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Preliminary communication

A CHELATE METHYLDISULPHIDO-LIGAND FROM METHYLATION OF CO-ORDINATED DISULPHUR. STRUCTURE OF $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]ClO_4$

G.R. CLARK and D.R. RUSSELL

Chemistry Department, University of Leicester, Leicester LE1 7RH (U.K.)

W.R. ROPER* and A. WALKER

Department of Chemistry, University of Auckland, Auckland (New Zealand)

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Summary

The co-ordinated disulphur molecule in $Os(S_2)(CO)_2(PPh_3)_2$ is methylated by methyltrifluoromethylsulphonate giving $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]SO_3CF_3$; x-ray crystal structure analysis of $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]ClO_4.\frac{1}{2}C_6H_6$, reveals that the S_2Me-ligand is bidentate, and attached in an almost symmetrical manner.

There are examples of co-ordinated dioxygen in Group VIII transition metal complexes reacting with sulphur dioxide, carbon dioxide, carbon disulphide, nitrogen dioxide, alkyl isocyanides, ketones, aldehydes and triphenylphosphine. These reactions have been reviewed.[1] In contrast, the reactivity of co-ordinated disulphur has been little studied apart from oxidation with periodate to complexes of S_2O and S_2O_2.[2] We have found that the zerovalent complexes $Ru(CO)_2(PPh_3)_3$ and $Os(CO)_2(PPh_3)_3$ with S_8 yield $Ru(S_2)(CO)_2(PPh_3)_2$ and $Os(S_2)(CO)_2(PPh_3)_3$ respectively, analogous to the previously reported dioxygen complexes,[3] and as part of an investigation of the chemistry of co-ordinated S_2 we describe here the methyldisulphido-ligand produced by direct methylation of S_2 with methyltrifluoromethylsulphonate.

1 equivalent of $Os(CO)_2(PPh_3)_3$ and ¼ equivalent of S_8 in

benzene under rigorously deoxygenated conditions slowly forms orange-coloured $Os(S_2)(CO)_2(PPh_3)_2$ in approximately 70% yield, (ν_{CO} 1998, 1944 cm^{-1}). $Ru(S_2)(CO)_2(PPh_3)_2$ forms similarly and has ν_{CO} 2000, 1955 cm^{-1}. 1 equivalent of $Os(S_2)(CO)_2(PPh_3)_2$ reacts rapidly with 1 equivalent of $CH_3SO_3CF_3$ forming pale yellow $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]SO_3CF_3$ (ν_{CO} 2045, 1980 cm^{-1}; ^1H n.m.r. τ, 8.0 (s) S-CH_3). This compound can be converted to a perchlorate and the i.r. spectra of both these salts show that the anions are not co-ordinated and suggest therefore that the S_2Me-ligand is bidentate. Reaction with iodide anion produces a compound which from solubility behaviour is no longer a salt and is probably $Os(\eta^1\text{-}S_2Me)I(CO)_2(PPh_3)_2$. This compound has not been thoroughly characterised because the solid is unstable, evolving an evil-smelling gas.

Cream-coloured crystals of $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]ClO_4\cdot\frac{1}{2}C_6H_6$ from CH_2Cl_2/C_6H_6 are triclinic, a = 14.23(1), b = 17.30(1), c = 10.44(1) A, α = 102.1(2), β = 102.7(2), γ = 105.5(1), Z = 2, space group $P\bar{1}$. Intensity data for the layers h k 0 through h k 10 were collected on a Stoe Weissenberg diffractometer using monochromatic Mo - K_α radiation and an ω scan technique. The structure was solved using conventional methods and at the present stage of least squares refinement the Os, Cl, S, and P atoms have been assigned anisotropic thermal parameters and R = 0.076 for 4693 observed reflections. The geometry of the cation is shown in the figure. The co-ordination about the osmium atom is distorted octahedral with trans phosphines. The S_2Me-ligand is nearly symmetrically co-ordinated to the metal in that the two Os-S distances differ by only 5σ. The S-S bond length is close to that found in S_8 (2.04 Å) and may be slightly shorter than those suggested to correspond to a bond order of 1.0 (2.05 - 2.08 Å). For comparison, we can note the S=S distance in S_2 (gas phase) is 1.887 Å. The overall geometry is remarkably similar to that in $[Ir(S_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$ where S-S is 2.066 Å[4]. The S(1)-C(Methyl) bond (1.82 Å) is normal. The angle C(Me)-S(1)-Os is 117.8°. At this stage of refinement

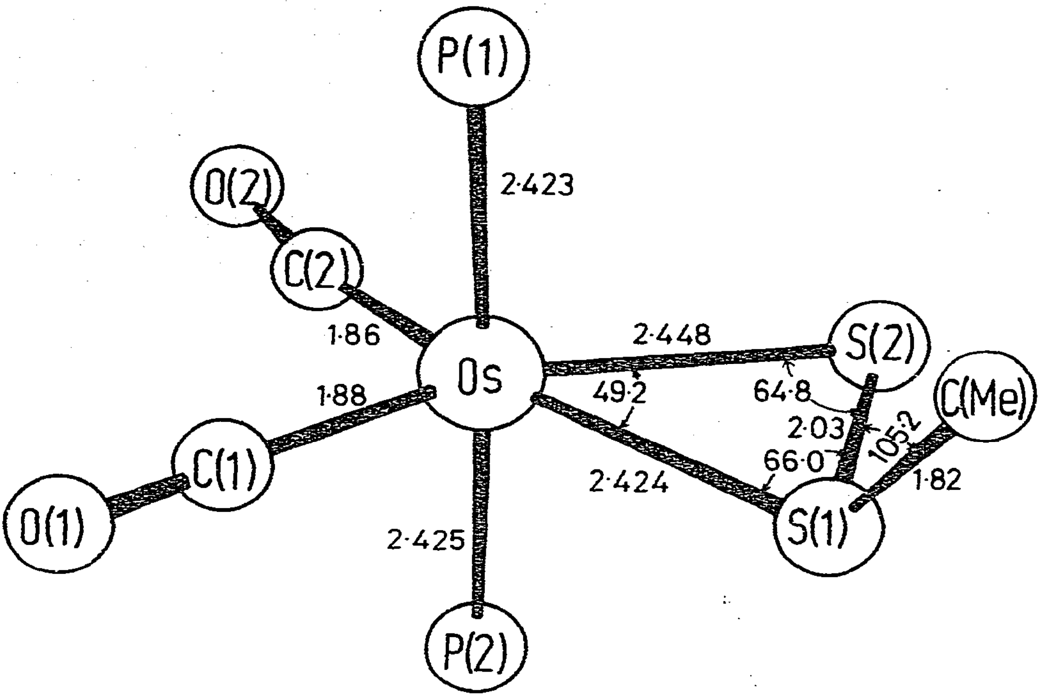

Fig. 1. Structure of $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]^+$

there is no significant difference between the two Os-CO distances.

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