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Spontaneous Formation of Heteroligated Pt^{II} Complexes with Chelating Hemilabile Ligands

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Abstract: The spontaneous formation of the heteroligated complex [PtCl(κ^2-$Ph_2PCH_2CH_2SMe$)($Ph_2PCH_2CH_2SPh$)]-Cl (**8a**) by a novel ligand rearrangement process has been observed. By using the weak-link approach, the relative arrangement of the alkyl and aryl groups can be controlled by abstraction of chloride from **8a** to form the closed complex [Pt(κ^2-$Ph_2PCH_2CH_2SMe$)(κ^2-$Ph_2PCH_2CH_2SPh$)][BF_4]$_2$ (**5**) and reopening using halide ions to form semi-open complexes [PtX(κ^2-$Ph_2PCH_2CH_2SMe$)($Ph_2PCH_2CH_2SPh$)]-BF_4 (**8b**; X = Cl^-) and (**8c**; X = I^-). Analogous procedures using $Ph_2PCH_2CH_2SMe$ and 1,4-($Ph_2PCH_2CH_2S$)$_2C_6H_4$ lead to heteroligated bimetallic complexes **7** and **9**, illustrating that this ligand rearrangement process can be used as a tool for the assembly of complementary metallosupramolecular structures.

Keywords: coordination modes · hemilabile ligands · platinum · supramolecular chemistry · transition metals

Introduction

We recently reported a novel halide-induced ligand rearrangement process in bisphosphane–Rh^I complexes, which results in metal complexes with heteroligated coordination environments.[1] This process was developed into a stepwise reaction that allows us to predictably construct square-planar Rh^I complexes with tweezer[2] (**1**) or "triple-decker"[3] (**2**) conformations that can be opened and closed reversibly (Scheme 1). A related procedure, also developed by our group, involving the stepwise addition of two different phosphane ligands leads to qualitatively similar heteroligated Rh^I macrocycles.[4] This reaction is quite powerful as it allows us to incorporate sophisticated functionality, including metallated and catalytically active salen moieties,[2,5] into metallosupramolecular structures[6] in a way that could facilitate cooperative interactions in the context of tweezer or "triple-decker" complexes. These molecules are essential for the development of allosteric regulators with regard to both catalysis and chemical sensing.[6f,7] Thus far, the utility of the reaction has been limited to Rh^I, which generally means that inert atmosphere conditions have to be used. Therefore, creating comparable capabilities with other metal centers that lead to air- and moisture-tolerant complexes could substantially extend the scope of utility of the allosteric systems as well as the range of molecules that can be used to initiate opening and closing of such complexes. Herein, we report a synthetic strategy to synthesize heteroligated Pt^{II} complexes bearing hemilabile aryl- and alkylthioether–phosphane ligands that are stable under ambient conditions. A large variety of synthetic methods are available to generate P,S ligands with functionalized alkyl and aryl groups, potentially allowing for the convergent assembly of complex supramolecular structures from relatively simple building blocks.

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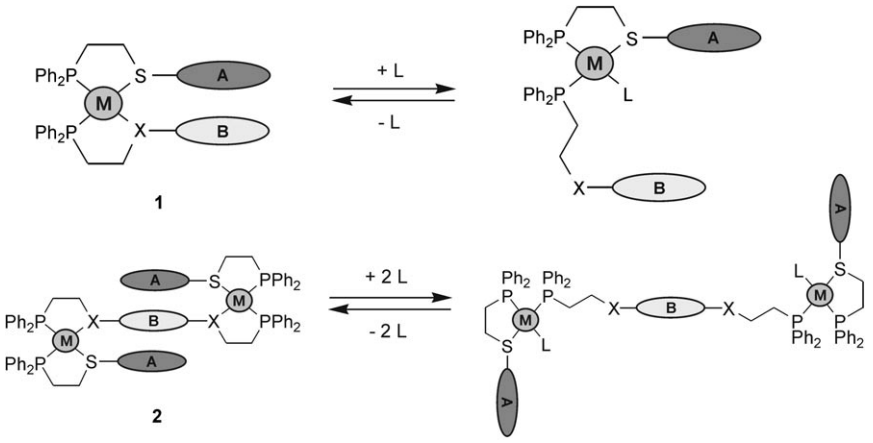
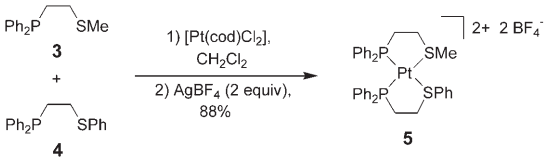
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. The Supporting Information contains $^{31}P\{^1H\}$ NMR spectra that illustrate the formation of complex **8a** via homoligated intermediate complexes.

Results and Discussion

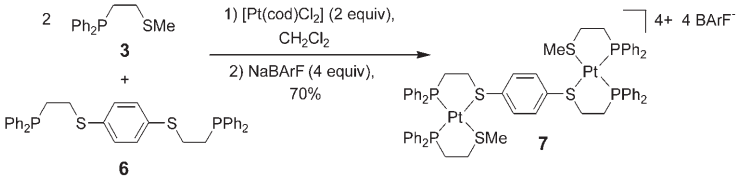
Synthesis of heteroligated complexes: Target structures **5** (Scheme 2) and **7** (Scheme 3) bear the *S*-alkyl and *S*-aryl groups in *cis* position with respect to each other to allow for cooperative effects or blocking of a catalytic site between



Scheme 1. M = metal; X = S,O; L = ligand; A, B = functional or catalytic groups.



Scheme 2.



Scheme 3.

functionalized alkyl and aryl groups, as has been realized with Rh^{I} structures using P,S and P,O ligands.[2,3,7a–e] They can be formed in a one-pot procedure, in which the semi-open precursor complexes **8a** (Scheme 4) or **9** (Scheme 5) are formed in situ, followed by chloride abstraction with $AgBF_4$ or NaBArF ($BArF^-$: $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$) to give **5** (88% yield) or **7** (70% yield), respectively. A single-crystal X-ray crystallographic study of **5** (Figure 1, Table 1)[8] shows that the methyl and phenyl groups of the two ligands are pointing away from each other and that the five-membered chelate rings assume a half-chair geometry. The Pt^{II} center exhibits a distorted square-planar geometry with P1-Pt1-P2 and S1-Pt1-S2 angles of 97.65(6) and 90.85(6)°, respectively. The Pt1–S1 and Pt1–S2 bond lengths are 2.3597(17) and 2.3536(17) Å, respectively.

Compound **8a**, the semi-open chloride precursor to structure **5**, is synthesized by the addition of one equivalent of $[Pt(cod)Cl_2]$ (cod: 1,5-cyclooctadiene) to one equivalent of $Ph_2PCH_2CH_2SMe$ (**3**) in CH_2Cl_2, followed by the addition of one equivalent of $Ph_2PCH_2CH_2SPh$ (**4**) at 24 °C in 89% yield (Scheme 4). Complex **8a** exhibits resonances in its $^{31}P\{^1H\}$ NMR spectrum at $\delta = 43.8$ (d, $^2J(P,P) = 14$ Hz, $^1J(Pt,P) = 3500$ Hz) and 8.5 ppm (d, $^2J(P,P) = 15$ Hz, $^1J(Pt,P) = 3148$ Hz), corresponding to the P atom of the κ^2-P,S-alkyl chelating ligand and to the P atom of the unchelated κ^1-P,S-aryl ligand, respectively.[9] A single-crystal X-ray crystallographic study confirms the solid-state *cis*-phosphane semi-open structure of **8a** (Figure 2, Table 1).[8] The Pt^{II} center exhibits a distorted square-planar geometry with P1-Pt1-P2, P2-Pt1-Cl1, and S1-Pt1-Cl1 angles of 99.46(5), 88.57(5), and 86.19(5)°, respectively. The Pt1–S1 and Pt1–Cl1 bond lengths are 2.3465(15) and 2.3497(14) Å, respectively. The preferential coordination of the alkylthioether moiety to the Pt^{II} center, while the arylthioether moiety remains uncoordinated, illustrates the significant influence of the substituent on the thioether group on its ability to undergo complexation with a metal.[10] This is likely due to the electron-withdrawing properties of the phenyl ring, resulting in a lower electron density on the S atom of the arylthioether ligand compared to the alkylthioether ligand.

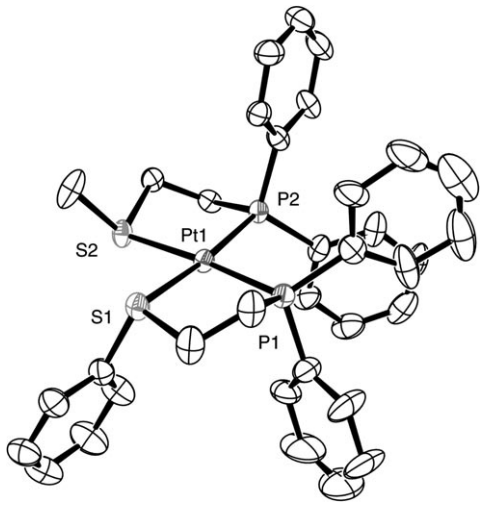
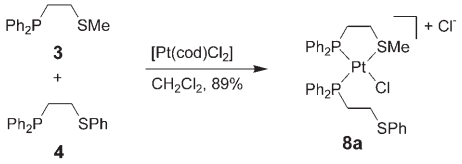


Figure 1. ORTEP diagram of $\mathbf{5}\cdot CH_2Cl_2\cdot 0.5$pentane with thermal ellipsoids drawn at 30% probability. Hydrogen atoms, counterions and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–P1 2.2669(17), Pt1–P2 2.2726(16), Pt1–S1 2.3597(17), Pt1–S2 2.3536(17), P1-Pt1-P2 97.65(6), P1-Pt1-S1 85.60(6), P2-Pt1-S2 86.13(6), S1-Pt1-S2 90.85(6), P1-Pt1-S2 175.43(6), P2-Pt1-S1 174.25(6).

When the bisbidentate phosphane ligand 1,4-$(Ph_2PCH_2CH_2S)_2C_6H_4$ (**6**) is used instead of bidentate ligand **4**, bimetallic complex **9** is formed in 90% yield (Scheme 5). It exhibits resonances in its $^{31}P\{^1H\}$ NMR spectrum at $\delta =$ 44.0 (d, $^2J(P,P) = 12$ Hz, $^1J(Pt,P) = 3514$ Hz) and at 8.9 ppm (d, $^2J(P,P) = 13$ Hz, $^1J(Pt,P) = 3146$ Hz), indicating that the

Table 1. Crystallographic data.

	5·CH_2Cl_2·0.5 pentane	**8a**·CH_2Cl_2
formula	$C_{38.5}H_{31.5}B_2Cl_2F_8P_2PtS_2$	$C_{36}H_{38}Cl_4P_2PtS_2$
M_r	1059.81	933.61
color, habit	colorless, plate	colorless, needle
crystal dimensions [mm]	0.30×0.30×0.10	0.15×0.10×0.05
space group	$C2/c$	$P\bar{1}$
crystal system	monoclinic	triclinic
a [Å]	37.718(3)	9.6990(13)
b [Å]	12.8281(12)	11.4350(15)
c [Å]	18.8568(17)	16.537(2)
α [°]	90	84.367(2)
β [°]	115.3160(10)	86.080(2)
γ [°]	90	85.345(2)
V [Å^3]	8247.7(13)	1815.8(4)
Z	8	2
ρ_{calcd} [g cm^{-3}]	1.707	1.708
radiation (λ [Å])	$Mo_{K\alpha}$ (0.71073)	$Mo_{K\alpha}$ (0.71069)
$F(000)$	4148	924
2θ range [°]	3.84 to 56.56	4.16 to 56.18
μ [mm^{-1}]	3.776	4.387
T [K]	100(2)	100(2)
reflns measured	34287	20752
independent reflns	9493	8083
	[R(int) = 0.0444]	[R(int) = 0.0427]
GOF on F^2	1.053	1.040
final R indices [$I>2\sigma(I)$]	$R1$ = 0.0517	$R1$ = 0.0446
	$wR2$ = 0.1361	$wR2$ = 0.1089
R indices (all data)	$R1$ = 0.0747	$R1$ = 0.0581
	$wR2$ = 0.1495	$wR2$ = 0.1152
Largest diff. peak/hole [e Å^{-3}]	2.424/−1.762	4.200/−2.467



Scheme 4.

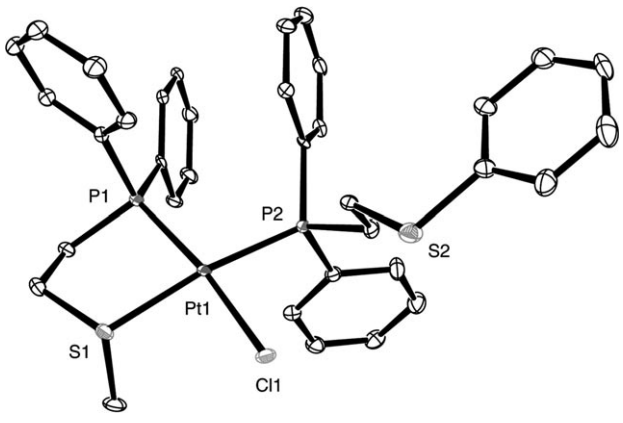
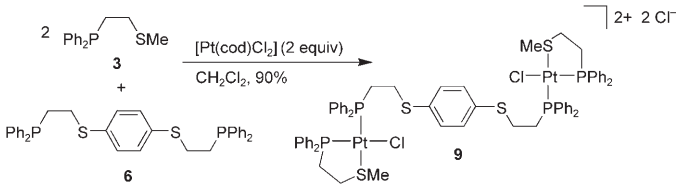


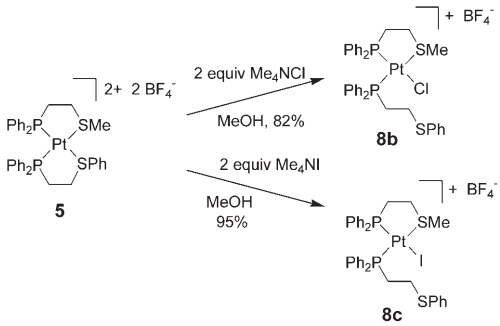
Figure 2. ORTEP diagram of **8a**·CH_2Cl_2 with thermal ellipsoids drawn at 30% probability. Hydrogen atoms, counterion and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1−P1 2.2241(14), Pt1−P2 2.2698(15), Pt1−S1 2.3465(15), Pt1−Cl1 2.3497(14), P1-Pt1-P2 99.46(5), P1-Pt1-S1 85.89(5), P2-Pt1-Cl1 88.57(5), S1-Pt1-Cl1 86.19(5), P1-Pt1-Cl1 171.92(5), P2-Pt1-S1 172.34(5).



Scheme 5.

coordination geometry around the Pt^{II} center is similar to complex **8a**. Furthermore, complex **9** exhibits molecular ion peaks in its ESIMS spectrum at m/z 1581.6 and 773.2, corresponding to the $[M-Cl]^+$ and $[M-2Cl]^{2+}$ ions.

Reactivity of closed complex 5: Initial investigations on the reactivity of condensed complex **5** with small molecules showed that selective cleavage of the Pt–S aryl bond is possible with halide molecules, giving the semi-open chloride complex **8b** or iodide complex **8c** through the addition of two equivalents of tetramethylammonium chloride or tetramethylammonium iodide in MeOH at 24 °C (Scheme 6, both



Scheme 6.

complexes contain BF_4^- as a counterion), while no opening of **5** is observed upon the addition of 20 equivalents of acetonitrile in CD_3OD after 24 h at 24 °C, according to in situ $^{31}P\{^1H\}$ NMR spectroscopy. Therefore, complementary reactivity with regard to Rh^I complexes was observed.[11]

Control reactions for ligand rearrangement process: To investigate whether the observed spontaneous formation of heteroligated Pt^{II} complexes is the result of a ligand rearrangement process, ligands **3** (2 equiv) and **4** (2 equiv) each were separately mixed with [Pt(cod)Cl_2] (1 equiv) in CD_2Cl_2/CH_2Cl_2 (1:5 v/v). The homoligated intermediates exhibit broad resonances in their $^{31}P\{^1H\}$ NMR spectra, indicating exchange processes that are fast on the NMR timescale at room temperature. This observation is consistent with literature references on the formation of homoligated Pt^{II} complexes with ligands **3** and **4**.[12,13] Upon mixing of the two solutions, the formation of heteroligated complex **8a** and the complete disappearance of the reactants was observed after 15 min, according to in situ $^{31}P\{^1H\}$ NMR spectroscopy (see Supporting Information). In a separate experi-

ment, $[Pt(cod)Cl_2]$ was added to a mixture of ligands **3** and **4** in CD_2Cl_2/CH_2Cl_2 (1:5 v/v), and complex **8a** was observed exclusively after 15 min, according to in situ $^{31}P\{^1H\}$ NMR spectroscopy.

Thus, the observed reaction constitutes a ligand rearrangement process leading from two different homoligated complexes to a single heteroligated complex. This example of spontaneous selective pairing of two P,S ligands A and B and a metal M in solution to form heteroligated A-M-B motifs instead of a mixture of A-M-A, B-M-B, and A-M-B motifs is one of relatively few examples of spontaneous complementary metallosupramolecular complexation[14] that is more frequently observed in organic supramolecular chemistry.[15]

Conclusion

We have presented a novel ligand rearrangement process that spontaneously leads to heteroligated Pt^{II} complexes coordinating to P,S-aryl and P,S-alkyl ligands. Condensation to closed complexes and reopening using halide ions illustrate how the weak-link approach[6e,f,7a–f,10,16,17] can be used to manipulate the coordination environment around Pt^{II} centers to make various heteroligated complexes with different relative arrangements of the thioether substituents. Because of the robustness of the Pt complexes with respect to oxygen and moisture and the high selectivity of the rearrangement process, the reaction is expected to become a valuable tool for the "programmed" assembly of complex functional supramolecular structures and allosteric catalysts.[7] The selective reactivity of the complexes with respect to various small molecules suggests potential applications for the development of sensors for small molecules. The interaction of nucleobases as N-donor ligands with respect to hemilabile, homoligated Pt^{II}–P,N complexes[18] indicates that a further extension to biologically relevant analyte molecules may be possible.

Experimental Section

General methods/instrument details: All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques or an inert atmosphere glovebox unless otherwise noted. CH_2Cl_2, acetonitrile, and hexanes were dried and purified through activated alumina columns as described by Grubbs et al. prior to use.[19] All solvents were degassed with nitrogen prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. All other chemicals were used as received from Aldrich Chemical Company or prepared according to literature procedures (**4**,[20] **6**,[17] NaBArF[21]). ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 300 and 75.5 MHz, respectively, and referenced to residual proton resonances in deuterated solvents. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 121.5 MHz and referenced relative to an external 85% H_3PO_4 standard. $^{19}F\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 282.5 MHz and referenced relative to an external $CFCl_3$ in $CDCl_3$ standard. All chemical shifts are reported in ppm. Electrospray mass spectra (ESIMS) were recorded on a Micromass Quatro II triple quadrupole mass spectrometer. Electron ionization mass spectra (EIMS) were recorded on a Fisions VG 70–250 SE mass spectrometer. Melting points were measured on a Mel-Temp 2 (Laboratory Devices) apparatus. Elemental analyses were performed by Quantitative Technologies, Whitehouse, NJ (USA).

(2-Methylthioethyl)diphenylphosphane (3):[22] $KPPh_2$ in THF (79 mL, 0.5 M, 39.5 mmol, 1 equiv) was added to 2-chloroethylmethyl sulfide (4.0 mL, 40.5 mmol, 1.03 equiv) over 15 min at 24 °C. The solution turned from yellow to red. After stirring for 3 h, the reaction solution was concentrated in vacuo and redissolved in CH_2Cl_2 (ca. 100 mL), washed with H_2O (3×75 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo to give a yellow oil. Recrystallization from MeOH gave **3** as an off-white powder (8.580 g, 83%). M.p. 54 °C; ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): $\delta = 7.46$–7.40 (m, 4H; arom), 7.39–7.33 (m, 6H; arom), 2.59–2.51 (m, 2H; -SCH_2CH$_2$P-), 2.37–2.32 (m, 2H; -SCH$_2$CH_2P-), 2.09 ppm (s, 3H; -SCH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 22 °C): $\delta = 138.7$ (d, ^1J(C,P) = 13.2 Hz; C_i-P), 133.2 (d, ^2J(C,P) = 19.0 Hz; C_o-P), 129.3 (s; C_p-P), 129.1 (d, ^3J(C,P) = 6.3 Hz; C_m-P), 31.1 (d, ^2J(C,P) = 21.7 Hz; -SCH$_2$CH$_2$PPh$_2$), 28.7 (d, ^1J(C,P) = 14.3 Hz; -CH$_2$PPh$_2$), 15.8 ppm (s; -SCH$_3$); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22 °C): $\delta = -16.8$ ppm (s); MS (EI): *m/z* calcd for $C_{15}H_{17}PS$ $[M]^+$: 260.0789; found: 260.0788; elemental analysis calcd (%) for $C_{15}H_{17}PS$: C 69.21, H 6.59; found: C 69.28, H 6.68.

[Pt(κ^2-Ph$_2$PCH$_2$CH$_2$SMe)(κ^2-Ph$_2$PCH$_2$CH$_2$SPh)][BF$_4$]$_2$ (5): A solution of $[Pt(cod)Cl_2]$ (100.7 mg, 0.269 mmol, 1 equiv) in CH_2Cl_2 (3 mL) was added dropwise to a stirring solution of ligand **3** (70.0 mg, 0.269 mmol, 1 equiv) in CH_2Cl_2 (3 mL) at 24 °C. The solution turned slightly yellow. After 5 min, a solution of **4**[20] (86.7 mg, 0.269 mmol, 1 equiv) in CH_2Cl_2 (3 mL) was added dropwise to the stirring reaction mixture. After 1 h, $AgBF_4$ (104.7 mg, 0.538 mmol, 2 equiv) was added to the reaction mixture, which turned cloudy. After 1 h, the reaction mixture was filtered through celite, followed by recrystallisation from CH_2Cl_2/hexanes, resulting in **5** as a white powder (229.3 mg, 88%). M.p. 168 °C; ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): $\delta = 7.84$–7.50 (m, 25H; arom), 3.8–2.1 ppm (m, 11H; aliph); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22 °C): $\delta = 46.4$ (d, ^2J(P,P) = 11 Hz, ^1J(Pt,P) = 3085 Hz), 45.8 ppm (d, ^2J(P,P) = 11 Hz, ^1J(Pt,P) = 3130 Hz); MS (ESI): *m/z* calcd for $C_{35}H_{36}BF_4P_2PtS_2$ $[M-BF_4]^+$: 864.1; found: 863.8; elemental analysis calcd (%) for $C_{35}H_{36}B_2F_8P_2PtS_2 \cdot 0.25C_6H_{14}$: C 45.03, H 4.09; found: C 44.92; H 3.81. A residual amount of hexane was observed by ^1H NMR spectroscopy after purification and extended drying in vacuo. Crystals of **5**·CH_2Cl_2·0.5 pentane suitable for single-crystal X-ray crystallography were obtained by slow diffusion of pentane into a saturated solution of **5** in CH_2Cl_2 (colorless plates).

[Pt$_2${κ^2:μ^2:κ^2-1,4-(Ph$_2$PCH$_2$CH$_2$S)$_2$C$_6$H$_4$}(κ^2-Ph$_2$PCH$_2$CH$_2$SMe)$_2$][BArF]$_4$ (7): A solution of $[Pt(cod)Cl_2]$ (21.6 mg, 0.0577 mmol, 2 equiv) in CH_2Cl_2 (3 mL) was added dropwise to a stirring solution of **3** (15.0 mg, 0.0576 mmol, 2 equiv) in CH_2Cl_2 (3 mL) at 24 °C. The solution turned slightly yellow. After 5 min, a solution of **6**[17] (16.3 mg, 0.0288 mmol, 1 equiv) in CH_2Cl_2 (3 mL) was added dropwise to the reaction mixture. After 30 min, NaBArF[21] (102.2 mg, 0.115 mmol, 4 equiv) was dissolved in CH_2Cl_2 (3 mL) and added to the reaction mixture, which turned cloudy. After 2 h, the reaction mixture was filtered through celite, followed by recrystallization from CH_2Cl_2/hexanes, resulting in **7** as a white powder (99.2 mg, 70%). M.p. 118 °C; ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): $\delta = 7.72$–6.95 (m, 92H; arom), 3.1–2.3 ppm (m, 22H; aliph); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22 °C): $\delta = 47.0$ (d, ^2J(P,P) = 11 Hz, ^1J(Pt,P) = 3093 Hz), 46.7 ppm (d, ^2J(P,P) = 11 Hz, ^1J(Pt,P) = 3020 Hz); MS (ESI): *m/z* calcd for $C_{128}H_{90}B_2F_{48}P_4Pt_2S_4$ $[M-2BArF]^{2+}$: 1601.7; found: 1601.7; elemental analysis calcd (%) for $C_{192}H_{114}B_4F_{96}P_4Pt_2S_4$: C 46.75, H, 2.33; found: C 46.98, H 2.03.

[PtCl(κ^2-Ph$_2$PCH$_2$CH$_2$SMe)(Ph$_2$PCH$_2$CH$_2$SPh)]Cl (8a): A solution of $[Pt(cod)Cl_2]$ (139.9 mg, 0.374 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added dropwise to a stirring solution of **3** (97.3 mg, 0.374 mmol, 1 equiv) in CH_2Cl_2 (5 mL) at 24 °C. The solution turned slightly yellow. After 5 min, a solution of **4**[20] (120.5 mg, 0.374 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added dropwise, and the reaction mixture was stirred for 1 h. Recrystallisation from CH_2Cl_2/hexanes resulted in **8a** as a white powder (310.5 mg, 89%). M.p. 166 °C; ^1H NMR (300 MHz, CD_2Cl_2, 22 °C): $\delta = 7.52$–7.15 (m,

25H; arom), 3.17–3.11 (m, 3H; -SCH_3), 2.99–2.92 (m, 4H; -CH_2-), 2.68–2.59 ppm (m, 4H; -CH_2-); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22°C): δ = 43.8 (d, ^2J(P,P) = 14 Hz, ^1J(Pt,P) = 3500 Hz), 8.5 ppm (d, ^2J(P,P) = 15 Hz, ^1J(Pt,P) = 3148 Hz); MS (ESI): *m/z* calcd for $C_{35}H_{36}ClP_2PtS_2$ $[M-Cl]^+$: 812.1; found: 812.4; elemental analysis calcd (%) for $C_{35}H_{36}Cl_2P_2PtS_2 \cdot CH_2Cl_2$: C 46.40, H 4.11; found: C 46.08, H 4.00. The CH_2Cl_2 molecule found in the combustion analysis is also observed in the crystal structure. Crystals of **8a**·CH_2Cl_2 suitable for single-crystal X-ray crystallography were obtained by slow evaporation of Et_2O into a saturated solution of **8a** in CH_2Cl_2 (colorless needles).

[PtCl(κ^2-Ph$_2$PCH$_2$CH$_2$SMe)(Ph$_2$PCH$_2$CH$_2$SPh)]BF$_4$ (8b): A solution of Me_4NCl (4.6 mg, 0.042 mmol, 2 equiv) in MeOH (anhydrous, 5 mL) was added to a stirring solution of complex **5** (20.0 mg, 0.0210 mmol, 1 equiv) in MeOH (anhydrous, 5 mL) at 24°C. The solution was colorless. After 30 min, the solution was concentrated in vacuo. Addition of CH_2Cl_2 (3 mL) and hexanes (ca. 1 mL), filtration through celite, and concentration in vacuo gave **8b** as a white powder (16.2 mg, 82%). M.p. 132°C; ^1H NMR (300 MHz, CD_2Cl_2, 22°C): δ = 7.54–7.15 (m, 25H; arom.), 3.14–3.09 (m, 3H; -SCH_3), 2.99–2.91 (m, 4H; -CH_2-), 2.68–2.59 ppm (m, 4H; -CH_2-); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22°C): δ = 43.7 (d, ^2J(P,P) = 15 Hz, ^1J(Pt,P) = 3505 Hz), 8.4 ppm (d, ^2J(P,P) = 15 Hz, ^1J(Pt,P) = 3118 Hz); $^{19}F\{^1H\}$ NMR (282.5 MHz, CD_2Cl_2, 22°C): δ = −152.94 (s; $^{10}BF_4$), −152.99 ppm (s; $^{11}BF_4$); MS (ESI): *m/z* calcd for $C_{35}H_{36}P_2PtS_2Cl$ $[M-BF_4]^+$: 812.1; found: 812.5; elemental analysis calcd (%) for $C_{35}H_{36}BClF_4P_2PtS_2 \cdot 0.5\,C_6H_{14}$: C 48.40, H 4.60; found: C 48.05, H, 4.42. A residual amount of hexane was observed by ^1H NMR spectroscopy after purification and extended drying in vacuo.

[PtI(κ^2-Ph$_2$PCH$_2$CH$_2$SMe)(Ph$_2$PCH$_2$CH$_2$SPh)]BF$_4$ (8c): A solution of Me_4NI (8.4 mg, 0.042 mmol, 2 equiv) in MeOH (anhydrous, 5 mL) was added to a stirring solution of complex **5** (20.0 mg, 0.0210 mmol, 1 equiv) in MeOH (anhydrous, 5 mL) at 24°C. The solution was yellow. After 30 min, the solution was concentrated in vacuo. Addition of CH_2Cl_2 (3 mL), filtration through celite, and concentration in vacuo gave **8c** as a yellow-orange powder (19.7 mg, 95%). M.p. 122°C; ^1H NMR (300 MHz, CD_2Cl_2, 22°C): δ = 7.57–7.14 (m, 25H; arom), 3.2–3.02 (m, 3H; -SCH_3), 2.90–2.63 ppm (m, 8H; -CH_2-); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22°C): δ = 49.2 (d, ^2J(P,P) = 11 Hz, ^1J(Pt,P) = 3343 Hz), 2.7 ppm (d, ^2J(P,P) = 12 Hz, ^1J(Pt,P) = 3073 Hz); $^{19}F\{^1H\}$ NMR (282.5 MHz, CD_2Cl_2, 22°C): δ = −152.97 (s; $^{10}BF_4$), −153.02 ppm (s; $^{11}BF_4$); MS (ESI): *m/z* calcd for $C_{35}H_{36}IP_2PtS_2$ $[M-BF_4]^+$: 904.0; found: 904.2; elemental analysis calcd (%) for $C_{35}H_{36}BF_4IP_2PtS_2$: C 42.38, H 3.66; found: C 42.10, H 3.55.

[Pt$_2$Cl$_2${μ^2-1,4-(Ph$_2$PCH$_2$CH$_2$S)$_2$C$_6$H$_4$}(κ^2-Ph$_2$PCH$_2$CH$_2$SMe)$_2$]Cl$_2$ (9): A solution of $[Pt(cod)Cl_2]$ (33.9 mg, 0.0906 mmol, 2 equiv) in CH_2Cl_2 (2 mL) was added dropwise to a stirring solution of **3** (23.6 mg, 0.0907 mmol, 2 equiv) in CH_2Cl_2 at 24°C (2 mL). The solution turned slightly yellow. After 5 min, a solution of **6**[17] (25.7 mg, 0.0454 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added dropwise and the reaction mixture was stirred for 1 h at 24°C. Recrystallisation from CH_2Cl_2/hexanes resulted in **9** as an off-white powder (65.8 mg, 90%). M.p. 186°C; ^1H NMR (300 MHz, CD_2Cl_2, 22°C): δ = 7.51–7.19 (m, 44H; arom), 3.18–3.05 (m, 6H; -SCH_3), 2.85–2.60 (m, 8H; -CH_2-), 2.48–2.28 ppm (m, 8H; -CH_2-); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 22°C): δ = 44.0 (d, ^2J(P,P) = 12 Hz, ^1J(Pt,P) = 3514 Hz), 8.9 ppm (d, ^2J(P,P) = 13 Hz, ^1J(Pt,P) = 3146 Hz); MS (ESI): *m/z* calcd for $C_{64}H_{66}Cl_3P_4Pt_2S_4$ $[M-Cl]^+$: 1581.1; found: 1581.6; *m/z* calcd for $C_{64}H_{66}Cl_2P_4Pt_2S_4$ $[M-2Cl]^{2+}$: 773.1; found: 773.2; elemental analysis calcd (%) for $C_{64}H_{66}Cl_4P_4Pt_2S_4$: C 47.52, H 4.12; found: C 47.92, H 4.42.

Control reactions

Reaction of acetonitrile with complex 5: Acetonitrile (5 µL, 0.1 mmol, 20 equiv) was added to a solution of complex **5** (5.0 mg, 0.0053 mmol, 1 equiv) in CD_3OD (0.75 mL) in a vial at 24°C and transferred into an air-free NMR tube. After 24 h, a $^{31}P\{^1H\}$ NMR spectrum was recorded, which showed no resonance upfield to 30 ppm, indicating the absence of unchelated phosphorus ligand.

Separate reaction of P,S ligands 3 and 4 with [Pt(cod)Cl$_2$], followed by mixing to give heteroligated complex 8a: A solution of $[Pt(cod)Cl_2]$ (7.2 mg, 0.0192 mmol, 1 equiv) in CH_2Cl_2 (1 mL) was added dropwise over 1 min to a stirring solution of **3** (10.0 mg, 0.0384 mmol, 2 equiv) in CH_2Cl_2 (1 mL) at 24°C. In a separate vial, a solution of $[Pt(cod)Cl_2]$ (7.2 mg, 0.0192 mmol, 1 equiv) in CH_2Cl_2 (1 mL) was added dropwise over 1 min to a stirring solution of **4** (12.4 mg, 0.0385 mmol, 2 equiv) in CH_2Cl_2 (1 mL). CD_2Cl_2 (0.4 mL) was added to each vial. A 1 mL aliquot of each solution was transferred into two air-free NMR tubes and $^{31}P\{^1H\}$ NMR spectra were recorded, showing broad resonances that are consistent with those given in reference [12a]. After 1 h, the two aliquots were recombined with the respective solutions and then the two solutions were mixed. After 5 min, a 1 mL aliquot was transferred into an air-free NMR tube and another $^{31}P\{^1H\}$ NMR spectrum was recorded after 10 min, showing the clean formation of complex **8a**.

Reaction of [Pt(cod)Cl$_2$] with a mixture of P,S ligands 3 and 4, resulting in heteroligated complex 8a: A solution of $[Pt(cod)Cl_2]$ (14.4 mg, 0.0385 mmol, 1 equiv) in CH_2Cl_2 (2 mL) and CD_2Cl_2 (0.75 mL) was added dropwise over 1 min to a stirring solution of **3** (10.0 mg, 0.0384 mmol, 1 equiv) and **4** (12.4 mg, 0.0385 mmol, 1 equiv) in CH_2Cl_2 (2 mL). A 1 mL aliquot was transferred into an air-free NMR tube after 5 min and a $^{31}P\{^1H\}$ NMR spectrum was recorded after 10 min, showing the clean formation of complex **8a**.

X-ray crystallography:[8] Crystallographic data are collected in Table 1. Colorless crystals of **5** and **8a** were mounted on fiber loops and cooled to 100 K. In both cases the centrosymmetric space group option was selected based on the results of the refinement. The structures were solved by direct methods, and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters, and contained idealized hydrogen atoms, except for the fractional and disordered pentane molecule in **5**. The asymmetric units contained cocrystallized solvent molecules in both cases: for **5**, CH_2Cl_2 and 0.5 pentane located on an inversion center, and for **8a** CH_2Cl_2. All software is contained in the SMART, SAINT and SHELXTL software libraries of the Bruker XRD corporation.

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