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Conversion of the cluster $[Os_3(CHCFc)(CO)_{10}]$ (CHCFc = ethynylferrocene) into $[Os_3(S)(CHCFc)(CO)_9]$ by reaction with sulphur. Crystal structures of these clusters and of $[Os_3H(C_2Fc)(CO)_9]$

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Abstract

By application of a method established for various alkynes, the cluster $[Os_3(CO)_{10}(MeCN)_2]$ was treated with ethynylferrocene (CHCFc) to give the alkyne cluster $[Os_3(\mu_3\text{-}CHCFc)(\mu\text{-}CO)(CO)_9]$ (**1**). This cluster loses CO thermally and by visible irradiation to form the hydrido-ferrocenylethynyl cluster $[Os_3H(\mu_3\text{-}C_2Fc)(CO)_9]$ (**2**), but if the decarbonylation is carried out in the presence of sulphur at room temperature under visible irradiation, the cluster $[Os_3(\mu_3\text{-}S)(\mu_3\text{-}CHCFc)(CO)_9]$ (**3**) is formed instead. The crystal structures of **1**, **2**, and **3** are reported. Clusters **1** and **3** are both 48-electron clusters containing μ_3-CH≡CFc ligands but, whereas **1** contains three Os–Os bonds, **3** contains only two. In **3** the triply bridging ligands occupy opposite faces of the Os_3 triangle, with the osmium atoms at the open edge of the triangle having σ-bonds to the alkyne ligand. The structure of **1** and the known structure of $[Os_3(PhC_2Ph)(CO)_{10}]$ are closely related, although cluster **1** contains one bridging CO ligand and the latter two semi-bridging CO ligands. The fluxionality of cluster **1** is considered in the light of these different structures.

Introduction

The μ_3-alkyne complexes $[Os_3(\text{alkyne})(CO)_{10}]$ are all of the same general type but there are different structures resulting from different arrangements of the carbonyl shell [1]. The cluster $[Os_3(PhC_2Ph)(CO)_{10}]$ has no bridging carbonyl

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ligands in the crystal [2,3], although there is a weak absorption around 1850 cm^{-1} in its solutions that can be assigned to an isomer containing a bridging carbonyl ligand. In this paper we describe some of our work on the use of ethynylferrocene [CH≡CFc; Fc = $(C_5H_4)Fe(C_5H_5)$] as a ligand in triosmium clusters which was initiated to see how the ferrocenyl substituent modifies the chemistry, and we present the single-crystal X-ray structure of $[Os_3(CHCFc)(CO)_{10}]$ (**1**), which adopts a different structure from that of the PhC_2Ph analogue. Normally terminal alkyne clusters of this type readily undergo thermal decarbonylation to give the oxidative addition product $[Os_3H(\mu_3\text{-}C{\equiv}CR)(CO)_9]$ [1] and in this respect the ferrocenyl compound **1** behaves as expected. However, decarbonylation of these clusters also occurs slowly at room temperature under visible irradiation, cluster **1** giving $[Os_3H(C_2Fc)(CO)_9]$ (**2**). In one such experiment we obtained a curious result. A solution of **1** in cyclohexane was allowed to stand in daylight and gave a different nonacarbonyl product (**3**) which was not a hydride and contained the alkyne ligand intact. Only after obtaining a mass spectrum and a single-crystal X-ray structure (reported in this paper) were we able to show that **3** is the sulphur-containing species $[Os_3(\mu_3\text{-}S)(\mu_3\text{-}CHCFc)(CO)_9]$ and we assume that the reaction solution had been contaminated with elemental sulphur or some sulphur compound.

After completion of this work a brief report appeared of compounds **1** and **2** and various related species, but no crystallographic studies were described [4].

Results and discussion

Synthesis of clusters

The synthesis of $[Os_3(CH{\equiv}CFc)(CO)_{10}]$ (**1**) from $[Os_3(CO)_{10}(MeCN)_2]$ by reaction with ethynylferrocene is a standard procedure used for many other alkynes (see Experimental and Scheme 1) [2,5–10]. The yield (70%) is, however, much higher than is generally observed for other alkynes. For many alkynes the lower yields result from a significant extent of alkyne coupling [11] leading to products such as $[Os_3(C_4H_2Fc_2)(CO)_9]$, which were not obtained in this case. Compound **1** is related spectroscopically to other alkyne clusters of this type and behaves chemically as expected. For example, it is converted thermally in refluxing heptane into the hydrido-compound $[Os_3H(C{\equiv}CFc)(CO)_9]$ (**2**) in good yield as the only isolable product (92%). This decarbonylation may also be carried out effectively by UV irradiation at room temperature. We also examined the use of visible light to induce this reaction and found that when a solution of cluster **1** in cyclohexane was kept in daylight (but not when it was kept in the dark) it was slowly converted into cluster **2**.

However, in one such attempt to carry out this conversion in daylight we were surprised to obtain a purple product **3** instead of the yellow compound **2**. This compound seemed very interesting because, although the IR $\nu(CO)$ spectrum clearly indicated that CO loss had occurred, since the absorption pattern is quite characteristic of a nonacarbonyl species, the μ_3-alkyne ligand evidently remained intact: the ^1H NMR spectrum showed a low-field signal at δ 9.25, as expected for a μ_3-terminal alkyne. Initially we thought that the product might be $[Os_3(CHCFc)(CO)_9]$, which would be stoichiometrically and structurally related to the known compound $[Os_3(PhC_2Ph)(CO)_7(dppm)]$ [12], that is with the alkyne perpendicular to an Os–Os bond. However, the high stability of **3** with respect to hydrogen atom transfer to

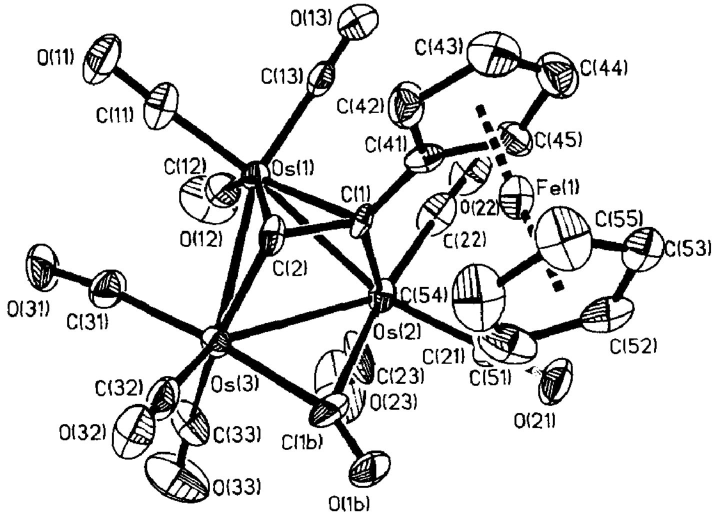


Fig. 1. Molecular structure of $[Os_3(CHCFc)(CO)_{10}]$ (cluster **1**).

osmium and its lack of reaction with CO are incompatible with this stoichiometry. The mass spectrum and a single-crystal X-ray structural study showed that compound **3** was $[Os_3(\mu_3\text{-}S)(\mu_3\text{-}CHCFc)(CO)_9]$, and that some sulphur impurity must have been introduced into the reaction mixture, leading to **3**. We have since shown that solutions of **1** in daylight in the presence of elemental sulphur do give **3** and that this is not formed, of course, if reagents and solvents are pure.

It seems likely that cluster **1** undergoes photochemical decarbonylation initially to $[Os_3(CHCFc)(CO)_9]$, which persists in solution long enough at room temperature to react with any suitable reagent present (such as sulphur), but in the absence of such a reagent isomerises to the hydrido-species **2**.

Structure of $[Os_3(CHCFc)(CO)_{10}]$ (cluster 1)

The molecular structure of **1** is shown in Fig. 1. Selected bond lengths and angles are in Table 1. The structure is compatible with 18-electron considerations, which require there to be three Os–Os bonds and the alkyne to be a 4-electron donor. This is bonded by two σ-Os–C bonds and an η^2-coordination through C(1) and C(2) to Os(1). Thus C(1)–C(2) is closely parallel to the Os(2)–Os(3) edge and the Os_3C_2 skeleton can be regarded as a *nido*-octahedron. The cyclopentadienyl rings are eclipsed, and the ferrocene group is directed away from Os(1) with the C_5H_4 ring closely coplanar with the C(1)C(2)Os(2)Os(3) ring, presumably to maximise $p\pi$–$p\pi$ bonding in the C(1)–C(41) bond. The presence of the ferrocenyl group does not seem to lead to any noticable distortion in the alkyne-to-metal cluster bonding.

One carbonyl ligand, C(1b)–O(1b), is bridging, and the other carbonyl ligands have OsCO angles in the range 172.3 to 178.1° and are normal terminal ligands. The bridging CO is, however, unsymmetrical, with Os(2)–C(1b) = 2.363(35) Å and Os(3)–C(1b) = 2.027(25) Å and angles Os(2)–C(1b)–O(1b) = 127.4(23)° and Os(3)–C(1b)–O(1b) = 151.9(28)°. There are only small differences in the coordination geometries of Os(2) and Os(3) as a result of this unsymmetrical arrangement. For example, the CO ligands *trans* to the bridge are positioned slightly differently; the angle C(31)–Os(3)–Os(1) of 73.7(9)° may be compared with the angle

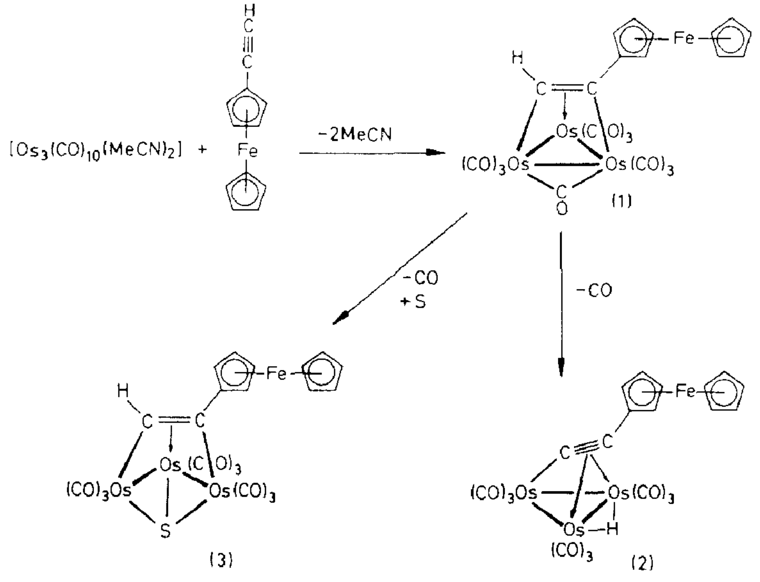
Table 1

Selected bond lengths (Å) and angles (°) for $[Os_3(CHCFc)(CO)_{10}]$ (cluster **1**)

Os(1)–Os(2)	2.743(1)	Os(3)–C(2)	2.13(2)
Os(1)–Os(3)	2.779(1)	Os(2)–C(1b)	2.36(4)
Os(2)–Os(3)	2.852(1)	Os(3)–C(1b)	2.03(3)
Os(1)–C(1)	2.35(2)	C(1)–C(2)	1.41(3)
Os(1)–C(2)	2.17(2)	C(41)–C(1)	1.46(3)
Os(2)–C(1)	2.11(2)	C(1b)–O(1b)	1.15(3)

	Range	Average
Os–CO (terminal)	1.88(3)–1.94(2)	1.902
C–O (terminal)	1.12(3)–1.19(4)	1.147
Fe–C (C_5H_4)	2.01(3)–2.06(3)	2.038
Fe–C (C_5H_5)	2.02(4)–2.08(3)	2.046
C–C (C_5H_4)	1.36(5)–1.44(4)	1.413
C–C (C_5H_5)	1.41(4)–1.46(4)	1.436

Os(3)–Os(1)–Os(2)	62.2(1)	C(1)–C(2)–Os(3)	112(2)
Os(2)–Os(3)–Os(1)	58.3(1)	Os(2)–C(1)–Os(1)	75.6(6)
Os(3)–Os(2)–Os(1)	71.3(5)	Os(3)–C(2)–Os(1)	80.4(8)
C(1)–Os(1)–Os(2)	48.3(4)	C(41)–C(1)–Os(2)	130(1)
C(2)–Os(1)–Os(3)	49.2(6)	C(41)–C(1)–Os(1)	124(1)
C(2)–Os(1)–C(1)	35.9(7)	C(41)–C(1)–C(2)	122(2)
C(1)–Os(2)–Os(1)	56.1(4)	C(1)–C(41)–C(42)	126(2)
C(2)–Os(3)–Os(1)	50.4(7)	C(1)–C(41)–C(45)	127(2)
C(2)–Os(3)–Os(2)	68.5(6)	C(1b)–Os(2)–Os(3)	44.5(6)
C(1)–Os(2)–Os(3)	71.3(5)	C(1b)–Os(3)–Os(2)	55(1)
C(1)–C(2)–Os(1)	79(1)	Os(3)–C(1b)–Os(2)	81(1)
C(2)–C(1)–Os(1)	65(1)	O(1b)–C(1b)–Os(2)	127(2)
C(2)–C(1)–Os(2)	108(1)	O(1b)–C(1b)–Os(3)	152(3)



Scheme 1

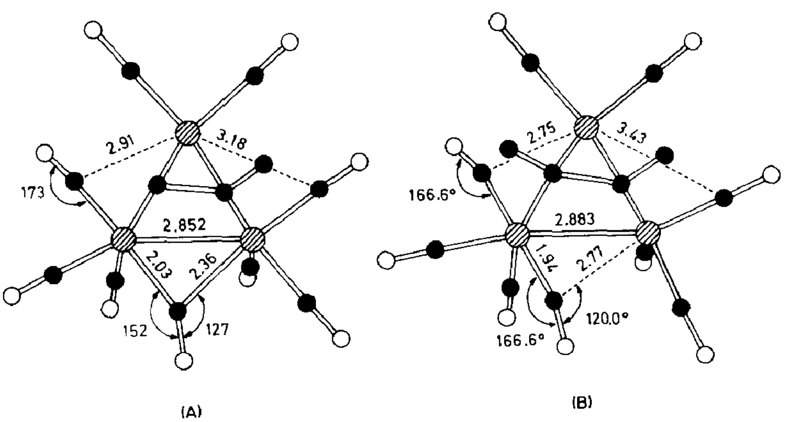


Fig. 2. A comparison of the structures of $[Os_3(CHCFc)(CO)_{10}]$ (A) (**1**) and of $[Os_3(PhC_2Ph)(CO)_{10}]$ (**B**) [2,3] stripping the alkynes down to the osmium-bound carbon atoms and atoms attached to these. The broken lines with lengths 2.75 and 2.77 Å in **B** indicate semi-bridging contacts, while other broken lines are non-bonding distances for comparison.

C(22)-Os(2)-Os(1) of 84.5(7)°. We believe that the slightly unsymmetrical geometry of cluster **1** does not arise from the presence of different substituents on the osmium-bound carbon atoms, since the symmetrical-alkyne cluster $[Os_3(PhC_2Ph)(CO)_{10}]$ is even less symmetrical [3]. The geometries of these two alkyne clusters are compared in Fig. 2. All the CO ligands in $[Os_3(PhC_2Ph)(CO)_{10}]$ were considered to be essentially terminal, although two semi-bridging ones have long range interactions with adjacent metal atoms indicated by broken lines in the Fig. 2. Although their structures are superficially very different, Figure 2 shows that they are actually very closely related. The structural details for **1** are consistent with small distortions from a structure with a symmetrical CO bridge towards the doubly semi-bridged geometry of the PhC_2Ph compound. Thus the carbonyl C(31)-O(31) has traces of incipient semi-bridging character as it is forced towards Os(1) as the bridging CO ligand is distorted from the symmetrical position. The Os(3)-C(31)-O(31) angle of 172.5(26)° and Os(1)-C(31) distance of 2.91 Å may be compared with the values of 166.6(8)° and 2.745(8) Å for the corresponding (semi-bridging) CO in the PhC_2Ph compound.

For different alkyne clusters of type $[Os_3(alkyne)(CO)_{10}]$ one could imagine a range of structures lying at various stages between those of the CHCFc and PhC_2Ph compounds. However, in solution and in the solid a good range of such compounds all have ν(CO) absorptions for the bridging carbonyl in the narrow range 1840-1850 cm^{-1}. Compound **1** has ν(CO) at 1844 cm^{-1} for a cyclohexane solution and at 1840 cm^{-1} for a KBr disc, showing that the solid state structure is also found in solution. The PhC_2Ph compound has no absorption in this region for the solid, but a weak absorption for the solution. These results indicate that in all cases one of the two extreme structures is adopted as a low energy state, and there is no intermediate structure observed which would be characterised by ν(CO) frequencies between 1850 cm^{-1} and normal terminal CO frequencies. In spite of this a superimposition of one structure on the other (Fig. 3) suggests that there should be little energy difference between the geometries and only a small energy barrier to their interconversion.

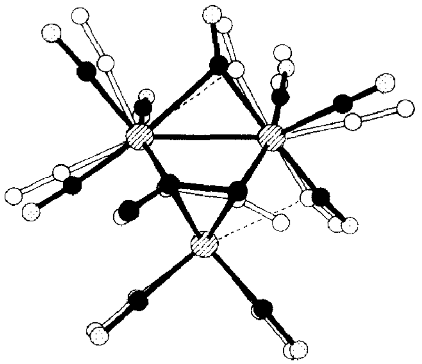


Fig. 3. The structures of $[Os_3(CHCFc)(CO)_{10}]$ (**1**) (on top with solid bonds) and of $[Os_3(PhC_2Ph)(CO)_{10}]$ [2,3] with the osmium atoms superimposed.

Compounds of the type $[Os_3(alkyne)(CO)_{10}]$ are fluxional in solution; in the case of compound **1** this can be seen in the ^1H NMR spectrum of the C_5H_4 group. Even with rapid rotation about the C(1)–C(41) bond the atoms C(42) and C(45), and likewise C(43) and C(44), are non-equivalent. Since the molecule is chiral, an inversion involving the motion of the C(1)–C(2) bond with respect to the metal triangle is required to produce a time-averaged plane of symmetry through the iron atom and hence exchange of the above pairs of carbon atoms. Figure 4 shows the

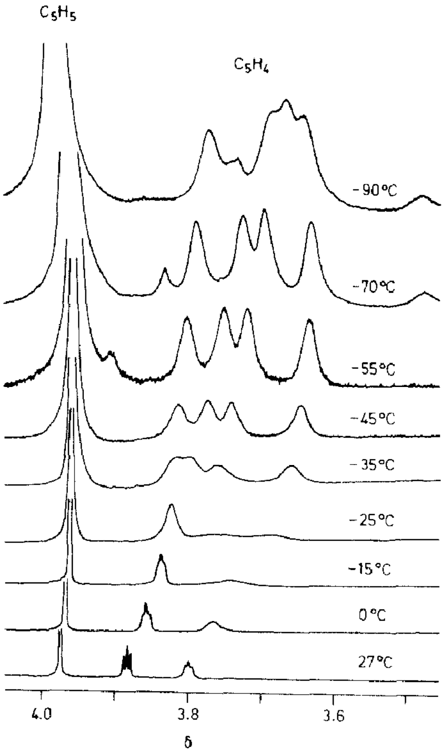
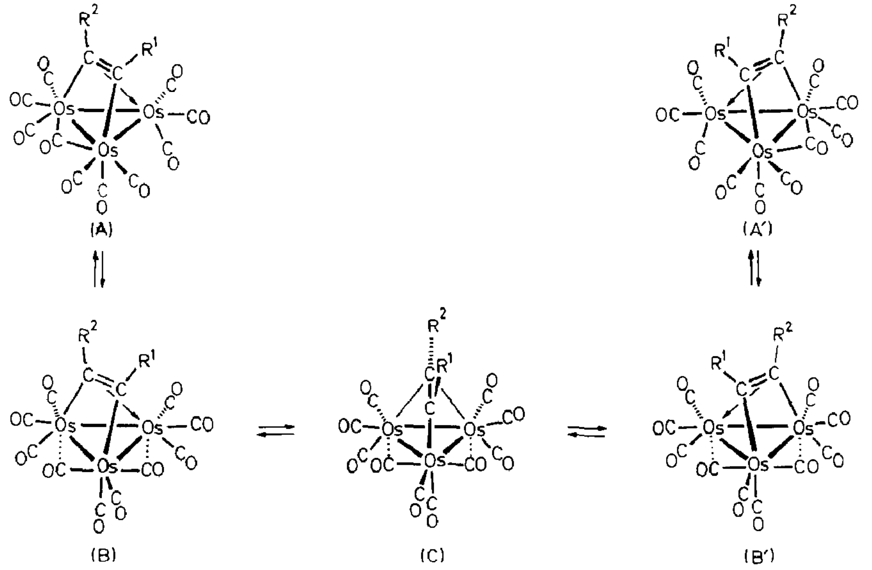


Fig. 4. ^1H NMR spectra of $[Os_3(CHCFc)(CO)_{10}]$ (**1**) recorded in $CDCl_3$ at 400 MHz in the C_5H_5 and C_5H_4 region.



Scheme 2

consequences of these exchanges in the ^{1}H NMR spectra. At room temperature there is a time-averaged plane of symmetry through the ferrocenyl group so that the C_5H_4 ligand gives an AA′BB′ spectrum. However, on cooling between 27 and −45 °C the two multiplets for the C_5H_4 group broaden and are resolved into four multiplets consistent with the structure in the crystal. Below −45 °C further weaker absorptions appear in this region of the spectrum, implying that there is another isomer which is exchanging rapidly above −45 °C with the major one but only slowly at low temperatures. This might be a another rotamer about the C(1)–C(41) bond or more likely an isomer with a different CO distribution. This could have a geometry like found for the PhC_2Ph compound in the crystal or like that of **1** but with the alkyne carbon atoms in reversed positions. It is notable that there are moderate temperature variations in the δ-values for the C_5H_4 group which possibly relate to rapid but changing equilibria between isomers above −45 °C.

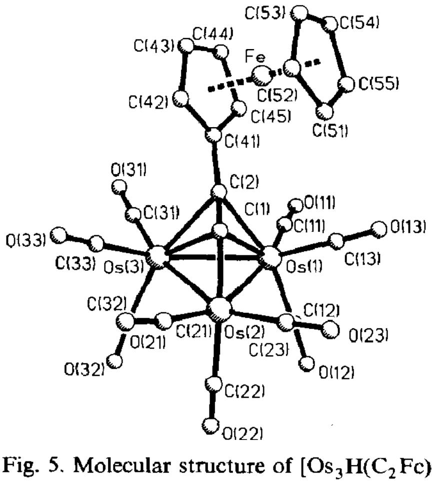


Fig. 5. Molecular structure of $[Os_3H(C_2Fc)(CO)_9]$ (cluster **2**).

Table 2

Selected bond lengths (Å) and angles (°) for [$Os_3H(C{\equiv}CFc)(CO)_9$] (cluster **2**)

Os(1)–Os(2)	2.8231(9)	Os(2)–C(2)	2.31(1)
Os(1)–Os(3)	2.8483(7)	Os(3)–C(1)	2.22(1)
Os(2)–Os(3)	2.8297(8)	Os(3)–C(2)	2.23(1)
Os(1)–C(1)	1.97(1)	C(1)–C(2)	1.31(2)
Os(2)–C(1)	2.24(1)	C(2)–C(41)	1.46(2)

	Range	Average
Os–CO	1.88(2)–1.93(1)	1.90
C–O	1.12(2)–1.18(2)	1.15
Fe–C (C_5H_4)	2.03(1)–2.08(2)	2.06
Fe–C (C_5H_5)	2.03(2)–2.10(2)	2.07
C–C (C_5H_4)	1.40(2)–1.50(2)	1.44
C–C (C_5H_5)	1.40(2)–1.50(2)	1.43

Os(2)–Os(1)–Os(3)	59.86(2)	Os(1)–Os(3)–C(2)	76.7(3)
Os(1)–Os(2)–Os(3)	60.51(2)	Os(2)–Os(3)–C(1)	51.0(4)
Os(1)–Os(3)–Os(2)	59.63(2)	Os(3)–Os(2)–C(1)	50.3(3)
Os(3)–Os(2)–C(2)	50.3(3)	Os(1)–C(1)–Os(2)	84.0(5)
Os(2)–Os(3)–C(2)	52.7(3)	Os(1)–C(1)–Os(3)	85.4(5)
Os(2)–Os(1)–C(1)	52.2(4)	Os(1)–C(1)–C(2)	153(1)
Os(3)–Os(1)–C(1)	51.0(3)	Os(2)–C(1)–Os(3)	78.7(4)
C(1)–Os(2)–C(2)	33.3(5)	Os(2)–C(2)–Os(3)	77.0(4)
C(1)–Os(3)–C(2)	34.1(5)	Os(2)–C(2)–C(41)	127(1)
Os(1)–Os(3)–C(1)	43.5(4)	Os(3)–C(2)–C(41)	137.4(8)
Os(1)–Os(2)–C(1)	43.9(4)	C(1)–C(2)–C(41)	144(1)
Os(1)–Os(2)–C(2)	76.1(3)		

In Scheme 2 a mechanism for the inversion leading to the changes in the ^1H NMR spectra in Fig. 4 is proposed in which the CO-bridged form **A** is in equilibrium with a PhC_2Ph-type structure **B**. It is structure **B** which inverts to **B′** via the intermediate (or transition state) **C** of C_s symmetry. In view of the structures displayed in Figs. 2 and 3, we expect a very small energy barrier between **A** and **B**, with the major barrier being that for the inversion process via **C**.

Structure of [$Os_3H(C{\equiv}CFc)(CO)_9$] (cluster 2)

The molecular structure is shown in Fig. 5 and selected bond lengths and angles are given in Table 2. The structure is of a known kind with the μ_3-alkynyl ligand behaving as a five-electron donor [13]. The main features of the coordination of the organic and the CO ligands are quite normal. The ^1H NMR spectrum of **2** shows that there is a plane of symmetry through the molecule even at − 90 °C, since only two multiplets are observed for the C_5H_4 group. The crystal structure is asymmetric, with the ferrocenyl group to one side. In solution a structure with a plane of symmetry may be adopted or, if the asymmetric geometry persists, there must be ready rotation or oscillation about the C(2)–C(41) bond to result in this time-averaged plane of symmetry.

Structure of [$Os_3(\mu_3\text{-}S)(\mu_3\text{-}CHCFc)(CO)_9$] (cluster 3)

The molecular structure is shown in Fig. 6 and selected bond lengths and angles are given in Table 3. With the S and CHCFc ligands as four-electron donors, compound **3** is a 50-valence-electron cluster and should therefore have two osmium–osmium bonds, and in agreement the Os–Os distances are 2.8095(9), 2.810(1), and 3.962(1) Å. The overall electron-count and geometry relate to those of $[Os_3(\mu_3\text{-}S)_2(CO)_9]$ for which the Os–Os distances are 2.814(1), 2.812(1), and 3.662(1) Å [14]. The longer non-bonded distance in **3** results from the fact that the alkyne ligand spans this edge through the two carbon atoms; these are σ-bonded to Os(1) and Os(3) and there is an η^2-interaction with Os(2). Figure 7 compares the geometries of attachment of the alkyne in clusters **1** and **3** in order to show the effect of opening up one of the Os–Os edges. The Os(1)–C(1)–C(2) and Os(3)–C(2)–C(1) angles in the open structure are understandably greater than the corresponding angles in **1** (by 18.1 and 17.2° respectively). The larger size of these angles for the open cluster **3** with respect to those in the closed structure **1** also affects the angle of the substituent at the alkyne. The other two angles at C(2) in **3** shown in Fig. 7 are correspondingly smaller than in the closed structure, the greatest contraction occurring in the C(1)–C(2)–C(41) angle, which is 112° in **3** compared with 122° in the closed structure. Thus a considerable variation in the interbond angles at the μ_3-alkyne on going from one structure to another is tolerated. The C(1)–C(2) bond increases from 1.405(28) to 1.47(3) Å on opening the cluster but this increase has little statistical significance.

An alkyne ligand also uses σ-M–C bonds to span the open edge of the metal triangle in the related open clusters $[Ru_3(\mu_3\text{-}S)(\mu_3\text{-}PhC_2Ph)(CO)_9]$ [15] and $[Os_3(\mu\text{-}Cl)(\mu_3\text{-}PhC_2Ph)(HgCl)(CO)_9]_2$ [16]. Likewise the μ_3-benzyne ligand in $[Os_3H(\mu\text{-}AsMe_2)(\mu_3\text{-}C_6H_4)(CO)_9]$ is linked by σ-Os–C bonds across the open edge with an η^2-interaction to the central Os atom [17]. This is not always the situation, since the C_6H_4 ligands in $[Os_3(\mu_3\text{-}PEt)(\mu_3\text{-}C_6H_4)(CO)_9]$ [18], $[Os_3(\mu_3\text{-}PMe)(\mu_3\text{-}C_6H_4)(CO)_9]$, $[Os_3(\mu_3\text{-}PMe)(\mu_3\text{-}C_6H_4)(CO)_8(PEt_3)]$ [19], and $[Os_3(\mu_3\text{-}AsC_6H_4Me)(\mu_3\text{-}C_6H_4)(CO)_9]$ [20] span Os–Os bonds by σ-Os–C bonds and not the adjacent open edge. It is not clear whether it is the replacement of S for PR (or AsR) or that

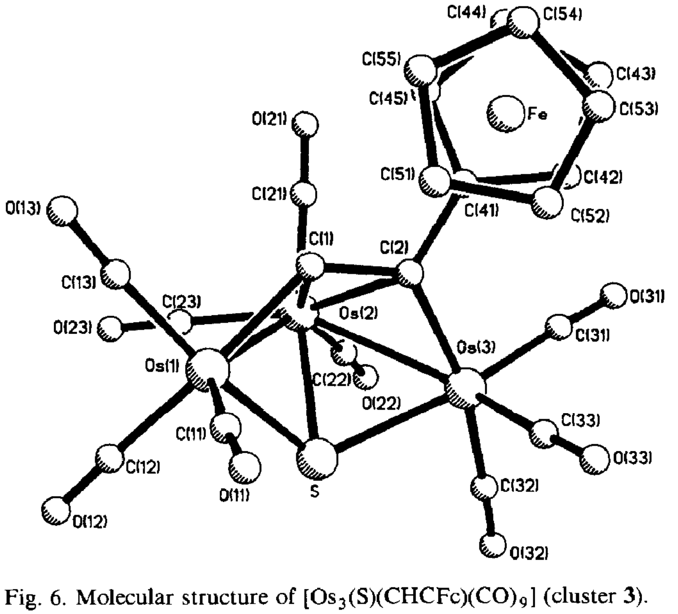


Fig. 6. Molecular structure of $[Os_3(S)(CHCFc)(CO)_9]$ (cluster **3**).

Table 3

Selected bond lengths (Å) and angles (°) for $[Os_3(S)(CHCFc)(CO)_9]$ (cluster **3**)

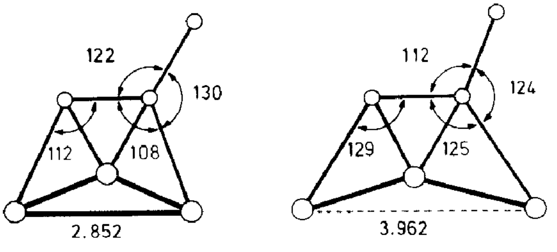
Os(1)–Os(2)	2.8095(9)	Os(1)–S	2.362(5)
Os(2)–Os(3)	2.810(1)	Os(2)–S	2.440(4)
Os(1)–C(1)	2.06(1)	Os(3)–S	2.384(4)
Os(3)–C(2)	2.06(2)	C(1)–C(2)	1.47(3)
Os(2)–C(1)	2.29(1)	C(2)–C(41)	1.49(2)
Os(2)–C(2)	2.39(1)		

	Range	Average
Os–CO (terminal)	1.85(2)–1.94(2)	1.89
C–O (terminal)	1.14(2)–1.16(2)	1.15
Fe–C (C_5H_4)	2.04(2)–2.06(2)	2.046
Fe–C (C_5H_5)	2.03(3)–2.06(2)	2.042
C–C (C_5H_4)	1.41(2)–1.45(3)	1.43
C–C (C_5H_5)	1.38(4)–1.41(4)	1.40

Os(1)–Os(2)–Os(3)	89.68(3)	Os(2)–Os(3)–C(2)	56.3(4)
Os(1)–S–Os(2)	71.6(1)	C(1)–Os(2)–C(2)	36.6(6)
Os(1)–S–Os(3)	113.2(1)	C(1)–Os(2)–S	78.3(3)
Os(2)–S–Os(3)	71.2(1)	C(2)–Os(2)–S	78.4(3)
Os(2)–Os(1)–S	55.50(9)	Os(1)–C(1)–C(2)	129.4(9)
Os(2)–Os(3)–S	55.33(9)	Os(3)–C(2)–C(1)	124.7(9)
Os(1)–Os(2)–S	52.9(1)	Os(2)–C(1)–C(2)	75.4(8)
Os(3)–Os(2)–S	53.4(1)	Os(2)–C(2)–C(1)	68.0(8)
Os(1)–Os(2)–C(1)	46.3(3)	C(1)–C(2)–C(41)	112(1)
Os(3)–Os(2)–C(2)	75.3(4)	Os(3)–C(2)–C(41)	124(1)
Os(2)–Os(1)–C(1)	53.4(4)		

of the alkyne for aryne that leads to the structural differences between $[Os_3(S)(alkyne)(CO)_9]$ and $[Os_3(PR)(aryne)(CO)_9]$. The aryne ligands in these compounds are mobile, and a structure analogous to that of **3** seems to easily accessible in the fluxional process and we should thus expect very small energy differences between these forms.

No results presented here indicate that ethynylferrocene behaves any differently from other alkynes in these systems. Ferrocenyl groups can have a stabilising effect on carbocationic character at an α-carbon but such effects are not encountered here. A strong π-donation by the ferrocenyl group would have the same effect as that of



Cluster (1)   Cluster (3)

Fig. 7. A comparison of the alkyne geometries in clusters **1** and **3** showing the consequences of the cleavage of a metal–metal bond of cluster **1** in forming cluster **3**.

the amino group in $[Os_3H_2(CHCNEt_2)(CO)_9]$, in which a perpendicular not parallel alkyne geometry is adopted [21]. We suggest that the presence of the ferrocenyl group may accelerate alkyne rotation. We have not studied this quantitatively but if the effect is present it is rather small. We believe that the chemistry described in this paper is likely to be found for other terminal alkynes.

Table 4

Crystallographic data for compounds **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{22}H_{10}FeO_{10}Os_3$	$C_{21}H_{10}FeO_9Os_3$	$C_{21}H_{10}FeO_9Os_3S$
M (g mol^{-1})	1060.76	1032.75	1064.81
Colour	red	orange	deep red
Size (mm^3)	$0.2\times0.4\times0.1$	$0.08\times0.1\times0.32$	$0.18\times0.18\times0.25$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/a$	$P2_1/c$	$P\bar{1}$
a (Å)	11.668(3)	7.633(1)	10.425(1)
b (Å)	12.617(3)	20.252(3)	15.049(2)
c (Å)	17.147(4)	16.591(1)	8.699(1)
α (°)	90	90	102.04(1)
β (°)	101.63(2)	109.58(1)	114.13(1)
γ (°)	90	90	83.04(1)
V (Å^3)	2472.7(9)	2416.4(5)	1217.2(5)
Z	4	4	2
D_c (g cm^{-3})	2.85	2.84	2.98
μ (Mo-K_α) (cm^{-1})	160.11	163.9	163.6
F (000)	1904	1848	984
No. of orientation reflns; range of 2θ	25; 20–34	25; 12–32	25; 12–22
Radiation, λ (Å)	Mo-K_α, 0.71073	Mo-K_α, 0.71073	Mo-K_α, 0.71073
Temp. (°C)	20	25	25
Scan mode	$\omega-2\theta$	ω	ω
2θ range (°)	$5\leqslant2\theta\leqslant50$	$5\leqslant2\theta\leqslant50$	$5\leqslant2\theta\leqslant52$
hkl range	$0, 0, -23\rightarrow16, 17, 23$	$-9, 0, 0\rightarrow9, 24, 18$	$-12, -18, 0\rightarrow12, 18, 10$
Total no. data	6262	4605	5093
No. unique data	5712	4383	4762
Structure solution	direct methods [x]	Patterson [y]	Patterson [y]
Acceptance criteria	$F_o\geqslant5\sigma(F_o)$	$F_o\geqslant3\sigma(F_o)$	$F_o\geqslant3\sigma(F_o)$
No. reflns used in refinement	3820	3064	2808
No. parameters in refinement	320	157	167
R [a]	0.0853	0.037	0.039
R'	0.0746	0.045	0.047
Weight w in weighting scheme	$1/[\sigma^2(F)+0.000556F^2]$	$4F^2/[\sigma^2(F)]^2$	$4F^2/[\sigma^2(F)]^2$
Max. shift to to error in final least squares refinement.	0.007	0.00	0.01
Max height in final diff. Fourier (eÅ^{-3})	4.5	2.1	1.19

[a] $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$.

Experimental

The cluster [$Os_3(CO)_{10}(MeCN)_2$] [22] and ethynylferrocene [23] were made as described previously. TLC was on silica [Merck, HF_{254} type 60].

Synthesis of [$Os_3(CHCFc)(CO)_{10}$] (1)

A solution of [$Os_3(CO)_{10}(MeCN)_2$] (0.015 g) and ethynylferrocene (0.023 g) in cyclohexane (20 cm^3) was heated under reflux under nitrogen for 20 min. Removal of the solvent and TLC on the residue [eluant: petroleum ether (b.p. 30–40 °C) gave one major orange-red band, which yielded compound **1** (0.012 g, 70%) as red crystals from dichloromethane/cyclohexane mixtures upon slow evaporation

Table 5

Fractional atomic coordinates ($\times 10^4$) for the cluster [$Os_3(CHCFc)(CO)_{10}$] (**1**)

Atom	*x*	*y*	*z*
Os(1)	737(1)	4511(1)	2771(1)
Os(2)	3131(1)	4353(1)	3113(1)
Os(3)	1990(1)	6076(1)	3720(1)
Fe(1)	3259(3)	5953(3)	731(2)
C(41)	2156(16)	5137(18)	1292(13)
C(42)	1522(22)	5807(29)	683(17)
C(43)	1821(27)	5500(36)	−54(15)
C(44)	2555(28)	4650(29)	83(18)
C(45)	2793(22)	4413(24)	920(16)
C(51)	4447(31)	6765(27)	1566(18)
C(52)	5038(21)	6103(23)	1081(20)
C(53)	4671(19)	6384(20)	274(17)
C(54)	3719(33)	7462(29)	1034(25)
C(55)	3875(32)	7280(22)	229(22)
C(1)	2179(13)	5228(16)	2144(12)
C(2)	1502(17)	5979(20)	2454(14)
C(1b)	3677(19)	6076(30)	3584(21)
O(1b)	4564(15)	6487(19)	3612(16)
C(11)	−799(20)	5053(20)	2484(18)
O(11)	−1759(15)	5372(20)	2286(16)
C(12)	485(21)	3582(25)	3582(17)
O(12)	398(25)	2998(21)	4078(15)
C(13)	384(18)	3502(27)	1943(16)
O(13)	168(15)	2874(20)	1474(14)
C(21)	4675(19)	4437(27)	2868(15)
O(21)	5560(14)	4447(18)	2710(14)
C(22)	2871(20)	3002(22)	2645(20)
O(22)	2776(17)	2213(17)	2357(18)
C(23)	3599(29)	3792(26)	4144(17)
O(23)	3765(32)	3393(29)	4793(17)
C(31)	456(21)	6039(26)	3987(17)
O(31)	−388(17)	6058(21)	4223(14)
C(32)	2035(19)	7600(26)	3676(19)
O(32)	2073(16)	8490(16)	3597(16)
O(33)	2995(31)	5760(26)	5508(14)
C(33)	2554(27)	5828(20)	4824(16)

(Found: C, 25.15; H, 0.95. $C_{22}H_{10}FeO_{10}Os_3$ calc: C, 24.9; H, 0.95%). IR (cyclohexane): ν(CO) 2098m, 2060s, 2052s, 2023vs, 2006s, 1998m, 1844w, br cm^{-1}; ^{1}H NMR ($CDCl_3$, 27 °C, 200 MHz) δ 9.24 (s, C*H*-C), 4.26 (m, 2H, C_5H_4), 4.19 (s, C_5H_5), 4.10 (m, 2H, C_5H_4).

Decarbonylation of compound (1)

(a) Thermal. A solution of cluster **1** (0.085 g) in heptane (50 cm^3 was refluxed under nitrogen for 2 h. Work-up as above gave one major yellow band, which yielded [$Os_3H(C{\equiv}CFc)(CO)_9$] (**2**) (0.076 g, 92%) as yellow crystals from cyclohexane/dichloromethane mixtures by slow evaporation (Found: C, 24.3; H, 1.1. $C_{21}H_{10}FeO_9Os_3$ calc: C, 24.4; H, 1.0%). IR (cyclohexane): ν(CO) 2099m, 2074s, 2052s, 2020s, 2013s, 2009sh, 2001m, 1994m, 1981m cm^{-1}; ^{1}H NMR ($CDCl_3$, 27 °C, 200 MHz): δ 4.42 (m, 2H, C_5H_4), 4.32 (m, 2H, C_5H_4), 4.19 (s, C_5H_5), − 20.6 (s, Os*H*).

Table 6

Fractional atomic coordinates for the cluster [$Os_3H(C_2Fc)(CO)_9$] (**2**)

Atom	*x*	*y*	*z*
Os(1)	0.35920(7)	0.59991(3)	0.82926(4)
Os(2)	0.10243(7)	0.63541(3)	0.91086(3)
Os(3)	0.06432(7)	0.68924(3)	0.74846(3)
O(11)	0.665(2)	0.5436(6)	0.9818(7)
O(12)	0.188(2)	0.4695(7)	0.7528(8)
O(13)	0.585(2)	0.6223(6)	0.7137(7)
O(21)	−0.169(2)	0.7086(7)	0.9801(8)
O(22)	−0.052(1)	0.4954(6)	0.8917(7)
O(23)	0.389(2)	0.6085(6)	1.0863(7)
O(31)	−0.080(2)	0.5851(7)	0.6112(8)
O(32)	−0.277(2)	0.7794(7)	0.6895(8)
O(33)	0.258(2)	0.7647(6)	0.6457(7)
C(11)	0.549(2)	0.5612(7)	0.9213(9)
C(12)	0.264(2)	0.5169(9)	0.783(1)
C(13)	0.504(2)	0.6125(8)	0.758(1)
C(21)	−0.076(2)	0.6785(8)	0.950(1)
C(22)	0.004(2)	0.5481(7)	0.9010(8)
C(23)	0.281(2)	0.6188(7)	1.0225(9)
C(31)	−0.027(2)	0.6255(8)	0.661(1)
C(32)	−0.146(2)	0.7447(8)	0.715(1)
C(33)	0.189(2)	0.7351(8)	0.6853(9)
C(1)	0.312(2)	0.6883(7)	0.8667(8)
C(2)	0.204(2)	0.7355(6)	0.8761(8)
Fe	0.3446(3)	0.8805(1)	0.9025(1)
C(41)	0.202(2)	0.7991(7)	0.9169(8)
C(42)	0.335(2)	0.8179(8)	0.998(1)
C(43)	0.284(2)	0.8842(8)	1.014(1)
C(44)	0.130(2)	0.9059(8)	0.947(1)
C(45)	0.073(2)	0.8513(8)	0.8825(9)
C(51)	0.495(2)	0.8562(9)	0.821(1)
C(52)	0.614(3)	0.881(1)	0.902(1)
C(53)	0.564(3)	0.947(1)	0.916(1)
C(54)	0.403(3)	0.964(1)	0.849(1)
C(55)	0.367(3)	0.907(1)	0.788(1)

(b) Photochemical in absence of sulphur. Dinitrogen was bubbled for 12 min through a solution of **1** (0.009 g) in heptane (12 cm^3) while it was being irradiated with a medium-pressure mercury UV lamp. The solution lightened from deep orange-red to orange-yellow. Chromatographic work-up as above gave compound **2** as yellow crystals (0.007 g, 90%). Also a solution of **1** (0.030 g) in purified cyclohexane (30 cm^3) left in daylight for 6 weeks underwent 25% conversion into cluster **2** with a 67% recovery of starting material, but no conversion occurred when an identical solution was kept in the dark for the same time.

(c) Photochemical in the presence of sulphur. A solution of **1** (0.045 g) in cyclohexane (50 cm^3) was allowed to stand over an excess of elemental sulphur in daylight for 3 weeks. Work up (TLC) gave recovered starting material (0.033 g), no detectable amount of cluster **2**, and $[Os_3(\mu_3\text{-}S)(\mu_3\text{-}CHCFc)(CO)_9]$ (**3**) as a purple oil

Table 7

Fractional atomic coordinates for the cluster $[Os_3(S)(CHCFc)(CO)_9]$ (3)

Atom	*x*	*y*	*z*
Os(1)	0.14093(6)	0.19774(4)	0.18963(7)
Os(2)	0.23174(6)	0.37331(4)	0.23561(7)
Os(3)	0.36637(6)	0.30751(4)	0.01031(7)
Fe	0.7157(2)	0.1814(2)	0.4720(3)
O(11)	0.179(2)	0.003(1)	0.037(2)
O(12)	0.183(1)	−0.208(1)	−0.019(2)
O(13)	0.165(1)	0.1587(9)	0.531(2)
O(21)	0.411(1)	0.4756(9)	0.585(1)
O(22)	0.965(1)	0.4187(9)	0.306(2)
O(23)	0.176(1)	0.533(1)	0.053(2)
O(31)	0.609(1)	0.4271(9)	0.089(1)
O(32)	0.200(2)	0.383(1)	−0.323(2)
O(33)	0.491(2)	0.141(1)	−0.144(2)
C(1)	0.434(1)	0.276(1)	0.251(2)
C(2)	0.344(1)	0.240(1)	0.317(2)
C(11)	0.161(2)	0.077(1)	0.098(2)
C(12)	−0.063(2)	0.203(1)	0.085(2)
C(13)	0.152(2)	0.172(1)	0.400(2)
C(21)	0.344(2)	0.437(1)	0.453(2)
C(22)	0.066(2)	0.401(1)	0.281(2)
C(23)	0.201(2)	0.473(1)	0.122(2)
C(31)	0.519(2)	0.382(1)	0.063(2)
C(32)	0.265(2)	0.356(1)	−0.196(2)
C(33)	0.441(2)	0.206(1)	−0.092(2)
C(41)	0.581(1)	0.287(1)	0.381(2)
C(42)	0.704(2)	0.283(1)	0.341(2)
C(43)	0.824(2)	0.292(1)	0.496(2)
C(44)	0.630(2)	0.299(1)	0.561(2)
C(45)	0.781(2)	0.302(1)	0.634(2)
C(51)	0.606(2)	0.066(2)	0.393(3)
C(52)	0.687(2)	0.078(2)	0.570(3)
C(53)	0.698(3)	0.059(2)	0.308(3)
C(54)	0.828(3)	0.079(2)	0.595(3)
C(55)	0.832(3)	0.066(2)	0.433(3)
S	0.1392(4)	0.2658(3)	−0.0326(5)

(0.005 g) that gave a few purple crystals suitable for an X-ray structure determination when kept under hexane. Elemental analytical data were not obtained but the parent molecular ion was observed; $m/e = 1070$ ($^{192}Os_3$ isotopomer; calc. 1070), significant fragmentation ions formed by successive CO loss and for $[Fe(C_5H_5)(C_5H_4C_2H)]^+$ were observed; IR ν(CO) (cyclohexane) 2096w, 2072s, 2053s, 2013s, 2004m, 1993m cm^{-1}; ^1H NMR ($CDCl_3$, 27 °C, 200 MHz) δ 9.25 (s, CH-C), 4.25 (s, C_5H_5), 4.10 (m, 2H, C_5H_4), 4.30 (m, 2H, C_5H_4).

Crystal structure determinations

Diffraction data for compound **1** were collected on a Nicolet R3m/V diffractometer and for compounds (**2**) and (**3**) on an Enraf–Nonius CAD4 diffractometer. Details of the data collection procedures and of the structure solutions are given in Table 4 together with the crystal data for the three structures. In each case corrections were made for Lorentz and polarisation effects and for decay by fitting the intensity data to three standard reflections collected periodically throughout the data collection. Empirical absorption corrections were carried out by the azimuthal scan method.

The structures were solved by methods indicated in Table 4 and refined by alternating cycles of full-matrix least squares and difference Fourier synthesis. Computations were carried out on Microvax II computers using SHELXTL PLUS [24] for compound **1** and SDP/VAX for compounds **2** and **3** [25]. Scattering factors for compounds **2** and **3** were taken from Cromer and Waber [26], anomalous dispersion effects were included in F_c [27], and the values of $\Delta f'$ and $\Delta f''$ were those of Cromer [28].

For compound **1** all non-hydrogen atoms with the exception of C(12) were refined anisotropically. The metal atoms for **2** and the Os, Fe, and S atoms for **3** were refined anisotropically; all other non-hydrogen atoms were refined isotropically. Hydrogen atoms were not included in the structural models.

Fractional atomic coordinates for **1**, **2**, and **3** are in Tables 5, 6, and 7 respectively. A complete table of bond lengths and angles and a list of observed and calculated structure factors are available from the authors.

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Note added in proof. In a recent paper the crystal structures of $[Os_3(EtC_2Et)(CO)_{10}]$ and of $[Os_3(EtC_2Et)(CO)_9(PPh_3)]$ were reported. The former has a structure close to that of **1** and the latter a structure close to that of $[Os_3(PhC_2Ph)(CO)_{10}]$ consistent with there being two distinct geometries accessible [E. Rosenberg, J. Bracker-Novak, R.W. Gellert, S. Aime, R. Gobetto, and D. Osella, J. Organomet. Chem., 365 (1989) 163].

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