

Synthesis, characterization, electrochemical properties and crystal and molecular structures of $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)]$ and $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CO}_2)]$

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Abstract

Two new air-stable triosmium clusters, $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)]$ (1) and $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CO}_2)]$ (2), were obtained from the reaction of the labilized cluster $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ and the corresponding ferrocenecarboxylic acid and were characterized by spectroscopic methods and single-crystal X-ray diffraction studies. The redox properties of both complexes were studied by cyclic voltammetry at ambient temperature; both exhibit a reversible electron transfer process.

Keywords: Osmium; Carbonyls; Cluster; Iron; Ferrocenes; Crystal structure

1. Introduction

Numerous transition metal complexes such as $(\text{Ph}_3\text{P})_3\text{RhCl}$ [1] and $[\text{Ni}(\text{cyclam})]^{2+}$ [2] have been shown to be effective catalysts for the reduction of carbon dioxide [3]. However, for these processes understanding of the nature of the intermediates and the reaction pathways is limited. To assist the search for a better catalyst for the reduction of carbon dioxide, the mechanism needs to be fully defined. The triosmium or triruthenium complexes of carboxylato ligands are potential models for the study of such process [4,5] and their electrochemical properties are definitely useful for the understanding of electrochemical activation of carbon dioxide. Despite their importance, structurally characterized cluster carboxylato complexes are fairly rare, especially in the case of osmium [6–11] and the electrochemical properties of such carboxylate-derived cluster complexes have not been much studied.

In this paper, we describe the synthesis and characterization of two new clusters derived from the ferro-

cenomonocarboxylic acid and 1,1'-ferrocenedicarboxylic acid. Voltammetric studies of these complexes have shown that both complexes undergo reversible electron transfer at the ferrocene centre, with the triosmium unit playing little part in the electron transfer process.

2. Results and discussion

Treatment of $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ with a stoichiometric amount of ferrocenomonocarboxylic acid in dichloromethane at room temperature gives an orange solution from which a good yield of $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)]$ (1) (54%) can be isolated. The reaction of $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ with 1,1'-ferrocenedicarboxylic acid in refluxing chloroform gives a mixture of products from which a moderate yield of $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CO}_2)]$ (2) (36%) can be obtained. Both complexes were fully characterized by spectroscopic methods (Table 1).

The IR spectra of both complexes in the carbonyl region show signals due to terminal carbonyl ligands only. The spectra are similar to those of carboxylato compounds such as $[\text{Os}_3\text{H}(\text{HCO}_2)(\text{CO})_{10}]$ [4] and

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Table 1
Spectroscopic data for $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)]$ (1) and $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CO}_2)]$ (2)

Compound	IR, νCO (cm^{-1}) ^a	¹ H NMR, δ (ppm) ^b	FAB-MS (m/z) ^c
1	2113w, 2074s, 2063m, 2027vs, 2018s, 2008w, 1985m	4.58 (<i>t</i> , 2H, $J = 2$ Hz, Cp) 4.30 (<i>t</i> , 2H, $J = 2$ Hz, Cp) 4.15 (<i>s</i> , 5H, Cp) – 10.24 (<i>s</i> , 1H, Os–H)	1085 (1086)
2	2113w, 2086w, 2074m, 2063m, 2029s, 2017s, 1984w	4.51 (<i>t</i> , 2H, $J = 2$ Hz, Cp) 4.26 (<i>t</i> , 2H, $J = 2$ Hz, Cp) – 10.28 (<i>s</i> , 1H, Os–H)	1975 (1976)

^a Recorded in *n*-hexane. *s* = Strong; *m* = medium; *w* = weak; *vs* = very strong.

^b 270 MHz spectra recorded in CDCl_3 at room temperature. *s* = Singlet; *t* = triplet.

^c Based on ¹⁹²Os (calculated values given in parentheses).

Table 2
Selected bond distances (\AA) and bond angles ($^\circ$) in $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)]$ (1)

Os(1)–Os(1*)	2.912(3)	Os(1)–Os(2)	2.872(2)
Os(1)–O(7)	2.13(2)	C(7)–O(7)	1.31(3)
C(7)–C(8)	1.49(8)	Fe–C(8)	2.10(5)
Fe–C(9)	2.03(3)	Fe–C(10)	2.10(3)
Fe–C(13)	2.01(5)	Fe–C(14)	2.11(5)
Fe–C(15)	1.99(9)		
Os(1)–Os(1*)–Os(2)	59.53(4)	Os(1)–Os(2)–Os(1*)	60.93(7)
Os(1*)–Os(1)–O(7)	82.2(6)	Os(1)–O(7)–C(7)	124(2)
O(7)–C(7)–O(7*)	126(4)	C(7)–C(8)–C(9)	122(2)
Os–C–O (average)	174.3		

Table 3
Final atomic coordinates and equivalent isotropic displacement coefficients, B_{eq} (\AA^2), for $[\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)]$ (1)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} ^a
Os(1)	0.6538(2)	0.11188(4)	0.1204(1)	3.33(4)
Os(2)	0.4566(3)	0.05357(6)	0.2500	3.71(5)
Fe(1)	0.358(1)	0.2602(2)	0.2500	3.9(2)
Cl(1)	0.867(8)	0.063(1)	0.7500	23(1)
Cl(2)	1.010(7)	0.134(1)	0.7500	25(1)
O(1)	0.870(4)	0.1790(9)	0.010(3)	8.7(9)
O(2)	0.953(4)	0.0531(8)	0.079(2)	6.9(7)
O(3)	0.466(4)	0.0823(8)	– 0.103(3)	7.0(7)
O(4)	0.770(7)	– 0.002(1)	0.2500	8(1)
O(5)	0.299(4)	0.0084(8)	0.040(2)	6.6(7)
O(6)	0.151(6)	0.113(1)	0.2500	6.1(9)
O(7)	0.461(3)	0.1567(5)	0.146(2)	3.5(5)
C(1)	0.780(5)	0.154(1)	0.050(3)	5.1(9)
C(2)	0.824(6)	0.076(1)	0.093(4)	5(1)
C(3)	0.524(5)	0.095(1)	– 0.022(3)	5.1(9)
C(4)	0.655(9)	0.018(2)	0.2500	5(1)
C(5)	0.358(6)	0.022(1)	0.117(4)	7(1)
C(6)	0.259(9)	0.089(2)	0.2500	5(1)
C(7)	0.411(8)	0.170(1)	0.2500	4(1)
C(8)	0.271(8)	0.201(2)	0.2500	4(1)
C(9)	0.220(4)	0.2216(9)	0.147(3)	4.1(8)
C(10)	0.104(4)	0.2533(10)	0.185(3)	4.1(7)
C(11)	1.04(2)	0.085(4)	0.7500	17(2)
C(13)	0.601(7)	0.270(1)	0.309(4)	9(1)
C(14)	0.510(6)	0.300(1)	0.353(4)	7(1)
C(15)	0.45(1)	0.316(2)	0.2500	10(2)

^a $B_{\text{eq}} = \frac{8}{3}\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha]$.

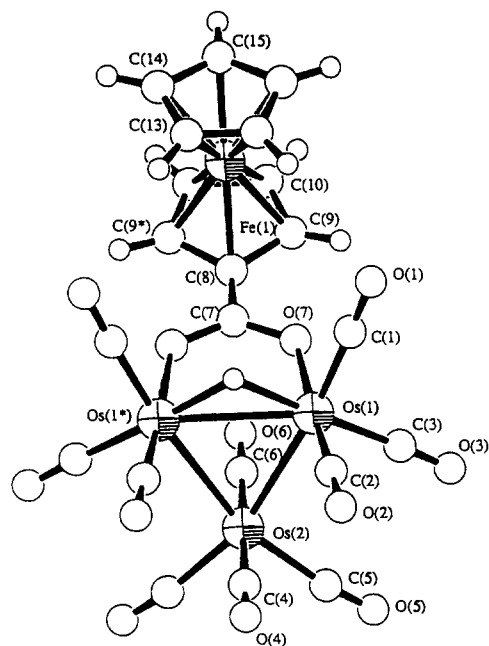


Fig. 1. Molecular structure of $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_5)] \cdot \text{CH}_2\text{Cl}_2$ (1). The solvent of crystallization is omitted.

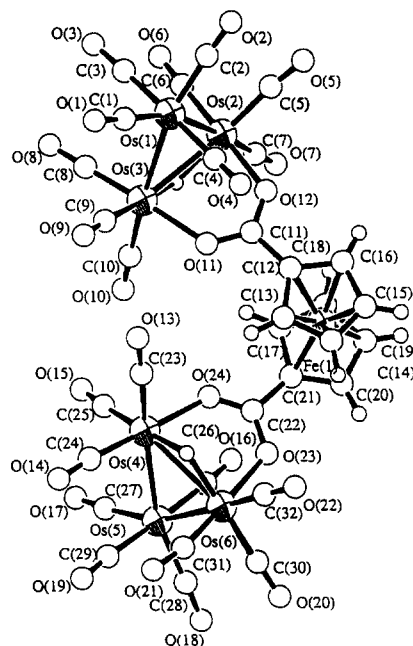


Fig. 2. Molecular structure of $[(\text{Os}_3\text{H}(\text{CO})_{10})_2(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CO}_2)](2)$.

$[(\text{Os}_3\text{H}(\text{CO})_{10})_2(\text{C}_2\text{O}_4)]$ [7]. The ^1H NMR spectrum of 1 shows the signals from the cyclopentadienyl protons in a 2:2:5 signal integration ratio in the range δ 4.58–4.15. The signal at δ –10.24 was assigned to

Os–H. In the case of 2, the ^1H NMR spectrum shows the cyclopentadienyl proton signals as two triplets at δ 4.26 and 4.52 and the Os–H resonance at δ –10.27.

Single crystals of 1 and 2 were obtained from a dichloromethane–*n*-hexane mixture. The structures of

Table 4

Selected bond distances (Å) and bond angles (°) in $[(\text{Os}_3\text{H}(\text{CO})_{10})_2(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CO}_2)]$ (2)

Molecule A		Molecule B	
Os(1)–Os(2)	2.862(1)	Os(7)–Os(8)	2.916(1)
Os(1)–Os(3)	2.858(1)	Os(7)–Os(9)	2.8662(9)
Os(2)–Os(3)	2.920(1)	Os(8)–Os(9)	2.859(1)
Os(4)–Os(5)	2.869(1)	Os(10)–Os(11)	2.903(1)
Os(4)–Os(6)	2.898(1)	Os(10)–Os(12)	2.867(1)
Os(5)–Os(6)	2.865(1)	Os(11)–Os(12)	2.871(1)
Os(2)–O(12)	2.10(1)	Os(7)–O(36)	2.12(1)
Os(3)–O(11)	2.15(1)	Os(8)–O(35)	2.13(1)
Os(4)–O(24)	2.14(1)	Os(10)–O(48)	2.13(1)
Os(6)–O(23)	2.16(1)	Os(11)–O(47)	2.14(1)
C(11)–O(11)	1.26(2)	C(43)–O(35)	1.25(2)
C(11)–O(12)	1.28(2)	C(43)–O(36)	1.27(2)
C(11)–C(12)	1.45(3)	C(43)–C(44)	1.49(2)
C(22)–O(23)	1.26(2)	C(54)–O(47)	1.29(2)
C(22)–O(24)	1.22(2)	C(54)–O(48)	1.30(2)
C(22)–C(21)	1.49(2)	C(54)–C(52)	1.46(2)
Os(2)–Os(1)–Os(3)	61.40(3)	Os(8)–Os(7)–Os(9)	59.26(2)
Os(1)–Os(2)–Os(3)	59.22(3)	Os(7)–Os(8)–Os(9)	59.51(2)
Os(1)–Os(3)–Os(2)	59.38(3)	Os(7)–Os(9)–Os(8)	61.23(3)
Os(5)–Os(4)–Os(6)	59.58(3)	Os(11)–Os(10)–Os(12)	59.67(3)
Os(4)–Os(5)–Os(6)	60.70(3)	Os(10)–Os(11)–Os(12)	59.53(3)
Os(4)–Os(6)–Os(5)	59.72(3)	Os(10)–Os(12)–Os(11)	60.79(3)
O(11)–C(11)–O(12)	124(1)	O(35)–C(43)–O(36)	125(1)
O(23)–C(22)–O(24)	124(1)	O(47)–C(54)–O(48)	126(1)
Os–C–O (average)	175.5	Os–C–O (average)	176.1

Table 5

Final atomic coordinates and equivalent isotropic displacement coefficients, B_{eq} (\AA^2), for $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CO}_2)]$ (2)

Atom	x	y	z	B_{eq}^a
Os(1)	0.62136(5)	0.42941(3)	0.0330(1)	3.52(2)
Os(2)	0.54479(4)	0.40642(3)	0.31133(10)	2.88(2)
Os(3)	0.67979(4)	0.38134(3)	0.2993(1)	2.90(2)
Os(4)	0.76976(4)	0.19640(3)	0.46087(10)	2.63(2)
Os(5)	0.77853(4)	0.13015(3)	0.70791(10)	2.97(2)
Os(6)	0.70885(4)	0.09847(3)	0.36056(10)	2.87(2)
Os(7)	0.90953(4)	-0.12667(3)	-0.29480(10)	2.53(2)
Os(8)	0.77634(4)	-0.09951(3)	-0.36480(9)	2.56(2)
Os(9)	0.85051(4)	-0.07687(3)	-0.02005(9)	2.75(2)
Os(10)	0.98895(4)	-0.31649(3)	-0.58442(10)	2.74(2)
Os(11)	0.92029(4)	-0.41282(3)	-0.6111(1)	3.10(2)
Os(12)	0.99414(4)	-0.38367(3)	-0.88786(10)	3.35(2)
Fe(1)	0.4989(1)	0.20761(9)	0.2760(4)	3.12(7)
Fe(2)	0.7220(1)	-0.29653(9)	-0.5252(4)	3.11(7)
O(1)	0.7373(10)	0.4416(7)	-0.188(2)	7.7(5)
O(2)	0.5125(9)	0.4702(6)	-0.175(2)	6.3(4)
O(3)	0.6782(9)	0.5278(7)	0.242(2)	7.1(4)
O(4)	0.5720(9)	0.3315(7)	-0.172(2)	6.9(4)
O(5)	0.4182(9)	0.4243(6)	0.092(2)	6.1(4)
O(6)	0.5805(7)	0.5053(5)	0.497(2)	4.6(3)
O(7)	0.4675(9)	0.3763(6)	0.612(2)	7.2(4)
O(8)	0.7676(9)	0.4732(6)	0.456(2)	6.6(4)
O(9)	0.7881(9)	0.3623(6)	0.062(2)	6.4(4)
O(10)	0.7261(8)	0.3304(6)	0.602(2)	5.7(4)
O(11)	0.6211(6)	0.3139(4)	0.193(2)	3.3(3)
O(12)	0.5181(6)	0.3353(4)	0.196(2)	3.2(2)
O(13)	0.7547(8)	0.2616(6)	0.181(2)	5.7(4)
O(14)	0.9100(7)	0.1869(5)	0.387(2)	4.4(3)
O(15)	0.8160(7)	0.2728(5)	0.775(2)	3.9(3)
O(16)	0.6468(8)	0.1583(5)	0.825(2)	5.4(3)
O(17)	0.8571(8)	0.1988(6)	1.023(2)	5.7(4)
O(18)	0.7571(8)	0.0375(6)	0.864(2)	5.5(4)
O(19)	0.9122(8)	0.1052(5)	0.589(2)	4.9(3)
O(20)	0.6639(8)	0.0068(6)	0.496(2)	5.9(4)
O(21)	0.8356(8)	0.0656(5)	0.240(2)	5.4(3)
O(22)	0.6247(10)	0.0665(7)	0.003(2)	7.5(5)
O(23)	0.6204(6)	0.1279(5)	0.425(2)	3.5(3)
O(24)	0.6677(6)	0.2020(4)	0.501(2)	2.9(2)
O(25)	1.0148(8)	-0.1470(5)	-0.017(2)	5.0(3)
O(26)	0.9523(8)	-0.1790(5)	-0.617(2)	5.3(2)
O(27)	1.0015(8)	-0.0374(5)	-0.323(2)	4.9(3)
O(28)	0.8269(7)	-0.0020(5)	-0.454(2)	4.8(3)
O(29)	0.6931(8)	-0.1298(6)	-0.723(2)	5.8(4)
O(30)	0.6549(8)	-0.0713(6)	-0.198(2)	5.8(4)
O(31)	0.7428(8)	-0.0314(5)	0.164(2)	5.0(3)
O(32)	0.9159(8)	0.0197(6)	-0.103(2)	5.3(3)
O(33)	0.7968(8)	-0.1754(6)	0.066(2)	5.7(4)
O(34)	0.9612(9)	-0.0698(6)	0.286(2)	6.2(4)
O(35)	0.7455(6)	-0.1704(4)	-0.323(1)	2.9(2)
O(36)	0.8482(6)	-0.1916(4)	-0.282(2)	3.2(2)
O(37)	1.0405(7)	-0.2404(5)	-0.797(2)	4.2(3)
O(38)	0.9779(7)	-0.2511(5)	-0.248(2)	4.5(3)
O(39)	1.1292(7)	-0.3292(5)	-0.448(2)	4.3(3)
O(40)	0.8366(9)	-0.4388(6)	-0.317(2)	6.8(4)
O(41)	1.0429(8)	-0.4514(5)	-0.462(2)	5.5(4)
O(42)	0.8623(9)	-0.5029(6)	-0.862(2)	6.7(4)
O(43)	0.9647(8)	-0.4752(6)	-1.143(2)	6.2(4)
O(44)	1.1248(9)	-0.4144(6)	-0.725(2)	6.2(4)
O(45)	0.8686(8)	-0.3504(6)	-1.050(2)	5.9(4)
O(46)	1.0774(8)	-0.3204(6)	-1.104(2)	5.8(4)
O(47)	0.8353(6)	-0.3808(5)	-0.698(2)	3.6(3)
O(48)	0.8898(6)	-0.3042(4)	-0.671(2)	3.2(3)
C(1)	0.692(1)	0.4356(9)	-0.105(3)	5.6(5)

Table 5 (continued)

Atom	x	y	z	B_{eq}^a
C(2)	0.555(1)	0.4560(7)	-0.096(3)	4.1(4)
C(3)	0.654(1)	0.4899(8)	0.166(3)	4.6(5)
C(4)	0.590(1)	0.3674(8)	-0.090(3)	4.3(5)
C(5)	0.467(1)	0.4199(7)	0.179(2)	3.5(4)
C(6)	0.5689(9)	0.4690(7)	0.422(2)	2.9(4)
C(7)	0.498(1)	0.3869(7)	0.497(3)	4.1(4)
C(8)	0.734(1)	0.4373(9)	0.394(3)	5.5(5)
C(9)	0.748(1)	0.3707(8)	0.147(3)	5.1(5)
C(10)	0.709(1)	0.3496(7)	0.486(3)	4.0(4)
C(11)	0.5576(10)	0.3047(7)	0.170(2)	3.0(4)
C(12)	0.5263(10)	0.2560(7)	0.112(2)	3.2(4)
C(13)	0.559(1)	0.2159(7)	0.081(3)	3.8(4)
C(14)	0.509(1)	0.1752(8)	0.032(3)	4.6(5)
C(15)	0.449(1)	0.1906(8)	0.031(3)	5.2(5)
C(16)	0.4564(10)	0.2392(7)	0.083(2)	3.3(4)
C(17)	0.5408(10)	0.2332(7)	0.529(2)	3.3(4)
C(18)	0.472(1)	0.2332(7)	0.513(3)	3.8(4)
C(19)	0.438(1)	0.1847(8)	0.456(3)	4.9(5)
C(20)	0.490(1)	0.1569(7)	0.436(3)	4.0(4)
C(21)	0.5505(9)	0.1854(7)	0.481(2)	2.9(4)
C(22)	0.6183(9)	0.1712(6)	0.466(2)	2.5(3)
C(23)	0.759(1)	0.2360(7)	0.288(3)	3.6(4)
C(24)	0.858(1)	0.1933(7)	0.421(3)	4.1(4)
C(25)	0.8013(10)	0.2442(7)	0.658(2)	3.2(4)
C(26)	0.694(1)	0.1463(8)	0.779(3)	4.8(5)
C(27)	0.830(1)	0.1720(8)	0.903(3)	4.0(4)
C(28)	0.764(1)	0.0724(8)	0.803(3)	3.8(4)
C(29)	0.865(1)	0.1158(8)	0.630(3)	4.7(5)
C(30)	0.681(1)	0.0423(9)	0.450(3)	5.4(5)
C(31)	0.783(1)	0.0746(8)	0.281(3)	5.0(5)
C(32)	0.660(1)	0.0798(8)	0.145(3)	5.1(5)
C(33)	0.974(1)	-0.1398(7)	-0.122(3)	3.7(4)
C(34)	0.9382(9)	-0.1601(7)	-0.495(2)	2.9(4)
C(35)	0.9653(10)	-0.0701(7)	-0.311(2)	3.3(4)
C(36)	0.8057(10)	-0.0393(7)	-0.417(2)	3.3(4)
C(37)	0.727(1)	-0.1192(7)	-0.590(3)	4.0(4)
C(38)	0.701(1)	-0.0834(7)	-0.257(3)	3.8(4)
C(39)	0.783(1)	-0.0491(7)	0.098(3)	4.0(4)
C(40)	0.890(1)	-0.0164(7)	-0.075(3)	3.7(4)
C(41)	0.813(1)	-0.1405(8)	0.029(3)	4.1(4)
C(42)	0.920(1)	-0.0724(7)	0.169(3)	3.6(4)
C(43)	0.7841(9)	-0.2003(6)	-0.306(2)	2.4(3)
C(44)	0.7520(9)	-0.2498(6)	-0.304(2)	2.8(4)
C(45)	0.681(1)	-0.2662(7)	-0.318(3)	3.8(4)
C(46)	0.671(1)	-0.3148(7)	-0.316(2)	3.6(4)
C(47)	0.737(1)	-0.3294(7)	-0.304(3)	3.8(4)
C(48)	0.7855(9)	-0.2896(6)	-0.297(2)	2.6(3)
C(49)	0.658(1)	-0.3148(8)	-0.763(3)	4.9(5)
C(50)	0.696(1)	-0.2685(7)	-0.751(3)	4.0(4)
C(51)	0.764(1)	-0.2712(7)	-0.728(3)	3.9(4)
C(52)	0.7728(10)	-0.3178(7)	-0.732(2)	3.3(4)
C(53)	0.707(1)	-0.3450(7)	-0.745(3)	4.0(4)
C(54)	0.836(1)	-0.3360(7)	-0.694(3)	3.6(4)
C(55)	1.0199(9)	-0.2699(7)	-0.717(2)	2.9(4)
C(56)	0.9825(10)	-0.2742(7)	-0.379(3)	3.5(4)
C(57)	1.0751(9)	-0.3252(6)	-0.501(2)	2.8(4)
C(58)	0.871(1)	-0.4288(8)	-0.429(3)	4.3(5)
C(59)	0.992(1)	-0.4409(8)	-0.522(3)	4.6(5)
C(60)	0.886(1)	-0.4695(8)	-0.764(3)	4.3(5)
C(61)	0.976(1)	-0.4414(8)	-1.044(3)	4.3(5)
C(62)	1.074(1)	-0.4038(7)	-0.779(3)	4.1(4)
C(63)	0.916(1)	-0.3633(7)	-0.985(3)	4.0(4)
C(64)	1.045(1)	-0.3450(7)	-1.018(3)	3.9(4)

$$^a B_{eq} = \frac{8}{3} \pi^2 [U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha].$$

the compounds were revealed by X-ray crystallographic studies. The molecular structure of **1**, together with the atomic labelling scheme is illustrated in Fig. 1. Relevant bond lengths and angles are tabulated in Table 2 and the final atomic coordinates are presented in Table 3. Cluster **1** possesses C_3 symmetry and is based on a triangular array of osmium atoms arranged in an isosceles manner ($\text{Os}(1)\text{--Os}(1^*) = 2.912(3)$ Å vs. $\text{Os}(1)\text{--Os}(2) = 2.872(2)$ Å). The structure of **1** is similar to that of $[\text{Os}_3\text{H}(\text{HCO}_2)(\text{CO})_{10}]$ [4]. Potential energy calculations [12] suggested that the bridging hydride, as is evident from ^1H NMR spectrum, bridges the $\text{Os}(1)\text{--Os}(1^*)$ edge; the non-bridged $\text{Os}\text{--Os}$ distance is similar to the average $\text{Os}\text{--Os}$ distance in the parent cluster $[\text{Os}_3(\text{CO})_{12}]$ [13]. The molecule is bisected by the crystallographic mirror planes with $\text{Os}(2)$, $\text{C}(7)$, $\text{C}(8)$, Fe , $\text{C}(15)$, $\text{C}(4)$, $\text{O}(4)$, $\text{C}(6)$ and $\text{O}(6)$ on the mirror plane.

Cluster **2** crystallized in the triclinic system and with two independent molecules (molecules A and B) in the asymmetric unit. An ORTEP drawing of the cluster $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2(\text{O}_2\text{CC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CO}_2)]$ (**2**) is depicted in Fig. 2 together with the atomic labelling scheme. Selected interatomic distances and angles for both molecules are given in Table 4 and the final atomic coordinates in Table 5. Each molecule contains two Os_3 triangles linked together by the 1,1'-ferrocene carboxylate ligand. Unlike the oxalate [7], succinic acid and acetylenedicarboxylate [11] derivatives, which have the two Os_3 clusters parallel to each other, cluster **2** has two Os_3 planes almost perpendicular to each other (mean dihedral angle $97.03(2)^\circ$). Moreover, the two Os_3 triangles point in opposite directions.

The mode of bonding of the carboxylate group to the triosmium unit has been observed previously. The geometries of carbonyl ligands in clusters **1** and **2** are indistinguishable from that for $[\text{Os}_3\text{H}(\text{HCO}_2)(\text{CO})_{10}]$ [4]. The carboxylate ligand takes up an essentially axial position and the five-membered $\text{Os}\text{--O}\text{--C}\text{--O}\text{--Os}$ plane is almost perpendicular to the triosmium triangle in both complexes. The dihedral angle between the triosmium plane and $\text{Os}\text{--O}\text{--C}\text{--O}\text{--Os}$ plane in **1** is 85.5° , whereas

in **2** the mean corresponding angle is 83.3° . In both complexes **1** and **2**, the bridging carboxylate has a mean $\text{O}\text{--C}\text{--O}$ angle and $\text{C}\text{--O}$ bond distances that lie in the normal range for delocalized carboxylate ligands (cluster **1** $126(4)^\circ$, $1.31(3)$ Å vs. cluster **2** $124(1)^\circ$, $1.26(2)$ Å (molecule A), and $125(1)^\circ$, $1.28(2)$ Å (molecule B)) [14].

In order to investigate the redox properties of complexes **1** and **2**, voltammetric measurements were undertaken with dichloromethane solutions. The results are summarized in Table 6. Ferrocenemonocarboxylic acid undergoes two electrochemical oxidations at a scan rate of 100 mV s^{-1} ; one appears at 0.09 V and the other close to 0.3 V (vs. Ag/AgNO_3). The wave at 0.09 V disappears when the scan rate is increased to 2.1 V s^{-1} . The chemical reversible redox process is believed to be due to the ferrocene/ferrocenium couple, while the irreversible process is probably due to the reduction of carboxylic acid to aldehyde.

Complex **1** exhibits a single reversible oxidation step at 0.394 V vs. Ag/AgNO_3 . The disappearance of the wave near 0.1 V is probably due to the carboxylic acid group coordinated to triosmium cluster forming carboxylate, which is difficult to reduce. The reversible oxidation wave of **1** is close to that of the ligand, leading us to believe that the $\text{Os}_3(\text{CO})_{10}\text{H}$ unit plays no role in the electron transfer process and that the oxidation wave is mainly due to the ferrocene/ferrocenium couple.

Complex **2** also exhibits a single reversible oxidation process. However, it requires a more positive potential for oxidation. The $E_{1/2}$ value is 0.713 V vs. Ag/AgNO_3 . Since the structure of **2** is closely related to that of **1**, we believe the electron transfer takes place at the ferrocene centre just as in the case of complex **1**, although cyclic voltammetric data for 1,1'-ferrocenedicarboxylic acid could not be obtained for comparison because of solubility problems.

The oxidation potential of **1** is comparable to that of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-COC}_5\text{H}_4\text{FeC}_5\text{H}_5)]$ ($E_{1/2} = 0.8 \text{ V}$ vs. Ag/AgCl ; 0.48 V vs. Ag/AgNO_3) [15], which also contains the ferrocenyl moiety. Complex **2** contains two linked Os_3 units for which the electron-withdrawing effect is more pronounced than that of the Os_3 group in **1**, and so, the ferrocenyl unit requires a more positive potential for oxidation.

Table 6

Redox potentials^a (V vs. Ag/AgNO_3) for the electrochemical processes undergone by ferrocenemonocarboxylic acid, clusters **1** and **2**^b

Compound	Formal electrode potential ^c (V)
Ferrocenemonocarboxylic acid ^d	0.407
Cluster 1	0.447
Cluster 2	0.713

^a Peak potential value, E_p , referred to 100 mV s^{-1} scan rate using $0.1 \text{ M NBu}_4\text{PF}_6$ in CH_2Cl_2 as supporting electrolyte.

^b The redox potential of 1,1'-ferrocenedicarboxylic acid cannot be determined owing to its poor solubility.

^c Formal electrode potential defined as $E = (E_p^a + E_p^c)/2$ for a chemically reversible processes.

^d An irreversible reduction wave appears at 0.09 V.

3. Experimental

3.1. Materials and general procedures

All reactions were carried out under dinitrogen by use of standard Schlenk-type techniques. All solvents were dried by standard methods and distilled before used. $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ was prepared as described previously [16]. Ferrocenemonocarboxylic acid and

1,1'-ferrocenedicarboxylic acid were used as obtained from Strem Chemicals. Products were isolated by preparative TLC on silica (Merck Kieselgel 60 GF₂₅₄) prepared as an aqueous slurry spread on glass plates.

Infrared spectra were recorded on a Nicolet 20SXC FT-IR spectrometer. The ¹H NMR spectra were recorded on a JEOL GSX 270 FT NMR spectrometer; chemical shifts are relative to internal SiMe₄. Fast atom bombardment (FAB) mass spectra were obtained with a Finnigan MAT 95 instrument.

3.2. Reaction of [Os₃(CO)₁₀(CH₃CN)₂] with ferrocenemonocarboxylic acid

To a solid mixture of [Os₃(CO)₁₀(CH₃CN)₂] (50 mg, 0.0536 mmol) and ferrocenemonocarboxylic acid (12.3 mg, 0.0535 mmol) were added 10 ml of dichloromethane. The mixture was stirred at room temperature for 1 h, during which the colour turned from yellow to orange. After removal of the solvent in vacuo, the orange residue was separated by TLC with n-hexane–dichloromethane (50:50, v/v) as eluent. The first orange band gave [HOs₃(CO)₁₀(O₂CC₅H₄FeC₅H₅)] (31.3 mg, 54%) (*R_f* ≈ 0.6). Orange crystals were formed by

slow evaporation of a CH₂Cl₂–n-hexane mixture during 1 day at room temperature.

3.3. Reaction of [Os₃(CO)₁₀(CH₃CN)₂] with 1,1'-ferrocenedicarboxylic acid

A solution of [Os₃(CO)₁₀(CH₃CN)₂] (50 mg, 0.0536 mmol) and a ten-fold excess of 1,1'-ferrocenedicarboxylic acid in chloroform (10 ml) was heated under reflux for 4 h. TLC separation with n-hexane–dichloromethane (50:50, v/v) as eluent gave [(Os₃H(CO)₁₀)₂(O₂CC₅H₄FeC₅H₄CO₂)] (17.9 mg, 36%) (*R_f* ≈ 0.1). Air-stable orange crystals were grown from a CH₂Cl₂–n-hexane mixture during 1 day at room temperature.

3.4. Electrochemical Measurements

Voltammetric measurements were performed with a Princeton Applied Research (PAR) Model 273A potentiostat connected to an interfaced computer. A standard three-electrode cell having a platinum wire counter electrode (Aldrich), an Ag/AgNO₃ reference electrode (Bioanalytical) and a glassy carbon working electrode (Bioanalytical) was employed. All measurements were

Table 7

Crystal data and data collection parameters ^a for [HOs₃(CO)₁₀(O₂CC₅H₄FeC₅H₅)] (1) and [(Os₃H(CO)₁₀)₂(O₂CC₅H₄FeC₅H₄CO₂)] (2)

Parameter	1	2
Formula	C ₂₂ H ₁₂ Cl ₂ FeO ₁₂ Os ₃	C ₃₂ H ₁₀ FeO ₂₄ Os ₆
Formula weight	1165.68	1975.46
Colour, habit	Orange, blocks	Orange, blocks
Crystal dimensions (mm)	0.22 × 0.32 × 0.34	0.30 × 0.32 × 0.42
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbcm</i> (No. 57)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	7.690(3)	20.170(4)
<i>b</i> (Å)	33.56(1)	28.869(6)
<i>c</i> (Å)	11.238(4)	7.703(4)
α (°)		97.12(3)
β (°)		96.09(2)
γ (°)		97.93(2)
<i>V</i> (Å ³)	2900(1)	4373(2)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	2.669	3.000
<i>F</i> (000)	2112.00	3504.00
μ (Mo K α) (cm ⁻¹)	138.24	177.56
2 θ range (°)	4–40	4–45
Scan rate in ω (° min ⁻¹)	16 (up to 4 scans)	16 (up to 4 scans)
Scan range (°)	0.73 + 0.35 tan θ	0.63 + 0.35 tan θ
Reflections collected	2997	11831
Unique reflections	1624 (<i>R</i> _{int} = 0.06)	11438 (<i>R</i> _{int} = 0.04)
Observed reflections	1074 (<i>I</i> > 3 σ (<i>I</i>))	8666 (<i>I</i> > 3 σ (<i>I</i>))
<i>R</i>	0.060	0.040
<i>R</i> _w	0.071	0.047
Goodness of fit	<i>S</i> = 2.590	<i>S</i> = 2.001
Number of parameters	104	575
Residual electron density (e Å ⁻³) (close to Os)	–1.79 to 1.55	–1.78 to 1.79

^a Details in common: temperature, 295 K; radiation, Mo K α (λ = 0.71073 Å); diffractometer, Rigaku AFC7R; scan mode, ω – 2 θ ; background measurement, 25% at both ends; weighting scheme: $w = 4F_0^2/\sigma^2F_0^2$.

carried out under N₂ in anhydrous deoxygenated dichloromethane.

The supporting electrolyte was 0.1 M tetra-n-butylammonium hexafluorophosphate (Aldrich) in CH₂Cl₂. Potentials were measured vs. the ferrocenium/ferrocene couple in the same solution. Positive feedback *iR* compensation was routinely applied.

3.5. X-Ray Analyses of 1 and 2

Orange crystals of **1** were mounted in a lithium glass capillary as they lose solvent of crystallization very rapidly. Crystals of **2** were mounted on a glass fibre. Intensity data for both **1** and **2** were collected on a Rigaku AFC7R diffractometer using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects and for absorption by the Ψ -scan method [17]. The crystal data and data collection parameters for both compounds are summarized in Table 7. The poor crystal quality of **1** and its weak diffraction precluded intensity measurement at 2θ of $> 40^\circ$. Both structures were solved by a combination of direct methods (SIR 88) [18] and Fourier difference techniques and refined by full-matrix least-squares analysis (Os, Fe anisotropic) until convergence was reached. The hydrogen atoms of the organic moieties were placed in calculated positions (C–H, 0.96 Å). All calculations were performed on a Silicon-Graphics computer using the program package TeXsan (from MSC) [19]. Final atomic coordinates for the two compounds are listed in Tables 3 and 5. Additional materials available from the Cambridge Crystallographic Data Centre include hydrogen atom coordinates, thermal parameters and a full list of bond lengths and angles.

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