 (s, 4, one of two diastereomers).

Comments: the alkene adducts (two possible diastereomers, depending on which side of S$_2$C$_6$H$_4$ ligand is attacked by ethylene) 4 are only sparingly soluble in chlorinated and aromatic NMR solvents (e.g., CDCl$_3$, CD$_2$Cl$_2$, toluene-d$_8$). In more strongly-coordinating solvents (acetone-d$_6$, acetonitrile-d$_3$, THF-d$_8$), the metal-bound DHBD(H,H) is displaced and metal decomposition products are observed as many $^1$H and $^{19}$F signals, for ill-defined (oligomeric [(Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$). In CDCl$_3$ and CD$_2$Cl$_2$, weak signals for 4 can be observed, and minor amounts of decomposition products (dihydrodithiin and [Mo(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$_x$) are formed as the adduct forms in situ, upon reaction of 2 and ethylene. Most of the product precipitates from solution in the form of brown-red microcrystals in weakly donating solvents. For preparative purposes, aliphatic solvents (e.g., hexanes) are ideal (see above, 4.5.12), where the alkene adducts precipitate from solution in the form of brown-red microcrystals and the decomposition pathway is suppressed.

4.5.14 Decomposition of 4 in CD$_3$CN

Compound 4 (6.1 mg, 0.010 mmol, mixture of diastereomers), isolated as described above (4.5.12), was combined with CD$_3$CN, which caused decomposition of the alkene adducts, dissolving the solid and giving a red-brown colored solution. The mixture was left at RT for ~ 15 min before analysis by $^1$H and $^{19}$F NMR spectroscopy. The NMR spectra show the
only products to be DHBD(H,H) and metal decomposition products ([Mo(S₂C₆H₄)(S₂C₂(CF₃)₂)]₃). The metal decomposition products appear as a large number of overlapping, low-intensity multiplets in the ¹H and ¹⁹F NMR spectra (not reported here, see 4.5.13 above for representative data). No alkene adducts (4) were observed (i.e., dissociation of the dihydrodithiin from metal is quantitative in this coordinating solvent). ¹H NMR (500 MHz, CD₃CN, dihydrodithiin only) δ 3.26 [s, 4H, dihydrodithiin (C₆H₂)₂], 7.01 [m, 2H, dihydrodithiin S₂(C₆H₄)], 7.14 [m, 2H, dihydrodithiin S₂(C₆H₄)].

4.5.15 Synthesis of (NEt₄)₂[Mo(S₂C₆H₄)(S₂C₂(CN)₂)(S₂C₂(CF₃)₂)] (5)

Complex 2 (99 mg, 0.16 mmol) was combined with hexanes (4-5 mL) in a 50 mL pyrex reaction vessel (sealable with a Teflon valve), giving a green solution with some suspended 2. Ethylene was introduced by allowing the gas to bubble through the hexanes/2 solution for 5 min to saturate the solution/atmosphere inside the vessel. The mixture was sealed under ethylene and allowed to react at RT, with stirring (protected from light), overnight (ca. 20 h). After overnight reaction, the green color associated with 2 had disappeared to give faintly violet colored supernatant solution with suspended fine brown-red solid material. From this mixture, the solvent/volatiles were removed under vacuum to afford brown solid residue. In air: To the brown residue was added Na₂S₂C₂(CN)₂ (61 mg, 0.33 mmol) in water/CH₃CN (1:1 v/v, 2.5 mL x 2 washings), giving, initially, a brown solution/suspension. The mixture was stirred at 70°C for 1 h, during which time a deep green colored homogeneous solution developed. Under vacuum, the volume of the solution was reduced by half (to ~ 2-3 mL). To this mixture was added NEt₄Br (168 mg, 0.80 mmol) in 1.5 mL of water, which immediately caused dark colored oily solid to precipitate. The oily solid was recovered (in air) by filtration. The solid product was washed with water (1 mL x 5), ethanol (1 mL x 5) and diethyl ether (1 mL x 10), which caused the product to become a tractable fine powder. The solid was dried in vacuo (dark blue powder, 92 mg, 67% based on 2). Anal. Calc. for C₃₀H₄₄F₂S₆N₄Mo: C 41.75, H 5.14, N 6.49, S 22.84; Found: C 41.50, H 5.40, N 6.02, S 22.84. ¹H NMR (500 MHz, acetone-d₆) δ 1.16 (m, 24H, N⁺(CH₂CH₃)₄ x 2), 3.13 (q, J_HH = 7.3 Hz, 16H, N⁺(CH₂Me)₄ x 2), 6.79 [m, 2H, S₂(C₆H₄)], 7.52 [m, 2H, S₂(C₆H₄)]. ¹⁹F NMR (470 MHz, acetone-d₆) δ -53.53 [s, 6F, (CF₃)₂]. X-ray quality crystals were grown by slow
diffusion of diethyl ether vapor into an acetone solution of 5. The crystal structure contains one tetraethylammonium [TEA] cation lying on a general position in the unit cell. During the refinement, areas of electron density were located in difference Fourier maps (on inversion centers) that were assigned as two additional [0.5 occupancy] tetraethylammonium cation molecules. The peak pattern of electron density illustrated that these molecules were highly disordered about the inversion centers. Attempts to model the disorder were unsuccessful. In the final cycles of refinement, the contribution to electron density corresponding to the disordered molecules was removed from the observed data using the SQUEEZE option in PLATON.\[33\] The resulting data vastly improved the precision of the geometric parameters of the remaining structure. The contribution of an additional molecule of TEA has been included in the molecular formula. The presence of two molecules of TEA in the molecular formula is confirmed by the charge balance and the other chemical analyses. A thermal ellipsoid plot for \([\text{Mo}(S_2C_6H_4)(S_2C_2(CN)_2)(S_2C_2(CF_3)_2)]^{2-}\) is shown in Figure 4.11(a) below, along with selected distances and angles.
**Figure 4.11** X-ray crystal structures of (a) $[\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)(\text{S}_2\text{C}_2(\text{CF}_3)_2)(\text{S}_2\text{C}_2(\text{CN})_2)]^{2-}$ and (b) $[\text{MoO}(\text{S}_2\text{C}_6\text{H}_4)(\text{S}_2\text{C}_2(\text{CF}_3)_2)]^{2-}$, using 30% probability ellipsoids. Tetraethylammonium counterions [partially disordered for (a), well-behaved for (b)] are not shown. For (b), one rotational orientation of the disordered trifluoromethyl group involving C3 is shown. Selected distances and angles: (a) $[\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)(\text{S}_2\text{C}_2(\text{CF}_3)_2)(\text{S}_2\text{C}_2(\text{CN})_2)]^{2-}$: Mo1-S1, 2.394(2); Mo1-S2, 2.397(2); Mo1-S3, 2.382(1); Mo1-S4, 2.379(1); Mo1-S5, 2.384(1); Mo1-S6, 2.371(1); S1-Mo1-S2, 80.80(6); S3-Mo1-S4, 80.95(5); S5-Mo1-S6, 80.32(5); ligand bend of $\text{S}_2\text{C}_6\text{H}_4$, $\text{S}_2\text{C}_2(\text{CF}_3)_2$, $\text{S}_2\text{C}_2(\text{CN})_2$, 2.7(2), 0.1(2), 0.5(2), respectively. (b) $[\text{MoO}(\text{S}_2\text{C}_6\text{H}_4)(\text{S}_2\text{C}_2(\text{CF}_3)_2)]^{2-}$: Mo1-S1, 2.383(1); Mo1-S2, 2.380(1); Mo1-S3, 2.389(1); Mo1-S4, 2.378(1); Mo1-O1, 1.702(3); S1-Mo1-S2, 82.62(4); S3-Mo1-S4, 83.26(4); ligand bend angles of $\text{S}_2\text{C}_6\text{H}_4$ and $\text{S}_2\text{C}_2(\text{CF}_3)_2$, 17.8(1) and 14.2(1), respectively.

### 4.5.16 Synthesis of $(\text{NEt}_4)_2[\text{MoO}(\text{S}_2\text{C}_6\text{H}_4)(\text{S}_2\text{C}_2(\text{CF}_3)_2)]$ (6)

Complex 2 (70 mg, 0.12 mmol) was combined with hexanes (4-5 mL) in a 50 mL pyrex reaction vessel, giving a green solution with some suspended 2. Ethylene was introduced by allowing the gas to bubble through the hexanes/2 solution for 5 min to saturated the
solution/atmosphere inside the vessel. The mixture was sealed under ethylene and allowed to react, with stirring (protected from light), overnight (approximately 20 h). After overnight reaction, the green color associated with 2 had disappeared to give faintly violet colored supernatant solution with suspended fine brown-red solid material. From this mixture, the solvent/volatiles were removed under vacuum to afford brown solid residue. Note: the following manipulations were done under anaerobic (argon) (but not anhydrous) conditions. NEt$_4$OH (0.13 mL of 35% w/w solution in water, 0.30 mmol) was added to the brown solid residue with EtOH (deoxygenated with argon purge) washings (1.5 mL x 2). Initially, a brown-red suspension was observed. The mixture was stirred at RT for 15 min and then heated at 50° C for 35 min. During this time, dark colored precipitate formed and the supernatant solution developed a faint blue color. The mixture was cooled to RT and the volatiles were removed under reduced pressure to afford crude product as a blue solid residue. Under inert (O$_2$/H$_2$O free) conditions: to the blue solid residue was added acetonitrile (2 mL), which mostly dissolved the solid, giving a blue solution. This solution was filtered. To the filtered solution was added THF (2 mL) and diethyl ether (3 mL). The resulting mixture was cooled overnight (~19 h), during which time pure product precipitated from the blue solution in the form of red-brown microcrystals. The red-brown solid was recovered by filtration. The solid was washed with (a) EtOH/THF (1:1 v/v, 1 mL x 5) and (b) diethyl ether (1 mL x 4) and then dried under vacuum. Yield: 57 mg, 67% based on 2.

Anal. Calc. for C$_{26}$H$_{44}$F$_6$S$_4$N$_2$O$_2$Mo: C 42.26, H 6.01, N 3.79, S 17.36; Found: C 42.25, H 5.77, N 3.63, S 17.86. $^1$H NMR (500 MHz, CD$_3$CN) δ 1.07 (m, 24H, N+($\text{CH}_2\text{CH}_3$)$_4$ x 2), 2.99 (q, $J_{\text{HH}}$ = 7.3 Hz, 16H, N+($\text{CH}_2\text{Me}$)$_4$ x 2), 6.76 [m, 2H, S$_2$(C$_6$H$_4$)], 7.50 [m, 2H, S$_2$(C$_6$H$_4$)]. $^{19}$F NMR (470 MHz, CD$_3$CN) δ -53.8. X-ray quality crystals were grown by vapor diffusion of THF into a CH$_3$CN solution of a (NEt$_4$)$_2$[MoO(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)] (red-orange plates). A thermal ellipsoid plot for [MoO(S$_2$C$_6$H$_4$)(S$_2$C$_2$(CF$_3$)$_2$)]$^{2-}$ is shown in Figure 4.11(b) above, along with selected distances and angles.

4.6 References


[14] We found, by UV-vis spectroscopy, the following approximate half-lives for reactions of molybdenum trisdithiolenes (0.16 mM) with ethylene in CH$_2$Cl$_2$ (ethylene-saturated solvent) at RT: for Mo(S$_2$C$_3$H$_4$)$_3$, t$_{1/2}$ > 2 h; for Mo(S$_2$C$_3$(CF$_3$)$_2$)$_3$, t$_{1/2}$ > 11 h (reaction not complete after 20 h); for Mo(S$_2$C$_3$H$_4$)$_2$(S$_2$C$_2$(CF$_3$)$_2$) (2) t$_{1/2}$ < 11 min.; for Mo(S$_2$C$_3$(CF$_3$)$_2$)$_2$(S$_2$C$_6$H$_4$) (1), t$_{1/2}$ < 1 min (reaction complete in 2 min);


[19] Crystallographic summary for structures reported here. For full details, the CIF/PDF files, deposited as CCDC-645333—645336, can be obtained from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.: data collection on Nonius-Kappa CCD diffractometer using Mo Kα (0.71073 Å), structure solution with direct methods, structure refinement on F$^2$ against all reflections, R$_1$ values reported here are for I > 2σ(I), wR$_2$ values are for all data. 2 C$_{32}$H$_{60}$F$_6$Mo$_5$S$_6$ (crystallizes as toluene solvate), MW = 694.66, green needle, triclinic, space group = P1̅, T = 150(1) K, a = 12.9104(5) Å, b = 13.8875(7) Å, c = 16.2347(9) Å, α = 106.797(2)°, β = 109.448(3)°, γ = 96.042(3)°, Z = 4, R$_1$ = 0.0468, wR$_2$ = 0.1310, GOF (F$^2$) = 1.031; 3: C$_{26}$H$_{50}$F$_2$Mo$_5$S$_6$ (crystallizes with partially disordered toluene, see experimental section for details on disorder, as well as twinning), MW = 854.73, red plate, monoclinic, space group = P 2$_1$/n, T = 120(2)
K, \( a = 12.9582(9) \) Å, \( b = 11.1308(6) \) Å, \( c = 21.4556(15) \) Å, \( \beta = 91.851(3)° \), \( Z = 4 \), \( R_1 = 0.0954 \), \( wR_2 = 0.2638 \), GOF (\( F^2 \)) = 1.100; 5 (two \( \text{NEt}_4^+ \) counter cations, see Supporting Information for details on disorder in one cation): \( \text{C}_{30}\text{H}_{44}\text{F}_6\text{Mo}_1\text{N}_4\text{S}_6 \), MW = 862.99, dark red needle, monoclinic, space group = \( P 2_1/c \), T = 150(2) K, \( a = 13.2228(7) \) Å, \( b = 19.4932(6) \) Å, \( c = 14.6543(8) \) Å, \( \beta = 90.1690(19)° \), \( Z = 4 \), \( R_1 = 0.0612 \), \( wR_2 = 0.1820 \), GOF (\( F^2 \)) = 0.973; 6 (two \( \text{NEt}_4^+ \) counter cations): \( \text{C}_{26}\text{H}_{44}\text{F}_6\text{Mo}_1\text{N}_2\text{O}_1\text{S}_4 \), MW = 738.81, orange needle, monoclinic, space group = \( P 2_11/n \), T = 150(2) K, \( a = 11.6275(5) \) Å, \( b = 18.5851(10) \) Å, \( c = 15.1232(5) \) Å, \( \beta = 94.295(3)° \), \( Z = 4 \), \( R_1 = 0.0536 \), \( wR_2 = 0.1342 \), GOF (\( F^2 \)) = 1.025.


[22] For DFT-calculated MOs of trisdithiolenes, see: Kirk, M. L.; McNaughton, R. L.; Helton, M. E., Chapter 3, p. 111 in ref. 20.


[25] This observation might be mechanistically relevant, by analogy, for the surprising reactions of 1,4-dithiins with certain cobalt complexes, reactions which generate metal-bound dithiolenes, under apparent alkyne extrusion: Kajitani, M.; Ochiai, R.; Kikuchi, R.; Okubo, M.; Akiyama, T.; Sugimori, A. Polyhedron 1990, 9, 1123.


[27] The mixed-dithiolene molybdenum oxo complex \([\text{MoO(S}_4\text{C}_2\text{CN})_2\text{(S}_4\text{C}_2\text{H}_2\text{)}_2]^-\) was made, along with other products (undirected approach), from \([\text{MeCN}]_4\text{MoO(Cl)}^+\) with \(\text{Na}_2\text{S}_4\text{C}_2\text{CN}_2\) and \(\text{Na}_2\text{S}_4\text{C}_2\text{H}_2\): (a) Donahue, J. P.; Goldsmith, C. R.; Nadiminti, U.; Holm, R. H. J. Am. Chem. Soc. 1998, 120, 12869. In another approach, \([\text{MoO(S}_4]_2^-\) undergoes substitution of one \([\text{S}_4]^-\) ligand with 1,2-arendithiols, yielding
[MoO(S₂(arene))]₂⁻ (where S₂(arene) = 1,2-benzenedithiolate or 3,6-dichloro-1,2-benzenedithiolate);
[MoO(S₂(arene))]₂⁻ can be treated with (HS)₂(arene') to furnish [MoO{S₂(arene)}{S₂(arene')}]²⁻ or with
MeCO₂C≡CCO₂Me to give [MoO{S₂(arene)}{(C₂S₂(CO₂Me)₂)]²⁻: (b) Sugimoto, H.; Suyama, K.; Sugimoto, K.;

Chapter 5

Catalytic Production of 2,3-Dihydro-1,4-benzodithiins: A New Application for Ligand-Based Reactivity of a Mixed-Ligand Molybdenum Trisdithiolene

5.1 Abstract

Activation of bis-o-phenylene tetrasulfide [BPTS, \((S_2C_6H_4)_2]\), to render it a practical benzodithiete equivalent for \([4+2]\) cycloadditions with alkenes, has been achieved with catalytic amounts of \(\text{Mo}(S_2C_2(CF_3)_2)(S_2C_6H_4)\) (1). The catalysis involves unusual ligand-based reactivity, and S,S-intraligand alkene adducts of 1 were directly observed as the catalyst resting state. A variety of substituted 2,3-dihydro-1,4-benzodithiins (DHBDs) were produced from BTPS and a selection of alkenes, including \(cis\)- and \(trans\)-disubstituted examples and allyl alcohol (with a hydroxyl group in addition to the alkene). For the reactions of \(cis\)- or \(trans\)-disubstituted alkenes, diastereospecificity was observed, such that \(cis\)- and \(trans\)-alkenes yielded \(cis\)- and \(trans\)-DHBDs, respectively (i.e., the alkene configuration is retained in the product). The work described below has been published.\(^1\)

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5.2 Introduction

Catalysis by transition metal complexes has enriched the toolbox of organic chemists to the extent that most multi-step organic syntheses are unthinkable without metal catalysis at important points of the synthesis sequence.\(^2\) The majority of transition-metal catalyzed transformations require direct coordination of a substrate to the metal (e.g., \(H_2\) activation via oxidative addition to rhodium(I), for Rh-catalyzed hydrogenation) at some critical point(s) in the catalytic cycle.\(^3\) A substrate may also interact with monoatomic metal-bound ligands, such as oxo groups or hydrides, without bonding directly to the metal.\(^4\) In a less common class of reactions, an organic molecule reacts with a comparatively complex (i.e., multiatomic) metal-activated ligand. Examples of the latter type of reactivity include stoichiometric metal-induced polarity reversal (\textit{umpolung}) of an
anilide ligand to make it amenable to nucleophilic attack, the “stepwise catalytic” activation of alkenes by coordination to the nitrogen atoms in cobalt dinitrosyl complexes, and, of course, the reactions of metal dithiolenes discussed in preceding chapters.

The ligand-based reactivity of metal bisdithiolenes was discovered in the 1960s and was studied rigorously for about a decade, before research in this area declined. After a relatively dormant period, research on the alkene reactivity of metal dithiolenes has intensified recently, due in part to potential applications and new mechanistic insights. In 2007 it was reported that the mixed-ligand trisdithiolene Mo(S2C2(CF3)2)2(S2C6H4) (compound 1) binds ethylene at the sulfur centers of the S2C6H4 ligand to form complex 2(H,H) (Step A in Scheme 5.1, R=R"=H) with a metal-chelating 2,3-dihydro-1,4-benzodithiin (see chapter 4). Compounds 1 and 2(H,H) were fully characterized [including a crystal structure for 2(H,H)]. It was found that 2,3-dihydro-1,4-benzodithiin [here DHBD(H,H)] could be cleanly displaced from the metal by ligand substitution, highlighting a possible novel approach to making DHBDs.

Both the parent 2,3-dihydro-1,4-dithiins (here DHDs; Figure 5.1A) and the benzannulated analogs, 2,3-dihydro-1,4-benzodithiins (DHBDs; Figure 5.1B), are interesting and useful compounds. For instance, 2,3-dihydro-1,4-dithiin tetroxide derivatives are active as non-peptide antagonists of the human galanin (hGAL-1) receptor. Mono-substituted (at the 5 or 6 positions, Figure 5.1A) 2,3-dihydro-1,4-dithiins can be converted into versatile alkenyl anion equivalents, to yield 5,6-disubstituted-2,3-dihydro-1,4-dithiins. The latter compounds can be viewed as protected cis-alkenes, and stereoselective alkene release from the heterocycle is easily achieved in good yield. 2,3-Dihydro-1,4-benzodithiins (DHBDs) have been proposed as precursors for naturally occurring benzenoid compounds, and highly symmetric polycyclic DHBDs are promising as precursors to organic ferromagnets and other advanced materials. Additionally, 2,3-disubstituted DHBDs have been explored as selective estrogen receptor modulators. Thus, catalytic production of DHBDs (or DHDs) from simple alkene precursors would be of interest as an efficient means of
Chapter 5 - Catalytic Production of 2,3-Dihydro-1,4-benzodithiins: A New Application for Ligand-Based Reactivity of a Molybdenum Trisdithiolene

generating these interesting sulfur heterocycles.

![Figure 5.1](image)

Figure 5.1 Nomenclature clarification: Parent (unsubstituted) DHD (A) and DHBD (B) with the ring numbering system shown. In some literature, the 2,3 and 5,6 positions are transposed. Also, in older reports the term ‘dithian’ is sometimes used to denote DHD.

5.3 Results and discussion

Catalytic cycles that exploit the reactivity of complex ligands are quite rare, and those involving sulfur-containing substrates are especially interesting because sulfur-containing molecules often cause catalyst poisoning. Until now, all of our molybdenum-mediated reactions producing DHBDs have been stoichiometric (see chapter 4). We now report that the alkene reactivity of Mo(S$_2$C$_2$(CF$_3$)$_2$(S$_2$C$_6$H$_4$)$_2$) (I) extends beyond ethylene to other alkenes and, most importantly, we have discovered a method for producing DHBDs catalytically, using I as a catalyst, according to an unusual mechanism that involves reactivity at a metal-bound dithiolene ligand.

5.3.1 Stoichiometric reactions

We discovered that compound 2(H,H) (formed from I and excess ethylene$^{12}$) reacts with excess bis-o-phenylene tetrasulfide [BPTS, (S$_2$C$_6$H$_4$)$_2$]$^{19}$ to regenerate I (83% yield by NMR)$^{20}$ while releasing free DHBD(H,H) (Figure 5.2). "Step B" (likely multiple steps, see below) in Scheme 5.1 has thus been realized.$^{21}$ Similarly, I reacts with excess 1-hexene to quantitatively form 2(H,$^n$Bu),$^{22}$ which can then be converted cleanly to I and DHBD(H,$^n$Bu) using excess BPTS.$^{23}$ Thus, the metal-coordinated DHBDs are displaced from 2(R,R$'$) and
the $S_2C_6H_4$ ligand is restored on the metal upon treatment of $2(R,R')$ with excess BPTS, or “dimeric$^{24} S_2C_6H_4$” (in CDCl$_3$ or CD$_2$Cl$_2$, 61-70$^\circ$C).

**Figure 5.2** $^{19}$F NMR (377 MHz, CD$_2$Cl$_2$) spectra showing that excess BPTS regenerates 1 (bottom) from of $2(H,H)$ (top). (Decomposition occurs as a rather minor side reaction, leading to some Mo($S_2C_2(CF_3)_2$)$_3$, labeled “*”) $^{25}$

These stoichiometric transformations address the key steps in a potential catalytic cycle. The full cycle, which aims to form DHBDs catalytically from alkenes and BPTS, is depicted in Scheme 5.1. Note that “Step B” in Scheme 5.1 almost certainly encompasses multiple steps. For example, it is possible that the DHBD is displaced by solvent (or excess alkene, if present), to form a bisdithiolene intermediate [$L_2Mo(S_2C_2(CF_3)_2)_2; L = $ solvent or alkene], which then reacts with BPTS to regenerate complex 1 (see below). Detailed mechanistic studies are needed to fully understand this transformation.
5.3.2 Catalytic production of DHBDs

We found that a catalytic amount of 1 (ca. 5 mol % relative to the “S$_2$C$_6$H$_4$” monomeric unit; 10 mol % with respect to dimeric BPTS) does indeed catalyze the formation of a variety of DHBDs from a selection of alkenes and BPTS. For the alkenes we screened, all of the corresponding DHBDs were obtained in fair to excellent NMR yields$^{20}$ (Table 5.1). The catalytic reactions were conducted in chlorinated solvents (CDCl$_3$ or CD$_2$Cl$_2$) or benzene-d$_6$ at 60-66°C (Table 5.1) in the presence of CD$_3$CN, which accelerates the DHBD-forming reactions (see below). High yields were obtained for simple/terminal alkenes (ethylene, 1-hexene or allyl alcohol) and for trans-2-pentene. The viability of allyl alcohol as a substrate in this reaction indicates that the method is not limited to non-polar (unfunctionalized) alkenes. Interestingly, the reactions of cis-disubstituted alkenes (cyclohexene or cis-2-pentene) gave lower yields of the corresponding DHBDs because of significant side-reactions giving polymeric material. Importantly, the reactions involving cis- and trans-2-pentene are diastereospecific, such that configuration of the alkene substrate is retained in the product. Specifically, the reaction of BPTS with cis-2-pentene (catalyzed by 1) produces DHBD(cis-Et,Me) (i.e., Et and Me groups cis in product) and none of the trans isomer (although polymeric byproduct is formed). Similarly, BPTS reacts with trans-2-pentene, in the presence of 1, to cleanly (no polymeric byproduct produced) furnish only DHBD(trans-Et,Me) and none of the cis isomer (Table 5.1).
Table 5.1 DHBD-yielding reactions catalyzed by 1

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Conditions (NMR yields)</th>
<th>Product(s)</th>
<th>Yield of DHBD</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene</td>
<td>20.5 h at 61°C (CDCl₃) [(S₂(C₆H₄))₂]₀ = 0.071 M excess ethylene [CD₃CN] = 0.48 M</td>
<td>![DHBD(H,H)]</td>
<td>NMR: 80% Isolated: 69%</td>
</tr>
<tr>
<td>1-hexene</td>
<td>2 h at 61°C (CDCl₃) [(S₂(C₆H₄))₂]₀ = 0.16 M [alkene]₀ = 0.30 M [CD₃CN] = 0.77 M</td>
<td>![DHBD(H,‘Bu)]</td>
<td>NMR: 96% Isolated: 67%</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>16.8 h at 65°C (C₆D₆) [(S₂(C₆H₄))₂]₀ = 0.14 M [alkene]₀ = 0.32 M [CD₃CN] = 0.77 M</td>
<td>![DHBD(C₆H₄,C₆H₄)] (+ polymer)</td>
<td>NMR: 71% Isolated: 50%</td>
</tr>
<tr>
<td>allyl alcohol</td>
<td>3 h at 61°C (CDCl₃) [(S₂(C₆H₄))₂]₀ = 0.14 M [alkene]₀ = 0.32 M [CD₃CN] = 0.77 M</td>
<td>![DHBD(H,CH₂OH)]</td>
<td>NMR: 89% Isolated: 58%</td>
</tr>
<tr>
<td>cis-2-pentene</td>
<td>17.8 h at 65°C (CD₂Cl₂) [(S₂(C₆H₄))₂]₀ = 0.14 M [alkene]₀ = 0.32 M [CD₃CN] = 0.77 M</td>
<td>![DHBD(cis-Me,Et)] (+ polymer)</td>
<td>NMR: 55% Isolated: 38%</td>
</tr>
<tr>
<td>trans-2-pentene</td>
<td>18.7 h at 61°C (CDCl₃) [(S₂(C₆H₄))₂]₀ = 0.14 M [alkene]₀ = 0.32 M [CD₃CN] = 0.77 M</td>
<td>![DHBD(trans-Me,Et)]</td>
<td>NMR: 94% Isolated: 80%</td>
</tr>
</tbody>
</table>

5.3.3 Distinguishing DHBD(cis- and trans-Et,Me)

To distinguish between the cis and trans isomers, the vicinal coupling constants Jₐc (Figures 3) were used, as the observed coupling constant between protons A and C should be significantly different for DHBD(cis-Et,Me) and DHBD(trans-Et,Me). Extracting the
experimental coupling constants from the $^1$H NMR data is not trivial and, for the \textit{trans} isomer in particular, we found it necessary to simulate (using Mestrec®) the experimental $^1$H NMR spectrum to ensure correct determination of the relevant coupling constants. See the experimental section for details on the simulations and for complete $^1$H NMR spectral assignments [all coupling constants and chemicals shifts for the [SCHMeCHeEtS] spin-systems for DHBD(\textit{cis-} and \textit{trans-}Et,Me)].

**Figure 5.3** Structures of DHBD(\textit{cis-}Et,Me) and DHBD(\textit{trans-}Et,Me) showing the proton labeling scheme for the 6-spin [SCHMeCHeEtS] system. The vicinal coupling constants, $J_{AC}$ (labeled in figure), were used to assign \textit{cis-} and \textit{trans-}stereochemistry.

For both the \textit{cis} and \textit{trans} dihydrodithiins, two major conformations of the six-membered dihydrodithiin ring are relevant here (Figure 5.4; this is neglecting conformers arising from folding along the S---S axis, or rotational isomerism of the Et group – which should have little bearing on $J_{AC}$). In the \textit{cis} isomer, DHBD(\textit{cis-}Et,Me), protons A and C should be separated by a dihedral angle of ca. 60° in both conformers [Figure 5.4(a) and (b)]. For the \textit{trans} form, one conformer [Figure 5.4(c)] places protons A and C at a dihedral angle of ca. 180°, and, in the other conformer [Figure 5.4(d)], the dihedral angle is ca. 60°. Thus, the dihedral angle between protons A and C is ca. 60° for \textit{cis} isomer, corresponding to an expected coupling constant ($J_{AC}$) of 2.5 Hz according to the Haasnoot-de Leeuw-Altona equation (a version of the Karplus relationship that includes substituent effects),\textsuperscript{26} regardless
of which conformer is more stable, since both conformers place $H^A$ and $H^B$ at a 60° dihedral angle. On the other hand, for the *trans* isomer, the observed (effective) coupling constant will be a weighted (by relative population) average of the vicinal coupling constants for pure forms (c) and (d) (Figure 5.4). The predicted (from torsion angles)$^{26}$ coupling constants are 10 Hz and 2.5 Hz for (c) and (d), respectively. While a 50% (c)/50% (d) population distribution should yield a 6.3 Hz effective (averaged) coupling constant, it can be expected that structure (c) should be very slightly disfavored in equilibrium, due to the *gauche*-dialkyl effect. The observed coupling constant for the *trans*-isomer thus should be significantly higher than 2.5 Hz but slightly lower than 6.3 Hz. In contrast, the vicinal hydrogen-hydrogen coupling constant for the *cis*-isomer should be very close to 2.5 Hz. The observed coupling constants for the two different isolated isomers of DHBD(Et,Me) are 2.61 Hz and 5.30 Hz, which safely allows assignment as *cis*- and *trans*-, respectively.

![Figure 5.4](image_url)

**Figure 5.4** Left: two ring conformers of DHBD(*cis*-Et,Me). Right: two ring conformers of DHBD(*trans*-Et,Me).

Additional confirmation of our assignments of DHBD(*cis*-Et,Me) and DHBD(*trans*-Et,Me) was obtained from 1D NOESY NMR experiments. Specifically, we selectively irradiated the doublet CH$_3$ signal (labeled “B” in Figure 5.3) for both the *cis* and *trans* isomers, while observing the response of $H^c$. The key results are summarized in Figure 5.5. When CH$_3^B$ was irradiated, a greater (by a factor of 2.8)$^{27}$ NOE response was observed for $H^c$ in the *trans* isomer, compared to the *cis* isomer, as expected on the basis of the Newman projections shown in Figure 5.4. That is, for the *trans* isomer, the dihedral angle between $H^c$ and the
methyl group is ca. 60° in both conformers [Figure 5.4(c and d)]. On the other hand, in the cis isomer, one conformer [Figure 5.4(a)] separates H^c and the methyl group by a dihedral angle of ca. 180°, meaning that these environments are separated by a greater distance, on average, than the corresponding environments in the trans isomer.

![Figure 5.5 1D NOESY NMR (500 MHz, CDCl₃) spectra showing the H^A/H^C regions (see Figure 5.3, above) for DHBD(cis-Et,Me) (top) and DHBD(trans-Et,Me) (bottom) and the relevant integrals.](image)

Thus, from the combined evidence of relative coupling constants (J_{AC}) and NOESY NMR experiments, we can confidently distinguish DHBD(cis-Et,Me) and DHBD(trans-Et,Me). Also, concerted synfacial alkene addition to complex 1 is expected (and symmetry-allowed^{12}), so cis-alkenes should yield cis-DHBDs and trans-alkenes should give trans-DHBDs.
5.3.4 Control experiments

A series of control experiments (see experimental section) for all alkenes used in this study verified that not even trace amounts of DHBDs were formed when 1 was not present in alkene/BPTS mixtures. We also tested other potential catalysts for forming DHBDs from alkenes and BPTS under otherwise similar conditions. A Lewis acid (B(C₆F₅)₃), a Brønsted acid ([H(OEt)₂][BF₄]), Lewis/Brønsted bases (NEt₃ and P(ⁿBu)₃), molybdenum(IV) sulfide and photolysis all failed to yield DHBDs. Additionally, we found that the radical inhibitor 2,6-di-tert-butyl-4-methylphenol (BHT, 30 mol %) does not inhibit catalysis in the reaction between 1-hexene and BPTS (with 1 as the catalyst). We therefore conclude that the catalysis operates according to the mechanism shown in Scheme 5.1.

5.3.5 Observation of the catalyst resting state and optimization of catalysis

¹⁹F and ¹H NMR spectroscopy were used to probe the resting state of the catalyst for the reactions involving 1-hexene and ethylene and, in both cases, the intraligand alkene adducts of 1 [2(H,H) or 2(H,ⁿBu)] were observed directly. For the ethylene reaction, compound 2(H,H), characterized by two singlets in the ¹⁹F NMR spectrum, (see Figure 5.2, above) is the dominant species present during catalysis (when CD₃CN is not present). The spectra for the catalyst resting state in the 1-hexene reactions – the alkene adduct 2(H,ⁿBu) – are considerably more complex than the spectra for 2(H,H): regardless of whether exo and/or endo isomers form (see discussion in experimental section), the resulting adduct(s) will have C₁ symmetry [versus C₅ symmetry for 2(H,H)]. Further, the ¹⁹F NMR spectra for 2(H,ⁿBu) exhibit temperature- and field- (400 MHz/500 MHz) dependence, indicating higher-order behaviour, which probably relates to impeded rotation of C-CF₃ bonds due to the increased steric bulk of metal-bound DHBD in 2(H,ⁿBu) compared to 2(H,H) [i.e., DHBD(H,H) versus ᵈBu-substituted DHBD(H,ⁿBu)]. More detailed NMR investigations are needed to assign the ¹H and ¹⁹F spectra for 2(H,ⁿBu), but reactivity studies confirm our assign of this species; recall from above that the adduct 2(H,ⁿBu), formed from reaction between 1 and 1-hexene, reacts with excess...
BPTS to regenerate complex 1, as does the fully characterized ethylene adduct 2(H,H).\(^{12}\)

The newly discovered catalysis was initially rather slow but proved to be amenable to significant acceleration upon optimization of conditions. In the 1-hexene reaction, for example, a turnover frequency (TOF)\(^{28}\) of 1.2 h\(^{-1}\) (in refluxing chloroform, 61°\(\text{C}\)) was measured for the first 2 h of the reaction when CD\(_3\)CN was not used.\(^{29}\) Interestingly, when CD\(_3\)CN (0.77 M, otherwise same conditions) was present in a parallel experiment, essentially complete conversion to DHBD(H,\(^n\)Bu) was observed in 2 h, causing a substantial increase in TOF\(^{28}\) to at least 9.7 h\(^{-1}\). Given that 2(R,R’) is the resting form of the catalyst, the steps (“Step B”, in Scheme 5.1) that release the metal-bound DHBD and regenerate complex 1 are expected to be rate-limiting. The presence of a more coordinating solvent would be expected to facilitate the rapid release of the chelating DHBD(R,R’) groups from the intermediates 2(R,R’). On the other hand, the resulting solvent adduct, (solvent)\(_2\)Mo(S\(_2\)C\(_2\)(CF\(_3\))\(_2\))\(_2\), must be sufficiently reactive to cleave BPTS to regenerate complex 1. We found that aromatic or chlorinated solvent/CD\(_3\)CN mixtures (ca. 25:1 v/v) gave the best catalytic results; higher concentrations of CD\(_3\)CN were problematic due to the low solubility of BPTS and 1 in polar solvents. Detailed mechanistic studies will be performed in the future to ascertain the precise role of CD\(_3\)CN in accelerating these catalytic reactions.

### 5.4 Conclusion

In conclusion, we have demonstrated that BPTS can be activated by complex 1 for reactions with alkenes to form 2,3-dihydro-1,4-benzodithiins (DHBDs). This is not only a new way to synthesize DHBDs\(^{30}\) but is also the first successful application of ligand-centered reactivity of a metal dithiolene in catalytic carbon-heteroatom bond formation.\(^{31}\) We have shown that the method can be applied to cis- and trans-disubstituted alkenes and allyl alcohol, with a hydroxyl functional group in addition to the alkene functionality. For the catalytic reaction involving ethylene and 1-hexene, the resting state of the catalyst, observed directly by NMR spectroscopy, was the corresponding alkene adduct of complex 1. Future work will broaden the scope of substrates.
Chapter 5 - Catalytic Production of 2,3-Dihydro-1,4-benzodithiins: A New Application for Ligand-Based Reactivity of a Molybdenum Trisdithiolene

5.5 Experimental Section

5.5.1 General Considerations

All experiments were conducted under inert atmosphere (nitrogen or argon), using glovebox (MBraun Unilab) or Schlenk-type techniques, except where noted. Benzene-1,2-dithiol (97%, Alfa Aesar), iodine (≥99%, Aldrich), bromine (reagent grade, Aldrich), 3,5-bis(trifluoromethyl)bromobenzene (BTBB) (99%, Aldrich), 1,2-dichloroethane (99.8%, Aldrich), triethylamine (99%, Aldrich), tributylphosphine (97%, Aldrich), tris(pentafluorophenyl)borane (95%, Aldrich), molybdenum(IV) sulfide (99%, <2 micron powder, Aldrich), HBF₄ (54 wt. % in diethyl ether, Aldrich), Vazo 52® (Dupont), ethylene (99.5%, BOC Canada), 1-hexene (≥99%, Aldrich), cyclohexene (99%, Aldrich), cis-2-pentene (98%, Aldrich), trans-2-pentene (99%, Aldrich), allyl alcohol (99%, Aldrich) and 2,6-di-tert-butyl-4-methylphenol (BHT) (99%, Aldrich) were obtained from commercial sources, as indicated. NMR (deuterated) solvents were purchased from Cambridge Isotopes or Aldrich. Silica gel (Alfa Aesar) was dried under vacuum at 100°C for >3 h, where noted. Acetonitrile-d₃ (CD₃CN), chloroform-d (CDCl₃), chloroform, pentane, triethylamine and the liquid alkenes were dried over activated molecular sieves (3Å, Aldrich) and deoxygenated with argon or nitrogen purges. Dichloromethane-d₂ (CD₂Cl₂) was dried over calcium hydride and vacuum-transferred prior to use. Benzene-d₆ (C₆D₆) was dried over sodium/benzophenone and vacuum-transferred from the purple ketyl prior to use. Mo(S₂C₃(CF₃)₂)(S₂C₆H₄) (I) was made using the literature procedure. BPTS ([S₂(C₆H₄)]₂) has been reported previously, but was prepared using a new procedure (see below) for the present study. Most of the NMR spectra were obtained on Bruker Avance III 400 MHz (¹H, ¹³C, ¹⁹F) or Unity/Inova Varian 500 MHz instruments (¹⁹F NMR VT experiments). Residual proton (¹H NMR) or carbon (¹³C NMR) peaks from the solvent were used as reference: ¹H (δ, ppm, benzene-d₆, 7.16, chloroform-d, 7.26; dichloromethane-d₂, 5.32); ¹³C ((δ, ppm, chloroform-d, 77.23). For ¹⁹F HMR spectra, BTBB (see above) was used as an internal standard (at -64.00 ppm); with BTBB at -64.00 ppm, external trifluoroacetic acid occurs at -76.52 ppm (in CDCl₃) or -76.42 ppm (in CD₂Cl₂). 1D
NOESY NMR experiments were recorded on a Unity/Inova Varian 500 MHz instrument. Spectra were collected at room temperature (RT, 20-25°C), except where noted. Mass spectrometry (EI) was performed at Advanced Instrumentation for Molecular Structure (AIMS), Toronto, ON, Canada on a Waters GC TOF instrument.

5.5.2 Synthesis of BPTS [(S$_2$C$_6$H$_4$)$_2$]

Benzene-1,2-dithiol (500 mg, 3.52 mmol) was added, in CHCl$_3$ (1.5 mL x 3) washings, to a 25 mL round-bottom flask containing I$_2$ (952 mg, 3.75 mmol) and CHCl$_3$ (8 mL) (and a stir bar). When the dithiol was added to the iodine solution, the color changed slightly from violet-red to brown-red. The flask was sealed with a septum. The mixture was stirred for 5 min and then NEt$_3$ (1.0 mL, 730 mg, 7.2 mmol) was added slowly (dropwise, over ca. 10 min) through the septum while vigorously stirring the solution. When addition of the amine was complete, the solution was orange with a small amount of insoluble viscous oil (polymer, see below). The mixture was stirred at ca. 30°C for 2 h. The solution was placed on a dry (not suspended in solvent) silica gel column (16 g of dry silica [70-230 mesh], inner column diameter: 2 cm). Once the orange solution was absorbed on the silica, additional CHCl$_3$ (enough to collected 25 mL of light yellow eluent) was passed through the column. Note that an orange band remained on the column. From the light yellow eluent, the solvent volume was reduced to ca. 8 mL under vacuum, causing a small amount of light yellow solid to precipitate from solution. More material was precipitated by the addition of pentane (or diethyl ether) (80 mL, added slowly, with stirring). The suspension was cooled (-35°C) overnight. The solid was recovered by filtration (15 mL glass frit funnel) and washed with pentane (or ether) (ca. 3 mL x 3) and then dried under vacuum (overnight at RT, do not heat). Yield (light yellow solid): 55-70% based on benzene-1,2-dithiol. $^1$H NMR (400 MHz, C$_6$D$_6$) δ 6.65 (m, 2H, Ar, byproduct, ca. 6%), 6.69 (m, 2H, Ar, byproduct) 6.70-6.81 (m, 4H, Ar, BPTS), 7.27 (m, 2H, Ar, byproduct), 7.41-7.51(m, 4H, Ar, BPTS). Trace pentane (or ether) was also observed in the $^1$H NMR spectrum. See Figure 5.6, below, for a representative NMR spectrum (aryl region). Also, see below for comments/discussion of the NMR data and the possible constitution of the byproduct. m/z (EI, reporting M$^+$ and base peaks and all peaks in between with intensities ≥ 10%) 280.0 (M$^+$, 21%), 216.0 (28%), 142.0
(12%), 141.0 (10%), 140.0 (S₂(C₆H₄), 100%). HRMS calcd for C₁₂H₈S₄ (M⁺) 279.9509, found 279.9507.

Figure 5.6 ¹H NMR (400 MHz, C₆D₆) spectrum for BPTS, as isolated. The possible identity of the unavoidable byproduct (labeled ‘*’ in the above spectrum) is discussed below.

5.5.2.1 Comments on BPTS

In the report containing the original synthesis of BPTS,¹⁹ it was noted that the molecular weights of the products were concentration-dependent in molten camphor and carbon disulfide. The authors also noted the propensity of BPTS to undergo polymerization when concentrated in solution and/or heated. Their synthesis, which used iodine to oxidize benzene-1,2-dithiol under high-dilution conditions in benzene, yielded ca. 50% oxidized product by mass, but approximately half of this material was insoluble in molten camphor (i.e., presumably high molecular weight species). An isolated yield for soluble/tractable material was not given.
Thus, the oxidation products of benzene-1,2-dithiol are highly reactive, particularly toward oligomerization/polymerization, and it is difficult to isolate soluble material with well-defined molecular weight, even under high dilutions conditions. Further, $^1$H NMR data for BPTS in the literature is sparse and possibly in error. For example, BPTS is reported to be one of several products in the reaction between o-benzyne and elemental sulfur.\textsuperscript{32} The reported $^1$H NMR data indicate a doublet of a doublet for BPTS at 8.66 ppm (in CDCl$_3$), corresponding to four protons. Presumably, there is another signal to account for the other four protons, possibly obscured by resonances from other products in the mixture. In our various attempts to oxidize benzene-1,2-dithiol to BPTS, we did not observe $^1$H NMR chemical shifts above 8 ppm (in CDCl$_3$ or C$_6$D$_6$) for any products, although it is possible that the reported shift at 8.66 ppm corresponds to another conformer of BPTS we have not observed. Rotational isomerism is possible for BPTS between $C_{2h}$ (chair) and $D_2$ (twist-boat) forms (Figure 5.7, A and B; both forms are present for (S$_2$C$_6$F$_4$)$_2$ at 300 K in toluene)\textsuperscript{33}, although crystallographically characterized BPTS showed the chair isomer\textsuperscript{34} and X-ray diffraction studies revealed only one type of crystal morphology in solid samples of BPTS.\textsuperscript{19}

![Figure 5.7 Conformational isomers of BPTS (A and B) and a possible structural isomer (C).](image)

When we attempted to oxidize the dithiol (initially ca. 0.09 M) with Br$_2$ (1 equiv), in ethanol or dichloromethane, the majority of the isolated material was intractable/insoluble (in chlorinated/aromatic/aliphatic solvents and in EtOH/MeOH and acetone) polymer. Further, we found that evaporation (to dryness) of CHCl$_3$ or CH$_2$Cl$_2$ solutions containing BPTS
resulted in considerable polymerization of the polysulfide to insoluble material, consistent
with the observation that BPTS “polymerized readily” at high concentration.19 Our best
results for the synthesis of BPTS, in terms of yield of soluble product and purity by 1H
NMR, were obtained using iodine as the oxidant (with amine present) in chloroform, as
described above.

The material we isolated was consistently contaminated with 5-10% of an unidentified
species with apparently lower symmetry than BPTS (in chair or twist-boat forms),
characterized by four equal-intensity multiplets in the 1H NMR spectrum (see Figure 5.635).
While we refer to BPTS as the dimer of highly reactive S2(C6H4) (observed by MS, see
above), the presence of higher oligomers (e.g., trimer or tetramer) is a possibility, given the
molecular weight dependence on concentration and the propensity of BPTS to polymerize.19
Thus, the byproduct could be a higher oligomer of the dithietene with a less symmetrical
structure than BPTS. Alternatively, this species could be a structural isomer of BPTS, with
one trisulfide and one monosulfide linkage connecting the two aryl rings (i.e., a 1,2,3,6-
tetra thiocin; see Figure 5.7, C), which would be consistent with our 1H NMR data showing a
species with four non-equivalent environments for aryl protons. The analogous
perfluorinated 1,2,3,6-tetra thiocin forms upon photolysis of the 1,2,5,6-tetra thiocin isomer of
(S2C6F4)2. This transformation is reversible for (S2C6F4)2: the 1,2,3,6-tetra thiocin isomer
slowly reverts to the 1,2,5,6-tetra thiocin in polar solvents.33

5.5.3 Synthesis of DHBD(H,H) (see Table 5.1 in section 5.3.2 for structure)

Complex 1 (10 mg, 0.015 mmol), BPTS (42 mg, 0.15 mmol) and CHCl3 (1.5 mL) were
combined in a 25 mL solvent bomb (Pyrex vessel sealable with a Teflon valve and a vacuum
adaptor side-arm) (with a stir bar). CD3CN (40 μL) was added. In air: the bomb was
quickly opened and ethylene gas was allowed to bubble gently through the solution for ca.
1.5 min. The bomb was resealed under ethylene. The bomb was placed in an oil bath (68°C)
and the solution was allowed to reflux, under ethylene, for 22.3 h. The solvent/volatiles
were removed under vacuum (at RT), affording dark brown oily residue. From this residue,
the product was distilled into the side-arm of the bomb, by heating the body of the bomb (but
not the side-arm) in an oil bath at 100°C under vacuum. The bomb was sealed to sequester the distilled product in the side-arm. In air, using undried solvent: The clear/colorless oil that condensed in the side-arm of the bomb was extracted with dichloromethane (1 mL x 3), after removing the silicone grease from the ground-glass joint of the side-arm. The solvent was removed, in vacuo (RT), from the combined extracts, affording clear, colorless oil. Yield: 35 mg, 69 % based on BPTS. ¹H NMR (400 MHz, CDCl₃) δ 3.26 (s, 4H, (CH₂)₂), 6.99 (m, 2H, Ar), 7.15 (m, 2H, Ar). See the ¹H NMR spectrum below (Figure 5.8). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 29.42, 125.41, 129.04, 131.55. m/z (EI) (reporting all peaks with m/z ≥ 140.0 and with intensities ≥ 10%) 168.0 (M⁺, 69%), 153.0 (base peak, 100%), 140.0 (35%). HRMS calcd for C₈H₉S₂ (M⁺) 168.0067, found 168.0071.

![Figure 5.8 ¹H NMR (400 MHz, CDCl₃) spectrum for purified (by vacuum distillation) DHD(H,H).](image-url)
5.5.4 Synthesis of DHBD(H⁸Bu)

Complex 1 (10 mg, 0.015 mmol) and 1-hexene (36 μL, 24 mg, 0.28 mmol) were combined in CHCl₃ (1.5 mL) and this solution was transferred to a 25 mL bomb containing BPTS (40 mg, 0.14 mmol). CD₃CN (35 μL) was added. The vessel was sealed under nitrogen and heated to reflux in an oil bath (65°C) for 45 h. The solvent/volatiles were removed under vacuum (at RT), affording dark green-brown oily residue. From this residue, the product was distilled into the side-arm of the bomb, by heating the body of the bomb (but not the side-arm) in an oil bath at 140°C under vacuum. The bomb was sealed to sequester the distilled product in the side-arm. In air, using undried solvent: The clear/colorless oil that condensed in the side-arm of the bomb was extracted with dichloromethane (1 mL x 3), after removing the silicone grease from the ground-glass joint of the side-arm. The solvent was removed, in vacuo (RT), from the combined extracts, affording clear, faintly green-blue (lightly tainted with trace catalyst residue) oil. Yield: 42 mg, 67 % based on BPTS. ¹H NMR (400 MHz, CDCl₃) δ 0.94 (t, ³JHH = 7.2 Hz, 3H, CH₃), 1.30-1.58 (m, 4H, (CH₂)₂), 1.76 (q, ³JHH = 7.7 Hz, 2H, CH₂), 2.98 (dd, ³JHH = 13.1 Hz, ³JHH = 8.3 Hz, 1H, SCH⁸H₈, cis to H⁸Bu), 3.22 (dd, ³JHH = 13.1 Hz, ³JHH = 3.2 Hz, 1H, SCH⁸H₈, trans to H⁸Bu), 3.47 (m, 1H, SCH (H⁸Bu)), 6.99 (m, 2H, Ar), 7.16 (m, 2H, Ar). See the ¹H NMR spectrum in Figure 5.9, below. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 14.13, 22.65, 29.13, 34.56, 35.62, 43.54, 125.01, 125.44, 128.68, 128.77, 131.50, 132.11. m/z (EI) (reporting M⁺ and base peaks and all peaks in between with intensities ≥ 10%) 224.1 (M⁺, 52%), 167.0 (41%), 153.0 (47%), 142.0 (32%), 140.0 (15%), 135.0 (12%), 134.0 (base peak, 100%). HRMS calcd for C₁₂H₁₆S₂ (M⁺) 224.0693, found 224.0691.
Figure 5.9 $^1$H NMR (400 MHz, CDCl$_3$) spectrum for purified (by vacuum distillation) DHD(H,nBu). The inset shows an expanded view of the resonances associated with the aliphatic (i.e., attached to sp$^3$ carbon) ring protons.

5.5.5 Synthesis of DHBD(C$_2$H$_4$C$_2$H$_4$)

Note: this compound has been reported previously. A procedure analogous to that used in the synthesis of DHBD(H,nBu) (see above; same solvents/concentrations) was used here, using cyclohexene as the alkene, with the following modifications: the catalyst/alkene/tetrasulfide mixture was heated (65°C) for 18 h; vacuum distillation of the product to the side-arm of the reaction vessel was carried out at 160°C. Yield (oily white solid at RT): 31 mg, 50 % based on BPTS. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.46 (m, 2H, CH$_2$), 1.70-1.92 (ov m, 4H, CH$_2$), 2.01 (m, 2H, CH$_2$), 3.57 (m, 2H, SCHR (x2)), 6.97 (m, 2H, Ar), 7.16 (m, 2H, Ar). Note: $^1$H NMR spectra of the crude material, before distillation, show contaminants with broad aliphatic and aryl resonances, probably indicating polymeric
byproduct (see below for discussion). See the $^1$H NMR spectrum of the purified product in Figure 5.10, below. $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ 23.25, 31.16, 44.06, 125.07, 128.55, 131.29. $m/z$ (EI) (reporting M$^+$ and base peaks and all peaks in between with intensities ≥ 10%) 222.1 (M$^+$, 61%), 179.0 (32%), 166.0 (24%), 153.0 (44%), 142.0 (31%), 141.0 (21%), 140.0 (100%). HRMS calcd for C$_{12}$H$_{14}$S$_2$ (M$^+$) 222.0537, found 222.0537.

**Figure 5.10** $^1$H NMR (400 MHz, CDCl$_3$) for purified (by vacuum distillation) DHD(C$_2$H$_4$,C$_2$H$_4$). The inset shows an expanded view of the resonances associated with the aliphatic ring protons.

### 5.5.6 Synthesis of DHBD(H,CH$_2$OH)

Complex 1 (10.2 mg, 0.015 mmol) was dissolved in CHCl$_3$ (1.5 mL) and the resulting deep green solution was added to a bomb containing BPTS (51 mg, 0.18 mmol). Allyl alcohol (19 μL, 16 mg, 0.28 mmol) and then CD$_3$CN (40 μL) were added. The vessel was sealed
and heated in an oil bath (68°C, reflux) for 2 h and 20 min. Note: the color of the solution changed from deep green to brown-green to brown-purple during this time. The solvent/volatiles were removed under reduced pressure, giving dark brown-purple oily residue. In air: this residue was redissolved in dichloromethane (3 mL); isopropanol (3 mL) was added. The volume of the resulting suspension was reduced by ca. ½ (to ca. 3 mL). The concentrated suspension was placed on a silica gel column (17 g of silica [230-400 mesh], suspended in isopropanol, inner column diameter: 2 cm). The reaction vessel was washed twice with isopropanol (1.5 mL) and these washings were also placed on the column. Isopropanol (20 mL) was passed through the column producing clear/colorless eluent (discarded). An additional 20 mL of isopropanol were passed through the column, giving very faintly green tinted eluent (kept). Note that a dark green-brown colored band remained on the bottom of the column. From the second 20 mL fraction, the solvent was removed under vacuum, yielding viscous (slightly green-brown) oil. This oil was redissolved in dichloromethane (ca. 5 mL) and the solvent was removed, again, under vacuum. Yield: 32 mg, 58% based on ally alcohol (excess of BPTS used to avoid difficulties in separating the product and unreacted alkene). $^1$H NMR (400 MHz, C$_6$D$_6$, sample filtered through Celite) $\delta$ 0.94 (t, $^{3}$J$_{HH}$ = 5.6 Hz, 1H, OH), 2.59-2.72 (ov m, 2H, H$^A$ and $^B$), 3.13 (m, 1H, H$^C$), 3.31(m, 1H, H$^D$ or $^E$), 3.44 (m, 1H, H$^D$ or $^E$), 6.69 (m, 2H, Ar), 7.10 (m, 2H, Ar). Figure 5.11, below, shows the $^1$H NMR spectrum of the product. $^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$, sample filtered through Celite) $\delta$ 30.62, 45.48, 64.93, 125.55, 126.27, 129.33, 129.81, 132.09, 132.85. $m/z$ (EI) (reporting M$^+$ and base peaks and all peaks in between with intensities $\geq$ 10%) 198.0 (M$^+$, 35%), 180.0 (16%), 167.0 (45%), 153.0 (53%), 142.0 (23%), 140.0 (17%), 135.0 (12%), 134.0 (base peak, 100%). HRMS calcd for C$_9$H$_{10}$OS$_2$ (M$^+$) 198.0173, found 198.0177.
Figure 5.11 $^1$H NMR (400 MHz, C$_6$D$_6$) spectrum for DHBD(H,CH$_2$OH), purified by column (silica gel) chromatography. The insets show expanded views of the resonances associated with the diastereotopic protons $^1$H$_{D,E}$ and aliphatic ring protons ($^1$H$_{A,B,C}$). Also shown is the structure of DHBD(H,CH$_2$OH), with the proton labeling scheme.

5.5.7 Synthesis of DHBD(cis-Et,Me) and $^1$H NMR spectral simulation

A procedure analogous to that used in the synthesis of DHBD(H,$^n$Bu) (section 5.5.4) was used here, using cis-2-pentene as the alkene, with the following modifications: no CD$_3$CN was used; the catalyst/alkene/tetrasulfide mixture was heated (65°C) for 21 h; vacuum distillation of the product to the side-arm of the reaction vessel was carried out at 170°C. Yield (blue-tinted oil): 23 mg, 38 % based on BPTS. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.09 (t, $^3$J$_{HH}$ = 7.4 Hz, 3H, CH$_2$CH$_3$), 1.39 (d, $^3$J$_{HH}$ = 6.9 Hz, 3H, SCH$_2$H$_3$), 1.62 (ov m, diastereotopic CH$_2$Me), 1.69 (ov m, diastereotopic CH$_2$Me), 3.38 (m, 1H, SCH$_2$Et, cis to H$_A$, see below), 3.57 (dq, $^3$J$_{HH}$ = 6.9 Hz, $^3$J$_{HH}$ = 2.6 Hz, 1H, SCH$_2$Me, cis to H$_C$), 6.96 (m, 2H, Ar), 7.11 (m, 2H, Ar). See Table 5.2 below for full $^1$H NMR details: all coupling
constants and chemical shifts are assigned for the [SCHMeCHEtS] spin system. Note: $^1$H NMR spectra of the crude material, before distillation, show contaminants with broad aliphatic and aryl resonances, probably indicating polymeric byproduct (see below for discussion). Figures 5.12 and 5.13 show the $^1$H NMR spectrum of the product, compared with the simulated spectrum. Simulating the spectrum (data in Table 5.2) gave accurate coupling constant information, which was used for assigning the product as the cis isomer. See discussion below. $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 12.11, 17.50, 25.11, 39.51, 49.35, 124.91, 125.00, 128.32, 128.51, 129.96, 130.66. m/z (EI) (reporting M$^+$ and base peaks and all peaks in between with intensities ≥ 10%) 210.1 (M$^+$, 61%), 181.0 (80%), 167.0 (56%), 166 (33%), 153.0 (75%), 149.0 (11%), 148.0 (36%), 147.0 (31%), 142.0 (25%), 141.0 (29%), 140.0 (base peak, 100%). HRMS calcd for C$_{11}$H$_{14}$S$_2$ (M$^+$) 210.0537, found 210.0533.

Figure 5.12 Comparison of experimental (bottom) and simulated (top) $^1$H NMR (400 MHz, CDCl$_3$, for experimental spectrum) spectra for DHBD(cis-Et,Me). The aromatic region is not shown. The inset shows the structure of DHBD(cis-Et,Me) and the proton labeling scheme. See Figure 5.13, below, for expanded views of the A/C and D/E regions.
Figure 5.13  Expanded views of the $^1$H NMR signals associated with ring protons A and C (cis) (left side; experimental spectrum on bottom, simulated spectrum on top) and diastereotopic protons D and E (right side; experimental spectrum on bottom, simulated spectrum on top). See Table 5.2, below, for the simulation parameters (coupling constants, etc.).

Table 5.2  $^1$H NMR parameters for DHBD(cis-Et,Me) used to simulate the experimental spectrum (aromatic protons not included). The coupling constant $J_{AC}$ (in bold) was used to identify the product as the cis isomer.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Number of protons</th>
<th>Chemical shift (ppm)</th>
<th>Coupling constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Fig. 5.12)</td>
<td>1</td>
<td>3.567</td>
<td>$J_{AB} = 6.85$</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>1.391</td>
<td>$J_{AC} = 2.61$</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>3.381</td>
<td>$J_{CD} = 9.20$</td>
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<tr>
<td>D</td>
<td>1</td>
<td>1.624</td>
<td>$J_{CE} = 5.50$</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>1.691</td>
<td>$J_{DE} = -14.00$</td>
</tr>
<tr>
<td>F</td>
<td>3</td>
<td>1.086</td>
<td>$J_{DF} = J_{EF} = 7.38$</td>
</tr>
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</table>

Line width (for simulation): 1.3
Spectral frequency: 400 MHz

5.5.8  Synthesis of DHBD(trans-Et,Me) and $^1$H NMR spectral simulation

A procedure analogous to that used in the synthesis of DHBD(H,nBu) (section 5.5.4) was used here, using trans-2-pentene as the alkene, with the following modifications: 40 $\mu$L of
CD$_3$CN were used (instead of 35 μL); the catalyst/alkene/tetrasulfide mixture was heated (68°C) for 22.3 h; vacuum distillation of the product to the side-arm of the reaction vessel was carried out at 150°C. Yield (oil): 50 mg, 80% based on BPTS. Note: in contrast to the reaction that gives DHBD(cis-Et,Me) (see above), no polymeric byproduct was formed in the present reaction. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.06 (t, $J_{HH} = 7.4$ Hz, 3H, CH$_2$CH$_3$), 1.48 (d, 6.8 Hz, 3H, SCHCH$_3$), 1.70 (ov m, 1H, diastereotopic CHHMe), 1.80 (ov m, 1H, diastereotopic CHHMe), 2.93 (m, 1H, SCH$^A$Et, trans to $H^C$, see below), 2.93 (m, 1H, SCH$^C$Me, trans to $H^A$), 7.00 (m, 2H, Ar), 7.18 (m, 2H, Ar). See Table 5.3 below for full $^1$H NMR details: all coupling constants and chemical shifts are assigned for the [SCHMeCHEtS] spin system. Figures 5.14 and 5.15 show the $^1$H NMR spectrum of the product, compared with the simulated spectrum. The simulated spectrum was used for assigning the product as the trans isomer. See discussion below. $^{13}$C[$^1$H] NMR (100 MHz, CDCl$_3$) $\delta$ 11.46, 22.72, 29.13, 41.16, 50.64, 125.16, 125.19, 128.81, 128.98, 130.70, 131.00. $m/z$ (EI) (reporting all peaks with $m/z \geq 140.0$ and with intensities $\geq 10\%$) 210.1 (M$^+$ and base peak, 100%), 181.0 (74%), 167.0 (25%), 166.0 (11%), 153.0 (24%), 148.0 (18%), 142.0 (14%), 140.0 (73%). HRMS calcd for C$_{11}$H$_{14}$S$_2$ (M$^+$) 210.0537, found 210.0535.
Figure 5.14 Comparison of experimental (bottom) and simulated (top) $^1$H NMR (400 MHz, CDCl$_3$, for experimental spectrum) spectra for DHBD($trans$-Et,Me). The aromatic region is not shown. The inset shows the structure of DHBD($trans$-Et,Me) and the proton labeling scheme. See Figure 5.15, below, for expanded views of the A/C and D/E regions.

Figure 5.15 Expanded views of the $^1$H NMR signals associated with ring protons A and C ($trans$) (left side; experimental spectrum on bottom, simulated spectrum on top) and diastereotopic protons D and E (right side; experimental spectrum on bottom, simulated spectrum on top). See Table 5.3, below, for the simulation parameters (i.e., coupling constants, etc.).
Table 5.3 ¹H NMR parameters for DHBD(trans-Et,Me) used to simulate the experimental spectrum (aromatic protons not included). The coupling constant \( J_{AC} \) (in bold) identifies the product as the trans isomer (see below for discussion).

<table>
<thead>
<tr>
<th>Environment</th>
<th>Number of protons</th>
<th>Chemical shift (ppm)</th>
<th>Coupling constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Fig. 5.14)</td>
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<td>3.254</td>
<td>( J_{AB} = 6.76 )</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>1.482</td>
<td>( J_{AC} = 5.30 )</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>2.928</td>
<td>( J_{CD} = 8.50 )</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>1.704</td>
<td>( J_{CE} = 5.05 )</td>
</tr>
<tr>
<td>E</td>
<td>1</td>
<td>1.804</td>
<td>( J_{DE} = -14.00 )</td>
</tr>
<tr>
<td>F</td>
<td>3</td>
<td>1.060</td>
<td>( J_{DF} = J_{EF} = 7.36 )</td>
</tr>
</tbody>
</table>

Line width (for simulation): 1.6
Spectral frequency: 400 MHz

See section 5.3.3, above, for a detailed discussion on how the above coupling constant data, combined with 1D NOESY experiments, were used to assign cis and trans configurations to the two forms DHBD(Et,Me).

5.5.9 Synthesis of DHBD(H,H) for NMR yield

Note: this compound has been reported previously\(^{37}\) and is commercially available. A CDCl₃ solution (1.0 mL) containing \( \mathbf{1} \) (5.0 mg, 0.0073 mmol) and 3,5-bis(trifluoromethyl)bromobenzene (BTBB) (4.0 μL, 6.8 mg, 0.023 mmol) was added to a 25 mL bomb containing BPTS (20 mg, 0.071 mmol) and a stir bar. CD₃CN (25 μL) was added and then ethylene gas was added to the vessel by allowing the gas to gently bubble through the solution for ca. 2 min. The vessel was sealed under ethylene. Note: within 5 min of adding the ethylene, the color of the solution changed from green-blue to brown-green. The mixture was heated to reflux in an oil bath (64°C) for 20.5 h. A portion of the resulting brown-yellow solution was placed in a J. Young NMR tube. Product proton integrations, relative to BTBB (internal standard) were used to determine the concentration/NMR yield of
the product [DHBD(H,H)]. NMR yield: 80%, based on BPTS. See above (section 5.5.3) for $^1$H, $^{13}$C NMR and mass spectrometry data for this compound.

### 5.5.10 Synthesis of DHBD(H,${}^n$Bu) for NMR yield

A CDCl$_3$ solution (0.50 mL) containing 1 (5.1 mg, 0.0074 mmol) and BTBB (9.0 μL, 15 mg, 0.050 mmol) was added to a J. Young NMR tube (sealable with Teflon valve) containing BPTS (22 mg, 0.079 mmol). CD$_3$CN (20 μL) and 1-hexene (19 μL, 13 mg, 0.15 mmol) were added and the tube was sealed under nitrogen. The mixture was heated to reflux in an oil bath (68°C) for 2 h. NMR yield (based on $^1$H integration vs. BTBB, see above): 96%, based on BPTS. See above (section 5.5.4) for full characterization data for this product. Note: a parallel experiment, with identical conditions to those described above, except CD$_3$CN was not added, gave an NMR yield of 12% for DHBD(H,${}^n$Bu) (2 h at 68°C, reflux). These experiments were used to calculate the TOFs reported in the manuscript {using TOF = [(moles of DHBD produced)/(moles of catalyst)]/time}. Note: when 1 is first reacted with excess 1-hexene, to form 2(H,${}^n$Bu) quantitatively (in <2 min), the resulting 2(H,${}^n$Bu)/1-hexene mixture reacts with BPTS (aside from order of addition, otherwise same conditions as above) to form DHBD(H,${}^n$Bu) catalytically. Thus, catalysis proceeds regardless of whether the catalyst starts in its alkene adduct form [2(H,${}^n$Bu)], or alkene-free form (complex 1), as expected from our mechanistic proposal (see main text).

### 5.5.11 Synthesis of DHBD(C$_2$H$_4$,C$_2$H$_4$) for NMR yield

The procedure was analogous to the one used for the synthesis of DHBD(H,${}^n$Bu) (section 5.5.10, see Table 5.1 for exact concentrations of alkene and BPTS), with the following modifications: cyclohexene was used as the alkene; the reaction was conducted in C$_6$D$_6$ (instead of CDCl$_3$); 1,2-dichloroethane was used as an internal standard (instead of BTBB); the reaction mixture was heated, in a J. Young NMR tube, at 65°C for 16.8 h. NMR yield of DHBD(C$_2$H$_4$,C$_2$H$_4$) (based on $^1$H integration vs. 1,2-dichloroethane): 71%, based on BPTS. See above (section 5.5.5) for characterization data for this product. Note: the crude product was contaminated with polymeric material, which was not volatile (i.e., did not transfer...
under vacuum at 160°C). This material has a $^1$H NMR spectral profile similar to that seen for the polymer produced in the synthesis of DHBD(cis-Et,Me) (see below).

### 5.5.12 Synthesis of DHBD(cis-Et,Me) for NMR yield

The procedure was analogous to the one used for the synthesis of DHBD(H,n-Bu) (section 5.5.10, see Table 5.1 for exact concentrations of alkene and BPTS), with the following modifications: cis-2-pentene was used as the alkene; the reaction was conducted in CD$_2$Cl$_2$ (instead of CDCl$_3$) to minimize the amount of polymeric byproduct (see below); the reaction mixture was heated, in a J. Young NMR tube, at 65°C for 17.8 h, with the NMR tube completely submerged in the oil bath (i.e., heated under autogenic pressure). NMR yield of DHBD(cis-Et,Me) (based on $^1$H integration vs. BTBB): 55%, based on BPTS. See above (5.5.7) for characterization data for this product. Note: the crude product was contaminated with polymeric material, which was not volatile (i.e., did not transfer under vacuum at 170°C). $^1$H NMR (for polymeric contaminants only) (400 MHz, CD$_2$Cl$_2$) $\delta$ 0.80-1.78 (br ov m), 1.98-2.36 (br ov m), 2.88-4.04 (br ov m), 6.46-7.76 (br ov m). See Figure 5.16, below, for a possible polymeric structure of the byproduct produced here and in the synthesis of DHBD(C$_2$H$_4$C$_2$H$_4$).

![Suggested structure for the polymeric byproduct observed in catalytic reactions between BPTS and internal cis alkenes](image)

**Figure 5.16** Suggested structure for the polymeric byproduct observed in catalytic reactions between BPTS and *internal cis* alkenes [i.e., cyclohexene (R=R'=C$_2$H$_4$) or cis-2-pentene (R=Me, R'=Et)].

Note: polymeric byproducts were not observed in the catalyzed reactions between BPTS and terminal alkenes (ethylene and 1-hexene). Also, some polymeric material was formed in mixtures containing BPTS and internal alkenes, even in the absence of 1 (see control experiments, below). Interestingly, however, the reaction of *trans*-2-pentene with BPTS...
(with 1 as catalyst) cleanly affords DHBD(trans-Et,Me) and polymeric byproduct is not produced.

5.5.13 Synthesis of DHBD(trans-Et,Me) for NMR yield

The procedure was analogous to the one used for the synthesis of DHBD(H,⁹Bu) (section 5.5.10, see Table 5.1 for exact concentrations of alkene and BPTS), with the following modifications: trans-2-pentene was used as the alkene; 9.0 μL (0.052 mmol) of BTBB (instead of 4.0 μL); the alkene/BPTS/catalyst reaction mixture was heated (68°C, reflux) for 18.7 h. NMR yield of DHBD(trans-Et,Me) (based on \(^1\)H integration vs. BTBB): 94%, based on BPTS. See above (section 5.5.8) for characterization data for this product. No polymeric byproduct was observed in this reaction.

5.5.14 Synthesis of DHBD(H,CH₂OH) for NMR yield

The procedure was analogous to the one used for the synthesis (section 5.5.10, see Table 5.1 for exact concentrations of alkene and BPTS) of DHBD(H,⁹Bu), with the following modifications: the alkene/BPTS/catalyst reaction mixture was heated (68°C, reflux) for 3 h to obtain near-complete consumption of BPTS. NMR yield of DHBD(H,CH₂OH) (based on \(^1\)H integration vs. BTBB): 89%, based on BPTS. See above (section 5.5.6) for characterization data for this product.

5.5.15 Observation of the catalyst resting state

The resting state of the catalyst, in reactions between ethylene or 1-hexene and BPTS, was assessed by \(^{19}\)F NMR spectroscopy. In both cases, the resting form is the corresponding alkene adduct of complex 1 [i.e., 2(R,R’)]. Compound 1 is known to react with ethylene rapidly and cleanly to form 2(H,H), its intraligand (at the S₃C₆H₄ ligand) ethylene adduct. This fully characterized complex is major species observed by \(^{19}\)F NMR (two singlets for \(C_s\)-symmetric adduct) in the catalytic reactions between ethylene and BPTS early in the reaction (also present when reaction is complete, along with various catalyst decomposition products) when CD₃CN was not present. For the present study, we showed, in a stoichiometric experiment, that 2(H,H) is converted back to 1, releasing free DHBD(H,H),
upon treatment with excess BPTS (see below for experimental details). The reactions involving 1-hexene gave much more complex spectra for the catalyst resting state, due to the $C_1$ symmetry of the adduct. When CD$_3$CN was not used, the major species observed (by $^{19}$F NMR) is the 1-hexene adduct of 1 (2(H,$^n$Bu), Figure 5.17) as (we propose) the exo isomer only (see below).

![Catalyst decomposition products](image)

**Figure 5.17** $^{19}$F NMR (377 MHz, CDCl$_3$, 23°C) spectrum showing the resting state of the catalyst in a reaction between 1-hexene and BPTS (with 1 as the catalyst, no CD$_3$CN). The inset shows an expanded view of the resonances associated with 2(H,$^n$Bu).

The above spectrum (Figure 5.17) was obtained after heating a 1-hexene/BPTS/1 mixture (initial concentrations: 0.28 M/0.15 M/15 mM; in CDCl$_3$) for 22 h at reflux. At this stage, the reaction to give DHBD(H,$^n$Bu) was ca. 60% complete (the reaction is faster when CD$_3$CN is present). In addition to 2(H,$^n$Bu), some minor products arising from catalyst decomposition are observed (labeled in Figure 5.17, <5% by integration). A $^{19}$F NMR spectrum of the same mixture, taken at an earlier point during the reaction (after ca. 1 h) is identical to the spectrum shown here, except the catalyst decomposition peaks were not
detectable. Thus, the catalyst has a finite lifetime, slowly decomposing to (presumably) inactive species.

We propose the $^{19}$F NMR spectrum shown in Figure 5.17 represents only the exo isomer of 2\((H,^nBu)\). The endo isomer appears unlikely to form on steric grounds, given the size/length of the alkyl \((^nBu)\) chain (i.e., there would be significant steric conflict between the trifluoromethyl groups and the dangling alkyl chain). The complexity of the spectrum is likely explained by higher order coupling between the fluorine atoms of the CF$_3$ groups, where C-CF$_3$ bond rotation is impeded by steric constraint caused by the metal-bound alkyl-substituted DHBD. Preliminary variable temperature (VT) NMR experiments show that the spectra for 2\((H,^nBu)\) are temperature-dependent (Figure 5.18) and also field-dependent, as expected for higher order spectra. Reactivity studies support our assignment of the $^{19}$F NMR data: 2\((H,^nBu)\) is converted to 1, releasing DHBD\((H,^nBu)\), when treated with excess BPTS (see below for experimental details). Recall that fully-characterized 2\((H,H)\)$^{12}$ is also converted to 1 and free DHBD\((H,H)\) when treated with excess BPTS (in CD$_2$Cl$_2$) (see experimental details below). When CD$_3$CN was present in catalytic runs, the $^{19}$F NMR spectra of the equilibrium mixture showed 2\((H,^nBu)\), as well as a new species, characterized by one sharp singlet (-55.4 ppm in CDCl$_3$), which is reasonably assigned as \((CD_3CN)_2Mo(S_2C_2(CF_3)_2)\). We found that having CD$_3$CN present accelerated the catalytic reactions between alkenes and BPTS, possibly because \((CD_3CN)_2Mo(S_2C_2(CF_3)_2)\) is more reactive toward BPTS than 2\((R,R')\).
5.5.16 Reaction of 2(H,H) with BPTS to generate 1 and DHBD(H,H)

Complex 1 (9.9 mg, 0.014 mmol) and BTBB (2.5 μL, 4.2 mg, 0.015 mmol) were combined in CD$_2$Cl$_2$ (0.7 mL). The tube was opened in air and ethylene was added by allowing the gas to gently pass through the solution for ca. 1 min. The tube was quickly resealed under an ethylene atmosphere. Ca. 10 min after adding the ethylene, $^1$H and $^{19}$F NMR spectra were obtained to verify quantitative conversion to 2(H,H) (see ref. 12 for NMR data for this compound and Figure 5.2 for a representative spectrum). Excess ethylene was removed by purging the solution with argon for ca. 1.5 min. Note: approximately 0.1 mL of solvent was lost to evaporation from purging with ethylene and argon. A $^1$H NMR spectrum was collected to confirm removal of excess ethylene. BTPS (10 mg, 0.036 mmol) was added, with an additional 0.1 mL of CD$_2$Cl$_2$, to the NMR tube. The entire tube was submerged in an oil bath and heated at 70°C (under autogenic pressure) for 18.8 h. Another $^{19}$F NMR spectrum was collected, which showed 83% yield (by integration relative to BTBB) of 1 (singlet, -56.03 in CD$_2$Cl$_2$), based the original concentration of the molybdenum trisdithiolen. The $^1$H NMR spectrum showed complete consumption of 2(H,H) and clean
production of DHBD(H,H) (singlet for (CH\textsubscript{2})\textsubscript{2} at 3.26 ppm in CD\textsubscript{2}Cl\textsubscript{2}), as well as unreacted BPTS.

5.5.17 Reaction of 2(H,\textsuperscript{n}Bu) with BPTS to generate 1 and DHBD(H,\textsuperscript{n}Bu)

1 (25 mg, 0.036 mmol) was combined with CDCl\textsubscript{3} (0.6 mL) and 1-hexene (5.0 μL, 3.4 mg, 0.040 mmol). After 45 min, \textsuperscript{1}H and \textsuperscript{19}F NMR spectra were obtained to verify conversion to 2(H,\textsuperscript{n}Bu) (see above for discussion). BPTS (12 mg, 0.043 mmol) was then added and the tube was resealed. The tube was heated in an oil bath at 66°C for 20.5 h. A \textsuperscript{19}F NMR spectrum shows reasonably clean conversion to 1 (singlet, -56.0 ppm in CDCl\textsubscript{3}) (see Figure 5.19); the \textsuperscript{1}H NMR spectrum shows DHBD(H,\textsuperscript{n}Bu) (see data above) and unreacted BPTS. \textsuperscript{19}F NMR (377 MHz, CDCl\textsubscript{3}) (for 2(H,\textsuperscript{n}Bu)) δ -54.66 to -54.34 (br ov m), -54.42 [s (apparently)], -54.30 to -54.07 (br ov m), -54.23 [s (apparently)].
For all alkene/BPTS reactions described here, control experiments were conducted without 1 present. Details as follows:

### 5.5.18 BPTS + excess ethylene (no catalyst)

The procedure was analogous to the one used for the synthesis of DHBD(H,H) (section 5.5.9), except 1 was not added to the reaction mixture. The reaction mixture (in CDCl$_3$) was heated at 66°C for 48.5 h, affording no DHBD(H,H). A $^1$H NMR spectrum showed unreacted starting materials.
5.5.19 BPTS + 2 equiv 1-hexene (no catalyst)

The procedure was analogous to the one used for the synthesis of DHBD(H,^n^Bu) (section 5.5.10), except 1 and CD₃CN were not added to the reaction mixture. The reaction mixture (in CDCl₃) was heated at 66°C for 45 h, affording no DHBD(H,^n^Bu). A ¹H NMR spectrum showed unreacted starting materials.

5.5.20 BPTS + 2 equiv cyclohexene (no catalyst)

The procedure was analogous to the one used for the synthesis of DHBD(C₂H₄,C₂H₄) (section 5.5.11), except 1 and CD₃CN were not added to the reaction mixture. The reaction mixture (in CDCl₃) was heated at 66°C for 21.5 h, affording no DHBD(C₂H₄,C₂H₄). A ¹H NMR spectrum showed unreacted starting materials and some polymeric material (ca. 10%), as seen above in the syntheses of DHBD(cis-Et,Me) and DHBD(C₂H₄,C₂H₄).

5.5.21 BPTS + 2 equiv cis-2-pentene (no catalyst)

The procedure was analogous to the one used for the synthesis of DHBD(cis-Et,Me) (section 5.5.12), except 1 was not added to the reaction mixture. The reaction mixture (in CDCl₃) was heated at 65°C for 23.5 h, affording no DHBD(cis-Et,Me) [or DHBD(trans-Et,Me)]. A ¹H NMR spectrum showed unreacted starting materials and some polymeric material (ca. 30%), as seen above in the syntheses of DHBD(cis-Et,Me) and DHBD(C₂H₄,C₂H₄).

5.5.22 BPTS + 2 equiv trans-2-pentene (no catalyst)

The procedure was analogous to the one used for the synthesis of DHBD(H,^n^Bu) (section 5.5.10), except 1 was not added to the reaction mixture and trans-2-pentene was used as the alkene. The reaction mixture (in CDCl₃) was heated at 66°C for 22.3 h, affording no DHBD(trans-Et,Me) [or DHBD(cis-Et,Me)]. A ¹H NMR spectrum showed unreacted starting materials and very broad peaks in the aromatic and aliphatic regions, indicating some polymerized material (ca. 15-20%) was formed.
5.5.23 **BPTS + 2 equiv allyl alcohol (no catalyst)**

The procedure was analogous to the one used for the synthesis of DHBD(H,\textsuperscript{n}Bu) (section 5.5.10), except 1 was not added to the reaction mixture and allyl alcohol was used as the alkene. The reaction mixture (in CDCl\textsubscript{3}) was heated at 66°C for 22.3 h, affording no DHBD(H,CH\textsubscript{2}OH). A \textsuperscript{1}H NMR spectrum showed only unreacted starting materials.

We screened a cross-section of other potential catalysts/conditions for the reaction between BPTS and 1-hexene, including a Lewis acid, Lewis bases, a Brønsted acid, molybdenum sulfide and photolytic conditions. The reaction between BPTS and cis-2-pentene was examined in the presence of a radical initiator. All of these experiments failed to produce DHBDs. Further, the catalytic reaction between BPTS and 1-hexene (with 1 present, 5 mol \%) was conducted in the presence 2,6-di-tert-butyl-4-methylphenol (BHT) to verify that the catalysis proceeds, to form DHBD(H,\textsuperscript{n}Bu), even in the presence of a radical inhibitor (i.e., to rule out a radical pathway). Details as follows:

5.5.24 **BPTS + 2 equiv 1-hexene (with NEt\textsubscript{3})**

The procedure was analogous to the one used for the synthesis of DHBD(H,\textsuperscript{n}Bu) (section 5.5.10), except 1 and CD\textsubscript{3}CN were not added to the reaction mixture. Instead, triethylamine (1.1 μL, 0.75 mg, 0.0074 mmol) was added. Note: when the amine was added, the solution became cloudy with very fine white-yellow precipitate, possibly indicating partial base-induced polymerization of BPTS. The BPTS/alkene/amine solution (in CDCl\textsubscript{3}) was heated at 66°C for 23 h, affording no DHBD(H,\textsuperscript{n}Bu). A \textsuperscript{1}H NMR spectrum showed unreacted starting materials.
5.5.25 BPTS + 2 equiv 1-hexene (with P(\text{Bu})_3)

The procedure was analogous to the one used for the synthesis of DHBD(H,\text{\textsuperscript{\textit{\textsuperscript{9}Bu)}} (section 5.5.10), except at ½ the concentration. Also, 1 and CD_3CN were not added to the reaction mixture. Instead, tributylphosphine (P(\text{Bu})_3) (18 \mu L, 15 mg, 0.072 mmol) was added. The BPTS/alkene/phosphine solution (in CDCl_3) was heated at 65\textdegree C for 20.5 h, affording no DHBD(H,\text{\textsuperscript{\textit{\textsuperscript{9}Bu)}}. A \textsuperscript{1}H NMR spectrum showed unreacted starting materials and polymeric material (ca. 20%), characterized by broad aliphatic/aryl peaks, similar to the polymeric byproduct seen in the syntheses of DHBD(C_2H_4,C_2H_4) and DHBD(cis-Et,Me).

5.5.26 BPTS + 2 equiv 1-hexene (with B(C_6F_5)_3)

The procedure was analogous to the one used for the synthesis of DHBD(H,\text{\textsuperscript{\textit{\textsuperscript{9}Bu)}} (section 5.5.10), except 1 and CD_3CN were not added to the reaction mixture. Instead, tris(pentafluorophenyl)borane (4.4 mg, 0.0085 mmol) was added. The BPTS/alkene/borane solution (in CDCl_3) was heated at 66\textdegree C for 22 h, affording no DHBD(H,\text{\textsuperscript{\textit{\textsuperscript{9}Bu)}}. A \textsuperscript{1}H NMR spectrum showed unreacted starting materials and polymeric material (ca. 20%), characterized by broad aliphatic and aryl peaks, similar to the polymeric byproduct seen in the syntheses of DHBD(C_2H_4,C_2H_4) and DHBD(cis-Et,Me).

5.5.27 BPTS + 2 equiv 1-hexene (with HBF_4)

The procedure was analogous to the one used for the synthesis of DHBD(H,\text{\textsuperscript{\textit{\textsuperscript{9}Bu)}} (section 5.5.10), except 1 and CD_3CN were not added to the reaction mixture. Instead, HBF_4 (54 wt. % in diethyl ether) (1.0 \mu L, 0.0073 mmol) was added. The BPTS/alkene/acid solution (in CDCl_3) was heated at 66\textdegree C for 16 h, affording no DHBD(H,\text{\textsuperscript{\textit{\textsuperscript{9}Bu)}}. A \textsuperscript{1}H NMR spectrum showed unreacted starting materials and polymeric material (ca. 10-15%), characterized by broad aliphatic and aryl peaks, similar to the polymeric byproduct seen in the syntheses of DHBD(C_2H_4,C_2H_4) and DHBD(cis-Et,Me).
5.5.28  **BPTS + 2 equiv 1-hexene (with MoS$_2$)**

The procedure was analogous to the one used for the synthesis of DHBD(H,$^n$Bu) (section 5.5.10), except 1 and CD$_3$CN were not added to the reaction mixture. Instead, MoS$_2$ (11 mg, 0.069 mmol) was added. The BPTS/alkene/MoS$_2$ mixture (in CDCl$_3$) was heated at 66°C for 16 h, affording no DHBD(H,$^n$Bu). A $^1$H NMR spectrum showed unreacted starting materials.

5.5.29  **BPTS + 2 equiv 1-hexene (photolytic conditions)**

The procedure was analogous to the one used for the synthesis of DHBD(H,$^n$Bu) (section 5.5.10), except 1 and CD$_3$CN were not added to the reaction mixture. The BPTS/alkene solution was taped to a fluorescent light tube (with aluminum foil backing to maximize light exposure) and irradiated for 17 h, affording no DHBD(H,$^n$Bu). A $^1$H NMR spectrum showed unreacted starting materials and polymeric material (ca. 20%), characterized by broad aliphatic/aryl peaks, similar to the polymeric byproduct seen in the syntheses of DHBD(C$_2$H$_4$C$_2$H$_4$) and DHBD(cis-Et,Me).

5.5.30  **BPTS + 2 equiv cis-2-pentene (with Vazo 52® radical initiator)**

The procedure was analogous to the one used for the synthesis of DHBD(cis-Et,Me) (section 5.5.12), except 1 was not added to the reaction mixture. Instead, Vazo 52® (11 mg, 0.069 mmol) was added. The BPTS/alkene/Vazo 52® mixture (in CDCl$_3$) was heated at 66°C for 18.5 h, affording no DHBD(H,$^n$Bu). A $^1$H NMR spectrum showed unreacted starting materials.

5.5.31  **BPTS + 2 equiv 1-hexene [catalyst: 1/CD$_3$CN; with BHT radical trap]**

A CDCl$_3$ solution (0.5 mL) containing 1 (5.0 mg, 0.0073 mmol) and BTBB (9.0 μL, 15 mg, 0.051 mmol) was added to a J. Young NMR tube containing BPTS (21 mg, 0.075 mmol) and 2,6-di-tert-butyl-4-methylphenol (BHT) (10 mg, 0.045 mmol). 1-Hexene (20 μL, 13.5 mg,
0.16 mmol) and then CD$_3$CN (20 μL) were added and the tube was sealed under nitrogen. The mixture was heated in an oil bath (68°C, reflux) for 3.25 h, giving clean conversion to DHBD(H,$^n$Bu) (95% $^1$H NMR yield, based on product integration relative to BTBB). Also visible in the $^1$H NMR spectrum (400 MHz, CDCl$_3$): unchanged BHT [δ 1.43 (s, 18H, C(CH$_3$)$_3$ x 2), 2.27 (s, 3H, CH$_3$), 5.02 (s, 1H, OH). Note: the aryl BHT peak (at ca. 7 ppm) is obscured by one of the aryl resonances of DHBD(H,$^n$Bu)].

5.6 References

Chapter 5 - Catalytic Production of 2,3-Dihydro-1,4-benzodithiins: A New Application for Ligand-Based Reactivity of a Molybdenum Trisdithiolene


[20] NMR yields were calculated by product peak integration relative to the internal standard 3,5-bis(trifluoromethyl)bromobenzene (BTBB).

[21] Experimental conditions: 2(H,H) (initially ca. 0.02 M) and BPTS (initially ca. 0.05 M) were heated (70°C) in CD₂Cl₂ for 18.8 h in a sealed J. Young NMR tube. See experimental section for more details.

[22] 2(H,₈Bu) exhibits a complex, higher-order ¹⁹F NMR spectrum, which is temperature and field-dependent. See the experimental section.

[23] Experimental conditions: 2(H,₈Bu) (initially ca. 0.06 M) and BPTS (initially ca. 0.07 M) were heated (66°C) in CDCl₃ for 20.5 h in a sealed J. Young NMR tube. See experimental section for more details.

[24] BPTS is the dimer of highly reactive benzodithiete, S₂C₆H₄; while BPTS is unreactive to alkenes (see control experiments in the experimental section), it reacts with itself: the molecular weight of “BPTS” is concentration-dependent (Ref. 19), pointing toward the formation of higher oligomers of S₂C₆H₄. Details on the difficulties associated with isolating pure BPTS (with well-defined molecular mass) are described in the experimental section.

[25] ¹⁹F NMR shift (BTBB standard) of the peak labelled ‘*’ is identical to that of authentic Mo(S₂C₂(CF₃)₂)₃, prepared as in: King, R. B. Inorg. Chem., 1963, 2, 641.


[27] The integrals were calibrated against the NOE signals for H₈; these integrals should be very similar for the cis and trans isomers because, in both cases, H₈ and CH₈₃ are held in rigid proximity (i.e., they share a geminal carbon and should be held at approximately the same distance) and the coupling constants, Jₐ₈b, are nearly equal (Tables 2 and 3), meaning that distortion of the signal for H₈, caused by direct J-coupling between the A and B environments, should be comparable in both cases.

[28] TOF values were calculated for the first 2 h of the reaction involving 1-hexene (in refluxing chloroform, 61°C), with and without CD₃CN present, using TOF = [(moles of DHBD produced)/(moles of catalyst)]/time. When CD₃CN was used, conversion to DHBD(H,₈Bu) was near-quantitative (96%, all of the alkene consumed); when CD₃CN was not used, the NMR yield of DHBD(H,₈Bu) (for 2 h reaction time) was only 12%, corresponding to a TOF of 1.2 h⁻¹; this TOF value is expected to decline when measured later in the reaction, as the concentration of the substrates (BPTS and 1-hexene) decreases and as the catalyst slowly decomposes.

[29] Conditions as described in Table 5.1 (for the 1-hexene reaction), except CD₃CN was not used.

[30] Existing syntheses of DHDs are very different from the alkene/oxidized sulfur compound/catalyst protocol described here. Some recent synthetic methods for DHDs: (a) Ref 16. (b) Preedasuriyachai, P.;


[35] Three multiplets, for the byproduct, are visible in C6D6 (see Figure 5.6) and four multiplets can be seen in CDCl3 (spectrum not shown).


Chapter 6

Nickel Dithiolene Chelate Rings in a New Role as $\eta^5$-Coordinating Ligands: Synthesis, Structural Characterization and Redox Reactivity of a Mixed-Valent ‘Fe$_2$Ni’ Bis-double-decker

6.1 Abstract

A bis-double-decker complex has been assembled from the nickel bisdithiolene complex $[\text{Ni}(\text{S}_2\text{C}_2\text{Me}_2)_2]^{n-}$ ($n = 1$ or 2) and two $[\text{Cp}^*\text{Fe}]^+$ units ($\text{Cp}^* = \text{C}_5\text{Me}_5$). The complex, $[(\eta^5-\text{Cp}^*=\text{Fe}-\mu-\eta^5,\eta^5-(\text{S}_2\text{C}_2\text{Me}_2)_2\text{Ni})-\text{Fe}-\eta^5-\text{Cp}^*]^n$, 1$,n$, was isolated in two charge states ($n = 0$, 1) depending on the initial charge state of the nickel bisdithiolene. Complex $1^+$ was crystallographically characterized as $1^+\text{PF}_6^-$ and $1^+\text{BF}_4^-$ and the structures show the nickel bisdithiolene units $\pi$-donating to iron centers in an $\eta^5$ mode. In both cases, the cations ($1^+$) are centrosymmetric with centers of inversion at nickel. A combination of experimental and computational (DFT) data strongly indicates highly delocalized spin density for odd-electron (“mixed-valent”) $1^+$. Reaction of $1$ with 1 or 2 equiv of $\text{HBF}_4$ leads to oxidation to form $1^+$ or $1^{2+}$, respectively. On an electrochemical timescale, reversibility is observed for the redox series $1/1^+/1^{2+}$, with an additional slower step for oxidation of $1^{2+}$. Most of the work detailed here has been published.$^1$ Antonio De Crisci (graduate student colleague) did the computational work described below, and Mitchell J. Kerr (undergraduate researcher) assisted with the syntheses.

6.2 Introduction

Although transition metal bisdithiolene complexes have been studied for decades, new properties and novel applications continue to be discovered. Bisdithiolene complexes show rich thermal (chapters 2-5) and photochemical (chapter 2) behavior.$^{2,3}$ In comparatively recent work, bisdithiolenes have been considered for sensing$^4$ and purification$^5$ applications, and have been incorporated into a variety of magnetic and conducting$^6$ materials. The unique chemical and spectroscopic properties of metal dithiolenes are related to their
delocalized electronic structures (see chapter 1). New synthetic strategies for the construction of dithiolene-derived supramolecular architectures, with extensive electronic conjugation, should lead to new properties and, likely, to new applications.

Using bisdithiolene complexes as ligands for other metal centers is a promising concept for the synthesis of new materials. This approach may involve appending specialized donating substituents to the dithiolene ligands [i.e., at the R groups in Figure 6.1(a)]. Alternatively, the dithiolene ligands themselves can engage in bonding with electrophilic centers, even in the absence of ligand-appended donor groups. The prototypical metal bisdithiolenes $[M(S_2C_2R_2)_2]^n$ (M = Ni, Pd, Pt; R = various substituents, n = 0, -1, -2) can, in principle, act as σ- or π-donor ligands (section 1.4.3.3). In the case of σ-donation, the dithiolene ligand uses electrons localized on one sulfur atom (η¹) to form a bond to a second metal [Figure 6.1(a),(b)] (or other electrophiles; e.g., alkyl cations), whereas in π-donation two or more contiguous atoms of the dithiolene MS₂C₂ unit are involved in bonding [η^x with x > 1; e.g., η⁴ or η⁵, Figure 6.1(a),(c)].

![Diagram](image_url)

**Figure 6.1** (A) General types of nucleophilic bonding by metal bisdithiolenes. (B) A literature example of a metal-dithiolene unit σ-bonding to another metal. (C) An example of a metal-dithiolene unit π-bonding to another metal.
\[\pi\]-Donation of dithiolenes is quite rare. Typical examples involve homometallic complexes of ruthenium\(^{10}\) [e.g., Figure 6.1(c)] or, less commonly, iron\(^{11}\) or manganese,\(^{12}\) as well as some hetero-metallic cases.\(^{13}\) Sandwich compounds of nickel bisdithiolenes, with a Ni-dithiolene chelate ring in an \(\eta^5\) \(\pi\)-donating mode, had not been demonstrated previously. A report from 2000,\(^{14}\) involving the monoanionic nickel bisdithiolene \([\text{Ni}(\text{S}_2\text{C}_6\text{H}_4)_2]^\text{−}\), proposed that the arene groups of the ligands, rather than the dithiolene NiS\(_2\)C\(_2\) rings, are used for bonding to \([\text{Cp}^\ast\text{Ru}]^\text{+}\) fragments (Figure 6.2A, \text{Cp}^\ast = \text{pentamethylcyclopentadienyl}). In fact, no structurally characterized example existed, prior to our work, for the general nickel bis-double-decker structure shown in Figure 6.2B, and isoelectronic Pd and Pt complexes are also unknown.

![Figure 6.2](image)

**Figure 6.2** (A) Proposed structure for \([\text{Ni}(\text{S}_2\text{C}_6\text{H}_4)_2(\text{RuCp}^\ast)_2]^\text{+}\).\(^{14}\) (B) Structure for a bis-double-decker complex where the Ni-dithiolene act as \(\eta^5\) \(\pi\)-donor ligands (e.g., complex 1\(^n\)).

### 6.3 Results and discussion

Here we describe the preparation of \(1\) and \(1^\text{+}\), novel bis-double-decker complexes in which a nickel bisdithiolene utilizes both of its NiS\(_2\)C\(_2\) rings as \(\pi\)-donors to \([\text{Cp}^\ast\text{Fe}]^\text{+}\) units, as depicted in Figure 6.2B. The resulting complexes are redox-active and the reduced forms, \(1\) and \(1^\text{+}\), may be oxidized to \(1^\text{+}\) and \(1^{2\text{+}}\), respectively, by treatment with acid (or ferrocenium hexafluorophosphate). Complex \(1^\text{+}\) was crystallographically characterized as its \(\text{PF}_6^\text{−}\) and \(\text{BF}_4^\text{−}\) salts to confirm the bis-double-decker structure shown in Figure 6.2B. Experimental and computational (DFT) investigations reveal that the lone electron in radical cationic \(1^\text{+}\) is delocalized over the entire molecule.
6.3.1 Syntheses of bis-double-decker complexes (1+ and 1) and X-ray structure for 1+

As discussed in chapter 1 (section 1.4.3.3), metal dithiolenes, particularly in their reduced forms, can behave as nucleophiles, forming either σ- or π-complexes, depending on the nature of the electrophile and on the electronic properties of the metal dithiolene. Thus, the monoanionic nickel bisdithiolene sodium salt Na[Ni(S$_2$C$_2$Me$_2$)$_2$]$^{15}$ reacts with two equiv of electrophilic [Cp*Fe(NCMe)$_3$](PF$_6$)$_{16}$ (with three labile sites at iron) in acetonitrile to form the bis-double-decker complex [$\eta^5$-Cp*-Fe-μ-η$^5$-((S$_2$C$_2$Me$_2$)$_2$Ni)-Fe-η$^5$-Cp*](PF$_6$) (1+PF$_6^-$, Scheme 6.1A) in 56% yield (Scheme 6.1A). Odd-electron 1+ gives a prominent near-infrared (NIR) band at 1702 nm, characteristic of a “mixed-valent”$^{17}$ system with some degree of electronic communication between two or more metals.$^{18,19}$ The effective magnetic moment for 1+ was found to be 2.1 (± 0.2) B.M. (Evans method, see 6.5.7 for details), consistent with one unpaired electron. The electronic structure of this complex (i.e., valence-trapped versus valence delocalized, Scheme 6.1B)$^{20}$ is discussed below.

Crystals of 1+PF$_6^-$ were obtained by diffusion of diethyl ether into a dichloromethane solution of 1+PF$_6^-$, and the results from a single-crystal X-ray structure determination$^{21}$ are shown in Figure 6.3A. The dithiolene units are almost planar. Deviations from the best plane are smaller than 0.06 Å, and are caused by a very slight (ca. 8 deg) bending along the S-S axes. The pentamethylcyclopentadienyl plane and the Ni-dithiolene plane are oriented in a parallel fashion, and the deviation from a perfectly parallel arrangement is only 4 deg (see legend of Figure 6.3). Furthermore, the iron center resides almost directly between the center of the cyclopentadienyl ring and the center of the dithiolene-nickel (C1-C2-S1-S2-Ni1) unit. Irrespective of the nature and strength of the iron-nickel interaction (the 2.6791 Å interatomic distance is well within bonding distance$^{22}$), the structural data demonstrate that the C1-C2-S1-S2-Ni1 rings coordinate to the iron centers in an η$^5$-fashion.$^{23}$

The neutral analogue, compound 1, is also accessible: combination of the dianionic bisdithiolene sodium salt Na$_2$[Ni(S$_2$C$_2$Me$_2$)$_2$]$^{15}$ with 2 equiv of [Cp*Fe(NCMe)$_3$](PF$_6$)$_{16}$ gives 1 (58%) (Scheme 6.1A). The $^1$H NMR spectrum of diamagnetic 1 shows all dithiolene
methyl groups to be equivalent, consistent with the structure shown in Scheme 6.1. The iron centers in 1 satisfy the 18-valence-electron rule: \([\text{Ni}(\text{S}_2\text{C}_2\text{Me}_2)_2]^2-\) is best described as Ni\textsuperscript{II} with two ene-dithiolate ligands\textsuperscript{24} and the \(\pi\)-system of each ene-dithiolate unit should act as a 6-electron donor, similar to cyclopentadienyl anion. Nonetheless, this compound is very susceptible to one-electron oxidation and rapidly decomposes in CDCl\textsubscript{3} (and slowly in CD\textsubscript{2}Cl\textsubscript{2}), probably through homolytic pathways initiated by electron transfer from 1 to generate 1\textsuperscript{+} and solvent-derived free radicals. In contrast to 1\textsuperscript{+}, complex 1 does not give a NIR absorption signal, as expected for an electronically saturated multimetallic system.

Scheme 6.1
Chapter 6 - Nickel Dithiolene Chelate Rings in a New Role as \( \eta^5 \)-Coordinating Ligands: Synthesis, Structural Characterization and Redox Reactivity of a Mixed-Valent ‘Fe\( \text{II} \)-Ni’ Bis-double-decker

**Figure 6.3** Structures of \( 1^+ \) (hydrogens omitted): (A) Crystal structure of \( 1^+PF_6^- \) (PF\(_6^-\) counterion not shown), using 30 % thermal ellipsoids. Ni1 resides on a crystallographic center of inversion. Selected distances and angles (Å, deg): Ni1-S1, 2.164(1); Ni1-S2, 2.163(1); C1-C2, 1.394(6); S1-Ni1-S2, 90.02(4); Fe1-S1, 2.266(1); Fe1-S2, 2.267(1); Fe1-C1, 2.072(4); Fe1-C2, 2.069(4); Fe1-Ni1, 2.6791(6); Fe1-C5, 2.090(4); Fe1-C6, 2.063(4); Fe1-C7, 2.075(4); Fe1-C8, 2.071(4); Fe1-C9, 2.088(4); Fe1-Centroid(C5-9), 1.683(4); Fe1-Centroid(Ni1,S1,S2,C1,C2), 1.657(3); Centroid-Fe1-Centroid, 175.9(1); dihedral angle \{Ni1-S1-S2\} vs \{C1-C2S1S2\}, 7.9(1); dihedral angle \{Ni1-S1-S2-C1-C2\} vs \{C5-C6-C6-C8-C9\}, 4.1(1). \( 1^+ \) in \( 1^+BF_4^- \) is extremely similar (experimental section). (B) Structure from UBLYP (SDD basis) geometry optimization; a spin isodensity surface corresponding to a 0.0013 value is superimposed.

6.3.2 Electronic structure of \( 1^+ \) (delocalized or valence-trapped?)

For potential applications (e.g., in magnetic, (semi-) conducting materials), mixed-valent systems with delocalized ground-states (i.e., electronic communication between the metals) are particularly desirable (see chapter 1, section 1.4.2). Concerning the electronic structure of mixed-valent \( 1^+ \), it is relevant that oxidation of the bridging unit, \([\text{Ni}(\text{S}_2\text{C}_2\text{Me}_2)_2]^{2-}\), without the \([\text{FeCp}^*]\)\(^+\) groups, would lead to removal of one electron from an essentially ligand-based HOMO (delocalized over both ligands, with a small coefficient at Ni; see sections 1.2.1 and 1.4.3.1).\(^2,24\) Thus, it appears likely that the unpaired electron in \( 1^+ \) is
delocalized over the whole molecule, including the dithiolene groups. Evidence presented in the following three sections will show that $1^+$ should indeed be regarded as a valence-delocalized system (versus valence-trapped, see Scheme 6.1B).

6.3.2.1 Crystalllographic evidence for a delocalized ground state

Complex $1^+$, in the crystallographically characterized $1^+\text{PF}_6^-$ (Figure 6.3), has a center of inversion (point group $C_i$), rendering both iron fragments equivalent. The core (iron-bis(dithiolene)nickel-iron) approximates even higher ($C_{2h}$) symmetry. The presence of an inversion center in the structure of $1^+\text{PF}_6^-$ seems to provide evidence against a localized Fe$^{\text{II}}$/Fe$^{\text{III}}$ description, but it cannot be regarded as conclusive proof of a truly delocalized ground state. Crystalllographic disorder and/or rapid intramolecular electron transfer between the iron centers in a Fe$^{\text{II}}$/Fe$^{\text{III}}$ localized state could also account for the center of inversion observed for $1^+\text{PF}_6^-$. However, there is no evidence for disorder caused by a valence-trapped Fe$^{\text{II}}$/Fe$^{\text{III}}$ state in the structure of $1^+\text{PF}_6^-$ (i.e., no abnormalities observed for the iron or Cp*-carbon ellipsoids). We crystallographically characterized $1^+$ as its BF$_4^-$ salt as well (see 6.5.9 below) and obtained a structure for $1^+$ that is virtually identical to its structure in $1^+\text{PF}_6^-$. again, the Ni atom lies on a center of inversion and Fe and Cp* ellipsoids show no signs of disorder. Thus, the metric data indicates that $1^+$ is either truly centrosymmetric, with a delocalized ground state, or, if the electronic structure is localized as Fe$^{\text{II}}$/Fe$^{\text{III}}$, electron transfer between the irons is very facile and occurs with minimal structural reorganization (Scheme 6.1B).  

6.3.2.2 Electrochemical evidence for a delocalized ground state

Further evidence for a delocalized ground state for $1^+$ was obtained from electrochemical data: the energy separation (i.e., the difference in potential) between successive electron transfer events in multimetallic complexes relates to the extent of valence delocalization. In practice, the comproporationation equilibrium constant, $K_c$ (Equation 6.1, $K_c = [(\text{MM})^+]^2/[[\text{MM}][\text{MM}^2^+]]$), is often used to evaluate the degree of electronic communication between the metals in mixed-valent systems. Its value relates to the stability
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of the mixed-valent versus isovalent states and, indirectly, to the extent of delocalization of the lone electron in the mixed-valent form.\(^{17,26}\) When the energetic separation of redox couples for successive electron transfers can be ascertained, the equilibrium constant can be computed according to \( K_c = \exp[nFR^{-1}(E_1^0 - E_2^0)T^{-1}] \).\(^{26}\)

\[
\text{(MM)}^{2+} + \text{MM} \rightleftharpoons 2 \text{(MM)}^+ \quad (M = \text{redox active metal})
\]

(6.1)

Thus, \( K_c \) for the \( \text{I}^{2+} + \text{I} \rightleftharpoons 2 \text{I}^+ \) equilibrium was calculated from electrochemical data and a value of \( 4.5 (\pm 5.6) \cdot 10^{10} \) was obtained (see section 6.5.13 for details on the calculation). The large error stems from the exponential relationship between \( K_c \) and \( (E_1^0 - E_2^0)/T \). However, the key point is that \( K_c \) is large (cf., \( K_c = 2.65 \cdot 10^5 \) for \( \text{BF}^{2+} + \text{BF} \rightleftharpoons 2 \text{BF}^+ \); \( \text{BF} = 1,1'\)-biferrocene),\(^{25b}\) establishing that the mixed-valent species (\( \text{I}^+ \)) is heavily favored over the isovalent\(^{17}\) forms and that the metals participating in the redox reactions are strongly coupled (i.e., valence-delocalized, Scheme 6.1B).

6.3.2.3 Computational (DFT) evidence for a delocalized ground state

Theory supports a truly delocalized ground state, based on a spin-unrestricted DFT (UBLYP) computation performed for \( \text{I}^+ \). A geometry optimization (Gaussian03,\(^{27}\) LANL2MB basis), without symmetry imposed, converges toward \( C_i \) symmetry. A calculation using a larger basis set (SDD, with added polarization functions on the sulfur atoms) predicts \( C_i \) symmetry (closely approximating \( C_{2h} \)) and yields structural parameters very similar to those seen in the crystal structures of \( \text{I}^+ \). The calculated structure of \( \text{I}^+ \) is shown in Figure 6.3B, along with the computed spin density, which is delocalized over both iron centers with significant spin contributions on the nickel bisdithiolene unit. Using a simplified model (methyils replaced with hydrogens) of \( \text{I}^+ \), an unsymmetrical valence-trapped state was enforced by geometry optimization in the presence of a simulated electric field; when the field was removed, the structure reverted back to the fully delocalized state (see experimental section for details). Thus, computational data further establishes the
delocalized nature of the $1^+$ radical and is consistent with structural and electrochemical results (see above).

6.3.3 Redox reactivity of $1^\text{m}$

Complex 1 is rapidly$^{28}$ oxidized by 1 equiv of HBF$_4$ to $1^+$; monocationic $1^+$ can be further oxidized to $1^{2+}$ by treatment with another equiv of HBF$_4$ (in dichloromethane). Dicationic $1^{2+}$ can also be generated by oxidation of $1^+$ with 1 equiv of ferrocenium hexafluorophosphate. Cyclic voltammetry on $1^+\text{PF}_6^-$ (Figure 6.4) reveals three one-electron transfer events. Rapid and reversible$^{29}$ electron transfer is observed between $1/1^+/1^{2+}$ (peak assignments in Figure 6.4$^{30}$). Oxidation of $1^{2+}$ is less facile and requires a relatively slow scan rate (< 100 mV/s) to observe reversible behavior, possibly indicating structural rearrangement. In Figure 6.4, the oxidation product is assigned as “$1^{3+}$”, but partial loss of [Cp*Fe]$^+$ in this highly oxidized species appears possible. Alternatively, slow diffusion of the highly charged trication ($1^{3+}$) could account for the apparently irreversible behavior at faster scan rates.

![Cyclic voltammogram for $1^+\text{PF}_6^-$](image)

Figure 6.4 Cyclic voltammogram for $1^+\text{PF}_6^-$ (~1 mM in acetonitrile, 0.1 M NBu$_4$PF$_6$ as supporting electrolyte, scan rate = 100 mV/s). Potentials are relative the ferrocene/ferrocenium couple.
6.4 Conclusion

In summary, we have synthesized a trimetallic bis-double-decker complex (in multiple charge states) with a new structural motif in which two dithiolene ligands act as π-donors to iron centers. Considerable evidence from experimental (structural and electrochemical) and computational (DFT) data point to a highly delocalized electronic structure for $1^+$, with the metals strongly coupled. This situation is distinct from somewhat related biferrocenium cations, which have moderately coupled metals and significant valence-trapped (Fe$^{III}$Fe$^{II}$) character. Consistent with delocalized frontier orbitals, compounds $1^n$ exhibit rich redox reactivity, as shown by cyclic voltammetry and by oxidation of $1$ and $1^+$ with H$^+$. These highly conjugated, redox-active species will be investigated for potential applications. More generally, the use of metal dithiolenes as ligands is a powerful method for making multimetallic complexes with interesting chemical and redox properties.

6.5 Experimental section

6.5.1 General considerations

Experiments were conducted in an inert (nitrogen or argon) atmosphere using standard glovebox (MBraun Unilab) and Schlenk-type techniques unless otherwise noted. Acetonitrile (Ominsolv®, Sigma Aldrich, low water content) was stored over activated molecular sieves (3 Å) and deoxygenated with a nitrogen or argon purge. Diethyl ether, tetrahydrofuran (THF), toluene and dichloromethane were dried/deoxygenated using an MBraun solvent purification system (MB SPS). Benzene-$d_6$ ($C_6D_6$) was dried over sodium/benzophenone and vacuum-transferred from the ketyl prior to use. Dichloromethane-$d_2$ ($CD_2Cl_2$) was dried by refluxing over calcium hydride and vacuum-transferred before using. Acetone-$d_6$ was dried over activated molecular sieves (3 Å) and was deoxygenated by purging with argon. All NMR solvents were purchased from Cambridge Isotopes. Hexafluorophosphoric acid (60 wt. % in water), tetrafluoroboric acid (54 wt. % in diethyl ether) and ferrocenium hexafluorophosphate were purchased from Sigma Aldrich. Silica gel (70-230 mesh) was purchased from Alfa Aesar and, where noted,
was dried/deoxygenated under vacuum at 130°C (with periodic nitrogen-back-fill-evacuate cycles) for > 6 h. Compound Ni(S₂C₂Me₂)₂ was made according to the literature procedure and reduced to its monoanion using NaBH₄; reduction to its dianion was achieved by using sodium metal (see details below). [Cp*Fe(NCMe)₃](PF₆) (Cp* = C₅Me₅) was prepared with modifications (see below for details) to the published synthesis. In the synthesis of [Cp*Fe(NCMe)₃](PF₆), photolysis was performed using a 160 W mercury vapor lamp (model: Westron Mega-Ray Self-Ballasted Zoologist). Cyclic voltammograms were collected on a BASi Epsilon electrochemical workstation. The electrochemical cell consisted of a platinum wire auxiliary electrode, nonaqueous Ag/Ag⁺ reference electrode, and platinum disk working electrode (polished with 1 μM diamond polish and then with alumina polish). Acetonitrile was used as solvent and was dried/deoxygenated as described above. NBu₄PF₆ (0.1 M) was used as the supporting electrolyte. The aqueous electrode was filled with a NBu₄PF₆ (0.1 M)/AgNO₃ (0.01 M) mixture in acetonitrile. Potentials are referenced relative to the ferrocene/ferrocinium (Fc/Fc⁺) couple (ferrocene, Fluka, ≥98% (sublimed), was added as internal standard, after collecting data without an internal standard). ¹H NMR spectra were collected on a Bruker Avance III 400 MHz instrument (at room temperature) and residual proton peaks were used as reference (δ, ppm, acetone-d₆, 2.05; acetonitrile-d₃ (CD₃CN), 1.94; C₆D₆, 7.16; CD₂Cl₂, 5.32). ¹³C NMR data was obtained using Bruker Avance III 400 MHz spectrometer at 100 MHz; the solvent peak was used as reference (δ, ppm, C₆D₆, 128.39). UV-vis and near-infrared (NIR) spectra were recorded on a Cary 14 spectrophotometer. Elemental analysis was carried out at Guelph (Chemisar) Laboratories, Guelph, ON, Canada. Mass spectrometry (ESI) was performed at Advanced Instrumentation for Molecular Structure (AIMS), Toronto, ON, Canada, using an AB/Sciex QStar mass spectrometer.

6.5.2 Reduction of Ni(S₂C₂Me₂)₂ to Na[Ni(S₂C₂Me₂)₂] with NaBH₄

Ni(S₂C₂Me₂)₂ (105 mg, 0.356 mmol) was combined with NaBH₄ (19 mg, 0.50 mmol) and THF (7 mL). The mixture was stirred for 2 h at ~35°C under positive nitrogen pressure (vented to a mineral oil bubbler). During this time, the color of the mixture changed from deep purple to magenta. The mixture was then filtered through Celite (~2 cm in a Pasteur
pipet); the mini-filter was washed with THF (1 mL x 2) to remove residual Na[Ni(S$_2$C$_2$Me$_2$)$_2$] on the Celite and these washings were combined with the rest of the filtrate. To the magenta colored filtrate, acetonitrile (1.5 mL) was added. The solvents were removed to give dark brown-red colored solid residue. The identity of this product was confirmed by comparison of its UV-vis spectral data with previously published data.$^{24b}$

6.5.3 Reduction of Ni(S$_2$C$_2$Me$_2$)$_2$ to Na$_2$[Ni(S$_2$C$_2$Me$_2$)$_2$] with sodium metal

Ni(S$_2$C$_2$Me$_2$)$_2$ (102 mg, 0.346 mmol) was combined with sodium metal (~300 mg, large excess, cut into thin sheets) and THF (7 mL). The mixture was refluxed under argon for 2 h (color change from deep purple to brown-yellow), with stirring, and then filtered through Celite (0.5-1 cm in 15 mL glass frit funnel). The filter frit/Celite was washed with THF (1 mL x 3) and these washings were combined with the filtrate. To the resulting brown solution, acetonitrile (1.5 mL) was added. The solvents were removed under reduced pressure, to give brown-yellow solid residue. The identity of this product was confirmed by comparison of its UV-vis spectral data with previously published data.$^{24b}$

6.5.4 Synthesis of [Cp*Fe(NCMe)$_3$](PF$_6$)

The following preparation is modified slightly from the published procedure: [Cp*Fe(CO)$_2$(NCMe)](PF$_6$) (340 mg, 0.78 mmol) was dissolved in acetonitrile (13 mL) and the resulting yellow solution was filtered through Celite (0.5 cm in 15 mL glass frit funnel). With argon purging through the solution (via a sparging tube), the sample was irradiated in a pyrex test tube (35 mL capacity; inner diameter: 2 cm), with the lamp (see above, section 6.5.1) placed ~10 cm from the reaction vessel (vessel kept at approximately room temperature by cooling with forced air), for 3 h. During this time, the yellow solution changed color to red-brown, and then to deep purple. Note that approximately one half of the solvent was lost to evaporation during this process, and (caution) carbon monoxide is evolved. The crude product was analyzed by $^1$H NMR spectroscopy (in acetone-d$_6$) and the data matched that for the reported compound.$^{16}$ For the syntheses of 1 and 1$^+$PF$_6^-$ (see
below), the product was generated by photolysis, as described above, and used in situ (without removing solvent, etc.).

6.5.5 Synthesis of $1 (\eta^5$-Cp*-Fe-$\mu$-$\eta^5$-$\eta^5$-((S$_2$C$_2$Me$_2$)$_2$Ni)-Fe-$\eta^5$-Cp*)

Na$_2$[Ni(S$_2$C$_2$Me$_2$)$_2$] (~0.4 mmol, made as in 6.5.3), partially dissolved/suspended in acetonitrile (6 mL), was added dropwise (over 10 min) to a stirred purple acetonitrile solution (7 mL) containing [Cp*Fe(NCMe)$_3$](PF$_6$) (~0.8 mmol, see 6.5.4). By the time addition of Na$_2$[Ni(S$_2$C$_2$Me$_2$)$_2$] was complete, green supernatant solution was observed, with dark colored precipitate visible. The mixture was protected from light and left to stir at RT for 18 h, under a static nitrogen atmosphere. The solvent was removed under vacuum to afford dark green colored residue. This residue was extracted with dichloromethane (1.5 mL x 5) and the dark green extracts were applied to a silica gel (dried, deoxygenated; see above) column (11 g of silica; suspended in diethyl ether; inner column diameter: 2 cm). A diethyl ether/dichloromethane (4:1 v/v) mixture (~25 mL) was passed through the column, which produced colorless eluent (discarded) and moved the dark green colored product towards the bottom of the column. An additional 30 mL of the same solvent mixture was passed through the column, giving dark green colored eluent (kept). The solvents were removed under reduced pressure to yield $1$ as dark green (nearly black) powder (141 mg, 58% yield based on Ni(S$_2$C$_2$Me$_2$)$_2$). Note that this complex is very susceptible to air-oxidation. $^1$H NMR (400 MHz, C$_6$D$_6$) (note: Compound $1$ decomposes rapidly in CDCl$_3$ and slowly in CD$_2$Cl$_2$) $\delta$ 1.76 (s, 30H, C$_5$(CH$_3$)$_5$ x 2), 1.99 (s, 12H, dithiolene CH$_3$ groups). $^{13}$C{$^1$H} NMR (100 MHz, C$_6$D$_6$) $\delta$ 11.39, 20.76, 83.65, 100.34. UV-vis-NIR (toluene, in 1 mm quartz cuvette): $\lambda_{max}(\varepsilon)$ = 340 (15000), 405 (shoulder, 5000), 596 (3000). Note: toluene absorbs strongly in the NIR region; we found it necessary to use a short-pathlength cuvette (1 mm) in order to effectively subtract the background solvent signal. In contrast to compound $1^+PF_6^-$ (below), there is no absorption in the 1000-2010 nm region. The spectrum is shown below (Figure 6.5).
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Figure 6.5 UV-vis-NIR spectrum of 1 (2.2 mM in toluene in 1 mm pathlength cuvette). Note the lack of a NIR signal (cf., 1\( ^+ \), which exhibits a strong signal at 1700 nm, see Figure 6.6 below).

6.5.6 Synthesis of 1\( ^+ \)PF\(_6 \)

Na[Ni(S\(_2 \)C\(_2 \)Me\(_2 \))] (\( \sim 0.4 \) mmol, section 6.5.2), dissolved in acetonitrile (3 mL), was added dropwise (over 10 min) to a stirred purple acetonitrile solution (7 mL) containing [Cp*Fe(NCMe)\(_3 \)](PF\(_6 \)) (\( \sim 0.8 \) mmol, see 6.5.4 above). By the time addition of Na[Ni(S\(_2 \)C\(_2 \)Me\(_2 \))] was complete, green supernatant solution was observed, with a significant amount of dark (apparently black) colored precipitate visible. The mixture was protected from light and left to stir at RT overnight (approximately 18 h), under a static nitrogen atmosphere. The solvent was removed under vacuum to afford dark (nearly black) colored residue. In air (solvents and silica gel undried): The dark colored residue was extracted with dichloromethane (1.5 mL x 5) and the extracts were placed on a silica gel column (14 g of silica; suspended in dichloromethane; inner column diameter: 2 cm). Dichloromethane (25-30 mL) was passed through column, giving, initially, colorless eluent and then faintly green-brown eluent (discarded). 25 mL of a dichloromethane/acetone (5:1 v/v) mixture was passed
through the column, giving, first, green-brown eluent and then colorless eluent (discarded). An additional 30 mL of the dichloromethane/acetone (5:1 v/v) mixture gave dark green-brown colored eluent (kept). From this final green-brown fraction, the solvents were removed under vacuum, giving $1^+$PF$_6^-$ as dark green (nearly black) microcrystalline solid material (164 mg, 56% yield based on Ni(S$_2$C$_2$Me$_2$)$_2$). X-ray quality crystals were grown by allowing diethyl ether vapor to diffuse into a dichloromethane solution of $1^+$PF$_6^-$. Anal. Calc. for C$_{28}$H$_{42}$F$_6$P$_1$S$_4$Fe$_2$Ni: C: 40.89%, H: 5.16%; Found: C: 40.78%, H: 5.11%. $^1$H NMR (400 MHz, acetone-d$_6$, [1$^+$PF$_6^-$] = 0.017 M, T $\approx$ 25$^\circ$C) (note: despite the odd-electron count for this compound, $^1$H NMR signals can be observed) δ -9.77 (br s, $\omega_{1/2}$ = 270 Hz, 30H, C$_5$(CH$_3$)$_5$ x 2), -5.46 (br s, $\omega_{1/2}$ = 165 Hz, 12H, dithiolene CH$_3$ groups (x 4)). UV-vis-NIR (dichloromethane, in 1 mm quartz cuvette): $\lambda_{\text{max}}(\varepsilon)$ = 774 (4800), 1702 (5700). Note: dichloromethane absorbs strongly in the NIR region; we found it necessary to use a short-pathlength cuvette (1 mm) in order to effectively subtract the background solvent signal. The spectrum is shown below (Figure 6.6):

![UV-vis-NIR spectrum](image)

**Figure 6.6** (A) UV-vis-NIR spectrum of 1$^+$ (2.3 mM in CH$_2$Cl$_2$ in 1.0 mm pathlength cuvette).
6.5.7 Determination of effective magnetic moment for $1^+$ using Evans method

Under atmospheric conditions (i.e., not under an inert gas): $1^+\text{PF}_6^-$ (2.67 mg, 0.00324 mmol) was weighed, on a high-resolution balance, directly into a J. Young NMR tube. A capillary tube containing pure CD$_2$Cl$_2$ was then added to the tube, followed by 0.80 mL of CD$_2$Cl$_2$, giving a green-brown solution with a concentration of 0.0041 ($\pm$ 0.00041) M (estimated error = 10%). After thoroughly mixing the sample, an NMR spectrum was collected (ca. 10 min after preparing sample) [$T = 24 \pm 1^\circ$C (297 $\pm$ 1 K), from the instrument panel, $\pm$ 1 is the estimated error]. From the spectrum (Figure 6.7), the separation between the residual solvent peaks was found to be 12 ($\pm$ 1.2) Hz (estimated error = 10%).

![Figure 6.7](image)

Figure 6.7 NMR (400 MHz, CD$_2$Cl$_2$) spectrum (horizontal scale in Hz) showing the separation of the residual solvent peaks ($\Delta\nu$) used in the determination of $\chi_m$ (broad/large peak associated with solvent in contact with $1^+$; the relatively narrow peak to the right is associated with pure CD$_2$Cl$_2$ in the capillary tube).

The magnetic susceptibility ($\chi_m$) is related to the frequency separation ($\Delta\nu$) by

$$\chi_m = (\Delta\nu)(477)[(Q)(\nu_1)(c)]^{-1}$$

where $\nu_1$ is the instrument field strength in Hz (here, $4.0 \cdot 10^8$ Hz); c is the concentration of the paramagnetic analyte in mol/L [here, 0.0041 ($\pm$ 0.00041) M]; Q depends on the type of magnet in the spectrometer ($Q = 2$ for superconducting magnets; $Q = 1$ for
electromagnets.\textsuperscript{31} A value of Q = 2 was used here, as the spectrometer was a Bruker Avance III 400 MHz instrument (with a superconducting magnet).

Thus, $\chi_m = 0.0018 \pm 0.0003$ L mol$^{-1}$

From $\chi_m$, the effective magnetic moment ($\mu_{\text{eff}}$) can be calculated using\textsuperscript{32}

$$\mu_{\text{eff}} = [(8)(\chi_m)(T)]^{1/2}$$

giving $\mu_{\text{eff}} = 2.1 \pm 0.2$ B.M. (consistent with one unpaired electron)

The sigma values ($\sigma$) (i.e., standard deviation) were calculated as the square root of the variance using the partial derivative method. Thus, the standard deviation for $\chi_m$ [here $\sigma(\chi_m)$] was computed by propagation of error in c and $\Delta\nu$ as follows:

$$\sigma(\chi_m) = \left\{(\frac{\partial\chi_m}{\partial\Delta\nu})^2[\sigma(\Delta\nu)]^2 + (\frac{\partial\chi_m}{\partial c})^2[\sigma(c)]^2\right\}^{1/2}$$

Similarly, the error in $\mu_{\text{eff}}$ was evaluated as

$$\sigma(\mu_{\text{eff}}) = \left\{(\frac{\partial\mu_{\text{eff}}}{\partial\chi_m})^2[\sigma(\chi_m)]^2 + (\frac{\partial\mu_{\text{eff}}}{\partial T})^2[\sigma(T)]^2\right\}^{1/2}$$

where $\sigma(\Delta\nu)$, $\sigma(c)$, $\sigma(\chi_m)$ and $\sigma(T)$ are the estimated errors (see above for these values) associated with the experimental determination of $\Delta\nu$, c, $\chi_m$ and T, respectively.

### 6.5.8 Synthesis of $1^+\text{PF}_6^-$ by treatment of 1 with HPF$_6$ (1 equiv)

Compound 1 (31 mg, 0.045 mmol), dissolved in dichloromethane (3 mL) (green solution) was treated with HPF$_6$ (~60 wt. % in water) (6 μL, ~0.04 mmol), under an atmosphere of argon. The mixture was stirred, at RT, under active argon pressure (vented to oil bubbler) for 0.5 h. The solvent/volatiles were removed in vacuo to give dark green colored residue. The UV-vis spectrum of this product agrees with that for $1^+\text{PF}_6^-$, synthesized from
Na[Ni(S$_2$C$_2$Me$_2$)$_2$] and [Cp*Fe(NCMe)$_3$](PF$_6$) (section 6.5.6). To further confirm the identity of the product, X-ray quality crystals were grown (diffusion of diethyl ether vapor into a dichloromethane of the product); the unit cell parameters matched those for compound 1$^+$PF$_6^-$, synthesized by combination of Na[Ni(S$_2$C$_2$Me$_2$)$_2$] (1 equiv) and [Cp*Fe(NCMe)$_3$](PF$_6$) (2 equiv) (6.5.6).

### 6.5.9 Reaction of 1 with HBF$_4$ (1 and 2 equiv) observed by UV-vis

In a sealable quartz (1 cm pathlength) cuvette, under a stream of argon, 4.0 mL of 0.3 mM solution of 1 in CH$_2$Cl$_2$ was treated with tetrafluoroboric acid (deoxygenated with argon purge, 0.24 M, 5.0 μL, 0.0012 mmol). Note: the diethyl ether used to prepare a dilute (0.24 M) solution of HBF$_4$ was not dried. The cuvette was sealed under argon, agitated by shaking, and a UV-vis spectrum was collected (data collection began ~ 1 min after adding acid) (scan range: 300-1100 nm). The spectrum shows complete conversion to 1$^+$, as determined by a characteristic peak with $\lambda_{\text{max}}$ at 774 nm ($\varepsilon = 5000$ M$^{-1}$cm$^{-1}$) and the absence of signals associated with neutral 1 (section 6.5.5). Immediately after collecting the above spectrum, another aliquot of tetrafluoroboric acid (deoxygenated with argon purge, 0.24 M, 5.0 μL, 0.0012 mmol) was added (under a stream of argon). After 2 h (at ~25°C), conversion to a new species, assigned as 1$^{2+}$ (see below), was complete. For 1$^{2+}$: UV-vis (dichloromethane): $\lambda_{\text{max}}(\varepsilon) = 372$ (9200, shoulder on a large band with peak absorbance above the instrument detection level), 516 (5600), 644 (9900), 860 (sh, 2700). The reaction between 1 and HBF$_4$ was used to synthesize 1$^+\text{BF}_4^-$, in a manner analogous to the synthesis of 1$^+$PF$_6^-$ by treatment of 1 with HPF$_6$ (above). X-ray quality crystals of 1$^+\text{BF}_4^-$ were grown by diffusion of ether into the dichloromethane solution of the product. The structure of 1$^+$ in 1$^+\text{BF}_4^-$ (see below, Figure 6.8) is very similar to its structure in 1$^+$PF$_6^-$ (see Figure 6.3).
Figure 6.8  Structure of 1⁺ in 1⁺BF₄⁻, using 30 % thermal ellipsoids. The hydrogen atoms and BF₄⁻ counterion are not shown. BF₄⁻ counterion is disordered over two positions. Ni1 resides on a crystallographic center of inversion. Selected distances and angles (Å, deg): Ni1-S1, 2.1655(7); Ni1-S2, 2.1609(7); C1-C2, 1.401(4); S1-Ni1-S2, 90.01(3); Fe1-S1, 2.2680(7); Fe1-S2, 2.2699(8); Fe1-C1, 2.076(2); Fe1-C2, 2.075(3); Fe1-Ni1, 2.6896(4); Fe1-C5, 2.079(3); Fe1-C6, 2.071(3); Fe1-C7, 2.061(3); Fe1-C8, 2.081(3); Fe1-C9, 2.087(3); Fe1-Centroid(C5-9), 1.682(3); Fe1-Centroid(Ni1,S1,S2,C1,C2), 1.663(3); Centroid-Fe1-Centroid, 175.9(1).

6.5.10  Reaction of 1 with HBF₄ (2 equiv) to form 1²⁺ (characterized by ESI MS)

Compound 1 (23 mg, 0.034 mmol) was combined with CH₂Cl₂ (3 mL) (green solution). Under a blanket of argon, HBF₄ (54 wt. % in diethyl ether) (9 μL, 0.066 mmol) was added (with stirring). The mixture was left to stir under positive argon pressure (vented to oil bubbler) for 22 h. After this time, a green mixture with a small amount of precipitate was observed. A portion of the resulting mixture was used to prepare a UV-vis sample in dichloromethane (sealable quartz cuvette, 1 cm pathlength); the spectrum indicates compound is 1²⁺ (see 6.5.10 for UV-vis data) is the product. From the remaining bulk solution/suspension, the solvent was removed under vacuum to afford very dark green solid residue. This residue was washed with diethyl ether (1 mL x 5) and dried in vacuo. A portion of the residual solid was analyzed by mass spectrometry. m/ε [ESI-TOF-MS]: 255.0 ([Cp*FeS₂]+ ?), 309.0 ([Cp*Fe(S₂C₂Me₂)]+), 338.0 (1²⁺, major), 485.0
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6.5.11 Reaction of $\mathbf{1}^+\text{PF}_6^-$ with $\text{Fc}^+\text{PF}_6^-$ (1 equiv) observed by $^1$H NMR and UV-vis

Compound $\mathbf{1}^+\text{PF}_6^-$ (12 mg, 0.015 mmol) was dissolved in CD$_2$Cl$_2$ (0.6 mL). The resulting green solution was transferred to a J. Young NMR tube containing ferrocenium hexafluorophosphate (5 mg, 0.015 mmol). The mixture was heated to reflux (under static nitrogen atmosphere) using an oil bath (set at 60°C) for 18 h. During this time, a significant amount of green-blue precipitate formed and the supernatant solution was deep green. The sample was allowed to cool to RT and a $^1$H NMR spectrum was obtained. Note: the sample exhibited paramagnetism and peaks were broad: $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 0.4-3.6 (br ov multiplets), 4.30 (br s, ferrocene). A portion of the NMR sample (solution/suspension) was used to prepare a UV-vis sample (diluted with CH$_2$Cl$_2$); the spectrum indicates compound is $\mathbf{1}^{2+}$ (see 6.5.8 for UV-vis data) is the product. Comments: the observation of ferrocene in $^1$H NMR spectrum indicates that the ferrocenium ion oxidizes $\mathbf{1}^+$, giving the same species that is formed by treatment of $\mathbf{1}$ with 2 equiv of HBF$_4$ (or $\mathbf{1}^+$ with 1 equiv of HBF$_4$), as determined by UV-vis. When $\mathbf{1}^+\text{PF}_6^-$ was treated with 1 equiv of ferrocenium hexafluorophosphate in CD$_3$CN (otherwise the same conditions) ferrocene was observed (4.16 ppm), upon oxidation of $\mathbf{1}^+\text{PF}_6^-$. However, the oxidized product, $\mathbf{1}^{2+}$, reacts with CD$_3$CN to give unidentified product(s).

6.5.12 Verification of single-electron-transfer steps for compound $\mathbf{1}^{n+}$ by CV

An acetonitrile solution containing $\mathbf{1}^+\text{PF}_6^-$ (1.2 mM) and ferrocene (Fc, 1.0 M) was subjected to a CV scan (scan rate: 100 mV/s; switching potentials: 1600 mV and -1000 mV). Peak currents for $\mathbf{1}/\mathbf{1}^+$, $\mathbf{1}^+/\mathbf{1}^{2+}$, Fc/Fc$^+$, $\mathbf{1}^{2+}/\mathbf{1}^{3+}$ integrated as 1, 1, 1.6, 1, respectively. The relative currents, calibrated against the one-electron transfer step of ferrocene show that each step in the $\mathbf{1}^{n+}$ redox chemistry is a one-electron transfer step. The higher current for the ferrocene/ferrocenium couple is predicted from the smaller hydrodynamic radius of ferrocene compared to $\mathbf{1}^{n+}$ (a geometric factor of ~ 2.5) and the inverse square-root
dependence of peak current on hydrodynamic radius.\textsuperscript{33} Also, compounds 1 and 1\textsuperscript{+} can be oxidized to 1\textsuperscript{+} and 1\textsuperscript{2+}, respectively, with 1 equiv of H\textsuperscript{+}, which provides additional independent evidence that the redox events for 1\textsuperscript{n}, observed by CV, are indeed one-electron transfer steps.

\section*{6.5.13 Calculation of $K_c$ for 1\textsuperscript{+}}

To calculate $K_c$, the energetic separation ($E_{1}^{0} - E_{2}^{0}$) between the reversible 1/1\textsuperscript{+} and 1\textsuperscript{+}/1\textsuperscript{2+} redox couples was obtained as the difference in the ($E_{\text{red}} - E_{\text{ox}}$)/2 values for the two couples [i.e., $| - 0.85 \text{ V} + 0.22 \text{ V} | = 0.63 (\pm 0.03) \text{ V}$ (with an estimated error of ca. 5%)].

$K_c$ was computed using the following expression:\textsuperscript{26}

$$K_c = \exp[nFR^{-1}(E_{1}^{0} - E_{2}^{0})T^{-1}]$$

with $n = 1$ (for one-electron transfer processes; see section 6.5.12 above); $F = 96485 \text{ C mol}^{-1}$ (Faraday constant); $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; $T = 298 (\pm 5) \text{ K}$ (estimated error in temperature)

Thus,

$$K_c = 4.5 (\pm 5.6) \cdot 10^{10}$$

This large value for $K_c$ shows that the mixed-valent state (1\textsuperscript{+}) is decidedly favored in the 1\textsuperscript{2+} + 1 $\rightleftharpoons$ 2 1\textsuperscript{+} equilibrium. The error ($\sigma$) in $K_c$ was calculated as described above (see section 6.5.7).
6.5.14 DFT Computations

6.5.14.1 General Computational Methods

Spin-unrestricted DFT computations were performed on a Windows PC, using the BLYP functional (UBLYP method), with Gaussian 03 for Windows. The counter anion was not included. Either the LANL2MB or the SDD atomic basis sets with effective core potentials (ECP) were used (see main body of the manuscript). The SDD basis set is the combination of the Huzinaga-Dunning double-ζ basis set on lighter elements (up to Argon) with the Stuttgart-Dresden relativistic effective core potential (RECP) on nickel and iron. To improve the accuracy of the calculation, addition of polarization functions to the sulfur atoms by augmenting the default SDD basis set, was incorporated into the calculation using the ‘ExtraBasis’ keyword in the input file. A single d primitive (single Gaussian) for all sulfurs was added with coefficients similar to that of the 6-311G(d,p) basis set, with an exponent of 0.65 with a weight of 1.0 and a scaling factor of 1.0. Final values were calculated to be 0.7836 for the cationic doublet as a doublet, indicating very low spin contamination. Initial geometry optimizations were done without symmetry using LANL2MB, and once it became clear that the structure converges into a centrosymmetric structure, the double-ζ SDD basis set was used and symmetry (exact symmetry, but the trimetallic core comes very close to even higher, symmetry), was imposed, for speed, during the final stages of the geometry optimization only. After a stationary point was located, vibrational analysis was performed at the same level of theory to determine if imaginary frequencies were present using no symmetry (nosymm). Compound showed no imaginary frequencies. Stability calculations were also performed on the SCF of the optimized structure using no symmetry (nosymm), to yield a stable wavefunction under default perturbations considered. The spin density was plotted using gOpenMol. Molecular orbital visualizations were created using Facio Version 11.5.1 using an iso-value of 0.04 unless otherwise stated.

For the atomic coordinates for determined at the UBLYP/SDD level of theory, see the supporting information for reference 1.
6.5.14.2 Analysis of the near-IR absorbance for \( \mathbf{1}^+ \): TDDFT

Preliminary TDDFT data (UBLYP/SDD, solvent was modeled with the PCM method) predict the lowest energy absorption band for \( \mathbf{1}^+ \) to be at 1570 nm, quite consistent with the experimental value of 1702 nm. As seen from the MO diagrams below (Figure 6.9), the charge transfer involves a donor orbital centered on the two iron centers and an acceptor orbital with primarily nickel dithiolene character.

![MO Diagrams](image)

**Figure 6.9** MOs involved in the NIR charge transfer transition of \( \mathbf{1}^+ \).

6.5.14.3 Computations on hydrogen-substituted (simplified) model

For the following computations (UBLYP/SDD), 14 methyl groups where replaced with 14 hydrogens, and the species are denoted as \( \mathbf{1H}_{14} \), \( \mathbf{1}^+\mathbf{H}_{14} \), etc.

Model computations relevant for the electronic ground-state structure of \( \mathbf{1}^+ \): A charge-trapped structure of \( \mathbf{1}^+\mathbf{H}_{14} \) (as a model for \( \mathbf{1}^+ \)) was created using the “field” keyword. With all symmetry turned off, an electric dipole field with strength of + 0.005 a.u., was added to the calculation on the axis that contained all three metals. In the presence of the field a geometry optimization was performed. The new geometry, which had significant lopsidedness, resulted in a dipole moment of 9.2268 Debye, in contrast with a dipole moment of 0 Debye in the fully delocalized structure. As a result of the application of the field, spin densities and Mulliken analysis reveal that both irons are not symmetrical, with
Mulliken spin densities values of Fe1 0.158980 and Fe2 0.717514. Upon a geometry optimization in the absence of the field (and with no symmetry constraints), the system converged back to the fully symmetrical (spin delocalized) geometry of $1^1 \text{H}_{14}$.

Comment on the electronic structure of $1^{2+}$: we observed paramagnetic broadening for the NMR spectra of $1^{2+}$. A computation on the simplified model $1^{2+}\text{H}_{14}$ indicated that a triplet ground-state structure (UBLYP/SDD) is more stable (by 3.9 kcal/mol) than the singlet (RBLYP/SDD) structure. While DFT energies of dicationic species are not expected to be very accurate, and while the triplet state may or may not be the ground state for the real system, this computational result is a strong indication that paramagnetic states can be low-lying and thermally accessible for $1^{2+}$.

6.6 References

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Na\(_2\)[Ni(S\(_2\)C\(_2\)Me\(_2\))\(_2\)] was made by reduction, using excess sodium metal; Na[Ni(S\(_2\)C\(_2\)Me\(_2\))\(_2\)] was obtained by reduction, using NaBH\(_4\) (see experimental section).


[17] The term “mixed-valent” is used to describe odd-electron multimetallic systems in which a metal is present in multiple whole-number oxidation states within a single molecule (e.g., M\(_n\)M\(_{n+1}\), n = whole number, “valence-trapped”). The term is also applied, somewhat misleadingly, to materials having a delocalized ground states where a lone electron shared equally between metals, resulting in non-integer oxidation states for the metals (e.g., M\(_{n+1/2}\)M\(_{n+1/2}\), “valence-delocalized”). The term “isovalent” pertains to arrangements with the metals in identical whole number oxidation states (e.g., M\(_n\)M\(_n\)).

[18] Marcus-Hush theory, based on a classical two-state model for intramolecular electron transfer, has been applied to the analysis of NIR transitions of mixed-valent systems to assess the extent of electronic delocalization (see ref. 19). This level of theory is useful when applied to bimetallic mixed-valent systems, when the metals are separated by a comparatively “innocent” (i.e., not redox-active) bridge and there is a measurable barrier to electron transfer between the metals (e.g., biferrocenium cations) (see ref. 19). However, Marcus-Hush theory is not appropriate for fully delocalized systems, particularly those with redox-active bridges (e.g., a nickel bisdithiolene bridge between the Fe atoms as in \( 1^+ \)), which potentially allow for multiple excited states.


[20] This analysis assumes a two-minus charge for the bridging nickel dithiolene unit in \( 1^+ \), which is likely an oversimplification considering the redox reactivity of metal bisdithiolenes and noninnocence of the dithiolene ligand (Chapter 1). See also ref. 18.

[21] Experimental details on X-ray crystallography: data collection on Nonius-Kappa CCD diffractometer using Mo K\(_\alpha\) (0.71073 Å) at 150(1) K, structure solution with direct methods, refinement on F\(^2\) against all reflections. Crystal data and structure refinement for \( 1^+ \) PF\(_6^–\): dark green block, crystal size = 0.23 x 0.16 x 0.11
mm, C_{38}H_{43}F_{14}Fe_{2}Ni_{1}P_{3}S_{4}, M = 822.24, triclinic, space group P -1, a = 8.3214(7) Å, b = 8.4045(6) Å, c = 13.0294(11) Å, α = 105.575(5)°, β = 101.908(4)°, γ = 103.120(4)°, Z = 1, V = 819.43(11) Å³. D_{calc} = 1.666 g cm⁻³, 7216 reflections collected of which 3646 were independent, GOF = 1.040, R1 = 0.0492 (data with I >2σ(I)), wR2 = 0.1308 (all data). Crystal data and structure refinement for 1⁺BF₄⁻: dark green needle, crystal size = 0.45 x 0.18 x 0.12 mm, C_{28}H_{42}B_{1}F_{4}Fe_{2}Ni_{1}S_{4}, M = 764.08, triclinic, space group P -1, a = 8.2743(2) Å, b = 8.3071(3) Å, c = 12.9787(5) Å, α = 105.1233(17)°, β = 101.2840(19)°, γ = 104.741(2)°, Z = 1, V = 799.37(5) Å³. D_{calc} = 1.587 g cm⁻³, 10562 reflections collected of which 3599 were independent, GOF = 1.047, R1 = 0.0369 (data with I >2σ(I)), wR2 = 0.0886 (all data). For Crystallographic Information Files (cif format) for these structures, see the supporting information for ref. 1.


[23] For a discussion of η⁵ versus η⁴ donation in structures of Rh/Ru tetrathiooxalate chelate rings:


[28] Conversion to 1⁺ is complete in <2 min (room temperature) by UV-vis spectroscopy ([HBF₄]₀ = [1]₀ = 0.3 mM in CH₂Cl₂).
[29] Under the conditions of our CV experiments, a peak separation (E_{ox} – E_{red}) of ca. 72 mV for ferrocene/ferrocenium couple was observed. Thus, redox couples with peak separation of 72 mV or less are considered reversible.

[30] Peak assignments are based on the observation that $1^+$ is oxidized by ferrocenium hexafluoro-phosphate, in a stoichiometric chemical oxidation experiment.


Chapter 7

Summary and Outlook

7.1 Overview

The preceding chapters have described our investigations into the ligand-based reactivity of metal bis- and trisdithiolenes. The following sections provide short summaries for each chapter, starting with chapter 2, with emphasis on key discoveries and with outlooks on future directions.

7.2 Chapter 2

Chapter 2 focused on the alkene-binding reactions of the nickel bisdithiolene \( \text{Ni(S}_2\text{C}_2\text{(CF}_3\text{)}_2\text{)}_2 \). We found that alkene addition to this complex proceeds, preferentially, in an intraligand fashion to yield decomposition products (when the reaction mixtures are free of reductants), seemingly undermining proposals to use \( \text{Ni(S}_2\text{C}_2\text{(CF}_3\text{)}_2\text{)}_2 \) in alkene purification schemes. However, we also discovered that the product selectivity can be reversed in favor of stable interligand adducts by adding monoanionic \( [\text{Ni(S}_2\text{C}_2\text{(CF}_3\text{)}_2\text{)}_2]^- \) (or a reductant to produce the anion \textit{in situ}) to \( \text{Ni(S}_2\text{C}_2\text{(CF}_3\text{)}_2\text{)}_2/\text{alkene} \) reaction mixtures. We have proposed a mechanism that addresses the possible role of the anion in determining product selectivity. Based on experiments utilizing selectively deuterated 1-hexene (\textit{trans-DHC}–\text{CH}°\text{Bu}), the symmetry-forbidden interligand addition of alkenes to \( \text{Ni(S}_2\text{C}_2\text{(CF}_3\text{)}_2\text{)}_2 \) proceeds with stereospecificity and is likely concerted. Future work should investigate, in greater detail, the mechanism of alkene binding in the presence of \( [\text{Ni(S}_2\text{C}_2\text{(CF}_3\text{)}_2\text{)}_2]^- \) to determine whether our proposed mechanism is correct, or whether a modified kinetic model is needed.
7.3 Chapter 3

Chapter 3 also dealt with the ligand-centered reactions of a metal bisdithiolene, but this study focused on Pt(S₂C₂(CF₃)₂)₂ and its reactions with 2,3-dimethyl-1,3-butadiene.² Although metal bisdithiolenes have been known to react with 1,3-conjugated dienes for decades, until our work only symmetry-allowed interligand S,S-addition had been observed. We found that Pt(S₂C₂(CF₃)₂)₂ reacts, initially, with 1 equiv of diene to rapidly form the expected interligand adduct. However, the interligand adduct isomerizes to a thermodynamic product in which two dienes have added to one dithiolene ligand [C,S-intraligand diene addition (x2)]. The double diene adduct possesses a new chiral bisthioether ligand (C₂ symmetry for the adduct and the ligand), formed by stereospecific diene addition. Ongoing work is directed at obtaining the chiral ligand, and/or its analogues, using catalytic amounts of Pt(S₂C₂(CF₃)₂)₂ (or another metal dithiolene).

7.4 Chapter 4

The synthesis of two new mixed-ligand molybdenum trisdithiolenes and their reactivity with ethylene were detailed in chapter 4.³ Specifically, we prepared the complexes Mo(S₂C₂(CF₃)₂)₂(S₂C₆H₄) and Mo(S₂C₆H₄)₂(S₂C₂(CF₃)₂) (an X-ray structure was presented for the latter compound), both of which react with ethylene in an intraligand fashion at the S₂C₆H₄ ligand. Molecular orbital and valence bond arguments were used to rationalize the mode of alkene binding. Interestingly, the intraligand adducts formed by the addition of ethylene to our new mixed-ligand trisdithiolenes are sufficiently stable to be characterized, in contrast to analogous adducts of bisdithiolenes. The metal-bound dihydrobenzodithiin, which is formed by ethylene addition, is labile, however, and can be displaced with a variety of nucleophiles to form new molybdenum bisdithiolenes, while releasing free dihydrobenzodithiin. These unusual adducts, especially the alkene adducts of Mo(S₂C₂(CF₃)₂)₂(S₂C₆H₄), with a dihydrobenzodithiin weakly bound to the metal, are therefore of interest as homogenous models for hydridesulfurization catalysts (four-coordinate MoS₄ environments), since the dihydrobenzodithiin cap can be easily removed to afford “Mo(S₂C₂(CF₃)₂)₂” analogues.
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7.5 Chapter 5

Chapter 5 describes how the ligand-based reactivity of the mixed-ligand trisdithiolene Mo(S2C2(CF3)2)2(S2C6H4) was used to generate dihydrobenzodithiins catalytically from a variety of alkenes and the tetrathiolate (S2C6H4)4 (i.e., oxidized benzene-1,2-dithiol). The catalysis involves unusual ligand-centered reactions and the resting state of the catalyst for the reactions involving ethylene and 1-hexene was found to be the corresponding intraligand alkene adducts of Mo(S2C2(CF3)2)2(S2C6H4). We also showed, in stoichiometric experiments, that these adducts can be converted to free dihydrobenzodithiins and Mo(S2C2(CF3)2)2(S2C6H4) by treatment with excess (S2C6H4)4. The catalysis leading to dihydrobenzodithiins is effective for both cis- and trans-disubstituted alkenes, although lower yields of dihydrobenzodithiins were obtained for cis-alkenes because of a side-reaction that yielded polymeric material. Significantly, for the reactions involving disubstituted alkenes, stereospecificity was observed, such that the configuration of the alkene was retained in the product (i.e., trans-alkenes give trans-dihydrobenzodithiins, etc.). Allyl alcohol was also viable as a substrate, indicating that the newly discovered catalysis is not limited in unfunctionalized alkenes. Ongoing efforts are aimed at broadening the scope of substrates: For example, more alkenes, including functionalized examples, will be screened in the dihydrobenzodithiin-forming reactions. Also, other oxidized substrates will be examined as potential alternatives to (S2C6H4)2 (e.g., other polysulfides, conjugated diimines, 1,2-benzoquinone derivatives).

7.6 Chapter 6

While the other chapters dealt with metal dithiolenes behaving as electrophiles, chapter 6 concerns new trimetallic complexes made by exploiting the nucleophilic properties of a reduced nickel bisdithiolene. Specifically, [Ni(S2C2Me2)]n− (n = 1, 2) reacts with [(MeCN)3FeCp*]+ (Cp* = cyclopentadienyl) (2 equiv) to form new Fe2Ni bis-double-decker complexes {[(η5-Cp*-Fe-μ-η5,η5-(S2C2Me2)2Ni)-Fe-η5-Cp*]m+; m = 0, 1}. These trimetallic complexes are redox active, as shown by cyclic voltammetry and chemical oxidation experiments. Experimental and computational data for the complex with m = 1 (i.e., the
monocationic bis-double-decker, see above) reveal that the lone electron is delocalized over all three metals, with significant spin contributions on the dithiolene ligands. Future efforts should focus on making polymeric derivatives based on the [Fe-μ-η⁵,η⁵-(S₂C₂Me₂)₂Ni] unit, by reacting a labile (uncapped, i.e., no Cp* group) Fe(II) salt (e.g., [(MeCN)₆Fe]²⁺) with [Ni(S₂C₂Me₂)₂]ⁿ⁺ (n = 1, 2). Such metallapolymeras should exhibit interesting properties, including redox reactivity and, possibly, electronic conductivity.

7.7 Final remarks

Metal dithiolenes are fascinating compounds with rich chemical, electrochemical, spectroscopic, solid-state and biological properties, which are related to the noninnocence of dithiolene ligands. Our work has focused, primarily, on electron-deficient metal dithiolenes behaving as electrophiles in reactions with alkenes and dienes, although chapter 6 addresses the use a reduced metal bisdithiolene as a nucleophile/ligand. We have contributed significantly to the field: for example, we provided much-needed fundamental insight into the reactions of nickel bisdithiolenes with simple alkenes. We have also reported the first fully-characterized mixed-ligand trisdithiolenes, including an example with three different dithiolene ligands attached to one molybdenum atom, in the first paper dealing extensively with the alkene binding of metal trisdithiolenes. These findings were applied to developing a catalytic process, which allows the fabrication of dihydrodithiins from alkenes and (S₂C₆H₄)₂, in a rare example of the ligand-centered reactivity of a metal dithiolene being exploited in a catalytic cycle.

7.8 References