Novel Reactivity and Low Temperature (−60 °C) X-Ray Crystal Structure Determination of Ru(CO)$_2$(η^2-SO$_2$·SO$_2$)(PPh$_3$)$_2$

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Summary   Crystals of the title complex have been obtained from SO$_2$ saturated benzene–heptane solutions of Ru(CO)$_3$-(PPh$_3$)$_2$, and an X-ray crystal structure determination at −60 °C has· shown not only η^2-SO$_2$ co-ordination to the ruthenium, but also a second molecule of SO$_2$ co-ordinated to the terminal oxygen of the η^2-SO$_2$, reaction with excess of SO$_2$ and PPh$_3$ under anaerobic conditions results in stoicheiometric production of Ru(SO$_4$)(CO)$_2$(PPh$_3$)$_2$ plus PPh$_3$S

During the synthesis and attempted crystallization of Ru(CO)$_2$(SO$_2$)(PPh$_3$)$_2$ an unusual reactivity was observed The complex slowly reacted with excess of SO$_2$ in the absence of oxygen to generate the bidentate sulphato-complex, Ru(SO$_4$)(CO)$_2$(PPh$_3$)$_2$,[1] the same complex that is obtained on reaction with molecular oxygen,[2] plus PPh$_3$S, and an as yet unidentified ruthenium species which appeared to contain bridging carbonyls   The reaction rate was enhanced by using liquid SO$_2$ as the solvent   The only products obtained in the presence of excess of PPh$_3$ were Ru(SO$_4$)(CO)$_2$(PPh$_3$)$_2$ and PPh$_3$S

Reinvestigation of the i r spectrum of Ru(CO)$_2$(SO$_2$)-(PPh$_3$)$_2$[2] revealed ν(SO) peaks at 1105 and 850 cm^{-1} which shifted to 1060 and 815 cm^{-1} when the complex was prepared with S^{18}O$_2$ This pattern indicated η^2-SO$_2$ co-ordination,[3] and the extremely low frequency of the second ν(SO) peak suggested substantial S–O bond lengthening that might be related to the unusual reactivity observed   These structural features have been verified through a single-crystal X-ray diffraction study
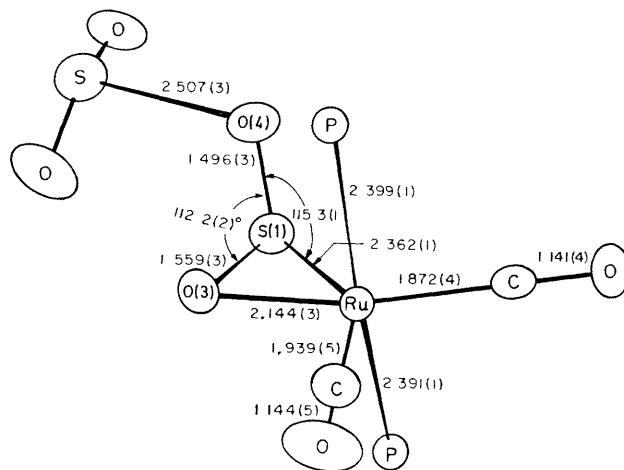
Crystal data   C$_{38}$H$_{30}$O$_6$P$_2$RuS$_2$, monoclinic, space group P2$_1$/n, a = 20 276(3), b = 16 158(3), c = 10 691(2), β = 96 42(1)°, D$_c$ = 1 54 g cm^{-3} for Z = 4 (T = −60 °C)   The structure was solved by Patterson and difference Fourier techniques and refined to R = 0 035 and R$_w$ = 0 035 for 3976 reflections †   As can be seen in the Figure, the geometry around the metal is trigonal bipyramidal with an equatorial η^2-SO$_2$ similar to that reported for RuClNO(η^2-SO$_2$)(PPh$_3$)$_2$[4] The dihedral angle between the S(1)–O(4) bond and the

FIGURE   X-Ray crystal structure of Ru(CO)$_2$(η^2-SO$_2$·SO$_2$)(PPh$_3$)$_2$

S(1)–Ru–O(3) plane is 107·9° as compared to 110·3° in the latter complex. In addition, another SO_2 is co-ordinated to the terminal oxygen of the η^2-SO_2. The geometry about the ligand-bound SO_2 is similar to that observed in metal halide- (and pseudo halide)-bound SO_2 which characteristically exhibits rather long S–X distances and pyramidal geometry about the sulphur atom.[5] The S–O distance of 2·5 Å is approximately midway between the sum of the Van der Waals radii (3·25 Å) and the sum of the covalent radii (1·7 Å).[6] The interaction is thus best described in terms of a bond order of less than one, consistent with the extreme lability of this second SO_2 molecule. This lability necessitated the low temperature structure determination and accounts for the failure to detect i.r. peaks of the ligand-bound SO_2 in spectra of Nujol mulls recorded at room temperature.

The bonding of η^2-SO_2 has been suggested to involve primarily π-donation from the metal to the LUMO of SO_2 which is antibonding with respect to the S–O bond and bonding with respect to the O–O vibration.[7] This type of interaction would be expected to lengthen S–O distances and increase the terminal oxygen basicity. It follows that such an increase in basicity should enhance co-ordination by Lewis acids like SO_2. The present complex exhibits the longest co-ordinated SO bond and the lowest ν(SO) value of any of the reported η^2-SO_2 complexes.

The exact relevance of this structure to the unusual reactivity observed remains to be determined, but since the reaction involves oxygen transfer from one SO_2 to another, interaction of a second SO_2 with bound SO_2 would not be an unreasonable first step in such a process.

This is the first report of electrophilic attack on an η^2-SO_2 and indicates that further studies of η^2-SO_2 with Lewis acids may lead to interesting results.

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