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Synthesis of 1,3-diaryltriazenido triruthenium and triosmium clusters: crystal structures of $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}C_6F_5NNNC_6F_5)]$ and $[Os_3(CO)_{11}Cl(\eta_2\text{-}C_6F_5NNNC_6F_5)]$

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New clusters $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}RNNNR)]$ (R = *p*-C_6F_4X; X = F **1**, Br **2**, I **3** or H **4**) were obtained from reactions of RN=NNHR with $[Ru_3(CO)_{12}]$ in toluene at 80 °C under vacuum, while the linear triosmium clusters $[Os_3(CO)_{11}Cl(\eta^2\text{-}RNNNR)]$ (R = *p*-C_6F_4X; X = F **5**, Br **6**, I **7** or H **8**) were obtained from RN=NNHR with $[Os_3(CO)_{11}(NCMe)]$ in CH_2Cl_2 at 60 °C under vacuum. The crystal structures of $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}C_6F_5NNNC_6F_5)]$ **1** and $[Os_3(CO)_{11}Cl(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **5** have been determined by single-crystal X-ray crystallography. The structure of **1** shows that the triazenide ligand bridges one Ru–Ru vector in the cluster at axial sites and forms a five-membered ring with π delocalization over the whole system. A hydride ligand was located which bridges another Ru–Ru vector equatorially and displays interesting fluxionality in solution. The chloride ligand in complex **5** co-ordinates equatorially at the first Os atom, while the triazenide occupies an axial and an equatorial site on the third Os in the linear cluster and forms a four-membered ring with π delocalization over the whole system. The linear cluster $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$, precursor of **5**, was also obtained. Carbon-13 NMR studies of this cluster and the mechanism of its formation are reported.

Triazenes have long been investigated as good ligands towards transition metals.[1] They can be either two- or four-electron donors, and a key to understanding their co-ordination chemistry is the mode of attachment to the metal. In early works, structures with monodentate,[2] bidentate [1] and bridging [2] triazenide ligands have been proposed on the basis of spectroscopic data. Recently, with the help of X-ray methods, the structures of $[\{Ni(dpt)_2\}_2]$ (dpt = 1,3-diphenyltriazenide),[3] $[\{Cu(dpt)_2\}_2]$,[4] $[\{Pd(C_3H_5)(dtt)\}_2]$ (dtt = 1,3-di-*p*-tolyltriazenide),[5] $[\{Cu(dmt)\}_4]$ (dmt = 1,3-dimethyltriazenide),[6] $[Re_2(dpb)_2Cl_4]$ (dpb = *N*,*N*′-diphenylbenzamidinate) [7] and $[\{Cr(dpt)_2\}]$ [8] were obtained which confirmed that the triazenide ligand bridges the metal centres in these compounds. While the structures of $[Co(dpt)_3]\cdot C_6H_5Me$,[9] *trans*-$[RuH(dtt)(CO)(PPh_3)_2]$,[10] $[\{(2\text{-}ClC_6H_4)_2N_3\}HgMn(CO)_5]$,[11] $[Re(dtt)(CO)_2(PPh_3)_2]$,[12] $[ReCl_2(dtt)(PPh_3)_2]$ [13] and $[Tc(dtt)(CO)_2(PMe_2Ph)_2]$ [14] revealed the presence of a bidentate triazenide co-ordinated to a single metal atom; *cis*-$[Pt(dpt)_2(PPh_3)_2]$ [10] contains monodentate dpt. Moreover, a novel Rh–Hg complex has been reported containing two triazenido groups, one chelating the rhodium atom and the other bridging a rhodium–mercury bond, and a dynamic process has been established consisting of interchange of the bridging and chelating triazenides *via* a monodentate intermediate.[15,16]

Despite extensive study of triazenes, their reactions with clusters do not appear to have received much attention. Only recently, triazenes have been found to react with the triruthenium cluster $[Ru_3(CO)_{12}]$ to give binuclear ruthenium(I) triazenido complexes of the form $[\{Ru(RNNNR)(CO)_3\}_2]$ (R = *p*-C_6H_4Me or *p*-C_6H_4Cl).[17] Their reactions with triosmium clusters have not been described. However, triosmium clusters with the general formula $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3R)]$ (R = H, Ph, Bu^n, CH_2Ph, cyclo-C_6H_{11} or $CPhCH_2$) [18,19] have been synthesized from reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with N_3SiMe_3 or the corresponding azides. We now report the reactions of 1,3-bis(polyfluorophenyl)triazenes with $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{11}(NCMe)]$ and the unusual structural properties of the new cluster derivatives.

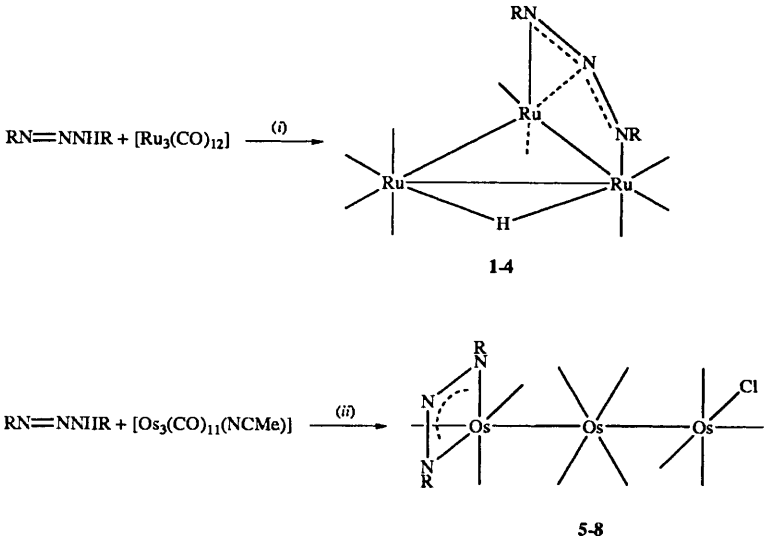
Results and Discussion

Reaction with $[Ru_3(CO)_{12}]$

Reactions of RN=NNHR (R = *p*-C_6F_4X; X = F, Br, I or H) with $[Ru_3(CO)_{12}]$ in toluene at 80 °C under vacuum for 4 h led to the formation of $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}RNNNR)]$ **1**–**4** in relatively good yields of 41–49% (Scheme 1). The products were purified by TLC and obtained as orange crystals from toluene. No corresponding products were formed when R = Ph or 2,4-$(O_2N)_2C_6H_3$ under the same conditions. The fluorine-containing triazenes and the non-fluorinated triazenes behave differently because of the electron-withdrawing polyfluorophenyl groups, which probably stabilize the triruthenium framework by reducing the electron density on the Ru.

Clusters **1**–**4** were characterized by spectroscopic studies (Table 1) and microanalysis (Table 2). The ^1H NMR spectra show a resonance attributable to the bridging hydride at δ_H −13.77 to −13.91. The ^{19}F NMR data show that the two polyfluorophenyl groups have different chemical shifts, reflecting the asymmetry of the ligand. The IR ν(CO) spectra for the four products are similar, indicating the same structure pattern; bands at *ca.* 1375–1372 and 1190–1210 cm^{-1} were attributed to the presence of bridging 1,3-diaryltriazenide ligands.[20] The UV bands, λ_2, of the new compounds refer to the largest wavelength absorption of the triazenide chromophore.[21] The bathochromic shift of this absorption is due to the replacement of the triazene proton [11] by Ru and the π delocalization over the ruthenium–triazenide system.

The fluxional behaviour of the bridging hydride has been studied and can be inferred from the 500 MHz ^1H NMR spectra shown in Fig. 1. The NMR spectrum at *ca.* −60 °C gave three singlet hydride signals at δ_H = −12.87, −14.05 and −14.06, indicating three isomers in a time-independent mol ratio of 1:2.5:2.5, which differ in the hydride sites (Scheme 2). The hydrides at $\delta \approx -14.00$ correspond to **1a** and **1b**, which are structurally similar and have a much faster rate of migration (coalesce at *ca.* −17 °C), whereas the hydride at δ −12.87,



Scheme 1 Reaction of RN=NNHR (R = p-C_6F_4X, X = F, Br, I or H) with $[Ru_3(CO)_{12}]$ or $[Os_3(CO)_{11}(NCMe)]$ (carbonyl groups omitted for clarity). (*i*) Toluene, 80 °C, vacuum, 4 h; (*ii*) CH_2Cl_2, 60 °C, vacuum, overnight

Table 1 Spectroscopic data for $[Ru_3(\mu\text{-H})(CO)_{10}(\mu\text{-RNNNR})]$ (R = p-C_6F_4X)

	^{1}H NMR[a]	^{19}F NMR[a]	IR[b] (cm^{-1})			UV[b] (nm)	
Cluster	(δ)	(δ, J/Hz)	ν(CO)	ν(R)	ν(Triazenide)	λ_1	λ_2
1 (X = F)	−13.91 (s, RuH)	−71.8 [d, $J(F_oF_m)$ = 9.77, 4 F], −78.8 [d, $J(F_mF_p)$ = 19.53, 1 F], −80.3 [t, $J(F_mF_p)$ = 19.53, 1 F], −85.1 (m, 4 F)	2124m, 2112w, 2104w, 2081vs, 2073m, 2071m, 2057vs, 2051vs, 2034s, 2017s, 2006s, 1990w, 1982w	1513m, 993w	1375m, 1148w	277	396w (sh)
2 (X = Br)	−13.82 (s, RuH)	−55.5 (s, 2 F), −56.7 (s, 2 F), −69.3 (s, 2 F), −73.3 (s, 2 F)	2124m, 2112w, 2104w, 2081vs, 2073m, 2069m, 2057vs, 2051vs, 2034s, 2018s, 2006s, 1990w, 1982w	1491m, 981w	1373m, 1140w	280	398w (sh)
3 (X = I)	−13.88 (s, RuH)	−42.5 (s, 2 F), −43.7 (s, 2 F), −68.6 (s, 2 F), −70.7 (s, 2 F)	2124m, 2112w, 2102w, 2081vs, 2073m, 2071m, 2057vs, 2051vs, 2033s, 2017s, 2006s, 1990w, 1982w	1488m, 974w	1373m	282	395w (sh)
4 (X = H)	−13.77 (s, RuH) 7.01 (m, 2 H)	−61.3 (s, 2 F), −62.6 (s, 2 F), −70.5 (s, 2 F), −74.7 (s, 2 F)	2124m, 2111w, 2081vs, 2072 (sh), 2057vs, 2051vs, 2033s, 2017s, 2005s, 1990w, 1981w	1514m, 943w	1372m, 1176w	274	394w (sh)

[a] In $CDCl_3$. [b] In hexanes.

Table 2 Analytical[a] data for the ruthenium and osmium clusters

		Analysis (%)		
Cluster	Yield[b] (%)	C	H	N
$[Ru_3(\mu\text{-H})(CO)_{10}(\mu\text{-RNNNR})]$ (R = p-C_6F_4X)				
1 (X = F)	42	27.5 (27.5)	0.2 (0.1)	4.9 (4.4)
2 (X = Br)	40	24.4 (24.4)	0.1 (0.1)	3.6 (3.9)
3 (X = I)	41	22.7 (22.5)	0.0 (0.1)	3.7 (3.6)
4 (X = H)	49	28.6 (28.6)	0.3 (0.3)	5.0 (4.6)
$[Os_3(CO)_{11}Cl(\eta^2\text{-RNNNR})]$ (R = p-C_6F_4X)				
5 (X = F)	44	21.3 (21.4)		3.3 (3.3)
6 (X = Br)	30	20.3 (19.6)		3.5 (3.0)
7 (X = I)	54	18.6 (18.3)		3.0 (2.8)
8 (X = H)	21	22.1 (22.0)	0.2 (0.2)	3.2 (3.4)
$[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **9**	47	22.0 (22.3)	0.2 (0.1)	3.0 (3.4)

[a] Required values are given in parentheses. [b] Based on the clusters $[Ru_3(CO)_{12}]$ or $[Os_3(CO)_{11}(NCMe)]$.

which is associated with **1c**, coalesces with those of **1a** and **1b** at *ca.* 23 °C to give a broad singlet at δ −13.97. Since the isomers have the mol ratio of 1 : 2.5 : 2.5, there is a 5 : 1 preference for the hydride to be on the open edge of the cluster. This could be rationalized in terms of the steric constraints of the pentafluorophenyl groups and the electron-deficient ruthenium centres bridged by the electron-withdrawing triazenide ligand, which was confirmed by the presence of the hydride in **1c** at relatively low field in the ^{1}H NMR spectrum. Therefore, in this case, the hydride is incorporated at the open edge both thermodynamically and kinetically and the dominant isomers were obtained during crystallization. Fluxionality of bridging hydride in nitrogen-containing clusters is relatively rare compared to that in clusters with phosphine ligands. There is no

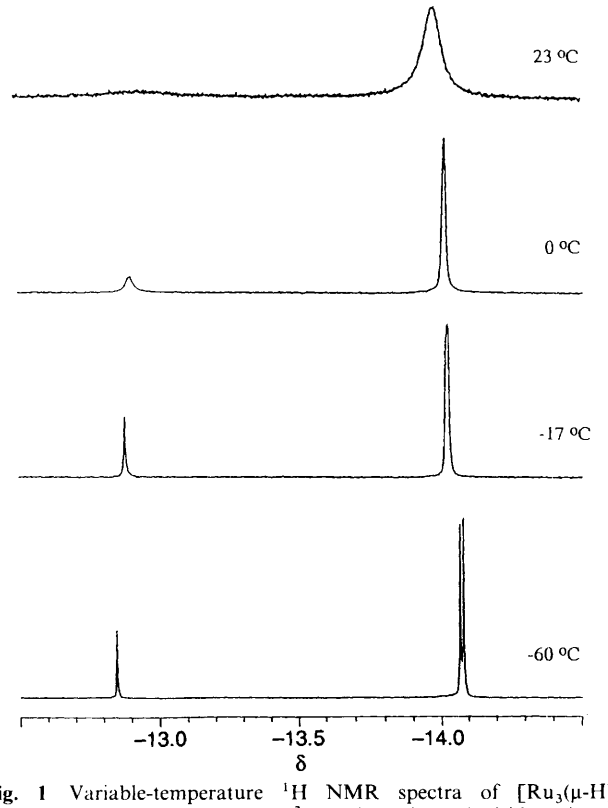
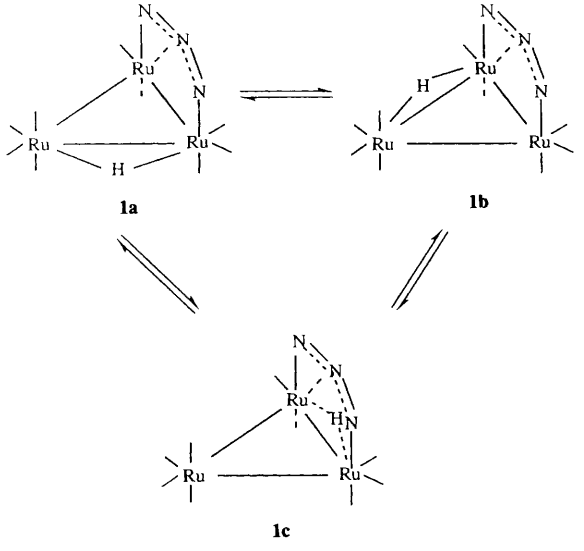


Fig. 1 Variable-temperature ^1H NMR spectra of $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}C_6F_5NNNC_6F_5)]$ **1** in $[^2H_8]$toluene in the hydride region



Scheme 2 Carbonyl and pentafluorophenyl groups omitted for clarity

report on the fluxional behaviour of the bridging hydride in the osmium analogues $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3R)]$[18,19] in which the hydride might bridge the most electron-rich Os–Os edge with the electron-donating triazenide ligand. Therefore, the most thermodynamically stable product was formed. That the hydride migration is not so easy in osmium clusters[22] may also contribute to the stability of this osmium cluster.

Reaction with $[Os_3(CO)_{11}(NCMe)]$

The reactions between RN=NNHR and $[Os_3(CO)_{11}(NCMe)]$ were carried out in CH_2Cl_2 at 60 °C under vacuum overnight and gave the major products $[Os_3(CO)_{11}Cl(\eta^2\text{-}RNNNR)]$ **5–8** (Scheme 1), which were separated by TLC. The products were characterized by spectroscopic studies (Table 3) and microanalysis (Table 2). The symmetrical arrangement of the triazenide ligand was shown by the observation of only one ^{19}F NMR resonance for the two polyfluorophenyl groups. The UV absorption bathochromic shift of λ_2 was also observed for these compounds, indicating the presence of π delocalization over the osmium–triazenide system. Infrared bands at *ca.* 1263 cm^{-1} are characteristic for bidentate triazenide ligands.[20]

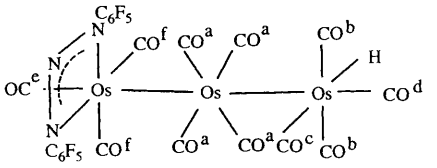
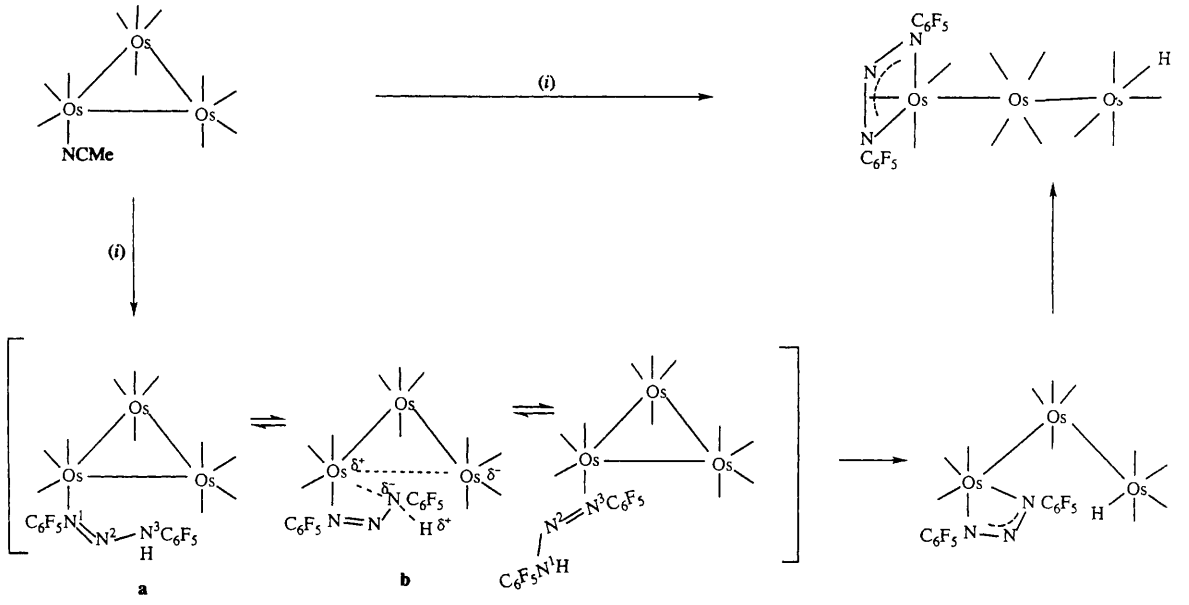


Fig. 2 Structure of $[Os_3H(CO)_{11}(C_6F_5NNNC_6F_5)]$ **9** showing the labelling of the CO groups

To investigate the mechanism of formation of these clusters the reaction of $C_6F_5N{=}NNHC_6F_5$ with $[Os_3(CO)_{11}(NCMe)]$ was studied closely. At room temperature in CH_2Cl_2 for 4 h or at 70 °C in hexane overnight, reaction led to the formation of the major compound $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **9**, which was characterized by analytical (Table 2) and spectroscopic data. The ^1H NMR spectrum indicates the existence of a terminal hydride at δ_H −9.87 which agrees very well with the chemical shift (*ca.* δ_H = −9.85, C_6D_6) obtained for the terminal hydride in the linear osmium complex $[Os_3H_2(CO)_{12}]$.[23] The IR absorption for the bidentate triazenide ligand was also observed at *ca.* 1264 cm^{-1}.[20] Compared with ^{13}C NMR data obtained by Gochin and Moss[24] for the linear triosmium cluster $[Os_3H_2(CO)_{12}]$, the peaks in the spectrum of compound **9** could be fully assigned (Fig. 2, Table 4). The peak at δ 188.5 has the strongest intensity and similar chemical shift to that of the four carbonyl groups on the central osmium atom in $[Os_3H_2(CO)_{12}]$;[24] therefore, it can be assigned to the four carbonyl groups (labelled CO^a in Fig. 2) on the central osmium atom in **9**. The peaks at δ 178.5, 174.1 and 165.8, which have similar chemical shifts and $^2J(^{13}C{-}^1H)$ to those of the four carbonyl groups on the terminal osmium atom bound to the hydride ligand in $[Os_3H_2(CO)_{12}]$,[24] can be assigned to the four carbonyl groups on the osmium atom having the terminal hydride, CO^b, CO^c and CO^d, respectively. The peak at δ 167.5, which remains as a singlet in the proton-coupled spectrum and appears at higher field, can be assigned to the carbonyl group CO^e *trans* to the Os–Os bond on the osmium atom bound to the triazenide ligand; that at δ 178.6, which also remains as a singlet in the proton-coupled spectrum but has higher intensity, can be assigned to the carbonyl groups CO^f on the same osmium atom.

Recently, Lu *et al.*[25] have described the synthesis of a similar linear triosmium complex $[Os_3Br(CO)_{10}(CNR)(\eta^3\text{-}C_3H_5)]$ (R = Pr or CH_2Ph) which was obtained *via* oxidative addition of allyl bromide to $[Os_3(CO)_{10}(CNR)(NCMe)]$ and partial heterolytic metal–metal bond fission. In our case the formation of **9** is believed to proceed *via* a similar mechanism with a monosubstituted intermediate $[Os_3(CO)_{11}(C_6F_5N{=}NNHC_6F_5)]$ **a** formed initially (Scheme 3). In this cluster the monodentate triazenide ligand undergoes rapid intramolecular N(1)–N(3) interchange *via* a five-co-ordinate chelated triazenido intermediate **b** as reported for mononuclear triazenido complexes.[26] Owing to the resonance stabilization of the triazenido anions $(RN{\cdot\cdot}N{\cdot\cdot}NR)^-$,[27] the N–H bond in 1,3-diaryltriazene might undergo facile cleavage very smoothly at this stage. With bidentate attachment of the triazenide ligand to the Os atom, the Os–Os bond is polarized and weakened and its dissociation occurs easily. The hydride ligand then transfers to the neighbouring Os atom to co-ordinate on the equatorial site.

Compound **9** could also be halogenated directly to $[Os_3(CO)_{11}Cl(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ after heating in CH_2Cl_2 at 60 °C. In most cases, methylene chloride could be used as a solvent for hydride complexes. However, it can react with



Scheme 3 (*i*) $C_6F_5N{=}NNHC_6F_5$, hexane, 70 °C

Table 3 Spectroscopic data for $[Os_3(CO)_{11}Cl(\eta^2\text{-RNNNR})]$ (R = *p*-C_6F_4X)

		IR[b] (cm^{-1})			UV[b] (nm)	
Cluster	^{19}F NMR[a]	ν(CO)	ν(R)	ν(Triazenide)	λ_1	λ_2
5	−74.71 (m, 4 F), −80.74 (m, 2 F), −85.20 (m, 4 F)	2138w, 2097vs, 2076w, 2057vs, 2026vs	1514m, 993w	1263m	245	366
6	−56.38 (m, 4 F), −74.31 (m, 2 F), −75.56 (m, 2 F)	2137w, 2096vs, 2069w, 2057vs, 2025vs	1492m, 978w	1263m	243	366
7	−43.61 (m, 4 F), −73.47 (m, 2 F), −75.36 (m, 2 F)	2138w, 2097vs, 2076w, 2057vs, 2026vs	1482m, 974w	1262m	252	389
8[c]	−62.06 (m, 2 F), −75.56 (m, 2 F)	2138w, 2097vs, 2075w, 2056vs, 2025vs	1492m, 978w	1263m	258	375

[a] In $CDCl_3$. [b] In hexanes. [c] ^{1}H NMR: [a] δ 6.99 (m, 2 H).

Table 4 Carbon-13 NMR data for $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNN\text{-}C_6F_5)]$[a]

δ[b] (Downfield from $SiMe_4$)	$^2J(^1H\text{–}^{13}C)$[b]/Hz	Assignment[b,c]
188.5 (188.0)	0 (0)	a (a)
178.6 (178.7)	8.3 (6)	b (b)
174.1 (174.1)	17.5 (18)	c (c)
165.8 (166.1)	5.8 (≈9)	d (d)
167.5	0	e
178.5	0	f

[a] In [$^2H_8$]toluene. [b] The data and labelling of CO groups in $[Os_3H_2(CO)_{12}]$[24] are given in parentheses. [c] See Fig. 2 for labelling of CO groups.

some hydride complexes, *e.g.* $[TaH_3(\eta\text{-}C_5H_5)_2]$ and $[NbH_3(\eta\text{-}C_5H_5)_2]$.[28] In our case it acts as a halogenating agent as well.

Molecular structure of $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}C_6F_5NNNC_6F_5)]$ 1

The molecular structure of complex **1** has been determined by single-crystal X-ray diffraction. Selected bond distances and angles are given in Table 5. The new cluster crystallized as two crystallographically independent but structurally similar molecules; each consists of a triangular cluster of ruthenium atoms with distances Ru(1)–Ru(2) 2.737(1), Ru(1)–Ru(3) 3.034(1) and Ru(2)–Ru(3) 2.890(1) Å (for molecule A). The structure of molecule A is shown in Fig. 3. Two nitrogen atoms in the triazene ligand, N(1) and N(3), co-ordinate at two axial sites of the Ru(1)–Ru(2) vector. The N(1), N(2), N(3), Ru(1) and Ru(2) atoms are nearly coplanar [largest deviation for N(2), 0.065 Å] and the plane defined by these atoms is almost orthogonal to that defined by the triruthenium atoms; the angle between them is 94.7°. The N(1)–N(2)–N(3) angle of 115.3° and the average N–N bond length of 1.302(4) Å agree very well with those reported for $[\{Ru(RNNNR)(CO)_2(NH_2R)\}_2]$ (R = *p*-C_6H_4Me).[17] The same bond length for N(1)–N(2) [1.300(4) Å] and N(2)–N(3) [1.303(4) Å], which is intermediate between a single- and a double-bond distance (1.44 and 1.24 Å, respectively),[29] as well as the near planarity of N(1), N(2), N(3), Ru(1) and Ru(2) indicates that there is extensive π delocalization over the ruthenium–triazenide system. A hydride ligand bridges the Ru(1) and Ru(3) atoms and lengthens the Ru(1)–Ru(3) bond by 0.180 Å compared to the value in $[Ru_3(CO)_{12}]$.[30] Its presence leads to asymmetry of the cluster, as shown by the different chemical shifts of the two pentafluorophenyl groups in the ^{19}F NMR spectrum. The average Ru–C distance for the axial carbonyl *trans* to the N atoms of the triazenide ligand [1.880(4) Å] is slightly shorter than that for the equatorial carbonyls. This trend is consistent with the proposal that *trans* axial groups compete for back donation of electron density from the same metal orbital, and that carbonyl is a better π acceptor than Ru or the N atom of the triazene.

Triazenide ligands have been observed previously in other

Table 5 Selected interatomic distances (Å) and angles (°) for $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}C_6F_5NNNC_6F_5)]$ **1**

		A		B			A		B
Ru–Ru	Ru(1)–Ru(2)	2.737(1)	Ru(4)–Ru(5)	2.743(1)	Ru_3 ring	Ru(1)–Ru(2)–Ru(3)	65.2(1)	Ru(4)–Ru(5)–Ru(6)	65.0(1)
	Ru(1)–Ru(3)	3.034(1)	Ru(4)–Ru(6)	3.032(1)		Ru(2)–Ru(1)–Ru(3)	59.8(1)	Ru(5)–Ru(4)–Ru(6)	59.9(1)
	Ru(2)–Ru(3)	2.890(1)	Ru(5)–Ru(6)	2.893(1)		Ru(1)–Ru(3)–Ru(2)	55.0(1)	Ru(4)–Ru(6)–Ru(5)	55.1(1)
Ligand ring	Ru(1)–N(1)	2.133(3)	Ru(4)–N(4)	2.135(3)	Ligand ring	Ru(2)–Ru(1)–N(1)	82.5(1)	Ru(5)–Ru(4)–N(4)	83.2(1)
	Ru(2)–N(3)	2.144(3)	Ru(5)–N(6)	2.142(3)		Ru(1)–Ru(2)–N(3)	83.0(1)	Ru(4)–Ru(5)–N(6)	82.1(1)
	N(1)–N(2)	1.300(4)	N(4)–N(5)	1.301(4)		Ru(1)–N(1)–N(2)	129.5(2)	Ru(4)–N(4)–N(5)	128.3(2)
	N(2)–N(3)	1.303(4)	N(5)–N(6)	1.299(4)		Ru(2)–N(3)–N(2)	128.4(2)	Ru(5)–N(6)–N(5)	129.6(2)
						N(2)–N(1)–C(111)	109.9(3)	Ru(5)–N(6)–C(411)	109.2(3)
Ru–C	Ru(1)–C(13)	1.881(4)	Ru(4)–C(41)	1.896(4)		N(2)–N(3)–C(211)	109.2(3)	N(5)–N(6)–C(511)	109.7(3)
(axial)	Ru(2)–C(21)	1.879(4)	Ru(5)–C(52)	1.881(4)		N(1)–N(2)–N(3)	115.3(3)	N(4)–N(5)–N(6)	115.4(3)
(equatorial)	Ru(1)–C(12)	1.959(4)	Ru(4)–C(42)	1.952(5)	Ru–Ru–C	Ru(1)–Ru(3)–C(33)	117.6(1)	Ru(4)–Ru(6)–C(62)	119.1(1)
	Ru(1)–C(11)	1.896(4)	Ru(4)–C(43)	1.896(5)		Ru(3)–Ru(1)–C(12)	116.9(1)	Ru(6)–Ru(4)–C(42)	114.5(1)
	Ru(2)–C(23)	1.927(4)	Ru(5)–C(53)	1.904(5)		Ru(1)–Ru(2)–C(22)	101.7(1)	Ru(4)–Ru(5)–C(52)	100.8(2)
	Ru(2)–C(22)	1.901(4)	Ru(5)–C(51)	1.916(5)		Ru(2)–Ru(1)–C(11)	85.7(1)	Ru(5)–Ru(4)–C(43)	86.5(1)
						Ru(3)–Ru(2)–C(23)	97.8(1)	Ru(6)–Ru(5)–C(51)	99.7(2)
						Ru(2)–Ru(3)–C(32)	87.1(1)	Ru(5)–Ru(6)–C(61)	86.1(2)
C–N	N(1)–C(111)	1.428(4)	N(4)–C(411)	1.430(4)	Ru–H–Ru	Ru(1)–H(1)–Ru(3)	113.8	Ru(4)–H(2)–Ru(6)	118.6
(ligand)	N(3)–C(211)	1.431(4)	N(6)–C(511)	1.431(4)					
Ru–H	Ru(1)–H(1)	1.848	Ru(4)–H(2)	1.752					
	Ru(3)–H(1)	1.774	Ru(6)–H(2)	1.775					

Table 6 Selected interatomic distances (Å) and angles (°) for $[Os_3(CO)_{11}Cl(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **5**

		A		B			A		B
Os–Os	Os(1)–Os(2)	2.888(1)	Os(4)–Os(5)	2.898(1)	Os–Os–Os	Os(1)–Os(2)–Os(3)	176.0(1)	Os(4)–Os(5)–Os(6)	172.8(1)
	Os(2)–Os(3)	2.878(1)	Os(5)–Os(6)	2.880(1)	Ligand ring	N(31)–Os(3)–N(33)	57.7(6)	N(61)–Os(6)–N(63)	58.6(7)
Ligand ring	Os(3)–N(31)	2.135(15)	Os(6)–N(61)	2.146(18)		Os(3)–N(31)–N(32)	98.2(10)	Os(6)–N(61)–N(62)	96.7(12)
	Os(3)–N(33)	2.126(22)	Os(6)–N(63)	2.115(20)		Os(3)–N(33)–N(32)	99.2(14)	Os(6)–N(63)–N(62)	99.5(15)
	N(31)–N(32)	1.307(28)	N(61)–N(62)	1.334(32)		N(31)–N(32)–N(33)	104.6(17)	N(61)–N(62)–N(63)	105.2(18)
	N(32)–N(33)	1.291(21)	N(62)–N(63)	1.292(23)		Os(2)–Os(3)–N(31)	89.9(4)	Os(5)–Os(6)–N(61)	89.7(5)
N–C (ligand)	N(31)–C(311)	1.425(24)	N(61)–C(611)	1.359(28)		Os(2)–Os(3)–N(33)	91.5(5)	Os(5)–Os(6)–N(63)	91.4(5)
	N(33)–C(331)	1.408(32)	N(63)–C(631)	1.452(33)	Os–Os–Cl	Os(2)–Os(1)–Cl(1)	89.4(2)	Os(5)–Os(4)–Cl(2)	89.5(2)
Os–Cl	Os(1)–Cl(1)	2.462(10)	Os(4)–Cl(2)	2.446(8)	Os–Os–C	Os(2)–Os(1)–C(11)	86.2(7)	Os(5)–Os(4)–C(41)	81.0(7)
Os–C	Os(1)–C(11)	1.963(30)	Os(4)–C(41)	1.978(22)		Os(2)–Os(1)–C(12)	86.6(7)	Os(5)–Os(4)–C(43)	88.7(6)
	Os(1)–C(12)	2.064(22)	Os(4)–C(42)	1.901(29)	Cl–Os–C	Cl(1)–Os(1)–C(12)	86.0(9)	Cl(2)–Os(4)–C(42)	85.1(12)
	Os(1)–C(13)	1.950(25)	Os(4)–C(43)	1.958(30)		Cl(1)–Os(1)–C(14)	92.0(11)	Cl(2)–Os(4)–C(44)	85.8(12)
	Os(1)–C(14)	1.989(25)	Os(4)–C(44)	1.924(29)		Cl(1)–Os(1)–C(13)	87.5(10)	Cl(2)–Os(4)–C(41)	90.8(9)
	Os(3)–C(31)	1.919(27)	Os(6)–C(61)	1.859(30)	C–Os–C	C(14)–Os(1)–C(11)	91.3(12)	C(44)–Os(4)–C(43)	90.6(13)
	Os(3)–C(32)	1.897(32)	Os(6)–C(62)	1.918(26)		C(12)–Os(1)–C(11)	89.9(10)	C(42)–Os(4)–C(44)	93.9(12)
	Os(3)–C(33)	1.890(24)	Os(6)–C(63)	1.850(29)					

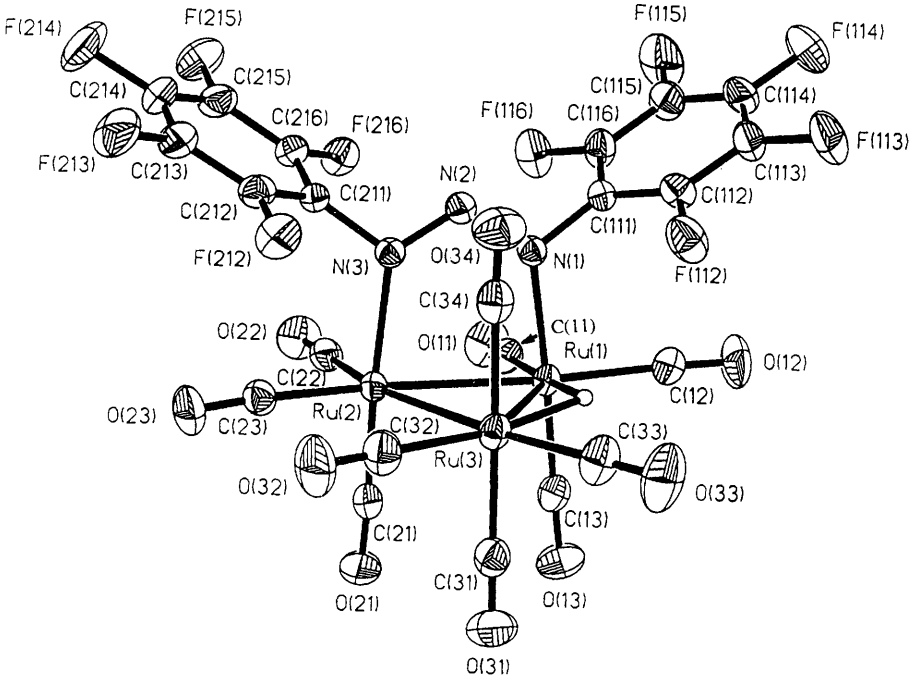


Fig. 3 Molecular structure of $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}C_6F_5NNNC_6F_5)]$ **1** showing the atom labelling

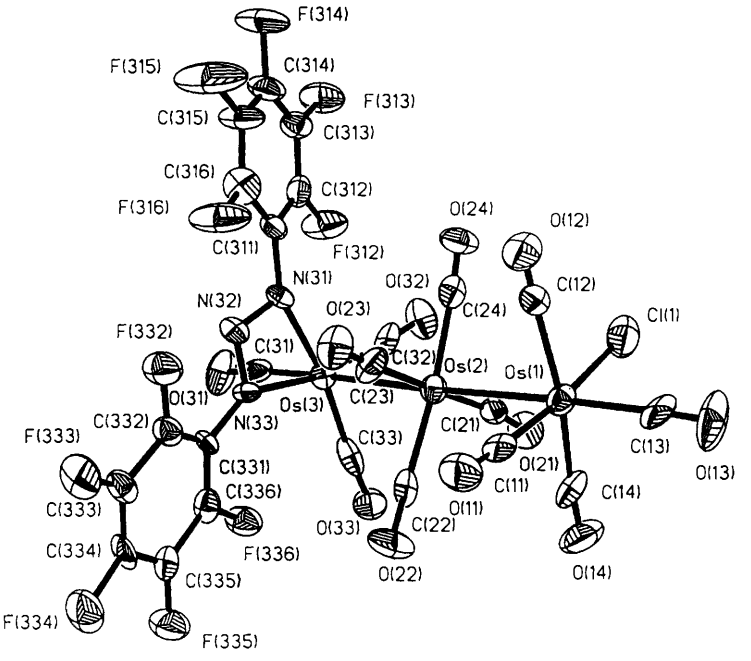


Fig. 4 Molecular structure of $[Os_3(CO)_{11}Cl(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **5** showing the atom labelling

cluster complexes such as $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3R)]$ (R = H, Ph, Bu^n, CH_2Ph, cyclo-C_6H_{11} or $CPhCH_2$).[18,19] The structure of these osmium clusters is similar to that of **1**: both are formally 48-electron species with the triazenide ligand acting as a three-electron donor. However, the locations of the hydride ligand are different: in the osmium clusters the hydride bridges the same Os–Os vector as that by the triazenide ligand; in **1** the hydride bridges one Ru–Ru vector while the triazenide bridges another. Therefore, the bond lengths for the two types of clusters are quite different. In the osmium clusters the three osmium atoms lie at the vertices of an approximately equilateral triangle; in **1** the three Ru–Ru bond lengths are different, one is normal, that bridged by the triazenide is 0.117 Å shorter than the value of 2.854(4) Å in $[Ru_3(CO)_{12}]$[30] and that bridged by the hydride is 0.180 Å longer than the value in $[Ru_3(CO)_{12}]$.[30] Adams and co-workers[31] have reported structural information on a number of triosmium clusters in which an Os–Os bond is bridged by a three-atom unit in an η fashion similar to that observed in **1**. In the cases where this bond is bridged by both an η group and a hydride it is generally slightly longer than the corresponding unbridged Os–Os bonds, while when the hydride is not present the bond length is shorter than that of the unbridged bonds. These trends also seem to apply to the corresponding triruthenium clusters.

Molecular structure of $[Os_3(CO)_{11}Cl(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ 5

The structure of complex **5** was determined by single-crystal X-ray diffraction. Selected bond lengths and angles are listed in Table 6. The complex crystallized as two crystallographically independent but structurally similar molecules. The structure of molecule A is shown in Fig. 4. The three osmium atoms are almost linear with Os–Os–Os 176.0(1)° (for molecule A). The Os–Os distances, 2.888(1) and 2.878(1) Å, are similar to those observed in $[Os_3(CO)_{12}]$,[32] 2.877(3) Å, and the linear cluster $[Os_3(CO)_{12}Cl_2]$,[33] 2.893(1) Å. The chloride ligand co-ordinates equatorially at the first Os atom with Os–Cl 2.462(10) Å, similar to that observed in $[Os_3(CO)_{12}Cl_2]$,[33] 2.43(1) Å. The triazenide ligand occupies an axial and equatorial site on the third Os forming an Os(3)–N(31)–N(32)–N(33) four-membered ring, which is almost coplanar [largest deviation from the plane for N(32), 0.0296 Å]. The Os(3)–N(31) and Os(3)–N(33) bond lengths [2.135(15) and 2.126(22) Å, respectively] are approximately the same, as are N(31)–N(32) and N(32)–N(33) [1.307(28) and 1.291(21) 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 $[RuH(dtt)(CO)(PPh_3)_2]$.[10] The N–N–N angle of 104.6(17)° is the same as that in $[RuH(dtt)(CO)(PPh_3)_2]$,[10] in which both nitrogen atoms are co-ordinated to the metal to form a four-membered chelate ring, and differs considerably from the values (mean 116°) found in cluster **1** and other complexes where the triazenide bridges two metal centres. This fact emphasizes the strained nature of the Os(3)–N(31)–N(32)–N(33) four-membered ring.

Some linear trinuclear osmium clusters have been reported;[34] however, one containing a triazenide ligand, as in **5**, has never been reported.

Experimental

Methodology

The starting materials $[Ru_3(CO)_{12}]$,[35] $[Os_3(CO)_{11}(NCMe)]$,[36] $C_6F_5N{=}NNHC_6F_5$[37] and *p*-$C_6F_4XNH_2$ (X = Br or I)[38] were prepared by published methods. The solvents hexane, toluene and CH_2Cl_2 for the reactions were dried by published methods.[39] 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, UV spectra on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer and NMR data in $CDCl_3$ on a JEOL FX 90Q FT or FT Bruker ACF 500 MHz spectrometer. Proton and ^{13}C shifts were with respect to $SiMe_4$ as internal reference and ^{19}F with respect to CF_3CO_2H as external reference. Mass spectra were recorded on a Hewlett-Packard 5988A mass spectrometer.

Crystallography

Crystal data for complexes **1** and **5** are summarized in Table 7, atomic coordinates in Tables 8 and 9. Diffraction intensities were collected at 298 K on a Siemens R3m/V X-ray diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), scan range $3.5 < 2\theta < 48.0°$. Indices $+h$, $-k$, $\pm l$ for **1** and $+h$, $+k$, $\pm l$ for **5**. All computations

were carried out on a Micro VAX 2000 computer using the SHELXTL PLUS program package.[40] The structures were solved by direct methods and a weighting scheme of the form $w^{-1} = \sigma^2(F) + gF^2$ was employed. Full-matrix, least-squares refinement with all non-hydrogen atoms being refined anisotropically. An empirical (ψ-scan) absorption correction was performed in each case. The position of the two hydrogen atoms in **1** were located from Fourier-difference maps.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Table 7 Crystallographic parameters for complexes **1** and **5***

	1	**5**
Formula	$C_{22}HF_{10}N_3O_{10}Ru_3$	$C_{23}ClF_{10}N_3O_{11}Os_3$
M	960.45	1290.3
D_c/g cm^{-3}	2.222	2.765
Crystal size/mm	0.2 × 0.25 × 0.3	0.30 × 0.30 × 0.40
a/Å	17.579(4)	14.496(3)
b/Å	19.142(4)	26.462(5)
c/Å	17.199(3)	17.409(3)
β/°	97.09(3)	111.82(3)
Reflections collected	9383	10 092
$F(000)$	3648	4656
Observed reflections	7139 [$F > 4.0\sigma(F)$]	5210 [$F > 6.0\sigma(F)$]
R,R' (obs. data)	0.0213, 0.0282	0.0440, 0.0544
R,R' (all data)	0.0307, 0.0325	0.0793, 0.0586
g	0.0010	0.0005
Goodness of fit	0.69	1.47

* Details in common: yellowish prism; monoclinic, space group $P2_1/c$; $Z = 8$.

Synthesis of RN=NNHR

The compounds RN=NNHR (R = *p*-C_6F_4X; X = Br, I or H) were prepared from the corresponding aniline by the published method for the synthesis of $C_6F_5N{=}NNHC_6F_5$;[37] *p*-$C_6HF_4NH_2$ was obtained from the reduction of *p*-$C_6BrF_4NH_2$ in Zn–NH_4Cl–ethanol–water. All of the new compounds were characterized by elemental analysis, NMR, IR and mass spectroscopy.

p-$C_6F_4BrN{=}NNHC_6F_4Br$-*p*: 63% yield, m.p. 145.5–146.5 °C (Found: C, 28.90; H, 0.30; N, 8.50. Calc. for $C_{12}HBr_2F_8N_3$: C, 28.90; H, 0.20; N 8.40%). NMR ($CDCl_3$): ^{1}H, δ 9.77 (s, 1 H); ^{19}F, δ −57.17 (s, 2 F), −57.34 (s, 2 F) and −74.08 (s, 4 F). IR (KBr): 3307m, 1640w, 1522vs, 1496s, 1467m, 1221s, 986s,

Table 8 Fractional atomic coordinates (× 10^4) for [$Ru_3(\mu\text{-H})(CO)_{10}(\mu\text{-}C_6F_5NNNC_6F_5)$] **1**

Atom	x	y	z	Atom	x	y	z
Ru(1)	397(1)	1261(1)	2090(1)	Ru(4)	4461(1)	1370(1)	8214(1)
Ru(2)	259(1)	1699(1)	3581(1)	Ru(5)	5370(1)	226(1)	8061(1)
Ru(3)	33(1)	2777(1)	2399(1)	Ru(6)	6135(1)	1560(1)	8001(1)
O(11)	815(2)	−156(2)	2797(2)	O(41)	4816(2)	1408(2)	9978(2)
O(12)	424(2)	784(2)	384(2)	O(42)	3537(2)	2727(2)	8278(2)
O(13)	2078(2)	1611(2)	2151(2)	O(43)	3164(2)	367(2)	8387(2)
O(21)	1952(2)	2000(2)	3930(2)	O(51)	6643(3)	−755(3)	7711(3)
O(22)	522(2)	359(2)	4510(2)	O(52)	5935(2)	87(2)	9785(2)
O(23)	21(2)	2588(2)	5003(2)	O(53)	4277(3)	−963(2)	8268(2)
O(31)	1760(2)	3112(2)	2626(2)	O(61)	7570(2)	744(3)	7742(2)
O(32)	−235(2)	3805(2)	3695(2)	O(62)	6810(2)	3030(2)	7907(2)
O(33)	−204(2)	3776(2)	992(2)	O(63)	5760(2)	1617(2)	6212(2)
O(34)	−1707(2)	2503(2)	2151(2)	O(64)	6531(2)	1558(2)	9794(2)
N(1)	−791(2)	1032(1)	2083(2)	N(4)	4211(2)	1269(2)	6973(2)
N(2)	−1207(2)	1037(1)	2657(2)	N(5)	4390(2)	759(2)	6529(2)
N(3)	−901(2)	1353(1)	3291(2)	N(6)	4906(2)	329(1)	6854(2)
C(11)	654(2)	379(2)	2552(2)	C(41)	4696(2)	1390(2)	9320(3)
C(12)	380(2)	981(2)	993(2)	C(42)	3882(2)	2240(2)	8227(2)
C(13)	1445(2)	1482(2)	2141(2)	C(43)	3660(3)	727(3)	8318(2)
C(21)	1311(2)	1903(2)	3774(2)	C(51)	6177(3)	−381(3)	7826(3)
C(22)	424(2)	854(2)	4159(2)	C(52)	5725(3)	162(2)	9135(3)
C(23)	72(2)	2261(2)	4467(2)	C(53)	4665(3)	−510(3)	8178(3)
C(31)	1128(3)	2968(2)	2552(2)	C(61)	7033(3)	1028(3)	7850(3)
C(32)	−127(2)	3415(2)	3232(2)	C(62)	6547(2)	2503(3)	7952(2)
C(33)	−112(3)	3409(2)	1501(2)	C(63)	5866(2)	1569(2)	6869(2)
C(34)	−1063(3)	2558(2)	2266(2)	C(64)	6370(2)	1536(2)	9143(3)
C(111)	−1185(2)	670(2)	1427(2)	C(411)	3624(2)	1685(2)	6548(2)
C(112)	−1400(2)	1010(2)	733(2)	C(412)	2894(2)	1418(2)	6331(2)
C(113)	−1738(2)	667(2)	79(2)	C(413)	2319(2)	1817(2)	5935(2)
C(114)	−1880(2)	−36(2)	115(2)	C(414)	2466(2)	2490(2)	5747(2)
C(115)	−1677(3)	−386(2)	801(2)	C(415)	3179(2)	2766(2)	5941(2)
C(116)	−1338(2)	−39(2)	1447(2)	C(416)	3752(2)	2370(2)	6343(2)
F(112)	−1260(2)	1699(1)	677(1)	F(412)	2734(1)	764(1)	6535(1)
F(113)	−1924(2)	1014(2)	−598(1)	F(413)	1614(1)	1556(1)	5755(2)
F(114)	−2209(2)	−371(2)	−526(2)	F(414)	1903(2)	2886(1)	5378(1)
F(115)	−1803(2)	−1076(1)	837(2)	F(415)	3332(2)	3430(1)	5754(2)
F(116)	−1124(2)	−398(1)	2106(1)	F(416)	4446(1)	2651(1)	6545(2)
C(211)	−1387(2)	1263(2)	3893(2)	C(511)	5010(2)	−231(2)	6326(2)
C(212)	−1696(2)	1827(2)	4240(2)	C(512)	5708(2)	−335(2)	6043(2)
C(213)	−2125(2)	1752(2)	4848(2)	C(513)	5842(2)	−917(2)	5608(2)
C(214)	−2260(2)	1102(3)	5119(2)	C(514)	5279(3)	−1403(2)	5437(2)
C(215)	−1982(2)	525(2)	4779(2)	C(515)	4571(2)	−1300(2)	5687(2)
C(216)	−1546(2)	607(2)	4172(2)	C(516)	4441(2)	−720(2)	6119(2)
F(212)	−1586(1)	2478(1)	3970(1)	F(512)	6274(1)	124(1)	6212(2)
F(213)	−2422(1)	2315(1)	5170(2)	F(513)	6530(1)	−1012(2)	5366(2)
F(214)	−2678(2)	1030(2)	5725(2)	F(514)	5417(2)	−1983(1)	5043(1)
F(215)	−2134(2)	−112(1)	5040(2)	F(515)	4021(2)	−1780(1)	5520(2)
F(216)	−1251(1)	39(1)	3863(1)	F(516)	3755(1)	−644(1)	6371(1)

Table 9 Fractional atomic coordinates ($\times 10^4$) for $[Os_3(CO)_{11}Cl(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	−59(1)	135(1)	1507(1)	C(636)	1626(23)	4207(9)	1192(20)
Os(2)	213(1)	1097(1)	2347(1)	O(11)	1513(14)	509(8)	887(14)
Os(3)	386(1)	2031(1)	3235(1)	O(12)	−1646(16)	659(8)	65(11)
Os(4)	5240(1)	6113(1)	3855(1)	O(13)	−276(19)	−915(7)	744(12)
Os(5)	4613(1)	5345(1)	2577(1)	O(14)	1501(16)	−250(8)	3130(14)
Os(6)	4253(1)	4566(1)	1345(1)	O(21)	80(14)	494(7)	3811(10)
Cl(1)	−1421(6)	59(3)	1981(5)	O(22)	2526(13)	998(8)	3109(12)
Cl(2)	6507(5)	6392(2)	3333(4)	O(23)	386(14)	1658(7)	868(10)
F(312)	−1931(10)	2479(6)	2657(10)	O(24)	−2039(13)	1317(7)	1678(12)
F(313)	−3750(11)	2812(6)	1716(10)	O(31)	672(17)	2974(6)	4314(12)
F(314)	−4097(11)	189(8)	193(10)	O(32)	−1177(15)	1614(7)	3824(11)
F(315)	−2670(13)	3147(10)	−431(11)	O(33)	1890(14)	1467(7)	4689(11)
F(316)	−878(12)	2765(8)	436(9)	O(41)	3673(14)	6742(7)	2479(13)
F(332)	1442(10)	2717(6)	1036(9)	O(42)	6014(21)	6973(8)	5088(16)
F(333)	3245(11)	2854(6)	1050(11)	O(43)	3714(13)	5690(7)	4525(12)
F(334)	4878(12)	2659(6)	2419(12)	O(44)	6830(16)	5369(8)	4913(12)
F(335)	4659(11)	2323(6)	3823(10)	O(51)	4888(14)	6114(7)	1374(12)
F(336)	2870(10)	2172(5)	3835(8)	O(52)	2386(13)	5606(8)	1888(12)
F(612)	6544(10)	4038(6)	1881(10)	O(53)	4297(15)	4619(6)	3816(11)
F(613)	8306(12)	3677(7)	2824(11)	O(54)	6799(13)	4989(8)	3074(12)
F(614)	8538(14)	3240(8)	4294(12)	O(61)	5916(13)	5036(7)	955(10)
F(615)	6999(14)	3187(7)	4800(12)	O(62)	2823(15)	5305(8)	131(12)
F(616)	5220(14)	3572(6)	3886(10)	O(63)	4029(14)	3778(8)	45(11)
F(632)	2918(13)	3675(6)	3187(10)	N(31)	−384(12)	2415(6)	2097(10)
F(633)	1062(13)	3523(6)	3019(12)	N(32)	389(13)	2573(6)	1951(9)
F(634)	−441(14)	3802(6)	1653(12)	N(33)	1142(12)	2379(6)	2537(12)
F(635)	−108(12)	4266(8)	442(12)	N(61)	4938(15)	4024(7)	2304(11)
F(636)	1756(10)	4453(6)	562(8)	N(62)	4108(15)	3878(6)	2404(11)
C(311)	−1320(16)	2618(8)	1583(14)	N(63)	3407(13)	4143(6)	1880(10)
C(312)	−2110(21)	2638(8)	1867(16)	C(11)	975(19)	360(9)	1108(13)
C(313)	−3031(19)	2817(9)	1400(17)	C(12)	−1124(19)	491(9)	517(16)
C(314)	−3190(20)	2995(11)	627(17)	C(13)	−229(21)	−543(9)	1038(14)
C(315)	−2481(21)	2973(12)	306(17)	C(14)	961(23)	−92(9)	2574(17)
C(316)	−1562(24)	2815(11)	771(17)	C(21)	64(17)	720(8)	3232(19)
C(331)	2065(15)	2456(8)	2458(16)	C(22)	1709(21)	1034(8)	2810(12)
C(332)	2182(18)	2610(8)	1739(16)	C(23)	354(20)	1452(9)	1415(19)
C(333)	3137(20)	2708(9)	1743(18)	C(24)	−1266(21)	1231(8)	1941(13)
C(334)	3945(21)	2609(9)	2435(23)	C(31)	528(17)	2635(10)	3879(16)
C(335)	3875(21)	2422(8)	3107(20)	C(32)	−583(22)	1759(8)	3610(12)
C(336)	2892(20)	2349(8)	3101(16)	C(33)	1333(21)	1697(10)	4148(16)
C(611)	5812(19)	3812(8)	2796(14)	C(41)	4210(19)	6503(9)	2982(14)
C(612)	6608(19)	3832(9)	2605(18)	C(42)	5716(24)	6648(10)	4631(20)
C(613)	7521(24)	3634(10)	3084(22)	C(43)	4273(20)	5844(8)	4290(13)
C(614)	7611(29)	3415(12)	3824(23)	C(44)	6223(25)	5640(11)	4514(17)
C(615)	6894(24)	3405(11)	4096(17)	C(51)	4836(19)	5833(9)	1845(16)
C(616)	5962(23)	3582(10)	3579(20)	C(52)	3187(20)	5488(9)	2156(13)
C(631)	2415(17)	4055(9)	1873(14)	C(53)	4366(17)	4893(9)	3328(16)
C(632)	2214(23)	3812(9)	2482(20)	C(54)	6044(20)	5133(10)	2939(14)
C(633)	1237(29)	3746(9)	2412(23)	C(61)	5239(21)	4878(9)	1072(12)
C(634)	486(25)	3886(11)	1720(24)	C(62)	3327(21)	5007(10)	556(18)
C(635)	622(24)	4114(9)	1111(20)	C(63)	4120(20)	4085(10)	539(17)

963vs, 833s and 766m cm^{-1}. Mass spectrum: *m/z* 501, 499, 497 (M^+), 257, 255 ($C_6F_4BrN_2^+$), 243, 241 ($C_6F_4BrN^+$), 229, 227 ($C_6F_4Br^+$).

p-$IC_6F_4N{=}NNHC_6F_4I$-*p*: 63% yield, m.p. 137–138 °C (Found: C, 24.10; H, 0.15; F, 25.45; N, 7.20. Calc. for $C_{12}HF_8I_2N_3$: C, 24.30; H, 0.15; F, 25.65; N, 7.10%). NMR ($CDCl_3$): ^{1}H, δ 9.80 (s); ^{19}F, δ −44.34 [d, 4 F, $J(F_oF_m)$ = 14.65 Hz] and −73.44 (s, 4 F). IR(KBr): 3306m, 1635w, 1513vs, 1485vs, 1462vs, 1445m, 1416s, 1215s, 1142m, 980s, 957vs and 805m cm^{-1}. Mass spectrum: *m/z* 593 (M^+), 303 ($C_6F_4IN_2^+$), 289 ($C_6F_4NI^+$) and 275 ($C_6F_4I^+$).

p-$HC_6F_4N{=}NNHC_6HF_4$-*p*: 46% yield, m.p. 88–89 °C (Found: C, 42.25; H, 1.00; F, 44.30; N, 12.45. Calc. for $C_{12}H_3F_8N_3$: C, 42.25; H, 0.90; F, 44.55; N, 12.30%). NMR ($CDCl_3$): ^{1}H, δ 9.82 (s, 1 H) and 6.95 [tt, $J(H\text{–}F_o)$ = 9.96, $J(H\text{–}F_m)$ = 5.28 Hz]; ^{19}F, δ −63.02 (s, 4 F) and −75.76 (s, 4 F). IR (KBr): 3308m, 2925m, 2854m, 1641w, 1511vs, 1421m, 1384w, 1265m, 1205m, 1175s, 955m, 932s and 742s cm^{-1}. Mass spectrum: *m/z* 341 (M^+), 177 ($C_6F_4N_2H^+$), 163 ($C_6F_4NH^+$), 149 ($C_6F_4H^+$) and 69 (CF_3^+).

p-$HC_6F_4NH_2$: 40% yield, b.p. 56 °C (5 mmHg, *ca.* 6.65 Pa) (Found: C, 43.60; H, 1.70; F, 46.30; N, 8.30. Calc. for $C_6H_3F_4N$: C, 43.65; H, 1.85; F, 46.05; N, 8.50%). NMR ($CDCl_3$): ^{1}H, δ 5.93 [tt, $J(H\text{–}F_o)$ = 9.53, $J(H\text{–}F_m)$ = 6.11 Hz] and 3.87 (NH_2, 2 H); ^{19}F, δ −68.40 (m, 2 F) and −88.80 (m, 2 F). IR (KBr): 3455m, 3407m, 1660m, 1611m, 1527s, 1267m, 1162m, 950m, 885m, 803m and 713m cm^{-1}. Mass spectrum: *m/z* 165 (M^+) 149 ($C_6F_4H^+$) and 144 ($C_6F_3NH_2^+$).

Reactions of RN=NNHR (R = *p*-C_6F_4X; X = F, Br, I or H)

With $[Ru_3(CO)_{12}]$. A solution of $[Ru_3(CO)_{12}]$ (50 mg, 0.078 mmol) and RN=NNHR (2 equivalents) in toluene (*ca.* 5 cm^3) was degassed, sealed in an ampoule and heated at 80 °C for 4 h. The solvent was removed under vacuum and the residue chromatographed on a silica gel TLC plate with hexane as eluent to give as the major products $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}RNNNR)]$ summarized in Table 2.

With $[Os_3(CO)_{11}(NCMe)]$. A solution of $[Os_3(CO)_{11}(NCMe)]$ (200.0 mg, 0.217 mmol) and an equimolar amount

of RN=NNHR in CH_2Cl_2 (*ca.* 10 cm^3) was degassed, sealed in an ampoule and heated at 60 °C overnight. The solvent was removed and the residue chromatographed on a silica gel TLC plate with hexane as eluent to give as the major products $[Os_3(CO)_{11}Cl(\eta^2\text{-RNNNR})]$ summarized in Table 2.

Formation of $[Os_3H(CO)_{11}(\eta^2\text{-}C_6F_5NNNC_6F_5)]$ 9

A solution of $[Os_3(CO)_{11}(NCMe)]$ (200.0 mg, 0.217 mmol) and an equimolar amount of $C_6F_5N{=}NNHC_6F_5$ (81.98 mg, 0.217 mmol) in hexane (*ca.* 10 cm^3) was degassed and heated at 70 °C overnight. The solvent was removed and the residue was chromatographed on a silica gel TLC plate to give the major product **9** (129.3 mg, 47% yield). IR (hexane): ν(CO) 2127w, 2088vs, 2068s, 2054m, 2033vs, 2025vs, 2014vs, 2004m, 1992w; $\nu(C_6F_5)$ 1515, 992; ν(triazenido) 1264 cm^{-1}. NMR($CDCl_3$): ^{19}F, δ −75.50 (m, 4 F), −80.91 (m, 2 F) and −85.14 (m, 4 F); ^1H, δ −9.87 (s, OsH).

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