

Table IX. Intermolecular Contacts (Å) ≤ 3.5 Å^a

C(16)-O(1) ^I	3.08	N(3)-C(35) ^{II}	3.32
O(1)-O(1) ^I	3.18	N(5)-C(4) ^{III}	3.40
N(4)-O(1) ^I	3.25	C(23)-C(35) ^{IV}	3.41
C(15)-O(1) ^I	3.26	C(24)-C(36) ^{IV}	3.42
C(38)-O(1) ^I	3.31		

^a Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z : (I) $-x, -y, -z$; (II) $-1/2 + x, 1/2 - y, -1/2 + z$; (III) $-1/2 + x, 1/2 - y, 1/2 - z$; (IV) $1 - x, -y, -z$.

the metal ion out of the macrocyclic plane.³⁸

The doming is not equal for the four isoindole groups. The maximum deviations from the plane of the four isoindole nitrogen atoms are 0.23 and 0.35 Å for phenyl carbon atoms in groups 2 and 3, while the maximum deviations in the same direction in groups 1 and 4 are 0.04 and 0.12 Å. Such a pattern was observed in aquo(phthalocyanato)magnesium(II).³⁶

There appears to be some variation in bond parameters of phthalocyanine complexes as the size of the central "hole" increases.³⁹ The C-N-C angle involving the azamethine nitrogen atom is the most sensitive bond parameter. This angle ranges from 121.7° in Fe(Pc)²⁵ (Ct-N = 1.93 Å) to 126.2° in Cl₂Sn(Pc)⁴⁰ (Ct-N = 2.05 Å). The average value of 125 (1)° found for this angle in PcOs(CO)(py) agrees with that

found in phthalocyanine complexes with similar Ct-N distances.^{35,39} The presence of a very heavy metal atom like osmium decreases the accuracy with which the lighter atoms can be determined, but within the observed standard deviations, the other bond parameters agree with those reported in the accurately determined structure of Zn(Pc)³⁹ and Sn(Pc).³⁴

A packing diagram of the unit cell is shown in Figure 3. Table IX lists the intermolecular contacts ≤ 3.5 Å. Most of the shortest contacts involve the carbonyl oxygen atom. Nonbonded contacts of this magnitude have been observed in other carbonyl complexes (e.g., [H₃OEP]⁺[Re₂(CO)₆Cl₃]⁻).⁴¹ Neither these nor any of the other intermolecular contacts are believed to have any significant effect on the structure.

The structure of PcRu(CO)(py) probably possesses a structure similar to that of PcOs(CO)(py).

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Registry No. PcRu(CO)(THF), 71870-08-1; PcRu(CO)(py), 67588-47-0; PcOs(CO)(THF), 71870-09-2; PcOs(CO)(py), 71870-10-5; Ru₃(CO)₁₂, 15243-33-1; Os₃(CO)₁₂, 15696-40-9; OsO₄, 20816-12-0.

Supplementary Material Available: Tables III-V containing calculated hydrogen atom positions, root-mean-square components of thermal ellipsoids, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of Two Square-Pyramidal Rhodium(I)-Sulfur Dioxide Complexes. Bonding Effects in Pyramidal-SO₂ Complexes

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The molecular structures of Rh(ttp)Cl(SO₂) and [Rh(ttp)(CO)(SO₂)](AsF₆), where ttp is bis(3-(diphenylphosphino)propyl)phenylphosphine, have been deduced by single-crystal X-ray diffraction. Both compounds contain square-pyramidal coordination units with apical pyramidal sulfur dioxide ligands. The neutral chloride compound is the most dissociatively and oxidatively stable pyramidal sulfur dioxide-metal complex yet reported and also has the shortest known metal-pyramidal SO₂ distance, 2.326 (5) Å. An M-SO₂ distance of 2.433 (6) Å is found for the carbonyl complex, which contains labile, reactive sulfur dioxide. A difference of about 90° is found in the orientation of the SO₂ group relative to the RhP₃L unit, an effect which is related to the π -bonding characteristics of L. A trans influence of 0.10 Å is seen for the Rh-P distance trans to Cl or CO, and the metal is only 0.08 Å out the basal plane for the carbonyl but 0.26 Å out of the plane for the chloride. These structural and chemical features are related to the donor/acceptor nature of Cl and CO. Crystal data: Rh(ttp)Cl(SO₂), *P*2₁/*a*, *Z* = 4, *a* = 21.327 (8) Å, *b* = 11.244 (3) Å, *c* = 14.617 (6) Å, β = 105.05 (2)°, *R* = 0.056 for 3515 reflections with *I* $\geq 2\sigma(I)$; [Rh(ttp)(CO)(SO₂)](AsF₆), *P*2₁/*c*, *Z* = 4, *a* = 11.138 (8) Å, *b* = 19.995 (2) Å, *c* = 20.229 (2) Å, β = 115.61 (6)°, *R* = 0.084 for 2295 reflections with *I* $\geq 2\sigma(I)$.

Introduction

The nature of the chemical bonding of sulfur dioxide to transition metals and other substrates continues to be a prime research area. In particular, there is much interest in determining those factors which dictate the mode of transition metal-SO₂ bonding (pyramidal, coplanar, or side-on-bonded SO₂) and the reactivity of the attached SO₂ (e.g., oxygen sensitivity or lability).¹⁻⁸ A recent study by Meek, Blum, and

co-workers attempted to address the latter subject by examining a series of Rh(I) complexes of the type [Rh(ttp)L(SO₂)]ⁿ⁺, where ttp is the triphosphine bis(3-(diphenyl-

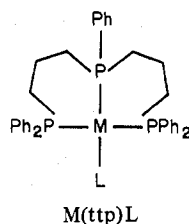
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Table I. X-ray Data Collection Description for Rh(ttp)Cl(SO₂) and [Rh(ttp)(CO)(SO₂)](AsF₆)

	Rh(ttp)Cl(SO ₂)	[Rh(ttp)(CO)(SO ₂)](AsF ₆)
chemical formula	RhP ₃ C ₃₆ H ₃₇ ClSO ₂	RhP ₃ C ₃₆ H ₃₇ SO ₃ AsF ₆
mol wt	764.8	946.5
systematic absence	0k0, k = 2n + 1; h0l, h = 2n + 1	0k0, k = 2n + 1; h0l, l = 2n + 1
space group	P2 ₁ /a	P2 ₁ /c
ρ _{obsd} , g/cm ³ (flotation)		1.563
ρ _{calcd} , g/cm ³	1.449	1.547
a, Å	21.327 (8)	11.138 (8)
b, Å	11.244 (3)	19.995 (2)
c, Å	14.617 (6)	20.229 (2)
β, deg	105.05 (2)	115.61 (6)
λ, Å	0.709 30	0.709 30
Z	4	4
temp, °C	22 ± 3	22 ± 3
base scan width, deg	2.0	2.0 in steps of 0.05°
scan rate, deg/min	2.0	2.0
θ _{min} , θ _{max} , deg	1, 45	3, 40
takeoff angle, deg	3.0	3.0
transmission coeff	0.929-0.950	0.865-0.889
no. of unique reflctns collected	4423	3672
no. of unique reflctns with I ≥ 2σ(I)	3515	2295
μ, cm ⁻¹	8.03	15.0
cryst dims, mm	0.074 × 0.400 × 0.082	0.084 × 0.180 × 0.100
cryst faces	{100}, {010}, {001}	{011}, {01T}, {100}
cell parameter refinement data	12 reflctns with 3θ ≥ 2θ ≥ 40°	12 reflctns with 18 ≥ 2θ ≥ 25°
diffractometer	computer-controlled Picker FACS-1	computer-controlled Picker FACS-1
R, R _w	0.056, 0.057	0.084, 0.077
max Δ/σ positional parameter	0.3	0.2

phosphino)propyl)phenylphosphine^{9,10} and $n = 1$ for neutral L and 0 for anionic L.



This ligand was designed to fit snugly around a square-planar or pyramidal metal ion with the size of Rh(I).^{11,12} This triphosphine ligand has been shown to be extremely useful in metal phosphine chemistry because of the geometric constraints and ligand-dissociation-inhibiting influence of its chelate nature.^{11,12}

The Rh(ttp)L-SO₂ studies revealed a large dependence of SO₂ lability and O₂ reactivity on L, even though infrared and NMR spectra indicated all the compounds had square-pyramidal coordination with pyramidal SO₂.^{9,10} For example, the L = Cl compound is completely unreactive to oxygen both in the solid state and in solution and fails to release SO₂ readily below 280 °C in a nitrogen atmosphere. Hence the chloride is the most dissociatively inert pyramidal MSO₂ compound known. By contrast, the L = CO compound contains an SO₂ ligand which is readily labilized and is readily oxidized by oxygen to sulfate. These interesting observations prompted us to carry out single-crystal studies on Rh(ttp)Cl(SO₂) and [Rh(ttp)(CO)(SO₂)](AsF₆) to see whether these physico-chemical properties could be correlated with the detailed molecular structures.

X-ray Crystallography

Crystals of Rh(ttp)Cl(SO₂) and [Rh(ttp)(CO)(SO₂)](AsF₆) were kindly supplied by Dr. P. Blum and Dr. D. W. Meek of The Ohio State University. The chloride compound was in the form of yellow-green needles and the carbonyl in the form of yellow-green platelets.

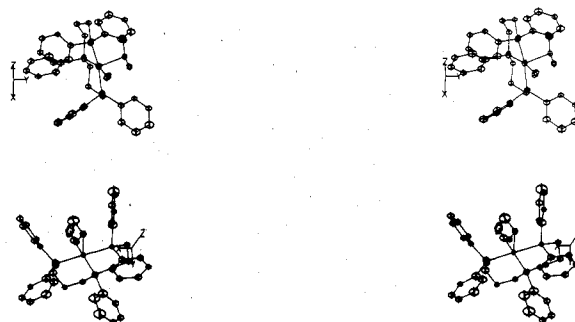


Figure 1. Stereoviews of the structures of Rh(ttp)Cl(SO₂) and [Rh(ttp)(CO)(SO₂)](AsF₆).

low-green needles and the carbonyl in the form of yellow-green platelets. Both were encased in a thin layer of Duco cement to inhibit possible deterioration in air. During data collection standards declined in intensity by about 3% for the two compounds. A correction was applied by using a least-squares polynomial fit. Details of data collection, other than those given in Table I, were as described previously.¹³ The structures were solved by the heavy-atom and direct methods and were refined in the conventional manner. Final positional and thermal parameters are presented in Tables II and III, and selected interatomic distances and angles are presented in Tables IV and V. Hydrogen atoms were not included in the refinements. The heights of the largest peaks in final difference Fourier syntheses were 1.5 e/Å³ (in the vicinity of the AsF₆ group) for [Rh(ttp)(CO)(SO₂)](AsF₆) and 0.8 e/Å³ (near a phenyl ring) for Rh(ttp)Cl(SO₂).

Description of the Structures

Stereoviews of the structures of Rh(ttp)Cl(SO₂) and [Rh(ttp)(CO)(SO₂)](AsF₆) are presented in Figure 1. The inner coordination units of the Rh(ttp)Cl(SO₂) molecule and the [Rh(ttp)(CO)(SO₂)]⁺ cation are shown in Figure 2. Both structures involve square-pyramidal rhodium coordination with the tridentate phosphine and Cl or CO in the base and pyramidal SO₂ in the apex. The coordination units differ significantly, however, in other aspects of their structure.

Of prime interest to the present study is the dependence of the M-SO₂ bonding on the ligand CO or Cl. Although the

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Table II. Fractional Coordinates and Thermal Parameters for RhCl(ttp)(SO₂)

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
Rh(1)	.31938(3)	-.08099(6)	.28113(5)	2.5(0)	2.0(0)	2.6(0)	.0(1)	1.1(1)	.2(1)
S(1)	.33975(11)	.09644(19)	.36533(16)	3.7(1)	2.1(1)	3.8(1)	.5(2)	1.7(2)	-.8(2)
O(1)	.40875(28)	.12262(51)	.38342(44)	4.4(4)	3.6(4)	6.9(5)	-1.8(6)	2.4(7)	-3.6(7)
O(2)	.32017(33)	.08513(55)	.45294(44)	9.8(5)	3.8(4)	6.1(4)	-1.7(6)	9.2(8)	-3.3(8)
Cl(1)	.24902(11)	.48689(20)	.86817(15)	4.0(1)	4.4(1)	3.8(1)	-1.2(2)	1.0(2)	-2.6(2)
P(1)	.09030(10)	.43598(20)	.78226(15)	2.7(1)	2.3(1)	3.0(1)	.3(2)	1.7(2)	.1(2)
P(2)	.12239(10)	.31190(19)	.59679(15)	2.7(1)	2.2(1)	2.6(1)	-.0(2)	.7(2)	-.4(2)
P(3)	.27501(11)	.36757(20)	.67407(16)	2.7(1)	2.8(1)	3.2(1)	.4(2)	1.4(2)	-.4(2)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
C(1)	.4179(4)	.0688(7)	.1488(5)	2.3(2)	C(2)	.3767(4)	.1649(8)	.1421(6)	3.0(2)
C(3)	.3867(5)	.2678(9)	.0897(7)	4.1(2)	C(4)	.4373(5)	.2684(9)	.0456(7)	4.3(2)
C(5)	.4789(5)	.1713(9)	.0531(7)	4.0(2)	C(6)	.4690(4)	.0687(8)	.1030(6)	3.2(2)
C(7)	.0912(4)	.3135(7)	.8652(6)	2.3(2)	C(8)	.0417(4)	.2284(8)	.8516(6)	3.6(2)
C(9)	.0488(5)	.1299(9)	.9156(7)	3.9(2)	C(10)	.1024(5)	.1210(9)	.9914(7)	4.4(2)
C(11)	.1506(5)	.2101(10)	.0077(7)	5.2(3)	C(12)	.1448(4)	.3068(8)	.9437(6)	3.7(2)
C(13)	.0086(4)	.4348(8)	.6995(6)	2.8(2)	C(14)	.4955(4)	.1640(7)	.6224(6)	2.7(2)
C(15)	.0367(4)	.3497(7)	.5493(6)	2.6(2)	C(16)	.1223(4)	.1530(8)	.6252(6)	2.7(2)
C(17)	.1501(4)	.1180(8)	.7176(6)	2.8(2)	C(18)	.3491(5)	.4942(9)	.2572(7)	4.5(2)
C(19)	.3776(5)	.4142(10)	.3275(7)	4.8(2)	C(20)	.4063(5)	.4476(9)	.4207(7)	5.0(2)
C(21)	.0925(4)	.0712(9)	.5531(7)	4.1(2)	C(22)	.1457(4)	.3181(8)	.4846(6)	2.8(2)
C(23)	.2148(4)	.2669(8)	.4917(6)	3.2(2)	C(24)	.2697(4)	.3498(7)	.5470(6)	2.7(2)
C(25)	.3448(4)	.4697(7)	.7043(6)	2.4(2)	C(26)	.1618(4)	.0877(8)	.2699(6)	3.1(2)
C(27)	.1076(4)	.1636(9)	.2537(6)	3.8(2)	C(28)	.0488(4)	.1231(8)	.2671(6)	3.7(2)
C(29)	.0417(5)	.0057(9)	.2919(7)	4.1(2)	C(30)	.4035(4)	.4275(8)	.6928(6)	3.3(2)
C(31)	.3056(4)	.2259(7)	.7304(6)	2.3(2)	C(32)	.3215(4)	.1314(8)	.6775(6)	3.4(2)
C(33)	.3412(5)	.0210(9)	.7239(7)	4.4(2)	C(34)	.1549(5)	.5053(9)	.1806(7)	4.1(2)
C(35)	.3298(5)	.1012(9)	.8715(7)	4.7(2)	C(36)	.3103(4)	.2131(9)	.8269(7)	3.7(2)

ANISOTROPIC THERMAL MOTION IS DEFINED BY $\text{EXP}(-2\text{P}1\text{X}^2 + \text{U}11\text{H}^2 + \text{U}22\text{K}^2 + \text{U}33\text{L}^2 + \text{U}12\text{HK} + \text{U}13\text{HL} + \text{U}23\text{KL})$
 WHERE U¹IJ = U¹JX¹IX²J AND U¹IJ IS MULTIPLIED BY 100 IN THE TABLE.

Table III. Fractional Coordinates and Thermal Parameters for [Rh(ttp)(CO)(SO₂)](AsF₆)

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
Rh(1)	.0096(2)	-.1554(1)	-.1501(1)	3.7(1)	3.5(1)	3.8(1)	-1.2(3)	3.7(2)	-1.1(2)
As(1)	.2760(3)	.3695(2)	.3474(2)	6.3(2)	7.3(2)	5.4(2)	2.5(4)	5.6(4)	1.4(4)
S(1)	.0042(6)	.0338(3)	.1507(5)	7.3(6)	3.3(4)	7.0(5)	.5(10)	7.4(10)	.7(10)
P(1)	.1670(6)	.1594(3)	.1007(3)	4.8(5)	4.3(4)	4.4(4)	.2(9)	5.1(8)	-1.1(8)
P(2)	-.1688(7)	.1614(4)	.0330(3)	4.9(5)	5.9(5)	3.4(4)	-2.9(10)	2.6(8)	-.7(8)
P(3)	-.1458(6)	.1574(3)	.2008(3)	4.5(5)	4.1(4)	4.5(4)	-.2(9)	5.1(8)	-.0(8)
F(1)	.3472(16)	.3318(10)	.4251(8)	10.4(15)	26.1(24)	7.0(12)	9.9(32)	7.2(22)	15.6(29)
F(2)	.4037(17)	.3469(13)	.3319(9)	10.7(15)	36.4(31)	12.7(15)	29.5(40)	16.0(26)	17.4(39)
F(3)	.2024(25)	.3056(10)	.3012(13)	19.2(26)	13.7(20)	25.5(27)	-6.7(39)	2.4(43)	-22.0(39)
F(4)	.2249(26)	.4133(11)	.2739(11)	34.6(35)	23.7(25)	13.3(18)	38.3(50)	33.1(44)	25.4(36)
F(5)	.1546(18)	.3975(12)	.3625(8)	14.0(17)	37.4(32)	9.2(14)	24.5(41)	18.5(27)	9.9(34)
F(6)	.3288(23)	.4399(10)	.3913(14)	17.2(25)	12.5(18)	29.4(32)	-4.9(37)	13.5(46)	-6.6(39)
O(1)	-.0059(19)	.0143(7)	.0795(9)	15.5(21)	4.9(12)	7.4(13)	-5.3(26)	13.2(28)	-4.9(21)
O(2)	.1227(20)	.0163(8)	.2119(11)	10.4(18)	4.6(13)	13.7(18)	1.8(26)	12.7(31)	2.6(25)
O(3)	.2267(15)	.1801(9)	.3032(8)	4.3(12)	13.3(16)	5.8(12)	1.6(27)	2.5(21)	-1.4(25)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
C(1)	.150(2)	.161(1)	.245(1)	3.3(6)	C(2)	.236(2)	.241(1)	.102(1)	3.8(6)
C(3)	.212(2)	.293(1)	.139(1)	3.6(5)	C(4)	.268(2)	.358(1)	.137(1)	4.9(6)
C(5)	.345(2)	.363(1)	.096(1)	5.5(6)	C(6)	.377(3)	.310(1)	.062(1)	5.9(7)
C(7)	.315(2)	.248(1)	.060(1)	4.7(6)	C(8)	.318(2)	.109(1)	.156(1)	3.7(6)
C(9)	.324(3)	.042(1)	.131(1)	5.9(7)	C(10)	-.435(3)	.503(1)	.322(1)	5.4(7)
C(11)	-.473(3)	.028(1)	.241(1)	6.5(7)	C(12)	-.479(3)	.092(1)	.263(1)	5.5(6)
C(13)	-.411(2)	.137(1)	.221(1)	3.6(5)	C(14)	.111(2)	.126(1)	.008(1)	3.1(5)
C(15)	-.014(2)	.339(1)	.453(1)	4.0(6)	C(16)	-.145(2)	.368(1)	.454(1)	3.3(5)
C(17)	-.236(3)	.247(1)	.010(1)	4.6(6)	C(18)	-.368(3)	.241(1)	.458(1)	5.4(7)
C(19)	-.412(3)	.176(1)	.441(1)	5.8(7)	C(20)	-.328(3)	.126(1)	.471(1)	6.1(7)
C(21)	-.196(3)	.367(1)	.021(1)	7.4(8)	C(22)	-.147(3)	.298(1)	.041(1)	6.4(7)
C(23)	-.315(2)	.108(1)	.020(1)	3.6(5)	C(24)	-.377(2)	.126(1)	.074(1)	3.5(5)
C(25)	-.301(2)	.103(1)	.153(1)	3.4(5)	C(26)	-.203(2)	.240(1)	.212(1)	2.6(5)
C(27)	-.315(3)	.245(1)	.228(1)	4.9(6)	C(28)	-.349(3)	.310(1)	.245(1)	5.8(7)
C(29)	-.275(3)	.363(1)	.242(1)	5.8(7)	C(30)	-.159(2)	.360(1)	.230(1)	4.4(6)
C(31)	-.128(2)	.295(1)	.214(1)	3.7(6)	C(32)	-.089(2)	.051(1)	.299(1)	4.2(6)
C(33)	-.018(2)	.164(1)	.353(1)	4.3(5)	C(34)	.038(3)	.135(1)	.424(1)	6.4(7)
C(35)	.026(3)	.066(1)	.434(1)	6.9(8)	C(36)	-.036(2)	.025(1)	.374(1)	5.3(7)
C(37)	-.079(2)	.121(1)	.294(1)	4.1(6)					

ANISOTROPIC THERMAL MOTION IS DEFINED BY $\text{EXP}(-2\text{P}1\text{X}^2 + \text{U}11\text{H}^2 + \text{U}22\text{K}^2 + \text{U}33\text{L}^2 + \text{U}12\text{HK} + \text{U}13\text{HL} + \text{U}23\text{KL})$
 WHERE U¹IJ = U¹JX¹IX²J AND U¹IJ IS MULTIPLIED BY 100 IN THE TABLE.

pyramidal SO₂ unit in both compounds has normal internal geometry for a pyramidal M-SO₂ group and a normal angle between the Rh-S vector and the resultant of the S-O vectors (118° for the carbonyl compound and 123° for the chloride), the Rh-S distances are remarkably different. In consonance with the observed inertness of Rh(ttp)Cl(SO₂) to SO₂ lability and oxidation, the Rh-S distance, 2.326 (5) Å, is the shortest metal-pyramidal SO₂ distance yet reported. This value is more

than 0.1 Å shorter than in the CO analogue, 2.433 (6) Å, and may be compared to the range of Rh-pyramidal SO₂ distances, 2.368 (5)-2.450 (2) Å, reported in previous structures (Table VI).¹⁴⁻²²

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Table IV. Selected Interatomic Distances (Å) for Rh(tp)Cl(SO₂) and [Rh(tp)(CO)(SO₂)](AsF₆)

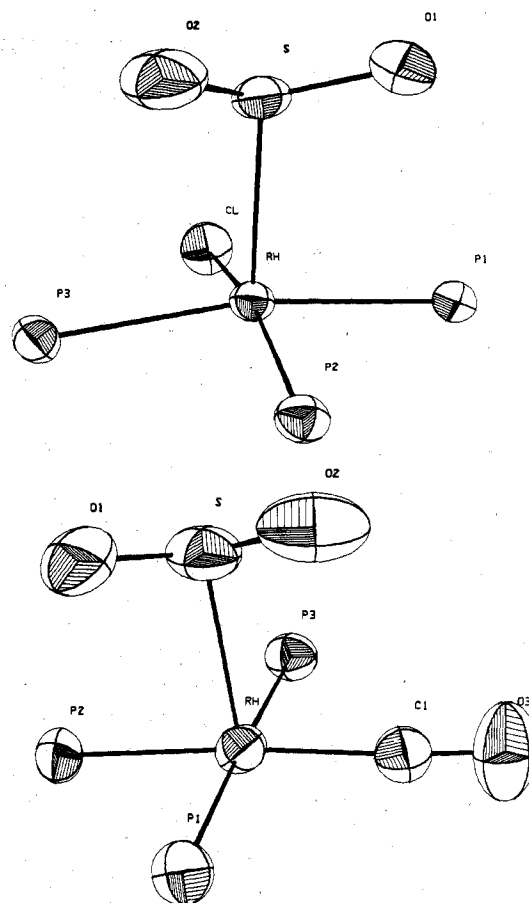
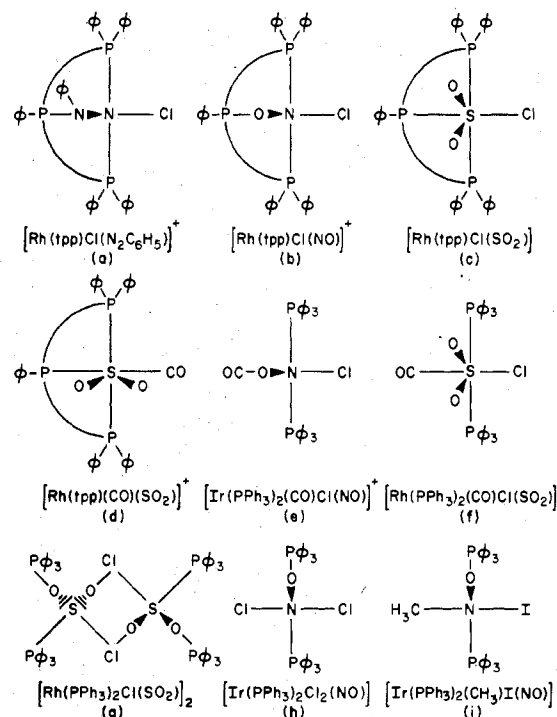
Rh(tp)Cl(SO ₂)		[Rh(tp)(CO)(SO ₂)](AsF ₆)
2.326 (5)	Rh-S	2.433 (6)
2.35 (2)	Rh-P1	2.364 (6)
2.24 (2)	Rh-P2	2.346 (6)
2.35 (1)	Rh-P3	2.362 (7)
2.41 (3)	Rh-Cl (C37)	1.89 (2)
1.457 (8)	S-O1	1.45 (1)
1.453 (9)	S-O2	1.41 (2)
1.840 (8)	P1-C1	1.82 (2)
1.829 (8)	P1-C7	1.86 (2)
1.85 (2)	P1-C13	1.82 (2)
1.56 (1)	C13-C14	1.52 (3)
1.56 (2)	C14-C15	1.59 (3)
1.83 (2)	P2-C15	1.82 (2)
1.836 (9)	P2-C16	1.85 (2)
1.841 (1)	P2-C22	1.86 (2)
1.56 (1)	C22-C23	1.56 (3)
1.55 (2)	C23-C24	1.53 (3)
1.844 (9)	P3-C24	1.91 (2)
1.84 (1)	P3-C25	1.83 (2)
1.83 (1)	P3-C31	1.84 (2)
	C37-O3	1.11 (2)
	As-F1	1.61 (1)
	As-F2	1.65 (2)
	As-F3	1.58 (2)
	As-F4	1.60 (2)
	As-F5	1.61 (2)
	As-F6	1.71 (2)

Table V. Selected Interatomic Angles (deg) for Rh(tp)Cl(SO₂) and [Rh(tp)(CO)(SO₂)](AsF₆)

Rh(tp)Cl(SO ₂)		[Rh(tp)(CO)(SO ₂)](AsF ₆)
94.65 (8)	S-Rh-P1	92.9 (3)
92.91 (8)	S-Rh-P2	92.5 (3)
96.89 (8)	S-Rh-P3	89.4 (3)
101.16 (8)	S-Rh-Cl(C37)	93.7 (7)
90.87 (8)	P1-Rh-P2	91.8 (2)
168.45 (9)	P1-Rh-P3	177.6 (2)
89.04 (8)	P1-Rh-Cl(C37)	89.6 (7)
89.06 (8)	P2-Rh-P3	88.7 (2)
165.89 (8)	P2-Rh-Cl(C37)	173.6 (7)
88.23 (8)	P3-Rh-Cl(C37)	89.7 (7)
108.1 (3)	Rh-S-O1	104.8 (7)
109.6 (3)	Rh-S-O2	103.7 (8)
111.4 (4)	O1-S-O2	116.6 (12)
	Rh-Cl-O3	174 (2)
	F-As-F(cis)	86-98
	F-As-F(trans)	172-175

Another important difference in the bonding in Rh(tp)-Cl(SO₂) and [Rh(tp)(CO)(SO₂)]⁺ is the distance of the metal above the approximate plane formed by the four basal ligands, 0.08 Å for the carbonyl and 0.26 Å for the chloride. This effect may also be seen clearly in the deviations of the P1-Rh-P3 angles (168.45 (9)° for the chloride and 177.6 (2)° for the carbonyl) from linearity. Likewise, the P2-Rh-Cl angle, 165.89 (8)°, is much smaller than the P2-Rh-CO angle, 173.6 (7)°. Among known pseudo-square-pyramidal-SO₂ complexes, our carbonyl complex by far contains the metal most nearly in the basal plane (Table VI). In [Rh(tp)(CO)(SO₂)]⁺ the metal is even closer to the basal plane than in the parent "planar" Rh(tp)Cl complex (deviation 0.14 Å).¹¹

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Figure 2. The inner coordination units of the Rh(tp)Cl(SO₂) molecule and the [Rh(tp)(CO)(SO₂)]⁺ cation.Figure 3. Idealized views of the structures of bent M-NO and pyramidal M-SO₂ complexes viewed in projection down the M-NO (M-SO₂) vectors.

A third important difference in the structures of Rh(tp)-Cl(SO₂) and [Rh(tp)(CO)(SO₂)]⁺ is the orientation of the

Table VI. Selected Structural Parameters for M-SO₂ and M-NO Complexes

complex	ref	Rh-S(N), Å	Rh-P1(P3), Å	Rh-P2, Å	Rh dev, ^a Å	Rh-Cl, Å	P-M-P, deg	L1-M-L2, deg
Rh(ttp)Cl(SO ₂)	<i>b</i>	2.326 (5)	2.35 (1)	2.24 (2)	0.26	2.41 (3)	168.5	165.9
[Rh(ttp)(CO)(SO ₂)] ⁺	<i>b</i>	2.433 (6)	2.363 (6)	2.346 (6)	0.08		177.6	173.6
Rh(PPh ₃) ₂ (CO)Cl(SO ₂)	14	2.450 (2)	2.355, 2.371 (2)		0.24	2.355 (2)	167.6	170.9
[Rh(PPh ₃) ₂ Cl(SO ₂) ₂] ⁺	15	2.368 (5)	2.298, 2.308 (5)		0.30	2.395, 2.425 (4) ^c	156, 158 ^e	
[Rh(ttp)Cl(N ₂ C ₆ H ₅)] ⁺	16	1.961 (7)	2.352, 2.368 (3)	2.274 (3)	0.22	2.403 (2)	172.6	165.2
[Rh(ttp)Cl(NO)] ⁺	11	1.909 (15)	2.374, 2.408 (3)	2.282 (4)	0.26	2.408 (4)	170.5	159.3
Rh(ttp)Cl	11		2.288 (1)	2.201 (2)	0.14	2.381 (2)	171.1	178.8
Ir(PPh ₃) ₂ (CO)Cl(SO ₂)	18b	2.49 (1)	2.328, 2.359 (8)		0.21	2.37 (1)	169.5	173
[Ir(PPh ₃) ₂ (CO)Cl(NO)] ⁺	18a	1.97 (1)	2.407 (3)		0.18	2.343 (3)	175.7	161.3
Ir(PPh ₃) ₂ Cl ₂ (NO)	20	1.94 (2)	2.367 (2)		0.33	2.348 (2)	170.2	157.4
[Ir(PPh ₃) ₂ (CO)I(NO)] ⁺	19	1.891 (3)	2.36 (1)		0.23		168.2	158
Ir(PPh ₃) ₂ (CH ₃)I(NO)	21	1.91 (2)	2.348 (3)		0.40		169.2	151
Ru(PPh ₃) ₂ Cl(NO)(NO)	22	1.85 (2), 1.74 (2) ^d	2.425 (6)		0.39	2.362 (6)	159.6	155.8

^a Out of plane. ^b Present study. ^c Bridging chlorides. ^d Linear Ru-NO. ^e For P-Rh-Cl.

SO₂ group with respect to the basal ligands (Figure 3). In the chloride the SO₂ bends away from chloride toward P2, the same bending sense as observed in the related complexes [Rh(ttp)Cl(NO)]⁺ and [Rh(ttp)Cl(N₂C₆H₅)]⁺.^{11,16} In contrast, in [Rh(ttp)(CO)(SO₂)]⁺ the SO₂ bends toward P1, i.e., approximately 90° away from the orientation adopted in the chloride complex.

An additional structural difference between Rh(ttp)Cl(SO₂) and [Rh(ttp)(CO)(SO₂)]⁺ lies in the magnitude of the Rh-P distance trans to chloride or carbonyl. Although the Rh-P1 and Rh-P3 distances, 2.35–2.36 Å, are very similar to the values observed in [Rh(ttp)Cl(NO)]⁺ and [Rh(ttp)Cl(N₂C₆H₅)]⁺, 2.352–2.408,^{11–16} in these same four compounds the Rh-P2 distances range from 2.24 to 2.35 Å. The Rh-P2 distance in the carbonyl compound is about 0.08 Å longer than in the other three structures, which contain trans chlorides. We attribute this effect to the stronger trans-labilizing influence of the carbonyl groups compared to that of chloride. The observed closer proximity of the metal to the basal ligand plane in the case of the carbonyl compound would be expected to enhance the trans effect.

Other geometric parameters of the Rh complexes and ttp ligands are unremarkable and entirely comparable to values found in other Rh-ttp complexes.^{11,16} Somewhat large thermal parameters and small but statistically significant deviations from octahedral symmetry were obtained for the refined AsF₆ group, possibly due to disorder or libration. The rather poor definition of the AsF₆ group largely accounts for the somewhat high *R* factor of 0.084 in the carbonyl compound. No unusual packing effects are evident in the two structures.

Discussion

The bonding analogy between bent/linear metal-nitrosyl complexes and pyramidal/coplanar metal-sulfur dioxide complexes is well recognized.^{3,6,18} The σ* and nondegenerate π* orbitals of sulfur dioxide are close in energy to d-orbital energies and comparable to corresponding σ* and π* orbitals in nitric oxide.³ Taking into account symmetry differences and the smaller σ*-π* separations in SO₂, the rules for predicting linear/bent M-NO and coplanar/pyramidal M-SO₂ geometries are usually parallel.³ As more examples of M-SO₂ structures are developed, further comparison of these two amphoteric ligands is possible. In this discussion we wish to correlate several features, appearing in the Rh(ttp)-SO₂ complexes described in this paper and in previously structured M-NO and M-SO₂ compounds, with proposed bonding models.

As mentioned above, the metal atom in [Rh(ttp)(CO)(SO₂)]⁺ lies much closer to the plane of the four basal ligands than in Rh(ttp)Cl(SO₂), [Rh(ttp)Cl(NO)]⁺, or even Rh(ttp)Cl. We feel this is a consequence of the excellent π-acceptor carbonyl, which will prefer the metal in the basal plane

so as to maximize π*(CO)-dπ back-bonding. In addition, if the basal coordination is brought closer to planar, the d orbitals are perturbed in such a way as to destabilize bonding to the axial ligand SO₂. Elevation of z² diminishes the σ*(SO₂)-z² interaction and depression of (xz,yz) diminishes any π*(SO₂)-dπ interaction as the ML₄ moiety becomes more nearly planar. Consequently, the M-SO₂ bond should be weakened as the basal coordination becomes more planar, thereby providing a rationale for the observations that the M-SO₂ distance is about 0.1 Å longer and the SO₂ is much more labile and reactive in the carbonyl compound than in the chloride.

The effect of basal planarity on the strength of the metal-axial ligand interaction may also be seen in the compounds Rh(PPh₃)₂(CO)Cl(SO₂) (Rh-SO₂ = 2.450 Å and Rh = 0.24 Å out of basal plane) and [Rh(PPh₃)₂Cl(SO₂)₂]⁺ (Rh-SO₂ = 2.368 Å and Rh = 0.30 Å out of basal plane). A similar effect on M-NO distances might be present also in metal nitrosyls, but the generally low precision of reported M-NO distances makes this type of analysis difficult. However, we do note that the presence of the acceptor CO in square-pyramidal nitrosyl complexes, as well as in the sulfur dioxide complexes, tends to reduce the distance of the metal from a least-squares plane through the four basal donors. Note, for example, this parameter in [Ir(PPh₃)₂(CO)Cl(NO)]⁺ is 0.18 Å vs. 0.33 Å in Ir(PPh₃)₂Cl₂(NO), and in [Ir(PPh₃)₂(CO)I(NO)]⁺ it is 0.23 Å vs. 0.40 Å in Ir(PPh₃)₂(CH₃)I(NO).

The factors involved in determining the rotational orientation of the bent axial nitrosyl in d⁸ square-pyramidal complexes have been extensively considered by several authors.^{6,23,24} For convenience, we reproduce here two previously developed rules, which may be of some utility in rationalizing orientational features of the present work (see especially ref 23 for underlying assumptions): (1) (a) In compounds of the type trans ML₂L'₂(NO), the nitrosyl group will bend in the plane of the poorer π donors. This rule can be rephrased in terms of the better acceptors with the understanding that excellent acceptors tend to promote linear nitrosyl geometries and drive the molecule to a trigonal-bipyramidal structure with the nitrosyl in the equatorial plane. (b) Increased σ-donating ability of the ancillary ligands also tends to promote bending. (2) In compounds of the type ML₂DA(NO), D = π donor trans to the π acceptor A, the NO group should bend in the DMA plane toward the acceptor. This stabilizing factor establishes a preference for the nitrosyl to lie in the DMA plane, as well as determining the direction of bending in this plane. Note that it is not necessary for one of the ligands to be a donor but only that a disparity in acceptor ability exist between the two ligands in question.

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Using these rules and the reasonable π -acceptor order $\text{CH}_3 < \text{Cl} < \text{I} < \text{PR}_3 \ll \text{CO} < \text{NO}$, one may rationalize all compounds definitely known to contain square-pyramidal, bent-nitrosyl structures. Situations exist for which the direction of bending is contrary to that expected by strict application of rule 1a (see Figure 3). For example, although the structure depicted in Figure 3e is in accord with both rules, in Figure 3b the bending is in the poorer acceptor plane. Presumably the structure is controlled by influence 2 plus the relatively stronger σ -donating ability of the PR_2Ph group compared to that of PRPh_2 (influence 1b).

One might ask to what extent these same rules apply to the SO_2 complexes. Unlike the nitrosyl case, for SO_2 the π^* orbital is nondegenerate and hence on bending there is no orbital which maintains a full π interaction with the metal. Thus, situations may be imagined for nitrosyl complexes in which the plane of bending is not determined entirely by the tendency for bending in a particular plane but also by the strength of the π bond in the perpendicular plane. Because sulfur dioxide complexes lack this complicating feature, they may provide a more sensitive test for these bonding concepts than nitrosyl complexes.

Inspection of Figure 3 shows that the SO_2 structures depicted in parts c and f are in line with the analogous nitrosyls and consistent with the theoretical predictions while those depicted in parts d and g are in need of further explanation. It is possible that the explanation for the $[\text{Rh}(\text{ttp})(\text{SO}_2)(\text{CO})]^+$ conformation is related to the presence of an excellent π acceptor and a good σ donor (moderate π acceptor) in the carbonyl plane. Since these factors favor the trigonal-bipyramidal (TBP) geometry, it is probable that if the SO_2 were oriented so that its π^* orbital could interact in this plane the TBP geometry would be the more stable. The observed structure may then be considered to be the result of a choice between the TBP and square-pyramidal coordination types, in addition to the preference for ligand bending in a particular plane. An excellent test of these arguments would be provided by the nitrosyl complex $[\text{Rh}(\text{ttp})(\text{CO})(\text{NO})]^{2+}$ since the driving force toward TBP cannot be avoided in this case. In the dimer $[\text{Rh}(\text{PPh}_3)_2\text{Cl}(\text{SO}_2)]_2$, the donors are cis and a good basal π -acceptor ligand is absent; the SO_2 does not bend toward any of the ligands.

It is interesting to note that $[\text{Rh}(\text{ttp})(\text{CO})(\text{SO}_2)](\text{AsF}_6)$ is unique in that it is the only structured square-pyramidal SO_2 complex which does not contain a π -donor ligand. In formally

$d^8 \text{ML}_4(\text{NO})$ complexes, π acceptors tend to favor trigonal-bipyramidal geometry with linear $\text{M}-\text{NO}$. In fact, all known structured complexes of this type have trigonal-bipyramidal geometry, i.e., $\text{Mn}(\text{CO})_4(\text{NO})$,²⁵ $\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{NO})$,²⁶ $\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{NO})$,²⁷ $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{NO})]^+$,²⁸ and $[\text{Ru}(\text{diphos})_2(\text{NO})]^+$.²⁹ This observation is consistent with more pronounced π acidity and greater tendency to bend on the part of SO_2 than of NO .

Conclusions

The nature of the ligand L in $[\text{Rh}(\text{ttp})\text{L}(\text{SO}_2)]^{n+}$ complexes decidedly influences the structure and reactivity of the complex. For L = the donor Cl, the SO_2 is remarkably stable to dissociation and oxidation and has the shortest known M-pyramidal SO_2 distance. For L = the π acceptor CO, the SO_2 is labile and air sensitive and has a relatively long Rh-S distance. For L = CH_3CN , a σ donor with neither substantial π -acceptor nor π -donor properties, intermediate chemical behavior is observed.¹⁰ The influence of strong basal acceptors in both square-pyramidal nitrosyls and SO_2 complexes is to make the basal coordination more planar, which in turn weakens the axial bond.

The orientation of the SO_2 group in most complexes can be rationalized by considering the effect of basal donors and acceptors on the $\text{ML}_4(\text{SO}_2)$ molecular orbitals. Although at present the predictive value of existing models is not great, this situation may be improved by additional studies.

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Registry No. $\text{Rh}(\text{ttp})\text{Cl}(\text{SO}_2)$, 50763-28-5; $[\text{Rh}(\text{ttp})(\text{CO})(\text{SO}_2)](\text{AsF}_6)$, 65106-24-3.

Supplementary Material Available: A listing of structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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