Novel Co-ordination of Sulphur Dioxide. The Crystal and Molecular Structure of Nitrosyl(sulphur dioxide)bis(triphenylphosphine)rhodium

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Summary Crystals of $[Rh(NO)(SO_2)(PPh_3)_2]$ have been obtained from SO_2-saturated solutions of $Rh(NO)(PPh_3)_3$ in benzene–heptane mixtures; the *X*-ray crystal structure shows the SO_2 ligand co-ordinated to the rhodium through the sulphur atom and through one of the oxygen atoms, while the RhNO angle is 140°.

SULPHUR DIOXIDE has been shown previously to interact reversibly with $[Rh(NO)(PPh_3)_3]$; however, the instability of the product toward loss of SO_2 and its ready reactivity with O_2 {forming $[Rh(NO)(SO_4)(PPh_3)_2]$} have prevented its isolation and characterization up to now.[1] In studies of SO_2 co-ordination to transition metals, we have found that this instability in similar systems depends partly on the existence of free PPh_3 in solution, which can displace the weakly bound SO_2 from the complex in solution. Thus, the reaction of $[Rh(NO)(PPh_3)_3]$ with excess of SO_2 has been carried out in benzene solution; heptane was then added to precipitate the $[Rh(NO)(SO_2)(PPh_3)_2]$, while the free PPh_3 is readily soluble in this solvent mixture. Crystals of $[Rh(NO)(SO_2)(PPh_3)_2]$ thus formed are stable to air for several days but rapidly react with oxygen in solution to yield the previously reported $[Rh(NO)(SO_4)(PPh_3)_2]$.

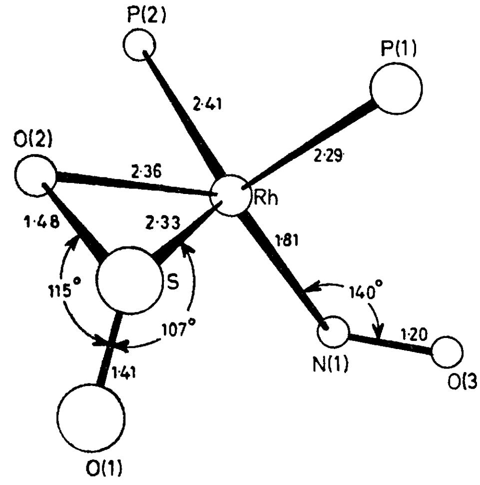

FIGURE. *X*-Ray structure of $[Rh(NO)(SO_2)(PPh_3)_2]$; distances in Å; ∠N(1)–Rh–P(1) = 102, N(1)–Rh–P(2) = 109, P(1)–Rh–P(2) = 109°; with SO defined as the midpoint of the S–O vector, ∠N(1)–Rh–SO = 127, P(1)–Rh–SO = 97, P(2)–Rh–SO = 111°. (Maximum e.s.d.s are 0·01 Å for distances and 0·9° for angles).

The i.r. spectrum (Nujol mull) shows bands attributable to $\nu(SO_2)$ at 1138 cm^{-1} and 948 cm^{-1}, with the latter being *ca.* 100 cm^{-1} lower than expected for *S*-bonded coplanar or pyramidal $M–SO_2$. $\nu(NO)$ is observed at 1600 cm^{-1}.

The molecular structure of this complex has been established by a single-crystal *X*-ray diffraction study. The compound crystallizes in the orthorhombic space group, *Pbca* with $a = 10·338(2)$, $b = 18·500(4)$, $c = 33·933(7)$ Å; $D_c = 1·477$ g cm^{-3}; $D_m = 1·47$ g cm^{-3}; $Z = 8$. The structure was solved by Patterson and difference Fourier techniques and refined to an unweighted R value of 0·07 for 2615 independent reflections. The co-ordination around rhodium is shown in the Figure along with pertinent distances and angles. The SO_2 clearly bonds to the rhodium through both the sulphur atom and one oxygen atom. As one might expect for co-ordination of this type, the S–O(2) distance (1·48 Å) is considerably longer than the S–O(1) distance (1·41 Å), while the O(1)–S–O(2) angle is the normal value found in *S*-bonded $M–SO_2$ complexes. The co-ordination geometry around the rhodium is tetrahedral, if one considers the SO-bonded SO_2 as a monodentate ligand (like ethylene, *etc.*) and the RhNO unit is clearly bent. This is only the second determination of a four-co-ordinate d^{10} mononitrosyl complex in which the M–NO geometry deviates significantly from linearity, the other being $[Ni(N_3)(NO)(PPh_3)_2]$[2,3] in which the MNO angle is 153°. It has been suggested that the observed distortion towards a square planar geometry for this Ni complex is related to the bent MNO unit.[3] However, in the structure presented here, the MNO angle is significantly smaller than that reported for the Ni complex with no commensurate distortion of the rhodium co-ordination geometry.

This structure thus represents the first reported for a transition-metal complex containing both NO and SO_2 as ligands and also establishes a novel mode for $M–SO_2$ bonding, similar to that observed for $M–CO_2$ and $M–CS_2$ in $[Ni(CO_2)(PCy_3)_2]$ (Cy = cyclohexyl)[4] and $[Pt(CS_2)(PPh_3)_2]$.[5]

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