Triosmium Alkylidyne Clusters containing Monophosphine and Chiral Diphosphine Ligands. Crystal and Molecular Structures of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CPBu^nPh_2)]$ and $(R)\text{-}[Os_3(\mu\text{-}H)_2(CO)_8\{\mu_3\text{-}CPPh_2CH(Me)CH_2PPh_2\}]$†

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The cluster $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ reacted with excess of butyldiphenylphosphine, in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu), to give the complex $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CPBu^nPh_2)]$ **1**. The optically active diphosphine $(R)\text{-}Ph_2PCH(Me)CH_2PPh_2$ reacted similarly to give two isomers, $(R)\text{-}[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CPPh_2CH(Me)CH_2PPh_2\}]$ **2a** and $(R)\text{-}[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CPPh_2CH_2CH(Me)PPh_2\}]$ **2b**, which have been spectroscopically characterised. Complex **2a** readily undergoes decarbonylation, followed by the formation of Os–P bond, to afford an octacarbonyl chiral cluster complex $(R)\text{-}[Os_3(\mu\text{-}H)_2(CO)_8\{\mu_3\text{-}CPPh_2CH(Me)CH_2PPh_2\}]$ **3**. The molecular structures of **1** and **3** have been established by X-ray crystallography. Complex **1** contains a triosmium alkylidyne metal core with the Bu^nPh_2P moiety bonded to the apical carbon atom through the phosphorus atom. On the other hand, the structure of **3**, which also contains a phosphine-substituted μ_3-C ligand bonded to three osmium atoms at the base, is characterised by the formation of a six-membered osmacycle with the centre of chirality being retained in the phosphine ligand of the complex.

The chemistry of the trihydrido osmium alkylidyne cluster $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ with nucleophilic reagents has been extensively studied.[1] These reactions, in the presence of a base, generally result in dihydrido alkylidyne clusters $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CY)]$ (Y = nitrogen[2,3] or sulfur[4] donor ligands). Little is known about phosphine-substituted derivatives of $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ employing the same synthetic methodology and the only structurally characterised example is the phosphite derivative $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CP(OMe)_3\}]$.[1]

We now report the results of the reaction between $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ and butyldiphenylphosphine and the chiral chelating diphosphine $(R)\text{-}Ph_2PCH(Me)CH_2PPh_2$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu). This particular system was chosen because it was hoped that the resulting zwitterionic cluster complexes containing phosphonium centres and negative charges formally on the triosmium atoms should provide an organometallic analogue of the phosphorus ylide which is a well-known versatile reagent in organic chemistry.[5] Besides, the production of a chiral cluster *via* incorporation of suitable chiral auxiliary for asymmetric catalysis is an ultimate goal of modern organometallic chemistry.[6] The chiral ligand $(R)\text{-}Ph_2PCH(Me)CH_2PPh_2$ has attracted particular attention in this aspect and its tendency to act as a bridging ligand in polynuclear metal complexes has been explored.[7]

Results and Discussion

The complex $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ reacts with butyldiphenylphosphine in a 1:10 molar ratio in the presence of 1 equivalent of dbu to give the complex $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CPBu^nPh_2)]$ **1** in 30% yield. Complex **1** has been fully characterised by spectroscopic methods (Table 1). The IR spectrum of **1** shows a spectral pattern in the $\nu(CO)$ absorption region quite characteristic of other $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CY)]$ (Y = Lewis base) complexes.[2,3] The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 shows a downfield resonance at δ 48.11 (*cf.* δ 17.10 in neat liquid of the unco-ordinated phosphine).[8] This is consistent with the phosphorus atom in phosphonium salts.

To characterise this complex structurally, a single-crystal X-ray analysis was undertaken. Single crystals of **1** suitable for X-ray diffraction study were grown from slow evaporation of a *n*-hexane–CH_2Cl_2 solution of **1** at room temperature for a period of two days. The molecular structure of **1** is shown in Fig. 1 together with the atomic numbering scheme adopted. Selected bond length and angle data are given in Table 2. The cluster geometry resembles that in other already structurally

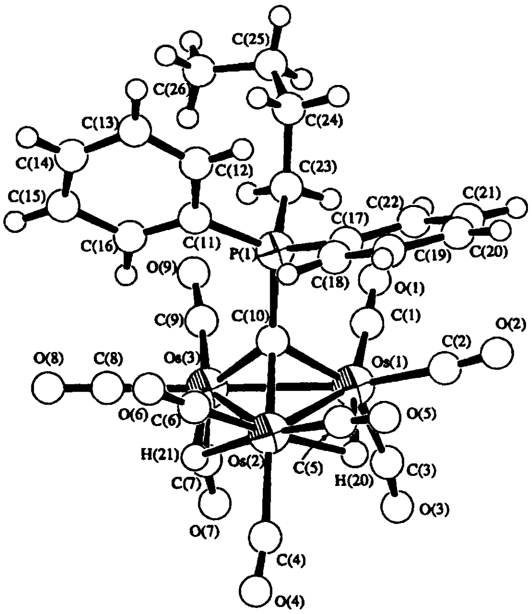

Fig. 1 Molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CPBu^nPh_2)]$ **1**

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Spectroscopic data for complexes **1**, **2a**, **2b** and **3**

Compound	IR(ν_{co})[a]/cm^{-1}	^{1}H NMR[b] (δ, J/Hz)	^{31}P NMR[b] (δ, J/Hz)	MS[c] (m/z)
1	2093s, 2054vs, 2023vs, 2003 (sh), 1977vs, 1953s, 1938s	7.51–7.95 (m, 10 H, C_6H_5), 2.71 (m, 2 H, PCH_2), 1.40 (m, 2 H, PCH_2CH_2), 1.27 (m, 2 H, CH_2CH_3), 0.85 (t, 3 H, J = 7.3, CH_3), −20.02 [d, 2 H, ^3J(PH) = 2.8, OsH]	48.11	1080 (1080)
2a	2094s, 2057vs, 2027vs, 2013 (sh), 1978s, 1958s, 1940s	7.13–8.08 (m, 20 H, C_6H_5), 2.96 (m, 1 H, CH_2), 2.65 (m, 1 H, CH), 2.41 (m, 1 H, CH_2), 1.52 [dd, 3 H, ^3J(HH) = 7.1, ^3J(PH) = 16.1, CH_3], −19.89 [d, 2 H, ^3J(PH) = 1.8, OsH]	50.71 [d, ^3J(PP) = 24.4, μ_3-$CPPh_2$], −16.89 [d, ^3J(PP) = 24.4, free PPh_2]	1250 (1250)
2b	2093s, 2055vs, 2025vs, 2012 (sh), 1977s, 1956s, 1939s	7.22–8.13 (m, 20 H, C_6H_5), 2.89 (m, 1 H, CH_2), 2.68 (m, 1 H, CH_2), 2.19 (m, 1 H, CH), 0.62 [dd, 3 H, ^3J(HH) = 14.7, ^3J(PH) = 6.8, CH_3], −20.07 [d, 2 H, ^3J(PH) = 1.8, OsH]	48.27 [d, ^3J(PP) = 36.7, μ_3-$CPPh_2$], 7.68 [d, ^3J(PP) = 36.7, free PPh_2]	1250 (1250)
3	2056s, 2017vs, 1972s, 1954s, 1927m	7.21–7.98 (m, 20 H, C_6H_5), 3.36 (m, 1 H, CH), 2.97 (m, 1 H, CH_2), 2.40 (m, 1 H, CH_2), 1.52 [dd, 3 H, ^3J(HH) = 7.1, ^3J(PH) = 2.0, CH_3], −18.36 (m, 1 H, OsH), −20.00 (m, 1 H, OsH)	44.68 (s, μ_3-$CPPh_2$), −27.27 (s, PPh_2Os)	1222 (1222)

[a] In CH_2Cl_2. [b] In CD_2Cl_2. [c] For M^+, required values in parentheses.

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

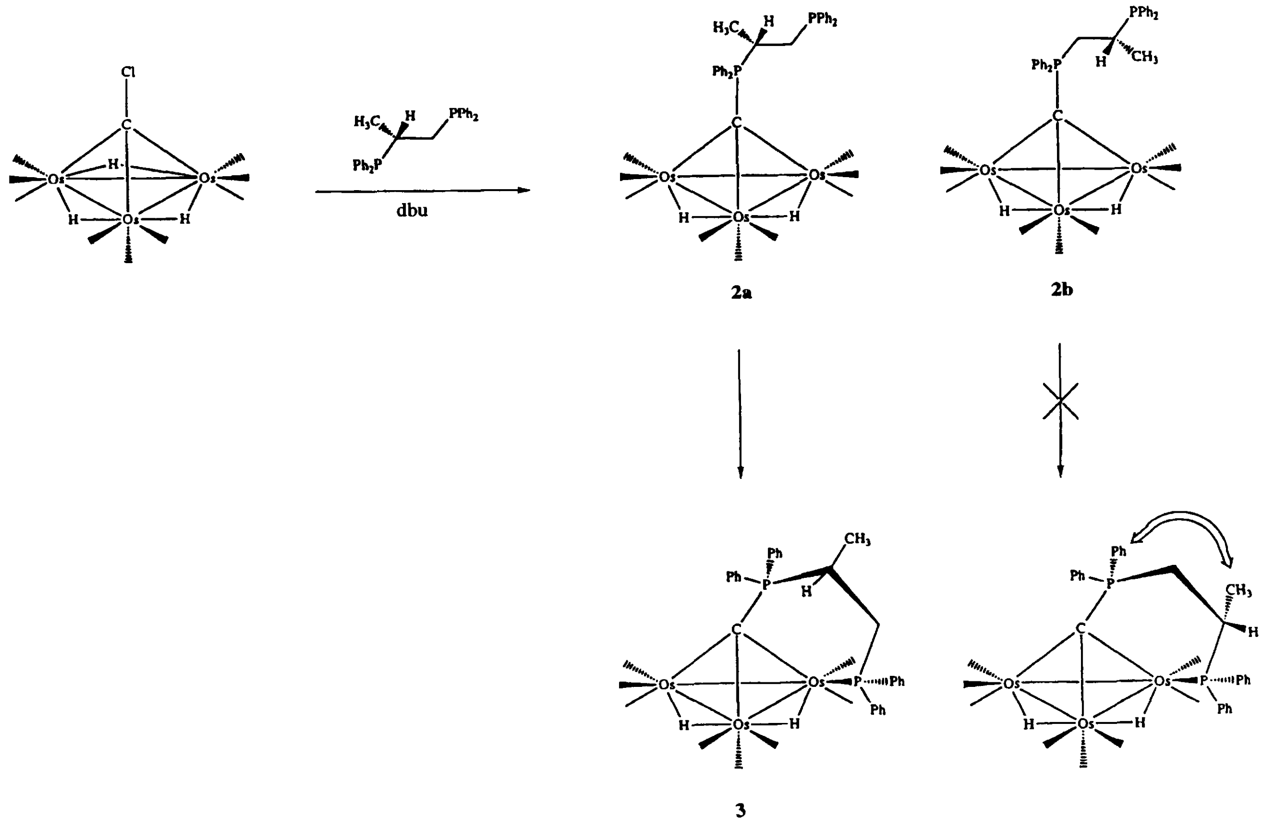
Os(1)–Os(2)	2.873(3)	Os(1)–Os(3)	2.737(5)
Os(2)–Os(3)	2.885(2)	Os(1)–C(10)	2.10(3)
Os(2)–C(10)	2.03(3)	Os(3)–C(10)	2.12(3)
P(1)–C(10)	1.80(3)	P(1)–C(11)	1.80(3)
P(1)–C(17)	1.81(3)	P(1)–C(23)	1.80(4)
C(23)–C(24)	1.51(6)	C(24)–C(25)	1.55(6)
C(25)–C(26)	1.41(7)		
Os(2)–Os(1)–Os(3)	61.9(1)	Os(1)–Os(2)–Os(3)	56.7(1)
Os(1)–Os(3)–Os(2)	61.4(1)	Os(1)–C(10)–P(1)	123(1)
Os(2)–C(10)–P(1)	131(1)	Os(3)–C(10)–P(1)	129(1)
C(10)–P(1)–C(11)	116(1)	C(10)–P(1)–C(17)	107(1)
C(10)–P(1)–C(23)	113(1)	P(1)–C(23)–C(24)	120(3)
C(23)–C(24)–C(25)	111(4)	C(24)–C(25)–C(26)	114(4)

characterised [$Os_3(\mu$-$H)_2(CO)_9(\mu_3$-$CY)$] complexes[2,3] and may be described as having a phosphoniomethylidyne ligand linked to three osmium atoms. A ruthenium cluster with similar geometry [$Ru_3(\mu$-$H)_2(CO)_9(\mu_3$-$CPPh_3)$] has previously been reported.[9] The Os(2)–C(10) bond [2.03(3) Å] is slightly shorter than the other two Os–C(alkylidyne) bonds [average 2.11(3) Å]. The two hydrides that show up in the ^{1}H NMR spectrum of **1** have been located by potential energy calculations[10] and they were found to bridge the edges Os(1)–Os(2) and Os(2)–Os(3). The bond distance P(1)–C(10) is 1.80(3) Å.

The reaction of [$Os_3(\mu$-$H)_3(CO)_9(\mu_3$-$CCl)$] with 1 equivalent of dbu in the presence of a 10-fold excess of the chiral diphosphine (R)-$Ph_2PCH(Me)CH_2PPh_2$ affords two non-interconvertible isomeric compounds, namely, [$Os_3(\mu$-$H)_2(CO)_9\{\mu_3$-$CPPh_2CH(Me)CH_2PPh_2\}$] **2a** (15% yield) and [$Os_3(\mu$-$H)_2(CO)_9\{\mu_3$-$CPPh_2CH_2CH(Me)PPh_2\}$] **2b** (20% yield), see Scheme 1. The spectroscopic data for these complexes are summarised in Table 1 and are fully consistent with the proposed structures. They both possess almost identical ν(CO) spectra and hence are structurally very similar. Their positive FAB mass spectra show the same parent ion peak at m/z = 1250, as expected, and the stepwise loss of nine carbonyl groups is also observed. Both complexes display three sets of multiplets in their ^{1}H NMR spectra due to the CH and CH_2 resonances of the phosphine ligand. The methyl protons of the organic moieties in **2a** and **2b** give rise to a doublet of doublets at δ 1.52 and 0.62 respectively by vicinal coupling to the neighbouring methine group and phosphorus–proton coupling. Two distinct sets of doublets in the hydride region were also observed for the two complexes (δ −19.89 for **2a** and δ −20.07 for **2b**). Isomer **2a** gives two doublets at δ 50.71 and −16.89 with $^3J_{PP}$ = 24.4 Hz in the ^{31}P-{^{1}H} NMR spectrum while **2b** gives two doublets at δ 48.27 and 7.68 with $^3J_{PP}$ = 36.7 Hz. The low-field doublets for **2a** and **2b** are assigned to the PPh_2 group co-ordinated to the μ_3-carbon atom, where partial positive charge has been created on the phosphorus atom by the electron-withdrawing properties of the 'Os_3C' core. Comparatively speaking, the other signal due to the free PPh_2 group remains more or less unshifted from those of the free ligand $Ph_2P'CH(Me)CH_2P''Ph_2$ (δ 3.03 for P′, δ −19.11 for P″). The phosphorus–phosphorus coupling, $^3J_{PP}$, in the range 20–40 Hz is typical of a monoco-ordinated diphosphine and is consistent with the potentially bidentate ligand co-ordinating to the metal framework through only one P atom.[11]

Complex **2a** readily decarbonylates under ambient conditions to give an octacarbonyl homometallic chiral cluster (R)-[$Os_3(\mu$-$H)_2(CO)_8\{\mu_3$-$CPPh_2CH(Me)CH_2PPh_2\}$] **3**. The conversion is about 60% complete after 24 h. The IR spectrum of **3** in the carbonyl stretching region has completely different features as compared to **2a** and **2b** and its mass spectrum (positive FAB mode) exhibits a parent ion at m/z = 1222 (28 amu less than **2a**) with sequential loss of eight carbonyls. The resonances due to the organic moieties were still observed in the ^{1}H NMR spectrum of **3** but instead there are two separate and complicated sets of hydride signals. The ^{31}P-{^{1}H} NMR spectrum of **3** consists of two singlets at δ 44.68 and −27.27 with the former signal also corresponding to the phosphorus atom directly attached to the apical carbon atom. However, an unexpected upfield shift of the ^{31}P NMR resonance of the osmium-co-ordinated PPh_2 group is observed.

In order unequivocally to establish the exact nature of the bonding of the ligand to the cluster framework and the



Scheme 1

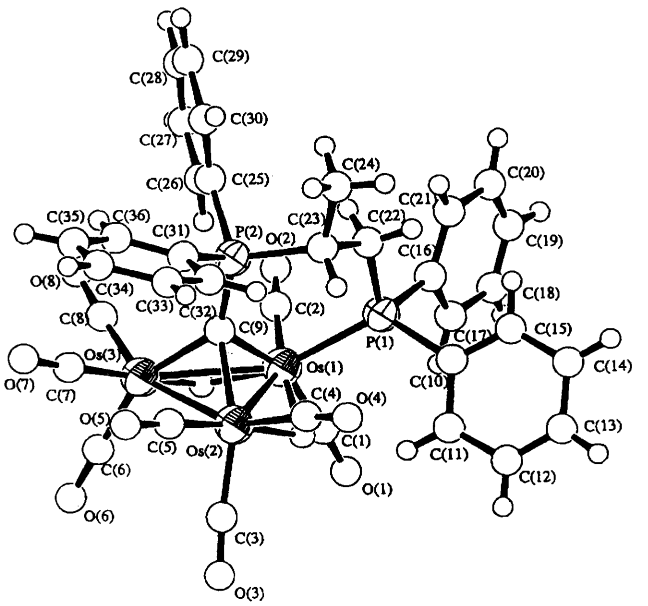


Fig. 2 Molecular structure of (*R*)-[$Os_3(\mu\text{-}H)_2(CO)_8\{\mu_3\text{-}CPPh_2CH(Me)CH_2PPh_2\}$] **3**

Table 3 Selected bond distances (Å) and bond angles (°) for **3**

Os(1)–Os(2)	2.911(1)	Os(1)–Os(3)	2.8953(9)
Os(2)–Os(3)	2.778(1)	Os(1)–C(9)	2.12(2)
Os(2)–C(9)	2.14(2)	Os(3)–C(9)	2.04(2)
Os(1)–P(1)	2.334(6)	P(2)–C(9)	1.77(2)
P(1)–C(10)	1.83(2)	P(1)–C(16)	1.84(2)
P(1)–C(22)	1.83(2)	C(22)–C(23)	1.53(3)
C(23)–C(24)	1.53(4)	P(2)–C(23)	1.84(3)
P(2)–C(25)	1.82(2)	P(2)–C(31)	1.80(2)
Os(2)–Os(1)–Os(3)	57.2(1)	Os(1)–Os(2)–Os(3)	61.1(1)
Os(1)–Os(3)–Os(2)	61.7(1)	Os(1)–C(9)–P(2)	126(1)
Os(2)–C(9)–P(2)	118(1)	Os(3)–C(9)–P(2)	137(1)
C(9)–P(2)–C(23)	112(1)	C(9)–P(2)–C(25)	115(1)
C(9)–P(2)–C(31)	112(1)	P(2)–C(23)–C(24)	114(1)
C(22)–C(23)–C(24)	107(2)	P(2)–C(23)–C(22)	109(1)
P(1)–C(22)–C(23)	121(1)	Os(1)–P(1)–C(10)	121.4(9)
Os(1)–P(1)–C(22)	113.6(8)	Os(1)–P(1)–C(16)	114.5(8)

stereochemical arrangement of the chiral complex **3**, an X-ray structure analysis was carried out on a single crystal obtained by slow evaporation of a *n*-hexane–CH_2Cl_2 solution of **3** at room temperature for a period of 3 days. The molecular structure of **3** is depicted in Fig. 2 together with the atomic numbering scheme used. Relevant bond distances and angles are given in Table 3. Compound **3** contains a phosphine-substituted μ_3-C ligand bonded to three osmium atoms at the base with the Os(3)–C(9) bond [2.04(2) Å] shorter than the others [average 2.13(2) Å]. The two hydride atoms, located by potential energy calculations, bridge the edges Os(1)–Os(2) and Os(1)–Os(3). A salient structural feature observed in the structure of **3** is the formation of a highly sterically favourable six-membered ring Os(1)–P(1)–C(22)–C(23)–P(2)–C(9) by replacing one terminal carbonyl ligand with the pendant PPh_2 group. The resulting six-membered ring adopts a stable chair conformation. The phosphorus atom P(1) is co-ordinated in pseudo-equatorial site to Os(1) and the methyl group at C(23) also occupies an equatorial position. The P(2)–C(9) and Os(1)–P(1) distances within the osmacycle are respectively 1.77(2) and 2.334(6) Å. The absolute structure for **3** was confirmed by X-ray diffraction study and the chelating chiral diphosphine displays the expected *R* configuration at C(23), creating a rather rigid chiral system on the triosmium surface. It

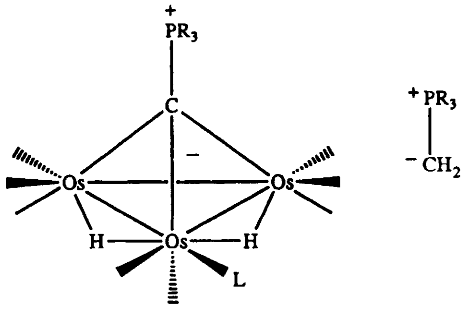


Fig. 3 Zwitterionic formulation of phosphine-containing alkylidyne clusters

Table 4 Crystal data and data collection parameters for **1** and **3**[a]

Compound	**1**	**3**
Formula	$C_{26}H_{21}O_9Os_3P$	$C_{36}H_{28}O_8Os_3P_2$
M	1079.02	1221.16
Colour, habit	Yellow plate	Pale yellow block
Crystal dimensions/mm	0.21 × 0.24 × 0.34	0.30 × 0.32 × 0.38
Space group	$C2/c$ (no. 15)	$P2_1$ (no. 4)
a/Å	29.511(7)	10.171(1)
b/Å	12.682(3)	17.573(2)
c/Å	16.944(5)	10.599(1)
β/°	111.61(2)	108.23(2)
U/Å^3	5895(3)	1799.3(4)
Z	8	2
D_c/g cm^{-3}	2.432	2.254
μ(Mo-Kα)/cm^{-1}	129.93	106.99
F(000)	3936	1132
T/K	298	298
Scan range/°	1.47 + 0.35 tan θ	0.55 + 0.35 tan θ
Reflections collected	4146	7099
Unique reflections	4067	7099
Observed reflections [$I > 3\sigma(I)$]	2445	5774
Transmission factors	0.314–1.000	0.265–1.000
g In weighting scheme $w = 4F_o^2/[\sigma^2(F_o^2) + gF_o^2]^2$	0.010	0.005
R[b]	0.068	0.057
R'[c]	0.079	0.066
Residual electron density/ e Å^{-3}[d]	2.40 to −2.83	1.87 to −2.05

[a] *Details in common*: monoclinic, ω–2θ scan mode, scan rate = 16.0° min^{-1}, data collection range 4 ≤ 2θ ≤ 45°, ψ-scan absorption correction. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [d] Close to Os.

was also found that the methylene protons on C(22) are magnetically non-equivalent and they appear as distinct signals in the ^{1}H NMR spectrum of **3**. However, no decarbonylation product of **2b** can be obtained under similar reaction conditions. This is probably due to the unfavourable steric interaction caused by the axial Me group and PPh$_2$ group in the corresponding six-membered ring in the chair conformation, see Scheme 1.

As far as bonding description of these neutral clusters is concerned, both spectroscopic (IR) and structural features suggest that the tertiary phosphine molecules add at the μ_3-carbon atom to give zwitterionic complexes containing phosphonium centres and negative charges on the cluster framework.[12] Basically, these zwitterionic formulations of the clusters may be viewed as the organometallic/inorganic analogue of the phosphorus ylide $R_3P{=}CH_2$ used frequently in synthetic organic chemistry, see Fig. 3.[13] It is believed that this system would provide a fertile area of metal-assisted organic reactions of phosphorus ylides and can hence gain a better understanding of some of the complicated reactions in the metal–phosphine–C$_1$ system.

Experimental

None of the compounds reported here is particularly air-sensitive, however all reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (CO stretching region). Dichloromethane was dried over CaH$_2$ and *n*-hexane was distilled from sodium–benzophenone in the presence of $O(CH_2CH_2OCH_2CH_2OMe)_2$. The starting cluster $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$[14] and the ligand butyldiphenylphosphine[15] were prepared as described previously. The ligand (*R*)-Ph$_2$PCH(Me)CH$_2$PPh$_2$ was purchased from Strem Chemicals Inc. and used as received. Infrared spectra were recorded on a BIO-RAD FTS-7 IR spectrometer using 0.5 mm solution cells. The ^{1}H and ^{31}P NMR spectra were recorded on a JEOL GSX 270FT-NMR spectrometer [SiMe$_4$ (δ = 0) for ^{1}H and 85% H_3PO_4 for ^{31}P]. Mass spectra were recorded on a Finnigan MAT 95 instrument with the fast atom bombardment technique. Routine separation of products were performed in the air by thin-layer chromatography with plates coated with Merck Kieselgel 60 GF$_{254}$.

Syntheses.—$[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CPBu^nPh_2)]$ **1**. The complex $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ (87.3 mg, 0.10 mmol) and the ligand PBu^{n}Ph$_2$ (0.24 g, 1.0 mmol) were dissolved in CH$_2$Cl$_2$ (20 cm^3). Dropwise addition of a dbu–CH$_2$Cl$_2$ solution (0.10 mmol) gave a yellow solution. The mixture was stirred at room temperature for 15 min and subsequently evaporated to dryness under vacuum. The residue was purified by TLC using *n*-hexane–acetone (95:5, v/v) as eluent. The complex **1** was isolated as a pale yellow solid (R_f = 0.70) in 30% yield (32 mg) (Found: C, 28.8; H, 2.05. Calc. for $C_{26}H_{21}O_9Os_3P$: C, 28.95; H, 1.95%).

$[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CPPh_2CH(Me)CH_2PPh_2\}]$ **2a** *and* $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu_3\text{-}CPPh_2CH_2CH(Me)PPh_2\}]$ **2b**. The cluster $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ (87.3 mg, 0.10 mmol) and the ligand (*R*)-Ph$_2$PCH(Me)CH$_2$PPh$_2$ (0.41 g, 1.0 mmol) in CH$_2$Cl$_2$ (25 cm^3) were stirred while a dbu–CH$_2$Cl$_2$ solution (0.10 mmol) was added dropwise. The mixture turned yellow immediately. After stirring for 15 min, the volume was reduced to 3 cm^3. Purification was accomplished by TLC using *n*-hexane–CH$_2$Cl$_2$ (80:20, v/v) as eluent to afford complexes **2a** (R_f = 0.70) and **2b** (R_f = 0.65) in respectively 15% (19 mg) and 20% (25 mg) yields (Found: C, 35.45; H, 2.15. Calc. for $C_{37}H_{28}O_9Os_3P_2$ **2b**: C, 35.6; H, 2.25%).

(*R*)-$[Os_3(\mu\text{-}H)_2(CO)_8\{\mu_3\text{-}CPPh_2CH(Me)CH_2PPh_2\}]$ **3**. Compound **2a** (20 mg, 0.016 mmol) was dissolved in CH$_2$Cl$_2$ (15 cm^3) under nitrogen to give a pale yellow solution. The mixture was allowed to stir for 24 h, resulting in a yellow solution. Following evaporation of most of the solvent, the mixture was subjected to preparative TLC using *n*-hexane–CH$_2$Cl$_2$ (80:20, v/v) as eluent to afford yellow crystals of (*R*)-$[Os_3(\mu\text{-}H)_2(CO)_8\{\mu_3\text{-}CPPh_2CH(Me)CH_2PPh_2\}]$ **3** (R_f = 0.40) in 50% yield (10 mg, 0.008 mmol) (Found: C, 35.2; H, 2.20. Calc. for $C_{36}H_{28}O_8Os_3P_2$: C, 35.4; H, 2.30%).

X-Ray Structure Analysis, Solution and Refinement.—Suitable crystals of compounds **1** and **3** for X-ray analysis were obtained by slow evaporation of a *n*-hexane–CH$_2$Cl$_2$ solution of the corresponding products at room temperature. The crystal and refinement data for **1** and **3** are summarised in Table 4. Intensity data were collected at room temperature on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using the ω–2θ scan method. The stability of the crystals was monitored at regular intervals using three standard reflections and no significant variation was observed. Intensity data were corrected for Lorentz and polarisation effects and semi-empirical absorption corrections (ψ-scan

Table 5 Atomic coordinates for compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Os(1)	0.655 87(6)	0.078 02(10)	0.035 48(10)
Os(2)	0.610 90(6)	0.067 93(10)	0.159 66(9)
Os(3)	0.560 70(5)	0.139 97(10)	−0.012 12(9)
P(1)	0.647 6(3)	0.318 8(6)	0.122 4(6)
O(1)	0.673(1)	0.200(3)	−0.101(2)
O(2)	0.763(1)	0.067(2)	0.143(2)
O(3)	0.644(1)	−0.127(3)	−0.071(2)
O(4)	0.577(1)	−0.140(3)	0.212(2)
O(5)	0.703(1)	0.053(2)	0.314(2)
O(6)	0.558 4(10)	0.201(2)	0.248(2)
O(7)	0.525(1)	−0.042(2)	−0.143(2)
O(8)	0.465(1)	0.219(2)	−0.009(2)
O(9)	0.558 8(10)	0.292(2)	−0.151(2)
C(1)	0.666(1)	0.148(3)	−0.050(2)
C(2)	0.724(2)	0.066(4)	0.109(3)
C(3)	0.652(2)	−0.056(4)	−0.031(3)
C(4)	0.592(2)	−0.071(3)	0.193(3)
C(5)	0.669(2)	0.061(3)	0.262(3)
C(6)	0.578(1)	0.149(3)	0.216(2)
C(7)	0.534(2)	0.029(4)	−0.098(3)
C(8)	0.501(1)	0.190(3)	−0.008(2)
C(9)	0.560(1)	0.227(3)	−0.099(2)
C(10)	0.624(1)	0.188(3)	0.091(2)
C(11)	0.609(1)	0.408(3)	0.152(2)
C(12)	0.629(1)	0.491(3)	0.212(3)
C(13)	0.600(1)	0.570(3)	0.225(2)
C(14)	0.552(2)	0.561(3)	0.187(3)
C(15)	0.529(2)	0.487(5)	0.127(4)
C(16)	0.562(2)	0.408(4)	0.115(3)
C(17)	0.704(1)	0.306(2)	0.214(2)
C(18)	0.704(1)	0.301(3)	0.293(2)
C(19)	0.746(2)	0.292(3)	0.359(3)
C(20)	0.790(2)	0.281(3)	0.344(3)
C(21)	0.789(1)	0.286(3)	0.266(3)
C(22)	0.747(1)	0.301(3)	0.199(2)
C(23)	0.657(1)	0.391(3)	0.038(2)
C(24)	0.676(2)	0.502(4)	0.053(3)
C(25)	0.664(2)	0.563(4)	−0.032(3)
C(26)	0.614(2)	0.584(5)	−0.075(4)

Table 6 Atomic coordinates for compound **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Os(1)	0.219 09(6)	0.290 317	0.749 40(5)
Os(2)	0.038 86(6)	0.169 00(4)	0.605 92(5)
Os(3)	0.095 10(6)	0.179 223	0.879 27(5)
P(1)	0.380 3(4)	0.300 6(2)	0.634 6(3)
P(2)	0.364 0(5)	0.109 8(2)	0.763 1(4)
O(1)	0.083(1)	0.446 4(7)	0.682(1)
O(2)	0.440(1)	0.353 2(6)	0.986(1)
O(3)	−0.263(2)	0.221 8(7)	0.496(1)
O(4)	0.100(2)	0.142 2(7)	0.347(1)
O(5)	−0.065(1)	0.006 8(7)	0.612(1)
O(6)	−0.170(2)	0.233 4(9)	0.925(2)
O(7)	0.026(2)	0.016 6(7)	0.925(1)
O(8)	0.284(1)	0.187 5(7)	1.167(1)
C(1)	0.143(2)	0.387 5(9)	0.710(1)
C(2)	0.354(2)	0.328 7(8)	0.899(1)
C(3)	−0.147(2)	0.205 1(10)	0.547(2)
C(4)	0.088(2)	0.155 8(8)	0.451(1)
C(5)	−0.021(2)	0.068 4(8)	0.609(1)
C(6)	−0.065(2)	0.211(1)	0.908(2)
C(7)	0.050(2)	0.078 7(9)	0.905(2)
C(8)	0.205(2)	0.187 3(8)	1.054(1)
C(9)	0.227(1)	0.170 3(8)	0.769(1)
C(10)	0.326(2)	0.321 0(7)	0.456(1)
C(11)	0.189(2)	0.334 2(8)	0.385(1)
C(12)	0.155(2)	0.359 2(9)	0.256(2)
C(13)	0.250(2)	0.369 5(9)	0.197(1)
C(14)	0.389(2)	0.358 5(10)	0.262(2)
C(15)	0.421(2)	0.332 9(9)	0.395(1)
C(16)	0.508(2)	0.377 6(8)	0.693(1)
C(17)	0.457(2)	0.450 2(9)	0.691(2)
C(18)	0.553(3)	0.512(1)	0.730(2)
C(19)	0.687(2)	0.499(1)	0.767(2)
C(20)	0.738(2)	0.431(1)	0.771(2)
C(21)	0.644(2)	0.368 0(9)	0.734(2)
C(22)	0.494(2)	0.218 0(8)	0.655(1)
C(23)	0.436(2)	0.137 4(8)	0.630(1)
C(24)	0.551(2)	0.085 1(10)	0.616(2)
C(25)	0.513(2)	0.106 2(8)	0.914(1)
C(26)	0.525(2)	0.162 9(9)	1.012(1)
C(27)	0.635(2)	0.163(1)	1.125(2)
C(28)	0.736(2)	0.108(1)	1.141(2)
C(29)	0.726(2)	0.051(1)	1.049(2)
C(30)	0.616(2)	0.052 5(10)	0.938(2)
C(31)	0.312(2)	0.011 6(8)	0.737(1)
C(32)	0.267(2)	−0.018 4(9)	0.610(2)
C(33)	0.218(2)	−0.092 6(9)	0.592(2)
C(34)	0.207(2)	−0.136 2(8)	0.699(2)
C(35)	0.250(2)	−0.104 7(9)	0.824(2)
C(36)	0.303(2)	−0.031 9(9)	0.842(1)

method) were also applied.[16] Scattering factors were taken from ref. 17 and anomalous dispersion effects [17b] were included in F_c. The structures were solved by a combination of direct methods (SIR 88)[18] and difference Fourier techniques and refined on F by full-matrix least-squares analysis. The hydrogen atoms of the organic moieties were placed in their idealised positions (C–H 0.95 Å), while all metal hydrides were estimated by potential energy calculations. The absolute configuration of **3** was established by analysing the trends of F_o *vs.* F_c for all the observed reflections and its Bijvoet mate. It is consistent with the configuration of the starting phosphine ligand. All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[19] Positional parameters for the non-hydrogen atoms are given in Tables 5 and 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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