tert-Butylimido Complexes of Osmium-(VIII), -(VII) and -(VI). X-Ray Crystal Structures of $[(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)(\mu\text{-}O)]_2$, $[Os(NBu^t)_2(\mu\text{-}NBu^t)]_2$ and $[Os(NBu^t)_2(\mu\text{-}NBu^t)]_2[BF_4]_2$†

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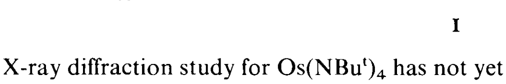
The interaction of OsO_4 with neat $NHBu^t(SiMe_3)$ gives the first homoleptic osmium(VIII) imido compound, $Os(NBu^t)_4$ **1**, together with the tetranuclear osmium(VI) oxo–imido complex $[(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)(\mu\text{-}O)]_2$ **2**. Complex **1** can be reduced to the osmium(VI) dimer, $[Os(NBu^t)_2(\mu\text{-}NBu^t)]_2$ **3**, by triphenylphosphine or by sodium amalgam in tetrahydrofuran; with trimethyloxonium tetrafluoroborate an unusual reduction reaction leads to the osmium(VII) dimeric cationic complex $[Os(NBu^t)_2(\mu\text{-}NBu^t)]_2[BF_4]_2$ **4**. The syntheses of $Os(NR)_3$, R = 2,6-$Me_2C_6H_3$ **5**, or 2,6-$Pr^i{}_2C_6H_3$ **6**, by interaction of OsO_4 with $NHR(SiMe_3)$ are reported. The X-ray crystal structures of **2**, **3** and **4** have been determined. Compound **2** has a chain tetrameric structure with two $(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)(\mu\text{-}O)$ units linked by a dioxo bridge. The outer Os atoms are four-co-ordinate, distorted tetrahedral, the inner Os atoms five-co-ordinate, square pyramidal. The bridging Os–N distances to the inner, five-co-ordinate osmiums are shorter than those to the outer osmiums; the terminal Os–N distances are essentially the same for both types of osmium. Compound **3** and the cation in **4** are dimers with imido bridges. The main difference between them is a significant shortening in the Os···Os distance in the osmium(VII) compound as a result of Os–Os single bond formation. This also results in a slight shortening of the Os–N bridge distances in **4** as compared to the neutral molecule **3**.

We have described the syntheses, some reactions and structures of the imido analogues of oxometalates of Group 6 elements, namely the compounds $Li_2M(NBu^t)_4$, M = Cr,[1] Mo[2] or W,[2] as well as $Li(Me_2NCH_2CH_2NMe_2)Re(NBu^t)_4$ and the rhenium(VI) neutral dimer, $[Re(NBu^t)_2(\mu\text{-}NBu^t)]_2$,[3a] which was the first homoleptic imido compound to be obtained.[3b] A preliminary note[1a] described the synthesis of the first homoleptic imido osmium(VIII) compound, $Os(NBu^t)_4$. The compound $Os(NBu^t)_3[N(O_2SC_6H_4Me)]$, has been reported[4] as having been prepared but no details have become available.

Details of our studies on osmium compounds are now given; analytical and physical data are given in Table 1 and spectroscopic data in Table 2.

Results and Discussion

Reactions of OsO_4 *with* $NHBu^t(SiMe_3)$.—The synthesis of a mixture of $OsO_2(NBu^t)_2$ and $OsO(NBu^t)_3$ by Nugent *et al.*[5] used the reaction of OsO_4 with $NHBu^t(SiMe_3)$ in hexane. By contrast, the reaction of neat $NHBu^t(SiMe_3)$ and OsO_4 leads to $Os(NBu^t)_4$ **1** in yields varying from 25 to 40%, together with other products one of which has been characterised. Compound **1** is a low melting point (*ca.* 30 °C) orange-red crystalline solid that is stable thermally to *ca.* 120 °C under N_2 or in vacuum. It is very soluble in common organic solvents and is monomeric as shown by cryoscopy in benzene. It is hydrolysed readily in moist air to a mixture of oxo–imido species; the only component of this mixture to be identified (by NMR spectroscopy) is $OsO_2(NBu^t)_2$.[6,7] The IR spectrum of $Os(NBu^t)_4$ shows a metal–imido absorption at 1238 cm^{-1} while the ^1H NMR spectrum (δ 1.48) is invariant over the ranges −80 to 25 °C (CD_2Cl_2) and 25–80 °C ($CDCl_3$) indicating equivalence of the Bu^t groups on the NMR time-scale. The $^{13}C\text{-}\{^1H\}$ chemical shifts at 30.25 and 72.61 ppm are those for the primary and tertiary carbons of Bu^t, respectively; the difference (Δ = 42.3 ppm) suggests that the imido group is nucleophilic in nature.[4,7] The electron impact (EI) mass spectrum shows the parent ion with the expected osmium isotopic envelope with additional low-intensity fragmentation peaks at higher mass. The major fragment ion, at *m/z* 390, could arise from agostic hydrogen interaction in the electrophilic parent ion leading to H transfer, loss of CH_3 and NBu^t and the formation of the ion **I**, equation (1). Other peaks in the spectrum correspond to the loss of 2-methylpropene and the NBu^t groups from $Os(NBu^t)_4$.



I

An X-ray diffraction study for $Os(NBu^t)_4$ has not yet proved possible owing to the low melting point and difficulty in obtaining suitable crystals; however electron diffraction studies are in progress.[8] The IR and NMR spectroscopic data are consistent with a tetrahedral geometry for $Os(NBu^t)_4$ in which all of the imido groups are equivalent; if an 18-electron structure is assumed, the molecule could be formulated with one linear and three bent $OsNBu^t$ groups that are equilibrating rapidly on the NMR time-scale since there is no change in the ^1H NMR

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† Di-μ-oxo-2:3κ^4*O*-tetra-μ-*tert*-butylimido-1:2κ^4*N*; 3:4κ^4*N*-hexakis(*tert*-butylimido-1κ^2*N*,2κ*N*,3κ*N*,4κ^2*N*)tetraosmium(VI), bis(μ-*tert*-butylimido)-bis[di(*tert*-butylimido)osmium(VI)] and bis(μ-*tert*-butylimido)-bis[di(*tert*-butylimido)osmium(VII)] bis(tetrafluoroborate).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical* and physical data for new compounds

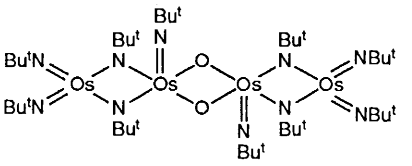
Compound	Colour	M.p./°C	Analytical data (%) C	H	N
1 $Os(NBu^t)_4$	Orange-red	*ca.* 30	40.6 (40.5)	7.6 (7.6)	11.0 (11.8)
2 $[(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)(\mu\text{-}O)]_2$	Red	120	32.4 (31.9)	6.0 (6.0)	9.3 (9.3)
3 $[Os(NBu^t)_2(\mu\text{-}NBu^t)]_2$	Yellow	150–155	35.6 (35.7)	6.7 (6.7)	10.2 (10.4)
4 $[Os(NBu^t)_2(\mu\text{-}NBu^t)]_2[BF_4]_2$	Orange	160–165 (decomp.)	29.0 (29.4)	5.4 (5.5)	8.4 (8.6)
5 $Os(NC_6H_3Me_2\text{-}2,6)_3$	Red-brown	165–169	51.6 (52.6)	4.5 (4.9)	7.2 (7.6)

* Calculated values in parentheses.

Table 2 Infrared,[a] nuclear magnetic resonance (^1H)[b] and mass spectral[c] data

Compound	^1H NMR δ	Assignment	IR ν/cm^{-1}	Assignment	MS *m/z*(%)	Assignment
1	1.48(s)	NBu^t	1238	$Os{=}NBu^4$	476(1.5)	$Os(NBu^t)_4{}^+$
					419(1.0)	$M^+ - Me_2C{=}CH_2$
					405(1.5)	$M^+ - NBu^t$
					390(100)	$M^+ - NMeBu^t$
2	1.56(m)	NBu^t(terminal)	1220	$Os{=}NBu^t$(terminal)	755(2.1)	$M/2^+$
	1.47(s)	NBu^t(terminal)	1195	$Os\text{–}\mu\text{–}NBu^t$	739(4.1)	$M/2 - O$
	1.12(s)	NBu^t(bridging)			698(0.5)	$M/2 - Me_2C{=}CH_2$
					684(0.4)	$M/2 - NBu^t$
					390(100)	$Os(NBu^t)_3(CH_2NBu^t)$
					334(3.4)	$390 - Me_2C{=}CH_2$
3	1.42	NBu^t(terminal)	1208	$Os{=}NBu^t$(terminal)	810(0.5)	M^+
	1.56	NBu^t(bridging)	1105	$Os\text{–}\mu\text{–}NBu^t$	753(5.2)	$M^+ - Me_2C{=}CH_2$
					739(15)	$M^+ - NBu^t$
4	1.75	NBu^t(bridging)	1220	$Os{=}NBu^t$(terminal)		
	1.50	NBu^t(terminal)	1150	$Os\text{–}\mu\text{–}NBu^t$		
			1050	BF_4(br)		
5	6.87	aromatic H	1150	$Os{=}NC_6H_3Me_2\text{-}2,6$	549(19.2)	M^+
	2.21	CH_3	1304	δ(C–N)	534(2.7)	$M^+ - Me$
			764	C–H aromatic		

[a] Bu^t and aryl bands not listed; spectra in Nujol mulls. [b] δ Relative to $SiMe_4$ at 298 K; $^{13}C\text{-}\{^1H\}$ for $Os(NBu^t)_4$, δ 30.25 (CH_3) and 72.61 (CMe_3) ppm; Solvent, $CDCl_3$. [c] EI Isotopic envelopes due to osmium isotopes were observed; only peaks corresponding to the highest abundance ^{192}Os (39.95%) are listed.



II

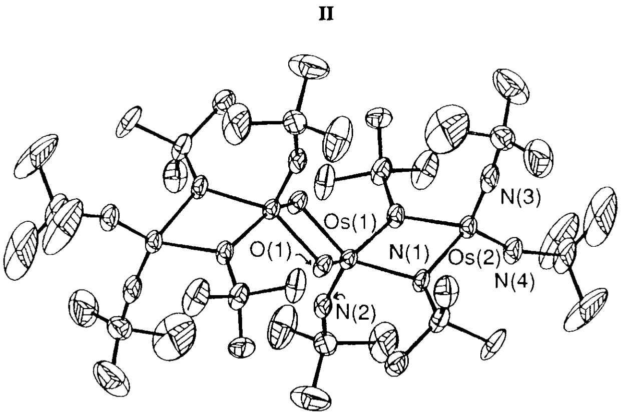


Fig. 1 The structure of $[(Bu^tN)_2Os(\mu\text{-}NBu^t{}_2)Os(NBu^t)(\mu\text{-}O)]_2$ **2**

spectrum down to −80 °C. There is only one band in the imido region of the IR spectrum suggesting that all the NBu^t groups are the same and probably bent.

From the reaction of OsO_4 and $NHBu^t(SiMe_3)$ a second compound, **2**, has been isolated and structurally characterised as having structure **II**, which contains two four-co-ordinate and two five-co-ordinate osmium(VI) centres. A diagram of the structure is shown in Fig. 1; selected bond lengths and angles are given in Table 3. The molecule is a chain tetramer which can be described conveniently as a dimer of dimers and has C_{2h} symmetry. Thus two dimeric units $(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)(\mu\text{-}O)$ are linked across a centre of symmetry by a dioxo bridge; the two oxygen atoms also lie on the two-fold axis and the mirror plane contains the metal atoms, the terminal imido nitrogens and relevant carbons. As a result the outer osmium atoms are four-co-ordinate, distorted tetrahedral with angles N–Os–N 73.5(3)°, involving bridging nitrogens and 118.2(7)°, involving the terminal nitrogens. The inner osmiums are five-co-ordinate, essentially square pyramidal, with the axial site occupied by a terminal imido group. There is no significant difference between the Os–N (terminal) distances at the two osmiums, in spite of the different co-ordination numbers, but the Os–N distances involving bridging imido groups are significantly different. Surprisingly, those to the inner, five-co-ordinate osmium atoms are *shorter* than those to the outer four-co-ordinate osmiums. These two features could reflect the greater steric compression in the co-ordination sphere of the outer '$Os(NBu^t)_4$' units, compared with the inner '$OsO_2(NBu^t)_3$' units. The Os-O bridges are symmetrical and the overall intramolecular steric compression is also reflected in the large Os ··· Os distances and 'acute' angles of *ca.* 70° at the metal atoms in the Os_2N_2 and Os_2O_2 rings. The terminal imido ligands have bent geometries (Os–N–C > 150°) consistent with their behaviour as predominantly four-electron ligands.

Table 3 Selected bond lengths in (Å) and angles in (°) for $[(Bu^tN)_2Os(\mu-NBu^t)_2Os(NBu^t)(\mu-O)]_2$ **2***

O(1)–Os(1)	1.941(7)	N(1)–Os(1)	1.938(10)
N(2)–Os(1)	1.708(12)	N(1)–Os(2)	1.966(10)
N(3)–Os(2)	1.732(14)	N(4)–Os(2)	1.668(15)
C(1)–N(1)	1.497(13)	C(11)–C(1)	1.551(18)
C(12)–C(1)	1.563(17)	C(13)–C(1)	1.538(17)
C(2)–N(2)	1.431(18)	C(21)–C(2)	1.561(19)
C(22)–C(2)	1.537(29)	C(3)–N(3)	1.408(18)
C(31)–C(3)	1.456(19)	C(32)–C(3)	1.592(39)
C(4)–N(4)	1.486(22)		
Os(1) • • • Os(2)	3.090(1)	Os(1) • • • Os(16)	3.130(1)
Os(1)–O(1)–Os(1B)	107.4(5)	N(1)–Os(1)–O(1)	93.0(4)
N(1)–Os(1)–N(1B)	74.7(6)	N(1)–Os(1)–O(1B)	140.4(3)
O(1B)–Os(1)–N(1B)	93.0(3)	N(2)–Os(1)–O(1)	112.3(4)
N(2)–Os(1)–N(1)	107.3(4)	N(1)–Os(2)–N(1B)	73.5(3)
N(3)–Os(2)–N(1)	115.5(5)	N(4)–Os(2)–Os(1)	126.7(5)
N(4)–Os(2)–N(1)	113.1(5)	N(4)–Os(2)–N(3)	118.2(7)
O(1)–Os(1)–O(1)	72.6(5)	Os(2)–N(1)–Os(1)	104.6(5)
C(1)–N(1)–Os(1)	129.2(8)	C(1)–N(1)–Os(2)	124.1(7)
C(11)–C(1)–N(1)	107.4(10)	C(12)–C(1)–N(1)	109.7(10)
C(12)–C(1)–C(11)	109.1(11)	C(13)–C(1)–N(1)	109.0(9)
C(13)–C(1)–C(11)	112.5(11)	C(13)–C(1)–C(12)	109.1(11)
C(2)–N(2)–Os(1)	154.4(12)	C(21)–C(2)–N(2)	107.9(11)
C(22)–C(2)–N(2)	106.4(16)	C(22)–C(2)–C(21)	112.0(13)
C(21)–C(2)–C(21B)	110.4(21)	C(3)–N(3)–Os(2)	174.9(13)
C(31)–C(3)–N(3)	111.6(11)	C(32)–C(3)–N(3)	103.2(21)
C(32)–C(3)–C(31)	103.1(16)	C(31)–C(3)–C(31B)	121.7(23)
C(4)–N(4)–Os(2)	156.8(13)	C(41)–C(4)–N(4)	109.2(13)
C(42)–C(4)–N(4)	104.1(20)	C(42)–C(4)–C(41)	110.1(17)
C(41)–C(4)–C(41B)	113.7(23)	N(1)–Os(1)–N(1)	74.7(6)
N(1)–Os(2)–N(1)	73.5(3)		

* Key to symmetry operations relating designated atoms to reference atoms at (*x*,*y*,*z*): (B) $-x$, $-y$, $-z$.

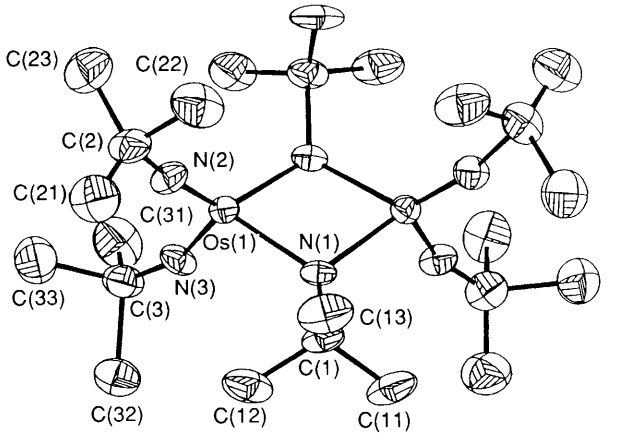


Fig. 2 The structure of $[Os(NBu^t)_2(\mu-NBu^t)]_2$

The spectroscopic data are in accord with the structure. The ^1H NMR spectrum has three singlets; the resonance at δ 1.56 can be assigned to the four terminal NBu^t groups, that at δ 1.12 to the bridging NBu^t groups and that at δ 1.47 to the NBu^t groups of the two internal Os atoms. The δ 1.56 and 1.12 signals show temperature-invariant fine structure that is possibly due to the slight inequivalence of the NBu^t protons entering the anisotropy region of the π-electron systems in certain conformations of the tetramer.

The mass spectrum of **2** does not show the parent ion but does show the fragment $(Bu^tN)_2Os(\mu-NBu^t)_2Os(NBu^t)O$ and losses due to 2-methylpropene, but not NBu^t as is common for most NBu^t complexes.

It is not clear if **2** is formed directly from OsO_4 or by reaction of $Os(NBu^t)_4$ with other oxo-imido species in the presence of an excess of $NHBu^t(SiMe_3)$ and $(Me_3Si)_2O$ formed in the reaction. The yield of $Os(NBu^t)_4$, however, decreases and that of **2** increases upon prolonged reaction times. The electrons required for reduction of Os^{VIII} could arise from $NHBu^t(SiMe_3)$ on oxidation to $[NBu^t(SiMe_3)]_2$. Minor amounts of $[Os(NBu^t)_2(\mu-NBu^t)]_2$ (see later) are also present in the reaction mixture according to NMR spectroscopy. Neither $Os(NBu^t)_4$ nor **2** is obtained from the reaction of OsO_4 with $NBu^t(SiMe_3)_2$, only $OsO_3(NBu^t)$.[7]

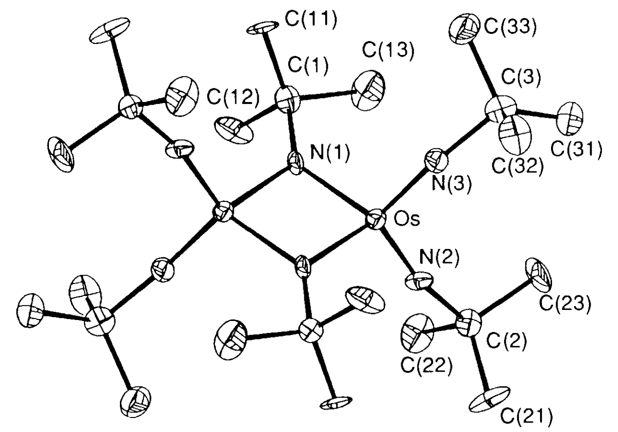


Fig. 3 The structure of the cation in $[Os(NBu^t)_2(\mu-NBu^t)]_2[BF_4]_2$ **4**

Reductions of $Os(NBu^t)_4$.—The tetraimide is reduced by tertiary phosphines (PPh_3, $PMePh_2$) in CH_2Cl_2 or tetrahydrofuran (thf) giving phosphine imides, $R_3P{=}NBu^t$, and the diamagnetic osmium(VI) dimer, $[Os(NBu^t)_2(\mu-NBu^t)]_2$ **3**, as the main osmium-containing product. Although the reaction is not clean, reduction of $Os(NBu^t)_4$ by Na–Hg in thf gives the same product as isolated by chromatography on Florisil.

The dimer is structurally similar to the rhenium(VI) analogue,[3] $[Re(NBu^t)_2(\mu-NBu^t)]_2$, which is diamagnetic with a Re–Re bond.

A diagram of the dimer **3** is shown in Fig. 2; selected bond lengths and angles are given in Table 4. The molecule has a two-fold axis of symmetry aligned perpendicular to the Os_2N_2 core, and the arrangement of the Bu^t groups is such that the overall molecular symmetry approximates quite closely to C_{2v}. The geometry around each osmium atom is very similar to that for the outer osmium in compound **2** and similarly in **3** the terminal imido groups are acting as four-electron ligands.

Unlike the reduction of $Os(NBu^t)_4$ with PPh_3 and $PMePh_2$ the interaction with PMe_3 gives a complex that will be described separately.

In the expectation of electrophilic attack on a nitrogen atom to give an $OsNMeBu^{t+}$ group **1** was treated with trimethyloxonium tetrafluoroborate. Although a fast reaction occurred at −78 °C work-up gave dark orange crystals of a new, reduced, dimeric species, $[Os(NBu^t)_2(\mu-NBu^t)]_2[BF_4]_2$ **4**. This contains osmium in the very rare[9] oxidation state of Os^{VII}, which is not observed in reductions with other reducing agents described above.

A diagram of the cation of **4** is shown in Fig. 3; selected bond lengths and angles are given in Table 5. The change from the neutral diosmium(VI) species **3** to this cationic diosmium(VII) species is reflected in a dramatic reduction in the Os . . . Os distance, from *ca.* 3.1 Å in **3** to 2.68 Å in **4**. This is consistent with the formation of a single Os–Os bond. In this centrosymmetric structure the Os–N–Os bridges are slightly unsymmetric, possibly as a result of the increased steric compression and particular orientation of the Bu^t groups on the bridging imido functions. The Os–N distances in the bridge, however, are slightly smaller than those in the neutral compound, but the terminal Os–N distances show no significant change. The spectroscopic data for **4** (Table 2) are in accord with the structure as determined.

Table 4 Selected bond lengths in (Å) and angles in (°) for $[Os(NBu^t)_2(\mu\text{-}NBu^t)]_2$ **3***

N(1)–Os(1)	1.953(127)	N(2)–Os(1)	1.589(25)
N(3)–Os(1)	1.821(18)	Os(1)–Os(1B)	3.120(4)
Os(1)–N(1B)	1.939(12)	C(1)–N(1)	1.529(22)
C(2)–N(2)	1.443(32)	C(3)–N(3)	1.500(4)
Os(1)–N(1)–Os(1B)	106.6(105)	N(2)–Os(1)–N(1)	123.3(13)
N(3)–Os(1)–N(1)	104.7(13)	N(3)–Os(1)–N(2)	116.1(10)
N(1)–Os(1)–N(1B)	72.8(11)	N(2)–Os(1)–N(1B)	127.2(13)
N(3)–Os(1)–N(1B)	104.3(12)	C(1)–N(1)–Os(1)	124.1(11)
C(2)–N(2)–Os(1)	161.5(22)	C(3)–N(3)–Os(1)	155.4(22)
C(11)–C(1)–N(1)	103.2(18)	C(12)–C(1)–N(1)	104.3(19)
C(13)–C(1)–N(1)	113.6(23)	C(21)–C(2)–N(2)	103.5(25)
C(22)–C(2)–N(2)	120.1(27)	C(23)–C(2)–N(2)	104.5(30)
C(32)–C(3)–N(3)	103.1(22)	C(31)–C(3)–N(3)	100.5(23)
C(33)–C(3)–N(3)	110.3(28)		

* Key to symmetry operations relating designated atoms to reference atoms at (*x*,*y*,*z*): (B) −*x*, −*y*, −*z*.

Table 5 Selected bond lengths in (Å) and angles in (°) for $[Os(NBu^t)_2(\mu\text{-}NBu^t)]_2[BF_4]_2$ **4***

N(1)–Os(1)	1.902(19)	N(1B)–Os(1)	1.927(20)
N(2)–Os(1)	1.715(18)	N(3)–Os(1)	1.710(19)
Os(1)–Os(1B)	2.677(5)	C(1)–N(1)	1.528(27)
C(2)–N(2)	1.446(26)	C(3)–N(3)	1.516(27)
N(2)–Os(1)–N(1)	111.8(8)	N(3)–Os(1)–N(1)	111.7(9)
N(3)–Os(1)–N(2)	115.2(9)	N(1B)–Os(1)–N(3)	111.1(8)
N(1B)–Os(1)–N(2)	113.3(7)	C(1)–N(1)–Os(1)	137.9(13)
C(2)–N(2)–Os(1)	168.7(16)	C(3)–N(3)–Os(1)	167.9(17)
C(11)–C(1)–N(1)	106.4(17)	C(12)–C(1)–N(1)	106.6(21)
C(13)–C(1)–N(1)	106.3(19)	C(21)–C(2)–N(2)	109.9(21)
C(22)–C(2)–N(2)	103.5(19)	C(23)–C(2)–N(2)	108.2(21)
C(31)–C(3)–N(3)	109.6(23)	C(32)–C(3)–N(3)	104.3(20)
C(33)–C(3)–N(3)	103.0(20)		

* Key to symmetry operations relating designated atoms to reference atoms at (*x*,*y*,*z*): (B) −*x*, −*y*, −*z*.

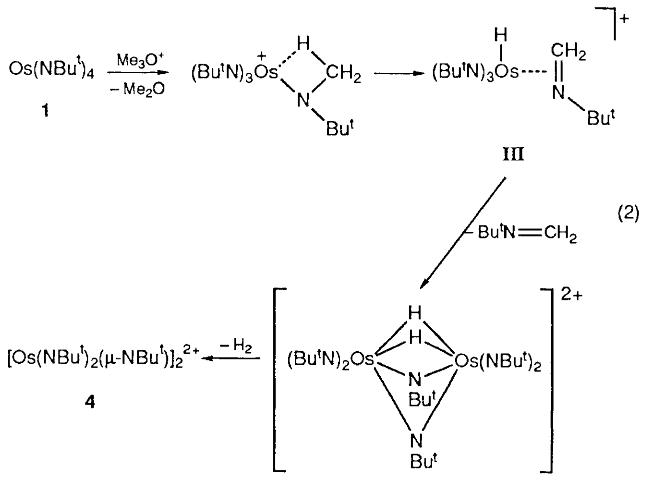


Table 6 Cyclic voltammetry*

Compound	Solvent	$E_{\frac{1}{2}}$/V
1	CH_2Cl_2	-1.67 (Os^{VII}–Os^{VIII})
3	CH_3CN	-0.05 (Os^{VI}–Os^{VII})
4	CH_3CN	-0.07 (Os^{VI}–Os^{VII}) -1.25 (Os^{V}–Os^{VI}) (-2.4) (?)
5	CH_2Cl_2	($+0.12$)(Os^{VI}–Os^{VII}) (-1.61)(Os^{V}–Os^{VI}) -2.05 (?)

* All values (V) referred to ferrocene–ferrocenium = 0.00 V. Sweep rate 100 mV s^{-1}. OE-PP2 instrument with 0.2 mol dm^{-3} $NBu^n{}_4PF_6$ as supporting electrolyte at 20 °C with platinum working, tungsten auxiliary and silver pseudo-reference electrodes. Values in parentheses indicate irreversible redox couples (E_p).

We are unaware of a precedent in which interaction of a complex with $Me_3O^+BF_4^-$ leads to reduction—here, one electron per osmium atom. The initial attack presumably involves electrophilic attack on $Os{=}NBu^t$ to give Os^+NMeBu^t. The reaction could then proceed as in equation (2) where there is hydride transfer from the methyl group, probably *via* initial agostic interaction with the electrophilic osmium centre [*cf.* equation (1)], leading to the species **III** for which there is an analogue in the compound[10] $Ta(NEt)_3(\eta^2\text{-}MeCH{=}NEt)$. Loss of $Bu^tN{=}CH_2$ (which could react with excess $Me_3O^+BF_4^-$) leads to the osmium(VIII) dimer **IV** from which reductive elimination of hydrogen produces the osmium(VII) dimeric cation **4**.

Although we have been unable to isolate any intermediates from the reaction, changes in the ^1H NMR spectra (25 °C, CD_2Cl_2) can be followed. The initial spectrum shows $Os(NBu^t)_4$ and Me_3O^+ peaks at δ 1.47 (NBu^t) and 3.2 (Me). After 5 min new peaks at δ 1.57 (NBu^t), 1.69 ($NMeBu^t$) and 3.45 (Me) appear which can be assigned to $[Os(NBu^t)_3(NMeBu^t)]^+$. After *ca.* 18 min the signal at δ 1.47 due to $Os(NBu^t)_4$ has disappeared while that at δ 1.57 due to NBu^t groups of the intermediate species remains and those at δ 1.69 and 3.45 have decreased in intensity. After 20 min the signal at δ 1.57 is still present while new peaks have appeared. Of these, a peak at δ 1.70 and a broad peak at δ *ca.* 5.7 can be assigned to the Bu^t and CH_2 groups of $Bu^tN{=}CH_2$; additionally there are small peaks at δ 1.41 and 1.17 which cannot be assigned. Signals due to the final product **4** have also now appeared together with a weak broad band at *ca.* δ −15 which we can ascribe to hydride in **III** or **IV**.

After 50 min, the peak at δ 1.57, attributed to the NBu^t groups of intermediate **III** or **IV** (or both), has disappeared and the final spectrum, which does not change further with time consists of (*a*) the bands at δ 1.75 ($\mu\text{-}NBu^t$) and 1.50 (NBu^t) of compound **4**, (*b*) bands at δ 5.7 and 1.70 assigned to $Bu^tN{=}CH_2$ but with much diminished intensity and (*c*) the bands at δ 1.41 and 1.17 with correspondingly increased intensity, which we consider to be due to the unidentified product of the reaction of $Bu^tN{=}CH_2$ with excess Me_3O^+ (which also appears at δ 3.2).

Other reactions of $Os(NBu^t)_4$ will be described separately.

Arylimido Compounds.—In addition to $Os(NBu^t)_4$, we have also synthesised by the same method using a neat silylamine, two diamagnetic osmium(VI) arylimido species, $Os(NR)_3$, R = $2,6\text{-}Me_2C_6H_3$, **5**, or $2,6\text{-}Pr^i{}_2C_6H_3$, **6**. The latter has also been described[11] during the course of this study, being prepared in 50% yield by the interaction of OsO_4 with the aryl isocyanate in refluxing heptane.

Compound **5** is monomeric in the gas phase (mass spectroscopy) and in solution (cryoscopy in benzene) and is thermally stable. It probably has a structure similar to that determined[11] for **6**.

The reduction of OsO_4 by the silylamine evidently leads to RN=NR (R = arene) and it may be noted that similar reactions using anilines with hydrogen atoms in the 2 position failed to give an isolable osmium(VI) product and only purple solutions of oxidised azo compounds were formed together with black osmium-containing precipitates insoluble in common organic solvents.

Electrochemistry of Compounds **1**, **3**, **4** *and* **5**.—The cyclic voltammetry data are collected in Table 6. For $Os(NBu^t)_4$ there is a reversible couple assignable as Os^{VII}–Os^{VIII} at −1.67 V

Table 7 Crystal data, details of intensity measurements and structure refinement

Compound	**2**	**3**	**4**
Formula	$C_{40}H_{70}N_{10}O_2Os_4$	$C_{24}H_{54}N_6Os_2$	$[C_{24}H_{54}N_6Os_2][BF_4]_2$
M	1504.02	807.133	980.742
Crystal system	Monoclinic	Monoclinic	Orthorhombic
a/ Å	16.072(3)	9.689(6)	13.946(1)
b/ Å	11.035(3)	18.060(5)	14.143(7)
c/ Å	17.579(3)	9.723(3)	19.025(4)
α/°	90	90	90
β/°	116.20(3)	96.79(3)	90
γ/°	90	90	90
U/Å^3	1398.98	1699.67	3752.46
Space group	$I2/m$	$C2$	$Pbca$
Z	2	2	4
D_c/g cm^{-3}	1.785	1.58	1.736
μ/cm^{-1}	87.32	74.98	65.33
F(000)	1440	784	1896
h,k,l, range	−11 to 11	0–6	0–15
	−16 to 16	0–12	0–15
	0–11	−6 to 6	0–20
Total no. of reflections	4136	1360	3033
No. of unique reflections	2063	1227	2614
No. of reflections used	1805	965	1179
Significance test	$[F > 3\sigma(F)]$	$[F > 3\sigma(F)]$	$[F > 5\sigma(F)]$
No. of parameters	144	146	230
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF_o^2]$	0.000 02	0.0002	0.0002
Final R	0.0391	0.0328	0.0440
Final R'	0.0364	0.0311	0.0379

Table 8 Fractional atomic coordinates (× 10^4) for $[(\mathrm{Bu^tN})_2\mathrm{Os}(\mu\text{-}\mathrm{NBu^t})_2\mathrm{Os}(\mathrm{NBu^t})(\mu\text{-O})]_2$ **2**

Atom	x	y	z
Os(1)	1031.4(3)	0	139.9(3)
Os(2)	1560.5(4)	0	−1359.8(3)
O(1)	0	1041(8)	0
N(1)	1428(5)	1066(7)	−514(4)
C(1)	1390(7)	2419(9)	−571(7)
C(11)	2212(10)	2840(11)	−743(10)
C(12)	1503(9)	2967(11)	289(8)
C(13)	445(9)	2804(10)	−1278(8)
N(2)	1886(7)	0	1158(7)
C(2)	2828(11)	0	1793(10)
C(21)	2981(11)	−1161(16)	2345(11)
C(22)	3434(14)	0	1318(16)
N(3)	633(8)	0	−2350(8)
C(3)	−172(13)	0	−3128(11)
C(31)	−296(16)	−1152(17)	−3568(11)
C(32)	−988(18)	0	−2847(26)
N(4)	2630(9)	0	−1279(8)
C(4)	3351(14)	0	−1592(15)
C(41)	3912(13)	−1132(18)	−1306(17)
C(42)	2805(28)	0	−2543(27)

(ΔE = 54 mV) in dichloromethane. The $E_{\frac{1}{2}}$ value for the analogous couple of OsO_4 in CH_2Cl_2 is 0.106 V (*vs.* Ag–AgCl)[12a,b] and −0.42 V *vs.* ferrocene-ferrocenium.[12b] The much more negative value for **1** is probably ascribable to the increased basicity of $\mathrm{NBu^t}$ compared to oxo groups. This type of difference was also found in the comparison of $\mathrm{OsO(NBu^t)(mes)_2}$ and $\mathrm{OsO_2(mes)_2}$ (mes = 2,4,6-$\mathrm{Me_3C_6H_2}$) where the $\mathrm{Os^V–Os^{VI}}$ $E_{\frac{1}{2}}$ values were, respectively, −1.89 and −1.28 V.[13]

For the dimeric compounds **3** and **4** we might have expected reversible one-electron steps $(\mathrm{VI–VI}) \rightleftharpoons (\mathrm{VI–VII})^+ \rightleftharpoons (\mathrm{VII–VII})^{2+}$. However, instead we observe a reversible two-electron couple at −0.05 and −0.07 V (ΔE = 30 and 32 mV), for **3** and **4** respectively, which is assigned to $\mathrm{Os^{VI}–Os^{VII}}$; the small $E_{\frac{1}{2}}$ difference can be disregarded, being within the limits of experimental error. Similar behaviour occurs in CH_2Cl_2. In addition **4** shows a reversible two-electron reduction at −1.25 V (ΔE = 32 mV) that can be ascribed to $\mathrm{Os^V–Os^{VI}}$ (*cf.* ref. 13). The nature of the irreversible couple at −2.4 V is not clear. Attempts to oxidise acetonitrile solutions of **3** chemically using various silver salts gave yellow-green solutions but neither $(\mathrm{VI–VII})^+$ nor $(\mathrm{VII–VII})^{2+}$ species could be isolated.

Table 9 Fractional atomic coordinates (× 10^4) for $[\mathrm{Os(NBu^t)_2}(\mu\text{-}\mathrm{NBu^t})]_2$ **3**

Atom	x	y	z
Os(1)	1167(1)	0	1245(1)
N(1)	−833(11)	77(19)	752(11)
N(2)	1186(24)	−666(13)	2121(26)
N(3)	1709(22)	927(10)	1811(19)
C(1)	−1901(17)	−88(17)	1744(18)
C(2)	2303(35)	−1405(21)	2557(28)
C(3)	2523(32)	1484(19)	2713(33)
C(11)	−3209(25)	382(16)	1125(29)
C(12)	−1333(26)	313(17)	3101(27)
C(13)	−2077(27)	−876(16)	1999(29)
C(21)	2057(38)	−1421(22)	4099(28)
C(22)	1692(38)	−2032(18)	1832(38)
C(23)	3993(31)	−1443(21)	2360(40)
C(32)	1389(33)	1860(19)	3508(33)
C(31)	3367(38)	1870(21)	1625(37)
C(33)	3686(30)	1106(22)	3628(33)

The arylimido complex **5** shows an irreversible oxidation wave at +0.12 V probably due to oxidation to $\mathrm{Os^{VII}}$, and also two reduction waves at −1.61 V (irreversible) and −2.05 V (quasi-reversible). Chemical reduction using Mg or Na–Hg in thf gives intractable mixtures while chemical oxidation by $AgBF_4$ gives a salt $[\mathrm{Os(NR)_2}(\mu\text{-F})]_2[\mathrm{BF_4}]_2$ that will be described separately.

Compound **6** shows no oxidation waves electrochemically

Table 10 Fractional atomic coordinates (× 10^4) for $[\mathrm{Os(NBu^t)_2(\mu\text{-}NBu^t)]_2[BF_4]_2}$ **4**

Atom	*x*	*y*	*z*
Os(1)	434(1)	489(1)	511(1)
N(1)	336(11)	641(10)	−479(9)
N(2)	1595(12)	289(11)	770(9)
N(3)	−144(11)	1374(13)	953(10)
C(11)	−295(18)	1837(14)	1289(13)
C(12)	1188(22)	840(17)	−1579(14)
C(13)	1295(22)	2083(20)	−658(17)
C(21)	2681(17)	−417(23)	−1619(14)
C(22)	3195(18)	36(20)	374(14)
C(23)	2777(18)	1309(18)	1285(18)
C(31)	400(23)	2723(19)	1651(13)
C(32)	−1166(18)	1883(21)	1921(14)
C(33)	−972(22)	2843(22)	774(16)
B(1)	5906(30)	470(36)	11754(23)
F(1A)	5561(46)	328(52)	12460(33)
F(2A)	5412(33)	606(36)	11157(20)
F(3A)	6098(37)	1157(38)	12086(25)
F(4A)	6433(33)	−339(36)	11764(31)
F(1B)	6643(33)	318(48)	11351(25)
F(2B)	6481(36)	1236(45)	11868(37)
F(3B)	5861(52)	−310(46)	12154(33)
F(4B)	5050(34)	392(48)	11652(33)
C(1)	631(14)	1366(19)	−1035(11)
C(2)	2565(15)	311(19)	1037(12)
C(3)	−450(20)	2256(14)	1347(13)

and is not oxidised by $\mathrm{Ag^+}$; however it has been oxidised to $\mathrm{OsO(NC_6H_3Pr^i{}_2\text{-}2,6)_3}$ by $\mathrm{Me_3NO}$.[11]

Experimental

Microanalyses were by Pascher and Imperial College Laboratories. Instruments used and experimental techniques have been described.[13] The silylamines $\mathrm{NHR(SiMe_3)}$, R = 2,6-$\mathrm{Me_2C_6H_3}$ or 2,6-$\mathrm{Pr^i{}_2C_6H_3}$, were prepared by interaction of LiNHR (prepared *in situ* from $\mathrm{NH_2R}$ and $\mathrm{LiBu^n}$ in thf at −20 °C) with $\mathrm{SiMe_3Cl}$ by a method analogous to that reported[14] while $\mathrm{NHBu^t(SiMe_3)}$ was prepared by interaction of $\mathrm{NH_2Bu^t}$ with $\mathrm{SiMe_3Cl}$.[15] All operations were carried out under argon or nitrogen.

Syntheses.—*Tetra*(tert-*butylimido*)*osmium*(VIII) **1** *and Di*-μ-*oxo*-2:3κ^{4}O-*tetra*-μ-tert-*butylimido*-1:2κ^{4}N; 3:4κ^{4}N-*hexakis*-(tert-*butylimido*-1κ^{2}N,2κN, 3κN, 4κ^{2}N)*tetraosmium* (VI) **2**. To $\mathrm{NHBu^t(SiMe_3)}$ (15 cm^3) was added $\mathrm{OsO_4}$ (0.75, 2.9 mmol); the solution immediately turned red-orange. After stirring at room temperature (15 min) the solution was refluxed (3 h), cooled and the volatiles removed under vacuum. The residue was extracted with hexane (2 × 20 cm^3) and the filtered solution concentrated (*ca.* 10 cm^2) and cooled (−20 °C) for 24 h to give red plates of the tetramer **2**, which were collected. Yield: 0.11 g (10% based on $\mathrm{OsO_4}$).

The solution was evaporated and the residue distilled (5 × 10^{-2} mm Hg, ≃ 6.6 Pa; 100 °C) using a short path distillation apparatus to give $\mathrm{Os(NBu^t)_4}$ **1** as an orange-red oil, which crystallised on cooling to *ca.* 20 °C.

Compound **1** can be directly obtained as follows. In a typical run, two 1 g ampoules of $\mathrm{OsO_4}$ were cleaned, dried and placed in a 100 cm^3 flask with side arm and magnetic stirring bar. After pumping for *ca.* 1 h $\mathrm{NHBu^t(SiMe_3)}$ (*ca.* 20 cm^3) was added and the ampoules broken. The red-brown mixture was refluxed under $\mathrm{N_2}$ (2 h), cooled, the volatiles removed under vacuum and the residue distilled under high vacuum to yield 1–1.5 g (*ca.* 25–40% based on $\mathrm{OsO_4}$) of **1**.

Bis(μ-tert-*butylimido*)-*bis*[*di*(tert-*butylimido*)*osmium* (VI)] **3**. To a solution of compound **1** (0.47 g, 1 mmol) in thf (20 cm^3) was added $\mathrm{PPh_3}$ (0.26 g) freshly recrystallised from EtOH. The mixture was refluxed under $\mathrm{N_2}$ (8 h), cooled and the volatiles removed *in vacuo*. The residue was transferred in hexane to a Florisil column (dried at 150 °C for 2 d and deactivated with dry thf) and eluted with hexane to give a fraction containing traces of $\mathrm{PPh_3}$ and $\mathrm{Ph_3P{=}NBu^t}$[16] (identified by ^{31}P NMR spectroscopy). Further elution using thf gave a yellow fraction containing **3**, which was evaporated and the solid crystallised from hexane. Yield: 0.1 g (*ca.* 25%). X-Ray quality crystals were obtained from MeCN at −20 °C.

The same product is obtained by reduction of **1** with Na–Hg in thf following the same work-up procedure.

Bis(μ-tert-*butylimido*)-*bis*[*di*(tert-*butylimido*)*osmium*(VII)] *Bis*(*tetrafluoroborate*) **4**. To a suspension of $\mathrm{Me_3O^+BF_4^-}$ (0.25 g, 1.7 mmol) in $\mathrm{CH_2Cl_2}$ (20 cm^3) at −78 °C was added a solution of compound **1** (0.24 g, 0.5 mmol) in hexane. The red-brown colour of **1** changed immediately to dark orange and when the solution warmed to room temperature it became yellow-green. After stirring (*ca.* 2 h) the solution was evaporated and the residue washed with hexane and $\mathrm{Et_2O}$. Extraction with $\mathrm{CH_2Cl_2}$ (10 cm^3) and addition of thf gave orange needles of **4** after cooling (−20 °C for 12 h). Yield: 0.09 g (35%). X-Ray quality crystals were obtained by layering of a $\mathrm{CH_2Cl_2}$ solution with $\mathrm{Et_2O}$.

$\mathrm{Os^{VI}(NR)_3}$, R = 2,6-$\mathrm{Me_2C_6H_3}$, **5** or 2,6-$\mathrm{Pr^i{}_2C_6H_3}$, **6**. In a typical reaction $\mathrm{OsO_4}$ (0.2 g) in neat $\mathrm{NHR(SiMe_3)}$ was heated at 100–120 °C for 2–3 h. The excess of silylamine was removed (120 °C, 0.05 mm Hg, ≃ 6.6 Pa), to a receiver at −196 °C, and the residue extracted with hexane, 5 × 20 cm^3 for the 2,6-dimethyl- or 3 × 20 cm^3 for the more soluble 2,6-diisopropylimido complex. The combined extracts were concentrated (to 40 and 20 cm^3 respectively) and cooled (−20 °C, 24 h) to give red-brown needles. The yields were 0.2 g (46%) and 0.35 g (62%) in two crops respectively. The isopropyl derivative is identical with that described.[13]

Crystallography.—Crystals of compounds **2**,**3** and **4** were sealed under argon in thin-walled glass capillaries. Following preliminary examination, unit-cell and intensity data were recorded using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo-Kα radiation, according to previously described procedures.[17] The structures were solved *via* direct **4** or Patterson methods, developed *via* difference syntheses and refined *via* least squares. No hydrogen atoms were included. Experimental and other details are listed in Table 7. Final atomic positional parameters are given in Tables 8–10. All calculations were made using SHELXS and SHELX 80[18] running on a T800 transputer hosted by an 80286 PC/AT and diagrams were drawn using SNOOPI.[19] Scattering factor data were as default in SHELX or from ref. 20.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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