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Some substitution reactions of planar hexanuclear osmium clusters *

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Abstract

The hexa-osmium clusters, $[Os_6(CO)_{18}]$ and $[Os_6(CO)_{21}]$, have been found to react with $P(OMe)_3$ to yield the blue-green planar cluster complexes $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$ ($n = 1$–6). The same substituted derivatives have been prepared by a range of other synthetic procedures. These include treatment of $[Os_6(CO)_{18}(MeCN)_n]$ ($n = 1$–3) (prepared by the direct reaction of $[Os_6(CO)_{18}]$ with MeCN) with the phosphite, treatment of $[Os_6(CO)_{21-n}(MeCN)_n]$ ($n = 1, 2$) [prepared either by the direct reaction of $[Os_6(CO)_{21}]$ with MeCN, or by catalytic dimerisation of $[Os_3(CO)_{12-n}(MeCN)_n]$ ($n = 1, 2$) with palladium dichloride as catalyst] with the phosphite, or by carbonylation of higher substituted products. The new substituted derivatives have been characterised by a combination of IR and NMR spectroscopy, and in some cases by single crystal X-ray diffraction studies. All fifteen possible derivatives have been characterised.

Introduction

A study [1] of the reaction of $[Os_6(CO)_{18}]$ with CO in solution revealed that a number of clusters are produced, including $[Os_3(CO)_{12}]$, $[Os_5(CO)_{16}]$, $[Os_5(CO)_{19}]$,

$$\begin{aligned}[Os_6(CO)_{18}] \xrightarrow{CO} {} & [Os_3(CO)_{12}] + [Os_5(CO)_{16}] + [Os_5(CO)_{19}] \\ & + [Os_7(CO)_{21}] + [Os(CO)_5] + \text{‘}[Os_6(CO)_{21}]\text{’} \\ & \qquad\qquad\qquad\qquad \text{(blue-purple solid)}\end{aligned}$$

Scheme 1. Products of the reaction of $[Os_6(CO)_{18}]$ with carbon monoxide.

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* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

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and $[Os_7(CO)_{21}]$, together with $[Os(CO)_5]$ and an insoluble blue-purple powder (Scheme 1), which is also the major product from the reaction of CO with solid $[Os_6(CO)_{18}]$. Characterisation of this product was prevented by its insolubility in common organic solvents, although EI mass spectroscopy suggested that it was a hexanuclear cluster, since it exhibited a strong peak in the mass spectrum corresponding to the ion $[Os_6(CO)_{20}]^+$. The formulation $[Os_6(CO)_{20}]$ was proposed on

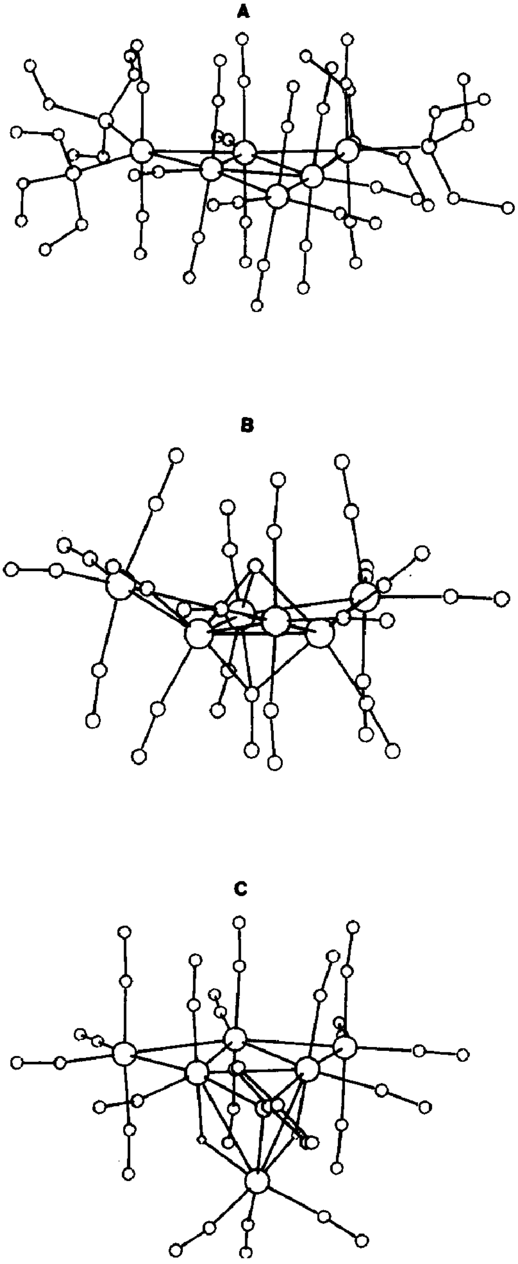


Fig. 1. Molecular structures of (a) $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$, (b) $[Os_6(CO)_{18}(\mu_3\text{-}CO)(\mu_3\text{-}O)]$ and (c) $[(\mu\text{-}H)_2Os_6(CO)_{18}(\mu_3\text{-}PPh)]$.

this basis and from the microanalysis (although this is not a particularly reliable guide for binary carbonyl clusters) and taking account of the observation that when the complex was heated, $[Os_6(CO)_{18}]$ was regenerated, apparently with the liberation of two equivalents of carbon monoxide [2]. As a consequence, in view of the apparent electron count of eighty-eight, the metal geometry was suggested to be a doubly edge-bridged tetrahedron.

Further work [2] showed that the reaction with $P(OMe)_3$ of either $[Os_6(CO)_{18}]$ or the blue-purple solid tentatively formulated as $[Os_6(CO)_{20}]$ produced a range of blue/green clusters, and a single crystal X-ray analysis of one of these, viz. $[Os_6(CO)_{17}\{P(OMe_3)_4\}]$, revealed an essentially planar arrangement of six Os atoms (Fig. 1a) [3]. On this basis the blue-purple solid was reformulated as the binary 'raft' carbonyl cluster $[Os_6(CO)_{21}]$. The difference in the percentage of carbon for the two formulations $[Os_6(CO)_{20}]$ and $[Os_6(CO)_{21}]$ is $< 0.5\%$ and therefore not truly diagnostic; however, a recent analysis of the carbonyl stretching frequencies in the IR solid state spectrum showed that the number of bands was consistent with a structure of D_{3h} symmetry, and a careful re-examination of the FAB mass spectrum has revealed a very weak peak corresponding to the molecular-ion $[Os_6(CO)_{21}]^+$ [4].

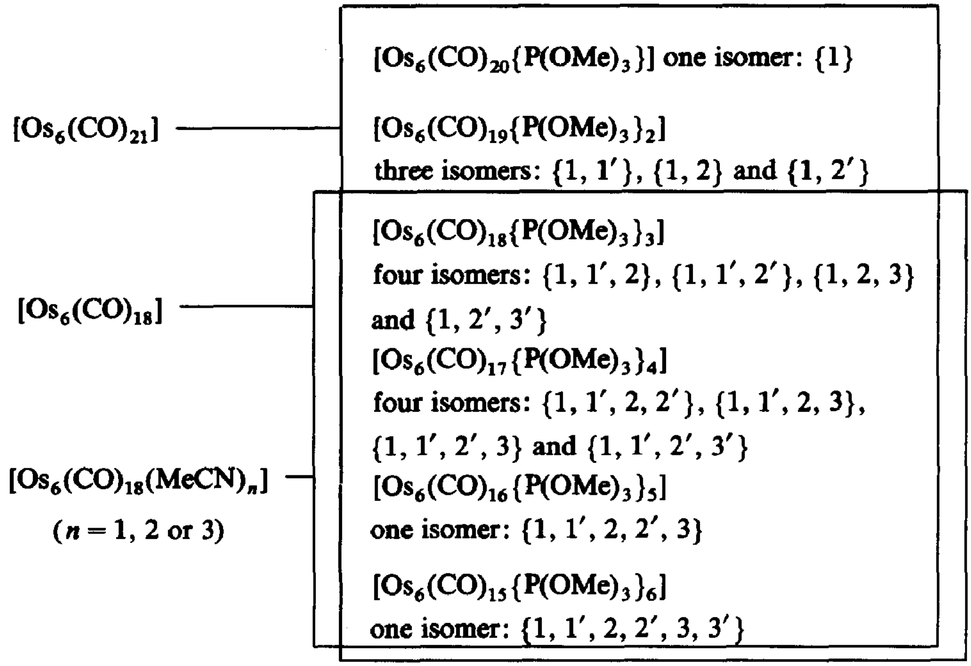
A similar planar metal geometry has also been reported for the 'oxo-raft' cluster $[Os_6(CO)_{18}(\mu_3\text{-}CO)(\mu_3\text{-}O)]$ (Fig. 1b), which was synthesised from $[Os_6(CO)_{21}]$ by direct reaction with O_2 in refluxing toluene [5]. The two capping ligands, a μ_3-O atom, and a μ_3-CO group, coordinate to the three Os atoms of the inner triangle and the outer triangles are slightly tilted towards the μ_3-O atom, resulting in short non-bonded distances between the axial carbonyls on the outer osmium atoms and the μ_3-O atom. A related metal geometry is also observed in the phosphido-hydrido cluster $[(\mu\text{-}H)_2Os_6(CO)_{18}(\mu_3\text{-}PPh)]$, although one of the outer triangles is considerably distorted from the idealised planar geometry (Fig. 1c) [6].

We report here on some further studies of raft molecules, and in particular of the synthesis and characterisation of the phosphite-substituted derivatives of the type $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$ ($n = 1$–6), and in addition discuss the pattern of substitution in $[Os_6(CO)_{21}]$. These studies represent the first step in an attempt to understand more fully the factors that influence the reactivity of such planar molecules towards molecular oxygen.

Results and discussion

Before we begin a detailed discussion of this work we comment on the nomenclature used for the various substituted derivatives. That nomenclature is shown in Fig. 2a. On the reasonable assumption that substitution occurs at the outer osmium atoms (1, 2, or 3) and at equatorial sites only (see below), there are fifteen possible substitution products and these correspond to the arrangements shown in Fig. 2b.

In the course of the work several new routes to these substituted derivatives were developed, and by use of these routes all fifteen possible equatorially substituted derivatives were prepared and characterised. The initial route to the substituted derivatives, which involved the reaction of parent carbonyls $[Os_6(CO)_{18}]$ or $[Os_6(CO)_{21}]$ with $P(OMe)_3$ in refluxing benzene, resulted in a complex mixture of substituted derivatives of the type $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$ ($n = 1$–6) (Scheme 2). In addition, a small percentage of other, lower nuclearity, products were produced



Scheme 2. Synthesis of substituted raft clusters directly from $[Os_6(CO)_{21}]$, $[Os_6(CO)_{18}]$, or $[Os_6(CO)_{18}(MeCN)_n]$ ($n = 1, 2$ or 3).

(see Experimental section). A more specific route was found fortuitously found. The parent carbonyl $[Os_6(CO)_{18}]$ dissolves in MeCN to give the adducts $[Os_6(CO)_{18}(MeCN)_n]$ ($n = 1$–3), and on standing these give the dianion $[Os_5(CO)_{15}]^{2-}$ and the dication $[Os(CO)_3(MeCN)_3]^{2+}$ (Scheme 3). However, when freshly prepared, the adducts are highly reactive, and on treatment with $P(OMe)_3$ yield a mixture of the tri-, tetra-, penta- and hexa-substituted derivatives (see

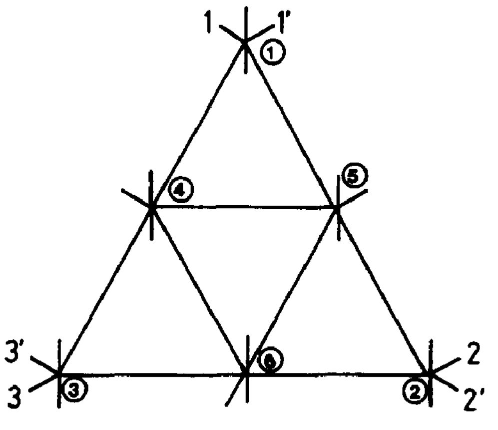
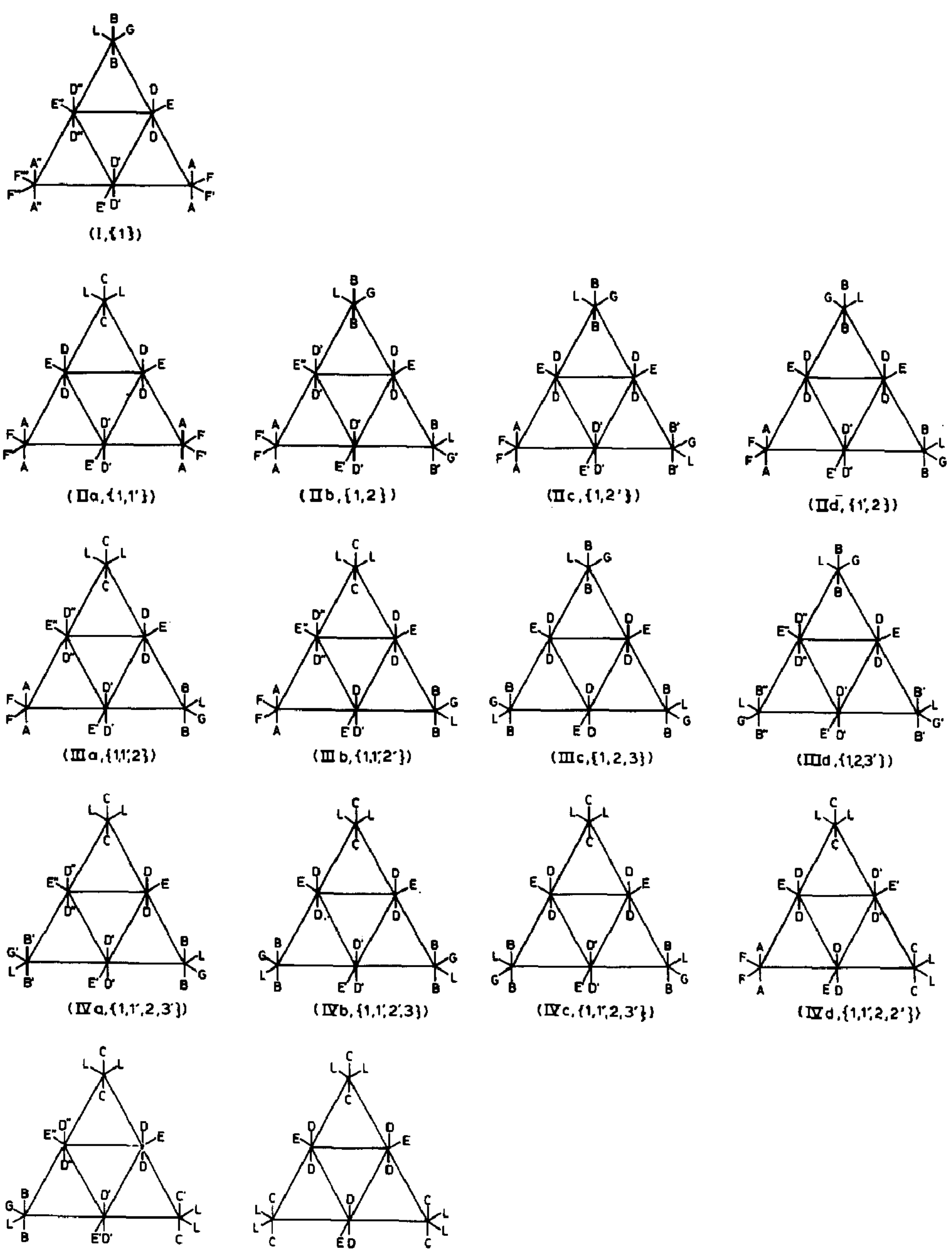


Fig. 2a. Nomenclature for substituted raft derivatives $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$ ($n = 1$–6). Note: Only the outer equatorial ligand positions need to be considered (see text).



(I,{1})

(IIa,{1,1'})
(IIb,{1,2})
(IIc,{1,2'})
(IId,{1',2})

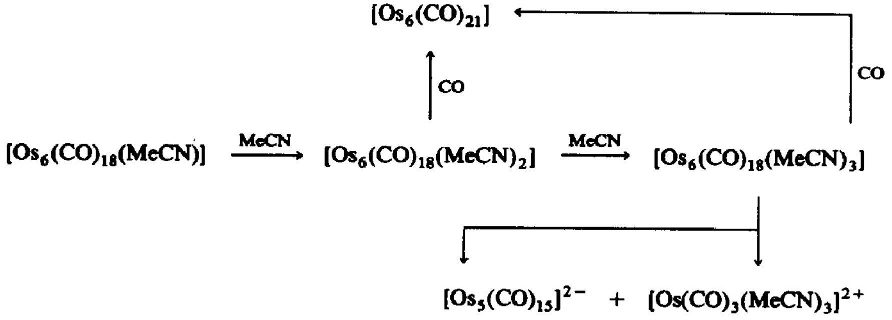
(IIIa,{1,1',2})
(IIIb,{1,1',2'})
(IIIc,{1,2,3})
(IIId,{1,2,3'})

(IVa,{1,1',2,3'})
(IVb,{1,1',2',3})
(IVc,{1,1',2,3'})
(IVd,{1,1',2,2'})

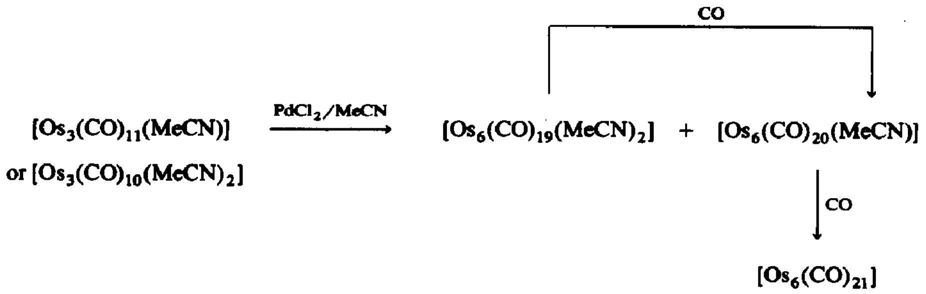
(V,{1,1',2,2',3})
(VI,{1,1,2,2',3,3'})

Fig. 2b. Possible substitution products.

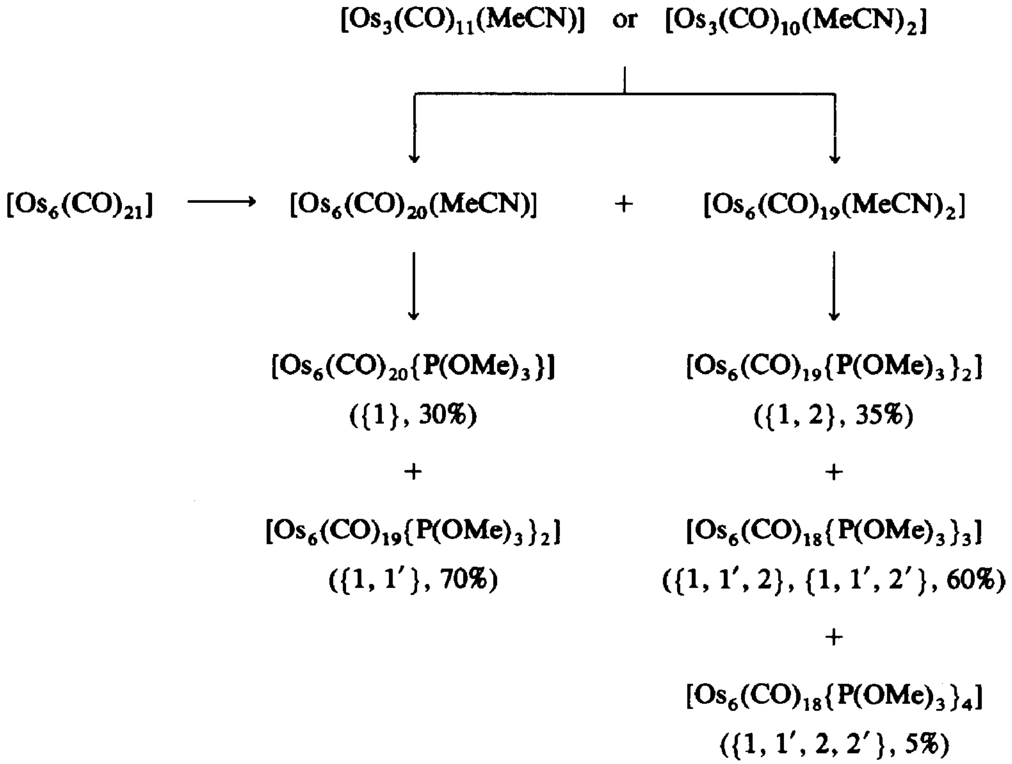
Scheme 2). We also found that the activated trinuclear clusters $[Os_3(CO)_{11}(MeCN)]$ or $[Os_3(CO)_{10}(MeCN)_2]$ in the presence of $PdCl_2$ [8] as catalyst undergo a coupling reaction to give the activated raft clusters $[Os_6(CO)_{21-n}(MeCN)_n]$ ($n = 1$, 2) in good yield (see Scheme 4) [9]. Reaction of these raft clusters in with $P(OMe)_3$ gives less substituted raft clusters of the type $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$ ($n = 1$–4), again in good yield (see Scheme 5). In addition, several intermediate substitution derivatives were synthesised in much improved yields by reaction with $P(OMe)_3$ of the



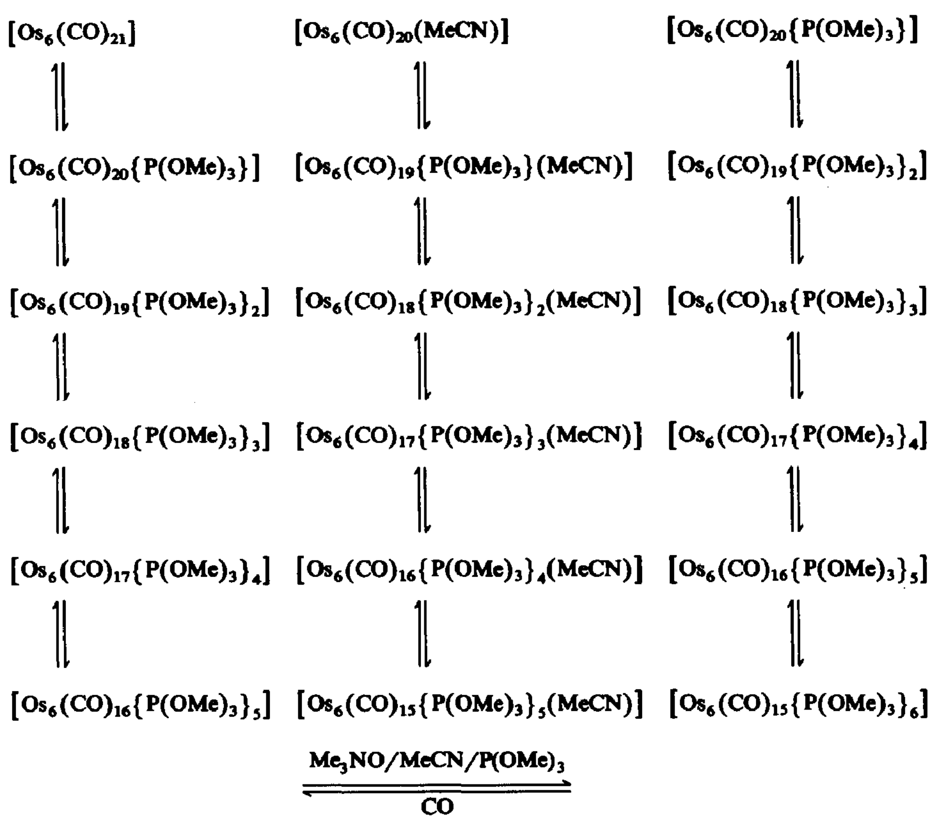
Scheme 3. Synthesis of the adducts $[Os_6(CO)_{18}(MeCN)_n]$ ($n = 1$, 2 or 3) from $[Os_6(CO)_{18}]$.



Scheme 4. Catalytic synthesis of $[Os_6(CO)_{19}(MeCN)_2]$ and $[Os_6(CO)_{20}(MeCN)]$ from $[Os_3(CO)_{11}(MeCN)]$ or $[Os_3(CO)_{10}(MeCN)_2]$.



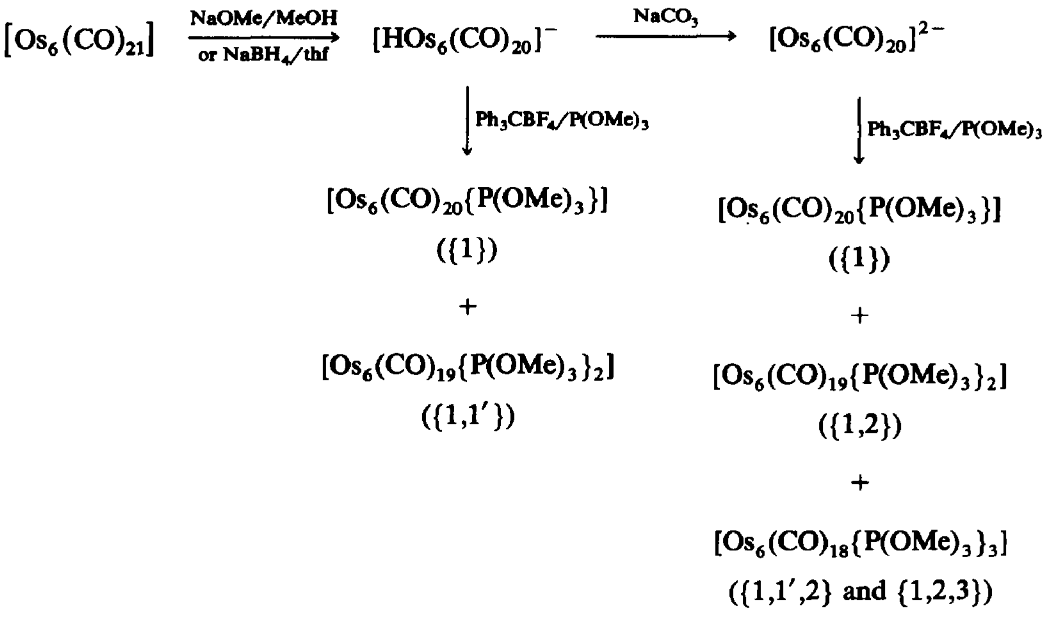
Scheme 5. Synthesis of substituted raft clusters from $[Os_6(CO)_{20}(MeCN)]$ or $[Os_6(CO)_{19}(MeCN)_2]$.



Scheme 6. Sequential synthesis of substituted raft clusters from $[Os_6(CO)_{21}]$ and $[Os_6(CO)_{20}(MeCN)]$.

activated species $[Os_6(CO)_{21-(n+m)}\{P(OMe)_3\}_n(MeCN)_m]$ (which were prepared by reaction of $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$ with $Me_3NO/MeCN$ in benzene or simply MeCN in refluxing benzene). We also observed that the substituted rafts $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$ ($n = 1$–6) readily react reversibly with carbon monoxide under mild conditions (1 atm, 25 °C) to give less substituted derivatives, providing an easy and systematic route (Scheme 6). Finally, $[Os_6(CO)_{21}]$ reacts with $NaBH_4$ in tetrahydrofuran or NaOMe in MeOH to form the monohydrido-anionic raft $[HOs_6(CO)_{20}]^-$ and with Na_2CO_3 in MeOH to form the dianion $[Os_6(CO)_{20}]^{2-}$; these anions react in turn with $P(OMe)_3$ in the presence of Ph_3CBF_4 to give high yields of the mono-, bis- and tris-substituted derivatives (Scheme 7). The products from these various reactions were readily separated by TLC on silica. All are blue-green, and are unstable in air (oxygen), in which they react to give the oxygen-raft species of the type described in the Introduction. The rate of this reaction with dioxygen depends on the degree of substitution (n), and this aspect of the work will be discussed in a future publication.

By a combination of these synthetic routes we have prepared the predicted total of fifteen derivatives. All were characterised on the basis of their IR and NMR spectra and in some cases by single crystal X-ray diffraction studies. In several instances, positional isomers in which substitution has occurred at the same osmium atom have been observed to undergo moderately rapid interconversion in solution and for this reason spectroscopic data in some cases were obtained only for isomeric



Scheme 7. Synthesis of substituted raft clusters from the anions $[HOs_6(CO)_{20}]^-$ or $[Os_6(CO)_{20}]^{2-}$.

mixtures (see below). Interconversion between derivatives in which L occupies sites on different osmium atoms is, in general, very slow.

Four of these substituted raft clusters have been previously characterised by single crystal X-ray crystallography as the {1} [7], {1,2} [2], {1,1′,2,2′} [19] and {1,1′,2,2′,3,3′} [2] derivatives. Full details of these X-ray studies will be presented elsewhere in a paper dealing in detail with the reactions that the substituted derivatives undergo and the significance of the structural variations they exhibit. All structural studies show that the $P(OMe)_3$ ligand(s) occupy equatorial sites on the outer osmium atoms. On this basis and on that of the information from detailed studies of the trinuclear osmium systems $[Os_3(CO)_{12-n}\{P(OMe)_3\}_n]$ ($n = 1$–6), we think it reasonable to assume that the same equatorial coordination mode persists for all derivatives (although, in this connection, it is noteworthy that the related MeCN derivatives $[Os_6(CO)_{21-n}(MeCN)_n]$ ($n = 1, 2$) appear to possess an axially rather than an equatorially substituted arrangement).

(a) Monosubstitution: $[Os_6(CO)_{20}\{P(OMe)_3\}]$ (I)

As expected, only one form (1), is observed and this is a product from most synthetic routes. It has been crystallographically characterised [7]. The highest peak in the FAB mass spectrum is at m/e 1836, which corresponds to the molecular-ion. This is in contrast with the EI mass spectrum, in which the highest peak corresponded to the species $[Os_6(CO)_{17}\{P(OMe)_3\}]^+$, clearly indicating that CO loss had occurred during the measurement. As noted above, this is a common problem with the EI spectra of planar derivatives of this type and possibly accounts for some of the problems encountered in the characterisation of the parent binary carbonyl, $[Os_6(CO)_{21}]$. The ^1H NMR spectrum of derivative I shows an expected doublet, at 3.73 ppm ($^3J(HP)$ 12.4 Hz) and the ^{31}P NMR spectrum shows only one singlet at

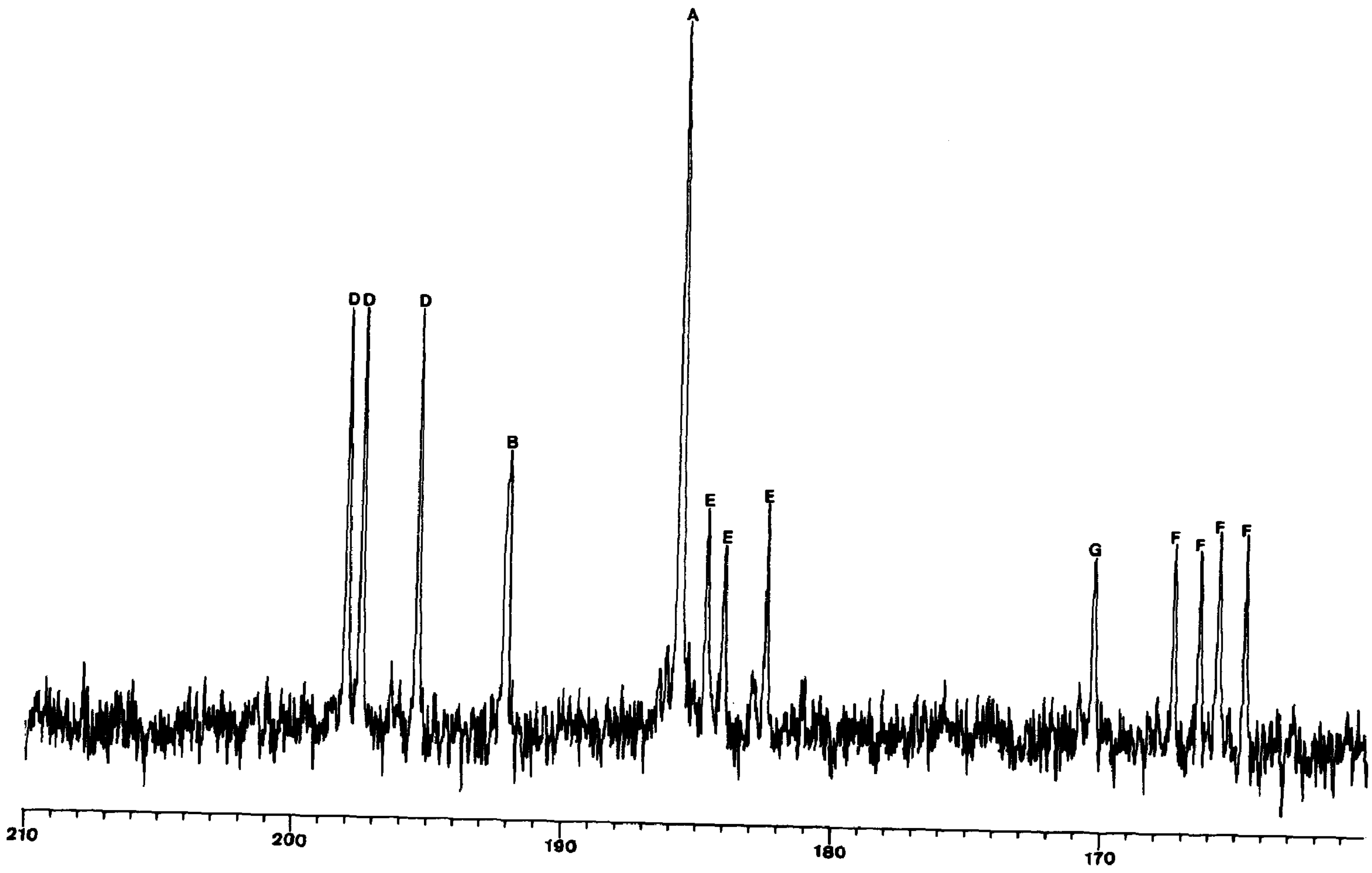


Fig. 3. ^{13}C NMR spectrum of {1} $[Os_6(CO)_{20}\{P(OMe)_3\}]$.

−58.92 ppm. In the ^{13}C NMR spectrum (Fig. 3) there are thirteen signals with an integration ratio of 2/2/2/2/4/1/1/1/1/1/1/1/1. Since the structure of I is known, the assignment of this spectrum is relatively simple. The eight signals of intensity one may be assigned to the eight different types of equatorial CO ligand, viz. $G/E/E^{I}/E^{II}/F/F^{I}/F^{II}/F^{III}$. The remaining five signals may be assigned to the pairs of axial CO ligands 2B, $(2A^{I}+2A^{II})$, 2D, $2D^{I}$, and $2D^{II}$. The accidental degeneracy of signals arising from $2A^{I}$ and $2A^{II}$ is understandable given their distance from the site of the molecular asymmetry.

(b) Bis-substitution: $[Os_6(CO)_{19}\{P(OMe)_3\}_2]$ (IIa–IId)

Four bis-substituted compounds IIa–IId were isolated. These correspond to substitution on one osmium atom (IIa) and two (IIb–IId). In every case, the parent molecular-ion (*m/e* 1932) was observed in the FAB mass spectrum. All the derivatives were characterised primarily from their NMR spectroscopic data.

The ^{1}H NMR spectrum of derivative IIa which corresponded to the symmetric 1,1-substitution exhibits at doublet at 3.64 ppm (*J*(HP) 11.8 Hz), and the ^{31}P NMR shows a single resonance, at −58.03 ppm. The ^{13}C NMR spectrum is also consistent with this symmetric structure, exhibiting eight signals in the integration ratio 4/2/2/2/4/1/2/2 (Fig. 4) that may be assigned to the CO ligands 4D/2C/2D′/2E/4A/E′/2F/2F′.

Derivative IIb was previously characterised by single crystal X-ray diffraction analyses as the 1,2-form. However, on dissolution this derivative undergoes moderately-rapid interconversion between the three related forms (IIb ⇄ IIc ⇄ IId). Thus, the ^{31}P NMR spectrum clearly shows the presence of three isomers (Fig. 5a).

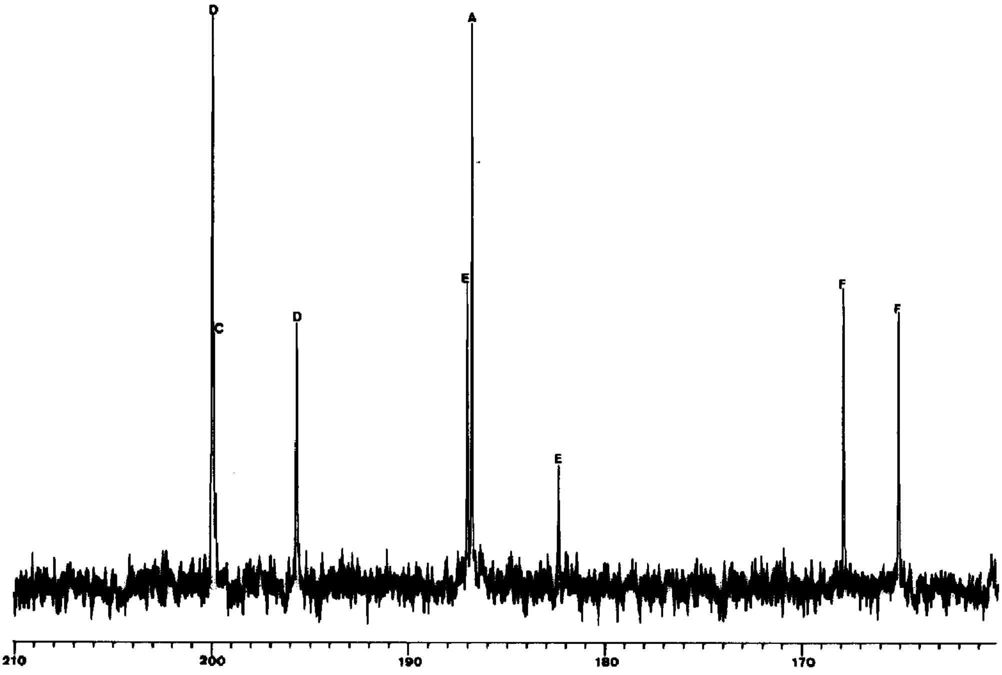


Fig. 4. ^{13}C NMR spectrum of {1,1} $[Os_6(CO)_{19}\{P(OMe)_3\}_2]$.

Monitoring the variation of this spectrum with time suggested that IIb, the 1,2-derivative, is the most abundant, and the two doublets (designated A_1 and A_2) in the region -57 to -61 ppm (^4J(PP) 6.8 Hz) may be assigned to this form.

The singlet resonances at ca. -56 ppm (C) and ca. -54 ppm (B) (Fig. 5a) may be assigned to one or other of the two possible arrangements {1,2′} and {1′,2}, although precise assignment is not possible on the basis of this evidence alone.

The ^{13}C NMR spectrum is also consistent with the presence of the same three isomers, and although again a detailed analysis of this spectrum is difficult a tentative assignment is given in Fig. 5b.

(c) Tris-substitution: $[Os_6(CO)_{18}\{P(OMe)_3\}_3]$ (IIIa–IIId)

Clear evidence for the four expected forms (IIIa–IIId) has been found. All were initially identified on the basis of their FAB mass spectra, each of which showed a strong molecular-ion at *m/e* 2028.

The four derivatives IIIa–IIId fall into two distinct classes. Derivatives IIIa and IIIb correspond to derivatives in which substitution has occurred at two of the three outer osmium atoms and so they are labelled {1,1′,2} and {1,1′,2′}. The two others,

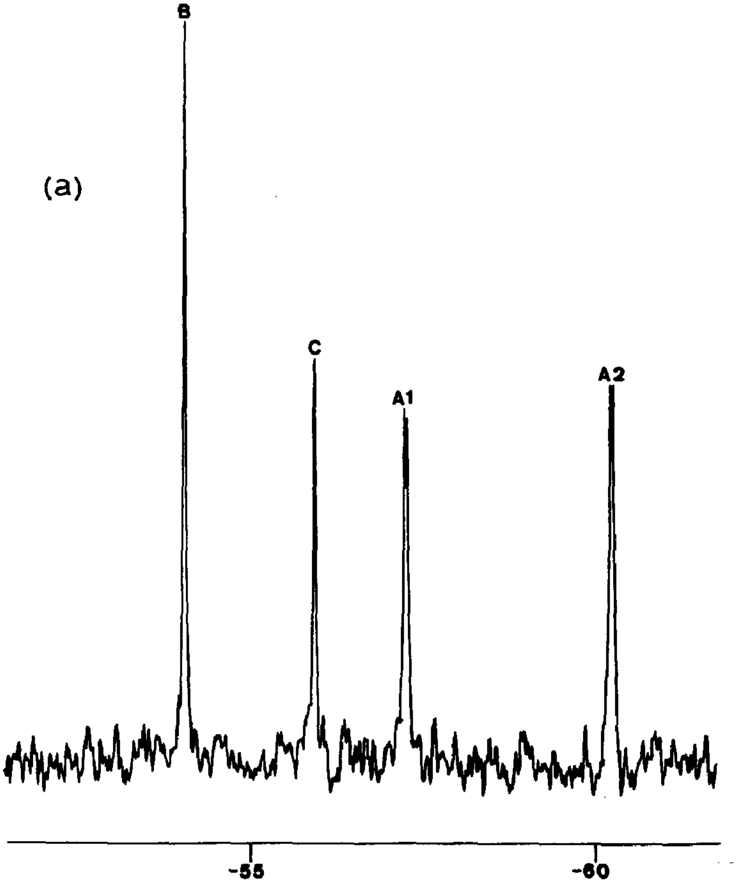


Fig. 5. (a) ^{31}P NMR spectrum of {1,2} $[Os_6(CO)_{19}\{P(OMe)_3\}_2]$.

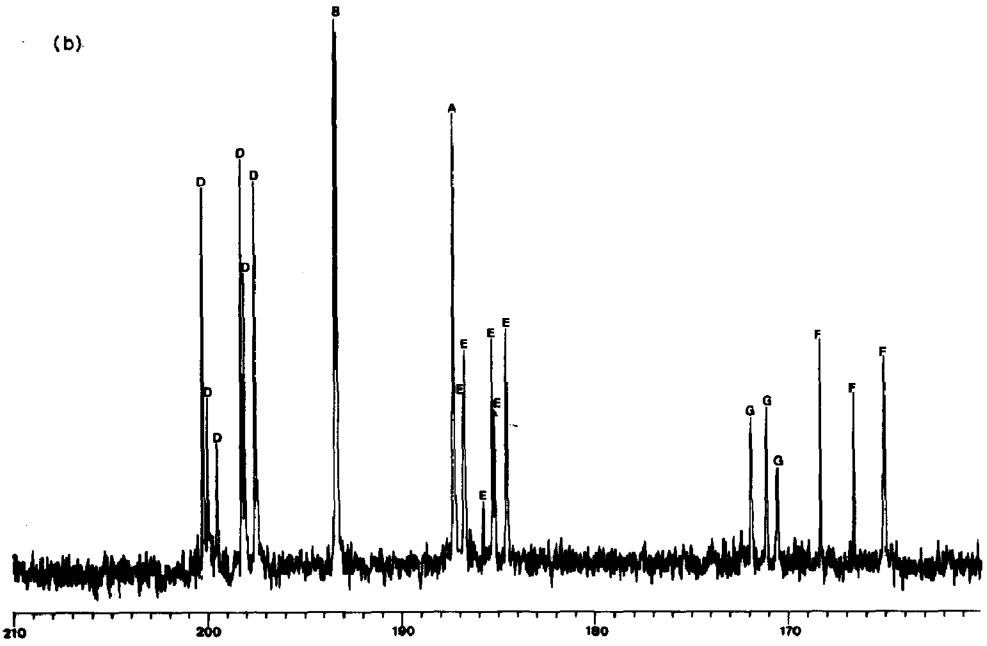


Fig. 5. (b) ^{13}C NMR spectrum of {1,2} [$Os_6(CO)_{19}\{P(OMe)_3\}_2$].

viz. IIIc and IIIa, correspond to the forms {1,2,3} and {1,2,3′}. In solution interconversion between forms IIIa $\rightleftarrows$ IIIb and between forms IIIc $\rightleftarrows$ IIId appears to occur fairly rapidly, but there is little or no interconversion between the two classes, i.e. between IIIa + IIIb and IIIc + IIId.

In the ^{13}P NMR spectrum of freshly dissolved IIIa or IIIb resonances associated with both forms appear. This is shown in Fig. 6a, in which the two independent sets of resonances are designated A and B. The ^{13}C NMR spectrum (Fig. 6b) is also consistent with the presence of two isomeric forms.

Similarly, the ^{31}P NMR spectra of samples of either IIIc or IIId (Fig. 7a) reveal the presence of an isomeric mixture. The singlet at ca. −58.5 ppm can be readily assigned to the most symmetric {1,2,3}-form IIIc and it follows that the three remaining signals (designated B_1, B_2 and B_3) must belong to the form IIId. Again, the ^{13}C NMR spectrum (Fig. 7b) contains resonances associated with the two different isomeric species.

(d) Tetra-substitution: [$Os_6(CO)_{17}\{P(OMe)_3\}_4$] (IVa–IVd)

All four isomeric possibilities (IVa–IVd) were isolated and characterised. In each case the molecular-ion (*m/e* 2121) is observed in the FAB mass spectrum. One derivative (IVd) was characterised previously as the {1,1′,2,2′}-form by single crystal X-ray diffraction analysis, and we shall discuss the NMR spectroscopic data for this derivative first.

The ^{1}H NMR spectrum of IVd consists of one doublet centred at 3.60 ppm, with *J*(HP) 11.8 Hz, which is consistent with bis-substitution at two osmium atoms. In the ^{31}P NMR spectrum two doublets of doublets are observed at −48.8 and −55.8 ppm, with coupling constants of 18.0 and 5.3 Hz, respectively (Fig. 8a). The ^{13}C

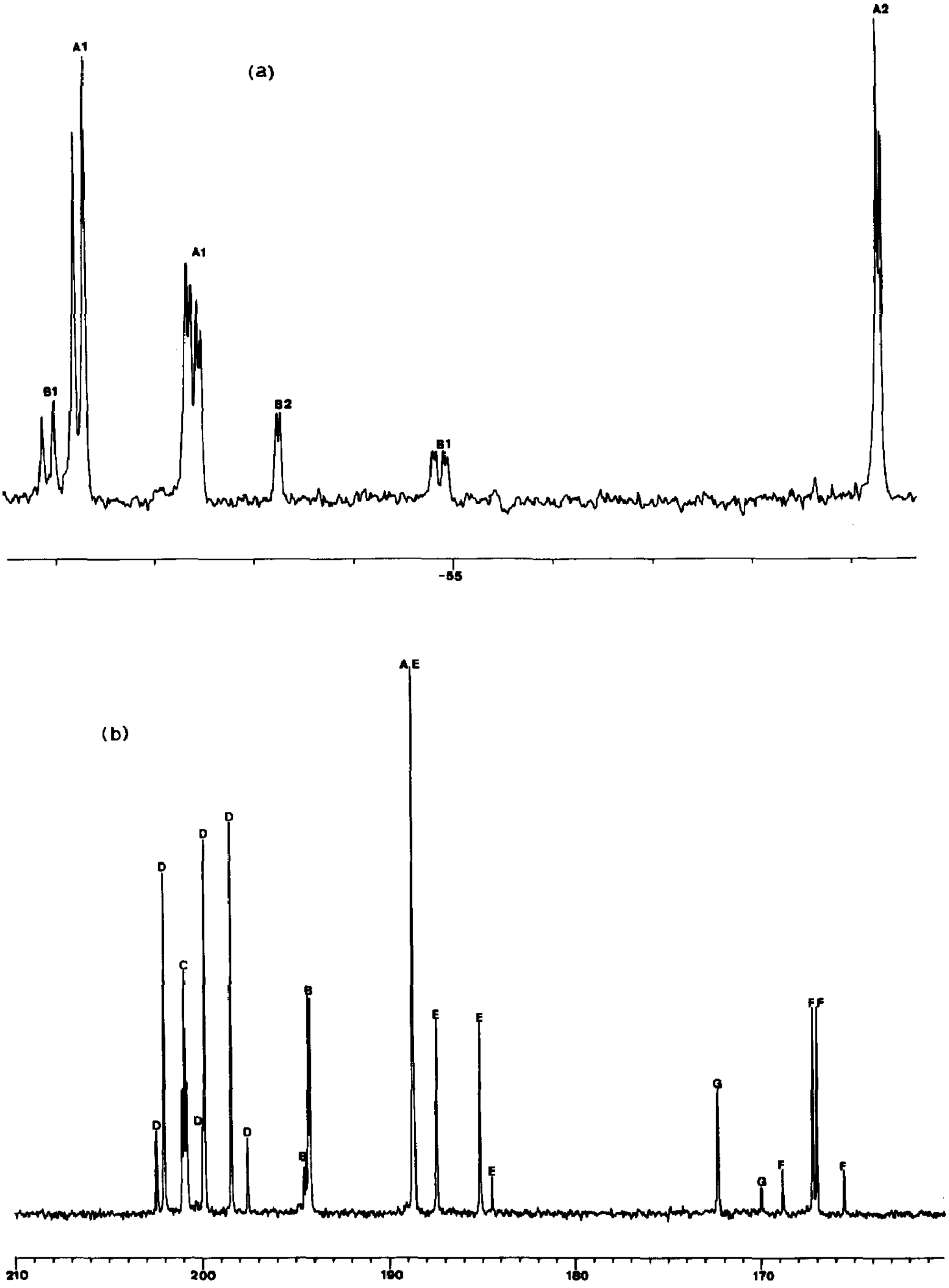


Fig. 6. (a) ^{31}P NMR spectrum of {1,1,2} $[Os_6(CO)_{18}\{P(OMe)_3\}_3]$ and (b) ^{13}C NMR spectrum of {1,1,2} $[Os_6(CO)_{18}\{P(OMe)_3\}_3]$.

NMR spectrum (Fig. 8b) exhibits seven signals in the integration ratio 2/4/4/1/2/2/2/ as expected (2D′/4C/4D/E′/2A/2E/2F).

In solution, the other three isomers (IVa–IVc) undergo moderately rapid interconversion. Thus, the ^{31}P NMR spectrum (Fig. 9a) is quite complicated, but can be understood in terms of a mixture of these three isomeric species (signals designated A, B and C). As expected for such a mixture the ^{13}C NMR spectrum is also complicated (see Fig. 9b), but may be to some extent interpreted in terms of the same isomeric mixture of IVa–IVc.

(e) Penta-substitution $[Os_6(CO)_{16}\{P(OMe)_3\}_5]$ *(V)*

There is only one form of this derivative, viz. that with {1,1′,2,2′,3}-substitution, and the formula was readily established from the FAB mass spectrum, which exhibited the expected parent-ion.

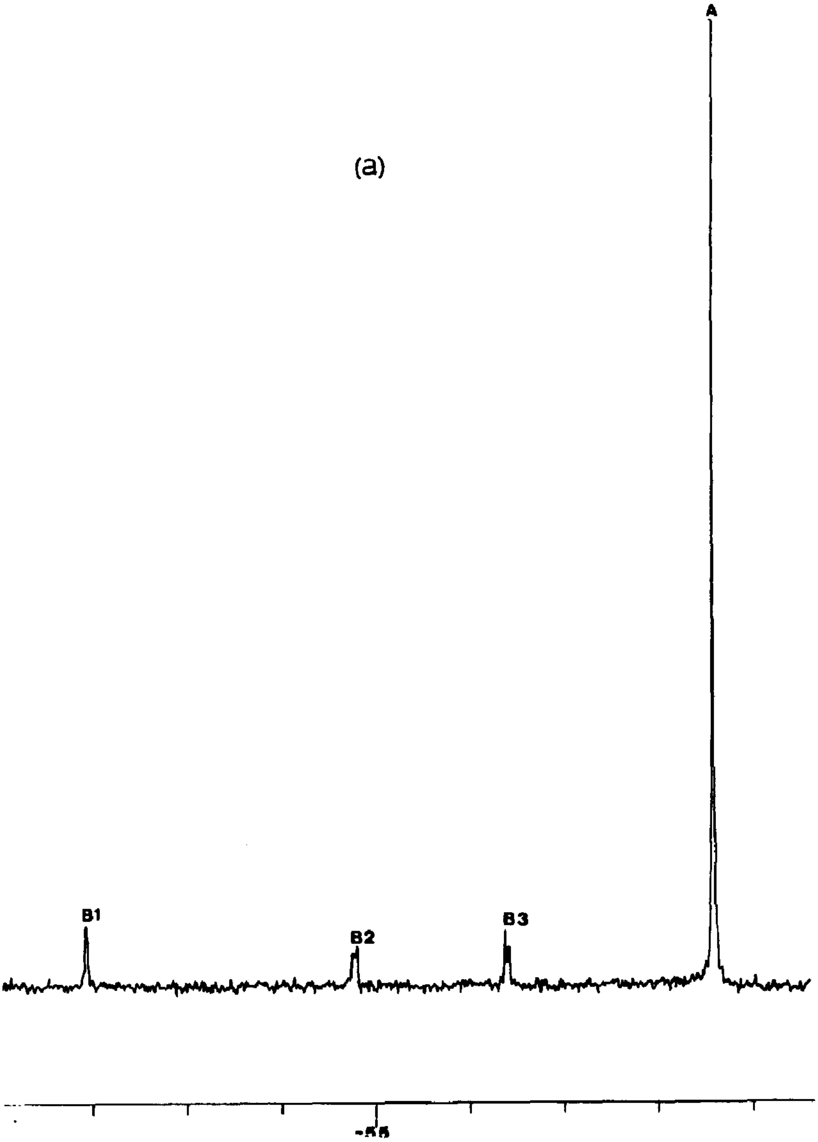


Fig. 7. (a) ^{31}P NMR spectrum of {1,2,3} $[Os_6(CO)_{18}\{P(OMe)_3\}_3]$.

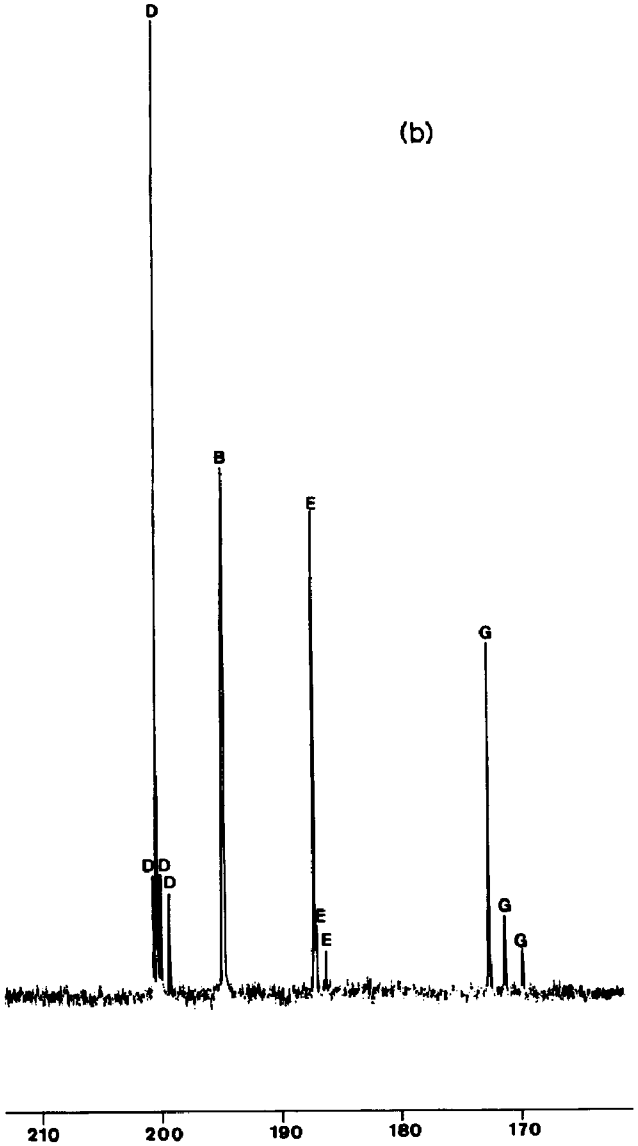


Fig. 7. (b) ^{13}C NMR spectrum of {1,2,3} [$Os_6(CO)_{18}\{P(OMe)_3\}_3$].

There are five signals in the ^{31}P NMR spectrum, which is consistent with the presence of five different P nuclei (Fig. 10a) as predicted for the {1,1′,2,′,3} structure. Four of these signals show coupling between P nuclei coordinated to the same Os atom, although the relatively poor resolution of the spectrum prevents further analysis. On the basis of the couplings discussed above, two of these four signals should show one coupling between P nuclei coordinated to different Os atoms, whereas the other two should show two such couplings. There should also be triplet due to the P nucleus on the mono-substituted Os atom. The recorded spectrum is consistent with such coupling. On the basis of the ^{1}H NMR data discussed above, two doublets would be predicted for this derivative, in a ratio of

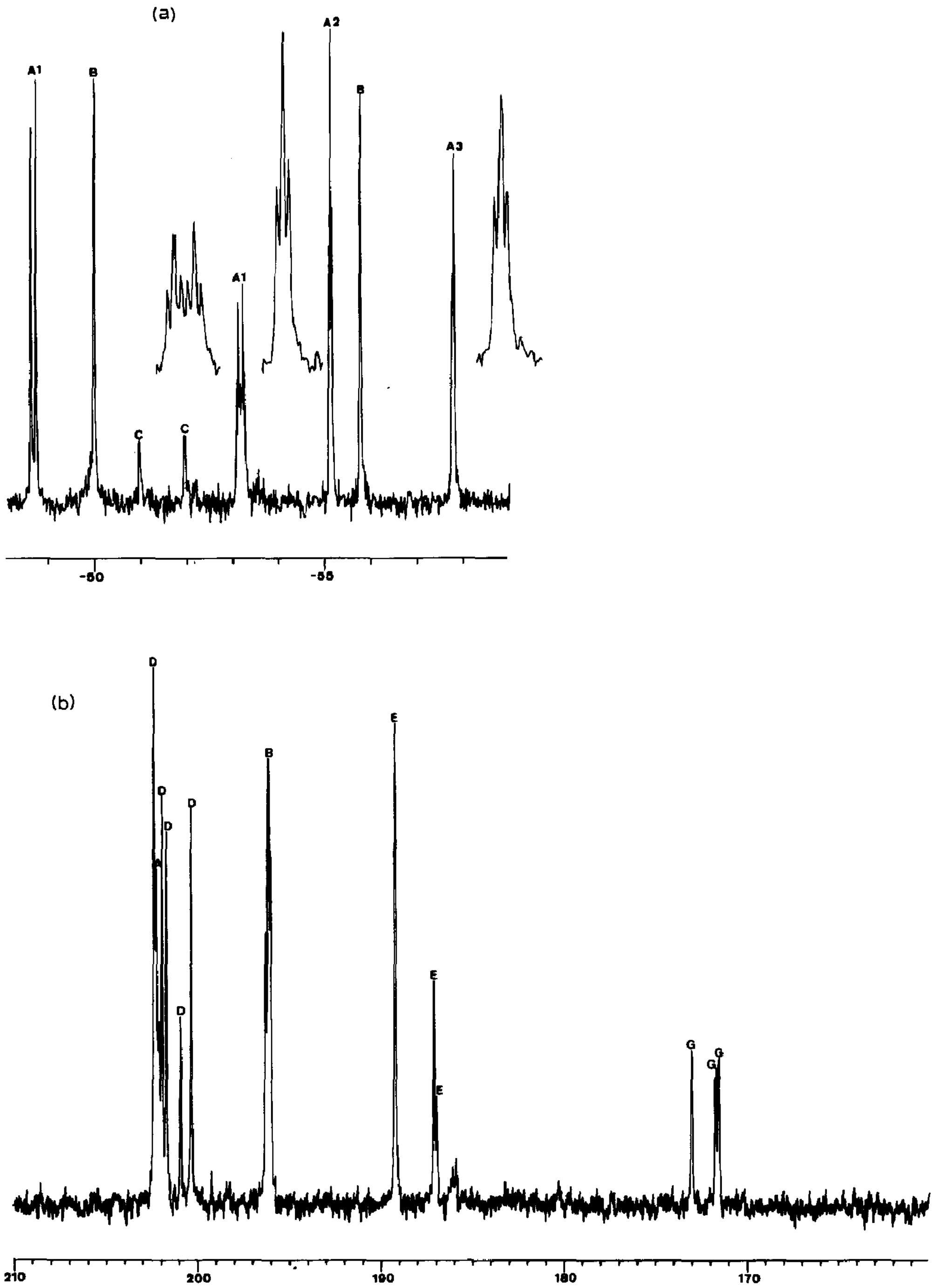


Fig. 8. (a) ^{31}P NMR spectrum of {1,1,2,2} $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$ and (b) ^{13}C NMR spectrum of {1,1′,2,2′} $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$.

4/1, the stronger signal having the smaller coupling constant. However, there are apparently no doublets in the spectrum, presumably because of overlap of the various resonances.

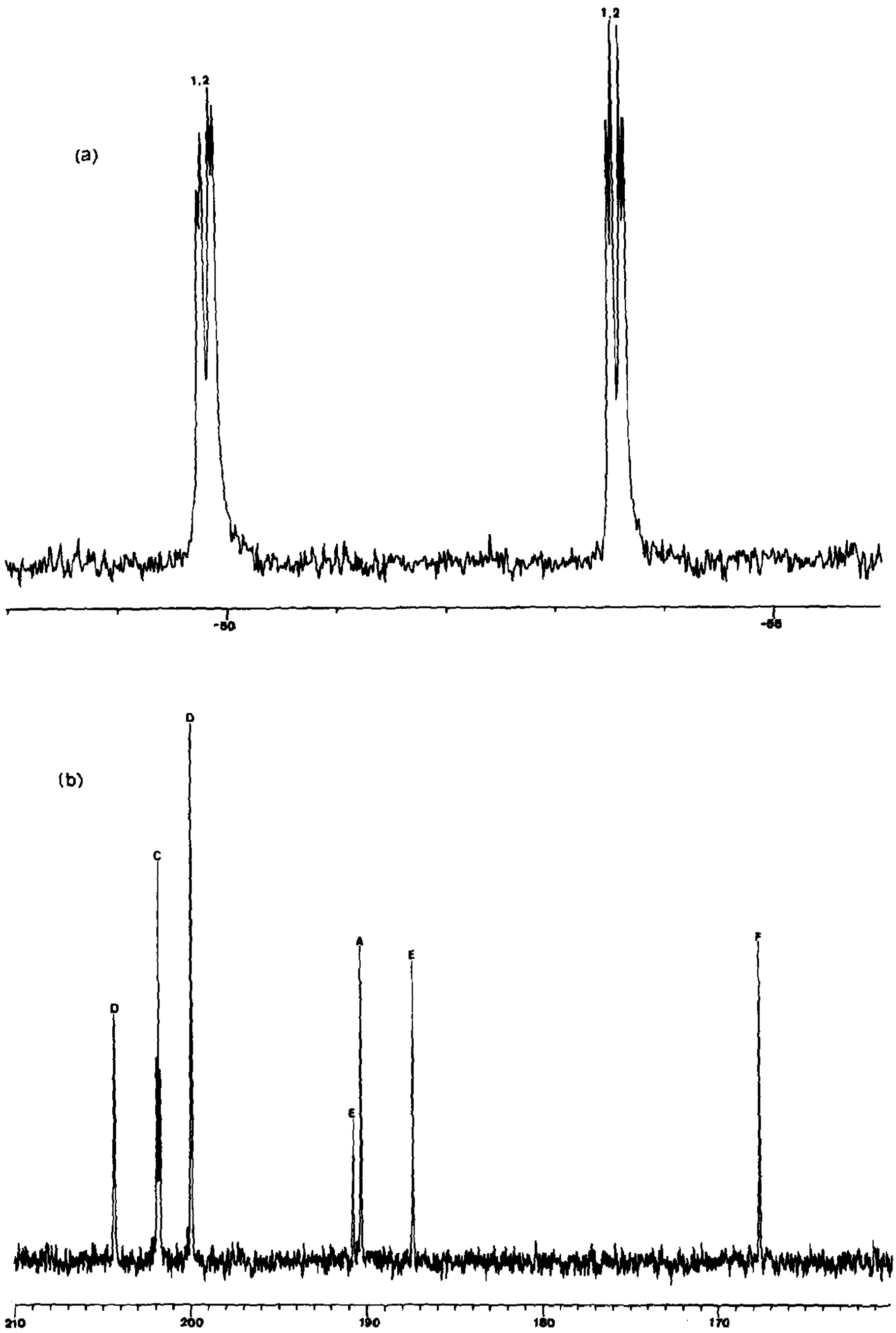


Fig. 9. (a) ^{31}P NMR spectrum of {1,1′,2,3} $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$ and (b) ^{13}C NMR spectrum of {1,1′,2,3} $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$.

(f) $[Os_6(CO)_{15}\{P(OMe)_3\}_6]$

This derivative was also shown crystallographically to have the {1,1′,2,2′,3,3′} structure [2], and, as expected, the spectroscopic data are very simple. The highest

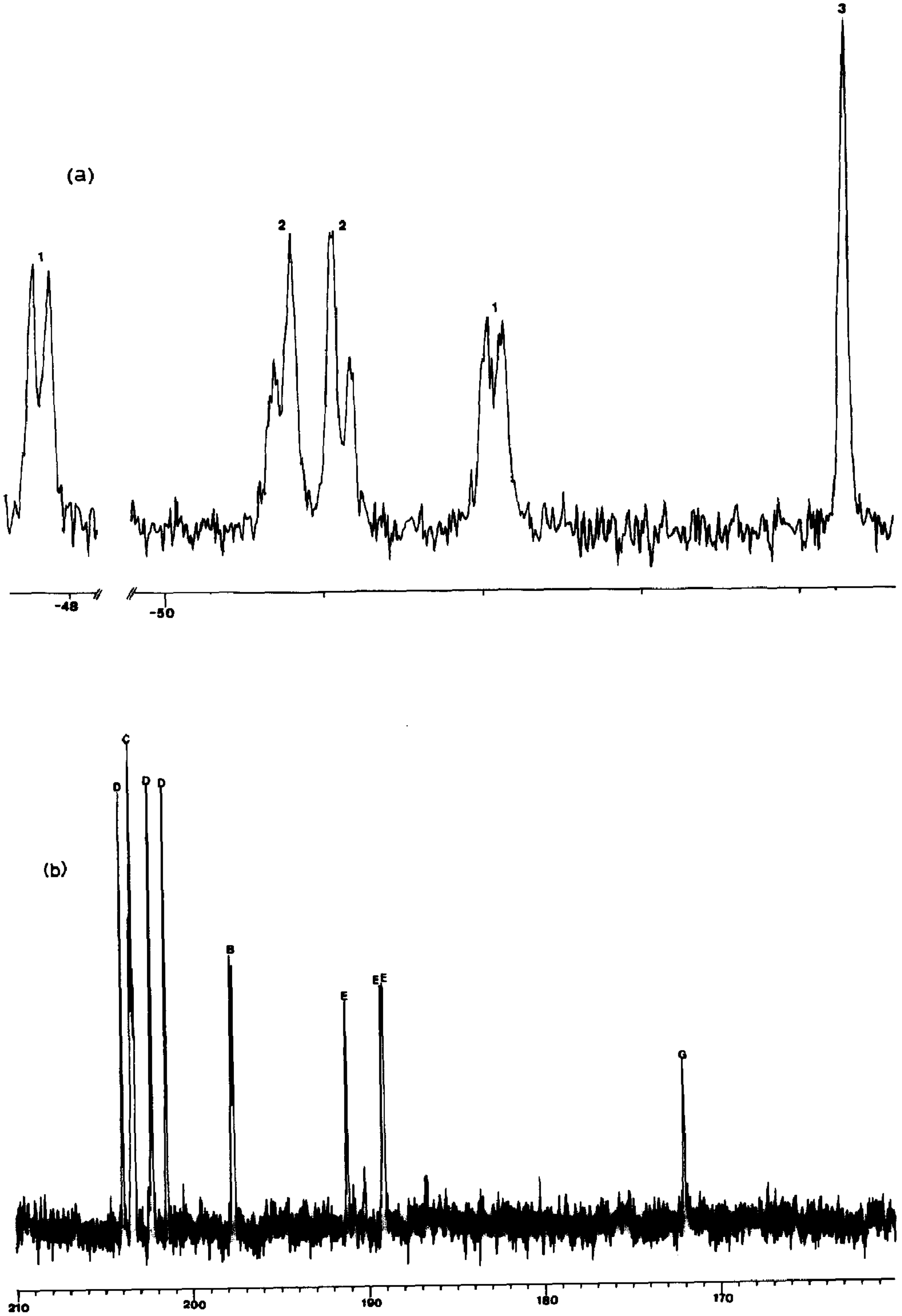


Fig. 10. (a) ^{31}P NMR spectrum of $\{1,1',2,2',3\}$ $[Os_6(CO)_{16}\{P(OMe)_3\}_5]$ and (b) ^{13}C NMR spectrum of $\{1,1',2,2',3\}$ $[Os_6(CO)_{16}\{P(OMe)_3\}_5]$.

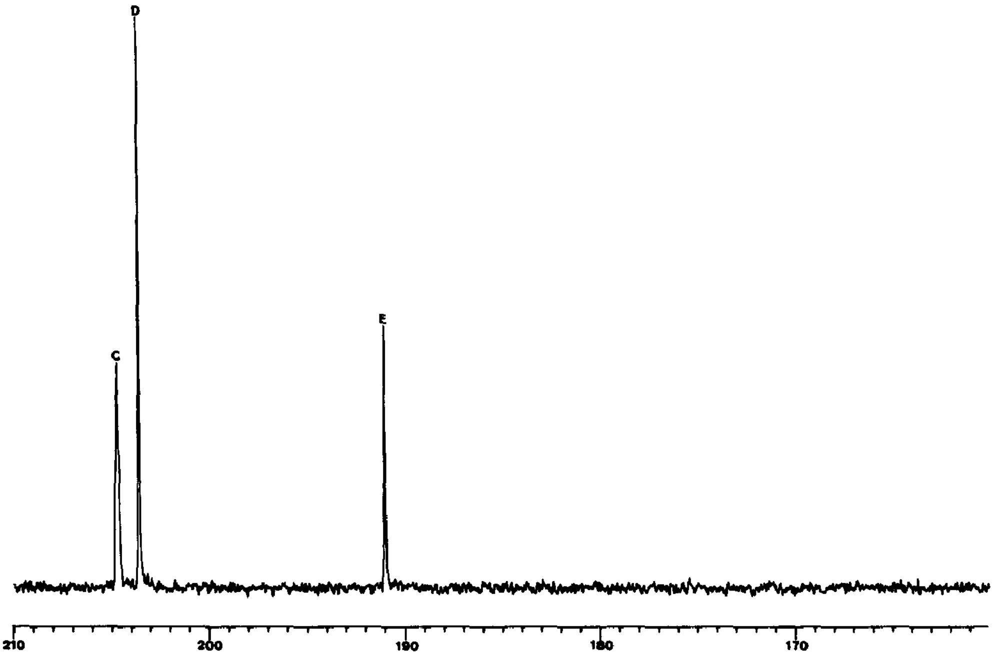


Fig. 11. ^{13}C NMR spectrum of {1,1′,2,2′,3,3′} [$Os_6(CO)_{15}\{P(OMe)_3\}_6$].

peak in the FAB mass spectrum corresponds to the molecular ion (*m/e* 2336). There is only one doublet in the ^{1}H NMR spectrum, at 3.57 ppm (^3J(HP) 10.9 Hz), one singlet in the ^{31}P NMR spectrum, and three signals in the ^{13}C NMR spectrum, due to C, D and E, in the ratio 2/2/1 (Fig. 11).

Conclusions

We have shown that the complete range of nine equatorially substituted derivatives of the parent raft cluster, [$Os_6(CO)_{21}$], together with their various isomeric forms, can be made by use of a range of synthetic routes. No substitution on any of the inner three osmium atoms seems to occur, or if it does then isomerisation to the more stable derivatives with substitution on the outer three osmium atoms must take place very rapidly,and we regard this as highly unlikely. The substitution pattern closely follows that established for the corresponding trinuclear systems, with only equatorial substitution being observed. However, it is clear that, because of the lower steric interaction between the bonded ligands, multiple substitution on the same osmium atom can occur, at least for trimethylphosphite. Preliminary experiments have revealed significant differences in the rates of reaction of these substituted raft clusters with molecular oxygen; with the rate varying with the degree and type of substitution. This aspect of the work will be considered elsewhere.

Experimental

Infrared spectra were recorded on a Perkin Elmer 983 or a Perkin Elmer 1710 FT spectrometer. ^{1}H NMR spectra were recorded on a Bruker WP80SY and WM250, and ^{13}C and ^{31}P NMR spectra on a Bruker AM400. Mass spectra were obtained with a Kratos MS 902 spectrometer. Microanalyses were carried out in this department. All manipulations were carried out under dry nitrogen by standard techniques. Dichloromethane, hexane, toluene, acetonitrile, benzene and methanol were dried by standard method and degassed before use. TLC plates prepared in this laboratory or purchased from Merck (20 × 20 cm glass coated with a 0.25 mm layer of Merck Kieselgel 60 F_{254}).

The following starting materials were prepared by previously described methods: $[Os_3(CO)_{10}(MeCN)_2]$ [20], $[Os_6(CO)_{21}]$ [4,7] and $[Os_6(CO)_{21-n}(MeCN)_n]$ [8,9] (n = 2). Trimethylphosphite was purchased from Aldrich and used as received; $Me_3NO \cdot 2H_2O$ was purchased from Aldrich, and was dried by Dean-Stark distillation in refluxing benzene.

Products from the reaction of $P(OMe)_3$ with the carbonyls $[Os_6(CO)_{21}]$ and $[Os_6(CO)_{18}]$

In a typical procedure, the carbonyl was heated in benzene with the appropriate amount of the phosphite. The reaction was followed by spot TLC. On completion the solution was filtered through coarse silica and the solvent removed in vacuo. The substituted derivatives were isolated and separated by TLC, and characterised by IR and NMR spectroscopy.

Products from the reaction of $Me_3NO/MeCN$ with the raft clusters $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$

In a typical procedure, a solution of the required raft derivative, $[Os_6(CO)_{21-n})\{P(OMe)_3\}_n]$, in MeCN was prepared, and n equivalents of a solution of Me_3NO in CH_2Cl_2 (1 mg/2 ml) were added dropwise. The reaction was monitored by spot TLC, further Me_3NO being added if necessary. The solution was filtered through coarse silica to remove unreacted Me_3NO, and the solvent was removed in vacuo. The MeCN derivatives were isolated by TLC, and characterised by IR and NMR spectroscopy.

Products of the reaction of the MeCN derivatives, $[Os_6(CO)_{18}(MeCN)_n]$ and $[Os_6(CO)_{21-n}(MeCN)_n]$ (n = 1, 2) with $P(OMe_3)$

In a typical reaction, a solution of $P(OMe)_3$ in CH_2Cl_2 (typically, 2 drops in 20 ml) was prepared, and 10–20 mg of the relevant MeCN derivative were added. The

Table 1

Products from the reaction of MeCN with the raft clusters $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$

$P(OMe)_3$ derivative	n	Eluent ($C_6H_{12}/CH_2Cl_2/MeCN$)	Product [a] yields
{1}	1	60/35/5	{1}[2] 85%
{1}	2	60/35/5	{1}[2,3] 95%
{1,1}	1	60/35/5	{1,1′}[2] 90%
{1,1}	2	60/35/5	{1,1′}[2,3] 95%
{1,2}	1	60/35/5	{1,2}[3] 95%
{1,1′,2}	1	40/55/5	{1,1′,2}[3] 95%
{1,1′,2,2′}	1	30/65/5	{1,1′,2,2′}[3] 95%

[a] $[n]$ indicates the site of the MeCN ligand.

Table 2

Products of the reaction of the MeCN derivatives with $P(OMe)_3$

MeCN derivative	Eluent (CH_2Cl_2/C_6H_{12})	Product [a] yields
[1]	50/50	{1} 30%
	50/50	{1,1′} 70%
[1,2]	50/50	{1,2} 35%
		{1,1′,2} 60%
		{1,1,2,2′} 5%
{1}[2]	50/50	{1,2} 65%
		{1,2,2′} 35%
{1}[2,3]	50/50	{1,2,3} 65%
		{1,2,2′,3} 30%
		{1,2,2′,3,3′} 5%
{1,1}[2]	50/50	{1,1′,2} 75%
		{1,1′,2,2′} 25%
{1,1}[2,3]	50/50	{1,1′,2,3} 75%
		{1,1′,2,2′,3} 20%
		{1,1′,2,2′,3,3′} 5%
{1,2}[3]	50/50	{1,2,3} 75%
		{1,2,3,3′} 25%
{1,1,2}[3]	100	{1,1′,2,3} 85%
{1,1,2,2}[3]	100	{1,1′,2,2′,3} 95%
		{1,1′,2,2′,3,3′} 5%

[a] [*n*] indicates site of MeCN ligand.

reaction was monitored by spot TLC. The solvent was removed in vacuo, and the products separated by TLC. The yields are shown below in Table 2. An additional product was isolated in low yield, and was characterised by IR and mass spectroscopy as $[Os_5(CO)_{16}\{P(OMe)_3\}_3]$.

Products of the reaction of the activated MeCN derivatives, $[Os_6(CO)_{21-(n+m)}\{P(OMe)_3\}_n(MeCN)_m]$, *with* $P(OMe)_3$

In a typical procedure, a solution of $P(OMe)_3$ in CH_2Cl_2 (typically, 2 drops in 20 ml) was prepared, and 10–20 mg of the relevant MeCN derivative were added. The reaction was monitored by spot TLC. The solvent was removed in vacuo and the products separated by TLC. The yields are shown in Table 2.

The reaction of the derivatives $[Os_6(CO)_{21-n}\{P(OMe)_3\}_n]$ *with CO*

In a typical procedure, a gentle stream of carbon monoxide was passed through a solution of the appropriate raft derivative until the presence of the required product was shown by spot TLC. The solvent was removed in vacuo, and the products separated by TLC.

Reaction of $P(OMe)_3$ *derivatives with* $P(OMe)_3$

In a typical reaction, a solution of a $P(OMe)_3$ raft derivative and 2 drops of $P(OMe)_3$ was stirred at room temperature. As no reaction occurred, the reaction was terminated after 2 h.

Substitution of $[Os_6(CO)_{21}]$ *by chemical oxidation*

A solution of [PPN][BH_4] (5 mg, 0.03 mmol) and [$Os_6(CO)_{21}$] (20 mg, 0.011 mmol) in CH_2Cl_2 (20 ml) was stirred for 10 min. The volume was then reduced to 5 ml, and the solution filtered to remove any changed [NEt_4][BH_4]. The product was characterised by IR and ^1H NMR spectroscopy as $[HOs_6(CO)_{20}]^-$. The solution was purged with N_2 for 30 min. Two drops of $P(OMe)_3$ were then added, and the solution was stirred for 30 min, during which no further reaction occurred. However, on addition of excess [Ph_3C][BF_4] an immediate reaction took place. The products were separated by TLC (eluent CH_2Cl_2/C_6H_{12}, 50/50), and identified by IR spectroscopy as the {1} derivative (6 mg).

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