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Chlorobis(tricyclohexylphosphine)(sulfur dioxide)rhodium(I). A Square Planar SO_2-Transition Metal Complex*

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The structure of chlorobis(tricyclohexylphosphine)(sulfur dioxide)rhodium(I) has been determined by single crystal X-ray techniques. The complex crystallizes in the space group $P2_1/c$ with cell constants of a *= 13.371(6),* b *=12.783(6),* c *= 23.293(10) Å and β = 105.01(2)°. Refinements using 2822 unique reflections for which* $I \geqslant 2\sigma(I)$ *included anisotropic temperature parameters for all atoms heavier than carbon and hydrogen atoms fixed in idealized positions converged to an unweighted* R *value of 6.6%.*

The coordination about the Rh atom is square planar with trans *phosphines and a η^1-planar SO_2 group. The conformation about the Rh–S bond is determined by O- - -H interactions.*

The bonding of SO_2 to the complex is discussed.

Introduction

We have had, in recent years, a continuing interest in the chemistry and structural aspects of sulfur dioxide-transition metal complexes. Of particular interest has been the demonstration of the utility of the various coordination modes of SO_2 (η^1-planar, η^1-pyramidal and η^2) as a test for bonding concepts [1, 2]. Additionally, correlations between the bonding mode, SO infrared stretching frequencies, and chemical activation are of interest [3]. Although several studies pertinent to SO_2 binding have been carried out, no structural information concerning complexes with square planar geometry about the transition metal has been produced for either the SO_2 ligand or the, in many ways similar, [1, 2] nitrosyl ligand. Recent reports [4, 5] of the existence of complexes of the type $RhCl(PR_3)_2L$ where R = Pr^i or Cy and L is ethylene, oxygen or nitrogen and the structural determination [5] of those three complexes when R = Pr^i led us to examine the chemistry of the analogous SO_2 complexes. The complex $RhCl(PPr^i_3)_2(SO_2)$ was prepared and found to crystallize in the space group $P2_1/c$, a = 8.086(4), b = 9.080(4), c = 17.039(8) Å and β = 93.74(3)° with z = 2 demanding that the rhodium atom reside on a $\bar{1}$ site. The resulting disorder between the *trans* chloro and SO_2 ligands could be only partially resolved even with the aid of rigid body refinements for the sulfur dioxide ligand. Although the results were judged inadequate for publication of the structural details, it is clear that the complex is square planar with *trans* phosphines and η^1-planar Rh–SO_2 bonding. The existence of this complex has more recently been reported by other authors [6].

The complex $RhCl[P(C_6H_{11})_3]_2(SO_2)$ has been reported [7] and suggested to contain four-coordinate rhodium. We have prepared and crystallized this complex and the results of the crystallographic investigation are reported herein.

Experimental

Crystal Preparation

The compounds $RhCl(PR_3)_2(SO_2)$ (R = Pr^i, Cy) were prepared by procedures similar to those recently published [6, 7]. Single crystals were grown by addition of ethanol to chloroform solutions of the complexes, and allowing the solutions to stand undisturbed at ambient temperature.

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 20% over the period of the data collection process. Correction curves for this decrease were estimated by least-squares refinement of a polynomial to the standards and applied to the data. The variance for $\overline{F^2}$ (denotes 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 is taken to be 0.015.

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TABLE I. Crystal Data.

Space Group	$P2_1/c$
a	13.371(6) A
b	12.783(6)
c	23.293(10)
β	105.01(2)°
z	4
$\mu(\mathrm{MoK}_\alpha)$	6.6 cm^{-1}
Developed faces; distance from origin	{110}, 0.06; {001}, 0.2 mm
max., min. transmission [9]	0.92, 0.93
data collected	$2\theta \leqslant 40°$*
no. of unique reflections	3599
no. observed $I \geqslant 2\sigma(I)$	2822
unweighted *R* value	6.6%

Diffractometer: Picker FACS-1, P. G. Lenhert's Disk Operating System, [10] Wang encoders, graphite monochromator, 3.5° takeoff angle, (1.5° + dispersion) continuous scans, 2θs symmetric background counts, MoK_α radiation (λ 0.709 30 A).

*The precentage of reflections for which $I \leqslant 3\sigma(I)$ was greater than 60% at 40°.

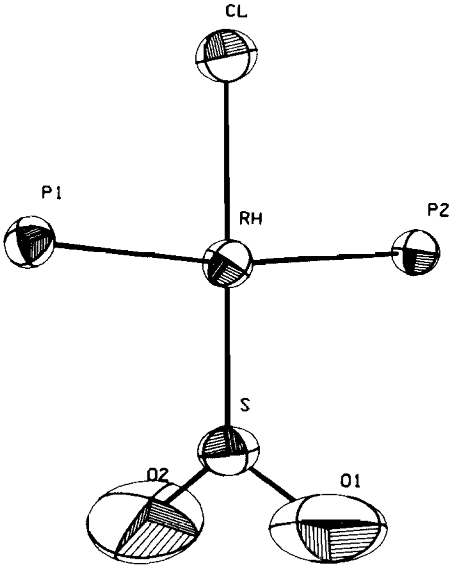

Fig. 1. ORTEP projection of the inner coordination sphere.

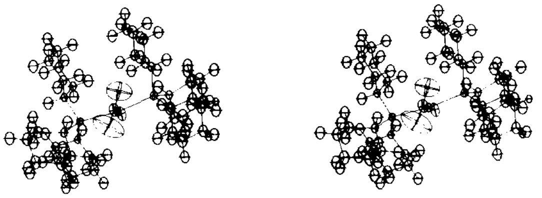

Fig. 2. Stereoview of the molecule.

The function minimized in the least-squares refinements was $\Sigma\, \mathrm{w}(|F_\mathrm{o}|-|F^*_\mathrm{c}|)^2$ where $\mathrm{w} = 4F^2_\mathrm{o}/\sigma(\bar{F}^2)^2$ and F^* includes a correction for secondary extinction [8].

The structure was solved by standard Patterson and Fourier techniques, and the refinements, including anisotropic thermal parameters on all atoms larger than carbon and hydrogen atoms placed in calculated positions (B = 5.0), converged to the *R* value listed in Table I. A final difference Fourier map contained a small peak ($\rho \approx 0.9$ e/Å^3) whose position could reasonably be interpreted as an oxygen atom bound to sulfur. Although such a peak could be the result of rotational disorder of the SO_2 ligand about the M–S bond, the second oxygen necessary for such an intepretation could not be located. All other peaks were very close to heavy atoms. Final parameters are presented in Table II.

Description of the Structure and Discussion

As can be seen from inspection of the distances and angles displayed in Table III and the ORTEP projection and stereoview of the structure shown in Figs. 1 and 2, the molecular structure may be described as square planar with respect to the rhodium atom coordination. The distances and angles are normal within the accuracy of the experiment and do not require further comment except for the P–Rh–P angle of 168.5° which is probably due to steric interference between the cyclohexyl rings.

The sulfur dioxide ligand shows short S–O distances and a rather small O–S–O angle, both of which are no doubt due to uncertainties associated with the large thermal motion of the oxygen atoms. In spite of this problem, it is clear that the SO_2 is bound in an η^1-planar fashion, *i.e.* the sum of the angles about the sulfur atom is 359.8° and the Rh–S distance is 2.069(4) Å, the latter being some 0.25 Å shorter than the shortest established distance for the η^1-pyramidal geometry [11].

The square planar geometry has been erroneously reported to be consistent with the η^1-pyramidal SO_2 geometry based on extended Hückel calculations [1]. The error is clearly of a typographical nature; the relevant frontier orbitals for the MCl_3^{2-} (C_{2v} symmetry) and their interaction with SO_2 are shown in Fig. 3. The diagrams are produced from calculations using the same program and parameters as reported previously [1]. A minimum was found in the sum of the one electron energies at the coplanar M–SO_2 conformation for all calculations performed, including those in which the M–S bond

TABLE II. Fractional Coordinates and Thermal Parameters for Chlorobis(trichlohexylphosphine) (Sulfur Dioxide)Rhodium.

Atom	X	Y	Z	U11	U22	U33	U12	U13	U23
Rh(1)	−0.31300(7)	0.17976(8)	0.13866(4)	2.3(1)	3.1(1)	3.7(1)	−0.2(1)	1.6(1)	0.4(1)
S(1)	−0.4057(3)	0.3071(3)	0.1439(2)	4.1(2)	3.5(2)	6.8(3)	1.4(4)	5.2(4)	0.7(5)
O(1)	−0.4488(12)	0.3738(12)	0.1007(7)	22.0(17)	22.8(17)	21.4(17)	38.4(29)	23.6(28)	25.5(29)
O(2)	−0.4391(11)	0.3330(10)	0.1933(6)	23.7(16)	10.7(11)	14.4(13)	18.0(22)	14.4(24)	−0.3(20)
Cl(1)	−0.2090(2)	0.0362(3)	0.1315(2)	4.6(2)	3.5(2)	9.0(3)	0.3(4)	6.9(4)	1.6(4)
P(1)	−0.4140(2)	0.0597(2)	0.1780(1)	2.6(2)	2.9(2)	3.5(2)	−0.4(3)	1.6(3)	−0.1(4)
P(2)	−0.1827(2)	0.2840(2)	0.1133(1)	2.4(2)	3.1(2)	2.9(2)	−0.1(3)	1.2(3)	0.6(4)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
C(1)	−0.4218(8)	−0.0695(9)	0.1426(5)	2.4(3)	C(2)	−0.4635(10)	−0.0644(10)	0.0758(6)	4.2(3)
C(3)	−0.4465(10)	−0.1700(12)	0.0479(6)	5.7(4)	C(4)	−0.4904(10)	−0.2590(11)	0.0752(6)	5.0(3)
C(5)	−0.4501(9)	−0.2632(10)	0.1399(6)	4.3(3)	C(6)	−0.4702(9)	−0.1594(10)	0.1684(5)	4.2(3)
C(7)	−0.3498(8)	0.0390(9)	0.2577(5)	2.7(3)	C(8)	−0.3267(9)	0.1421(10)	0.2905(6)	3.9(3)
C(9)	−0.2773(11)	0.1295(11)	0.3555(6)	5.5(4)	C(10)	−0.1801(11)	0.0647(10)	0.3658(6)	5.0(3)
C(I1)	−0.2027(9)	−0.0393(11)	0.3366(6)	4.4(3)	C(12)	−0.2507(9)	−0.0275(10)	0.2705(6)	4.1(3)
C(13)	−0.5455(8)	0.1049(9)	0.1788(5)	2.5(3)	C(14)	−0.6063(9)	0.0412(10)	0.2145(5)	4.1(3)
C(15)	−0.7036(10)	0.1005(10)	0.2184(6)	4.6(3)	C(16)	−0.7718(9)	0.1250(10)	0.1567(6)	4.0(3)
C(17)	−0.7133(10)	0.1834(12)	0.1215(6)	5.8(4)	C(18)	−0.6167(10)	0.1222(10)	0.1173(6)	4.5(3)
C(19)	−0.1209(8)	0.2161(8)	0.0624(5)	2.2(2)	C(20)	−0.0313(8)	0.2673(9)	0.0436(5)	3.1(3)
C(21)	0.0192(9)	0.1919(10)	0.0095(5)	3.9(3)	C(22)	−0.0574(10)	0.1471(10)	−0.0437(6)	4.4(3)
C(23)	−0.1496(10)	0.0997(10)	−0.0269(6)	4.5(3)	C(24)	−0.2000(8)	0.1754(10)	0.0066(5)	3.3(3)
C(25)	−0.2202(8)	0.4183(9)	0.0856(5)	2.7(3)	C(26)	−0.2905(9)	0.4169(9)	0.0220(5)	3.5(3)
C(27)	−0.3357(10)	0.5270(11)	0.0049(6)	5.3(3)	C(28)	−0.2517(11)	0.6071(11)	0.0106(6)	5.5(4)
C(29)	−0.1789(10)	0.6078(11)	0.0722(6)	5.0(3)	C(30)	−0.1320(9)	0.4986(10)	0.0886(5)	4.1(3)
C(31)	−0.0779(8)	0.3091(9)	0.1812(5)	2.4(2)	C(32)	−0.1165(8)	0.3733(9)	0.2268(5)	3.1(3)
C(33)	−0.0278(9)	0.3988(10)	0.2810(5)	4.0(3)	C(34)	0.0256(9)	0.3010(10)	0.3090(6)	4.4(3)
C(35)	0.0625(9)	0.2346(10)	0.2655(5)	3.9(3)	C(36)	−0.0257(8)	0.2089(9)	0.2117(5)	2.9(3)

Anisotropic thermal motion is defined by exp(−2pixpi(U′11HH + U′22KK + U′33LL + U′12HK + U′13HL + U′23KL) where U′ij = UijXbiXbj and Uij is multiplied by 100 in the Table.

TABLE III. Selected Distances and Angles.

Distances (Å)	Rh–S	2.069(4)
	Rh–Cl	2.333(3)
	Rh–P(1)	2.379(3)
	Rh–P(2)	2.386(3)
	S–O(1)	1.33(1)
	S–O(2)	1.38(1)
Angles (°)	Rh–S–O(1)	127.4(7)
	Rh–S–O(2)	124.5(6)
	S–Rh–Cl	179.4(2)
	S–Rh–P(1)	94.4(1)
	S–Rh–P(2)	93.6(1)
	Cl–Rh–P(1)	85.9(1)
	Cl–Rh–P(2)	86.3(1)
	P(1)–Rh–P(2)	168.3(1)
	O(1)–S–O(2)	107.9(8)

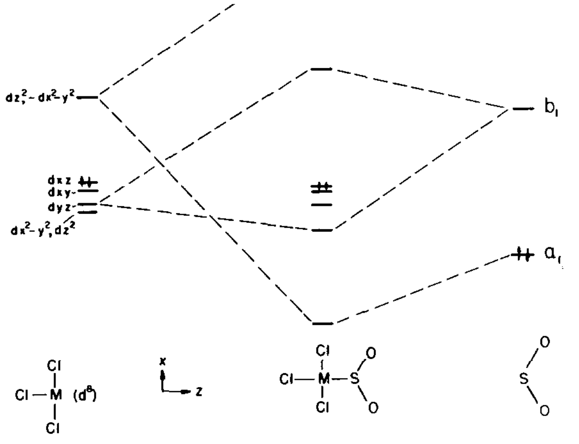

Fig. 3. Interaction diagram for MCl_3SO_2 as produced from extended Hückel calculations. Parameters used in the calculations were taken from Reference 1 with M–S = 2.1 A.

distance was assumed to be 2.45 Å and the rotational conformation was taken to be either staggered or eclipsed with respect to the *cis* M–Cl bonds.

The preference for the η^1-planar M–SO_2 geometry over the η^1-pyramidal is evident by inspection of the orbital diagram. The η^1-pyramidal geometries are associated with those situations in which the complex fragment (before reaction with SO_2) contains a filled sigma orbital at the prospective coordination site. The interaction with sulfur dioxide (coplanar M–

SO_2) then produces a diagram in which the HOMO is a σ type orbital, mostly metal in character and antibonding with respect to the M–S bond. The LUMO is a bonding (wrt M–S) orbital whose principle components are the sulfur p orbital perpendicular to the SO_2 plane and the $d\pi$ metal orbital. It is the interaction between these two molecular orbitals which accounts for the deep minimum at the η^1-pyramidal conformation as described in previous publications [1, 2].

In the present case the situation is quite different in that the ML_3 (d^8) fragment presents to the SO_2 an *empty* sigma type orbital and filled π orbitals, a situation which is ideally suited for the coplanar M–SO_2 geometry observed here. One should notice, however, that the orbital template discussed above is quite similar to that expected for a C_{4v} ML_5 (d^6) complex, and that the octahedral complexes have been shown to exhibit the η^2 as well as η^1-planar M–SO_2 geometries [12–15]. It is reasonable to suggest then that the choice for the square planar complexes is between η^1-planar and η^2 coordination but that the η^1-pyramidal geometry is not likely. The η^1-pyramidal conformation cannot be definitely excluded, however, since the participation of dz^2 in the filled orbital labeled ($dx^2 - y^2, dz^2$) is sensitive to the nature of the ancillary ligands.

Ample precedent exists for the complexing of small molecules in a η^2 fashion for the present $RhCl(PCy_3)_2$ complex [7] and the related triisopropylphosphine complex, and a recent crystal structure of chlorobis(triisopropylphosphine)-4-methyl-N-sulfinylanilinerhodium [6] shows the sulfur-bound η^1-planar structure while spectroscopic studies are indicative of η^1-planar to "π–N=S" linkage isomerization in solution [6].

In the present structure we find the torsional angle between the least square of the inner coordination sphere of the complex and the SO_2 plane to be 53.6°, a value which is similar to the angle of *ca.* 60° found in the above mentioned sulfinylaniline complex [6]. The shortest oxygen to hydrogen intermolecular contacts are O(1)- - -H1 (2.65, 2.64 Å) and O(2)- - -H1 (2.80, 2.39 Å). The structure also contains intramolecular contacts of 2.66 Å for O(1)- - -H and 2.74 Å for O(2). If the SO_2 ligand is rotated so that the ligand plane is parallel to the least squares plane of the rhodium inner coordination sphere, O- - -H contacts of *ca.* 2.0 Å result. One can therefore conclude that the conformation of SO_2 about the Rh–S bond is determined by steric rather than electronic factors. Notice, also, the large values for the oxygen amplitudes of vibration perpendicular to the SO_2 plane compared to those of the sulfur atom (Fig. 2). Since no appreciable instability is expected for the SO_2 out of plane wagging motion (*vide supra*) this must attest to a rather low barrier to rotation about the Rh–S bond.

Several attempts were made to isolate analogous complexes with phosphines other than PPr^i_3 and PCy_3. Reaction of $[RhCl(cyclooctene)_2]_2$ with two equivalents of PR_3 (R_3 = Et_3, Me_2Ph, Bzl_3, Bu^t_3) in benzene followed by SO_2 addition gave oily or otherwise intractable products. Use of PPh_2Me led to precipitation of the known [16] five-coordinate species, $RhCl(PPh_2Me)_3(SO_2)$, which presumably contains η^1-pyramidal SO_2 from infrared evidence [3]. Thus, as is often the case, PPr^i_3 and PCy_3 possess just the right combination of steric and electronic properties to stabilize complexes with novel coordination features. As a further demonstration of the substantial role that can be exercised by the organo groups of a phosphine in determining the coordination geometry of a complex, attempts to prepare $RhCl(PR_3)_2(SO_2)$ where R = Ph led only to isolation of the five-coordinate chloride-bridged dimer $[RhCl(PPh_3)_2(SO_2)]_2$ [3, 17]. Solutions of the latter as well as $RhCl(PPh_2Me)_3(SO_2)$ are reactive towards oxygen to form sulfates, while $RhCl(PR_3)_2(SO_2)$ (R = Pr^i or Cy) does not show this behavior [3]. Further studies of the effects of ancillary ligands on metal–SO_2 coordination geometry and reactivity are in progress.

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