

The preparation and aspects of the chemistry of some tertiary-phosphine, arsine and stibine complexes of hexaosmium clusters *

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Abstract

Good routes have been developed to the mono- and bis-substituted derivatives $[\text{Os}_6(\text{CO})_{17}\text{L}]$ ($\text{L} = \text{P}(\text{OMe})_3$, PEt_3 , PPh_2Me , PPh_3 , AsPh_3 or SbPh_3) and $[\text{Os}_6(\text{CO})_{16}\text{L}'_2]$ ($\text{L}' = \text{PPh}_3$, PPh_2Me), which have structures based on the same bicapped tetrahedral Os_6 -unit established for $[\text{Os}_6(\text{CO})_{18}]$. The $[\text{Os}_6(\text{CO})_{16}\text{L}'_2]$ compounds apparently exist in more than one isomeric form and small amounts of the tris-substituted derivatives $[\text{Os}_6(\text{CO})_{15}\text{L}'_3]$ are also observed. The mono-substituted hexaosmium cluster $[\text{Os}_6(\text{CO})_{17}\text{L}]$ undergoes reaction with Me_3NO in CH_2Cl_2 to yield the previously unknown hydrido-hexaosmium anion $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ which on reaction with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ first gives the neutral hexaosmium dihydride $[\text{H}_2\text{Os}_6(\text{CO})_{16}\text{L}]$ and then the cation $[\text{H}_3\text{Os}_6(\text{CO})_{16}\text{L}]^+$. The bis-substituted hexaosmium cluster $[\text{Os}_6(\text{CO})_{16}\text{L}_2]$ reacts similarly with $\text{Me}_3\text{NO}/\text{CH}_2\text{Cl}_2$ to give the hydrido-anion $[\text{HOs}_6(\text{CO})_{16}\text{L}_2]^-$.

Introduction

Earlier [1], we reported the preparation and partial characterisation of the new, anionic osmium cluster $[\text{HOs}_6(\text{CO})_7\text{L}]^-$ as the product of the reaction of with Me_3NO in dichloromethane. Evidence led us to suggest that the structure of this anion had the same bicapped tetrahedral geometry for the Os_6 core as that previously observed for the isoelectronic parent molecule $[\text{Os}_6(\text{CO})_{18}]$ but, in the absence of X-ray data, this could not be confirmed. We now report further more extensive studies of this and a number of other related reactions which have led to an improved route to mono-, bis- and tris-substituted derivatives of the type $[\text{Os}_6(\text{CO})_{17}\text{L}]$ ($\text{L} = \text{P}(\text{OMe})_3$, PPh_3 , PEt_3 , PPh_2Me , AsPh_3 , $\text{As}(\text{p-tol})_3$, and SbPh_3), $[\text{Os}_6(\text{CO})_{16}\text{L}'_2]$ and $[\text{Os}_6(\text{CO})_{15}\text{L}'_3]$ ($\text{L}' = \text{PPh}_3$ and PPh_2Me) and the previously unknown hydrido-anions $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ and $[\text{HOs}_6(\text{CO})_{15}\text{L}_2]^-$. The replacement of one CO ligand in $[\text{HOs}_6(\text{CO})_{17}]^-$ by the ligand L has permitted a full characterisation of these intriguing anionic species by NMR spectroscopy.

* Dedicated to Professor Peter L. Pauson on the occasion of his retirement.

Results and discussion

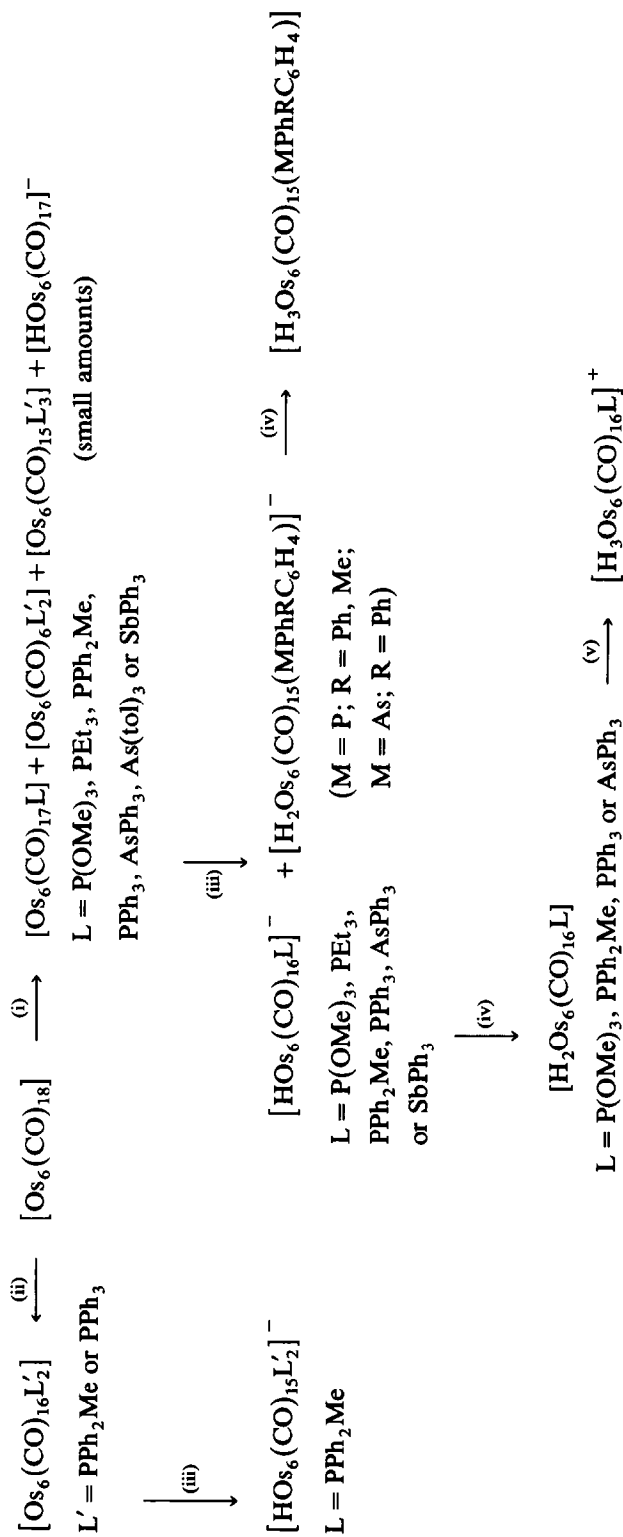
The preparation of the mono-, bis- and tris-substituted derivatives $[\text{Os}_6(\text{CO})_{18-n}\text{L}_n]$ ($n = 1, 2$ or 3)

Substituted derivatives of the type $[\text{Os}_6(\text{CO})_{18-n}\text{L}_n]$ ($n = 1$ or 2) have been prepared previously [1–3] from the reaction of the acetonitrile derivatives $[\text{Os}_6(\text{CO})_{18-n}(\text{MeCN})_n]$ with L. In addition adducts of the type $[\text{Os}_6(\text{CO})_{17-n}(\text{MeCN})_{2+n}]$ (Fig. 1) have also been observed. This route, being a two-step process, is inconvenient, and the yields of the desired substitution products are often low as a result of difficulties involved in the synthesis and purification of the relatively unstable intermediate acetonitrile derivatives. Consequently, in this work the possibility of incorporating the ligand L directly by the reaction of $[\text{Os}_6(\text{CO})_{18}]$ with Me_3NO in the presence of L has been investigated. At room temperature, the reaction of $[\text{Os}_6(\text{CO})_{18}]$ in dichloromethane with Me_3NO (1 : 1) and L has proved to be non-specific, producing not only the expected mono-substituted complex $[\text{Os}_6(\text{CO})_{17}\text{L}]$ but also the bis-substituted complex $[\text{Os}_6(\text{CO})_{16}\text{L}'_2]$ and very small amounts of the tris-substituted complex $[\text{Os}_6(\text{CO})_{15}\text{L}'_3]$ (see Scheme 1) as well as large proportion of the anionic cluster $[\text{HOs}_6(\text{CO})_{17}]^-$. However, on cooling the reaction mixture to 0°C during the addition of Me_3NO , the competitive formation of $[\text{HOs}_6(\text{CO})_{17}]^-$ and the further reaction of the mono-substituted product with Me_3NO with the consequential formation of higher substituted products is minimised. If the reaction mixture is then allowed to warm up slowly to room temperature, the derivative $[\text{Os}_6(\text{CO})_{17}\text{L}]$ is produced in ca. 70–90% yield.

This method has also been used to synthesise a wide range of other mono-substituted derivatives (see Scheme 1). Bis-substituted derivatives have also been prepared in high yield by this route, using two equivalents of Me_3NO in the initial reaction mixture. In this case a mixture of isomers of the bis-derivative $[\text{Os}_6(\text{CO})_{16}\text{L}'_2]$, which is identical to that obtained [1] by treatment of $[\text{Os}_6(\text{CO})_{16}(\text{MeCN})_2]$ with L' , is produced. Spectroscopic data for these new substituted hexaosmium derivatives are presented in Table 1 and are similar to those of the previously structurally characterised species $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$ and $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_3)_2]$ [4].

^{13}C NMR studies of the derivatives $[\text{Os}_6(\text{CO})_{18-n}(\text{PPh}_3)_n]$ ($n = 1$ or 2)

In the structure of $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$ (Fig. 2), which has been established by single crystal X-ray analysis [5], the C_{2v} symmetry of the bicapped tetrahedral hexa-osmium is lost as a result of the incorporation of the phosphine ligand on one of the capping osmium atoms. As a consequence, the all carbonyl groups are inequivalent and, in the absence of any CO exchange processes, seventeen different ^{13}C signals should be observed in the ^{13}C NMR spectrum. At 180 K, the ^{13}C NMR spectrum of 20% ^{13}C enriched sample shows the expected seventeen carbonyl resonances (Fig. 3a). The two peaks (G and L) in this spectrum which are split by ^{31}P – ^{13}C coupling [$J(^{31}\text{P}$ – $^{13}\text{C}) = 9$ Hz] can be assigned unambiguously to the carbonyls on the PPh_3 -substituted osmium centre. Assignment of the remaining resonances in the slow exchange limiting spectrum has been made on the basis of the temperature behaviour (see below) and is not unambiguous. The temperature dependent ^{13}C NMR spectra of $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$ over the temperature range 180–360 K are shown in Fig. 3a. As the temperature is raised first to 190 K the three signals assigned to carbonyls DMO are seen to collapse. At 210 K, the three



- (i) $\text{Me}_3\text{NO/MeCN}$: $\text{Os}_6(\text{CO})_{18}$ (1 : 1) in the presence of L at 195 K
 (ii) $\text{Me}_3\text{NO/MeCN}$: $\text{Os}_6(\text{CO})_{18}$ (2 : 1) in the presence of $2\text{L}'$ at 195 K
 (iii) $\text{Me}_3\text{NO/CH}_2\text{Cl}_2$: Os_6 precursor (2 : 1)
 (iv) $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in CH_2Cl_2
 (v) Excess $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in CH_2Cl_2

Scheme 1. The formation of $[\text{Os}_6(\text{CO})_{17}\text{L}]$, $[\text{Os}_6(\text{CO})_{16}\text{L}'_2]^-$ and $[\text{H}_2\text{Os}_6(\text{CO})_{16}\text{L}]$ from $[\text{Os}_6(\text{CO})_{18}]$.

Table 1

Spectroscopic data for new derivatives

Compound	IR, $\nu(\text{CO})$ (cm^{-1}) ^b	Mass spect. (m/e)	¹ H NMR δ^c (ppm)
<i>(i) Os₆(CO)_{18-n}(L)_n</i> (<i>n</i> = 1 or 2)			
Os ₆ (CO) ₁₇ PPh ₃ ^a	2089(w), 2056(s), 2034(vs,sh), 2025(vs) 1976(w)	–	7.4 (m)
Os ₆ (CO) ₁₇ PEt ₃	2091(w), 2056(s), 2033(vs), 2025(vs), 1998(w), 1974(vw)	1746(1746)	2.25 (m) 1.18 (dt, $J_1(^1\text{H}-^{31}\text{P}) = 7.8$, $J_2 = 17.8$ Hz)
Os ₆ (CO) ₁₇ PPh ₂ Me	2091(w), 2057(s), 2036(vs), 2025(vs), 1978(w)	1828(1828)	7.6 (m) 2.47 (d, $J(^1\text{H}-^{31}\text{P}) = 10$ Hz)
Os ₆ (CO) ₁₇ AsPh ₃	2091(m), 2077(w), 2057(s), 2034(w), 2026(s), 1977(w)	1934(1934)	7.4 (m)
Os ₆ (CO) ₁₇ As(Tol) ₃	2091(w), 2076(w), 2057(s), 2034(vs), 2026(s), 1976(w)	1948(1948)	7.37 (m) 2.45 (s)
Os ₆ (CO) ₁₇ SbPh ₃	2091(mw), 2057(s), 2934(vs), 2027(s), 1999(mw), 1977(w)	1981(1981)	7.5 (m)
Os ₆ (CO) ₁₆ (PPh ₃) ₂ ^a isomer I	2079(w), 2038(m), 2017(s), 1973(w)	–	7.4–7.6 (m)
isomer II	2066(w), 2057(w), 2029(s), 2022(s,sh), 1961(w)	–	7.50 (m)
Os ₆ (CO) ₁₆ (PPh ₂ Me) ₂ isomer I	2081(mw), 2037(m), 2019(vs), 1972(w)	2000 (2000)	7.5 (m) 2.55 (d, $J(^1\text{H}-^{31}\text{P}) = 10$ Hz)
isomer II	2067(w), 2031(vs), 2023(s), 2004(m), 1961(w)	–	7.5 (m) 2.51 (d, $J(^1\text{H}-^{31}\text{P}) = 10$ Hz)
isomer III	2083(mw), 2048(m), 2072(vs), 2004(m), 1985(mw), 1953(w)	–	7.5 (m) 2.33 (d, $J(^1\text{H}-^{31}\text{P}) = 10$ Hz) 2.25 (d, $J(^1\text{H}-^{31}\text{P}) = 10$ Hz)
<i>(ii) [H₂Os₆(CO)₁₅{PPhR(C₆H₄)}]⁻ and</i> <i>[H₃Os₆(CO)₁₅{PPh₂(C₆H₄)}]⁺</i>			
[H ₂ Os ₆ (CO) ₁₅ (PPh ₂ (C ₆ H ₄))]⁻	2066(m), 2007(s,br)	–	7.6–7.3 (m) – 8.83 (d, $J(^1\text{H}-^{31}\text{P}) = 9.5$ Hz) – 13.52 (s)
[H ₃ Os ₆ (CO) ₁₅ (PPh ₂ (C ₆ H ₄))]⁺	2084(ms), 2046(s), 2031(vs), 1993(m), 1932(w)	–	7.6–7.3 (m) – 8.16 (dd, $J_1(^1\text{H}-^{31}\text{P}) = 6.2$, $J_2(^1\text{H}-^{31}\text{P}) = 1.4$ Hz) – 10.03 (d, $J(^1\text{H}-^{31}\text{P}) = 6.2$ Hz) – 14.41 (dd, $J_1(^1\text{H}-^{31}\text{P})$ = 10.5 Hz, $J_2(^1\text{H}-^{31}\text{P})$ = 1.4 Hz)
[H ₂ Os ₆ (CO) ₁₅ (PPhMe(C ₆ H ₄))]⁻	2045(w), 2015(m) 1998(vs)	–	7.4 (m) 2.52 (d, $J(^1\text{H}-^{31}\text{P}) = 10$ Hz) – 8.9 (d, $J(^1\text{H}-^{31}\text{P}) = 9$ Hz) – 13.12 (s)

Table 1 (continued)

Compound	IR, $\nu(\text{CO})$ (cm^{-1}) ^b	Mass spect. (m/e)	¹ H NMR δ (ppm) ^c
<i>(iii) H₂Os₆(CO)₁₆(L)</i> (L = P(OMe) ₃ , PEt ₃ , AsPh ₃)			
H ₂ Os ₆ (CO) ₁₆ P(OMe) ₃	2088(w), 2068(m), 2028(s,br)	—	3.54 (d, $J(^1\text{H}-^{31}\text{P}) = 12$ Hz) -9.73 (d, $J(^1\text{H}-^{31}\text{P}) = 16.4$ Hz) -16.4 (d, $J(^1\text{H}-^{31}\text{P}) = 4.8$ Hz)
H ₂ Os ₆ (CO) ₁₆ PEt ₃	2089(w), 2067(m), 2028(s)	—	2.22 (m) 1.48 (dt, $J_1(^1\text{H}-^{31}\text{P}) = 7.8$ Hz, $J_2(^1\text{H}-^{31}\text{P}) = 18$ Hz) -10.01 (d, $J(^1\text{H}-^{31}\text{P}) = 16$ Hz) -16.89 (d, $J(^1\text{H}-^{31}\text{P}) = 5.6$ Hz)
H ₂ Os ₆ (CO) ₁₆ AsPh ₃	2088(w), 2066(m), 2030(s,br)	—	7.4 (m) -10.01 (s)
<i>(iv) [H₃Os₆(CO)₁₆L]⁺</i> (L = P(OMe) ₃ , PEt ₃ , AsPh ₃)			
[H ₃ Os ₆ (CO) ₁₆ P(OMe) ₃] ⁺	2090(mw), 2069(m,sh), 2055(s), 2039(vs),	—	3.94 (d, $J(^1\text{H}-^{31}\text{P}) = 12$ Hz) -10.67 (d, $J(^1\text{H}-^{31}\text{P}) = 8$ Hz, 2H) -15.83 (s, 1H)
[H ₃ Os ₆ (CO) ₁₆ PEt ₃] ⁺	2032(s,sh), 2010(m) 2089(mw), 2067(mw), 2051(s), 2039(vs),	—	2.22 (m) 1.48 (dt, $J_1 = 7.8$ Hz, $J_2 = 18$ Hz) -11.06 (d, $J_1(^1\text{H}-^{31}\text{P}) = 7.6$ Hz, 2H) -16.63 (s, 1H)
[H ₃ Os ₆ (CO) ₁₆ AsPh ₃] ⁺	2089(mw), 2068(m), 2047(m), 2028(vs)	—	7.5 (m) -10.01 (d, $J(^1\text{H}-^{31}\text{P}) = 7.8$ Hz, 2H) -16.65 (s, 1H)

^a Data known for fully characterised derivative presented for comparison. ^b in CH₂Cl. ^c in CD₂Cl₂.

signals associated with carbonyls ANQ also collapse and then at 230 K signals due to carbonyls BHE. This is followed by the collapse of signals CFI at 270 K and at 360 K, the collapse of signals J, P and K. Finally, at 360 K, two broad peaks and one moderately sharp peak are observed in the regions of ~ 180 ppm, ~ 174 ppm,

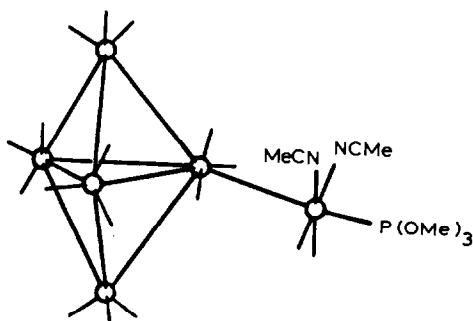


Fig. 1. The molecular structure of [Os₆(CO)₁₇P(OMe)₃(MeCN)₂].

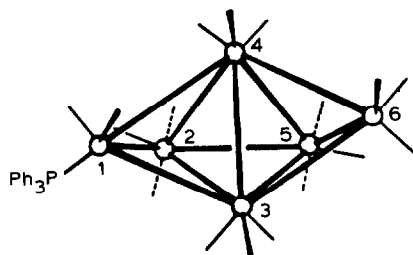


Fig. 2. The molecular structure of $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$.

and ~ 172 ppm respectively. These three, rather poorly resolved peaks, rather than the expected five peaks are observed because of the accidental degeneracy of the weighted average values of the coalesced peaks BEH + CFI, ANQ + JPK, and DMO + GL, respectively. It is thus apparent that five groups of three carbonyls and one group of two carbonyls may be identified as occupying sites on the six individual osmium atoms. It would also appear that, just as with $[\text{Os}_6(\text{CO})_{18}]$, fluxional behaviour corresponds to rotation of the three ligands about each of the independent osmium atoms [1 to 6]. Two-dimensional ^{13}C NMR (NOESY) experiments have been carried out on the compound $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$ to investigate the

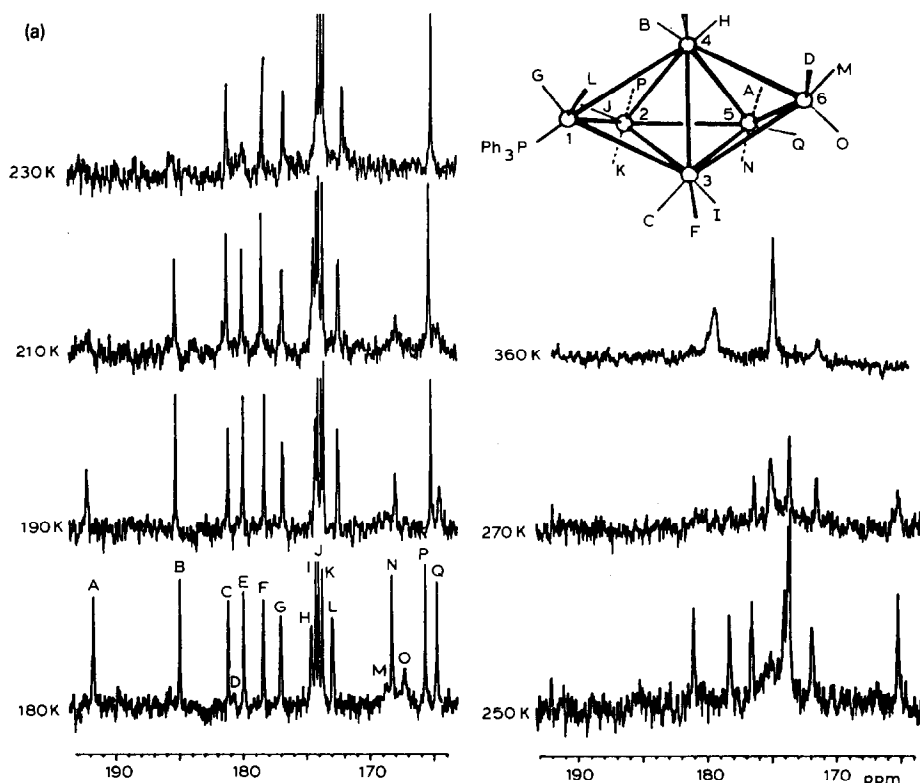


Fig. 3a. Temperature dependent ^{13}C NMR spectra of $[\text{Os}_6(\text{CO})_{17}(\text{PPh}_3)]$ in the range 180–360 K; recorded in toluene- d_8 .

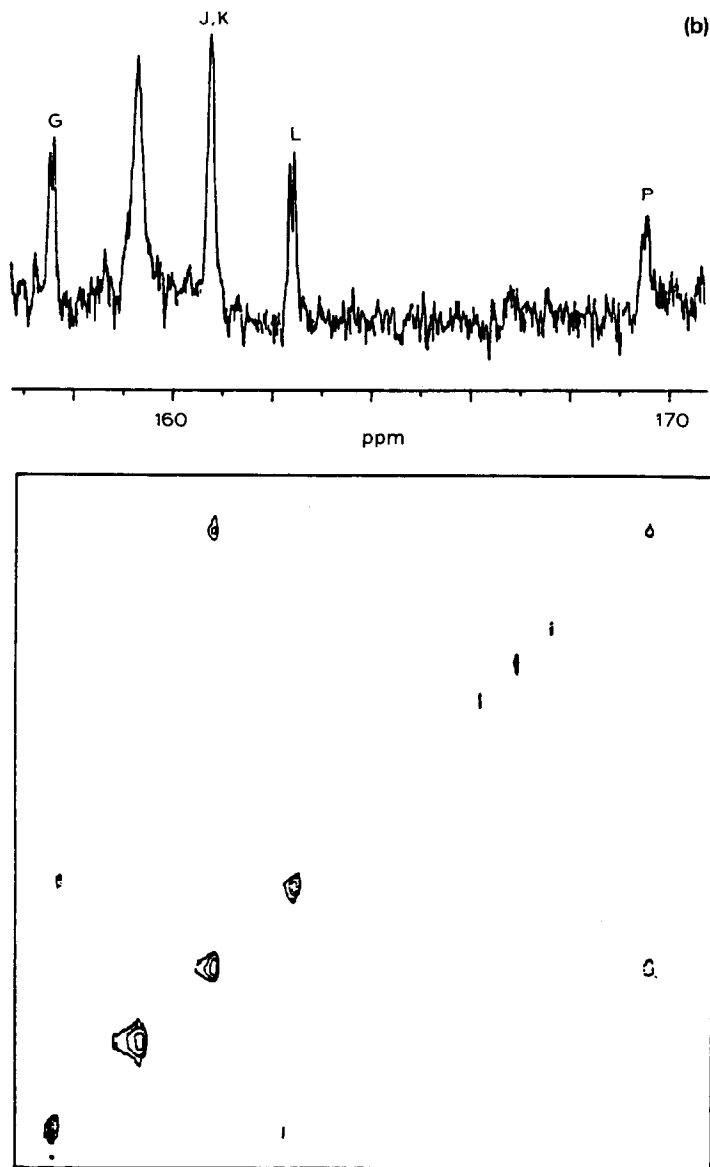


Fig. 3b. Contour plot of the 2D ^{13}C NOESY spectrum of $[\text{Os}_6(\text{CO})_{17}(\text{PPh}_3)]$ recorded at 270 K with $\tau_m = 0.05$.

exchange processes occurring at 270 K and 360 K. A contour plot of the 2D NOESY spectrum recorded at 270 K with $\tau_m = 0.01$ s is shown in Fig. 3b. Assuming, as before, that at the low level of ^{13}C enrichment used in this experiment, no direct ^{13}C - ^{13}C dipolar interaction will be observed, the cross peaks between signals G and L and between signals J, K and P can be attributed to exchange between these interconnected sites. In contrast, none of the ^{13}C NOESY spectra recorded at 360 K using varying values for τ_m showed any cross peaks indicative of CO site exchange at this temperature.

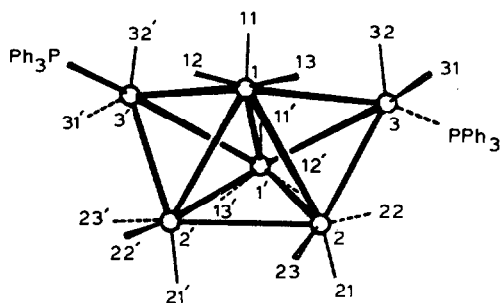


Fig. 4. Molecular structure of the more stable isomer of $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_3)_2]$.

Finally, it is important to note that the variable temperature ^{31}P NMR study of this cluster has shown that there is no change in the ^{31}P chemical shift of the PPh_3 ligand over the temperature range 180–380 K, so that any exchange process clearly does not involve a change in the ligand environment from one metal atom to another or the dissociation of the PPh_3 ligand at high temperature.

The ^{13}C NMR study of $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_3)_2]$

A sample of the more stable isomer of ^{13}C enriched $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_3)_2]$ was prepared by heating a mixture of the isomers of $[\text{Os}_6(^{13}\text{C})_{16}(\text{PPh}_3)_2]$ obtained from the reaction of $[\text{Os}_6(^{13}\text{C})_{18}]$ with Me_3NO (2 equiv.) in the presence of PPh_3 . This thermodynamically more stable isomer has the symmetrical solid state structure shown in Fig. 4 [4].

The ^{13}C NMR spectrum of the enriched sample of $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_3)_2]$ at 200 K is completely consistent with this structure, showing eight carbonyl resonances of equal intensity, two of which are split by ^{31}P - ^{13}C coupling. In the solid state structure a network of incipient bridging carbonyls is observed in which the strongest interactions are between carbonyl groups on the relatively electron rich centres $\text{Os}(2)$, $\text{Os}(2')$, $\text{Os}(1)$ and $\text{Os}(1\text{H}')$ and the electron-poor capping atoms (3) and (3'). It is possible that these secondary interactions are retained at low temperature in solution. On this basis, the signals at 201.4 and 195.7 ppm could be assigned to the pairs of carbonyls (22), (22') and (12), (13). The peaks showing ^{13}C - ^{31}P coupling can be assigned unambiguously to the equivalent carbonyls on osmiums (3) and (3'). The remaining peaks are tentatively assigned on the basis of the observed variable temperature data (Fig. 5). As the temperature is raised the collapse of the series of peaks corresponding to the carbonyl ligands on the three independent osmium atoms is observed in a manner similar to that observed for $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$ and discussed above.

The temperature dependence of the ^{13}C spectra of $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_3)_2]$ can thus be adequately explained in terms of a localised CO exchange process. Since the molecule has overall C_2 symmetry there are only three different osmium centres, and localised CO site exchange will average the CO groups on the equivalent osmium centres. Thus, the three peaks in the spectrum at 370 K correspond to the averages of the carbonyls on osmium atoms (2,2'), osmium atoms (1,1') and osmium atoms (3,3') respectively. It is thus entirely similar to the fluxional behaviour exhibited by $[\text{Os}_6(\text{CO})_{18}]$ and $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$.

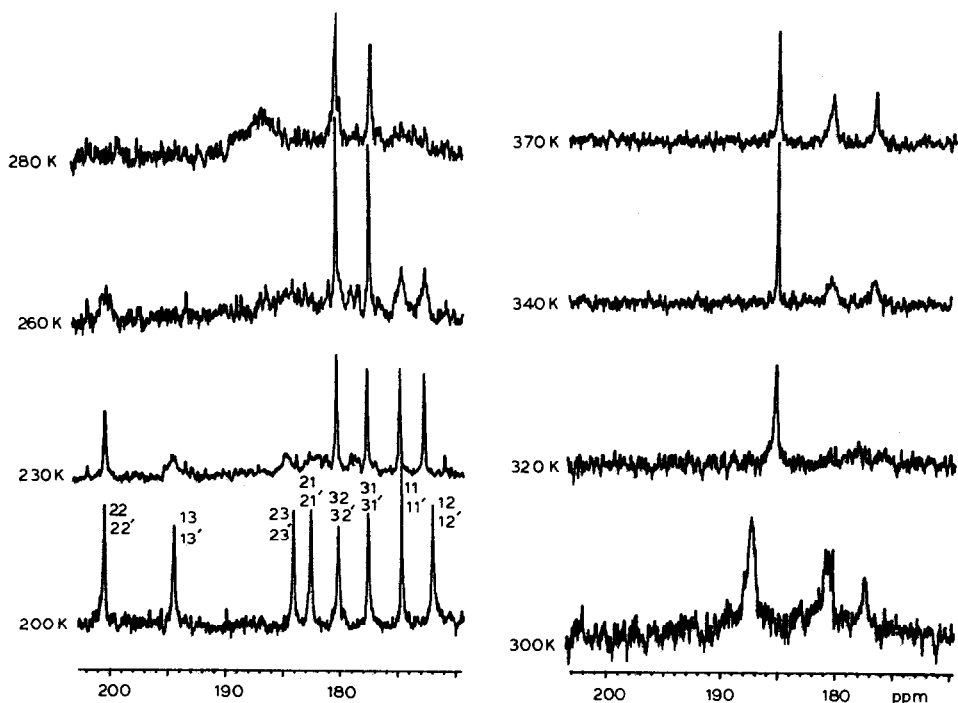


Fig. 5. Temperature dependent ^{13}C NMR spectrum of $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_3)_2]$ in the range 200–370 K recorded in toluene- d_8 .

Reactions of $[\text{Os}_6(\text{CO})_{17}\text{L}]$ with Me_3NO (1 : 2) to produce the anion $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$

Treatment of $[\text{Os}_6(\text{CO})_{17}\text{L}]$ with two equivalents of Me_3NO in CH_2Cl_2 , results in a colour change from brown to dark red and formation of an anionic hydrido-species as the major product (80%). This has been formulated, on the basis of spectroscopic data (Table 2), as the expected anionic product $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$. An additional very minor orange anionic product has been identified from its IR and ^1H NMR data as the anion $[\text{HOs}_5(\text{CO})_{14}\text{L}]^-$. However, in the case of $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$,

Table 2

Spectroscopic data for the anions, $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ ($\text{L} = \text{P}(\text{OMe})_3, \text{PEt}_3, \text{PPh}_2\text{Me}, \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$)

Compound ^a	IR, $\nu(\text{CO})$ (cm^{-1})	^1H NMR ^b , δ (ppm)	^{31}P NMR (ppm)
$[\text{HOs}_6(\text{CO})_{16}\text{P}(\text{OMe})_3]^-$	2064(mw), 2022(ms), 2002(s)	3.74 (d, $J(^1\text{H}-^{31}\text{P}) = 12$ Hz) -9.65 (d, $J(^1\text{H}-^{31}\text{P}) = 10$ Hz)	-35.74
$[\text{HOs}_6(\text{CO})_{16}\text{PEt}_3]^-$	2062(mw), 2025(m), 2003(s)	2.25(m) 1.53 (dt, $J_1(^1\text{H}-^{31}\text{P}) = 7.8$ Hz, $J_2(^1\text{H}-^{31}\text{P}) = 18$ Hz) -9.64 (d, $J(^1\text{H}-^{31}\text{P}) = 10.5$ Hz)	-74.3
$[\text{HOs}_6(\text{CO})_{16}\text{PPh}_2\text{Me}]^-$	2059(w), 2021(m), 2004(s)	2.40 (d, $J(^1\text{H}-^{31}\text{P}) = 10$ Hz) -9.60 (d, $J(^1\text{H}-^{31}\text{P}) = 10$ Hz)	-
$[\text{HOs}_6(\text{CO})_{16}\text{AsPh}_3]^-$	2087(vw), 2062(m), 2017(s), 2001(vs)	7.3 (m) -9.61 (s)	-

^a All compounds separated and characterised as PPN^+ salts. ^b Recorded at 260 K.

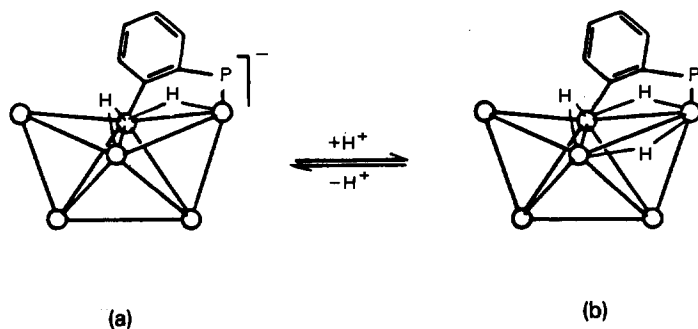


Fig. 6. Molecular structures of $[\text{H}_2\text{Os}_6(\text{CO})_{15}\text{PPh}_2\text{C}_6\text{H}_4]^-$ (a) and $[\text{H}_3\text{Os}_6(\text{CO})_{15}\text{PPh}_2\text{C}_6\text{H}_4]$ (b).

reaction with Me_3NO produces, in addition to the expected anion $[\text{HOs}_6(\text{CO})_{16}\text{PPh}_3]^-$, a mixture of other anionic species of which a brown product is the major component. The IR spectrum of this product, as the Et_4N^+ salt, is similar to that of $[\text{HOs}_6(\text{CO})_{16}\text{PPh}_3]^-$, however, the ^1H NMR spectrum shows two broad hydride signals at δ 8.83 and δ 13.52. On cooling to 260 K, these signals are resolved into a singlet and a doublet ($J(^{31}\text{P}-^1\text{H}) = 9.5$ Hz) resonance respectively. In the phenyl region of the spectrum, a set of three coupled resonances each integrating for one proton, as well as a complex multiplet integrating for eleven protons is observed. The coupled phenyl resonances resemble part of the ABCD spin pattern expected for protons in an asymmetrically ortho-substituted C_6H_4 ring. Assuming that the fourth resonance for the C_6H_4 ring proton is concealed by the multiplet due to the other phenyl protons (as the integration of the phenyl region suggests) the ^1H NMR spectrum of this compound is consistent with its formulation as the orthometallated anionic species $[\text{H}_2\text{Os}_6(\text{CO})_{15}(\text{PPh}_2\text{C}_6\text{H}_4)]^-$. This species, which is isoelectronic with $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$ and the orthometallated species, $[\text{HOs}_6(\text{CO})_{16}(\text{C}_6\text{H}_4\text{N})]$, is proposed to have the bicapped tetrahedral structure shown in Fig. 6a. The hydrido positions shown in the figure have not been established with certainty; however, comparison with the structure of $[\text{HOs}_6(\text{CO})_{16}(\text{C}_6\text{H}_4\text{N})]$ leads us to suggest that shown in 6a. Such a structure is consistent with our reported data.

Acidification of this anion with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ produces a neutral red compound which is formulated as $[\text{H}_3\text{Os}_6(\text{CO})_{15}(\text{PPh}_2\text{C}_6\text{H}_4)]$ [Fig. 6b] on the basis of its spectroscopic data (Table 1). Again, the precise location of the hydrido ligands has not been established and their location in 6b follows from the proposed structure of the dihydrido species 6a and is again consistent with our recorded data. Similar orthometallated compounds are also obtained on reaction of $[\text{Os}_6(\text{CO})_{17}\text{L}]$ ($\text{L} = \text{PPh}_2\text{Me}$, AsPh_3 , $\text{As}(p\text{-tol})_3$ or SbPh_3) with Me_3NO (1:2) in CH_2Cl_2 , in addition to the expected anion $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$.

Fluxional behaviour and the proposed structure of the anion $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ in solution

The ^1H NMR spectrum of $[\text{HOs}_6(\text{CO})_{16}\text{P}(\text{OMe})_3]^-$ shows a broad hydride resonance (linewidth ca. 30 Hz) at $\delta - 9.62$ at room temperature which, on cooling to 260 K, is resolved into a sharp doublet with two pairs of doublet ^{187}Os satellites [$J(^{187}\text{Os}-^1\text{H}) = 32.2$ Hz, 52.30 Hz]. This low temperature spectrum is consistent

with the presence of only one isomer which must contain a hydride ligand bridging two inequivalent osmium atoms one of which is the phosphite substituted osmium centre. On heating above 290 K the hydride signal collapses and above 350 K, a broad singlet at $\delta - 9.16$ is observed. This process is completely reversible on cooling. The variable temperature ^{31}P NMR data for $[\text{HOs}_6(\text{CO})_{16}\text{P}(\text{OMe})_3]^-$ are also consistent with a fluxional processes. At 240 K, a sharp singlet is observed at -35.7 ppm which, on heating to 370 K, collapses and is replaced by a new peak at -40.15 ppm. On the basis of these observations we conclude that the fluxional behaviour is similar to that of $[\text{HOs}_6(\text{CO})_{17}]^-$ with H-migration occurring over the cluster surface. Such a migration would cause a change in the environment of the $\text{P}(\text{OMe})_3$ ligand and hence a shift of the ^{31}P resonance at higher temperatures. However, the possibility that the process is due to the migration of the phosphite ligand cannot be excluded on the basis of this evidence alone.

Variable temperature ^{13}C NMR studies have also been carried out on several of the substituted anions in the attempt to determine the structure of the anion in solution and nature of the fluxional process. For these studies, ^{13}C enriched samples of the anions $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ ($\text{L} = \text{PEt}_3, \text{PPh}_3, \text{AsPh}_3$) (ca. 20%) as the PPN^+ salts were prepared from the corresponding ^{13}C -enriched derivatives $[\text{Os}_6(\text{CO})_{17}\text{L}]$. The ^{13}C NMR spectrum of $[\text{HOs}_6(\text{CO})_{16}\text{AsPh}_3]^-$ is temperature dependent in the range 170–340 K. At the low temperature limit the ^{13}C NMR

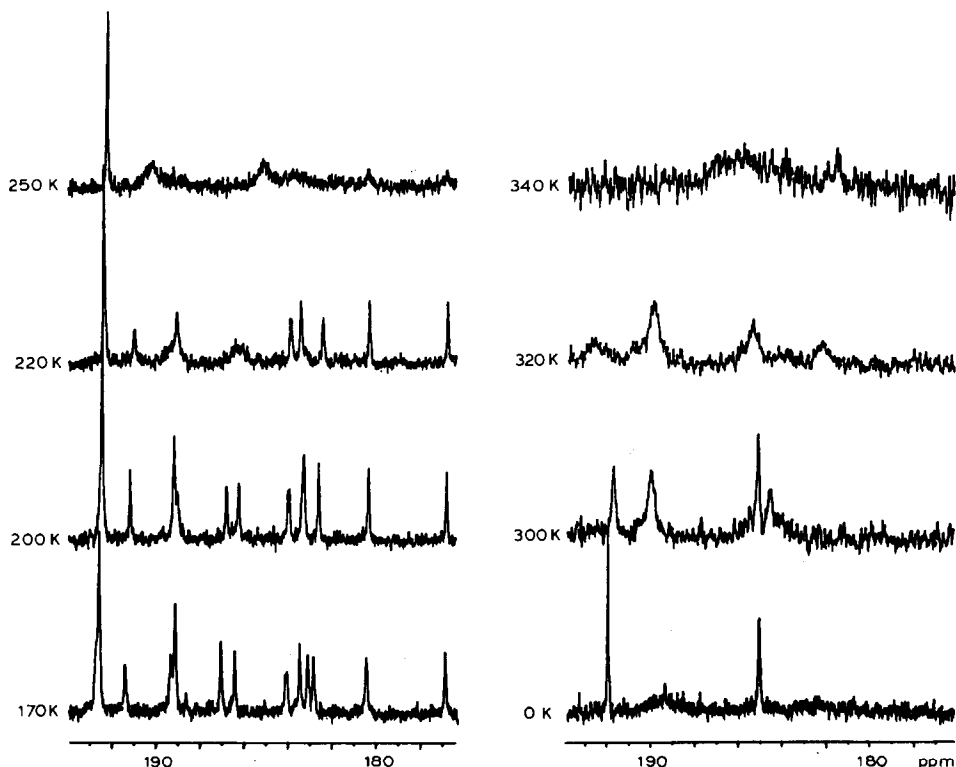


Fig. 7. Variable temperature ^{13}C NMR spectrum of $[\text{HOs}_6(\text{CO})_{16}(\text{AsPh}_3)]^-$ in the range 170–340 K recorded in CD_2Cl_2 and $\text{C}_2\text{D}_2\text{Cl}_4$.

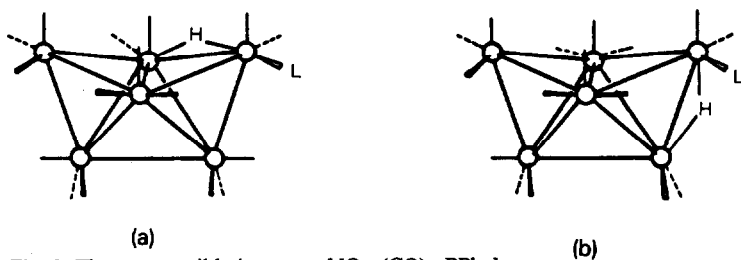


Fig. 8. The two possible isomers of $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$.

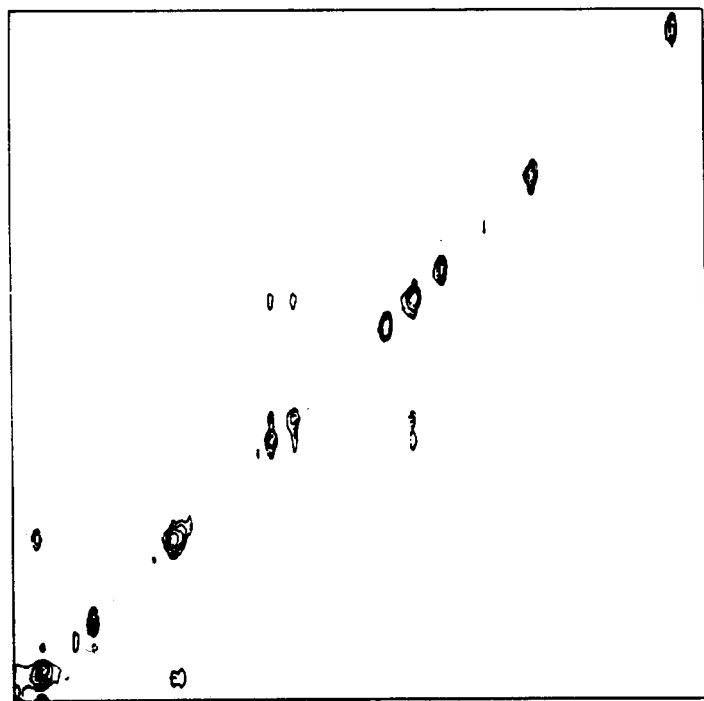
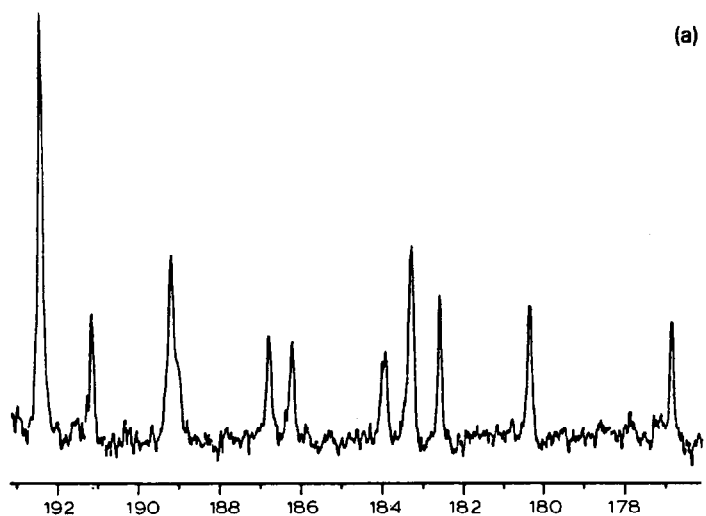


Fig. 9a. Contour plot of the 2D ^{13}C NOESY spectrum of $[\text{HOs}_6(\text{CO})_{16}(\text{AsPh}_3)]^-$ recorded at 200 K with $\tau_m = 0.01$ s.

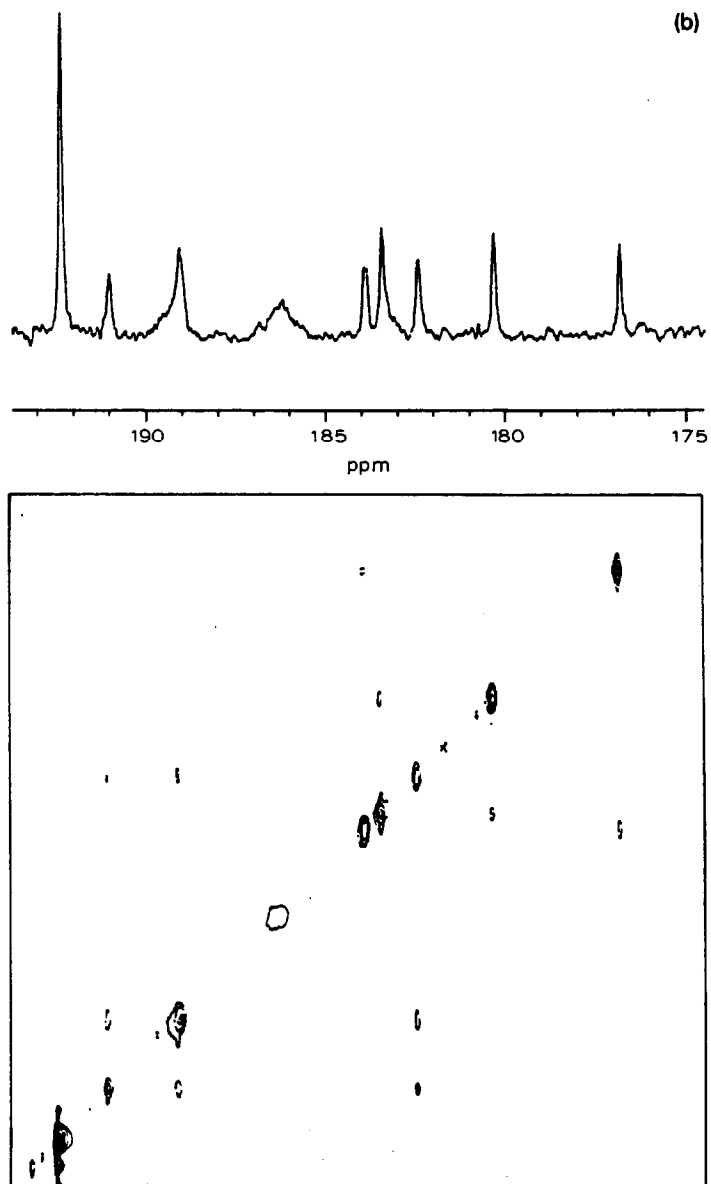


Fig. 9b. Contour plot of the 2D ^{13}C NOESY spectrum of $[\text{HOs}_6(\text{CO})_{16}(\text{AsPh}_3)]^-$ recorded at 220 K with $\tau_m = 0.01$ s.

spectrum is consistent with the existence of only one isomer of the anion of thirteen CO signals integrating for a total of sixteen carbonyl groups are observed (Fig. 7). The width of the signals at 191.7 and 188.9 ppm (integrating for 3 and 2 carbonyl groups respectively) in the low temperature spectrum and the asymmetry of the carbonyl resonances suggests that this spectrum does not represent the slow exchange limit. However, some structural information can be derived from this spectrum. The number of CO resonances observed at low temperature is consistent

only with a highly asymmetric structure for the anion and the pattern of ^{31}P - ^{13}C and ^1H - ^{13}C coupling in $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ ($\text{L} = \text{PPh}_3, \text{PEt}_3$) confirms that the hydride ligand is bonded to the phosphine-substituted osmium centre. Two possible structures for the anion, based on the crystallographically determined structure of $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$ [4], are shown in Fig. 8; in (b) the asymmetry of the structure derives from the position of phosphine-substitution on the capping osmium atom.

The variable temperature behaviour of the anion $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ ($\text{L} = \text{PEt}_3, \text{PPh}_3, \text{AsPh}_3$) is identical to that of $[\text{HOs}_6(\text{CO})_{17}]^-$. Two dimensional ^{13}C NOESY experiments carried out on $[\text{HOs}_6(\text{CO})_{16}\text{AsPh}_3]^-$ at 200 K and 220 K (Figs. 9a and 9b) show that at these temperatures CO fluxionality is limited to localised site exchange around the different osmium centres. However, on heating above 300 K, complete CO scrambling must occur since all signals collapse and merge to give one broad signal at 340 K. As in the case of $[\text{HOs}_6(\text{CO})_{17}]^-$, this behaviour is in contrast to that of the neutral parent clusters $[\text{Os}_6(\text{CO})_{17}\text{L}]$.

The lower energy barrier to CO migration in the anions may be rationalised as before in terms of the effect of the increased electron density on the cluster favouring the formation of CO bridges. Carbonyl exchange via a polytopal rearrangement seems unlikely in this case since this would also scramble of the position of the ligand L and would be expected to result in the formation of the several different isomers of $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ in solution.

Reaction of $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_2\text{Me})_2]$ with Me_3NO (1 : 2)

Preliminary investigations of the reaction of the thermodynamically most stable isomer of $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_2\text{Me})_2]$ with Me_3NO suggest that this reaction is completely analogous to that of the mono-substituted derivatives. Treatment of $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_2\text{Me})_2]$ with two equivalents of Me_3NO in CH_2Cl_2 produces mainly an anionic species, the spectroscopic data of which are consistent with its formulation as the expected anion $[\text{HOs}_6(\text{CO})_{15}(\text{PPh}_2\text{Me})_2]^-$ (Table 1). The room temperature ^1H NMR data of this anion indicate it is fluxional in solution. On cooling to 240 K, a sharp doublet hydride resonance at $\delta = 8.9$ and two doublets attributable to the methyl hydrogens of the PPh_2Me groups, are observed. These low temperature ^1H NMR data are consistent with the anion having an asymmetric structure, in contrast to the parent cluster $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_2\text{Me})_2]$ which appears, on the basis of IR and ^1H NMR data to be structurally analogous to the symmetrically substituted isomer of $[\text{Os}_6(\text{CO})_{16}(\text{PPh}_3)_2]$ and consistent with the ^1H NMR data (Fig. 10).

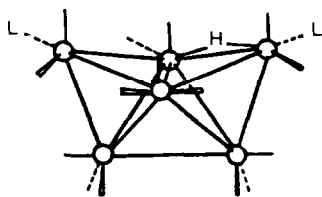


Fig. 10. Possible structure of the anion $[\text{HOs}_6(\text{CO})_{15}(\text{PPh}_2\text{Me})_2]^-$.

Table 3

 ^{13}C NMR data for $\text{H}_2\text{Os}_6(\text{CO})_{16}\text{PEt}_3$ in toluene- d^8

Chemical shift (ppm)	Integration	Multiplicity	Coupling constant (Hz)
189.5	1	s	
187.4	1	d	$J(^1\text{H}-^{13}\text{C}) = 4.4$
186.5	1	s	
183.5	1	d	$J(^1\text{H}-^{13}\text{C}) = 4.4$
182.9	1	dd	$J(^{31}\text{P}-^{13}\text{C}) = 8$
182.7	1	d	$J(^1\text{H}-^{13}\text{C}) = 5$
182.3	1	s	
180.2	1	s	
178.3	1	s	
177.9	3	s	
177.6	1	s	
177.4	1	s	
176.9	1	dd	$J(^{31}\text{P}-^{13}\text{C}) = 6.7$
175.0	1	s	$J(^1\text{H}-^{13}\text{C}) = 2$

Reactions of $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ ($\text{L} = \text{P}(\text{OMe})_3, \text{PEt}_3, \text{PPh}_2\text{Me}, \text{PPh}_3, \text{AsPh}_3$) with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$

Treatment of the anions $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in CH_2Cl_2 results in the formation of red products (ca. 80%) which, on the basis of spectroscopic data (Table 1), are formulated as the neutral dihydrides $[\text{H}_2\text{Os}_6(\text{CO})_{16}\text{L}]$. The ^1H NMR data for these derivatives (Table 1) show that, in contrast to $[\text{H}_2\text{Os}_6(\text{CO})_{17}]$, the hydride ligands in these compounds are not fluxional at room temperature. The compounds $[\text{H}_2\text{Os}_6(\text{CO})_{16}\text{L}]$ are considerably more soluble than $[\text{H}_2\text{Os}_6(\text{CO})_{17}]$ so a low temperature ^{13}C NMR study could be more readily undertaken. The ^{13}C NMR spectrum of $[\text{H}_2\text{Os}_6(\text{CO})_{16}\text{PEt}_3]$ (ca. 30% ^{13}C enriched) at 187 K shows fourteen signals, thirteen of intensity 1 and one of intensity 3, six of which are split by $^{31}\text{P}-^{13}\text{C}$ and/or $^1\text{H}-^{13}\text{C}$ coupling in the CO region (Table 3). This indicates that the compound has a highly asymmetric structure in which the two hydride ligands occupy bridging positions, similar to that of $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$. In this case, on the basis of the ^1H data, they are thought to be bonded to the phosphine-substituted osmium atom according to the structure shown in Fig. 11a. However, we are unable at present to interpret fully the more detailed aspects of the ^{13}C NMR data.

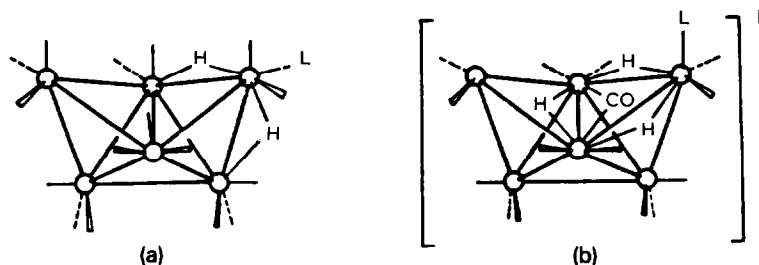


Fig. 11. The structure of $\text{H}_2\text{Os}_6(\text{CO})_{16}\text{L}$ (a) and $[\text{H}_3\text{Os}_6(\text{CO})_{16}\text{L}]^+$ (b).

In the presence of excess acid, these dihydride compounds react to give orange products which are formulated, on the basis of the ^1H NMR data (Table 1), as the trihydrido cation $[\text{H}_3\text{Os}_6(\text{CO})_{16}\text{L}]^+$. In the ^1H NMR spectra of these trihydrido cations two broad hydride signals are observed at room temperature; on cooling these broad signals are resolved into a doublet in the region of 11 ppm [$J(^{31}\text{P}-^1\text{H}) \sim 8$ Hz] and a singlet in the region of -16 ppm of relative intensity 2:1. On this basis, the cation probably has the structure shown in Fig. 11b in which two protons span edges adjacent to the ligand bearing osmium atom and the third proton occupies a unique edge of the bicapped tetrahedron.

Conclusions

In this work we have established good synthetic routes to the mono- and bis-substituted derivatives $[\text{Os}_6(\text{CO})_{17}\text{L}]$ and $[\text{Os}_6(\text{CO})_{16}\text{L}_2]$ which have structures based on the same bicapped tetrahedral Os_6 -unit established for $[\text{Os}_6(\text{CO})_{18}]$. The $[\text{Os}_6(\text{CO})_{16}\text{L}_2]$ compounds apparently exist in more than one isomeric form and there is evidence for the formation of small amounts of the tris-substituted product $[\text{Os}_6(\text{CO})_{15}\text{L}_3]$. These mono- and bis-substituted compounds, like $[\text{Os}_6(\text{CO})_{18}]$, react with Me_3NO in CH_2Cl_2 to produce the anionic derivatives $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ and $[\text{HOs}_6(\text{CO})_{15}\text{L}_2]^-$ which, on reaction with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, go on the form hydrido-species of the type $[\text{H}_2\text{Os}_6(\text{CO})_{16}\text{L}]$ and $[\text{H}_3\text{Os}_6(\text{CO})_{16}\text{L}]^+$.

Experimental

General

All manipulations were carried out under dry nitrogen using standard techniques. All solvents were dried and freshly distilled under nitrogen before use.

Infrared spectra were recorded using a Perkin Elmer 983 spectrometer. NMR spectra were recorded using a Bruker WP250 and a Bruker AM400 machine. Mass spectra were recorded using a Kratos MS 902 machine and microanalyses were carried in the microanalytical section of this department. TLC plates were prepared in this laboratory (20 × 20 on glass coated with a 0.20 mm layer of Merck Kiesel gel 60F₂₅₄).

Synthesis of the compounds $[\text{Os}_6(\text{CO})_{18-n}\text{L}_n]$ ($n = 1, 2$)

In a typical synthesis of a mono-substituted derivative, $[\text{Os}_6(\text{CO})_{18}]$ (20 mg) was dissolved in CH_2Cl_2 (20 ml) and an excess of the ligand L added. The mixture was cooled to 195 K and a solution of Me_3NO (0.9 mg) in CH_2Cl_2 (2 ml) added dropwise over 10 min with stirring. The reaction mixture was allowed to warm up slowly to room temperature with stirring, then reduced in volume and the products separated by TLC eluting with 40% CH_2Cl_2 /hexane. Typically three bands separated; a brown band identified as $[\text{Os}_6(\text{CO})_{18}]$ (5%), a yellow-brown band which gave the mono-substituted product, $[\text{Os}_6(\text{CO})_{17}\text{L}]$ (80–90%) and a dark-brown band consisting of the bis-substituted product (5–10%). The product, $[\text{Os}_6(\text{CO})_{17}\text{L}]$, was generally crystallised from CH_2Cl_2 /hexane as a dark brown solid.

The disubstituted derivatives, $[\text{Os}_6(\text{CO})_{16}\text{L}'_2]$, were isolated in high yield by a similar route, using two equivalents of Me_2NO , under the same conditions and working up the reaction mixture as described above. The derivatives prepared were

identified by IR and ^1H NMR spectroscopy and mass spectrometry (Table 1). Samples of ^{13}C enriched $[\text{Os}_6(\text{CO})_{17}\text{L}]$ (ca. 20% enrichment) were prepared by this route from $[\text{Os}_6(^{13}\text{C})_{18}]$.

Reaction of the derivative $[\text{Os}_6(\text{CO})_{17}\text{L}]$ with Me_3NO

In a typical reaction, $[\text{Os}_6(\text{CO})_{17}\text{L}]$ (20 mg) was dissolved in CH_2Cl_2 (20 ml) and a solution of Me_3NO (2.2 mg) in CH_2Cl_2 (2 ml) was added dropwise with stirring over 5 minutes. The solution immediately became red-brown in colour and its IR spectrum showed a shift in the $\nu(\text{CO})$ bands to lower wavenumbers ($\approx 2004\text{ cm}^{-1}$). The product, $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$, was generally separated as the PPN^+ salt, by TLC, eluting with 80% CH_2Cl_2 /hexane. In the case of the reaction of $[\text{Os}_6(\text{CO})_{17}\text{PPh}_3]$ with Me_3NO (1 : 2), the orange product formulated as $[\text{H}_2\text{Os}_6(\text{CO})_{15}(\text{Ph}_2\text{P}(\text{C}_6\text{H}_4))]^-$ was also separated as the PPN^+ salt by TLC. The anionic products were characterised by IR, ^1H NMR and ^{31}P NMR spectroscopy. Samples of ^{13}C enriched $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ ($\text{L} = \text{PEt}_3, \text{PPh}_3, \text{As}(\text{Tol})_3$) (ca. 20% enrichment) were prepared from the corresponding enriched $[\text{Os}_6(\text{CO})_{17}\text{L}]$ derivative by the method described above.

Reactions of $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$

Generally, a solution of $[\text{HOs}_6(\text{CO})_{16}\text{L}]^-$ (ca. 10 mg) in CH_2Cl_2 was prepared as described above and approximately one equivalent of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ added with stirring. An immediate colour change to bright red was observed and the IR spectrum showed formation of a neutral ($\nu(\text{CO})$ 2028(s) cm^{-1}). These products were isolated by filtration of the reaction mixture through silica and extracting with CH_2Cl_2 and were characterised by IR and ^1H NMR spectroscopy and mass spectrometry. The cations $[\text{H}_3\text{Os}_6(\text{CO})_{16}\text{L}]^+$ were obtained by treatment of a CH_2Cl_2 solution of $[\text{H}_2\text{Os}_6(\text{CO})_{16}\text{L}]$ with excess $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. Samples of ^{13}C enriched $[\text{H}_2\text{Os}_6(\text{CO})_{16}\text{PEt}_3]$ and the corresponding cation were prepared for the ^{13}C NMR studies by treatment of $[\text{HOs}_6(\text{CO})_{16}\text{PEt}_3]^-$ with the appropriate amount of CF_3COOH in a NMR tube.

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