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General Strategy for the Synthesis of Rigid Weak-Link Approach Platinum(II) Complexes: Tweezers, Triple-Layer Complexes, and Macrocycles

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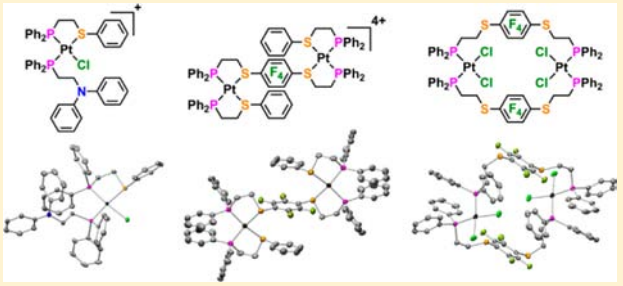
Supporting Information

ABSTRACT: Air-stable, heteroligated platinum(II) weak-link approach (WLA) tweezer and triple-layer complexes that possess P,X−Aryl hemilabile ligands (P^ = $Ph_2PCH_2CH_2$−, X = chalcoethers or amines) have been synthesized via the halide-induced ligand rearrangement (HILR) reaction, using a one-pot, partial chloride-abstraction method. The approach is general and works with a variety of phosphine-based hemilabile ligands; when a P,S−Ph ligand is used as the relatively strongly chelating ligand, heteroligated complexes are formed cleanly when an ether- (P,O−Ph), amine- (P,N−Ph_2), or fluorinated thioether-based (P,S−C_6F_4H) hemilabile ligand is used as the weakly chelating counterpart. The HILR reaction has also been used to synthesize bisplatinum(II) macrocycles free of oligomeric material without having to resort to the high-dilution conditions typical for macrocycle synthesis. This approach is complementary to the traditional WLA to the synthesis of macrocyclic complexes which typically proceeds via fully closed, chloride-free intermediates. The structures of the complexes may be toggled between semiopen (with only one chelating ligand) and fully closed (with both ligands chelating) via the abstraction and addition of chloride.



INTRODUCTION

Within the discipline of coordination chemistry, the weak-link approach (WLA)[1−6] has emerged as a powerful means to assemble complicated supramolecular structures (Scheme 1). Unlike the symmetry-interaction approach (SIA)[7−11] and directional bonding approach (DBA),[12−26] which lead to static, rigid structures, the WLA results in dynamic complexes that may be toggled between rigid and flexible states via the introduction and removal of elemental anions or small-molecule "effectors". Functional units such as catalytic sites, redox-active moieties, host−guest recognition sites, and fluorophores may be incorporated into the ligands in such a way that the structural change results in a marked change in the properties of the complex.[27−33] Allosteric regulation of this type resembles the behavior of many enzymes, and examples of this aspect of biomimicry are otherwise rare in coordination chemistry.[6,34−37]

The WLA for the synthesis of macrocyclic complexes employs symmetric homoditopic ligands that possess rigid cores and two hemilabile[38−41] phosphino−chalcoether (P,X; X = S, O, Se) or phosphino−amine (P,N) moieties (Scheme 1).[2,3,5,6] Upon chelation to a d^8 metal center [e.g., rhodium(I), palladium(II)] and in the absence of coordinating anions, the favored *cis* geometry of the phosphine ligands promotes the clean formation of bimetallic macrocyclic assemblies while preventing the formation of polymeric and oligomeric by-products.[1] A reaction often used in conjunction with the WLA is the halide-induced ligand rearrangement (HILR) reaction,[5,42−45] in which a ligand-sorting process between electron-rich and electron-poor hemilabile ligands leads exclusively to heteroligated structures, thus allowing for an extra level of complexity to be incorporated into WLA architectures (**2**, **3**, **6**, **7**, **8**, and **9**, Scheme 1).

Functional allosteric enzyme mimics synthesized via the WLA rely on the precise positioning of active groups that are incorporated into the hemilabile ligand. This is achieved by using rigid ligands in which the weakly coordinating atom (Scheme 1) is bound directly to an aryl group. In the case of rhodium(I), rigid, heteroligated aryl−aryl complexes may be synthesized cleanly and reliably using P,S−aryl and P,O−aryl ligands as the strong and weak binders, respectively. However, the sensitivity of rhodium(I) WLA complexes to air limits their compatibility with certain reaction environments, and accordingly, a recent focus of our work has been the expansion of the WLA to include the chemistry of more stable d^8 metals such as nickel(II), palladium(II), and platinum(II).[32,43,44,46−50] We have demonstrated that heteroligated tweezers and triple-layer

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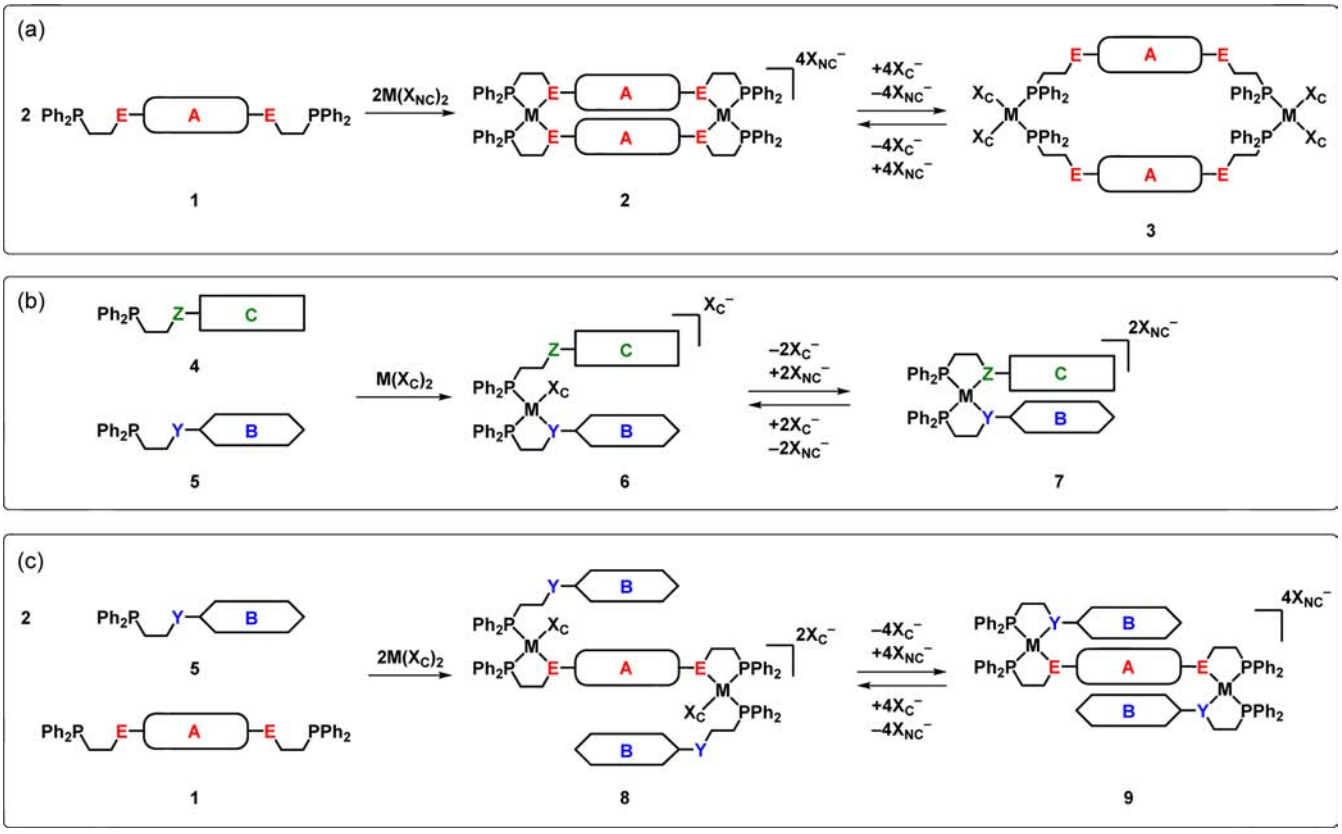
Scheme 1. Weak-Link Approach to the Synthesis of Macrocycles and Heteroligated Tweezer and Triple-Layer Complexes[a]



[a](a) The traditional WLA for the synthesis of macrocycles utilizes ditopic bidentate ligands (**1**) and d^8 metal precursors (M) paired with noncoordinating anions (X_{NC}^-). The synthesis proceeds via the templated formation of a condensed intermediate (**2**) that may be opened reversibly by various coordinating ligands (X_C^-) to form the fully open species (**3**). (b and c) The HILR reaction results in a ligand sorting process that cleanly produces heteroligated species. These may be toggled between semiopen (**6**, **8**) and closed structures (**7**, **9**) via the removal and addition of coordinating anions. E, Y, and Z represent the weak-link ligands, which are usually chalcoethers or amines. A, B, and C can be functional groups (e.g., catalysts, recognition sites, redox active moieties).

complexes form cleanly and spontaneously with palladium(II) and platinum(II) when alkyl- and aryl-based hemilabile ligands are used in combination (e.g., Scheme 2; compound **22**).[43,44,46,47] One shortcoming of this assembly technique is that alkyl-based ligands are inherently flexible and thus unsuitable for the construction of rigid architectures in which supramolecular properties are controlled with structural changes. A general, modular route to rigid, heteroligated aryl−aryl′ palladium(II) and platinum(II) complexes, which is compatible with many functional ligands, is highly desirable. However, typical synthetic approaches to aryl−aryl′ palladium-(II) and platinum(II) complexes have failed so far, resulting in dynamic mixtures which contain multiple species. Herein we report a new method for the clean and quantitative synthesis of rigid, platinum(II) WLA assemblies (Scheme 1; **2**, **3**, **6**, **7**, **8**, **9**) via partial abstraction of chloride in either protic or nonpolar solvents. Using this method, heteroligated tweezers, triple layer complexes, and binuclear macrocycles have been obtained from a variety of aryl-based hemilabile P,S, P,O, and P,N ligands. These complexes serve as models for functional, air-stable WLA systems.

RESULTS AND DISCUSSION

Heteroligated Tweezer Compounds. We focused on simple heteroligated tweezer complexes constructed from phosphine-based (P,X) hemilabile ligands. We explored combinations of aryl-based hemilabile ligands that fulfilled two principal criteria: (a) the difference in chelating strength between the ligands is sufficiently high to favor the clean formation of heteroligated species and (b) the ligands are synthetically accessible, i.e., their incorporation into more complex molecules is relatively straightforward. Thus, the phenyl-terminated thioether ligand $Ph_2PCH_2CH_2SPh$ (P,S−Ph; **10**) was chosen as the strongly chelating ligand (Scheme 2), and three different weakly binding ligands (Scheme 2) were evaluated in order to increase the potential generality of the system: 2,3,5,6-tetrafluorophenyl thioether, $Ph_2PCH_2CH_2SC_6F_4H$ (P,S−C_6F_4H; **11**); phenyl ether, $Ph_2PCH_2CH_2OPh$ (P,O−Ph; **12**); and the diphenylamine derivative, $Ph_2PCH_2CH_2NPh_2$ (P,N−Ph_2; **13**). Importantly, the chemical attachment of these P,X moieties onto functional molecules, for example, porphyrins and salens or large sterically hindering groups, is relatively simple via established synthetic procedures.[51,52]

The dynamic behavior of d^8 metal complexes which possess two hemilabile ligands has been investigated in detail by our group and others.[53−63] For the specific cases of platinum(II)-based tweezer complexes with the general formula $PtCl_2(Ph_2PCH_2CH_2SR)_2$ (R = aryl, alkyl), the equilibria describing the distribution of chloride anions between the inner and outer coordination spheres is shown in Scheme 2b. In general, aprotic solvents such as dichloromethane shift the

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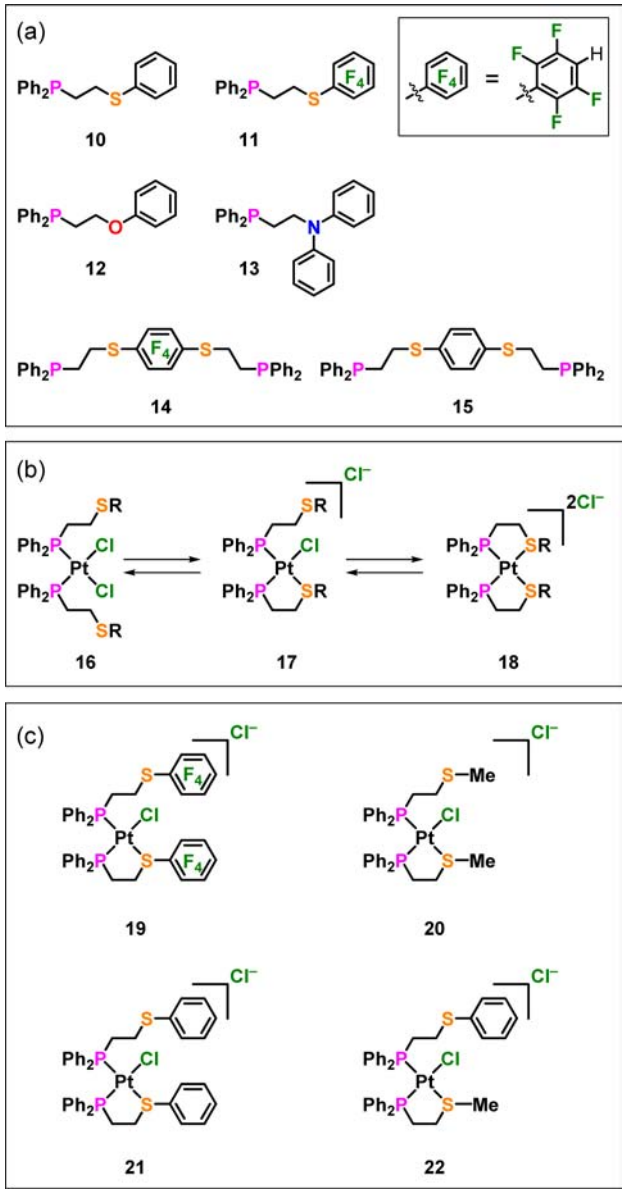
Scheme 2. (a) Model Ligands 10−15 Used in This Study; (b) Distribution of Chloride Anions between the Inner and Outer Coordination Spheres [Fully Open (16), Semiopen (17), and Fully Closed Species (18)]; (c) Examples of Platinum(II) WLA Tweezer Complexes with Weak (19), Strong (20), and Intermediate Strength (21) Chelating P,S Ligands[a]



[a]Complex **22** is a heteroligated alkyl−aryl complex.

equilibria to the left as drawn, favoring fully open species (**16**, Scheme 2b), in which there are two inner-sphere chlorides and both ligands are nonchelating, or semiopen species (**17**) that possess one chelating ligand and one outer-sphere chloride. In protic solvents such as methanol, outer-sphere chloride anions are stabilized by hydrogen bonding, thus shifting the equilibrium to the right and favoring closed species (**18**).[64−66] The distribution of products in solution is also related to the strength of the thioether coordination. In the cases of complexes with weakly coordinating hemilabile ligands (e.g., R = C_6F_4H; **19**), the equilibrium favors fully open or semiopen species. For example, the homoligated complex $PtCl_2(P,S-C_6F_4H)_2$ (**19**), which possesses weakly coordinating ligands, exists as a static, semiopen species in methanol and as a static, fully open species in dichloromethane. On the other hand, closed species are favored when strongly chelating hemilabile ligands (e.g., R = Me; **20**) are used. For example, the homoligated complex $[Pt(P,S-Me)_2]Cl_2$ (**20**), which possesses strongly chelating ligands, exists exclusively as the fully closed species in methanol as determined by $^{31}P\{^1H\}$ NMR spectroscopy, whereas in dichloromethane, a fast "windshield wiper" exchange[67] between equivalent semiopen structures is observed. When ligands of intermediate chelating strength are involved, the behavior lies somewhere between these two extremes. For example, the homoligated complex $PtCl_2(P,S-Ph)_2$ (**21**) dissolved in dichloromethane undergoes dynamic equilibrium between fully open (**16**) and semiopen (**17**) structures as the outer-sphere chloride ion competes with the weakly chelating ligand, whereas in methanol the chlorides are solvated to the extent that dynamic equilibrium between semiopen (**17**) and fully closed (**18**) structures is observed.[64−66]

When a strongly chelating ligand is paired with a relatively weakly chelating ligand (e.g., P,S−Me and P,S−Ph; **22**) in dichloromethane, the equilibrium favors the formation of *heteroligated* semiopen species (e.g., **17**); the system is stabilized via the maximization of the number of strong Pt−S interactions formed through the chelation of the P,S−Me ligand.[44,47] Importantly, in dichloromethane, the chelation of the P,S−Me ligand is strong enough to prevent the second chloride anion from binding to the platinum center, and no contribution from the fully open species is observed.[44,45]

Because we were targeting the formation of heteroligated aryl−aryl′ complexes, we hypothesized that they could be made by pairing P,S−Ph (**10**) with comparatively weakly chelating ligands such as $P,S-C_6F_4H$ (**11**), P,O−Ph (**12**), or $P,N-Ph_2$ (**13**). As a point of entry we decided to explore the chemistry of the fluorinated ligand **11**. The fluorinated P,S ligand system was of particular interest to us because of the synthetic accessibility of the fluorinated hemilabile subunit, $[(Ph_2PCH_2CH_2S)-C_6F_4-]$.[51,52]

The combination of ligands **10** and **11** with $PtCl_2(cod)$ (cod = 1,5-cyclooctadiene) in a 1:1:1 ratio in dichloromethane resulted in an unresolvable and dynamic mixture of species, as determined by in situ $^{31}P\{^1H\}$ NMR spectroscopy.[68] Presumably, this is due to the presence of fully open species which interfere with the thermodynamically controlled ligand sorting process. The cod byproduct was removed via precipitation with hexanes to give a white solid that was used for all subsequent reactions. Further evidence that ligand sorting does not occur satisfactorily in dichloromethane solution was obtained via the abstraction of both chloride anions using silver hexafluorophosphate. The abstraction, which essentially traps the various species present in solution, resulted in a mixture of closed homoligated and heteroligated complexes. In contrast, when the white solid that was obtained from the hexane precipitation was dissolved in methanol, the semiopen heteroligated tweezer **23a** formed quantitatively (Scheme 3). The in situ $^{31}P\{^1H\}$ NMR spectrum exhibits defined doublets and associated ^{195}Pt satellites at δ 10.20 ($^1J_{Pt-P}$ = 3235 Hz, $^2J_{P-P}$ = 14 Hz), which is consistent with a nonchelated ligand with the phosphorus *trans* to a S-bound phenyl thioether, and δ 45.74 ($^1J_{Pt-P}$ = 3486 Hz, $^2J_{P-P}$ = 14 Hz), which is consistent with a chelated ligand with the phosphorus atom *trans* to a chloride. The coupling constants

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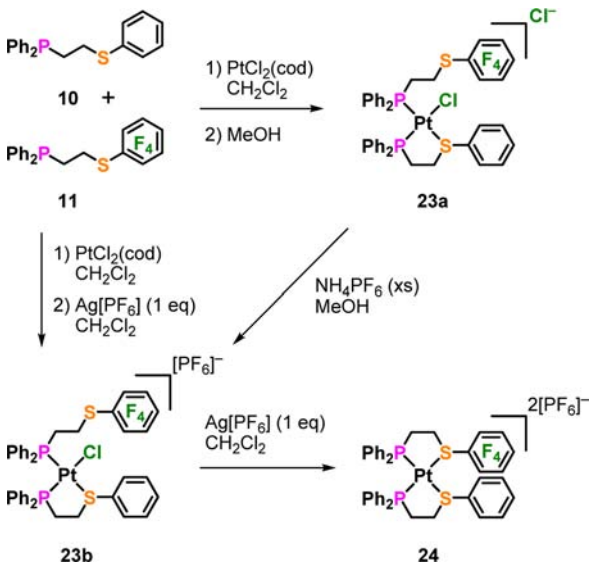
Scheme 3. Synthesis of Heteroligated Tweezer Compounds 23a, 23b, and 24



are consistent with a mutual *cis* coordination of the phosphorus atoms to the platinum center.[68] Removal of the methanol followed by dissolution in dichloromethane regenerated the unresolvable mixture, demonstrating the highly dynamic nature of the system. Importantly, the addition of a methanolic solution of ammonium hexafluorophosphate to the semiopen complex, also in methanol, resulted in the immediate precipitation of the heteroligated hexafluorophosphate salt **23b** in high yield. Unlike the parent dichloride complex **23a**, compound **23b** retains its semiopen structure when redissolved in dichloromethane, as discussed below. Slow diffusion of hexanes into a solution of **23b** in dichloromethane resulted in the growth of crystals suitable for single-crystal X-ray diffraction analysis (Figure 1a). In the solid state, the platinum center has a square planar geometry. The nonfluorinated ligand **10** is chelating whereas the fluorinated ligand **11** is coordinated only through the phosphine. The phosphines have a mutual *cis* orientation, and the remaining coordination site is occupied by a chloride.

To improve the generality of the approach, we sought a route to the stable, semiopen complex **23b** that did not involve the precipitation of the complex from methanol. We reasoned that a major factor in the spontaneous formation of heteroligated complexes in methanol is the solvation and effective removal of a single chloride anion from the inner to the outer coordination sphere. With only one chloride available for inner-sphere coordination and no contribution from fully open dichloride species, a HILR ligand sorting process can occur that leads to well-defined products. The HILR process does not occur in aprotic dichloromethane because of the greater coordinating strength of the chloride to the platinum center in this solvent. This results in the formation of fully open species that have two chloride ions coordinated to the platinum center, thus disrupting the thermodynamic landscape of the reaction. We hypothesized that the chemical removal of a single chloride ion in a nonprotic solvent such as dichloromethane using a single equivalent of a silver-based abstraction agent would mimic the action of methanol, thus leading to heteroligated complexes. Indeed, as mentioned earlier, the semiopen complex **23b**, which is synthesized in methanol and possesses only a single chloride

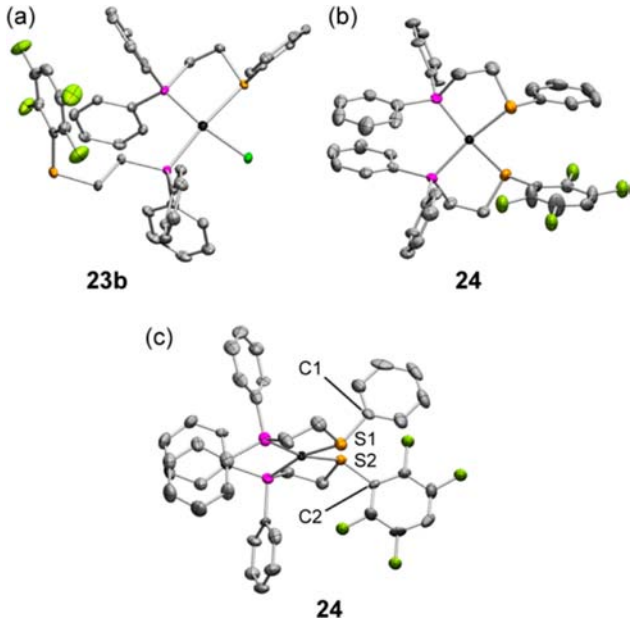


Figure 1. Molecular structures of compounds **23b** (a) and **24** (b and c) determined via single-crystal X-ray diffraction. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, occluded solvent molecules, and anions are omitted for clarity. Atom color code: Pt = black; P = magenta; S = orange; Cl = green; F = yellow-green; C = gray.

anion, retains its semiopen structure when dissolved in dichloromethane. Thus, the addition of a single equivalent of silver hexafluorophosphate to the mixture of species formed from P,S−Ph and P,S−C_6F_4H in dichloromethane resulted in the precipitation of silver chloride and the clean formation of the semiopen, heteroligated complex **23b** over several hours (Scheme 3). The in situ $^{31}P\{^1H\}$ NMR spectrum is essentially identical to that of compound **23b** isolated from methanol. As mentioned above, if both chlorides are removed simultaneously, the HILR process does not have time to operate, and a mixture of fully chelated species is obtained.

The fully closed, heteroligated complex **24** could be synthesized via the addition of 1 equiv of silver hexafluorophosphate to a solution of semiopen complex **23b** in dichloromethane. In situ $^{31}P\{^1H\}$ NMR spectroscopy indicated a quantitative conversion: the spectrum contains only two downfield doublets (δ 45.46 and δ 46.36) with a mutual coupling of 13 Hz and $^{195}Pt-^{31}P$ coupling constants of 3087 and 3252 Hz, respectively, which is consistent with a fully closed complex. The $^{195}Pt-^{31}P$ coupling constants may be used to assign the NMR signals: the signal δ 45.46 exhibits a coupling constant of 3087 Hz, thus suggesting that the corresponding phosphorus atom is *trans* to the phenyl thioether. The signal at δ 46.36, which exhibits a larger coupling constant of 3252 Hz, corresponds to the phosphorus atom *trans* to the weakly coordinating tetrafluorophenyl thioether. Subsequent single-crystal X-ray diffraction analysis revealed that, in the solid state, complex **24** has a fully closed, heteroligated structure with a square planar coordination geometry (Figure 1b). Similar to other closed tweezer complexes, the planes of the sulfur-bound aryl groups are approximately parallel and the groups are staggered; i.e., the C1−S1−S2−C2 dihedral angle is 87.6(5)° (Figure 1c). All other characterization data are consistent with this structural assignment. In methanol or dichloromethane, the semiopen

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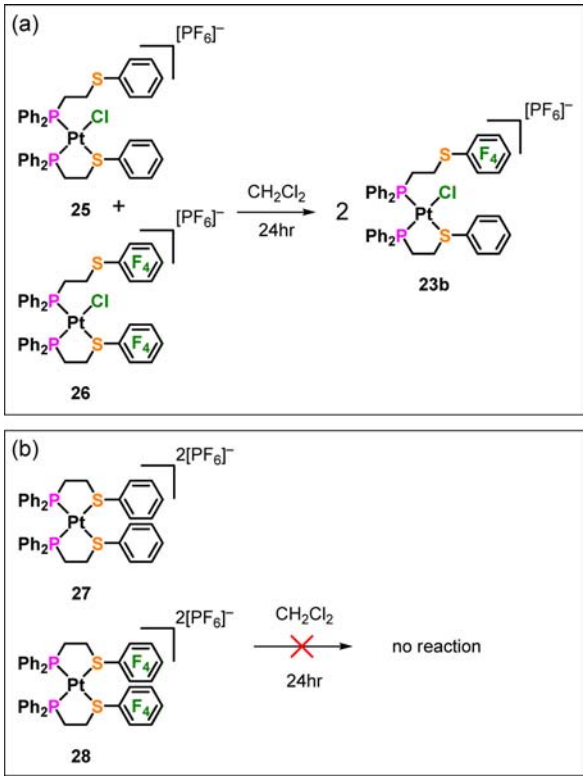
complex **23b** may be regenerated from the fully closed compound **24** upon the addition of a single equivalent of tetraethylammonium chloride, demonstrating the reversibility of the system.

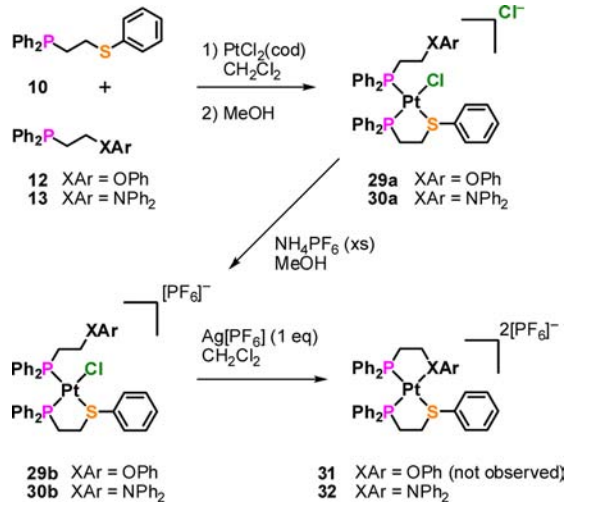
To confirm that the HILR reaction is operating in this Pt(II) system, equimolar quantities of the homoligated semiopen complexes **25** and **26** were stirred together in dichloromethane at room temperature. Over the course of 24 h, complete rearrangement to the heteroligated species occurred (Scheme 4a). In the case of the fully closed species **27** and **28**, on the other hand, no ligand sorting occurred (Scheme 4b). Thus, it appears from the aforementioned reactions that the chemistry of the platinum(II) system with a single chloride removed from the inner coordination sphere closely resembles that of the analogous Rh(I) system.

Scheme 4. Formation of Heteroligated Tweezer 23b from Homoligated Species 25 and 26 (a) via the Halide-Induced Ligand Rearrangement Reaction while (b) No Reaction Occurs between Fully Closed Complexes 27 and 28



To expand the scope and explore the potential generality of the reaction, we performed an analogous series of reactions using the related phosphine−phenyl ether and phosphine−diphenylamino ligands **12** and **13**, respectively, as the weak chelators (Scheme 5). Indeed, the reactions proceeded in a manner similar to those performed with the P,S−C_6F_4H ligand **11** (Scheme 3), and heteroligated, semiopen complexes were obtained cleanly and in good yields. In both cases, methanol was required to induce the ligand sorting process, and the addition of methanolic ammonium hexafluorophosphate resulted in the precipitation of pure semiopen species as the hexafluorophosphate salts **29b** and **30b** (Scheme 5). The semiopen complexes maintained their composition in dichloromethane, as determined by $^{31}P\{^{1}H\}$ NMR spectroscopy. The solid-state structures were determined in both cases via single-crystal X-ray diffraction analyses (Figure 2). Similar to compound **23b** (Figure 1), both **29b** and **30b** have semiopen heteroligated structures in the solid state. The platinum centers of all three complexes have square planar coordination geometries with a *cis* disposition of the phosphine ligands. In **29b** and **30b**, the P,S−Ph ligand **10** is chelating whereas the P,O−Ph ligand **12** and P,N−Ph_2 ligand **13** are monodentate, and a single chloride occupies the fourth coordination site. Attempts to generate the heteroligated, fully closed phosphine−phenyl ether complex **31**, using a variety of chloride-abstracting agents (silver hexafluorophosphate, silver tetrafluoroborate, trimethylsilyl trifluoromethanesulfonate, and trimethyloxonium tetrafluoroborate) in dichloromethane, failed. In all cases, in situ $^{31}P\{^{1}H\}$ NMR spectroscopy revealed that no reaction had taken place. Presumably, the observation that **29b** (Scheme 5) does not form the fully closed species is attributable to the very low affinity of the phenyl ether for the platinum center. In contrast, the fully closed, heteroligated diphenylamino species **32** was obtained from the semiopen species **30b** cleanly and quantitatively via the reaction with a single equivalent of silver hexafluorophosphate in dichloromethane, as evidenced by spectroscopic analyses.

Scheme 5. Synthesis of Heteroligated Tweezer Compounds 29−32 that Contain P,O−Ph and P,N−Ph_2 Ligands



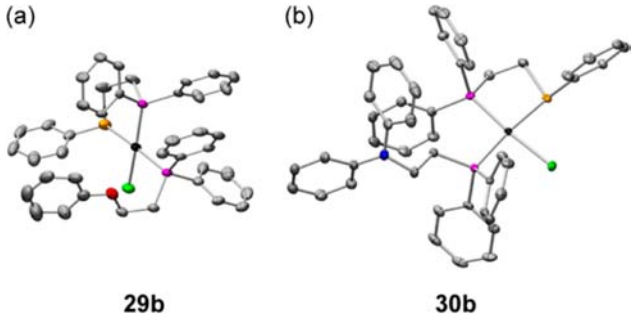


Figure 2. Molecular structures of compounds (a) **29b** and (b) **30b** determined via single-crystal X-ray diffraction. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, occluded solvent molecules, and anions are omitted for clarity. Atom color code: Pt = black; P = magenta; S = orange; O = red; N = blue; Cl = green; F = yellow-green; C = gray.

Triple-Layer Complexes. We have previously shown that WLA complexes based on rhodium(I) can be the basis for

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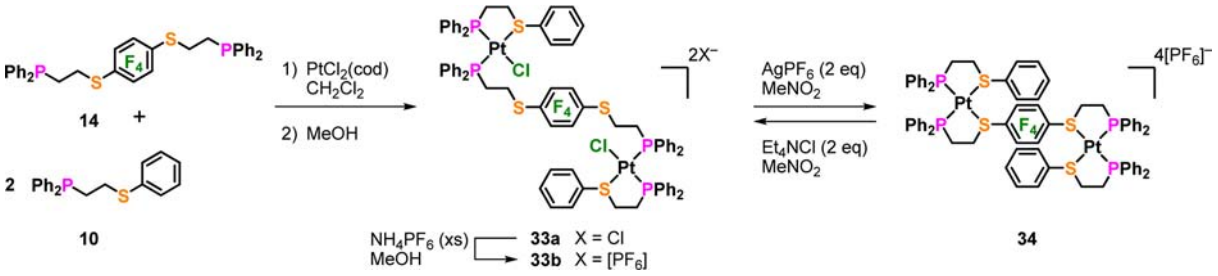
Scheme 6. Synthesis of Triple Layer Complexes 33−34



powerful allosteric systems in which monometallic catalysts that are buried in the central layer of a triple-layer assembly may be reversibly exposed by addressing allosteric "hinge" sites with small-molecule or elemental effectors (Scheme 1c).[33] These allosteric catalysts display no background activity in the "off" state, and considering the large amount of synthetically accessible monometallic catalysts, we are eager to further explore this particular avenue of research. At present, this chemistry is restricted by the air-sensitivity of rhodium(I), and there is a need to develop the chemistry of platinum(II)-based systems in order to exploit their higher stability and use a greater scope of allosteric effector.[47] For these studies we focused on the combination of fluorinated and nonfluorinated thioether ligands (Scheme 6) and assumed that, as in the case of the heteroligated tweezers, the related P,N triple-layer complex would behave in an essentially identical manner.

Thus, in an analogous fashion to the synthesis of the heteroligated tweezers, the combination of fluorinated ditopic ligand **14**, nonfluorinated ligand **10**, and $PtCl_2$(cod) in a 1:2:2 ratio in dichloromethane produced a dynamic and unresolvable mixture of compounds (Scheme 6). The cod byproduct was removed via precipitation with hexanes to give a white solid that was used for all subsequent reactions. When this solid was dissolved in methanol, the mixture equilibrated over a period of minutes to produce a single semiopen species **33a**, as characterized using in situ $^{31}P\{^1H\}$ NMR spectroscopy. The spectrum closely resembles that of the related tweezer complex **23a** (Scheme 3), with a doublet at δ 9.10 ($^1J_{Pt-P}$ = 3257 Hz, $^2J_{P-P}$ = 15 Hz), which corresponds to the nonchelating ligand, and a doublet at δ 43.30 ($^1J_{Pt-P}$ = 3452 Hz, $^2J_{P-P}$ = 15 Hz), which corresponds to the chelating ligand. This indicates the clean formation of the semiopen triple-layer complex. The addition of a methanolic solution of ammonium hexafluorophosphate to the solution resulted in the immediate precipitation of semiopen hexafluorophosphate salt **33b** (Scheme 6). Similar to the tweezer complex **23a** (Scheme 3), the replacement of chloride with the hexafluorophosphate anion stabilizes the structure; the $^{31}P\{^1H\}$ NMR spectrum of **33b** in dichloromethane is essentially identical to that of the nonabstracted complex **33a** in methanol. The semiopen triple-layer structure of **33b** was subsequently confirmed using single-crystal X-ray diffraction analysis (Figure 3a). The ditopic ligand **14** bridges the two platinum centers, and both of the P,S moieties are coordinated only through phosphine. Both the P,S−Ph ligands in **33b** are chelating, and there is a mutual *cis* arrangement of phosphines at each platinum center. Chloride anions occupy the remaining coordination sites. All other characterization data for **33b** are consistent with the proposed structure.

Abstraction of the remaining chlorides from **33b** using silver hexafluorophosphate in nitromethane generates the fully closed

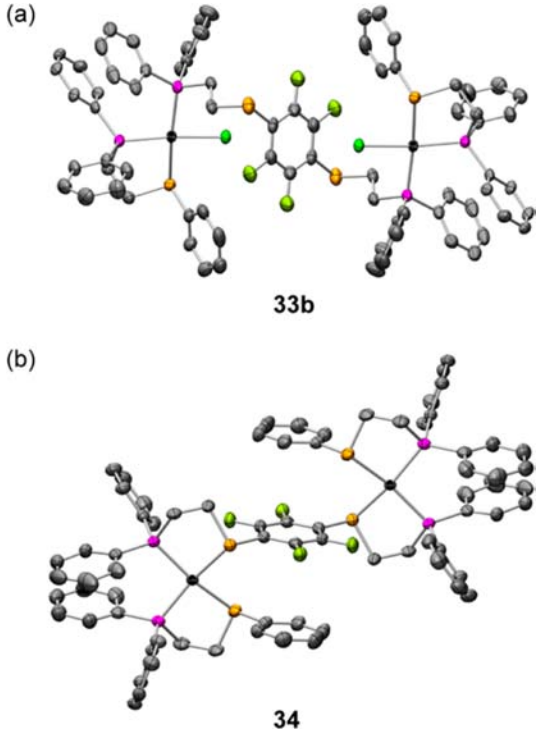


Figure 3. Molecular structures of compounds (a) **33b** and (b) **34** determined via single-crystal X-ray diffraction. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, occluded solvent molecules, and counteranions are omitted for clarity. Atom color code: Pt = black; P = magenta; S = orange; Cl = green; F = yellow-green; C = gray.

triple-layer complex **34** (Scheme 6). The choice of nitromethane is important in the case of the condensed, tetracationic model complexes described in this report because of their low solubility in common solvents such as dichloromethane, methanol, and acetonitrile. Furthermore, the solubility of silver chloride is sufficiently low in nitromethane for effective abstraction and simple purification via filtration. Similar to the fully closed tweezer complex **24**, the in situ $^{31}P\{^1H\}$ NMR spectrum of **34** contains closely spaced doublets at δ 46.76 ($^1J_{Pt-P}$ = 3129 Hz, $^2J_{P-P}$ = 13 Hz) and δ 47.06 ($^1J_{Pt-P}$ = 3229 Hz, $^2J_{P-P}$ = 13 Hz), indicating that the reaction proceeds quantitatively. The magnitudes of the $^{195}Pt-^{31}P$ coupling constants suggest that the signals at δ 46.76 and 47.06 correspond to the phosphorus atoms *trans* to the phenyl thioether and tetrafluorophenyl thioether, respectively. Compound **34** was separated from silver chloride by filtration and isolated via precipitation with diethyl ether (Scheme 6). Single-crystal X-ray diffraction analysis confirmed the fully closed triple-layer structure (Figure 3b). The ditopic ligand (**14**)

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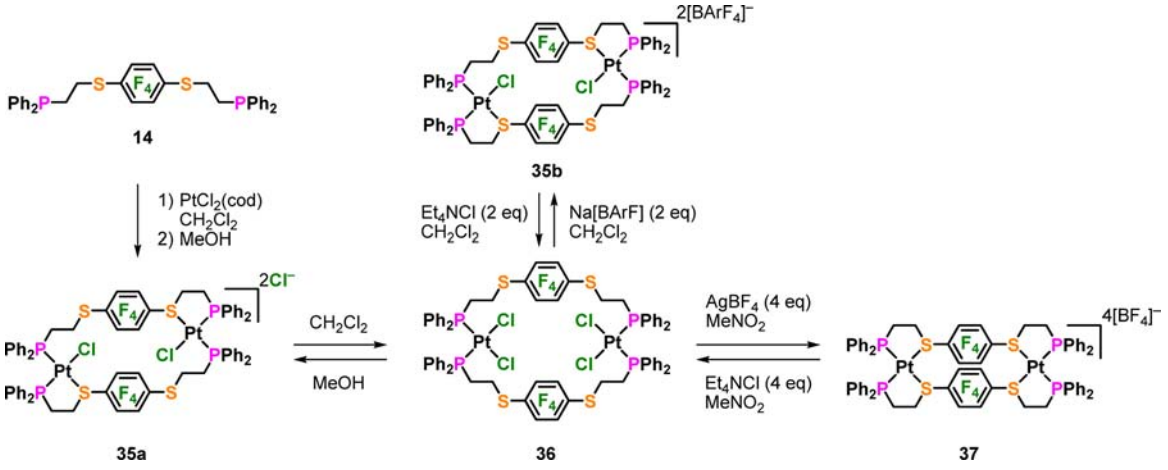
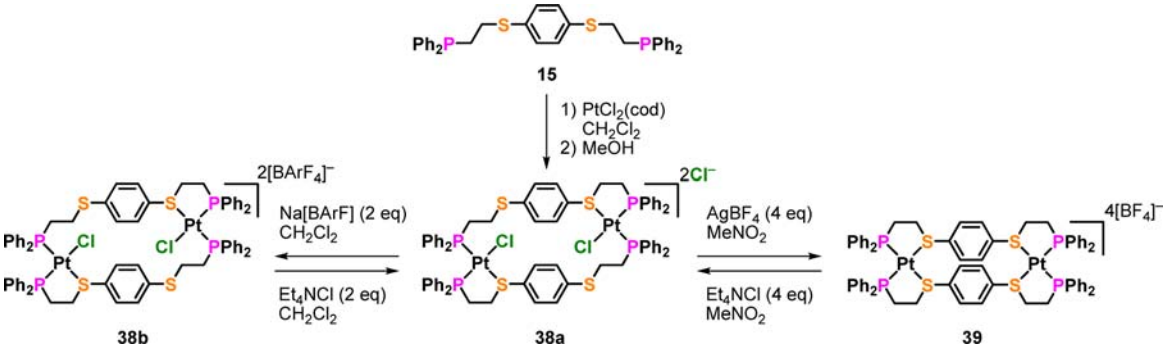
Scheme 7. Syntheses of Macrocyclic Complexes 35−37



Scheme 8. Syntheses of Macrocyclic Complexes 38 and 39



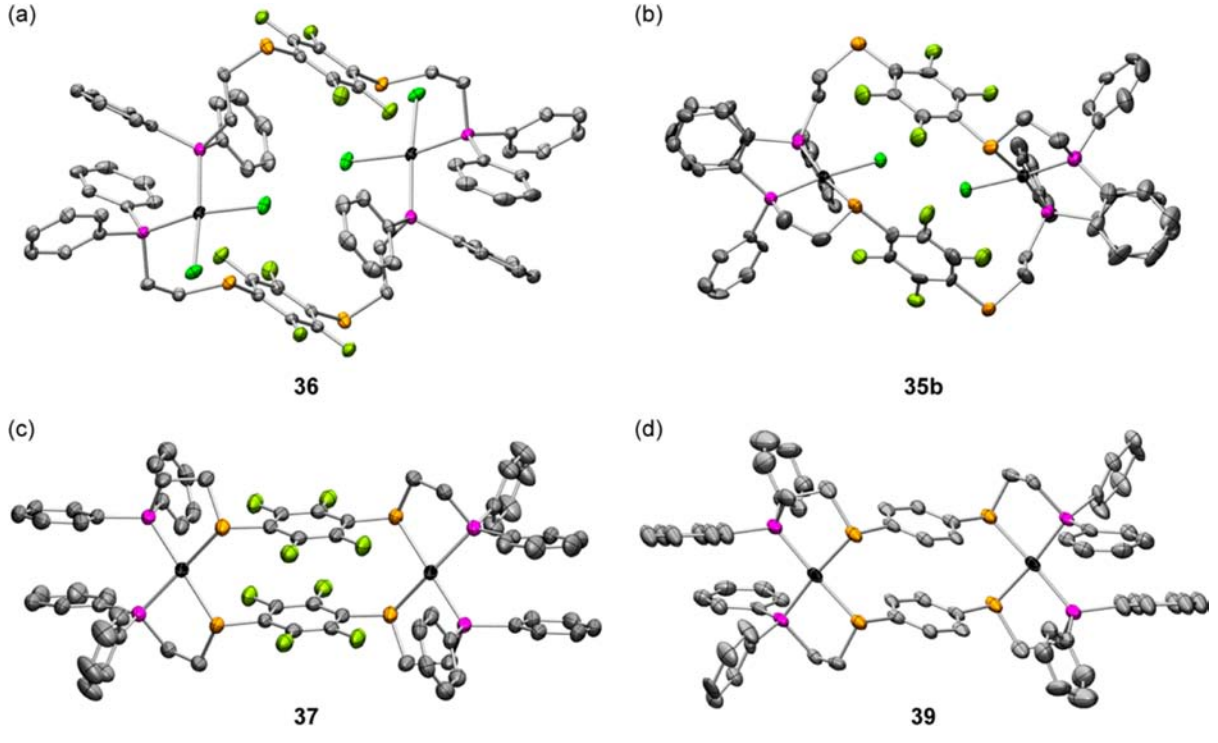


Figure 4. Molecular structures of compounds (a) **36**, (b) **35b**, (c) **37**, and (d) **39** (PF_6 salt) determined via single-crystal X-ray diffraction. Thermal ellipsoids for a−c are drawn at 50% probability. Thermal ellipsoids for d are drawn at 30% probability. Hydrogen atoms, occluded solvent molecules, and counteranions are omitted for clarity. Atom color code: Pt = black; P = magenta; S = orange; Cl = green; F = yellow-green; C = gray.

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bridges the platinum centers, and the central tetrafluorophenylene ring and phenyl groups are arranged in a staggered, parallel fashion.

Bisplatinum(II) Macrocycles. As mentioned in the Introduction, the original WLA to the synthesis of macrocylic supramolecular complexes proceeds via a fully closed "condensed" intermediate (Scheme 1a).[1] This intermediate forms cleanly because a *cis* ligand geometry is produced around the first metal center, thus positioning the remaining chelating moieties of the symmetrical, ditopic ligands rigidly and mutually adjacent and favoring cyclization. Strongly coordinating ligands such as chloride disrupt this templating effect because they compete more effectively for the metal center than the weak-link heteroatom. To avoid this, d^8 metal precursors with noncoordinating counteranions, such as $[Rh(nbd)_2][BF_4]$ (nbd = norbornadiene) or $[Pd(CH_3CN)_4][BF_4]_2$), are typically used to synthesize WLA macrocycles.[1−3] Our observation that the HILR reaction was operating in platinum(II) tweezer and triple-layer complexes led us to consider if bisplatinum(II) macrocycles could be obtained in the presence of chloride with a greater degree of thermodynamic control. We hypothesized that the reversibility inherent in the HILR reaction would result in the degradation of oligomeric and polymeric material, and favor the concomitant formation of discrete macrocycles. Model systems based on fluorinated and nonfluorinated ditopic ligands **14** and **15** (Schemes 7 and 8), respectively, were chosen to investigate this possibility for the reasons of synthetic accessibility previously stated.

The reaction of equimolar quantities of fluorinated ditopic ligand **14** and $PtCl_2(cod)$ in dichloromethane at room temperature resulted in the complete consumption of the starting materials, as determined by in situ $^{31}P\{^1H\}$ NMR spectroscopy. The cod byproduct was removed via precipitation with diethyl ether to give a white solid mixture of products (vide infra) that was used for subsequent reactions.

A solution of this mixture of products in methanol was heated for several hours at 40 °C. The in situ $^{31}P\{^1H\}$ NMR spectrum of the solution exhibits two symmetrical, slightly broadened signals with associated ^{195}Pt satellites at δ 44.81 ($^1J_{Pt-P}$ = 3452 Hz) and δ 9.58 ($^1J_{Pt-P}$ = 3402, $^2J_{P-P}$ = 14 Hz) that indicate the clean conversion to a single semiopen species with *cis* phosphines (**35a**). In a similar fashion to the other semiopen species in this study, the downfield signal corresponds to the chelating ligand, and the upfield signal corresponds to the nonchelating ligand. The addition of diethyl ether to this solution resulted in the precipitation of a white crystalline solid. Single-crystal X-ray diffraction analysis (Figure 4a) revealed that, upon crystallization, the outer-sphere chloride anions coordinate to the platinum to produce the fully open complex (**36**) in which the ligands are coordinated through the phosphorus atoms only, and a square planar *cis* coordination geometry around each platinum is observed. A crystallographic inversion center is located at the center of the macrocycle, and the tetrafluorophenylene rings are parallel planar (Figure 4a). The $^{31}P\{^1H\}$ NMR spectrum of a solution of the white crystalline solid **36** in dichloromethane displays a single, sharp resonance at δ 6.45 with corresponding ^{195}Pt satellites ($^1J_{Pt-P}$ = 3615 Hz), indicating that, in dichloromethane, the solution structure resembles the solid-state structure (Figure 4a); i.e., two chloride ligands are coordinated to each platinum center, and the ligands are nonchelating with a mutual *cis* geometry.

To stabilize the semiopen macrocycle in nonprotic solvents, one chloride anion per platinum was abstracted from **36** using Na[BArF] in 1,2-dichloroethane ([BArF] = tetrakis(3,5-bis-[trifluoromethyl]phenyl)borate). The in situ $^{31}P\{^1H\}$ NMR spectrum of this solution resembles that of the unabstracted complex **35a** in methanol, and contains two defined doublets with associated ^{195}Pt satellites at δ 42.52 ($^1J_{Pt-P}$ = 3419 Hz, $^2J_{P-P}$ = 14 Hz) and δ 9.02 ($^1J_{Pt-P}$ = 3409 Hz, $^2J_{P-P}$ = 15 Hz) that indicate the formation of a single semiopen species (**35b**): the signal at δ 45.52 is consistent with a chelating ligand in which the phosphorus atom is *trans* to a chloride, and the signal at δ 9.02 is consistent with a nonchelating ligand in which the phosphorus atom is *trans* to a tetrafluorophenylene thioether. Single crystals were obtained via the slow diffusion of hexanes into a solution of **35b** in dichloromethane. X-ray diffraction analysis confirmed the macrocyclic, semiopen structure of **35b** (Figure 4b). The coordination sphere of each platinum center has a square planar geometry and contains one chelating ligand and one nonchelating phosphine-bound ligand in a *cis* arrangement. The remaining site is occupied by a chloride ligand, which is directed into the center of the macrocycle. Each ligand bridges the two platinum centers and is chelating through one P,S moiety and nonchelating through the other. The molecule possesses a quasi-C_2 symmetry axis that is aligned perpendicularly to the plane of the macrocycle.

Treatment of fully open macrocycle **36** with 4 equiv of silver tetrafluoroborate in nitromethane resulted in the clean formation of the condensed tetracationic macrocycle **37** (Scheme 7). The $^{31}P\{^1H\}$ NMR spectrum of **37**, measured in nitromethane-d_3, contains a single, sharp singlet at δ 51.01 with corresponding ^{195}Pt satellites ($^1J_{Pt-P}$ = 3209 Hz), indicative of a highly symmetrical molecule that possesses only chelating ligands. The structure was confirmed using single-crystal X-ray diffraction analysis (Figure 4c). The macrocycle **37**, which is isostructural with its rhodium(I) and iridium(I) analogues $[(\kappa^2{:}\mu{:}\kappa^2$-(1,4-bis[(2′-(diphenylphosphino)ethyl)-thio]-2,3,5,6-tetrafluorobenzene)$_2M_2][BF_4]_2$ (M = Rh, Ir),[1,69] is centrosymmetric and possesses cofacial fluorophenylene rings.

The semiopen macrocycle **35b** was regenerated from closed complex **37** in nitromethane via the addition of 1 equiv of tetraethylammonium chloride per platinum atom (Scheme 7). Similarly, the addition of tetraethylammonium chloride to a solution of the semiopen complex **35b** in dichloromethane cleanly generated the fully open complex **36**.

Importantly, when the initial heating step in methanol was not performed, thus effectively bypassing the semiopen complex **35a** (Scheme 7), subsequent chloride-abstraction reactions resulted in mixtures of complexes. Because ligand **14** is weakly chelating, the chloride ligands bind strongly to the platinum centers in dichloromethane thus preventing the HILR reaction from occurring. The initial products of the reaction, which form a mixture of fully open species that includes the desired macrocycle **36** along with presumably oligomeric material and larger macrocyclic species, are thus trapped. As successive chloride anions are abstracted, the mixture of oligomers and macrocycles is conserved. For example, when one chloride per platinum atom was abstracted from a sample of compound **36** that had not been heated in methanol, several products were observed via $^{31}P\{^1H\}$ NMR spectroscopy. In addition to the resonances arising from compound **35b** (vide supra), pairs of doublets are also observed at approximately δ 10 and 44, indicating the presence of other species that possess semiopen coordination geometries at the platinum centers.[68,43,44,47]

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A similar set of reactions was conducted with the nonfluorinated ligand **15** (Scheme 8). Unlike in the case of the fluorinated ligand, the combination of equimolar quantities of **15** and $PtCl_2$(cod) in dichloromethane resulted in fluxional species as indicated by the presence of a single, very broad signal centered at δ 14 in the $^{31}P\{^1H\}$ NMR spectrum (Scheme 8). The cod was removed by precipitation with hexanes to give a white solid. Similar to the abstraction of chloride in the fluorinated system, if a methanol-induced HILR reaction was not performed, the abstraction of chloride from **38a** using 2 equiv of Na[BArF] produced a mixture of species with semiopen coordination, whereas abstraction with 4 equiv of silver tetrafluoroborate in nitromethane produced a mixture of complexes with fully closed coordination. This suggests that the initial reaction in dichloromethane produces a mixture of oligomeric and polymeric materials. However, when the initial mixture of species was stirred in methanol at 50 °C for several hours, subsequent abstraction reactions proceeded cleanly and in high yields (Scheme 8). Thus, in methanol at room temperature, two broad signals are present in the $^{31}P\{^1H\}$ NMR spectrum at δ 45.48 ($^1J_{Pt-P}$ = 3500 Hz) and δ 10.84 ($^1J_{Pt-P}$ = 3270 Hz), indicative of a fluxional semiopen species (**38a**): the signal at δ 45.48 is consistent with a chelating ligand in which the phosphorus atom *trans* to a chloride, and the signal at δ 10.84 is consistent with a nonchelating ligand in which the phosphorus atom is *trans* to a phenylene thioether. Removal of the methanol under reduced pressure produced **38a** as a yellow oil that was used in subsequent reactions. The addition of 2 equiv of Na[BArF] to a solution of **38a** in dichloromethane resulted in the clean formation of semiopen complex **38b** that could be separated from the sodium chloride byproduct by filtration and then isolated via precipitation with hexanes (Scheme 8). The $^{31}P\{^1H\}$ NMR spectrum recorded in dichloromethane contains signals at δ 44.44 ($^1J_{Pt-P}$ = 3508 Hz) and δ 9.57 ($^1J_{Pt-P}$ = 3231 Hz), which is consistent with the proposed semiopen structure. The fully closed species **39** was obtained from the semiopen complex **38a** via the complete abstraction of chloride using silver tetrafluoroborate or hexafluorophosphate in nitromethane. The $^{31}P\{^1H\}$ NMR spectrum of the tetrafluoroborate salt of **39** recorded in nitromethane contains a single signal at δ 49.51 ($^1J_{Pt-P}$ = 3103 Hz), which is consistent with a condensed structure.[68] The structural assignments for the fully closed complexes were confirmed by single-crystal X-ray diffraction on crystals of the hexafluorophosphate salt (Figure 4d) and tetrafluoroborate salt (see SI) of **39**.

CONCLUSIONS

The work described in this report effectively brings the chemistry of the WLA out of the glovebox and onto the bench. Over the past several years we have made a thorough study of the WLA chemistry of rhodium(I) and used this chemistry to develop a platform for allosteric catalysis that is both tailorable and predictable. Nevertheless, rhodium(I)-based WLA chemistry is fundamentally limited in that it must be performed in the absence of air. In contrast, the platinum(II) complexes described in this report are stable to air and moisture and can be synthesized with no special precautions. The ability to synthesize heteroligated aryl−aryl platinum(II)-based WLA complexes using a variety of hemilabile ligands not only allows us to make all of our previously reported rhodium(I) systems stable to air, but also allows for the exploration of new allosteric oxidation catalysts that are incompatible with rhodium(I). Another important aspect of this work is the development of a dynamic, nontemplated synthesis of WLA macrocycles. The formation of macrocyclic species via the inherently reversible HILR reaction, which necessarily occurs in the presence of halide, is a fundamentally different approach to the traditional stepwise, templated WLA synthesis[70] that must be conducted in the absence of halide (Scheme 1a). Work toward the next generation of air-stable enzyme mimics based on platinum(II) WLA complexes is underway in our laboratories.

EXPERIMENTAL SECTION

General Methods/Instrument Details. The syntheses of platinum(II) complexes and all manipulations were done under ambient conditions. All solvents were anhydrous grade, purchased from Sigma-Aldrich, and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. Compounds **10**,[65] **11**,[45] **12**,[71] **13**,[33] **15**,[70] and **25**−**28**[49] were prepared according to literature procedures or adaptations thereof. All other chemicals were purchased from Aldrich Chemical Co. and were used as received. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ^1H NMR spectra were referenced internally to residual protons in the deuterated solvents (dichloromethane-d_2 = δ 5.32; 1,2-dichloroethane-d_4 = δ 3.72; nitromethane-d_3 = δ 4.33; methanol-d_4 = 3.31). ^{31}P and $^{31}P\{^1H\}$ NMR spectra were referenced to an external 85% H_3PO_4 standard (δ 0), and $^{19}F\{^1H\}$ NMR spectra were referenced an external $CFCl_3/CDCl_3$ standard (δ 0). Elemental analyses were performed by Intertek Pharmaceutical Services, Whitehouse, NJ. Electrospray ionization (ESI) mass spectra were recorded on an Agilent 6120 LC−TOF instrument in positive ion mode.

Synthesis. *1,4-Bis[(2-(diphenylphosphino)ethyl)thio]-2,3,5,6-tetrafluorobenzene (**14**).* 2-(Diphenylphosphino)ethylthiol (500 mg, 2.03 mmol), hexafluorobenzene (120 μL, 193 mg, 1.04 mmol), cesium carbonate (1.323 g, 4.06 mmol), and tetrabutylammonium bromide (11 mg, 34 μmol) were dissolved in degassed tetrahydrofuran (7 mL) and stirred under nitrogen at room temperature for 18 h. The reaction was monitored using TLC (silica, 1:1 dichloromethane/hexanes, R_f = 0.5). The mixture was filtered through a glass frit, and the retentate was washed with dichloromethane. The solvent was removed from the filtrate under reduced pressure to give a crystalline off-white solid. Column chromatography (silica, 200 mL, ϕ = 5 cm, 1:1 dichloromethane/hexanes, R_f = 0.5) gave compound **14** as a white crystalline solid. Yield = 97% (632 mg, 0.990 mmol). ^1H NMR (400 MHz, CD_2Cl_2) δ 2.32 (m, 4H), 2.99 (m, 4H), 7.35 (m, 20H); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ −16.68; ^{19}F NMR (376 MHz, CD_2Cl_2) δ −134.07. Spectral data match those previously reported.[69]

*[cis-PtCl(Ph$_2$PCH$_2$CH$_2$SC$_6$HF$_4$-κP)(Ph$_2$PCH$_2$CH$_2$SPh-κ^2)][PF$_6$] (**23b**).* A solution of *cis*-$PtCl_2$(cod) (190 mg, 0.507 mmol) in dichloromethane (10 mL) was added to a solution of **10** (164 mg, 0.507 mmol) and **11** (201 mg, 0.507 mmol) in dichloromethane (5 mL) in a 50 mL oven-dried Schlenk flask. The resulting mixture was stirred vigorously for 15 min and then concentrated to ca. 3 mL under reduced pressure. Hexanes (50 mL) were added, and the resulting cloudy suspension was stored at −20 °C for one hour. The suspension was then filtered using a fritted funnel, and the white retentate was washed with hexanes (3 × 10 mL). The retentate was dissolved in methanol (10 mL) and stirred vigorously for 30 min. To this solution was added a solution ammonium hexafluorophosphate (490 mg, 3.0 mmol) in methanol (3 mL). The resulting suspension was stirred vigorously for 30 min. The mixture was filtered using a fritted funnel, and the retentate was washed with diethyl ether (3 × 10 mL). The retentate (**23b**) was dried in vacuo. Yield = 93% (506 mg, 0.463 mmol). ^1H NMR (400 MHz, CD_2Cl_2) δ 2.77−3.09 (br m, 8H), 7.22−7.81 (br m, 26H); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ 9.13 (d, $^2J_{P-P}$ = 15 Hz [d, $^1J_{Pt-P}$ = 3207 Hz]), 44.29 (d, $^2J_{P-P}$ = 15 Hz [d, $^1J_{Pt-P}$ = 3474 Hz]). Anal. Calcd for $C_{40}H_{34}ClF_{10}P_3PtS_2$: C 43.98, H 3.14. Found: C 43.67, H 2.79. HRMS (ESI+) m/z Calcd for $[M - PF_6]^+$: 947.0847. Found: 947.0866.

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*[cis-Pt(Ph$_2$PCH$_2$CH$_2$SC$_6$HF$_4$-κ^2)(Ph$_2$PCH$_2$CH$_2$SPh-κ^2)][PF$_6$]$_2$ (**24**).* A solution of **23b** (250 mg, 0.228 mmol) in dichloromethane (15 mL) was added to a solution of silver hexafluorophosphate (58 mg, 0.228 mmol) in dichloromethane (5 mL) in a 25 mL vial covered in aluminum foil. The resulting mixture was stirred vigorously for 1 h and then filtered through a Celite pad in a fritted funnel. The Celite was washed with dichloromethane (3 × 10 mL). The filtrate was collected and concentrated to ca. 3 mL under reduced pressure. Hexanes (50 mL) were added and the cloudy suspension was stored at −20 °C for 1 h. The suspension was filtered using a fritted funnel, and the white retentate was washed with hexanes (3 × 10 mL). The retentate (**24**) was dried in vacuo. Yield = 96% (264 mg, 0.219 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.72−3.09 (br m, 8H), 7.37−7.61 (br m, 26H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 45.46 (d, $^2J_{P-P}$ = 13 Hz [d, $^1J_{Pt-P}$ = 3087 Hz]), 46.36 (d, $^2J_{P-P}$ = 15 Hz [d, $^1J_{Pt-P}$ = 3250 Hz]). Anal. Calcd for $C_{40}H_{34}F_{16}P_4PtS_2{\cdot}CH_2Cl_2$: C 38.27, H 2.82. Found: C 38.61, H 2.64. HRMS (ESI+) *m*/*z* Calcd for [M − 2PF$_6$ + Cl]$^+$: 947.0847. Found: 947.0869.

*[cis-PtCl(Ph$_2$PCH$_2$CH$_2$OPh-κP)(Ph$_2$PCH$_2$CH$_2$SPh-κ^2)][PF$_6$] (**29b**).* A solution of *cis*-PtCl$_2$(cod) (254 mg, 0.679 mmol) in dichloromethane (10 mL) was added to a solution of **10** (219 mg, 0.679 mmol) and **12** (208 mg, 0.679 mmol) in dichloromethane (5 mL) in a 50 mL oven-dried Schlenk flask. The resulting mixture was stirred vigorously for 15 min and then concentrated to ca. 3 mL under reduced pressure. Hexanes (50 mL) were added, and the cloudy suspension was stored at −20 °C for 1 h. This suspension was filtered using a fritted funnel, and the white retentate was washed with hexanes (3 × 10 mL). The retentate was dissolved in methanol (10 mL) and stirred vigorously at 50 °C overnight. This solution was cooled to room temperature, and a solution of ammonium hexafluorophosphate (1.5 g, 9.2 mmol) in methanol (3 mL) was added. The resulting suspension was stirred vigorously for 3 h. The mixture was filtered using a fritted funnel, and the white retentate was washed with diethyl ether (3 × 10 mL). The retentate (**29b**) was dried in vacuo. Yield = 66% (450 mg, 0.448 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.76−3.13 (br m, 6H), δ 4.38−4.42 (br m, 2H), 6.81−7.49 (br m, 30H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 12.06 (d, $^2J_{P-P}$ = 15 Hz [d, $^1J_{Pt-P}$ = 3200 Hz]), 44.79 (d, $^2J_{P-P}$ = 15 Hz [d, $^1J_{Pt-P}$ = 3513 Hz]). Anal. Calcd for $C_{40}H_{38}ClF_6OP_3PtS{\cdot}0.25CH_2Cl_2$: C 47.14, H 3.78. Found: C 47.27, H 3.40. HRMS (ESI+) *m*/*z* Calcd for [M − (PF$_6$)]$^+$: 859.1449. Found: 859.1453.

*[cis-PtCl(Ph$_2$PCH$_2$CH$_2$NPh$_2$-κP)(Ph$_2$PCH$_2$CH$_2$SPh-κ^2)][PF$_6$] (**30b**).* A solution of *cis*-PtCl$_2$(cod) (98 mg, 0.262 mmol) in dichloromethane (10 mL) was added to a solution of **10** (85 mg, 0.262 mmol) and **13** (100 mg, 0.262 mmol) in dichloromethane (5 mL) in a 50 mL oven-dried Schlenk flask. The resulting mixture was stirred vigorously for 15 min and then concentrated to ca. 3 mL under reduced pressure. Hexanes (50 mL) were added, and the cloudy suspension was stored at −20 °C for 1 h. This suspension was filtered using a fritted funnel, and the white retentate was washed with hexanes (3 × 10 mL). The retentate was dissolved in methanol (10 mL) and stirred vigorously for 30 min. To this solution was added a solution of ammonium hexafluorophosphate (256 mg, 1.57 mmol) in methanol (3 mL). The resulting suspension was stirred vigorously for 30 min. The mixture was filtered using a fritted funnel, and the white retentate was washed with diethyl ether (3 × 10 mL). The retentate (**30b**) was dried in vacuo. Yield = 91% (257 mg, 0.238 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.56−3.84 (br m, 8H), 6.64−7.53 (br m, 35H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 6.18 (d, $^2J_{P-P}$ = 15 Hz [d, $^1J_{Pt-P}$ = 3182 Hz]), 44.31 (d, $^2J_{P-P}$ = 15 Hz [d, $^1J_{Pt-P}$ = 3485 Hz]). Anal. Calcd for $C_{46}H_{43}ClF_6NP_3PtS$: C 51.19, H 4.02, N 1.30. Found: C 51.07, H 4.03, N 1.19. HRMS (ESI+) *m*/*z* calcd for [M − 2PF$_6$]$^{2+}$: 872.0793. Found: 872.0802.

*[cis-Pt(Ph$_2$PCH$_2$CH$_2$NPh$_2$-κ^2)(Ph$_2$PCH$_2$CH$_2$SCPh-κ^2)][PF$_6$]$_2$ (**32**).* A solution of **30b** (100 mg, 0.092 mmol) in dichloromethane (10 mL) was added to a solution of silver hexafluorophosphate (23 mg, 0.092 mmol) in dichloromethane (5 mL) in a 25 mL vial covered in aluminum foil. The resulting mixture was stirred vigorously for 1 h and then filtered through a Celite pad in a fritted funnel. The Celite was washed with dichloromethane (3 × 10 mL). The filtrate was collected and concentrated to ca. 3 mL under reduced pressure. Hexanes (50 mL) were added, and the cloudy suspension was stored at −20 °C for 1 h. The suspension was filtered using a fritted funnel, and the retentate was washed with hexanes (3 × 10 mL). The retentate (**32**) was dried in vacuo. Yield = 94% (103 mg, 0.086 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.69−3.13 (br m, 8H), 6.92−7.52 (br m, 35H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 28.37 (d, $^2J_{P-P}$ = 14 Hz [d, $^1J_{Pt-P}$ = 3279 Hz]), 32.97 (d, $^2J_{P-P}$ = 14 Hz [d, $^1J_{Pt-P}$ = 3355 Hz]). Anal. Calcd for $C_{46}H_{43}F_{12}NP_4PtS$: C 46.47, H 3.65, N 1.18. Found: C 46.54, H 3.39, N 1.17. HRMS (ESI+) *m*/*z* Calcd for [M − PF$_6$]$^+$: 933.1928. Found: 933.1927.

*[cis-Pt$_2$Cl$_2$(κP:μ:κP-1,4-{Ph$_2$PCH$_2$CH$_2$S}$_2$C$_6$F$_4$)(Ph$_2$PCH$_2$CH$_2$SPh-κ^2)$_2$][PF$_6$]$_2$ (**33b**).* A solution of *cis*-PtCl$_2$(cod) (234 mg, 0.626 mmol) in dichloromethane (15 mL) was added to a solution of **10** (202 mg, 0.626 mmol) and **14** (200 mg, 0.313 mmol) in dichloromethane (10 mL) in a 50 mL oven-dried Schlenk flask. The resulting mixture was stirred vigorously for 15 min before being concentrated to ca. 5 mL under reduced pressure. Hexanes (50 mL) were added, and the cloudy suspension was stored at −20 °C for 1 h. The suspension was filtered using a fritted funnel, and the white retentate was washed with hexanes (3 × 20 mL). The retentate was dissolved in methanol (15 mL) and stirred vigorously for 30 min. To this solution was added a solution of ammonium hexafluorophosphate (612 mg, 3.75 mmol) in methanol (3 mL). The resulting suspension was stirred vigorously for 30 min. The mixture was filtered using a fritted funnel, and the retentate was washed with diethyl ether (3 × 20 mL). The retentate (**33b**) was dried in vacuo. Yield = 97% (617 mg, 0.303 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.72−2.88 (br m, 16H), 7.17−7.53 (br m, 50H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 8.39 (d, $^2J_{P-P}$ = 14 Hz [d, $^1J_{Pt-P}$ = 3037 Hz]), 43.10 (d, $^2J_{P-P}$ = 14 Hz [d, $^1J_{Pt-P}$ = 3479 Hz]). Anal. Calcd for $C_{74}H_{66}Cl_2F_{16}P_6Pt_2S_4{\cdot}CH_2Cl_2$: C 43.08, H 3.25. Found: C 43.21, H 3.09. HRMS (ESI) *m*/*z* calcd for [M − 2(PF$_6$)]$^{2+}$: 872.0794. Found: 872.0799.

*[cis-Pt$_2$(κ^2:μ:κ^2-1,4-{Ph$_2$PCH$_2$CH$_2$S}$_2$C$_6$F$_4$)(Ph$_2$PCH$_2$CH$_2$SPh-κ^2)$_2$][PF$_6$]$_4$ (**34**).* A solution of **33b** (200 mg, 0.098 mmol) in nitromethane (10 mL) was added to a solution of silver hexafluorophosphate (50 mg, 0.196 mmol) in nitromethane (5 mL) in a 25 mL vial covered in aluminum foil. The resulting mixture was stirred vigorously for 1 h and then filtered through a Celite pad in a fritted funnel. The Celite was washed with nitromethane (3 × 10 mL). The filtrate was collected and concentrated to ca. 3 mL under reduced pressure. Ether (50 mL) was added, and the cloudy suspension was stored at −20 °C for 1 h. The suspension was filtered using a fritted funnel, and the white retentate was washed with hexanes (3 × 10 mL). The retentate (**34**) was dried in vacuo. Yield = 93% (198 mg, 0.087 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.54−3.63 (br m, 16H), 7.39−7.71 (br m, 50H); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 46.76 (d, $^2J_{P-P}$ = 13 Hz [d, $^1J_{Pt-P}$ = 3129 Hz]), 47.06 (d, $^2J_{P-P}$ = 13 Hz [d, $^1J_{Pt-P}$ = 3229 Hz]). Anal. Calcd for $C_{74}H_{66}F_{28}P_8Pt_2S_4{\cdot}2.5CH_2Cl_2$: C 37.26, H 2.90. Found: C 37.01, H 2.80. HRMS (ESI+) *m*/*z* Calcd for [M − 4(PF$_6$) + 2Cl]$^{2+}$: 871.0810. Found: 871.0790.

*[cis-Pt$_2$Cl$_2$(κP:μ:κ^2-1,4-{Ph$_2$PCH$_2$CH$_2$S}$_2$C$_6$F$_4$)$_2$]Cl$_2$ (**35a**).* A solution of *cis*-PtCl$_2$(cod) (58.7 mg, 0.157 mmol) in dichloromethane (2 mL) was added to a solution of **14** (100.3 mg, 0.157 mmol) in dichloromethane (3 mL) in a 20 mL vial. The vial was sealed, and the solution was stirred at room temperature for 6 h. The solution was concentrated to ca. 0.5 mL under reduced pressure, and diethyl ether (20 mL) was added. The resulting suspension was stirred vigorously overnight in the sealed vial. The suspension was filtered using a fritted funnel, and the retentate was washed with diethyl ether (3 × 10 mL). Methanol (7 mL) was added to the retentate, and the mixture was stirred on the frit until the retentate dissolved (15 min). The solution was transferred to a 25 mL round-bottomed flask, and a further 8 mL of methanol was used to wash the frit. The methanolic solutions were combined and stirred at 40 °C for 16 h. The solution was then concentrated to ca. 2 mL under reduced pressure, and diethyl ether (20 mL) was added. The mixture was allowed to stand for 24 h, resulting in the precipitation of a white, microcrystalline solid. The mixture was filtered using a fritted funnel, and the retentate was washed with diethyl ether (2 × 5 mL). The retentate **35a** was dried in

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vacuo. Yield = 94% (131.4 mg, 73.8 μmol). ^{1}H NMR (400 MHz, CD_3OD) δ 2.8−3.5 (b, 16 H), 7.28−7.62 (br m, 40H); $^{31}P\{^1H\}$ NMR (162 MHz, CD_3OD) δ 9.60 (d, $^2J_{P-P}$ = 11 Hz [d, $^1J_{Pt-P}$ = 3402 Hz]), 44.81 (s [d, $^1J_{Pt-P}$ = 3452 Hz]); ^{19}F NMR (376 MHz, CD_3OD) δ −131.0 (br s). HRMS (ESI+) *m*/*z* Calcd for $[M - 2Cl]^{2+}$: 869.0398. Found: 869.0400.

*[cis-Pt$_2$Cl$_2$(κP:μ:κ^2-1,4-{Ph$_2$PCH$_2$CH$_2$S}$_2$C$_6$F$_4$)$_2$][BArF]$_2$ (**35b**).* A solution of **35a** (33.6 mg, 18.9 μmol) in methanol (3 mL) was stirred in a 20 mL vial at 50 °C for 24 h. The solution was passed through a 0.2 μm PTFE filter, and 1,2-dichloroethane (4 mL) was added to the filtrate. The solution was concentrated under reduced pressure to ca. 3 mL, and 1,2-dichloroethane (4 mL) was added. The solution was again concentrated under reduced pressure to ca. 3 mL and the dilution/concentration process repeated a further two times. The solution was then transferred to a 20 mL vial containing sodium tetrakis(3,5-bis[trifluoromethyl]phenyl)borate (Na[BArF]) (32.9 mg, 37.1 μmol), and the mixture was sealed and stirred at room temperature for 16 h, resulting in a small quantity of fine, white precipitate. The suspension was passed through a 0.2 μm PTFE filter, and the filtrate was concentrated in vacuo to give **35b** as an off-white solid. Yield = 87% (56.1 mg, 16.2 μmol). ^{1}H NMR (400 MHz, 1,2-$C_2D_4Cl_2$) δ 2.80−3.21 (br m, 16 H), 7.18, 7.35, 7.55, 7.74 (four m, 64H in total); $^{31}P\{^1H\}$ NMR (162 MHz, 1,2-$C_2D_4Cl_2$) δ 9.02 (d, $^2J_{P-P}$ = 15 Hz [d, $^1J_{Pt-P}$ = 3397.1 Hz]), 42.52 (d, $^2J_{P-P}$ = 14 Hz [d, $^1J_{Pt-P}$ = 3433.5 Hz]); ^{19}F NMR (376 MHz, 1,2-$C_2D_4Cl_2$) δ −129.79 (br s, 8F), −63.11 (s, ca. 48F). Anal. Calcd for $C_{132}H_{80}B_2Cl_2F_{56}P_4Pt_2S_4$: C 45.76, H 2.33. Found: C 45.85, H 2.16. HRMS (ESI) *m*/*z* Calcd for $[M - 2(BArF)]^{2+}$: 867.5370. Found: 867.5386. Single crystals of **35b** suitable for X-ray diffraction studies were grown by slow liquid−liquid diffusion of *n*-hexane into a solution of **35b** in dichloromethane in a 5 mm NMR tube

*[cis-Pt$_2$Cl$_4$(κP:μ:κP-1,4-{Ph$_2$PCH$_2$CH$_2$S}$_2$C$_6$F$_4$)$_2$] (**36**).* Compound **36** was obtained by dissolving **35a** in dichloromethane: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.55 (br s, 8H), 3.08 (br s, 8H), 7.25−7.60 (m, 40 H); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ 6.48 (s [d, $^1J_{Pt-P}$ = 3617 Hz]); ^{19}F NMR (376 MHz, CD_2Cl_2) δ −133.66 (s). Single crystals of **36** suitable for X-ray diffraction studies were grown by slow liquid−liquid diffusion of diethyl ether into a solution of **35a** in methanol in a 5 mm NMR tube.

*[cis-Pt$_2$(κ^2:μ:κ^2-1,4-{Ph$_2$PCH$_2$CH$_2$S}$_2$C$_6$F$_4$)$_2$][BF$_4$]$_4$ (**37**).* A solution of *cis*-$PtCl_2$(cod) (59.0 mg, 0.158 mmol) in dichloromethane (2 mL) was added to a solution of **14** (100.8 mg, 0.158 mmol) in dichloromethane (3 mL) in a 20 mL vial, and the resulting solution was capped and stirred at room temperature for 4 h. The solution was concentrated to ca. 1 mL under reduced pressure, and diethyl ether (20 mL) was added. The resulting suspension was stirred vigorously for 1 h in the sealed vial. The suspension was filtered using a fritted funnel, and the retentate was washed with diethyl ether (10 mL) and *n*-pentane (10 mL). Warm methanol (10 mL) was added to the retentate, and the mixture was stirred on the frit until the retentate dissolved (15 min). The solution was transferred to a 25 mL round-bottomed flask and stirred at 40 °C for 16 h. The solution was then concentrated to ca. 1 mL under reduced pressure, and nitromethane (3 mL) was added. The solution was concentrated to ca. 2 mL under reduced pressure, and nitromethane (1 mL) was added. The solution was added to solid silver tetrafluoroborate (62.8 mg, 0.323 mmol) in a 10 mL vial. The mixture was stirred in the sealed vial at room temperature, protected from light, for 1 h. A white solid precipitated which was removed via filtration through a 0.2 μm PTFE filter. The filtrate was allowed to stand in a sealed vial, protected from light, for 24 h. A brown solid precipitated which was removed via filtration through a 0.2 μm PTFE filter. Diethyl ether (20 mL) was added to the filtrate, and the resulting mixture was allowed to stand at room temperature for 24 h. The crystalline material thus formed was isolated via filtration using a fritted funnel, washed on the frit with diethyl ether (10 mL), and dried in vacuo. Yield = 80% (127.0 mg, 63.0 μmol). ^{1}H NMR (400 MHz, CD_3NO_2) δ 3.0−3.7 (br m, 16H), 7.58, 7.72 (two m, 40H in total), 3.21−2.80 (br m, 16 H); $^{31}P\{^1H\}$ NMR (162 MHz, CD_3NO_2) δ 51.01 (s [d, $^1J_{Pt-P}$ = 3209 Hz]); ^{19}F NMR (376 MHz, CD_3NO_2) δ −151.41 (s, $^{11}BF_4$, 13B), −151.36 (s, $^{10}BF_4$, 3B), −123.80 (br s, 4F), −122.70 (br s, 4F). Anal. Calcd for $C_{68}H_{56}B_4F_{24}P_4Pt_2S_4{\cdot}2CH_3NO_2$: C 39.35, H 2.92. Found: C 39.16, H 2.78. Satisfactory mass spectra could not be obtained for this compound. Single crystals suitable for X-ray diffraction studies were grown by slow liquid−liquid diffusion of diethyl ether into a solution of **37** in nitromethane in a 5 mm NMR tube.

*[cis-Pt$_2$Cl$_2$(κP:μ:κ^2-1,4-{Ph$_2$PCH$_2$CH$_2$S}$_2$C$_6$H$_4$)$_2$][BArF]$_2$ (**38b**).* A solution of $PtCl_2$(cod) (132.2 mg, 0.353 mmol) in dichloromethane (10 mL) was added to a solution of **15** (200.0 mg, 0.353 mmol) in dichloromethane (10 mL) in a 30 mL vial. The solution was stirred under nitrogen at room temperature for 2 h. The solution was concentrated to ca. 1 mL under reduced pressure. To the solution was added hexanes (20 mL), and the resulting suspension was filtered using a fritted funnel. The retentate was washed with hexanes (2 × 10 mL) and dried in vacuo. The white solid was dissolved in methanol (10 mL) and transferred to a 30 mL vial. The methanolic solution was stirred at 50 °C for 1 h. The methanol was removed in vacuo to give a yellow solid, which was dissolved in nitromethane (10 mL). To the nitromethane solution was added a solution of NaBArF (310.2 mg, 0.35 mmol) in nitromethane (5 mL), and the resulting solution was stirred overnight. A white solid precipitated, which was removed via filtration through a 0.2 μm PTFE filter. The filtrate was collected, and the nitromethane was removed under reduced pressure to afford 543.2 mg of compound **38b** (92%, 0.164 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.72 (s, 16H), 7.55 (s, 8H), 7.25−7.65 (br m, 40H), 2.69−3.17 (br m, 16H); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ 44.44 (br s [d, $^1J_{P-Pt}$ = 3508 Hz]), 9.57 (br s [d, $^1J_{P-Pt}$ = 3230 Hz]). Anal. Calcd for $C_{132}H_{88}B_2Cl_2F_{48}P_4Pt_2S_4$: C 47.74, H 2.67. Found: C 47.52, H 2.30. HRMS (ESI+) *m*/*z* Calcd for $[M - (BArF)]^{2+}$: 797.0746. Found: 797.0765.

*[cis-Pt$_2$(κ^2:μ:κ^2-1,4-{Ph$_2$PCH$_2$CH$_2$S}$_2$C$_6$H$_4$)$_2$][BF$_4$]$_4$ (**39**).* A solution of $PtCl_2$(cod) (9.2 mg, 24.6 μmol) in dichloromethane (2 mL) was added to a solution of **15** (13.9 mg, 24.6 μmol) in dichloromethane (2 mL) in a 20 mL vial. The solution was stirred under nitrogen at room temperature for 2 h. The solution was concentrated to ca. 0.5 mL under reduced pressure. To the solution was added hexanes (10 mL), and the resulting suspension was filtered using a fritted funnel. The retentate was washed with hexanes (2 × 5 mL) and dried. The white solid was dissolved in methanol (5 mL) and transferred to a 20 mL vial. The methanolic solution was stirred under nitrogen at 50 °C for 1 h. The methanol was removed in vacuo to give a yellow solid, which was dissolved in nitromethane (3 mL). The nitromethane solution was added dropwise to a solution of silver tetrafluoroborate (9.7 mg, 49.8 μmol) in nitromethane (1 mL). The mixture was stirred under nitrogen at room temperature, protected from light, overnight. A white solid precipitated, which was removed via filtration through a 0.2 μm PTFE filter. The fitrate was collected and stirred overnight with activated carbon. The mixture was filtered, and the nitromethane was removed from the filtrate under reduced pressure to afford 15.2 mg of compound **39** (66%, 8.1 μmol). ^{1}H NMR (400 MHz, CD_3NO_2) δ 7.6 (br m, *ca.* 48H), 3.55 (br s, 8H), 3.14 (br s, 8H); $^{31}P\{^1H\}$ NMR (162 MHz, CD_3NO_2) δ 49.54 (s [d, $^1J_{P-Pt}$ = 3102 Hz]). Anal. Calcd for $C_{68}H_{64}B_4F_{16}P_4Pt_2S_4{\cdot}CH_3NO_2$: C 42.90, H 3.50, N 0.73. Found: C 43.10 H 3.39, N 0.86. (The slight discrepancy may be due to residual activated carbon in sample.) Satisfactory mass spectra could not be obtained for this compound.

X-ray Crystallography. 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.

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■ ASSOCIATED CONTENT

Supporting Information

NMR spectra for all compounds. Crystallographic data for complexes **23b**, **24**, **29b**, **30b**, **33b**, **34**, **35b**, **36**, **37**, and **39** (BF_4 and PF_6 salts) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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