# Preparation and Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of Isonitrile Substituted Derivatives of $[Os_3(CO)_{12}]$

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The preparation of the complexes $[Os_3(CO)_{12-n}(CNR)_n]$ ($n$ = 1 or 2 for R = Me, $C_6H_4OMe$, $Bu^n$, or $Bu^t$; $n$ = 3 or 4 for R = $Bu^n$ or $Bu^t$) is described. A variable-temperature $^{13}C$ n.m.r. spectroscopic study of these complexes shows that, for $n$ = 1, only the axial isomer is present in significant concentrations in solution at low temperatures, except for the most bulky ligand, $CNBu^t$, for which an equilibrium mixture of the axial and equatorial isomer is obtained at −60 °C. Above 0 °C these isomers interconvert rapidly on the n.m.r. time scale. For $n$ = 2 only the *trans*-diaxially substituted isomers are present at low temperatures except in the case of $CNBu^t$ for which a mixture of the *trans*-diaxial and a diequatorially substituted isomer is obtained. For the trisubstituted complex both $CNBu^n$ and $CNBu^t$ give a mixture of isomers at low temperature which again interconvert rapidly at higher temperatures. The same is true of the tetrasubstituted complex with $CNBu^n$ as a ligand but with $CNBu^t$ only an all-axially substituted isomer is found.

THE reaction of $[Os_3(CO)_{12}]$ with organophosphines has been extensively studied.[1–5] In general such reactions lead, in the first instance, to simple substitution products of the type $[Os_3(CO)_{12-x}L_x]$ and, for L = $PEt_3$, $PEt_2Ph$, and $PMePh_2$, the complete range of complexes with $x$ = 1—3 has been reported.[3] *X*-Ray diffraction studies[6] and $^{13}C$ n.m.r. spectroscopy[7] show that substitution normally occurs progressively on different metal centres and that the substituting ligands occupy equatorial sites. This preference for equatorial substitution can be accounted for in steric terms, since simple calculations on $[Os_3(CO)_{12}]$ show that equatorial sites in the approximately anticuboctahedral structure are less sterically hindered than axial sites.[8] That axial substitution of organophosphines is also possible in $[M_3(CO)_{12}]$ derivatives, however, has been recently demonstrated by the preparation of $[Ru_3(CO)_9\{SiMe(PBu_2)_3\}]$, in which the sterically constrained ligand caps the $Ru_3$ triangle.[9]

The reaction of isonitrile ligands with $[Os_3(CO)_{12}]$ has been far less well studied than the reactions with organophosphines. Apart from a preliminary report by us on the pyrolysis of some of the complexes now reported in this paper[10] only the disubstituted complexes $[Os_3(CO)_{10}L_2]$ (L = CNMe or $CNCH_2Ph$) are mentioned in the literature,[11] and no details of their preparation or properties were given. Such substituted derivatives are, however, of considerable interest since their pyrolysis provides a valuable route to higher nuclearity clusters which are not readily accessible by other means.[10]

We now report the preparation and some spectroscopic properties of the complexes $[Os_3(CO)_{12-n}(CNR)_n]$ ($n$ = 1 or 2 for R = Me, $C_6H_4OMe$-*p*, $Bu^n$, or $Bu^t$; $n$ = 3 or 4 for R = $Bu^n$ or $Bu^t$). Infrared and $^{13}C$ n.m.r. data have enabled us to show that the substituting ligands can occupy either axial or equatorial sites depending on the steric requirements of the ligand and the degree of substitution. Several of the complexes exist in solution as equilibrium mixtures of isomers which in most cases interconvert rapidly on the n.m.r. time scale at room temperature. For the less highly substituted complexes, the axial isomers are in general the more abundant, and the preference of organophosphines for equatorial rather than axial sites in analogous complexes is therefore almost certainly due to the more sterically demanding nature of these ligands rather than to electronic factors.

## RESULTS AND DISCUSSION

*Preparation*, $^1H$ *N.M.R. and I.r. Data*.—The substituted derivatives were all prepared by refluxing a toluene solution of $[Os_3(CO)_{12}]$ with the appropriate ligand for *ca.* 2 h. A complex: ligand ratio of 1 : 3 gave mainly the mono- and di-substituted derivatives; in order to obtain the more highly substituted complexes in good yield it was necessary to add a further quantity of the ligand after the 2 h period and then continue to reflux for a further 2 h. The failure to obtain tri- and tetra-substituted complexes containing CNMe or $CNC_6H_4OMe$-*p* by this means was due to practical difficulties rather than to the inherent instability of these complexes. The polymerisation of the ligand which took place during the reaction rendered chromatographic separation of the metal complexes extremely difficult.

The isonitrile complexes prepared all gave excellent mass spectra, showing prominent molecular ions and stepwise loss of carbonyl and isonitrile down to an $Os_3^+$ core. Indicative of the stability of the metal triangle is the observation of peaks due to doubly charged species *e.g.* $[Os_3(CO)_9(CNBu^t)_3]^{2+}$. Infrared and $^1H$ n.m.r. data for the new complexes are given in Table 1 and analytical data in Table 2. The complexes $[Os_3(CO)_{10}(CNC_6H_4OMe\text{-}p)_2]$ and $[Os_3(CO)_8(CNBu^n)_4]$ did not crystallise well, and satisfactory microanalytical data for these two complexes were not obtained.

The $^1H$ n.m.r. spectra of the complexes were recorded only at room temperature and indicated that a single ligand environment was present in all the complexes, including the tetrasubstituted derivatives for which none of the possible isomers have equivalent isonitrile ligands. This could be due to a lack of resolution but it more probably reflects the fluxional nature of the complexes as revealed by their $^{13}C$ n.m.r. spectra (see below).

The solution i.r. spectra of all the monosubstituted isonitrile derivatives are essentially identical, both in hexane and in dichloromethane. All the ν(CO) bands are due to terminal carbonyl groups as in $[Os_3(CO)_{12}]$ itself but the pattern of bands is very different from that observed for the (equatorially) monosubstituted phosphine derivatives.[3] This evidence alone suggests that the isonitrile ligand is axially rather than equatorially substituted, although more conclusive evidence comes from the $^{13}C$ n.m.r. data. The ν(NC) bands in all the complexes show a marked shift to higher frequencies from the free-ligand values and for $[Os_3(CO)_{11}(CNBu^n)]$ this is as much as 57 $cm^{-1}$. The average value of ν(NC) decreases as *n* increases, suggesting that relatively more charge is delocalised into the CNR π* orbitals as the number of CO groups available for this purpose decreases.

The disubstituted complexes give solution i.r. spectra in the carbonyl region which are very similar for all the CNR ligands studied but quite different from those found for disubstituted organophosphine complexes.[3] Since the latter are equatorially substituted,[7] axial positions are indicated for the CNR ligands and this is confirmed by the $^{13}C$ n.m.r. data (see below). The simplicity of the i.r. spectra makes it extremely unlikely that more than one isomer is present.

TABLE 1

Infrared and $^1H$ n.m.r. data for isonitrile substituted derivatives of $[Os_3(CO)_{12}]$

| Compound | ν(CNR) [a] | ν(CO) [a] | $^1H$ n.m.r. (δ/p.p.m.) [b] |
|---|---|---|---|
| $[Os_3(CO)_{11}(CNBu^n)]$ | 2 195m | 2 102s, 2 054s, 2 041s, 2 023s, 2 004s, 1 990s | 4.0 (2 H, t, $^4J$(H–H) 6.0, $CNCH_2$–)<br>1—2 (7 H, m) |
| $[Os_3(CO)_{11}(CNBu^t)]$ | 2 177m | 2 100m, 2 054s, 2 039s, 2 021s, 2 005s, 2 000 (sh), 1 988s, 1 986 (sh) | 1.5 (s) |
| $[Os_2(CO)_{11}(CNMe)]$ | 2 203m | 2 101m, 2 054s, 2 041s, 2 022s, 2 003s, 1 989s, 1 986 (sh) | 3.8 (s) |
| $[Os_3(CO)_{11}(CNC_6H_4OMe\text{-}p)]$ | 2 164m | 2 097s, 2 055s, 2 040s, 2 022s, 2 015 (sh), 2 006s, 2 002 (sh), 1 990s, 1 986 (sh) | 3.8 (s, 3 H, $CH_3$)<br>6.85, 6.95, 7.2, 7.3 (4 H, AB, –$C_6H_4$–) |
| $[Os_3(CO)_{10}(CNBu^n)_2]$ | 2 180m | 2 072m, 2 054m, 2 041 (sh), 2 031 (sh), 2 026s, 2 004 (sh), 1 997 (sh), 1 987s, 1 975s, 1 969s | 3.95 (2 H, t, $CNCH_2$–)<br>1.1 (7 H, m) |
| $[Os_3(CO)_{10}(CNBu^t)_2]$ | 2 164m | 2 069m, 2 026 (sh), 2 024s, 2 003 (sh), 1 996 (sh), 1 987s, 1 973s, 1 966s | 1.5 (s) |
| $[Os_3(CO)_{10}(CNMe)_2]$ | 2 149m | 2 073m, 2 042m, 2 033 (sh), 2 028s, 1 997m, 1 988s, 1 977s, 1 971s | 3.7 (s) |
| $[Os_3(CO)_{10}(CNC_6H_4OMe\text{-}p)_2]$ | 2 147m | 2 069m, 2 056m, 2 036 (sh), 2 029s, 2 007 (sh), 2 001 (sh), 1 992s, 1 979s, 1 974s | 3.8 (3 H, s, $CH_3$)<br>6.8, 6.9, 7.15, 7.25 (4 H, AB, –$C_6H_4$–) |
| $[Os_3(CO)_9(CNBu^n)_3]$ | 2 170m,<br>2 154 (sh) | 2 057 (sh), 2 053m, 2 039m, 2 021s, 1 986s, 1 972s, 1 966 (sh), 1 956s, 1 936m | 3.9 (2 H, t, $^4J$(H–H) 6.5, $CNCH_2$)<br>1—2 (7 H, m) |
| $[Os_3(CO)_9(CNBu^t)_3]$ | 2 154m,<br>2 134 (sh) | 2 065m, 2 051m, 2 034m, 2 010s, 1 985m | 1.5 (s) |
| $[Os_3(CO)_8(CNBu^n)_4]$ | 2 162s,<br>2 138 (sh) | 2 040 (sh), 2 020s, 1 997s, 1 974s, 1 959s, 1 944s, 1 934 (sh), 1 922 (sh) | 6.15 (2 H, t, $^4J$(H–H) 6.5, $CNCH_2$–)<br>1—2 (7 H, m) |
| $[Os_3(CO)_8(CNBu^t)_4]$ | 2 136s,<br>2 110 (sh) | 2 043 (sh), 2 034m, 2 013m, 1 992s, 1 997 (sh), 1 970s, 1 956s, 1 943s, 1 933s | 1.5 (m) |

[a] Recorded in $C_6H_{12}$ ($cm^{-1}$). [b] In $CD_2Cl_2$ solution at 100 MHz and 35 °C; *J*(Hz); s = singlet, t = triplet, m = multiplet, AB = AA′BB′ quartet.

TABLE 2

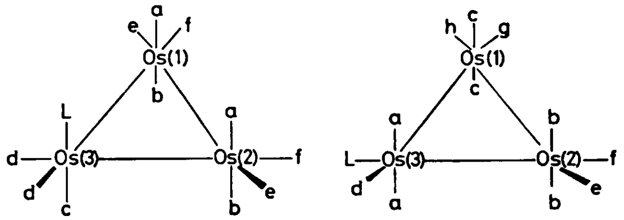
Analytical data for $[Os_3(CO)_{12-n}(CNR)_n]$ derivatives

| Complex | Analysis (%) * C | H | N |
|---|---|---|---|
| $[Os_3(CO)_{11}(CNBu^t)]$ | 18.8 (20.0) | 0.7 (0.9) | 1.9 (1.5) |
| $[Os_3(CO)_{11}(CNBu^n)]$ | 20.7 (20.0) | 1.6 (0.9) | 1.5 (1.5) |
| $[Os_3(CO)_{11}(CNMe)]$ | 17.9 (17.0) | 0.6 (0.3) | 1.4 (1.5) |
| $[Os_3(CO)_{11}(CNC_6H_4OMe\text{-}p)]$ | 23.0 (22.5) | 0.9 (0.7) | 1.3 (1.4) |
| $[Os_3(CO)_{10}(CNBu^t)_2]$ | 24.0 (23.6) | 1.9 (1.8) | 2.8 (3.8) |
| $[Os_3(CO)_{10}(CNBu^n)_2]$ | 23.0 (23.6) | 2.1 (1.8) | 2.2 (2.8) |
| $[Os_3(CO)_9(CNBu^t)_3]$ | 26.9 (26.7) | 3.0 (2.5) | 3.7 (3.9) |
| $[Os_3(CO)_8(CNBu^t)_4]$ | 30.4 (29.8) | 3.5 (3.2) | 4.9 (5.0) |

* Calculated values are given in parentheses.

*Carbon*-13 *N.M.R. Data.*—(*a*) *Monosubstituted derivatives.* Figure 1(*a*) and 1(*b*) shows the idealised structures of equatorially and axially substituted $[Os_3(CO)_{11}L]$ complexes with the lettering indicating chemically equivalent carbonyl groups.

In the absence of exchange, the equatorially substituted isomer would be expected to give rise to eight signals of relative intensity 2 : 2 : 2 : 1 : 1 : 1 : 1 : 1. The axially substituted species would be expected to show six resonances of relative intensity 2 : 2 : 2 : 2 : 2 : 1.



(*a*) (*b*)

FIGURE 1 The possible isomers for $[Os_3(CO)_{11}L]$ derivatives

The spectra of $[Os_3(CO)_{11}(CNBu^n)]$ and $[Os_3(CO)_{11}(CNC_6H_4OMe\text{-}p)]$ (Table 3) each show five resonances in their low-temperature limiting spectra with intensity ratios of 2 : 2 : 1 : 4 : 2. This is consistent with the axially substituted structure, 1(*a*), with an accidental degeneracy of two of the resonances a, b, d, e, and f. In contrast, the reported spectrum of $[Os_3(CO)_{11}(PEt_3)]$ shows the eight resonances expected for the equatorial isomer, 1(*b*).[7] In the case of the phosphine complex the axial carbonyls can be assigned, since these are of relative intensity two, while equatorial carbonyls are of unit intensity. The axial ligands occur to lower field compared with equatorial carbonyls. Transferring this rule of thumb to the isocyanide case means that for $[Os_3(CO)_{11}(CNBu^n)]$ the resonance at 183.7 p.p.m. (Table 3) can be assigned to carbonyl c, while a and b each give rise to one of the signals at 184.3 and 185.2 p.p.m.; although which belongs to which is not clear. The most likely degenerate pair of resonances would seem to be those from carbonyls e and f, and so the signal at 173.2 p.p.m. is assigned to these, leaving the one at 171.7 p.p.m. for carbonyls d. The degeneracy of e and f would seem unlikely to be anything other than accidental, there being no precedent for a scrambling process interconverting only these two sites.

TABLE 3

Carbon-13 n.m.r. data for $[Os_3(CO)_{12-n}(CNR)_n]$ complexes

| Complex | Temperature (°C) | Solvent | δ/p.p.m.* | |
|---|---|---|---|---|
| | | | CO | Other assignments |
| $[Os_3(CO)_{11}(CNBu^t)]$ | −60 | $CH_2Cl_2$ | *Isomer A:* 186.6(2), 185.1(2), 184.3(1), 176.3(2), 174.8(4)<br>*Isomer B:* 189.8, 183.7, 173.0, 172.9, 171.5 | |
| | 50 | $CH_2Cl_2$ | 180.7 | $CNC(CH_3)_3$ 29.9 |
| $[Os_3(CO)_{11}(CNBu^n)]$ | −80 | $CH_2Cl_2$ | 185.2(2), 184.3(2), 183.7(1), 173.2(4), 171.7(2) | |
| $[Os_3(CO)_{11}(CNC_6H_4OMe\text{-}p)]$ | −95 | $CH_2Cl_2$ | 184.8(2), 184.2(2), 183.4(1), 172.8(4), 171.4(2) | |
| | 90 | Toluene | 178.3 | |
| $[Os_3(CO)_{10}(CNBu^t)_2]$ | −80 | $CH_2Cl_2$ | *Isomer A:* 187.7(2), 186.6(2), 179.0(2), 178.4(4)<br>*Isomer B:* 192.3(2), 190.1(2), 188.8(2), 180.7(1), 177.6(1), 177.0(1), 176.2(1) | |
| | 35 | $CH_2Cl_2$ | 183.9 | $CNC(CH_3)_3$ 29.8 |
| $[Os_3(CO)_{10}(CNBu^n)_2]$ | −60 | $CH_2Cl_2$ | 189.9(2), 188.9(2), 178.6(2), 177.2(4) | $CNBu^n$ 44.3, 29.5, 18.6, 2.1 |
| | 80 | Toluene | 180.6 | |
| $[Os_3(CO)_{10}(CNC_6H_4OMe\text{-}p)_2]$ | −80 | $CHCl_2$ | 187.3(2), 186.3(2), 176.1(2), 174.8(4) | $CNC_6H_4OMe\text{-}p$ 127.2, 113.5 |
| | 90 | Toluene | 180.3 | |
| $[Os_3(CO)_9(CNBu^n)_3]$ | −80 | $CH_2Cl_2$ | *Isomer A:* 193.2(2), 188.6(1), 187.5(1), 179.3(1), 178.7(1), 178.2(1), 177.3(1), 176.9(1)<br>*Isomer B:* 189.7(1), 188.3(2), 178.0(6) | |
| | 25 | $CH_2Cl_2$ | 183.1 | |
| $[Os_3(CO)_9(CNBu^t)_3]$ | −85 | $CH_2Cl_2$ | *Isomer A:* 192.3(2), 187.6(1), 186.6(1), 180.4(1), 179.1(1), 177.6(1), 177.2(1), 176.1(1)<br>*Isomer B:* 190.1(1), 189.0(2), $\left.\begin{matrix}178.45\\178.3\end{matrix}\right\}(6)$ | |
| | 70 | Toluene | 184.4 | |
| $[Os_3(CO)_8(CNBu^n)_4]$ | −90 | $CD_2Cl_2/CHCl_2F$ | *Isomer A:* 195.0(1), 194.4(1), 191.1(1), 189.7(1), 189.3(1), 180.9(1), 179.0(2)<br>*Isomer B:* 193.4(2), 181.6(4), 179.9(2) | |
| | 30 | $CH_2Cl_2$ | 185.9 | |
| $[Os_3(CO)_8(CNBu^t)_4]$ | −95 | $CH_2Cl_2$ | 194.1(2), 187.2(2), 178.9(4) | |
| | 25 | $CH_2Cl_2$ | 187.0 | |

* Relative intensities in parentheses. Referenced with respect to solvent as internal standard (δ $CH_2Cl_2$ = 53.9, δ $CH_3C_6H_5$ = 137.7) with δ $SiMe_4$ = 0.

On warming the samples of $[Os_3(CO)_{11}(CNBu^n)]$ and $[Os_3(CO)_{11}(CNC_6H_4OMe\text{-}p)]$ above −60 °C evidence for fluxionality of these species is obtained. Between *ca.* −50 and 0 °C a gradual broadening of resonances a, b, and e/f is observed although e/f broadens less markedly than a or b, suggesting that perhaps only e or f is involved. Resonances c and d remain sharp over this temperature range. A partial scrambling of the CO groups is clearly occurring, such a process having been observed previously for $[Os_3(CO)_{11}(PEt_3)]$.[7] For this phosphine derivative the data could be explained if it was assumed that any rearrangement process involving transfer of the $PEt_3$ ligand from an equatorial to an axial position has a high activation-energy barrier relative to processes which do not require this transfer. A similar assumption is necessary if the data for the isonitrile complexes is to be accounted for. Thus if the CNR group is constrained to occupy an axial site, the pairwise exchange of CO groups according to the Cotton mechanism[12] can only take place along the edge Os(1)–Os(2) of the metal-atom triangle. This would result in the scrambling of carbonyls a, b, and e in accord with our data. Above 0 °C, before the coalescence of the signals due to a, b, and e is complete, resonances c and d also start to broaden and at 90 °C a single averaged signal is observed. This complete scrambling of all the CO groups could be achieved in a number of ways. It is possible that the axially substituted isomer may be in rapid equilibrium with a low concentration of the equatorially substituted isomer, the equilibrium process presumably involving a polytopal rearrangement of the terminal ligands on the substituted metal atom.[13,14] Alternatively, the CNR ligand may pass from one metal atom to another *via* an intermediate in which it acts as a bridging ligand. Either of these possibilities would allow CO scrambling *via* pairwise opening and closing of CO bridges along the other edges of the metal-atom triangle and hence lead to total exchange.

That it is at least possible for the CNR ligand to occupy an equatorial site in a monosubstituted complex is indicated by the $^{13}$C n.m.r. spectrum of [$Os_3(CO)_{11}(CNBu^t)$]. At −60 °C the spectrum is much more complicated than that due to [$Os_3(CO)_{11}(CNBu^n)$] showing a total of ten $^{13}$CO resonances. The most likely explanation of this more complicated spectrum is that both the axial and equatorial isomers are present in solution. Indeed five resonances (at 186.6, 185.1, 184.3, 176.3, and 174.8 p.p.m.) of relative intensity 2 : 2 : 1 : 2 : 4 can be assigned to the axial isomer by comparison with the spectrum of [$Os_3(CO)_{11}(CNBu^n)$]. On warming to −30 °C three of these signals broaden preferentially, leaving those at 184.3 (intensity one) and 174.8 (intensity four) as relatively sharp. Assuming that the same limited scrambling process as found for [$Os_3(CO)_{11}(CNBu^n)$] operates, then the resonances at 186.7, 185.1, and 176.3 p.p.m. must be assigned to carbonyls a, b, and e. Since that of unit intensity must arise from carbonyl c, the signal at 174.8 p.p.m. must arise from a degeneracy of d and f. In fact this peak does possess an unresolved shoulder. That d and f should have very similar chemical shifts in [$Os_3(CO)_{11}(CNBu^t)$] whereas e and f are degenerate for the other CNR ligands used is perhaps a little surprising, but may possibly be due to distortion of the molecule by the bulky CNBu$^t$ group.

The remaining five resonances in the spectrum of [$Os_3(CO)_{11}(CNBu^t)$] at −60 °C must be due to the equatorial isomer. Because this is clearly present at a lower concentration than the axial isomer the relative intensities of these resonances are more difficult to estimate. Three of them, at 173.0, 172.9, and 171.5 p.p.m., are at positions typical of equatorial carbonyl groups. Another, at 183.7 p.p.m., can be assigned to a pair of axial carbonyls. The fifth, at 189.8 p.p.m., is also at a chemical shift typical of axial carbonyls but is broad. For the low-temperature limiting spectrum of the equatorial isomer a further three resonances (one due to a pair of axial carbonyls and two due to equatorial carbonyl groups) should be present. Their absence suggests the onset of coalescence at −60 °C, and indeed when the temperature is raised to −30 °C the signal at 189.9 p.p.m. disappears and is replaced by a much stronger signal at 185.5 p.p.m. This signal overlaps one of the resonances from the axially substituted isomer, but is of approximately the correct relative intensity to represent the six carbonyl groups aa, cc, d, and g [Figure 1(*b*)] scrambling along the edge Os(1)–Os(3) as found in [$Os_3(CO)_{11}(PEt_3)$].[7] Unfortunately it was not possible to record the $^{13}$C spectrum of [$Os(CO)_{11}(CNBu^t)$] below −60 °C due to the insolubility of the complex, and a low-temperature limiting spectrum for the equatorial isomer was therefore not obtained. On raising the temperature above 0 °C all resonances, from both axial and equatorial isomers, were observed to broaden and collapse, giving rise to a single resonance at 180.7 p.p.m. at 50 °C. At this temperature then, interconversion of the axial and equatorial isomers is rapid on the n.m.r. time scale.

The above evidence shows that [$Os_3(CO)_{11}(CNR)$] complexes can exist either as axially or as equatorially substituted isomers. The fact that less bulky RNC ligands favour the axial position suggests that this position is electronically preferred. The same may be true of substitution by organophosphorus ligands, and the fact that all monosubstituted phosphine derivatives prepared to date exist in an equatorially substituted form may merely reflect the greater steric bulk of organophosphines as opposed to isonitrile ligands. Subsequent to the completion of our $^{13}$C n.m.r. study an *X*-ray crystal-structure determination of [$Ru_3(CO)_{11}(CNBu^t)$] has revealed that for this complex the axial isomer alone is present in the solid state. By analogy with the osmium system it might have been expected that a mixture of isomers would be present for the complex in solution. However, the molecule is fluxional down to −100 °C and no information on this point could be obtained.[14]

(*b*) *Disubstituted derivatives*. The $^{13}$C n.m.r. spectra of [$Os_3(CO)_{10}(CNBu^n)_2$] and [$Os_3(CO)_{10}(CNC_6H_4OMe\text{-}p)_2$] at low temperatures both show four lines of intensity ratio 2 : 2 : 2 : 4. For the diequatorial isomer [Figure 2(*a*)], found for [$Os_3(CO)_{10}(PEt_3)_2$], seven resonances of relative intensity 2 : 2 : 2 : 1 : 1 : 1 : 1 are expected, while the *cis*-diaxial isomer, 2(*b*), should show six resonances of intensity ratio 2 : 2 : 2 : 2 : 1 : 1. The *trans*-diaxial isomer, 2(*c*), is expected to give rise to five resonances of equal intensity while an axial/equatorial isomer, 2(*d*) or 2(*e*), has ten non-equivalent carbonyl groups. Of these possibilities the diequatorial isomer 2(*a*) can be eliminated on the basis of the i.r. data as discussed above. The other possible diequatorial isomer, 2(*f*), is less likely than 2(*a*) on steric grounds, quite apart from the fact that 2(*a*) is preferred over 2(*f*) for [$Os_3(CO)_{10}(PEt_3)_2$].[7] The axial/equatorial isomers, 2(*d*) and 2(*e*), would almost certainly give rise to a more complex i.r. spectrum than is observed and the fit of the $^{13}$C n.m.r. data with either of these isomers is also extremely poor. The *trans*-diaxial isomer, 2(*c*), requires one accidental degeneracy in its $^{13}$C n.m.r. spectrum while the *cis*-diaxial isomer, 2(*b*), requires e and f to be degenerate and also one other degeneracy. The $^{13}$C data, therefore, together with the fact that 2(*c*) is sterically more favourable than 2(*b*), strongly suggest that 2(*c*) is the isomer present in solution. Of the four $^{13}$C n.m.r. resonances observed at low temperatures the two at lower field may be assigned to axial carbonyls, as for the monosubstituted complexes and for [$Os_3(CO)_{10}(PEt_3)_2$]. The accidental degeneracy required to fit the data to 2(*c*) seems most likely to be between the equatorial pairs c and d, and the remaining resonance at 178.6 p.p.m. is then due to e.

Again, as for the monosubstituted derivatives, the spectrum of $[Os_3(CO)_{10}(CNBu^t)_2]$ at low temperatures is more complicated than those of the other disubstituted derivatives, and the presence of more than one isomer is indicated. A mixture of the *trans*-diaxial and the diequatorial isomer 2(*a*) seems most likely, and the number of carbonyl resonances is as required for such a mixture assuming one accidental degeneracy in the diaxial isomer as observed for the other disubstituted isonitrile derivatives. The tentative assignment of the 11 resonances observed to either the diaxial or diequatorial isomer (Table 3) is made on the basis of a comparison with the spectra of these other derivatives and with that of $[Os_3(CO)_{10}(PEt_3)_2]$.[7]

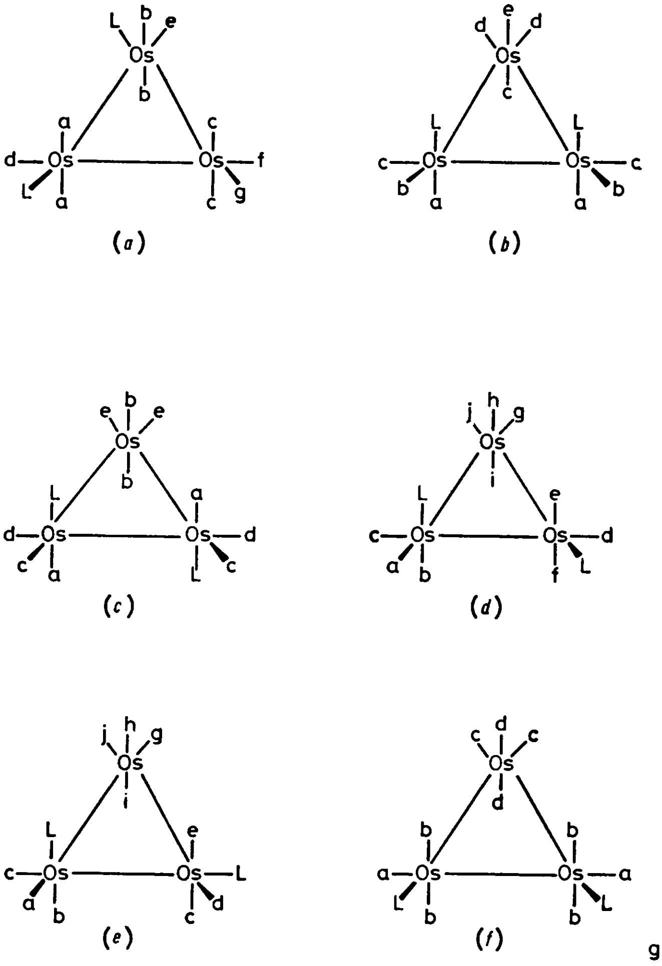


FIGURE 2 The possible isomers for $[Os_3(CO)_{10}L_2]$ derivatives

On warming a sample of $[Os_3(CO)_{10}(CNBu^n)_2]$ from $-60$ °C to $-30$ °C two of the resonances (at 189.9 and 178.6 p.p.m.) which are due to a or b and e [Figure 2(*c*)] start to broaden. The only reasonable choice for the resonance at 189.9 p.p.m. is then b, the broadening being due to a polytopal rearrangement on the unsubstituted osmium atom. On further warming to 0 °C the resonance at 177.2 p.p.m. also begins to broaden, whilst the signal at 188.9 p.p.m. is still sharp. This may indicate the onset of a second partial scrambling process and one possibility which would account for the data is in-plane scrambling of c, d, and e, the so called 'merry-go-round' process.[15] Above 0 °C, however, and before coalescence due to these partial scrambling processes is complete, broadening of all the carbonyl resonances is observed, due to the onset of complete scrambling. No firm conclusions about the second partial scrambling process can therefore be drawn. The variable-temperature behaviour of $[Os_3(CO)_{10}(CNC_6H_4OMe\text{-}p)_2]$ is identical to that of the $CNBu^n$ derivative, but for $[Os_3(CO)_{10}(CNBu^t)_2]$ the complexity of the $^{13}C$ spectrum (due to the mixture of isomers) is such that nothing can be deduced about the nature of any partial scrambling processes. It is, however, significant that at 35 °C all the CO signals have collapsed to a single resonance at 183.9 p.p.m., indicating that isomer interconversion is rapid on the n.m.r. time scale at this temperature.

(*c*) *Trisubstituted derivatives.* For both $[Os_3(CO)_9(CNBu^n)_3]$ and $[Os_3(CO)_9(CNBu^t)_3]$ the complexity of the $^{13}C$ n.m.r. spectra at $-80$ °C is such that at least two isomers must be present in solution in each case. Although the spectra are broadly similar for the two complexes the relative intensities of the signals differ considerably. By a careful comparison of these relative intensities it is possible to separate the signals into two groups (Table 3) each presumably corresponding to one isomer. Of the six possible isomers for trisubstituted complexes {assuming one substituent per metal atom as found for $[Os_3(CO)_9(PEt_3)_3]^7$} the $^{13}C$ n.m.r. data are most compatible with the isomers shown in Figure 3(*a*) and 3(*b*). Thus the group of signals of relative intensity 6 : 2 : 1 is as required for isomer 3(*b*) if it is assumed that carbonyls aa, a′a′, and a″a″ are either accidentally degenerate or undergoing in-plane scrambling at $-80$ °C {as observed for $[Ru_3(CO)_{10}(\text{diazene})]$ [16]}. The former seems the more likely as for $[Os_3(CO)_9(CNBu^t)_3]$ the accidental degeneracy is in fact partially resolved. The eight signals not due to 3(*b*) can be assigned to 3(*a*) if it is assumed (not unreasonably) that carbonyls a and a′ are degenerate.

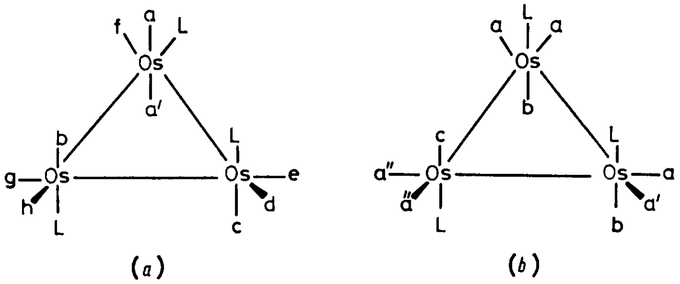


FIGURE 3 Two of the six possible isomers for $[Os_3(CO)_9L_3]$ derivatives

On warming solutions of either of the trisubstituted complexes, all the signals broaden and collapse and, at

24 °C in $CH_2Cl_2$ for the $CNBu^n$ complex and at 70 °C in toluene for the $CNBu^t$ complex, a single averaged signal is observed indicating rapid isomer interconversion.

(*d*) *Tetrasubstituted derivatives*. In the tetrasubstituted complexes $[Os_3(CO)_8L_4]$ it can be assumed that one metal atom will carry two substituents and the other metal atoms one each. The $^{13}C$ n.m.r. spectra of the tetrasubstituted derivatives reveal that, in contrast to the less highly substituted derivatives, it is for L = $CNBu^t$ that the simplest spectrum is obtained. Three resonances at δ 194.1, 187.2, and 178.9 p.p.m. of relative intensity 2 : 2 : 4 are observed at −60 °C. On the basis of a comparison of chemical shifts with those of less highly substituted derivatives this seems most likely to correspond to an isomer with two axial and six equatorial CO groups. Of the two possible isomers of this type 4(*a*) is clearly preferable to 4(*b*) on steric grounds and fits the $^{13}C$ n.m.r. data assuming carbonyls c and c′ are accidentally degenerate. A similar assumption was necessary in the case of the monosubstituted and disubstituted derivatives. It is not possible to exclude entirely the alternative possibility of an isomer with four axial and four equatorial CO groups on the basis of the chemical shift comparison alone. Of the several isomers of this type, however, none fits the $^{13}C$ n.m.r. data at all well. Isomer 4(*c*), for example, would give rise to seven or eight resonances and the number of accidental degeneracies required effectively rule out this and all other isomers of this type.

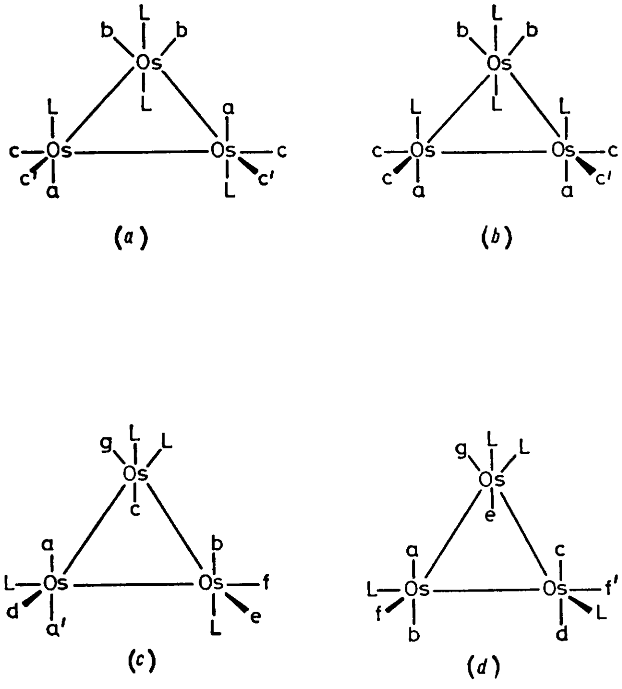


FIGURE 4 Some of the possible isomers for $[Os_3(CO)_8L_4]$ derivatives

The $^{13}C$ spectrum of $[Os_3(CO)_8(CNBu^n)_4]$ at −90 °C shows, in addition to the resonances attributable to 4(*a*), a further seven resonances. Five of these have chemical shifts typical of axial carbonyls and are of unit intensity. The other two are to higher field and have intensities of one and two. Such a spectrum is as required for isomer 4(*d*) if it is assumed that f and f′ are degenerate. This seems a reasonable assumption, since both are in equatorial positions on metals which each carry one substituent. Furthermore both f and f′ are *trans* to a CNR group through a metal–metal bond.

On warming the sample above −90 °C all resonances broaden and collapse, and at 35 °C a single line due to the carbonyl groups in both isomers is observed. Obviously isomer interconversion and carbonyl scrambling are rapid at this temperature, but it is not possible to determine the mechanism of these processes without further experimental data.

## EXPERIMENTAL

All manipulations were carried out under dry oxygen-free nitrogen. Solvents were dried, deoxygenated, and distilled before use according to standard literature methods.

Infrared spectra were recorded as cyclohexane solutions in 0.1 or 0.5 mm $CaF_2$ cells on a Perkin-Elmer 257 spectrometer using polystyrene as calibrant. Mass spectra were obtained using an A.E.I. M.S.12 instrument. Hydrogen-1 n.m.r. spectra were recorded using a Varian Associates HA100 instrument operating at 100 MHz. Tetramethylsilane or the solvent were used as internal calibrants. Carbon-13 n.m.r. spectra were recorded using a Varian Associates XL-100 instrument operating in the Fourier-transform mode at 25.2 MHz. Spectra were obtained over a range of spectral widths (10 000, 5 000, and 300 Hz) with appropriate acquisition times and calibrated relative to $SiMe_4$ using the solvent resonances as internal standard. Variation of the standard with temperature remained uncorrected. At > −50 °C *ca*. 0.05 mol dm$^{-3}$ tris(pentane-2,4-dionato)chromium(III) was added as a shiftless relaxation agent. Below this temperature the relaxation agent was found to be unnecessary. The lowest temperature at which the spectra were recorded was governed by the solubility of individual complexes. Samples for spectroscopic study were prepared using $[Os_3(CO)_{12}]$ *ca*. 20% enriched with $^{13}CO$. Microanalyses were carried out at the University of Cambridge Chemical Laboratory.

*Preparation of* $[Os_3(CO)_{12-n}(CNBu^t)_n]$ ($n$ = 1—4).—The compound $[Os_3(CO)_{12}]$ (0.45 g, 0.5 mmol) was dissolved in toluene (100 cm$^3$), $CNBu^t$ (0.125 g, 1.5 mmol) was added, and the mixture refluxed for 2 h. If any unreacted $[Os_3(CO)_{12}]$ remained at the end of the 2 h period further small quantities of $CNBu^t$ were added and the reflux continued until monitoring of the reaction by t.l.c. (thin-layer chromatography) showed that this had been consumed. The solvent was then removed *in vacuo* and the residue dissolved in a minimum of dichloromethane. The products were separated by t.l.c. on silica using 10% ethyl acetate–90% cyclohexane as eluant. The other derivatives with CNMe, $CNC_6H_4OMe$-*p*, and $CNBu^n$ as the substituting ligands were similarly prepared.

We thank Johnson, Matthey and Co. for the generous loan of $OsO_4$ and one of us (P. D. G.) thanks the S.R.C. for a maintenance grant.

[9/1239 *Received*, 6*th August*, 1979]

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