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Reactivity of $Pt(PCy_3)_2$ and $Pt[P(t\text{-}Bu)_3]_2$ with SO_2 and CS_2

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The first structurally characterized three-coordinate bis(phosphine)platinum(0)–sulfur dioxide complex is described, $Pt(PCy_3)_2SO_2$. The complex crystallized in the monoclinic space group $C2/c$ with $a = 23.328$ (4) Å, $b = 15.181$ (3) Å, $c = 25.207$ (4) Å, and $\beta = 126.17$ (1)° with $Z = 8$ ($T = -100$ °C). The effect of subtle electronic and steric changes on the reactivity of $Pt(PCy_3)_2$ and $Pt[P(t\text{-}Bu)_3]_2$ with the small molecules SO_2, CS_2, and O_2 is demonstrated. Evidence is presented for the first example of a bridged $Pt_3(\mu\text{-}CS_2)_3(PR_3)_3$ moiety.

Introduction

The study of SO_2 derivatives of zerovalent platinum compounds and transition-metal–SO_2 complexes in general, has received considerable attention in the past 6 years as exemplified by the 293 references cited in two recent reviews.[1,2] While there has been much synthetic work on nickel-triad compounds, 2-coordinate tertiary phosphine–platinum(0) compounds are rare.[3] This is reflected in the absence of any structurally characterized 3-coordinate Pt(tertiary phosphine)$_2$(SO_2) complexes. Moody et al.[4] and Cook and Jauhal[5] formulated an unstable species derived from $Pt(SO_2)_2(PPh_3)_2$ as being $Pt(SO_2)(PPh_3)_2$, but due to the high dissociation pressures of SO_2, only indirect evidence for its identity was offered. With this exception, literature[2] descriptions of the reaction of SO_2 with Pt(0)–phosphine complexes have been limited to the formation of 4-coordinate species. In general, with small ligands, the preferred coordination number for zerovalent Ni, Pd, and Pt is 4,[6] giving the metal an inert-gas configuration.

In 1977, Tolman published an excellent review[7] concerning the steric effects of phosphorus ligands on a variety of physical and chemical properties of organometallic compounds. He presented a strong case for the argument that steric effects are generally at least as important as electronic effects and oftentimes are the dominant consideration. The reports by Otsuka et al.[8] and Green et al.[9] describing the first syntheses of alkyl $Pt(PR_3)_2$ complexes and their resulting reactivity toward small molecules aptly illustrated the importance of steric factors in stabilizing the metal center with ligand bulk.

This paper contains the results of our investigation of the reactivity of SO_2 toward Pt–bulky phosphine complexes that are coordinatively and electronically unsaturated. In order to strengthen the likelihood that $Pt(PR_3)_2$ would coordinate only small molecules in a third coordination site and at the same time circumvent addition of a third phosphine, careful attention was paid to phosphine size. Our strategy was to employ cone angles of the ligands, a measure of steric bulk,[7] to emphasize variations in reactivity of these complexes toward small molecules. Since ligands with cone angles greater than 160° appear to favor 2-coordination, $Pt(PCy_3)_2$ and $Pt[P(t\text{-}Bu)_3]_2$ (cone angles 170 and 182°, respectively) were selected as a result of previously reported[8b] differences in reactivity toward H_2, O_2, and small HX compounds. Further, Strohmeier and Muller[10] have shown that phosphines can be ranked according to their electronic effects (on the basis of CO stretching frequencies in $Ni(CO)_3L$ species). Since PCy_3 and $P(t\text{-}Bu)_3$ show nearly identical electronic parameters in this study ($\nu = 2056.4$ and 2056.1 cm^{-1}, respectively),[7] we reasoned significant differences in ligand nucleophilicity could be ruled out.

The crystal and molecular structure of $Pt(SO_2)(PCy_3)_2$ is presented here, along with a comparison of its reactivity and that of the $P(t\text{-}Bu)_3$ analogue toward O_2, SO_2, and CS_2.

Experimental Section

All reactions were carried out in a nitrogen atmosphere except where noted. Phosphines were purchased from Strem Chemicals and SO_2 from the Matheson Co. As required, SO_2 was purified by trap to trap distillation. All solvents used in this study were reagent grade, dried over activated molecular sieve or sodium metal, and degassed by freeze–thaw procedures. Infrared spectra (Nujol mulls) were recorded on a Perkin-Elmer Model 180 or Model 683 spectrophotometer, and elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

The starting materials $Pt(PCy_3)_2$ (**1**) and $Pt[P(t\text{-}Bu)_3]_2$ (**2**) were prepared according to the methods of Stone[11] and Otsuka,[8a] respectively, the latter with the minor modification of filtering under N_2 an *n*-hexane solution of **2** through a frit layered with a 1-cm pad of chromatographic grade alumina. Great care is necessary to avoid the presence of O_2 at all stages of the preparation of **1**. Synthesis of **2** was initially attempted according to the literature procedure of Goel et al.[12] However, we were unable to isolate a crystalline material, and the infrared spectrum for the viscous white product did not correspond to the above referenced[8a] report. As previously described,[8] $Pt(O_2)(PCy_3)_2$ (**4**) was prepared by reaction of **1** with O_2 in solution or in the solid state, while **2** was found to be totally unreactive toward O_2 as a dry solid or in solution.

Reactions of Bis(tricyclohexylphosphine)platinum(0). (1) With Sulfur Dioxide. Purified sulfur dioxide was passed over a stirred solution of **1** (0.15 g, 0.2 mmol) in *n*-hexane (35 mL) at room temperature. Immediate SO_2 absorption occurred, producing a dark yellow solution. After 30 min, the vessel was closed off (under SO_2) and the mixture stirred for 2 h, during which time a fine greenish yellow solid was suspended in the mustard green solution. Following concentration to ca. 3 mL, filtration, and recrystallization from cold (0 °C) hexane, lime green crystals of $Pt(SO_2)(PCy_3)_2$ (**3**) (0.11 g, 67%) were isolated; mp 131–133 °C dec.

Variation of solvents (THF, ether, pentane, petroleum ether, toluene, benzene) produces the same product **3**, differing only in solubility. As described below, extended exposure of **3** to air results in the formation of a sulfato complex, and hence **3** should be stored under an inert atmosphere. Evacuation (10^{-5} torr) of **3** (0.15 g, 0.18 mmol) produced no change in color, melting point, or infrared spectrum, nor was there evidence of SO_2 dissociation after 48 h. Formulation of **3** as $Pt(SO_2)(PCy_3)_2$ resulted from infrared (Table III) and X-ray crystal analysis (see below).

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$Pt(PCy_3)_2$ (0.12 g, 0.15 mmol) was placed in a break-seal tube and 1.4 g (22 mmol) of purified SO_2 was condensed into the vessel, which was then sealed and warmed to room temperature with stirring. After 18 h, the mustard yellow solution was taken to dryness in vacuo, yielding a green solid whose infrared spectrum and melting point were identical with those of **3**.

(2) With Carbon Disulfide. Excess degassed CS_2 (13 g, 17 mmol) was condensed into a 100-mL vessel containing 50 ml of an *n*-hexane solution of **1** (0.15 g, 0.2 mmol). As the stirred mixture warmed to room temperature (20 min), a peach-colored solid separated from the light orange solution. After 2 h of stirring under N_2, the solution was concentrated at reduced pressure to ca. 5 mL and filtered, and the light orange solid was recrystallized from cold hexane and dried (10^{-5} torr) for 3 h, giving pink crystals of $Pt(CS_2)(PCy_3)_2$ (**5**) in high yield (0.14 g, 87%); mp 213–216 °C dec. Anal. Calcd for $PtC_{37}H_{66}P_2S_2$: C, 53.40; H, 7.99; P, 7.44; S, 7.70; Pt, 23.44. Found: C, 53.46; H, 7.93; P, 7.33; S, 7.80; Pt, 23.61.

Utilization of **5** proved to be the preferred method for synthesis of **3**, as (relative to **1**) **5** is reasonably insensitive to small amounts of dioxygen. This permitted use of commercial (unpurified) SO_2 in displacing CS_2 over a 1-h period from an *n*-hexane solution of **5** to give a quantitative yield of pure **3**. This inertness was further illustrated when **5** (0.10 g, 0.12 mmol) in 40 mL of hexane was mixed with 500 torr (6.8 mmol) each of O_2 and SO_2 in a 250-mL flask, forming a bright yellow solution, and subsequently reduced to dryness in vacuo after 10 min, with the lime green solid product proving to be nearly pure **3** as shown by its infrared spectrum. Under the same conditions, the vessel was left closed overnight, producing the yellow crystalline product $Pt(SO_4)(PCy_3)_2$ (**6**) described below.

Reactions of (Sulfur dioxide)bis(tricyclohexylphosphine)platinum(0). (1) With Dioxygen. A large excess of SO_2 (7.0 g, 110 mmol) was condensed into a pressure vessel containing **3** (0.10 g, 0.13 mmol); the contents were subsequently warmed to room temperature, stirred for 1 h, and cooled to −196 °C, and 250 mL of O_2 (690 torr, 9.4 mmol) was admitted to the vessel. Rewarming to room temperature after 10 h of stirring produced a clear, pale yellow solution. After the solution was cooled to −196 °C, uncoordinated O_2 was removed in vacuo and free SO_2 subsequently removed by trapping as the contents warmed to room temperature, the pale yellow solid **6** being dried overnight (10^{-5} torr). Consistent with the observation of moderate air stability for solid **3**, 3 h was required before complete conversion to **6** occurred when 45 mL of an *n*-hexane solution of **3** (0.10 g, 0.13 mmol) was saturated with O_2. The infrared spectrum for **6** (Table III) shows sulfate frequencies similar to those reported by Horn et al.[13] and Levison and Robinson[14] for the analogous $Pt(SO_4)(PPh_3)_2$. Anal. Calcd for $PtC_{36}H_{66}P_2SO_4$: C, 50.75; H, 7.81; P, 7.27; S, 3.76; Pt, 22.89. Found: C, 51.24; H, 7.79; P, 7.17; S, 3.89; Pt, 21.16.

In contrast to the relatively slow reaction of **3** with O_2 to form the sulfato complex, **4** immediately reacts with SO_2 to give **6**. *n*-Hexane (35 mL) was condensed onto **4** (0.15 g, 0.19 mmol), and the contents were warmed to room temperature with stirring (**4** partially dissolves). As SO_2 passed over the solution, all of **4** immediately dissolved, and within 30 s a precipitate appeared in the solution, with copious amounts of a curdy yellow solid being deposited over a 2–3-min period. After 5 min, the reaction appeared complete and the solution was reduced to ca. 5 mL, cooled (0 °C), and filtered and the pale yellow solid (0.13 g, 81%) dried in vacuo for 1 h. It was characterized via infrared analysis as being **6**, with no evidence of **4** or **3** being present.

(2) With Carbon Disulfide. *n*-Hexane (35 mL) was condensed onto **3** (0.14 g, 0.17 mmol), excess CS_2 was admitted, (2.0 g, 26 mmol), and the mixture was warmed to room temperature. The initially lime green solution turned yellow within 5 min, yielding a pale yellow precipitate. After being stirred overnight, the solution was concentrated to 8 mL and filtered, and the pale orange solid was dried in vacuo for 1 h and characterized as **5** via infrared measurements. To determine the effect of adding an equimolar amount of CS_2 on the reactivity of **3**, 0.15 g (0.18 mmol) of $Pt(SO_2)(PCy_3)_2$ was added to 35 mL of *n*-hexane. To this was added (under a SO_2 atmosphere) a 10-mL *n*-hexane solution containing 0.014 g (0.18 mmol) of CS_2 saturated with SO_2. The green solid collected from the lemon-lime solution after 3 h proved to be pure **3** as confirmed by its IR spectrum.

Table I. X-ray Data

space group	$C2/c$
a	23.328 (4) Å
b	15.181 (3) Å
c	25.207 (4) Å
β	126.17 (1)°
Z	8
μ(Mo Kα)	41.2 cm^{-1}
developed faces	{001}, {110}, [100]
dist from origin	0.062, 0.148, 0.165 mm
max, min transmission[15]	0.608, 0.366
data collcd	$2\theta \leqslant 50°$
no. of unique reflcns	6371
no. obsd $I \geqslant 2\sigma(I)$	5186
unweighted R value	2.4%
weighted R value	3.0%
temp	−100 °C
diffractometer and counting technique	Picker FACS-1, P. G. Lenhert's disk operating system,[16] Wang encoders, graphite monochromator, 3.5° takeoff angle, (1.5 + dispersion)° continuous scans, 20-s symmetric background counts, Mo Kα_1 radiation (λ 0.709 30 Å)

Reactions of Bis(tri-*tert*-butylphosphine)platinum(0). (1) With Sulfur Dioxide. The reaction of **2** (0.20 g, 0.33 mmol) with SO_2 was carried out in a fashion similar to that for **3** to obtain a yellow precipitate (mp 205–207 °C dec) of $Pt(SO_2)[P(t\text{-}Bu)_3]_2$ (**7**) in 55% yield (0.23 g). As previously noted,[8b] the title compound was insensitive to dioxygen, so unpurified tank SO_2 was utilized throughout. The reaction conditions were duplicated in THF, ether, pentane, and toluene, giving the same results with poorer yields. Anal. Calcd for $PtSO_2P_2C_{24}H_{54}$: C, 43.42; H, 8.20; P, 9.33; S, 4.82; Pt, 29.38. Found: C, 43.65; H, 8.44; P, 9.08; S, 5.02; Pt, 29.68. Reaction of **2** with a mixture of SO_2 and O_2 also produced only **7**.

(2) With Carbon Disulfide. In contrast to the case of **5**, the reaction of **2** (0.15 g, 0.25 mmol) with CS_2 (1.3 g, 17 mmol) gave orange crystals of $Pt_3(CS_2)_3[P(t\text{-}Bu)_3]_3$ (**8**) in quantitative yield. Anal. Calcd for $Pt_3C_{39}H_{81}S_6P_3$: C, 32.95; H, 5.77; P, 6.54; S, 13.52; Pt, 41.19. Found: C, 34.15; H, 5.96; P, 7.00; S, 13.09; Pt, 34.98. The high C, H, and P analyses suggested the sample was contaminated with displaced $P(t\text{-}Bu)_3$, so the reaction was repeated and the sample washed with *n*-hexane prior to analysis. Anal. Found: C, 33.77; H, 5.94; P, 6.98; S, 13.57; Pt, 37.93. A proton NMR spectrum obtained at 60 MHz on a Varian EM-360 spectrometer revealed one doublet (δ 1.1, J_{P-H} = 12 Hz) in C_6D_6/CS_2 solution, as compared to that of uncomplexed $P(t\text{-}Bu)_3$ in C_6D_6, which showed a doublet (δ 0.8, J_{P-H} = 10 Hz).

Contrary to the case of **5**, exposure of a stirred solution of **8** (0.12 g, 0.18 mmol) in 40 mL of *n*-hexane to excess SO_2 over an 8-h period did not result in the displacement of CS_2. This was verified by lack of a color change in the pale orange solid and identification of its infrared spectrum as pure, unreacted **8**.

Reactions of (Sulfur dioxide)bis(tri-*tert*-butylphosphine)platinum(0). (1) With Dioxygen. A 0.06-g (0.1-mmol) sample of **7** was dissolved in ca. 20 mL of *n*-hexane saturated with O_2, the mixture stirred overnight, solvent subsequently removed (10^{-3} torr), and the yellow solid dried in vacuo for 3 h. Unlike **3**, only the starting material **7** was present as confirmed via infrared analysis.

(2) With Carbon Disulfide. The reaction of **7** (0.06 g, 0.1 mmol) in 15 mL of *n*-hexane with CS_2 (0.4 g, 5.3 mmol) was carried out as described above for **3**, and the coordinated SO_2 was similarly displaced to form **8** as confirmed by infrared analysis.

X-ray Measurements, Solution, and Refinements. Pertinent information concerning the cell, crystal morphology, and intensity measurements is given in Table I. Two standard reflections measured after every 50 reflections varied by less than 2% over the period of the data collection process. Correction curves for this variation were estimated by least-squares refinement of a polynomial to the standards and applied to the data. The variance for $\overline{F^2}$ (the average of F^2 over equivalent reflections) was computed from $\sigma^2(\overline{F^2}) = \sigma_c^2(\overline{F^2}) + \sigma_N^2(\overline{F^2})^2$ where σ_c^2 is the variance due to counting statistics and σ_N

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Table II. Selected Distances (Å) and Angles (deg)

Pt-S	2.299 (1)	P1-Pt-P2	165.72 (4)
Pt-P1	2.304 (1)	S-Pt-P1	95.03 (4)
Pt-P2	2.309 (1)	S-Pt-P2	97.39 (4)
S-O1	1.465 (3)	Pt-S-O1	104.8 (1)
S-O2	1.461 (3)	Pt-S-O2	104.1 (1)
		O1-S-O2	113.1 (2)

is taken to be 0.015.

The function minimized in the least-squares refinements was $\sum w(|F_o| - |F_c^*|)^2$ where $w = 4F_o^2/\sigma^2(F^2)$ and F^* includes a correction for secondary extinction.[17] Neutral-atom scattering factors[18] were used with appropriate dispersion terms.[18]

The location of the Pt atom was determined from the Patterson map; the structure was determined from standard difference Fourier methods. Refinements of the structure with anisotropic thermal parameters for atoms heavier than carbon and without hydrogen atoms converged to an unweighted R value of 3.9%. At this point, hydrogen atoms were added at calculated positions (C-H = 1.0 Å, B_H = 5.0) and were held fixed in subsequent calculations. Final refinements included anisotropic thermal parameters for carbon atoms. A final difference map showed a ghost of the cyclohexyl ring involving C19-C24 with peaks that varied from 0.6 to 1.4 e/Å^3. Since the population of this ghost ring is small ($\sim^1/_6$) and the isotropic thermal parameters of the parent ring are consistent with the remaining carbon atoms in the structure, no attempt was made to refine the structure further. Selected distances and angles are presented in Table II and final parameters are listed in Table IV.

Results and Discussion

Molecular Structure of $Pt(SO_2)(PCy_3)_2$. The X-ray crystal analysis shows this to be a 3-coordinate complex with an η^1-pyramidal SO_2. The Pt atom is 0.12 Å out of the plane defined by the sulfur and two phosphorus atoms. The SO_2 is oriented so that the oxygens lie closer to P2 and are nearly symmetrically disposed with respect to the above-mentioned plane (1.03 and 1.33 Å for O1 and O2, respectively). The angle between the Pt-S vector and the vector defined by the sum of the S-O vectors of 116.9° is normal for η^1-pyramidal complexes.

On the basis of several previous structural studies and related discussions,[2] it is clear that SO_2 adopts the η^1-pyramidal geometry only when the transition-metal fragment acts as a σ base. As pointed out by Ryan et al.,[2] the orbital template for C_{2v}-$ML_2(d^{10})$ metal fragments is compatible with all three known M-SO_2 geometries, η^1-planar, η^1-pyramidal, and η^2, though the relatively higher energy of the metal a_1 LUMO suggests that the former is least likely. Furthermore, several structural investigations of $ML_2(d^{10})$ fragments bonded to ligands that are π acids fully document the ability of these fragments to act as π bases.[19] The enhanced π-donating ability of C_{2v}-ML_2 fragments has been investigated from a theoretical point of view by several authors.[20] Since η^2-SO_2 has been shown to be favored by π-donating ML_n fragments,[2] it is indeed interesting that the present structure exhibits η^1-pyramidal SO_2 and points to the unique ability of SO_2 to act as a sensitive probe of the nature of the frontier orbitals on transition-metal fragments. Clearly, in the present case the L_2Pt fragment prefers to make use of its σ-donating ability to coordinate SO_2.

A further point of interest is the observation that the SO_2 group bends in the molecular plane. Although we could find no discussion in the literature for planar ML_2A (A = amphoteric ligand) complexes, the five-coordinate ML_4A complexes where NO is contained in the equatorial plane of a trigonal bipyramid have been discussed by Hoffmann et al.[20] We have carried out model calculations[21] on $Pt(PH_3)_2$ and find that it is topologically similar, even at a bond angle of 160°, to that described by Hoffmann et al. for the equatorial plane of a trigonal bipyramid, where it has been pointed out that the tendency for nitrosyl to bend (if it bends) perpendicular to the equatorial plane rather than in that plane can be attributed to the formation of the metal fragment-nitrosyl π interaction in the equatorial plane.[20]

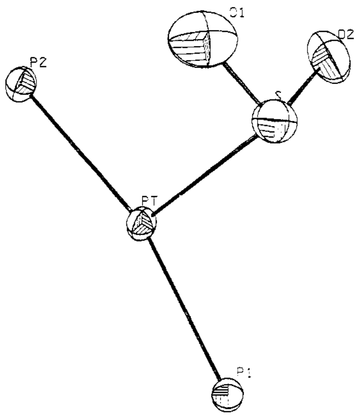

Figure 1. ORTEP projection of $Pt(PCy_3)_2(SO_2)$. Carbon atoms are omitted for clarity.

Unlike nitrosyl, the SO_2 ligand lacks a good π-accepting orbital perpendicular to its bending direction, and therefore the tendency to bend in a particular direction depends only on the degree of stabilization gained by adopting the η^1-pyramidal geometry. This stabilization is determined, in a second-order Jahn-Teller sense, by the degree of interaction between the two low-lying antibonding σ and π^* orbitals in the hypothetical η^1-planar complex.[2] The present structure then makes a valuable comment on the relative effectiveness of this interaction to induce bending independent of the π-bonding stabilization in the perpendicular direction and nicely complements the related nitrosyl structures.

It is somewhat surprising to note that the P-Pt-P angle has opened to 165.72° upon coordination to SO_2, given the 160.5° angle for $Pt(PCy_3)_2$ reported by Immirzi and co-workers.[22] However our calculations for $Pt(PH_3)_2$ and $Pt(CO)_2$ show a relatively flat minimum at 180°, which leads us to believe that the structural results may be a result of steric effects. It is also interesting to note the relatively short Pt-S distance of 2.299 Å observed in this 3-coordinate complex as compared to the longer distances (2.37-2.46 Å) found for the four-coordinate Pt(0) complexes also containing the η^1-pyramidal geometry. Presumably the lower coordination number permits closer access of SO_2 to the platinum center.

Reactivity of PtP_2 and $PtXP_2$ toward SO_2 (P = PCy_3, P-(*t*-Bu)$_3$; X = CS_2, SO_2). While one 3-coordinate and a substantial number of 4-coordinate platinum(0)-phosphine-SO_2 complexes have been reported in the literature,[1,2] the synthetic appraoch has uniformly been displacement of coordinated ligands from PtL_3 and PtL_4 moieties. Further, the only previously reported 3-coordinate complex, $Pt(SO_2)(PPh_3)_2$,[4,5] is coordinated with a phosphine unit that is not particularly bulky (cone angle 145°),[7] thus proving to be unstable, especially in solution, and reactive toward other small molecules such as CS_2 and O_2. We reasoned that sterically crowded PtP_2 complexes might alter the nature of SO_2 coordination and its

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Table III. Characteristic IR Data (cm^{-1}) in Nujol

complex	complex no.	ν(S–O)	δ(S–O)	ν(C–S)	δ(C–S)	ν(M–C)	ν(O–O)
free SO_2[a]		1362, 1151	518				
$Pt(SO_2)(PPh_3)_2$[b]		1182, 1149, 1035					
$Pt(SO_2)(PCy_3)_2$	3	1162, 1029	508				
$Pt(SO_2)[P(t\text{-}Bu)_3]_2$	7	1173, 1035	509[c]				
$Pt(SO_4)(PPh_3)_2$[d]		1146, 651, 536, 316					
$Pt(SO_4)(PCy_3)_2$	6	1277, 1158, 883, 650					
free CS_2[e]				1196, 1117			
$Pt(CS_2)(PPh_3)_2$[f]				1146	651	536	
$Pt(CS_2)(PCy_3)_2$	5			1133	658	g	
$Pt_3(CS_2)_3[P(t\text{-}Bu)_3]_3$	8			1111	743	513[h]	
$Pt(O_2)(PCy_3)_2$	4						820

[a] Gas-phase spectrum; ref 30. [b] References 2, 5. [c] Tentative assignment based on increased intensity of absorption compared to that of **2**. [d] References 24a,d. [e] Reference 24c. [f] Reference 24a. [g] Phosphine bands interfere with assignment. [h] This band may be a shift of the parent phosphine 503-cm^{-1} vibration.

Table IV. Coordinates and Thermal Parameters for $Pt(PCy_3)_2(SO_2)$[a]

atom	x	y	z	atom	x	y	z
Pt1	0.19075 (1)	0.00037 (1)	−0.21480 (1)	S1	0.08058 (6)	0.06542 (8)	−0.27827 (6)
O1	0.0385 (2)	0.0082 (2)	−0.3359 (2)	O2	0.0941 (2)	0.1522 (2)	−0.2938 (2)
P1	0.19998 (5)	0.00616 (7)	−0.11868 (5)	C1	0.1627 (2)	−0.0955 (2)	−0.1095 (2)
C2	0.1993 (2)	−0.1789 (2)	−0.1109 (2)	C3	0.1650 (2)	−0.2623 (3)	−0.1073 (2)
C4	0.0856 (2)	−0.2651 (3)	−0.1621 (2)	C5	0.0496 (2)	−0.1830 (3)	−0.1600 (2)
C6	0.0823 (2)	−0.0992 (3)	−0.1648 (2)	C7	0.2927 (2)	0.0134 (2)	−0.0435 (2)
C8	0.3450 (2)	−0.0263 (3)	−0.0554 (2)	C9	0.4222 (2)	−0.0186 (3)	0.0055 (2)
C10	0.4324 (2)	−0.0591 (3)	0.0654 (2)	C11	0.3824 (2)	−0.0165 (2)	0.0779 (2)
C12	0.3049 (2)	−0.0258 (3)	0.0190 (2)	C13	0.1495 (2)	0.0966 (2)	−0.1143 (2)
C14	0.1466 (2)	0.0953 (3)	−0.0552 (2)	C15	0.0953 (2)	0.1661 (3)	−0.0630 (2)
C16	0.1172 (2)	0.2568 (3)	−0.0709 (2)	C17	0.1232 (3)	0.2585 (3)	−0.1277 (2)
C18	0.1736 (2)	0.1876 (3)	−0.1208 (2)	P2	0.19900 (6)	−0.03608 (7)	−0.29899 (5)
C19	0.1580 (2)	0.0435 (3)	−0.3676 (2)	C20	0.1352 (3)	0.0186 (3)	−0.4335 (3)
C21	0.0856 (3)	0.0900 (3)	−0.4844 (2)	C22	0.1264 (3)	0.1788 (3)	−0.4626 (3)
C23	0.1527 (3)	0.2033 (3)	−0.3967 (3)	C24	0.1955 (2)	0.1328 (3)	−0.3451 (2)
C25	0.2954 (2)	−0.0437 (3)	−0.2613 (2)	C26	0.3300 (2)	−0.1166 (3)	−0.2091 (2)
C27	0.4112 (2)	−0.1103 (3)	−0.1669 (2)	C28	0.4375 (2)	−0.1139 (3)	−0.2095 (2)
C29	0.4020 (2)	−0.0433 (3)	−0.2628 (2)	C30	0.3209 (2)	−0.0489 (3)	−0.3051 (2)
C31	0.1527 (2)	−0.1416 (3)	−0.3382 (2)	C32	0.1502 (2)	−0.2027 (3)	−0.2913 (2)
C33	0.1043 (3)	−0.2837 (3)	−0.3270 (2)	C34	0.1279 (3)	−0.3337 (3)	−0.3634 (2)
C35	0.1306 (2)	−0.2734 (3)	−0.4093 (2)	C36	0.1783 (2)	−0.1936 (3)	−0.3732 (2)

[a] Anisotropic thermal parameters are published as supplementary data.

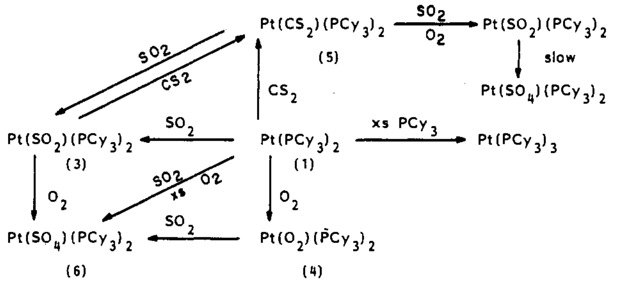

Figure 2. Reactions of $Pt(PCy_3)_2$.

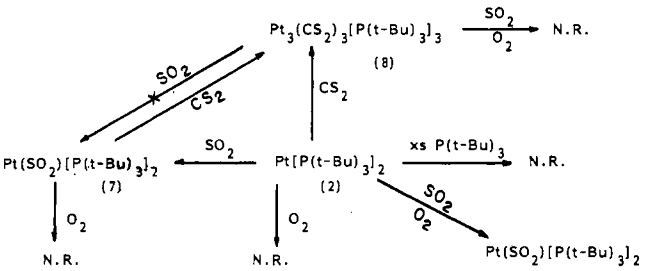

Figure 3. Reactions of $Pt[P(t\text{-}Bu)_3]_2$.

subsequent reactivity with other chemical species. Selection of PCy_3 and $P(t\text{-}Bu)_3$ was predicated on their nearly identical electron donor/acceptor properties (according to the method of Tolman[6a] and Strohmeier and Muller[10]) and their large size (cone angles 170 and 182°, respectively[7]). Diagrams depicting the various reactions studied and the products found are shown in Figures 2 and 3.

It is important to emphasize the greatly reduced reactivity of $Pt[P(t\text{-}Bu)_3]_2$ in comparison to $Pt(PCy_3)_2$ and especially for both complexes with respect to platinum–phosphine analogues with smaller steric bulk. For example, Ghatak et al.[23] reported the reaction of $Pt(SO_2)(PPh_3)_3$ with CS_2, in the presence of excess SO_2, to form the dithiocarbonate complex $Pt(CS_2O)(PPh_3)_2$.[24] The latter product was also obtained when SO_2 gas was passed through a benzene solution of $Pt(CS_2)(PPh_3)_2$. In sharp contrast, we found CS_2 and SO_2 to readily displace one another from $PtX(PCy_3)_2$, depending on which moiety was in excess. Interestingly, $Pt(SO_2)[P(t\text{-}Bu)_3]_2$ was irreversibly converted to the first reported example of a bridged trimeric CS_2 complex, $Pt_3(CS_2)_3[P(t\text{-}Bu)_3]_3$ (**8**), in the presence of excess CS_2. For neither system were we able to obtain dithiocarbonate complexes when SO_2 and CS_2 were used as reagents. However, the authentic $Pt(S_2CO)(PCy_3)_2$ (but not $Pt(S_2CO)[P(t\text{-}Bu)_3]_2$) was prepared according to a literature method[24a] starting with $PtO_2(PCy_3)_2$ and reacting

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with CS_2. Presumably the difference in reactivity lies in the well-known ability of Pt–PPh_3 complexes to assume a coordination number of 4, whereas PCy_3 and P(*t*-Bu)$_3$ ligands do not readily permit cis coordination of an intermediate species containing both SO_2 and CS_2.

Steric and Electronic Influences on Reactivity. We have observed both SO_2 and CS_2 coordination to Pt(PCy_3)$_2$, infrared (Table III) and X-ray results showing coordination of SO_2 to be η^1-pyramidal and infrared data strongly supporting η^2 bonding for CS_2. The similarity of the infrared data for **3** and **7** suggests that the latter also contains η^1-pyramidal SO_2, although infrared diagnostics can be misleading for a d^{10} system.[2]. Clearly, **7** does not contain η^2-SO_2, however.

The coordination of CS_2 with Pt(PCy)$_2$ and Pt[P(*t*-Bu)$_3$]$_2$ warrants further comment. Otsuka[3] has pointed out that addition to ML_2 (M = Pt, Pd; L = bulky phosphines) species is limited to small substrates, e.g. HX (X = H, Cl, $OCOCH_3$, etc.), that form trans complexes and that these ML_2 complexes do not accept two-center π acids that require cis alignment of the phosphine ligands. Thus, relying on steric arguments, he accounts for the inertness of M[P(*t*-Bu)$_3$]$_2$ toward dioxygen. While we also found Pt[P(*t*-Bu)$_3$]$_2$ to be unreactive with dioxygen, carbon disulfide reacts in a facile manner. This appeared somewhat puzzling to us initially until it was realized that phosphine dissociation had occurred upon reaction with CS_2 and that the product appeared to be a trinuclear cluster[25] instead of the expected product, Pt(CS_2)[P(*t*-Bu)$_3$]$_2$. There is little doubt CS_2 is bonded to Pt(PCy_3)$_2$ as a π acid in an η^2 fashion, as supported by its infrared frequencies (Table III). Hayward et al.[24a] assigned four bands in the spectrum of Pt(CS_2)(PPh_3)$_2$ as ν(C=S) 1146, ν(C—S) 651, ν(M—C) 536, and ν(M—S) 316 cm^{-1}. At about the same time, the crystal structure for the latter material was published and CS_2 was in fact found to be coordinated in a two-center mode.[24d] While we were unable to identify the ν(M—C) and ν(M—S) frequencies due to interference from phosphine vibrations, the appearance of a very strong ν(C=S) 1133 cm^{-1} and a strong ν(C—S) absorption at 658 cm^{-1} safely permits formulation of η^2 coordination through one sulfur and one carbon atom of CS_2 for the Pt(CS_2)(PCy_3)$_2$ complex. The infrared spectrum of the proposed trinuclear cluster Pt_3(CS_2)$_3$[P(*t*-Bu)$_3$]$_3$ shows a decrease in the ν(C=S) absorption (1111 vs. 1133 cm^{-1}), suggesting a bridged CS_2 species rather than a simple adduct. Not surprisingly, Pt_3(CS_2)$_3$[P(*t*-Bu)$_3$]$_3$ was so stable that it resisted all attempts to replace the CS_2 even in the presence of excess SO_2.

We have observed that Pt(CS_2)(PCy_3)$_2$ is unreactive toward oxygen but the CS_2 ligand is rapidly displaced by SO_2. Since the formation of the sulfato complex apparently (vide infra) requires intermediate formation of Pt(O_2)(PCy_3)$_2$, we have prepared pure Pt(SO_2)(PCy_3)$_2$, even in the presence of small amounts of O_2, by first preparing Pt(CS_2)(PCy_3)$_2$ and subsequently reacting it with tank SO_2.

Given the similar electronic (inductive) nature of both phosphine ligands, the slightly larger steric bulk and concomitant reduced compressibility of P(*t*-Bu)$_3$ apparently work in concert to prevent formation of dioxygen, sulfate (see below), and dithiocarbonate complexes. This is in notable contrast to the ready conversion of Pt(PCy_3)$_2$ to the latter species. This compressibility has been noted by several workers[7,8a,26] and in part must account for the formation of the tris(phosphine) complex Pt(PCy_3)$_3$[3,26] whereas Pt[P(*t*-Bu)$_3$]$_3$[8a] cannot be obtained. In this connection, we noted no infrared evidence for intramolecular metalation of tri-*tert*-butylphosphine in our compounds in contrast to that reported by Goel and Montemayor[27] for *trans*-PtCl[C_4H_8P(*t*-Bu)$_2$]P(*t*-Bu)$_3$.

Reactions with Dioxygen. Although an infrared spectral comparison of **3** and **7** suggests similar SO_2 environments (Table III), Pt(SO_2)[P(*t*-Bu)$_3$]$_2$ failed to react with molecular oxygen, while exposure of Pt(SO_2)(PCy_3)$_2$ to an oxygen atmosphere or exposure of Pt(O_2)(PCy_3)$_2$ to sulfur dioxide resulted in the formation of Pt(SO_4)(PCy_3)$_2$.

The sulfate appears to be bidentate, as supported by the appearance of four characteristic[13,29] ν(SO) bands, analogous to those observed for Pt(SO_4)(PPh_3)$_2$ (Table III). At present it is not clear whether the steric constraints of the bidentate sulfate product hinder this reaction for **7** or whether the inability to form an initial oxygen adduct dominates the chemistry for Pt[P(*t*-Bu)$_3$]$_2$. In any case, **7** represents the only (presumably) η^1-pyramidal Pt–SO_2 complex that does not undergo the sulfato reaction.

Malatesta and Cenini[28] have commented on the attention given oxygen activation by transition metals in recent years. Qualitatively, our data support the concept that prior coordination of Pt with O_2 is necessary in order to promote the formation of metal–sulfato or –dithiocarbonato complexes from SO_2 or CS_2, respectively. That is, as outlined in Figure 2, we observed conversion of Pt(SO_2)(PCy_3)$_2$ to Pt(SO_4)(PCy_3)$_2$ to be much slower than the corresponding conversion of Pt(O_2)(PCy_3)$_2$ to Pt(SO_4)(PCy_3)$_2$. Similar behavior was also observed for the relative inertness of Pt(CS_2)(PCy_3)$_2$ with oxygen in comparison to the rapid reaction of Pt(O_2)(PCy_3)$_2$ with CS_2 to form the dithiocarbonate complex. The slow conversion of Pt(CS_2)(PCy_3)$_2$ to Pt(SO_4)(PCy_3)$_2$ in a mixture of SO_2 and O_2 and the formation of only Pt(SO_2)([P(*t*-Bu)$_3$]$_2$ when oxygen-insensitive[8b] Pt[P(*t*-Bu)$_3$]$_2$ was mixed with an equimolar mixture of SO_2 and O_2 also support this contention. Also, Mingos[1] has noted Pt(SeO_2)(PPh_3)$_2$ does not react with molecular oxygen under mild conditions, whereas SeO_2 does react with Pt(O_2)(PPh_3)$_2$ to yield Pt(SeO_4)(PPh_3)$_2$. This is consistent with the hypothesis of the importance of prior Pt–O_2 coordination.

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Registry No. **1**, 55664-33-0; **2**, 60648-70-6; **3**, 85995-08-0; **4**, 62945-65-7; **5**, 85976-69-8; **6**, 85976-70-1; **7**, 85995-09-1; **8**, 85976-71-2; SO_2, 7446-09-5; CS_2, 75-15-0; O_2, 7782-44-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positions, calculated distances and angles, and observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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