trend may result, in part, from the involvement of in-plane metal d orbitals with both σ and π bonding to ligands.

Nickel(0) and platinum(0) have been shown from various studies to be stronger π-bonding metals than their d^8 divalent ions.[24,25] Structurally shorter M–C distances and longer C–C distances would be expected for olefin complexes of the zerovalent metals of this series relative to their divalent analogs. Although comparative data are only available for Pt, such seems to be the case. The present structural result suggests that Pd(0) behaves in an anomalous way. Estimates of d_π bonding ability for the d^{10} series Ni(0), Pd(0), and Pt(0) have been related to the $d^{10} \rightarrow d^9p^1$ promotion energy of the atom.[25] Values of 1.72, 4.23, and 3.28 eV for the respective metal atoms clearly suggest that of the series Pd would be the least effective d_π metal.[4] The relatively long Pd–C bond lengths, short coordinated olefin C–C distances, and ligand planarity of $Pd(DBA)_3$ strongly indicate a lower affinity for olefin coordination for Pd(0).

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Registry No. $Pd(DBA)_3 \cdot C_6H_6$, 41812-89-9.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2955.

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Bonding in Sulfur Dioxide Complexes Active toward Oxygenation. Molecular Structure of the Benzene Solvate of Tris(triphenylphosphine)(sulfur dioxide)platinum

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The crystal and molecular structure of tris(triphenylphosphine)(sulfur dioxide)platinum has been determined as its benzene solvate from three-dimensional X-ray data. Crystals of the complex are hexagonal, space group $P6_3$, with unit cell parameters $a = 18.722$ (6) Å, $c = 10.008$ (5) Å, and $V = 3038$ Å^3. Refinement by least-squares procedures using 375 independent reflections gave a final R factor of 0.067. There are two molecules of complex per unit cell ($\rho_{\text{exptl}} = 1.18$ (5), $\rho_{\text{calcd}} = 1.168$ g/cm^3) with crystallographically required threefold symmetry. The benzene solvate has been found to have a fractional occupancy of approximately 0.5. The complex is four coordinate, essentially trigonal pyramidal in geometry with the SO_2 in the apical position (P–Pt–P = 118.4 (4), P–Pt–S = 97.2 (2)°). Oxygen atoms of the SO_2 are disordered about the threefold axis. Bonding between the Pt and phosphine ligands is relatively strong (Pt–P = 2.280 (9) Å) while SO_2 coordination is weak (Pt–S = 2.399 (13) Å). The open trigonal base of the pyramid exposes the basic metal to electrophilic attack.

Introduction

Structural studies on sulfur dioxide adducts of transition metal complexes have indicated that bonding between the metal center and the SO_2 molecule can occur in two forms.[1-3] The M–SO_2 group in the complex $[RuCl(NH_3)_4(SO_2)]^+$ was found to have a strong Ru–S bond collinear with the SO_2 plane.[1] Recent work on the complexes $MCl(SO_2)(P(C_6H_5)_3)_2(CO)$ (M = Rh, Ir) has indicated an entirely different coordination geometry for the M–SO_2 group.[2,3] Significantly longer M–S bond lengths were found with the SO_2 plane bent severely away from the direction of the M–S bond. The SO_2 has been viewed to add oxidatively to the metal in these latter complexes with the change in electronic structure of the sulfur resulting in the bent bonding configuration. The M–S bond in this coordination configuration is qualitatively similar to the N–S bond found in amine-SO_2 charge-transfer complexes where the SO_2 group bonds as a Lewis acid.[4] The SO_2 in $[RuCl(NH_3)_4(SO_2)]^+$, however, bonds as a Lewis base with considerable M–SO_2 π bonding.

The coordination of SO_2 to nucleophilic transition metals has attracted recent attention with the interest in the metal-catalyzed oxygenation of SO_2 to SO_4^{2-}.[5] Virtually all molecular oxygen complexes have been found to react with SO_2 to form coordinated sulfate while a few select SO_2 complexes react with O_2 to give SO_4^{2-}. The complexes $M(SO_2)(P(C_6H_5)_3)_{2,3}$ (M = Pd, Pt) have been found to undergo oxygenation forming $M(SO_4)(P(C_6H_5)_3)_2$.[6,7] Recently $Ru(CO)_2(P(C_6H_5)_3)_2(SO_2)$ and $Ru(Cl)(SO_2)(NO)(P(C_6H_5)_3)_2$ have been reported to form $Ru(SO_4)(CO)_2(P(C_6H_5)_3)_2$[8] and $Ru(SO_4)(Cl)(NO)(P(C_6H_5)_3)_2$[9] on exposure to air. In order to attempt to correlate the activity of coordinated SO_2 with its bonding properties to metals the molecular structure of one of the more active members of this series, the benzene solvate of $Pt(SO_2)(P(C_6H_5)_3)_3$, has been determined crystallographically.

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Table I. Final Positional, Thermal, and Group Parameters for $Pt(P(C_6H_5)_3)_3(SO_2)\cdot 1.5C_6H_6$

Atom[a]	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.3333	0.6667	0.1000	0.0043 (2)	0.0043 (2)	0.0055 (2)	0.0027 (2)	0.0000	0.0000
S	0.3337	0.6667	0.3397 (13)	0.0090 (15)	0.0090 (15)	0.0089 (17)	0.0042 (15)	0.0000	0.0000
P	0.2935 (5)	0.5309 (5)	0.0715 (5)	0.0042 (5)	0.0044 (6)	0.0043 (10)	0.0006 (4)	−0.0005 (5)	−0.0007 (5)
O(1)	0.373 (7)	0.625 (5)	0.414 (8)	0.009 (4)	0.011 (4)	0.007 (8)	0.001 (4)	−0.004 (6)	0.002 (6)
O(2)	0.294 (7)	0.707 (5)	0.411 (8)	0.010 (4)	0.010 (4)	0.008 (8)	0.001 (4)	0.005 (6)	0.001 (6)

Group[c]	x_c	y_c	z_c	ϕ	θ	ρ
R(1)	0.1129 (10)	0.3970 (8)	0.1841 (15)	−2.61 (3)	−2.57 (2)	0.47 (2)
R(2)	0.4068 (7)	0.4562 (8)	0.1778 (14)	−0.25 (3)	−2.14 (2)	0.74 (3)
R(3)	0.2800 (7)	0.4921 (9)	−0.2438 (15)	2.19 (1)	−2.99 (2)	−1.71 (1)
BZ	0.1989 (16)	0.1616 (24)	0.0311 (24)	−0.64 (3)	2.95 (3)	−1.50 (3)

[a] Estimated standard deviations of the least significant figures are given in parentheses here and in succeeding tables. [b] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] x_c, y_c, and z_c are the fractional coordinates of the rigid group centers. The angles ϕ, θ, and ρ are in radians and have been previously defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

Crystal Preparation

A sample of the complex $Pt(P(C_6H_5)_3)_3(SO_2)$ was synthesized by the slow addition of SO_2 to a benzene solution of $Pt(P(C_6H_5)_3)_4$ without stirring.[6] Over the period of several hours large dark purple needles of the complex formed which were then isolated and stored under nitrogen. After several hours of exposure to air the crystals gave poor diffraction patterns and had begun to decompose to $Pt(P(C_6H_5)_3)_2(SO_4)$. A crystal of dimensions 0.12 × 0.12 × 0.53 mm was coated with an inert resin to avoid decomposition and prepared for crystallographic study.

Collection and Reduction of the X-Ray Data

The crystal chosen resembled a hexagonal needle and was mounted along the length of the needle. Weissenberg and precession photographs of the *hk*0, *hk*1, *hk*2, *h*0*l*, and *h*1*l* zones indicated that the crystal belonged to the hexagonal system, mounted along the c^* axis. The observed extinction pattern of 00*l*, $l = 2n + 1$, is consistent with the centrosymmetric space group $P6_3/m$ (C_{6h}^2, No. 176) and acentric space groups $P6_3$ (C_6^6, No. 173) and $P6_322$ (D_6^6, No. 182).[10] The lattice constants were determined at ambient room temperature from a least-squares refinement of the angular settings of 15 strong, independent reflections centered on a Picker four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are $a = 18.722$ (6) Å, $c = 10.008$ (5) Å, and $V = 3038$ Å^3. Owing to the instability of the complex and crystal deterioration due to loss of benzene solvate when crystals are placed in a foreign solvent, only an approximate experimental density of 1.18 (5) g/cm^3 could be obtained. This value, however, agrees well with a value of 1.168 g/cm^3 for two formula weights of composition $Pt(P(C_6H_5)_3)_3(SO_2)\cdot 1.5C_6H_6$ per unit cell. The mosaic spread of the crystal was determined using the narrow-source open-counter ω-scan technique.[11] The average width at half-height was found to be acceptable at 0.18°. An independent set of intensity data was collected by the θ–2θ scan technique using Zr-filtered Mo Kα peak with allowances made for the Kα_1–Kα_2 separation at higher 2θ values. The data set was collected within the angular range $4.5° \leq 2\theta \leq 40°$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded 9000 counts/sec during the scan. The attenuators used were brass foil of thickness chosen to give an approximate attenuation factor of 2.5. During data collection the intensities of four standard reflections in different regions of reciprocal space were monitored after every 100 reflections measured. None of these standards deviated from its mean value by more than 3% during the time required to collect the data. Data were processed in the usual way with values of I and $\sigma(I)$ corrected for Lorentz, polarization, and absorption effects. With a linear absorption coefficient of 24.9 cm^{-1} transmission coefficients ranged from 0.72 to 0.98. The intensities of a total of 706 reflections were measured of which 415 were observed to be greater than 2σ. Several reflections of this group were related by space group symmetry and were averaged to give the 375 observed, independent reflections included in the refinement.

Solution and Refinement of the Structure

In each of the three possible choices of space group, crystallographic symmetry is imposed on the molecule. In $P6_3/m$ the molecule is required to have either $\bar{3}$ or $\bar{6}$ symmetry; in $P6_322$, 32 symmetry; or in $P6_3$, threefold symmetry. Of these choices only $P6_3$ is consistent with a reasonably ordered molecular geometry. Of the two sets of special positions for $P6_3$ set 2(a) was eliminated on the basis of packing considerations and set 2(b) was chosen for the Pt and also the S atom. It is of interest that the threefold symmetry imposed on the molecule seems to occur generally for $ML(P(C_6H_5)_3)_3$ complexes where L is sufficiently small and the chirality of the phosphine ligands correct.[12] The z coordinate of the Pt was chosen at 0.100 to fix the origin of the space group while the sulfur was chosen to lie approximately 2.30 Å above the Pt along the z coordinate in the initial cycle of refinement. After two cycles of least-squares refinement of the z coordinate of sulfur, the isotropic thermal parameters of Pt and S, and a single scale factor, the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ were 0.23 and 0.32, respectively. The positions of the phosphorus and phosphine carbon atoms were determined from a subsequent Fourier. A cycle of refinement including the triphenylphosphine ligand reduced the discrepancy indices to $R_1 = 0.137$ and $R_2 = 0.147$. A Fourier based on phases from this refinement indicated the positions of carbon atoms of the benzene solvate appearing at approximately half the height of the phosphine carbons. Also the positions of the one-third oxygen atoms of the SO_2 were indicated.

The complete trial structure was refined by least-squares procedure in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. The standard deviations $\sigma(F^2)$ were estimated from counting statistics according to the formula given by Corfield, *et al.*,[13] with a value of 0.03 for the uncertainty parameter. In all calculations the atomic scattering factors for the nonhydrogen atoms were those of Cromer and Waber,[14] while the hydrogen scattering factors were taken from the tabulation of Stewart, *et al.*[15] The effects of anomalous dispersion were included in the calculated structure factors with the appropriate values of $\Delta f'$ and $\Delta f''$ for the Pt, S, and P atoms taken from the report by Cromer.[16] Throughout the refinement, the phenyl rings and benzene solvate molecule were treated as rigid groups of D_{6h} symmetry (d(C–C) = 1.392 Å) in the manner described previously. A fractional occupancy factor of 0.5 was arbitrarily assigned to the benzene solvate group. This value is consistent with analytical data on the complex obtained by Robinson[6] and also with the height of solvate peaks on the Fourier. Three cycles of least-squares refinement with isotropic temperature factors assigned to nongroup atoms, single thermal parameters assigned to each group, and one scale factor reduced the discrepancy factors to $R_1 = 0.098$ and $R_2 = 0.108$. Three more cycles of refinement with anisotropic thermal parameters assigned to nongroup atoms and individual isotropic thermal parameters assigned to group atoms converged with discrepancy factors of $R_1 = 0.069$ and $R_2 = 0.072$. The positions of the hydrogen atoms of the phenyl rings were then included (d(C–H) = 0.98 Å) in a subsequent structure factor calculation. The final discrepancy factors for the refinement are $R_1 = 0.067$ and $R_2 = 0.070$. The largest parameter changes on the final cycle

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of refinement occurred for the oxygen atoms where values changed by approximately 40% of their standard deviations. Changes of other parameters during this cycle were considerably smaller. The estimated standard deviation of an observation of unit weight is 0.98. A final difference Fourier map showed residual electron density in the vicinity of the fractional oxygen atoms at about 60% their height. It was clear from a previous Fourier, however, that the positions of these atoms were not well defined. The final positional and thermal parameters of the structure are given in Table I. Derived positional and thermal parameters of the groups are given in Table II. Table III contains root-mean-square vibrational amplitudes of anisotropically refined atoms. A table of the final F_o and $|F_c|$ values for the 375 reflections used in the refinement is available.[17]

Description and Discussion of the Structure

The structure consists of well-separated $Pt(P(C_6H_5)_3)_3(SO_2)$ molecules and benzene molecules of crystallization. In Figure 1 the inner coordination geometry of the $Pt(P(C_6H_5)_3)_3(SO_2)$ molecule is presented with the oxygen atoms shown in one of the three equivalent orientations required by the crystallographic threefold symmetry. In Figure 2 a stereoview of the entire molecule is shown. Principal intramolecular distances and angles are given in Table IV. All intermolecular contacts are normal.

The coordination geometry of the $Pt(P(C_6H_5)_3)_3(SO_2)$ molecule could be described as a distorted tetrahedron although the value of 97.2 (2)° for the S-Pt-P angle and the approximate planarity of the PtP_3 group results in a geometry more closely resembling a trigonal pyramid with the SO_2 occupying the apical position. The Pt atom is displaced only 0.33 Å from the P_3 plane while greater deviations of 0.36, 0.51, and 0.55 Å have been found for the MP_3 groups of the trigonal-bipyramidal complexes $Rh(H)(CO)(P(C_6H_5)_3)_3$,[18] $[Ir(H)(NO)(P(C_6H_5)_3)_3]^+$,[19] and $Ru(H)(NO)(P(C_6H_5)_3)_3$,[20] respectively. The Pt-P distance of 2.280 (9) Å agrees well with values found in three-coordinate Pt(0) complexes.[21] Values of 2.25-2.28 (1) Å have been reported for the respective olefin complexes $Pt(P(C_6H_5)_3)_2(C_2H_4)$,[22] $Pt(P(C_6H_5)_3)_2(C_2Cl_4)$,[23] and $Pt(P(C_6H_5)_3)_2(C_2(CN)_4)$.[24] These values are all significantly shorter than values within the range 2.333 (8)-2.352 (8) Å reported for $Pt(P(C_6H_5)_3)_3(CO)$[25] where the carbonyl group π bonds strongly with the metal. The P-Pt-P angle of 118.4 (4)° for $Pt(P(C_6H_5)_3)_3(SO_2)$ is more closely related to values of 115-122° reported for $Pt(P(C_6H_5)_3)_3$[21] rather than the more regularly tetrahedral complex $Pt(P(C_6H_5)_3)_3(CO)$ with values within the range of 109.6 (2)-113.7 (3)°. While bonding to the phosphine ligands is strong, bonding to the SO_2 is weak. The Pt-S distance of 2.399 (13) Å is long compared with a sum of radii of 2.36 Å and values of 2.227 (9) and 2.218 (9) Å found for $Pt_2S(CO)(P(C_6H_5)_3)_3$.[26] The present value is considerably longer than the value of 2.073 (3) Å found for $[Ru(Cl)(NH_3)_4(SO_2)]^+$;[1] however, it is shorter than values of 2.450 (2) and 2.49 (1) Å reported for the bent SO_2 groups in $M(Cl)(SO_2)(P(C_6H_5)_3)_2(CO)$ (M = Rh, Ir), respectively.[2,3] The dihedral angle of 90 (3)° between the P_3 and SO_2 planes reflects the basic nature of the SO_2 ligand in the present complex while the long Pt-S bond length indicates the absence of significant Pt-SO_2 π bonding. This result is somewhat surprising in view of the nucleophilic nature of the metal; however, it agrees with the observed lability of the SO_2 ligand.[6]

Table II. Derived Positional and Isotropic Thermal Parameters for Group Carbon Atoms

Atom	x	y	z	B, Å^2
		R(1)		
C(1)	0.036 (1)	0.341 (1)	0.237 (2)	6.4 (9)
C(2)	0.043 (1)	0.400 (2)	0.145 (2)	4.4 (8)
C(3)	0.106 (2)	0.338 (1)	0.276 (2)	6.3 (9)
C(4)	0.190 (1)	0.453 (2)	0.131 (2)	6.8 (9)
C(5)	0.183 (1)	0.395 (2)	0.223 (2)	8.3 (9)
C(6)	0.120 (1)	0.456 (1)	0.092 (4)	4.2 (7)
		R(2)		
C(1)	0.456 (3)	0.426 (3)	0.228 (2)	7.1 (9)
C(2)	0.422 (2)	0.403 (2)	0.102 (2)	6.5 (7)
C(3)	0.441 (1)	0.480 (2)	0.305 (1)	6.9 (9)
C(4)	0.358 (3)	0.486 (3)	0.128 (2)	7.5 (9)
C(5)	0.392 (2)	0.510 (2)	0.254 (2)	7.5 (9)
C(6)	0.372 (1)	0.433 (2)	0.051 (1)	4.4 (9)
		R(3)		
C(1)	0.276 (1)	0.475 (1)	−0.380 (1)	4.7 (7)
C(2)	0.338 (1)	0.551 (1)	−0.330 (2)	4.7 (8)
C(3)	0.219 (1)	0.417 (1)	−0.293 (2)	7.5 (8)
C(4)	0.284 (1)	0.509 (1)	−0.108 (1)	3.1 (7)
C(5)	0.222 (1)	0.434 (1)	−0.157 (2)	6.4 (9)
C(6)	0.341 (1)	0.567 (1)	−0.194 (2)	7.4 (9)
		BZ		
C(1)	0.194 (3)	0.145 (3)	−0.105 (3)	15 (5)
C(2)	0.153 (3)	0.081 (2)	−0.015 (5)	6 (2)
C(3)	0.240 (3)	0.226 (3)	−0.059 (4)	7 (3)
C(4)	0.204 (3)	0.178 (3)	0.167 (3)	4 (2)
C(5)	0.245 (3)	0.242 (3)	0.077 (5)	10 (5)
C(6)	0.158 (3)	0.097 (2)	0.122 (4)	9 (4)

Table III. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Pt	0.167 (3)	0.229 (3)	0.268 (4)
S	0.212 (11)	0.328 (10)	0.395 (12)
P	0.144 (8)	0.211 (9)	0.315 (10)
O(1)	0.155 (33)	0.301 (36)	0.508 (42)
O(2)	0.162 (35)	0.314 (39)	0.521 (44)

Table IV. Principal Bond Distances and Angles

Atoms	Distance, Å	Atoms	Angle, deg
Pt-P	2.280 (9)	S-Pt-P	97.2 (5)
Pt-S	2.399 (13)	P-Pt-P′	118.5 (4)
S-O(1)	1.51 (5)	O(1)-S-O(2)	122 (4)
S-O(2)	1.47 (5)	O(1)-S-Pt	119 (2)
P-S	3.511 (13)	O(2)-S-Pt	119 (2)
P-O(2)	3.55 (2)		
P-P′	3.920 (10)		

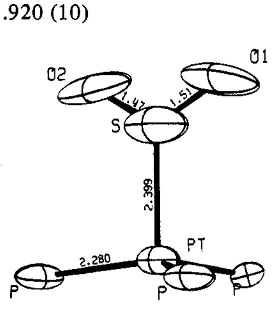

Figure 1. Perspective view of the inner coordination geometry of the $Pt(P(C_6H_5)_3)_3(SO_2)$ molecule.

Structural results on the related isoelectronic series Pt(P-

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(17) See paragraph at end of paper regarding supplementary material.

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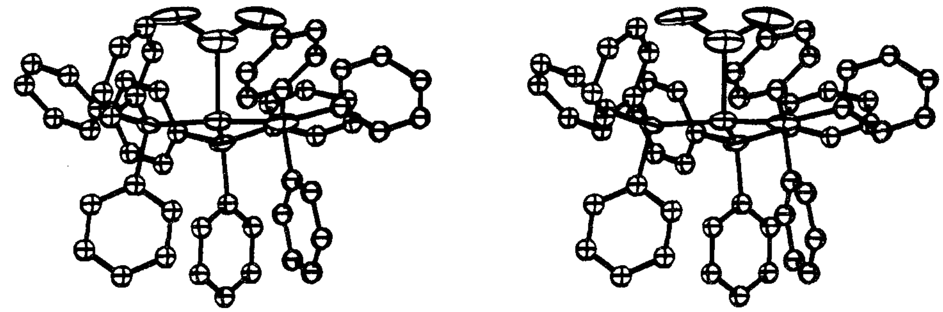


Figure 2. Stereoscopic view of the entire $Pt(P(C_6H_5)_3)_3(SO_2)$ molecule.

Table V. Bonding Parameters for Pseudotetrahedral Complexes of d^{10} Metals with π-Acceptor Ligands[a]

	$Pt(SO_2)L_3$	$Pt(CO)L_3$[c]	$Pt(CO)L_3$[d]	$Ir(NO)L_3$
$\Delta(M-P_3)$,[b] Å	0.33	0.70		1.04
M-X, Å	2.399 (13)	1.86 (3)	1.84 (2)	1.67 (2)
M-P, Å	2.280 (9)	2.340 (8)	2.36 (1)	2.31 (1)
P-M-X, deg	97.2 (5)	107 (1)	113 (1)	116.8 (5)
P-M-P, deg	118.5 (4)	111.4 (3)	105.7 (7)	101.3 (6)
Reference		25	27	24

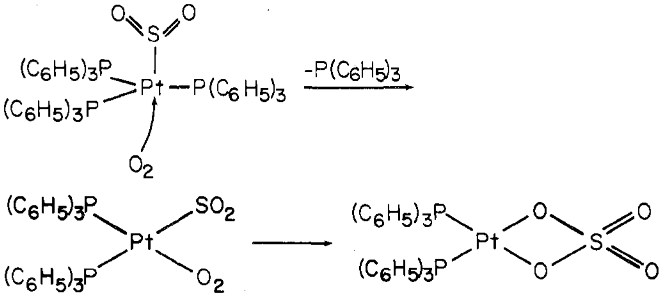
[a] $L = PPh_3$. [b] $\Delta(M-P_3)$ refers to the displacement of the metal atom from the trigonal phosphine plane. [c] Monoclinic form of $Pt(CO)L_3$. [d] Trigonal form of $Pt(CO)L_3$.

$(C_6H_5)_3)_3(SO_2)$, $Pt(P(C_6H_5)_3)_3(CO)$,[25,27] and $Ir(P(C_6H_5)_3)_3(NO)$,[12] show a trend toward metal displacement from the P_3 plane similar to that observed for trigonal-bipyramidal complexes containing hydride and a strong π-acceptor ligand in axial positions (Table V). Displacement values of 0.33 Å for $Pt(P(C_6H_5)_3)_3(SO_2)$, 0.70 Å for $Pt(P(C_6H_5)_3)_3(CO)$, and 1.04 Å for $Ir(P(C_6H_5)_3)_3(NO)$ increase as the strength of the bond to the apical ligand increases. Electron pair repulsions between the M-P and M-X bonds have been proposed to account for similar displacements in the five-coordinate complexes.[19] Distortion of these d^{10}, four-coordinate complexes with bulky triphenylphosphine ligands from an ideal *trigonal-pyramidal* geometry may therefore be related to the acidity of the ligand and basicity of the metal. A consequence of the metal displacement from the trigonal P_3 plane is the trend toward larger X-M-P and smaller P-M-P angles. This is particularly evident for the complex $Ir(P(C_6H_5)_3)_3(NO)$ with values reflecting distortion well beyond the more regularly tetrahedral geometry of the platinum-carbonyl complexes.

Bonding parameters for the SO_2 ligand are within error of values reported for other SO_2 complexes. Distances of 1.47 (5) and 1.51 (5) Å for the S-O bonds are not significantly longer than values of 1.40-1.47 Å reported previously[28,29] and a value of 1.43 (2) Å for solid SO_2.[30] The O(1)-S-O(2) angle of 122 (4)° compares well with a value of 119 (2)° reported for solid SO_2 but is larger than values of 114-116° found for coordinated SO_2. Unfortunately, with disorder of the oxygen atoms resulting in large errors for the oxygen positions, significant comparisons of these bond distances and angles are impossible.

Oxygenation of $Pt(P(C_6H_5)_3)_3(SO_2)\cdot 1.5C_6H_6$

Certain structural features of the $Pt(P(C_6H_5)_3)_3(SO_2)$ molecule may be related to the reactivity of the complex toward oxygenation of the SO_2. It is important to point out that the linear coordination configuration of the $Pt-SO_2$ group is not unique to this complex and most systems with SO_2 bonded in a similar way do not undergo oxygenation. Additionally the weak Pt-S bond probably does little to increase the activity of the sulfur. Although coordinatively saturated, the Pt remains strongly nucleophilic, and the open base of the trigonal pyramid exposes the metal to electrophilic attack. These features point to an oxygenation mechanism which first involves addition of an O_2 molecule to the metal rather than direct attack at the SO_2 sulfur or insertion into the Pt-S bond. The oxidative addition of O_2 would be accompanied by loss of a phosphine, followed by intramolecular rearrangement to give the sulfate complex $Pt(SO_4)(P(C_6H_5)_3)_2$[5]



The low density of the crystal cell and porosity resulting from the fractional occupancy of the solvate contribute to the unusually high reactivity of crystalline $Pt(P(C_6H_5)_3)_3(SO_2)\cdot 1.5C_6H_6$.[6]

While little direct evidence exists for such a mechanism, the molecular structure of $Pt(P(C_6H_5)_3)_3(SO_2)$ certainly suggests that the metal center is the initial site of attack by O_2. This view is consistent with a mechanism proposed by Valentine, *et al.*,[9] involving an intermediate with both SO_2 and O_2 simultaneously coordinated to the metal. It is interesting that the nucleophilicity required of the metal precludes oxygenation of bent SO_2 complexes. In these compounds the basicity of the metal is reduced by the Lewis acidity of the apical SO_2.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2959.

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