5288 *Inorg. Chem.* **2001,** *40,* 5288−5289

Insertion Reactions of $(PPh_3)_2Pt(SR)_2$ with CS_2, where R = H, CMe_3, $CHMe_2$, 4-C_6H_4Me; Structure of $(PPh_3)Pt(SC_6H_4Me)(S_2CS\text{-}4\text{-}C_6H_4Me)$

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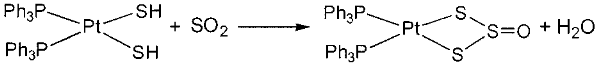
Received July 24, 2000

Introduction

Recently we reported[1] the reaction of **1** with SO_2 to give **2** (Equation 1). Both complexes catalyze the industrially important Claus reaction; they are the first homogeneous catalysts to do so. The Claus reaction involves the reaction of SO_2 with H_2S to give sulfur and water. Equation 1 is thought to be the first step in the reaction.



(1)

1 **2**

Although SO_2 readily inserts into M−C bonds,[2] and there are a few reports of SO_2 insertion into M−N[3] and M−O[4] bonds, there are no reports, to our knowledge, of SO_2 insertion into M−S bonds. Therefore, the reaction of **1** with SO_2 is thought to involve insertion into the S−H bond.[1] On the other hand, CS_2 readily inserts into M−S bonds;[5] however, its reactivity with the MSH moiety has not been studied except for one example.[5a] Therefore, we have conducted a study of the reactivity of CS_2 with *cis*-$(PPh_3)_2Pt(SH)_2$, **1**, and the thiolate complexes $(PPh_3)_2Pt(SR)_2$, **4a−c**, the results of which are reported below.

Experimental Section

All experiments were performed under nitrogen using vacuum lines and Schlenk techniques. Complexes **1**[7] and **4a−c**[8] were prepared according to published procedures. CS_2 (Aldrich) was used as received. Nuclear magnetic resonance spectra were recorded under nitrogen on a Varian XL-200 or JEOL-270 spectrometer. Chemical shifts are in ppm relative to TMS (for ^1H) and H_3PO_4 (for ^{31}P) at 0 ppm. Infrared spectra were recorded on an Analect AQS-20 Fourier transform infrared (FT-IR) spectrophotometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia. Melting points were obtained on a Thomas Hoover Capillary melting point apparatus and are uncorrected.

$(PPh_3)_2Pt(S_2CS)$ (3). In a 100 mL Schlenk flask, carbon disulfide (10.0 mL) was added to a solid sample of *cis*-$(PPh_3)_2Pt(SH)_2$ (0.10 g, 0.13 mmol). The solution became yellow after stirring overnight. The volatile compounds were removed under vacuum. Recrystallization of the residue from methylene chloride/hexanes gave yellow crystals (0.09 g, 85%). Mp: 265−267°. IR (KBr, cm^{-1}): $\nu_{C=S}$ 1060(s). ^1H NMR ($CDCl_3$): δ 7.20 (m, PPh_3). ^{31}P NMR ($CDCl_3$): δ 18.3 ($J_{Pt-P} = 3146$ Hz). Anal. Calcd for $C_{37}H_{30}P_2PtS_3{\cdot}CH_2Cl_2$: C, 50.00; H, 3.53; S, 10.54. Found C, 49.81; H, 3.65; S, 10.02.

$(PPh_3)Pt(SCHMe_2)(S_2CSCHMe_2)$ (5a). In a 100 mL Schlenk flask, carbon disulfide (10.0 mL) was added to a solid sample of *cis*-$(PPh_3)_2Pt(SCHMe_2)_2$ (0.050 g, 0.057 mmol). The solution became dark red almost immediately, and the stirring was continued for 4 h. The volatile compounds were removed under vacuum. Recrystallization of the residue from hot hexanes gave purple crystals (0.031 g, 79%). Mp: 129−131°. IR (KBr, cm^{-1}): $\nu_{CS\ of\ CS3}$ 985(s), $\nu_{CS\ of\ SR}$ 799(s), 925(m). ^1H NMR ($CDCl_3$): δ 1.32 (d, 6H, $SCH(CH_3)_2$), 1.42 (d, 6H, $SCH(CH_3)_2$), 2.99 (septet, 1H, $SCH(CH_3)_2$), 4.06 (septet, 1H, $SCH(CH_3)_2$), 7.28 (m, 9H, PPh_3), 7.62 (m, 6H, PPh_3). ^{31}P NMR ($CDCl_3$): δ 17.8 ($J_{Pt-P} = 3780$ Hz). Anal. Calcd for $C_{25}H_{29}PPtS_4$: C, 43.91; H, 4.27; S, 18.76. Found: C, 44.53; H, 4.33; S, 18.40.

$(PPh_3)Pt(SCMe_3)(S_2CSCMe_3)$ (5b). In a 100 mL Schlenk flask, carbon disulfide (10.0 mL) was added to a solid sample of *cis*-$(PPh_3)_2Pt(SCMe_3)_2$ (0.050 g, 0.056 mmol). The solution became dark red almost immediately, and the stirring was continued for 4 h. The volatile compounds were removed under vacuum. Recrystallization of the crude residue from hot hexanes gave purple crystals (0.031 g, 78%). Mp: 160−162°. IR (KBr, cm^{-1}): $\nu_{CS\ of\ CS3} = 988$(m), $\nu_{CS\ of\ SR} = 768$(s), 922(m). ^1H NMR ($CDCl_3$): δ 1.35 (s, 9H, $SC(CH_3)_3$), 1.61 (s, 9H, $SC(CH_3)_3$), 7.37 (m, 9H, PPh_3), 7.67 (m, 6H, PPh_3). ^{31}P NMR ($CDCl_3$): δ 17.1 ($J_{Pt-P} = 3780$ Hz). Anal. Calcd for $C_{27}H_{33}PPtS_4$: C, 45.56; H, 4.67; S, 18.02. Found C, 45.50; H, 4.86; S, 15.93.

$(PPh_3)Pt(S\text{-}4\text{-}C_6H_4Me)(S_2CS\text{-}4\text{-}C_6H_4Me)$ (5c). In a 100 mL Schlenk flask, carbon disulfide (10.0 mL) was added to a solid sample of *trans*-$(PPh_3)_2Pt(S\text{-}4\text{-}C_6H_4Me)_2$ (0.05 g, 0.052 mmol). The solution became dark red after it was stirred overnight. The volatile compounds were removed under vacuum. Recrystallization of the residue from methylene chloride/hexanes gave red crystals (0.035 g, 86%). Mp: 196−198°. IR (KBr, cm^{-1}): $\nu_{CS\ of\ CS3}$ 980 (s), $\nu_{CS\ of\ SR}$ 805(s), 943(s). ^1H NMR ($CDCl_3$): δ 2.24 (s, 3H, $SC_6H_4CH_3$), 2.34 (s, 3H $SC_6H_4CH_3$), 6.88 (d, 2H, $SC_6H_4CH_3$), 7.12 (d, 2H, $SC_6H_4CH_3$), 7.25 (d, 2H, SC_6H_4Me), 7.29 (d, 2H, SC_6H_4Me), 7.45 (m, 9H, PPh_3), 7.60 (m, 6H, PPh_3). ^{31}P NMR ($CDCl_3$): δ 16.8 ($J_{Pt-P} = 3730$ Hz). Anal. Calcd for $C_{33}H_{29}PPtS_4$: C, 50.82; H, 3.75; S, 16.45. Found: C, 49.77; H, 3.55; S, 15.08.

X-ray Structure Determination for 5c (Table 1).

Data for a red crystal of dimensions 0.48 × 0.35 × 0.17 mm was measured on a Rigaku AFC6S diffractometer using $\omega/2\theta$ scan mode and Cu Kα radiation. In all, 9408 reflections were measured of which 4731 were used for structure solution and refinement. The structure was solved by the Patterson method (SHELXS-96)[9] and refined on F^2 using SHELXL-96.[9] All non-hydrogen atoms are isotropic and were introduced in calculated positions. The structure was checked for missed symmetry and solvent voids using PLATONS.[10]

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10.1021/ic000825+ CCC: $20.00

Table 1. Crystallographic Data for **5c**

empirical formula $C_{33}H_{29}S_4PPt$	FW 779.86
a 10.2050(10) Å	space group triclinic $P1$
b 11.206(2) Å	T 20 °C
c 15.235(2) Å	λ 1.54056
α 93.14(2)°	d_{calc} 1.636 g/cm^{-3}
β 92.54(2)°	μ 11.388 mm^{-1}
γ 114.14(1)°	trans range 0.02−0.14
V 1583.2(4) Å^3	R_1 ($I > 2\sigma I$, all) 0.0390/0.0411[a]
Z 2	ωR_2 ($I > 2\sigma I$, all) 0.1073/0.1101[b]
reflns measured 9408	
unique refln (R_{int}) 4731 (0.053)	

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $\omega R_2 = [\sum\omega(F_o^2 - F_c^2)^2/\sum(\omega\,(F_o^2)^2)]^{1/2}$.

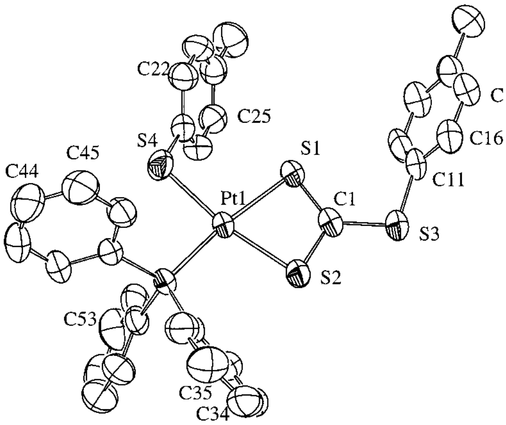
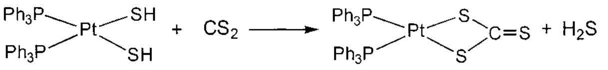


Figure 1. ORTEP drawing of $(PPh_3)Pt(SCS_2\text{-}4\text{-}C_6H_4Me)(S\text{-}4\text{-}C_6H_4\text{-}Me)$ **(5c)**. Selected bond lengths (Å) and angles (deg): Pt−P, 2.246(2); Pt−S(1), 2.382(2); Pt−S(2), 2.326(2); Pt−S(4), 2.293(2); P−Pt−S(1), 172.26(6); P−Pt−S(2), 98.72(6); P−Pt−S(4), 91.03(7); S(4)−Pt−S(2), 169.73(7); S(4)−Pt−S(1), 96.48; S(2)Pt−S(1), 73.68(6).

Results and Discussion

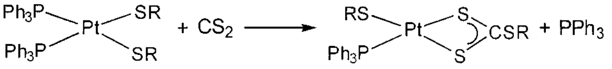
Complex **1** reacted with CS_2 to give $(PPh_3)_2Pt(S_2CS)$, **3**, in 85% yield with evolution of H_2S (Equation 2).



(2)

1 **3**

The yellow, air stable complex was identified by its spectroscopic properties[6] and elemental analysis. The thiolato complexes **4a−c** also reacted with CS_2 to give the thiolato−thioxanthato complexes $(PPh_3)Pt(SR)(S_2CSR)$ **5a−c** in 78% to 86% yield (Equation 3).



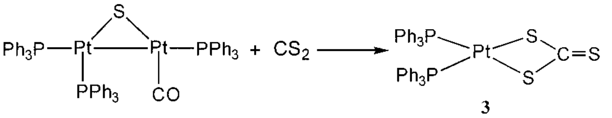
(3)

4a-c **5a-c**

R= $CHMe_2$(**a**), CMe_3 (**b**), 4-C_6H_4Me (**c**)

The spectroscopic properties and elemental analyses of **5a−c** suggested that only one CS_2 molecule had been incorporated while one PPh_3 ligand had been lost. This was confirmed by the X-ray structure determination of **5c** shown in Figure 1. Complexes **1** and **4a** did not react with CO_2 or COS at room temperature in THF or CH_2Cl_2.

The reactivity of CS_2 with **1** is similar to that of SO_2[1] in that only one molecule of each is incorporated, leading to elimination of H_2S and H_2O to give **3** and **2**, respectively. In the case of CS_2, the probable intermediate contains the PtSC(S)SH moiety, which reacts internally with the other SH ligand. Similar intermediates were proposed[5a] in the sequential reaction of CS_2 with two molecules of $CpRu(PPh_3)_2SH$ to give $Cp_2Ru_2(PPh_3)_3\text{-}CS_3$, which contains a bridging CS_3 ligand. The chemistry of CS_2 with **1** is similar to the Claus chemistry observed between **1** and SO_2. Complex **3** has also been prepared[6] via Equation 4.



(4)

3

Complexes **4a−c**, which do not contain the reactive Pt−SH moiety, react with CS_2 probably via an intermediate containing a monodentate thioxanthato ligand which becomes bidentate via loss of a PPh_3 ligand. The reactions between **4a−c** and CS_2 were monitored by NMR spectroscopy. The rates of reaction with complexes containing electron releasing groups ($CHMe_2$, CMe_3) were much faster than that containing 4-C_6H_4Me. There was no evidence of any intermediates. The rate increases with increasing CS_2 concentrations, decreases in the presence of added PPh_3, and is invariant in the presence of CO. These observations are very similar to those[5] made for the reactions of CS_2 with $CpRu(PPh_3)_2SR$ and $CpW(CO)_2(PPh_3)SR$. These latter reactions are thought to proceed via loss of PPh_3 and precoordination of CS_2 to the metal atoms followed by electrophilic attack by the CS_2 ligand on the sulfur atom of the thiolato ligand. The reactions of **4** with CS_2 are also consistent with precoordination of CS_2.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada and the Quebec Department of Education for financial support. We thank McGill University for Fellowship support of M.E.

Supporting Information Available: X-ray crystallographic file, in CIF format, for the structure determination of **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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