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Structure of η^5-Cyclopentadienyl(sulfur dioxide)ethenylrhodium(I), $(C_5H_5)Rh(C_2H_4)SO_2$. A d^8 Complex with a Planar MSO_2 Group

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The structure of $(C_5H_5)Rh(C_2H_4)SO_2$ has been determined by single-crystal x-ray techniques. The compound crystallizes in the orthorhombic space group *Pcmn* with cell constants of a = 7.230 (3), b = 8.420 (2), and c = 14.124 (2) Å. The structure was refined to an unweighted R value of 0.029 using the 696 reflections ($2\theta \leq 50°$) whose intensities were observed to be greater than 2σ above background (813 were measured) on an automated Picker four-circle diffractometer (Mo Kα radiation). The Rh atom is on the crystallographic mirror plane with the C_5H_5 and ethylene groups perpendicular to the plane. The SO_2 moiety is contained in the same plane, the Rh–S distance being 2.096 (2) Å. Important distances and angles are Rh–C = 2.201 (6)–2.223 (7) Å for the C_5H_5 ring, Rh–C = 2.155 (6) Å for the ethylene group, S–O = 1.442 (7) and 1.430 (8) Å, Rh–S–O = 124.3 (4) and 121.4 (4)°, and O–S–O = 114.4 (5)°. The S–Rh–C_2H_4 midpoint angle is 92.8 (2)°. This is the first structure to be reported for a d^8 transition metal complex with a planar M–SO_2 group, a result which is discussed in terms of a general molecular orbital model for transition metal–sulfur dioxide complexes.

Introduction

Transition metal nitrosyl complexes have, over the past few years, been the subject of intensive research efforts.[1,2] Foremost among the reasons for this interest is the utility of the nitrosyl ligand as a probe to the bonding in such complexes, since the M–N–O geometry (i.e., "linear" vs. "bent") is delicately related to the d-electron population, coordination geometry, and the specific transition metal. It has recently been pointed out that the SO_2 ligand is at least as interesting in this regard[3] since transition metal complexes with both "coplanar" and "bent" M–SO_2 moieties are known. A molecular orbital treatment of the bonding in M–SO_2 compounds, similar to that applied to M–NO systems, was used successfully[3] to rationalize geometry in the five crystallographically determined transition metal complexes containing terminal M–SO_2 moieties and to predict structures for several hypothetical and/or structurally undetermined systems. However, the potential of SO_2 as a bonding probe can only be realized when sufficient structural information is available to make practical a comparison with the extensively studied ligand NO.

The only structural information available for d^8 transition metal–sulfur dioxide complexes is afforded by the two five-coordinate Vaska-type adducts $(Ph_3P)_2(CO)ClMSO_2$ where M = Ir and Rh.[4,5] Both of these can be classified as having square-pyramidal geometry with the SO_2 axially bound through the sulfur atom and both exhibit pyramidal geometry about the sulfur atom. Pyramidal sulfur is also found in the d^{10} pseudotetrahedral complexes $(Ph_3P)_3PtSO_2$ and $(Ph_3P)_2Pt(SO_2)_2$.[6,7] In contrast, the two known six-coordinate structures $[Ru(NH_3)_4Cl(SO_2)]Cl$ and $Mn(C_5H_5)(CO)_2(SO_2)$, are both d^6 cases containing a planar M–SO_2 moiety.[8,9] The observed sulfur geometries are all readily explicable using the above-mentioned M–SO_2 bonding model.

The structure presented in this paper is part of an ongoing program in this laboratory to characterize metal complexes containing a terminally bound SO_2 ligand.[3,6,7] Aside from the important question of the geometry at the sulfur atom and its relevance to the M–SO_2 bonding, $(C_5H_5)Rh(C_2H_4)SO_2$ presents the opportunity to compare M–SO_2, M–C_2F_4, and M–C_2H_4 bonding since the analogous compound $(C_5H_5)Rh(C_2H_4)(C_2F_4)$ has been previously synthesized and structurally determined.[10-14]

Experimental Section

In air, $CpRh(C_2H_4)SO_2$ is stable in the solid state for at least 1 week. When a benzene solution was exposed to an O_2 stream for 30 min and then air for more than 6 h, the recovered, sublimable solid had an infrared spectrum identical with that of the starting material. The complex is slightly unstable thermally, however, slowly darkening in color if not stored in a freezer.

The compound was prepared from $CpRh(C_2H_4)_2$[10] (Cp = η^5-C_5H_5) by Cramer's method.[11] Dark red crystals of a size appropriate for single-crystal x-ray investigation were grown by sublimation onto a water-cooled cold finger at ambient temperature under high-vacuum conditions. A crystal with approximate dimensions 115 × 165 × 82 μ was mounted parallel to the b axis and used for all subsequent experimental work. The diffraction pattern showed Laue symmetry *mmm* and extinctions consistent with the space group *Pcmn* (or $Pc2_1n$), i.e., $0kl$, $l = 2n + 1$, and $hk0$, $h + k = 2n + 1$. The cell constants estimated from least-squares refinement of 12 high-order reflections whose positions were measured on an automated Picker four-circle diffractometer are a = 7.230 (2), b = 8.420 (2), and c = 14.124 (3) Å (Mo Kα radiation, λ 0.70930 Å). The calculated density for Z = 4 is 2.009 g cm^{-3}.

Intensities were measured for two quadrants of the reciprocal sphere ($2\theta \leq 50°$) using θ–2θ scans of 2° at 1°/min, 20-s background counts at each end of the scan, and graphite-monochromatized Mo Kα radiation. Of the 813 unique reflections (after averaging equivalent reflections) so determined, 696 were judged to be observed according to the criterion $I \geq 2\sigma(I)$ where $\sigma(I) = [T + B + [0.015(T - B)]^2]^{1/2}$, T being the total count for each scan and B the estimated background. The intensity of the two standard reflections measured after every 50 reflections was found to decrease by approximately 2%. This decrease in intensity was corrected for using a polynomial determined by least-squares fitting of the standard reflection curves. Transmission factors[15] were applied, with the crystal being described by the six bounding planes {001}, {010}, and {$\bar{1}$01}, and varied between 0.83 and 0.86 (μ = 23.0 cm^{-1}).

The structure, including all hydrogen atom positions, was determined using standard Patterson and difference Fourier techniques assuming *Pcmn* to be the correct choice for the space group. Refinement was carried out as described in previous publications[16] using neutral atom scattering factors[17] for all atoms and appropriate anomalous scattering terms for rhodium.[18] In the final refinement, which included a secondary extinction term[19,20] and anisotropic thermal motion for all atoms heavier than hydrogen, no parameter shift was greater than 0.2 esd and the unweighted R value was 0.029. A final difference Fourier map showed residuals such that $|\rho(x)| \leq 0.7$ e/Å^3, the largest of which were in the vicinity of the Rh atom. Final atomic parameters are given in Table I and selected distances and angles are presented in Table II.

Description of the Structure

The structure (Figures 1 and 2) consists of discrete $Rh(Cp)(C_2H_4)SO_2$ molecules. The Rh atom occupies special position 4c, thus requiring the molecule to have C_m symmetry. Also contained in the symmetry plane are the three atoms comprising the SO_2 group, the midpoint of the ethylene ligand, and one of the Cp carbon atoms with its attached hydrogen atom. Both the Cp and ethylene ligands are bisected by the crystallographic mirror plane. The analogous compound[14]

Table I. Final Atomic Parameters[a,b]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.1197 (2)	0.2500	0.0601 (1)	0.0121 (1)	0.0122 (1)	0.00255 (3)	0.0000	−0.0004 (1)	0.0000
S	−0.1334 (9)	0.2500	−0.0122 (5)	0.0143 (4)	0.0160 (4)	0.0059 (1)	0.0000	−0.0053 (4)	0.0000
O1	−0.151 (3)	0.2500	−0.114 (1)	0.031 (2)	0.023 (1)	0.0060 (4)	0.0000	−0.015 (2)	0.0000
O2	−0.195 (2)	0.2500	−0.462 (2)	0.013 (1)	0.032 (2)	0.0120 (7)	0.0000	−0.001 (1)	0.0000
C1(C_2H_4)	0.230 (3)	0.331 (2)	0.438 (1)	0.022 (1)	0.022 (1)	0.0034 (3)	0.007 (2)	−0.002 (1)	0.002 (1)
C2(Cp)	0.040 (5)	0.2500	0.211 (2)	0.019 (2)	0.042 (4)	0.003 (5)	0.0000	0.006 (2)	0.000
C3(Cp)	0.152 (3)	0.382 (3)	0.196 (1)	0.043 (3)	0.017 (1)	0.003 (3)	0.011 (3)	−0.004 (2)	−0.002 (1)
C4(Cp)	0.320 (3)	0.331 (3)	0.167 (1)	0.027 (2)	0.035 (2)	0.0034 (3)	−0.027 (3)	−0.006 (1)	0.001 (1)

	x	y	z	B, Å^2		x	y	z	B, Å^2
H1	0.37 (3)	0.09 (3)	−0.04 (1)	6 (2)	H4	0.12 (2)	0.03 (2)	0.20 (1)	5 (2)
H2	0.20 (3)	0.13 (2)	−0.11 (1)	5 (2)	H5	0.41 (3)	0.41 (2)	0.15 (1)	9 (3)
H3	−0.06 (4)	0.2500	0.23 (2)	5 (3)					

[a] g = extinction coefficient = 2.2 (3) × 10^{-5}. [b] See ref 16 for definition of β's.

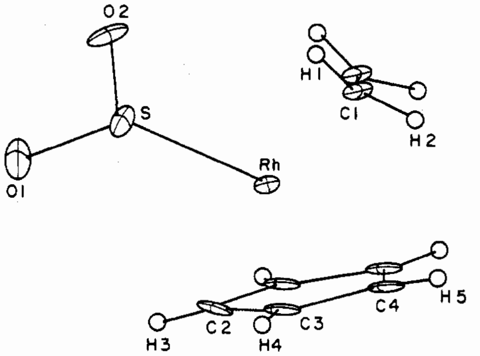

Figure 1. Molecular structure of CpRh(C_2H_4)SO_2.

Table II. Selected Distances (Å) and Angles (deg)[a]

	Distances		
Rh–S	2.096 (2)	C2–C3(Cp)	1.387 (11)
Rh–C1(C_2H_4)	2.155 (6)	C3–C4(Cp)	1.357 (11)
Rh–C2(Cp)	2.203 (9)	C4–C4′(Cp)	1.367 (4)
Rh–C3(Cp)	2.223 (7)	C1–H1	1.02 (7)
Rh–C4(Cp)	2.201 (6)	C1–H2	0.89 (7)
S–O1	1.442 (7)	C2–H3	0.80 (10)
S–O2	1.430 (8)	C3–H4	0.75 (8)
C1–C1(C_2H_4)	1.366 (15)	C4–H5	0.96 (9)
	Angles		
Rh–S–O1	124.3 (4)	C3–C2–C3′	105.7 (11)
Rh–S–O2	121.4 (4)	H1–C1–H2	134 (5)
O1–S–O2	114.4 (5)	C1–C1′–H1	127 (4)
S–Rh–C1(C_2H_4)	92.7 (2)	C1–C1′–H2	114 (5)
S–Rh–C2(Cp)	103.9 (3)	C3–C2–H3	127.1 (6)
S–Rh–C3(Cp)	120.7 (3)	C2–C3–H4	126 (6)
S–Rh–C4(Cp)	155.5 (3)	C4–C3–H4	125 (6)
Rh–C1–C1′	71.5 (2)	C3–C4–H5	117 (5)
C2–C3–C4	109.0 (9)	C4–C4–H5	135 (5)
C3–C4–C4′	108.1 (6)		

[a] Primed and unprimed atoms are related by the mirror plane.

Rh(Cp)(C_2H_4)(C_2F_4) possesses a pseudo mirror plane bisecting the C_2H_4, C_2F_4, and Cp groups with the unique Cp carbon atom being located "trans" to the ethylene, as observed in Rh(Cp)(C_2H_4)SO_2.

The Rh–SO_2 moiety is required by symmetry to be planar, in contrast to the two previously reported d^8 structures which exhibited pyramidal geometry at the sulfur. The Rh–S distance, 2.096 (2) Å, is in the expected range for a planar Rh–SO_2 (vide infra).[8,9] In the two other known structures containing planar M–SO_2 the M–S distances are 2.072 (3) Å ([Ru(NH_3)$_4$Cl(SO_2)]Cl)[9] and 2.037 (5) Å [Mn(Cp)(CO)$_2$$SO_2$].[8] The geometry of coordinated SO_2 groups does not seem to vary greatly among different coordination types or from that of uncoordinated SO_2; the S–O distances, 1.442 (7) and 1.430 (8) Å, and the O–S–O angle, 114.4 (5)°, observed in the present structure agree with the previously reported values.[3–9,21,22]

The Rh–C_2H_4 coordination exhibits an Rh–C distance (2.155 (6) Å) which is among the shortest found in Rh(I)–C_2H_4 structures while the C–C ethylene distance (1.366 (5) Å) is relatively long.[14,23] In addition, the distance to the average position of the ethylene hydrogen atoms is 0.15 Å farther from the Rh atom than is the plane which contains the carbon atoms and whose normal is defined by the vector between Rh and the midpoint of the C–C bond. In the related C_2F_4 compound the plane of the ethylene hydrogens was 0.18 Å from the midpoint of the ethylene carbon atoms.

The Rh–C (2.201 (6)–2.223 (7) Å) and C–C (1.357 (11)–1.387 (11) Å) distances for the Cp ring are consistent with parameters observed in many similar structures. In Rh(Cp)(C_2H_4)(C_2F_4), the Cp C–C bond approximately "trans" to the C_2F_4 group was reported to be significantly shorter (1.286 (12) Å) than the other Cp C–C distances (1.344 (12)–1.405 (7) Å), an observation attributed to a trans influence on the part of the C_2F_4 ligand. No significant trends in the Rh–C and C–C distances involving the Cp group are

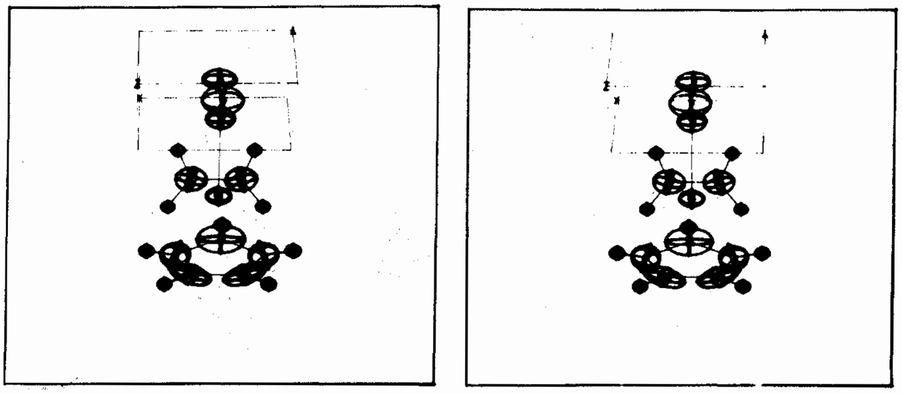

Figure 2. Stereoview of the structure.

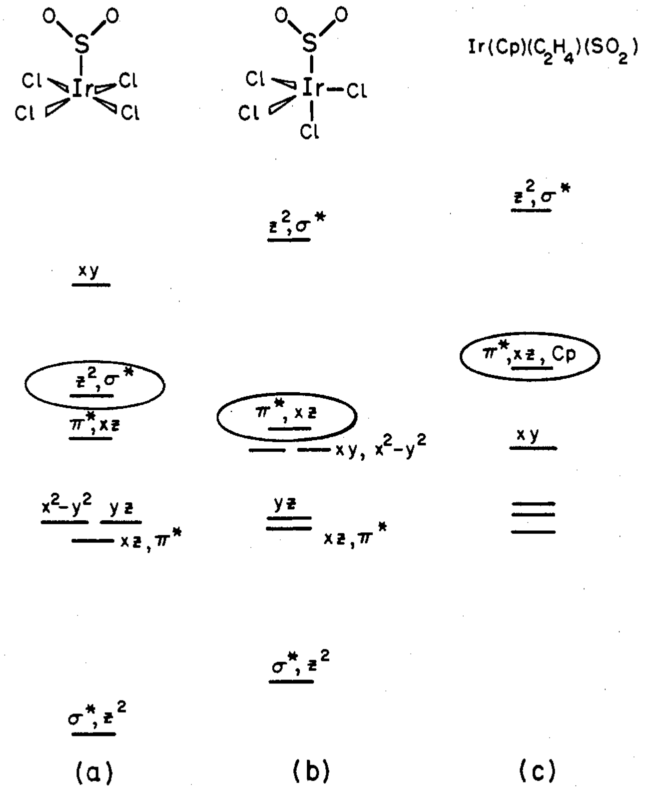

Figure 3. Proposed MO diagrams for five-coordinate $IrSO_2$ complexes in (a) square pyramid, (b) trigonal bipyramid, and (c) present structure. The circled orbitals are the LUMO for the d^8 cases. The SO_2 acceptor orbital is denoted by π^* here and in the text. Only MO's in the HFMO and LUMO regions are shown and the labels identify the primary Ir atom orbital contributions to these MO's and their bonding character with respect to SO_2. The M–S bond defines the z direction and x is perpendicular to the SO_2 plane.

discernible in the present structure.

Discussion

As pointed out in the Introduction, $Rh(Cp)(C_2H_4)SO_2$ is the first structure determination for a d^8 transition metal complex containing a planar $M{-}SO_2$ species. The difference between this molecule and the two previously reported d^8 $M{-}SO_2$ complexes ($M(PPh_3)_2(CO)ClSO_2$, M = Rh, Ir), both of which are pseudo-square-pyramidal cases with axial SO_2 ligands, may be understood by comparing the molecular orbital diagrams presented in Figure 3 for hypothetical square-pyramidal and trigonal-bipyramidal $[IrCl_4(SO_2)]^{3-}$ species. These diagrams are derived from extended Hückel calculations performed as previously described.[3] Notice that for the square-pyramidal d^8 case the orbital labeled (π^*, xz) is the highest filled molecular orbital (HFMO) and the orbital labeled (z^2, σ^*) is the lowest unfilled molecular orbital (LUMO). These two orbitals interact so as to stabilize (π^*, xz) as the SO_2 is bent, resulting in the observed bent structures for square-pyramidal d^8 systems.[3] In the trigonal-bipyramidal case, however, neither the (z^2, σ^*) nor the (π^*, xz) orbital is filled, and consequently a planar $M{-}SO_2$ moiety is predicted. Note that for the model $Ir(Cp)(C_2H_4)SO_2$ calculations (Figure 3c), a pattern of orbitals similar to the trigonal-bipyramidal $IrCl_4SO_2$ case arises, consistent with the observed planar structure.

A significant feature of the structures of $Rh(Cp)(C_2H_4)SO_2$ and $Rh(Cp)(C_2H_4)(C_2F_4)$ is the rotational angle about the $Rh{-}SO_2$ and $Rh{-}C_2F_4$ bonds. In these two compounds the π-acceptor orbitals on SO_2 and C_2F_4 have exactly the same orientation with respect to the metal, ethylene, and Cp. The MO calculations favor the observed conformation by 5 kcal/mol over the hypothetical orientation with the SO_2 plane parallel to ethylene and show the same effects to be operative in the analogous C_2F_4 compound. That the perturbation stabilizing the observed SO_2 rotational orientation derives from the π-bonding influence of the ethylene ligand is supported by calculations for both SO_2 conformations when ethylene is replaced by the σ-bonding ligand chloride (Ir–Cl = 2.35 Å). In this case the difference in stability is computed to be less than 0.4 kcal/mol.

It is interesting to note that our calculations indicate a much deeper energy minimum with respect to bending of the SO_2 groups in the observed conformation, compared to the hypothetical "rotated SO_2" structure. This effect illustrates the stabilizing influence of the ethylene π^* orbital on the coplanar $M{-}SO_2$ conformation. Evidence for a cooperative effect between the SO_2 and ethylene π-acceptor orbitals is supported by Cramer's NMR studies on $Rh(Cp)(C_2H_4)L$ which show the barrier to rotation for the ethylene group to be ca. 15.0 kcal/mol for L = C_2F_4 and ca. 12 kcal/mol for L = SO_2.[11]

It is legitimate to question whether the observed orientations of SO_2 in $Rh(Cp)(C_2H_4)SO_2$ and of C_2F_4 in $Rh(Cp)(C_2H_4)(C_2F_4)$ are the result of steric rather than electronic effects. Indeed, in $Rh(Cp)(C_2H_4)(C_2F_4)$ two short intramolecular H–F contacts (2.35, 2.42 Å) are observed. However, when a rotation of 90° about the $Rh{-}C_2F_4$ bond is carried out, more drastic interactions are not noted. Furthermore, in the SO_2 complex the shortest O–H(ethylene) contacts (ca. 2.7 Å) actually occur in the observed conformation.

In summary, the structure determination for $Rh(Cp)(C_2H_4)SO_2$ has revealed a new type of transition metal–sulfur dioxide complex and has afforded a needed test of current bonding concepts. As the versatility of the SO_2 ligand becomes more widely known, the number of types of $M{-}SO_2$ compounds is certain to grow and allow further evaluation of the bonding model.

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Registry No. $(C_5H_5)Rh(C_2H_4)SO_2$, 12247-81-3.

Supplementary Material Available: Listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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