Triosmium Clusters containing the Ligands CNH_2, NCHCN, and NCMeCN derived from Cyanide Ion, Cyanogen, and Acetonitrile

Antony J. Deeming,* Susan Donovan-Mtunzi, and Shariff E. Kabir
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ
Alejandro J. Arce and Ysaura De Sanctis
Departamento de Quimica, Universidad Simon Bolivar, Caracas, Venezuela

The addition of cyanide ion to $[Os_3H_2(CO)_{10}]$ gives $[Os_3H_2(CN)(CO)_{10}]^-$ as four isomers in solution. Subsequent protonation at nitrogen leads *via* intermediates to the aminomethylidyne complex $[Os_3H(\mu\text{-}CNH_2)(CO)_{10}]$, the characterisation of which was assisted by the synthesis of the corresponding $^{13}CNH_2$, $C^{15}NH_2$, and deuteriated analogues. Hydrogen exchange at the CNH_2 ligand is slow in neutral solution but is both acid- and base-catalysed. Rather than displacing acetonitrile from $[Os_3H(CO)_{10}(MeCN)(PMe_2Ph)]PF_6$, cyanide ion adds at MeCN to give two main isomers of $[Os_3H(NCMeCN)(CO)_9(PMe_2Ph)]$. Related complexes $[Os_3H(NCHCN)(CO)_9L]$ (L = CO or PMe_2Ph) were obtained by reaction of $[Os_3H_2(CO)_9L]$ with cyanogen (C_2N_2) at room temperature. Rotation about the C=N bonds in the iminyl complexes is sufficiently slow to allow the separation of isomers when L = PMe_2Ph. The isomeric form $[Os_3H(NHCCN)(CO)_{10}]$ was also obtained.

Although the cyanide ion is isoelectronic with carbon monoxide, only a little work has been done to incorporate cyanide into metal carbonyl compounds and no simple cyanocarbonyl clusters are apparently known. Our initial idea was to prepare anionic clusters such as $[Os_3(CN)_x(CO)_{12-x}]^{x-}$, isoelectronic with $[Os_3(CO)_{12}]$, but we have found that reactions of $[Os_3(CO)_{12-x}(MeCN)_x]$ (x = 1 or 2) with cyanide ion leads to insoluble and intractable solids which are probably mixtures. This paper describes the incorporation of cyanide into Os_3 clusters as aminomethylidyne (CNH_2) and the cyanoiminyl ligands N=CR(CN) (R = H or Me) and NH=C(CN). These are interesting new ligands in clusters but we have been unable to synthesise simple cyano-clusters except for isomers of $[Os_3H_2(CN)(CO)_{10}]^-$ in solution.

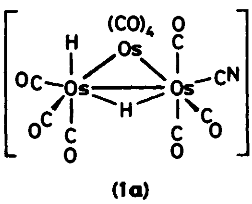
Results and Discussion

An Aminomethylidyne Cluster.—The purple dihydride $[Os_3H_2(CO)_{10}]$ is known to form yellow adducts $[Os_3H_2(CO)_{10}L]$ with neutral ligands L (L = PR_3, CO, RNC, *etc.*) in which one of the hydride ligands becomes terminally bonded.[1–8] Hydride ion as KH or halide ion as $[N(PPh_3)_2]X$, where X = Cl, Br, or I, adds similarly to give the anions $[Os_3H_2X(CO)_{10}]^-$ which may be isolated as $[N(PPh_3)_2]^+$ salts.[6,9] We have now added $[N(PPh_3)_2]CN$ to give the anionic cluster $[N(PPh_3)_2][Os_3H_2(CN)(CO)_{10}]$, (**1**). The terminal and bridging hydride ligands rapidly exchange but ^1H, ^{13}C, and ^{15}N n.m.r. spectra at −70 °C of appropriately enriched samples of (**1**) (using 90% ^{13}CN or 98.8% $C^{15}N$) showed the compound to exist in solution as three main isomers (intensity ratio 1:2:5) and a fourth in very low concentration was observed clearly only in the ^{15}N n.m.r. spectrum (see Experimental section and Table 1 for details). These isomers each contain a terminal and a bridging hydride ligand (about δ −10 and −19 respectively). The presence of four isomers can be accounted for if the cyanide ligand can occupy each of the four non-equivalent terminal sites at one osmium atom, structures (**1a**)—(**1d**). In related compounds, tertiary phosphines have been shown to occupy just one of the equatorial sites[1–3,5] whereas smaller ligands such as hydride[9] or isocyanides[6,7] occupy axial sites and then interconverting isomers are observed. The rapid interconversion of terminal and bridging hydride ligands in these systems is well studied.[1–11]

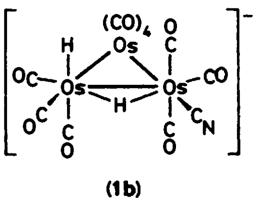
Table 1. Proton and ^{15}N n.m.r. data for the four isomers of $[Os_3H_2(CN)(CO)_{10}]^-$ (**1a**)—(**1d**)

Isomer	^1H N.m.r.[a] δ(terminal)	δ(bridging)	J(HH)/ Hz	δ(^{15}N)[b]
Major	−10.30 (d)	−19.63 (d)	4.0	−84.8
Intermediate	−10.37 (d)	−19.52 (d)	4.0	−87.1
Minor	−10.25 (d)	−19.57 (d)	4.1	−83.6
Very minor	−9.48 (d)	*c*	3.5	−86.3

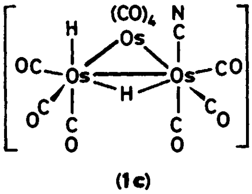
[a] Recorded in CD_2Cl_2 at −70 °C. Using ^{13}CN, the hydride signals around δ −19 become triplets, those at around δ −10 double doublets. [b] Chemical shifts relative to $MeNO_2$. [c] Obscured by the more intense signals around δ −19.



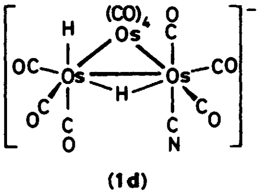
(**1a**)



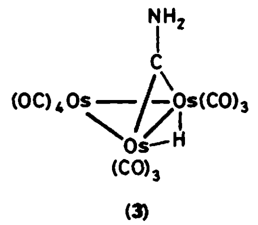
(**1b**)



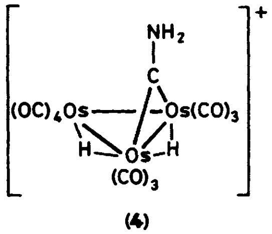
(**1c**)



(**1d**)



(**3**)

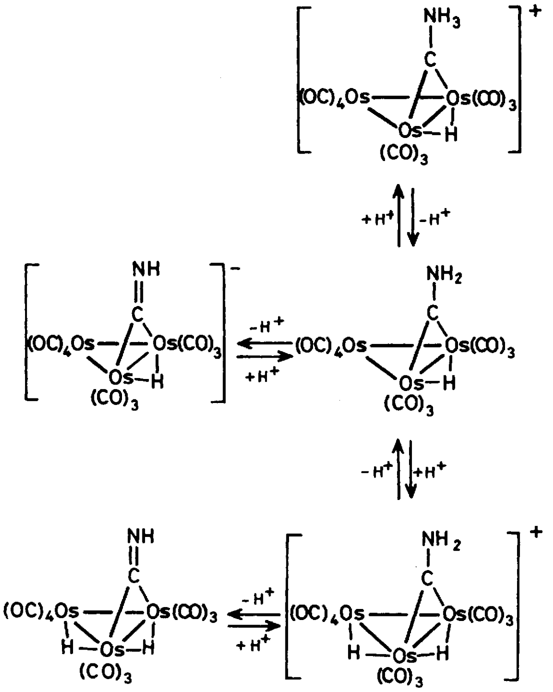


(**4**)

Table 2. Selected i.r.[a] and n.m.r.[b] data for $[Os_3H(CNH_2)(CO)_{10}]$, (3)

Ligand[c]	$\delta(^1H)$	$\delta(^{13}C$ or $^{15}N)$	$\nu(NH)^d/cm^{-1}$	$\delta(NH_2)^d/cm^{-1}$	$\nu(CN)^d/cm^{-1}$
$^{12}C^{14}NH_2$	8.65 (s)		3 427	1 642	1 482
	−16.52 (s)		3 346		
$^{13}C^{14}NH_2$	8.70 (s)	297.4 (dt)[e]	3 428	1 641	1 449
	−16.52 (d)	[$J(CNH)$ 2.6, $J(COsH)$ 5.8]	3 346		
$^{12}C^{15}NH_2$	8.83 (d)	−206.5 (t)[f]	3 418	1 633	1 471
	−16.69 (s)	[$J(NH)$ 91.5]	3 339		

[a] $^{12}C^{14}NH_2$ Compound: $\nu(CO)$ (cyclohexane) 2 101w, 2 057vs, 2 050s, 2 018vs, 2 005vs, 1 991s, 1 982m, 1 976 (sh), and 1 950vw cm^{-1}. [b] Recorded in $CDCl_3$ or CD_2Cl_2; δ in p.p.m.; *J* in Hz. [c] 90% ^{13}C or 98.8% ^{15}N as appropriate. [d] Nujol or hexachlorobutadiene; $\nu(ND)$ for CND_2 compound at 2 578 and 2 437 cm^{-1}. [e] Relative to $SiMe_4$. [f] Relative to $MeNO_2$.



Scheme.

Addition of a five-fold excess of CF_3CO_2H to compound (**1**) in CD_2Cl_2 at −70 °C gives the isomers of (**1**) in a rapidly equilibrating mixture with corresponding isomers of $[Os_3H_2(CNH)(CO)_{10}]$, (**2**), which also contain terminal and bridging hydride ligands. It is because we observe only a single set of ^1H and ^{15}N n.m.r. signals which vary with the temperature and concentration that we believe (**2**) is incompletely formed under these conditions. On standing at room temperature this solution gives, in addition to ^{15}N n.m.r. signals for (**1**) and (**2**), a triplet [δ −179.8, $J(^{15}NH)$ = 92 Hz] growing then decreasing in intensity to be replaced by another triplet [δ −206.5, $J(^{15}NH)$ = 91.5 Hz]. The triplet patterns seem likely to be due to CNH_2 groups and work-up involving t.l.c. on silica gave $[Os_3H(CNH_2)(CO)_{10}]$, compound (**3**) (30% yield), corresponding to the second triplet. Compound (**3**) was characterised by its mass spectrum ($^{192}Os_3$-based parent molecular ion at *m/e* 885) and data in Table 2. Key spectroscopic data correspond closely to those of $[Os_3H(CNMe_2)(CO)_{10}]$ derived from NMe_3[12] and of $[Os_3H(CNHBu^t)(CO)_{10}]$ formed from $[Os_3H_2(CO)_{10}]$ and Bu^tNC.[7,8] Compound (**3**) is formally derived by insertion of hydroisocyanic acid (HNC) into an Os–H bond.

Since well resolved ^{15}N–H coupling is observed at room temperature, there is no rapid proton exchange at nitrogen. Evaporation to dryness of a solution of $[Os_3H(CNH_2)(CO)_{10}]$ (**3**) in neat MeOD gives $[Os_3H(CND_2)(CO)_{10}]$ [$\nu(ND)$ 2 578 and 2 437 cm^{-1}]. However, a solution of (**3**) in $CDCl_3$ with a 10-fold excess of MeOD only gave very slow exchange, this being far from complete after 1 h at 25 °C. Addition of NEt_3 (0.1 mol per mol Os_3) or CF_3CO_2H (0.1 mol per mol Os_3) gave rapid exchange to equilibrium conditions within the time taken to obtain a ^1H n.m.r. spectrum (less than 1 min). The Scheme shows our proposals for these acid- and base-catalysed exchanges. Presumably NEt_3 catalysis involves reversible deprotonation at nitrogen but the H^+ catalysis could involve either protonation at osmium or nitrogen atoms, the most obvious nucleophilic centres. If an excess of trifluoroacetic acid is added to a chloroform solution of compound (**3**) there is complete protonation to $[Os_3H_2(CNH_2)(CO)_{10}]^+$ (**4**) which is characterised by its ^1H n.m.r. spectrum [δ −15.73 (d) and −20.14 (d), *J* = 1 Hz]. Treatment with water regenerated the deprotonated starting material (**3**). In the metal-protonated form the CNH_2 protons would be much more acidic than in (**3**) and undergo rapid exchange. We cannot, however, rule out that a reversible protonation at nitrogen, which is more rapid, is not occurring, but the nucleophilicity of the NH_2 group is certainly low. For example, there is no reaction between (**3**) and methyl iodide.

The addition of $[NBu_4]OH$ in methanol to a solution of cluster (**3**) in dichloromethane leads to $[NBu_4][Os_3H(CO)_{11}]$ as the main compound in solution but we cannot be sure that this is formed by C–N cleavage.

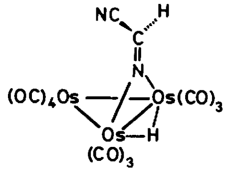
Cluster (**3**) is one of a series of known alkylidyne clusters of the type $[Os_3H(\mu\text{-}CX)(CO)_{10}]$ where X = H,[13] CH_2CHMe_2,[14] Ph,[15] OMe,[16] NMe_2,[12] *etc.* When X = H there is a donor–acceptor interaction between the osmium atom of the $Os(CO)_4$ group and the electrophilic CH group which moves as a result towards a triply bridging mode. When X is a good π donor there should be p_π–p_π bonding between X and the alkylidyne carbon atom and for compound (**3**) $\nu(CN)$ at 1 482 cm^{-1} is consistent with this. In this case there is no need for any direct bonding interaction between the CNH_2 group and the third osmium atom in the $Os(CO)_4$ group. We have illustrated (**3**) without this multiple bonding, but clearly the zwitterionic form with a positive charge at nitrogen, negative charge at osmium, and a double carbon–nitrogen bond has some contribution. The metal atoms are certainly more nucleophilic than nitrogen and are protonated, and furthermore the $\nu(CO)$ values for (**3**) are a little lower than for other members of the series $[Os_3H(\mu\text{-}CX)(CO)_{10}]$.

Cyanoiminyl Clusters.—Oxidative addition of cyanogen (NCCN) to nickel(0) complexes leads to nickel(II) dicyano complexes.[17] Using a similar approach, we treated $[Os_3(CO)_{10}$-

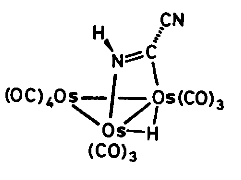
Table 3. Spectroscopic data for cyanoiminyl clusters (**5**)—(**8**)

			^{1}H N.m.r.^{c}		
Cluster	ν(CO)^a/cm^{-1}	ν(CN)^b/cm^{-1}			
[**5**) $[Os_3H^x(NCH^yCN)(CO)_{10}]$	2 107m, 2 072vs, 2 058s, 2 024vs, 2 011s, 2 003s, 1 987m	2 220w	7.59 (d)	H^y	$J(H^xH^y)$
			−14.90 (d)	H^x	0.9
(**6**) $[Os_3H^x(NH^yCCN)(CO)_{10}]$	2 108m, 2 067vs, 2 057s, 2 029vs, 2 013s, 2 003s, 1 986m	2 204w^d	10.1 (s, br)	H^y	
			−14.89 (s)	H^x	
(**7a**) $[Os_3H^x(NCH^yCN)(CO)_9(PMe_2Ph)]$	2 090s, 2 053s, 2 015vs, 2 008 (sh), 2 002 (sh), 1 990ms, 1 983ms, 1 975m, 1 954m	2 214w	6.09 (d)	H^y	$J(H^yP)$ 2.9
			2.16 (d)	Me	J 9.9
			2.06 (d)	Me	J 9.9
			−14.80 (d)	H^x	$J(H^xP)$ 7.9
(**7b**) $[Os_3H^x(NCH^yCN)(CO)_9(PMe_2Ph)]$	2 090s, 2 053s, 2 015vs, 2 005 (sh), 2 002 (sh), 1 990ms, 1 983ms, 1 975m, 1 954m	2 214w	7.44 (d)	H^y	$J(H^yP)$ 6.2
			2.09 (d)	Me	J 9.8
			2.06 (d)	Me	J 9.8
			−14.70 (d)	H^x	$J(H^xP$ 7.9)
(**8**) $[Os_3H^x(NCMe^yCN)(CO)_9(PMe_2Ph)]^e$	2 093s, 2 052vs, 2 022 (sh), 2 019vs, 2 003s, 1 994s, 1 983m, 1 975m, 1 962w		7.4 (m)	Ph	
			2.33 (d)	Me	J 10
			2.25 (d)	Me	J 10
			2.24 (s)	Me	
			2.23 (d)	Me	J 10
			2.21 (d)	Me	J 10
			−15.24 (d)	H^x	$J(H^x)$ 9
			−15.32 (d)	H^x	$J(H^x)$ 9

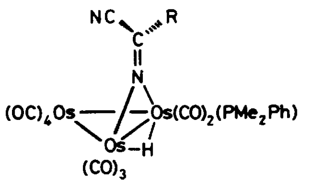
^{a} In cyclohexane. ^{b} Nujol mull. ^{c} Recorded at 200 MHz in $CDCl_3$ at 27 °C. ^{d} ν(NH) 3 271 cm^{-1} (Nujol). ^{e} Mixture of two isomers.



(**5**)

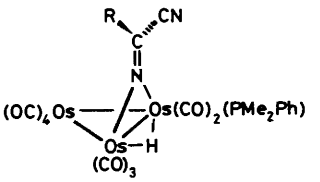


(**6**)



(**7a**) R = H

(**8a**) R = Me



(**7b**) R = H

(**8b**) R = Me

$(MeCN)_2]$ with cyanogen but did not obtain $[Os_3(CN)_2(CO)_{10}]$, only intractable materials. However, $[Os_3H_2(CO)_{10}]$ in dichloromethane reacts slowly with cyanogen to give a mixture of isomers of $[Os_3H(C_2HN_2)(CO)_{10}]$ which were separated by t.l.c. on silica. These were characterised as $[Os_3H(\mu\text{-}N{=}CHCN)(CO)_{10}]$ (**5**) (55%) and $[Os_3H(\mu\text{-}NH{=}CCN)(CO)_{10}]$ (**6**) (20%) (see Table 3). Both have very similar i.r. and n.m.r. data except for the ^{1}H n.m.r. signals for the N=CHCN and NH=CCN protons. We assign the compound giving a sharp doublet at δ 7.59 to (**5**) and the one with the broad singlet at δ 10.1 to (**6**) in the expectation that the NH signal would be broad. The cyano-groups absorb at 2 220 and 2 204 cm^{-1} for (**5**) and (**6**) respectively. To our knowledge these are the first examples of the insertion of cyanogen into metal–hydrogen bonds, only oxidative-addition products being previously obtained. However, there are several examples of compounds of the type $[Os_3H(\mu\text{-}NCHR)(CO)_{10}]$ related to (**5**)[18–21] and of the type $[Os_3H(\mu\text{-}RN{=}CR')(CO)_{10}]$ related to (**6**).[8,12,21,22]

A similar insertion reaction of cyanogen into $[Os_3H_2(CO)_9(PMe_2Ph)]$ gave only one regioisomer, that corresponding to (**5**), that is $[Os_3H(N{=}CHCN)(CO)_9(PMe_2Ph)]$ (**7**). By careful chromatography, however, this material could be separated into two isomers (**7a**) and (**7b**). The ν(CO) and ν(CN) absorptions for (**7a**) are almost indistinguishable from those of (**7b**) but there are distinct ^{1}H n.m.r. differences (Table 3). The hydride signals are very similar for (**7a**) and (**7b**) with the same value for J_{PH}. This suggests that isomerism does not result from different (*e.g.* axial and equatorial) sites of phosphine co-ordination but rather from *cis–trans* isomerisation about the C=N bond. The barrier to rotation about this bond must be sufficiently large to allow the separation of isomers.

Attempting to prepare $[Os_3H(CN)(CO)_9(PMe_2Ph)]$, we treated $[Os_3H(CO)_{10}(MeCN)(PMe_2Ph)]PF_6$ with $[NEt_4]CN$. The Experimental section describes how we prepared this hydrido-cation along with its by-product $[Os_3H(CF_3CO_2)(CO)_{10}(PMe_2Ph)]$, which thermally decarbonylates to the nonacarbonyl. We had introduced the PMe_2Ph ligand to reduce the electrophilicity of the cluster to prevent nucleophilic attack at the incorporated CN. However, the reaction with cyanide ion gave $[Os_3H(NCMeCN)(CO)_9(PMe_2Ph)]$ (**8**) which is closely related to (**7**) and likewise exists as isomers but in this case we could not separate them. These isomers are probably (**8a**) and (**8b**) but the overlap of n.m.r. signals prevented proper assignments and this remains speculative.

Experimental

The salts $[N(PPh_3)_2]CN$, $[N(PPh_3)_2]^{13}CN$, and $[N(PPh_3)_2]C^{15}N$ were prepared by reported methods using KCN, $K^{13}CN$ (90% ^{13}C), or $KC^{15}N$ (99.8% ^{15}N),[23] the enriched samples being obtained from Merck, Sharp, and Dohme (Canada) Ltd. Cyanogen (C_2N_2) was prepared by adding a saturated aqueous solution of NaCN to solid copper(II) sulphate.[24] Proton, ^{31}P, and ^{13}C n.m.r. spectra were recorded on a Varian XL200 spectrometer, ^{15}N n.m.r. spectra on a Bruker WH400 spectrometer, and i.r. spectra on a Perkin-Elmer 983 spectrometer.

Reaction of $[Os_3H_2(CO)_{10}]$.—*With* $[N(PPh_3)_2]CN$. The addition of $[N(PPh_3)_2]CN$ (0.019 g) to a purple solution of the dihydrido-cluster (0.030 g) in CD_2Cl_2 (0.5 cm^3) at -70 °C led to a yellow solution within 5 min. The ^1H n.m.r. spectrum indicated complete conversion into the anionic clusters $[Os_3H_2(CN)(CO)_{10}]^-$, isomers (**1a**)—(**1d**) (see Table 1); ν(CO) (CH_2Cl_2) 2 090w, 2 064s, 2 056vs, 2 042s, 2 005vs, 1 968m, and 1 947 (sh); ν(CN) 2 133 cm^{-1}. Using ^{13}C-labelled cyanide, $[N(PPh_3)_2]CN$ (0.019 g, 1 mol per mol Os_3) was added to a CD_2Cl_2 solution (0.5 cm^3) of $[Os_3H_2(CO)_{10}]$ (0.030 g) at -70 °C and the formation of labelled clusters was followed by ^{13}C n.m.r. spectra. The hydride signals at around δ -19 became triplets (J_{CH} = 4 Hz) and the terminal hydride signals around δ -10 became poorly resolved double doublets. Likewise ^{15}N n.m.r. spectra of a solution of $[Os_3H_2(CO)_{10}]$ (0.230 g) and $[N(PPh_3)_2]C^{15}N$ (0.146 g) in CD_2Cl_2 (3 cm^3) were recorded at -70 °C (Table 1). Treatment of this solution with CF_3CO_2H (0.153 cm^3) allowed the formation of $[Os_3H(C^{15}NH_2)(CO)_{10}]$ to be followed by ^{15}N n.m.r. spectroscopy.

With cyanide ion followed by acidification. The salt $[N(PPh_3)_2]CN$ (0.601 g) was added to a solution of the dihydride (0.946 g) in CH_2Cl_2 (25 cm^3) at -78 °C under a nitrogen atmosphere. The colour changed from purple to yellow (5 min) and after 30 min the solution was allowed to warm to room temperature. Trifluoroacetic acid (0.428 cm^3, 5 mol per mol Os_3) was added and after 20 h solid sodium hydrogencarbonate (around 0.5 g) was added. The mixture was stirred for 4 h, the solution decanted, and the solvent removed under vacuum. T.l.c. separation [SiO_2: eluant, pentane–dichloromethane (10:3 v/v)] gave a yellow band yielding a yellow solid which was recrystallised from dichloromethane–hexane mixtures to give $[Os_3H(CNH_2)(CO)_{10}]$ (**3**) as yellow crystals (0.297 g, 30%) (Found: C, 15.1; H, 0.5; N, 1.5. $C_{11}H_{13}NO_{10}Os_3$ requires C, 15.0; H, 0.35; N, 1.6%). The corresponding compounds $[Os_3H(^{13}CNH_2)(CO)_{10}]$ and $[Os_3H(C^{15}NH_2)(CO)_{10}]$ were prepared similarly from $[N(PPh_3)_2]^{13}CN$ and $[N(PPh_3)_2]C^{15}N$ respectively.

With cyanogen. Cyanogen gas was bubbled for a few minutes through a solution of the dihydride (0.267 g) in dichloromethane (25 cm^3) at -40 °C. The flask was sealed and kept at room temperature for 3 d by which time the purple solution had become yellow-brown. Removal of the solvent under reduced pressure gave a brown solid which was separated by t.l.c. [SiO_2; eluant, light petroleum (b.p. < 40 °C)–dichloromethane (10:1 v/v)] to give two yellow bands which gave $[Os_3H(NCHCN)(CO)_{10}]$, (**5**) (0.147 g, 55%), as a yellow solid (Found: C, 16.2; H, 0.2; N, 3.0. $C_{12}H_2N_2O_{10}Os_3$ requires C, 16.0; H, 0.3; N, 3.0%), and its isomer $[Os_3H(NHCCN)(CO)_{10}]$, (**6**) (0.050 g, 20%), also as a yellow solid (Found: C, 16.7; H, 0.3; N, 3.0%).

Exchange of $[Os_3H(CNH_2)(CO)_{10}]$ (**3**) *with* MeOD.—The CNH_2 compound (0.015 g) in $CDCl_3$ (0.5 cm^3) in an n.m.r. tube was treated with MeOD (0.006 g, 10-fold excess) and the ^1H n.m.r. spectrum recorded over a period. This experiment was repeated except that CF_3CO_2H (0.0002 cm^3, 0.1 mol per mol Os_3) or NEt_3 (0.0002 cm^3, 0.1 mol per mol Os_3) was added. The exchange of the CNH_2 protons with Me*OD* was followed in each case. In a synthetic scale experiment the CNH_2 compound (0.020 g) was dissolved in MeOD (3 cm^3). After 2 h at room temperature the solvent was removed to give the corresponding CND_2 compound quantitatively.

Reaction of $[Os_3H(CNH_2)(CO)_{10}]$ (**3**) *with* $[NBu_4]OH$.—A solution of compound (**3**) (0.033 g) in CH_2Cl_2 (2 cm^3) changed immediately from yellow to red on addition of $[NBu_4]OH$ (0.073 cm^3 of a 1 mol dm^{-3} solution in methanol, 2 mol per mol Os_3). The i.r. spectrum indicated that the main solute was $[NBu_4][Os_3H(CO)_{11}]$ with small quantities of an unknown compound.

Protonation of $[Os_3H(CNH_2)(CO)_{10}]$ (**3**).—Trifluoroacetic acid (0.018 cm^3, 10 mol per mol Os_3) was added to a solution of compound (**3**) (0.020 g) in $CDCl_3$ (0.5 cm^3). Proton n.m.r. spectra indicated complete conversion into $[Os_3H_2(CNH_2)(CO)_{10}]^+$, (**4**). The solution was diluted with CH_2Cl_2 (10 cm^3), treated with a few drops of water, and finally extracted with light petroleum (b.p. 30—40 °C). T.l.c. separation [SiO_2; eluant, light petroleum (b.p. 30—40 °C)–dichloromethane (10:3 v/v)] gave starting compound (**3**) (0.012 g).

Synthesis of $[Os_3H_2(CO)_9(PMe_2Ph)]$.—A method somewhat modified from that reported was used.[2] Addition of PMe_2Ph (0.042 g) to a purple solution of $[Os_3H_2(CO)_{10}]$ (0.258 g) in cyclohexane (20 cm^3) gave a yellow precipitate of $[Os_3H_2(CO)_{10}(PMe_2Ph)]$. The suspension was refluxed for 40 min and the solvent removed under vacuum. T.l.c. [SiO_2; eluant, light petroleum (b.p. < 40 °C)–dichloromethane (3:1 v/v)] gave the product as purple-brown crystals (0.175 g, 68%).

Reaction of Cyanogen with $[Os_3H_2(CO)_9(PMe_2Ph)]$.—Cyanogen was bubbled through a solution of the dihydride (0.100 g) in dichloromethane (20 cm^3) at about -40 °C. The flask was sealed and kept at room temperature for 3 d. The solvent was removed from the yellowish solution and t.l.c. separation as above gave an isomeric mixture of $[Os_3H(NCHCN)(CO)_9(PMe_2Ph)]$ (0.057 g, 57%) as a single band. The isomers in 2:1 ratio (^1H n.m.r. evidence) were separated by careful rechromatography [SiO_2; eluant, chloroform–light petroleum (b.p. < 40 °C) (1:1 v/v)].

Synthesis of $[Os_3H(CO)_{10}(MeCN)(PMe_2Ph)]PF_6$.—Trimethylamine oxide ($Me_3NO{\cdot}2H_2O$, 0.068 g, 1.25 mol per mol Os_3) was added to a solution of $[Os_3(CO)_{11}(PMe_2Ph)]$ (0.492 g) in dichloromethane (70 cm^3) and acetonitrile (6 cm^3). After 30 min the solution was filtered through silica and the solvent removed to give $[Os_3(CO)_{10}(MeCN)(PMe_2Ph)]$ (0.472 g, 95%), characterised by i.r. and n.m.r. data. The compound was redissolved in dichloromethane (30 cm^3) and CF_3CO_2H (0.353 cm^3, 10 mol per mol Os_3) added. The colour changed from orange to yellow and the solvent was removed under vacuum. A methanolic solution of NH_4PF_6 (0.020 g) was added to a solution of the osmium compound in methanol (30 cm^3) and water added dropwise to give a yellow precipitate which was recrystallised from CH_2Cl_2–Et_2O mixtures to give $[Os_3H(CO)_{10}(MeCN)(PMe_2Ph)]PF_6$ (0.372 g, 69%) as yellow crystals (Found: C, 20.55; H, 1.25; N, 1.15; P, 5.05. $C_{20}H_{15}F_6NO_{10}Os_3P_2$ requires C, 20.45; H, 1.3; N, 1.2; P, 5.25%). The solvent was removed from the mother-liquor under vacuum and the residue chromatographed [t.l.c. (SiO_2); eluant, pentane–diethyl ether (10:1 v/v)] to give $[Os_3H(CF_3CO_2)(CO)_{10}(PMe_2Ph)]$ (0.100 g, 20%) as yellow crystals from n-hexane (Found: C, 21.8; H, 1.3; O, 17.75; P, 3.0. $C_{20}H_{12}F_3O_{12}Os_3P$ requires C, 21.1; H, 1.1; O, 17.4; P, 2.8%).

Thermolysis of $[Os_3H(CF_3CO_2)(CO)_{10}(PMe_2Ph)]$.—A solution of this by-product from the above reaction (0.050 g) in heptane (25 cm^3) was heated under reflux for 16 h. Removal of the solvent and chromatography [t.l.c. (SiO_2); eluant, light petroleum (b.p. < 40 °C)–diethyl ether (10:1 v/v)] gave $[Os_3H(CF_3CO_2)(CO)_9(PMe_2Ph)]$ as yellow crystals (0.033 g, 67%) from hexane–dichloromethane mixtures (Found: C, 21.2; H, 1.1; P, 2.9. $C_{19}H_{12}F_3O_{11}Os_3P$ requires C, 21.25; H, 1.15; P, 2.9%).

Reaction of [$Os_3H(CO)_{10}(MeCN)(PMe_2Ph)$]$PF_6$ *with* [NEt_4]CN.—A solution of [NEt_4]CN (0.020 g) and the cluster cation (0.152 g) in dry dichloromethane (20 cm^3) was stirred at room temperature for 1.5 h. Removal of the solvent and t.l.c. [SiO_2; eluant, light petroleum (b.p. 30—40 °C)–diethyl ether (10:1 v/v)] gave [$Os_3H(NCMeCN)(CO)_9(PMe_2Ph)$] as a yellow solid (0.057 g, 46%) (Found: C, 23.35; H, 1.45; N, 3.15; P, 3.05. $C_{20}H_{15}N_2O_9Os_3P$ requires C, 24.4; H, 1.45; N, 2.7; P, 3.0%).

Acknowledgements

We thank the S.E.R.C. (A. J. D.) for financial support and the Association of Commonwealth Universities for a studentship (for S. E. K.).

References

1 A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, 1975, **88**, C21.
2 A. J. Deeming and S. Hasso, *J. Organomet. Chem.*, 1976, **114**, 313.
3 J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. DeBoer, *J. Am. Chem. Soc.*, 1975, **97**, 4145.
4 M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.
5 J. B. Keister and J. R. Shapley, *Inorg. Chem.*, 1977, **16**, 2397.
6 J. B. Keister and J. R. Shapley, *Inorg. Chem.*, 1982, **21**, 3304.
7 R. D. Adams and N. M. Golembeski, *Inorg. Chem.*, 1979, **18**, 1909.
8 R. D. Adams and N. M. Golembeski, *J. Am. Chem. Soc.*, 1979, **101**, 2579.
9 S. Kennedy, J. J. Alexander, and S. G. Shore, *J. Organomet. Chem.*, 1981, **219**, 385.
10 E. Rosenberg, E. V. Anslyn, C. Barner-Thorsen, S. Aime, D. Osella, R. Gobetto, and L. Milone, *Organometallics*, 1984, **3**, 1790.
11 S. Aime, D. Osella, L. Milone, and E. Rosenberg, *J. Organomet. Chem.*, 1981, **213**, 207.
12 C. Choo Yin and A. J. Deeming, *J. Organomet. Chem.*, 1977, **133**, 123.
13 J. R. Shapley, M. E. Cree-Uchiyama, G. M. St. George, M. R. Churchill, and C. Bueno, *J. Am. Chem. Soc.*, 1983, **105**, 140.
14 M. Green, A. G. Orpen, and C. J. Schaverien, *J. Chem. Soc., Chem. Commun.*, 1984, 37.
15 W-Y. Yeh, J. R. Shapley, Y-J. Li, and M. R. Churchill, *Organometallics*, 1985, **4**, 767.
16 P. D. Gavens and M. J. Mays, *J. Organomet. Chem.*, 1978, **162**, 389; L. M. Bavaro and J. B. Keister, *ibid.*, 1985, **287**, 357 and refs. therein.
17 M. Basato, B. Corain, G. Favero, and P. Rosano, *J. Chem. Soc., Dalton Trans.*, 1984, 2513.
18 Z. Dawoodi, M. J. Mays, and A. G. Orpen, *J. Organomet. Chem.*, 1981, **219**, 251.
19 M. Laing, P. Sommerville, P. J. Wheatley, M. J. Mays, and Z. Dawoodi, *Acta Crystallogr., Sect B*, 1981, **37**, 2230.
20 R. D. Adams, D. A. Katahira, and L-W. Yang, *J. Organomet. Chem.*, 1981, **219**, 241.
21 R. D. Adams, D. A. Katahira, and L-W. Yang, *J. Organomet. Chem.*, 1981, **219**, 85.
22 R. D. Adams and N. M. Golembeski, *Inorg. Chem.*, 1978, **17**, 1969.
23 A. Martinsen and J. Songstad, *Acta Chem. Scand., Ser. A*, 1977, **31**, 645.
24 G. J. Janz, *Inorg. Synth.*, 1969, **5**, 43.

Received 7th July 1986; *Paper* 6/1352