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Chelating Effect as a Driving Force for the Selective Formation of Heteroligated Pt(II) Complexes with Bidentate Phosphino-Chalcoether Ligands

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The halide-induced ligand rearrangement reaction (HILR) has been employed to provide selective and exclusive in situ formation of heteroligated Rh(I), Pd(II), and Pt(II) complexes with bidentate phosphino-chalcoether ligands. To gain insights on the nature of this unique reaction, we explored this process via the stepwise addition of bidentate phosphino-chalcoether (P, X; X = S or Se) and relevant monodentate phosphine ligands with a Pt(II) metal precursor. The corresponding monoligated complexes were obtained in quantitative yields by reacting 1 equiv of a P, X bidentate ligand with Pt(II) and were fully characterized via single crystal X-ray diffraction studies and heteronuclear (^{31}P, ^{77}Se, and ^{195}Pt) NMR spectroscopy in solution. These species were further reacted with a second equivalent of either a bidentate ligand or the monodentate ethyl diphenylphosphine ligand, resulting in the clean formation of the heteroligated species or, in the case of the monodentate ligand with an electron-withdrawing bidentate ligand, a mixture of products. On the basis of competitive exchange reactions between these heteroligated, homoligated, and monoligated complexes, we conclude that ligand chelation plays a crucial role in the Pt(II) HILR. The in situ preferable formation of the stable monoligated complex allows for ligand sorting to occur in these systems. In all cases where the heteroligated product results, the driving force to these species is ligand chelation.

Introduction

Coordination chemistry-based approaches for constructing supramolecular structures are well-established, with three general substrategies emerging: the directional bonding,[1] symmetry interaction,[2] and weak-link approaches.[3] While the former two approaches result in rigid structures with well-defined cavities, the weak-link approach (WLA) is unique as it yields flexible species where the distances between the chemically active functionalities can be modulated via reversible chemistry on metal centers coordinated to hemilabile ligands (**1**−**6**, Scheme 1).[4] Metals that have been explored in the context of the WLA include Rh(I),[5] Ru(II), [6] Pd(II),[5a,f,7]

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(1) (a) Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifenberger, R. *Science* **1996**, *272*, 1323. (b) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1989**, *111*, 5962. (c) Klosterman, J. K.; Yamauchi, Y.; Fujita, M. *Chem. Soc. Rev.* **2009**, *38*, 1714. (d) Lee, S. J.; Lin, W. *Acc. Chem. Res.* **2008**, *41*, 521. (e) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (f) Lu, Z.; Knobler, C. B.; Furukawa, H.; Wang, B.; Liu, G.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *131*, 12532. (g) Piermattei, A.; Giesbers, M.; Marcelis, A. T. M.; Mendes, E.; Picken, S. J.; Crego-Calama, M.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **2006**, *45*, 7543. (h) Spokoyny, A. M.; Kim, D.; Sumrein, A.; Mirkin, C. A. *Chem. Soc. Rev.* **2009**, *38*, 1218. (i) Wurthner, F.; You, C.-C.; Saha-Moller Chantu, R. *Chem. Soc. Rev.* **2004**, *33*, 133. (j) Amijs, C. H. M.; van Klink, G. P. M.; van Koten, G. *Dalton Trans.* **2006**, 308.

(2) (a) Albrecht, M. *Chem. Soc. Rev.* **1998**, *27*, 281. (b) Faiz, J. A.; Heitz, V.; Sauvage, J.-P. *Chem. Soc. Rev.* **2009**, *38*, 422. (c) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349. (d) Flamigni, L.; Collin, J.-P.; Sauvage, J.-P. *Acc. Chem. Res.* **2008**, *41*, 857. (e) Lehn, J.-M. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 4763. (f) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2008**, *130*, 11423. (g) Stoddart, J. F. *Chem. Soc. Rev.* **2009**, *38*, 1521.

(3) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022.

(4) (a) Gianneschi, N. C.; Bertin, P. A.; Nguyen, S. T.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 10508. (b) Gianneschi, N. C.; Cho, S.-H.; Nguyen, S. T.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5503. (c) Gianneschi, N. C.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 1644. (d) Masar, M. S., III; Gianneschi, N. C.; Oliveri, C. G.; Stern, C. L.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 10149. (e) Oliveri, C. G.; Gianneschi, N. C.; Nguyen, S. T.; Mirkin, C. A.; Stern, C. L.; Wawrzak, Z.; Pink, M. *J. Am. Chem. Soc.* **2006**, *128*, 16286. (f) Yoon, H. J.; Heo, J.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 14182. (g) Yoon, H. J.; Mirkin, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 11590.

(5) (a) Eisenberg, A. H.; Ovchinnikov, M. V.; Mirkin, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 2836. (b) Farrell, J. R.; Eisenberg, A. H.; Mirkin, C. A.; Guzei, I. A.; Liable-Sands, L. M.; Incarvito, C. D.; Rheingold, A. L.; Stern, C. L. *Organometallics* **1999**, *18*, 4856. (c) Farrell, J. R.; Mirkin, C. A.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 465. (d) Gianneschi, N. C.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 5326. (e) Jeon, Y.-M.; Heo, J.; Brown, A. M.; Mirkin, C. A. *Organometallics* **2006**, *25*, 2729. (f) Wiester, M. J.; Mirkin, C. A. *Inorg. Chem.* **2009**, *48*, 8054.

(6) Kuwabara, J.; Stern, C. L.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 10074.

(7) (a) Eisenberg, A. H.; Dixon, F. M.; Mirkin, C. A.; Stern, C. L.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **2001**, *20*, 2052. (b) Spokoyny, A. M.; Reuter, M. G.; Stern, C. L.; Ratner, M. A.; Seideman, T.; Mirkin, C. A. *J. Am. Chem. Soc.* **2009**, *131*, 9482.

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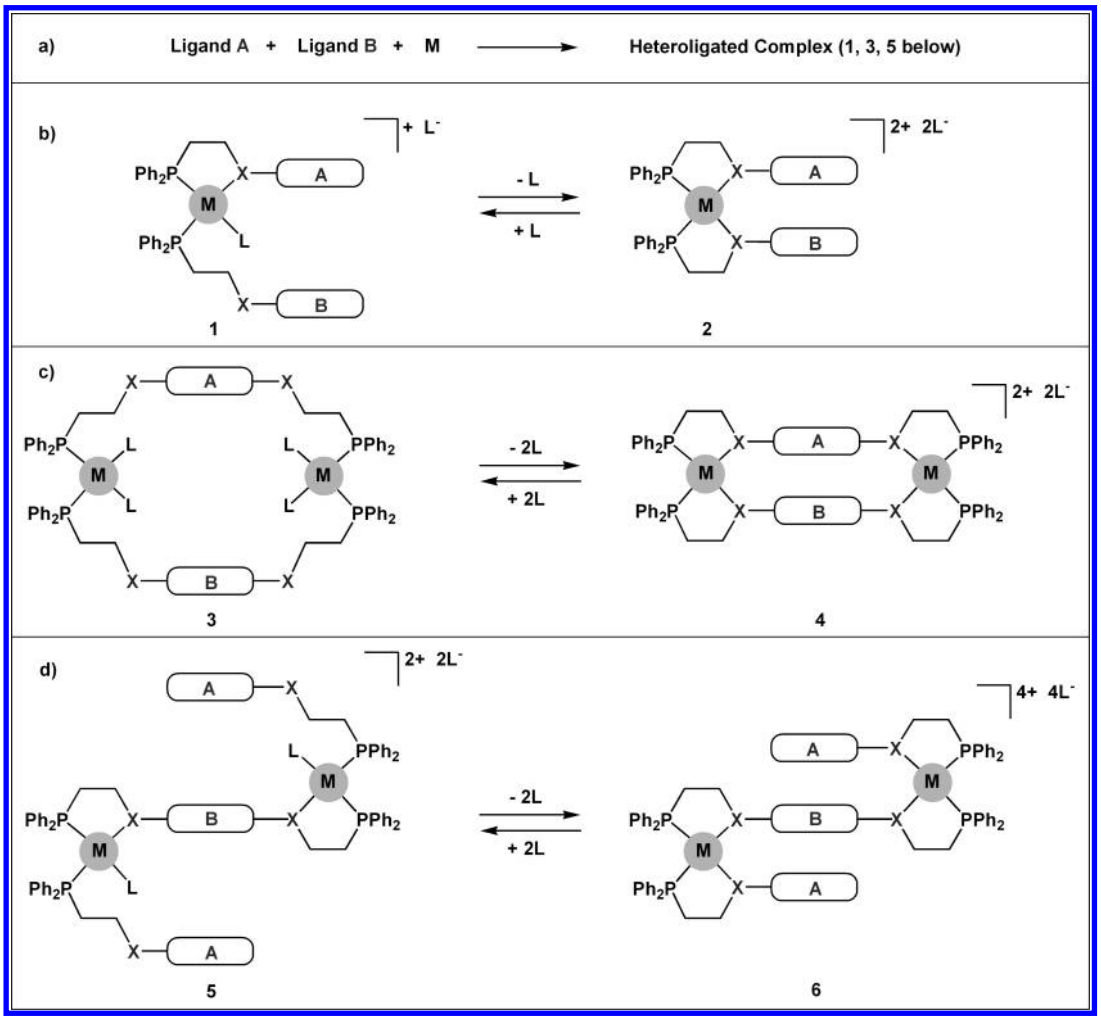
Scheme 1. Weak-Link Approach (WLA) to Making Heteroligated Structures[a]



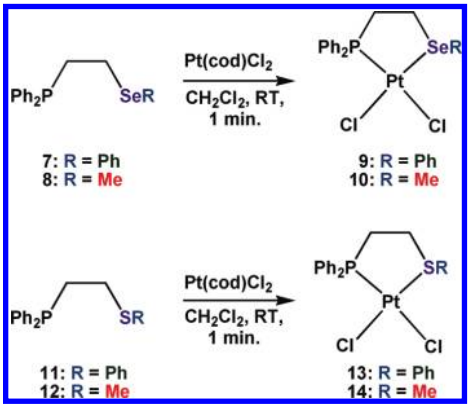
[a] (a) The WLA can be used to make heteroligated structures in quantitative yield via a multicomponent assembly process that involves bidentate ligands and a metal precursor (M). This makes the WLA an ideal method for the construction of a wide variety of coordination complexes including: (b) tweezers **2**, (c) macrocycles **3** and **4**, and (d) triple-layer complexes **6**. The geometry of the complexes can be further manipulated via reversible chemistry on the metal regulatory sites coordinated to hemilabile ligands. Here, X represents the "weak-link" moiety (usually a chalcoether or amine) and A and B are functional groups (e.g., catalytic center,[4d−f] or recognition site,[11] etc.). When A = B the resulting complex is homoligated. When L (an elemental anion or small molecule) is coordinated to the metal center, the complex is "semi-open" (**1** and **5**) or "fully open" (**3**). Conversely, **2**, **4**, and **6** are "closed" complexes.

Ir(I),[8] Cu(I),[9] and Pt(II).[10] Since Pt(II) often provides structures that are resistant to degradation in air, it has been the focus of many recent studies.[7b,10] The hemilabile, bidentate ligands commonly used to synthesize WLA systems employ strong-binding phosphines and weak-binding sites that incorporate chalcoethers (O, S, or Se) and amines. The diverse toolbox of metals and ligands explored thus far has resulted in the synthesis of increasingly sophisticated molecular architectures including tweezers (**2**, Scheme 1b),[7a] triangular prisms,[8] macrocycles (**3** and **4**, Scheme 1c),[5a,d,f] and triple-layer complexes (**6**, Scheme 1d).[5e]

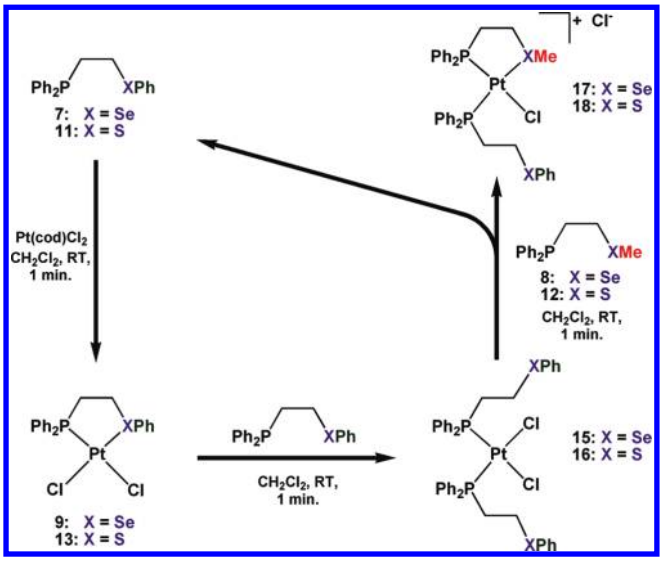
While studying WLA systems, we discovered the halide-induced ligand rearrangement reaction (HILR), a process involving the above-mentioned d^8 transition metals and bidentate, hemilabile ligands that is dependent on the presence of a halide ion and allows for the quantitative formation of heteroligated structures (Scheme 1).[11] This type of multicomponent self-assembly (Scheme 1a) is unusual in Pt(II) coordination chemistry.[10,12] While 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,[5b,c] we showed that Pt(II) systems can employ P, S and/or phosphine-selenoether (P, Se) ligands to make A-Pt(II)-B heteroligated structures. Further investigation has led us to conclude that the strength of the binding

(8) Ovchinnikov, M. V.; Holliday, B. J.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 4927.
(9) Masar, M. S., III; Mirkin, C. A.; Stern, C. L.; Zakharov, L. N.; Rheingold, A. L. *Inorg. Chem.* **2004**, *43*, 4693.
(10) (a) Spokoyny, A. M.; Rosen, M. S.; Ulmann, P. A.; Stern, C.; Mirkin, C. A. *Inorg. Chem.* **2010**, *49*, 1577. (b) Ulmann, P. A.; Brown, A. M.; Ovchinnikov, M. V.; Mirkin, C. A.; DiPasquale, A. G.; Rheingold, A. L. *Chem.—Eur. J.* **2007**, *13*, 4529.
(11) (a) Brown, A. M.; Ovchinnikov, M. V.; Stern, C. L.; Mirkin, C. A. *J. Am. Chem. Soc.* **2004**, *126*, 14316. (b) Oliveri, C. G.; Ulmann, P. A.; Wiester, M. J.; Mirkin, C. A. *Acc. Chem. Res.* **2008**, *41*, 1618.
(12) (a) Baxter, P.; Lehn, J. M.; DeCian, A.; Fischer, J. *Angew. Chem.* **1993**, *105*, 92. (b) Baxter, P. N. W.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Chem.—Eur. J.* **1999**, *5*, 113. (c) Kuil, M.; Goudriaan, P. E.; Van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Commun.* **2006**, 4679. (d) Schmittel, M.; Kalsani, V. *Top. Curr. Chem.* **2005**, *245*, 1. (e) Yoshizawa, M.; Nagao, M.; Kumazawa, K.; Fujita, M. *J. Organomet. Chem.* **2005**, *690*, 5383.

Scheme 2. Synthesis of Phosphino-Selenoether (P, Se) and Phosphino-Thioether (P, S) Monoligated Complexes



Scheme 3. Formation of Heteroligated Complexes with the Electron-Withdrawing XPh Ligand **7** or **11** (X = Se or S)[a]



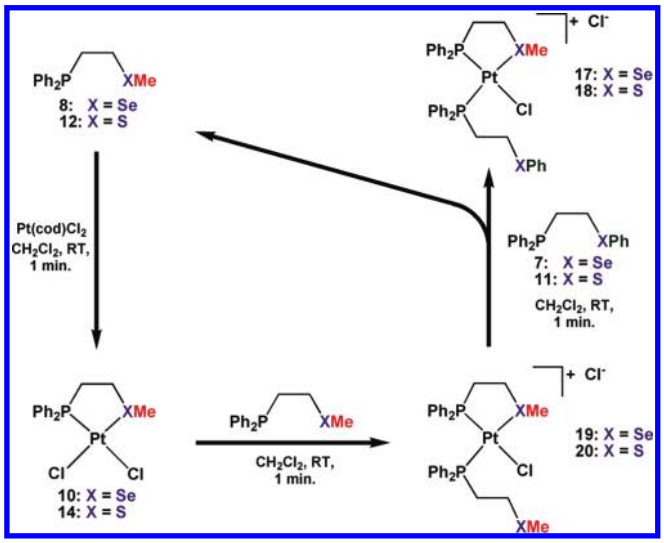
[a] Addition of 1 equiv of the electron-donating ligand **8** or **12** to the homoligated complex **15** or **16** results in the formation of the heteroligated semi-open species **17** or **18**, and the release of 1 equiv of the electron-withdrawing ligand **7** or **11**, respectively.

interaction between the Pt(II) and the chalcogen, modulated via the aryl or alkyl moiety on the chalcoether, is crucial for the formation of these heteroligated motifs.[10,13]

We are interested in developing a fundamental understanding of the critical factors underlying the formation of the heteroligated species in Pt(II) WLA complexes, which have remained unclear until now. In general, controlling the assembly of multicomponent systems remains an underdeveloped area of research.[12,14] Through a stepwise addition of ligands to a Pt(II) precursor, we now show that the bidentate nature of these ligands is crucial for the clean formation of the heteroligated species. The ligand's chelating ability drives the first step of the ligand addition to the Pt(II) metal toward the clean, preferential formation of the monoligated Pt(II) chelate. If this chelation is strong, the desired heteroligated product is observed when a second bidentate ligand (P, Se or P, S) with a

(13) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759.
(14) Bar, A. K.; Mostafa, G.; Mukherjee, P. S. *Inorg. Chem.* **2010**, *49*, 7647.

Scheme 4. Formation of Heteroligated Complexes with the Electron-Donating XMe Ligand **8** or **12** (X = Se or S)[a]



[a] Addition of 1 equiv of the electron-withdrawing ligand **7** or **11** to the homoligated, semi-open complex **19** or **20** results in the formation of the heteroligated semi-open species **17** or **18**, and the release of 1 equiv of the electron-donating ligand **8** or **12**, respectively. The experiments with the thioether ligands were performed in dichloromethane, and those with the selenoether ligands, in 1,2-dichloroethane.

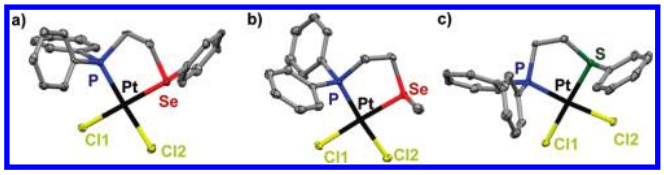


Figure 1. Crystal structures of complexes **9**, **10**, and **13**, respectively, drawn with 50% thermal ellipsoid probability. The crystal structure of complex **14** was previously reported by Yang et al.[19] When applicable, only one stereoisomer in the unit cell is shown. In all cases, hydrogens, solvent molecules, and anions are omitted for clarity. Platinum atoms are black; sulfur, green; selenium, red; phosphorus, blue; and carbon, gray. See Table 1 for selected bond lengths and angles. Crystallographic information can be found in the Supporting Information, Table S1.

weaker chalcoether chelate is introduced. If this first chelation is weak, the second bidentate ligand must be a strong chelator to obtain the desired heteroligated product. Furthermore, when a non-chelating phosphine is introduced to the monoligated complex, heteroligated structures are not always observed. Competitive displacement reactions indicate that the first chelation, forming the monoligated product, has a significantly larger stabilization on the metal than does the second ligand. The stability of the monoligated complexes allows for ligand sorting to occur in the HILR, which we think is a crucial aspect in approaching the design of more sophisticated structures in this family of complexes. The extent of stabilization of monoligated complexes is dependent on the electron-donating or -withdrawing nature of the functionality appended to the chalcoether. Here we examine how ligand electronics and overall chelating ability are intimately related, resulting in the clean assembly of Pt(II) heteroligated WLA species, providing important fundamental insights into the coordination chemistry of Pt(II) with phosphino-chalcoether ligands and the above-mentioned multicomponent self-assembly processes.

Table 1. Selected Bond Lengths and $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$Chemical Shifts for Complexes **9** through **14**

compound	Pt−P (Å)	Pt−X (Å)	Pt−Cl1 (Å)[a]	Pt−Cl2 (Å)[a]	$^{31}P\{^1H\}$ (ppm)	$^{77}Se\{^1H\}$ (ppm)
9	2.205(2)	2.3727(7)	2.319(2)	2.352(2)	39.6	499 (d)
10	2.212 (1)	2.3726(4)	2.3309(8)	2.372(1)	39.6	352 (d)
13	2.2175(5)	2.2600(6)	2.3229(6)	2.3665(4)	39.5	
14	2.210(4)	2.256(4)	2.325(3)	2.367(4)	39.6	

[a] Cl1 is trans to the chalcogen (X) and Cl2 is cis to X (X = Se or S).

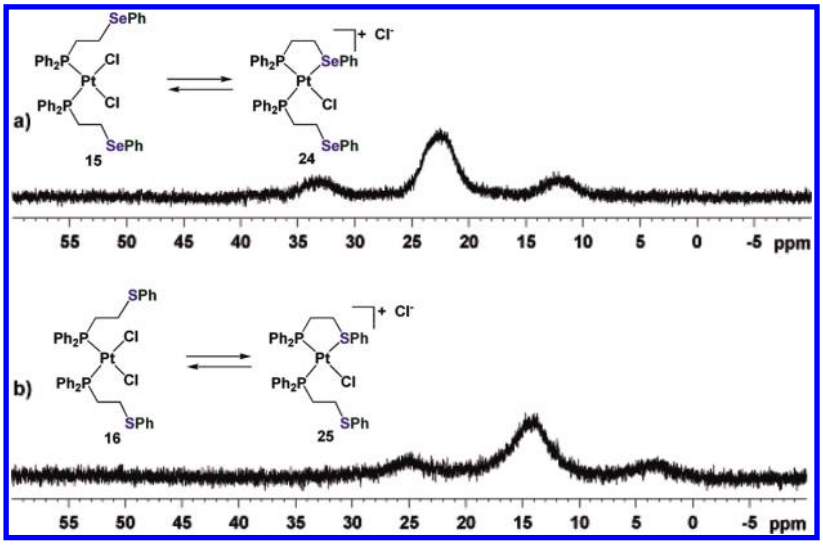


Figure 2. (a) $^{31}P\{^1H\}$ NMR spectra of complex **15** at room temperature. (b) $^{31}P\{^1H\}$ NMR spectra of complex **16** at room temperature.

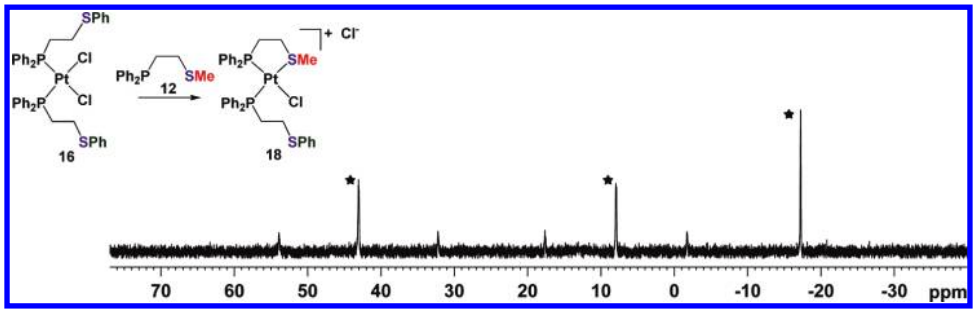


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of the products formed by adding ligand **12** to complex **16**. The main resonances of interest are marked with a star, and the associated ^{195}Pt satellite resonances are located about 10 ppm upfield and downfield of the main resonance.

Results and Discussion

Monoligated Complexes. A general synthesis for all monoligated complexes entails mixing 1 equiv of the desired hemilabile ligand **7**, **8**, **11**, or **12**, prepared via literature methods,[10a,15] with the Pt(II) precursor (Pt(cod)Cl_2, cod = cyclooctadiene, 1 equiv) in dichloromethane (CH_2Cl_2), resulting in quantitative formation of complexes **9**, **10**, **13**, and **14** within a few minutes (Scheme 2). $^{31}P\{^1H\}$ NMR and, where appropriate, $^{77}Se\{^1H\}$ NMR spectroscopies were used to probe the environment of the strong- and weak-binding moieties, respectively. Monoligated complex **9** exhibits a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ 39.6 with characteristic Pt satellites (J_{P-Pt} = 3580 Hz)[10a,16] and a doublet in the $^{77}Se\{^1H\}$ NMR spectrum at δ 499 (J_{Se-P} = 10 Hz) also with characteristic and well-resolved ^{195}Pt satellites (J_{Se-Pt} = 588 Hz).[10a,17] The singlet in the $^{31}P\{^1H\}$ NMR spectrum for monoligated complex **10** has a similar chemical shift of δ 39.6 (J_{P-Pt} = 3650 Hz), while the doublet in the $^{77}Se\{^1H\}$ NMR spectrum at δ 352 (J_{Se-P} = 13 Hz, J_{Se-Pt} = 477 Hz) is quite different, consistent with the significantly larger electron-donating ability of the SeMe group compared to the SePh group. Consistent with this hypothesis, the Pt−P coupling constant for complex **10** is greater than that of complex **9**.[18] Similarly, the thioether analogues of **9** and **10**, **13** and **14**, respectively, exhibit $^{31}P\{^1H\}$ NMR chemical shifts of δ 39.5 (J_{Pt-P} = 3590 Hz) and δ 39.6 (J_{Pt-P} = 3590 Hz), consistent with the conclusion that the electronic environment of the phosphine is not greatly affected by the electron-donating ability of the substituent on the chalcoether

(15) Cunningham, T. J.; Elsegood, M. R. J.; Kelly, P. F.; Smith, M. B.; Staniland, P. M. *Dalton Trans.* **2010**, *39*, 5216.
(16) White, S.; Kalberer, E. W.; Bennett, B. L.; Roddick, D. M. *Organometallics* **2001**, *20*, 5731.
(17) (a) Hassan, F. S. M.; McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1501. (b) Briggs, J. R.; Crocker, C.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1981**, 575.
(18) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

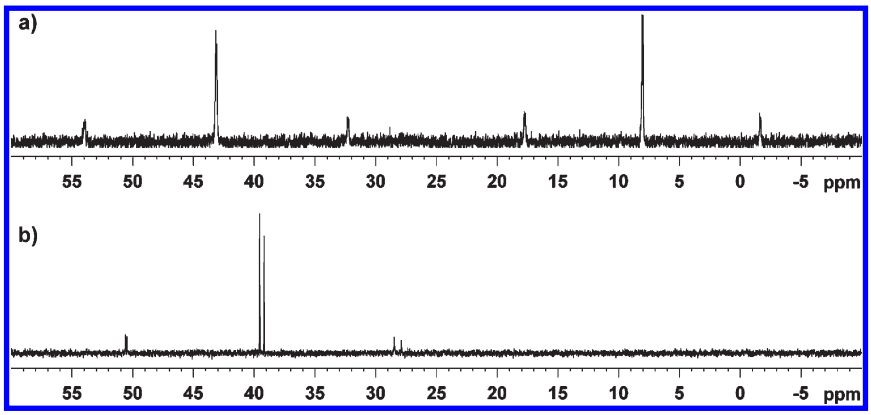
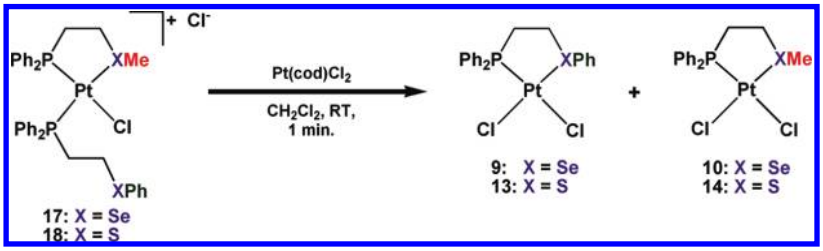
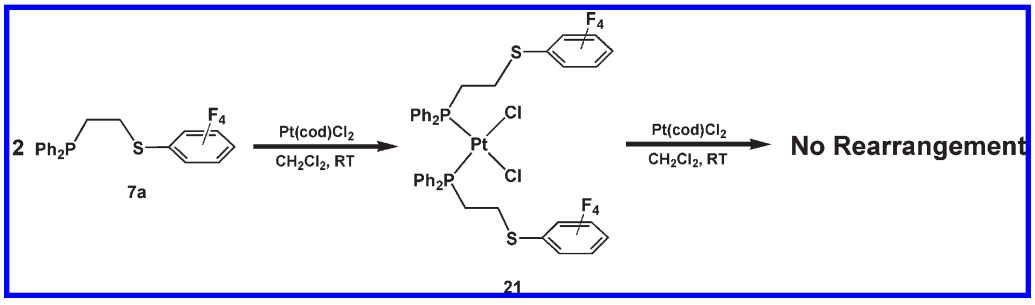


Figure 4. (a) $^{31}P\{^{1}H\}$ NMR spectra of complex **18**. (b) Upon addition of 1 equiv of $Pt(cod)Cl_2$ to complex **18**, the monoligated complexes **13** and **14** form.

Scheme 5. Upon Addition of a Second Equivalent of $Pt(cod)Cl_2$ to the Heteroligated Complex **17** or **18**, the Monoligated Complexes **9** and **10** or **13** and **14** Form, Respectively



Scheme 6. Upon Addition of a Second Equivalent of $Pt(cod)Cl_2$ to the Fully-Open Complex **21**, No Reaction Occurs



moiety. Electrospray ionization mass spectroscopy, single crystal X-ray diffraction studies, and elemental analyses of complexes **9**, **10**, **13**, and **14** confirmed their composition.

It is noteworthy that only species **9**, **10**, **13**, and **14** form under the reaction conditions outlined above; there are no observable quantities of the diligated species, which suggests that the formation of the monoligated complexes is preferential over a mixture of the homoligated analogues **15**, **16**, **19**, and **20** (Schemes 3 and 4) and the Pt(II) precursor under these conditions (note that the term homoligated is used to designate that 2 equiv of the same P, X ligands are coordinated to one metal center). This clean formation of the monoligated product is driven by the chelating ability of ligands **7**, **8**, **11**, and **12**, respectively (Scheme 2).

Complexes **9**, **10**, **13**, and **14** were further characterized by single-crystal X-ray diffraction studies (Figure 1). A comparison between the Pt−Cl1 bond for the Cl trans to the chalcoether moiety in complexes **9** and **10** reveals that the chalcoether with the more electron-donating substituent exhibits a larger trans influence than its electron-withdrawing analogue as evidenced by the elongation of the Pt−Cl1 bond in complex **10** as compared with the analogous Pt−Cl1 bond in complex **9**, 2.3309(8) Å and 2.319(2) Å, respectively (Table 1). This is consistent with the conclusion that the Pt−Se interaction in **10** is stronger than in **9**.

A similar conclusion can be made for the analogous thioether complexes **13** and **14**, where the Pt−Cl1 bond in **13** is shorter than that in **14**, 2.3229(6) Å and 2.325(3) Å, respectively. The corresponding Pt−S bond lengths reflect this trend, with the Pt−S bond being longer in complex **13**, at 2.2600(6) Å, than in **14**, at 2.256(4) Å. The difference in Pt−X bond strengths between complexes with an electron-donating or withdrawing ligand proves to be important when constructing diligated complexes, as described below.

Diligated (Homoligated or Heteroligated) Complexes. The stepwise addition of hemilabile ligands (P, S or P, Se) to either the monoligated complexes with an electron-withdrawing XPh (X = Se or S) group, **9** or **13**, or an electron-donating XMe (X = Se or S) group, **10** or **14**, as depicted in Schemes 3 and 4, ultimately leads to clean formation of the heteroligated species in all cases.

The species formed upon the addition of a second P, X ligand to complex **9** was characterized by NMR spectroscopy (Figure 2a). For example, the addition of a second

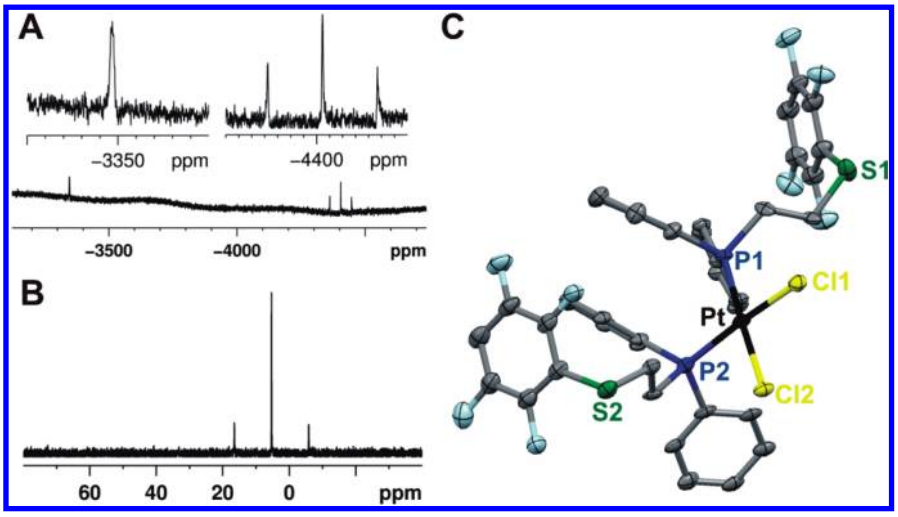
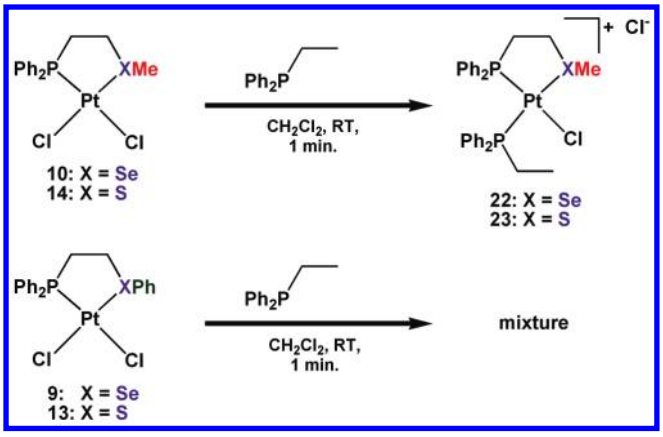


Figure 5. Upon the addition of 1 equiv of Pt(cod)Cl_2 to complex **21**, no rearrangement occurs as shown in the (a) ^{195}Pt NMR spectra of complex **21** where the resonance for the Pt(II) precursor is observed at ~ −3350 ppm and that of complex **21** is observed at ~ −4400 ppm, and (b) $^{31}P\{^1H\}$ NMR spectra of complex **21**. (c) Crystal structure of complex **21**, drawn with 50% thermal ellipsoid probability. Hydrogens and solvent molecules are omitted for clarity. Platinum atoms are black; sulfur, green; phosphorus, blue; and carbon, gray. Crystallographic information can be found in the Supporting Information, Table S1.

Scheme 7. Upon Addition of 1 equiv of the Monodentate Ligand Ethyl Diphenylphosphine (EDP) to Either Complex **10** or **14**, the Heteroligated Complex **22** or **23** Forms, Respectively; However, When EDP Is Added to Either Complex **9** or **13**, the Result Is a Mixture of Products



equivalent of the electron-withdrawing ligand **7** to a stirring solution of complex **9** in dichloromethane results in the formation of a complex that exhibits a broad resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 24.8 (J_{P-Pt} = 3430 Hz). This resonance has been assigned to the homoligated complex **15** (Figure 2a) and compares well with isolectronic and isostructural model complexes.[10b] The analogous thioether complex **16** also exhibits a broad resonance in the $^{31}P\{^1H\}$ NMR spectrum, significantly upfield of the resonance for **15** (Figure 2b), observed at δ 14.36 (J_{P-Pt} = 3530 Hz) (Figure 2b).

This chemical shift for complex **15** roughly lies between the $^{31}P\{^1H\}$ NMR resonance of the closed, homoligated SePh-Pt(II)-SePh complex (Supporting Information, Figures 1 and 2), in which the selenoethers in both P, Se hemilabile ligands are chelating to the Pt(II) center, that occurs at δ 49.7 (J_{P-Pt} = 4180 Hz) and the resonance at δ 12.3 assigned to the unbound chalcoether in the semiopen complex **17** (Figure 2). This indicates that the interaction of the selenoether moiety with the Pt center in complex **15** is dynamic, where one chalcoether is coordinating and

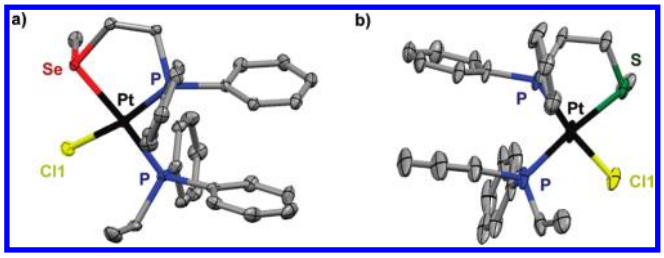


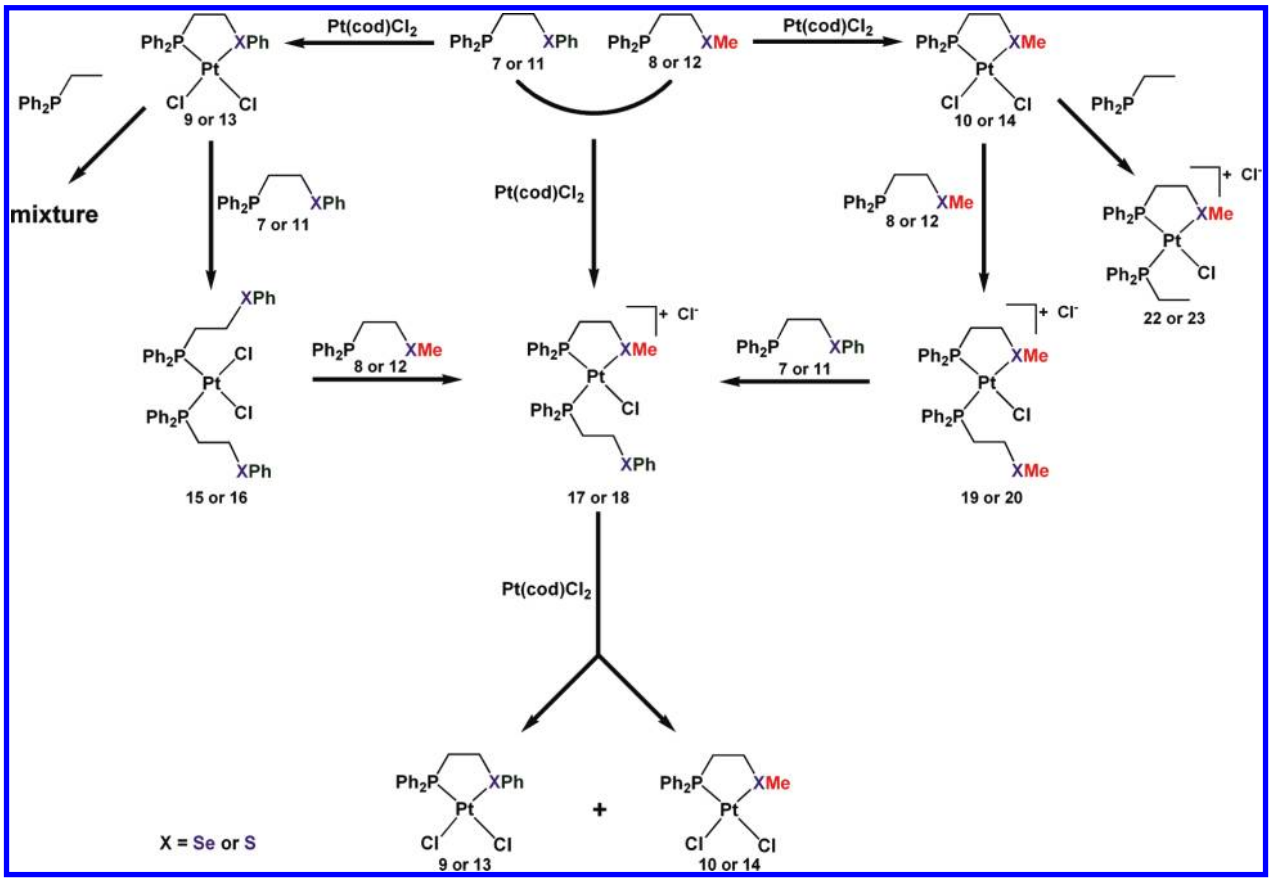
Figure 6. Crystal structures of **19** and **20**, respectively, drawn with 50% thermal ellipsoid probability. In all cases, hydrogens, solvent molecules, and anions are omitted for clarity. Only one stereoisomer in the unit cell is shown. Platinum atoms are black; sulfur, green; selenium, red; phosphorus, blue; and carbon, gray. Crystallographic information can be found in the Supporting Information, Table S1.

releasing at the Pt(II) center.[20] Cooling a solution of complex **15** or **16** to −60 °C in dichloromethane-d_2 freezes out various species, as observed via $^{31}P\{^1H\}$ NMR spectroscopy, although many resonances are still broad. In the case of the selenoether complex **15** (Scheme 3), the semiopen complex appears as two broad resonances at −60 °C, with the chelating ligand **7** at δ 43.7 (J_{P-Pt} = 3500 Hz) and the non-chelating ligand **7** at δ 9.17 (J_{P-Pt} = 3160 Hz), and the single resonance at δ 50.1 (J_{P-Pt} = 3190 Hz) can be assigned to the fully closed complex. In the case of the thioether complex **16** (Figure 3) at −60 °C, only the semiopen species is observed as two broad resonances in the $^{31}P\{^1H\}$ NMR spectrum, with the chelating ligand **11** at δ 45.2 (J_{P-Pt} = 3500 Hz) and the non-chelating ligand **11** at δ 8.08 (J_{P-Pt} = 3130 Hz). The presence of the closed complex at −60 °C in the $^{31}P\{^1H\}$ NMR spectrum of complex **15** but not for complex **16**, coupled with the differences in their room temperature $^{31}P\{^1H\}$ NMR spectra (Figure 2), suggests that

(19) Yang, J.; Huang, D.; Li, G.; Zhang, L. *Huaxue Xuebao* **1993**, *51*, 1145.

(20) (a) Barthel-Rosa, L. P.; Maitra, K.; Nelson, J. H. *Inorg. Chem.* **1998**, *37*, 633. (b) Liu, J.; Jacob, C.; Sheridan, K. J.; Al-Mosule, F.; Heaton, B. T.; Iggo, J. A.; Matthews, M.; Pelletier, J.; Whyman, R.; Bickley, J. F.; Steiner, A. *Dalton Trans.* **2010**, *39*, 7921.

Scheme 8. Comprehensive Scheme Summarizing the Reactions of Hemilabile Phosphino-Chalcoether Ligands with Pt(II)



the selenoether-Pt(II) interaction is slightly stronger than the analogous thioether-Pt(II) interaction.

When ligand **8** is added to complex **15**, it chelates to the Pt(II) center, displacing 1 equiv of ligand **7** to form **17**, which can be unequivocally confirmed by $^{31}P\{^1H\}$ NMR spectroscopy as evidenced by a singlet at δ −15.7. Complex **17** does not undergo exchange in solution like complex **15**, a consequence of the significantly stronger chelating ability of ligand **8** as compared with its aryl analogue, **7**. Indeed this chelation is a significant driving force for the formation of the heteroligated complex **17**. This provides a means of rearrangement, or ligand sorting in this process. Note that it is known that complex **9** will react with ligand **8** directly to form the heteroligated product **17**.[10a]

The monoligated complex **10** reacts with 1 equiv of electron-donating ligand **8** to form the homoligated complex **19**, which exhibits a broad resonance at δ 44.1 ($J_{Pt\text{-}P}$ = 3300 Hz) in its $^{31}P\{^1H\}$ NMR spectrum. With complex **19**, one chalcoether is under dynamic exchange between metal bound and unbound states,[10] which is characteristic of isolectronic and isostructural model complexes.[10b] Upon addition of 1 equiv of ligand **7** to complex **19**, the heteroligated, semiopen complex **17** is formed, releasing 1 equiv of the SeMe ligand as evidenced by a diagnostic resonance for ligand **8** at δ −15.7 in the $^{31}P\{^1H\}$ NMR spectrum (Scheme 4). Consequently, it is only when ligands of different chelating abilities are present that the heteroligated species is formed.

Chelating Effect. The results of the competition experiments discussed thus far (Schemes 3 and 4) indicate that the chelating ability of the ligand is crucial for the formation of the heteroligated product. In support of this, a heteroligated semiopen complex will form the corresponding monoligated complexes if a second equivalent of Pt(cod)Cl_2 is introduced (Figure 4, Scheme 5). This qualitatively indicates that the stabilization energy is higher for the binding of the first ligand to the Pt(II) metal center than for the second. It should be noted that when 1 equiv of Pt(cod)Cl_2 is added to solutions of **15**, **16**, **19**, or **20**, that the corresponding monoligated complexes form, **9**, **13**, **10**, or **14**, respectively.

Further evidence of the chelating effect's role in heteroligated complex formation comes from experiments with complex **21**, which is synthesized from the addition of ligand **7a** to Pt(cod)Cl_2 in dichloromethane (Scheme 6). The addition of a second equivalent of the Pt(II) precursor to complex **21** does not result in the formation of two monoligated complexes from this diligated species (Figure 5). Here, both of the thioethers do not coordinate to the Pt(II) center because of the electron-withdrawing perfluorinated substituent, thus precluding rearrangement from occurring.

To directly examine the role of the bidentate ligand, ethyl diphenylphosphine (EDP) was employed as a monodentate, non-chelating analogue. When 1 equiv of EDP was added to the monoligated complex **10** or **14**, the expected heteroligated complex formed in quantitative yield (Scheme 7). Complexes **22** and **23** were characterized by $^{31}P\{^1H\}$ NMR and, where appropriate, $^{77}Se\{^1H\}$ NMR spectroscopy; single-crystal X-ray diffraction studies (Figure 6); and electrospray ionization mass spectrometry.

However, if the EDP was added to complex **9** or **13**, a mixture of products was observed (Scheme 7); that is,

heteroligation did not occur in the same manner as in the previous cases. This reinforces the idea that a chelate comprising a strongly electron-donating moiety stabilizes the Pt(II) center and is a required element for the HILR reaction.

Heteroligated complex formation via the WLA with Pt(II) is summarized in Scheme 8.

Conclusion

While controlled heteroligated species formation has been described as a "challenging design job,"[21] our system employs relatively simple design parameters for the successful synthesis of heteroligated structures in quantitative yield. Unlike other motifs that heavily rely on steric constraints or the coordination preferences of the metal center(s) to achieve heteroligated structures,[21] we have demonstrated that the chelating effect in combination with rationally designed P, X-type hemilabile ligands provides a driving force for heteroligated complex formation. This was established by a series of competitive exchange reactions between heteroligated, homoligated, and monoligated complexes, which are either products or intermediates in the Pt(II) HILR reaction. The preferential formation of the monoligated species is a critical factor for ligand rearrangement, which provides stable intermediates. Clean formation of heteroligated complexes with one bidentate and one monodentate ligand occurs only if the bidentate ligand strongly chelates to the Pt(II) metal center. Consequently, attempts to make heteroligated complexes result in a mixture of products when a monodentate ligand is combined with a weakly chelating bidentate ligand in the same complex. Overall, this understanding may help in constructing supramolecular assemblies based on the weak-link approach (WLA) and design other ligands that can, with the right metals, lead to similar processes. Finally, the rationale presented here suggests that the influence of the chelating effect in this system should be applicable not only to P, X-type ligands, but to other hemilabile ligands with a variety of metals.

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 at ambient conditions. Dichloromethane (DCM), diethyl ether, ethanol, and hexanes 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. Ligands **7**,[10a] **7a**,[22] **8**,[10a] **11**,[10b] and **12**,[10b] were synthesized according to previously described procedures. All NMR spectra were recorded on a Bruker Advance 400 MHz NMR spectrometer. ^{1}H spectra were referenced to residual proton and carbon resonances in the deuterated solvents. ^{31}P{^{1}H}, ^{77}Se{^{1}H}, and ^{195}Pt NMR spectra were referenced to H_3PO_4, Me_2Se, and Na_2PtCl_6 standards, respectively. For ^{77}Se acquisition, relaxation delays of 0.01 s or less were usually sufficient because of the fast relaxation of the Pt(II) complexes studied. Electrospray ionization (ESI) mass spectra were recorded on a Micromass Quatro II triple quadrupole mass spectrometer or an Agilent LC/MS MSD1100 mass spectrometer. Elemental analyses were performed by Quantitative Technologies, Whitehouse, NJ. [The inability to obtain accurate EA results is not unknown in Pt-containing complexes. Likely, this is due to incomplete combustion and formation of platinum hydroxide and/or platinum carbides as byproducts, which would decrease the experimental values of the carbon and hydrogen content in some samples, as observed.[23]] Single crystals suitable for X-ray diffraction studies were obtained by layering diethyl ether over a dichloromethane solution of the relevant complex.

General Procedure for Formation of Monoligated Complexes. A solution of the ligand (**7**, **8**, **11**, or **12**) (0.33 mmol, 1 equiv) in dichloromethane (5 mL) was added dropwise to a solution of the platinum precursor [Pt(cod)Cl$_2$] (125 mg, 0.33 mmol, 1 equiv) in dichloromethane (5 mL) at room temperature. 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 monoligated complex (in situ ^{31}P{^{1}H} NMR yields = 100%, isolated yields >95%).

General Procedure for Formation of Heteroligated Semiopen Complexes. A solution of ligand A (**7** or **11**) (0.33 mmol, 1 equiv) in dichloromethane (5 mL) was added dropwise to a solution of the platinum precursor [Pt(COD)Cl$_2$] (125 mg, 0.33 mmol, 1 equiv) in dichloromethane (5 mL) at room temperature. The solution was allowed to stir for 5 min before ligand B (**8** or **12**), dissolved in dichloromethane (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{^{1}H} NMR yields = 100%, isolated yields >95%).

General Procedure for Formation of Heteroligated Complexes with One Monodentate Ligand. A solution of the bidentate ligand (**8** or **12**) (0.33 mmol, 1 equiv) in dichloromethane (5 mL) was added dropwise to a solution of the platinum precursor [Pt(cod)Cl$_2$] (125 mg, 0.33 mmol, 1 equiv) in dichloromethane (5 mL) at room temperature. The solution was allowed to stir for 5 min before the monodentate ligand, ethyl diphenylphosphine (EDP), dissolved in dichloromethane (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{^{1}H} NMR yields = 100%, isolated yields >95%).

General Procedure for Conversion of Heteroligated Semiopen Complexes to Monoligated Complexes. A solution of the semiopen heteroligated complex in dichloromethane was prepared as described above. A solution of the platinum precursor [Pt(cod)Cl$_2$] (125 mg, 0.33 mmol, 1 equiv) in dichloromethane (5 mL) at room temperature 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 monoligated complexes (in situ ^{31}P{^{1}H} NMR yields = 100%, isolated yields >95%).

Characterization. **9.** ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C, TMS): δ 8.10−7.40 (m, 15 Ar H), δ 3.09−2.70 (m, 3 Aliph H); δ 2.53−2.35 (m, 1 Aliph H); ^{31}P{^{1}H} NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ 39.6, J_{P-Pt} = 3580 Hz; HRMS (ESI): m/z calcd for $C_{20}H_{19}Cl_2PPtSe$ [M-Cl]$^+$: 600.9804; found: 600.9736; Anal. Calcd for $C_{20}H_{19}Cl_2PPtSe \cdot {}^1/_2CH_2Cl_2$: C, 36.33; H, 2.97. Found: C, 36.72; H, 2.82.

10. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C, TMS): δ 7.95−7.21 (m, 10 Ar H), δ 2.91−2.36 (m, 7 Aliph H); ^{31}P{^{1}H}

(21) De, S.; Mahata, K.; Schmittel, M. *Chem. Soc. Rev.* **2010**, *39*, 1555.
(22) Brown, A. M.; Ovchinnikov, M. V.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4207.
(23) Bennett, M. A.; Canty, A. J.; Felixberger, J. K.; Rendina, L. M.; Sunderland, C.; Willis, A. C. *Inorg. Chem.* **1993**, *32*, 1951.

NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ 39.6, J_{P-Pt} = 3650 Hz; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{17}Cl_2PPtSe$ [*M*-Cl]$^+$: 538.9648; found: 538.9543; Anal. Calcd for $C_{15}H_{17}Cl_2PPtS \cdot {}^3/_2CH_2Cl_2$: C, 28.29; H, 2.88. Found: C, 28.80; H, 2.49.

13. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C, TMS): δ 8.10−7.43 (m, 15 Ar H), δ 3.11−2.78 (m, 2 Aliph H), δ 2.59−2.33 (m, 2 Aliph H); $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ 39.5, J_{P-Pt} = 3590 Hz; HRMS (ESI): *m*/*z* calcd for $C_{20}H_{19}Cl_2PPtS$ [*M*-Cl]$^+$: 553.0360; found: 553.0374; Anal. Calcd for $C_{20}H_{19}Cl_2PPtS \cdot {}^1/_2CH_2Cl_2$: C, 39.03; H, 3.20. Found: C, 39.98; H, 2.94.

14. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C, TMS): δ 7.96−7.10 (m, 10 Ar H), δ 2.99−2.36 (m, 7 Aliph H); $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ 39.6, J_{P-Pt} = 3590 Hz; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{17}Cl_2PPtS$ [*M*-Cl]$^+$: 491.0203; found: 491.0117; Anal. Calcd for $C_{15}H_{17}Cl_2PPtS$: C, 34.23; H, 3.26. Found: C, 34.56; H, 3.21.

21. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C, TMS): δ 7.48−7.03 (m, 22 Ar H), δ 3.13−2.30 (m, 8 Aliph H); $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ 4.99, J_{P-Pt} = 3620 Hz; HRMS (ESI): *m*/*z* calcd for $C_{40}H_{30}Cl_2F_8P_2PtS_2$ [*M*-Cl]$^+$: 1018.0473; found: 1018.0527; Anal. Calcd for $C_{42}H_{44}Cl_2F_8P_2PtS_2$: C, 45.55; H, 2.87. Found: C, 45.04; H, 2.86.

22. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C, TMS): δ 7.79−7.15 (m, 22 Ar H), δ 3.74−2.00 (m, 12 Aliph H); $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ 41.9, J_{P-P} = 13.0, J_{P-Pt} = 3550 Hz; δ 12.8, J_{P-P} = 13.5, J_{P-Pt} = 3150 Hz; HRMS (ESI): *m*/*z* calcd for $C_{29}H_{32}Cl_2P_2PtSe$ [*M*-Cl]$^+$: 753.0559; found: 753.0494; Anal. Calcd for $C_{29}H_{32}Cl_2P_2PtSe \cdot CH_2Cl_2$: C, 41.30; H, 3.93. Found: C, 41.45; H, 3.74.

23. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C, TMS): δ 7.76−7.17 (m, 20 Ar H), δ 4.01−2.05 (m, 12 Aliph H); $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ 43.4, J_{P-P} = 15.2, J_{P-Pt} = 3540 Hz; δ 12.9, J_{P-P} = 15.4, J_{P-Pt} = 3130 Hz; HRMS (ESI): *m*/*z* calcd for $C_{29}H_{32}Cl_2P_2PtS$ [*M*-Cl]$^+$: 705.1114; found: 705.1042; Anal. Calcd for $C_{29}H_{32}Cl_2P_2PtS \cdot {}^1/_3CH_2Cl_2$: C, 46.54; H, 4.35. Found: C, 46.12; H, 4.37.

X-ray Crystallography. Crystallographic data are collected in the Supporting Information, Table S1. Single crystals were mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated Mo Kα or Cu Kα radiation. 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 **9**−**10**, **13**−**14**, **21**−**23** in cif file format. Further details are given in supporting Figures 1 and 2 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.