A novel hexaosmium cluster [$Os_6(\mu$-H)(CO)$_{19}(\mu$-CO)(η^2-$C_6F_5NNNC_6F_5$)] formed from an isomeric intermediate [$Os_6(\mu$-H)(CO)$_{20}$(NCMe)$_2(\eta^2$-$C_6F_5NNNC_6F_5$)] *via* a capping process

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A novel hexaosmium cluster [$Os_6(\mu$-H)(CO)$_{19}(\mu$-CO)(η^2-$C_6F_5NNNC_6F_5$)] is obtained in the reaction of C_6F_5N=$NNHC_6F_5$ with [Os_3(CO)$_{10}$(NCMe)$_2$] and is fully characterized in the solid state by single-crystal X-ray diffraction analysis; investigation of its formation revealed the interesting capping of one end of a linear triosmium fragment onto the triangular face of [Os_3(CO)$_{10}$(NCMe)$_2$] *via* a 'spiked' isomeric intermediate [$Os_6(\mu$-H)(CO)$_{20}$(NCMe)$_2(\eta^2$- $C_6F_5NNNC_6F_5$)], of which the structure in solution was proposed based on ^{13}C NMR studies.

Since the structures of the high-nuclearity osmium carbonyl clusters [Os_6(CO)$_{18}$][1] and [Os_7(CO)$_{21}$][1] were elucidated, this field has received much attention and enormous numbers of such species have been reported.[2] For increasing nuclearity, pyrolysis and redox condensation have been widely used but in general give a variety of products with variable yields.[2] Designed synthesis still presents a problem and study on reaction mechanisms is viewed as a highly complex subject. We report here a novel hexaosmium–triazenido cluster [Os_6(μ-H)(CO)$_{19}(\mu$-CO)(η^2-$C_6F_5NNNC_6F_5$)] **3**. Investigation of its formation revealed the interesting capping of one end of a linear triosmium fragment on the face of triangular cluster [Os_3(CO)$_{10}$(NCMe)$_2$] *via* a 'spiked' isomeric intermediate [$Os_6(\mu$-H)(CO)$_{20}$(NCMe)$_2(\eta^2$-$C_6F_5NNNC_6F_5$)] **2**, of which the structure in solution was proposed based upon ^{13}C NMR studies.

The carbonyl complexes with terminal hydride ligand have been employed as building blocks for controlled build-up of carbonyl clusters *via* their 'metal–hydride coupling' reaction with cluster precursors with labile ligands.[3] In our current work, a linear triosmium cluster with terminal hydride ligand [Os_3H(CO)$_{11}(\eta^2$-$C_6F_5NNNC_6F_5$)][4] obtained from reaction of C_6F_5N=$NNHC_6F_5$ with [Os_3(CO)$_{11}$(NCMe)] and was found to react readily with [Os_3(CO)$_{10}$(NCMe)$_2$] to give the 'spiked' cluster [$Os_6(\mu$-H)(CO)$_{21}$(NCMe)(η^2-$C_6F_5NNNC_6F_5$)].[5] Another linear triosmium cluster [Os_3H(CO)$_{10}$(NCMe)(η^2-$C_6F_5NNNC_6F_5$)] **1** was expected to be an effective building block as it bears both terminal hydride and labile ligand MeCN. Because of the presence of the labile ligand MeCN, clusters more complicated than the 'spiked' species might be obtained *via* the loss of MeCN and formation of metal–metal bonds assisted by hydride ligand.

In our attempt to synthesize this cluster from the similar reaction of C_6F_5N=$NNHC_6F_5$ with [Os_3(CO)$_{10}$(NCMe)$_2$] in CH_2Cl_2 at room temp overnight, a variety of compounds was formed in this reaction. Clusters [$Os_6(\mu$-H)(CO)$_{20}$(NCMe)$_2(\eta^2$-$C_6F_5NNNC_6F_5$)] **2** (two isomers: **2a**, 4%; **2b**, 3%) and [Os_6(μ-H)(CO)$_{19}(\mu$-CO)(η^2-$C_6F_5NNNC_6F_5$)] **3** (8%) were isolated by TLC and characterized by spectroscopic and analytical methods.† Cluster **2** is the major product in the initial reaction mixture, but it is not stable in solution and was converted mainly into **3** at room temp. in CH_2Cl_2 over a period of several hours or even at −20 °C over a period of several weeks. The remaining products isolated are currently being characterized.

A single-crystal X-ray diffraction study was undertaken to elucidate the solid-state molecular structure of **3** (Fig. 1).‡ Its metallic framework reveals the delicate capping of one end of the linear triosmium cluster on the face of the triangulo-osmium cluster to form a hexanuclear cluster with two-nuclear 'antenna' linking to a tetrahedron, a geometry hitherto not reported for metal carbonyl clusters. The metal atoms Os(1), Os(2) and Os(3) are almost linear with Os–Os–Os 177.0(1)°. The Os(2)–Os(3) distance, 2.932(2) Å, is slightly longer than that of Os(1)–Os(2), 2.883(2) Å, and that observed for the Os–Os bonds in [Os_3(CO)$_{12}$].[6] The triazenido ligand occupies an axial and equatorial site of the first Os atom centre to form an Os(3)N(1)N(2)N(3) four-membered ring, which is almost coplanar [the largest deviation from the plane is for N(2) at 0.0259 Å]. The Os(1)–N(1) and Os(1)–N(3) bond lengths 2.127(12) and 2.138(14) Å, respectively, are approximately the same, as are the N(1)–N(2) and N(2)–N(3) bond lengths, 1.330(19) and 1.315(19) Å, respectively, indicating that the ligand chelates in a chemically equivalent environment and there is extensive π-delocalization over the entire ring. This feature is common to other related compounds, such as [RuH(dtt)(CO)(PPh$_3$)$_2$] (dtt = 1,3-di-*p*-tolyltriazenido).[7] The N–N–N angle of 103.4(12)° has a similar value to the

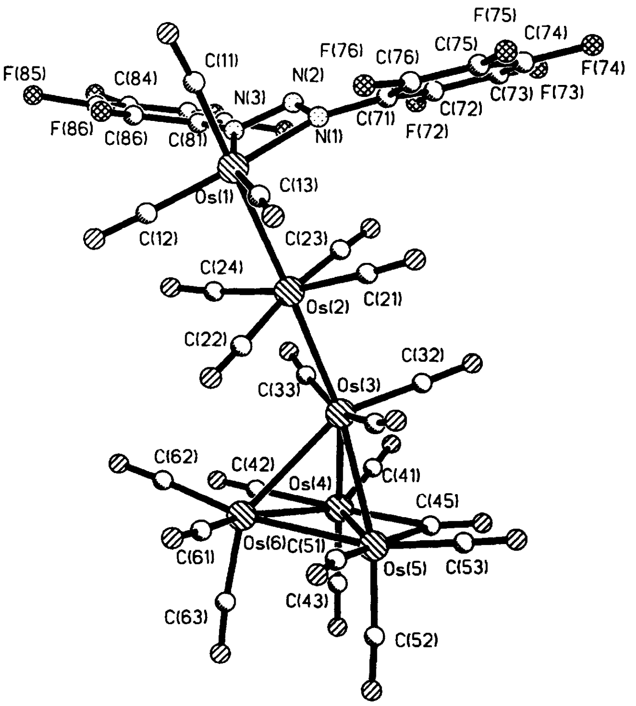
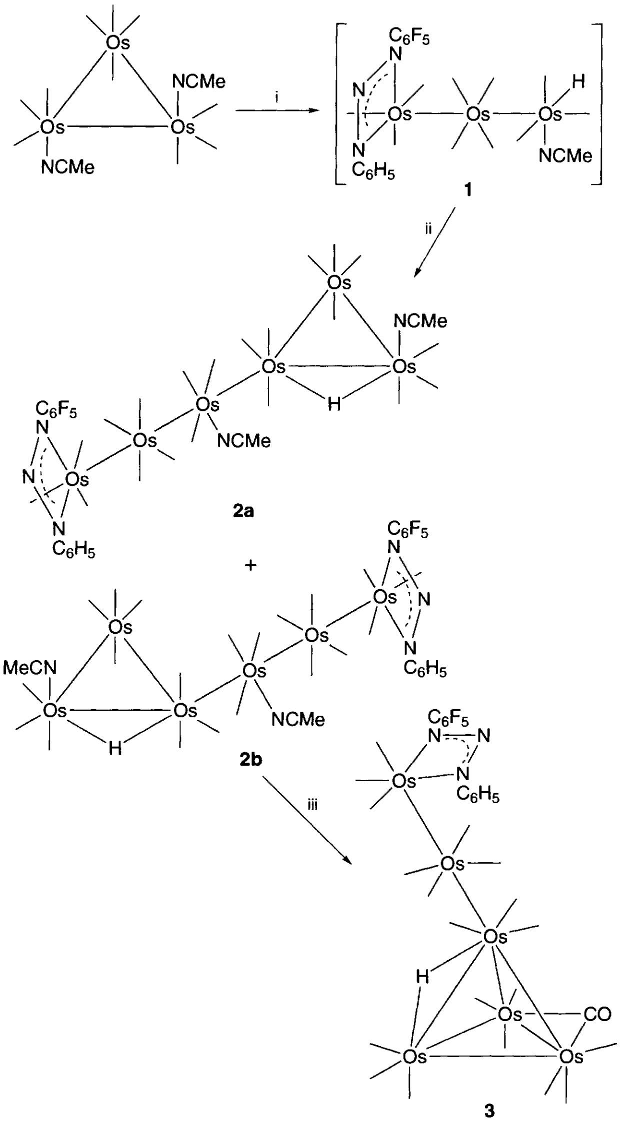


Fig. 1 The molecular structure of $Os_6(\mu$-H)(CO)$_{19}(\mu$-CO)(η^2-$C_6F_5NNNC_6F_5$)] **3**, showing the labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Important bond lengths (Å) and angles (°) are mentioned in the text.

corresponding angle in $[RuH(dtt)(CO)(PPh_3)_2]$,[7] in which both nitrogen atoms are coordinated to the metal to form a four-membered chelated ring. The third Os in the linear portion asymmetrically caps the triangular face with two short and one long bond [2.853(2), 2.880(1) and 2.966(1) Å, respectively]. One bridging CO ligand spans one edge of the triangular face, while the remaining 19 CO groups are terminal. Although the hydride was not located directly in the X-ray analysis, its position could be inferred by the elongated Os(3)–Os(6) bond and distorted CO(62) ligand, which is bent away from the metal–metal bond.

The study on the formation of compounds **3** was also carried out (Scheme 1). Although intermediate **1** has not been separated and fully characterised, its terminal hydride resonance, which appeared at δ −10.07 in the ^1H NMR spectrum, was detected in the initial reaction mixture in CD_2Cl_2.[4] Bearing the terminal hydride, intermediate **1** undergoes a 'metal–hydride coupling' reaction with $[Os_3(CO)_{10}(NCMe)_2)]$ to give 'spiked' isomeric intermediate **2**, of which the proton-coupled and decoupled ^{13}C NMR spectra recorded at −10 °C in $[^2H_8]$toluene are consistent with the feature that the linear portion 'spikes' at equatorial sites of the triangular framework *cis* or *trans* to the hydride ligand (Scheme 1).† Intermediate **2** was not stable and subsequent metal–metal bond formation is easily achieved to lead to the 'capped' cluster **3**. Similar changes have also been observed in other clusters. Upon pyrolysis, the 'spiked' cluster $[Os_4H_2(CO)_{14}(NCMe)]$ afforded the tetrahedral cluster $[Os_4H_2(CO)_{13}]$ *via* a sequential loss of two-electron ligands and formation of new metal–metal bonds with consequent closing of the cluster.[3] In our case, cluster **3** was formed by loss of two MeCN ligands, formation of two Os–Os metal bonds and change of one terminal CO ligand to bridging CO. Thus, each osmium atom in the resultant cluster obeys the 18-electron rule.



Scheme 1 *Reagents and conditions*: i, $C_6F_5N{=}NNHC_6F_5$, CH_2Cl_2, room temp.; ii, $[Os_3(CO)_{10}(NCMe)_2]$; iii, CH_2Cl_2, −2MeCN, room temp.

Attempts to isolate the reactive cluster **1** turned out to be unsuccessful. However, the formation of the new cluster **3** demonstrated the potential application of the clusters with terminal hydride and labile ligands in controlled synthesis of clusters under mild conditions. In these processes, the synthesis is initially directed by the intermolecular 'metal–hydride coupling' reaction, which could result in simple 'spiked' clusters such as **2**. Because of the presence of the hydride and the labile ligand MeCN, these 'spiked' clusters could convert easily to 'capped' clusters by losing MeCN and forming metal–metal bonds. This 'capping' process might consist of a series of intramolecular 'metal–hydride coupling' reactions between the hydride and the labile ligand MeCN. Thus, through elegantly designed clusters (complexes) containing terminal hydride and a labile ligand, controlled synthesis of clusters with special metal frameworks such as **3** can be achieved. Furthermore, as these clusters are formed under very mild conditions, their intermediates could be separated and provide elusive experimental evidence enabling the mechanism of their formation to be proposed.

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Footnotes

† *Selected spectroscopic data*: for **2**, isomer **a**: IR ν(CO) (CH_2Cl_2) 2107w, 2085m, 2065m, 2057m, 2032w, 2022m, 2002s cm^{-1}. ^1H NMR ($CDCl_3$, δ) −16.4 (s, 1 H), 2.5 (s, 6 H); ^{19}F NMR −77.8 (d, J_{FF} 24.41 Hz, 4 F), −85.0 (t, J_{FF} 29.29 Hz, 2 F), −88.1 (m, 4 F). Isomer **b**: IR ν(CO) (CH_2Cl_2) 2105w, 2088s, 2063m, 2056m, 2038w, 2018m, 2005s, 1982m cm^{-1}. ^1H NMR ($CDCl_3$, δ) −16.2 (s, 1 H), 2.5 (s, 6 H); ^{19}F −77.1 (d, J_{FF} 19.53 Hz, 4 F), −83.3 (t, J_{FF} 24.41 Hz, 2 F), −87.1 (m, 4 F). ^{13}C NMR data for **2a** and **b** are consistent with the structures proposed in Scheme 1. For **3**: IR ν(CO) (CH_2Cl_2) 2120w, 2098m, 2081w, 2064vs, 2027vs, 1999w, 1818w cm^{-1}. ^1H NMR ($CDCl_3$, δ) −22.5 (s); ^{19}F −75.4 (d, J_{FF} 19.53 Hz, 4 F), −80.3 (t, J_{FF} 19.53 Hz, 2 F), −84.9 (t, J_{FF} 19.54 Hz, 4 F). Satisfactory microanalyses were obtained for **2a**, **b** and **3**.

‡ *Crystal data* for **3**: deep yellow prism, $C_{32}HF_{10}N_3O_{20}Os_6$; M = 2078.6, triclinic, space group $P\bar{1}$, a = 9.346(2), b = 15.516(5), c = 16.823(4) Å, α = 71.37(2), β = 78.76(2), γ = 75.85(2), U = 2223.4(10) Å^3, Z = 2, D_c = 3.103 g cm^{-1}, $F(000)$ = 1838, λ = 0.71073 Å, μ(Mo-Kα) = 17.198 mm^{-1}. Intensity data were collected for a crystal of dimensions 0.3 × 0.2 × 0.2 mm mounted on a Siemens R3 m/v diffractometer by the ω-scan method ($3.5 < 2\theta < 50°$); of 8388 reflections measured, 5659 were considered observed [$F > 4.0\sigma(F)$]. The structure was solved (direct methods) and refined (full-matrix least squares) using the Siemens SHELXTL PLUS program (PC version), give final R and R_W values of 0.0505 and 0.0571 respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/40.

References

1 R. Mason, K. M. Thomas and D. M. P. Mingos, *J. Am. Chem. Soc.*, 1973, **95**, 3802.
2 M. D. Vargas and J. N. Nicholls, *Adv. Inorg. Chem. Radiochem.*, 1986, **30**, 123.
3 J. Lewis and J. R. Moss, *J. Organomet. Chem.*, 1993, **444**, C51, and references cited therein.
4 H. G. Ang, L. L. Koh and G. Y. Yang, *J. Chem. Soc., Dalton Trans.*, 1996, 1573.
5 H. G. Ang, L. L. Koh and G. Y. Yang, unpublished work.
6 M. R. Churchill and B. G. de Boer, *Inorg. Chem.*, 1977, **16**, 878.
7 L. D. Brown and J. A. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 1597.

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