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Selective Formation of Heteroligated Pt(II) Complexes with Bidentate Phosphine-Thioether (P,S) and Phosphine-Selenoether (P,Se) Ligands via the Halide-Induced Ligand Rearrangement Reaction

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Bidentate phosphine-selenoether (P,Se) ligands were synthesized, and their heteroligated Pt(II) complexes were made and studied. The unique "P,S/P,Se" ligand coordination to Pt(II) can be realized via the halide-induced ligand rearrangement reaction. In all cases, the exclusive formation of semi-open heteroligated complexes was achieved as shown by ^{31}P and ^{77}Se NMR spectroscopy and from single crystal X-ray diffraction studies. This is the first example of the use of ^{77}Se NMR spectroscopy to characterize these types of structures through direct observation of the weak-link interaction with the metal center. Heteroligated structure formation is believed to be driven by the relative electron-donating ability of the substituent groups on the seleno or thioether moieties. This effect is studied by comparing the structures of corresponding "P,SMe" and "P,SeMe" complexes bearing a hemilabile "P,SCH_2CF_3" group, which is less sterically demanding than "P,SPh" but is similar in terms of electron withdrawing ability.

Introduction

The most general and utilized strategies for synthesizing supramolecular complexes include the directional bonding,[1] symmetry interaction,[2] and weak-link approaches.[3] Researchers frequently target rigid structures with well-defined cavity sizes and shapes; however, structurally flexible complexes are often desired, especially when one wants to mimic the properties of a biological system.[4] The weak-link approach (WLA) is unique among these three synthetic strategies in that it produces species that can be dynamically interconverted between structurally rigid and flexible states via small-molecule coordination chemistry.[5] This property makes the WLA particularly attractive for the preparation of sophisticated allosteric structures that can be up- or down-regulated via the interaction of small molecules with regulatory sites strategically located within the complex.[6]

The WLA relies on the use of hemilabile ligands and metal ions to rapidly assemble supramolecular structures in which the ligands chelate via both strong and weak binders

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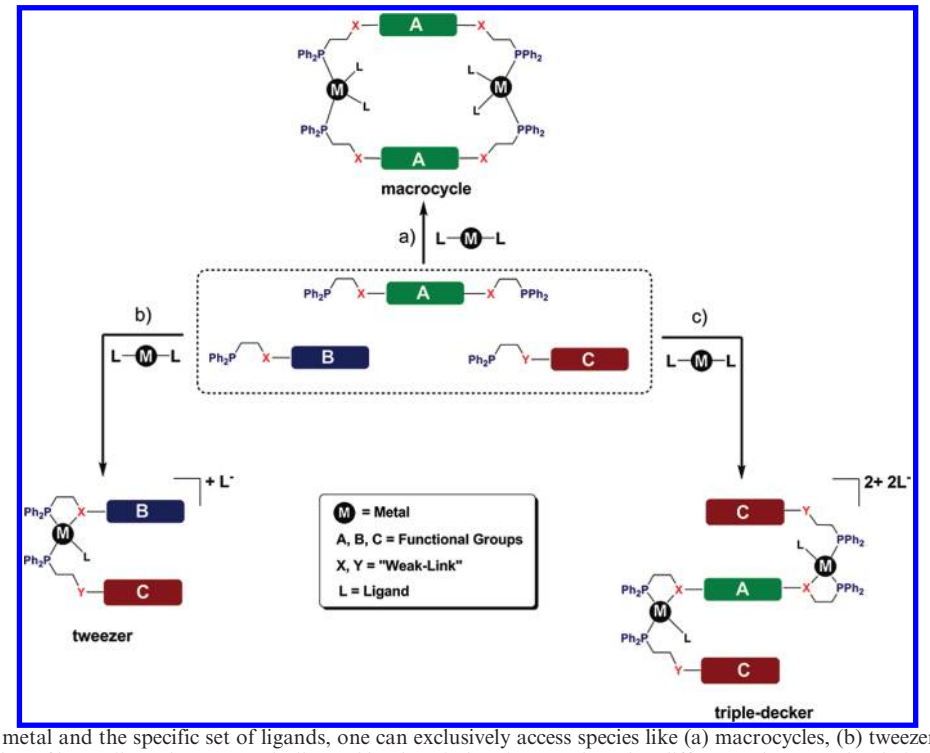
Scheme 1. WLA Is a Versatile Method for Constructing a Variety of Supramolecular Complexes[a]



[a] Depending on the metal and the specific set of ligands, one can exclusively access species like (a) macrocycles, (b) tweezers, and (c) triple-decker complexes. The formation of heteroligated structures is dictated by the relative electron-donating differences between the chalcogens (X and Y, where X is a stronger binder than Y) and the presence of a halide ancillary ligand (L), which constitutes the basis of halide induced ligand rearrangement (HILR). In all cases, one can reversibly abstract L and access the corresponding condensed species.

(Scheme 1).[7,8] Structures realized thus far include tweezers,[9a] macrocycles,[9b,d,g] triple-decker complexes,[9f] and triangular prisms.[9c] The weak binders can be selectively and reversibly displaced with small molecules, thus inducing a dramatic shape and size change in the chemically active pockets in these complexes.[8]

Bidentate phosphine-ether (P,O) ligands with Rh(I) were the first ligand−metal combinations studied in the context of the WLA.[7,8] Since then, the WLA has been studied with a wide variety of ligands and metals, including Ru(II), Pd(II), Ir(I), and Cu(I).[9] This synthetic tool box has allowed researchers to construct allosteric enzyme mimics,[5e] multimetallic complexes with catalytic properties that resemble important biological systems like PCR,[5f] and enantiomerically pure structures with the ability to selectively recognize and sequester one enantiomer in a racemic mixture.[5d]

Subsequent to the initial development of the WLA, we discovered a new reaction involving d^8 transition metals that allows one to easily prepare heteroligated structures (Scheme 1b and c).[10] In Rh(I) systems, this reaction works well with phosphine-ether (P,O) and phosphine-thioether (P,S) ligands to form exclusively A-Rh(I)-B mixed ligand structures. Since the formation of such motifs is dependent on the presence of a halide ion, this new reaction within the WLA family is called the halide-induced ligand rearrangement (HILR).[10]

To evaluate the generality of the HILR, we have explored analogous chemistry with Pd(II) and Pt(II).[11] When air stability is necessary, the use of Pt(II) provides clean access to A-Pt(II)-B products with P,S ligands.[11a,c] Until now, all ligands studied in the context of the WLA have contained either P,O; P,S; and, to a lesser extent, P,N moieties. These ligands and metal combinations are a rich platform for complex construction, but they offer no convenient way to probe the interaction between the weak-binding nuclei and the metal. As the complexity of the structures we synthesize grows and obtaining a definitive structure via X-ray analysis becomes more difficult, additional, routine characterization techniques are necessary and represent an important advance. Therefore, we have synthesized a series of model P,Se hemilabile ligands and their corresponding WLA complexes. NMR-active ^{77}Se nuclei were used to probe the nature of the Se-metal interaction.[12] These

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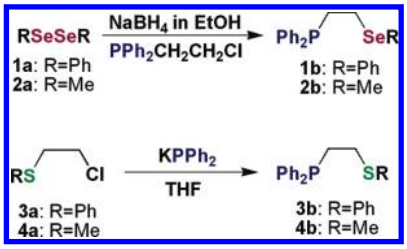
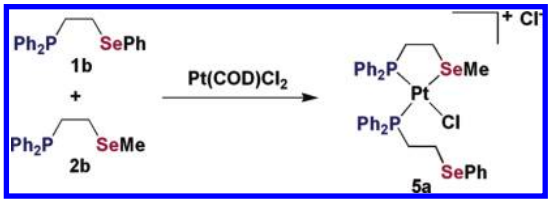
Scheme 2. Syntheses of P,Se Ligands **1b** and **2b** and P,S Ligands **3b** and **4b**



Scheme 3. Synthesis of the Semi-Open P,Se Complex **5a**



ligands are the first of a new class of selenoether hemilabile ligands.[13] Not only do they expand the toolbox of WLA chemistry, but they also provide important fundamental insights into the coordination chemistry of P,Se-type ligands with Pt(II).

Results and Discussions

Syntheses of Ligands. There are several existing methods in the synthetic literature for introducing a selenoether moiety within a molecule.[14] From these available routes, we chose one developed by the Sharpless group that involves the in situ reduction of diselenide precursors (**1a** or **2a**) and the use of the reduced product in the subsequent nucleophilic substitution of an alkyl halide in 1-chloroethanediphenylphosphine (Scheme 2).[13c] This reaction proceeds cleanly in 70−80% yield with no significant degradation of the diphenylphosphine moiety.

Although the dimethyldiselenide precursor has an extremely pungent odor, ligands **1b** and **2b**, when purified, are odorless. Importantly, the synthetic approach for **1b** and **2b** should be easily adaptable to other diselenide synthons bearing other functional groups (R in Scheme 2) compatible with $NaBH_4$. Ligands incorporating thioether moieties, such as **3b** and **4b**, were synthesized as reported previously from thioether precursors **3a** and **4a** (Scheme 2).[11a]

Synthesis of Heteroligated Semi-Open Complexes. Upon mixing ligands **1** (1 equiv) and **2** (1 equiv) with the Pt(II) precursor ($Pt(cod)Cl_2$, cod=cyclooctadiene, 1 equiv) in 1,2-dichloroethane, the heteroligated semi-open complex **5a** forms in quantitative yield (Scheme 3). The reaction was also performed in dichloromethane and 1,1,2,2-tetrachloroethane (TCE) to evaluate the role of solvent effects on the synthesis and $^{31}P\{^1H\}$ NMR spectroscopy of these compounds was performed. In 1,2-dichloroethane, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture exhibits two resonances at δ 42.1 (d, J_{P-P} = 13 Hz) and δ 10.8 (d, J_{P-P} = 11 Hz), assigned to the phosphines of **5a** on chelating ligand **2b** and non-chelating ligand **1b**, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **5a** in dichloromethane also exhibits two resonances, with a broad signal at 10.8 ppm. Upon gradually cooling **5a** to −50 °C in CD_2Cl_2, this signal broadens further and a broad resonance at δ 46.7 emerges, indicating the chelation of the chalcogen in ligand **1b**. To work at higher temperatures, we studied **5a** in TCE, which at room temperature exhibits a spectrum almost identical to **5a** in dichloromethane. Upon heating this complex to 50 °C, the broad peak at 10.8 ppm sharpens into a well-resolved doublet. The observed changes in the NMR spectra are likely a result of a fluxional closing process associated with ligand **1b** that is fast on the NMR time scale at higher temperatures, but that is slow enough to induce signal broadening at lower temperatures. This dynamic process is also affected by solvent polarity. In favor of this argument, the HILR confirmation experiment[11a,c] in dichloromethane, which is less polar than 1,2-dichloroethane, reveals slow rearrangement and incomplete formation of the heteroligated species even after 12 h. In contrast, the same experiment in 1,2-dichloroethane results in a spontaneous rearrangement within minutes. A quantitive assessment of solvent and temperature effects on heteroligated structure formation of Pt(II) WLA complexes will be addressed in subsequent work. The signal broadening in the $^{31}P\{^1H\}$ NMR spectrum could also result from the dipole−dipole relaxation pathway provided by the ^{77}Se nucleus in non-chelating ligand **1b** in complex **5a**. If this were indeed the case, the restrained ^{77}Se nucleus in chelating ligand **2b** would not contribute to the resonance broadening in the ^{31}P NMR spectrum of **5a** via a dipole−dipole relaxation pathway.[15] Consistent with these assumptions, the resonance for the P atom farthest from the nonchelated selenoether does not exhibit significant broadening. The phosphorus atom that is part of chelating ligand **2b** in **5a** exhibits a larger P−Pt coupling constant (J_{P-Pt} = 3538 Hz) than the analogous phosphorus atom in non-chelating ligand **1b** (J_{P-Pt} = 3152 Hz) because of the *trans*-directing nature of the SeMe group.[16] A single crystal X-ray diffraction study of **5a** is consistent with this observation: the P−Pt bond involving the P atom *trans* to the bound selenoether moiety is elongated (~2.28 Å) relative to the bond involving the P atom *trans* to the chloride (~2.23 Å) (Figure 1). Electrospray ionization mass spectroscopy (m/z $[M-Cl]^+$ = 907) and elemental analysis are consistent with the proposed composition and structure of complex **5a**.

The mixed P,S/P,Se heteroligated species **6a** and **7a** (Scheme 4) can be synthesized by combining two of the ligands from the pool of **1b**−**4b**, where one ligand features an electron withdrawing group on the chalcogen and the other an electron donating group, with 1 equiv of

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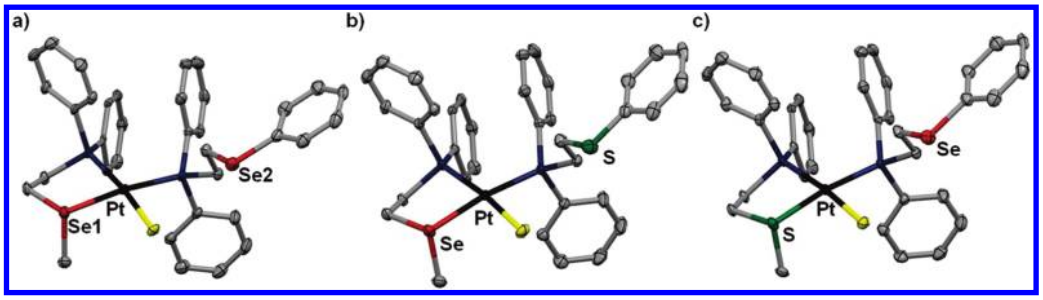
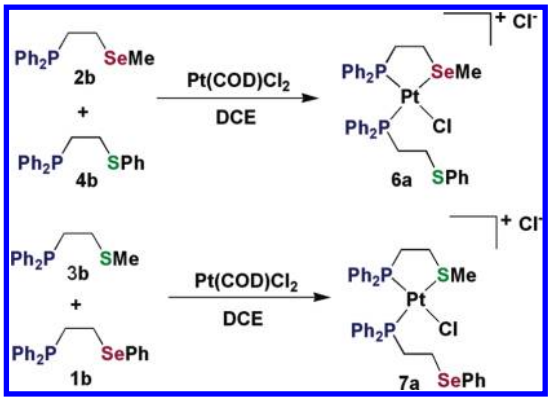


Figure 1. Crystal structures of the semi-open complexes **5a**, **6a**, and **7a** drawn with 50% thermal ellipsoid probability. In all cases, hydrogens, solvent molecules, and anions are omitted for clarity. Only one enantiomer is shown. Platinum atoms are black; sulfur, green; selenium, red; phosphorus, blue; chlorine, yellow; and carbon, gray. Selected bond lengths [Å] and angles [deg]: (a) **5a**: Pt1−Se1 2.462(6), Pt1−P1 2.236(1), Pt1−P2 2.285(1), Pt1−Cl1 2.362(1), P1−Pt1−P2 99.40(4), Se1−Pt1−Cl1 85.91(3), P2−Pt1−Cl1 88.62(4), P1−Pt1−Se1 86.15(3), P2−Pt1−Se1 172.63(3), P1−Pt1−Cl1 171.96(4) (b) **6a**: Pt1−Se1 2.4605(3), Pt1−P1 2.2334(7), Pt1−P2 2.2750(7), Pt1−Cl1 2.3589(8), P1−Pt1−P2 99.64(3), Se1−Pt1−Cl1 85.91(2), P2−Pt1−Cl1 88.43(3), P1−Pt1−Se1 86.09(2), P2−Pt1−Se1 172.53(2), P1−Pt1−Cl1 171.92(3) (c) **7a**: Pt1−S1 2.354(1), Pt1−P1 2.2829(9), Pt1−P2 2.2377(9), Pt1−Cl1 2.3593(9), P1−Pt1−P2 99.30(3), S1−Pt1−Cl1 86.40(3), P2−Pt1−S1 85.91(3), P1−Pt1−Cl1 88.52(3), P1−Pt1−S1 172.57(3), P2−Pt1−Cl1 172.1(3).

Scheme 4. Formation of Heteroligated Semi-Open Mixed P,Se/P,S Pt(II) Complexes



the Pt(II) precursor. Four different heteroligated complexes can be synthesized in this manner (the P,SMe/P,SPh complex was synthesized in a previous report).[11a] Interestingly, in the solid state, **5a**−**7a** are isostructural, having nearly identical orientations of major functional units, the same space group ($P\bar{1}$), and the same unit cell parameters. Each unit cell of the heteroligated species comprises a racemic mixture of enantiomers crystallized in a 1:1 ratio (see Supporting Information). P−Pt bond distances (Table 1), for which P is both *trans* to the Cl and *trans* to the chalcoether, are statistically identical in all structures. Comparison between the Pt−Se (2.46 Å) and Pt−S (2.35 Å) bond distances reveal similar Pt-chalcogen interactions when atomic radii are taken into account (Se, 1.16 Å; S, 1.02 Å).[17]

^{77}Se Characterization. ^{77}Se nuclei (Spin = 1/2) are useful for NMR spectroscopy because of their relatively high natural abundance (7.63%) and large chemical shift range.[15] The Se atoms in ligands **1b** and **2b** exhibit doublets at δ 334 (J_{Se-P} = 11 Hz) and δ 125 (J_{Se-P} = 11 Hz), respectively. Upon metalation to form **5a**, **6a**, and **7a**, the ^{77}Se{^{1}H} NMR spectra reveal that the Se atoms in both the non-chelating ligand **1b** and the chelating ligand **2b** exhibit a downfield chemical shift. For the chelating ligand **2b**, the resonance for the Se atom shifts downfield by ~210 ppm, whereas a modest ~30 ppm shift is observed for the analogous Se atom in non-chelating ligand **1b**. The ^{77}Se{^{1}H} NMR spectrum of complex **5a** exhibits a singlet at δ 360 assigned to the Se atom of the non-chelated SePh moiety in ligand **1b** and a poorly resolved doublet of doublets (appearing as a broad doublet) at δ 332 for the Se atom in chelating ligand **2b** (Figure 2). In contrast, the ^{77}Se{^{1}H} NMR spectrum of **6a** is well-resolved, revealing a doublet of doublets for the Se atom ($^{1}J_{Se-P}$ = 11 Hz, $^{2}J_{Se-P}$ = 134 Hz) with the expected Pt satellites (J_{Se-Pt} = 49 Hz). The relatively weak interaction between the Se and the Pt atoms results in a smaller *J*-value for the Pt(II) satellites compared to other reported systems, such as with Pt-selenide complexes.[18] The signal broadening in the ^{77}Se{^{1}H} NMR spectrum of complex **5a** and its absence in the analogous spectrum of complex **6a** may be explained if the rate of the fluxional closing and opening process is slower for complex **5a**. This hypothesis is supported by the observation of a broad doublet at δ 254 in the ^{77}Se{^{1}H} NMR spectrum of complex **5a** at −50 °C. Indeed, this shift is consistent with the ^{77}Se{^{1}H} resonance for **5a** after chloride abstraction (see next section). Since we did not observe solvent-induced sharpening of these resonances at both low and high temperatures, the presence of the chemical shift anisotropy (CSA) relaxation pathway (available because of the presence of the ^{77}Se nucleus) cannot be dismissed. In favor of the presence of the CSA pathway, the signals in the ^{77}Se{^{1}H} NMR spectra of **5a** and **7a** are broad, and the Pt satellites are not resolved.[19]

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Table 1. Selected Bond Lengths and $^{31}P\{^1H\}$ Chemical Shifts for Heteroligated Complexes **5a**−**7a** in 1,2-Dichloroethane-d^4

compound	Pt−P (Å)	Pt−P (Å)	Pt−Cl (Å)	$^{31}P_{chelate}\{^1H\}$ (ppm)	$^{31}P_{nonchelate}\{^1H\}$ (ppm)
5a	2.236(1)	2.285(1)	2.362(1)	42.1	10.8
6a	2.233(1)	2.275(1)	2.358(1)	42.2	8.1
7a	2.237(1)	2.283(1)	2.359(1)	43.1	11.5

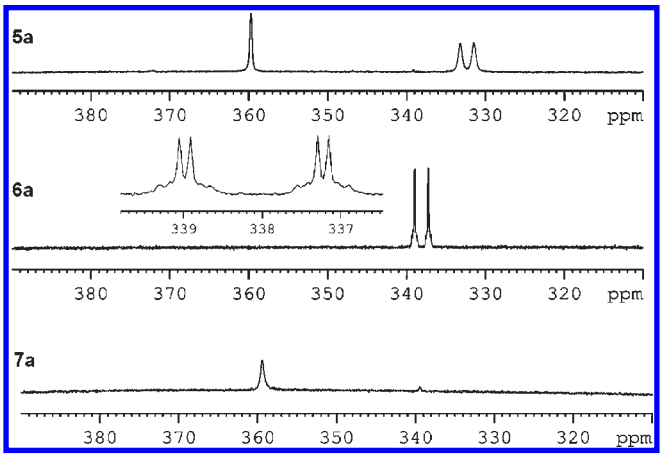
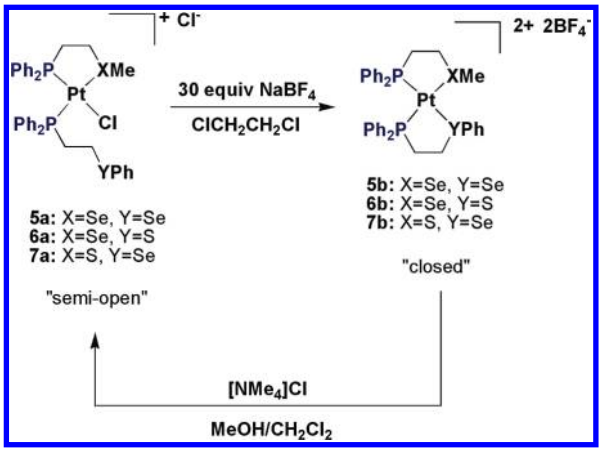


Figure 2. $^{77}Se\{^1H\}$ NMR spectra of semi-open complexes taken in dichloromethane-d^2.

Scheme 5. Reversible Conversion of Semi-Open Complexes to the Closed Form



Closed Complexes. Semi-open complexes can be converted to the corresponding closed species via chloride abstraction (Scheme 5). Initially, $AgBF_4$ was used as a chloride abstraction agent, but it led to a mixture of products when used in slight excess, possibly because of ligand and complex oxidation. A cleaner conversion was accomplished with a 30-fold total excess of $NaBF_4$. In a typical procedure, a semi-open complex is stirred for a day with $NaBF_4$ at room temperature in dichloroethane, followed by filtration and recrystallization of the product in ether. Solution-phase $^{31}P\{^1H\}$ NMR spectroscopy of the reaction mixtures showed almost quantitative conversion to the fully closed complexes **5b**−**7b** (Scheme 5). Upon addition of 2 equiv of NMe_4Cl to any of the closed species, they revert back to the semi-open state as observed by $^{31}P\{^1H\}$ NMR spectroscopy.

The phosphorus atoms in the P,YPh moieties in the closed complexes **5b**−**7b** exhibit a downfield shift of approximately 34 ppm in the $^{31}P\{^1H\}$ NMR spectra compared to the analogous semi-open species as a result of the chalcogen coordinating to the Pt center (Scheme 5).[20] In the same spectra, the phosphorus resonances for the P,XMe moieties are shifted downfield by only approximately 3 ppm, consistent with a significantly smaller electronic change at the site.

The limited solubility of the closed species **5b**−**7b** precluded us from obtaining high-quality ^{77}Se NMR spectra of them. Nevertheless, in the $^{77}Se\{^1H\}$ NMR spectrum of the closed complex **6b**, we observe a doublet of doublets (J_{Se-P} = 97 Hz) at δ 268 ppm, approximately 64 ppm upfield relative to the analogous resonance in the $^{77}Se\{^1H\}$ NMR spectrum of the semi-open species **6a**. A doublet in the $^{77}Se\{^1H\}$ NMR spectrum is observed for **5b** at the same chemical shift, δ 268 ppm; however, J_{Se-P} could not be determined because of signal broadening. In both **5b** and **6b**, this upfield shift is consistent with redistribution of electron density on the Se atom after chloride abstraction from **5a** and **6a**. Since the chelation of the SePh moiety in **5b** and the SPh moiety in **6b** adds electron density to the Pt(II) centers, the need for electron donation from the SeMe moiety is diminished. This, for example, in **5b**, results in a significant bond shortening (0.02 Å) between the selenium and the carbon atoms in the SeMe moiety and a corresponding bond elongation (0.02 Å) between the selenium and the carbon atoms in the SePh group. Species **6b** and **7b** were also characterized by single crystal X-ray diffraction (Figure 3). As with the semi-open species, their closed analogues are isostructural with each unit cell consisting of a 1:1 ratio of enantiomers. In all cases, the geometry around the Pt(II) center is nearly square planar, with the phosphorus atoms in the two chelates coordinating in a *cis* fashion, consistent with the P,S/P,S complexes reported earlier.[11a,c] In the $^{77}Se\{^1H\}$ NMR spectrum of complex **7b**, the peak corresponding to the Se atom in the SePh moiety (ca. δ 342) is significantly broadened. As postulated in the discussion of the ^{77}Se NMR spectra of complexes **5a** and **7a** above, the broadening is due to the presence of the chemical shift anisotropy relaxation pathway provided by the ^{77}Se nucleus. Consequently, cooling complex **7b** to −50 °C does not sharpen the peaks in the ^{77}Se NMR spectrum, and no information on the coupling constant between the P and Pt nuclei in the complex could be obtained. In the $^{31}P\{^1H\}$ NMR spectra of the closed species, the presence of a large number of invertomers (at −50 °C) provides further complications. Unfortunately, since the closed species were not sufficiently soluble at temperatures below −50 °C, it was not possible to clearly observe and assign resonances for the frozen conformations.[18c]

Sterics versus Electronics. There are several possible explanations for the selective formation of the heteroligated species. In all cases, we observe that these species

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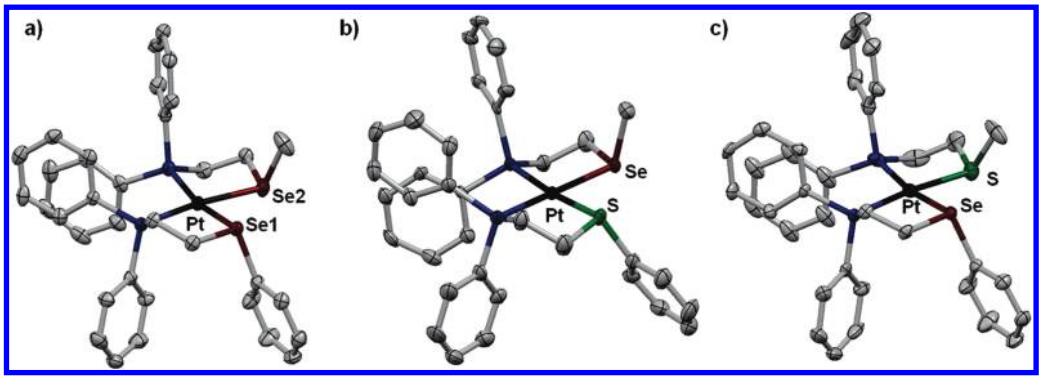
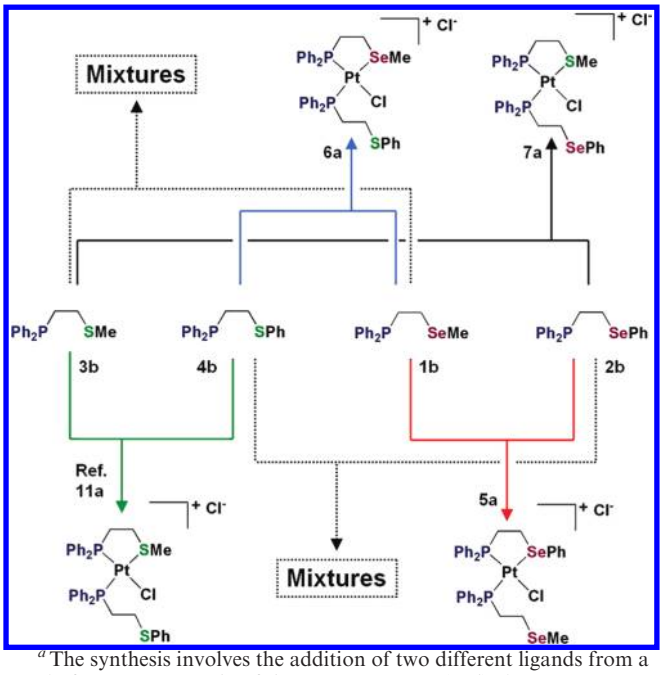


Figure 3. Crystal structures of semi-open complexes **5b**, **6b**, and **7b** drawn with 50% thermal ellipsoid probability. In all cases, only one isomer in the unit cell is shown; hydrogens, solvent molecules, and anions are omitted for clarity. Platinum atoms are black, sulfur, green; selenium, red; phosphorus, blue; and carbon, gray. Selected bond lengths [Å] and angles [deg]: (a) **5b**: Pt1−Se1 2.4715(6), Pt1−P1 2.2725(9), Pt1−P2 2.268(1), Pt1−Se2 2.4549(4), P1−Pt1−P2 100.22(4), Se1−Pt1−Se2 88.43(2), P2−Pt1−Se2 85.67(3), P1−Pt1−Se1 86.28(3), P2−Pt1−Se1 168.71(3), P1−Pt1−Se2 173.32(3) (b) **6b**: Pt1−Se1 2.472(7), Pt1−S1 2.365(2), Pt1−P1 2.263(2), Pt1−P2 2.281(2), P1−Pt1−P2 97.98(6), Se1−Pt1−S1 90.02(4), P2−Pt1−S1 88.28(6), P1−Pt1−Se1 85.56(4), P2−Pt1−Se1 175.64(5), P1−Pt1−S1 174.31(6) (c) **7b**: Pt1−Se1 2.475(1), Pt1−P1 2.268(2), Pt1−P2 2.273(3), Pt1−S1 2.352(2), P1−Pt1−P2 98.87(8), Se1−Pt1−S1 89.71(6), P2−Pt1−S1 85.54(8), P1−Pt1−Se1 86.46(6), P2−Pt1−Se1 170.85(7), P1−Pt1−S1 174.06(8).

Scheme 6. Summary of the Reactions for the Synthesis of Heteroligated Complexes[a]



[a] The synthesis involves the addition of two different ligands from a pool of **1b**−**4b** to 1 equiv of the Pt precursor, $Pt(cod)Cl_2$.

form quantitatively only if the functional groups on the chalcogen (S or Se) in the ligand pair we introduce have significantly different electron donating abilities. Indeed, the reactions involving **1b** and **3b** or **2b** and **4b** and the Pt(II) precursor do not result in the formation of one semi-open species, but instead result in the formation of mixtures (Scheme 6).

For the combination of ligands **1b** and **3b**, the inability to form a single complex can be explained either by the weak chelating ability of these ligands or by steric reasons. Steric repulsion between the two phenyl groups could potentially explain the instability of the XPh/YPh species, leading to the formation of the heteroligated complex when the much smaller chalcogen-Me-containing ligand is introduced to this system. To address whether the formation of the heteroligated Me/Ph species is dictated by steric interactions or by differences in the

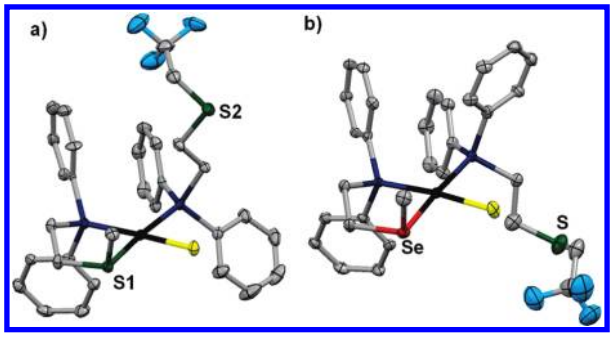
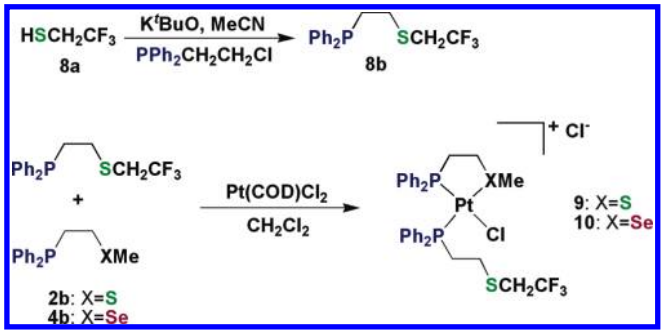


Figure 4. Crystal structures of semi-open complexes **9** (a) and **10** (b) drawn with 50% thermal ellipsoid probability. In all cases, hydrogens, solvent molecules, and anions are omitted for clarity. Platinum atoms are black, sulfur, green; selenium, red; phosphorus, dark blue; carbon, gray; and fluorine, light blue. Selected bond lengths [Å] and angles [deg]: (a) **9**: Pt1−S1 2.340(2), Pt1−P1 2.243(2), Pt1−P2 2.277(2), Pt1−Cl4 2.346(2), P1−Pt1−P2 101.19(6), S1−Pt1−Cl4 84.64(6), P2−Pt1−Cl4 86.93(6), P1−Pt1−S1 87.12(6), P2−Pt1−S1 171.41(6), P1−Pt1−Cl4 170.97(6) (b) **10**: Pt1−Se1 2.461(5), Pt1−P1 2.228(1), Pt1−P2 2.284(1), Pt1−Cl1 2.360(1), P1−Pt1−P2 98.91(5), Se1−Pt1−Cl1 86.41(4), P2−Pt1−Cl1 88.03(5), P1−Pt1−Se1 86.68(4), P2−Pt1−Se1 174.20(4), P1−Pt1−Cl1 173.00(5).

Scheme 7. Synthesis of P,SCH_2CF_3 Ligand **8b** and the Corresponding Heteroligated Pt(II) Complexes with Ligands **2b** and **4b**



electronic properties of the ligands, we have synthesized the P,SCH_2CF_3 ligand **8b** from the thiol derivative **8a** (Scheme 7).

This ligand was intended to be less sterically demanding than the P,SPh ligand, but still electron withdrawing, to elucidate the driving force of this reaction. When ligand

8b was reacted with either **2b** or **4b** and the Pt precursor, we observed quantitative formation of the semi-open heteroligated species **9** and **10**, respectively, as confirmed by $^{31}P\{^1H\}$ NMR spectroscopy and single crystal X-ray crystal diffraction studies. One can probe the Pt-SeMe interaction in complex **10** via $^{77}Se\{^1H\}$ NMR spectroscopy. This analysis reveals a doublet of doublets at 336.5 ($^1J_{Se-P} = 11$ Hz, $^2J_{Se-P} = 129$ Hz), similar to what is observed in case of **5a**. A small downfield shift of 3 ppm is observed via $^{19}F\{^1H\}$ NMR for both complexes **9** and **10** relative to the chemical shift of the Se atom in ligand **8b**, which is consistent with the slight change in the electronic environment at the CF_3 moiety. Analysis of the single-crystal X-ray diffraction data for complexes **9** and **10** (Figure 4) is consistent with the observations made from the $^{77}Se\{^1H\}$ NMR spectra. The near square-planar geometries on Pt(II) of **9** an **10**, bond angles, and lengths are in good correlation with the analogous properties observed in **5a**−**7a**. It is therefore reasonable to propose that a difference in electron donating ability between the two ligands is crucial in the formation of Pt(II) heteroligated complexes. Additional mechanistic studies examining this process in a quantitative manner will be reported in subsequent work.

A comparison can be made between selenoether coordination behavior and the behavior of the thioether analogues. While the O,R and S,R chemistries differ significantly, $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectroscopic analyses and solid-state crystal structures of Se, R-containing complexes show no significant differences in the Pt-chalcogen interaction from the case of S,R-containing complexes. In both seleno- and thioether coordination chemistries, the strength of the heteroatom-metal interaction is mainly dictated by the electron donating or withdrawing nature of its substituent. Additionally, the study of WLA systems benefits from the presence of the selenoether moiety: ^{77}Se NMR spectroscopy provides a convenient probe of the interaction between the weak-link moiety and the Pt center. Given that selenoether and thioether coordination chemistries are very similar for Pt(II), information obtained from ^{77}Se NMR spectroscopy of selenoether-containing WLA complexes can be extended to their thioether analogues.

Conclusions

The halide-induced ligand rearrangement facilitates the synthesis of mixed-ligand systems that form as dictated by the substituent on the chalcoether moieties. Clean formation of the heteroligated WLA species is observed only when the ligand pair includes a weak and a strong electron donor at the chalcogen site. In contrast to the behavior of O,R ligands in WLA systems, analysis of the complexes presented here indicates little difference between selenoether and thioether coordination chemistry with Pt(II) in both solution and the solid state. Therefore, through analysis of the P,Se version of such complexes by ^{77}Se NMR spectroscopy, we can draw conclusions that can be extended to the P,S analogues with Pt(II).

Experimental Section

General Methods/Instrument Details. All phosphine-based ligands were prepared and stored using standard Schlenk techniques under an inert nitrogen atmosphere. The syntheses of Pt(II) complexes and all manipulations were done under ambient conditions. All solvents were purchased as anhydrous grade from Sigma-Aldrich and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. All other chemicals were used as received from Aldrich Chemical Co. or prepared according to literature procedures.[11a,c] All NMR spectra were recorded on a Bruker Avance 400 MHz. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to residual proton and carbon resonances in the deuterated solvents. $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra were referenced to H_3PO_4 and Me_2Se standards, respectively. $^{19}F\{^1H\}$ NMR spectra were referenced to an external $CFCl_3$ (in $CDCl_3$) standard. Electrospray ionization (ESI) mass spectra were recorded on a Micromass Quatro II triple quadrupole mass spectrometer; high-resolution APPI (atmospheric pressure ion) on an Agilent 6210 LC-TOF with Agilent 1200 HPLC induction mass-spec system instrument. Elemental analyses were performed by Quantitative Technologies, Whitehouse, NJ.

(2-Phenylselenoethyl)diphenylphosphine 1. Diphenyldiselenide (Ph_2Se_2, 0.6 g, 1.9 mmol) was dissolved in anhydrous EtOH (20 mL) in a 50 mL Schlenk flask equipped with a magnetic stir bar at room temperature. Approximately 180 mg of $NaBH_4$ was added slowly to a reaction mixture kept under nitrogen. After 5 min, reduction of the diselenide was complete as indicated by the disappearance of the solution's yellow color. A 0.95 g portion (3.8 mmol) of 1-chloroethanephosphine was added to the flask, and the reaction mixture was refluxed for 18 h. The product mixture was filtered to remove salts while hot, and all volatiles were evaporated in vacuo. The residual oily substance was extracted with dichloromethane and washed with brine, followed by column chromatography on silica eluted with 1:1 mixture of hexane/dichloromethane. Recrystallization from cold ethanol (−20 °C) afforded **1** as a white solid (1.1 g, 78%). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C): δ −15.3 (s); $^{77}Se\{^1H\}$ NMR (76.34 MHz, 25 °C): δ 334.3 (d, $J_{Se-P} = 11$ Hz); ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.41−7.15 (m, 15H, ArH), 2.87 (m, 2H, AliphH), 2.39 (m, 2H, AliphH); $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ 138.5 (d, $J_{C-P} = 15$ Hz), 133.2 (d, $J_{C-P} = 19$ Hz), 133.1 (s), 129.7 (s), 129.3 (s), 129.1 (d, $J_{C-P} = 7$ Hz), 127.4 (s), 29.6 (d, $J_{C-P} = 16$ Hz), 23.8 (d, $J_{C-P} = 21$ Hz). HRMS (APPI, MeOH): m/z calcd for $C_{20}H_{19}PSe$ $[M+H]^+$: 371.0462; found: 371.0471.

(2-Methylselenoethyl)diphenylphosphine 2. ***Caution!*** *Dimethyldiselenide emits a strong garlic-like odor in extremely low concentrations. This reaction should be handled with proper attire in a well-ventilated laboratory.*

Compound **2** was prepared using the same procedure as in **1** from 0.75 g (4 mmol) of dimethyldiselenide (Me_2Se_2) and 2.0 g (8 mmol) of 1-chloroethanephosphine to afford **2** as a white solid (2.1 g, 85%). $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ −15.2 (s). ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ 7.41−7.23 (m, 10H, ArH), 2.52 (m, 2H, AliphH), 2.38 (m, 2H, AliphH), 1.94 (br s, 3H, AliphH); $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ 138.8 (d, $J_{C-P} = 15$ Hz), 133.3 (d, $J_{C-P} = 19$ Hz), 129.3 (s), 129.1 (d, $J_{C-P} = 7$ Hz), 29.8 (d, $J_{C-P} = 15$ Hz), 21.2 (d, $J_{C-P} = 20$ Hz), 4.5 (s); $^{77}Se\{^1H\}$ NMR (76.34 MHz, 25 °C): δ 125.1 (d, $J_{Se-P} = 11$ Hz). HRMS (APPI, MeOH): m/z calcd for $C_{15}H_{17}PSe$ $[M+H]^+$: 309.0306; found: 309.0319.

(2-(2,2,2-Trifluoroethane)thioethyl)dipheynlphosphine 8. One g (1.1 equiv) of K^{t}BuO was added to 0.95 g (8.2 mmol) of 2,2,2-trifluoroethanethiol dissolved in 10 mL of dry acetonitrile, and the mixture was stirred for 30 min at room temperature. A 2.04 g portion (8.2 mmol) of 1-chloroethanephosphine dissolved in 5 mL of dry acetonitrile were added to the reaction mixture that was allowed to stir for 48 h at room temperature. All volatiles were evaporated in vacuo, and the residue was extracted with ether and brine. The organic extract was evaporated in vacuo

Table 2. Crystallographic Data

	(**5a**·CH_2Cl_2)	(**6a**·CH_2Cl_2)	(**6b**)	(**9**·CH_2Cl_2)
formula	$C_{36}H_{38}Cl_4P_2PtSe_2$	$C_{36}H_{38}Cl_4P_2PtSSe$	$C_{39}H_{52}BF_4O_4P_2PtSSe$	$C_{32}H_{35}Cl_4F_3P_2PtS_2$
fw	1027.41	980.51	1126.07	939.55
color, habit	colorless plate	colorless needle	colorless needle	colorless needle
cryst dimens [mm]	0.500 × 0.316 × 0.030	0.519 × 0.09 × 0.02	0.17 × 0.06 × 0.04	0.56 × 0.08 × 0.03
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$
a [Å]	9.7387(11)	9.7594(4)	17.1537(3)	9.5260(3)
b [Å]	11.5991(13)	11.4970(5)	12.7690(2)	12.7111(3)
c [Å]	16.6505(18)	16.6076(6)	18.0712(3)	15.8835(4)
α [deg]	83.477(2)	83.721(2)	90	108.108(2)
β [deg]	86.362(2)	86.262(2)	94.8700(10)	90.6480(10)
γ [deg]	85.674(2)	85.680(2)	90	100.0850(10)
V [Å^3]	1860.5(4)	1843.94(13)	3943.95(11)	1795.32(8)
Z	2	2	4	2
ρ_{calcd} [g cm^{-3}]	1.834	1.766	1.751	1.738
radiation (λ, D [Å])	Mo Kα (0.71073)	Mo Kα (0.71073)	Cu Kα (1.54178)	Mo Kα (0.71073)
μ [mm^{-1}]	6.126	5.251	9.475	4.449
T [K]	100(2)	100(2)	100(2)	100(2)
F(000)	996	960	2068	924
min/max transmn	0.1114/0.8310	0.2507/0.9012	0.2879/0.6917	0.1907/0.8969
2θ range [deg]	1.77 to 28.75	2.06 to 34.50	4.32 to 67.17	1.72 to 30.68
reflns collected	16962	30926	26361	37308
indep reflns	8588	14339	6805	10835
R_{int}	0.0293	0.0471	0.0790	0.0884
refinement method	full-matrix least-squares on F^2			
data/restraints/params	8588/0/407	14339/0/407	6805/0/407	10835/6/399
final R indices [$I^2 > 2\sigma(I)$]	$R1$ = 0.0365, $wR2$ = 0.0893	$R1$ = 0.0335, $wR2$ = 0.0800	$R1$ = 0.0393, $wR2$ = 0.1026	$R1$ = 0.0502, $wR2$ = 0.1251
R indices [all data]	$R1$ = 0.0491, $wR2$ = 0.0956	$R1$ = 0.0509, $wR2$ = 0.0860	$R1$ = 0.0535, $wR2$ = 0.1065	$R1$ = 0.0633, $wR2$ = 0.1293
GOF(F^2)	1.047	0.881	1.048	1.115
largest diff peak/hole [e Å^{-3}]	3.319/−2.060	3.057/−1.535	1.883/−1.653	4.087/−2.785

	(**10**·CH_2Cl_2·H_2O)	(**5b**·CH_2Cl_2)	(**7a**·CH_2Cl_2)	(**7b**)
formula	$C_{32}H_{37}Cl_4F_3OP_2PtSSe$	$C_{36}H_{38}B_2Cl_2F_8P_2PtSe_2$	$C_{36}H_{38}Cl_4P_2PtSSe$	$C_{35}H_{36}B_2F_8P_2PtSSe$
fw	1004.47	1130.13	980.51	1042.37
color, habit	colorless plate	colorless block	colorless needle	colorless tabular
cryst dimens [mm]	0.28 × 0.13 × 0.02	0.35 × 0.26 × 0.14	0.476 × 0.116 × 0.116	0.302 × 0.138 × 0.080
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$
a [Å]	9.86540(10)	37.7059(6)	9.7524(7)	37.375(4)
b [Å]	10.06650(10)	13.6290(2)	11.5428(9)	13.3976(15)
c [Å]	18.4500(2)	17.2281(3)	16.6607(13)	17.394(2)
α [deg]	91.6080(10)	90	84.0610(10)	90
β [deg]	93.8850(10)	115.7880(10)	86.2950(10)	114.810(13)
γ [deg]	96.5660(10)	90	85.7670(10)	90
V [Å^3]	1814.88(3)	7971.7(2)	1857.3(2)	7905.8(17)
Z	2	8	2	8
ρ_{calcd} [g cm^{-3}]	1.838	1.883	1.753	1.752
radiation (λ, D [Å])	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ [mm^{-1}]	5.350	5.626	5.213	4.673
T [K]	100(2)	100(2)	100(2)	100(2)
F(000)	980	4368	960	4086
min/max transmn	0.3128/0.8823	0.2435/0.4980	0.2693/0.5934	0.3809/0.7016
2θ range [deg]	1.11 to 30.55	1.20 to 30.02	1.78 to 28.76	1.63 to 28.67
reflns collected	36443	111134	17259	36032
indep reflns	11034	11614	8626	9602
R_{int}	0.0638	0.0977	0.0238	0.0985
refinement method	full-matrix least-squares on F^2			
data/restraints/params	11034/0/415	11614/0/479	8626/0/411	9602/0/412
final R indices [$I^2 > 2\sigma(I)$]	$R1$ = 0.0421, $wR2$ = 0.0971	$R1$ = 0.0349, $wR2$ = 0.0956	$R1$ = 0.0317, $wR2$ = 0.0800	$R1$ = 0.0646, $wR2$ = 0.1460
R indices [all data]	$R1$ = 0.0619, $wR2$ = 0.1097	$R1$ = 0.0597, $wR2$ = 0.1062	$R1$ = 0.0371, $wR2$ = 0.0837	$R1$ = 0.0823, $wR2$ = 0.1510
GOF(F^2)	0.986	1.067	1.060	1.059
largest diff peak/hole [e Å^{-3}]	4.131/−2.579	3.243/−2.008	2.588/−1.460	2.323/−4.051

and purified via column chromatography on silica with 6:4 hexane/dichloromethane, which afforded **8** as a slightly yellowish oil (2 g, 75%). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C): δ − 20.4 (s). ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ 7.52−7.30 (m, 10H, ArH), 3.11 (q, 2H, AliphH), 2.74 (m, 2H, AliphH), 2.34 (m, 2H, AliphH); $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ 134.8 (d, J_{C-P} = 14 Hz), 129.6 (d, J_{C-P} = 19 Hz), 125.9 (s), 125.6 (d, J_{C-P} = 7 Hz), 123.1 (d, J_{C-F} = 276 Hz), 31.6

(q, J_{C-F} = 25 Hz), 26.8 (d, J_{C-P} = 22 Hz), 25.2 (d, J_{C-P} = 15 Hz); $^{19}F\{^1H\}$ NMR (376.46 MHz, CD_2Cl_2, 25 °C): δ − 70.3 (s). HRMS (APPI): *m*/*z* calcd for $C_{16}H_{16}PSF_3$ $[M+H]^+$: 329.0735; found: 329.0744.

General Procedure for Formation of Heteroligated Semi-Open Complexes. A solution of ligand A (**2** or **4**) (0.33 mmol) in $ClCH_2CH_2Cl$ (5 mL) was added dropwise to a solution of $[Pt(cod)Cl_2]$ (125 mg, 0.33 mmol, 1 equiv) in dichloroethane (5 mL) at room temperature. The solution was allowed to stir for 5 min before ligand B (0.33 mmol) (**1**, **3**, or **8**), dissolved in dichloroethane (5 mL), was added dropwise. After 20 min, the solvent was reduced to about 1 mL in vacuo, and 10 mL of diethyl ether was added, precipitating a white solid. The solid was filtered and washed with an additional amount of ether (5 mL) to afford the analytically pure heteroligated complex (in situ $^{31}P\{^1H\}$ NMR yields = quantitative, isolated yields >95%).

General Procedure for the Formation of Heteroligated Closed Complexes. To a solution of a heteroligated semi-open complex (0.3 mmol) in 10 mL of dichloroethane or dichloromethane, about 1 g (9 mmol, 30 eq., 15 eq. per Cl^-) of $NaBF_4$ was added, and the solution was left vigorously stirring for 24 h. After passing the resulting mixture through Celite and reducing the volume of solvent to about 1 mL in vacuo, diethyl ether was used to precipitate the solid product. This product was then filtered and washed with additional amount of ether (ca. 10 mL) to afford the closed heteroligated complex (in situ $^{31}P\{^1H\}$ NMR yields = quantitative, isolated yields >95%).

Characterization Summary of 5a−b, 6a−b, 7a−b, 9, and 10. In all cases a small residual amount of reaction solvent was observed in the ^1H NMR even after prolonged drying *in vacuo*. This is consistent with presence of solvent molecules in the unit cells of the corresponding crystal structures and elemental analysis data, as well as with previously reported work.[11a,c]

[PtCl(κ^2-PPh$_2$SCH$_2$CH$_2$SeMe)(PPh$_2$CH$_2$CH$_2$SePh)]Cl (5a). ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ 7.92−6.84 (m, 25ArH), 3.77−2.28 (m, 11 AliphH); $^{31}P\{^1H\}$ NMR (100.62 MHz, DCE-d^4, 25 °C): δ 42.1 (d, J_{P-P} = 12 Hz, J_{P-Pt} = 3538 Hz), 10.8 (d, J_{P-P} = 11 Hz, J_{P-Pt} = 3152 Hz); $^{77}Se\{^1H\}$ NMR (76.34 MHz, 25 °C): δ 359.7 (bs), δ 332.4 (bd, J_{Se-P} = 131 Hz); MS (ESI): *m*/*z* calcd for $C_{35}H_{36}P_2PtSe_2Cl$ $[M-Cl]^+$: 907; found: 907; Anal. Calcd for $C_{35}H_{36}P_2Se_2PtCl_2$: C, 44.60; H, 3.85. Found: C, 44.38; H, 3.59.

[Pt(κ^2-PPh$_2$SCH$_2$CH$_2$SeMe)(κ^2-PPh$_2$CH$_2$CH$_2$SePh)][BF$_4$]$_2$ (5b). ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ 7.71−6.96 (m, 25ArH), 3.47−2.14 (m, 11H, AliphH); $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, DCE-d^4): δ 47.0 (bs, J_{P-Pt} = 3126 Hz), 44.8 (bs, J_{P-Pt} = 3362 Hz); $^{77}Se\{^1H\}$ NMR (76.34 MHz, 25 °C): δ 268.1 (d, J_{Se-P} = 98 Hz); $^{19}F\{^1H\}$ NMR (376.46 MHz, 25 °C) δ −150.77 (s, $^{10}BF_4$), −150. 82 (s, $^{11}BF_4$). MS (ESI): *m*/*z* calcd for $C_{35}H_{36}P_2PtSe_2BF_4$ $[M-BF_4]^+$: 959; found: 959; Anal. Calcd for $C_{35}H_{36}P_2PtSe_2B_2F_8$: C, 40.11; H, 3.47. Found: C, 41.93; H, 3.35.

[PtCl(κ^2-PPh$_2$SCH$_2$CH$_2$SeMe)(PPh$_2$CH$_2$CH$_2$SPh)]Cl (6a). ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ 7.91−6.90 (m, 25ArH), 3.71−2.23 (m, 11AliphH); $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, DCE-d^4): δ 42.2 (d, J_{P-P} = 15 Hz, J_{P-Pt} = 3538 Hz), 8.1 (d, J_{P-P} = 14 Hz, J_{P-Pt} = 3167 Hz); $^{77}Se\{^1H\}$ NMR (76.34 MHz, 25 °C): δ 338.2 (dd, J_{Se-P} = 134 and 11 Hz, J_{Se-Pt} = 49 Hz). MS (ESI): *m*/*z* calcd for $C_{35}H_{36}P_2PtSeSCl$ $[M-Cl]^+$: 861; found: 861; Anal. Calcd for $C_{35}H_{36}P_2SSePtCl_2$: C, 46.94; H, 4.05. Found: C, 47.51; H, 3.71.

[Pt(κ^2-PPh$_2$SCH$_2$CH$_2$SeMe)(κ^2-PPh$_2$CH$_2$CH$_2$SPh)][BF$_4$]$_2$ (6b). ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ 7.78−6.91 (m, 25ArH), 3.47−2.19 (m, 11AliphH); $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, DCE-d^4): δ 47.2 (bs, J_{P-Pt} = 3106 Hz), 43.1 (d, J_{P-P} = 15 Hz, J_{P-Pt} = 3464 Hz); $^{77}Se\{^1H\}$ NMR (76.34 MHz, 25 °C): δ 268.0 (d, J_{SeP} = 97 Hz); $^{19}F\{^1H\}$ NMR (376.46 MHz, 25 °C) δ −151.77 (s, $^{10}BF_4$), −150.83 (s, $^{11}BF_4$). MS (ESI): *m*/*z* calcd for $C_{35}H_{36}P_2PtSeSBF_4$ $[M-BF_4]^+$: 911; found: 911; Anal. Calcd for $C_{35}H_{36}P_2SSePtB_2F_8$: C, 42.11; H, 3.63. Found: C, 43.12; H, 3.60.

[PtCl(κ^2-PPh$_2$SCH$_2$CH$_2$SMe)(PPh$_2$CH$_2$CH$_2$SePh)]Cl (7a). ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ 7.79−6.91 (m, 25ArH), 3.72−2.21 (m, 11AliphH); $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, DCE-d^4): δ 43.1 (d, J_{P-P} = 3517 Hz, J_{P-Pt} = 3517 Hz), 11.5 (d, J_{P-P} = 15 J_{P-Pt} = 3125 Hz); $^{77}Se\{^1H\}$ NMR (76.34 MHz, 25 °C): δ 359.5 (bs) MS (ESI): *m*/*z* calcd for $C_{35}H_{36}P_2PtSeSCl$ $[M-Cl]^+$: 861; found: 861; Anal. Calcd for $C_{35}H_{36}P_2SSePtCl_2$: C, 46.94; H, 4.05. Found: C, 47.43; H, 4.07.

Pt(κ^2-PPh$_2$SCH$_2$CH$_2$SMe)(κ^2-PPh$_2$CH$_2$CH$_2$SePh)][BF$_4$]$_2$ (7b). ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ 7.71−6.92 (m, 25ArH), 3.25−2.43 (m, 11AliphH); $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, DCE-d^4): δ 47.3 (d, J_{P-Pt} = 3192 Hz), 46.9 (bs, J_{P-Pt} = 3030 Hz); $^{77}Se\{^1H\}$ NMR (76.34 MHz, 25 °C): δ 341.5 (bs); $^{19}F\{^1H\}$ NMR (376.46 MHz, 25 °C) δ −150.95 (s, $^{10}BF_4$), −151.00 (s, $^{11}BF_4$). MS (ESI): *m*/*z* calcd for $C_{35}H_{36}P_2PtSeSBF_4$ $[M-BF_4]^+$: 911; found: 911; Anal. Calcd for $C_{35}H_{36}P_2SSePtB_2F_8$: C, 42.11; H, 3.63. Found: C, 43.52; H, 3.64.

[PtCl(κ^2-PPh$_2$SCH$_2$CH$_2$SMe)(PPh$_2$CH$_2$CH$_2$SCH$_2$CF$_3$)]Cl (9). NMR (400.13 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2): δ 7.79−7.92 (b, 20ArH), 3.28−2.39 (b, 13AliphH); $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, DCE-d^4): δ 47.0 (d, J_{P-P} = 15 Hz, J_{P-Pt} = 3517 Hz), 9.1 (d, J_{P-P} = 14 Hz, J_{P-Pt} = 3186 Hz); $^{19}F\{^1H\}$ NMR (376.46 MHz, 25 °C): δ − 66.3 (s). MS (ESI): *m*/*z* calcd for $C_{31}H_{33}ClF_3P_2S_2Pt$ $[M-Cl]^+$: 818; found: 818; Anal. Calcd for $C_{31}H_{33}Cl_2F_3P_2S_2Pt$: C, 43.47; H, 3.89. Found: C, 43.39; H, 3.82.

[PtCl(κ^2-PPh$_2$SCH$_2$CH$_2$SeMe)(PPh$_2$CH$_2$CH$_2$SCH$_2$CF$_3$)]Cl (10). ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2): δ 8.00−6.89 (b, 20ArH), 3.81−2.05 (b, 13AliphH); $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, DCE-d^4): δ 42.4 (d, J_{P-P} = 14 Hz J_{P-Pt} = 3536 Hz), 9.0 (d, J_{P-P} = 14 Hz, J_{P-Pt} = 3190 Hz); $^{77}Se\{^1H\}$ NMR (76.34 MHz, 25 °C): δ 336.5 (dd, $^1J_{Se-P}$ = 11 Hz, $^2J_{Se-P}$ = 129); $^{19}F\{^1H\}$ NMR (376.46 MHz, CD_2Cl_2, 25 °C): δ −70.3. MS (ESI): *m*/*z* calcd for $C_{31}H_{33}ClF_3P_2SSePt$ $[M-Cl]^+$: 865; found: 865; Anal. Calcd for $C_{31}H_{33}Cl_2F_3P_2SSePt$: C, 41.30; H, 3.69. Found: C, 42.27; H, 3.46.

General Procedure for Conversion of Closed Complexes to Semi-Open. A solution of Me_4NCl (0.1 mmol) in methanol (5 mL) was added to a solution of closed complex (0.1 mmol) in dichloromethane (5 mL), resulting in a pale yellow solution. $^{31}P\{^1H\}$ NMR spectroscopy after 20 min showed predominantly the semi-open complex.

Control Reactions Confirming the Occurrence of the HILR in Complex Formation.[11a] A mixture of ligand A (**2** or **4**) (0.33 mmol) and B (**1**, **3**, or **8**) (0.33 mmol) in 10 mL of 1,2-dichloroethane was added dropwise to a solution of the platinum precursor $[Pt(cod)Cl_2]$ (125 mg, 0.33 mmol) in 5 mL of 1,2-dichloroethane at room temperature. A $^{31}P\{^1H\}$ NMR spectrum recorded after 5 min indicated the presence of only heteroligated species.

X-ray Crystallography. Crystallographic data collected for Pt(II) complexes **5a−b**, **6a−b**, **7a−b**, **9**, and **10** is summarized in Table 2. Single crystals of semi-open complexes suitable for crystallographic analysis were grown in an NMR tube from a dichloromethane solution layered with diethyl ether. Closed complexes were grown by slow evaporation (ca. 3 days) from dichloromethane in NMR tubes. Single crystals were mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated MoK\R radiation and CuK\R for **6b**. Data were collected using Bruker APEXII detector and processed using APEX2 from Bruker. All structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions, but not refined. Their

positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

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Supporting Information Available: Crystallographic data for complexes **5a**−**b**, **6a**−**b**, **7a**−**b**, **9**, and **10** in cif file format. This material is available free of charge via the Internet at http://pubs.acs.org.