

# Synthesis, characterisation and electrochemistry of the novel ferrocenyldienediyltriosmium cluster $[\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^4\text{-Fe}[\text{C}_5\text{H}_4(\text{C}_2\text{SiMe}_3)_2\}]_2]$

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The reaction between  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  and  $[\text{Fe}\{\text{C}_5\text{H}_4(\text{C}_2\text{SiMe}_3)_2\}]_2$  yielded  $[\text{Os}_3(\text{CO})_{10}\{\mu_3\text{-}\eta^2\text{-Fe}[\text{C}_5\text{H}_4(\text{C}_2\text{SiMe}_3)_2\}]_2$  **1** and the decarbonylated product of this complex,  $[\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^4\text{-Fe}[\text{C}_5\text{H}_4(\text{C}_2\text{SiMe}_3)_2\}]_2$  **2**, the structure of which has been shown by X-ray crystallography to incorporate a triosmium cluster linked *via* a metallobutadienyl ligand to a ferrocene unit; the cyclic voltammogram of **2** shows a reversible one-electron oxidation of the ferrocene unit and an irreversible two-electron reduction for the triosmium unit.

Recent reports have indicated that organic complexes and polymers which contain ferrocene or metal-alkyne units exhibit novel physical properties which may have applications in the electronics industry.<sup>1,2</sup> We have been undertaking a series of studies which involve the incorporation of both ferrocene and metal-alkyne units into the same heterobimetallic complex.<sup>3</sup> These systems exhibit 'donor-acceptor' characteristics and show potential for non-linear optical behaviour.<sup>4,5</sup> In this communication we describe a novel extension of this work to include diyne systems and report the linkage of a ferrocene derivative to a triosmium cluster unit *via* a co-ordinated diyne.

The reaction of the activated cluster  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ <sup>6</sup> with the bis(trimethylsilylalkynyl)-substituted ferrocene derivative  $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4(\text{C}_2\text{SiMe}_3)_2\}]_2$ <sup>7</sup> at room temperature, in dichloromethane, led to an instantaneous change from orange to deep red, and after 0.5 h the IR spectrum of the reaction mixture shows that none of the starting material remains. Separation and purification of the reaction mixture by TLC afforded two red bands. The first, characterised as  $[\text{Os}_3(\text{CO})_{10}\{\mu_3\text{-}\eta^2\text{-Fe}[\text{C}_5\text{H}_4(\text{C}_2\text{SiMe}_3)_2\}]_2$  **1** by spectroscopic techniques,<sup>†</sup> was obtained in 70% yield, and readily decarbonylates in solution over 2 d to  $[\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^4\text{-Fe}[\text{C}_5\text{H}_4(\text{C}_2\text{SiMe}_3)_2\}]_2$  **2** which was isolated as the second red band from the initial reaction in 25% yield. This decarbonylation step is hindered by the absence of visible light.

The IR spectrum of compound **1** indicates the presence of both bridging and terminal carbonyl ligands, and the absorption at  $2145\text{ cm}^{-1}$  is indicative of the presence of a free alkyne group.<sup>†</sup> The <sup>13</sup>C NMR data, at room temperature, are consistent with the presence of nine terminal carbonyl ligands; a signal corresponding to a bridging carbonyl was not observed but these are often very weak, and the IR spectrum is a better guide to their presence. The mass spectrum corresponds to the formulation proposed and the structure shown. The geometry is similar to that found for many triosmium alkyne-substituted complexes.<sup>8</sup>

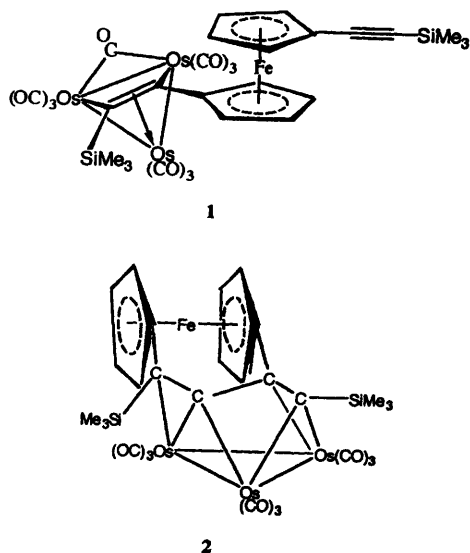
Complex **2** was initially characterised by spectroscopic techniques.<sup>†</sup> The IR spectrum showed the presence of only terminal carbonyl ligands, and no absorption corresponding to a free alkyne. The <sup>13</sup>C NMR spectrum showed four signals corresponding to four dienediyl carbons, in addition to signals corresponding to carbonyl, cyclopentadienyl and trimethylsilyl groups. The mass spectrum gave a molecular ion consistent with the formulation **2**, and this was confirmed by a single-crystal X-ray analysis.<sup>‡</sup>

The crystal structure of compound **2** has two independent but

structurally similar molecules in the asymmetric unit. The molecular structure **2** is shown in Fig. 1 together with selected bond parameters. The osmium triangle is capped by a dienediyl fragment derived from both alkyne functionalities of the substituted ferrocene; as a consequence of this the ferrocene unit lies over the top of the triangle acting as a bridging group. The dienediyl forms  $\pi$  interactions with Os(11) and Os(12) and two  $\sigma$  interactions with Os(13). Although not statistically significant the dienediyl shows alternate short-long-short-long C-C distances along the C(115)-C(116)-C(117)-C(123) chain. The twisted configuration of the dienediyl unit is related to that of the diene in  $[\text{Os}_3(\text{CO})_{10}(s\text{-trans-C}_4\text{H}_6)]$ <sup>11</sup> where this ligand co-ordinates to two of the Os atoms of the metal triangle. It is interesting that for this reaction product **2** to have formed the

<sup>†</sup> The compound  $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  (50 mg, 0.05 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (25  $\text{cm}^3$ ),  $[\text{Fe}\{\text{C}_5\text{H}_4(\text{C}_2\text{SiMe}_3)_2\}]_2$  (20 mg, 0.053 mmol) was added and a change from orange to deep red occurred instantaneously. The mixture was stirred for 1 h. The resulting brown-red  $\text{CH}_2\text{Cl}_2$  solution was evaporated to dryness under reduced pressure. The resulting oily residue was redissolved in the minimum of  $\text{CH}_2\text{Cl}_2$  (2  $\text{cm}^3$ ) and purified by TLC. Elution with  $\text{CH}_2\text{Cl}_2$ -hexane (1:9) afforded the major product **1** (high  $R_f$ ) as a red air-sensitive solid (70%) and the minor product **2** (low  $R_f$ ) as a red, air-stable oily solid (25%). Complex **2** was recrystallised from  $\text{CH}_2\text{Cl}_2$ -hexane, affording dark red air-stable crystals (Found: C, 28.80; H, 2.10. Calc. for  $\text{C}_{29}\text{H}_{26}\text{FeO}_9\text{Os}_3\text{Si}_2$ : C, 28.95; H, 2.15%). Spectroscopic data: **1**, IR ( $\text{CH}_2\text{Cl}_2$ ) 2145w, 2094m, 2086 (sh), 2055vs, 2036 (sh), 2017s, 1999 (sh) and 1832w (br)  $\text{cm}^{-1}$ ; NMR (250 MHz,  $\text{CD}_2\text{Cl}_2$ ), <sup>1</sup>H,  $\delta$  4.52 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 4.43 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 4.40 (m, 2 H,  $\text{C}_5\text{H}_4$ ), 4.21 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 4.18 (m, 2 H,  $\text{C}_5\text{H}_4$ ), 4.16 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 0.26 (s, 9 H, SiMe<sub>3</sub>) and 0.15 (s, 9 H, SiMe<sub>3</sub>); <sup>13</sup>C,  $\delta$  177.78-169.49 (10 s, 10 C, CO), 104.26 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 90.51 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 74.54-68.43 (8 s, 8 C,  $\text{C}_5\text{H}_4$ ), 4.18 (s, 3 C, SiMe<sub>3</sub>) and 0.56 (s, 3 C, SiMe<sub>3</sub>); negative FAB spectrum  $m/z$  1229; **2**, IR ( $\text{CH}_2\text{Cl}_2$ ) 2085s, 2050s, 2035vs, 2010m, 1997m 1975m and 1960 (sh)  $\text{cm}^{-1}$ ; NMR (250 MHz,  $\text{CD}_2\text{Cl}_2$ ), <sup>1</sup>H,  $\delta$  4.40 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 4.30 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 4.17 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 4.11 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 4.04 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 3.98 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 3.65 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 3.48 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 0.44 (s, 9 H, SiMe<sub>3</sub>) and 0.06 (s, 9 H, SiMe<sub>3</sub>); <sup>13</sup>C, 176.82-168.54 (9 s, 9 C, CO), 141.02 (s, 1 C, C), 135.90 (s, 1 C, C), 123.56 (s, 1 C, C), 122.00 (s, 1 C, C), 94.45 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 91.10 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 74.50 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 72.80 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 72.08 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 70.81 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 70.55 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 70.37 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 69.51 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 68.35 (s, 1 C,  $\text{C}_5\text{H}_4$ ), 2.67 (s, 3 C, SiMe<sub>3</sub>) and 1.03 (s, 3 C, SiMe<sub>3</sub>); negative FAB spectrum  $m/z$  1201.

<sup>‡</sup> Crystal data:  $\text{C}_{29}\text{H}_{26}\text{FeO}_9\text{Os}_3\text{Si}_2$ ,  $M = 1201.13$ , orange tablets, crystal dimensions  $0.10 \times 0.15 \times 0.20$  mm, triclinic, space group  $P1$  (no. 2),  $a = 16.677(9)$ ,  $b = 19.048(8)$ ,  $c = 11.005(4)$  Å,  $\alpha = 94.98(4)$ ,  $\beta = 104.45(4)$ ,  $\gamma = 93.68(4)^\circ$ ,  $U = 3359(3)$  Å<sup>3</sup>,  $D_c = 2.375$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 2216$ , Mo-K $\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo-K}\alpha) = 11.854$  mm<sup>-1</sup>,  $T = 293(2)$  K. Rigaku AFC5R four-circle diffractometer, 9843 reflections collected in the range,  $\theta$  3.51-22.52°, 8761 unique absorption-corrected data ( $R_{\text{int}} = 0.0530$ ). Structure solved by direct methods (Os atoms) (SHELXTL PLUS<sup>9</sup>) and refined with all non-hydrogen atoms anisotropically by full-matrix least squares based on  $F^2$  (SHELXL 93<sup>10</sup>); the H atoms were placed in idealised positions and allowed to ride on the relevant C atom. Refinement converged at  $R1 = 0.0345$ ,  $wR2 = 0.0767$  for 6017 unique data with  $F > 4\sigma(F)$ , and  $R1 = 0.0884$  and  $wR2 = 0.0914$  (all data), goodness of fit = 1.035, weighting scheme  $w = 1/[\sigma^2(F_o^2) + (0.251P)^2]$  where  $P = 2F_o^2/3$ . 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 186/285.



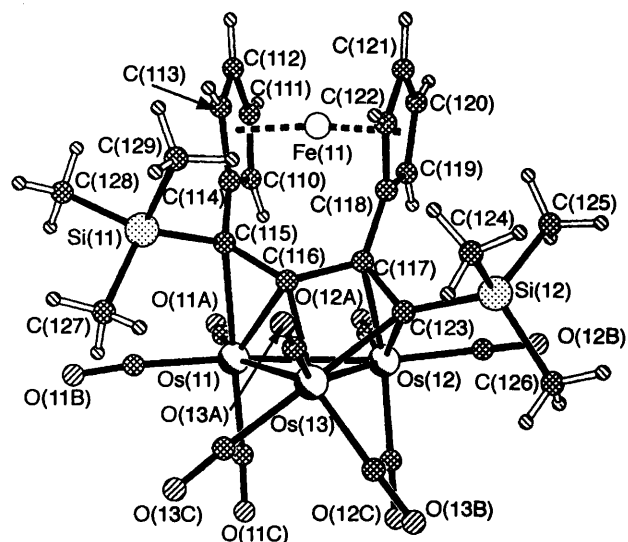
Si(11)Me<sub>3</sub> group has undergone a 1,2 shift from C(116) to C(115) and a C–C bond has formed between C(116) and C(117). Overall, the dienediyl acts as a six-electron donor and the cluster counts as a 48-electron system, typical of the closed triangular metal arrangement.

A number of triosmium clusters co-ordinated in one manner or another to a ferrocene derivative are known,<sup>12,13</sup> but the structure of **2** is novel with the presence of the face-capping dienediyl ferrocene. Also the 1,2-silyl migration to generate **2** is unusual. This chemistry is most closely related to recent work on catalytic studies of [Ru<sub>3</sub>(CO)<sub>12</sub>] with bis(silylethynyl)ferrocene where a novel cyclocarbonylation, involving 1,2-silyl migration of the silylethynyl group generating a transition-metal vinylidene intermediate, to give a cyclopent-3-ene-1,2-dione derivative is observed.<sup>14</sup> While no cluster complex was isolated in the reaction with [Ru<sub>3</sub>(CO)<sub>12</sub>], **2** might be viewed as an intermediate related to a similar process facilitating the silyl migration, the slower kinetics of the osmium system allowing for the isolation of the intermediate. Related trinuclear ruthenacycle complexes having a [2]ferrocenophane skeleton, [Ru<sub>3</sub>(CO)<sub>8</sub>{Fe(C<sub>5</sub>H<sub>4</sub>CCR)<sub>2</sub>}] (R = Ph or SiMe<sub>3</sub>), which contain a central diynyl unit, but which do not show the 1,2-silyl migration have also been isolated from the reaction with [Ru<sub>3</sub>(CO)<sub>12</sub>].<sup>15</sup>

A cyclic voltammetric study of compound **2**, in dichloromethane, revealed a reversible one-electron oxidation at 0.776 V and an irreversible two-electron reduction at -0.997 V. By comparison the cyclic voltammogram of [Fe{C<sub>5</sub>H<sub>4</sub>(C<sub>2</sub>-SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] shows a one-electron reversible oxidation at 0.662 V. The positive shift in the oxidation of [Fe{C<sub>5</sub>H<sub>4</sub>(C<sub>2</sub>-SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] relative to ferrocene (0.55 V vs. Ag–AgCl reference electrode) is a reflection of the ability of the triple bonds to accept electron density from the iron(II) centre. The reversible oxidation of **2** can be assigned as being based on the ferrocenyl fragment. Its positive shift with respect to [Fe{C<sub>5</sub>H<sub>4</sub>(C<sub>2</sub>-SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] is attributable to an increase of the electron-withdrawing ability of the unsaturated carbon chain upon co-ordination to the cluster. The irreversible reduction in **2** can be assigned to the osmium cluster fragment, and this unit plays little part in the electron-transfer process.

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**Fig. 1** Molecular structure of compound **2** with the atom numbering scheme. Selected bond lengths and angles (second molecule in square brackets): Os(11)–Os(12) 2.900(2) [2.907(1)], Os(12)–Os(13) 2.796(1) [2.794(2)], Os(11)–Os(13) 2.831(2) [2.842(2)], Os(12)–C(123) 2.199(11) [2.189(12)], Os(12)–C(117) 2.230(12) [2.249(11)], Os(11)–C(115) 2.420(13) [2.398(11)], Os(11)–C(116) 2.254(13) [2.279(12)], Os(13)–C(116) 2.143(12) [2.173(12)], Os(13)–C(123) 2.142(13) [2.170(14)], C(123)–C(117) 1.46(2) [1.45(2)], C(117)–C(116) 1.49(2) [1.46(2)], C(116)–C(115) 1.42(2) [1.41(2)], C(115)–Si(11) 1.879(13) [1.880(14)], C(123)–Si(12) 1.946(12) [1.909(12)], C(114)–C(115) 1.50(2) [1.52(2)] and C(117)–C(118) 1.49(2) [1.50(2)] Å; Os(11)–Os(12)–Os(13) 59.56(5) [59.77(4)], Os(11)–Os(13)–Os(12) 62.06(4) [62.08(4)], Os(12)–Os(11)–Os(13) 58.38(4) [58.15(4)], C(115)–C(116)–C(117) 128.5(11) [131.9(11)], C(116)–C(117)–C(123) 101.5(10) [105.6(10)], C(117)–C(123)–Si(12) 127.3(10) [128.8(10)], Si(11)–C(115)–C(114) 110.7(9) [110.4(8)] and Si(12)–C(115)–C(116) 119.3(9) [121.2(9)]°

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