The Preparation, Characterisation, and Some Reactions of $[Os_3(CO)_{11}(NCMe)]$ †

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The cluster $[Os_3(CO)_{11}(NCMe)]$ has been prepared from the reaction of $[Os_3(CO)_{12}]$ with NMe_3O in the presence of MeCN. This cluster reacts with ligands L (L = CO, PPh_3, $CH_3C_6H_4SO_2CH_2NC$-*p*, C_2H_4, or C_5H_5N) to produce $[Os_3(CO)_{11}L]$ derivatives and with HX (X = Cl, Br, or I) to form $[Os_3(CO)_{11}HX]$, $[Os_3(CO)_{10}HX]$ (X = Cl, Br, or I) and $[Os_3(CO)_9HX]$ (X = I). Evidence for the formation of an uncharacterised intermediate, possibly $[Os_3(CO)_{11}(NCMe)H]X$, is also presented. Possible structures of these complexes are also discussed.

THE use of amine oxides (NR_3O) to remove co-ordinated carbon monoxide was first reported by Shvo and Hazum.[1] The carbon monoxide is removed as carbon dioxide and the mechanism of oxidation is considered to involve the nucleophilic addition of the amine oxide (R = Me) on the co-ordinated carbonyl ligand. Since this initial report there have been others and the method has been applied not only to other mononuclear carbonyls but also to clusters.[2,3] In this paper we report the preparation of $[Os_3(CO)_{11}(NCMe)]$ from the reaction of $[Os_3(CO)_{12}]$ with NMe_3O in the presence of MeCN and its reactions with a wide range of ligands, L, to produce the derivatives $[Os_3(CO)_{11}L]$ (L = CO, PPh_3, $CH_3C_6H_4SO_2CH_2NC$-*p*, C_2H_4, or C_5H_5N) and with HX (X = Cl, Br, or I) to form $[Os_3(CO)_{11}HX]$, $[Os_3(CO)_{10}HX]$, and $[Os_3(CO)_9HX]$ (X = I). Some aspects of this work have been communicated previously.[4]

RESULTS AND DISCUSSION

Preparation and Characterisation of $[Os_3(CO)_{11}(NCMe)]$.—Dodecacarbonyltriosmium in dichloromethane reacts with trimethylamine oxide in methyl alcohol in the presence of a little methyl cyanide at room temperature to yield almost quantitatively the methyl cyanide complex $[Os_3(CO)_{11}(NCMe)]$. The reaction was monitored by i.r. spectroscopy by following the disappearance of the bands [ν(CO)] due to $[Os_3(CO)_{12}]$. In general, slightly more than a stocheiometric amount of NMe_3O was required. After separation, the complex $[Os_3(CO)_{11}(NCMe)]$ was obtained as air-stable yellow crystals. The i.r. and ^1H n.m.r. spectra are given in Table 1. The ^1H n.m.r. spectrum (*ca.* 25 °C) shows one signal at τ 7.26 (s) which may be assigned to CH_3CN of the co-ordinated NCMe ligand. Under electron impact the complex undergoes decomposition and no parent ion was observed; however, the complex does give satisfactory analytical data (see Experimental section).

Reaction of $[Os_3(CO)_{11}(NCMe)]$ *with Other Donor Ligands* L.—Complexes of the type $[Os_3(CO)_{11}L]$ may also be prepared from the reaction of $[Os_3(CO)_{12}]$ with NMe_3O in the presence of the appropriate ligand L. However, better yields of these derivatives were obtained by treating the preformed complex $[Os_3(CO)_{11}(NCMe)]$ with the ligand L. Thus, treatment of $[Os_3(CO)_{11}(NCMe)]$ with CO, PPh_3, or $CH_3C_6H_4SO_2CH_2NC$-*p* led to the formation of the known compounds $[Os_3(CO)_{12}]$, $[Os_3(CO)_{11}(PPh_3)]$, and $[Os_3(CO)_{11}(CNR)]$ (see ref. 5) in quantitative amounts. Significantly, no di- or tri-substituted complexes, $[Os_3(CO)_{10}L_2]$ and $[Os_3(CO)_9L_3]$, were obtained emphasising the advantages offered by this milder synthetic route. The spectroscopic properties of the monosubstituted derivatives are recorded in Table 1.

On reaction of $[Os_3(CO)_{11}(NCMe)]$ with ethylene or pyridine the clusters $[Os_3(CO)_{11}(C_2H_4)]$ and $[Os_3(CO)_{11}(C_5H_5N)]$ were obtained. Although mass spectroscopic data could not be obtained for these compounds {decomposition in the spectrometer seems to produce some $[Os_3(CO)_{12}]$} they were fully characterised on the basis of their analytical and other spectroscopic data. For $[Os_3(CO)_{11}(C_2H_4)]$ a resonance was observed in the ^1H n.m.r. at τ 7.42 (singlet) at room temperature. This information may be taken to indicate that the ethylene is rotating rapidly at this temperature since it is difficult to imagine a structure for this complex in which all four protons are equivalent in the ground state. A single-crystal *X*-ray analysis of this compound, although allowing the Os_3 triangle to be fully characterised, could not be completed because of crystal disorder.

For $[Os_3(CO)_{11}(C_5H_5N)]$ the ^1H n.m.r. spectrum (25 °C) exhibits three signals at τ 1.20 (d, 2 H), 2.42 (m, 1 H), and 2.74 (m, 2 H), as expected for a co-ordinated C_5H_5N group.

The ^1H n.m.r. and i.r. spectra for the $[Os_3(CO)_{11}L]$ clusters are summarised in Table 1 and the structures shown in Figure 1.

In general, for simple substitution products of the type $[Os_3(CO)_{11}L]$, the substituting ligand L occupies an equatorial site.[5,6] This preference for equatorial substitution can be accounted for in steric terms since simple calculations [5,7] on $[Os_3(CO)_{12-x}L_x]$ systems show that equatorial sites in (approximately) anticuboctahedral structures of ligands are less sterically hindered than axial sites. For CNR ligands the substituting ligand can occupy either an axial or an equatorial site depending on the steric requirements of the R group. In solution, both isomeric forms are known to exist although in the solid state the related complex $[Ru_3(CO)_{11}(CNBu^t)]$ [6] has been shown to exist as the axial isomer alone.

It is worth noting that the complexes $[Os_3(CO)_{11}(C_2H_4)]$ and $[Os_3(CO)_{11}(C_5H_5N)]$ represent postulated [8,9] but unobserved intermediate products in the reactions of

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† Undecacarbonyl(methyl cyanide)triosmium (3*Os*–*Os*).

TABLE 1

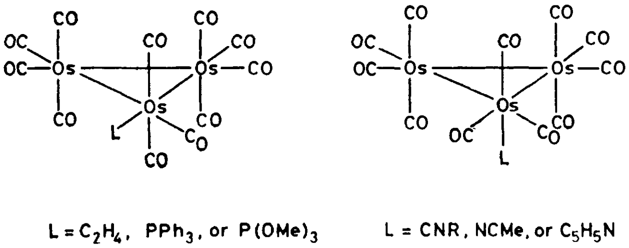
Spectroscopic properties of $[Os_3(CO)_{11}L]$ derivatives

Compound	I.r.[a]	^1H n.m.r. (τ)[b]	Molecular weight (mass spectrum)[c]
$[Os_3(CO)_{11}(NCMe)]$	2 103w, 2 052s, 2 040s, 2 020m, 2 000vs, 1 984 (sh), 1 981m, 1 969vw, 1 960vw	7.26 (3 H, s)	
$[Os_3(CO)_{11}(C_5H_5N)]$	2 104w, 2 051s, 2 035vs, 2 018m, 2 004vs, 1 998 (sh), 1 979 (sh), 1 975m, 1 960vw, 1 948vw	1.20 (s H, d), 2.42 (1 H, m), 2.74 (2 H, m)	
$[Os_3(CO)_{11}(C_2H_4)]$	2 117w, 2 064s, 2 048s, 2 027vs, 2 009m, 2 005m, 1 995m, 1 983w, 1 967w	7.42 (4 H, s)	
$[Os_3(CO)_{11}(PPh_3)]$	2 108ms, 2 055s, 2 035s, 2 109s, 2 000ms, 1 989ms, 1 978m		
$[Os_3(CO)_{11}(CNMe)]$	2 101ms, 2 054s, 2 041s, 2 022s, 2 003s, 1 989s, 1 986 (sh)		
$[Os_3(CO)_{11}(CNBu^t)]$	2 102ms, 2 054s, 2 041s, 2 023s, 2 004s, 1 990s		
$[Ru_3(CO)_{11}(CNBu^t)]$	2 092ms, 2 043 (sh), 2 036s, 2 012 (sh) 2 004s, 1 989 (sh)		
$[Os_3(CO)_{11}\{P(OMe)_3\}]$	2 111m, 2 055s, 2 039m, 2 021s, 2 002w, 1 992m, 1 981w, 1 967vw		
$[Os_3(CO)_{11}(CH_3C_6H_4SO_2CH_2CN\text{-}p)]$	2 099w, 2 056s, 2 042,s 1 994s, 1 981m, 1 977 (sh)		
$[Os_3(CO)_{11}HCl]$	2 142vw, 2 099s, 2 079vs, 2 066vs, 2 052s, 2 034vs, 2 026s, 2 023s, 2 013m, 1 990w, 1 976w	25.98 (1 H, s)	m/e — 922
$[Os_3(CO)_{11}HBr]$	2 143vw, 2 100s, 2 081vs, 2 068s, 2 056s, 2 037vs, 2 026m, 2 016m, 1 996m, 1 978w	26.93 (1 H, s)	m/e = 966
$[Os_3(CO)_{10}(PPh_3)HCl]$	2 113w, 2 077s, 2 064s, 2 031vs, 2 019s, 2 012m, 2 001w, 1 992w, 1 977w, 1 965w	2.48 (15 H, m), 24.59 (1 H, d); J(PH) 12.7 Hz	m/e = 1 128
$[Os_3(CO)_9HI]$	2 095w, 2 067s, 2 043s, 2 012s, 2 003w, 1 968br, w[d]		
$[Os_3(CO)_9(PPh_3)HI]$ Isomer (*a*)	2 095vw, 2 090w, 2 063s, 2 058 (sh), 2 035s, 2 007s, 1 997m, 1 970w, 1 964vw, 1 957vw	2.51 (15 H, m), 26.69 (0·5 H, s), 26.86 (0.5 H, s)[e]	m/e — 1 218
$[Os_3(CO)_9(PPh_3)HCl]$ Isomer (*b*)	2 097vw, 2 092w, 2 066s, 2 062 (sh), 2 038s, 2 029 (sh), 2 019m, 2 009s, 1 998s, 1 984w, 1 972m, 1 965m, 1 960m, 1 954w	2.58 (15 H, m), 24.62 (0.5 H, s), 24.78 (0.5 H, s)[e,f]	
$[Os_3(CO)_{11}(NCMe)H]Cl$	2 149w, 2 108s, 2 087s, 2 075 (sh), 2 062s, 2 040 (sh), 2 021w, 2 010 (sh)		

[a] In cyclohexane. [b] In $CDCl_3$ unless stated otherwise. [c] Based on ^{192}Os, ^{37}Cl, and ^{81}Br. [d] Taken from octane reaction mixture [e] See text. [f] Recorded in CD_2Cl_2.

$[Os_3(CO)_{12}]$ with C_2H_4 or C_5H_5N. Reaction of the parent dodecacarbonyl with these ligands takes place only at elevated temperatures when the derivatives $[Os_3(CO)_9(C{=}CH_2)H_2]$ [9] and $[Os_3(CO)_{10}(C_5H_4N)H]$ [8] were obtained as the simplest products. We find that $[Os_3(CO)_{11}(C_2H_4)]$ and $[Os_3(CO)_{11}(C_5H_5N)]$ undergo conversion to these products on heating in n-octane in the presence of excess of ligand. Thus the two reaction pathways (*a*) and (*b*) (Scheme 1) have been established.

Reaction of $[Os_3(CO)_{11}(NCMe)]$ *with* HX (X = H, Cl, *or* Br).—These reactions are outlined in Scheme 2. The reaction of $[Os_3(CO)_{11}(NCMe)]$ with H_2 gives $[Os_3(CO)_{11}H_2]$ [10,11] which readily loses CO to form $[Os_3(CO)_{10}H_2]$.



L = C_2H_4, PPh_3, or $P(OMe)_3$

L = CNR, NCMe, or C_5H_5N

FIGURE 1 Molecular structures of $[Os_3(CO)_{11}L]$ clusters

In the reaction with HX (X = Cl or Br) the compound $[Os_3(CO)_{11}HX]$ is formed initially but on heating in cyclohexane for *ca.* 10 min CO ejection occurs and the previously reported [12] cluster $[Os_3(CO)_{10}HX]$ is formed.

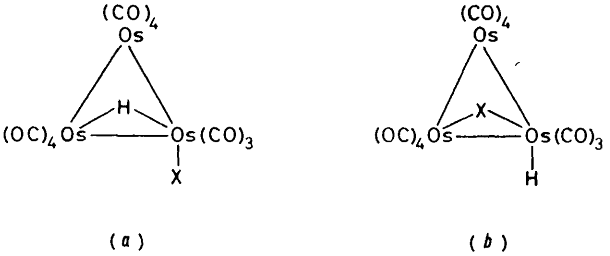
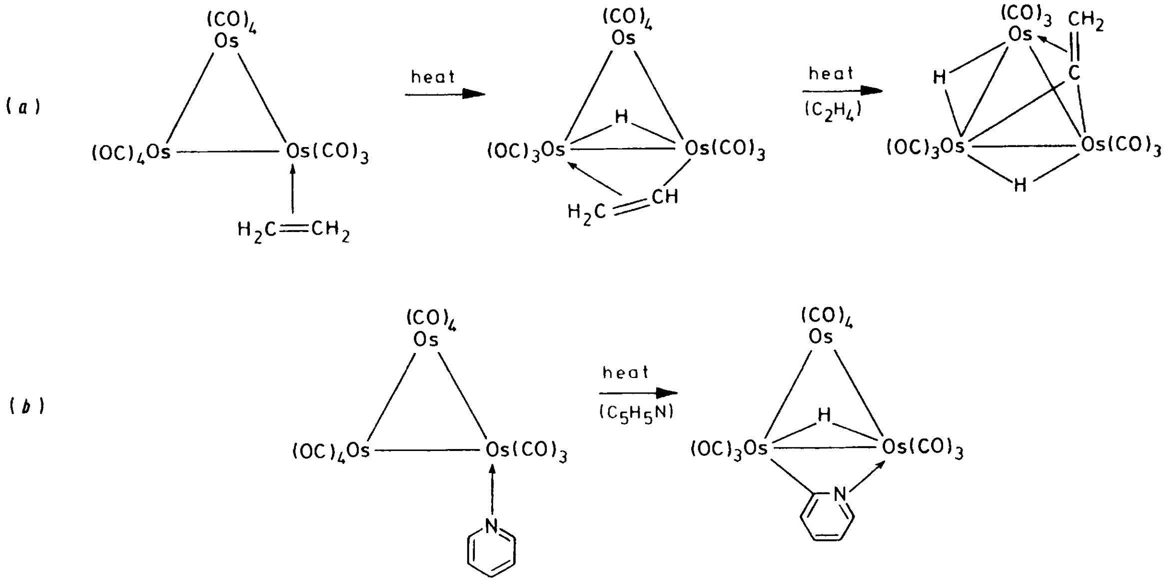


FIGURE 2 Possible isomeric forms of $[Os_3(CO)_{11}HX]$

The i.r. spectra of the $[Os_3(CO)_{11}HX]$ compounds (Table 1) are similar to that of $[Os_3(CO)_{11}H_2]$ and on this basis we propose a structure involving one bridging and one terminal ligand [Figure 2, (*a*) and (*b*)]. The ^1H n.m.r. spectra of these complexes exhibit a single hydride resonance at τ 25.98 (X = Cl) and 25.96 (X = Br) consistent with either structure (*a*) or (*b*). We tend to favour structure (*a*) which involves a bridging H ligand and a terminally bound halide on the following grounds.

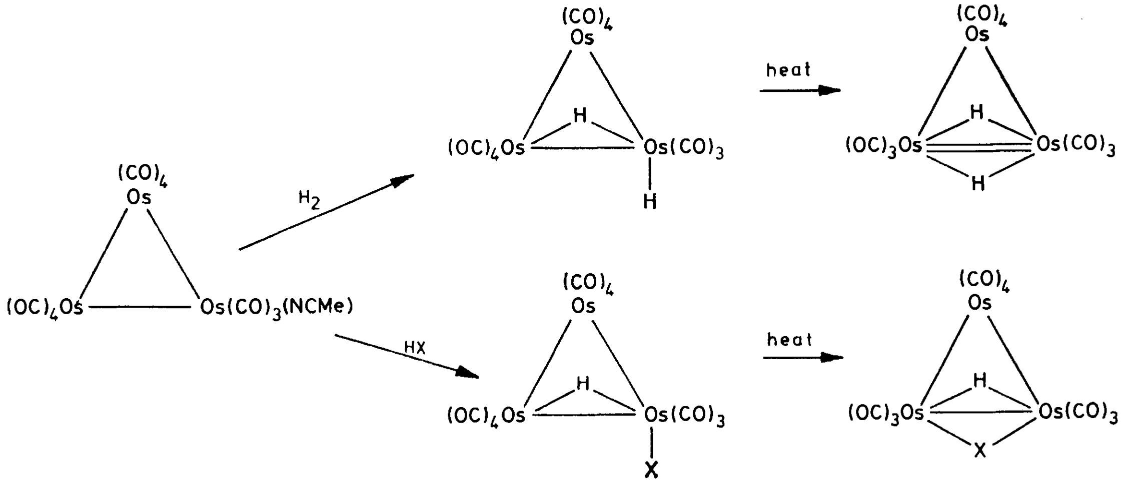


SCHEME 1 The effect of heat on (*a*) $[Os_3(CO)_{11}(C_2H_4)]$ and (*b*) $[Os_3(CO)_{11}(C_5H_5N)]$

First, terminal hydrides tend to react with CCl_4 or $CHCl_3$ to generate chloride-containing species whereas bridging hydrides are apparently more resistant to attack.[13,14] We find that $[Os_3(CO)_{10}H_2]$ is stable in CCl_4 over a period of several days but $[Os_3(CO)_{11}H_2]$ undergoes reaction to produce $[Os_3(CO)_{11}HCl]$. No evidence for the formation of $[Os_3(CO)_{11}Cl_2]$ {or $[Os_3(CO)_{10}Cl_2]$} from $[Os_3(CO)_{10}HCl]$ with CCl_4, which might have been expected if the second H ligand was terminally bound, was found. Secondly, the complex $[Os_3(CO)_{10}HCl]$ readily adds PPh_3 to produce $[Os_3(CO)_{10}(PPh_3)HCl]$ which was identified on the basis of its analytical data. Its i.r. spectrum shows a doublet signal at τ 24.59 [J(P-H) = 12.7 Hz]; evidence compatible with the presence of a bridging H ligand. It is reasonable to conclude, therefore, that the closely related complex $[Os_3(CO)_{11}HCl]$ has a similar structure [*viz.* (*a*)].

On heating in cyclohexane the complex $[Os_3(CO)_{10}(PPh_3)HCl]$ loses CO to form a complex, which, on the basis of its mass spectrum and analytical data, was formulated as $[Os_3(CO)_9(PPh_3)HCl]$. However, this complex has an i.r. spectrum [ν(CO)] quite unlike those of either $[Os_3(CO)_9(PR_3)H_2]$ [11] [Figure 3(*a*)] or $[Os_3(CO)_9(SPh)(PR_3)H]$ [15] [Figure 3(*b*)] but is related to that of $[Os_3(CO)_9(SR)(PPh_3)H]$ for which structure 3(*c*) has been established.[16] We therefore propose structure 3(*d*) for this cluster.

Treatment of $[Os_3(CO)_{11}(NCMe)]$ with HI led to the isolation of $[Os_3(CO)_{10}HI]$. Attempts to isolate other possible products of this reaction {*e.g.* $[Os_3(CO)_{11}HI]$} failed, but by monitoring the reaction [i.r. ν(CO)] two intermediate compounds were detected. The second of these intermediates was identified {from a comparison of its i.r. spectrum with that of $[Os_3(CO)_{11}HX]$} as $[Os_3(CO)_{11}HI]$. The first intermediate has not been fully characterised but in view of the relatively high values of the CO stretching vibrations in the i.r. (Table 1) we suggest that it is an ionic complex of the $[Os_3(CO)_{11}$-



SCHEME 2 The reactions of $[Os_3(CO)_{11}(NCMe)]$ with H_2 and HX (X = Cl or Br)

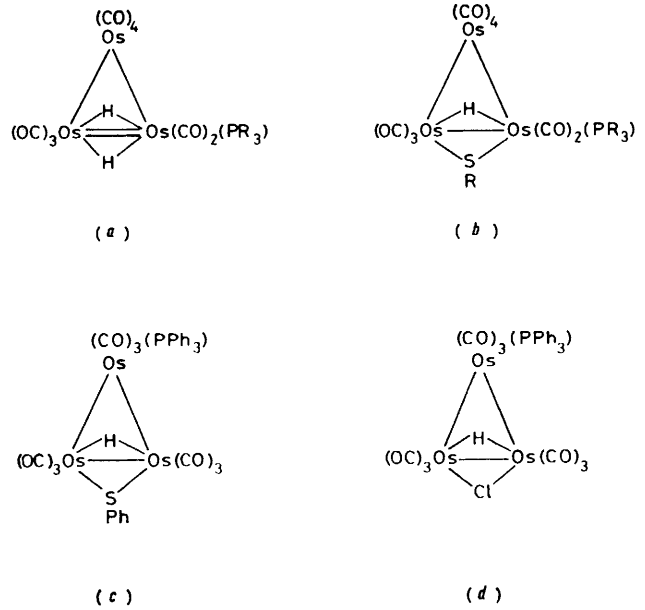


FIGURE 3 Molecular structures of (a) $[Os_3(CO)_9(PR_3)H_2]$, (b) $[Os_3(CO)_9(SR)(PR_3)H]$, (c) $[Os_3(CO)_9(SPh)(PPh_3)H]$, and proposed structure for $[Os_3(CO)_9(PPh_3)HCl]$ (d)

(NCMe)H]X type. A similar intermediate has also been detected in the reaction of $[Os_3(CO)_{11}(NCMe)]$ with HX (X = Cl or Br), and an ionic derivative of a related type has been observed [16] in the reaction of $[Os_3(CO)_{12}]$ with HX.[9]

On heating $[Os_3(CO)_{10}HI]$ in n-octane two halogenocarbonyl complexes were produced. One was readily identified as $[Os_2(CO)_6I_2]$ [17] but the other could not be isolated. However, the i.r. spectrum of this second compound closely resembled that of $[Os_3(CO)_9(SR)H]$ [Figure 4(*a*)]. Furthermore, treatment of this complex with CO led to the reformation of $[Os_3(CO)_{10}HI]$. On these grounds we formulate this second complex as $[Os_3(CO)_9HI]$ and propose structure 4(*b*) in which the I atom functions as a five-electron donor and spans three osmium atoms.

Addition of PPh_3 to a solution of $[Os_3(CO)_9HI]$ immediately produces the new adduct $[Os_3(CO)_9(PPh_3)HI]$ which has an i.r. spectrum closely similar to that of $[Os_3(CO)_9(PPh_3)HCl]$ (Table 1). For both $[Os_3(CO)_9(PPh_3)HCl]$ and $[Os_3(CO)_9(PPh_3)HI]$ two ^1H n.m.r. signals are observed in the high-field region and the i.r. spectra are more complicated than might be anticipated in view of their proposed structures. We therefore suggest that two isomeric forms of these complexes exist corresponding to the axial and equatorial site occupation by the PPh_3 ligand (Figure 5).

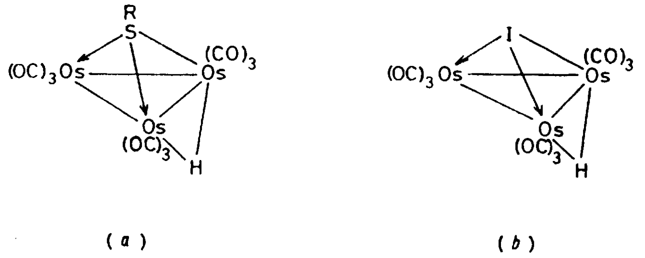


FIGURE 4 Molecular structures of (*a*) $[Os_3(CO)_9(SR)H]$ and (*b*) $[Os_3(CO)_9HI]$

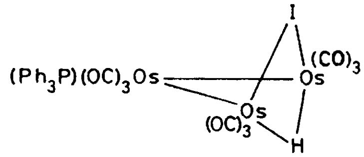
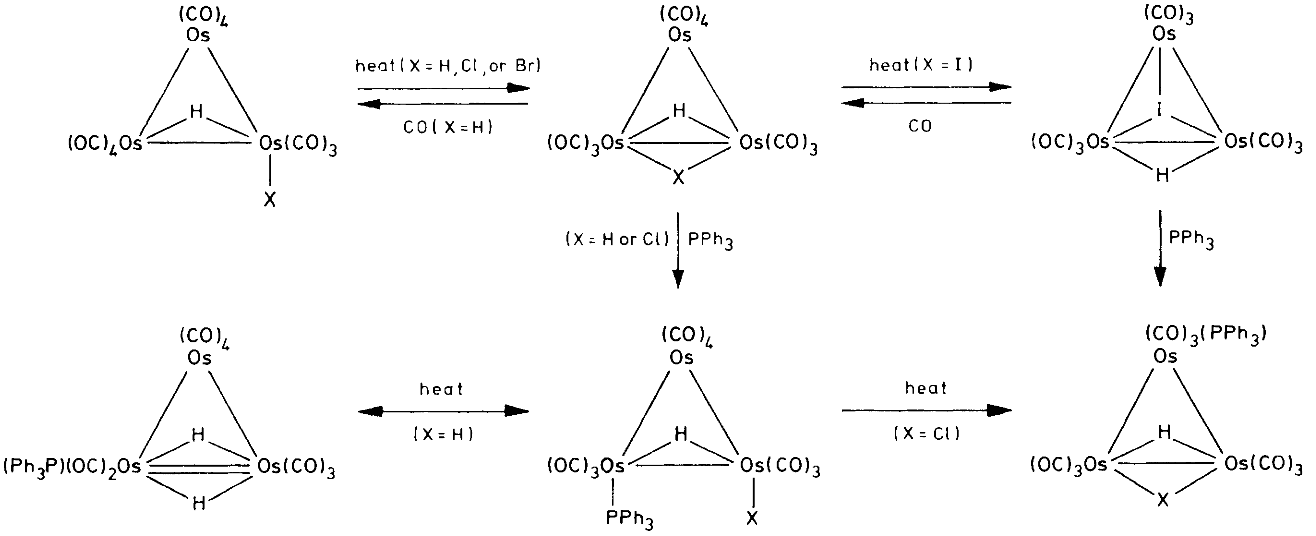


FIGURE 5 Molecular structure of $[Os_3(CO)_9(PPh_3)HI]$; PPh_3 ligand may occupy axial or equatorial site

The overall reaction sequence of the $[Os_3(CO)_{11}HX]$ systems described above is outlined in Scheme 3.

Preparation of $[Os_3(CO)_{10}(NCMe)_2]$.—Further reaction of $[Os_3(CO)_{11}(NCMe)]$ with NMe_3O in MeCN gives



SCHEME 3 The substitution reactions of $[Os_3(CO)_{10}HX]$ compounds

$[Os_3(CO)_{10}(NCMe)_2]$ in high yield. This cluster has previously been prepared from $[Os_3(CO)_{10}H_2]$.[18] No further reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with NMe_3O to produce $[Os_3(CO)_9(NCMe)_3]$ was observed, possibly reflecting the diminished tendency of the remaining CO groups to undergo nucleophilic attack.[19] Further work on this complex is in hand.

Some Other Reactions.—Reaction of $[Os_3(CO)_{11}(NCMe)]$ with a number of other donor ligands was attempted. With some (C_2H_5OH, C_6H_{10}, and C_6H_8) no reaction occurred at room temperature and on heating only the formation of a little $[Os_3(CO)_{12}]$ was observed. For others (H_2O and Pr^iSH) the known decacarbonyls were produced {*viz*. $[Os_3(CO)_{10}(OH)H]$ and $[Os_3(CO)_{10}(SPr^i)H]$}.

EXPERIMENTAL

The compound $[Os_3(CO)_{12}]$ was prepared by a high-pressure route from OsO_4 and CO in ethanol and used without further purification. Hydrogen iodide was prepared by the reaction of water with red phosphorus and iodine. Water was removed from $NMe_3O{\cdot}2H_2O$ (Aldrich Chemicals Ltd.) by sublimation but no special precautions were taken to rigorously exclude water from this hygroscopic reagent and this did not appear to influence reactions adversely. Microanalytical data (Cambridge) are recorded in Table 2.

TABLE 2

Microanalytical data for new compounds *

Compound	Analysis (%)							
	Required				Found			
	C	H	N	P	C	H	N	P
$[Os_3(CO)_{11}(NCMe)]$	16.95	0.35	1.50		17.2	0.50	1.20	
$[Os_3(CO)_{11}(C_5H_5N)]{\cdot}CH_2Cl_2$	20.6	0.60	1.35		20.55	0.60	0.90	
$[Os_3(CO)_{11}(C_2H_4)]$	17.25	0.45			17.95	0.65		
$[Os_3(CO)_{11}HCl]$	14.45	0.10			14.45	0.25		
$[Os_3(CO)_{10}(PPh_3)HCl]$	29.9	1.40		2.70	29.7	1.60		2.95
$[Os_3(CO)_9(PPh_3)HCl]$	29.5	1.40		2.75	29.9	1.70		2.85

* Determined at Cambridge.

Preparation of $[Os_3(CO)_{11}(NCMe)]$ (1).—The compound $[Os_3(CO)_{12}]$ (100 mg) was dissolved in CH_2Cl_2 (150 cm^3) containing MeCN (1 cm^3). A solution of NMe_3O in methanol (*ca*. 40 mg cm^{-3}) was added carefully until the peaks in the i.r. spectrum due to $[Os_3(CO)_{12}]$ had just disappeared (*ca*. 4 cm^3). The solvent was removed under vacuum and the residue recrystallised from the minimum volume of hot MeCN to give a bright yellow microcrystalline product. Additional product was obtained on removal of further solvent from the mother-liquor followed by thin-layer chromatography (t.l.c.) of the residue [eluting with hexane–diethyl ether–MeCN (60 : 35 : 5)]. Total yield 81 mg.

Reactions of (1) *with Donor Ligands*.—Complex (1) (20 mg) was dissolved in cyclohexane (30 cm^3) and the ligand L (L = PPh_3 or $CH_3C_6H_4SO_2CH_2NC$-*p*) added (a few mg) or passed through the solution (L = CO). The solution was then warmed for 3 min after which the i.r. spectrum indicated the quantitative formation of $[Os_3(CO)_{11}L]$.

For L = C_5H_5N, the solution of (1) was refluxed for 4 min in the presence of C_5H_5N in order that the complete conversion of (1) to $[Os_3(CO)_{11}(C_5H_5N)]$ (3) took place. Complex (3) was isolated by removing the solvent under vacuum and crystallising the residue from CH_2Cl_2–pentane. The product was obtained as orange-yellow needles (yield 75%).

For L = C_2H_4, complex (1) (40 mg) in CH_2Cl_2 was stirred under ethylene at room temperature for 2 h when the i.r. spectrum showed conversion to $[Os_3(CO)_{11}(C_2H_4)]$ (2). The complex was obtained as yellow-green crystals by concentrating the reaction solution and cooling. The product was purified by crystallisation from pentane (yield 20 mg).

Effect of Heat on Complexes (2) *and* (3).—Complex (2) (20 mg) was refluxed in n-octane (25 cm^3) and C_2H_4 passed through for 3 h. At this stage an i.r. spectrum of the solution showed that only $[Os_3(CO)_{12}]$ (*ca*. 80%) and $[Os_3(CO)_9(C{=}CH_2)H_2]$ (20%) were present.

Complex (3) (20 mg) was refluxed in n-octane (25 cm^3) in the presence of several drops of pyridine for 25 min after which time an i.r. spectrum showed the major species to be $[Os_3(CO)_{10}(C_5H_4N)H]$.

Reaction of (1) *with* H_2 *and* HX.—Hydrogen gas was passed through a solution of complex (1) (20 mg) in CH_2Cl_2 (10 cm^3) for 1 h at room temperature when the slow formation of $[Os_3(CO)_{11}H_2]$ was observed. The CH_2Cl_2 was removed under vacuum and the residue dissolved in C_6H_{12} (20 cm^3). This solution was refluxed for 10 min under H_2 when the solution became purple and the i.r. indicated that mainly $[Os_3(CO)_{10}H_2]$ was present.

Complex (1) (100 mg) was dissolved in CH_2Cl_2 (40 cm^3) and HX passed through at room temperature for 5 min (X = Cl or Br) or 10 min (X = I). In each case a similar i.r. spectrum was obtained {$[Os_3(CO)_{11}(NCMe)H]X$?}. The solvent was removed under vacuum and the residue was dissolved in $CHCl_3$. For X = Cl, the i.r. spectrum of this solution showed that $[Os_3(CO)_{11}HCl]$ was now present. For X = Br or I a similar spectrum was obtained initially but this slowly changed to that of $[Os_3(CO)_{11}HX]$ (30 min). For X = I, similar results were obtained except that the spectrum continued to change to that of $[Os_3(CO)_{10}HI]$. The yellow compounds $[Os_3(CO)_{11}HX]$ (X = Cl or Br) were isolated by t.l.c., eluting with CH_2Cl_2–hexane (60 : 40) (yields *ca*. 50%). Attempts to isolate $[Os_3(CO)_{11}HI]$ in this way were unsuccessful.

Reaction of $[Os_3(CO)_{10}HCl]$ *with* PPh_3.—The compound $[Os_3(CO)_{10}HCl]$ was prepared by treating (1) with HCl in refluxing cyclohexane for 10 min. This complex (30 mg) was dissolved in cyclohexane (30 cm^3) and PPh_3 (10 mg) added. After leaving in the dark for 3 days the i.r. spectrum of this solution showed that conversion to $[Os_3(CO)_{10}(PPh_3)HCl]$ had occurred. The solvent was removed and the products separated by column chromatography on silica [eluting with CH_2Cl_2–hexane (60 : 40)] to give pale yellow $[Os_3(CO)_{10}(PPh_3)HCl]$ (as slowest moving band) (yield 20 mg).

The compound $[Os_3(CO)_{10}(PPh_3)Cl]$ was heated in cyclohexane for 1 h when the solution changed from yellow to orange. The solvent was removed and the product separated by t.l.c. [eluting with pentane–CH_2Cl_2 (80 : 20)] to give orange $[Os_3(CO)_9(PPh_3)HCl]$ as the major product (yield 11 mg).

Effect of Heat on $[Os_3(CO)_{10}HI]$.—The compound $[Os_3(CO)_{10}HI]$ (50 mg) was heated in n-octane (30 cm^3) for 2.5 h. An i.r. spectrum of this solution showed the presence of two species. The solvent was removed and after t.l.c. (eluting with hexane) $[Os_2(CO)_6I_2]$ and $[Os_3(CO)_{10}HI]$ were obtained.

The compound $[Os_3(CO)_{10}HI]$ (50 mg) was treated in the same way. Carbon monoxide was bubbled through for 10 min when one set of peaks in the i.r. spectrum was replaced by those of $[Os_3(CO)_{10}HI]$.

A solution of $[Os_3(CO)_{10}HI]$ (50 mg) was again refluxed for 2.5 h and cooled. Triphenylphosphine (5 mg) was added and i.r. showed immediate reaction of ' $Os_3(CO)_9HI$ '. The solvent was removed followed by t.l.c. of the residue, eluting with hexane, to give orange $[Os_3(CO)_9(PPh_3)HI]$ (yield 7 mg).

Further Reaction of (1) *and* MeCN.—Complex (1) (25 mg) in MeCN (20 cm^3) was treated with a solution of NMe_3O in MeCN (*ca.* 1 mg cm^{-3}). The i.r. spectrum of the product in cyclohexane was similar to that reported[18] [2 077w, 2 025 (sh), 2 019vs, 1 982s, 1 953m] for $[Os_3(CO)_{10}(NCMe)_2]$. Addition of PPh_3 to this compound gave a quantitative yield of $[Os_3(CO)_{10}(PPh_3)_2]$.

A solution of NMe_3O in MeCN (4 mg in 4 cm^3 MeCN) was added to a solution of $[Os_3(CO)_{10}(NCMe)_2]$ in the same solvent. No new compound was formed after 2 days (as evidenced by the i.r. spectrum of the reaction solution).

We thank Johnson Matthey and Co. Ltd. for their generous loan of OsO_4 and the S.R.C. for financial support.

[0/856 *Received, 5th June,* 1980]

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