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Insertion of Elemental Sulfur and SO_2 into the Metal−Hydride and Metal−Carbon Bonds of Platinum Compounds

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Elemental sulfur (S_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 = $Cy_2PC_2H_4PCy_2$). Unlike the parent compounds, the S-inserted complexes do not undergo reductive elimination to form the corresponding alkane- or arenethiols. 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.[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)Pt^0] (dcpe = $Cy_2PC_2H_4PCy_2$) species.[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_8). While rare, there are a few reported cases of elemental sulfur insertion into transition-metal−ligand bonds.[4,6] Early work by Legzdins showed an example of insertion of a single sulfur atom from elemental sulfur into a metal−carbon bond.[6] A recent report by Hillhouse demonstrated the facile insertion of sulfur into the metal−aryl bond in a (bipy)-Ni(aryl)(alkyl) complex.[7] All other examples of using elemental sulfur resulted in a sulfur-chain fragment (S_x) 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_2 into group 8 metal−carbon bonds.[8] In this paper, similar insertions of SO_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_2 group from the metal to form methylsulfinic acid.

Results and Discussion

Synthesis of Sulfur Insertion Adducts. Addition of elemental sulfur (S_8) to a benzene or THF solution of Pt(dcpe)(R)H (R = Me, $CH_2{}^tBu$, Ph) leads to the quantitative formation of the new products Pt(dcpe)(R)(SH) (R = Me (**1**), $CH_2{}^tBu$ (**2**), Ph (**3**)). NMR spectroscopy proved to be ideal for following the progress of these reactions. For example, addition of elemental sulfur (S_8) to a THF-d_8 solution of Pt(dcpe)(Me)H led to complete reaction within 5 min. The ^1H NMR spectrum showed that the methyl resonance of Pt(dcpe)(Me)H at δ 0.67 (dd, $J_{PtH} = 70$ Hz) had shifted upfield to δ 0.36 (dd, $J_{PtH} = 62$ Hz). A more dramatic change was seen in the hydride resonance, which shifted downfield from the signal for the starting material at δ −0.445 (dd, $J_{PtH} = 1150$ Hz) to δ −0.917 (dd, $J_{PtH} = 62$ Hz) with a large change in the Pt−H coupling constant. ^{31}P NMR spectroscopy provided another handle for monitoring the reaction. The ^{31}P NMR spectrum of **1** in THF-d_8 displays a resonance at δ 62.33 (s, $J_{PtP} = 3064$ 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.[2,3] A second resonance is seen in the ^{31}P NMR spectrum at δ 67.02 ($J_{PtP} = 1811$ 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_8. Another synthetic route was devised to allow for complete characterization which also allowed for the elimination of problems involving removal of unreacted S_8

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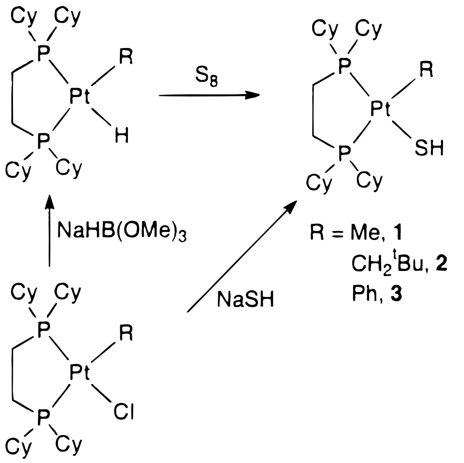
in the samples. The nucleophilic attack of SH^- (from NaSH) on the metal alkyl or aryl halides was used to generate large quantities of **1** cleanly (eq 1). Crystals of **1** were obtained by cooling a supersaturated hot acetone solution. Both the methyl and the sulfhydryl groups were sufficiently disordered 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.



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Compounds **2** and **3**, the CH_2CMe_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_2CMe_3)H] and the reaction monitored by NMR spectroscopy until all traces of the starting material were consumed. The hydride resonance shifted downfield in the ^1H NMR spectrum to δ −0.457 (J_{PtH} = 61 Hz) upon sulfur insertion. Two resonances were observed in the ^{31}P NMR spectrum, one at δ 57.88 (J_{PtP} = 3210 Hz) assigned to the phosphorus *trans* to the SH group and another at δ 64.07 (J_{PtP} = 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_6D_6 solution of Pt(dcpe)(Ph)H. The hydride resonance in the ^1H NMR spectrum shifted downfield to δ 0.168 (J_{PtH} = 65 Hz) following sulfur insertion. Two resonances were observed in the ^{31}P NMR spectrum at δ 54.58 (J_{PtP} = 3025 Hz) for the phosphorus *trans* to the SH group, and at δ 60.55 (J_{PtP} = 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.

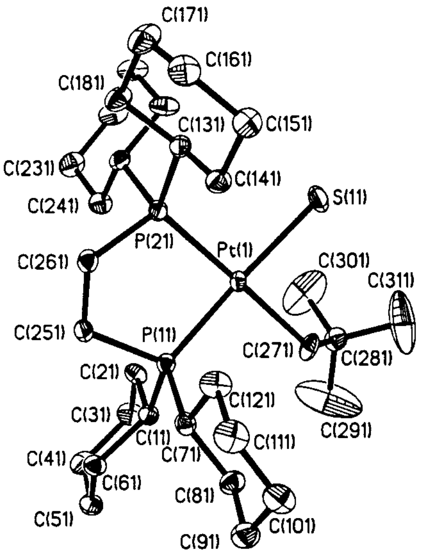

Figure 1. ORTEP drawing of [Pt($Cy_2PC_2H_4PCy_2$)($CH_2{}^tBu$)(SH)] (**2**). Ellipsoids are shown at the 30% level.

For comparison, the methylene-bridged chelating phosphine analogue of **1**, [Pt($Cy_2PCH_2PCy_2$)(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 δ −26.76 (J_{PP} = 43 Hz, J_{PtP} = 1376 Hz) and δ −28.36 (J_{PP} = 43 Hz, J_{PtP} = 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

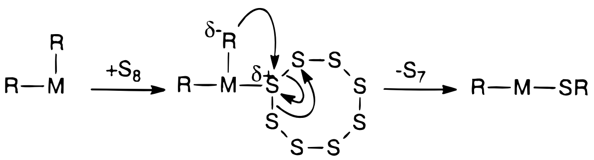

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Table 1. Summary of Crystallographic Data for Complexes 2, 3, and 7

	2	**3**	**7**
	Crystal Parameters		
chem formula	$C_{35}H_{68}OP_2PtS$	$C_{35}H_{60}OP_2PtS$	$C_{47}H_{77}ClN_2O_2Pt$
fw	793.98	785.92	932.65
cryst syst	monoclinic	monoclinic	orthorhombic
space group (No.)	$C2/c$ (15)	$P2_1/n$ (14)	$Pca2_1$ (29)
Z	16	4	4
a, Å	46.3269(6)	10.7275(2)	18.4367(2)
b, Å	17.0101(3)	22.1317(4)	10.6432(1)
c, Å	20.4152(1)	15.3769(2)	17.2377(1)
β, deg	112.334(1)	102.330(1)	90
V, $Å^3$	14880.9(3)	3566.5(1)	3387.43(5)
ρ_{calcd}, g cm^{-3}	1.418	1.464	1.562
cryst dimens, mm^3	0.20 × 0.22 × 0.38	0.20 × 0.30 × 0.40	0.05 × 0.20 × 0.20
temp, °C	−80	−80	−80
	Measurement of Intensity Data and Refinement Parameters		
radiation (λ, Å)		Mo Kα (0.710 73)	
2θ range, deg	3−47	3−56	4−56
total no. of data	30 939	20 776	19 069
no. of unique data	10 536	8245	7612
R_{int}, R_σ (%)[a]	3.48, 4.09	4.21, 6.24	6.32, 9.74
no. of obsd data ($I > 2\sigma(I)$)	8679	6690	5870
no. of params varied	677	354	314
μ, mm^{-1}	3.938	4.108	4.480
abs cor		empirical (SADABS)	
range of transmissn factors	0.648−0.928	0.708−0.928	0.783−0.928
Flack param			0.011(9)
GOF	1.037	1.178	1.086
R1(F_o), wR2(F_2^o) obsd (%)	3.32, 6.94	5.46, 8.21	6.07, 8.45
R1(F_o), wR2(F_2^o) all (%)	4.66, 7.39	7.56, 8.78	8.86, 9.24

[a] $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum[F_o^2]$, and $R_\sigma = \sum[\sigma(F_o^2)]/\sum[F_o^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [(\text{Max};0,F_o^2) + 2F_o^2]/3$.

Table 2. Selected Distances (Å) and Angles (deg) for Pt(dcpe)($CH_2{}^tBu$)(SH) (2), Pt(dcpe)(Ph)(SH) (3), and Pt(dcpe)(SO_2Me)Me (7)

	2[a]	**3**	**7**
	Distances		
Pt1−P1	2.232(3)	2.291(2)	2.316(2)
Pt1−P2	2.282(3)	2.242(2)	2.266(2)
Pt1−C27	2.141(11)	2.075(6)	2.136(8)
Pt1−S1	2.336(4)	2.339(2)	2.335(2)
	Angles		
P1−Pt1−P2	86.8(1)	87.43(5)	86.74(9)
S1−Pt1−C27	88.2(9)	86.7(2)	90.5(2)
P1−Pt1−S1	172.0(9)	93.74(6)	90.91(8)
P1−Pt1−C27	92.2(5)	179.6(2)	177.5(2)
P2−Pt1−S1	92.8(12)	178.62(6)	172.67(8)
P2−Pt1−C27	178.3(4)	92.1(2)	91.6 (2)

[a] Values listed are for the average of two independent molecules.

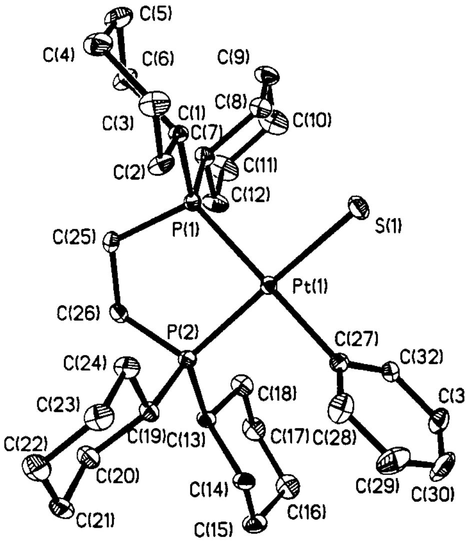

Figure 2. ORTEP drawing of [Pt($Cy_2PC_2H_4PCy_2$)(Ph)(SH)] (**3**). Ellipsoids are shown at the 30% level.

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 terminally bound sulfur groups such as $Pt(PPh_3)_2(SH)_2$ (**A**; Pt−S = 2.360(2) Å),[9] Pt(dppe)(SC_5H_4N)$_2$ (**B**; Pt−S = 2.358(1) Å),[10] and *cis*-{Pt(SCH_2Ph)(μ-SCH_2Ph)($PMePh_2$)}$_2$ (**C**; Pt−$S_{terminal}$ = 2.342(5) Å).[11] They are also similar but slightly shorter than those seen in bridging sulfur groups such as *cis*-{Pt(SCH_2Ph)(μ-SCH_2Ph)($PMePh_2$)}$_2$ (**C**; Pt−$S_{bridging}$ = 2.380 Å),[11] [Pt_2(μ-S)(SCH_2Ph)$_2$(μ-dppm)$_2$] (**D**; Pt−$S_{bridging}$ = 2.347(3) Å),[12] [{Pt(Me)$_2$(μ-S(Et)$_2$)}$_2$] (**E**; Pt−S = 2.356(3) Å),[13] and the mixed-oxidation-state complex [{Pt(dppe)}(μ-SMe)$_2${Pt(Me)$_3$Cl}] (**F**; Pt^{II}−S = 2.386 (4) Å, Pt^{IV}−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(P^iBu_3)$_2$(SH)$_2$] (**G**; Pd−S = 2.305(1) Å),[15] and

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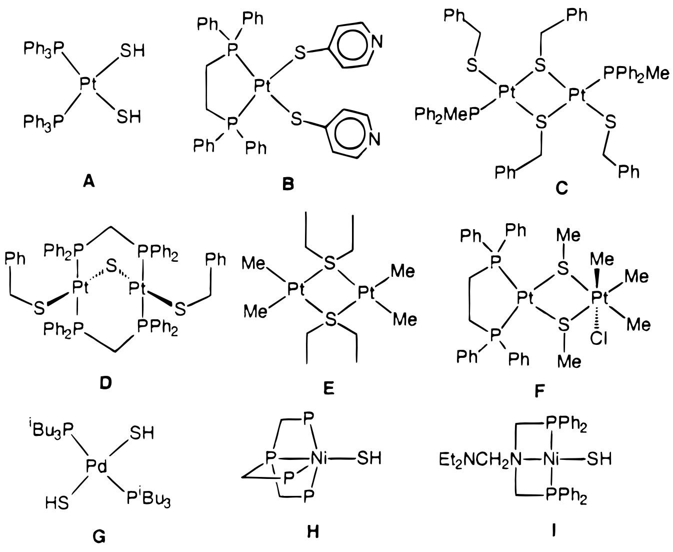
Chart 1



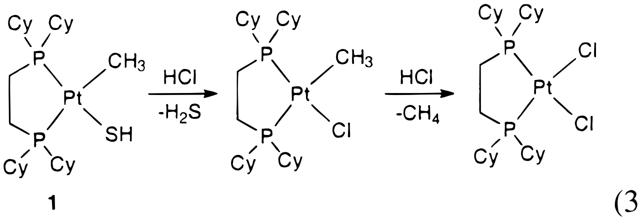
much longer than those seen for the two nickel species **H** (Ni−S = 2.256(11) Å[16]) and **I** (Ni−S = 2.188(3) Å[17]). The Pt−P bond lengths are also comparable to those of previously reported compounds, with the Pt−P bound *trans* to the SH group being longer then those of the Pt−P bond *cis* to the SH group.[18]

The bond angles around the Pt atoms in complexes **2** and **3** range between 86.7 and 93.7°, with both the P−Pt−P and the S−Pt−C angles being similar. The largest angular deviation from square planar in the complex is between the phosphorus atoms and the alkyl/aryl 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.

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 through sulfur insertion, and finally reductively eliminate the derivatized methyl compound. All attempts to induce **1** to reductively eliminate methanethiol thermally failed. At 130 °C, methane was lost but no evidence for the formation of MeSH could be seen by NMR spectroscopy. As the reaction proceeded, the ^{1}H NMR spectrum showed the disappearance of resonances corresponding to both the methyl and the SH groups, while the ^{31}P 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 CH_4 was seen to eliminate at 80 °C in THF-d_8.

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 H_2S and ultimately Pt(dcpe)Cl_2 with the additional loss of CH_4 (eq 3). **1** also reacted rapidly with I_2 and Br_2. The addition of solid I_2 to a solution of **1** in CD_2Cl_2 converted all of **1** quantitatively to Pt(dcpe)I_2, as determined by NMR spectroscopy. When a solution of **1** in CD_2Cl_2 was reacted with Br_2, the reaction was much slower, allowing for the observance of the Pt^{IV} intermediate that must also be formed in the I_2 reaction. The Pt^{IV} species then converts to form [Pt($Cy_2PC_2H_4PCy_2$)Br_2], 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.



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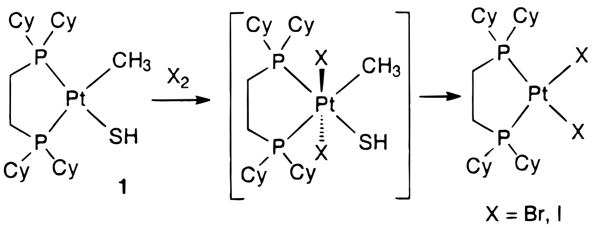

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The reaction of MeI was also investigated, since similar reactions of Pt^{II} species to form the corresponding Pt^{IV} species are known in the literature.[20,21] MeI was reacted with a solution of **1** in CD_2Cl_2. After 20 h, all **1** had been quantitatively converted to Pt(dcpe)I_2. As in the cases of reactions with the halogens, no NMR evidence was seen to indicate the formation of MeSH or Me_2S.

In an attempt to see how stable these systems were toward other sulfur sources, **1** was reacted with H_2S. When a sample of **1** was dissolved in C_6D_6 and then sealed under 1 atm of H_2S, **1** was completely converted to Pt(dcpe)$(SH)_2$ (**6**), with the loss of CH_4. An alternate synthetic route to this product was discovered using the nucleophilic reactivity of SH^- toward the metal dihalide to confirm the generation of Pt(dcpe)$(SH)_2$.

When a solution of **1** in THF-d_8 was exposed to near-UV light from a Xe/Hg lamp, the system decomposed.

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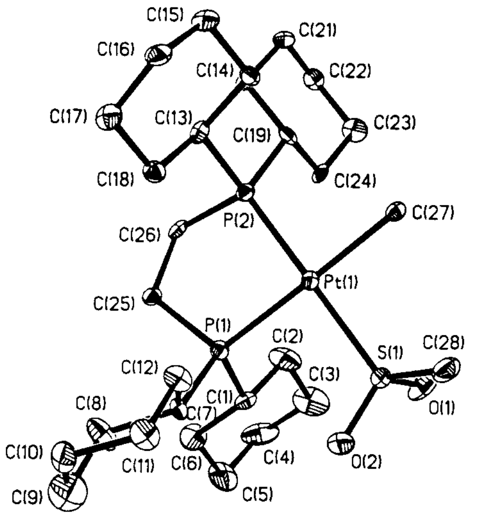
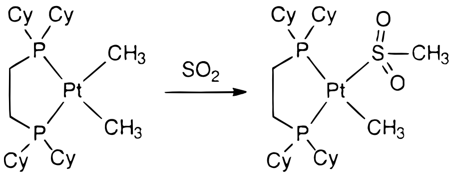


Figure 3. ORTEP drawing of [Pt($Cy_2PC_2H_4PCy_2$)(SO_2Me)-Me] (**7**). Ellipsoids are shown at the 30% level.

^{1}H NMR spectroscopy provided evidence for the formation of a small quantity of CH_4, but no MeSH was observed.

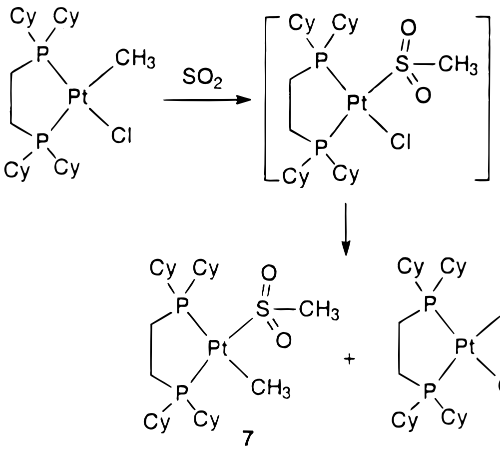
SO_2 Insertion into Pt−C Bonds. Addition of 1 atm of SO_2 to a solution of Pt(dcpe)(Me)$_2$ in THF-d_8 leads to the quantitative formation (on the basis of NMR) of the new product **7** after 20 h at ambient temperature (eq 5). The clear solution does not change color during the course of the reaction, and no intermediates can be seen while monitoring the reaction by NMR spectroscopy. The ^{1}H NMR spectrum of the product, Pt(dcpe)(SO_2Me)-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 SO_2-inserted methyl is masked by resonances of the chelating phosphine ligand. Two singlet resonances are observed in the ^{31}P 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.



(5)

Crystals of **7** were obtained by layering a methylene chloride solution with hexanes. The X-ray structure (Figure 3) shows that SO_2 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 SO_2 is capable of inserting into group 8 metal−carbon bonds in Cp*Rh(PMe$_3$)-(R)Cl (R = Me, Ph).[8] Addition of 1 atm of SO_2 to a solution of Pt(dcpe)(Me)Cl did not result in the expected Pt(dcpe)(SO_2Me)Cl but instead resulted in a 1:1 ratio of Pt(dcpe)(SO_2Me)Me (**7**) and Pt(dcpe)Cl$_2$ (eq 6). Presumably, the SO_2 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 SO_2 insertion being necessary prior to disproportionation.



(6)

Attempts to synthesize the phenyl analogue of **7** have failed to yield the phenylsulfinate species. Addition of 1 atm of SO_2 to a solution of Pt(dcpe)Ph$_2$ (**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.[22]

It had been reported that mineral acids are able to react with metal−sulfinate groups to give the corresponding sulfinic acids.[8] When 12 M HCl(aq) was added to a sample of **7**, both methylsulfinic acid and methane were formed along with [Pt($Cy_2PC_2H_4PCy_2$)Cl$_2$], as determined by ^{1}H and ^{31}P spectra. An authentic sample of methylsulfinic acid was synthesized from the commercially available Na salt, and the ^{1}H 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 SO_2 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 SO_2-inserted species.

Experimental Section

General Considerations. All manipulations were performed under an N$_2$ atmosphere, either on a high-vacuum line

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using modified Schlenk techniques or in a Vacuum Atmospheres Corp. glovebox. Tetrahydrofuran and benzene were distilled from sodium−benzophenone ketyl under N_2. Dichloromethane was distilled from CaH_2. Alkane solvents were made olefin-free by stirring over H_2SO_4, washing with aqueous $KMnO_4$ and water, and distilling from sodium−benzophenone ketyl under N_2. Dichloromethane-d_2, benzene-d_6, *p*-xylene-d_{10}, and tetrahydrofuran-d_8 were purchased from Cambridge Isotope Laboratories, dried over either CaH_2 (in the case of CD_2Cl_2) or sodium−benzophenone ketyl, distilled under vacuum, and stored in ampules with Teflon-sealed vacuum line adapters. The preparations of Pt(dcpe)(Me)H,[3] Pt(dcpe)(Me)Cl,[3] Pt(dcpe)($CH_2{}^tBu$)Cl,[23] Pt(dcpe)($CH_2{}^tBu$)H,[23] Pt(dcpe)(Ph)H,[23] Pt(dcpe)(Ph)Cl,[23] Pt(dcpe)Cl_2,[3] Pt(dcpe)I_2,[24] Pt(dcpe)Br_2,[25] Pt(dcpe)$(Me)_2$,[26] and Pd(cod)(Me)Cl[27] have been previously reported. NaSH was purchased from Alfa. S_8, MeI, Br_2, and I_2 were purchased from Aldrich Chemical Co. and used without further purification.

All ^1H NMR and ^{31}P NMR spectra were recorded on a Bruker AMX400 spectrometer. All ^1H chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced using the chemical shifts of residual solvent resonances (C_6H_6, δ 7.15; THF, δ 3.58; CH_2Cl_2, δ 5.32; *p*-xylene, δ 7.22). ^{31}P NMR spectra were referenced to external 30% H_3PO_4 (δ 0.0). Unless otherwise noted, all NMR-scale reactions were carried out in NMR tubes equipped with Teflon seals and connected to a high-vacuum line. Any solvents used were then vacuum-transferred into the tube and then resealed. Analyses were obtained from Desert Analytics. A Siemens SMART CCD area detector diffractometer equipped with an LT-2 low-temperature unit was used for X-ray crystal structure determination.

***cis*-Sulfhydrylmethyl[bis(dicyclohexylphosphino)ethane]platinum(II) (1). Method A.** To a solution of 100 mg (0.150 mmol) of Pt(dcpe)(Me)Cl in about 6 mL of dry THF was added 3.4 mg (0.63 mmol) of NaSH. The resulting yellow solution was stirred at ambient temperature for 15 h, resulting in an orange-tan solution that was evaporated to dryness. The residue was extracted with H_2O and CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, and evaporated to dryness on a rotary evaporator to yield a tan solid. Recrystallization from a CH_2Cl_2 solution layered with hexanes yielded white crystals of Pt(dcpe)(Me)(SH) (**1**; 93 mg, 93%). ^1H NMR (THF-d_8): δ −0.917 (dd, J_{PH} = 6, 15 Hz, J_{PtH} = 62 Hz, 1 H, SH), 0.361 (dd, J_{PH} = 5, 6 Hz, J_{PtH} = 62 Hz, 3 H, CH_3), 1.2−2.4 (m, 48 H, $Cy_2PC_2H_4PCy_2$). ^1H NMR (C_6D_6): δ 0.195 (dd, J_{PH} = 5, 16 Hz, J_{PtH} = 61 Hz, 3 H, CH_3), 1.0−2.4 (m, 49 H, $Cy_2PC_2H_4PCy_2$ and SH). ^1H NMR (*p*-xylene-d_{10}): δ −0.106 (dd, J_{PH} = 6, 16 Hz, J_{PtH} = 62 Hz, 1 H, SH), 0.888 (dd, J_{PH} = 5, 6 Hz, J_{PtH} = 63 Hz, 3 H, CH_3), 1.0−2.5 (m, 48 H, $Cy_2PC_2H_4PCy_2$). ^{31}P NMR (THF-d_8): δ 62.33 (s, J_{PtP} = 3064 Hz), 67.02 (s, J_{PtP} = 1811 Hz). ^{31}P NMR (C_6D_6): δ 59.94 (s, J_{PtP} = 3070 Hz), 64.89 (s, J_{PtP} = 1800 Hz).). ^{31}P NMR (*p*-xylene-d_{10}): δ 64.98 (s, J_{PtP} = 3047 Hz), 70.01 (s, J_{PtP} = 1792 Hz). Anal. Calcd for $C_{27}H_{52}P_2PtS$: C, 48.71; H, 7.87. Found: C, 48.39; H, 7.67.

Method B. A 14 mg (0.02 mmol) amount of Pt(dcpe)(Me)H and 2.0 mg (0.03 mmol) of S_8 were added to an NMR tube and dissolved in about 1 mL of dry, oxygen-free THF-d_8. The resulting yellow solution was mixed at ambient temperature for $^1/_2$ h, at which time the material had quantitatively converted to Pt(dcpe)(Me)(SH) (**1**)**,** as determined by NMR spectroscopy.

***cis*-Sulfhydrylneopentyl[bis(dicyclohexylphosphino)ethane]platinum(II) (2). Method A.** To a solution of 25 mg (0.035 mmol) of Pt(dcpe)($CH_2{}^tBu$)Cl in about 0.5 mL of dry THF-d_8 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 H_2O and CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, and evaporated to dryness on a rotary evaporator to yield a tan solid. Recrystallization from a CH_2Cl_2 solution layered with hexanes yielded white crystals of Pt(dcpe)($CH_2{}^tBu$)(SH) (**2**; 56 mg, 73%). ^1H NMR (THF-d_8): δ −0.457 (dd, J_{PH} = 6, 16 Hz, J_{PtH} = 61 Hz, 1 H, SH), 1.095 (s, 15 H, t-Bu), 1.2−2.6 (m, 50 H, $Cy_2PC_2H_4PCy_2$ and CH_2). ^{31}P NMR (THF-d_8): δ 57.88 (s, J_{PtP} = 3210 Hz), 64.07 (s, J_{PtP} = 1626 Hz). Anal. Calcd for $C_{31}H_{60}P_2PtS\cdot{}^1/_2CH_2Cl_2$: C, 49.50; H, 8.04. Found: C, 49.46; H, 8.31.

Method B. A 14 mg (0.02 mmol) amount of Pt(dcpe)($CH_2{}^tBu$)H and 2.0 mg (0.03 mmol) of S_8 were added to an NMR tube and dissolved in about 1 mL of dry, oxygen-free THF-d_8. The resulting yellow solution was mixed at ambient temperature for 1 h, at which time the material had quantitatively converted to Pt(dcpe)($CH_2{}^tBu$)(SH) (**2**)**,** as determined by NMR spectroscopy.

***cis*-Sulfhydrylphenyl[bis(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 H_2O and CH_2Cl_2. All organic layers were combined, dried with $MgSO_4$, and evaporated to dryness on a rotary evaporator to yield a tan solid. Recrystallization from a CH_2Cl_2 solution layered with hexanes yielded amber crystals of Pt(dcpe)(Ph)(SH) (**3**; 68 mg, 68%). ^1H NMR (C_6D_6): δ 0.168 (dd, J_{PH} = 6, 16 Hz; J_{PtH} = 65 Hz, 1 H, SH), 0.8−2.5 (m, 48 H, $Cy_2PC_2H_4PCy_2$), 7.03 (t, J_{PH} = 7 Hz, 1 H, Ph), 7.26 (t, J_{PH} = 7 Hz, 2 H, Ph), 7.80 (t, J_{PH} = 6 Hz, J_{PtH} = 46 Hz, 2 H, Ph). ^{31}P NMR (C_6D_6): δ 54.58 (s, J_{PtP} = 3025 Hz), 60.55 (s, J_{PtP} = 1720 Hz). Anal. Calcd for $C_{32}H_{54}P_2PtS\cdot CH_2Cl_2$: C, 48.77; H, 6.94. Found: C, 48.70; H, 7.13.

Method B. A 25 mg (0.036 mmol) amount of Pt(dcpe)(Ph)H and a 4.0 mg (0.016 mmol) amount of S_8 was added to an NMR tube and dissolved in about 1 mL of dry, oxygen-free C_6D_6. 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).** To a solution of 150 mg (0.42 mmol) of Pt(COD)(Me)Cl in 5 mL of CH_2Cl_2 was added 175 mg (0.429 mmol) of $Cy_2PCH_2PCy_2$. 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 CH_2Cl_2 solution layered with hexanes yielded white crystals of Pt($Cy_2PCH_2PCy_2$)(Me)Cl (221 mg, 79.8%). ^1H NMR (CD_2Cl_2) δ 0.388 (dd, J_{PH} = 6, 9 Hz, J_{PtH} = 59 Hz, 3 H, Me), 1.2−2.4 (m, 44 H, $Cy_2PCH_2PCy_2$). ^{31}P NMR (CD_2Cl_2): δ −19.17 (d, J_{PP} = 42 Hz, J_{PtP} = 2799 Hz), −21.19 (d, J_{PP} = 42 Hz, J_{PtP} = 2799 Hz). Anal. Calcd for $C_{26}H_{49}ClP_2Pt\cdot CH_2Cl_2$: C, 43.88; H, 6.96. Found: C, 44.13; H, 7.42.

***cis*-Sulfhydrylmethyl[bis(dicyclohexylphosphino)methane]platinum(II) (4).** A solution of 78 mg (0.12 mmol) of Pt($Cy_2PCH_2PCy_2$)(Me)Cl in 6 mL of THF was treated with 14 mg (0.25 mmol) of NaSH and stirred at ambient temperature for 15 h. The resulting orange-tan solution was evaporated and the residue extracted with H_2O and CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, and evaporated to dryness on a rotary evaporator to yield a tan solid. Recrystallization from a CH_2Cl_2 solution layered with hexanes yielded white crystals of Pt($Cy_2PCH_2PCy_2$)(Me)(SH) (**4**; 56 mg, 73%). ^1H NMR (CD_2Cl_2): δ −0.658 (dd, J_{PH} = 5, 15 Hz, J_{PtH} = 58 Hz, 1 H, SH), 0.352 (dd, J_{PH} = 5, 7 Hz, J_{PtH} = 66 Hz, 3 H,

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Me), 1.1−2.4 (m, 44 H, Cy), 3.06 (t, $J_{PH} = 9$ Hz, 2 H, CH_2). ^1H NMR (THF-d_8): δ −0.910 (dd, $J_{PH} = 6$, 22 Hz, $J_{PtH} = 61$ Hz, 1 H, SH), 0.355 (dd, $J_{PH} = 5$, 7 Hz, $J_{PtH} = 67$ Hz, 3 H, Me), 1.2−2.4 (m, 44 H, Cy), 3.19 (t, $J_{PH} = 9$ Hz, 2 H, CH_2). ^{31}P NMR (CD_2Cl_2): δ −27.95 (d, $J_{PP} = 42$ Hz, $J_{PtH} = 1374$ Hz), −28.98 (d, $J_{PP} = 42$ Hz, $J_{PtH} = 2803$ Hz). ^{31}P NMR (THF-d_8): δ −26.76 (d, $J_{PP} = 43$ Hz, $J_{PtH} = 1376$ Hz), −28.36 (d, $J_{PP} = 43$ Hz, $J_{PtH} = 2727$ Hz). Anal. Calcd for $C_{26}H_{50}P_2PtS\cdot{}^1/_3CH_2Cl_2$: C, 46.51; H, 7.51. Found: C, 46.52; H, 7.73.

Reaction of Pt(dcpe)(Me)(SH) and *p*-Xylene-d_{10}. A 12 mg (0.018 mmol) amount of Pt(dcpe)(Me)(SH) was added to an NMR tube and dissolved in about 1 mL of dry, oxygen-free *p*-xylene-d_{10}, followed by immersion in a 130 °C oil bath. After 24 h of heating, the starting material had quantitatively converted into a new product with the loss of CH_4, as determined by NMR spectroscopy. Recrystallization of the product from a *p*-xylene-d_{10} solution layered with hexanes resulted in a yellow powder assigned as $[Pt(dcpe)(\mu\text{-}S)]_2$. ^1H NMR (*p*-xylene-d_{10}): δ 1.3−3.0 (m). ^{31}P NMR (*p*-xylene-d_{10}): δ 65.01 (s, $J_{PtH} = 2648$ Hz). Anal. Calcd for $C_{52}H_{96}P_4Pt_2S_2$: C, 48.06; H, 7.45. Found: C, 47.71; H, 7.79.

***cis*-Chloromethyl[bis(dicyclohexylphosphino)ethane]palladium(II).** A solution of 90 mg (0.34 mmol) of Pd(COD)(Me)Cl in 15 mL of C_6H_6 was treated with 14 mg (0.34 mmol) of $Cy_2PC_2H_4PCy_2$. The tan 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 CH_2Cl_2 solution layered with hexanes. ^1H NMR ($CDCl_3$): δ 0.483 (dd, $J_{PH} = 8$, 2 Hz, 3 H, Me), 1.1−2.1 (m, 48 H, $Cy_2PC_2H_4PCy_2$). ^{31}P NMR ($CDCl_3$): δ 60.66 (d, $J_{PP} = 18$ Hz), 75.99 (d, $J_{PP} = 19$ Hz). Anal. Calcd for $C_{27}H_{51}ClP_2Pd\cdot 2CH_2Cl_2$: C, 46.48; H, 7.40. Found: C, 46.99; H, 7.22.

***cis*-Sulfhydrylmethyl[bis(dicyclohexylphosphino)ethane]palladium(II) (5).** A solution of 65 mg (0.11 mmol) of Pd(dcpe)(Me)Cl in 10 mL of THF was treated with 28 mg (0.50 mmol) of NaSH. The solution was stirred at ambient temperature for 2 h, resulting in an orange solution. The solution was evaporated and extracted with H_2O and CH_2Cl_2. All organic layers were combined, dried with $MgSO_4$, and evaporated to dryness on a rotary evaporator to yield an orangish tan solid. Recrystallization from a CH_2Cl_2 solution layered with hexanes yielded amber crystals of Pd(dcpe)(Me)(SH) (**5**; 48 mg, 74%). ^1H NMR (C_6D_6): δ 0.248 (dd, $J_{PH} = 5$, 16 Hz, 3 H, Me), 0.225 (dd, $J_{PH} = 6$, 8 Hz, 3 H, Me), 1.1−2.1 (m, 48 H, $Cy_2PC_2H_4PCy_2$). ^{31}P NMR (C_6D_6): δ 68.28 (d, $J_{PP} = 20$ Hz), 63.26 (d, $J_{PP} = 17$ Hz). Anal. Calcd for $C_{27}H_{52}P_2PdS\cdot CH_2Cl_2$: C, 50.79; H, 8.22. Found: C, 50.39; H, 7.96.

Reaction of Pt(dcpe)(Me)(SH) with 12 M HCl. A 22 mg (0.033 mmol) amount of Pt(dcpe)(Me)(SH) (**1**) was added to a standard NMR tube and dissolved in 1 mL of C_6D_6. Two drops of 12 M HCl(aq) was added to the tube and mixed for 1 h, resulting in the formation of a white precipitate. Filtration of the white precipitate followed by NMR spectroscopic analysis indicated that the starting material had been converted to Pt(dcpe)Cl_2.

Reaction of Pt(dcpe)(Me)(SH) with 6 M HCl. A 15 mg (0.023 mmol) amount of Pt(dcpe)(Me)(SH) (**1**) was added to a standard NMR tube and dissolved in 0.5 mL of C_6D_6. To the sample was added 0.008 mL (0.048 mmol) 6 M HCl(aq), and this solution was mixed for 15 h. NMR spectroscopic analysis of the resulting yellow solution indicated the formation of Pt(dcpe)(Me)Cl and the presence of H_2S.

Reaction of Pt(dcpe)(Me)(SH) with I_2. A 22 mg (0.033 mmol) amount of Pt(dcpe)(Me)(SH) (**1**) and a 10 mg (0.040 mmol) amount of I_2 were placed in a standard NMR tube and dissolved in about 1 mL of CD_2Cl_2, followed by sonication to ensure all the I_2 dissolved. After 1 h at ambient temperature, the starting material had been quantitatively converted to Pt(dcpe)I_2, as determined by NMR spectroscopy.

Reaction of Pt(dcpe)(Me)(SH) with Br_2. 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 CD_2Cl_2. A 1.8 μL aliquot of Br_2 (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)Br_2, with some of the Pt^{IV} complex remaining. The presence of the Pt^{IV} species, presumably *cis*-Pt(dcpe)(Me)(SH)Br_2, is based on the ^{31}P NMR spectrum (CD_2Cl_2), which showed a resonance at δ 41.06 (s, $J_{PtP} = 2028$ Hz).

Reaction of Pt(dcpe)(Me)(SH) with MeI. 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 CD_2Cl_2. The NMR tube was unsealed, and 0.002 mL of MeI (0.032 mmol) was added. After 20 h at ambient temperature, the starting material had been quantitatively converted to Pt(dcpe)I_2, as determined by NMR spectroscopy.

***cis*-Disulfhydryl[bis(dicyclohexylphosphino)ethane]platinum(II) (6).** A solution of 40 mg (0.058 mmol) of Pt(dcpe)Cl_2 in 6 mL of THF was treated with 14 mg (0.25 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 H_2O and CH_2Cl_2. The organic fractions were combined, dried over $MgSO_4$, and evaporated to dryness on a rotary evaporator. Recrystallization from a CH_2Cl_2 solution layered with hexanes yielded yellow crystals of Pt(dcpe)$(SH)_2$ (**6**; 39 mg, 98%). ^1H NMR (C_6D_6): δ 0.282 (dd, $J_{PH} = 6$, 9 Hz, $J_{PtH} = 59$ Hz, 2 H, SH), 1.0−2.4 (m, 48 H, $Cy_2PC_2H_4PCy_2$). ^{31}P NMR (C_6D_6): δ 64.08 (s, $J_{PtP} = 2799$ Hz). Anal. Calcd for $C_{26}H_{50}P_2PtS_2$: C, 52.47; H, 8.47. Found: C, 52.22; H, 8.56.

Reaction of Pt(dcpe)(Me)(SH) with H_2S. A 8 mg (0.012 mmol) amount of Pt(dcpe)(Me)(SH) (**1**) was added to an NMR tube and dissolved in about 0.5 mL of dry oxygen-free C_6D_6. The NMR tube was briefly opened to 1 atm of H_2S gas. After 20 h at ambient temperature, the sample was evaporated to remove excess H_2S and then redissolved in C_6D_6. The starting material had been quantitatively converted to Pt(dcpe)$(SH)_2$, as determined by NMR spectroscopy.

Photolysis of Pt($Cy_2PC_2H_4PCy_2$)(Me)(SH). A 13 mg (0.020 mmol) amount of Pt(dcpe)(Me)(SH) (**1**) was added to an NMR tube and dissolved in about 1 mL of dry, oxygen-free THF-d_8. Photolysis of the sample using a Xe/Hg lamp (λ_{max} >300 nm) for 24 h resulted in decomposition of the starting material and generation of a small quantity (~10%) of CH_4, as determined by NMR spectroscopy.

***cis-(*Methylsulfinato)methyl[bis(dicyclohexylphosphino)ethane]platinum(II) (7).** A 24 mg (0.037 mmol) amount of Pt(dcpe)$(Me)_2$ was added to an NMR tube and dissolved in about 1 mL of dry, oxygen-free THF-d_8. The NMR tube was briefly opened to 1 atm of SO_2 gas. After 20 h at room temperature, the starting material had been quantitatively converted to Pt(dcpe)(SO_2Me)Me (**7**), as determined by NMR spectroscopy. The product was isolated by removal of the solvent under vacuum and recrystallization from a CH_2Cl_2 solution layered with hexanes. ^1H NMR (THF-d_8): δ 0.557 (dd, $J_{PH} = 6$, 4 Hz, $J_{PtH} = 61$ Hz, 3 H, Me), 1.1−2.6 (m, 52 H, $Cy_2PCH_2PCy_2$ and Me). ^{31}P NMR (THF-d_8): δ 53.36 (s, $J_{PtP} = 2499$ Hz), 71.73 (s, $J_{PtP} = 1919$ Hz). Anal. Calcd for $C_{28}H_{54}O_2P_2PtS\cdot 2CH_2Cl_2$: C, 40.87; H, 6.63. Found: C, 40.97; H, 7.03.

Reaction of Pt(dcpe)(Me)Cl and SO_2. A 20 mg (0.030 mmol) amount of Pt(dcpe)(Me)Cl was added to a NMR tube and dissolved in about 1 mL of dry, oxygen-free THF-d_8. The NMR tube was briefly opened to 1 atm of SO_2 gas. After 24 h at 65 °C, the starting material had completely reacted to form a 1:1 ratio of Pt(dcpe)(SO_2Me)Me (**7**) and Pt(dcpe)Cl_2, as determined by NMR spectroscopy.

Reaction of Pt(dcpe)(SO_2Me)Me and 12 M HCl. A 15 mg (0.020 mmol) amount of Pt(dcpe)(SO_2Me)Me (**7**) was added to a standard NMR tube and dissolved in 1 mL of THF-d_8.

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)Cl_2, $MeSO_2H$, and CH_4.

***cis*-Diphenyl[bis(dicyclohexylphosphino)ethane]platinum(II).** A solution of 80 mg (0.116 mmol) of Pt(dcpe)Cl_2 in 6 mL of THF was treated with 20 mg (0.238 mmol) of PhLi and stirred at ambient temperature for 2 h. The resulting milky solution was quenched with a saturated NH_4Br solution and evaporated, and the residue was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$ and evaporated to dryness on a rotary evaporator to yield a white solid. Recrystallization from a CH_2Cl_2 solution layered with hexanes resulted in white crystals of Pt(dcpe)Ph_2 (58 mg, 64%). ^{1}H NMR (C_6D_6): δ 0.8−2.0 (m, 48 H, $Cy_2PC_2H_4PCy_2$), 6.92 (t, $J_{PH} = 7$ Hz, 2 H, Ph), 7.21 (m, 4 H, Ph), 7.79 (t, $J_{PH} = 7$ Hz, $J_{PtH} = 58$ Hz, 4 H, Ph). ^{31}P NMR (C_6D_6): δ 55.24 (s, $J_{PtP} = 1725$ Hz). Anal. Calcd for $C_{38}H_{58}P_2Pt{\cdot}CH_2Cl_2$: C, 54.67; H, 7.06. Found: C, 54.52; H, 7.60.

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.[28] Data were corrected for absorption with the SADABS[29] 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 F^2 (Siemens, SHELXTL,[30] version 5.04). All 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 CH_2Cl_2 solvent in the asymmetric unit. The final residuals and goodness-of-fit values,[31] 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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[28] It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10× the listed value. It should be noted that the SAINT program could not improve the original cell produced by SMART for **11**, and hence the final unit cell is based upon only 168 reflections.

[29] The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

[30] SHELXTL: Structure Analysis Program, version 5.04; Siemens Industrial Automation Inc.: Madison, WI, 1995.

[31] GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n and p denote the number of data and parameters. R1 = $(\sum||F_o| - |F_c||)/\sum|F_o|$, and wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [(\mathrm{Max};0,F_o^2) + 2F_c^2]/3$.