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Reactions of the linear triosmium cluster $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ with $[Os_3(CO)_{12-n}(NCMe)_n]$ (n = 1 or 2): crystal structures of $[Os_4(\mu\text{-}H)(CO)_{14}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ and $[Os_5(\mu\text{-}H)(CO)_{17}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$

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Reaction of the linear triosmium carbonyl cluster $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ with $[Os_3(CO)_{11}(NCMe)]$ in hexane at 60 °C under vacuum afforded the 'spiked' tetraosmium cluster $[Os_4(\mu\text{-}H)(CO)_{14}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **1**. Reaction with $[Os_3(CO)_{10}(NCMe)_2]$ in CH_2Cl_2 at room temperature gave the 'spiked' hexaosmium cluster $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **2**. Cluster **2** is reactive and converts into the 'spiked' pentaosmium cluster $[Os_5(\mu\text{-}H)(CO)_{17}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **3** and a known cluster $[Os_5(CO)_{16}]$ respectively when heated with and without $C_6F_5N{=}NNHC_6F_5$. Clusters **1** and **3** were characterized by single-crystal X-ray crystallography. The structure of **1** consists of a triangular unit with a $Os(CO)_3(\eta^2\text{-}C_6F_5NNNC_6F_5)$ portion 'spiked' equatorially to it. The two nitrogen atoms in the triazenide ligand occupy an axial and an equatorial position in the $Os(CO)_3(\eta^2\text{-}C_6F_5NNNC_6F_5)$ group. The hydride ligand bridges, in a *cis* manner, the Os–Os edge where the $Os(CO)_3(\eta^2\text{-}C_6F_5NNNC_6F_5)$ portion is attached. The structure of **3** adopts a '4 + 1 spiked' geometry hitherto unknown. Its metal core consists of a planar 'kite-like' Os_4 unit with the $Os(CO)_3(\eta^2\text{-}C_6F_5NNNC_6F_5)$ portion 'spiked' to one of the equatorial co-ordination sites of an osmium atom. The two nitrogen atoms in the triazenide ligand and the hydride are bonded as in cluster **1**. Based upon ^{13}C NMR studies, the structure of cluster **2** in solution was also deduced to have a 'spiked' feature with the linear triosmium fragment $Os_3(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)$ bound to one atom in the osmium triangle at an equatorial co-ordination site. The transformation of cluster **2** and the formation of cluster **1** are also briefly discussed.

Pyrolysis and redox reactions of carbonyl clusters have been shown to give a variety of products with high nuclearity.[1] However, these reactions presented difficulties in efficient separation and mechanism studies. Recently, a stepwise build-up of carbonyl clusters has been achieved *via* 'metal hydride coupling' reaction of a metal complex *e.g.* $[Os_nH_2(CO)_{4n}]$ (n = 1–3) with clusters containing labile ligand(s) *e.g.* MeCN.[2] We have also reported the synthesis of a novel Os_6 cluster $[Os_6(\mu\text{-}H)(CO)_{19}(\mu\text{-}CO)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$,[3] as shown in Scheme 1. Studies have shown that it is formed *via* a 'spiked' isomeric intermediate $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ resulting from 'metal hydride coupling' reactions between the unstable linear cluster $[Os_3H(CO)_{10}(NCMe)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ and the triangular cluster $[Os_3(CO)_{10}(NCMe)_2]$. These findings stimulated us to explore systematically the application of the linear triosmium cluster $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$, obtained from the reaction of $C_6F_5N{=}NNHC_6F_5$ with $[Os_3(CO)_{11}(NCMe)]$,[4] in the synthesis of 'spiked' clusters and their transformation from open to closed clusters. We present here the study of 'metal hydride coupling' reactions of the linear triosmium cluster $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ with $[Os_3(CO)_{12-n}(NCMe)_n]$ (n = 1 or 2), together with the reactivities of the adduct $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$.

Results and Discussion

Reaction of $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ with $[Os_3(CO)_{11}(NCMe)]$

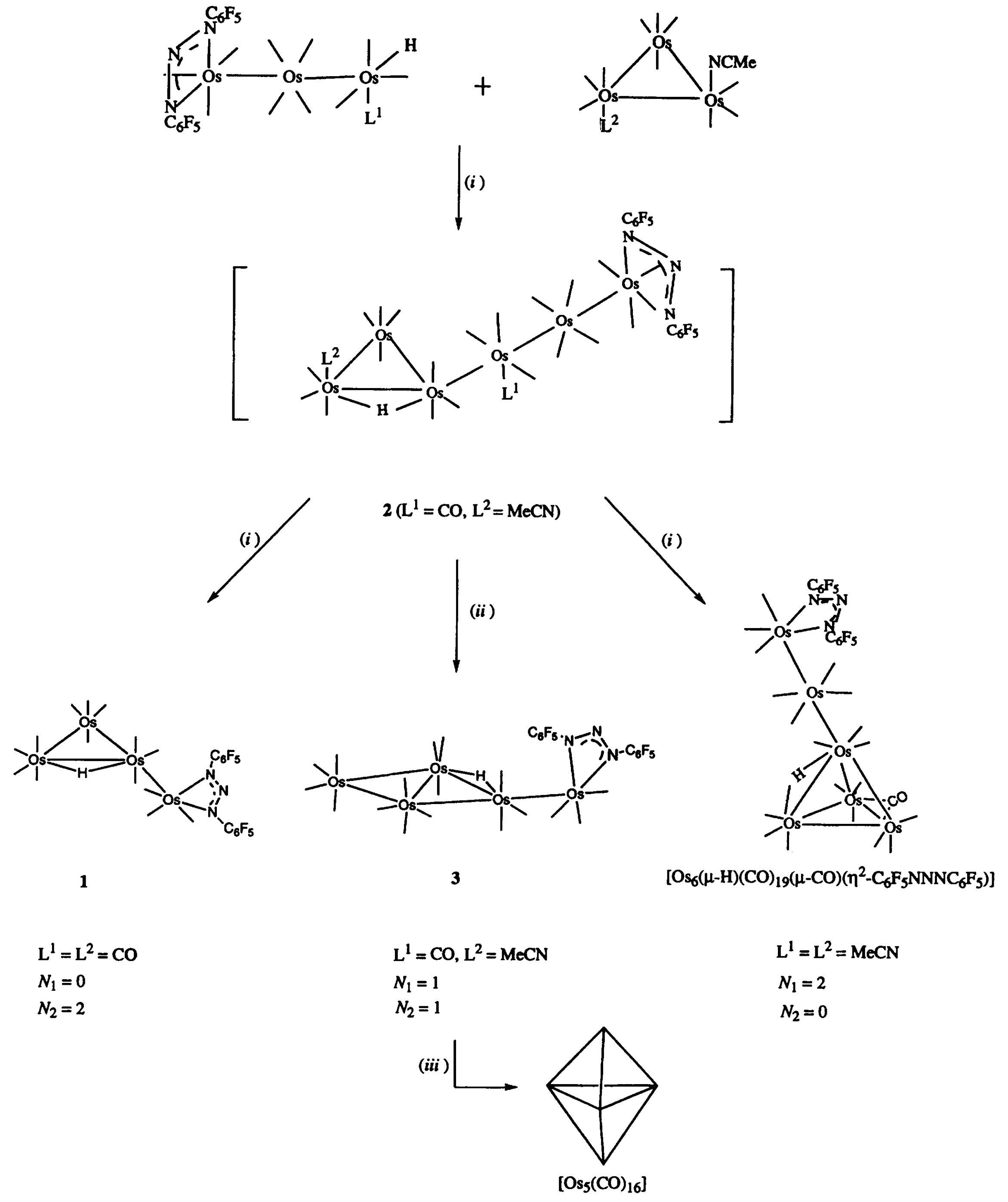
Treatment of the linear cluster $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ with an equivalent amount of $[Os_3(CO)_{11}(NCMe)]$ in hexane at 60 °C under vacuum provided a major product $[Os_4(\mu\text{-}H)(CO)_{14}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **1**, isolated as an orange solid (15.1%) after thin-layer chromatography (TLC). Cluster **1** was characterized by spectroscopy (Table 1) and microanalysis. Its IR absorption in the carbonyl region shows multiple peaks for terminal carbonyl groups. The band at 1263 cm^{-1} is characteristic for a bidentate triazenide ligand.[5] The ^1H NMR spectrum shows the presence of bridging hydride at δ −19.21, while the ^{19}F NMR spectrum exhibits the same chemical shifts for the two C_6F_5 groups, indicating a symmetrical arrangement of the triazenide ligand.

Reaction of $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ with $[Os_3(CO)_{10}(NCMe)_2]$

Addition of $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ to a solution of $[Os_3(CO)_{10}(NCMe)_2]$ in CH_2Cl_2 at room temperature afforded an orange compound $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **2** (37.0%). Its IR spectrum shows only terminal CO stretching, consistent with the proposed structure based upon ^{13}C NMR studies (Tables 1 and 2). As for cluster **1**, the band at 1252 cm^{-1} is due to the bidentate triazenide ligand.[5] The ^1H NMR spectrum shows a singlet at δ −16.8, attributed to a bridging metal hydride. The symmetrical arrangement of the triazenide ligand is also shown by the identical chemical shifts of the two C_6F_5 groups in the ^{19}F NMR spectrum.

Carbon-13 NMR study of cluster 2

To elucidate the structure of cluster **2**, $^{13}C\text{-}\{^1H\}$ and $^{13}C\text{-}^1H$ NMR spectra (Fig. 1) were recorded and they display two resonances of relative intensity four, one resonance of intensity two and eleven of intensity one due to the carbonyl ligands (Table 2). The proton-coupled spectrum reveals $^2J(^{13}C\text{-}^1H)$ coupling on resonances j, f, g, i, h and e. A tentative assignment of these resonances is shown in Fig. 1 and Table 2. The peak at



Scheme 1 (*i*) CH_2Cl_2, room temperature; (*ii*) $C_6F_5N{=}NNHC_6F_5$, hexane, 60–70 °C, vacuum; (*iii*) toluene, 90 °C, vacuum. N_1 = Number of new Os–Os bonds formed; N_2 = number of $Os(CO)_4$ units eliminated

Table 1 Spectroscopic data for osmium clusters

	NMR (δ, $CDCl_3$)		IR (cm^{-1}, CH_2Cl_2)		
Cluster	^1H	^{19}F	ν(CO)	ν(C_6F_5)	ν(triazenide)
1	−19.21 (s)	−75.2 (m, 4 F), −81.0 (m, 2 F), −85.8 (m, 4 F)	2134w, 2094w, 2075vs, 2056vs, 2031m, 2022m, 2005m, 1968w, 1944w	1514m, 992w	1263m
2	−16.8 (s, 1 H), 2.57 (s, 3 H)	−75.4 (m, 4 F), −81.9 (m, 2 F), −85.7 (m, 4 F)	2119w, 2095m, 2077w, 2053w, 2063m, 2031s, 2021vs	1514m, 990w	1252m
3	−14.14 (s)	−74.8 (m, 2 F), −75.4 (m, 2 F), −80.7 (m, 1 F), −81.7 (m, 1 F), −85.4 (m, 4 F)	2118w, 2126w, 2098s, 2079m, 2061s, 2042s, 2026s	1515m, 991w	1252m

the highest field (δ 167.80) remains as a broad singlet in the proton-coupled spectrum and can therefore be assigned to the carbonyl carbon (CO^a) *trans* to the Os–Os bond at the end of the linear portion with the triazenide ligand. This broadening is presumably due to the coupling between ^{13}C and ^{15}N nuclei. The peak at δ 179.05, which also remains broad in the proton-

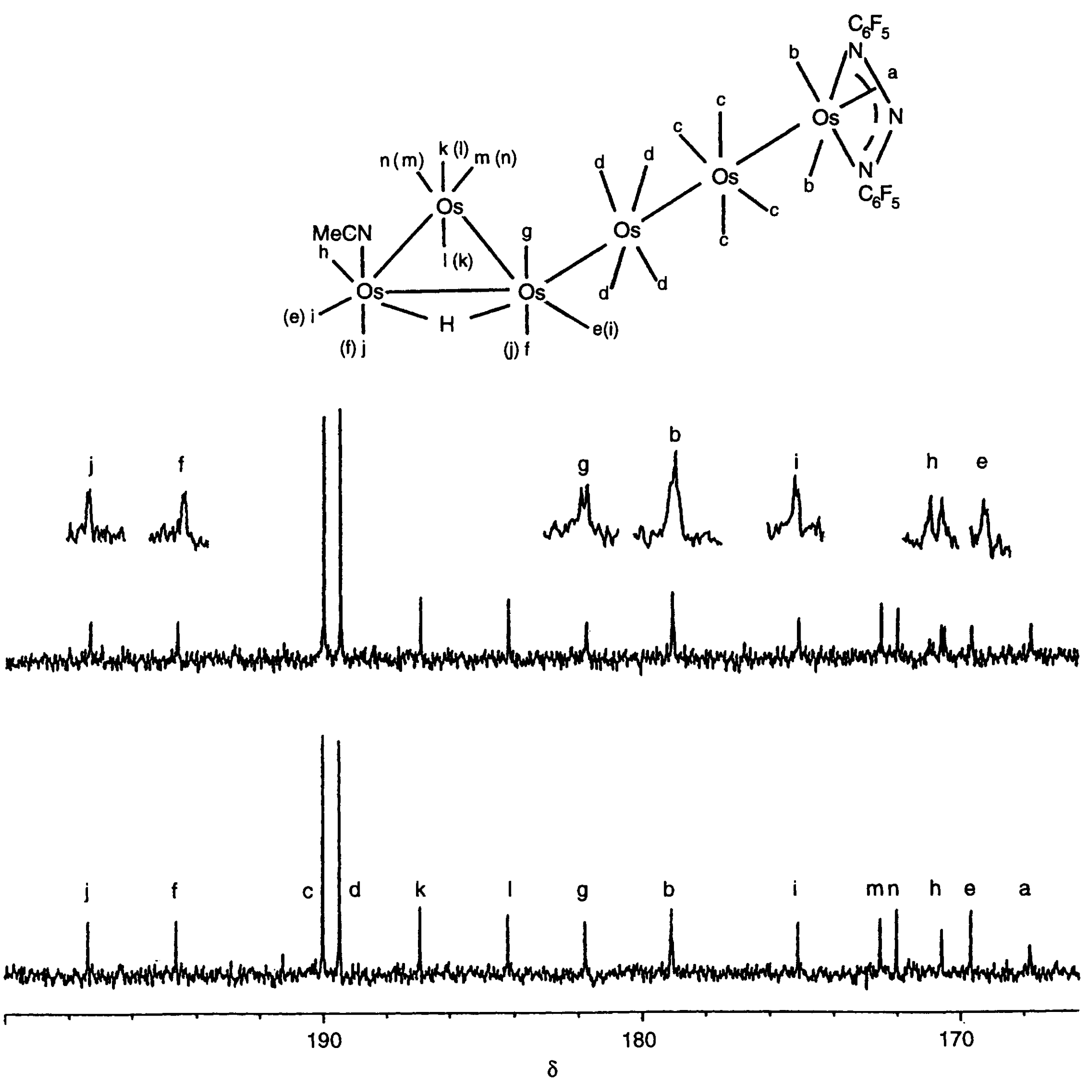


Fig. 1 Proton-coupled (upper) and decoupled (lower) ^{13}C NMR spectra in the carbonyl region for cluster 2

Table 2 Carbon-13 NMR data for cluster 2

δ (CD_2Cl_2, downfield from $SiMe_4$)	$^2J(^1H-^{13}C)$/Hz	Assignment
197.38	2.87	j
194.62	2.86	f
189.99	0	c
189.47	0	d
186.93	0	k
184.19	0	l
181.78	5.03	g
179.05	br	b
175.12	3.37	i
172.54	0	m
172.02	0	n
170.58	12.69	h
169.67	3.82	e
167.80	br	a

coupled spectrum but has the intensity of two nuclei, can be assigned to the two carbonyl carbon nuclei (CO^b) at the same osmium atom of the linear portion. The two peaks at δ 189.99 and 189.47, both of which have intensity four and remain as singlets in the proton-coupled spectrum, can be assigned to the carbonyl groups (CO^c and CO^d) on the other two osmium atoms in the linear portion, where rotation about the Os–Os bonds in solution is presumably fast on the NMR time-scale rendering the rotamers indistinguishable. The peak at δ 170.58 with the largest value of $^2J(^{13}C-^1H)$ in the proton-coupled spectrum can be assigned to the carbonyl carbon (CO^h) *trans* to the hydride. The peaks at δ 197.38 and 194.62, which have the smallest values of $^2J(^{13}C-^1H)$, 2.87 and 2.86 Hz, respectively, are tentatively assigned to the carbonyl groups (CO^j and CO^f) at the axial sites of the Os atoms attached to the bridging hydride. The peaks at δ 175.12 and 169.67 with $^2J(^{13}C-^1H)$ of 3.37 and 3.82 Hz, respectively are tentatively assigned to the carbonyl carbon nuclei (CO^i and CO^e) *cis* to the hydride, and that at δ 181.78 with $^2J(^{13}C-^1H)$ of 5.03 Hz to the carbonyl carbon (CO^g) at the axial site. As the chemical shift of the CO carbon *trans* to the Os–Os bond is at relatively high field, the peaks at δ 172.54 and 172.02, which remain as singlets in the proton-coupled spectrum, can be assigned to the equatorial carbonyl carbon nuclei (CO^m and CO^n) on the osmium atom without a bridging hydride. The singlets at δ 186.93 and 184.19 are at relatively low field and can be assigned to the axial carbonyl carbon nuclei (CO^k and CO^l) on the same osmium atom. Although the assignment of the CO groups in this cluster is tentative due to limited literature data on the magnitude of $^2J(^{13}C-^1H)$ coupling constants in such systems, the pattern of the ^{13}C NMR spectra are fully consistent with an 'equatorially spiked' arrangement of the linear fragment $Os_3(CO)_{11}(\eta^2-C_6F_5NNNC_6F_5)$ on the triangular portion $Os_3(\mu-H)(CO)_{10}(NCMe)$.

Reactivity of cluster 2

Cluster 2 was converted into a dark red cluster $[Os_5(\mu-H)(CO)_{17}(\eta^2-C_6F_5NNNC_6F_5)]$ 3 (34.5%) when heated with an equivalent amount of $C_6F_5N{=}NNHC_6F_5$ in hexane at 60–70 °C under vacuum. As for cluster 1, the IR spectroscopic data reveal the bidentate co-ordination mode for the triazenide

Table 3 Selected interatomic distances (Å) and angles (°) for cluster **1**

Os(1)–Os(2)	2.850(2)	Os(1)–Os(3)	3.042(2)
Os(1)–Os(4)	2.880(2)	Os(2)–Os(3)	2.899(2)
Os(4)–N(1)	2.19(3)	Os(4)–N(3)	2.16(3)
N(1)–N(2)	1.18(5)	N(2)–N(3)	1.34(5)
Os(1)–C(11)	1.93(3)	Os(1)–C(12)	1.91(4)
Os(1)–C(13)	1.87(4)	Os(2)–C(21)	1.83(4)
Os(2)–C(22)	1.90(6)	Os(2)–C(23)	1.87(5)
Os(2)–C(24)	1.87(5)	Os(3)–C(31)	2.01(4)
Os(3)–C(32)	2.02(4)	Os(3)–C(33)	1.86(5)
Os(3)–C(34)	2.01(4)	Os(4)–C(41)	1.92(5)
Os(4)–C(42)	1.97(4)	Os(4)–C(43)	2.03(4)
N(1)–C(106)	1.37(5)	N(3)–C(306)	1.40(5)
Os(1)–Os(2)–Os(3)	63.9(1)	Os(1)–Os(3)–Os(2)	57.3(1)
Os(2)–Os(1)–Os(3)	58.8(1)	Os(3)–Os(1)–Os(4)	108.2(1)
Os(2)–Os(1)–Os(4)	166.7(1)	N(1)–N(2)–N(3)	110.7(33)
Os(4)–N(1)–N(2)	97.9(24)	Os(4)–N(3)–N(2)	95.2(22)
Os(1)–Os(4)–C(42)	175.8(11)	Os(1)–Os(3)–C(32)	115.5(11)
Os(1)–Os(4)–C(43)	87.8(11)	Os(1)–Os(4)–C(41)	84.3(13)

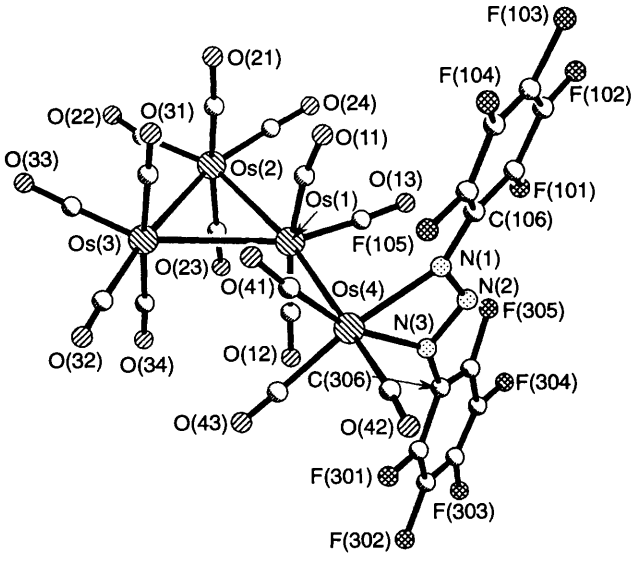


Fig. 2 Molecular structure of compound **1** showing the atom labelling. The C atoms of the CO and C_6F_5 groups bear the same numbering as the corresponding O or F atoms

ligand and the presence of terminal carbonyl ligands (Table 1). The resonance of the bridging hydride ligand was seen at δ −14.14 in the ^1H NMR spectrum. The arrangement of the triazenide ligand is also symmetrical as shown by the identical chemical shifts of the two C_6F_5 groups in the ^{19}F NMR spectrum. When heated in toluene at 90 °C under vacuum in the absence of $C_6F_5N{=}NNHC_6F_5$ cluster **2** was converted into a known cluster $[Os_5(CO)_{16}]$.[6] On standing in CH_2Cl_2 at room temperature, cluster **2** can also be converted slowly into **3**. Upon heating compound **3** in toluene at 90 °C cluster $[Os_5(CO)_{16}]$ was also obtained as a major product. Compared with the formation of the hexaosmium cluster $[Os_6(\mu\text{-}H)(CO)_{19}(\mu\text{-}CO)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ [3] which we obtained previously, the build-up of Os–Os bonds on the triangular portion is dependent on the presence of labile ligands (MeCN) in the intermediates $[Os_6(\mu\text{-}H)(CO)_{20}L^1(L^2)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ (Scheme 1). In the case of $[Os_6(\mu\text{-}H)(CO)_{20}L^1(L^2)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **2** (L^1 = CO, L^2 = MeCN) the presence of one labile ligand MeCN in the triangular portion allows the formation of one additional Os–Os bond upon its conversion into cluster **3**. In the case of cluster **2** ($L^1 = L^2$ = MeCN), where one MeCN ligand is present in the triangular part and the other at the osmium atom attached to the triangular metal core, $[Os_6(\mu\text{-}H)(CO)_{19}(\mu\text{-}CO)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ was obtained with the formation of two additional Os–Os bonds and loss of two MeCN ligands. Cluster **1** was obtained directly from the reaction of $[Os_3(CO)_{11}(NCMe)]$ with $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5\text{-}NNNC_6F_5)]$ in hexane at an elevated temperature of 60 °C or in a polar solvent *e.g.* CH_2Cl_2 or tetrahydrofuran at room temperature. The intermediate **2** ($L^1 = L^2$ = CO) was not obtained in either reaction. In this case, no additional metal–metal bond would be formed during the transformation.

It has been suggested that in osmium cluster chemistry the addition of a pair of electrons to a cluster is concomitant with breaking of a metal–metal bond.[7] Based upon our observation, it can be concluded that the formation of a metal–metal bond is consistent with loss of a two-electron donor ligand (*e.g.* MeCN or CO). This kind of process was also believed to occur in the formation of high-nuclearity carbonyl clusters *via* pyrolysis methods, in which co-ordinatively unsaturated species were involved and condensed to the products by forming new metal–metal bonds.[8] This feature was also present in the transformation of cluster **3** to $[Os_5(CO)_{16}]$, in which three new Os–Os bonds were formed with the loss of one CO (two-electron donor) and one $C_6F_5N{=}NNHC_6F_5$ ligand (four-electron donor). It is also interesting that the formation of cluster **1** was accompanied by the elimination of two $Os(CO)_4$ units, while in the transformation of cluster **2** to **3** one $Os(CO)_4$ was expelled from the system and no $Os(CO)_4$ was lost during the formation of $[Os_6(\mu\text{-}H)(CO)_{19}(\mu\text{-}CO)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$.

Crystal structure of cluster 1

The molecular structure of compound **1** was determined by single-crystal X-ray diffraction analysis. Relevant bond lengths and bond angles are given in Table 3. The structure (Fig. 2) consists of a metal-co-ordinated triangular cluster having four metal–metal bonds and a total of 64 electrons, in which a 17-electron portion, $Os(CO)_3(\eta^2\text{-}C_6F_5NNNC_6F_5)$ 'spikes' the triangular $(\mu\text{-}H)Os_3(CO)_{11}$ fragment. One Os–Os edge in the osmium triangle is bridged by a hydride ligand, while the triazenide ligand is attached to the osmium atom co-ordinated to the triangle. The osmium atom of the $Os(CO)_3(C_6F_5\text{-}NNNC_6F_5)$ ligand is positioned at a distance of 0.1623 Å above the plane formed by the other three osmium atoms. This deviation from planarity may be the result of steric hindrance between the bulky C_6F_5 group on N(1) and the carbonyls CO(11) and CO(13) on Os(1). The geometry around the Os(4) atom is close to octahedral and the orientation of the $Os(CO)_3(C_6F_5NNNC_6F_5)$ unit is such that the carbonyl ligands are staggered with respect to those bonded to Os(1) as evidenced by the torsion angles [C(41)–Os(4)–Os(1)–C(11) 49.0(1.8), C(43)–Os(4)–Os(1)–C(12) −49.7(1.7) and N(1)–Os(4)–Os(1)–C(13) 29.5(1.5)°]. The unbridged Os(1)–Os(4) bond is 2.880(2) Å. The triazenide ligand occupies both an axial and an equatorial site of the fourth osmium atom centre to form a Os(4)–N(1)–N(2)–N(3) four-membered ring, which is almost planar [largest deviation from the plane 0.0281 Å for N(2)]. The presence of the hydride ligand was not located directly. However it was inferred to bridge the Os(1)–Os(3) vector, which is longer than the other Os–Os bond lengths in the osmium triangle. A singly hydrogen-bridged Os–Os bond usually has a length around 3.0 Å {*e.g.* 2.989(1) Å in $[Os_3(\mu\text{-}H)(H)(CO)_{11}]$[9] and 3.0185(6) Å in $[Os_3(\mu\text{-}H)(H)(CO)_{10}(PPh_3)]$[10]}. The bond length of Os(1)–Os(3) in **1** is 3.042(2) Å, which falls within the specified range. Furthermore, the average Os–Os–C_{eq} angle for $[Os_3(CO)_{12}]$ is 98.2°,[9] but the Os(1)–Os(3)–C(32) angle for **1** is 115.5(11)°. This difference is also attributable to the presence of the bridging hydride. Analysis of the Os–Os bond lengths (Å) in the osmium triangle of **1** shows that while most are longer than the Os–Os distance in the parent $[Os_3(CO)_{12}]$, Os(1)–Os(2) is significantly shorter than the average found in $[Os_3(CO)_{12}]$. This shortening of the Os(1)–Os(2) bond which is *trans* to the Os(1)–Os(4) bond may

Table 4 Selected interatomic distances (Å) and angles (°) for cluster **3**

Os(1)–Os(2)	2.814(1)	Os(1)–Os(3)	2.959(1)
Os(2)–Os(3)	2.947(1)	Os(2)–Os(4)	2.911(1)
Os(3)–Os(4)	3.053(1)	Os(4)–Os(5)	2.869(1)
Os(5)–N(1)	2.12(2)	Os(5)–N(3)	2.11(1)
N(1)–N(2)	1.33(3)	N(2)–N(3)	1.28(2)
Os(1)–C(11)	1.89(2)	Os(1)–C(12)	1.89(2)
Os(1)–C(13)	2.00(2)	Os(1)–C(14)	1.94(2)
Os(2)–C(21)	1.87(1)	Os(2)–C(22)	1.94(2)
Os(2)–C(23)	1.93(2)	Os(3)–C(31)	1.90(2)
Os(3)–C(32)	1.95(2)	Os(3)–C(33)	1.96(2)
Os(3)–C(34)	1.95(2)	Os(4)–C(41)	1.89(2)
Os(4)–C(42)	1.94(2)	Os(4)–C(43)	1.99(2)
Os(5)–C(51)	1.89(2)	Os(5)–C(52)	1.92(2)
Os(5)–C(53)	1.94(2)	N(1)–C(61)	1.41(2)
N(3)–C(71)	1.44(2)		
Os(2)–Os(1)–Os(3)	61.3(1)	Os(3)–Os(2)–Os(4)	62.8(1)
Os(1)–Os(2)–Os(3)	61.8(1)	Os(1)–Os(3)–Os(2)	56.9(1)
Os(2)–Os(3)–Os(4)	58.0(1)	Os(2)–Os(4)–Os(3)	59.2(1)
Os(4)–Os(2)–C(21)	132.9(5)	Os(1)–Os(2)–C(21)	102.5(5)
Os(4)–Os(5)–C(51)	175.0(6)	Os(4)–Os(5)–N(1)	88.1(4)
Os(4)–Os(5)–N(3)	91.8(4)	N(1)–N(2)–N(3)	102.6(16)
Os(5)–N(1)–N(2)	98.9(11)	Os(5)–N(3)–N(2)	101.0(11)

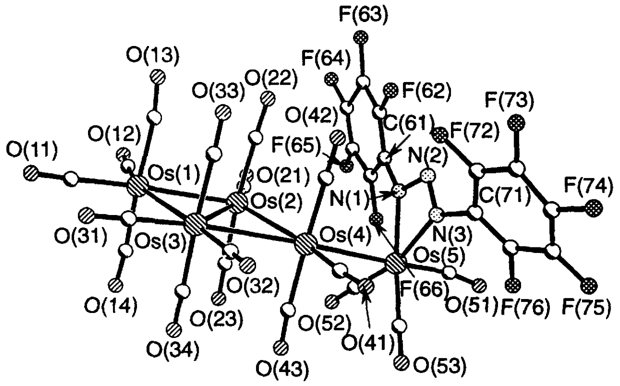


Fig. 3 Molecular structure of compound **3** showing the atom labelling. The C atoms of the CO and C_6F_5 groups bear the same numbering as the corresponding O or F atoms

be taken to indicate that the $Os(CO)_3(C_6F_5NNNC_6F_5)$ portion is a weak donor ligand and this is consistent with the electron-withdrawing property of the triazenide ligand. The fourteen carbonyl groups in **1** are all terminal with Os–C and C–O bond lengths of 1.83(4)–2.03(4) and 1.02(5)–1.18(7) Å respectively.

Crystal structure of cluster 3

The molecular structure of cluster **3** has been determined by single-crystal X-ray diffraction. Selected bond distances and angles are given in Table 4. This cluster could be described as being derived from the unusual planar tetraosmium cluster $[Os_4(CO)_{15}]$.[11] Its metal core consists of a planar 'kite-like' Os_4 unit with an osmium bound to one of the equatorial coordination sites of an osmium atom, a structure which has not been reported before (Fig. 3). As was found in $[Os_4(CO)_{15}]$, the Os_4 unit in this cluster is almost planar [dihedral angle between the planes Os(1)–Os(2)–Os(3) and Os(2)–Os(1)–Os(4) 2.4°]. The fifth osmium Os(5) lies essentially in this plane [deviation from the plane defined by Os(1)–Os(2)–Os(3) and Os(4) 0.349 Å]. The hydride was not located directly; however, it was inferred to bridge the Os(2)–Os(4) vector, the length [2.911(1) Å] of which is similar to those found in other clusters {*e.g.* 2.989(1) Å in $[Os_3(\mu\text{-}H)(H)(CO)_{11}]$[9] and 3.0185(6) Å in $[Os_3(\mu\text{-}H)(H)(CO)_{10}(PPh_3)]$[10]}. The location of the hydride at Os(2)–Os(4) is also confirmed by the comparison of the diequatorial angles Os(4)–Os(2)–C(21) [132.9(5)°] and Os(1)–Os(2)–C(21) [102.5(5)°]. The former is larger by 30.4°. The Os–Os unbridged bond lengths in this cluster are only slightly different from the corresponding ones in $[Os_4(CO)_{15}]$. The diagonal Os(2)–Os(3) bond is 2.947(1) Å and is the same as that in $[Os_4(CO)_{15}]$. The bond length of Os(1)–Os(2) [2.814(1) Å] is significantly shorter than the average value of 2.877(3) Å for an Os–Os bond in $[Os_3(CO)_{12}]$, but larger than the corresponding bond length of 2.772(1) Å in $[Os_4(CO)_{15}]$. The Os(2)–Os(4) bond length [2.911(1) Å] is larger than both the average value in $[Os_3(CO)_{12}]$[9] and the corresponding bond length of 2.772(1) Å in $[Os_4(CO)_{15}]$. The bond length of Os(1)–Os(3) [2.959(1) Å] is also longer than average bond length in $[Os_3(CO)_{12}]$ and slightly shorter than the corresponding bond length of 2.997(1) Å in $[Os_4(CO)_{15}]$. Long and short Os–Os bonds are common in osmium clusters, but the cause is not well understood. In the case of $[Os_4(CO)_{15}]$ or its derivative $[Os_4(CO)_{14}(PMe_3)]$[12] the unusual bond lengths were rationalized in terms of three-centre two-electron metal–metal bonds. Therefore, the short bonds were assigned a bond order of 1.5 and the long bond an order of 0.5, consistent with an 18-electron configuration for each metal atom. As described above, in the case of this cluster, long and short Os–Os bonds are also observed. Although the average unbridged bond length [2.943(1) Å] is not very different from that in $[Os_4(CO)_{15}]$ [2.897(1) Å], the bond lengths in cluster **3** are very similar, in contrast to what was observed in $[Os_4(CO)_{15}]$. This may be due to the presence of the bridging hydride and the 'spiked' unit $Os(CO)_3(\eta^2\text{-}C_6F_5NNNC_6F_5)$, which may assist in the delocalization of electrons in the whole Os_4 unit and thus reduce the difference in electron density for each metal–metal bond.

The fifth osmium atom 'spikes' on the Os_4 unit at Os(4) at the equatorial site. The geometry around the Os(5) atom is close to octahedral and the orientation of the $Os(CO)_3(\eta^2\text{-}C_6F_5NNNC_6F_5)$ group is such that the carbonyl ligands are staggered with respect to those bonded to Os(4) as evidenced by the torsion angles [C(43)–Os(4)–Os(5)–C(52) 43.3(7), C(41)–Os(4)–Os(5)–C(53) 45.2(7) and C(42)–Os(4)–Os(5)–N(3) 24.8(6)°]. The bidentate triazenide ligand chelates Os(5) to form a four-membered ring Os(5)–N(1)–N(2)–N(3), which is almost planar [largest deviation 0.0052 Å, for N(2), from the plane defined by Os(5)–N(1)–N(2)–N(3)] and perpendicular to the plane of the Os_4 unit (dihedral angle between these two planes 96.8°).

Experimental

Methodology

The starting materials $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$,[4] $[Os_3(CO)_{10}(NCMe)_2]$,[13] $[Os_3(CO)_{11}(NCMe)]$[14] and $C_6F_5N{=}NNHC_6F_5$[15] were prepared by published methods. The solvents hexane, toluene and CH_2Cl_2 for the reactions were dried by published methods.[16] Thin-layer chromatography was performed in air on plates coated with silica (Merck Kieselgel 60GF). Infrared spectra were recorded on a Perkin-Elmer 983G spectrometer, NMR in $CDCl_3$ on a JEOL FX 90Q FT or FT Bruker ACF 500 MHz spectrometer; ^1H and ^{13}C NMR spectra were measured with respect to $SiMe_4$ as internal reference, and ^{19}F with respect to CF_3CO_2H as external reference.

Crystallography

Crystal data for compounds **1** and **3** are summarized in Table 5. Diffraction intensities were collected at 298 K on a Siemens R3m/V X-ray diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å), scan range $7.0 < 2\theta < 45.0$ for **1** and $3.5 < 2\theta < 50.0°$ for **3**, indices $+h$, $+k$, $\pm l$ for **1** and $+h$, $\pm k$, $\pm l$ for **3**. All computations were carried out on a Micro VAX 2000 computer using the SHELXTL PLUS program package.[17] The structures were solved by direct

Table 5 Summary of crystallographic data for compounds **1** and **3**

	1	**3**
Formula	$C_{26}HF_{10}N_3O_{14}Os_4$	$C_{29}HF_{10}N_3O_{17}Os_5$
M	1530.1	1804.3
D_c/g cm^{-3}	2.664	3.024
Colour, habit	Orange blocks	Brown blocks
Crystal dimensions/mm	0.33 × 0.22 × 0.11	0.35 × 0.25 × 0.15
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	13.040(3)	8.975(2)
b/Å	18.839(4)	12.668(3)
c/Å	15.652(3)	17.619(4)
α/°		82.50(3)
β/°	97.51(3)	85.83(3)
γ/°		88.27(3)
U/Å^3	3812(3)	1980.4(10)
Z	4	2
Reflections collected	6953	7479
Observed reflections [$F > 4.0\sigma(F)$]	3275	5340
R, R' (observed data)	0.0744, 0.0966	0.0467, 0.0581
(all data)	0.1438, 0.1285	0.0647, 0.0671
Goodness of fit	1.13	1.13
$F(000)$	2736	1604
μ(Mo-Kα)/mm^{-1}	13.403	16.104
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0042F^2$	$\sigma^2(F) + 0.0016F^2$
Minimum, maximum transmission	0.0370, 0.0726	0.1601, 0.9805

methods, using full-matrix, least-squares refinement (based on *F*) with all non-hydrogen atoms being refined anisotropically except for the C atoms of the CO ligands and the C_6F_5 groups in cluster **1**, and C and F atoms of the C_6F_5 groups in cluster **3**, which were refined isotropically. Owing to large deviations, seven and four observed reflections were omitted for cluster **1** and **3**, respectively. The bond lengths (C–C 1.38, C–F 1.32 Å) of the C_6F_5 groups in **3** were fixed because of high thermal motion. An empirical (ψ-scan) correction was performed in each case.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/204.

Reactions of $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$

With $[Os_3(CO)_{11}(NCMe)]$. A mixture of $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ (56.0 mg, 0.045 mmol) and $[Os_3(CO)_{11}(NCMe)]$ (50.0 mg, 0.054 mmol) in hexane (4 cm^3) was introduced in a Schlenk tube (50 cm^3). The system was evacuated and the Schlenk apparatus was placed in an oil-bath at 60–70 °C for 16 h. The resultant orange solution was evaporated to dryness and subjected to TLC, using hexane–CH_2Cl_2 (7:3 v/v) as eluent, to give $[Os_4(\mu\text{-}H)(CO)_{14}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **1** (R_f = 0.5, 12.5 mg, 15.1%) as the major product (Found: C, 20.10; H, 0.20; F, 12.6; N, 2.75. Calc. for $C_{26}HF_{10}N_3O_{14}Os_4$: C, 20.4; H, 0.05; F, 12.4; N, 2.75%).

With $[Os_3(CO)_{10}(NCMe)_2]$. A mixture of $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ (57.0 mg, 0.046 mmol) and $[Os_3(CO)_{10}(NCMe)_2]$ (50.0 mg, 0.053 mmol) in CH_2Cl_2 (4 cm^3) was introduced in a Schlenk tube (50 cm^3). The system was evacuated and refilled with N_2 (1 atm, 101 325 Pa). After stirring overnight, the resultant orange solution was evaporated to dryness and subjected to TLC, using hexane–CH_2Cl_2 (6:4 v/v) as eluent, to give $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **2** (R_f = 0.5, 36.5 mg, 37.0%) as the major product (Found: C, 19.6; H, 0.20; N, 2.75. Calc. for $C_{45}H_4F_{10}N_3O_{21}Os_6$: C, 19.55; H, 0.20; N, 2.60%).

Reaction of compound 2 with $C_6F_5N{=}NNHC_6F_5$

A mixture of $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ (50.0 mg, 0.023 mmol) and $C_6F_5N{=}NNHC_6F_5$ (8.8 mg, 0.023 mmol) in hexane (4 cm^3) in a Schlenk tube (50 cm^3) was degassed and heated at 60–70 °C overnight. The resultant red solution was evaporated to dryness and subjected to TLC, using hexane–CH_2Cl_2 (9:1 v/v) as eluent, to give a red compound $[Os_5(\mu\text{-}H)(CO)_{17}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **3** (R_f = 0.35, 12.9 mg, 34.5%) as the major product (Found: C, 19.3; H, 0.25; N, 2.60. Calc. for $C_{29}HF_{10}N_3O_{21}Os_5$: C, 19.2; H, 0.05; N, 2.60%).

Pyrolysis of compound 2

A solution of $[Os_6(\mu\text{-}H)(CO)_{21}(NCMe)(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ (50.0 mg, 0.023 mmol) in toluene (4 cm^3) in a Schlenk reaction tube was degassed and heated at 90 °C overnight. The resultant dark brown mixture was evaporated to dryness and subjected to TLC, using hexane–CH_2Cl_2 (7:3 v/v) as eluent, to give the major cluster $[Os_5(CO)_{16}]$ (R_f = 0.60, 8.3 mg), characterized by comparison of its IR spectrum with literature data[6] (Found: C, 13.88. Calc. for $C_{16}O_{16}Os_5$: C, 13.75%).

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