Preliminary communication

REACTIONS OF CS_2 WITH METAL CLUSTER CARBONYLS OF THE IRON TRIAD: SYNTHESIS AND X-RAY STRUCTURE OF $Os_3(CO)_8(CS)S_2$

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Summary

The reaction of $Os_3(CO)_{12}$ with CS_2 in hexane at 130°C under 10 atm. CO/Ar (1/1) pressure gives $Os_3(CO)_8(CS)S_2$ as the major hexane eluted product. This has been fully characterised by spectroscopic and single crystal X-ray crystallographic techniques.

Few reactions of CS_2 with metal cluster carbonyls and their derivatives have been reported [1—7]. The reaction with $Co_2(CO)_8$ has shown [1—3] that the CS_2 molecule can be easily broken down, and may rearrange on the cluster core to give carbide, sulphide and various C_xS_y groups (e.g. x, y = 2, 2 [1,3]; 1, 2 [2]) as the products.

Whilst there are three examples of μ_2-CS groups coordinated to bimetal centres joined by metal—metal bonds [8—10], there are only two characterised complexes where CS has been found coordinated to a larger cluster core. In $[(\eta^5-C_5H_5)Co]_3(\mu^3-CS)]$ [11] the CS ligand caps the Co_3 triangle, while in $H_2Os_3(CO)_7(CS)S_2$ [7] the CS ligand is terminal.

In this communication we report the reaction of CS_2 with $Os_3(CO)_{12}$. Two hexane eluted products were obtained, $Os_3(CO)_8(CS)S_2$ and a much smaller quantity of the known complex $Os_3(CO)_9S_2$ [12]. A variety of reaction conditions were employed, both in the autoclave, and in refluxing solvent under N_2 at 1 atm. For the latter, refluxing CS_2, hexane, MeOH and EtOH gave no reaction, whilst in n-heptane a very slow reaction occurs from which only $Os_3(CO)_{12}$ and a little totally insoluble material were obtained. In refluxing n-octane, traces of $Os_3(CO)_8(CS)S_2$ and $Os_3(CO)_9S_2$ were identified by mass spectral and $\nu(CO)$ infrared data. In the autoclave, the optimum conditions for producing $Os_3(CO)_8(CS)S_2$ were to use an excess of CS_2 in hexane under a low pressure of CO/Ar at 130° C (see Experimental).

In the employed conditions, $Os_3(CO)_8(CS)S_2$ and $Os_3(CO)_9S_2$ comprise the total product eluted by n-hexane (ca. 15%). The heavy orange baseline of this chromatograph eluted in an acetone/hexane mixture to give a large number of

bands of similar intensity and R_F value; identification of these has not proved possible as yet.

The molecular geometry of $Os_3(CO)_8(CS)S_2$ has been established by a single-crystal X-ray analysis. The structure is shown in Fig. 1 and some important bond parameters are given in Table 1. As in $H_2Os_3(CO)_7(CS)S_2$ [7], the Os_3 core forms a wide "V", so that one edge of the Os_3 triangle ($Os(1)\cdots Os(3)$ 3.642(3) Å) is non-bonding. The two S atoms act as μ_3-ligands, and cap either side of the Os_3 triangle. The $S\cdots S$ distance of 3.030(12) Å suggests that there is little direct interaction. The terminal thiocarbonyl group is linear and occupies an equatorial site on $Os(1)$. The $C(11)$—$S(3)$ distance in this ligand indicates the presence of significant C—S multiple bonding.

Spectroscopic studies indicate that this structure is retained in solution, and details of spectroscopic and analytical data are given in Table 2.

The product $Os_3(CO)_8(CS)S_2$ may be regarded as both a parent compound of $H_2Os_3(CO)_7(CS)S_2$ [7], which has a similar structure except that two edge
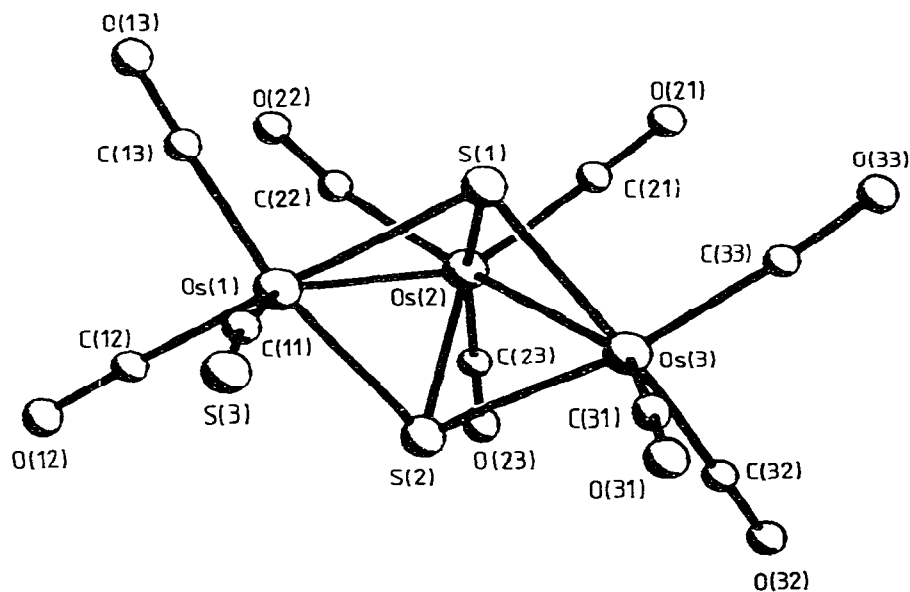

Fig. 1. The molecular structure of $Os_3(CO)_8(CS)S_2$.

TABLE 1

BOND LENGTHS (Å) AND ANGLES (°) IN $Os_3(CO)_8(CS)S_2$

Os(1)—Os(2) 2.830(2)	Os(1)—S(1) 2.380(9)
Os(2)—Os(3) 2.780(2)	Os(2)—S(1) 2.440(9)
Os(1)—C(11) 1.890(1)	Os(3)—S(1) 2.400(9)
C(11)—S(3) 1.471(14)	Os(1)—S(2) 2.365(10)
	Os(2)—S(2) 2.408(11)
	Os(3)—S(2) 2.381(9)
Os(1)—Os(2)—Os(3) 81.0(1)	Os(1)—S(1)—Os(2) 71.9(2)
Os(1)—C(11)—S(3) 172.2(25)	Os(1)—S(1)—Os(3) 99.3(3)
Os(2)—Os(1)—C(11) 144.2(9)	Os(2)—S(1)—Os(3) 70.1(3)
S(1)—Os(1)—C(11) 97.7(11)	Os(1)—S(2)—Os(2) 72.7(3)
S(2)—Os(1)—C(11) 102.2(11)	Os(1)—S(2)—Os(3) 100.3(4)
	Os(2)—S(2)—Os(3) 71.0(3)

TABLE 2

IR ν(CO)(cm^{-1})^a	2091m, 2074m, 2067s, 2051ms, 2040(sh), 2019(sh), 2013s, 1995m, 1982(sh)
ν(CS)(cm^{-1})^b	1324
^{1}H NMR	blank
Mass spectrum^c	m/e 908 − 8(CO) − (CS) − (S) − (S)
M.p. (°C)	127—128
Microanalysis^d	C, 12.59 (11.89); H, 0.19 (00); S, 10.85 (10.57)

^{a}Perkin—Elmer 257 grating IR spectrometer; cyclohexane solution; relative to 2143 cm^{-1} band of CO (g). ^{b}Perkin—Elmer 557 grating IR spectrometer, CH$_2$Cl$_2$ solution; relative to 1603 cm^{-1} band of polystyrene. ^{c}AEI MS 12: using tris(perfluoroheptyl)-s-triazine reference, 70 eV, 100°C. ^{d}Expected values in parentheses: C, H performed by University Chemical Laboratory Macroanalytical Service; S performed by Butterworth's, London.

bridging hydrides "replace" one of the carbonyl groups on Os(2), and as a derivative of Os$_3$(CO)$_9$S$_2$ [12].

The tendency for thiocarbonyl ligands to either μ_2- or μ_3-bridge metal cluster units has been noted [11,13]. However, in both Os$_3$(CO)$_8$(CS)S$_2$ and H$_2$Os$_3$(CO)$_7$(CS)S$_2$ [7] a terminal thiocarbonyl group has been observed. This may result simply from the length of the Os—Os bonds, as it is noted that the occurrence of bridging CO ligands diminishes rapidly with an increase in metal—metal bond length [14].

Experimental

Reactions were carried out in a Roth laboratory autoclave of 50 ml capacity. Os$_3$(CO)$_{12}$ was prepared by a literature method [15]. CS$_2$ was AR grade and was stored over 5A molecular sieve. Hexane, CH$_2$Cl$_2$ and cyclohexane (except that used for TLC) were distilled under N$_2$ over CaH$_2$ and stored under N$_2$. Operations to fill the autoclave were performed whilst flushing with N$_2$ and, once filled, the autoclave was purged by pressuring to ca. 50 atm. with either CO or Ar, and this operation repeated several times. In a typical reaction, 100 mg Os$_3$(CO)$_{12}$, 5 ml CS$_2$ and 40 ml hexane were used; 10 atm. of CO/Ar (1/1) was introduced and the autoclave heated at 130°C for 10 h.

After transfer to a Schlenk tube, the reaction mixture was evaporated to dryness and extracted with ca. 20 ml of warm cyclohexane. Chromatography of this solution (thin silica plates, Merck Kieselgel 60) eluting with hexane gives two very close yellow bands; care must be taken not to allow total solvent evaporation from the silica since Os$_3$(CO)$_8$(CS)S$_2$ decomposes rapidly on dry silica. The R_F values of Os$_3$(CO)$_8$(CS)S$_2$ and Os$_3$(CO)$_9$S$_2$ are very similar and often these have to be removed from the plates together; however, the former predominates in the mixture and can be crystallised pure from the solution. Os$_3$(CO)$_9$S$_2$ was identified by its presence in the ν(CO) infrared and mass spectra. Crystallisation was achieved by cooling a hexane solution in stages from room temperature to −5°C; this gives amber crystals (ca. 12% yield).

Crystal data: C$_9$O$_8$Os$_3$S$_3$, mol. wt. 902.87, triclinic, a 9.630(12), b 9.982(7), c 9.978(8) Å, α 99.62(6), β 116.11(8), γ 89.67(8)°, V 845.7 Å^3, D_c 3.54 g cm^{-3} for Z = 2, μ(Mo-K_α) 228.6 cm^{-1}, space group $P\bar{1}$. 2828 intensities (3.0 < 2θ < 55.0°) were recorded on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo-K_α radiation and an $\omega/2\theta$ scan technique. Absorption and Lp corrections were applied and the reflections averaged to give 2205 unique observed

intensities $|F > \epsilon_7(F)|$. The Os atoms were located by multisolution Σ_2 sign expansion, and the remaining atoms from a difference synthesis. The structure was refined by full-matrix least squares with all atoms assigned anisotropic thermal parameters; weak constraints were placed on the Os—C bond lengths to make them 1.89 Å. The current residuals are $R = 0.101$ and $R_w = \Sigma w^{\frac{1}{2}} \Delta w^{\frac{1}{2}} |F_0| = 0.099$.

Acknowledgements

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