# $[Os_3(CO)_9H(SR)]$, a Highly Reactive Molecule. The *X*-Ray Structure of a π-Bound Ethylene Adduct $[Os_3(CO)_9H(C_2H_4)(SMe)]$

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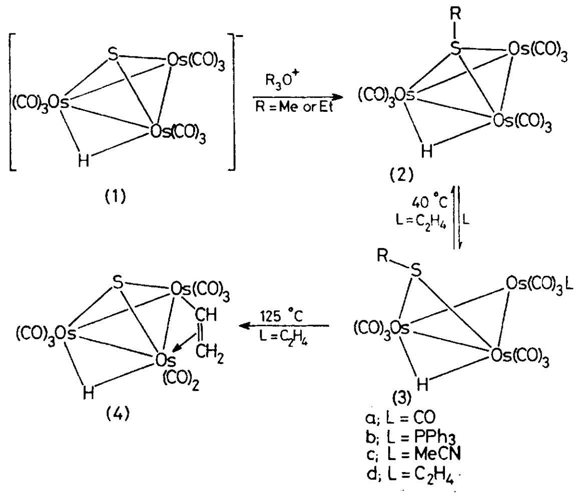
*Summary* The high reactivity of $[Os_3(CO)_9H(SR)]$ (R = Me or Et), associated with a variable co-ordination of the sulphur ligand, has enabled a range of adducts to be prepared; in particular the first *X*-ray diffraction study of a cluster containing ethylene π-bound to a single metal centre is reported.

There is considerable interest in molecules containing ligands which can generate additional co-ordination sites by changing the nature of their co-ordination. Thus for one-metal systems it has been proposed that the bending of linear nitrosyls or the π to σ conversion of π-allyl complexes may produce additional sites (in each case by changing from three-electron to one-electron donors). For two-metal species other systems are possible in addition. For example in $[Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2]$[1] the unusual four-electron donating bridging carbonyl can change to a normal two-electron donating terminal ligand, providing a site for the addition of carbon monoxide. We now present a system dependent on three metal atoms which involves a change from five- to three-electron donation by the SR ligand in $[Os_3(CO)_9H(SR)]$. This confers high reactivity upon the molecule and the chemical behaviour contrasts with that often found in attempts to substitute carbonyl groups in a cluster with other ligands.



Scheme

Initial attempts to prepare $[Os_3(CO)_9H(SR)]$ (R = Me or Et) by heating the easily prepared complex $[Os_3(CO)_{10}H(SR)]$ did not lead to the desired product. Consequently a different approach was adopted. The anion $[Os_3(CO)_9HS]^-$ (**1**) was prepared in good yield by treating $[Os_3(CO)_9H_2S]$[2] with methanolic potassium hydroxide, followed by precipitation as the yellow bis(triphenylphosphine)imminium salt. Treatment of (**1**) with $R_3O^+$ salts (R = Me or Et) in dry dichloromethane led to the formation of $[Os_3(CO)_9H(SR)]$ (**2**). The complexes (**2**) are not very stable under the reaction conditions and are conveniently trapped in high yield as ethylene adducts from which they can subsequently be easily regenerated (*vide infra*). The structure of (**1**) is similar to that of $[Ru_3(CO)_9H_2S]$[3] with a proton removed from one metal–metal edge.[4] It is proposed that the complexes (**2**) have an analogous structure to that of $[Fe_3(CO)_9H(SR)]$[5] where the sulphur atom spans all three metal atoms and is formally a five-electron donor to the metal triangle.

When carbon monoxide was bubbled through the solution of (**2**) the previously characterised compounds $[Os_3(CO)_{10}H(SR)]$ (**3a**) were formed. These are known to have the structure shown in the Scheme[6] where the sulphur ligand now spans two osmium atoms. Thus a site for the extra carbonyl ligand is provided by the sulphur ligand changing from face-bridging (five-electron donor) to edge-bridging (three-electron donor).

Treatment of (**2**) with triphenylphosphine, acetonitrile, and ethylene led to the formation of the adducts (**3b**), (**3c**), and (**3d**), respectively. The adduct (**3d**; R = Me) was also prepared in lower yield by treating $[Os_3(CO)_{10}H(SMe)]$ with trimethylamine oxide in dichloromethane under an ethylene atmosphere. The structure of this adduct was determined by *X*-ray diffraction. Pale yellow, approximately equidimensional crystals were deposited from n-pentane solution. A crystal of approximate dimensions 0·075 × 0·125 mm was chosen for analysis.

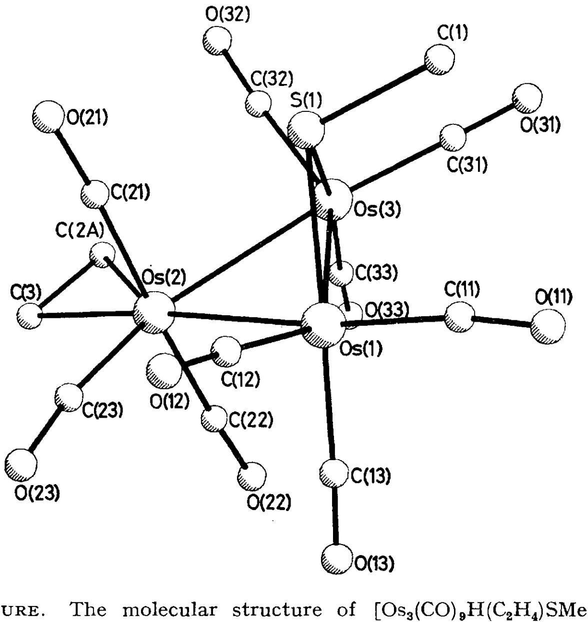


Figure. The molecular structure of $[Os_3(CO)_9H(C_2H_4)SMe]$. Some important bond parameters include: Os(1)–Os(2) 2·852(1), Os(1)–Os(3) 2·842(1), Os(2)–Os(3) 2·847(1), Os(1)–S(1) 2·402(7), Os(3)–S(1) 2·402(6), Os(2)–C(2A) 2·23(4), Os(2)–C(3) 2·23(4), C(2A)–C(3) 1·42 Å; ∠Os(2)–Os(1)–Os(3) 60·0(1), Os(1)–Os(2)–Os(3) 59·8(1), Os(1)–Os(3)–Os(2) 60·2(1), Os(1)–S(1)–Os(3) 72·5(2)°.

*Crystal data:* $C_{12}H_8O_9Os_3S$, $M = 808{\cdot}8$, monoclinic, $a = 10{\cdot}333(4)$, $b = 15{\cdot}735(5)$, $c = 11{\cdot}792(4)$ Å, $\beta = 98{\cdot}07(2)°$, $U = 1898.3$ Å$^3$; $D_c = 2{\cdot}83$ g cm$^{-3}$, $Z = 4$, $\mu$(Mo-$K_\alpha$) $= 201{\cdot}69$ cm$^{-1}$; space group $P2_1/n$. 3795 intensities ($3{\cdot}0 < 2\theta < 50{\cdot}0°$) were measured on a Nonius CAD 4 diffractometer, using zirconium filtered Mo-$K_\alpha$ radiation, and an $\omega/2\theta$ scan technique. These data were corrected for absorption, and averaged to give 2014 unique observed $[I > 2{\cdot}5\sigma(I)]$ reflections.†

The three osmium atoms were located by multisolution $\Sigma_2$ sign expansion, and the non-hydrogen atoms from a subsequent difference electron density synthesis. The ethylene ligand and the equatorial carbonyl group bonded to Os(2) were found to be positionally disordered in a *ca.* 2 : 1 ratio. In order to obtain a suitable model for refinement of the disordered unit the four Os–C (ethylene) distances were constrained to be equal, as were the two C–O carbonyl distances, and these bond lengths were allowed to refine. The ethylene C–C distances were fixed at 1·42 Å, and the Os–C (carbonyl) lengths at 1·89 Å. Full-matrix least-squares refinement, with the Os and S atoms assigned anisotropic thermal parameters, yielded residuals of $R$ 0·055 and $R'[= (\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_0|] = 0{\cdot}057$.

The molecular geometry is shown in the Figure, which includes the atom numbering scheme, and some important bond lengths and angles. Only one arrangement of the ethylene ligand and equatorial carbonyl is shown for clarity. The three osmium atoms define an almost equilateral triangle, the shortest edge of which is symmetrically bridged by the sulphur atom of the methanethiolato ligand. The $Os_2S$ plane makes an angle of 103·5° with the metal triangle. The hydride ligand is thought to bridge the same Os–Os edge and lie on the opposite side of the triangle. A similar configuration has been reported for $[Os_3(CO)_{10}H(SEt)]$.[6] All nine carbonyls are linear and terminal, occupying axial and equatorial sites as found in $[Os_3(CO)_{12}]$,[7] but with an axial carbonyl on each Os(1) and Os(3) replaced by the bridging methanethiolato group, and a single equatorial carbonyl replaced by a $\pi$-bonded ethylene ligand on Os(2). The organic group is coplanar with the metal triangle (maximum deviation 0·010 Å), but, because of the disorder of this ligand and the equatorial carbonyl group, it is difficult to assess the detailed geometry of the olefin–metal arrangement.

The ethylene ligand is easily displaced thermally from (**3d**) to give either (**2**), or in the presence of other ligands L, complexes of the type $[Os_3(CO)_9H(SR)L]$. On heating (**3d**) in n-octane under an ethylene atmosphere $[Os_3(CO)_8H(CH{:}CH_2)S]$ (**4**) was formed. This conversion of a $\pi$-bound ethylene into a vinyl ligand has been proposed previously with regard to the interaction of $[Os_3(CO)_{12}]$ with ethylene but has not previously been observed. The compound (**4**) was also prepared, in higher yield, by the reaction of $[Os_3(CO)_8H_2(C_2H_4)S]$ {from $[Os_3(CO)_9H_2S]$ and $Me_3NO$ under ethylene} with acetylene. The weakly bound ethylene ligand is displaced by the acetylene molecule which then inserts into an Os–H bond {in a manner similar to that proposed for the reaction of $[Os_3(CO)_{10}H_2]$ and acetylene}.[8]

It was not possible to displace thermally the more strongly bound ligands L (*i.e.* CO and $PPh_3$) from (**3**), but preliminary results indicate that the related ruthenium compound $[Ru_3(CO)_{10}H(SPr^i)]$ undergoes reversible carbon monoxide loss to $[Ru_3(CO)_9H(SPr^i)]$ in refluxing hexane. This did not occur for $[Os_3(CO)_{10}H(SPr^i)]$ even under more vigorous conditions. In a similar manner $[Os_3(CO)_{10}HI]$ loses carbon monoxide reversibly to give $[Os_3(CO)_9HI]$.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre' University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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