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# A New Series of Sulfur Dioxide Complexes. The Preparation, Characterization, and Reactivity of the Sulfur Dioxide Adducts of a Series of Rhodium(I) Complexes Containing Triphosphine Ligands

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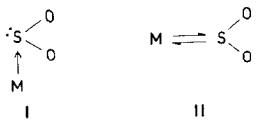
It has been pointed out that the sulfur dioxide ($SO_2$) moiety may be as useful a probe for investigating metal ligand bonding in coordination compounds as is the nitrosyl (NO) ligand [1–4]. The $SO_2$ ligand can bond to a metal atom through the sulfur atom in one of two spatial arrangements, *i.e.*, bent (I, where the sulfur atom is acting as a Lewis acid) with approximately tetrahedral geometry around the sulfur atom, and coplanar with the metal (II, where the sulfur acts as a $\sigma$ electron donor and a $\pi$ electron acceptor).

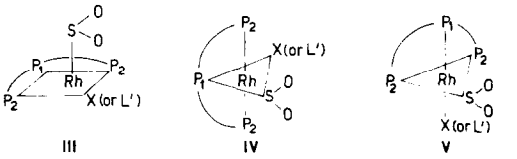


I II

Structures of complexes with both "bent" ([Rh($Ph_3P$)$_2$(CO)Cl($SO_2$)] [5], [Ir($Ph_3P$)$_2$(CO)Cl($SO_2$)] [6], [($Ph_3P$)$_3$Pt($SO_2$)] [2], and [($Ph_3P$)$_2$Pt($SO_2$)$_2$] [3]) and coplanar ([Ru($NH_3$)$_4$Cl($SO_2$)]Cl [7]. (Mn($C_5H_5$)-(CO)$_2$($SO_2$)] [8] and [($C_5H_5$)Rh($C_2H_4$)($SO_2$)] [1] M–$SO_2$ groups have been determined and correlations of the geometry with electronic, chemical and physical properties of the complexes have been attempted. In general, if the metal–$SO_2$ adduct exhibits the "bent" geometry, the S=O infrared stretching frequencies occur near 1200 and 1050 $cm^{-1}$, the $SO_2$ is labile, and complexes containing coordinated sulfate are formed on exposure to $O_2$. On the other hand if the metal–$SO_2$ groups are coplanar, the S=O stretching frequencies appear near 1300 and 1100 $cm^{-1}$, the $SO_2$ group is not labile and sulfates are not formed upon air oxidation [9]. However, there are some exceptions to the above generalization; for example, Sacconi *et al.* [10] found the M–$SO_2$ group of Ni($CH_3C(CH_2PPh_2)_3$)$SO_2$ to be planar, but the S=O stretching frequencies occur at 1190, 1055 and 1045 $cm^{-1}$ and the compound is air sensitive.

A yellow–green rhodium–sulfur dioxide adduct prepared by this group [11, 12], Rh(ttp)Cl·$SO_2$, has $\nu_{SO}$ at 1155 and 1030 $cm^{-1}$, which is consistent with a bent geometry for the Rh–$SO_2$ moiety and provides a direct analogy to the known structure of Rh($PPh_3$)$_2$(CO)Cl($SO_2$) [5]. The Rh(ttp)-Cl·$SO_2$ compound appeared unusual, however, since the $SO_2$ group was not labile and it did not react upon exposure to molecular $O_2$ at ambient conditions [13].

In order to determine which factors influence the reactivity of a bonded $SO_2$ group we have prepared a series of rhodium–$SO_2$ adducts of the type: RhLX·$SO_2$ and [RhLL′($SO_2$)]Y (where L is a linear triphosphine, X is a coordinated anion, L′ is a neutral ligand and Y is a noncoordinated anion). By varying X and L′ we can increase or decrease the basicity at the rhodium center and determine how this influences the reactivity of the bonded $SO_2$. The choice of L influences not only the basicity at rhodium but it also controls the geometry around the rhodium atom. In addition, the linear triphosphine ligand ttp readily facilitates the use of phosphorus-31 NMR to "measure" the *trans* influence of the ligand *trans* to $P_1$ [14]. In this work we have used the $^1J_{P_1-Rh}$ values to ascertain that the ligand opposite $P_1$ in the parent compound is still opposite $P_1$ in the $SO_2$ adduct. For example, the first three compounds listed in the Table have $^1J_{P_1-Rh}$ values of 147.5, 138.7 and 113.8 Hz, respectively. The parent compounds Rh(ttp)Cl, Rh(ttp)$N_3$ and Rh(ttp)CN have $^1J_{P_1-Rh}$ values of 162.5, 152.8 and 122.6 Hz, respectively, which is the same trend as their $SO_2$ adducts and suggests similar geometries and relative placement of atoms in the basal plane of the two series of compounds [15].



III IV V

Three logical geometries can be proposed for these compounds, *i.e.*, III, IV and V. Structures III and V are very nearly the same, the degree of distortion at the $P_2$–Rh–$P_2$ bond angle being the distinguishing feature. At the outset of this investigation, the square-pyramidal structure III appeared most likely to be the structure, by analogy with [Rh(ttp)Cl(NO)]-$PF_6$ and with [Rh($Ph_3P$)$_2$(CO)Cl($SO_2$)]. However, if the steric requirements of ttp are sufficiently large compared to $Ph_3P$ and CO, some distortion around the $P_2$–Rh–$P_2$ bond angle could lead to structure V. An expansion of the S–Rh–X (or L′) bond angle would result in structure IV. The phosphorus-31 data does not exclude any of these geometries and X-ray structural data is needed for the final assignment of structure.

The antisymmetric and symmetric S=O stretching frequencies for these compounds are reported in the

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TABLE. Spectral Data on the Sulfur Dioxide Complexes.

| Compound | $SO_2$ | | $\delta P_1$ | $\delta P_2$ | $\delta P_3$ | $J_{P_1-P_2}$ | $J_{P_1-P_3}$ | $J_{P_2-P_3}$ | $J_{P_1-Rh}$ | $J_{P_2-Rh}$ | $J_{P_3-Rh}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\nu_{asym}$ | $\nu_{sym}$ | ppm | ppm | ppm | hz | hz | hz | | | |
| $Rh(ttp)Cl\cdot SO_2$[a] | 1155 | 1033 | −15.5 | −2.5 | − | 39.3 | − | − | 147.5 | 113.8 | − |
| $Rh(ttp)N_3\cdot SO_2$ | 1152 | 1023 | −13.1 | −2.9 | − | 41.6 | − | − | 138.7 | 116.7 | − |
| $Rh(ttp)CN\cdot SO_2$ | 1154 | 1030 | 0.1 | −5.7 | − | 43.0 | − | − | 113.8 | 117.2 | − |
| $[Rh(ttp)(CH_3CN)(SO_2)]PF_6$ | 1180 | 1038 | −12.7 | −2.1 | − | 39.5 | − | − | 145.6 | 111.0 | − |
| $[Rh(ttp)(PPhMe_2)(SO_2)]AsF_6$[b] | 1167 | 1028 | 14.1 | −0.0 | 22.9 | 47.6 | 242.0 | 33.1 | 111.1 | 116.7 | 110.3 |
| $[Rh(ttp)(PEt_3)(SO_2)]AsF_6$[c] | 1178 | 1033 | 16.0 | −0.9 | 13.1 | 47.9 | ~240 | 30.6 | 109.4 | 119.1 | 105.7 |
| $[Rh(ttp)(CO)(SO_2)]AsF_6$ | 1225 (1210) | 1063 | 11.3 | −3.7 | − | 47.2 | − | − | 113.6 | 113.6 | − |

[a]ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$. ① ② [b]Monophosphine–P. ③ [c]Due to the very low intensity of several peaks, this spectrum has not been fully simulated and $J_{P_1-P_3}$ is accurate only to two significant figures.

Table; all of the values are similar and in the range generally found for the "bent" arrangement in $SO_2$ complexes. The carbonyl complex $[Rh(ttp)(CO)(SO_2)]AsF_6$ has $\nu_{SO}$ absorptions (at 1225 and 1063 $cm^{-1}$) somewhat higher than those of the other compounds, and this can be attributed to the apparent reduced basicity of rhodium in this case due to the $\pi$-acceptor nature of CO.

Although the chemical properties of these $SO_2$ complexes have not been studied thoroughly yet, a major difference in reactivity toward oxygen has been noted. For example, $Rh(ttp)Cl\cdot SO_2$ is unreactive at 25 °C both in the solid state and in solution [12, 13], whereas $[Rh(ttp)(CH_3CN)(SO_2)]PF_6$ shows significant reaction with $O_2$ in the solid state after one month; in solution the reaction is complete after only a few moments' exposure. These compounds appear to have reasonably non-labile $SO_2$ groups since both may be recrystallized or heated *in vacuo* (0.1 torr, 57 °C) for 18 h without loss of $SO_2$. On the other hand, both $[Rh(ttp)(PEt_3)(SO_2)]AsF_6$ and $[Rh(ttp)(CO)(SO_2)]AsF_6$ lose $SO_2$ readily when refluxed in methanol if a positive pressure of $SO_2$ is not maintained.

Both $[Rh(ttp)(PEt_3)(SO_2)]AsF_6$ and $[Rh(ttp)(PPhMe_2)(SO_2)]AsF_6$ exhibit a surprising lability of the monophosphine ligands. At room temperature, an acetone solution of either compound is yellow (the compounds are orange in the solid state and in solution at lower temperatures) and the $^{31}P$ NMR spectra indicate that the rhodium compound present has ttp as the only phosphine ligand. The $^{31}P$ NMR parameters of this species are very similar to those of $[Rh(ttp)(CH_3CN)(SO_2)]PF_6$ but it is not known whether the species is five coordinate, $[Rh(ttp)(acetone)(SO_2)]AsF_6$ or only four coordinate $[Rh(ttp)(SO_2)]AsF_6$. If the temperature is lowered to 223 °K the predominant pattern in the NMR is that due to $[Rh(ttp)(PEt_3)(SO_2)]^+$ or $[Rh(ttp)(PPhMe_2)(SO_2)]^+$, respectively, although the first pattern is still present to some extent. As long as the solution is not heated or flushed with $N_2$ the $SO_2$ remains coordinated.

We are presently obtaining crystal structure determinations on several of these compounds. We shall report these results along with a more extensive discussion of experimental details and results in a subsequent paper. In addition, we shall report the differences in $O_2$ sensitivity observed for $Rh-SO_2$ complexes of other triphosphine ligands.


1 R. R. Ryan, P. G. Eller and G. J. Kubas, *Inorg. Chem.*, *15*, 797 (1976).
2 P. G. Eller, R. R. Ryan and D. C. Moody, *Inorg. Chem.*, *15*, 2442 (1976).
3 D. C. Moody and R. R. Ryan, *Inorg. Chem.*, *15*, 1823 (1976).
4 D. C. Moody and R. R. Ryan, *Chem. Commun.*, (1977).
5 K. W. Muir and J. A. Ibers, *Inorg. Chem.*, *8*, 1921 (1969).
6 J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, *5*, 405 (1966).
7 L. H. Vogt, Jr., J. L. Katz and S. E. Wiberley, *Inorg. Chem.*, *4*, 1157 (1965).
8 C. Barbeau and R. J. Dubey, *Can. J. Chem.*, *51*, 3684 (1973).
9 G. J. Kubas, *Abstracts 172nd National Amer. Chem. Soc. Meeting*, San Francisco, Calif., No. 240, September 3 (1976).
10 P. Dapporto, S. Midollini, A. Orlandine and L. Sacconi, *Inorg. Chem.*, *15*, 2768 (1976).
11 T. E. Nappier, Jr., and D. W. Meek, *J. Am. Chem. Soc.*, *94*, 306 (1972).
12 T. E. Nappier, Jr., D. W. Meek, R. M. Kirchner and J. A. Ibers, *J. Am. Chem. Soc.*, *95*, 4194 (1973).
13 In the solid state it is stable towards $O_2$ indefinitely. In solution it was exposed to $O_2$ for more than 1 hr at one atmospheric $O_2$ pressure with no evidence of a chemical reaction.
14 P. R. Blum and D. W. Meek, unpublished data (1977).
15 D. W. Meek, D. L. DuBois and J. A. Tiethof, *Adv. in Chem. Ser.*, *150*, 335 (1976).
16 P. S. Braterman, R. J. Cross, L. Manojlovic-Muir, K. W. Muir and G. B. Young, *J. Organomet. Chem.*, *84*, C40 (1975).