Synthesis, characterisation and electrochemical analysis of a bis(ferrocenyl) vinyl allyl ether-substituted triosmium cluster

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From the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with ethynylferrocene was isolated the known cluster $[Os_3(CO)_{10}\{(C_5H_5)FeC_5H_4CCH\}]$ **1**; in addition the bis(ferrocenyl)-substituted triosmium cluster $[Os_3(CO)_9\{[(C_5H_5)FeC_5H_4CCH]_2CO\}]$ **2** was obtained in reasonable yield. Both ^1H and $^{13}C-\{^1H\}$ NMR studies of **2** indicate that the ferrocenyl groups are inequivalent. A single-crystal X-ray analysis of **2** showed that on co-ordination to the triosmium cluster the two ethynylferrocene groups have been linked *via* a metal carbonyl to give a composite ligand that may be described as a 2,6-bis(ferrocenyl) vinyl allyl ether. An electrochemical analysis of the compounds $(C_5H_5)FeC_5H_4CCH$, **1** and **2** reveals reversible one-electron oxidations attributable to the ferrocenyl moiety, with the two well separated redox processes found in **2** indicating inequivalent ferrocenyl sites. In addition, irreversible two-electron cluster-based oxidation processes were observed for **1** and **2**.

The interaction of alkyne substrates with transition-metal clusters has attracted a great deal of interest over the last two decades.[1,2] One of the major reasons has been the desire to use cluster-bound substrates as model systems for the interaction of organic adsorbates on catalytic metal surfaces.[3–5] The structural characterisation of cluster complexes involving unsaturated ligands[6,7] has provided a wealth of examples of how these substrates might interact with a metal surface. In addition, there has been interest in the reaction of transition-metal clusters with unsaturated compounds, with the possible view of utilising these systems as polymerisation catalysts. Recent reports have demonstrated that such systems may effect cyclo-dimerisation and -trimerisation of the bound substrate.[8] Transformations at the cluster surface are not limited to reactions between the unsaturated ligands, with many documented cases of other bound or introduced ligands being involved in subsequent transformations. Such an example is the coupling of a metal carbonyl ligand with a cluster-bound acetylene, as was observed in the compound $[Ru_3(CO)_7\{PhC\text{-}C(CO)Ph\}(C_6H_6)]$.[9] This interaction of a metal carbonyl with bound acetylene ligands, whilst relatively uncommon, has been observed for several other compounds. Some of the more unusual examples are clusters in which the carbonyl is involved in the linkage between two acetylene groups.[10,11] It is of interest that no product from alkyne coupling was documented for the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with ethynylferrocene in refluxing cyclohexane.[12] That report is in contrast to the results reported for the reactions of $[Os_3H_2(CO)_{10}]$ and $[Ru_3(CO)_{12}]$ with ethynylferrocene.[13,14] In this paper we report the synthesis, characterisation and electrochemical analysis of a bis(ferrocenyl)-substituted triosmium cluster obtained by the coupling of two ethynylferrocene ligands.

Results and Discussion

Reaction of the bis(acetonitrile)-substituted triosmium cluster $[Os_3(CO)_{10}(MeCN)_2]$ with 1.5 molar equivalents of ethynylferrocene in dichloromethane yielded the compound $[Os_3(CO)_9\{[(C_5H_5)FeC_5H_4CCH]_2CO\}]$ **2** in reasonable yield (43.5%) as an air-stable red crystalline solid. In addition, the previously reported[12] monosubstituted cluster $[Os_3(CO)_{10}\{(C_5H_5)FeC_5H_4CCH\}]$ **1** was also isolated from the reaction mixture in moderate yield (19.5%). The formulation of **2** was originally based on spectroscopic and analytical data. The ^1H NMR spectrum exhibited peaks at δ 8.87 and 7.28 attributable to the acetylenic protons. In addition single resonances at δ 4.29 and 4.21 were observed, which may be assigned to the two unsubstituted cyclopentadienyl rings of the ferrocene groups. The protons of the substituent-bearing cyclopentadienyl rings gave rise to a complicated multiplet in the region δ 4.26–4.82. The peaks attributable to the acetylenic protons show a dramatic increase in chemical shift compared with that observed for the unco-ordinated ethynylferrocene (δ 2.71). The above results clearly indicate that the two ethynylferrocene groups are inequivalent, with a dramatic difference in the magnetic environment of the acetylenic protons, occurring on co-ordination to the triosmium cluster. This inequivalence was also observed in the $^{13}C-\{^1H\}$ NMR spectrum, with peaks attributable to all of the carbon atoms of the substituent-bearing cyclopentadienyl rings appearing as individual resonances, indicating a lack of fluxional behaviour on the NMR time-scale. In the mass spectrum obtained by fast atom bombardment, the parent ion is observed with the predicted isotopic pattern, together with fragmentation peaks due to the successive loss of ten carbonyl ligands.

Molecular structure of complex 2

The molecular structure of complex **2** has been determined by a single-crystal X-ray diffraction analysis (Fig. 1). Selected bond lengths and angles are presented in Table 1. The structure consists of a discrete monomer with a triangular metal framework as expected, with osmium–osmium distances lying within the range 2.7861(11)–2.8830(14) Å. There are nine metal-bound carbonyl ligands, eight of which are terminally co-ordinated, whilst the other bridges between Os(2) and Os(3) in a highly asymmetric manner [Os(2)–C(23) 1.96(2), Os(3)–C(23) 2.23(2) Å]. On co-ordination to the metal cluster the two ethynylferrocene groups have been linked together through a C–O moiety derived from a metal carbonyl ligand. The composite ligand thus formed coordinates to the metal framework in an asymmetric μ_3 fashion. The bonding of Os(2)

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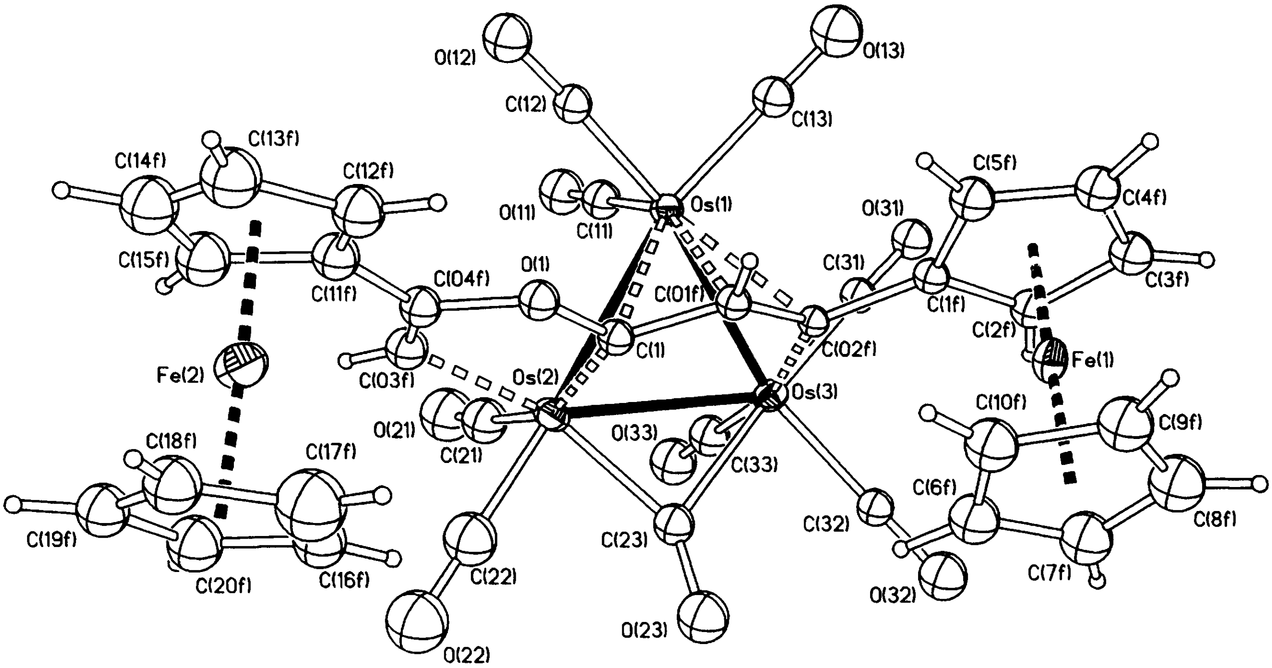

Fig. 1 Molecular structure of $[Os_3(CO)_9\{[(C_5H_5)FeC_5H_4CCH]_2CO\}]$ **2**

Table 1 Selected bond lengths (Å) and angles (°) for $[Os_3(CO)_9\{[(C_5H_5)FeC_5H_4CCH]_2CO\}]$ **2**

Os(1)–Os(2)	2.8351(12)	Os(3)–C(02f)	2.136(12)
Os(1)–Os(3)	2.7861(11)	O(1)–C(1)	1.38(2)
Os(2)–Os(3)	2.8830(14)	O(1)–C(04f)	1.42(2)
Os(1)–C(1)	2.334(14)	C(1)–C(01f)	1.43(2)
Os(1)–C(01f)	2.303(13)	C(01f)–C(02f)	1.40(2)
Os(1)–C(02f)	2.341(12)	C(02f)–C(1f)	1.49(2)
Os(2)–C(1)	2.022(13)	C(03f)–C(04f)	1.31(2)
Os(2)–C(03f)	2.08(2)	C(04f)–C(11f)	1.49(2)
C(1)–O(1)–C(04f)	110.4(10)	C(01f)–C(02f)–C(1f)	114.0(11)
O(1)–C(1)–C(01f)	113.3(11)	C(01f)–C(02f)–Os(3)	123.4(9)
O(1)–C(1)–Os(2)	118.3(9)	C(1f)–C(02f)–Os(3)	122.5(9)
C(01f)–C(1)–Os(2)	128.1(10)	C(01f)–C(02f)–Os(1)	70.9(7)
O(1)–C(1)–Os(1)	118.5(9)	C(1f)–C(02f)–Os(1)	123.0(9)
C(01f)–C(1)–Os(1)	70.9(8)	C(04f)–C(03f)–Os(2)	114.9(12)
Os(2)–C(1)–Os(1)	80.9(5)	C(03f)–C(04f)–O(1)	118.4(14)
C(02f)–C(01f)–C(1)	120.3(12)	C(03f)–C(04f)–C(11f)	134(2)
C(02f)–C(01f)–Os(1)	73.9(7)	O(1)–C(04f)–C(11f)	107.7(13)
C(1)–C(01f)–Os(1)	73.3(8)		

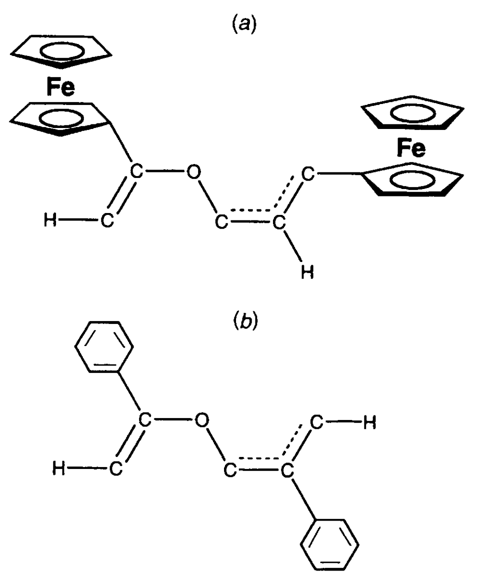

Fig. 2 2,6- and 2,5-Substituted vinyl allyl ethers as observed for complex **2** (*a*) and $[Os_3(CO)_9\{(PhCCH)_2CO\}]$ **3**[11] (*b*) respectively

and Os(3) to the ligand may be described in terms of σ interactions with Os(2)–C(03f), Os(2)–C(1) and Os(3)–C(02f) exhibiting similar bond distances of 2.08(2), 2.022(13) and 2.136(12) Å respectively. In contrast the co-ordination of the ligand to Os(1) through the carbon atoms C(1), C(01f) and C(02f) may be thought of as a π-allyl interaction with bond lengths of 2.334(14), 2.303(13) and 2.341(12) Å, respectively. The insertion of the carbonyl moiety between the two acetylenic groups of the ethynylferrocene ligands occurs in such a manner that the carbonyl carbon atom is co-ordinated to the β-carbon of one of the acetylenic groups. In comparison, the carbonyl oxygen atom is bound to the α-carbon of the second ethynylferrocene and hence the composite ligand thus formed may be described as a disubstituted vinyl allyl ether, with ferrocenyl substituents at the 2 and 6 positions [Fig. 2(*a*)]. The relative lack of accuracy for the bond lengths and angles associated with the light atoms within the structure precludes a detailed examination of the bonding within the ligand framework. However the observed bond distances within the composite ligand are in accord with the description as a vinyl allyl ether. In addition there appears to be a significant degree of electronic delocalisation within the vinyl allyl ether moiety, with bond lengths ranging from 1.31(2) [C(03f)–C(04f)] to 1.43(2) Å [C(1)–C(01f)]. Also, the delocalisation is indicated by the near planarity observed within the vinyl allyl ether linkage; the atoms C(1f), C(02f), C(01f) and C(1) lie within a plane, as do the atoms C(11f), C(03f), C(04f) and O(1), with an angle of 3(1)° being observed between these planes.

The vinyl allyl ether may be considered as a six-electron donor, with the cluster having an overall electron count of 48 as expected. However, the 18-electron rule is not obeyed for the individual metal atoms with Os(3) and Os(1) having electron counts of 17 and 19 respectively. This discrepancy may account for the presence of the highly asymmetric bridging carbonyl ligand, with Os(3) being formally electron deficient and hence forming an interaction with the carbonyl to redress this deficiency.

The insertion of a metal carbonyl between alkyne ligands co-ordinated to a triosmium cluster has been reported previously for the reaction between phenylacetylene and triosmium dodecacarbonyl,[11] where an analogous compound was formed but with the phenyl substituents in the 2 and 5 positions of the vinyl allyl ether [**3** in Fig. 2(*b*)]. Hence, the vinyl allyl ether in **2** can be thought of as an isomer of that observed in **3**, with the latter formed by insertion of a metal carbonyl between the α-carbon atoms of the two phenylacetylene ligands. It is not apparent why the link between the two acetylenic groups occurs between the α-carbon atoms in **3**, whereas in **2** it occurs between an α-carbon atom of one of the ethynylferrocene ligands and a β-carbon atom of the other. It is feasible that the greater steric bulk of the ferrocenyl substituents is responsible for the reactivity difference; however electronic considerations may also have important implications and hence cannot be entirely discounted.

In view of the results outlined above and the report by Deeming and co-workers[12] that no product obtained from alkyne coupling was observed at elevated temperatures, it seems likely that compound **1** is not an intermediate in the formation of **2**. A feasible reaction pathway is that the two labile acetonitrile ligands are initially replaced by two incoming $(C_5H_5)FeC_5H_4CCH$ ligands co-ordinated in a π fashion, each acting as a two-electron donor. Insertion of the metal carbonyl between the two co-ordinated ethynylferrocene groups and a concomitant rearrangement of the resulting composite ligand would result in the formation of **2**.

Electrochemical analysis of $(C_5H_5)FeC_5H_4CCH$ and compounds 1 and 2

A cyclic voltammetric study of compound **2** (Fig. 3) in CH_2Cl_2–0.5 mol dm^{-3} $[NBu^n_4][BF_4]$ revealed two reversible one-electron oxidations, as confirmed by coulometry, at 0.575 and 0.73 V. There was also a two-electron irreversible oxidation, as confirmed by stirred voltammetry with the E_{anodic} at 1.51 V and a multi-electron reduction with $E_{cathodic}$ at -1.02 V. A cyclic voltammogram of **1** (Fig. 4) revealed a reversible one-electron oxidation, as confirmed by coulometry, at 0.68 V. Irreversible two-electron oxidations and reductions, as indicated by stirred voltammetry, were observed with $E_{cathodic}$ and E_{anodic} at -1.04 and 1.54V respectively. In addition, the irreversible two-electron reduction resulted in the formation of redox-active daughter products with E_{anodic} of -0.10 and 0.42 V. We attribute this behaviour to a chemical rearrangement of the cluster upon reduction.

Cyclic voltammetry of ethynylferrocene revealed a reversible one-electron oxidation at 0.72 V, as previously reported.[15] The positive shift in the oxidation relative to ferrocene is a reflection of the ability of the triple bond to accept electron density from the iron(II) metal centre. The reversible oxidations of compounds **1** and **2** can be confidently assigned as being based on the ethynylferrocene fragment. The negative shift in the reversible oxidation of **1** with respect to ethynylferrocene is attributable to the reduction of the electron-withdrawing ability of the triple bond upon co-ordination to the cluster. There is a larger negative shift for the oxidation of the first ferrocene fragment in the electrochemistry of **2** and we would tentatively assign this oxidation to the ferrocene co-ordinated to the carbon directly bridging Os(1) and Os(3). We would expect this ferrocene fragment to be in a less electron-withdrawing environment than the second group, to which we would assign the second reversible oxidation. The irreversible oxidations and reductions, by comparison with ferrocene and ethynylferrocene which show no other electrochemical processes within the potential window, must be assigned to cluster-based redox processes.

In situ UV/VIS/NIR spectroelectrochemistry

Absorption spectral data are given in Table 2. A comparison of the spectra of ferrocene and $(C_5H_5)FeC_5H_4CCH$ indicate that the band at 37 820 cm^{-1} for the latter species must be due to a electronic transition involving orbitals based on the acetylene triple bond. A low-energy band was exhibited by both **1** and **2** which, by comparison with the spectra of ferrocene and ethenylferrocene, we tentatively assign as a charge transfer from a primarily ferrocene-based HOMO (highest occupied molecular orbital) to a cluster-based LUMO (lowest unoccupied molecular orbital). Interestingly, complex **1** has only one visible transition, whereas **2**, which contains two electrochemically and structurally different ferrocene centres, exhibits two visible transitions. By analogy with the spectra of ferrocene and $(C_5H_5)FeC_5H_4CCH$, absorptions at higher energy must be due to cluster-based electronic transitions.

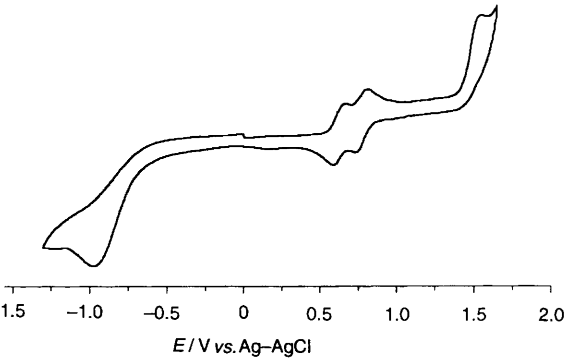

Fig. 3 Cyclic voltammogram of complex **2** in CH_2Cl_2–0.5 mol dm^{-3} $[NBu^n_4][BF_4]$

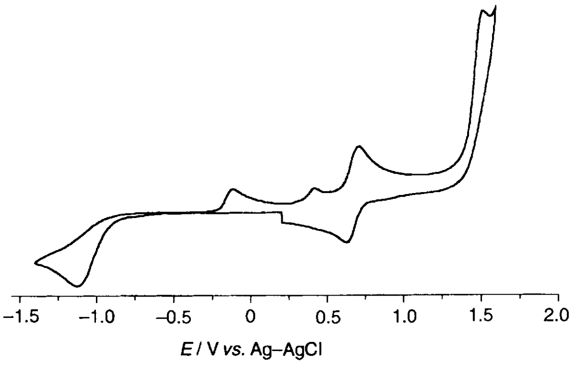

Fig. 4 Cyclic voltammogram of complex **1** in CH_2Cl_2–0.5 mol dm^{-3} $[NBu^n_4][BF_4]$

Both complexes $\mathbf{2}^+$ and $\mathbf{1}^+$ exhibit a low-energy band which, by analogy with ferrocenium and ethenylferrocene can confidently be assigned as a charge transfer from an orbital primarily based on the C_5H_5 ligands to a MO based primarily on the iron(III) centre. The bands are shifted to much lower energy upon co-ordination to the cluster compared to the free ligand. Complex $\mathbf{2}^{2+}$ exhibits two low-energy bands at 11 510 and ≈17 000 cm^{-1}. By comparison with $\mathbf{2}^+$ these can be assigned as charge-transfer transitions from C_5H_5 ligands to MOs based on the two ferrocenium centres. Interestingly the two bands have a similar separation to that observed for the ferrocene to cluster-based charge-transfer bands in the neutral molecule.

Experimental

All reactions were performed under an atmosphere of purified dinitrogen by standard Schlenk and vacuum-line techniques.[16] Subsequent work-up of products was carried out without precautions to exclude air. Solvents used were distilled from appropriate drying agents under dinitrogen.[17] Routine separations of products were performed by thin-layer chromatography using commercially available glass plates, precoated to 0.25 mm thickness with Merck Kieselgel 60 PF_{254}.

Table 2 Band positions (cm^{-1}) and absorption coefficients (dm^3 mol^{-1} cm^{-1}) in the UV/VIS spectra

Compound	Neutral	Monocation	Dication
2	20 260 (6 300) 26 850 (8 900)	10 190 (750) 25 930 (9 800)	11 510 (940) ≈17 000 (≈600) 25 510 (10 200) 39 870 (38 200)
1	23 320 (3 100)	11 900 (360)	
$(C_5H_5)FeC_5H_4CCH$	22 580 (220) 37 820 (8 100)	14 320 (380) 34 580 (≈10 700) 38 340 (≈10 700)	
$[Fe(C_5H_5)_2]$	22 600 (100) 30 710 (60)	16 170 (480)	

Infrared spectra were recorded as dichloromethane solutions on a Perkin-Elmer 1710 Fourier-transform spectrometer, ^1H and $^{13}C-\{^1H\}$ NMR spectra on a Bruker AC-250 spectrometer referenced to external tetramethylsilane and positive-ion fast atom bombardment mass spectra on a Kratos MS-50 mass spectrometer using *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were performed in this department by standard techniques. The compounds $[Os_3(CO)_{10}(MeCN)_2]$ and $(C_5H_5)FeC_5H_4CCH$ were prepared according to literature procedures.[18,19] Electrochemical studies were performed using a DELL 466-DL personal computer with a general purpose electrochemical system (GPES) Version 4 software connected to an Autolab system containing a PSTAT10 potentiostat. Cyclic voltammetric experiments were executed using a standard three-electrode configuration with platinum micro-working (0.5 mm diameter) and counter electrodes and a Ag–AgCl reference electrode against which ferrocene–ferrocenium was measured at 0.55 V. The salt $[NBu^n{}_4]_2[IrCl_6]$, which exhibits a Ir^{IV}–Ir^{III} reduction at 0.105 V, was used as the internal reference. Ferrocene was not suitable due to its oxidation's close proximity to the redox processes of interest. Redox potentials are quoted for a scan rate of 100 mV s^{-1}. Bulk electrolysis was effected in a compartmentalised H-type cell with platinum basket and mesh working and counter electrodes respectively; the reference electrode was as before. All electrochemical measurements were performed in nitrogen-purged dichloromethane solutions at 293 K containing 0.5 mol dm^{-3} $[NBu^n{}_4][BF_4]$. *In situ* UV/VIS/NIR spectroelectrochemistry was performed at an optically transparent electrode (OTE) cell in a Perkin-Elmer Lambda 9 spectrophotometer.[20] Oxidations were performed at 253 K. After each oxidation, reduction to the original starting material was effected to ensure full chemical reversibility for the redox step.

Synthesis of $[Os_3(CO)_9\{[(C_5H_5)FeC_5H_4CCH]_2CO\}]$ 2

To a solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.233 g, 0.25 mmol) in dichloromethane (50 cm^3) was added $(C_5H_5)FeC_5H_4CCH$ (0.068 g, 0.325 mmol) and the resulting red mixture stirred at room temperature for 1 h. Removal of the solvent and chromatography eluting with a 35% dichloromethane–hexane mixture afforded two products. The first was obtained as orange crystals (R_f = 0.67; 0.052 g, 19.5%) and identified on the basis of its IR spectrum as the previously reported cluster **1**.[12] The second compound was recrystallised from dichloromethane–hexane to yield red crystals of the desired product **2** (R_f = 0.53; 0.138 g; 43.5%) [Found: C, 32.3; H, 1.5%; *m/z* 1276. $C_{34}H_{20}Fe_2O_{10}Os_3$ requires C, 32.15; H, 1.60%; *M* (based on ^{192}Os) 1276]; $\tilde{\nu}_{max}$/cm^{-1} (pentane) 2091s, 2056vs, 2051s (sh), 2022s, 2014m, 1999m and 1836w (CO); $\delta_H(CDCl_3)$ 8.87 (1 H, s, C=CH), 7.28 (1 H, s, C=CH), 4.82–4.26 (m, 8 H, C_5H_4), 4.29 (s, 5 H, C_5H_5) and 4.21 (s, 5 H, C_5H_5); $\delta_C(CDCl_3)$ 199.6 (1 C, C≡O), 196.9 (2 C, C≡O), 181.6 (1 C, C≡O), 177.0 (1 C, quaternary C), 175.2 (1 C, quaternary C), 174.4 (3 C, C≡O), 172.4 (1 C, C≡O), 171.2 (1 C, quaternary C), 167.9 (1 C, C≡O), 156.2 (1 C, *ipso*-C of C_5H_5), 106.5 (1 C, C≡*C*H), 93.6 (1 C, *ipso*-C of C_5H_5), 89.6 (1 C, C≡*C*H), 74.3 (1 C, C_5H_5), 72.3 (1 C, C_5H_5), 70.4 (1 C, C_5H_5), 70.2 (5 C, C_5H_5), 69.3 (5 C, C_5H_5), 69.0 (1 C, C_5H_5), 68.6 (1 C, C_5H_5), 67.9 (1 C, C_5H_5), 66.7 (1 C, C_5H_5) and 65.9 (1 C, C_5H_5); *m/z* 1276 (M^+), 1248 (*M* – CO), 1220 (*M* – 2CO), 1192 (*M* – 3CO), 1164 (*M* – 4CO), 1136 (*M* – 5CO), 1108 (*M* – 6CO), 1080 (*M* – 7CO), 1052 (*M* – 8CO), 1024 (*M* – 9CO) and 996 (*M* – 10CO).

Crystallography

Crystal data and data-collection parameters. $C_{34}H_{20}Fe_2O_{10}Os_3$ **2**, M = 1270.80, monoclinic, space group $P2_1/n$ [no. 14 (alternative setting)], a = 8.465(2), b = 35.629(5), c = 11.561(2) Å, β = 101.56(3)°, U = 3416.1(14) Å^3 (by least-squares refinement on diffractometer angles from 25 centred reflections, $10.5 < \theta < 15.0°$), T = 293 K, graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å, Z = 4, D_c = 2.471 Mg m^{-3}, $F(000)$ = 2336, red needle with dimensions 0.35 × 0.20 × 0.05 mm, μ(Mo-Kα) = 12.003 mm^{-1}, semi-empirical absorption correction based on ψ scans, transmission factors 0.66–1.00; Rigaku AFC7R diffractometer, ω scans, data-collection range $2.5 < \theta < 22.5°$, $+h$, $+k$, $\pm l$, three standard reflections showed no significant variation in intensity; 4816 reflections measured, 4465 unique (R_{int} = 0.0365) which were used in all calculations.

Structure solution and refinement. The structure was solved by a combination of direct methods and Fourier techniques. During the refinement process it was noted that one of the cyclopentadienyl rings [C(16f)–C(20f)] exhibited 50% disorder and its alternative position [C(21f)–C(25f)] was located from a Fourier-difference electron-density synthesis and included in subsequent cycles of refinement. Hydrogen atoms were placed in calculated positions and refined using a riding model. Anisotropic thermal motion was assumed only for the osmium and iron atoms. Full-matrix least-squares refinement on $F_{obs}{}^2$ for 4465 data and 224 parameters converged to $wR2$ = 0.0950 (all data), conventional $R1$ = 0.0431 (observed data), $(\Delta/\sigma)_{max}$ = 0.001, goodness of fit = 1.028. The function minimised was $\Sigma w(F_{obs}{}^2 - F_{calc}{}^2)^2$, $w = 1/[\sigma^2(F_{obs}{}^2) + (0.0229P)^2 + 31.0728P]$ where $P = (F_{obs}{}^2 + 2F_{calc}{}^2)/3$ and σ was obtained from counting statistics. A final Fourier-difference electron-density synthesis revealed maximum and minimum residual electron-density peaks of 1.03 and −0.86 e Å^{-3}, which were in close proximity to osmium atoms. The crystallographic computing programs SHELXS 86 and SHELXL 93 were used throughout the structure solution and refinement process.[21,22]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the

CCDC for this material should quote the full literature citation and the reference number 186/166.

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