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An Experimental and Computational Comparison of Phosphorus and Selenium-Based Ligands for Catalysis

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Draft

Abstract

In order to compare and contrast the bonding and reactivity of organoselenium ligands with organophosphines in coordination complexes, a new palladium(II) complex of the *Se,N*-chelating ligand *o*-(NH₂)(X)C₆H₄ (X = SePh, **2**) was prepared. Its characterization by NMR spectroscopy, single-crystal X-ray diffraction and Density Functional Theory calculations is contrasted with the Pd^{II} complex of the related *P,N* chelating ligand (X = PPh₂, **1**). These techniques indicate the phenylseleno moiety is a weaker σ donor to the PdCl₂ fragment than the diphenylphosphino group. Both complexes were suitable to catalyze the Suzuki-Miyaura coupling of *p*-tolylboronic acid and 4-bromobenzaldehyde.

Key Words: organoselenium compounds, coordination chemistry, X-ray crystallography, Density Functional Theory, Suzuki-Miyaura coupling

Introduction

Rational ligand design is an essential tool for homogeneous catalysis research. Amongst the many reported ligand scaffolds, a common element for palladium-based catalysts is the incorporation of organophosphorus donors. Phosphines are valued for their strong σ -donor ability in conjunction with the ability to act as a π -acid. Over the last several decades there has been a growing interest in the use of selenoether-type ligands as alternatives to phosphines. Organoselenium ligands and their complexes to metals such as nickel, palladium, and rhodium are often air- and moisture-stable, and have shown catalytic activity in a number of transformations including carbon-carbon coupling reactions.¹ Ligand synthesis often involves the use of an organic diselenide such as Ph_2Se_2 with NaBH_4 to effect convenient selenylation of organic halides via a PhSe^- equivalent.

A variety of scaffolds have been explored; some examples of multidentate hard-soft selenoether-containing ligands are illustrated in Chart 1. Palladium(II) complexes of the ligands **A**² and **B**³ are effective Suzuki-Miyaura catalysts, while ligands **C**,⁴ **D**,⁵ and **E**⁶ have been used to catalyze the Heck reaction. Ligand **D** is commercially available from Sigma-Aldrich, and $[(2,6\text{-PhSeCH}_2)_2\text{C}_6\text{H}_3]\text{PdX}$ can also catalyze, for example, the boronation of allylic alcohols ($\text{X} = \text{Cl}$),⁷ and the allylation of aldehydes with organotin reagents ($\text{X} = \text{OAc}$).⁸ As further examples are reported, selenium-based catalysts with activities surpassing even state-of-the-art phosphine-based systems have emerged.⁵

Chart 1.

However, the reasons for such differences in activity are not well-understood. The strong electron donor ability of Se has been cited as an advantage of selenium-containing ligands, however detailed electronic structure studies or direct comparisons between phosphine and selenoether ligands to this end remain rare. Additionally, the identity of the active catalyst is at times uncertain. In some systems, the Pd^{II} coordination complex serves as a pre-catalyst which forms palladium selenide nanoparticles under thermal conditions, and these have been implicated as the source of Pd(0) particles (the “true catalyst”) for Heck transformations.⁹ This does not, however, preclude single-site catalysis in other processes, and mechanistic details are scant for many reported selenium-containing catalyst systems.

This contribution examines two [Pd(L)Cl₂] complexes where L is either a chelating phosphine or selenoether ligand, both of which contain the same *ortho*-substituted aniline framework and differ only by the second heteroatom donor (–SePh or –PPh₂). It is therefore possible to make a direct comparison of their structures, NMR properties, and σ donor ability. Additionally, their effectiveness as catalysts in a Suzuki-Miyaura coupling reaction is evaluated.

Results and Discussion

Synthesis and NMR Characterization of Metal Complexes. The ligands *o*-(NH₂)(X)C₆H₄ (**1**: X = PPh₂,¹⁰ **2**: X = SePh¹¹) were prepared according to the reported procedures, from 2-fluoroaniline and 2-chloronitrobenzene, respectively. Palladium(II) complexes of the ligands were targeted to furnish diamagnetic complexes amenable to NMR studies, and with a square-planar geometry for evaluation of the relative thermodynamic *trans*-effect of P and Se donor sites. The chelating ligands were separately reacted with [PdCl₂(COD)] (COD = 1,5-cyclooctadiene) in CH₂Cl₂ at room temperature (Equation 1). The resultant complexes, [PdCl₂(*o*-(NH₂)(X)C₆H₄)] (**3**: X = PPh₂; **4**: X = SePh), precipitated from the reaction mixtures in high yields (83-100%). The phosphine complex **3** has been previously prepared using another method and investigated as an anti-cancer agent,¹² while the selenoether complex **4** has not been reported. Complex **3** is a yellow solid, with no appreciable solubility in hydrocarbons, THF, Et₂O, or CH₂Cl₂; it is sparingly soluble in hot MeCN and soluble in DMSO. Complex **4** is an orange solid which is similarly insoluble in common organic solvents, slightly more soluble than **3** in MeCN and very soluble in DMSO.

Evidence of *X,N*-coordination in both cases was clearly observed by NMR spectroscopy. The ³¹P NMR spectrum of **3** (*d*₆-DMSO) indicates a singlet resonance shifted by +66.6 ppm compared to the free ligand **1**, and the NH₂ singlet resonance in the ¹H NMR spectrum is similarly shifted by +2.75 ppm. For the *Se,N*-complex **4**, the ⁷⁷Se NMR signal appears 178 ppm downfield of the

signal for **2**. The NH₂ group, in addition to being significantly shifted by +2.40 ppm in the ¹H NMR spectrum compared to free ligand, also manifests as two closely spaced broad singlets with a separation of 13 Hz. This is consistent with two diastereotopic protons which are not rapidly exchanged on the NMR timescale, as would be expected for a square-planar complex featuring two stereochemically distinct faces. Here, the steric differentiation is provided by the SePh donor group, with a phenyl substituent projecting out of one side of the molecular plane and a lone pair out of the other. An interesting feature of the ¹H NMR spectrum of **4** is the visibility of low intensity signals corresponding to the free ligand (those not overlapping with product signals). These resonances are observed even in recrystallized samples, suggesting a solution equilibrium in *d*₆-DMSO (in the slow exchange regime) where the solvent competes with **2** for coordination to palladium, rather than contamination by unreacted **2**. All resonances of the product spectrum become broadened at higher temperature, which seems to support this hypothesis. Additionally, in CD₃CN no signals for the free ligand are visible.

X-Ray Crystallography. As the solid-state structure of **3** has not been previously reported, and **4** is a new compound, we pursued X-ray quality single crystals of these complexes for diffraction studies. Suitable crystals of **3**•2DMSO and **4**•MeCN were grown in their respective solvents. Thermal ellipsoid plots are shown in Figures 1 and 2; selected metrical parameters are presented in Table 1. The two structures are overall consistent with the solution-state NMR data, indicating square-planar palladium(II) chloride complexes of the *cis*-chelating ligands **1** and **2** (sum of angles around Pd: 360.1 and 360.2°, respectively). With the exception of the phenyl groups and amino protons, all atoms in complexes **3** and **4** are nearly coplanar – the largest deviations from planarity involve chlorine atoms. The PdCl₂ moiety is slightly twisted out

of the mean plane in **3** (displacements of chlorine atoms +0.099 and -0.078 Å) and one chlorine atom in **4** is 0.095 Å from the mean plane. The selenium atom in complex **4** is chiral – the centrosymmetric structure contains a 1:1 mixture of enantiomers.

The Pd–Se distance in **4** is ca. 7% elongated compared to the Pd–P distance in **3**, consistent with the larger covalent radius of selenium. The lower *s*-character of the selenium-centred bonding orbitals is also borne out in the metrical data: the bond angles around selenium are noticeably smaller than those for phosphorus, e.g. the Pd–X–C_{phenyl} angles for **3** and **4** are 101.31(6) and 115.56(3)–118.94(10)°, respectively. Another notable feature of the X-ray data are the Pd–Cl distances: those distances *trans* to the NH₂ group in each complex are not significantly different (**3**: 2.3001(9) Å; **4**: 2.3017(5) Å), while those *trans* to phosphorus and selenium differ by ca. 0.03 Å (**3**: 2.3607(8) Å; **4**: 2.3352(5) Å). In the context of the thermodynamic *trans*-effect,¹³ the Ph₂P group is therefore observed to be a stronger σ donor than the PhSe group in the presently studied system. This is consistent with other findings that heavy chalcogenoethers are modest σ donors compared to organophosphines.^{14,15}

Both crystal structures feature well-ordered lattice solvent molecules. In the (*P,N*) complex **3**, the NH₂ protons are each hydrogen-bonded to one crystallographically unique DMSO molecule with N–H···O distances of 2.823(4) and 2.821(4) Å. This secondary bonding motif has been observed for related metal complexes, including the octahedral ruthenium(II) complex [RuCl₂(**1**)(CO)₂]•4DMSO,¹⁶ and the square-planar palladium(II) complex [PdCl₂(4,5-dax)]•2DMSO (4,5-dax = 4,5-diaminoxylene).¹⁷ The crystal structure of (*Se,N*) complex **4** features a lattice acetonitrile molecule, but it does not engage in any significant secondary bonding interactions. The closest intermolecular contacts to the NH₂ protons in **4** are two N–H···Cl interactions

(3.295(2) and 3.331(2) Å), generating a staircase-type packing arrangement (Figure 3). With H $\cdots$ Cl distances of 2.53(3) and 2.54(3) Å, these contacts are in the range of “medium” length hydrogen bonds involving metal-bound chlorine atoms.¹⁸ No intermolecular Pd $\cdots$ Se interactions are detected.

Figure 1. Thermal ellipsoid plot (50% probability) of **3**•2DMSO – carbon-bound hydrogen atoms are omitted for clarity.

Figure 2. Thermal ellipsoid plot (50% probability) of one enantiomer of complex 4•MeCN – carbon-bound hydrogen atoms and the lattice solvent molecule are omitted for clarity.

Figure 3. Packing diagram for complex 4, showing N-H...Cl hydrogen bonds.

Computational Studies. To probe the electronic structure of the related complexes **3** and **4**, DFT calculations were conducted on these structures using the M06 functional, which is corrected for dispersion and has been found to give more accurate bond lengths for transition metal complexes compared to non-dispersion corrected functionals, e.g. B3LYP.¹⁹ First to third row atoms were modeled using the 6-31G(d,p) basis set, whereas cc-pVTZ basis set with SDB relativistic effective core potentials were used for palladium and selenium.

The optimized structures featured metrical parameters very similar to the crystal data, mainly differing by rotation of phenyl rings in the absence of crystal packing forces. Notably, the larger elongation of the Pd–Cl bond *trans* to P versus that *trans* to Se is preserved in these gas-phase calculations (2.3450 versus 2.3177 Å), suggesting the difference is unlikely due to a packing or hydrogen bonding effect. Analysis of the frontier orbitals (Figure 4) indicated the HOMO compositions as mostly Cl(p), P(p) or Se(p), and Pd(d) orbital combinations, while the LUMOs also have larger contributions from N(p) and are σ -antibonding with respect to the PdL₄ square planes. HOMO-LUMO gaps of 4.28 eV for **3** and 4.07 eV for **4** are observed. The first ionization energies, estimated using Koopman's theorem, of 6.31 eV (**3**) and 6.43 eV (**4**) indicate the phosphine complex is more susceptible to oxidation, as would be expected.²⁰

Figure 4. Frontier orbitals of complexes **3** and **4**.

Qualitative values of $\Delta G_{\text{rxn}}^\circ$ for Eqn 1 were estimated computationally in the gas phase (-62.5 kJ mol $^{-1}$ for **3** and $+0.5$ kJ mol $^{-1}$ for **4**). The formation of the phosphine complex **3** is predicted to be more favourable than the selenoether complex **4** and hence ligand **1** is a stronger chelate ligand towards PdCl $_2$ relative to COD than **2**. This is consistent with the higher *trans* influence of **1** versus **2** observed in the X-ray data, as well as the experimental NMR spectral data for **4** which suggested dynamic behaviour involving some degree of dissociation of **2** in d_6 -DMSO solution.

Catalysis Experiments. To test the relative catalytic competencies of complexes **3** and **4**, they were employed in the Suzuki-Miyaura coupling reaction of *p*-tolylboronic acid with 4-bromobenzaldehyde, utilizing conditions similar to those reported for the Cu I -catalyzed coupling of arylboronate esters with aryl iodides using the *P,N*-chelating ligand 1- t Bu $_2$ P-2-NMe $_2$ C $_6$ H $_4$.²¹ Conversion as measured by GC-MS was investigated for the two complexes, in addition to [PdCl $_2$ (COD)], under several reaction conditions (Table 2). DMF was used as the reaction solvent to ensure solubility of the catalyst.

In the absence of a palladium complex <10% conversion was observed at 120 °C, while 5 mol% of [PdCl $_2$ (COD)], **3**, or **4** afford quantitative conversion. At 50 °C, the selenium-containing complex **4** shows higher conversion than the phosphine complex **3**, however does not outperform [PdCl $_2$ (COD)] and all complexes yield <50% conversion. Finally, at room temperature no catalyst exceeds 25% conversion, and the COD complex reaches higher yields than both **3** and **4**, which are equal at 13%.

Conclusions

The new palladium(II) complex (**4**) of a chelating organoselenium ligand has been prepared and characterized by a number of methods in order to contrast its properties with the phosphine-ligated analogue **3**. Experimental evidence from ^1H NMR spectra and X-ray structural analysis indicate the phenylselenyl substituent has a lower σ -donor ability towards Pd^{II} and ligand **2** is general is more weakly bound, which was corroborated computationally by DFT, including free energy calculations. Both complexes **3** and **4** are active catalysts in the Suzuki-Miyaura coupling of an arylboronic acid with an aryl bromide, albeit with activities not significantly higher than the simple COD complex of PdCl_2 .

Future studies will examine the donor ability of a wider range of selenium (and tellurium) donor ligands as compared to other heteroatoms such as N and P. The coordination chemistry of **2** towards other transition metals such as nickel and copper will be investigated to study their structures and reactivity, with the possibility of improving solubility of complexes through variation of the substitution patterns on the aromatic ring and selenium centre. Additionally, the mechanism of catalytic processes involving heavy chalcogenoethers will be probed computationally and experimentally.

Experimental Section

General Considerations. All manipulations were conducted under an inert atmosphere of argon using standard glovebox or Schlenk/vacuum line techniques, except where noted. The solvents dichloromethane, diethyl ether, and toluene (ACS grade) were sparged with argon and dried by passage through two columns of activated alumina, before storage in PTFE-sealed glass vessels; diethyl ether was stored over Na/benzophenone. Solvents were transferred by vacuum

distillation into PTFE-sealed storage flasks over activated 4 Å molecular sieves for Schlenk manipulations. Acetonitrile was dried by stirring over CaH_2 overnight, and then distilled onto activated 3 Å molecular sieves. d_6 -DMSO was dried over activated 4 Å molecular sieves, and degassed using at least three freeze-pump-thaw cycles.

The reagents $[\text{PdCl}_2(\text{COD})]$ ²² and $o\text{-(NH}_2\text{)}(\text{X})\text{C}_6\text{H}_4$ ($\text{X} = \text{PPh}_2$,¹⁰ SePh ¹¹) were prepared according to the literature procedures. DMSO (anhydrous), *p*-tolylboronic acid, 4-bromobenzaldehyde, cesium fluoride, and 4-nitrobenzaldehyde were purchased from commercial sources and used as received. Melting points were recorded from samples sealed under argon in capillary tubes.

Instrumentation. NMR spectra were collected on a Bruker 400 MHz Avance III spectrometer. Chemical shifts are reported in parts per million (ppm). ^1H and ^{13}C resonances are referenced to residual protons or carbon atoms in the deuterated solvent. For other nuclei, the external standards Ph_2Se_2 in CDCl_3 (^{77}Se) and $\text{H}_3\text{PO}_4(\text{aq})$ (^{31}P) were utilized. Elemental analyses were performed by Canadian Microanalytical Ltd. (Delta, BC, Canada). GC/MS analysis was conducted using an Agilent 5975C system. High resolution mass spectra (HRMS) were obtained using a quadrupole ion trap mass spectrometer with electrospray ionization (ESI).

Synthesis of 3. To a mixture of ligand **1** (168 mg, 0.61 mmol) and $[\text{PdCl}_2(\text{COD})]$ (157 mg, 0.55 mmol) was added CH_2Cl_2 (25 mL). The yellow solution was stirred for 1 h at room temperature, during which time a yellow precipitate formed. The volatiles were removed in vacuo, and the resultant solid was washed with Et_2O (3×5 mL). After drying in vacuo, **3** was obtained as a yellow powder in quantitative yield. Solution ^1H and ^{31}P NMR spectral data in d_6 -DMSO matched that reported in the literature.¹² Anal. calcd. (%) C 47.55, H 3.55, N 3.08; found C

47.38, H 3.41, N 3.09. An X-ray quality single crystal of **3**•2DMSO was grown from a layered DMSO/toluene solution at room temperature.

Synthesis of 4. Complex **4** was prepared in a method analogous to that used for complex **3**, using ligand **2** (162 mg, 0.65 mmol) and [PdCl₂(COD)] (171 mg, 0.60 mmol), and isolated as an orange powder (211 mg, 83%, m.p. >240 °C (dec.)). ¹H NMR (*d*₆-DMSO): δ 7.88-7.68 (overlapping m and d, *J*_{HH}(d) = 13 Hz, 4H, aromatic CH (m) and NH₂ (d)), 7.61-7.37 (m, 7H, aromatic CH); low intensity resonances corresponding to *ca.* 12% free ligand **2** were observed at δ 7.27-7.13 (m, aromatic CH), 6.82 (d, *J*_{HH} = 8 Hz, aromatic CH), 6.54 (t, *J*_{HH} = 8 Hz, aromatic CH), 5.32 (br s, NH₂). ¹³C{¹H} NMR (*d*₆-DMSO): δ 147.3 (s), 137.9* (s), 133.5 (s), 131.6* (s), 131.2 (s), 130.7 (s), 130.2 (s), 129.4* (s), 128.8 (s), 128.1 (s), 126.3* (s), 125.7 (s); resonances marked with an asterisk match ¹³C chemical shifts for the free ligand **2**. Of these 4 resonances (of 12 total), two are likely overlapping signals from **2** and **4**, and two are from **2**. ⁷⁷Se{¹H} NMR (*d*₆-DMSO): δ 482. HRMS (ESI) *m/z*: [M + Na]⁺ calcd. for C₁₂H₁₁Cl₂NPdSeNa: 447.83608, found: 447.83519. Anal. calcd. (%) C 33.87, H 2.61, N 3.29; found C 33.21, H 2.43, N 3.25. An X-ray quality single crystal of **4**•MeCN was grown from a slowly cooled concentrated solution of the complex in warm acetonitrile.

X-ray Crystallography. Data were collected for a suitable crystal of each complex with a Bruker APEX-II CCD diffractometer at 193 K using APEX2.²³ Cell refinement and data reduction were carried out using SAINT,²⁴ and numerical absorption correction was applied using SADABS.²⁵ Using Olex2,²⁶ the structure was solved with SHELXS²⁷ structure solution program using the Patterson method for **3** and direct methods for **4**. Least squares refinement of the structure was carried out against *F*² using SHELXL.²⁸ The structures were well-ordered and no

special considerations were needed for the refinements. Carbon-bound hydrogen atoms were placed in calculation positions and treated in a riding-model approximation, while nitrogen-bound hydrogen atoms were located in the difference electron map and allowed to refine isotropically. The N–H hydrogen atoms in **3** were restrained to a length of 0.89 Å. All non-hydrogen atoms were modeled anisotropically. Selected crystal data are given in Table 3.

General Procedure for Catalytic Reactions. In a glovebox, the boronic acid (0.1 mmol), aryl halide (0.1 mmol), cesium fluoride (0.15 mmol), and catalyst (5 mol%) were weighed into a vial equipped with a stir bar. Dimethylformamide was added (0.5 mL), and the vial was sealed with a PTFE-lined screw cap. The vial was heated to the reaction temperature for 14 h. After cooling to room temperature, an internal standard (4-nitrobenzaldehyde, 20 µL of a 0.5 M solution in acetonitrile) was added and the reaction mixture was diluted with ethyl acetate (2 mL), filtered through a plug of silica gel in a Pasteur pipet, and analyzed by EI GC-MS. Reaction conversion were determined by integration of the total ion current and using the separately determined relative response factors of the product and internal standard.

DFT Calculations. Starting from crystal structure coordinates, gas-phase closed-shell geometry optimizations of complexes **3** and **4** were performed with GAMESS²⁹ using the M06 functional.³⁰ The 6-31G(d,p) basis set was used for C, H, N, and P, while relativistic effective core potentials as implemented in SDB-cc-pVTZ were applied to Se and Pd.³¹ Molecular orbital plots were generated at a contour level of 0.03 using wxMacMolPlt.³²

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Supplementary Material

Further computational details, including coordinates for optimized geometries, are tabulated in Supplementary Material, available on the journal website at www.nrcresearchpress.com/journal/cjc. CCDC 1414987-1414988 contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)).

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Table 1. Selected Bond Lengths (Å) and Angles (°) for Complexes [(*o*-(NH₂)(X)C₆H₄)PdCl₂].

	X = PPh ₂ (3)	X = SePh (4)
Pd1–N1	2.048(3)	2.0456(18)
Pd1–X1	2.2050(8)	2.3575(3)
Pd1–Cl1	2.3001(9)	2.3017(5)
Pd1–Cl2	2.3607(8)	2.3352(5)
X1–C1	1.806(3)	1.933(2)
N1–C2	1.458(4)	1.459(3)
Cl1–Pd1–Cl2	94.51(3)	94.18(2)
Pd1–X1–C7	118.94(10)	101.31(6)
Pd1–X1–C13	115.56(10)	–
X1–Pd1–N1	85.61(8)	88.07(5)
X1–C1–C2–N1	3.3(4)	2.6(3)

Table 2. Comparative Use of **3**, **4**, and [PdCl₂(COD)] for a Suzuki-Miyaura Coupling Reaction^a

Entry	Catalyst	Temperature (°C)	Time (h)	Yield (%)
1	none	120 °C	14	9 ^b
2	[PdCl ₂ (COD)]	120	14	>95%
3	3	120	14	>95%
4	4	120	14	>95%
5	[PdCl ₂ (COD)]	50	14	35 ^b
6	3	50	14	20 ^b
7	4	50	14	36 ^b
8	[PdCl ₂ (COD)]	23	14	24 ^b
9	3	23	14	13 ^b
10	4	23	14	13 ^b

^aConditions: boronic acid (0.1 mmol), aryl bromide (0.1 mmol), DMF (0.5 mL) catalyst (5 mol%),

CsF (0.15 mmol); ^bYields measured by GC/MS versus the internal standard 4-nitrobenzaldehyde.

Table 3. Crystallographic Data for **3•2DMSO** and **4•MeCN**.

Compound	3•2(C₂H₆OS)	4•C₂H₃N
Empirical formula	C ₂₂ H ₂₈ Cl ₂ NO ₂ PPdS ₂	C ₁₄ H ₁₄ N ₂ Cl ₂ SePd
Formula weight	610.84	466.53
Temperature (K)	193(2)	193(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	10.9748(6)	10.7926(6)
<i>b</i> (Å)	18.4224(10)	7.3379(4)
<i>c</i> (Å)	13.0833(7)	20.5576(12)
α (°)	90	90
β (°)	105.6894(7)	99.4615(7)
γ (°)	90	90
Volume (Å ³)	2546.7(2)	1605.91(16)
<i>Z</i>	4	4
<i>D</i> _{calcd} (g cm ⁻³)	1.593	1.93
μ (mm ⁻¹)	1.185	3.745
<i>F</i> (000)	1240	904
Crystal size (mm ³)	0.335 × 0.082 × 0.041	0.446 × 0.192 × 0.09
Radiation	MoK α (λ = 0.71073 Å)	MoK α (λ = 0.71073 Å)
θ range for data collection (°)	1.959 to 27.6	1.913 to 28.25
Index ranges	-14 ≤ <i>h</i> ≤ 14, -23 ≤ <i>k</i> ≤ 23, -16 ≤ <i>l</i> ≤ 16	-14 ≤ <i>h</i> ≤ 12, -9 ≤ <i>k</i> ≤ 9, -27 ≤ <i>l</i> ≤ 27
Reflections collected	21623	11808

Independent reflections	5876 [$R_{\text{int}} = 0.0434$]	3864 [$R_{\text{int}} = 0.0202$]
Data/restraints/parameters	5876/2/292	3864/0/190
Goodness-of-fit on F^2	1.04	1.04
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0364$, $wR_2 = 0.0875$	$R_1 = 0.0210$, $wR_2 = 0.0518$
Final R indexes [all data]	$R_1 = 0.0498$, $wR_2 = 0.0959$	$R_1 = 0.0245$, $wR_2 = 0.0534$
Largest diff. peak/hole ($\text{e } \text{\AA}^{-3}$)	1.18/-0.59	0.57/-0.45

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Figure Captions

Figure 1. Thermal ellipsoid plot (50% probability) of **3**•2DMSO – carbon-bound hydrogen atoms are omitted for clarity.

Figure 2. Thermal ellipsoid plot (50% probability) of one enantiomer of complex **4**•MeCN – carbon-bound hydrogen atoms and the lattice solvent molecule are omitted for clarity.

Figure 3. Packing diagram for complex **4**, showing N–H $\cdots$ Cl hydrogen bonds.

Figure 4. Frontier orbitals of complexes **3** and **4**.

Graphical Abstract

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