Insertion of Elemental Sulfur and SO\textsubscript{2} into the Metal–Hydride and Metal–Carbon Bonds of Platinum Compounds

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Elemental sulfur (S\textsubscript{8}) has been found to insert only one sulfur atom into the metal–hydride bonds of the platinum alkyl and aryl hydride complexes [(dcpe)PtRH] (dcpe = Cy\textsubscript{2}PC\textsubscript{2}H\textsubscript{4}PCy\textsubscript{2}). Unlike the parent compounds, the S-inserted complexes do not undergo reductive elimination to form the corresponding alkane- or arenedithiols. Methane is lost from the methyl sulfhydryl complex. Sulfur dioxide was also found to insert into a platinum–methyl bond to form the corresponding S-bound sulfinate, which upon reacting with mineral acids generates methylsulfinic acid.

Introduction

The selective activation and transformation of C–H bonds has been a major driving force behind much current research in organometallic chemistry.\textsuperscript{(1)} In 1986, Whitesides was able to develop a platinum-based system that was able to selectively activate C–H bonds in alkanes and arenes by the oxidative addition of the C–H bond to the coordinatively unsaturated [dcpe]Pt0 (dcpe = Cy\textsubscript{2}PC\textsubscript{2}H\textsubscript{4}PCy\textsubscript{2}) species.\textsuperscript{(2,3)} This paper explores the potential use of this chemistry to develop a way of activating methane and other alkyl and aryl compounds, followed by insertion of sulfur-bearing species to synthesize sulfur-bearing organic compounds.

One convenient sulfur source capable of insertion chemistry is elemental sulfur (S\textsubscript{8}). While rare, there are a few reported cases of elemental sulfur insertion into transition-metal–ligand bonds.\textsuperscript{(4,6)} Early work by Legzdins showed an example of insertion of a single sulfur atom from elemental sulfur into a metal–carbon bond.\textsuperscript{(6)} A recent report by Hillhouse demonstrated the facile insertion of sulfur into the metal–aryl bond in a (bipy)-Ni(aryl)(alkyl) complex.\textsuperscript{(7)} All other examples of using elemental sulfur resulted in a sulfur-chain fragment (S\textsubscript{8}) being inserted.

In this paper, three new compounds are presented that are able to cleanly insert one sulfur atom into their M–H bonds. All three examples are based on the group 10 metal system studied by Whitesides. The reactivity of these species is also presented. We recently reported the insertion of SO\textsubscript{2} into group 8 metal–carbon bonds.\textsuperscript{(8)} In this paper, similar insertions of SO\textsubscript{2} into the M–C bonds of group 10 metal complexes are reported. We have also been able to show that it is possible to release the RSO\textsubscript{2} group from the metal to form methylsulfinic acid.

Results and Discussion

Synthesis of Sulfur Insertion Adducts. Addition of elemental sulfur (S\textsubscript{8}) to a benzene or THF solution of Pt(dcpe)(R)H (R = Me, CH\textsubscript{3}Bu, Ph) leads to the quantitative formation of the new products Pt(dcpe)(R)(SH) (R = Me (1), CH\textsubscript{3}Bu (2), Ph (3)). NMR spectroscopy proved to be ideal for following the progress of these reactions. For example, addition of elemental sulfur (S\textsubscript{8}) to a THF-d\textsubscript{8} solution of Pt(dcpe)(Me)H led to complete reaction within 5 min. The \textsuperscript{1}H NMR spectrum showed that the methyl resonance of Pt(dcpe)(Me)H at \(\delta\ 0.67\) (dd, \(J_{PH} = 70\) Hz) had shifted upfield to \(\delta\ 0.36\) (dd, \(J_{PH} = 62\) Hz). A more dramatic change was seen in the hydride resonance, which shifted downfield from the signal for the starting material at \(\delta\ 0.445\) (dd, \(J_{PH} = 1150\) Hz) to \(\delta\ 0.917\) (dd, \(J_{PH} = 62\) Hz) with a large change in the Pt–H coupling constant. \textsuperscript{31}P NMR spectroscopy provided another handle for monitoring the reaction. The \textsuperscript{31}P NMR spectrum of 1 in THF-d\textsubscript{8} displays a resonance at \(\delta\ 62.33\) (s, \(J_{PP} = 3064\) Hz), which corresponds to the phosphorus trans to the SH group. This large Pt–P coupling constant is seen in other complexes of phosphorus groups trans to either halides or main-group metals.\textsuperscript{2,3} A second resonance is seen in the \textsuperscript{31}P NMR spectrum at \(\delta\ 67.01\) (J\textsubscript{PP} = 1811 Hz) with a Pt–P coupling constant similar to those seen for the starting materials. Curiously, no P–P coupling is observed.

1 decomposes in solution in the presence of excess S\textsubscript{8}. Another synthetic route was devised to allow for complete characterization which also allowed for the elimination of problems involving removal of unreacted S\textsubscript{8}.
in the samples. The nucleophilic attack of \( \text{SH}^- \) (from NaSH) on the metal alkyl or aryl halides was used to generate large quantities of 1 cleanly (eq 1). Crystals of 1 were obtained by cooling a supersaturated hot acetone solution. Both the methyl and the sulfhydryl groups were sufficiently disordered to prevent a satisfactory X-ray structure of 1 from being obtained, but the model indicated that only a single sulfur atom had inserted into the M–H bond.

Compounds 2 and 3, the CH$_2$CMe$_3$ and Ph derivatives, were synthesized similarly. In the case of 2, elemental sulfur was added to a THF-d$_8$ solution of [Pt-(dcpe)(CH$_2$CMe$_3$)$_2$H] and the reaction monitored by NMR spectroscopy until all traces of the starting material were consumed. The hydride resonance shifted downfield in the $^1$H NMR spectrum to $\delta$ ~0.457 (J$_{PH}$ = 61 Hz) upon sulfur insertion. Two resonances were observed in the $^{31}$P NMR spectrum, one at $\delta$ 57.88 (J$_{PP}$ = 3210 Hz) assigned to the phosphorus trans to the SH group and another at $\delta$ 64.07 (J$_{PP}$ = 1626 Hz) assigned to the phosphorus trans to the neopentyl group. As in the case of 1, compound 2 appears to be unstable in solution with excess S$_8$; therefore, the NaSH route was used to generate larger quantities of 2 (eq 1).

Crystals of 2 were obtained by layering a solution of 2 in methylene chloride with hexanes. The X-ray structure (Figure 1) shows that insertion of a single sulfur atom has occurred into the M–H bond. Crystallographic data are listed in Table 1, and selected distances and angles are given in Table 2.

The platinum phenyl sulfhydryl complex 3 was synthesized by addition of elemental sulfur (S$_8$) to a C$_6$D$_5$ solution of Pt(dcpe)(Ph)$_2$H. The hydride resonance shifted downfield in the $^1$H NMR spectrum to $\delta$ ~0.168 (J$_{PH}$ = 65 Hz) following sulfur insertion. Two resonances were observed in the $^{31}$P NMR spectrum at $\delta$ 54.58 (J$_{PP}$ = 3025 Hz) for the phosphorus trans to the SH group, and at $\delta$ 60.55 (J$_{PP}$ = 1720 Hz) for the phosphorus trans to the phenyl group. Unlike the cases of 1 and 2, the reaction with S$_8$ was slower in the case of 3, taking up to 2 h to consume all of the starting material. The platinum phenyl sulfhydryl complex 3 also appears to be more stable in solution with excess S$_8$. Nevertheless, an alternate synthetic route was used to obtain pure, S$_8$-free samples of 3.

Crystals of 3 were obtained by layering a solution of 3 in methylene chloride with hexane. The X-ray structure (Figure 2) shows that only one S atom insertion has occurred into the M–H bond. Crystallographic data are listed in Table 1, and selected distances and angles are given in Table 2.

For comparison, the methylene-bridged chelating phosphine analogue of 1, [Pt(C$_2$P$_2$CH$_2$PC$_2$H$_2$)(Me)(SH)] (4) was synthesized by way of the NaSH route. The $^{31}$P NMR spectrum of 4 showed large changes from those of the ethylene-bridged compounds. The resonances of 4 are shifted ~80 ppm upfield from those of 1, appearing at $\delta$ ~26.76 (J$_{PP}$ = 43 Hz, J$_{PP}$ = 1376 Hz) and $\delta$ ~28.36 (J$_{PP}$ = 43 Hz, J$_{PP}$ = 2727 Hz). The P–P coupling can now be seen, and each resonance appears as a doublet. In compounds 1–3, the P–P coupling must be small and is not observable in the NMR spectra.

**Structures of Complexes 2 and 3.** Complexes 2 and 3 are structurally similar, except for the alkyl or aryl group bound to the platinum center. In each case, they consist of mononuclear neutral molecules (Figures 1 and 2) with no significant intermolecular interactions. The platinum metal is coordinated to two phosphorus atoms, one carbon atom, and one sulfur atom in a slightly distorted square planar geometry.

The three X-ray structures of 1–3 definitively prove that only one sulfur atom was inserted into the Pt–H bonds. Of the previously reported cases of elemental sulfur insertions, only the studies by Legzdins$^6$ and Hillhouse$^7$ showed single-sulfur-atom insertions. In the case of the W–C insertion, a mechanism was proposed to explain the observation of single-atom insertion, in which it was proposed that the tungsten species first coordinated with the S$_8$ and the bound S atom then underwent intramolecular nucleophilic attack by an alkyl group with concomitant expulsion of the residual sulfur fragment (eq 2). It was also found that the
Insertion into M–H and M–C Bonds of Pt Compounds

Table 1. Summary of Crystallographic Data for Complexes 2, 3, and 7

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Table 2. Selected Distances (Å) and Angles (deg) for Pt(dcpe)(CH₂Bu)(SH) (2), Pt(dcpe)(Ph)(SH) (3), and Pt(dcpe)(SO₂Me)Me (7)

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Table 2. Selected Distances (Å) and Angles (deg) for Pt(dcpe)(CH₂Bu)(SH) (2), Pt(dcpe)(Ph)(SH) (3), and Pt(dcpe)(SO₂Me)Me (7)

Figure 2. ORTEP drawing of [Pt(Cy₃PC₂H₄PCy₃)(Ph)(SH)] (3). Ellipsoids are shown at the 30% level.

tungsten species was able to further react with more elemental sulfur. Unlike the previous tungsten case, we saw no indication of sulfur insertion into the Pt–C bonds.

The Pt–S bond lengths in 2 and 3 are similar to those previously reported in the literature (Chart 1). They are similar to other terminal bound sulfur groups such as Pt(PPh₃)(SH)₂ (A; Pt–S = 2.360(2) Å),⁹ Pt(dppe)-(SC₂H₄N₂)₂ (B; Pt–S = 2.358(1) Å),¹⁰ and cis-[Pt(SCH₂-Ph)(µ-SCH₂Ph)(PMMe₂)]₂ (C; Pt–Sterminal = 2.342(5) Å).¹¹ They are also similar but slightly shorter than those seen in bridging sulfur groups such as cis-[Pt(SCH₂-Ph)(µ-SCH₂Ph)(PMMe₂)]₂ (C; Pt–Sbridging = 2.380 Å).¹¹ [Pt₂(µ-S)(SCH₂Ph)(µ-dppm)]₂ (D; Pt–Sbridging = 2.347(3) Å),¹² [Pt₂(µ-S)(SCH₂Ph)(µ-dppm)]₂ (E; Pt–S = 2.356-3 Å),¹³ and the mixed-oxidation-state complex ([Pt(dppm)(µ-SMe₂)]₂) (F; Pt–S = 2.386 (4) Å, Ptiv–S = 2.468 (4) Å).¹⁴ The Pt–S bond lengths are also longer than those seen in sulfur groups bound to the other group 10 metals, such as in the palladium species trans-[Pd(PBu₃)₂(SH)₂] (G; Pd–S = 2.305(1) Å),¹⁵ and

NMR spectroscopy. As the reaction proceeded, the evidence for the formation of MeSH could be seen by normally failed. At 130 °C, methane was lost but no induce the derivatized methyl compound. All attempts to through sulfur insertion, and finally reductively elimi-
cation of the alkyl or aryl group has little effect on the geometry around the metal center.

Reactivity of the Sulfur-Inserted Species. One of the major reasons for studying the insertion of S into Pt—H bonds was the desire of finding a system that could activate methane, derivatize the methyl group or the sulfur atom, indicating that the bulk of the alkyl or aryl group has little effect on the geometry around the metal center.

addition of solid I₂ to a solution of 1 in CD₂Cl₂ converted all of 1 quantitatively to Pt(dcpe)I₂, as determined by NMR spectroscopy. When a solution of 1 in CD₂Cl₂ was reacted with Br₂, the reaction was much slower, allowing for the observance of the PtIV intermediate that must also be formed in the I₂ reaction. The PtIV species then converts to form [Pt(Cy₂P₂C₂H₄PCy₂)Br₂], as determined by NMR spectroscopy and compared to known samples (eq 4). In both cases, there was no evidence in the NMR spectra for formation of MeSH upon generation of the dihalide species.

The reaction of MeI was also investigated, since similar reactions of PtII species to form the corresponding PtIV species are known in the literature.20,21 MeI was reacted with a solution of 1 in CD₂Cl₂. After 20 h, all 1 had been quantitatively converted to Pt(dcpe)I₂, as determined by ¹H NMR spectroscopy. As the reaction proceeded, the ¹H NMR spectrum showed the disappearance of resonances corresponding to both the methyl and the SH groups, while the ³¹P NMR spectrum showed the formation of a singlet for a new symmetric chelating-phosphine-containing species. On the basis of analytical data, this complex is assigned as the sulfur-bridged dimer [Pt(dcpe)(μ-S)]₂. The lack of reductive elimination of the C—S bond in this system stands in contrast to the nickel system studied by Hillhouse, which eliminated C—S bonds readily.7 Hartwig has also seen facile reductive elimination of C—S bonds in (diphos)Pd(Ar)(SR) compounds.19

To see if a palladium species might be more reactive toward reductive elimination, the corresponding complex Pd(dcpe)(Me)(SH) (5) was synthesized from the reaction of Pd(dmpe)(Me)Cl and NaSH. This compound was found to be more thermally labile, as expected, but as with the platinum case only CH₄ was seen to eliminate at 80 °C in THF-d₈.

The sulfur-inserted species were seen to be reactive toward both mineral acids and halogens. 1 reacted with aqueous HCl to form Pt(dcpe)(Me)Cl with the loss of H₂S and ultimately Pt(dcpe)Cl₂ with the additional loss of CH₄ (eq 3). 1 also reacted rapidly with I₂ and Br₂. The

![Chart 1](image-url)
1H NMR spectroscopy provided evidence for the formation of a small quantity of CH₄, but no MeSH was observed.

**SO₂ Insertion into Pt–C Bonds.** Addition of 1 atm of SO₂ to a solution of Pt(dcpe)(Me)₂ in THF-d₈ leads to the quantitative formation (on the basis of NMR) of the new product 7 after 20 h at ambient temperature (eq 5). The clear solution does not change color during the course of the reaction, and no intermediates can be seen while monitoring the reaction by NMR spectroscopy. The 1H NMR spectrum of the product, Pt(dcpe)(SO₂Me)-Me (7), exhibits one methyl resonance (δ 0.557) in a location similar to that of the starting material. The other methyl resonance corresponding to the SO₂-inserted methyl is masked by resonances of the chelating phosphine ligand. Two singlet resonances are observed in the 31P NMR spectrum at δ 53.36 (J_PtP = 2499 Hz) and δ 71.73 (J_PtP = 1919 Hz). As seen with the sulfur-inserted compounds, there is both a large and a small Pt–P coupling constant, with the phosphorus atom trans to the sulfinate group having the larger Pt–P coupling.

Crystals of 7 were obtained by layering a methylene chloride solution with hexanes. The X-ray structure (Figure 3) shows that SO₂ insertion has occurred into the Pt–C bond in a [1,1] fashion, giving an S-sulfinate (eq 5). Crystallographic data are listed in Table 1, and selected distances and angles are given in Table 2.

Previously, we reported that SO₂ is capable of inserting into group 8 metal–carbon bonds in Cp*Rh(PMe₃)-(R)Cl (R = Me, Ph). Addition of 1 atm of SO₂ to a solution of Pt(dcpe)(Me)Cl did not result in the expected Pt(dcpe)(SO₂Me)Cl but instead resulted in a 1:1 ratio of Pt(dcpe)(SO₂Me)Me (7) and Pt(dcpe)Cl₂ (eq 6). Pre-

![Figure 3. ORTEP drawing of [Pt(Cy₂PC₂H₄PCy₂)(SO₂Me)-Me] (7). Ellipsoids are shown at the 30% level.](image)

sumably, the SO₂ inserts into the Pt–C bond of Pt(dcpe)-(Me)Cl, but the product then rapidly disproportionates with any remaining starting material to form the 1:1 mixture of observed products. Failure to induce Pt-(dcpe)(Me)Cl to disproportionate with itself at elevated temperatures lends support for the SO₂ insertion being necessary prior to disproportionation.

Attempts to synthesize the phenyl analogue of 7 have failed to yield the phenylsulfinate species. Addition of 1 atm of SO₂ to a solution of Pt(dcpe)Ph₂ (8) failed to produce any new products. This may be caused by the increased bulk of a phenyl group relative to a methyl group and the increased Pt–C bond strength in the Pt–Ph compound vs the Pt–Me compound..

It had been reported that mineral acids are able to react with metal–sulfinate groups to give the corresponding sulfinic acids. When 12 M HCl(aq) was added to a sample of 7, both methylsulfinic acid and methane were formed along with [Pt(Cy₂PC₂H₄PCy₂)Cl₂], as determined by 1H and 31P spectra. An authentic sample of methylsulfinic acid was synthesized from the commercially available Na salt, and the 1H NMR spectrum matched that seen in the reaction with HCl.

**Conclusion**

Three new transition-metal compounds have been found to undergo a clean sulfur insertion into their M–H bonds. In each case, the sulfur atom, from elemental sulfur, reacts with the metal systems quantitatively under mild conditions. Alternate synthetic routes utilizing the nucleophilic addition of SH⁻ have been developed in order to allow complete characterization of these S-inserted species. In none of the cases does reductive elimination of an arene- or alkanethiol occur. The platinum sulfhydryl compounds were shown to be reactive toward mineral acids and halogens. Also, a new transition-metal compound has been found to undergo a clean SO₂ insertion into its M–C bond. This insertion proceeds quantitatively under mild conditions. Methylsulfinic acid has been shown to form upon reactions of mineral acids with the SO₂-inserted species.

**Experimental Section**

**General Considerations.** All manipulations were performed under an N₂ atmosphere, either on a high-vacuum line.

using modified Schlenk techniques or in a Vacuum Atmospheres Corp. glovebox. Tetrahydrofuran and benzene were distilled from sodium–benzophenone ketyl under N2. Dichloromethane was distilled from CaH2. Alkane solvents were made olefin-free by stirring over H2O2, washing with aqueous KMnO4 and water, and distilling from sodium–benzophenone ketyl under N2. Dichloromethane–d2, benzene–d6, p-xylene–d10, and tetrahydrofuran–d6 were purchased from Cambridge Isotope Laboratories, dried over either CaH2 (in the case of CDCl3) or sodium–benzophenone ketyl, distilled under vacuum, and stored in ampules with Teflon-sealed vacuum line adapters. The preparations of Pt(dcpe)(Me)H, Pt(dcpe)(Me)Cl, Pt(dcpe)(CH2tBu)Cl, Pt(dcpe)(Ph)H, Pt(dcpe)(Ph)Cl, Pt(dcpe)(Bu)Cl, Pt(pdcdcpBr), Pt(dcpe)(Me)2 and Pd(pdcdcp)Cl2 have been previously reported. 31P NMR spectra were referenced to external 30% H3PO4 (distilled from sodium using modified Schlenk techniques or in a Vacuum Atmospheres. The preparations of Pt(dcpe)(Me)H, Pt(dcpe)(Me)Cl, Pt(dcpe)(CH2tBu)Cl, Pt(dcpe)(Ph)H, Pt(dcpe)(Ph)Cl, Pt(dcpe)(Bu)Cl, Pt(pdcdcpBr), Pt(dcpe)(Me)2 and Pd(pdcdcp)Cl2 have been previously reported. 31P NMR spectra were referenced to external 30% H3PO4 (distilled from sodium using modified Schlenk techniques or in a Vacuum Atmospheres. 

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**cis-Sulfhydrylnneoptenyli[bis(dicyclohexylphosphino)ethane]platinum(II) (1).** **Method A.** To a solution of 25 mg (0.035 mmol) of Pt(dcpe)(CH2tBu)Cl in about 0.5 mL of dry THF–d8 was added 2.2 mg (0.039 mmol) of NaSH. The resulting yellow solution was stirred at ambient temperature for 15 h, resulting in an orange-tan solution that was evaporated; the residue was then extracted with H2O and CH2Cl2. The organic layers were combined, dried over MgSO4, and evaporated to dryness on a rotary evaporator to yield a tan solid. Recrystallization from a CH2Cl2–hexane mixture yielded white crystals of Pt(dcpe)(CH2tBu)(SH)(2) (25, 56%, 6). 

**Method B.** A 14 mg (0.022 mmol) amount of Pt(dcpe)(CH2tBu)Cl and 2.0 mg (0.03 mmol) of S8 were added to an NMR tube and dissolved in about 1 mL of dry, oxygen-free THF–d8. The resulting yellow solution was mixed at ambient temperature for 1 h, at which time the material had quantitatively converted to Pt(dcpe)(CH2tBu)(SH)(2), as determined by NMR spectroscopy.

**cis-Sulfhydrylbis(dicyclohexylphosphino)ethane]platinum(II) (3).** **Method A.** To a solution of 101 mg (0.14 mmol) of Pt(dcpe)(Ph)Cl in 6 mL of THF was added 16 mg (0.30 mmol) of NaSH. The solution was stirred at ambient temperature for 2 h, resulting in a yellow solution. The solution was evaporated and the residue extracted with H2O and CH2Cl2. All organic layers were combined, dried with MgSO4, and evaporated to dryness on a rotary evaporator to yield a tan solid. Recrystallization from a CH2Cl2–hexane mixture yielded white crystals of Pt(dcpe)(Ph)(SH)(3) (68%, 68). 

**Method B.** A 25 mg (0.036 mmol) amount of Pt(dcpe)(Ph)H and a 4.0 mg (0.016 mmol) amount of S8 was added to an NMR tube and dissolved in about 1 mL of dry, oxygen-free CH2Cl2. The resulting yellow solution was mixed at ambient temperature for 2 h, at which time the material had quantitatively converted to Pt(dcpe)(Ph)(SH)(3), as determined by NMR spectroscopy.

**cis-Chloromethyl[bis(dicyclohexylphosphino)methane]platinum(II) (4).** To a solution of 150 mg (0.42 mmol) of Pt(COD)(Me)Cl in 5 mL of CH2Cl2 was added 175 mg (0.429 mmol) of CuPC2HPCy2. The solution was stirred for 20 h, resulting in a tan colored solution. The solution was concentrated to a tan oil and washed with hexanes to remove residual cyclooctadiene. Recrystallization from a CH2Cl2–hexane mixture yielded white crystals of Pt(CuPC2HPCy2)(Me)(CH2Cl2) (221 mg, 79.8%). 

**Method B.** A 14 mg (0.022 mmol) amount of Pt(dcpe)(Me)H and 2.0 mg (0.03 mmol) of S8 were added to an NMR tube and dissolved in about 1 mL of dry, oxygen-free THF–d8. The resulting yellow solution was mixed at ambient temperature for 2 h, at which time the material had quantitatively converted to Pt(dcpe)(Me)(SH)(1), as determined by NMR spectroscopy.
Reactivity of Pt(dcpe)(Me)(SH) with Br₂. A 14 mg (0.021 mmol) amount of Pt(dcpe)(Me)(SH) (1) was added to a standard NMR tube and dissolved in 0.5 mL of CDCl₃. A 1.8 μL aliquot of Br₂ (0.035 mmol) was added to the tube, and this solution was mixed for 1 h, at which time the solution had turned orange. NMR analysis indicated that most of the starting material had converted to Pt(dcpe)Br₂, with some of the PtIV complex remaining. The presence of the PtIV species, presumably dσ-Pt(dcpe)(Me)(SH)Br₂, is based on the 31P NMR spectrum (CDCl₃), which showed a resonance at δ 41.06 (s, JpP = 2028 Hz).

Reactivity of Pt(dcpe)(Me)(SH) with MeO. A 21 mg (0.032 mmol) amount of Pt(dcpe)(Me)(SH) (1) was added to a NMR tube and dissolved in about 1 mL of dry oxygen-free CDCl₃. The NMR tube was unsealed. After 10 h at ambient temperature, the starting material had been quantitatively converted to Pt±(3dcpe)±(Me)±(SH)±Cl±(2), as determined by NMR spectroscopy.

cis-Diisulfhydryl[bis(dicyclohexylphosphino)ethane]platinum(II) (5). A solution of 40 mg (0.058 mmol) of Pt(dcpe)-Cl in 6 mL of THF was treated with 14 mg (0.025 mmol) of NaSH. The solution was stirred at ambient temperature for 15 h, resulting in a cloudy yellow solution. The solution was evaporated and the residue extracted with H₂O and CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, and evaporated to dryness on a rotary evaporator. Recrystallization from a CH₂Cl₂ solution layered with hexanes yielded yellow crystals of cis-Pt(dcpe)(Me)(SH)Cl₂, mp 173 mg, 74%). 1H NMR (CDCl₃): δ 6.50 (s, JpP = 18 Hz), 7.60 (d, JpP = 19 Hz). Anal. Calcd for C₂₇H₄₂P₂Pd₂S₂: C, 46.48; H, 7.40. Found: C, 46.52; H, 7.73.

cis-Chloromethyl[bis(dicyclohexylphosphino)ethane]- palladium(II) (5). A solution of 90 mg (0.34 mmol) of Pd(COD)-(Me)Cl in 15 mL of C₆H₆ was treated with 28 mg (0.34 mmol) of Pt(dcpe)(Me)(Cl) (157 mg, 88%). The product was recrystallized from a CH₂Cl₂ solution layered with hexanes. 1H NMR (CDCl₃): δ 3.54 (t, JpP = 4 Hz, 2 H, 3, Me), 1.31–1.81 (m, 48 H, 6 PC₂PCH₂PCy₂). 31P NMR (CDCl₃): δ 6.85 (s, JpP = 18 Hz). Anal. Calcd for C₂₇H₅₁ClP₂Pd: C, 46.52; H, 7.73.

cis-Sulphhydrylmethyl[bis(dicyclohexylphosphino)ethane]- palladium(II) (5) (5). A solution of 65 mg (0.11 mmol) of Pd(dcpe)(Me)Cl in 10 mL of THF was treated with 28 mg (0.34 mmol) of Cy₂PC₂H₄PCy₂. The solution was stirred for 2 h, resulting in a clear solution that was evaporated in vacuo to produce an ivory-colored powder of Pd(dcpe)(Me)Cl (173 mg, 88%). The product was recrystallized from a CH₂Cl₂ solution layered with hexanes. 1H NMR (CDCl₃): δ 1.038 (d, JpP = 8, 2 Hz, 3, Me), 1.1–1.8 (m, 48 H, 6 PC₂PCH₂PCy₂). 31P NMR (CDCl₃): δ 60.66 (d, JpP = 19 Hz). Anal. Calcd for C₂₇H₅₂P₂Pd: C, 46.48; H, 7.40. Found: C, 46.52; H, 7.72.

Two drops of 12 M HCl(aq) was added to the tube. After 4 h at ambient temperature, a clear solution and a white precipitate formed. NMR spectroscopic analysis showed that the starting material had quantitatively converted to Pt(dcpe)Cl₂, as indicated by the presence of a single resonant peak in the NMR spectrum.

X-ray Experimental Details for 2, 3, and 7. The X-ray intensity data were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal-focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of either 10 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.6°). The total data collection time was approximately 6 h. Frames were integrated to 0.90 Å for 2 and to 0.75 Å for 3 and 7 with the Siemens SAINT program. Laue symmetry revealed monoclinic crystal systems for 2 and 3 and an orthorhombic crystal system for 7. The final unit cell parameters (at ~80 °C) were determined from the least-squares refinement of three-dimensional centroids of ~5000 reflections for all the crystals. Data were corrected for absorption with the SADABSA program.

The space group assignments are provided in Table 1. The structures were solved by using direct methods and refined employing full-matrix least squares on F² (Siemens, SHELXTL, version 5.04). Of the non-H atoms of the molecular species were refined anisotropically for all the data sets, except for C(9) in 7, which tended toward NPD. The hydrogen atoms were included in idealized positions for all the structures. For a Z value of 4, 3 contained one molecule and an acetone solvent, which was disordered over two positions, in the asymmetric unit. Hydrogen atoms were not included for the disordered solvent atoms. For a Z value of 16, 2 contained two molecules and two THF solvents in the asymmetric unit. For a Z value of 4, 7 contained one molecule and a CH₂Cl₂ solvent in the asymmetric unit. The final residuals and goodness-of-fit values, as well as further details of the data collection and refinement, are provided in Table 1.

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Supporting Information Available: Tables of crystallographic data, atom coordinates, thermal parameters, and bond distances and angles for 2, 3, and 7 (23 pages). Ordering information is given on any current masthead page.

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