Reactions of CS_2 with Metal Cluster Carbonyls of the Iron Triad: Reaction of $[Os_6(CO)_{18}]$ and *X*-Ray Crystal Structure of $[Os_4(CO)_{12}(CS)S]$ †

By **Peter V. Broadhurst, Brian F. G. Johnson, Jack Lewis,*** and **Paul R. Raithby,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The reaction of $[Os_6(CO)_{18}]$ with excess CS_2 in heptane at 165 °C under CO pressure gives the known compounds $[Os_3(CO)_8(CS)S_2]$ (1) and $[Os_3(CO)_9S_2]$ (2), and also $[Os_4(CO)_{12}(CS)S]$ (3). A single crystal *X*-ray diffraction study shows that in (3) the four Os atoms adopt a ' butterfly ' configuration, but with an Os ··· Os separation of 3.598(2) Å across the ' backbone ', which is non-bonding. Three of the Os atoms are capped by a μ_3-S ligand, while a CS ligand, which acts as a four-electron donor, lies on the other side of the metal framework. The carbon atom of this ligand is co-ordinated to all four metal atoms but the sulphur atom is only co-ordinated to one. The molecule (3) crystallises in space group $P\bar{1}$ with $a = 14.834(6)$, $b = 10.048(5)$, $c = 7.682(5)$ Å, $\alpha = 108.84(3)$, $\beta = 92.99(3)$, $\gamma = 95.64(3)$°, and $Z = 2$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked-cascade least squares to $R = 0.058$ for 3 249 observed diffractometer data.

THIOCARBONYL groups are known to act as two-, four-, and six-electron donors. The two-electron donors are of μ-CS type, observed in $[Os_3(CO)_7(CS)S_2H_2]$ [1] and $[Os_3(CO)_8(CS)S_2]$,[2] and of the μ_3-CS type in $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$.[3,4] Related four-electron donors are found in $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)\{(\mu_3\text{-}CS)Cr(CO)_5\}]$ [3,4] and $[Fe_4(CO)_{12}(CS)S]$,[5] and a six-electron donor exists in $[Fe_5(CO)_{13}(CS)S_2]$.[6]

Here we report the preparation of $[Os_4(CO)_{12}(CS)_2S]$ from the reaction of $[Os_6(CO)_{18}]$ with CS_2. An *X*-ray crystal structure analysis shows it to have a different geometry to $[Fe_4(CO)_{12}(CS)S]$.[5]

RESULTS AND DISCUSSION

The reaction of $[Os_6(CO)_{18}]$ with an excess of CS_2 in heptane was performed at 165 °C under 45 atm ‡ pressure of CO for 4 h. Yields of *ca.* 8% of $[Os_3(CO)_9S_2]$ (2) [7] and of $[Os_4(CO)_{12}(CS)S]$ (3) resulted together with traces of $[Os_3(CO)_8(CS)S_2]$ (1) [2] and two other products which have not been identified but which on the basis of mass spectroscopic data may be Os_4 (*m*/*e* 1 256) and Os_2 (*m*/*e* 748) species.

Under the reaction conditions employed $[Os_6(CO)_{18}]$ may also be converted to $[Os_3(CO)_{12}]$ in reasonable yield.[8] It appeared possible, therefore, that at least some of the products were derived from the triosmium carbonyl. When reacted with CS_2 under similar conditions, $[Os_3(CO)_{12}]$ gave only the Os_3 products (1) and (2) in about the same yield as above. Thus, $[Os_4(CO)_{12}(CS)S]$ (3) and the two other, unidentified products must result from the direct reaction of $[Os_6(CO)_{18}]$.

Infrared spectroscopic data suggest that $[Os_4(CO)_{12}(CS)S]$ (3) is not isostructural with its iron analogue; there are significant differences in the ν(CO) patterns and the value of ν(CS) in (3) is significantly lower, at 843 cm^{-1} {*cf.* 963 cm^{-1} in $[Fe_4(CO)_{12}(CS)S]$ [5]}. The structure was established by single-crystal *X*-ray analysis and is shown in Figure 1. Some selected bond parameters are listed in Table 1.

TABLE 1

Selected bond parameters

(*a*) Bond lengths (Å)			
Os(1)–Os(2)	2.829(1)	Os(1)–S(1)	2.445(4)
Os(1)–Os(4)	2.852(1)	Os(2)–S(1)	2.419(4)
Os(2)–Os(3)	2.812(1)	Os(3)–S(1)	2.434(5)
Os(3)–Os(4)	2.859(1)	Os(1)–C(1)	2.206(19)
Os(4)–S(2)	2.447(5)	Os(2)–C(1)	2.161(19)
S(2)–C(1)	1.757(18)	Os(3)–C(1)	2.164(14)
		Os(4)–C(1)	2.107(18)
(*b*) Bond angles (°)			
Os(2)–Os(1)–Os(4)	93.6(1)	Os(2)–Os(1)–S(1)	54.0(1)
Os(1)–Os(2)–Os(3)	79.3(1)	Os(4)–Os(1)–S(1)	86.9(1)
Os(2)–Os(3)–Os(4)	93.8(1)	Os(1)–Os(2)–S(1)	54.9(1)
Os(1)–Os(4)–Os(3)	78.1(1)	Os(3)–Os(2)–S(1)	54.8(1)
Os(2)–Os(1)–C(1)	48.9(5)	Os(2)–Os(3)–S(1)	54.3(1)
Os(4)–Os(1)–C(1)	47.1(5)	Os(4)–Os(3)–S(1)	86.9(1)
Os(1)–Os(2)–C(1)	50.3(5)	Os(4)–S(2)–C(1)	57.4(6)
Os(3)–Os(2)–C(1)	49.5(4)	Os(1)–C(1)–S(2)	119.5(8)
Os(2)–Os(3)–C(1)	49.4(5)	Os(2)–C(1)–S(2)	129.7(9)
Os(4)–Os(3)–C(1)	47.1(5)	Os(3)–C(1)–S(2)	123.1(10)
Os(1)–Os(4)–C(1)	50.1(5)	Os(4)–C(1)–S(2)	78.0(7)
Os(3)–Os(4)–C(1)	48.8(4)		

The Os_4 core can be described either as a distorted square with one osmium, Os(4), above the plane, or as a ' butterfly ' unit not bonded across the Os(1)–Os(3) ' backbone '. The bonded osmium–osmium distances indicate single-bond interactions and there are three terminal carbonyl ligands associated with each osmium.

A μ_3-S ligand caps the Os(1)Os(2)Os(3) triangle, lying 1.61 Å from this plane, and on the other side of the Os_4 unit is bonded the thiocarbonyl ligand. The carbon atom of the CS group is nearly equidistant from all four osmium atoms. The average Os–C separation of 2.16(2) Å is significantly less than the sum of covalent radii (2.21 Å) indicating a strong interaction. The sulphur bonds to Os(4) only. The C–S distance is 1.757(18) Å and approaches that typical for a single C–S bond (1.81 Å).

There is a non-crystallographic plane of symmetry bisecting the plane containing the Os(2), Os(4), C(1), S(2),

† Dodecacarbonyl-μ_3-sulphido-μ_4-(thiocarbonyl-*C*,σ-*S*)-tetra-osmium(4 *Os*–*Os*).

‡ Throughout this paper: 1 atm = 101 325 Pa.

and S(1) atoms and the overall symmetry of the molecule leads to the simple ν(CO) pattern observed.

Assuming a normal four-electron donation by the μ_3-S group, the CS ligand must formally donate four electrons for the cluster to be considered 'electron precise', *i.e.* to obey the 18-electron rule.

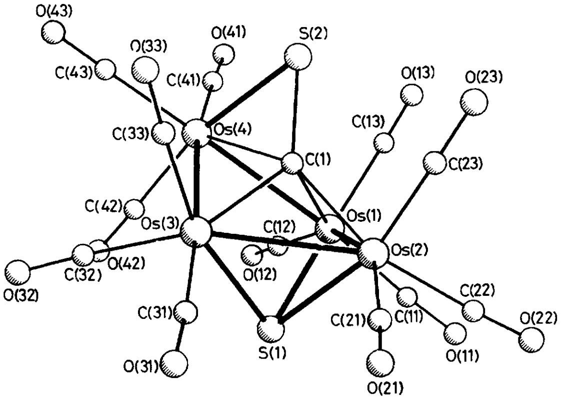

FIGURE 1 Molecular structure of $[Os_4(CO)_{12}(CS)S]$

The C–S separation in (3) is significantly longer than in $[Fe_5(CO)_{13}(CS)S_2]$ [6] where the group acts as a six-electron donor but is bonded similarly at the carbon. The values of ν(CS) are consistent with the observed bond lengths. This increase in bond length may be a consequence of the larger Os_4 unit compared to Fe_4, but it is also reasonable to consider that the extra two electrons donated in the iron case are derived from a lone pair isolated at the sulphur atom rather than from the C–S π bonding.

TABLE 2

Examples of bonding of CO ligands [a]

Bond type	No. of e⁻ donated	Example	C–O/Å	Bond order	M–C/Å	Ref.
μ–C, σ–O	4	$[Mn_2(dppm)_2(CO)_5]$ [b]	1.10(1)	3	1.93(1), 2.01(1)	*c*
μ_4–C, σ–O	4	$[Fe_4(CO)_{13}H]^-$	1.26(1)	1.74	1.81(1), 3 × 2.10(2)	*d*
μ_3–C, μ–O	6	$[\{Nb(\eta^5\text{-}C_5H_5)\}_3(CO)_7]$	1.30(1)	1.54	1.97(1), 2 × 2.22(3)	*e*

[a] Typical bond lengths: C–O 1.43, C=O 1.20, C≡O 1.13 Å. [b] dppm = Bis(diphenylphosphino)methane. [c] C. J. Commons and B. F. Hoskins, *Aust. J. Chem.*, 1975, **28**, 1663. [d] M. Manassero, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 1976, 919. [e] W. A. Herrmann, H. Biersack, M. L. Ziegler, K. Weidenhammer, R. Siegel, and D. Rehder, *J. Am. Chem. Soc.*, 1981, **103**, 1692; W. A. Herrmann, M. L. Ziegler, K. Weidenhammer, and H. Biersack, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 960.

There is no increase in the C–S bond length between the four- and six-electron donor cases. This may be taken to indicate that there is little tendency for the CS ligand to co-ordinate *via* any C–S multiple bond in the Chatt–Dewar manner. This is also supported by the observation that in both $[Os_4(CO)_{12}(CS)S]$ (3) and $[Fe_5(CO)_{13}(CS)S_2]$ [6] the metal–carbon distances for the bonded CS group are similar to those observed in certain carbide clusters, *e.g.* $[Os_5C(CO)_{15}]$.[9] This suggests that the Os_4–C, Os–C, and C–S interactions are largely independent with no use of C–S π orbitals in the interaction with Os_4.

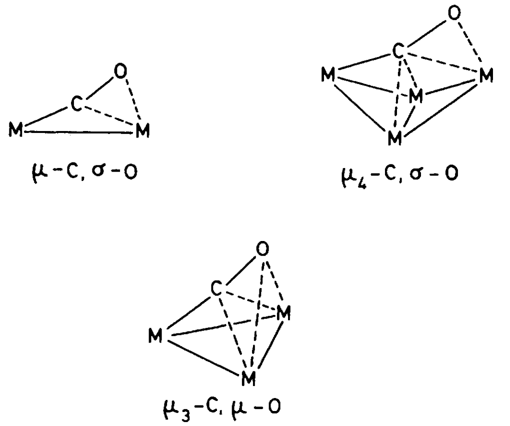

FIGURE 2 CO bonding modes which donate four or six electrons to a cluster core

Comparing the examples of the thiocarbonyl ligand which donate more than two electrons with the corresponding class of carbonyl ligand suggests that whereas CS π bonding is largely lost, this is not the case with CO. Data are given in Figure 2 and Table 2 for the CO complexes and in Figure 3 and Table 3 for the CS derivatives.

Examination of these data suggests that there is some retention of C–O π bonding. First, using bond length as a criterion, the bond orders variously exceed 1.5 indicating some multiple bonding, although metal back-donation to ligand π* orbitals in both linear and Chatt–Dewar fashions would also be expected to reduce the bond order.

Second, the metal–carbon distance is least between a carbon and a metal atom which have a nearest-to-

TABLE 3

Examples of bonding of CS ligands *

Bond type	No. of e⁻ donated	Example	C–S/Å	Bond order	M–C/Å	Ref.
μ_3–C, σ–S (i)	4	$[Fe_4(CO)_{12}(CS)S]$	1.70(1)	1.54	1.88(1), 2.01(1), 2.03(1)	5
μ_3–C, σ–S (ii)	4	$[\{Co(\eta^5\text{-}C_5H_5)\}_3(S)\{(CS)Cr(CO)_5\}]$	1.68(2)	1.64	3 × 1.91(2)	3, 4
μ_4–C, σ–S	4	$[Os_4(CO)_{12}(CS)S]$	1.76(2)	1.27	4 × 2.16(2)	—
μ_4–C, μ–S	6	$[Fe_5(CO)_{13}(CS)S_2]$	1.71(2)	1.50	4 × 1.96(2)	6

* Typical bond lengths: C–S 1.82, C=S 1.60 Å.

linear M–C–O arrangement. This suggests different types of M–C interaction, the shortest corresponding to a metal–carbon interaction as found for a terminal carbonyl group, the rest to interactions of the C–O π bond in a fashion analogous to certain co-ordination modes of olefinic and acetylenic ligands.

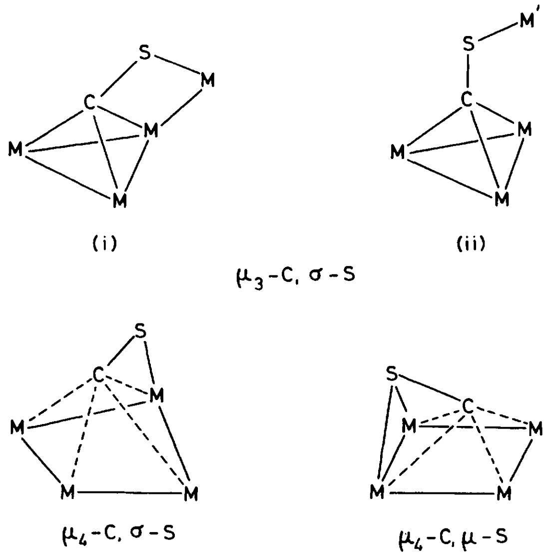

FIGURE 3 CS bonding modes which donate four or six electrons to a cluster core

For the thiocarbonyl cases, the C–S bond lengths suggest a slightly lower bond order. Also, with one exception, the CS carbon is equidistant from each metal atom indicating equivalent interactions. This would not be the case if part of the donation were from C–S π bonding and suggests that the M_n–C, M–S, and C–S interactions are independent. In the exception, $[Fe_4(CO)_{12}(CS)S]$,[5] the sulphur is bonded to a metal atom attached terminally to a triangular unit and is likely to cause the observed distortion towards this side of the triangle: it *does not* correspond to a *quasi*-linear M–C–S arrangement.

This difference in behaviour corresponds with the weaker (p_π–p_π) bonding between carbon and sulphur than between carbon and oxygen, demonstrating that the former is lost more readily.

However, this apart, it has been demonstrated that the thiocarbonyl ligand displays a wide variety of co-ordination modes to match the range observed for the carbonyl ligand.

EXPERIMENTAL

Reactions were performed in a Röth laboratory autoclave of 100 cm³ capacity. The autoclave was charged while flushing with N_2 and, once sealed, was purged of any air by pressuring to *ca.* 50 atm with the reaction gas and then venting, performing this a few times. Reaction solvents had been distilled under N_2 over an appropriate drying agent, precleaning saturated hydrocarbons by stirring over concentrated H_2SO_4. Thin-layer chromatography was employed for separation using Merck pre-coated Kieselgel $60F_{254}$ plates of 0.25 mm thickness. $[Os_6(CO)_{18}]$ was prepared by a literature method[10] and AR grade CS_2 was stored over 5 Å molecular sieve before use.

Typically, $[Os_6(CO)_{18}]$ (200 mg, 0.126 mmol) and CS_2 (3 cm³) in n-heptane (40 cm³) were reacted under 45 atm CO at 165 °C for 4 h. After removal of solvent, the product mixture was redissolved in the minimum of CH_2Cl_2 and separated, eluting with CH_2Cl_2–hexane (15 : 85). This gave four bands, (*a*)—(*d*). These were identified as (*a*), a mixture of $[Os_3(CO)_8(CS)S_2]$ (1)[2] and $[Os_3(CO)_9S_2]$ (2);[7] crystallisation from hexane solution yielded (2) in 8% yield, the trace quantity of (1) being identified by spectroscopic means. (*b*), $[Os_4(CO)_{12}(CS)S]$ (3), crystallised from benzene–hexane solution by cooling in 8% yield. (*c*) and (*d*) were the two as yet unidentified products, which are present in low yield. Spectroscopic and analytical data for (3) are given in Table 4.

TABLE 4

Spectroscopic and analytical data for $[Os_4(CO)_{12}(CS)S]$

Infrared	ν(CO)[a]/cm^{-1}	2 077s, 2 058w, 2 023ms, 2 019 (sh), 2 007mw, 1 986vw
	ν(CS)[b]/cm^{-1}	843m

Mass spectrum:[c] *m*/*e* 1 180
M.p.: *ca.* 185 °C (decomp.)
Analysis[d] (%): C, 13.6 (13.3); H, 0.35 (0.00)

[a] Perkin-Elmer 257 spectrophotometer, in cyclohexane solution with NaCl solution cells (0.5 mm), with the CO absorption at 2 143 cm^{-1} as reference. [b] Perkin-Elmer 557 spectrophotometer, Nujol mull with NaCl plates, with the polystyrene absorption at 1 603 cm^{-1} as reference (for ^{192}Os). [c] A.E.I. MS12 at 70 eV and 90 °C using tris(perfluoroheptyl)-triazene as reference. [d] Performed by the University Chemical Laboratory microanalytical service; calculated values in parentheses.

TABLE 5

Atom co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	7 024(1)	8 656(1)	3 208(1)
Os(2)	8 663(1)	7 735(1)	1 803(1)
Os(3)	7 673(1)	5 135(1)	1 553(1)
Os(4)	6 656(1)	6 370(1)	4 607(1)
S(1)	7 160(3)	6 859(5)	232(6)
C(1)	7 877(12)	7 141(18)	3 784(22)
S(2)	8 194(4)	7 294(6)	6 082(6)
C(11)	7 119(19)	10 122(25)	2 149(39)
O(11)	7 185(17)	11 078(20)	1 604(32)
C(12)	5 738(15)	8 703(22)	3 211(31)
O(12)	4 988(11)	8 788(18)	3 240(25)
C(13)	7 260(15)	9 995(21)	5 701(28)
O(13)	7 380(14)	10 738(17)	7 149(23)
C(21)	9 404(13)	6 812(21)	−100(28)
O(21)	9 815(11)	6 229(19)	−1 228(24)
C(22)	8 919(15)	9 436(26)	1 144(29)
O(22)	9 099(14)	10 431(17)	827(29)
C(23)	9 670(16)	8 182(21)	3 556(29)
O(23)	10 274(11)	8 477(16)	4 694(23)
C(31)	8 258(16)	4 189(22)	−619(29)
O(31)	8 578(13)	3 564(17)	−1 911(22)
C(32)	6 663(16)	3 682(21)	790(26)
O(32)	6 044(12)	2 816(17)	261(25)
C(33)	8 309(15)	4 212(21)	3 001(28)
O(33)	8 689(12)	3 711(18)	3 902(25)
C(41)	6 021(17)	7 486(24)	6 615(30)
O(41)	5 673(14)	8 168(20)	7 769(24)
C(42)	5 584(15)	5 719(21)	2 961(32)
O(42)	4 298(10)	5 336(18)	2 029(22)
C(43)	6 607(15)	4 671(24)	5 324(31)
O(43)	6 628(12)	3 696(18)	5 706(26)

Crystal Structure Determination.—Orange 'wedge-shaped' crystals of [$Os_4(CO)_{12}(CS)S$] (3) were deposited from hexane. 4 274 Intensities were recorded on a Stoe four-circle diffractometer using graphite-monochromated Mo-K_α radiation, and a crystal of dimensions *ca.* 0.24 × 0.22 × 0.11 mm. Unit-cell dimensions were determined from the angular measurements of 20 strong reflections with $15 < 2\theta < 25°$. Data were collected in the range $3.0 < 2\theta < 55.0°$ using an ω/θ scan technique. Two reflections were monitored periodically throughout data collection and showed no significant variation.

A semi-empirical absorption correction, based on a pseudo-ellipsoid model, and Lorentz polarization corrections were applied, and equivalent reflections averaged to give 3 249 unique observed reflections [$F > 5\sigma(F)$].

Crystal data. $C_{13}O_{12}Os_4S_2$, $M = 1\,173.1$, Triclinic, $a = 14.834(6)$, $b = 10.048(5)$, $c = 7.682(5)$ Å, $\alpha = 108.84(3)$, $\beta = 92.99(3)$, $\gamma = 95.64(3)°$, $U = 1\,074.14$ Å^3, $F(000) = 1\,019.6$, D_m not measured, $Z = 2$, $D_c = 3.626$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 238.2$ cm^{-1}. Space group $P\bar{1}$ (no. 2) from the successful refinement.

The four Os atoms were located by multisolution Σ_2 sign expansion, and all the remaining atoms from a subsequent difference electron-density synthesis. The structure was refined by blocked-cascade least squares with all atoms assigned anisotropic thermal parameters. In the final cycles of refinement the weighting scheme $w = [\sigma^2(F) + 0.0004|F|^2]^{-1}$ was introduced. The converged residuals were $R = 0.058$ and $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o = 0.053$. Complex neutral-atom scattering factors [11] were employed throughout the refinement.

Table 5 lists the final atomic co-ordinates while details of anisotropic thermal parameters, bond lengths and angles, molecular least-squares planes, and observed and calculated structure factors are in Supplementary Publication No. SUP 23303 (25 pp.).*

[2/144 *Received, 25th January, 1982*]

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.