

Tetraosmium carbonyl clusters containing μ -NH₂ amido ligands: syntheses, crystal structures and reactivities

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Treatment of [Os₄(μ -H)₄(CO)₁₂] with *O*-tert-butylhydroxylamine hydrochloride (tBuONH₂·HCl) afforded two amino ligand containing osmium clusters [Os₄(μ -H)₄(CO)₁₁(η^1 -NH₂O^tBu)] (**1**) and [Os₄(μ -H)₄(CO)₁₁{(μ -H)₃Os(CO)₂(η^1 -NH₂O^tBu)₂Cl}] (**2**) in moderate yields. For the same reaction, in the presence of one equivalent of [Os₃(CO)₁₂], the novel heptaosmium carbonyl cluster [Os₇(μ -H)₂(CO)₁₁(μ -NH₂)] {Os₃(μ -H)(CO)₁₁} (**3**) was isolated together with **1** and **2**. This heptaosmium cluster **3** displays an uncommon metal skeleton, where the tetraosmium tetrahedron and the triosmium triangle are connected by a metal–metal bond. Upon the addition of hydrobromic acid (HBr) to a solution of **1**, a pair of geometric isomers, unsupported butterfly [Os₄(μ -H)₄(CO)₁₁(μ -NH₂)Br] (**4a**) and supported butterfly [Os₄(μ -H)₄(CO)₁₁(μ -NH₂)Br] (**4b**) clusters were formed. They are the first examples of μ -NH₂ amido tetraosmium carbonyl clusters, which serve as good models for the adsorbed nitrogen atoms on a stepped metal surface. Refluxing of **4a** in toluene for several hours, afforded a new triosmium μ -NH₂ amido cluster [Os₃(μ -H)₂(CO)₉(μ -NH₂)Br] (**5**). Addition of an excess of triphenylcarbenium tetrafluoroborate [Ph₃C][BF₄] to a solution of **4a** in dichloromethane gave another tetrahedral μ -NH₂ amido tetraosmium cluster [Os₄(μ -H)₂(CO)₁₁(μ -NH₂)Br] (**6**) in moderate yield upon elimination of two hydrides.

Introduction

The chemistry of late transition metal carbonyl clusters possessing amino¹ and amido² ligands has been extensively investigated in the last decade. Much of the interest stems from the comparison of their reactivity to that of nitrogen atoms bound to metal surfaces. The formation and cleavage of N–H bonds on metal surfaces is believed to be an integral part of several important heterogeneously catalyzed reactions such as the Haber process³ and the oxidation of ammonia.⁴ The bonding relationship between coordinated transition metal clusters and surface-absorbed NH_x moieties is illustrated in Scheme 1.^{5–8}

However, to our knowledge, only very few examples of μ -NH₂ amido containing transition metal clusters are well characterized, these include [M₃(μ -H)(CO)₁₀(μ -NH₂)] (M = Os,⁶ Ru⁹), [Os₃(μ -H)(CO)₉(μ -NH₂)(PPh₃)₃]¹⁰ and [Ru₃(CO)₁₀(μ -NH₂)(μ_3 -Hg){Mo(η^5 -C₅H₅)(CO)₃}]¹¹. Most examples are trinuclear systems, which model a flat metal surface. Recently, we have prepared and fully characterized the first examples of tetraosmium carbonyl clusters containing μ -NH₂ amido ligands. The μ -NH₂ amido containing supported butterfly tetraosmium cluster [Os₄(μ -H)₄(CO)₁₁(μ -NH₂)Br] **4a** serves as a good model

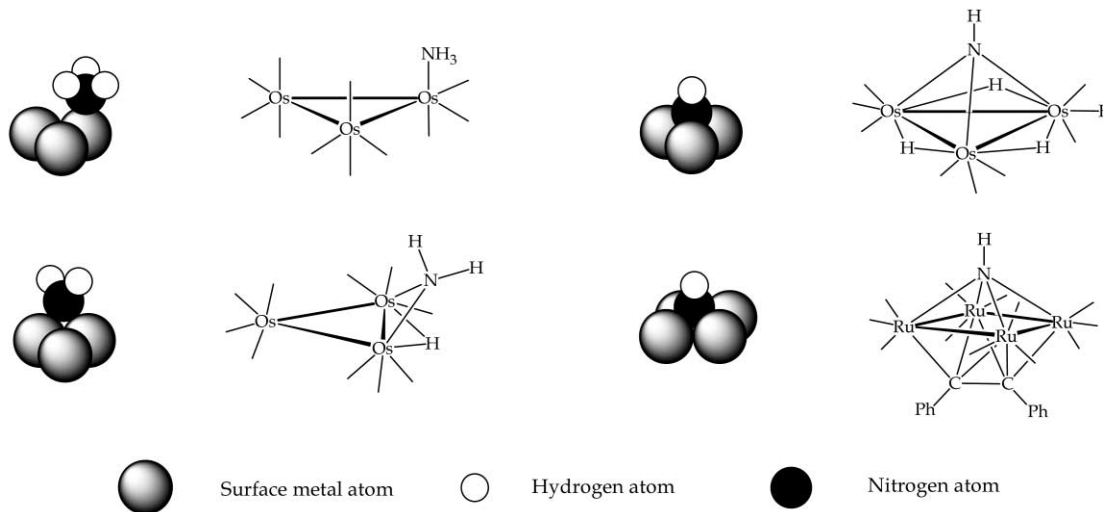
for adsorbed nitrogen atoms on a stepped metal surface. The transformation of amino clusters to amido clusters is demonstrated.

Experimental

General

All reactions and manipulations were carried out under argon using standard Schlenk techniques, except for the chromatographic separations. Solvents were purified by standard procedures and distilled prior to use.¹² Reactions were monitored by analytical thin-layer chromatography (Merck Kieselgel 60 F₂₅₄) and the products were separated by thin-layer chromatography on plates coated with silica (Merck Kieselgel 60 F₂₅₄). All chemicals, unless otherwise stated, were purchased commercially and used as received. [Os₄(μ -H)₄(CO)₁₂]¹³ was prepared by the literature methods.

Infrared spectra were recorded on a Bio-Rad FTS-135 IR spectrometer, using 0.5 mm calcium fluoride solution cells, ¹H NMR spectra on a Bruker DPX300 spectrometer using CD₂Cl₂ and referenced to SiMe₄ (δ 0). Variable-temperature ¹H NMR



Scheme 1

spectra were obtained on a Bruker DPX500 spectrometer. Positive ionization fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT 95 mass spectrometer, using *m*-nitrobenzyl alcohol as matrix solvent. Microanalyses were performed by Butterworth Laboratories, UK.

Syntheses

Reaction of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ with *O*-tert-butylhydroxylamine hydrochloride ($\text{tBuONH}_2\cdot\text{HCl}$). The complex $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ (110 mg, 0.1 mmol) was dissolved in dichloromethane (30 cm³) and mixed with one equivalent of *O*-tert-butylhydroxylamine hydrochloride at 0 °C. One equivalent of trimethylamine-*N*-oxide was then added dropwise to the solution mixture. Upon stirring for 1 h, the solution turned dark yellow. The solvent was removed under reduced pressure. Chromatography of the residue on preparative TLC plates eluting with *n*-hexane–dichloromethane (1 : 1, v/v) afforded the complexes $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}\{\eta^1\text{-NH}_2\text{O}^t\text{Bu}\}]$ **1** (40 mg, 34%) and $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}\{(\mu\text{-H})_3\text{Os}(\text{CO})_2(\eta^1\text{-NH}_2\text{O}^t\text{Bu})_2\text{Cl}\}]$ **2** (9 mg, 6%).

$[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)]\{\text{Os}_3(\mu\text{-H})(\text{CO})_{11}\}$ (3**).** The complexes $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}]$ (110 mg, 0.1 mmol) and $[\text{Os}_3(\text{CO})_{12}]$ (91 mg, 0.1 mmol) were dissolved in dichloromethane (30 cm³) and the mixture stirred with one equivalent of *O*-tert-butylhydroxylamine hydrochloride at 0 °C. One equivalent of trimethylamine-*N*-oxide was added slowly. After 1 h, the yellow solution turned orange. The solvent was removed under reduced pressure and the residue chromatographed on TLC plates using *n*-hexane–dichloromethane (1 : 1, v/v) as eluent. The first brown band was found to be $[\{\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)\}\{\text{Os}_3(\mu\text{-H})(\text{CO})_{11}\}]$ **3** (26 mg, 13%). Complexes **1** and **2** were also isolated in 23 and 4% yield, respectively.

Reaction of **1 with hydrobromic acid (HBr).** A solution of **1** (23 mg, 0.02 mmol) in dichloromethane (30 cm³) was stirred with three drops of hydrobromic acid (33% HBr). The solution was allowed to stir for 30 min and the solvent was then dried *in vacuo*. The dark yellow residue was subjected to TLC separation with *n*-hexane–dichloromethane (1 : 1, v/v) as eluent. Two consecutive yellow bands were characterized as $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\mu\text{-NH}_2)\text{Br}]$ **4a** (16 mg, 68%) and $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\mu\text{-NH}_2)\text{Br}]$ **4b** (3 mg, 13%).

Thermolysis of **4a.** A solution of **4a** (23 mg, 0.02 mmol) in toluene (30 cm³) was refluxed under argon atmosphere for 24 h. The solution gradually changed from yellow to pale yellow. After cooling, the solvent was evaporated *in vacuo*. Chromatography of the residue on silica eluting with *n*-hexane–dichloromethane (1 : 1, v/v) afforded the complex $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu\text{-NH}_2)\text{Br}]$ **5** (5 mg, 27%).

Reaction of **4a towards triphenylcarbenium tetrafluoroborate $[\text{Ph}_3\text{C}][\text{BF}_4]$.** A solution of **4a** (23 mg, 0.02 mmol) in dichloromethane (30 cm³) was stirred with excess triphenylcarbenium tetrafluoroborate $[\text{Ph}_3\text{C}][\text{BF}_4]$ under an argon atmosphere. The initial yellow solution changed to green upon stirring for 5 h. After reducing the solvent volume, the residue was separated by preparative TLC on silica, with an eluent of *n*-hexane–dichloromethane (1 : 1, v/v). The intense green band was isolated as $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)\text{Br}]$ **6** (7 mg, 30%).

X-Ray crystallography

Single crystals were grown from their appropriate solvent systems under favorable conditions. Intensity data were collected at ambient temperature using a Bruker SMART CCD 1000 diffractometer with graphite monochromated Mo- $K\alpha$ radiation using ω scan type. Details of the intensity data collection and crystal data are given in Table 1, while the selected bond parameters are shown in Table 2. The data were corrected for Lorentz

Table 1 Crystal data and data collection parameters for 1–6

	1	2	3	4a	4b	5	6
Empirical formula	$\text{C}_{15}\text{H}_{15}\text{NO}_{12}\text{Os}_4$	$\text{C}_{21}\text{H}_{39}\text{N}_2\text{O}_{15}\text{ClO}_5$	$[\text{C}_{22}\text{H}_5\text{NO}_{22}\text{Os}_7]\cdot\text{CH}_2\text{Cl}_2$	$\text{C}_{11}\text{H}_6\text{NO}_{11}\text{BrOs}_4$	$\text{C}_{11}\text{H}_6\text{NO}_{11}\text{BrOs}_4$	$\text{C}_9\text{H}_4\text{NO}_9\text{BrOs}_3$	$\text{C}_{11}\text{H}_4\text{NO}_{11}\text{BrOs}_4$
Formula weight	1162.08	1535.92	2051.61	1168.87	1168.87	920.64	1166.86
Crystal color, habit	Yellow, block	Orange, block	Brown, block	Yellow, block	Yellow, needle	Yellow, plate	Yellow, plate
Crystal dimensions/mm	$0.12 \times 0.11 \times 0.09$	$0.33 \times 0.12 \times 0.10$	$0.24 \times 0.22 \times 0.11$	$0.22 \times 0.20 \times 0.14$	$0.32 \times 0.09 \times 0.07$	$0.32 \times 0.30 \times 0.08$	$0.27 \times 0.21 \times 0.09$
Crystal system	Orthorhombic	Triclinic	Triclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	<i>Pbca</i> (no. 61)	<i>P1</i> (no. 2)	<i>P1</i> (no. 2)	<i>Pbcn</i> (no. 60)	<i>P1</i> (no. 2)	<i>P2_1/c</i> (no. 14)	<i>P2_1/c</i> (no. 14)
<i>a</i> /Å	15.986(1)	10.022(1)	9.363(1)	17.842(1)	8.5990(8)	13.392(1)	8.985(1)
<i>b</i> /Å	17.119(1)	14.121(1)	14.601(1)	15.729(1)	9.6870(8)	9.7620(6)	9.147(1)
<i>c</i> /Å	17.981(1)	15.772(2)	15.911(1)	15.101(1)	14.047(1)	14.773(1)	24.149(2)
α /°	—	104.16(1)	64.99(2)	—	91.88(1)	—	—
β /°	—	96.08(2)	85.13(1)	—	102.76(1)	—	93.12(1)
γ /°	—	107.32(1)	82.34(2)	—	113.96(1)	—	—
<i>V</i> /Å ³	4920.8(4)	2027.2(5)	1952.6(4)	4237.9(4)	1033.0(2)	1764.9(2)	1981.8(3)
<i>Z</i>	8	2	2	8	2	4	4
<i>D</i> _c /g cm ⁻³	3.137	2.516	3.489	3.664	3.758	3.465	3.911
μ (Mo- α)/cm ⁻¹	206.33	157.23	228.84	258.35	264.99	238.41	276.24
Reflections collected	31060	12880	12297	26281	6315	10910	12406
Unique reflections	6224	8851	8497	5335	4444	4229	4749
Observed reflections [<i>I</i> > 1.5 σ (<i>I</i>)]	2743	5590	5386	3881	3673	3207	2800
<i>R</i>	0.0583	0.081	0.057	0.038	0.079	0.035	0.066
<i>R</i> _w	0.0514	0.091	0.055	0.051	0.095	0.046	0.048
Goodness of fit, <i>S</i>	1.011	1.96	1.147	1.56	2.58	1.30	1.54

Table 2 Selected bond distances (Å) and angles (°) for **1–6**

	1	2	3	4a	4b	5	6
Os(1)–Os(2)	2.803(2)	2.962(2)	2.797(1)	2.8109(8)	2.828(1)	2.8310(6)	2.955(2)
Os(1)–Os(3)	2.943(2)	2.960(2)	2.966(1)	2.8728(7)	3.049(1)	3.0424(6)	2.756(2)
Os(1)–Os(4)	2.951(2)	2.769(2)	2.902(1)		3.070(1)		2.925(2)
Os(2)–Os(3)	2.816(2)	2.822(2)	2.957(1)	2.9407(7)	2.981(1)	2.8198(7)	2.982(2)
Os(2)–Os(4)	2.988(2)	2.963(2)	2.730(1)	2.9942(7)	3.037(1)		2.788(2)
Os(3)–Os(4)	2.999(2)	2.976(2)	2.787(1)	3.1141(7)			2.730(2)
Os(5)–Os(6)			2.853(1)				
Os(5)–Os(7)			3.049(1)				
Os(6)–Os(7)			2.917(1)				
Os(2)–Os(5)			2.872(1)				
Os(4)–Os(5)		3.29					
Os(5)–Cl(1)		2.407(7)					
Os(1)–Br(1)						2.600(1)	
Os(3)–Br(1)					2.544(3)		2.558(3)
Os(4)–Br(1)				2.555(2)			
Os(3)–N(1)					2.15(2)	2.08(1)	2.00(2)
Os(4)–N(1)	2.15(2)				2.13(2)		
Os(5)–N(1)		2.09(3)					
Os(5)–N(2)		2.19(3)					
Os(1)–N(1)			2.15(2)	2.14(1)			2.21(2)
Os(2)–N(1)			2.06(2)	2.07(1)		2.09(1)	
N(1)–O(12)	1.40(3)						
N(1)–O(14)		1.41(3)					
N(2)–O(15)		1.44(3)					
Os(2)–Os(5)–Os(6)			165.66(4)				
Os(2)–Os(5)–Os(7)			110.87(4)				
Os(1)–N(1)–Os(2)			83.3(6)	83.9(4)			
Os(1)–N(1)–Os(3)							81.7(8)
Os(3)–N(1)–Os(4)					112.3(9)		
Os(2)–N(1)–Os(3)						85.0(4)	
Os(4)–N(1)–O(12)	109(1)						
Os(5)–N(1)–O(14)		110(1)					
Os(5)–N(2)–O(15)		111(2)					
N(1)–Os(5)–N(2)		89(1)					

and polarization effects. The structures were solved by direct methods (SIR92¹⁴ or SHELXS86¹⁵), and expanded using Fourier techniques (DIRDIF94).¹⁶ Non-hydrogen atoms were refined anisotropically whenever possible, while the rest were refined isotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan¹⁷ crystallographic software package of the Molecular Structure Corporation.

CCDC reference numbers 192358–192364.

See <http://www.rsc.org/suppdata/dt/b2/b208321c/> for crystallographic data in CIF or other electronic format.

Results and discussion

The preparations of **1–6** is summarized in Scheme 2. These compounds have been fully characterized by elemental analyses, infrared, ¹H NMR and mass spectroscopic methods. The spectroscopic data are tabulated in Table 3. In addition, their solid-state structures have been established by single crystal X-ray diffraction analyses.

The formation of **1** is simply a substitution reaction, replacing a carbonyl ligand with the amino ligand, while the isolation of pentaosmium cluster **2** is rather unexpected. Two metal fragments, [Os(^tBuONH₂)₂(CO)₂Cl] and [Os₄(μ-H)₄(CO)₁₁], are connected by three bridging hydrides, which suggests that the mononuclear osmium fragment probably arises from the decomposition of the robust parent cluster [Os₄(μ-H)₄(CO)₁₂].

A broad hydride signal was observed in the ¹H NMR spectrum of **1** at room temperature and variable-temperature ¹H NMR studies were conducted for **1** from 298 to 233 K. Two sets of four sharp singlet peaks are resolved at 233 K which correspond to two isomers, namely **1a** and **1b**, in the solution of **1** probably arising from the different disposition of hydrides.¹⁸

The solid-state structure of **1** is depicted in Fig. 1. A distorted tetrahedral osmium metal core is observed in **1**, with the Os–Os bond distances within the range 2.803(2)–2.999(2) Å, which is similar to the values observed in other tetraosmium systems.¹⁸ The amine ligand is terminally coordinated to the Os(4) metal centre through the nitrogen N(1), with an Os(4)–N(1) dative bond distance [2.15(2) Å] slightly shorter than the corresponding Os–N distance [2.22(3) Å] observed in [Os₄(μ-H)₄(CO)₁₁-(η¹-NH₂Ph)].¹⁹

The molecular structure of **2** is shown in Fig. 2. The metal framework of **2** consists of five osmium atoms. Four of them form a distorted tetrahedron while the fifth osmium is bonded to the tetrahedron by three bridging hydrides; the Os(5)···Os(4) bond distance (3.29 Å) is too long to be considered as a metal–metal bond, which is supported by the ¹H NMR study. This supported osmium moiety is rather robust as evidenced from mass spectrometry. The fragmentation of the mononuclear fragment [Os(CO)₂(^tBuONH₂)₂Cl] is far less facile relative to dissociation of ^tBuONH₂ or CO ligands.

The Os(5)–N(1) and Os(5)–N(2) bond distances [2.09(3) and 2.19(3) Å] are comparable to the corresponding values observed in **1**. The latter Os–N bond in **2** is slightly longer than the former, probably because of the stronger influence of the CO ligand. The chloride ligand, probably originating from the starting material [^tBuONH₂·HCl], is bonded terminally to Os(5) with a bond length of 2.407(7) Å. A 78 cluster-valence electron count is observed for **2**.

Recently, Lee and Wong reported that two μ₄-NH containing clusters, [Ru₆(μ-H)(CO)₁₆(μ-CO)₂(μ₄-NH)(μ-OCH₃)] and [Ru₅(μ-H)₃(CO)₁₃(μ₄-NH)(μ₃-OCH₃)], which were obtained from the hydrogenation of [Ru₃(CO)₉(μ₃-CO)(μ₃-NOCH₃)] in the presence of [Ru₃(CO)₁₂].²⁰ It was suggested that metal cluster expansion together with nitrogen functionality trans-formation is possible. An equimolar amount of clusters [Os₄-

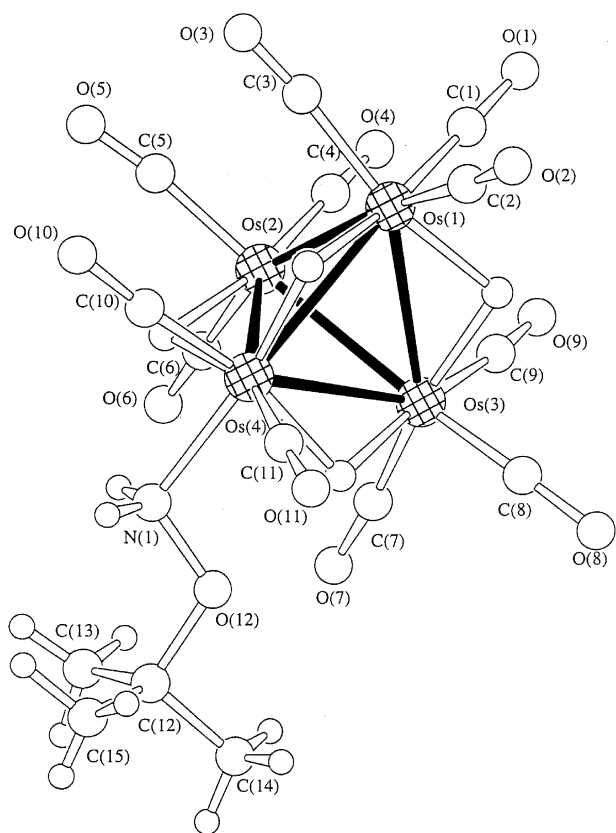
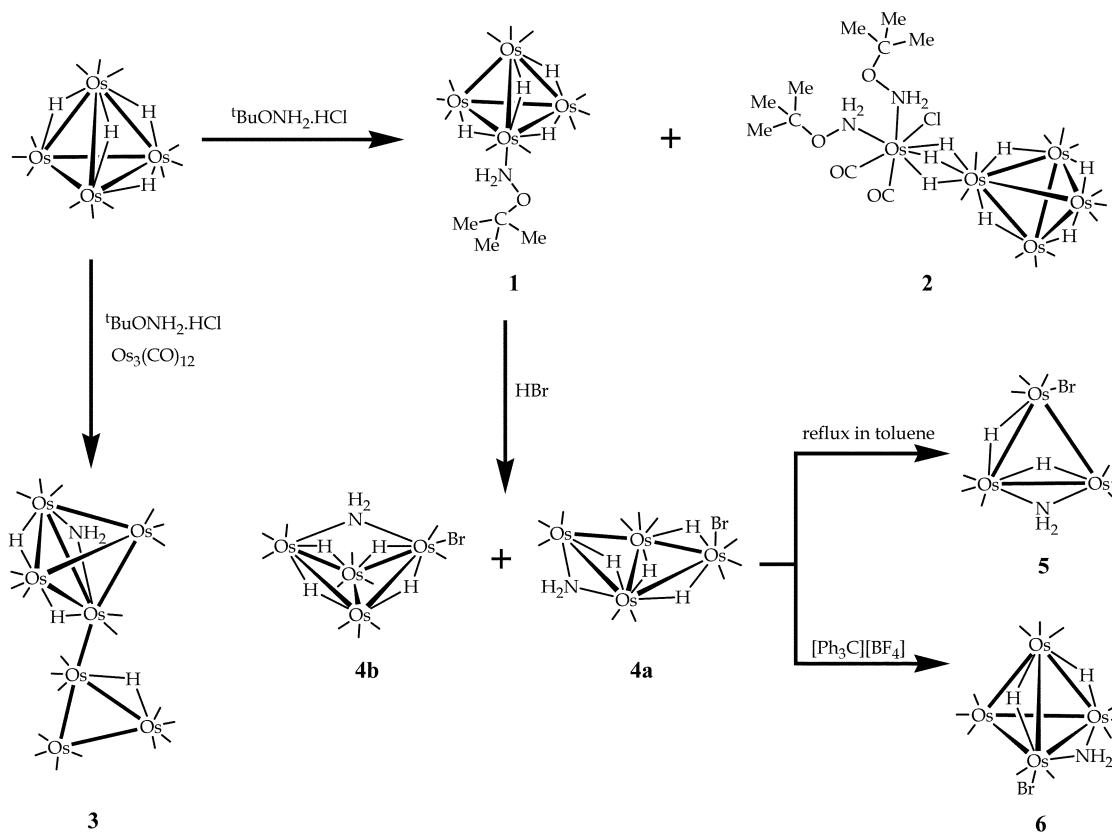


Fig. 1 The molecular structure of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\eta^1\text{-NH}_2\text{O}^t\text{Bu})]$ **1** with the atom numbering scheme.

$(\mu\text{-H})_4(\text{CO})_{12}$ and $[\text{Os}_3(\text{CO})_{12}]$ were stirred with an excess of *O*-*tert*-butylhydroxylamine hydrochloride in dichloromethane at ambient temperature. A new brown cluster $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)\{\text{Os}_3(\mu\text{-H})(\text{CO})_{11}\}]$ **3** was isolated in moderate

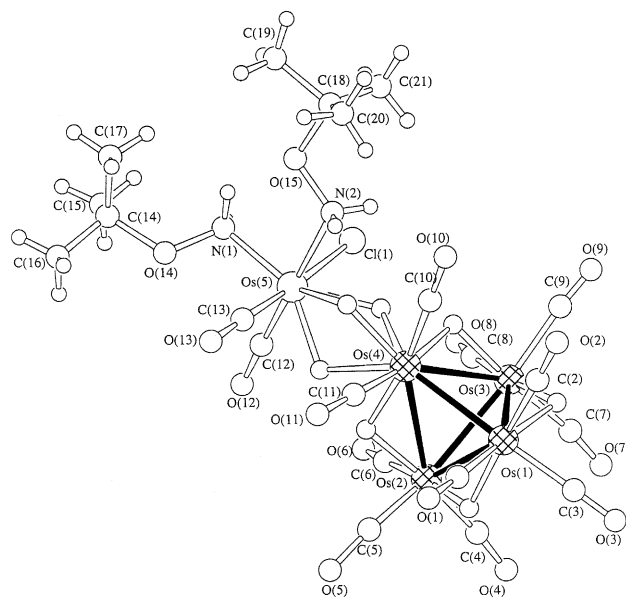


Fig. 2 The molecular structure of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}\{(\mu\text{-H})_3\text{Os}(\text{CO})_2(\eta^1\text{-NH}_2\text{O}^t\text{Bu})_2\text{Cl}\}]$ **2** with the atom numbering scheme.

yield together with **1** and **2**. To our knowledge, this is the first example of a $\mu\text{-NH}_2$ amido ligand containing heptaosmium cluster.

Cluster **3** consists of a tetraosmium tetrahedron $[\text{Os}(1), \text{Os}(2), \text{Os}(3), \text{Os}(4)]$ and a triosmium triangle $[\text{Os}(5), \text{Os}(6), \text{Os}(7)]$, having an $\text{Os}(2)\text{-Os}(5)$ bond distance of 2.872(1) Å (Fig. 3). The $\text{Os}(2)$, $\text{Os}(5)$ and $\text{Os}(6)$ metal centers $[\text{Os}(2)\text{-Os}(5)\text{-Os}(6), 165.66(4)^\circ]$ are arranged almost in a linear manner. The amido ligand asymmetrically bridges the $\text{Os}(1)$ and $\text{Os}(2)$ metal centres with a bite angle of $83.3(6)^\circ$ and the $\text{Os}(1)\text{-N}(1)$ and $\text{Os}(2)\text{-N}(1)$ bond distances are 2.15(2) and 2.06(2) Å, respectively. The ligand bridged $\text{Os}(1)\text{-Os}(2)$ bond [2.797(1) Å] is relatively short. The dihedral angle between the $\text{Os}(1)\text{-Os}(2)\text{-}$

Table 3 Spectroscopic and analytical data for **1-6**

Cluster	IR $\nu(\text{CO})/\text{cm}^{-1}$	$^1\text{H NMR}^c$ (δ , J/Hz)	Analysis ^d (%)				MS ^d (m/z)
			C	H	N		
1	2093w, 2060s, 2033s, 2010m, 2003m, 1983w ^a	1a	6.08 (s, 2H, NH ₂) 1.25 (s, 9H, methyl) -18.65 (s, br, 4H, hydride)	15.4 (15.50)	1.3 (1.30)	1.2 (1.20)	1162 (1162)
		1b	-13.64 (s, 1H, hydride) -15.36 (s, 1H, hydride) -18.28 (s, 1H, hydride) -18.41 (s, 1H, hydride)	-14.28 (s, 1H, hydride) -14.93 (s, 1H, hydride) -18.18 (s, 1H, hydride) -20.86 (s, 1H, hydride)			
2	2093w, 2076m, 2060s, 2033m, 2016m, 1993w, 1985w ^b	7.43 (d, $J_{\text{HH}} = 6.6$, 1H, NH ₂) 6.67 (d, $J_{\text{HH}} = 5.9$, 1H, NH ₂) 6.54 (d, $J_{\text{HH}} = 6.7$, 1H, NH ₂) 6.40 (d, $J_{\text{HH}} = 7.3$, 1H, NH ₂)	16.5 (16.42)	1.8 (1.90)	1.7 (1.82)	1535 (1535)	
3	2097w, 2064m, 2047w, 2029w, 2016s, 2004w, 1985s ^a	4.62 (s, 1H, NH ₂) 4.55 (s, 1H, NH ₂)	13.3 (13.43)	0.3 (0.26)	0.7 (0.71)	1966 (1966)	
4a	2126m, 2093s, 2060s, 2045s, 2028w, 2016w, 1983w ^b	3.06 (s, 1H, NH ₂) 2.59 (s, 1H, NH ₂) -13.45 (s, 1H, hydride)	11.3 (11.17)	0.5 (0.51)	2.4 (2.37)	1169 (1169)	
4b	2126w, 2099w, 2070s, 2048s, 2026w ^b	0.19 (s, 1H, NH ₂) -0.20 (s, 1H, NH ₂) -14.06 (s, 1H, hydride)	11.2 (11.17)	0.5 (0.51)	2.3 (2.37)	1089[M - Br] ⁺ (1169)	
5	2122w, 2093s, 2066s, 2045m, 2037w, 2022w, 2012s, 1991w ^a	4.87 (s, br, 2H, NH ₂) -15.44 (t, $J_{\text{HH}} = 1.7$, 1H, hydride) -16.13 (d, $J_{\text{HH}} = 1.2$, 1H, hydride)	11.8 (11.74)	0.5 (0.44)	1.6 (1.52)	921 (921)	
6	2113w, 2084s, 2060s, 2037s, 2012w ^b	5.55 (s, br, 1H, NH ₂) 4.94 (s, br, 1H, NH ₂)	11.3 (11.32)	0.4 (0.35)	1.2 (1.20)	1167 (1167)	

^aIn *n*-hexane. ^bIn CH₂Cl₂. ^cIn CD₂Cl₂. ^dCalculated values in parentheses.

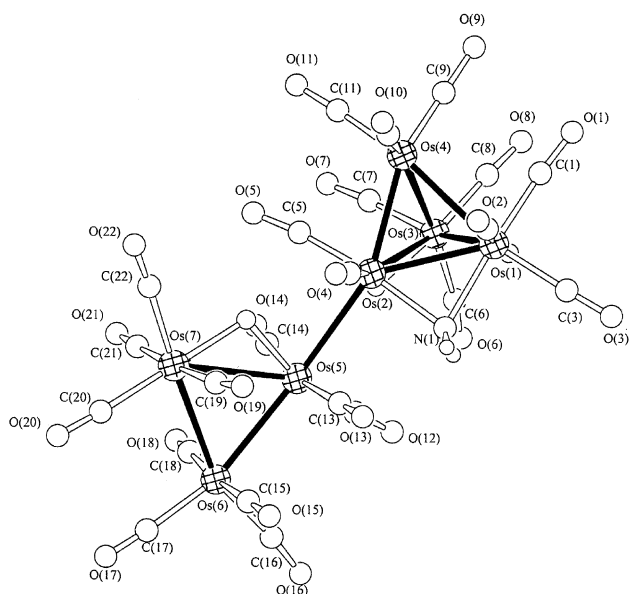


Fig. 3 The molecular structure of $[\{\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)\}\{\text{Os}_3(\mu\text{-H})(\text{CO})_{11}\}]$ **3** with the atom numbering scheme.

Os(3) and Os(1)–Os(2)–N(1) planes is 109.50° . The characteristic 106 cluster-valence electron count is observed for **3** when the bridging amido ligand is regarded as a three-electron donor. The mechanism of the formation of **3** is not clear. However, no clusters arising from the coupling of two triosmium units were isolated from the reaction mixture. It is believed that the $t\text{-BuONH}_2$ ligand first attacks the tetraosmium cluster to give some intermediates that further react with triosmium cluster to give **3**. However, we do not observe the formation of **3** from the reaction of **1** and $[\text{Os}_3(\text{CO})_{12}]$.

Cluster **1** is believed to be a good precursor for amido ($\mu\text{-NH}_2$) or nitrene ($\mu_3\text{-NH}/\mu_4\text{-NH}$) containing metal clusters. The good leaving group *tert*-butylhydroxy ($t\text{BuO}$) is supposed to be eliminated easily upon protonation, and the remaining amino ligand will coordinate to the metal core effectively. A few drops of hydrobromic acid were added to a solution of **1** in dichloromethane at room temperature. The isomeric clusters $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\mu\text{-NH}_2)\text{Br}]$ **4a** and $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\mu\text{-NH}_2)\text{Br}]$ **4b** were isolated in high and moderate yields, respectively. (Scheme 3) The formation of **4a** seems to be more favourable in dichloromethane solution at ambient temperature according to the reaction yield obtained. The polarities of these isomers are significantly different according to their R_f values on chromatography

separation; relatively non-polar cluster **4a** is more soluble in common organic solvents.

The mass spectra of **4a** and **4b** show different fragmentation patterns. The parent ion envelope of **4a** observed at $m/z = 1169$ agrees with the molecular formula, while a molecular ion peak was not observed in the mass spectrum of **4b**, probably due to facile fragmentation of Br ligand in the ionization process. In addition, the ^1H NMR spectrum of **4a** reveals that two amido proton signals are located at δ 3.06 and 2.59, which are comparable to the values observed in **3**. However, the amido proton ^1H NMR signals of **4b** are significantly shielded to δ 0.19 and -0.20 , and seems to be very electron rich. The differences in the fragmentation pattern and the ^1H NMR chemical shift of the amido proton signals of **4a** and **4b** are believed correlate with their structural geometry.

The molecular structures of **4a** and **4b** are depicted in Figs. 4 and 5, respectively. The architecture of **4a** consists of a butterfly

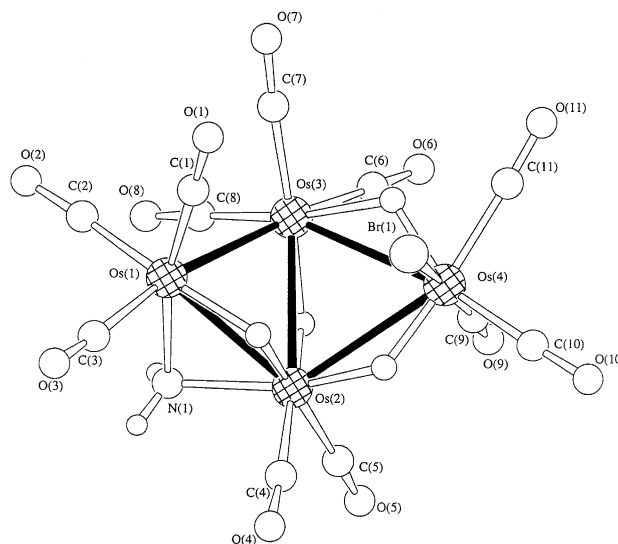
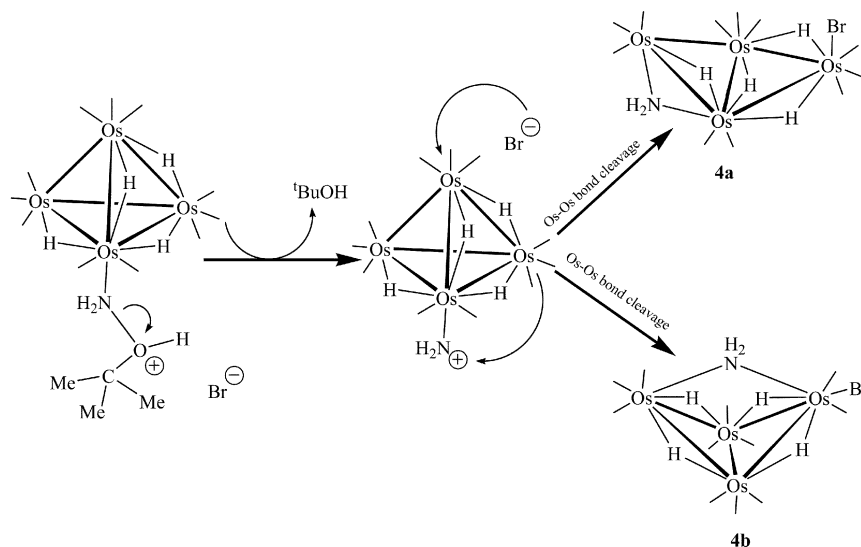
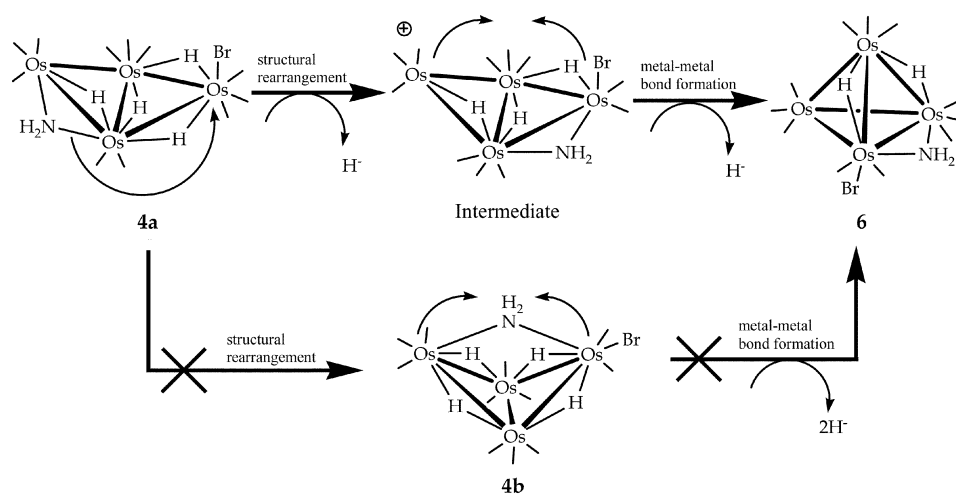


Fig. 4 The molecular structure of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\mu\text{-NH}_2)\text{Br}]$ **4a** with the atom numbering scheme.

arrangement of four osmium atoms, which is derived from the parent tetrahedron geometry by opening up one metal–metal bond. This is the common configuration observed for 62-electron clusters and is in agreement with the theories of cluster bonding.²¹ This is one of very few examples of 62-electron butterfly clusters with no supporting ligand between wingtip osmium metals.²² The dihedral angle between two wings of the



Scheme 3



Scheme 4

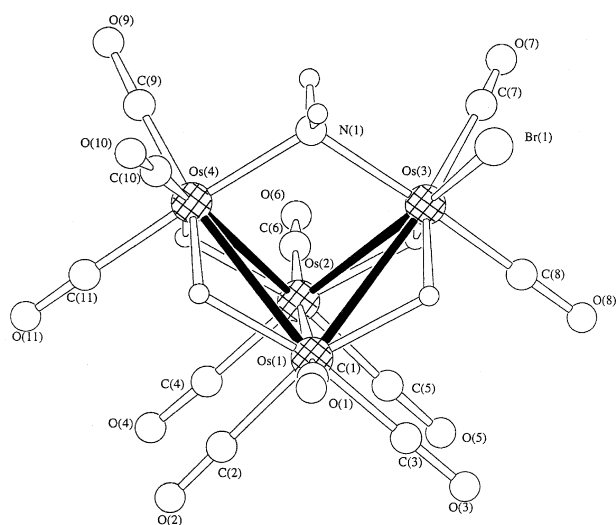


Fig. 5 The molecular structure of $[\text{Os}_4(\mu\text{-H})_4(\text{CO})_{11}(\mu\text{-NH}_2)\text{Br}]$ **4b** with the atom numbering scheme.

butterfly, $\text{Os}(1)\text{-Os}(2)\text{-Os}(3)$ and $\text{Os}(2)\text{-Os}(3)\text{-Os}(4)$, is 122.08° , which is significantly larger than the angle of $112.2(1)^\circ$ observed in another unbridged $[\text{Os}_4\text{H}_3(\text{CO})_{12}(\text{NCMe})_2]^+$ cation.^{22c} This dihedral angle associated with **4a** is within the range of values observed in a variety of alkyne-capped butterfly structures ($112.7\text{-}144.1^\circ$).²³ The metal-metal bond lengths within the butterfly core are observed in the range $2.8109(8)\text{-}3.1141(7)$ Å which are similar to those in other tetraosmium butterfly systems,²⁴ while the hinge $\text{Os}(2)\text{-Os}(3)$ bond bridged by a hydride is uncommon. The hydride bridged $\text{Os}(3)\text{-Os}(4)$ [$3.1141(7)$ Å] is exceptionally long, while the doubly bridged $\text{Os}(1)\text{-Os}(2)$ bond [$2.8109(8)$ Å] is the shortest metal-metal bond implying that the shortening effect of the bridging amido ligand is significant. The NH_2 ligand is asymmetrically bridged to the $\text{Os}(1)\text{-Os}(2)$ bond with a bite angle of $83.9(4)^\circ$, having $\text{Os}(1)\text{-N}(1)$ and $\text{Os}(2)\text{-N}(1)$ bond lengths of $2.14(1)$ and $2.07(1)$ Å, respectively. The dihedral angle between the $\text{Os}(1)\text{-Os}(2)\text{-Os}(3)$ and $\text{Os}(1)\text{-Os}(2)\text{-N}(1)$ planes is 107.41° . The bromide, from hydrobromic acid, is terminally bonded to $\text{Os}(4)$ with a bond length of $2.555(2)$ Å.

The molecular structure of **4b** has a supported butterfly tetraosmium metal framework. The amido ligand bridges the wingtip osmium metals, $\text{Os}(3)$ and $\text{Os}(4)$, with a bite angle $\text{Os}(3)\text{-N}(1)\text{-Os}(4)$ of $112.3(9)^\circ$. The $\text{Os}(3)\text{-N}(1)$ and $\text{Os}(4)\text{-N}(1)$ bond distances are $2.15(2)$ and $2.13(2)$ Å respectively, which are comparable to the corresponding values observed in **4a**. The dihedral angle between the $\text{Os}(1)\text{-Os}(2)\text{-Os}(3)$ and $\text{Os}(1)\text{-Os}(2)\text{-Os}(4)$ planes is 83.17° which is significantly smaller than those found in other supported butterfly systems.²⁴

Refluxing of **4a** in toluene for several hours afforded a new pale yellow cluster $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu\text{-NH}_2)\text{Br}]$ **5**. Cluster **4a** undergoes a thermolytic fragmentation process instead of the oligomerization reaction observed as in the case of ruthenium.²⁰ Molecules of **5** consist of an isosceles triangle of osmium atoms with the shortest $\text{Os}(2)\text{-Os}(3)$ edge [$2.8198(7)$ Å] bridged on both sides by an amido (NH_2) and hydride ligands (Fig. 6). The bridging amido ligand and the metal hydride are

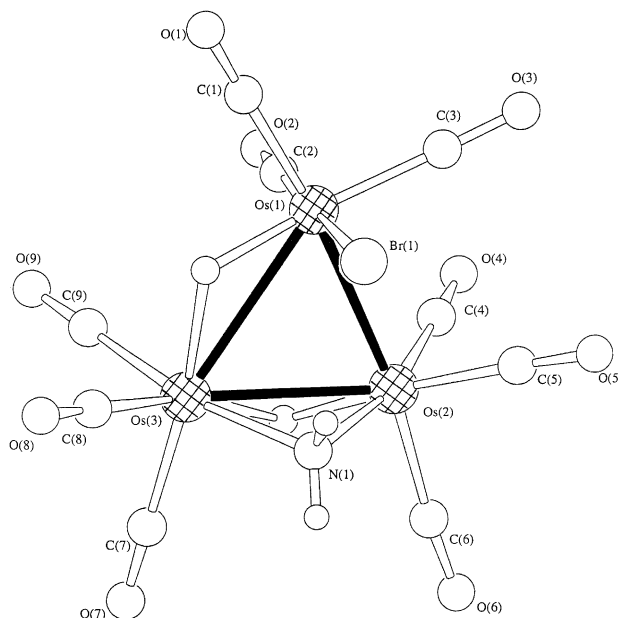


Fig. 6 The molecular structure of $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu\text{-NH}_2)\text{Br}]$ **5** with the atom numbering scheme.

located on the opposite sides of the triosmium plane and show dihedral angles of 101.06 and 124.73° relative to the triosmium plane.

An excess of triphenylcarbenium tetrafluoroborate was added to a solution of **4a** in dichloromethane in order to remove the hydrides in the metal core. This suggests that the amido ligand may undergo ligand transformation to give the $\mu_3\text{-}$ or $\mu_4\text{-NH}$ nitrene ligand, which acts as a four-electron donor in the electron deficient tetraosmium metal core. However, another green amido tetrahedral tetraosmium cluster $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)\text{Br}]$ **6**, instead of a nitrene cluster, was isolated in this reaction.

The solid-state structure of **6** is depicted in Fig. 7. Two hydrides are removed by triphenylcarbenium ion during the reaction, affording an unstable dication with 60 cluster valence

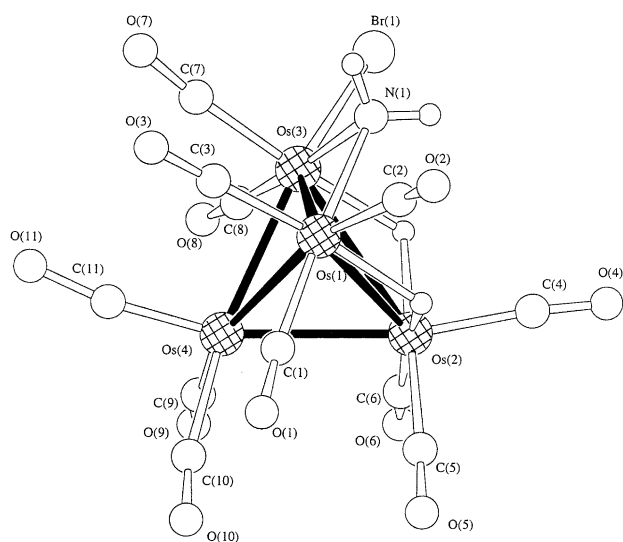


Fig. 7 The molecular structure of $[\text{Os}_4(\mu\text{-H})_2(\text{CO})_{11}(\mu\text{-NH}_2)\text{Br}]$ **6** with the atom numbering scheme.

electrons. In order to eliminate the electron deficiency, the butterfly metal framework changes back to tetrahedral by forming a metal–metal bond instead of a nitrene cluster. The amido ligand asymmetrically bridges $\text{Os}(1)\text{--Os}(3)$, and the dihedral angle between the $\text{Os}(1)\text{--N}(1)\text{--Os}(3)$ and $\text{Os}(1)\text{--Os}(2)\text{--Os}(3)$ planes is 71.40° . The bromide ligand is bonded to $\text{Os}(3)$, with a $\text{Os}(3)\text{--Br}(1)$ bond distance of $2.558(3)$ Å. The fact that the bromide and amido ligands are bonded to the same osmium atom in **6** implies that an intermediate compound with migration of the amido ligand is presumably involved in the process. Cluster **4b** is not this intermediate compound since it does not give **6** in reaction with triphenylcarbenium ion (Scheme 4)

Conclusion

The transformation of the amino cluster to $\mu\text{-NH}_2$ amido clusters has been demonstrated in this work. The first examples of osmium metal clusters containing $\mu\text{-NH}_2$ amido ligands were prepared and fully characterized. They are believed to be important cluster analogues for the reactivity study of metal surface bound nitrogen atom towards molecular hydrogen.

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