Journal of Organometallic Chemistry, 187 (1980) 141—145
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Synthesis and Characterisation of a Thiocarbonyl containing Osmium Cluster

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(Received November 9th, 1979)

Summary

Reaction of CS_2 with $H_2Os_3(CO)_8(MeCN)S$ in cyclohexane yields a product $H_2Os_3(CO)_7(CS)S_2$. This has been characterised by NMR and mass spectroscopy, and by X-ray analysis, and has been shown to contain a terminal thiocarbonyl ligand.

The chemistry of metal carbonyl clusters is well developed but no general synthetic methods exist for the preparation of the isostructural thiocarbonyl clusters. Only the μ_3-thiocarbonyl containing cluster $[(\eta^5\text{-}C_5H_5)Co]_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ has been characterised [1].

Reaction of CS_2 with polynuclear metal carbonyls has led to a variety of species which do not contain thiocarbonyl ligands. Adams [2] found that the reaction of $H_2Os_3(CO)_{10}$ with CS_2 yielded $[HOs_3(CO)_9]_2(\mu\text{-}S_2CH_2)$. On refluxing $Ru_3(CO)_{12}$ in CS_2 an insoluble powder of stoichiometry $[Ru(CO)_3CS]_n$ is isolated [3]. Also, when refluxed in CS_2, $Co_2(CO)_8$ reacts to give $Co_6(CO)_{12}CS_2$ and

$[Co_3(CO)_9(CS)]_2$ [4] which contain two μ_3-S and one μ_3-C atom, and an S-C_2-S linkage, respectively [5].

This tendency for the formation of μ_3-S ligands with break up of the thiocarbonyl group is exemplified in reactions of CS_2 and CSX_2 (X = Cl, NH_2) with a variety of Os_3 clusters. The principal products of these reactions were $H_2Os_3(CO)_9S$ from CSX_2 with $H_2Os_3(CO)_{10}$ and $Os_3(CO)_9S_2$ from CS_2 with $Os_3(CO)_{11}(C_2H_4)$ [6].

However, when $H_2Os_3(CO)_8(MeCN)S$ [7], which already contains a μ_3-S group, is refluxed with CS_2 in cyclohexane a yellow solid is obtained. Purification by t.l.c. leads to the isolation of $H_2Os_3(CO)_7(CS)S_2$ as a major reaction product. The molecular geometry was elucidated by an X-ray analysis. A plot of the molecule is shown in Fig. 1 and some bond lengths and angles are presented in Table 1. The asymmetric unit contains two crystallographically independent molecules, one of which is disordered.

In this structure the three Os atoms define a triangle with one side lengthened (Os .... Os 3.70 Å) so that there is no direct metal-metal bond along this edge. Two μ_3-S atoms cap above and below the Os_3 plane such that the cluster core resembles that in

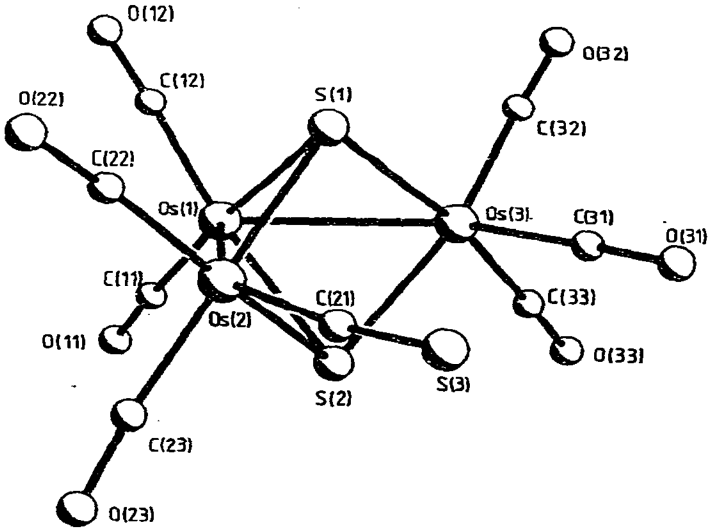

Fig. 1

Table 1

Bond Lengths (Å) and Bond Angles (°) for $H_2Os_3(CO)_7(CS)S_2$

Os(1)-Os(2)	2.813(1)	Os(1)-S(2)	2.427(17)
Os(1)-Os(3)	2.808(1)	Os(2)-S(2)	2.464(18)
Os(1)-S(1)	2.435(14)	Os(3)-S(2)	2.401(18)
Os(2)-S(1)	2.373(12)	Os(2)-C(21)	1.90 (2)
Os(3)-S(1)	2.431(12)	C(21)-S(3)	1.43 (2)
Os(2)-Os(1)-Os(3)	82.8(1)	Os(2)-C(21)-S(3)	168.6 (20)

$Fe_3(CO)_9S_2$ [8]; the S .... S distance of 3.077 Å indicates little direct interaction. The linear thiocarbonyl ligand occupies an equatorial site on one of the terminal metal atoms in the Os_3 chain. The hydrides were not located in the X-ray analysis but empirical potential energy calculations [9], based on the ligand distribution, indicates that these atoms bridge the two Os-Os bonds such that they are trans to the equatorial carbonyl and thiocarbonyl ligands, and hence trans to each other. The ^1H NMR spectrum is in agreement with this positioning. The hydride ligands resonate as an AB quartet at 23.14 τ and 24.99 τ , respectively, with J_{AB} = 16.9 H_z. Since CS is a better π-acceptor and σ-donor then CO it is proposed that the hydride trans to the thiocarbonyl will have its resonance shifted downfield to that trans to a carbonyl.

The strength of the Os-C bond linking the thiocarbonyl relative to that linking a carbonyl is illustrated by the mass spectrum cf the complex. This reveals that the thiocarbonyl group is removed only after the sequential loss of the two hydrides and the seven carbonyl groups.

Experimental

Laboratory grade solvents were used throughout. In a typical experiment $H_2Os_3(CO)_8(MeCN)S$ (0.1 g) and an excess of CS_2(5 cm^3) in cyclohexane (50 cm^3) were refluxed under a nitrogen atmosphere until i.r. monitoring indicated that no $H_2Os_3(CO)_8(MeCN)S$ remained (*ca*. 2 h). The reaction solution was cooled, filtered and evaporated to low volume and the mixture was separated by t.l.c. on thin silica plates eluting with 40% CH_2Cl_2/60% hexane. This yielded three bands, the first being $H_3Os_3(CO)_9S$ (*ca*. 15%) and the second being $H_2Os_3(CO)_7(CS)S_2$: the third has not yet been fully characterised. The latter two compounds are unstable on dry silica, so total evaporation of solvent from the plates should be avoided. $H_2Os_3(CO)_7(CS)S_2$ was crystallised from CH_2Cl_2/hexane mixtures giving amber crystals (*ca*. 10%). ^1H NMR (CD_2Cl_2) shows an AB pattern τ 23.14 ppm (1H), τ 24.99 ppm (1H); J_{AB} 16.9 Hz. IR(cm^{-1}) shows ν(CO) 2102 w, 2076 m, 2029 s, 2021 m, 1971 w and ν(CS) 1325 m. Mass spectrum shows $^m/_e$ 882-2H-7CO-CS-S.

Crystal Data. $C_8H_2O_7Os_3S_3$, mol. wt. 876.88, monoclinic, a 14.437(3), b 11.730(3), c 9.819(4) Å, β 104.79(2)°, V 1607.7 Å^3, D_c 3.62 g cm^{-2} for Z = 4, μ(Mo K_α) 240.43 cm^{-1}; space group $P2_1$. Intensity data ($2\theta < 60.0°$) were recorded on a Stoe AED four-circle diffractometer with monochromated Mo K_α radiation and an ω/θscan technique. The structrue was refined by full-matrix least squares to R - 0.046 and R_w = 0.045 for 2877 unique observed intensities.

Acknowledgements

We thank the S.R.C. for financial support and Imperial Chemical Industries Ltd. for a grant to J.R.T.

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