Synthesis, characterisation, electrochemistry and reactivity of osmium–palladium carbonyl complexes containing 1,1′-bis(diphenylphosphino)ferrocene (dppf); molecular structures of $[Os_5PdC(CO)_{14}(\mu\text{-dppf})]$, $[OsPd(\mu\text{-}I)_2I_2(CO)_2(\mu\text{-dppf})]_2$ and $[\{Os_5C(CO)_{14}\}_2(\mu\text{-dppf})]$

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The hexanuclear osmium–palladium carbonyl carbide cluster $[Os_5PdC(CO)_{14}(\mu\text{-dppf})]$ **1** [dppf = 1,1′-bis(diphenylphosphino)ferrocene] has been synthesized in 56% yield by the reaction of $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$ with $[Pd(dppf)(H_2O)_2][O_3CCF_3]_2$. When treated with iodine in CH_2Cl_2 at ambient conditions, compound **1** underwent cluster degradation to give the macrocyclic complex $[OsPd(\mu\text{-}I)_2I_2(CO)_2(\mu\text{-dppf})]_2$ **2**. Thermolysis of complex **1** in refluxing chloroform gave the dppf bridged dimeric cluster $[\{Os_5C(CO)_{14}\}_2(\mu\text{-dppf})]$ **3**. The structures of **1**–**3** were characterised by IR, ^1H, ^{31}P NMR and mass spectroscopies and X-ray crystallography. Electrochemical investigations revealed that complex **1** underwent a reversible one-electron oxidation at the ferrocene centre followed by a quasi-reversible oxidation of the metal cluster core.

One of our interests is the synthesis and reactivity of osmium–palladium mixed-metal carbonyl clusters.[1–6] We have recently reported the reactions of the osmium carbide cluster $[Os_5C(CO)_{15}]$ with palladium reagents containing phosphorus donor ligands such as $[Pd(PPh_3)_4]$ or $[Pd(PPh_3)_2Cl_2]$ which led to the formation of the heterometallic complexes $[Os_5PdC(CO)_{12}(\mu\text{-CO})_2(PPh_3)_2]$ and $[Os_5PdC(CO)_{15}(\mu\text{-Cl})_2(PPh_3)]$ respectively in moderate yields.[5] The former product is found to consist of a square-based pyramidal core of five osmium atoms with a $Pd(PPh_3)$ group capping a triangular face of the pyramid. The metal core of the second complex consists of a butterfly of four osmium atoms with the two 'wing-tip' osmium atoms bridged by the Pd atom and an additional $Os(PPh_3)(CO)_3$ moiety connected to the apex. Both metal cores contain Pd−C (carbide) bonds. To our knowledge, structurally characterised examples containing Pd−C (carbide) bonds are rare and it is believed that the carbide may have a stabilising effect on the overall geometry of the clusters.[7,8] The properties of this carbon atom and the chemistry of this carbide bond are potentially interesting.[9] In addition, 1,1′-bis(diphenylphosphino)ferrocene (dppf), a member of the ferrocenylphosphine family, has been extensively employed as a chelating agent for transition-metal complexes which show interesting properties and is also widely utilised in metal carbonyl complexes.[10–14] To date, there have been only a few examples of cluster complexes that contain both carbide and dppf.[15] The idea of combining the properties of these two sets of fascinating molecules has significant appeal.

As part of our ongoing studies of the chemistry of osmium–palladium mixed-metal carbonyl clusters, we report some reactivities of compound $[Os_5PdC(CO)_{14}(\mu\text{-dppf})]$ **1**, which is prepared by the reaction of $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$ and $[Pd(dppf)(H_2O)_2][O_3CCF_3]_2$.

Results and Discussion

Syntheses

Ionic coupling has been shown to be an effective way to increase the metal nuclearity of a cluster in a systematic and controlled fashion. Even under mild conditions rapid coupling reactions between the ions are observed.[16–18] We have recently reported the reaction of $[Os_5C(CO)_{14}]^{2-}$ with $[M(C_6H_6)(MeCN)_3]^{2+}$ (M = Os or Ru) in CH_2Cl_2 at room temperature, which led to the formation of some arene derivatives of hexanuclear carbide clusters, and led us to believe that systematic cluster build-up using $[Os_5C(CO)_{15}]$ is possible.[19]

When the activated pentaosmium carbide cluster $[Os_5C(CO)_{14}]^{2-}$ was allowed to react with a stoichiometric amount of $[Pd(dppf)(H_2O)_2]^{2+}$ at room temperature, $[Os_5PdC(CO)_{14}(\mu\text{-dppf})]$ **1** was obtained as dark red crystals in 56% yield. The formation of complex **1** in good yields offered us the opportunity to study its reactivity. Treating a solution of **1** in CH_2Cl_2 with a suspension of 5 equivalents of iodine in CH_2Cl_2 led to the formation of the unprecedented macrocyclic complex $[OsPd(\mu\text{-}I)_2I_2(CO)_2(\mu\text{-dppf})]_2$ **2**, which could be isolated as a brown solid in relatively low yield (6%). In addition, we observed significant decomposition of the starting cluster. The mechanism leading to **2** is not well understood at this stage. However, we believe that the oxidation by I_2 caused cluster degradation to give some fragments containing Os and Pd metals bridged by a dppf ligand prior to the formation of complex **2**. In order to investigate the cluster metal core rearrangement about the osmium–palladium heterometallic bond, we heated **1** in chloroform (61 °C) to reflux for approximately 48 h. The only product isolated upon TLC separation is a linking cluster $[\{Os_5C(CO)_{14}\}_2(\mu\text{-dppf})]$ **3**. Under thermal conditions, **1** was found to undergo Os−Pd bond cleavage, with palladium metal being deposited, leaving the pendant dppf ligand to bond to another $\{Os_5C(CO)_{14}\}$ fragment to form complex **3**. This observation leads to the impression that polar Os−Pd bonds are weaker than the Os−Os bond in **1** and that it is the subsequent formation of the thermodynamically favourable cluster $[\{Os_5C(CO)_{14}\}_2(\mu\text{-dppf})]$ **3** that provides the driving force for this conversion.

The complexes **1**–**3** were fully characterised by conventional spectroscopic [IR, ^1H, ^{31}P NMR and fast atom bombardment (FAB) mass spectra] techniques and elemental analyses, see Table 1. The ^1H and ^{31}P NMR signals due to the organic moieties of all the complexes are fully consistent with their structures and all the mass spectra exhibit molecular ion envelopes which agree with the formulae of the compounds, with ion peaks corresponding to CO losses also being present. The signals due to protons of the cyclopentadienyl rings are observed at δ 4.58 while the phenyl rings protons are observed in the

Table 1 Spectroscopic data for compounds **1**–**3**

Compound	IR ν(CO)/cm$^{-1\,a}$	^{1}H NMR/δ^b	^{31}P NMR/δ^c	Mass spectra (*m*/*z*)^d
1	2077s, 2036s, 2018m, 2010m, 1983w	7.58 (m, 20 H), 4.58 (s br, 8 H)	29.62 (s), −8.23 (s)	2374 (2374)
2	2115w, 2049s, 2022m, 1984m	7.34 (m, 40 H)	35.46 (s), −84.31 (s)	2999 (2997)
3	2096w, 2061s, 2049m, 2026m, 2015m (sh)	7.33 (m, 20 H)	−11.81 (s)	3350 (3347)

^{a} Recorded in CH_2Cl_2. ^{b} Recorded in CD_2Cl_2 at 298 K. ^{c} Recorded in $CDCl_3$ at 298 K. ^{d} Calculated value in parentheses.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Os(1)–Os(2)	2.186(2)	Os(1)–Os(3)	2.915(2)
Os(1)–Os(4)	2.843(2)	Os(1)–Os(5)	2.895(2)
Os(2)–Os(3)	2.852(2)	Os(2)–Os(5)	2.935(2)
Os(2)–Pd	2.974(3)	Os(3)–Os(4)	2.902(2)
Os(4)–Os(5)	2.997(2)	Os(5)–Pd	2.767(2)
Os(1)–C(15)	2.28(3)	Pd–C(15)	2.04(3)
Os(2)–C(15)	2.17(2)	Os(3)–C(15)	2.05(3)
Os(4)–C(15)	2.06(2)	Os(5)–C(15)	2.07(2)
Pd–C(15)	2.04(3)	Pd–P(1)	2.327(8)
Os(4)–P(2)	2.386(7)	Fe–C $(C_5H_4)_{average}$	2.05(1)
Os(2)–Os(1)–Os(3)	59.65(4)	Os(2)–Os(1)–Os(4)	94.90(4)
Os(2)–Os(1)–Os(5)	61.83(4)	Os(3)–Os(1)–Os(4)	60.92(4)
Os(3)–Os(1)–Os(5)	89.61(4)	Os(4)–Os(1)–Os(5)	62.97(4)
Os(1)–Os(2)–Os(3)	61.89(4)	Os(1)–Os(2)–Os(5)	60.40(4)
Os(1)–Os(2)–Pd	95.11(6)	Os(3)–Os(2)–Os(5)	90.05(5)
Os(3)–Os(2)–Pd	68.34(5)	Os(5)–Os(2)–Pd	55.84(5)
Os(1)–Os(3)–Os(2)	58.46(4)	Os(1)–Os(3)–Os(4)	58.32(4)
Os(2)–Os(3)–Os(4)	92.50(4)	Os(1)–Os(4)–Os(3)	60.76(4)
Os(3)–Os(4)–Os(5)	87.56(4)	Os(1)–Os(5)–Os(2)	57.77(4)

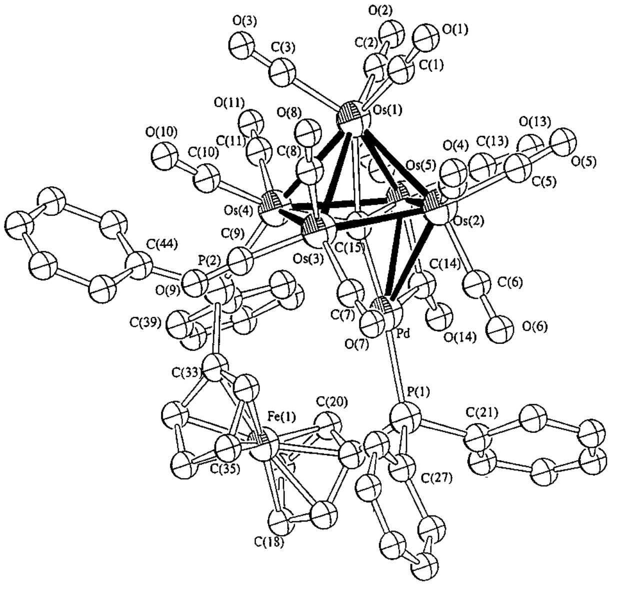

Fig. 1 The molecular structure of $[Os_5PdC(CO)_{14}(\mu\text{-dppf})]$ **1** with the atom numbering scheme

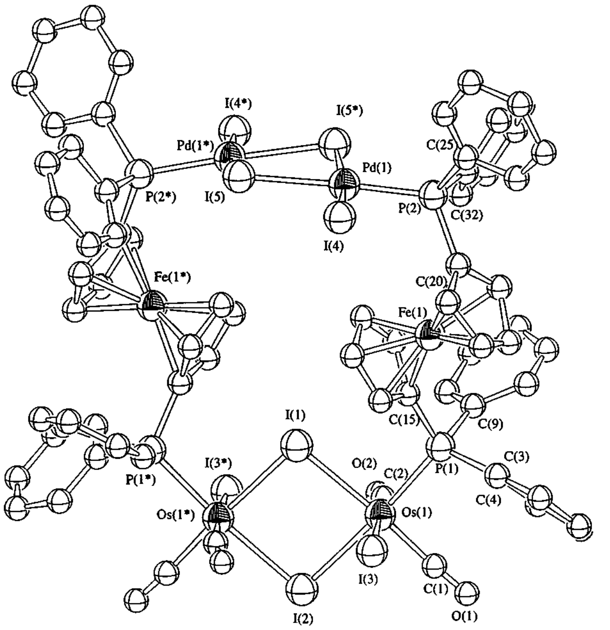

Fig. 2 The molecular structure of $[OsPd(\mu\text{-I})_2I_2(CO)_2(\mu\text{-dppf})]_2$ **2** with the atom numbering scheme

range δ 7.35–7.58. These values are comparable to those of other dppf-substituted complexes.[20–23] The structures of complexes **1**–**3** have been established by X-ray crystallography.

Molecular structures of compounds 1–3

Dark red crystals of **1** suitable for a diffraction study were grown from a saturated solution of $CHCl_3$–cyclohexane at room temperature. The molecular structure of **1** is depicted in Fig. 1, while selected bond distances and angles are given in Table 2. Three molecules of $CHCl_3$, as the solvent of crystallisation, were present in the crystal lattice. The compound consists of 88 cluster valence electrons which can be rationalised by the Effective Atomic Number (EAN) rule[24] and the Condensed Polyhedral Approach,[25] although there are many mixed-metal clusters of Os and Pt that do not obey simple electron-counting rules.[26–28] The single-crystal X-ray structural determination has shown that the metal core of **1** is essentially isostructural with that observed in $[Ru_6C(CO)_{15}(\mu\text{-dppf})]$, which was prepared by the reaction of $[Ru_6C(CO)_{17}]$ with dppf in refluxing tetrahydrofuran (thf).[15] A salient structural feature is the formation of an Os_5PdC metal core. The metal core of **1** can be described as a hinged square-based Os_5 pyramid, with Pd hinged at the basal metal atoms Os(2) and Os(5) and supported by P(1) of the bridging dppf ligand for which two very long Os · · · Pd separations [Os(3)–Pd 3.271(2) and Os(4)–Pd 3.272(2) Å] are observed. The carbide carbon atom is displaced from the centroid of the four metals constituting the square-based pyramid by 0.296(8) Å and toward Pd. The average Os(basal)–Os(basal) [2.926(3) Å] and Os(apical)–Os(basal) [2.867(4) Å] bond distances in **1** are slightly longer than the corresponding parameters in $[Os_5C(CO)_{15}]$, 2.88(2) and 2.85(3) Å, respectively.[29] The distorted cluster core is surrounded by 13 terminal carbonyls and one CO bridging the Os(5)–Pd vector. The presence of this bridging carbonyl group across this bond has a striking shortening effect [0.207(2) Å] as compared with the non-bridged Os(2)–Pd bond. However, no significant difference was observed[5] in $[Os_5PdC(CO)_{12}(\mu\text{-CO})_2(PPh_3)_2]$ between the supported and unbridged Os–Pd bonds. All carbonyls are essentially linear except that the Os(2)–C(6)–O(6) angle [171(2)°] is slightly distorted. Such a structural distortion is attributed to the close proximity of the Pd atom and the phenyl rings to the above mentioned carbonyl. The dppf ligand is ligated in the vicinal position, bridging the hinged Pd metal and the basal metal Os(4); so the two phosphorus atoms are in different environments.

Single crystals of complex **2** suitable for X-ray analysis were obtained by slow evaporation of a *n*-hexane–CH_2Cl_2 solution at room temperature for a period of 3 d. Fig. 2 shows the molecular structure of **2** and some important bond lengths and angles

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

Os(1)–I(1)	2.749(3)	Os(1)–I(2)	2.785(3)
Os(1)–I(3)	2.765(3)	Os(1)–P(1)	2.367(9)
I(4)–Pd(1)	2.581(4)	I(5)–Pd(1)	2.668(3)
I(5*)–Pd(1)	2.608(4)	Pd(1)–P(2)	2.288(8)
P(1)–C(15)	1.82(4)	P(1*)–C(15*)	1.84(3)
Fe–C $(C_5H_4)_{\mathbf{average}}$	2.02(1)		
I(1)–Os(1)–I(2)	84.12(7)	I(1)–Os(1)–I(3)	90.29(7)
I(1)–Os(1)–P(1)	91.2(2)	I(2)–Os(1)–I(3)	87.04(7)
I(2)–Os(1)–P(1)	173.9(2)	I(3)–Os(1)–P(1)	89.1(2)
Os(1)–I(1)–Os(1*)	96.7(1)	Os(1)–I(2)–Os(1*)	95.1(1)
Pd(1)–I(5)–Pd(1*)	95.4(1)	I(4)–Pd(1)–I(5)	88.6(1)
I(4)–Pd(1)–I(5*)	171.1(1)	I(4)–Pd(1)–P(2)	89.9(3)
I(5)–Pd(1)–I(5*)	83.2(1)	I(5)–Pd(1)–P(2)	176.9(3)
I(5*)–Pd(1)–P(2)	98.4(3)		

Symmetry code: $1 - x, y, \frac{1}{2} - z$.

Table 4 Selected bond lengths (Å) and angles (°) for complex **3**

Os(1)–Os(2)	2.840(4)	Os(1)–Os(3)	2.833(3)
Os(1)–Os(4)	2.844(3)	Os(1)–Os(5)	2.852(3)
Os(2)–Os(3)	2.864(3)	Os(2)–Os(5)	2.852(3)
Os(3)–Os(4)	2.940(3)	Os(4)–Os(5)	2.915(3)
Os(6)–Os(7)	2.833(4)	Os(6)–Os(8)	2.831(4)
Os(6)–Os(9)	2.819(3)	Os(6)–Os(10)	2.871(3)
Os(7)–Os(8)	2.852(3)	Os(7)–Os(10)	2.849(4)
Os(8)–Os(9)	2.924(4)	Os(9)–Os(10)	2.922(3)
Os(1)–C(29)	2.19(5)	Os(6)–C(30)	2.15(4)
Os(4)–P(1)	2.35(1)	Os(9)–P(2)	2.37(1)
Fe–C $(C_5H_4)_{\mathbf{average}}$	2.06(4)		
Os(2)–Os(1)–Os(3)	60.64(8)	Os(2)–Os(1)–Os(4)	92.44(8)
Os(2)–Os(1)–Os(5)	60.15(8)	Os(3)–Os(1)–Os(4)	62.39(7)
Os(3)–Os(1)–Os(5)	91.68(8)	Os(4)–Os(1)–Os(5)	61.58(7)
Os(1)–Os(2)–Os(3)	59.56(8)	Os(1)–Os(2)–Os(5)	60.12(8)
Os(3)–Os(2)–Os(5)	91.03(9)	Os(1)–Os(3)–Os(4)	58.98(7)
Os(2)–Os(3)–Os(4)	89.97(8)	Os(1)–Os(4)–Os(3)	58.63(7)
Os(7)–Os(6)–Os(8)	60.45(9)	Os(7)–Os(6)–Os(9)	92.96(9)
Os(6)–Os(7)–Os(8)	59.74(9)	Os(6)–Os(7)–Os(10)	60.71(9)
Os(6)–Os(8)–Os(9)	58.58(8)	Os(7)–Os(8)–Os(9)	90.3(1)
Os(6)–Os(9)–Os(8)	58.99(9)	Os(6)–Os(9)–Os(10)	59.98(7)
Os(6)–Os(10)–Os(9)	60.45(9)	Os(6)–Os(10)–Os(7)	59.38(9)

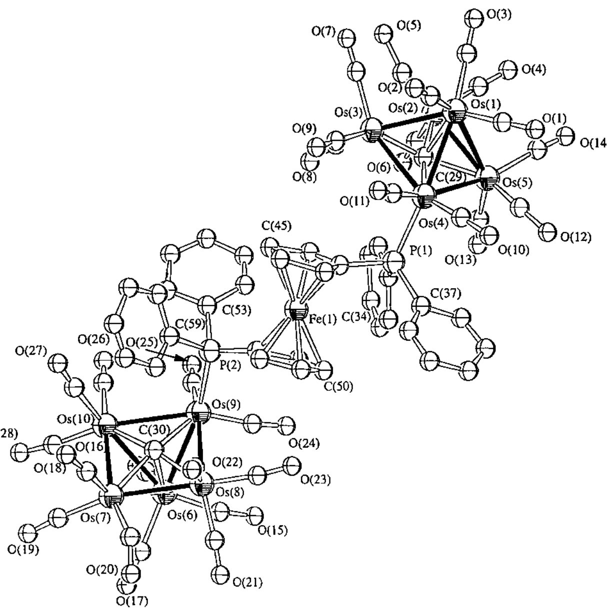

Fig. 3 The molecular structure of $[\{Os_5C(CO)_{14}\}_2(\mu\text{-dppf})]$ **3** with the atom numbering scheme

are given in Table 3. Complex **2** crystallises in the monoclinic space group *C*2/*c* with one half-molecule in the asymmetric unit. Structurally, complex **2** can be regarded as possessing an arrangement of the planar $\{Pd(\mu\text{-}I)I\}_2$ unit and the octahedral $\{Os(\mu\text{-}I)(CO)_2I\}_2$ unit linked by dppf ligands acting as a spacer. The molecule is related by a crystallographic two-fold symmetry with I(1), I(2) on this axis. The plane defined by Pd(1), I(5), Pd(1*) and I(5*) is orthogonal to the plane defined by Os(1), I(1), Os(1*) and I(2). The two iodide ligands asymmetrically bridge the two Pd atoms with Pd(1)–I(5) 2.668(3) and Pd(1)–I(5*) 2.608(4) Å which are almost identical with that of $[NBu^n{}_4]_2[Pd_2I_6]$[3] [Pd–$I_{\mathbf{average}}$ 2.596(1) Å] which possesses a square Pd_2I_2 core. However the Pd_2I_2 ring in **2** is a distorted square with Pd(1)–I(5)–Pd(1*) 95.4(1) and I(5)–Pd(1)–I(5*) 83.2(1)°.

Orange-red crystals of **3** suitable for a diffraction analysis were obtained by slow evaporation of **3** in a *n*-hexane–CH_2Cl_2 mixture at −20 °C for a period of 2 d. A perspective view of the molecular structure of complex **3** is shown in Fig. 3, together with relevant bond parameters in Table 4. Complex **3** reveals a bridging ferrocenylphosphine unit axially and singly linking two pentaosmium $\{Os_5C(CO)_{14}\}$ moieties. The *anti* arrangement of the two $\{Os_5C(CO)_{14}\}$ units helps to ease the inter-ligand repulsion otherwise imposed. The two Os–P bond lengths in the dppf-bridged cluster are almost equal [Os(4)–P(1) 2.35(1) and Os(9)–P(2) 2.37(1) Å]. It is well established that dppf is flexible and can co-ordinate to mononuclear metal centres,[30–36] bridge dimetallic frameworks[37] and bind to clusters[38] in chelating, pendant, edge-bridging and even linking mode. In the two $\{Os_5C(CO)_{14}\}$ moieties, the presence of the bridging dppf group has little effect on the Os(apical)–Os(basal) bonds [Os(1)–Os(4) 2.844(3) and Os(6)–Os(9) 2.819(3) Å]. However, the two Os(basal)–Os(basal) bonds associated with the phosphine substituted metal atoms Os(4) and Os(9) are significantly longer [Os(3)–Os(4) 2.940(3), Os(4)–Os(5) 2.915(3); Os(8)–Os(9) 2.924(4) and Os(9)–Os(10) 2.922(3) Å] compared to the average of 2.858(1) and 2.850(1) Å for the other two bonds in each pentaosmium unit respectively.

As far as the conformations of the C_5H_5 and C_5H_4 rings of the dppf group in complexes **1**–**3** are concerned, the eclipsed nature of the rings is confirmed by the X-ray structural determination and produces an average distance of 1.655, 1.629 and 1.655 Å from their centroids to the iron atom in **1**, **2** and **3** respectively. The two rings of dppf (C_5H_5 and C_5H_4) are almost parallel and eclipsed with the dihedral angle between the C_5H_4 planes of 2.51, 3.85 and 3.95° in **1**, **2** and **3** respectively. The average C–C bond lengths in both the C_5H_5 and C_5H_4 rings are 1.41(4), 1.46(4) and 1.44(7) Å, respectively for **1**, **2** and **3**, whereas the corresponding mean Fe–C (cyclopentadienyl) distance is 2.05(1), 2.02(1) and 2.06(4) Å. The remaining interatomic distances and angles in the molecules compare well with the values reported for other ferrocene and cluster derivatives.[39,40]

Electrochemistry

In order to investigate the redox properties of the dppf containing complexes **1**–**3**, electrochemistry of all the complexes (including the parent compounds) has been investigated in CH_2Cl_2 using cyclic voltammetry with NBu_4BF_4 as the supporting electrolyte. We would like to explore the electrochemical activity of individual ferrocenyl sites and its effect on the overall redox behaviour of the complex. Redox potential values obtained in this study are in Table 5.

Complexes **1** and **2** exhibit a quasi-reversible oxidation at +0.614 and +0.876 V respectively. Since no redox waves have been observed in this range for other osmium carbonyl clusters, these may be assigned to be ferrocenyl centred oxidations instead of cluster centred. An irreversible oxidation is also found for cluster **1** at +1.008 V, but no such process is detected for complexes **2** and **3** under the same experimental conditions.

Compared to free dppf, the oxidation potential of the corresponding ferrocene–ferrocenium redox couples of complex **1** are only anodically shifted by 50 mV. The magnitude of the shift is slightly smaller than those of the other complexes where ferrocenyl groups have been used as redox spectators.[23] This result indicates poor communication between the cluster and ferrocenyl fragment in complex **1**.

Experimental

Materials and methods

All reactions and manipulations were carried out under an inert atmosphere using standard Schlenk techniques. Solvents were purified by standard procedures and freshly distilled prior to use. All chemicals, except where stated, were purchased commercially and used as received. The complex $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$[41,42] and $[Pd(dppf)(H_2O)_2][O_3CCF_3]_2$[43] were prepared by literature methods. Infrared spectra were recorded on a Bio-Rad FTS-7 IR spectrometer, using 0.5 mm calcium fluoride solution cells, proton NMR spectra on a Bruker DPX 300 NMR spectrometer using CD_2Cl_2 and referenced to $SiMe_4$ (δ 0), ^{31}P spectra on a Bruker DPX 500 NMR spectrometer using $CDCl_3$ as solvent with 85% H_3PO_4 as reference. Mass spectra were recorded on a Finnigan MAT 95 instrument by the fast atom bombardment technique, using *m*-nitrobenzyl alcohol or α-thioglycerol as the matrix solvents. Microanalyses were performed by Butterworth Laboratories, UK. Cyclic voltammetric measurements were made with a Princeton Applied Research (PAR) model 273A potentiostat, the supporting electrolyte was 0.2 mol dm^{-3} NBu_4BF_4 in CH_2Cl_2. A standard three-electrode cell comprising of a platinum wire counter electrode (Aldrich), an Ag–$AgNO_3$ reference electrode (Bioanalytical) and a glassy carbon working electrode (Bioanalytical) was employed. All electrochemical experiments were carried out at ambient temperature and the system was calibrated using ferrocene as the internal standard. Positive feedback internal resistance compensation was routinely applied. Routine purification of products was carried out in air by thin-layer chromatography on plates coated with Merck Kieselgel 60 GF_{254}.

Table 5 Electrochemical data for complexes **1**–**3** and related molecules in CH_2Cl_2 at 298 K[a]

Compound	Formal electrode potential/V[b]
1	+1.008, +0.614
2	+0.876
3	—
$[Os_5C(CO)_{15}]$	+1.025, +0.701
$[PdCl_2(dppf)]$	+0.876

[a] Analyses performed in dry, deoxygenated CH_2Cl_2 solutions containing 0.2 mol dm^{-3} NBu_4BF_4, scan rate 50 mV s^{-1}. [b] Formal electrode potential is defined as $E = (E_{pa} + E_{pc})/2$ for a chemically reversible process where E_{pa} and E_{pc} are the anodic and cathodic electrode potentials respectively.

Preparation of $[Os_5PdC(CO)_{14}(\mu\text{-dppf})]$ 1

A solution of $[N(PPh_3)_2]_2[Os_5C(CO)_{14}]$ (30 mg, 0.012 mmol) in CH_2Cl_2 (30 cm^3) was stirred with $[Pd(dppf)(H_2O)_2][O_3CCF_3]_2$ (12 mg, 0.012 mmol) at room temperature under a nitrogen atmosphere. The initial yellow solution immediately changed to red upon stirring. Stirring was continued for 1 h and the solvent was then removed under reduced pressure. The residue was redissolved in CH_2Cl_2 (2 cm^3) and separated by preparative TLC using the eluent (*n*-hexane–CH_2Cl_2, 70:30, v/v) to afford one red band (R_f 0.5). Extraction with CH_2Cl_2 gave complex **1** in 56% yield (16 mg, 0.006 mmol) (Found: C, 25.96; H, 1.40. Calc. for $C_{52}H_{31}Cl_9FeO_{14}Os_5P_2Pd$: C, 26.28; H, 1.31%).

Reaction of complex 1 with iodine

Complex **1** (10 mg, 0.0042 mmol) was dissolved in CH_2Cl_2 (10 cm^3). A five-fold excess of iodine (5 mg, 0.021 mmol) dissolved in CH_2Cl_2 (10 cm^3) was gradually introduced to the solution at room temperature over 3 h. The mixture gradually turned from bright red to deep brown, it was stirred for a further 5 h after all

Table 6 Crystallographic data and data collection parameters for compounds **1**–**3**

Compound	**1**·$3CHCl_3$	**2**·CH_2Cl_2	**3**·CH_2Cl_2
Empirical formula	$C_{52}H_{31}Cl_9FeO_{14}Os_5P_2Pd$	$C_{74}H_{60}Cl_4Fe_2I_8O_4Os_2P_4Pd_2$	$C_{65}H_{30}Cl_2FeO_{28}Os_{10}P_2$
M	2374.08	2999.12	3349.64
Crystal dimensions/mm	0.24 × 0.28 × 0.33	0.12 × 0.28 × 0.31	0.22 × 0.23 × 0.28
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*1 (no. 2)	*C*2/*c* (no. 15)	*P*1 (no. 2)
a/Å	14.531(2)	22.516(2)	10.153(1)
b/Å	18.344(3)	14.889(1)	12.416(1)
c/Å	14.468(3)	26.014(2)	31.960(3)
α/°	112.78(1)	90.0	84.11(2)
β/°	115.66(1)	99.56(2)	83.37(2)
γ/°	87.38(2)	90.0	80.49(2)
$U/Å^3$	3170(1)	8600(1)	3932.6(8)
Z	2	4	2
$D_c/g\ cm^{-3}$	2.487	2.316	2.829
μ/cm^{-1}	109.60	67.95	164.34
F(000)	2180	5536	2988
T/K	298	296	296
Diffractometer	AFC7R	MARRESEARCH Image Plate	AFC7R
Maximum 2θ/°	45.0	51.3	45.0
Scan range/ω	0.73 + 0.35 tan θ	—	0.65 + 0.35 tan θ
Reflections collected	8695	32 441	10 969
Unique reflections	8304	5901	10 264
Observed reflections [$I > 3.00\sigma(I)$]	5038	2226	5806
Transmission factors	0.5897–1.0000	—	0.3888–1.0000
P in weighting scheme $w = [\sigma_c^2(F_o) + P^2/4(F_o^2)]^{-1}$	0.0060	—	0.002
R,*R′* Indices (observed data)	0.052, 0.058	0.062, 0.064	0.082, 0.092
Goodness of fit indicator	2.57	1.87	3.25
Largest Δ/σ	0.06	0.03	0.08
Number of parameters	334	257	470
Residual extrema in the final difference map (close to Os)/e $Å^{-3}$	3.30, −1.41	1.62, −0.86	3.86, −3.88

the starting materials had been consumed. After reducing the volume, the filtrate was separated by preparative TLC on silica, with an eluent of *n*-hexane–CH_2Cl_2 (40 : 60, v/v). Compound **2** was isolated as a deep brown crystalline solid in 6% yield (R_f 0.2, 0.8 mg, 0.000 25 mmol) (Found: C, 29.13; H, 1.92. Calc. for $C_{74}H_{60}Cl_4Fe_2I_8O_4Os_2P_4Pd_2$: C, 29.61; H, 2.00%).

Thermolysis of complex 1

A suspension of complex **1** in distilled chloroform (61 °C) was refluxed under nitrogen. The solution gradually changed from bright red to dark brown during which time palladium metal also deposited. Thermolysis was continued until no starting materials remained (48 h, as confirmed by IR spectroscopy and TLC). The reaction mixture was then filtered to remove the very fine powder of palladium metal and the solvent from the resulting filtrate was then removed *in vacuo*. The dark brown residue was redissolved in CH_2Cl_2 (2 cm^3) and TLC separation (*n*-hexane–CH_2Cl_2, 40 : 60, v/v) afforded one major pale orange band. Crystallisation from CH_2Cl_2–*n*-hexane gave orange-red microcrystals of $[\{Os_5C(CO)_{14}\}_2(\mu\text{-dppf})]$ **3** in 12% yield (3 mg, 0.001 mmol).

When the complex $[Os_5C(CO)_{15}]$ was reacted with dppf in refluxing $CHCl_3$ for 24 h, compound **3** was also obtained in 78% yield (Found: C, 23.38; H, 0.94. Calc. for $C_{65}H_{30}Cl_2FeO_{28}Os_{10}P_2$: C, 23.29; H, 0.90%).

X-Ray data collection and structural determination of complexes 1–3

All pertinent crystallographic data and other experimental details are summarised in Table 6. Data were collected at ambient temperature either on a Rigaku AFC7R diffractometer (complexes **1** and **3**) or a MAR research image plate scanner (compound **2**), using Mo-Kα radiation ($\lambda = 0.710\ 73$ Å) with a graphite-crystal monochromator in the incident beam. For complexes **1** and **3**, all the data were collected at room temperature (298 K) using the ω–2θ scan technique with a scan rate of 16.0 min^{-1} (in ω). For compound **2**, 65 3° frames with an exposure time of 5 min per frame were used. The diffracted intensities were corrected for Lorentz and polarisation effects. The ψ scan method was employed for semiempirical absorption corrections for **1** and **3**.[44] However, no absorption correction was made for **2**. Scattering factors were taken from ref. 45*a* and anomalous dispersion effects[45b] were included in F_c.

The structures were solved by direct methods (SIR 88)[46] and expanded by Fourier-difference techniques. The solutions were refined on *F* by full-matrix least-squares analysis with Os, Pd and I atoms refined anisotropically. The hydrogen atoms of organic moieties were placed in their ideal positions. All the hydrogen atoms were included in the structure factors but the parameters were fixed without further refinement. Calculations were performed on a Silicon-Graphics computer, using the program package TEXSAN.[47]

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.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/554.

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References

1 S. Chan and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1994, 1605.
2 S. Chan and W.-T. Wong, *J. Organomet. Chem.*, 1995, **489**, C78.
3 S. Chan, S.-M. Lee, Z. Lin and W.-T. Wong, *J. Organomet. Chem.*, 1996, **510**, 219.
4 S. Chan and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1995, 3987.
5 J. W.-S. Hui and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1996, 2887.
6 J. W.-S. Hui and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1997, 1515.
7 M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.*, 1981, **28**, 203.
8 M. Tachikawa, A. C. Sievert, E. L. Muetterties, M. R. Thompson, C. S. Day and V. W. Day, *J. Am. Chem. Soc.*, 1980, **102**, 1725.
9 F. Wells, *Structural Chemistry*, Clarendon Press, Oxford, 4th edn., 1975, pp. 756–761.
10 Y. K. Yan, H. S. O. Chan, T. S. A. Hor, K.-L. Tan, L.-K. Liu and Y.-S. Wen, *J. Chem. Soc., Dalton Trans.*, 1992, 423.
11 T. S. A. Hor, H. S. O. Chan, K.-L. Tan, L.-T. Phang, Y. K. Yan, L.-K. Liu and Y.-S. Wen, *Polyhedron*, 1991, **10**, 2437.
12 M. I. Bruce, W. R. Cullen, P. A. Humphrey, O. bin Shawkataly, M. R. Snow and E. R. T. Tiekink, *Organometallics*, 1990, **9**, 2910.
13 U. Casellato, B. Corain, R. Graziani, B. Longato and G. Pilloni, *Inorg. Chem.*, 1990, **29**, 1193.
14 G. Pilloni, R. Graziani, B. Longato and B. Corain, *Inorg. Chim. Acta*, 1991, **190**, 165.
15 A. J. Blake, A. Harrison, B. F. G. Johnson, E. J. L. McInnes, S. Parsons, D. S. Shephard and L. J. Yellowlees, *Organometallics*, 1995, **14**, 3160.
16 M. Tachikawa, R. L. Greets and E. L. Muetterties, *J. Organomet. Chem.*, 1981, **213**, 11.
17 M. J. Mays, P. R. Raithby, P. L. Taylor and K. Henrick, *J. Organomet. Chem.*, 1982, **224**, C45.
18 A. Fumagalli, G. Longoni, P. Chini, A. Albinati and S. Bruckner, *J. Organomet. Chem.*, 1980, **202**, 329.
19 J. W.-S. Hui and W.-T. Wong, *J. Organomet. Chem.*, 1996, **524**, 211.
20 I. R. Butler, W. R. Cullen, T.-J. Kim, S. J. Rettig and J. Trotter, *Organometallics*, 1985, **4**, 972.
21 D. T. Hill, G. R. Girard, F. L. McCaber, R. K. Johnson, P. D. Stupik, J. H. Zhang, W. M. Reiff and D. S. Eggleston, *Inorg. Chem.*, 1989, **28**, 3529.
22 T. M. Miller, K. J. Ahmed and M. S. Wrighton, *Inorg. Chem.*, 1989, **28**, 2347.
23 W.-Y. Wong and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1996, 3209.
24 B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 225.
25 D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 706.
26 D. M. P. Mingos and A. S. May, in *The Chemistry of Metal Cluster Complexes*, eds. D. F. Shriver, H. D. Daesz and R. D. Adams, VCH, New York, 1990, ch. 2.
27 C. Couture and D. H. Farrar, *J. Chem. Soc., Dalton Trans.*, 1987, 2253.
28 See, for example, (*a*) R. D. Adams and T. S. A. Hor, *Inorg. Chem.*, 1984, **23**, 4723; (*b*) L. J. Farrugia, *Adv. Organomet. Chem.*, 1990, **31**, 301.
29 P. F. Jackson, B. F. G. Johnson, J. Lewis and J. N. Nicholls, *J. Chem. Soc., Chem. Commun.*, 1980, 564.
30 U. Casellato, D. Ajo, G. Valle, B. Corain, B. Longato and R. Graziani, *J. Crystallogr. Spectrosc. Res.*, 1988, **18**, 583.
31 S. Onaka, A. Mizuno and S. Takagi, *Chem. Lett.*, 1989, 2037.
32 D. T. Hill, G. R. Girard, F. L. McCabe, R. K. Johnson, P. D. Stupik, J. H. Zhang, W. M. Reiff and D. S. Eggleston, *Inorg. Chem.*, 1989, **28**, 3529.
33 A. Houlton, D. M. P. Mingos, D. M. Murphy, D. J. Williams, L.-T. Phang and T. S. A. Hor, *J. Chem. Soc., Dalton Trans.*, 1993, 3629.
34 L.-T. Phang, S. C. F. Yeung, T. S. A. Hor, S. B. Khoo, Z.-Y. Zhou and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1993, 165.
35 J. T. Lin, S. Y. Wang, P. S. Huang, Y. M. Hsiao, Y. S. Wen and S. K. Yeh, *J. Organomet. Chem.*, 1990, **388**, 151.
36 See, for example, M. I. Bruce, I. R. Butler, W. R. Cullen, G. A. Koutsantonis, M. R. Snow and E. R. T. Tiekink, *Aust. J. Chem.*, 1988, **41**, 963; T. M. Miller, K. J. Ahmed and M. S. Wrighton, *Inorg. Chem.*, 1989, **28**, 2347; A. L. Rheingold, B. S. Haggerty, A. J. Edwards, C. E. Housecroft, A. D. Hattersley and N. Hinze, *Acta Crystallogr., Sect. C*, 1994, **50**, 1411; B. S. Haggerty, C. E. Housecroft, A. L. Rheingold and B. A. M. Shaykh, *J. Chem. Soc., Dalton Trans.*, 1991, 2175 and refs. therein.
37 Y. K. Yan, H. S. O. Chan, T. S. A. Hor, K.-L. Tan, L.-K. Liu and Y.-S. Wen, *J. Chem. Soc., Dalton Trans.*, 1992, 423.

38 See, for example, S. T. Chacon, W. R. Cullen, M. I. Bruce, O. bin Shawkataly, F. W. B. Einstein, R. H. Jones and A. C. Willis, *Can. J. Chem.*, 1990, **68**, 2001; S. Onaka, A. Mizuno and S. Takagi, *Chem. Lett.*, 1989, 2037; T.-J. Kim, S.-C. Kwon, Y.-H. Kim, N. H. Heo, M. M. Teeter and A. Yamano, *J. Organomet. Chem.*, 1991, **426**, 71.

39 W.-Y. Wong, W.-T. Wong and K. K. Cheung, *J. Chem. Soc., Dalton Trans.*, 1995, 1399.

40 A. J. Arce, P. A. Bates, S. P. Best, R. J. H. Clar, A. J. Deeming, M. B. Hursthouse, R. C. S. McQueen and N. I. Powell, *J. Chem. Soc., Chem. Commun.*, 1988, 478.

41 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. N. Nicholls, J. Puga, P. R. Raithby, M. J. Rosales, M. Schroder and M. D. Vargas, *J. Chem. Soc., Dalton Trans.*, 1983, 2447.

42 C. R. Eady, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1975, 2606.

43 P. J. Stang, B. Olenyuk, J. Fan and A. M. Arif, *Organometallics*, 1996, **15**, 904.

44 A. C. T. North, D. C. Philips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

45 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4; (*a*) Table 2.2B; (*b*) Table 2.3.1.

46 M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidor, R. Spagna and D. Viterbo, SIR 88, *J. Appl. Crystallogr.*, 1989, **22**, 389.

47 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

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