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Citation

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Transition Metal Complexes of an (S,S)-1,2-Diphenylethylamine Functionalized N-Heterocyclic Carbene: a New Member of the Asymmetric NHC Ligand Family

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ABSTRACT: By a simple S<sub>N</sub>2 reaction between N-methylimidazole and a chiral sulfamidate, the first proligand of a new class of enantiopure NHC-CHPh-CHPh-NH<sub>2</sub> ligands can be prepared in high yield. This proligand, with molecular formula [(S,S)-H<sub>2</sub>NCHPhCHPh-NC<sub>3</sub>H<sub>3</sub>N-CH<sub>3</sub>](PF<sub>6</sub>), when reacted with a slight excess of lithium or potassium bis(trimethylsilyl)amide, produces the corresponding NHC-CHPh-CHPh-NH<sub>2</sub> ligand, “kaibene”. In the presence of the silver(I) starting materials AgPF<sub>6</sub> or AgI, two Ag(kaibene):X complexes (X = PF<sub>6</sub> or I) and one helical kaibene silver polymer [Ag(kaibene)]<sub>n</sub>(PF<sub>6</sub>)<sub>n</sub> can be prepared. Using the suitable silver complex, we successfully transferred kaibene to ruthenium(II), iridium(I) and nickel(II). The ruthenium complex [Ru(p-cymene)(kaibene)(Cl)]PF<sub>6</sub> with a base in THF is a moderately active catalyst at 50 °C and 25 bar H<sub>2</sub> for the hydrogenation of acetophenone but with no enantioselectivity.

INTRODUCTION

Enantiopure alcohols and amines are essential building blocks for the synthesis of drugs, fragrances and agrochemicals. One of the many ways to efficiently generate such molecules is via the asymmetric hydrogenation of the corresponding ketones or imines using a transition metal catalyst. However most hydrogenation catalysts, including recently reported iron-based catalysts, contain asymmetric chelating phosphine ligands which can potentially introduce harmful contaminants into products destined for medical applications. A possible solution to this problem is to replace the phosphines with N-heterocyclic carbenes (NHC) since these organic ligands might be less toxic while maintaining a σ-donor strength that is similar or greater than that of a phosphine. Our group previously reported achiral NHC-Q-NH<sub>2</sub> ligands with linking groups Q for use with precious metals like Ru (1, 2 and 4) and Ir (3) (Scheme 1). The complexes of these ligands showed moderate to exceptional catalytic reactivity under mild conditions (25 – 50 °C, 9 – 26 atm) towards the complete hydrogenation of ketones, imines (only 2), and esters (only 2). Our theoretical calculations support the proposed mechanism involving an “N-H” effect in the hydrogenation of these substrates with polar bonds where a metal-hydride (M-H) and an amine-hydrogen (N-H) group deliver a pair of hydrogens from the catalyst to the polar unsaturated bond of a ketone, imine or ester in a cooperative fashion. Complexes 1, 2 and 4 and a primary amino carbene ruthenium complex reported by Cross et al. are moderately active catalysts for the transfer hydrogenation of acetophenone using isopropanol, but the conversions for this equilibrium process are not complete.
Our objective is the synthesis of enantiomerically pure asymmetric ligands that chelate transition metals via NHC and amine donors in order to take advantage of this rate-enhancing “N-H” effect. Many asymmetric N-heterocyclic carbenes (NHC) ligand designs are known but there are only a few examples with the NHC-Q-NH₂ structure. A palladium complex containing such an NHC-Q-NH₂ ligand with a 1,2-trans-cyclohexyl linker Q between an NHC and primary amino group (Fig. 1, 5) was described by Bonnet et al in 2004 but it was formed on the metal by a hydrolysis side reaction. A related ligand with a 1,10-binaphthyl-2,2’-diamine linker was also formed on palladium by hydrolysis (Fig. 1, 6). Ligands with the amino group directly attached to an aromatic backbone such as that of 6 are not expected to form amido complexes that are reactive enough to efficiently split dihydrogen in a bifunctional catalytic reaction. We are targeting ligands with the amino group attached to an aliphatic carbon to enhance the basicity of the amido group in the catalytic cycle.

Here we describe the synthesis directly from methylimidazole of the first of a new class of such ligands 7 (R² = Me, “(S,S)-kaibene”) where Q is an (S,S)-1,2-diphenylethandiyl linker along with its silver, nickel, iridium and ruthenium complexes including a chiral, helical coordination silver polymer. Enantiopure 1,2-diphenylethylene diamine (dpen) has proven to be an effective group in catalyst structures for inducing asymmetry in the products of a wide variety of catalytic transformations including asymmetric hydrogenation (AH). Kaibene’s similar structure to dpen when coordinated in a bidentate fashion suggests that it might have these valuable characteristics.
RESULTS AND DISCUSSION

Synthesis of a Chiral NH₂-tethered NHC Ligand “kaibene.” In order to synthesize the required imidazolium salt (S,S)-9, a sulfamidate precursor 8 37,38 in the configuration (R, S) was first refluxed in a solution of 50% v/v N-methylimidazole (about 10 equivalents) in toluene for 90 min (Scheme 2). During the course of heating, the initially insoluble sulfamidate suspension precipitated as a white powder. The white powder as the Boc protected intermediate can be isolated in almost quantitative yield by cooling the reaction mixture to room temperature and adding an excess of diethyl ether. To deprotect the Boc group, we simply used excess 37% HCl(aq) instead of the standard trifluoroacetic acid or HCl in dioxane treatment. After neutralization and salt metathesis, the product (S,S)-9 can be collected in 90% yield. Its enantiopurity was confirmed by NMR after making the Mosher amide. 39 In principle the enantiomer (R,R)-9 can also be prepared since the corresponding sulfamidate can be prepared from a commercially available amino alcohol. In addition other sulfamidates derived from amino alcohols could be prepared in principle. For example the synthesis of related imidazolium salts with a -CHPh-CHMe-NMeSO₃⁻ tether has been reported. 40

Scheme 2. Synthesis of the Imidazolium Salt Precursor to “(S,S)-kaibene”

![Scheme 2](image)

The presence of the Boc protecting group is crucial in order to obtain an enantiopure product. In a different experiment where the Boc protection group on the sulfamidate was first removed by potassium imidazolide, subsequent reaction with N-methylimidazole consistently gave a mixture of S,S and R,S diastereomers in a 3:1 ratio independent of varying the reaction temperature and solvent polarity. This observation can be explained through a competing S_N1 reaction with the ongoing S_N2 reaction. We suspect that, without the Boc group, the nitrogen atom is better able to stabilize the carbocation intermediate formed during the S_N1 mechanism, thus yielding the undesired diastereomer. The use of the correct reaction time is also important to prevent side reactions. Prolonged heating led to an undesired side product which is formed by a slow but irreversible E2 elimination from (S,S)-9 where the imidazolium functions as good leaving group.

Synthesis of Silver Complexes for use in Transmetallation Reactions. Typically NHC complexes are prepared by the transmetallation of the ligand from silver (e.g. complex 4 of Scheme 1) or nickel (complexes 1-3) and usually silver oxide is utilized to make silver derivatives. We found that the imidazolium salt (S,S)-9 is not sufficiently acidic to be deprotonated by silver (I) oxide in an aprotic, low dielectric constant solvent such as CH₂Cl₂ or THF. In order to synthesize
the corresponding silver complex, it is necessary to use a silver reagent in combination with the
strong base hexamethyldisilylamide as the alkaline metal salt (MHMDS, M=Li, K); this likely
produces the free (S,S)-kaibene (Scheme 3) which is rapidly trapped by a silver cation. We tried to
directly deprotonate the imidazolium salt with various strong bases to generate the NHC in situ but
the system decomposed. By using this method, three different silver complexes were made (Scheme
3).

**Scheme 3. Synthesis of a Coordination Polymer (10) and Two Monometallic Silver
Complexes (11, 12) Starting from (S,S)-9**

In order to prepare 10 we reacted one equivalent of base and silver ion per imidazolium salt
precursor in a THF solution over a period of four days until a white precipitate slowly formed.
This substance was collected via filtration and all unreacted starting materials and lithium salt by-
products were washed away by use of THF. A recrystallization using a slow diffusion of diethyl ether into a saturated acetonitrile solution gave colourless crystals which revealed the formation of a 1-D silver NHC-NH$_2$ polymer 10 as illustrated in Scheme 3. The crystal structure (Figure 2) reveals that the polymer is in a $\Lambda$(M)-helical configuration with each silver ion coordinated by an
NHC carbon and an amino nitrogen of the (S,S)-kaibene with a nearly linear C-Ag-N angle of 177.0(2)°.

Figure 2. A \( \Lambda(M) \)-helical coordination polymer 10 of silver with (S,S)-kaibene. Selected bond lengths (Å) and angles (°): Ag1-C1 2.053(5), Ag1-N3a 2.135(4), C1-Ag1-N1a 177.0(2). PF\(_6\) and a diethyl ether molecule are removed for clarity.

Complex 10 has an unusually short Ag-C bond distance of 2.053(5) Å in comparison to known Ag-NHC complexes with two coordinate silver in the literature. This is in the 6\(^{th} \) percentile of Ag-NHC distances which range from 2.02 to 2.16 Å in 390 structures with two coordinate silver as determined by searching the 2015 Cambridge Structural Database. This is ascribed to the fact that amine donors have among the weakest trans influence of neutral donors.\(^{41} \) The only other complex with a crystallographically characterized [N(amine)-Ag-C(NHC)]\(^+ \) structure is the dimeric complex [Ag\(_2\)(NEt\(_2\)CH\(_2\)CH\(_2\)NC\(_2\)H\(_2\)NMe)\(_2\)](NTf\(_2\))\(_2\).\(^{42} \) It has a comparable Ag-C distance but a longer Ag-N distance (2.178(3) vs 2.135(4) in 10) because of the larger size of the substituents on nitrogen and their poorer ability to stabilize the positive charge. While some coordination polymers of silver and NHC ligands are known, none have adopted an asymmetric structure like that of 10.\(^{43-45} \) Further investigation showed that the oligomerization process is extremely slow at room temperature as the white product did not appear in the solution until approximately the third day of the reaction. Attempts to isolate the product before this precipitate is observed yielded unidentified decomposition products. Although the formation of such a polymer is interesting and unprecedented, this polymer is only soluble in DMSO and acetonitrile which limits its use in the synthesis of other metal complexes.

In order to increase the solubility of a silver NHC complex, the ratio of silver to ligand was reduced to half to disfavour the formation of the polymer. The reaction of (S,S)-9 with AgPF\(_6\) and base resulted in the formation of the silver bis(kaibene) complex 11 as the PF\(_6\) salt while that with AgI and base produced the neutral silver bis(kaibene) iodide complex 12. Complex 12 can also be prepared from 11 by reaction with potassium iodide (Scheme 3). It is noteworthy that the presence of excess KI is necessary to obtain 12 in high purity; if not, the product appears more metallic, probably due the formation of silver (0). In contrast to compound 10 which is light stable, compounds 11 and 12 are light sensitive; colourless solutions of 11 or 12 turned brown after 18 h when illuminated with overhead fluorescent lights. Both complexes were characterized by NMR
and by EA and single crystals of 12 suitable for X-ray diffraction were grown from a saturated CH₂Cl₂/hexane solution (Figure 3).

**Figure 3.** Molecular structure of 12. (Left: atom numbering; right: orientation showing the T-shape with trans carbenes). Selected bond lengths (Å) and angles (°): Ag1A-C1A 2.103(1), Ag1A-C19A 2.095(2), Ag1A-I1A 3.251(8), C19A-Ag1A-C1A 165.9(6), C19A-Ag1A-I1A 93.3(4), C1A-Ag1A-I1A 100.6(4). CH₂Cl₂ molecules are removed for clarity.

Complex 12 contains a “T-shaped” three coordinate silver center with the two NHC ligands in an approximate trans orientation (Figure 3). There are two molecules A and B in each asymmetric unit with C-Ag-C angles 165.9(6)° for A and 160.3(5)° for B. The Ag-I bond forms two angles with the two Ag-C bonds, one in range of 94° and the other 103° for each molecule. The Ag-NHC distance appears to be longer in 12 (2.095(2) to 2.103(1) Å) than 10 (2.053(5)) because of the higher trans influence of carbene versus amine. Although a Ag-I bond is drawn by the crystallographic software in Fig. 3, the Ag-I distance (3.251(8) Å) is actually longer than the sum of the covalent radii of silver and iodine (2.84 Å, 1.45 Å for silver and 1.39 Å for iodine). Therefore the iodide serves mainly as a counterion and its position can be attributed to a balance of electrostatic attractions and steric interaction. It should also be noted that the voids in this lattice host a large number of CH₂Cl₂ molecules. This compound has a characteristic NHC carbon shift at 181.5 ppm in the ¹³C NMR spectrum, which falls within the expected range of transition metal NHC compounds.

**Synthesis of Ru, Ni and Ir Complexes of Kaibene.** The ruthenium p-cymene complex with kaibene is prepared by reacting the dichloro(p-cymene)ruthenium dimer with compound 12 in THF at reflux (Scheme 4). Notably, it is important to add an excess of a non-halide salt such as KPF₆ or NaBPh₄ during the reaction to remove one chloride ligand from the dimer. This generates a vacant site on the ruthenium for kaibene, breaks apart the dimer, and makes the ruthenium center more Lewis acidic to facilitate ligand transmetallation. In contrast, trial reactions done without one of these salts, or with only a stoichiometric amount of them, tended to produce multiple products. Unfortunately, both 13 and 14 are obtained as equal quantities of two diastereomers having opposite chirality at ruthenium, independent of the choice of the counter anion. This might explain our failure to obtain single crystals for X-ray crystallography. As an alternative approach, we use 2D NMR and mass spectrometry techniques to elucidate the structures in solution.
Scheme 4. Synthesis of the Half-sandwich Ruthenium Complexes 13 and 14 using the Transmetallation Reagent 12

The $^{13}$C NMR spectrum of compound 13 in CD$_2$Cl$_2$ reveals two NHC signals at 174.2 and 171.3 ppm, one for each of the diastereomers. This is a significant chemical shift difference from that of the starting silver reagent at 181.5 ppm thus providing evidence for coordination. Also, this NMR shift is near to 174.0 ppm observed for its achiral analogue compound 4. To further validate that kaibene is chelated to ruthenium via both the NHC and NH$_2$ parts, a 2D $^1$H-$^{15}$N gHSQC experiment was conducted (Figure 4). As expected for the presence of two diastereomers, two sets of NH$_2$ peaks are observed in the $^{15}$N dimension of the spectrum at -2.61 and 3.76 ppm. More importantly, each of these nitrogen signals correlates to two diastereotopic hydrogen atoms through one-bond interactions. An NMR spectrum of 13 in DMSO-$d_6$ was also collected. In this spectrum, NH signals are found at 4.00, 4.13, 4.51, 5.60 ppm compared to 3.21, 3.93, 5.18, 5.60 ppm for 13 in CD$_2$Cl$_2$. The NH peak at 4.51 ppm shows a clear doublet of doublet pattern as expected. This confirms the coordination of the NH$_2$ functional group in 13 since, upon binding to Ru(II), the two hydrogen atoms on the nitrogen are no longer able to achieve chemical equivalence via inversion at nitrogen.

Figure 4. $^1$H-$^{15}$N gHSQC spectrum of 13 in CD$_2$Cl$_2$ ($f_1$ $^{15}$N, $f_2$ $^1$H).
In addition to ruthenium, we also transferred kaibene from silver to nickel(II) and iridium(I) using silver complexes 11 and 12 respectively (Scheme 5). After reacting 11 with approximately two equivalents of nickel(II) chloride in the presence of KI over a five day period, we obtained a bis(kaibene) nickel (II) dimer with bridging iodides (15, Scheme 5) in approx. 64% yield, using kaibene as the limiting reagent. Experiments were also conducted in the absence of KI. However, the product mixture was never as pure as that obtained in the experiment performed with KI addition. In contrast to compounds 13 and 14, we observed only one doublet $^1$H NMR signal for the NH$_2$ group at 1.66 ppm ($J_{HH} = 5.1$ Hz) which integrates as two protons. The use of 2D $^1$H-$^1$H correlation determined that the CH hydrogen on the CHPh group adjacent to the NH$_2$ group is responsible for this coupling. It is likely that the amine groups are not coordinated and are freely inverting. We also observe similar NH$_2$ resonances for complexes 11 (1.56 ppm, $J = 4.3$ Hz) and 12 (1.77 ppm, $J = 5.5$ Hz) which are known to have no amine coordination because of the linear coordination mode favored by silver(I); this is seen in the solid state structure of compound 12. The $^{13}$C signal for 15 at 186.01 ppm provides evidence for NHC coordination while mass spectrometry reveals the presence of [Ni(kaibene)$_2$]$^{2+}$ fragments. $^{19}$F NMR and elemental analysis suggest the presence of PF$_6^-$ as the counter anion for this system. All of these analytical data suggest that the nickel compound 15 contains a nickel (II) center and has a stoichiometric ratio kaibene:nickel = 2:1. On the basis that nickel (II) complexes tend to have a square planar arrangement due to their $d^{10}$ configuration we propose that the structure of 15 is an iodide-bridged nickel dimer as illustrated in Scheme 5. A similar nickel (II) NHC dimeric structure was reported but it contains only one bulky IPr NHC ligand. Interestingly, the use of compound 11 as the transmetallation reagent to generate compound 15 was crucial. The use of the analogous compound 12 always led to a mixture of products. We speculate that the silver(I) cation in 11 without halide coordination can act as a halide abstracting agent to first convert NiCl$_2$ into the better Lewis acid [NiCl]$^+$ to favor the coordination of the kaibene.
Similarly, the analogous iridium complex 16 can be synthesized by refluxing chloro(1,5-cyclooctadiene)iridium(I) dimer with complex 12 in THF. Complex 11 can also be used but the yield is lower. In early attempts we reacted complex 11 with the iridium precursor at room temperature with an excess of KI but only obtained compound 12. To rationalize this, we believe that the temperature of THF at reflux is required to make the cyclooctadiene ligand labile for substitution. Initially we attempted to isolate an Ir(cod)(kaibene)Cl compound similar to our previous active catalyst 3. However, we believe that the strong trans influence of the kaibene carbon labilizes the alkene ligand so that no [Ir(cod)(kaibene)]⁺ complex is observed in the product.

We propose a structure [Ir(kaibene)₂I]₂ for compound 16 with uncoordinated amino groups that is similar to that of compound 15 since we also observe a clean doublet representing the NH₂ at 1.78 ppm (d, J₁HH = 5.7 Hz, 2H) in the ¹H NMR spectrum. The NHC ¹³C shift in the NMR spectrum is 186.53 ppm. We observed an [Ir(kaibene)₂]⁺ fragment in mass spectrometry which indicates a ratio of kaibene:iridium = 2:1 and this is consistent with the elemental analysis. It is noteworthy that we also observe an [Ir(kaibene)₂(cod)]⁺ fragment in the mass spectrum as the major species but no obvious cod signal in the proton NMR spectrum. Trace amounts of this complex must ionize much more efficiently under the ESI conditions than dimeric complex 16. No similar iridium(I) structures have been reported but a reaction intermediate was proposed to have an [Ir(NHC)₂Cl]₂ structure with bridging chlorides.⁵⁰ Compound 16 was tested for the hydrogenation of acetophenone and but no catalytic reactivity was observed under the conditions that we used (50 °C, 25 bar H₂).

**Catalytic hydrogenation of acetophenone using compound 13.** First we examined the transfer hydrogenation capability of ruthenium complex 13 since the analogous compound 4 showed moderate reactivity in transfer hydrogenation. At 75 °C with 0.5% catalyst 13 loading along with 4% KOTBu, there was 40% conversion to 1-phenylethanol after 3.5 hours, using isopropanol
as the sacrificial hydrogen source as well as the solvent. We attribute the poor activity to the low solubility of the precatalyst in the solution. The enantioselectivity of this reaction is low (5%). This is possibly due to the diastereomeric composition of the precatalyst. However this is also consistent a mechanism, as proposed for the analogous achiral complex 4, where the activated catalyst transfers a hydride to acetophenone in the inner coordination sphere with the amine group of the NHC ligand decoordinated and thus inducing little enantioselectively.\textsuperscript{16}

We then tested precatalyst 13 for direct hydrogenation (Figure 5) and find that it is more effective here than in transfer hydrogenation. The e.e. is 0% indicating that the presence of diastereomers of the catalyst is detrimental to catalytic asymmetric applications or that this catalytic reaction also proceeds via an inner sphere hydride transfer mechanism with the tethered NH\textsubscript{2} decoordinated. The activity of the catalyst system (TOF 200 h\textsuperscript{-1}) is less than that of the achiral analogue 4 (Scheme 1, TOF 600 h\textsuperscript{-1}) possibly for steric reasons.

\begin{center}
\includegraphics[width=0.8\textwidth]{figure5.png}
\end{center}

\textbf{Figure 5.} Catalytic hydrogenation of acetophenone using compound 13

We lowered the catalyst loading and measured a reaction profile of conversion versus time and observed no activation period. This provides evidence against the formation of catalytically active nanoparticles which typically display an induction period. The reaction profile shows a continuously declining rate of reaction with conversion. The use of a higher substrate concentration gave a similar profile with no significant enhancement in TOF.

\section*{Conclusions}

In summary, a new approach to synthesize primary amine tethered NHC proligands is reported and this method can be used to generate enantiopure asymmetric ligands. Here we reported the first ligand of this class (S,S)-H\textsubscript{2}N-CHPh-CHPh-NHC “kaibene” that can be prepared in 90% yield and analytical purity as the imidazolium salt. In the presence of HMDS base, three silver complexes can be produced depending on the source of silver and the stoichiometric ratio between the ligand and metal. With one equivalent of silver per ligand, the first \( \Lambda \)-helical coordination polymer of silver 10 was synthesized and structurally characterized by X-ray crystallography. The use of a half equiv. of silver per ligand generates compounds 11 and 12 with the molecular formula \( \text{Ag(kaibene)}_2X \) (\( X = \text{I or PF}_6 \)) and these bis(kaibene) silver compounds are good transmetallation reagents that can be used for the synthesis of Ru(II), Ni(II) and Ir(I) kaibene complexes (13-16). The ruthenium complexes 13 and 14 [Ru(p-cymene)(kaibene)(Cl)]\(\_2\)\( (X = \text{PF}_6, \text{BPh}_4) \) exist as two diastereomers and their amine coordination was confirmed by 2D \(^{1}\text{H}-^{15}\text{N}\) gHSQC. In contrast, Ni and Ir complexes display interesting dimeric structures with the formulae [NiI(kaibene)]\(\_2\)(\( \text{PF}_6\)) and [IrI(kaibene)]\(\_2\) where the primary amine groups are not coordinating. Complex 13 showed poor transfer hydrogenation capacity and moderate direct hydrogenation activity (TOF 200 h\textsuperscript{-1})
using acetophenone as the test substrate but the presence of the two diastereomers or decoordination of the amino group would explain why little or no enantioselectivity is observed.

**EXPERIMENTAL SECTION**

**General Considerations.** The synthesis of the ligand was conducted in the air. All of the synthesizes of transition metal complexes were performed under an argon or nitrogen atmosphere using standard Schlenk-line and glove box techniques unless stated otherwise. The sulfamidate precursor was prepared according to the reported literature method. All solvents were degassed and dried using standard procedures prior to all manipulations and reactions unless stated otherwise. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Sigma Aldrich, degassed, and dried over activated 3 Å molecular sieves prior to use. All other reagents were purchased from commercial sources and utilized without further purification. NMR spectra were recorded at ambient temperature and pressure using a Varian Gemini 400 MHz spectrometer (400 MHz for 1H, 100 MHz for 13C, 376 MHz for 19F), Agilent DD2-500 MHz spectrometer (500 MHz for 1H, 125 MHz for 13C) or an Agilent DD2-600 MHz spectrometer (600 MHz for 1H, 151 MHz for 13C, 564 MHz for 19F) unless stated otherwise. The 1H-15N gHSQC was measured using an Agilent DD2-700 MHz spectrometer. The 1H and 13C NMR were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane (TMS). Only selected NMR data is listed below. A complete assignment of resonances and coupling constants for the compounds with numbered atoms is found in the Supporting Information.

**3-((1S,2S)-2-amino-1,2-diphenylethyl)-1-methyl-1H-imidazol-3-ium hexafluorophosphat e, (S,S)-9.** A round bottom flask was charged with a magnetic stirring bar, the sulfamidate (4S,5R)-1,2,3-oxazathiolidine-3-carboxylic acid, 4,5-diphenyl-1,1-dimethylethyl ester, 2,2-dioxide (1.0 g, 2.66 mmol), N-methylimidazole (2.2 mL, 27.6 mmol) and 2 mL of toluene and then the solution was refluxed for 1.5 h. The reaction mixture turned from cloudy to clear and then to cloudy during the reflux. After cooling to room temperature, 20 mL of diethyl ether was added and the mixture was stirred for another 20 min. A white precipitate of the Boc-protected (S,S)-9 formed and was collected via filtration. 5 mL of conc. HCl (37% wt in H2O) was used to dissolve this white powder and the mixture was stirred for another hour. The acidic solution was then neutralized with sodium carbonate and then to it was added 0.5 g of potassium hexafluorophosphate. The mixture stirred for 18 h to allow salt metathesis. The white precipitate that formed was filtered and the filtrate was extracted with 50 mL CH2Cl2 (CH2Cl2) three times and the extracts were combined with the precipitate. Evaporation of all volatiles under vacuum gave a white solid which was then dissolved in a minimum amount of CH2Cl2. Insoluble compounds were filtered off and then product was precipitated by the addition of an excess hexanes; this mixture was stirred for 2 h and then filtered and dried in vacuo. Yield: 1.02 g (90%). 1H NMR (DMSO-d6, 298K, δ): 9.42 (s, NCHN, 1H), 7.97 (dd, 3JH=2.4 Hz, 4JH=1.7 Hz, CH of imid., 1H), 7.71 (dd, 3JH=2.4 Hz, 4JH=1.6 Hz, CH of imid., 1H), 7.48-7.08 (m, Ph on the backbone, 10H), 5.72 (d, 3JH=10, CHPh-imid., 1H), 4.83 (d, 3JH=10.1 Hz, CHPh-NH2, 1H), 3.88 (s, CH3, 3H). 13C[1H] NMR (DMSO-d6, 298K, δ): 142.98 (NCHN), 137.05 (Ph), 136.71 (Ph), 129.5-127.5 (aromatic CH), 124.02 (CH of imid.), 122.10 (CH of imid.), 70.12 (CHPh-imid), 58.20 (CHPhNH2), 36.40 (CH3). 19F NMR (DMSO-d6, 298K, δ): -70.16 (d, PF6). 31P NMR (DMSO-d6, 298K, δ): -114.17 (septet, PF6). MS (ESI, methanol; m/z): 278.1653 [M − PF6]#. Anal. Calcd for C18H20F6N3P: C, 51.07; H, 4.76; N, 9.93. Found: C, 50.68; H, 5.19; N, 9.89.

**Note:** All of the following syntheses of the Ag complexes were conducted at 28 °C without any heating.

[Ag(kaibene)(PF6)]n 10. A 20 mL vial was charged with (S,S)-9 (40 mg, 0.094 mmol), AgPF6 (26 mg, 0.10 mmol) and a stirring bar. The mixture was dissolved in 2 mL of THF. LiHMDS (16 mg, 0.10 mmol), dissolved in a minimum THF, was added with vigorous stirring. The vial was
then wrapped in aluminium foil to avoid photolytic side reactions and stirred for 4 days. Over time a white/grey precipitate formed. The precipitate was then collected by filtration and washed with cold THF. X-ray quality crystals were grown by slow diffusion of diethyl ether into a saturated solution of 10 in acetonitrile. Yield: 23.5 mg (94%). $^1$H NMR (DMSO-$d_6$, 298K, $\delta$): 7.93 (s, $CH$ of imid., 1H), 7.71 (s, $CH$ of imid., 1H), 7.68-7.15 (m, Ph on the backbone, 10H), 5.97 (d, $CHPh$-imid., 1H), 5.56 (broad m, $CHPhNH_2$, 1H), 4.33 (broad m, $NH_2$, 2H), 3.83 (s, $CH_3$, 3H). $^1$H - $^{13}$C HSQC NMR (DMSO-$d_6$, 298K, $\delta$): 131.58-124.73 (aromatic $CH$), 126.64 (CH of imid.), 118.76 (CH of imid.), 73.32 (CHPh-imid.), 56.64 (CHPhNH$_2$), 39.52 (CH$_3$). MS failed due to low volatility and decomposition in protic solvents. Anal. Calcd for C$_{36}$H$_{38}$AgF$_6$N$_6$P: C, 40.78; H, 3.61; N, 7.93. Found: C, 41.74; H, 3.81; N, 9.99. Unsatisfactory analyses were measured even in the presence of V$_2$O$_5$ because of a combustion problem due to the presence of the hexafluorophosphate anion as previously reported in the literature.\textsuperscript{31}

\[ \text{[Ag(kaibene)$_2$](PF$_6$), 11.} \] A 20 mL vial was charged with (S,S)-9 (300 mg, 0.709 mmol), AgPF$_6$ (99 mg, 0.39 mmol) and a stirring bar. With vigorous stirring, the mixture was dissolved in 5 mL of THF and then a solution of KHMDS (177 mg, 0.887 mmol) in 3 mL THF was added. The vial was then protected with aluminium foil to avoid photolytic side reactions and the solution was stirred for 18 h. Over time an insoluble precipitate formed. The reaction mixture was then filtered to remove insoluble materials and the residue was washed with more THF. The volatiles were then removed in vacuo and the residue was dissolved in CH$_2$Cl$_2$ again. The CH$_2$Cl$_2$ solution was filtered through a pad of celite to remove any insoluble compounds and then treated with an excess of hexanes to cause the formation of an oily substance at -30°C. Removal of the supernatant and drying the residue in the dark gave a fluffy yellow-white solid. Yield: 240 mg (84%). $^1$H NMR (DMSO-$d_6$, 298K, $\delta$): 7.97 (s, $CH$ of imid., 2H), 7.54 (s, $CH$ of imid., 2H), 7.5-7.0 (m, Ph on the backbone, 20H), 5.68 (d, $^3$J$_{HH}$=9.4 Hz, CHPh-imid., 2H), 5.03 (dt, $^3$J$_{HH}$=9.4, 4.8 Hz, CHPh-NH$_2$, 2H), 3.82 (s, $CH_3$, 6H), 1.98 (d, $^3$J$_{HH}$=4.8 Hz, NH$_2$, 4H). $^{13}$C [$^1$H] NMR (DMSO-$d_6$, 298K, $\delta$): $C_{NH_2}$ was not detected due to the low solubility of 11, 142.72 (Ph), 138.73 (Ph), 129.0-126.5 (aromatic CH), 123.38 (CH of imid.), 120.37 (CH of imid.), 72.03 (CHPh-imid.), 57.70 (CHPh-NH$_2$), 38.29 (CH$_3$). MS unavailable due to water sensitivity. Anal. Calcd for C$_{36}$H$_{38}$AgF$_6$N$_6$P•0.5CH$_2$Cl$_2$: C, 51.57; H, 4.62; N, 9.89. Found: C, 50.92; H, 5.27; N, 9.33.

\[ \text{Ag(kaibene)$_2$I, 12: Route (a) from 11.} \] A magnetic stirring bar, 11 (200 mg, 0.248 mmol), potassium iodide (KI) (100 mg, 0.602 mmol) and 7 mL of THF were added to a round bottom flask and the mixture was stirred 18 h while protecting the reaction from light. The reaction mixture was then filtered to remove unreacted KI and the residue was washed with more THF. The volatiles were then removed in vacuo and residue was dissolved in CH$_2$Cl$_2$. The CH$_2$Cl$_2$ solution was filtered through a pad of celite to remove any insoluble matter and then the addition of excess hexanes caused the formation of a white powder. Yield: 132 mg (68%). \textbf{Route (b) from (S,S)-9.} A 40 mL vial was charged with (S,S)-9 (500 mg, 1.18 mmol), KI (500 mg, 3.01 mmol) and a stirring bar and then 10 mL THF was added to form a suspension. With vigorous stirring, AgI (144 mg, 0.613 mmol) was added followed by a KHMDS solution (KHMDS (1.43 mmol, 285 mg) dissolved in 4 mL THF). More THF was added to make up a total volume at about 40 mL. The vial was then protected with aluminium foil to avoid photolytic side reactions and the mixture was stirred for 18 h. The reaction mixture was then filtered to remove insoluble compounds and the residue was washed with CH$_2$Cl$_2$ (5 mL x 3). The washings were combined and then evaporated and the residue was dissolved in CH$_2$Cl$_2$. The CH$_2$Cl$_2$ solution was filtered through a pad of celite to remove any insoluble compounds and then treated with an excess of hexanes to cause the formation of product as a white precipitate. Yield: 423 mg (91%). $^1$H NMR (DMSO-$d_6$, 298K, $\delta$): 7.96 (d, $^3$J$_{HH}$=1.8 Hz,
CH of imid., 2H), 7.52 (d, J_{HH}=1.6 Hz, CH of imid., 2H), 7.45-7.05 (m, Ph on the backbone, 20H), 5.76 (d, J_{HH}=9.6 Hz, CHP-imid., 2H), 5.02 (dt, J_{HH}=9.6, 5.8 Hz, CHPH-NH$_2$, 2H). 3.81 (s, CH$_3$, 6H), 1.97 (d, J_{HH}=5.8 Hz, NH$_2$, 4H). $^{13}$C$^1$H NMR (DMSO-d$_6$, 298K, $\delta$): 181.49 (C$_{NH}$), 142.87 (Ph), 138.88 (Ph), 129.0-126.5 (aromatic CH), 123.27 (CH of imid.), 120.1 (CH of imid.), 72.10 (CHP-imid.), 57.76 (CHPH-NH$_2$), 38.26 (CH$_3$). MS unavailable due to water sensitivity. Anal. Calcd for C$_{65}$H$_{33}$N$_6$AgF$_0$.5CH$_2$Cl$_2$; C, 52.69; H, 4.73; N, 10.10. Found: C, 53.07; H, 4.63; N, 10.07. Single crystals for the X-ray diffraction study were obtained by slow evaporation of a saturated hexane/CH$_2$Cl$_2$ solution.

[Ru(p-cymene)(kaibene)(Cl)]PF$_6$, 13. In a 25 mL Schlenk flask charged with a stirring bar, 12 (40 mg, 0.051 mmol), [Ru(p-cymene)Cl$_2$] (30 mg, 0.049 mmol) and KPF$_6$ (40 mg, 0.26 mmol) were suspended in 4 mL THF. The reaction mixture was then refluxed for 3 h and stirred at room temperature for 18 h. Then, all of the THF was evaporated and the residue was redissolved in CH$_2$Cl$_2$ and filtered through a pad of celite. The addition of excess diethyl ether to the CH$_2$Cl$_2$ filtrate caused the formation of a yellow powder. The solution was then cooled to -30°C for further crystallization. The precipitate was then collected via filtration, washed with diethyl ether and dried in vacuum. Yield: 48 mg (71%). $^1$H NMR (CD$_2$Cl$_2$, 298K, $\delta$): see Supporting Information. $^{13}$C$^1$H NMR (CD$_2$Cl$_2$): 174.20 (C$_{NH}$, isomer B), 171.31 (C$_{NH}$, isomer A) and see Supporting Information. MS (ESI, methanol; m/z): 548.1412 [M – PF$_6$]$^+$. Anal. Calcd for C$_{38}$H$_{38}$N$_6$AgF$_0$.5PrCl: C, 48.52; H, 4.80; N, 6.06. Found: C, 45.35; H, 4.23; N, 5.62. Unsatisfactory analyses were measured even in the presence of V$_2$O$_5$ because of a combustion problem.$^{31}$

[Ru(p-cymene)(kaibene)(Cl)] BPh$_4$, 14. This was synthesized using the same procedure to make compound 13, starting with 12 (40 mg, 0.051 mmol), [Ru(p-cymene)Cl$_2$] (30 mg, 0.049 mmol) and NaBPh$_4$ (70 mg, 4.18 mmol). Yield: 76 mg (89%). The $^1$H NMR spectrum is nearly identical to that of 12 except for the extra aromatic peaks due to the BPh$_4$ anion.

[Ni(kaibene)$_2$]$_2$(PF$_6$)$_2$, 15. A 20 mL vial was charged with NiCl$_2$ (12 mg, 0.093 mmol), 11 (35 mg, 0.043 mmol), KI (63 mg, 0.38 mmol) and a stirring bar and the mixture was suspended in 3 mL of THF with vigorous stirring for 18 h, protected from light. The reaction mixture was then filtered to remove insoluble materials and the residue was washed with more THF. All of the volatiles were then evaporated and the residue was dissolved in CH$_2$Cl$_2$ again. The CH$_2$Cl$_2$ solution was filtered through a pad of celite to remove any insoluble compounds and then stirred for five days. The CH$_2$Cl$_2$ solution was filtered through a pad of celite again and all of the CH$_2$Cl$_2$ was removed under vacuum. The residue was then recrystallized from THF/diethyl ether as a light yellow powder. Yield: 25 mg (64%). $^1$H NMR (CD$_2$Cl$_2$, 298K, $\delta$): 7.37-7.15 (m, Ph, 40H), 7.49 (d, J$_{HH}$=1.8 Hz, CH of imid., 4H), 7.04 (d, J$_{HH}$=1.8 Hz, CH of imid., 4H), 5.99 (d, J$_{HH}$=8.5 Hz, CHP-imid., 4H), 4.93 (dt, J$_{HH}$=8.5, 5.1 Hz, CHPH-NH$_2$, 4H), 3.77 (s, CH$_3$, 12H), 1.68 (d, J$_{HH}$=5.1 Hz, NH$_2$, 8H). $^{13}$C$^1$H NMR (CD$_2$Cl$_2$): 186.01 (C$_{NH}$), 142.21 (Ph), 138.67 (Ph, isomer A), 130.0-127.0 (Ph), 122.70 (CH of imid.), 120.54 (CH of imid.), 71.95 (CHP-imid.), 59.50 (CHPH-NH$_2$), 39.34 (CH$_3$). $^{19}$F NMR (CD$_2$Cl$_2$, 298K, $\delta$): -72.95 (d, PF$_6$). MS (ESI, methanol; m/z): 306.1255 [Ni(kaibene)$_2$]$^{2+}$. Anal. Calcd for C$_{72}$H$_{76}$F$_2$N$_{12}$P$_2$N$_{12}$L$_2$; C, 48.84; H, 4.33; N, 9.49. Found: C, 47.40; H, 4.60; N, 9.13. Unsatisfactory carbon analyses but acceptable hydrogen and nitrogen content were measured, even the in the presence of V$_2$O$_5$, because of a combustion problem due to the presence of the hexafluorophosphate anion.$^{31}$

[IrI(kaibene)$_2$]$_2$, 16. A 20 mL vial was charged with chloro(1,5-cyclooctadiene)iridium(I) dimer (50 mg, 0.074 mmol), 12 (120 mg, 0.152 mmol), KI (240 mg, 1.45 mmol) and a stirring bar and the mixture was suspended in 12 mL of THF with vigorous stirring for 18 h at 66 °C, protected
from light. The reaction mixture was then filtered to remove insoluble materials and the residue was washed with more THF. All of the volatiles were then evaporated and the residue was dissolved in CH$_2$Cl$_2$ again. The CH$_2$Cl$_2$ solution was filtered through a pad of celite again and all of the CH$_2$Cl$_2$ was removed under vacuum. The residue was then recrystallized from CH$_2$Cl$_2$/diethyl ether as a light yellow powder. Yield: 104 mg (80%). $^1$H NMR (CD$_2$Cl$_2$, 298K, $\delta$): 7.51 (d, $^3J_{HH}$=1.8 Hz, CH of imid., 4H), 7.45-7.10 (m, Ph on the backbone, 4H), 7.06 (d, $^3J_{HH}$=1.8 Hz, CH of imid., 4H), 6.18 (d, $^3J_{HH}$=9.0 Hz, CHPH-imid., 4H), 4.87 (dt, $^3J_{HH}$=9.0, 5.6 Hz, CHPH-imid., 4H), 3.75 (s, C$_3$H$_3$), 1.78 (d, $^3J_{HH}$=5.6 Hz, NH$_2$, 8H). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$): 186.53 (C$\equiv$NHC), 142.60 (Ph), 139.14 (Ph), 130.0-127.5 (Ph), 122.66 (CH of imid.), 120.21 (CH of imid.), 71.52 (CHPh-imid.), 59.87 (CHPh-NH$_2$), 39.36 (CH$_3$). MS (ESI, methanol; $m/z$): 747.2795 [Ir(kaibene)$_2$]$^{2+}$. Anal. Calcd for C$_{72}$H$_{76}$N$_6$Ir$_2$: C, 49.48; H, 4.38; N, 9.62. Found: C, 48.66; H, 4.82; N, 8.58.

ASSOCIATED CONTENT

NMR data for the complexes. CIF files of crystal structure data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

NSERC Canada is thanked for a Discovery Grant to R. H. M. and two graduate scholarships to K. Y. W. The authors acknowledge the Canadian Foundation for Innovation, project number 19119, and the Ontario Research Fund for funding of the Centre for Spectroscopic Investigation of Complex Organic Molecules and Polymers. R. H. M. thanks the Canada Council for the Arts for a Killam Research Fellowship.

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(S,S) - KaibenePF_6 → [ML_n] (M=Ni, Ir or Ru)

ketone hydrogenation catalyst → [Ru(ρ-cymene)(Kaibene)Cl](PF_6)

[Ag], base
Transition Metal Complexes of an (S,S)-1,2-Diphenylethylamine Functionalized N-Heterocyclic Carbene: a New Member of the Asymmetric NHC Ligand Family

Kai Y. Wan, Alan J. Lough and Robert H. Morris*
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Supporting Information

Figure S1: $^1$H NMR spectrum (400 MHz, DMSO-d$_6$, 298K) of (S,S)-9

Figure S2: $^{13}$C($^1$H) NMR spectrum (100 MHz, DMSO-d$_6$, 298K) of (S,S)-9

Figure S3: gCOSY ($^1$H-$^1$H) NMR spectrum (400 MHz, DMSO-d$_6$, 298K) of (S,S)-9

Figure S4: gHSQC ($^1$H-$^{13}$C) NMR spectrum (400 MHz, DMSO-d$_6$, 298K) of (S,S)-9

Figure S5: $^{19}$F NMR spectrum (376 MHz, DMSO-d$_6$, 298K) of (S,S)-9

Figure S6: $^{31}$P NMR spectrum (162 MHz, DMSO-d$_6$, 298K) of (S,S)-9

Figure S7: $^1$H NMR spectrum (400 MHz, DMSO-d$_6$, 298K) of 10

Figure S8: gCOSY ($^1$H-$^1$H) NMR spectrum (400 MHz, DMSO-d$_6$, 298K) of 10

Figure S9: gHSQC ($^1$H-$^{13}$C) NMR spectrum (700 MHz, DMSO-d$_6$, 298K) of 10

Figure S10: $^1$H NMR spectrum (500 MHz, DMSO-d$_6$, 298K) of 11

Figure S11: $^{13}$C($^1$H) NMR spectrum (126 MHz, DMSO-d$_6$, 298K) of 11

Figure S12: gHSQC ($^1$H-$^{13}$C) NMR spectrum (500 MHz, DMSO-d$_6$, 298K) of 11

Figure S13: $^1$H NMR spectrum (700 MHz, DMSO-d$_6$, 298K) of 12

Figure S14: $^{13}$C($^1$H) NMR spectrum (126 MHz, DMSO-d$_6$, 298K) of 12

Figure S15: gHSQC ($^1$H-$^{13}$C) NMR spectrum (500 MHz, DMSO-d$_6$, 298K) of 12

Figure S16: $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298K) of 13

Figure S17: $^{13}$C($^1$H) NMR spectrum (126 MHz, CD$_2$Cl$_2$, 298K) of 13

Figure S18: gCOSY ($^1$H-$^1$H) NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298K) of 13

Figure S19: gHSQC ($^1$H-$^{13}$C) NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298K) of 13

Figure S20: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298K) of 15

Figure S21: $^{13}$C($^1$H) NMR spectrum (100 MHz, CD$_2$Cl$_2$, 298K) of 15

Figure S22: $^{19}$F NMR spectrum (376 MHz, CD$_2$Cl$_2$, 298K) of 15

Figure S23: gCOSY ($^1$H-$^1$H) NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298K) of 15

Figure S24: gHSQC ($^1$H-$^{13}$C) NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298K) of 15

Figure S25: $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298K) of 16

Figure S26: $^{13}$C($^1$H) NMR spectrum (126 MHz, CD$_2$Cl$_2$, 298K) of 16

Figure S27: gCOSY ($^1$H-$^1$H) NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298K) of 16

Figure S28: gHSQC ($^1$H-$^{13}$C) NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298K) of 16

S1
3-((1S,2S)-2-amino-1,2-diphenylethyl)-1-methyl-1H-imidazol-3-ium hexafluorophosphate (S,S)-9. %). 1H NMR (DMSO-d6, 298K, δ): 9.42 (s, 1H; H2), 7.97 (dd, 1H; H4, 3JHH=2.4 Hz, 4JHH=1.7 Hz), 7.71 (dd, 1H; H3, 3JHH=2.4 Hz, 4JHH=1.6 Hz), 7.48-7.08 (m, 10H; H9-H18), 5.72 (d, 1H; H5, 3JHH=10.1 Hz), 4.83 (d, 1H; H6, 3JHH=10.1 Hz), 3.88 (s, 3H; H1).

Figure S1: 1H NMR spectrum (400 MHz, DMSO-d6, 298K) of (S,S)-9
3-((1S,2S)-2-amino-1,2-diphenylethyl)-1-methyl-1H-imidazol-3-ium hexafluorophosphate, (S,S)-9 \[\text{\textsuperscript{13}C}\{\text{H}\} \text{NMR (DMSO-\text{d}_6, 298K, } \delta ) \]: 142.98 (C2), 137.05 (C7), 136.71 (C8), 129.5-127.5 (C9-C18), 124.02 (C3), 122.10 (C4), 70.12 (C5), 58.20 (C6), 36.40 (C1).

Figure S2: \[\text{\textsuperscript{13}C}\{\text{H}\} \text{NMR spectrum (100 MHz, DMSO-\text{d}_6, 298K) of (S,S)-9}\]
Figure S3: gCOSY (\(1^1\)H-\(1^1\)H) NMR spectrum (400 MHz, DMSO-\(d_6\), 298K) of (S,S)-9
Figure S4: gHSQC ($^1$H-$^{13}$C) NMR spectrum (400 MHz, DMSO-$d_6$, 298K) of (S,S)-9
Figure S5: $^{19}$F NMR spectrum (376 MHz, DMSO-$d_6$, 298K) of (S,S)-9
Figure S6: $^{31}$P NMR spectrum (162 MHz, DMSO-d$_6$, 298K) of (S,S)-9
[Ag(kaibene)(PF₆₆)]ₙ, 10. ¹H NMR (DMSO-d₆, 298K, δ): 7.93 (s, 1H; H4), 7.71 (s, 1H; H3), 7.68-7.15 (m, 10H; H9-H18), 5.97 (broad s, 1H; H5), 5.56 (broad s, 1H; H6), 4.33 (broad s, 2H; H19), 3.83 (s, 3H; H1).

Figure S7: ¹H NMR spectrum (400 MHz, DMSO-d₆, 298K) of 10
Figure S8: gCOSY (¹H-¹H) NMR spectrum (400 MHz, DMSO-d$_6$, 298K) of 10
[Ag(kaibene)(PF₆)]ₙ, 10. $^1$H - $^{13}$C HSQC NMR (DMSO-$d_6$, 298K, $\delta$): 131.58-124.73 (C9-C18), 126.64 (C3), 118.76 (C4), 73.32 (C5), 56.64 (C6), 39.52 (C1).

Figure S9: gHSQC ($^1$H-$^{13}$C) NMR spectrum (700 MHz, DMSO-$d_6$, 298K) of 10
[Ag(kaibene)$_2$](PF$_6$), 11. $^1$H NMR (DMSO-$d_6$, 298K, $\delta$): 7.97 (s, 2H; H4), 7.54 (s, 2H; H3), 7.50-7.00 (m, 20H; H9-H18), 5.68 (d, 2H; H5, $^3J_{HH}=9.4$ Hz), 5.03 (dt, 2H; H6, $^3J_{HH}=9.4$, 4.8 Hz), 3.83 (s, 6H; H1), 1.98 (d, 4H; H19, $^3J_{HH}=4.8$ Hz).

Figure S10: $^1$H NMR spectrum (500 MHz, DMSO-$d_6$, 298K) of 11
[Ag(kaibene)$_2$][PF$_6$], 11. $^{13}$C{H} NMR (DMSO-$d_6$, 298K, $\delta$): $C_{NHIC}$ was not detected due to the low solubility of 11, 142.72 (C7), 138.73 (C8), 129.0-126.5 (C9-C18), 123.38 (C3), 120.37 (C4), 72.03 (C5), 57.70 (C6), 38.29 (C1).

Figure S11: $^{13}$C{H} NMR spectrum (126 MHz, DMSO-$d_6$, 298K) of 11
Figure S12: gHSQC (\textsuperscript{1}H-\textsuperscript{13}C) NMR spectrum (500 MHz, DMSO-\textit{d}_6, 298K) of 11
Ag(kaibene)$_2$I, 12. $^1$H NMR (DMSO-$d_6$, 298K, $\delta$): 7.96 (d, 2H; H4, $^3J_{HH}$=1.8 Hz), 7.52 (d, 2H; H3, $^3J_{HH}$=1.6 Hz), 7.45-7.05 (m, 20H; H9-H18), 5.76 (d, 2H; H5, $^3J_{HH}$=9.6 Hz), 5.02 (dt, 2H; H6, $^3J_{HH}$=9.6, 5.8 Hz), 3.81 (s, 6H; H1), 1.97 (d, 4H; H19, $^3J_{HH}$=5.8 Hz).

Figure S13: $^1$H NMR spectrum (700 MHz, DMSO-$d_6$, 298K) of 12
Ag(kaibene)$_2$I, 12. $^{13}$C{H} NMR (DMSO-d$_6$, 298K, $\delta$): 181.49 (C2), 142.87 (C7), 138.88 (C8), 129.0-126.5 (C9-C18), 123.27 (C3), 120.13 (C4), 71.73 (C5), 57.76 (C6), 38.26 (C1).

Figure S14: $^{13}$C{H} NMR spectrum (126 MHz, DMSO-d$_6$, 298K) of 12
Figure S15: gHSQC ($^1$H-$^{13}$C) NMR spectrum (500 MHz, DMSO-$d_6$, 298K) of 12
[Ru(p-cymene)(kaibene)(Cl)] PF₆, 13. ¹H NMR (CD₂Cl₂, 298K, δ):

Figure S16: ¹H NMR spectrum (500 MHz, CD₂Cl₂, 298K) of 13
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<td>H6</td>
<td>t, $^3J_{HH}=7.0$ Hz</td>
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<tr>
<td>1.12</td>
<td>3</td>
<td>H29</td>
<td>d, $^3J_{HH}=6.9$ Hz</td>
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[Ru(p-cymene)(kaibene)(Cl)]PF$_6$, 13. $^{13}$C-$^1$H NMR (CD$_2$Cl$_2$):

Figure S17: $^{13}$C-$^1$H NMR spectrum (126 MHz, CD$_2$Cl$_2$, 298K) of 13
[Ru(p-cymene)(kaibene)(Cl)]PF₆, 13. $^{13}\text{C-}^{1\text{H}}$ NMR (CD₂Cl₂):

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<td>90.0-82.0</td>
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<td>18.86</td>
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</tr>
</tbody>
</table>

Figure S18: gCOSY ($^{1\text{H-}}^{1\text{H}}$) NMR spectrum (500 MHz, CD₂Cl₂, 298K) of 13
Figure S19: gHSQC ($^1$H-$^{13}$C) NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298K) of 13
[Nil(kaibene)$_2$]$_2$(PF$_6$)$_2$, 15. $^1$H NMR (CD$_2$Cl$_2$, 298K, $\delta$): 7.49 (d, 4H; H4, $^3$J$_{HH}$=1.8 Hz), 7.37-7.15 (m, 40H; H9-H18), 7.04 (d, 4H; H3, $^3$J$_{HH}$=1.8 Hz), 5.99 (d, 4H; H5, $^3$J$_{HH}$=8.5 Hz), 4.93 (dt, 1H; H6, $^3$J$_{HH}$=8.5, 5.1 Hz), 3.77 (s, 12H; H1), 1.68 (d, 8H; H19, $^3$J$_{HH}$=5.1 Hz).

Figure S20: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298K) of 15
[Ni(kaibene)$_2$(PF$_6$)$_2$], 15. $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$): 186.01 (C2), 142.21 (C7), 138.67 (C8), 130.0-127.0 (C9-C18), 122.70 (C3), 120.54 (C4), 71.95 (C5), 59.50 (C6), 39.34 (C1).

Figure S21: $^{13}$C{$^1$H} NMR spectrum (100 MHz, CD$_2$Cl$_2$, 298K) of 15
Figure S22: $^{19}$F NMR spectrum (376 MHz, CD$_2$Cl$_2$, 298K) of 15
Figure S23: gCOSY ($^1$H-$^1$H) NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298K) of 15
Figure S24: gHSQC ($^1$H-$^{13}$C) NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298K) of 15
[Ir(kaibene)$_2$], 16. $^1$H NMR (CD$_2$Cl$_2$, 298K, $\delta$): 7.51 (d, 4H; H4, $^3$J$_{HH}=1.8$ Hz), 7.45-7.10 (m, 40H; H9-18), 7.06 (d, 4H; H3, $^3$J$_{HH}=1.8$ Hz), 6.18 (d, 4H; H5, $^3$J$_{HH}=9.0$ Hz), 4.87 (dt, 4H; H6, $^3$J$_{HH}=9.0$, 5.6 Hz), 3.75 (s, 12H; H1), 1.78 (d, 8H; H19, $^3$J$_{HH}=5.6$ Hz).

Figure S25: $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$, 298K) of 16
[Ir(kaibene)$_2$], 16. $^{13}$C\{$^1$H} NMR (CD$_2$Cl$_2$): 186.53 (C2), 142.60 (C7), 139.14 (C8), 130.0-127.5 (C9-C18), 122.66 (C3), 120.21 (C4), 71.52 (C5), 59.87 (C6), 39.36 (C1).

Figure S26: $^{13}$C\{$^1$H} NMR spectrum (126 MHz, CD$_2$Cl$_2$, 298K) of 16
Figure S27: gCOSY (1H-1H) NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298K) of 16
Figure S28: gHSQC (\(^1H-^{13}C\)) NMR spectrum (400 MHz, CD\(_2\)Cl\(_2\), 298K) of 16