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"Bent" vs. Coplanar M–SO_2 Coordination. The Structure of the Sulfur Dioxide Adduct, $Pt(PPh_3)_3(SO_2)\cdot 0.7SO_2$[1]

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An x-ray structure determination of the compound $Pt(PPh_3)_3(SO_2)\cdot 0.7SO_2$ conclusively demonstrates the presence of a pyramidal Pt–SO_2 moiety, in contrast to conclusions reached earlier for a disordered benzene solvate form of the same compound. The Pt–SO_2 geometry in the present compound is characteristic of that found in other well-defined structures containing nonplanar M–SO_2 groups, with a long Pt–S bond of 2.368 (3) Å and Pt–S–O angles of 107.4 (3) and 106.7 (3)°. In other details, the geometry of the pseudotetrahedral coordination unit agrees with the earlier study, with P–Pt–P angles and P–Pt–S angles in the ranges 115.51 (9)–120.91 (9) and 93.3 (1)–99.6 (1)°, respectively. These results are evaluated in light of a recently proposed bonding scheme for M–SO_2 complexes, and compared with pseudotetrahedral complexes containing linear M–NO groups. Cell data: space group $P\bar{1}$, $Z = 2$, $a = 13.723$ (6), $b = 14.325$ (7), $c = 12.626$ (7) Å, $\alpha = 111.18$ (4), $\beta = 90.58$ (4), $\gamma = 91.86$ (3), $\rho_{calcd} = 1.51$ g/cm³, $R = 0.037$, and $R_w = 0.043$ for 3868 diffractometer-collected reflections with $I \geq 2\sigma(I)$.

Introduction

Crystal structure analyses have been reported for seven complexes in which a sulfur dioxide molecule is attached directly to a transition metal.[2-7] Two cases are square-pyramidal d^8 Vaska-type adducts, $[M(PPh_3)_2(CO)Cl(SO_2)]$, where M = Rh and Ir, which are characterized by long M–S bonds (Rh–S = 2.45 Å, Ir–S = 2.49 Å) and by distinctly nonplanar, or "bent", M–SO_2 moieties (M–S–O = 104–108°).[2] Recently the formally pentacoordinate complex $Rh(\pi\text{-}C_5H_5)(C_2H_4)(SO_2)$ was shown to contain a coplanar Rh–SO_2 moiety with a short Rh–S distance of 2.096 (2) Å.[3] Two other well-defined examples of coplanar M–SO_2 moieties with short M–S distances are afforded by the d^6 hexacoordinate complexes $[Ru(NH_3)_4Cl(SO_2)]Cl$,[4] with Ru–S = 2.07 Å, and $Mn(\pi\text{-}C_5H_5)(CO)_2(SO_2)$,[5] with Mn–S = 2.05 Å. The other two structurally characterized M–SO_2 complexes are the tetracoordinate platinum–phosphine complexes $Pt(PPh_3)_2(SO_2)_2$, shown unambiguously in a previous paper[6] to contain two bent Pt–SO_2 groups with long Pt–S bonds of 2.391 (2) and 2.464 (2) Å, and $Pt(PPh_3)_3(SO_2)\cdot{}^3/_2C_6H_6$,[7] previously claimed to contain a *coplanar* Pt–SO_2 moiety with a *long* Pt–S bond, 2.40 Å. This latter result seemed highly unusual and provoked a reexamination of that structure.

The benzene solvate of $Pt(PPh_3)_3(SO_2)$ crystallizes in a hexagonal cell with space group restraints requiring the molecule to possess threefold symmetry, and hence a threefold disorder of the oxygen atoms in the Pt–SO_2 group is demanded. Clearly, selection of a disordered *bent* model would be equally acceptable on the basis of the reported crystallographic results and, in fact, such a selection gives a reasonable "bent" M–SO_2 geometry. Indeed, we find that using a bent Pt–SO_2 model in which a *single* oxygen atom is refined (hence redundant, or overlapping, oxygen positions are generated by the threefold operator for the two oxygen atoms of the SO_2 group), refinement proceeds to convergence with a reasonable pyramidal M–SO_2 geometry. However, our attempts to repeat the reported refinement with a coplanar M–SO_2 group led to divergence and totally unrealistic thermal parameters for the oxygen atoms.

Further, Fourier syntheses revealed a triangle of oxygen peaks about the threefold axis, consistent with the above bent M–SO_2 model but clearly inconsistent with a coplanar M–SO_2 model (for which a hexagon of oxygen peaks should be observed). We invariably obtained these results, using either the reported structure factors or a low temperature (−78 °C) data set collected by us, and using several different least-squares codes. These results and the implications from the structure of $Pt(PPh_3)_2(SO_2)_2$[6] clearly favor the bent Pt–SO_2 model for $Pt(PPh_3)_3(SO_2)$. To dispel any question of the correctness of this interpretation, we have solved the structure of the SO_2-solvated, triclinic form of this compound. The coordination unit in this structure is well-ordered and unambiguously contains a bent M–SO_2 moiety, with geometry characteristic of the previously observed bent M–SO_2 structures.

The importance of this structure lies in its relevance to a proposed bonding model for M–SO_2 complexes,[8] to previous attempts to correlate reactions (e.g., oxygenation) of the bound ligand with M–SO_2 geometry,[7,9] and to the comparison of the pyramidal-coplanar M–SO_2 dichotomy with the bent-linear dichotomy in metal nitrosyl complexes.[10–12]

Experimental Section

Red-brown platelets of the title compound were prepared by the synthesis originally reported for $Pt(PPh_3)_3(SO_2)\cdot{}^3/_2C_6H_6$, substituting toluene for benzene as the solvent.[13] Although crystals prepared by this method appeared visually to be well formed, nearly a dozen crystals were rejected because of severe splitting observed in diffractometer ω scans. The crystal finally selected was still of mediocre quality, with ω peak splittings up to 0.3° (total width at half height less than 0.6°) along the principal crystallographic directions. Precession photographs, careful examination of the crystal packing, and a unit cell reduction revealed no symmetry higher than triclinic for these crystals. A crystal of dimensions 250 × 250 × 50 μm was coated with Duco cement and mounted on a Picker FACS-I diffractometer. The cell constants least squares adjusted to the setting angles of 12 high-order reflections are: (Mo Kα radiation, λ 0.709 30 Å) $a = 13.723$ (6), $b = 14.325$ (7), $c = 12.626$ (7), $\alpha = 111.18$ (4), $\beta = 90.58$ (4), and $\gamma = 91.86$ (3). Assuming two molecules in the cell thus chosen, the calculated density is 1.51 g/cm^3 and the six crystal faces are {100}, {010} (major face), and {001}. Intensities were measured in the hemisphere $h, \pm k, \pm l$ ($\theta \leq 20°$) using a standard θ–2θ scan technique (1.5° scan at 2° min^{-1} with 20 s backgrounds). From the 4546 reflections so measured, 4231 unique reflections were obtained after averaging equivalent reflections, and 3868 were judged to be observed according to the criterion $I \geq 2\sigma(I)$ where $\sigma^2(I) = (T + B) + [0.015(T - B)]^2$. A fluctuation of approximately 3% was observed in the intensities of two standard reflections (measured after every 50 observations) and a correction was applied using a least-squares polynomial. Absorption corrections[14] were applied with transmission factors ranging from 0.439 to 0.826 ($\mu = 34.0$ cm^{-1}).

The Pt position was deduced from a Patterson function and the remaining nonhydrogen atoms were located by routine application of Fourier/least-squares techniques. Scattering factors were taken from Cromer's tabulation[15] and anomalous dispersion terms were used for Pt, P, and S.[16] No attempt was made to account for hydrogen atoms. A full-matrix least-squares refinement of the 61 Pt, P, S, O, and C positions, a secondary extinction parameter,[17,18] anisotropic thermal parameters for P, Pt, S, and O, and isotropic parameters for the C atoms was carried out and resulted in conventional discrepancy values of $R = 0.053$ and $R_w = 0.053$. A difference Fourier synthesis revealed peaks of height 5.8 e$^-$/Å^3 at ($^1/_2$,0,$^1/_2$) and 2.2 e$^-$/Å^3 at ($^1/_2$,–0.03,0.41), in addition to several other smaller peaks ranging downward from 0.8 e$^-$/Å^3 in reasonable locations for lattice SO_2 oxygens. An attempt was made to account for this scattering density by introducing three rigid SO_2 groups[19] with sulfur atoms fixed at ($^1/_2$,0,$^1/_2$), as suggested by the difference Fourier synthesis, and refining three orientational parameters and a population parameter for each group. A single isotropic thermal parameter was refined for the oxygen atom, and sulfur was also refined isotropically. This final refinement converged with $R = 0.037$ and $R_w = 0.043$ and fractional occupancies of 0.18, 0.32, and 0.25 for the three lattice SO_2 groups. A final difference Fourier synthesis contained as the principal features peaks of height 1.3 e$^-$/Å^3 near the S atom and 0.7 e$^-$/Å^3 in the vicinity of a phenyl ring, indicating the disorder model to be adequate. No evidence was found for disorder or alternative positions for the oxygen atoms of the metal-ligated SO_2 group. In the final cycle of refinement, no parameter shifted by more than 0.10 esd and the standard deviation of an observation of unit weight was 3.1.

Views of the coordination unit are shown in Figures 1 and 2. Refined atomic parameters are given in Table I and selected distances and angles are tabulated in Table II. A listing of structure factors is available in the supplementary material.

Discussion

The structure of $Pt(PPh_3)_3(SO_2)$ is well-ordered and unambiguously contains a pyramidal Pt–SO_2 moiety. This result conflicts with the original interpretation of the disordered structure of the benzene solvate of the same compound.[7] The Pt–S distance observed here, 2.368 (3) Å, is somewhat shorter than values previously observed for pyramidal M–SO_2 species (2.39–2.49 Å)[2,6] but dramatically greater than the range observed for coplanar species (2.05–2.10 Å).[3–5] The Pt–S–O angles, 107.4 (3) and 106.7 (3)°, are typical for pyramidal M–SO_2 as is the angle of 123.0° between the M–S vector and the SO_2 plane. We believe, therefore, that our reinterpretation of the benzene-solvated structure as containing a pyramidal Pt–SO_2 group is correct (see Introduction).

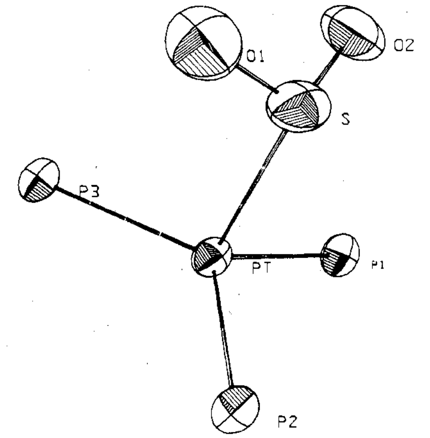

Figure 1. A view of the central coordination unit for $Pt(PPh_3)_3(SO_2)$.

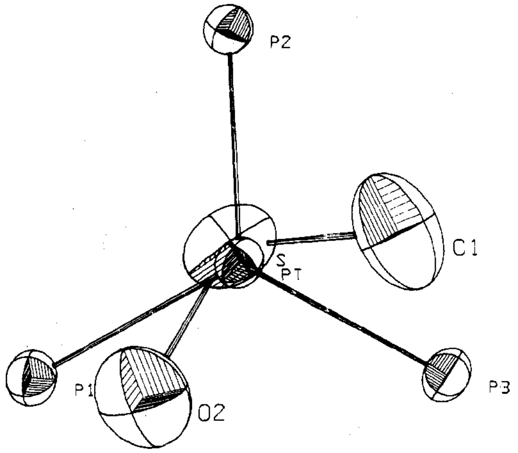

Figure 2. A view of the $Pt(PPh_3)_3(SO_2)$ molecule normal to the plane of the three phosphorus atoms.

The geometry of the $Pt(PPh_3)_3$ fragment is essentially the same in the two structure determinations. The three P–Pt–P angles vary slightly in our determination from 115.5 to 120.9°, but the average agrees with the value 118.4° previously found.[7] Our P–Pt–S angles, 93.26 to 99.60°, also agree satisfactorily with the previous value of 97.2°. The observed rotational orientation of the SO_2 group (Figure 2) is almost exactly the same as that obtained in our refinements for the benzene-solvated form and further supports the bent model for the solvated crystal.

Another feature of interest in the present structure is the large P–Pt–P angles of 115.51 (9), 120.91 (9), and 119.79 (9)° with platinum lying 0.78 Å from the plane of the three phosphorus atoms. In $Pt(PPh_3)_3(CO)$[20] and $Ir(PPh_3)_3(NO)$,[21] the P–M–P angles are 105.7 and 101.3°, respectively. As has been pointed out by Hoffmann et al.,[11] this angle is expected to be large for L_3MA complexes of this general type when there is little or no π interaction between the transition metal and the ligand A. The large value for this angle is then consistent with the bent M–SO_2 geometry and a predominantly σ metal–sulfur interaction.

In Figure 2 is shown a projection of the Pt–SO_2 unit onto the plane of the three phosphine atoms. Note that the P(1)–Pt–P(2) angle is closed down to 115.5 (2)° and that the

Table I. Final Positional and Thermal Parameters[a]

	x	y	z	B		x	y	z	B
Pt	0.230 00 (3)	0.310 36 (3)	0.224 92 (3)	[b]	C28	0.505 6 (9)	0.733 5 (9)	0.463 2 (9)	4.7 (3)
S	0.243 1 (2)	0.425 8 (2)	0.414 4 (2)	[b]	C29	0.580 9 (9)	0.266 8 (9)	0.483 5 (10)	4.8 (3)
O1	0.153 8 (6)	0.418 3 (6)	0.468 3 (6)	[b]	C30	0.404 9 (8)	0.235 1 (8)	0.471 8 (9)	4.0 (2)
O2	0.264 0 (5)	0.523 8 (5)	0.408 2 (6)	[b]	C31	0.313 7 (7)	0.069 6 (7)	0.144 5 (7)	2.6 (2)
P1	0.343 6 (2)	0.394 3 (2)	0.148 7 (2)	[b]	C32	0.248 4 (7)	0.052 3 (7)	0.053 2 (8)	3.2 (2)
P2	0.291 3 (2)	0.178 7 (2)	0.272 4 (2)	[b]	C33	0.668 1 (9)	0.099 7 (9)	0.052 6 (10)	5.2 (3)
P3	0.062 6 (2)	0.315 1 (2)	0.192 2 (2)	[b]	C34	0.396 8 (9)	0.916 9 (9)	0.037 2 (10)	5.5 (3)
C1	0.348 0 (7)	0.326 4 (7)	0.994 5 (7)	2.5 (2)	C35	0.740 8 (8)	0.033 7 (8)	0.047 5 (9)	4.3 (2)
C2	0.667 6 (7)	0.627 3 (7)	0.083 9 (8)	3.1 (2)	C36	0.389 8 (8)	0.003 9 (8)	0.138 9 (9)	4.1 (2)
C3	0.641 0 (8)	0.835 8 (8)	0.160 0 (9)	3.9 (2)	C37	0.978 5 (7)	0.263 6 (7)	0.271 4 (7)	2.4 (2)
C4	0.638 5 (7)	0.777 9 (7)	0.042 8 (8)	3.1 (2)	C38	0.853 4 (8)	0.280 6 (8)	0.412 4 (9)	4.2 (2)
C5	0.670 0 (8)	0.686 1 (8)	0.202 0 (9)	4.0 (2)	C39	0.848 3 (8)	0.176 4 (8)	0.384 7 (9)	4.0 (2)
C6	0.658 0 (8)	0.787 8 (9)	0.238 8 (9)	4.4 (3)	C40	0.975 6 (7)	0.159 5 (8)	0.245 8 (8)	3.2 (2)
C7	0.473 0 (7)	0.406 3 (7)	0.192 4 (8)	2.5 (2)	C41	0.917 7 (7)	0.325 4 (7)	0.354 5 (8)	3.1 (2)
C8	0.547 0 (7)	0.371 1 (8)	0.116 8 (8)	3.5 (2)	C42	0.909 9 (8)	0.116 1 (8)	0.300 8 (8)	3.7 (2)
C9	0.493 6 (8)	0.458 1 (8)	0.308 5 (9)	4.5 (3)	C43	0.007 8 (7)	0.434 1 (7)	0.208 1 (8)	2.7 (2)
C10	0.646 4 (8)	0.388 5 (8)	0.157 6 (9)	4.5 (3)	C44	0.976 3 (8)	0.606 1 (8)	0.328 6 (9)	4.1 (2)
C11	0.666 8 (9)	0.438 9 (9)	0.270 8 (10)	5.3 (3)	C45	0.922 6 (8)	0.617 0 (9)	0.239 2 (10)	4.7 (3)
C12	0.592 3 (10)	0.477 1 (10)	0.348 5 (10)	5.8 (3)	C46	0.912 3 (9)	0.539 9 (9)	0.137 0 (10)	5.0 (3)
C13	0.323 2 (7)	0.523 2 (7)	0.160 7 (7)	2.4 (2)	C47	0.954 2 (8)	0.446 2 (8)	0.119 3 (9)	3.9 (2)
C14	0.399 3 (7)	0.590 7 (8)	0.164 5 (8)	3.4 (2)	C48	0.019 8 (7)	0.513 2 (8)	0.310 9 (8)	3.3 (2)
C15	0.226 5 (8)	0.552 8 (8)	0.165 4 (9)	4.1 (2)	C49	0.029 3 (7)	0.237 8 (7)	0.044 6 (7)	2.3 (7)
C16	0.207 3 (9)	0.652 5 (9)	0.175 7 (10)	5.3 (3)	C50	0.924 7 (8)	0.831 8 (8)	0.152 7 (8)	3.7 (2)
C17	0.380 7 (8)	0.689 9 (8)	0.175 6 (9)	4.1 (2)	C51	0.899 9 (7)	0.776 1 (7)	0.038 4 (8)	2.9 (2)
C18	0.284 2 (8)	0.720 9 (8)	0.182 2 (9)	4.5 (3)	C52	0.018 3 (8)	0.874 3 (8)	0.184 6 (9)	4.0 (2)
C19	0.221 8 (7)	0.120 5 (7)	0.358 5 (7)	2.3 (2)	C53	0.934 6 (7)	0.195 0 (7)	0.013 2 (8)	3.2 (2)
C20	0.246 6 (8)	0.025 3 (8)	0.357 0 (8)	3.7 (2)	C54	0.088 9 (8)	0.861 5 (8)	0.101 7 (9)	3.8 (2)
C21	0.197 8 (8)	0.983 8 (8)	0.429 2 (9)	4.2 (2)	S2[c]	0.500 0	0.000 0	0.500 0	12.1 (4)
C22	0.897 1 (8)	0.868 5 (8)	0.496 9 (8)	4.1 (2)	O3	0.438 (6)	−0.086 (6)	0.492 (7)	14.7 (9)
C23	0.150 1 (7)	0.173 2 (7)	0.429 5 (8)	3.2 (2)	O4	0.524 (16)	0.065 (4)	0.615 (2)	14.7 (9)
C24	0.126 7 (8)	0.038 4 (8)	0.502 2 (8)	3.8 (2)	O5	0.591 (3)	0.024 (2)	0.458 (5)	14.7 (9)
C25	0.406 5 (7)	0.207 1 (7)	0.353 2 (7)	2.4 (2)	O6	0.499 (7)	0.028 (4)	0.622 0 (3)	14.7 (9)
C26	0.582 8 (9)	0.240 1 (9)	0.365 2 (10)	5.1 (3)	O7	0.442 (7)	−0.060 (5)	0.401 (4)	14.7 (9)
C27	0.493 8 (8)	0.210 5 (8)	0.298 9 (9)	4.0 (2)	O8	0.456 (6)	0.009 2 (2)	0.607 (3)	14.7 (9)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.002 37 (3)	0.003 13 (3)	0.003 34 (4)	0.000 80 (4)	0.000 52 (4)	0.002 20 (4)
S1	0.005 5 (2)	0.005 5 (2)	0.003 7 (2)	0.002 9 (3)	−0.000 8 (4)	0.000 4 (3)
O1	0.008 4 (7)	0.007 1 (6)	0.006 6 (7)	−0.001 1 (10)	0.005 1 (11)	0.003 0 (11)
O2	0.007 1 (6)	0.004 0 (5)	0.007 6 (7)	−0.000 9 (9)	0.001 6 (10)	0.000 7 (10)
P1	0.002 7 (2)	0.003 9 (2)	0.004 4 (2)	0.000 1 (3)	0.000 3 (3)	0.003 6 (3)
P2	0.002 7 (2)	0.003 7 (2)	0.004 2 (2)	0.000 8 (3)	0.000 7 (3)	0.003 5 (3)
P3	0.002 5 (2)	0.003 8 (2)	0.004 6 (2)	0.000 9 (3)	0.000 3 (3)	0.003 0 (3)

[a] Anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. [b] Refined anisotropically. [c] S2 and O3–O6 were refined as three rigid groups, with S fixed at 0.500, 0, 0.500 and with thermal parameters for O atoms constrained to be equal. Final occupancies are: (S, O3, O4) 0.18 (2); (S, O5, O6) 0.32 (3); (S, O7, O8) 0.25 (2).

Pt–S vector is rotated 3.7° from the normal to the plane of the three phosphine atoms. This motion of the SO_2 group from the *z* axis of the molecule may be a direct consequence of maximizing the $\pi^*(SO_2)$–d_{z^2} interaction, in a manner reminiscent of square-pyramidal bent NO complexes.[10,11]

This structure is the second example of a d^{10} pseudotetrahedral complex containing a *pyramidal* M–SO_2 group, the other example being $Pt(PPh_3)_2(SO_2)_2$.[6] These results are significant with respect to current bonding concepts for so-called "amphoteric" ligands such as SO_2 and NO, for which the rules for predicting planar-pyramidal (linear-bent) geometries have been thought to be similar. Of particular interest in the present case is the fact that all of the structurally characterized pseudotetrahedral metal–nitrosyls [with the notable exception of $Ni(PPh_3)_2(N_3)(NO)$][22] exhibit linear or only slightly bent M–NO geometry (see ref 10 and the references cited therein), e.g., $Ir(PPh_3)_3(NO)$. Indeed, it is generally assumed that for L_3MNO complexes the limiting stereochemical choices are either (a) tetrahedral with a linear M–NO moiety or (b) square planar with a bent MNO group.[10-12] This "rule" persists even in the absence of *any* evidence for a structure which falls into category (b) and depends on the assumption that as the nitrosyl is bent there is increasing transfer of electron density from the transition metal to the nitrogen atom until the nitrogen atom has a stereochemically active lone pair of electrons; the electronic configuration of the metal atom would then be effectively d^8, thereby favoring a square planar conformation. It is easily demonstrated that the factors which determine the charge transfer to the nitrosyl as the ligand is bent[10,11] (and for the SO_2 ligand as well)[8] are more subtle than those which govern the resulting minimum energy conformation, and the "rule" described above is therefore somewhat suspect.

In comparing the ligands NO and SO_2 it is significant that the EHMO (extend Hückel) approach indicates that their π^* orbitals are of approximately the same energy, and both are in the energy range of a typical transition metal d orbital. However, the ionization energy of the σ^* orbital for NO is considerably larger than that of SO_2. One might then expect, in a transition metal complex, that these two sets of orbitals, which in this simple model dictate the metal–ligand geometry, will be closer in energy for SO_2 than in the nitrosyls and that the *tendency* for pyramidal SO_2 complexes is greater than for bent nitrosyl complexes. We feel that the structure presented here is a consequence of this effect. A possible interaction diagram representing the binding of SO_2 to an $IrCl_3$ fragment is presented in Figure 3. The principal interactions between the metal and the SO_2 group are the $\pi^*(SO_2)$–d_{xz} and $\sigma^*(SO_2)$–d_{z^2} interactions using the coordinate system defined in Figure 3. If the symmetry of the direct product between a

Table II. Selected Distances and Angles[a]

Distances, Å			
Pt-S	2.368 (3)	P1-C13	1.829 (9)
Pt-P1	2.355 (3)	P2-C19	1.847 (9)
Pt-P2	2.353 (2)	P2-C25	1.825 (9)
Pt-P3	2.337 (2)	P2-C31	1.833 (9)
S-O1	1.428 (8)	P3-C37	1.839 (9)
S-O2	1.453 (7)	P3-C43	1.830 (10)
P1-C1	1.838 (9)	P3-C49	1.836 (9)
P1-C7	1.837 (9)		

Angles, deg	
Pt-S-O1	107.4 (3)
Pt-S-O2	106.7 (3)
O1-S-O2	114.2 (5)
S-Pt-P1	96.41 (10)
S-Pt-P2	93.26 (9)
S-Pt-P3	99.60 (9)
P1-Pt-P2	115.51 (9)
P1-Pt-P3	120.91 (9)
P2-Pt-P3	119.79 (9)
Pt-P1-C1	108.6 (3)
Pt-P1-C7	120.5 (3)
Pt-P1-C13	119.6 (3)
C1-P1-C7	102.5 (4)
C1-P1-C13	103.2 (4)
C7-P1-C13	99.9 (4)
Pt-P2-C19	122.0 (3)
Pt-P2-C25	115.5 (3)
Pt-P2-C31	111.0 (3)
C19-P2-C25	99.3 (4)
C19-P2-C31	101.6 (4)
C25-P2-C31	105.4 (4)
Pt-P3-C37	118.0 (3)
Pt-P3-C43	120.0 (3)
Pt-P3-C49	110.5 (3)
C37-P3-C43	101.9 (4)
C43-P3-C49	101.7 (4)
C43-P3-C49	102.1 (4)

[a] Observed ranges for C-C, C-C-C, and P-C-C parameters were 1.36 (1)-1.44 (1) Å, 118.0-121.3°, and 116.0-123.1°, respectively.

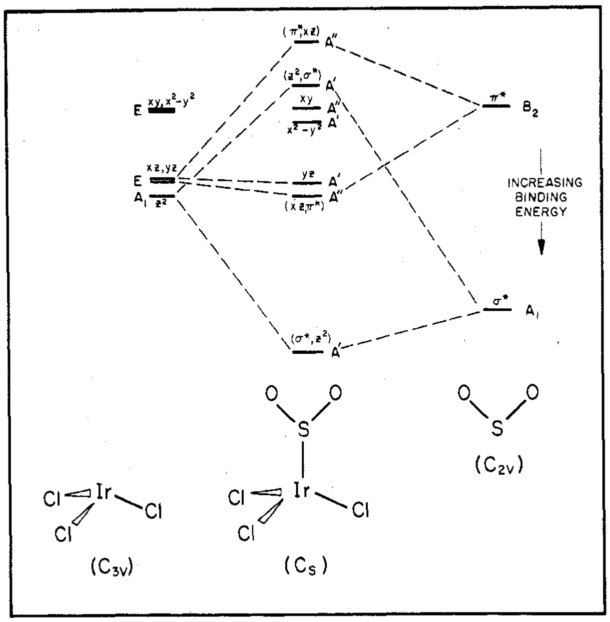

Figure 3. A diagram representing the possible interaction of a pyramidal $IrCl_3$ moiety with SO_2. The z axis is along the M-S vector and the y axis lies in the M-SO_2 plane. For a d^{10} metal configuration, the MO scheme is filled through the (z^2, σ^*) orbital.

filled and an unfilled molecular orbital is the same as that for a bending vibration of the M-SO_2 moiety (A″), second-order Jahn-Teller arguments will predict a bent M-SO_2 geometry if the energy difference between these orbitals is sufficiently small. Notice that this conclusion is independent of the order of the two orbitals in question. It should be noted, however, that this symmetry argument is possible only with a starting coplanar model in which the MSO_2 group and one MSL group are coplanar, as otherwise a bending vibration for M-SO_2 will not lower the molecular symmetry.

Calculations using the EHMO approach as described in ref 8 have also been carried out for model $M(CO)_3(SO_2)$ compounds. As noted previously for $ML_3(NO)$ models,[11] the exact energy differences (and even ordering) between levels is strongly parameter dependent in a calculation of this type and predictions of either pyramidal (bent) or coplanar (linear) geometries are possible with appropriate selection of ligand, transition metal, and specific complex geometry. A clear trend, however, is an enhancement of the stability of the coplanar M-SO_2 (linear M-NO) geometry when good π-acceptor ligands are present, an effect which others have suggested for equatorially substituted square pyramidal M-NO complexes.[11] It is noteworthy that all structurally characterized four-coordinate nitrosyl and SO_2 complexes do, in fact, contain π acceptors as the adjunct ligands.

In summary, this structure illustrates graphically a distinct difference in the bonding characteristics of SO_2 and NO toward transition metals and demonstrates the danger of general application of heuristically simple bonding schemes based on NO^+-NO^- and SO_2-SO_2^{2-} dichotomies. Indeed, efforts to prepare pseudotetrahedral ML_3X complexes with bent M-NO groups (or coplanar M-SO_2 groups) would appear far from hopeless.

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Registry No. $Pt(PPh_3)_3(SO_2) \cdot 0.7SO_2$, 59821-94-2.

Supplementary Material Available: Table of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

References and Notes

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