The Reaction of $[Os_3(\mu\text{-}H)_2(CO)_9L]$ (L = CO or PEt_3) with Dimethylcyanamide, Me_2NCN: *X*-Ray Crystal Structure of $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}]$† and the Reactions of this Complex with Acids

Jon Banford, Martin J. Mays,* and Paul R. Raithby
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

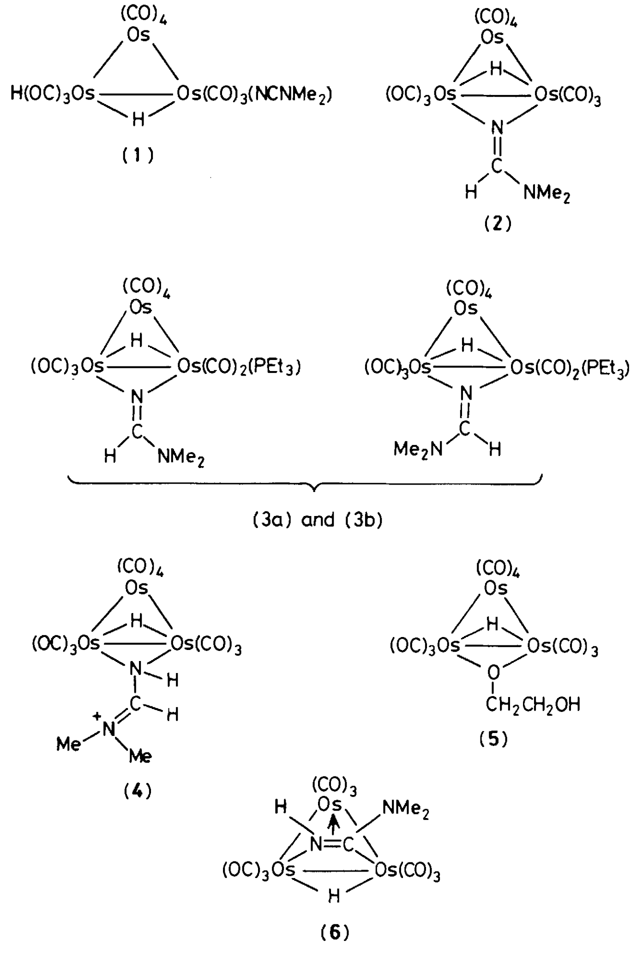
The reaction of $[Os_3H_2(CO)_{10}]$ with Me_2NCN gives a 1 : 1 adduct, $[Os_3H(\mu\text{-}H)(NCNMe_2)(CO)_{10}]$ (**1**), which, on reflux in hexane solution, rearranges to give $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}]$ (**2**). The complex $[Os_3H_2(CO)_9(PEt_3)]$ reacts similarly to give $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_9(PEt_3)]$ (**3**) which exists in solution as a mixture of two isomers which could not be separated by t.l.c. An *X*-ray diffraction study of complex (**2**) shows that both the $NCHNMe_2$ group and the hydride bridge the short edge [Os–Os 2.795(1) Å] of an isosceles Os_3 triangle. The ten carbonyl groups are all terminal, four bonded to the unique Os, and three to each of the Os atoms which are also co-ordinated to the bridging ligands. Complex (**2**) reacts with strong acids, HX (X = CF_3CO_2 or Cl), and, in the presence of $HBF_4{\cdot}R_2O$ (R = Me or Et), with weak acids (X = CH_3CO_2, MeO, HO, or $HOCH_2CH_2O$) to give complexes of the type $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$. The mechanism of this reaction is discussed in the light of a study by ^1H n.m.r. spectroscopy of the protonation of (**2**) at low temperatures. Results of the thermolysis and attempted hydrogenation of complex (**2**) are also reported.

We have recently reported the reaction of the activated nitrile CF_3CN with $[Os_3H_2(CO)_{10}]$ to give $[Os_3(\mu\text{-}H)(\mu\text{-}NCHCF_3)(CO)_{10}]$ and $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NHCCF_3)(CO)_{10}]$[1] and have further studied the reactions of these two molecules with molecular hydrogen.[2]

A rather different example of an activated nitrile is provided by dimethylcyanamide (cyanodimethylamine), Me_2NCN, and in this paper we describe the reaction of $[Os_3(\mu\text{-}H)_2(CO)_9L]$ (L = CO or PEt_3) with this nitrile. For L = CO the reaction gives a single product, $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}]$ (**2**) in quantitative yield. The reaction of (**2**) with a variety of acids, HX, either alone or in the presence of $HBF_4{\cdot}R_2O$ (R = Me or Et) provides a simple high-yield route to a wide range of complexes of the form $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$ and evidence as to the mechanism of this reaction is presented.

Results and Discussion

(*a*) *Reaction of* $[Os_3H_2(CO)_{10}]$ *with* Me_2NCN.—When a hexane solution of $[Os_3H_2(CO)_{10}]$ is treated with an excess of Me_2NCN at room temperature a copious pale yellow precipitate is formed. This precipitate analyses as the 1:1 adduct $[Os_3H_2(NCNMe_2)(CO)_{10}]$ (**1**) and its i.r. spectrum (Table 1) in hexane solution shows a similar pattern of ν(CO) bands to that obtained for other adducts of the type $[Os_3H_2(CO)_{10}L]$.[3,4] It is clearly more stable than the one previously reported 1:1 nitrile adduct of $[Os_3H_2(CO)_{10}]$ (with PhCN) which is not isolated as a solid and is only stable in nitrile solution.[3] Nevertheless, on dissolution in CH_2Cl_2, complex (**1**) reverts entirely to $[Os_3H_2(CO)_{10}]$ unless a large excess of Me_2NCN is also present. Attempts to record the mass spectrum of (**1**) gave only peaks due to $[Os_3H_2(CO)_{10}]$, and the ready dissociation of (**1**) in polar solvents (it is only slightly soluble in non-polar solvents) precluded an ^1H n.m.r. spectrum from being obtained. We tentatively assign to this adduct the structure shown in Figure 1.



(1) (2) (3a) and (3b) (4) (5) (6)

Figure 1. Proposed structures for new osmium complexes

---

† 1,1,1,2,2,2,3,3,3,3-Decacarbonyl-1,2-μ-(dimethylaminomethyleneamino-*N*)-1,2-μ-hydrido-*triangulo*-triosmium.

Supplementary data available (No. SUP 56207, 6 pp.): H-atom co-ordinates, thermal parameters, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: atm = 101 325 Pa.

Table 1. Infrared, mass spectroscopic, and ^1H n.m.r. data for new osmium complexes

			^1H N.m.r.[b]		
Compound	$\tilde{\nu}(CO)^a/cm^{-1}$	m/z (^{192}Os)	δ/p.p.m.	Assignment	J/Hz
(**1**) $[Os_3H(\mu\text{-}H)(NCNMe_2)(CO)_{10}]$	2 200vs [ν(CN), free], 2 166m [ν(CN), co-ordinated], 2 100m, 2 062vs, 2 046vs, 2 017vs, 1 993s, 1 980m, 1 964m	858[c]			
(**2**) $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}]$	2 101m, 2 061s, 2 051s, 2 017vs, 2 007s, 1 996m, 1 988s, 1 982(sh), 1 974m	928	7.08(s)	CH	
			3.07(s)	$N(CH_3)_2$	
			−14.52(s)	Os–H	
(**3**) $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_9(PEt_3)]^d$	2 084m, 2 043s, 2 004vs, 1 998s, 1 991s, 1 979m, 1 970m, 1 962m, 1 938m	1 018	7.30(s)	CH [Isomer (**3a**)]	
			6.89(s)	CH [Isomer (**3b**)]	
			3.05(s)	$N(CH_3)_2$ [Isomer (**3b**)]	
			2.97(s)	$N(CH_3)_2$ [Isomer (**3a**)]	
			2.2—0.9(m)	$P(CH_2CH_3)$ [Isomer (**3a**) and (**3b**)]	
			−14.48(d)	Os–H [Isomer (**3a**) and (**3b**)]	J(PH) = 7
(**5**) $[Os_3(\mu\text{-}H)(\mu\text{-}OCH_2CH_2OH)(CO)_{10}]$	2 111w, 2 071vs, 2 059s, 2 023vs, 1 999s, 1 989m, 1 982m	918	3.67(t)	CH_2CH_2OH	J(HH) = 4.4
			3.48(dt)	CH_2CH_2OH	J(HH) = 5.0, 4.4
			1.59(t)	OH	J(HH) = 5.0
			−12.51(s)	Os–H	$J(^{187}Os\text{-}H)$ = 37
(**6**) $[Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}NHCNMe_2)(CO)_9]$	2 087w, 2 059s, 2 030s, 2 003vs, 1 986m, 1 968w, 1 945m		5.62(s)	NH	
			3.41(s)	NCH_3	
			3.15(s)	NCH_3	
			−15.76(s)	Os–H	

[a] Complex (**1**) in hexane, (**2**)—(**5**) in cyclohexane. [b] Recorded at 298 K in CD_2Cl_2 except for complex (**4**) (213 K); s = singlet, d = doublet, t = triplet, dt = doublet of triplets, and m = multiplet. [c] Decomposition to $[Os_3H_2(CO)_{10}]$ in mass spectrometer. [d] Mixture of isomers, ratio (**3a**):(**3b**) from ^1H n.m.r. is 1:1.4.

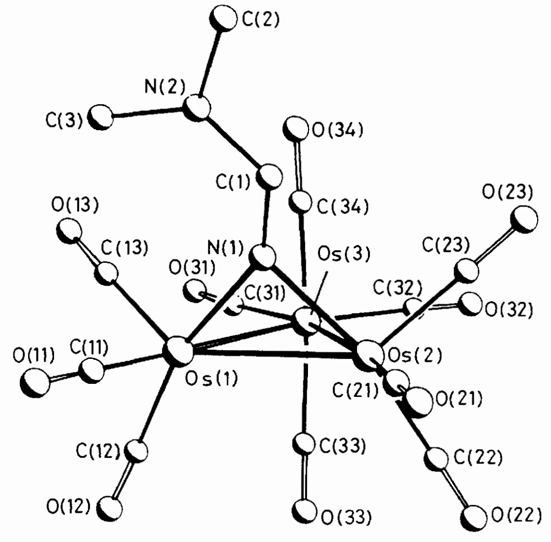


Figure 2. Molecular structure of $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}]$ (**2**) including the atom numbering scheme

When the initially obtained precipitate and solution of complex (**1**) in hexane were heated to reflux the yellow colour of the solution changed to russet brown and an i.r. spectrum indicated that partial dissociation to starting materials had taken place. After *ca.* 8 min, however, the solution had again become yellow and, after work-up, the complex $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}]$ (**2**) was obtained from the solution in high yield. No other osmium complexes were present in significant concentrations and, in this respect, the reaction differs from that of $[Os_3H_2(CO)_{10}]$ with CF_3CN which, in addition to a product analogous to (**2**), gives a second isomer, $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NHCCF_3)(CO)_{10}]$ in approximately the same yield.[1]

Table 2. Selected bond lengths (Å) and angles (°) for $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}]$ (**2**)

Os(1)–Os(2)	2.795(1)	Os(1)–N(1)	2.061(11)
Os(1)–Os(3)	2.843(1)	Os(2)–N(1)	2.078(10)
Os(2)–Os(3)	2.846(1)	N(1)–C(1)	1.30(2)
Os(1)–C(11)	1.91(2)	C(1)–N(2)	1.37(2)
Os(1)–C(12)	1.90(2)	N(2)–C(2)	1.43(2)
Os(1)–C(13)	1.89(2)	N(2)–C(3)	1.42(2)
Os(2)–C(21)	1.94(2)	Os(3)–C(31)	1.93(2)
Os(2)–C(22)	1.93(2)	Os(3)–C(32)	1.95(2)
Os(2)–C(23)	1.88(2)	Os(3)–C(33)	1.96(2)
		Os(3)–C(34)	1.93(2)
Os(2)–Os(1)–Os(3)	60.6(1)	Os(2)–Os(1)–N(1)	47.8(3)
Os(1)–Os(2)–Os(3)	60.5(1)	Os(3)–Os(1)–N(1)	81.2(4)
Os(1)–Os(3)–Os(2)	58.8(1)	Os(1)–Os(2)–N(1)	47.3(3)
Os(1)–N(1)–Os(2)	84.9(4)	Os(3)–Os(2)–N(1)	80.8(3)
Os(1)–N(1)–C(1)	147.9(10)	N(1)–C(1)–N(2)	128.1(14)
Os(2)–N(1)–C(1)	126.3(9)	C(1)–N(2)–C(2)	116.6(13)
Os(2)–N(2)–C(3)	119.3(13)	C(1)–N(2)–C(3)	124.1(13)

The identity of complex (**2**) was initially established from spectroscopic data (Table 1) and its molecular structure was then investigated in more detail by *X*-ray analysis.

(*b*) *X-Ray Crystal Structure of Compound* (**2**).—The structure of (**2**) is shown in Figure 2 and selected bond parameters are listed in Table 2. The molecule comprises an isosceles triangle of osmium atoms with ten terminal carbonyl groups, four being bonded to the unique osmium atom and three to each of the other two. The short osmium–osmium vector is bridged by nitrogen atom N(1) of the organic ligand and, although the hydride ligand was not located directly, the disposition of the carbonyl ligands indicates that it too bridges Os(1)–Os(2) on the opposite side of the metal-atom triangle to N(1). The atoms Os(1), Os(2), N(1), C(1), N(2), C(2), C(3) exhibit near-exact planarity and the angle between this plane and that of the metal-atom triangle is 108.5°. The planarity of the ligand suggests that there must be some multiple bonding between N(2) and C(1) as well as between N(1) and C(1), involving the *p* orbitals on each of these atoms perpendicular to the plane of the ligand. Multiple bonding between C(1) and N(1) is confirmed by the C(1)–N(1) bond length of 1.30(2) Å which is comparable to that found in related structures,[5–9] and the C(1)–N(2) bond length of 1.37(2) Å, which whilst significantly longer than C(1)–N(1) is still considerably shorter than that expected for a single bond. The multiple-bond character in the C(2)–N(1) bond is not, however, sufficient to prevent rotation about this bond at room temperature which is rapid on the n.m.r. time-scale, since only a single ^1H n.m.r. resonance due to the two methyl groups is observed.

The structure of (**2**) is similar to that of a variety of $[Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}]$ compounds, where X is a three-electron donor. In particular the bonding in the Os(μ-H)(μ-N)Os unit follows the same trends as in a series of related molecules.[10] The bridged Os(1)–Os(2) bond is *ca.* 0.05 Å shorter than the average value of 2.845(2) Å for the two unbridged Os–Os bonds, and all these distances are shorter than the bond length of 2.877(2) Å in $[Os_3(CO)_{12}]$.[11] The resultant Os(1)–Os(2) distance not only indicates the electronic bond-shortening influence of the bridgehead nitrogen atom, which counteracts the known bond-lengthening influence of a bridging hydride,[6] but also is consistent with the observation that the reduced steric influence of a small bridgehead atom permits a shorter bridged metal–metal distance.[12]

(*c*) *Reaction of* $[Os_3H_2(CO)_9(PEt_3)]$ *with* Me_2NCN.—The reaction of $[Os_3H_2(CO)_9(PMe_2Ph)]$ with CF_3CN proceeds in an analogous fashion to that of $[Os_3H_2(CO)_{10}]$ with this substrate and gives an isomeric mixture of products containing either the (μ-$NCHCF_3$) or the (μ-η^2-$NHCCF_3$) ligand.[13] Using $[Os_3H_2(CO)_9(PEt_3)]$ and with Me_2NCN as the substrate, however, t.l.c. indicated that only one product was present in significant yield and this was identified by mass and ^1H n.m.r. spectroscopy as $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_9(PEt_3)]$ (**3**). The ^1H n.m.r. spectrum of (**3**) shows two sets of signals for both the CH and the Me protons, these presumably being due to the presence of *syn* (**3a**) and *anti* (**3b**) isomers (Figure 1). A similar mixture of *syn* and *anti* isomers of $[Os_3(\mu\text{-}H)(\mu\text{-}NCHCF_3)(CO)_9(PMe_2Ph)]$ was obtained from the reaction of $[Os_3(\mu\text{-}H)(\mu\text{-}NCHCF_3)(CO)_{10}]$ with PMe_2Ph, and these isomers, though not separable by t.l.c. were isolated by hand-picking of crystals.[13] The failure to separate (**3a**) and (**3b**) by t.l.c. could be due to relatively rapid isomer interconversion (albeit not on the n.m.r. time-scale) resulting from a low degree of restricted rotation around the C(1)–N(1) bond. This does not seem unreasonable in the light of the expected competition between the lone pairs of electrons on N(1) and N(2) for the vacant *p* orbital on the carbon atom, C(1), in complex (**3**).

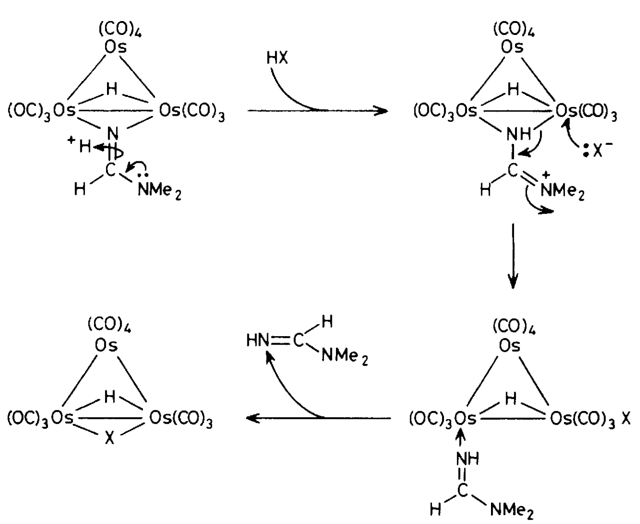
Complex (**3**) may also be synthesised [again as an inseparable mixture of (**3a**) and (**3b**)] by refluxing (**2**) with PEt_3 in hexane solution. The yield obtained by this route is significantly lower than *via* the reaction of $[Os_3(\mu\text{-}H)_2(CO)_9(PEt_3)]$ with Me_2NCN.

(*d*) *Reactions of* $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}]$ (**2**) *with Strong Acids*.—Addition of an excess of trifluoroacetic acid to a dichloromethane solution of complex (**2**) at room temperature gave, after 15 min at room temperature, a pale yellow solution from which the known complex[14] $[Os_3(\mu\text{-}H)(\mu\text{-}O_2CCF_3)(CO)_{10}]$ was isolated in near quantitative yield. With HCl gas in place of CF_3CO_2H a similar yield of $[Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}]$ was obtained.

In an attempt to elucidate the mechanism of this reaction the experiment with CF_3CO_2H was repeated at −60 °C and the changes monitored by ^1H n.m.r. spectroscopy. One drop of the acid was added to a solution of complex (**2**) in [$^2H_2$]dichloromethane at 0 °C in an n.m.r. tube which was then rapidly cooled to −60 °C in the spectrometer. The spectrum showed no trace of starting material and was in accord with that expected for the protonated species $[Os_3(\mu\text{-}H)(\mu\text{-}NHCHNMe_2)(CO)_{10}]^+$ (**4**) (Figure 1). Thus, in addition to peaks due to excess of CF_3CO_2H and the bridging hydride ligand (at δ −12.35), two doublet signals each of relative intensity 1 were observed at δ 7.07 and 5.20 [*J*(HH) = 18.1 Hz] corresponding respectively to the coupled CH and NH protons. Singlet resonances, each of relative intensity 3, at δ 3.16 and 2.68, may be assigned to the two non-equivalent NCH_3 groups which are now locked in position by the multiple bond between the C and N atoms corresponding to C(1) and N(2) in complex (**2**). This has now become a full double bond by virtue of the protonation of the lone pair of electrons on N(1). The structure proposed for (**4**) is closely related to that found for $[Os_3(\mu\text{-}H)(\mu\text{-}CHCHNEt_2)(CO)_{10}]$.[15] Protonation of N(2) in (**2**) as an alternative to protonation of N(1) cannot be entirely excluded but seems less likely on the basis of the n.m.r. results. Such protonation would almost certainly not have led to the observation of inequivalent methyl groups in complex (**4**) and coupling between the NH proton and the methyl protons might have been expected.

On warming to room temperature the signals due to complex (**4**) diminish in intensity and new signals appear at δ 3.20, 2.78, −10.30, and −11.96. The identity of the species giving rise to these signals could not be established but, after several hours at room temperature, they were no longer seen and the only metal hydride-containing species present in solution was $[Os_3(\mu\text{-}H)(\mu\text{-}O_2CCF_3)(CO)_{10}]$. There were also a number of small peaks in the region δ 0—10 which presumably result from decomposition of the ejected organic ligand.

A possible mechanism for the reaction of HX with complex (**2**) is shown in the Scheme and, in an attempt to isolate other intermediates, the reaction of (**2**) with an acid containing a poorly co-ordinating anion, $HBF_4\cdot Et_2O$, was investigated. After 0.5 h at room temperature, excess of acid was neutralised with $NaHCO_3$ and the known compounds $[Os_3(\mu\text{-}H)(\mu\text{-}$



Scheme. Possible mechanism for the reaction of complex (**2**) with HX

OEt)(CO)$_{10}$][14] and [Os$_3$(μ-H)(μ-OH)(CO)$_{10}$][16,17] were then identified spectroscopically as the only osmium-containing species present in significant amounts. The (μ-OEt) ligand is presumably scavenged from the HBF$_4$·Et$_2$O, whilst the (μ-OH) ligand must come from trace water present in the reaction mixture. The formation of the (μ-OH) complex presumably results from water reacting as a weak acid in the presence of HBF$_4$·Et$_2$O (see below), but it is more difficult to postulate a mechanism for the formation of the (μ-OEt) complex.

(*e*) *Reactions of* [Os$_3$(μ-H)(μ-NCHNMe$_2$)(CO)$_{10}$] *with Weak Acids in the Presence of* HBF$_4$·R$_2$O (R = Me *or* Et).—Reaction of complex (**2**) with acetic acid led to no colour change and, after several hours at room temperature, removal of the solvent and the acid *in vacuo* gave essentially quantitative recovery of the starting material. Presumably acetic acid is not a sufficiently strong acid to protonate (**2**) and destabilise it with respect to ejection of the bridging (N=CHNMe$_2$) ligand. On addition of HBF$_4$·Et$_2$O to a solution of (**2**) and glacial acetic acid in CH$_2$Cl$_2$, however, there is an immediate colour change and, after 20 min at room temperature followed by neutralisation of the excess of acid with NaHCO$_3$, the known complex [Os$_3$(μ-H)(μ-O$_2$CCH$_3$)(CO)$_{10}$][14] was isolated in near-quantitative yield after work-up. This reaction may be understood in terms of the mechanism shown in the Scheme, with the strong acid, HBF$_4$·Et$_2$O, bringing about protonation of complex (**2**) and the weak acid, CH$_3$CO$_2$H, providing the counter ion.

Weaker acids than acetic acid, including water and alcohols, were found to react in the same fashion, although product yields were lower. Thus using similar conditions and work-up procedures to those employed in the reaction of complex (**2**) with CH$_3$CO$_2$H, water gives a *ca.* 60% yield of [Os$_3$(μ-H)(μ-OH)(CO)$_{10}$] together with unreacted starting material, and methanol gives a 75% yield of [Os$_3$(μ-H)(μ-OMe)(CO)$_{10}$],[17] again with unreacted starting material as the only other complex present in significant concentration. Ethylene glycol, HOCH$_2$CH$_2$OH, in excess also reacts to give a 65% yield of the previously unreported species [Os$_3$(μ-H)(μ-OCH$_2$CH$_2$OH)(CO)$_{10}$] (**5**) (Figure 1) which was characterised by microanalysis and its i.r., mass, and ^{1}H n.m.r. spectra (Table 1). Attempts to prepare a cluster containing two Os$_3$ units, linked *via* an OCH$_2$CH$_2$O bridge, by using a deficiency of ethylene glycol in the above reaction were not successful.

Since the formation of complex (**2**) from [Os$_3$H$_2$(CO)$_{10}$] is quantitative, the reaction of (**2**) with acids, HX, either alone or in the presence of HBF$_4$·R$_2$O, provides a route to complexes of the type [Os$_3$(μ-H)(μ-X)(CO)$_{10}$] in yields at least as high {based on [Os$_3$(CO)$_{12}$]} as those obtained by previously published methods starting from [Os$_3$(CO)$_{10}$(C$_6$H$_8$)][14] or [Os$_3$(CO)$_{10}$(NCMe)$_2$].[18]

(*f*) *Thermolysis of Complex* (**2**).—The complex [Os$_3$(μ-H)(μ-NCHCF$_3$)(CO)$_{10}$] is unchanged after several hours in refluxing octane at 125 °C but loses a carbonyl ligand at higher temperatures to give [Os$_3$(μ-H)(μ$_3$-η^2-NCHCF$_3$)(CO)$_9$] in low yield together with considerable decomposition.[1] Complex (**2**) is similarly resistant to thermolysis but, after 10 h in refluxing decane (174 °C), no traces of starting material remained and a pale yellow complex (**6**) giving a molecular ion in its mass spectrum at *m/e* 900 was obtained in *ca.* 30% yield together with much brown tarry material. This mass spectrum is consistent with (**6**) being formed by loss of a CO group from (**3**), but the i.r. spectrum of (**6**) (Table 1) is quite different from that of [Os$_3$(μ-H)(μ$_3$-η^2-NCHCF$_3$)(CO)$_9$] and closely resembles that of the isomeric complex [Os$_3$(μ-H)(μ$_3$-η^2-NHCCF$_3$)(CO)$_9$].[1] The ^{1}H n.m.r. spectrum of (**6**) is also more consistent with a complex of this latter type showing, in addition to a metal hydride singlet at δ −15.76, two singlet resonances due to non-equivalent methyl groups and a rather broad unresolved signal at δ 5.62 which may be assigned to an NH proton. This proton is also revealed by a stretching vibration at 3 309 cm^{-1} in the i.r. spectrum of (**6**) and, on the basis of the spectroscopic evidence, we formulate (**6**) as [Os$_3$(μ-H)(μ$_3$-η^2-NHCNMe$_2$)(CO)$_9$] with the structure shown in Figure 1. The non-equivalence of the methyl groups observed in the ^{1}H n.m.r. spectrum can then be attributed to restricted rotation about the Me$_2$N–C bond, and suggests that there is significant overlap between the lone pair of electrons on the NMe$_2$ nitrogen atom and the appropriate *p* orbital on carbon. Unfortunately, despite repeated attempts, complex (**6**) could not be obtained in a crystalline form suitable for the *X*-ray diffraction study needed to confirm the above suggestion.

In an attempt to reverse the thermolysis reaction and perhaps obtain the other isomer of (**2**), complex (**6**) was kept under an atmosphere of CO, first at room temperature for 18 h then at 80 °C (refluxing hexane) for 6 h. At the conclusion of this experiment (**6**) was recovered unchanged from solution.

(*g*) *Hydrogenation of Complex* (**2**).—Treatment of complex (**2**) with hydrogen gas at 1 atm pressure at 69 °C led to complete recovery of starting material after 12 h. After 18 h at 140 °C under 50 atm of hydrogen, however, no starting material remained and [Os$_4$(μ-H)$_4$(CO)$_{12}$] was the only osmium complex which could be recovered from solution. At intermediate temperatures mixtures of starting material and this osmium complex were obtained. The reaction of (**2**) with hydrogen thus differs from that of [Os$_3$(μ-H)(μ-NCHCF$_3$)(CO)$_{10}$] with hydrogen, which led to complexes containing the partially hydrogenated ligand.[2] Presumably the ligand in (**2**) is also hydrogenated but is then more readily lost from the complex to give [Os$_3$H$_2$(CO)$_{10}$]. Under the conditions of the experiment this would be rapidly converted into the observed product.[19] The fate of the hydrogenated ligand was not determined.

Experimental

Unless otherwise stated all experiments were carried out in an atmosphere of dry nitrogen. Dry, oxygen-free solvents were used when appropriate. Solvents were distilled from an appropriate drying agent and were stored over 4A or 5A molecular sieves. Octane was washed with concentrated H$_2$SO$_4$, shaken with Na$_2$CO$_3$, and stored over sodium wire. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using 0.5-mm sodium chloride cells and were calibrated with CO gas. Mass spectra were recorded on an A.E.I. MS12 spectrometer using tris(perfluoroheptyl)-*s*-triazine introduced indirectly as calibrant. Proton n.m.r. spectra were recorded on Bruker WH400 and WD250, and Varian XL-100-12 and CFT-20 instruments in the Fourier-transform mode, and solvent resonances were used as secondary standards to calibrate spectra.

All chromatography was carried out on commercial Merck t.l.c. plates coated with a 0.25-mm layer of silica. The plates were loaded by careful application of the mixture in dichloromethane and products were also extracted with this solvent. Microanalyses were carried out at the Chemical Laboratory, University of Cambridge. The complexes [Os$_3$H$_2$(CO)$_{10}$][19] and [Os$_3$H$_2$(CO)$_9$(PEt$_3$)][20] were prepared by standard literature methods.

Preparations.—[Os$_3$H$_2$(NCNMe$_2$)(CO)$_{10}$] (**1**). A solution of [Os$_3$H$_2$(CO)$_{10}$] (0.05 g, 0.059 mmol) in hexane (15 cm^3) was treated with Me$_2$NCN (0.05 cm^3, 0.070 g, 1.00 mmol). The purple solution instantly became pale yellow and, after about 15 s, a copious yellow precipitate was obtained. After stirring for 5 min the solution was taken to dryness under reduced pressure yielding more of complex (**1**) as a pale yellow powder; yield 99% (Found: C, 17.0; H, 0.9; N, 3.0. C$_{13}$H$_8$N$_2$O$_{10}$Os$_3$ requires C, 16.9; H, 0.9; N, 3.0%).

$[Os_3H(NCHNMe_2)(CO)_{10}]$ (**2**). A solution of $[Os_3H_2(CO)_{10}]$ (0.40 g, 0.469 mmol) in hexane (125 cm^3) was treated with Me_2NCN (0.75 cm^3, 1.05 g, 15.0 mmol) to give the pale yellow solution and a precipitate of complex (**1**) as above. The solution was brought to reflux whereupon the precipitate redissolved to give a russet-brown solution, which, after 8 min at reflux, had again changed to a bright yellow. After cooling to room temperature, solvent was removed under reduced pressure to give an orange gum which was redissolved in diethyl ether. The ether was removed and the solid redissolved three or four times until a bright yellow solid remained. This was redissolved in the minimum quantity of CH_2Cl_2 and placed on t.l.c. plates. One elution with CH_2Cl_2–hexane (1:9) gave a bright yellow band (together with several very faint yellow bands at higher and lower R_f values) which was crystallised by cooling a hot saturated hexane solution to room temperature yielding yellow platelets, 0.330 g (76%) (Found: C, 17.0; H, 0.9; N, 3.0. $C_{13}H_8N_2O_{10}Os_3$ requires C, 16.9; H, 0.9; N, 3.0%).

$[Os_3H(NCHNMe_2)(CO)_9(PEt_3)]$ (**3**). A solution of $[Os_3H_2(CO)_9(PEt_3)]$ (0.050 g, 0.053 mmol) in hexane (25 cm^3) was treated with Me_2NCN (0.5 cm^3, 0.70 g, 10.0 mmol). The solution promptly changed colour from purple-grey to pale yellow, but a sample eluted at this stage with CH_2Cl_2–hexane (1:3) on a t.l.c. chip gave one major grey spot, corresponding to $[Os_3H_2(CO)_9(PEt_3)]$, together with several other faint yellow bands. After refluxing for 10 min, however, no trace of starting material remained and the solution was bright yellow. The solvent was removed under reduced pressure and the orange oil remaining was treated several times with diethyl ether as in the preparation of complex (**2**) until it yielded a yellow solid. This was dissolved in the minimum of CH_2Cl_2 and placed on t.l.c. plates. Two elutions with CH_2Cl_2–hexane (1:3) gave one bright yellow band with a few very faint yellow bands above and below it. The major band was recrystallised by cooling a warm hexane solution at room temperature to give clumps of tiny needle-shaped orange crystals of (**3**). Yield 0.043 g (80%) (Found: C, 21.5; H, 2.1; N, 2.6; P, 3.2. $C_{18}H_{23}N_2O_9Os_3P$ requires C, 21.3; H, 2.3; N, 2.8; P, 3.1%).

Reactions of Complex (**2**) *with Strong Acids*.—(*a*) *With* CF_3CO_2H. A solution of complex (**2**) (0.050 g, 0.054 mmol) in CH_2Cl_2 (10 cm^3) was treated with CF_3CO_2H (0.10 cm^3, 1.35 mmol) to give an immediate colour change from bright yellow to amber-orange which reverted within 90 s to pale yellow. After 15 min the solvent and excess of acid were removed *in vacuo* yielding a yellow solid which was identified by its i.r., ^1H n.m.r., and mass spectra as the known complex $[Os_3H(O_2CCF_3)(CO)_{10}]$.[14] Yield, 0.049 g (95%).

(*b*) *With* HCl. Hydrogen chloride gas was passed through a solution of complex (**2**) (0.025 g, 0.027 mmol) in CH_2Cl_2 (10 cm^3). The colour of the solution changed from bright yellow to a paler shade then reverted to bright yellow, all within 30 s, and a test t.l.c. chip at this stage showed that reaction was complete. Removal of the solvent under reduced pressure gave a yellow solid which was identified by means of its i.r. spectrum as the known complex $[Os_3H(Cl)(CO)_{10}]$.[3] Yield, 0.0245 g (100%).

(*c*) *With* $HBF_4 \cdot Et_2O$. A solution of complex (**2**) (0.044 g, 0.048 mmol) in CH_2Cl_2 (10 cm^3) was treated with $HBF_4 \cdot Et_2O$ (0.10 cm^3). The colour of the solution changed from bright orange to yellow over 25 min and it was then shaken with excess of $NaHCO_3$ for 5 min to neutralise the acid. After filtration through Celite, solvent was removed under reduced pressure to give an orange-yellow gum which was redissolved in the minimum quantity of CH_2Cl_2 and applied to t.l.c. plates. Elution with dichloromethane–hexane (1:6) gave two yellow bands separated by several other very faint bands. The yellow band with the higher R_f value yielded a yellow solid, on evaporation of the solvent, which was recrystallised by cooling a saturated solution in warm hexane to give yellow blocks. These were identified by i.r., mass, and ^1H n.m.r. spectroscopy as the known complex $[Os_3H(OEt)(CO)_{10}]$[14] (0.025 g, 58%). The other yellow band also yielded a yellow solid which was identified on the basis of its i.r. and mass spectra as the known complex $[Os_3H(OH)(CO)_{10}]$[16,17] (0.008 g, 21%).

Reactions of Complex (**2**) *with Weak Acids in the Presence of* $HBF_4 \cdot R_2O$.—(*a*) *With* CH_3CO_2H. A solution of complex (**2**) (0.025 g, 0.027 mmol) and glacial acetic acid (0.05 cm^3, 0.833 mmol) in CH_2Cl_2 (10 cm^3) was treated with $HBF_4 \cdot Et_2O$ (0.05 cm^3). The initially orange solution changed to pale yellow over about 20 min and the acid was then neutralised with an excess (*ca.* 0.5 g) of $NaHCO_3$. The solution was stirred for 5 min and was then filtered through Celite. Removal of the solvent under reduced pressure yielded a yellow gum which, after removal of all traces of CH_3CO_2H *in vacuo*, became a pale yellow solid. This was identified by i.r., ^1H n.m.r., and mass spectroscopy as the known complex $[Os_3H(O_2CMe)(CO)_{10}]$[14] (0.024 g, 97%).

(*b*) *With* MeOH. A solution of complex (**2**) (0.025 g, 0.027 mmol) and methanol (0.5 cm^3) in CH_2Cl_2 (10 cm^3) was treated with $HBF_4 \cdot Me_2O$ (0.2 cm^3). After 0.5 h the solution had become a clear yellow and it was then treated as in (*a*) to give a yellow oil after removal of solvent. This was applied to the t.l.c. plates which were then eluted with dichloromethane–hexane (1:7) to give two yellow bands. The more intense band, with the higher R_f value, gave a yellow solid, identified by its i.r. and mass spectrum as the known complex $[Os_3H(OMe)(CO)_{10}]$[17] (0.018 g, 75%). The weaker band gave a yellow solid identified by its i.r. spectrum as unreacted $[Os_3H(NCHNMe_2)(CO)_{10}]$.

(*c*) *With water*. A solution of complex (**2**) (0.025 g, 0.027 mmol) in CH_2Cl_2 (5 cm^3) containing water (0.1 cm^3) was treated with $HBF_4 \cdot Me_2O$ (0.15 cm^3). After 15 min the solution had become orange-yellow and it was then treated as in (*a*) to give a yellow oil after removal of solvent. This was applied to t.l.c. plates which were eluted with dichloromethane–hexane (1:1) to give two yellow bands. The band with the higher R_f value gave a yellow solid identified by i.r. spectroscopy as unreacted (**2**) (0.008 g, 32%). The band with the lower R_f value gave a yellow solid identified by i.r. and mass spectroscopy as $[Os_3H(OH)(CO)_{10}]$ (0.014 g, 60%).

(*d*) *With* $HOCH_2CH_2OH$. A solution of complex (**2**) (0.100 g, 0.108 mmol) in CH_2Cl_2 (20 cm^3) was treated with $HOCH_2CH_2OH$ (0.5 cm^3). After vigorous stirring a separate layer of $HOCH_2CH_2OH$ was still present and this was removed with a pipette (*ca.* 0.3 cm^3). To the remaining solution $HBF_4 \cdot Me_2O$ (0.5 cm^3) was added, giving an orange solution with a yellow-orange precipitate. Further addition of $HBF_4 \cdot Me_2O$ (0.5 cm^3) caused this precipitate to redissolve. After 1 h the solution was neutralised with excess of $NaHCO_3$ and heated as in (*a*) to give, after removal of solvent, a yellow oil. This was applied to t.l.c. plates and elution with dichloromethane–hexane (1:1) gave two yellow bands. The band with the higher R_f value gave a brownish yellow gum, shown by i.r. spectroscopy to be impure $[Os_3H(OMe)(CO)_{10}]$.[17] The lower band yielded a yellow solid which was recrystallised by cooling a warm saturated hexane solution to room temperature to give amber rhomboids of complex (**5**) (0.064 g, 65%) (Found: C, 15.6; H, 0.7. $C_{12}H_6O_{12}Os_3$ requires C, 15.8; H, 0.7%).

X-Ray Structure Determination of Complex (**2**).—Suitable crystals of $[Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}]$ (**2**) were obtained as yellow plates from hexane solution.

Crystal data. $C_{13}H_8N_2O_{10}Os_3$, $M = 992.81$, triclinic, $a = 7.403(1)$, $b = 9.302(2)$, $c = 15.067(4)$ Å, $\alpha = 94.75(2)$, $\beta = 95.13(2)$, $\gamma = 96.98(2)^\circ$, $U = 1\,021$ Å^3 (by least-squares refinement of diffractometer angles for 15 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P\bar{1}$ (no. 2, by suc-

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for [$Os_3(\mu\text{-}H)(\mu\text{-}NCHNMe_2)(CO)_{10}$] (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	−58(1)	1 149(1)	1 651(1)	C(21)	1 492(24)	832(21)	4 179(10)
Os(2)	613(1)	2 275(1)	3 444(1)	O(21)	2 045(21)	51(17)	4 623(9)
Os(3)	−756(1)	4 031(1)	2 145(1)	C(22)	2 707(23)	3 730(18)	3 773(10)
N(1)	−1 432(14)	758(14)	2 755(7)	O(22)	3 975(17)	4 512(13)	3 976(8)
C(1)	−2 686(19)	−55(17)	3 108(10)	C(23)	−802(21)	3 050(19)	4 292(11)
N(2)	−4 017(16)	−1 101(14)	2 681(8)	O(23)	−1 698(17)	3 554(18)	4 792(9)
C(2)	−5 200(24)	−1 861(22)	3 235(13)	C(31)	−1 655(24)	4 578(18)	996(13)
C(3)	−4 252(24)	−1 478(23)	1 740(11)	O(31)	−2 291(24)	4 922(18)	337(10)
C(11)	398(19)	−826(15)	1 463(9)	C(32)	−902(27)	5 762(20)	2 941(12)
O(11)	661(15)	−1 982(11)	1 343(8)	O(32)	−949(23)	6 793(17)	3 355(11)
C(12)	1 684(18)	1 836(16)	882(11)	C(33)	1 801(22)	4 611(19)	1 944(11)
O(12)	2 758(15)	2 181(13)	412(8)	O(33)	3 248(15)	4 987(13)	1 834(9)
C(13)	−2 019(21)	1065(18)	748(10)	C(34)	−3 114(22)	3 074(18)	2 375(10)
O(13)	−3 176(14)	1 126(13)	203(7)	O(34)	−4 544(15)	2 562(17)	2 475(10)

cessful refinement), D_m not measured, $Z = 2$, $D_c = 3.228$ g cm^{-3}, $F(000) = 816$, crystal dimensions $0.09 \times 0.37 \times 0.42$ mm, $\mu(\text{Mo-}K_\alpha) = 186.62$ cm^{-1}.

Data collection and processing.[21] Syntex $P2_1$ diffractometer, ω—2θ mode with scan range from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$, scan speed 2.5—29.3° min^{-1}, graphite-monochromated Mo-K_α radiation; 2 816 reflections measured ($3.0 < 2\theta < 50.0°$, $+h, \pm k, \pm l$), 2 365 unique [merging $R = 0.008$ after empirical absorption correction based on 408 azimuthal scan data from 17 independent reflections (maximum, minimum transmission factors 0.99, 0.32)], giving 2 359 with $F > 3\sigma(F)$. No crystal decomposition during data collection.

Structure analysis and refinement. Direct methods (Os atoms) followed by Fourier difference techniques. Blocked-cascade least-squares refinement with all non-hydrogen atoms anisotropic and methyl hydrogens in idealised positions with one, overall, refined U_{iso} [= 0.18(4) Å^2]. The weighting scheme $w = [\sigma^2(F) + 0.0015F^2]^{-1}$ with $\sigma(F_o)$ from counting statistics[21] gave satisfactory agreement analyses. Final R and R' were 0.039 and 0.041.

All computations were performed on the IBM 3081 computer at the University of Cambridge using a modified version of SHELX 76.[22] Neutral atom scattering factors[23] were employed throughout. Final atomic co-ordinates for the non-hydrogen atoms are presented in Table 3.

References

1 Z. Dawoodi, M. J. Mays, and P. R. Raithby, *J. Organomet. Chem.*, 1981, **219**, 103.

2 Z. Dawoodi, M. J. Mays, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1984, 433.

3 A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, 1976, **114**, 313.

4 J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. DeBoer, *J. Am. Chem. Soc.*, 1975, **97**, 4145.

5 Z. Dawoodi, M. J. Mays, and A. G. Orpen, *J. Organomet. Chem.*, 1981, **219**, 251.

6 M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 1843.

7 M. R. Churchill and K-K. G. Lin, *Inorg. Chem.*, 1975, **14**, 1675.

8 D. Bright and O. S. Mills, *Chem. Commun.*, 1967, 245.

9 M. J. Mays, D. W. Prest, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1982, 2021.

10 M. R. Churchill, F. J. Hollander, J. R. Shapley, and J. B. Keister, *Inorg. Chem.*, 1980, **19**, 1272; M. R. Churchill and H. J. Wasserman, *ibid.*, 1981, **20**, 1580; M. R. Churchill and H. J. Wasserman, *ibid.*, p. 2905; K. Burgess, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1982, 263; B. F. G. Johnson, J. Lewis, P. R. Raithby, and S. W. Sankey, *J. Organomet. Chem.*, 1982, **228**, 135.

11 M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.

12 M. R. Churchill and R. G. Lashewycz, *Inorg. Chem.*, 1979, **18**, 1926, 3261.

13 R. D. Adams, D. A. Katahira, and L. W. Yang, *J. Organomet. Chem.*, 1981, **219**, 85.

14 E. G. Bryan, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, 1328.

15 M. R. Churchill and R. A. Lashewycz, *Inorg. Chem.*, 1979, **18**, 848.

16 C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1973, **57**, C84.

17 B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc. A*, 1968, 2859.

18 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407.

19 S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942.

20 A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, 1975, **88**, C21.

21 B. F. G. Johnson, P. R. Raithby, and C. Zuccaro, *J. Chem. Soc., Dalton Trans.*, 1980, 99.

22 SHELX 76, A crystallographic structure solution package, G. M. Sheldrick, University of Cambridge, 1976.

23 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 27*th September* 1984; *Paper* 4/1663