Some Reactions of Tetrakis(*tert*-butylimido)osmium(VIII). X-Ray Crystal Structures of $Os(NBu^t)O(O_2CBu^t)_2(NH_2Bu^t)_2\cdot Bu^tCO_2H$, $(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)X_2$ (X = Cl or I) and $[Os_2(NBu^t)_4(\mu\text{-}NBu^t)_2]I_3$†

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Reactions of $Os(NBu^t)_4$ with carboxylic acids and halogens have been studied. Acetic and pivalic acids give different oxo carboxylate complexes, the acetate being $Os(NBu^t)O(O_2CMe\text{-}O)(O_2CMe\text{-}OO')$-$(NH_2Bu^t)$ **1** and the pivalate $Os(NBu^t)O(O_2CBu^t\text{-}O)_2(NH_2Bu^t)_2$ **2**. The osmium(VI) compounds $(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)X_2$ (X = I, **3**; or Cl, **5**) have been obtained by interaction of $Os(NBu^t)_4$ with, respectively, I_2 and PPh_4I in 1,2-$C_2H_4Cl_2$; the iodine reaction also produces the paramagnetic mixed-valence diosmium(VI, VII) compound $[Os_2(NBu^t)_4(\mu\text{-}NBu^t)_2]I_3$ **4**. The X-ray crystal structures of compounds **2–5** have been determined: **2** is octahedral with *trans*-NH_2Bu^t and *trans*-carboxylate groups; **3** and **5** are isomorphous with tetrahedral and trigonal-bipyramidal osmium atoms, the latter having *trans*-halogens, a linear NBu^t and two NBu^t bridging goups. Compound **4** is similar to the dimeric compounds previously described and completes the series $[Os(NBu^t)_2(\mu\text{-}NBu^t)]_2^{0,+,2+}$.

The synthesis and some reactions[1] of $Os(NBu^t)_4$ have been described. Additional reactions with carboxylic acids and halogens are now reported, and structures of some of the compounds formed have been determined by X-ray diffraction. Analytical and physical data for new compounds are given in Table 1.

Results and Discussion

Reaction of $Os(NBu^t)_4$ *with Carboxylic Acids.*—Acetic and pivalic acids in dichloromethane react rapidly at low temperature with $Os(NBu^t)_4$ to give the respective osmium(VI) compounds, $Os(NBu^t)O(O_2CMe)_2(NH_2Bu^t)$ **1** and $Os(NBu^t)$-$O(O_2CBu^t)_2(NH_2Bu^t)_2\cdot Bu^tCO_2H$ **2**. The compounds are both very soluble in hexane and in diethyl ether and consequently on the small scale of synthesis used the high solubility makes it difficult to get yields of crystals of more than *ca.* 20% although the overall yield is higher. Propionic and butyric acid react similarly but the products are oils.

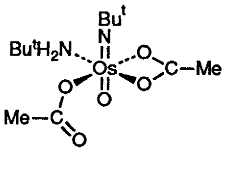
The acetate **1** has been characterised only spectroscopically since suitable crystals for X-ray study could not be obtained. The data indicate the structure **1** with both unidentate and bidentate acetate groups. The mass spectrum shows the correct molecular ion in addition to ions corresponding to loss of Bu^t, O and $MeCO_2$ groups. The IR spectrum can be assigned using standard criteria[2] and comparison with data for the ion *cis*-$[OsO_2(O_2CMe)_2]^-$;[3] the bands at 1581 and 1636 cm^{-1} can be assigned to the asymmetric stretches of unidentate and chelate acetate, respectively.

The structure of the pivalate **2** has been determined by X-ray crystallography and a diagram of the molecule is shown in Fig. 1; bond lengths and angles are given in Table 2. The molecular geometry is octahedral with a *trans,trans,trans* disposition of the oxo, imido, two monodentate carboxylate and two amine ligands. The interbond angles are all within a few degrees of idealised values. Particular features of the geometry worthy of comment are the *trans* disposition of the two π-bonding imido and oxo ligands (see below), the shorter Os≦N *vs.* Os≦O bonds, reflecting the greater π-donating capability of the organoimido function, and the proximal arrangement of the unco-ordinated carboxylate carbonyl oxygens. This latter feature is logically explained by hydrogen bonding between these two oxygens and one of the amine donors [N(2)], where the distances

Table 1 Analytical and physical data for the osmium compounds

Compound	Colour	M.p./°C	Analysis (%)* C	H	N
1 $Os(NBu^t)O(O_2CMe)_2$ (NH_2Bu^t)	Orange	140–145 (decomp.)	32.3 (32.3)	5.8 (5.8)	7.7 (6.7)
2 $Os(NBu^t)O(O_2CBu^t)_2$ $(NH_2Bu^t)_2\cdot Bu^tCO_2H$	Orange	78–80	44.5 (44.9)	8.3 (8.2)	5.5 (5.8)
3 $Os_2(NBu^t)_3(\mu\text{-}NBu^t)_2I_2$	Red	224–225	24.3 (24.3)	4.7 (4.6)	6.9 (7.1)
4 $[Os_2(NBu^t)_4(\mu\text{-}NBu^t)_2]I_3$	Red	142–145	24.4 (24.3)	4.6 (4.5)	7.1 (7.1)
5 $Os_2(NBu^t)_3(\mu\text{-}NBu^t)_2Cl_2$	Red-black	>240	30.0 (29.8)	5.6 (5.4)	8.7 (8.7)

* Calculated values in parentheses. For mass spectra see Experimental section.



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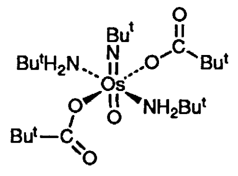

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† Bis(*tert*-butylamine)(*tert*-butylimido)oxobis(pivalato-κ*O*)osmium–pivalic acid (1/1), bis(μ-*tert*-butylimido)tris(*tert*-butylimido-1κ*N*,2κ²*N*)-dichloro-2κ²*Cl* (or -diiodo-2κ²*I*)-diosmium and bis(μ-*tert*-butylimido)-bis[bis(*tert*-butylimido)osmium] triiodide.

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

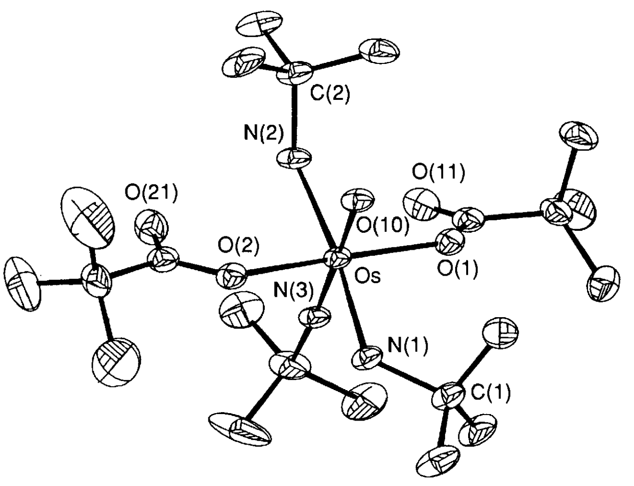


Fig. 1 The structure of $Os(NBu^t)O(O_2CBu^t)_2(NH_2Bu^t)_2$ **2**

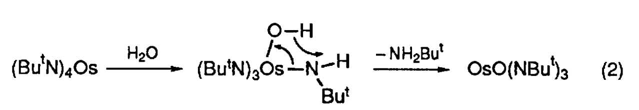
Table 2 Selected bond lengths (Å) and angles (°) for $Os(NBu^t)O(O_2CBu^t)_2(Bu^tNH_2)_2$ **2**

O(10)–Os	1.761(6)	O(1)–Os	1.972(6)
O(2)–Os	1.957(6)	N(1)–Os	2.098(7)
N(2)–Os	2.088(7)	N(3)–Os	1.749(7)
C(01)–O(1)	1.258(8)	C(02)–O(2)	1.291(8)
C(1)–N(1)	1.518(10)	C(2)–N(2)	1.522(10)
C(3)–N(3)	1.436(9)		
O(1)–Os–O(10)	88.7(3)	O(2)–Os–O(10)	85.6(3)
O(2)–Os–O(1)	172.1(2)	N(1)–Os–O(10)	85.5(3)
N(1)–Os–O(1)	92.5(3)	N(1)–Os–O(2)	81.6(3)
N(2)–Os–O(10)	92.7(3)	N(2)–Os–O(1)	94.1(3)
N(2)–Os–O(2)	91.7(3)	N(2)–Os–N(1)	173.1(2)
N(3)–Os–O(10)	177.4(2)	N(3)–Os–O(1)	93.6(3)
N(3)–Os–O(2)	91.9(3)	N(3)–Os–N(1)	93.5(3)
N(3)–Os–N(2)	88.1(3)	C(02)–O(2)–Os	126.8(5)
C(1)–N(1)–Os	129.7(5)	C(2)–N(2)–Os	125.2(5)
C(3)–N(3)–Os	176.2(5)		

O(11) ··· N(2) and O(21) ··· N(2) are *ca.* 2.7 Å. Hydrogen-atom positions were not confirmed, however. Hydrogen bonding also occurs between the pivalic acid molecule of crystallisation and the complex. Relevant interactions are from the protonated carboxylate on the acid to the oxo function on the complex, O(100) ··· O(10) 2.54 (1) Å and from the acid carbonyl to the co-ordinated amine *not* involved in intramolecular hydrogen bonding, with O(200) ··· N(1) 2.82(1) Å.

For both compounds the *trans*-imido oxo structure for osmium(VI), d^2, is most likely for electronic reasons[4] and results in a diamagnetic 18e system. The mechanism of the formation of these osmium(VI) compounds is not clear. Reaction (1) in Scheme 1 could generate water which then leads to initial hydrolysis of $Os(NBu^t)_4$ as in equation (2). Hydrolysis of $Os(NBu^t)_4$ in CH_2Cl_2 has been found[1] to give oxo imido species and similar replacements of imido groups by oxo groups on hydrolysis are known for tungsten[5a] and molybdenum[5b] compounds. However, while protonation of the lone pairs on the bent Os=NBu^t groups of $Os(NBu^t)_4$ by the carboxylic acid could lead to NH_2Bu^t and an intermediate with a Os–NHBu^t group and having ionic or, more likely, co-ordinated carboxylate groups, some form of two-electron reduction to Os^{VI} is still required. One possibility is that there is a reductive elimination

$$2MeCO_2H \longrightarrow (MeCO)_2O + H_2O \qquad (1)$$



$$(Bu^tN)_4Os \xrightarrow{H_2O} (Bu^tN)_3Os{-}N(H)(Bu^t)\cdots O{-}H \xrightarrow{-NH_2Bu^t} OsO(NBu^t)_3 \qquad (2)$$

Scheme 1

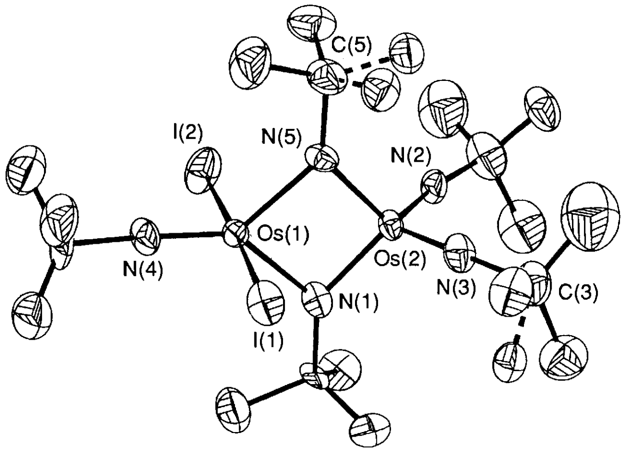


Fig. 2 The structure of $(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)I_2$; the chloride analogue is isostructural but does not show the methyl disorder at C(3) and C(5)

Table 3 Selected bond lengths (Å) and angles (°) for $(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)X_2$ (X = I, **3**; or Cl, **5**

Compound	**3**	**5**
Os(1)–Os(1)	2.749(4)	2.740(4)
X(1)–Os(1)	2.783(5)	2.409(8)
X(2)–Os(1)	2.719(5)	2.377(8)
N(1)–Os(1)	1.987(26)	1.939(17)
N(4)–Os(1)	1.610(23)	1.646(19)
N(5)–Os(1)	2.020(26)	1.925(20)
N(1)–Os(2)	1.848(26)	1.877(16)
N(2)–Os(2)	1.716(21)	1.791(18)
N(3)–Os(2)	1.719(24)	1.689(22)
N(5)–Os(2)	1.874(22)	1.871(20)
C(1)–N(1)	1.434(32)	1.497(27)
C(2)–N(2)	1.451(33)	1.338(27)
C(3)–N(3)	1.573(39)	1.445(33)
C(4)–N(4)	1.455(32)	1.512(28)
C(5)–N(5)	1.554(37)	1.508(31)
X(1)–Os(1)–Os(2)	89.9(2)	88.4(2)
X(2)–Os(1)–Os(2)	91.0(2)	90.9(3)
X(2)–Os(1)–X(1)	177.9(1)	177.5(2)
N(1)–Os(1)–Os(2)	42.2(7)	43.2(4)
N(1)–Os(1)–X(1)	89.0(7)	88.3(6)
N(1)–Os(1)–X(2)	90.3(7)	89.6(6)
N(4)–Os(1)–Os(2)	176.5(8)	174.6(6)
N(4)–Os(1)–X(1)	87.6(9)	92.4(7)
N(4)–Os(1)–X(2)	91.6(9)	88.5(7)
N(4)–Os(1)–N(1)	140.2(10)	142.1(7)
N(5)–Os(1)–X(1)	89.2(7)	89.8(7)
N(5)–Os(1)–X(2)	92.8(7)	91.3(7)
N(5)–Os(1)–N(1)	85.1(10)	86.2(8)
N(5)–Os(1)–N(4)	134.4(10)	131.7(8)
N(2)–Os(2)–N(1)	116.1(11)	113.2(8)
N(3)–Os(2)–N(1)	113.8(10)	114.6(9)
N(3)–Os(2)–N(2)	109.6(12)	110.6(10)
N(5)–Os(2)–N(1)	93.5(11)	89.6(8)
N(5)–Os(2)–N(2)	114.3(9)	114.4(9)
N(5)–Os(2)–N(3)	108.6(12)	113.1(10)
Os(2)–N(1)–Os(1)	91.6(11)	91.8(7)
C(1)–N(1)–Os(1)	131.8(18)	134.0(12)
C(1)–N(1)–Os(2)	136.6(19)	134.1(13)
C(2)–N(2)–Os(2)	166.8(23)	162.7(17)
C(3)–N(3)–Os(2)	167.6(22)	173.9(19)
C(4)–N(4)–Os(1)	176.1(23)	169.1(15)
Os(2)–N(5)–Os(1)	89.8(10)	92.4(9)
C(5)–N(5)–Os(1)	134.5(19)	134.4(15)
C(5)–N(5)–Os(2)	135.8(20)	133.1(15)

of Bu^{t}HN groups from Os^{VIII} to give the hydrazine (Bu^{t}HN)$_2$. We are unaware of any precedent for such reductive elimination and further studies on the course of the reaction are in progress.

Reaction of Os(NBu^t)$_4$ *with Iodine and* PPh$_4$I *in* CH$_2$Cl$_2$.—Interaction of Os(NBu^t)$_4$ with iodine in CH$_2$Cl$_2$ leads to two products **3** and **4** that can be easily separated on account of their different solubilities in organic solvents. Spectroscopic and X-ray study confirms the structures **3** and **4** where the osmium oxidation states are VI,VI and VI,VII respectively. The chlorine analogue of **3**, compound **5**, has been obtained by the interaction of Os(NBu^t)$_4$ in 1,2-dichloroethane with tetraphenylphosphonium iodide, where the chlorine in the product is derived from the solvent.

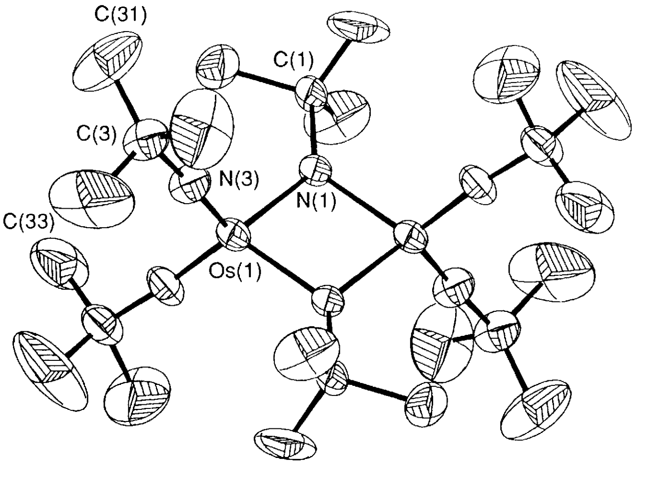
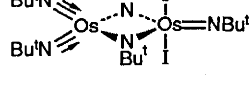


Fig. 3 The structure of [Os$_2$(NBu^t)$_4$(μ-NBu^t)$_2$]$^+$ in the triiodide salt

Table 4 Selected bond lengths (Å) and angles (°) for [Os$_2$(NBu^t)$_4$(μ-NBu^t)$_2$]I$_3$ **4**

N(1)–Os(1)	1.925(10)	N(3)–Os(1)	1.711(8)
C(1)–N(1)	1.496(12)	C(3)–N(3)	1.415(10)
I(1)–I(2)	2.910(4)	Os(1)–Os(1B)	2.921(4)
N(3)–Os(1)–N(1)	113.4(4)	C(1)–N(1)–Os(1)	133.7(7)
C(3)–N(3)–Os(1)	171.2(7)	N(3)–Os(1)–N(3B)	117.7(4)
N(1)–Os(1)–N(1B)	81.8(3)	N(3)–Os(1)–N(1B)	112.6(4)
N(1)–Os(1)–N(3B)	113.4(4)	Os(1)–N(1)–Os(1B)	98.2(3)
C(1)–N(1)–Os(1B)	128.1(7)	I(2)–I(1)–I(2B)	180.0(3)



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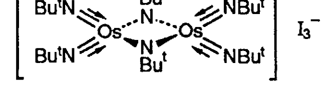

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The osmium(VI) dimers **3** and **5** are moderately air-stable and diamagnetic. Formally they can be derived from the previously[1] structurally characterised osmium(VI) dimer [Os(NBu^t)$_2$(μ-NBu^t)]$_2$, by replacement of one terminal *tert*-butylimido group by two halogen atoms. It may be noted that removal of a Bu^{t}N group by chlorine has been observed in the 'reductive halogenation' of Cr^{VI}(NBu^t)$_2$Cl$_2$ to give Cr^V(NBu^t)Cl$_3$.[6]

The structure of compound **3** is shown in Fig. 2 and that of **4** in Fig. 3; bond distances and angles are given in Tables 3 and 4. Compounds **3** and **5** are isostructural in the non-centrosymmetric space group $P2_1$, although the molecules have approximate mirror symmetry [the plane containing C(41), C(4), N(4), Os(1), Os(2), N(1), N(5), C(1) and C(5)]. In **3** there is disorder in two of the *tert*-butyl groups which does not occur in **5**. This molecular symmetry is arbitrarily oriented to the monoclinic axis, however. One of the osmium atoms, Os(2), has the tetrahedral geometry found in the neutral dimer mentioned above, but the geometry of Os(1), where the dihalogen/imido substitution has occurred, has changed considerably to distorted trigonal bipyramidal. The two halogen atoms are mutually *trans* and axial and the main distortion is in the equatorial N$_3$ plane where the Os$_2$N$_2$ ring structure requires a much reduced (from the ideal 120°) N(1)–Os(1)–N(5) angle of 85°. The substitution of one bivalent imido function by the two halogens has not led to the expected *cis* arrangement.

The osmium–imido bonding shows considerable differences. The equatorial Os–N bond distance of the terminal *tert*-butylimido ligand on the trigonal-bipyramidal Os(1) centre is much shorter than those of the two terminal ligands on tetrahedral Os(2), highlighting the much stronger π-bonding possibility in the former case. On the other hand, the Os–N–Os bridges are strongly asymmetric, with much shorter bonds to

Table 5 Crystal data, details of intensity measurements and structure refinement

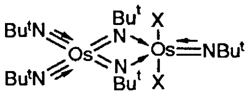
Compound	**2**	**3**	**4**	**5**
Molecular formula	$C_{22}H_{49}N_3O_5Os\cdot C_5H_9O_2$	$C_{20}H_{45}I_2N_5Os_2$	$C_{24}H_{54}I_2N_6Os_2$	$C_{20}H_{45}Cl_2N_5Os_2$
M	690.94	989.82	1187.85	806.92
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	18.693(3)	10.129(2)	11.544(1)	10.158(2)
b/Å	10.262(3)	10.697(3)	14.339(1)	10.616(3)
c/Å	19.390(5)	15.249(2)	12.738(1)	14.526(5)
α/°	90	90	90	90
β/°	118.87(2)	103.98(1)	107.54(1)	104.61(2)
γ/°	90	90	90	90
U/Å^3	3284.99	1603.28	1955.35	1513.53
Space group	$P2_1/n$	$P2_1$	$C2/m$	$P2_1$
Z	4	2	2	2
D_c/g cm^{-3}	1.397	2.050	2.018	1.771
μ/cm^{-1}	37.22	193.05	154.38	204.49
F(000)	1420	916	1102	727
Total no. of reflections	5355	3095	5668	2991
No. of unique reflections	4868	2974	1831	2831
No. of reflections used [$F > 3\sigma(F)$]	4108	2360	1536	2452
No. of parameters	416	281	91	261
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.000 29	Unit weights	0.010 23	0.003 28
Final R	0.0263	0.0398	0.0477	0.0522
Final R'	0.0274	0.0398	0.0490	0.0530

Table 6 Fractional atomic coordinates ($\times 10^4$) for $Os(NBu^t)O(O_2CBu^t)_2(Bu^tNH_2)_2{\cdot}Bu^tCO_2H$ **2**

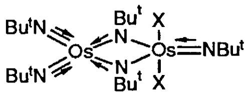
Atom	*x*	*y*	*z*
Os	2562.7(1)	2150.0(2)	244.0(1)
O(10)	2692(3)	2144(4)	−596(3)
O(1)	1848(3)	3681(5)	−194(3)
O(2)	3192(3)	528(4)	533(3)
N(1)	1619(3)	827(5)	−385(3)
N(2)	3595(3)	3279(5)	890(3)
N(3)	2446(3)	2082(5)	1085(3)
C(1)	738(4)	1093(8)	−956(4)
C(2)	4120(4)	3857(7)	571(4)
C(3)	2403(5)	1983(7)	1802(5)
C(11)	708(5)	1915(8)	−1616(4)
C(12)	375(5)	1713(9)	−491(6)
C(13)	333(5)	−155(9)	−1290(6)
C(21)	4519(5)	2833(9)	337(6)
C(22)	4785(5)	4579(9)	1264(5)
C(23)	3606(5)	4721(7)	−101(4)
C(31)	1645(6)	2693(10)	1701(6)
C(32)	3158(6)	2553(10)	2444(5)
C(33)	2331(8)	581(10)	1945(7)
C(01)	1938(4)	4684(7)	218(4)
C(10)	1308(5)	5688(7)	−283(4)
O(11)	2438(3)	4859(5)	897(3)
C(101)	1575(5)	6241(8)	−854(6)
C(103)	458(5)	5121(10)	−778(7)
C(102)	1273(7)	6666(10)	280(6)
C(02)	3857(4)	309(7)	1172(4)
C(20)	4159(5)	−1001(7)	1221(5)
O(21)	4217(3)	1045(5)	1696(3)
C(201)	4782(9)	−1286(12)	2080(7)
C(202)	4529(11)	−1080(16)	693(9)
C(203)	3442(8)	−1899(10)	953(11)
O(100)	6984(4)	−473(5)	1371(4)
O(200)	7970(4)	584(6)	1391(5)
C(100)	7483(5)	453(7)	1610(4)
C(03)	7384(5)	1377(7)	2147(4)
C(301)	6923(8)	2465(10)	1653(7)
C(302)	8228(6)	1854(12)	2706(7)
C(303)	6965(9)	761(11)	2577(7)

Table 7 Fractional atomic coordinates ($\times 10^4$) for $(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)I_2$ **3**

Atom	*x*	*y*	*z*
Os(1)	8 083(1)	0	2 077(1)
Os(2)	6 927(1)	1 767(1)	2 968(1)
I(1)	7 511(2)	1 487(2)	534(1)
I(2)	8 579(3)	−1 517(3)	3 551(2)
N(1)	6 253(24)	401(24)	2 258(14)
N(2)	6 793(18)	1 712(24)	4 068(13)
N(3)	6 321(24)	3 175(20)	2 494(16)
N(4)	8 809(23)	−966(22)	1 533(14)
N(5)	8 699(20)	1 543(25)	2 829(13)
C(1)	4 953(24)	−184(23)	1 932(18)
C(2)	6 565(35)	1 958(34)	4 956(19)
C(3)	5 542(35)	4 434(29)	2 192(24)
C(4)	9 377(36)	−1 887(34)	1 024(22)
C(5)	10 078(32)	2 239(35)	3 150(24)
C(11)	5 061(38)	−1 257(36)	1 286(28)
C(12)	4 458(28)	−624(33)	2 747(20)
C(13)	3 927(28)	756(34)	1 384(23)
C(21)	7 054(31)	3 147(32)	5 272(22)
C(22)	5 061(39)	1 800(44)	4 863(22)
C(23)	7 315(48)	978(48)	5 636(32)
C(41)	8 593(39)	−2 445(43)	289(30)
C(42)	10 595(40)	−2 439(43)	1 697(29)
C(43)	10 235(38)	−976(42)	424(25)
C(51)	11 051(35)	1 649(49)	2 672(28)
C(52)	10 595(37)	1 478(44)	4 174(25)
C(53)	9 835(55)	3 547(55)	2 706(44)
C(53B)	9 923(61)	3 435(66)	3 573(48)
C(31)	6 112(58)	5 358(60)	2 934(41)
C(32)	4 025(42)	4 245(43)	2 173(34)
C(33)	4 648(65)	4 185(63)	1 267(48)
C(33B)	5 982(55)	4 910(53)	1 380(38)



I



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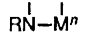
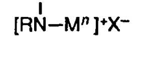


$$\begin{array}{cc} X & X \\ | & | \\ RN- & M^n \end{array}$$

III



$$\begin{array}{l} X \\ | \\ {[RN-M^n]^+X^-} \end{array}$$

IV

tetrahedral Os(2) than to Os(1), with canonicals of the form **I** and a representation as $Os^{IV}Os^{VIII}$ rather than $Os^{VI}Os^{VI}$, or **II**, which retains the $Os^{VI}Os^{VI}$ distribution. For both **I** and **II**, however, the tetrahedral osmium atom has access to an excess of 18e if all the imido groups were to use their full π-bonding capability as shown. It is pertinent to note that all the terminal imido groups are linear, consistent with some contribution from the 4e bonding mode $Bu^tN\overset{\rightarrow}{\equiv}Os$.

Table 8 Fractional atomic coordinates ($\times 10^4$) for $[Os_2(NBu^t)_4(\mu\text{-}NBu^t)_2]I_3$ **4**

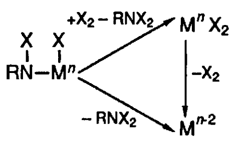
Atom	*x*	*y*	*z*
Os(1)	301.7(4)	0	123.4(4)
I(2)	3270(2)	0	6290(2)
I(1)	5000	0	5000
N(1)	1118(9)	0	89(9)
N(3)	468(7)	−1021(7)	1981(8)
C(1)	2425(11)	0	127(13)
C(11)	3257(15)	0	1427(19)
C(12)	2696(12)	900(10)	−340(18)
C(3)	707(11)	−1784(8)	2742(11)
C(31)	1969(16)	−1905(14)	3274(20)
C(32)	36(21)	−2606(15)	2143(22)
C(33)	−37(24)	−1635(18)	3497(21)

In the structure of compound **4** both anion and cation lie on positions of symmetry 2/*m*. For the cation the mirror plane is coincident with the Os_2N_2 ring. Thus the two osmium atoms are crystallographically and structurally equivalent. The complex is formally a mixed-oxidation-state $Os^{VI}Os^{VII}$ system, and falls between the previously described[1] neutral $Os^{VI}Os^{VI}$ and dicationic $Os^{VII}Os^{VII}$ complexes. For the neutral complex, the Os–Os distance was 3.1 Å and in the dication, in which direct Os–Os bonding is postulated, 2.68 Å. In the present monocation **4** the distance is 2.921(4) Å. The bridges are symmetrical and the bridging and terminal Os–N distances are similar to those in the dication. Compound **4** shows no NMR spectrum, being paramagnetic with a magnetic moment (by Evans' NMR method) corresponding approximately to one unpaired electron per cation. The I_3^- ion is linear and symmetrical by virtue of crystallographic site symmetry.

The mechanism of the reaction of $Os(NBu^t)_4$ and I_2 is not clear. Initial free-radical or polar additions of halogen across M–N bonds would form intermediates of the type **III** or **IV** that could decompose by different pathways such as substitution by halide followed by reductive elimination as in Scheme 2. Dimerisation of reactive intermediates would give the products; for **4**, these would have to be in non-equivalent oxidation states. There is no evidence for the mixed-oxidation-state species **4** in the cyclic voltammograms[1] of either $[Os^{VI}(NBu^t)_2(\mu\text{-}NBu^t)]_2$

Table 9 Fractional atomic coordinates ($\times 10^4$) for (Bu^{t}N)$_2$Os(μ-NBu^t)$_2$Os(NBu^t)Cl$_2$ **5**

Atom	*x*	*y*	*z*
Os(1)	8 335(1)	0	2 072(1)
Os(2)	7 214(1)	1 752(1)	3 035(1)
Cl(1)	7 884(7)	1 411(6)	728(4)
Cl(2)	8 678(7)	−1 412(7)	3 383(5)
N(1)	6 538(15)	390(15)	2 229(10)
N(2)	7 008(17)	1 555(18)	4 216(12)
N(3)	6 632(21)	3 178(20)	2 595(15)
N(4)	9 150(18)	−1 002(17)	1 548(13)
N(5)	8 965(20)	1 401(18)	2 908(14)
C(1)	5 148(23)	−145(23)	1 826(16)
C(2)	6 674(22)	1 746(25)	5 039(15)
C(3)	6 125(27)	4 430(26)	2 321(20)
C(4)	9 754(21)	−1 800(21)	895(16)
C(5)	10 341(25)	1 979(27)	3 335(19)
C(11)	5 310(27)	−1 329(27)	1 161(19)
C(12)	4 648(28)	−698(28)	2 678(21)
C(13)	4 221(27)	814(27)	1 238(21)
C(21)	7 266(31)	732(31)	5 813(24)
C(22)	5 172(33)	2 104(32)	4 930(26)
C(23)	7 338(30)	3 287(30)	5 426(22)
C(31)	6 621(32)	5 410(32)	3 190(25)
C(32)	4 552(31)	4 397(32)	2 033(26)
C(33)	6 586(31)	4 662(31)	1 330(24)
C(41)	8 679(28)	−2 442(28)	131(22)
C(42)	10 447(29)	−2 830(29)	1 562(22)
C(43)	10 515(28)	−981(27)	345(21)
C(51)	11 315(31)	1 888(33)	2 847(21)
C(52)	11 037(32)	1 225(32)	4 253(26)
C(53)	10 454(31)	2 796(33)	4 173(27)



Scheme 2

or [Os^{VII}(NBu^t)$_2$(μ-NBu^t)]$_2{}^{2+}$, nor can **4** be obtained by chemical reduction of Os(NBu^t)$_4$ or oxidation of [Os(NBu^t)$_2$(μ-NBu^t)]$_2$.

The interaction of the halides **3** and **5** with silver oxide gives rise to the tetraosmium compound [(Bu^{t}N)$_2$Os(μ-NBu^t)$_2$Os(NBu^t)(μ-O)]$_2$ that has been previously[1] structurally characterised. Both **3** and **5** are also reduced by sodium amalgam in tetrahydrofuran (thf) to a neutral compound, Os$_3$(NBu^t)$_8$, identical to that produced by interaction of Os(NBu^t)$_4$ with trimethylphosphine. This compound will be described separately.

Experimental

The general techniques used and instrumentation have been described.[7] Analyses were by Pascher, Imperial College and University College, London. Mass spectra were recorded by electron impact, NMR spectra in CDCl$_3$ *vs.* SiMe$_4$ and IR spectra in Nujol mulls unless otherwise specified. The synthesis of Os(NBu^t)$_4$ has been described.[1] All reagents were thoroughly dried and all operations were carried out in vacuum or under purified Ar or N$_2$.

Reaction of Os(NBu^t)$_4$ *with Carboxylic Acids: (Acetato-*κO*)(acetato-*κ^{2}O,O′*)(*tert*-butylamine)(*tert*-butylimido)oxo-osmium(*VI*)* **1** *and Bis(*tert*-butylamine)(*tert*-butylimido)oxo-bis(pivalato-*κO*)osmium(*VI*)* **2**.—To a solution of Os(NBu^t)$_4$ (0.4 mmol) in CH$_2$Cl$_2$ (10 cm^3) at −78 °C was added on excess of either anhydrous acetic or pivalic acid (*ca.* 0.2 cm^3). The orange-brown solution which became red-brown was allowed to warm to room temperature, stirred for *ca.* 1 h when the volatiles were removed in vacuum. The residue was washed with hexane, dissolved in the minimum of diethyl ether which was filtered, then concentrated and cooled (−20 °C) to give orange crystals of compound **1** or **2** in yields 15–20%. Mass spectrum of **2**: *m*/*z* 513 (*M* − Bu^{t}CO$_2$H), 497 (*M* − Bu^{t}CO$_2$H − O), 457 (*M* − Bu^{t}CO$_2$H − Me$_2$C=CH$_2$) and 442 (*M* − Bu^{t}CO$_2$H − NBu^t). IR of **1**: 1636, 1581, 1558, 1400 [C(O)O]; 1207 (NBu^t); and 928 cm^{-1} (OsO). NMR: ^{1}H, **1**, δ 2.16 (s, 6 H, O$_2$CMe), 1.75 (s, 9 H, NH$_2$*Bu*^{t}) and 1.50 (s, 9 H, NBu^t); **2**, 6.13 (s, br, N*H*$_2$Bu^t), 1.41 (s, 18 H, O$_2$CBu^t), 1.28 (s, 9 H, Bu^{t}N), 1.23 (s, 9 H, O$_2$CBu^t) and 1.19 (s, 18 H, NH$_2$*Bu*^{t}).

In the acetic acid reaction some blue crystals were deposited initially on warming to room temperature but attempts to recrystallise these very air-sensitive crystals led only to decomposition.

Reaction of Os(NBu^t)$_4$ *with Iodine: Bis(*μ-tert*-butylimido)tris(*tert*-butylimido-*1κN,2κ^{2}N*)diiodo-*2κ^{2}I*-diosmium* **3** *and Bis(*μ-tert*-butylimido)-bis[bis(*tert*-butylimido)osmium] Triiodide* **4**.—To a solution of Os(NBu^t)$_4$ (0.4 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added I$_2$ (0.25 g, excess) and the dark brown solution stirred (2 h) then evaporated in vacuum. Excess of iodine was sublimed to a cooled probe (solid CO$_2$) and the residue extracted with hexane (2 × 30 cm^3); the extracts were filtered, concentrated (to *ca.* 5 cm^3) and cooled (−20 °C) to give red crystals of compound **3** in *ca.* 40% yield. The residue insoluble in hexane was extracted into dichloromethane (*ca.* 10 cm^3), filtered and layered with Et$_2$O. Diffusion for 24 h afforded red crystals of compound **4** in *ca.* 30% yield. Mass spectrum of **3**: *m*/*z* 735 (*M* − I$_2$), 679 (*M* − I$_2$ − Me$_2$C=CH$_2$) and 664 (M − I$_2$ − NBu^t). IR: **3**, 1288, 1202, 1183 (NBu^t); **4**, 1220 and 1205 cm^{-1} (NBu^t). NMR of **3**: δ 1.91 (s, 9 H, terminal NBu^t), 1.89 (s, 18 H, μ-NBu^t) and 1.41 (s, 18 H, terminal NBu^t).

*Bis(*μ-tert*-butylimido)tris(*tert*-butylimido-*1κN,2κ^{2}N*)-dichloro-*2κ^{2}Cl*-diosmium* **5**.—To a solution of Os(NBu^t)$_4$ (0.5 mmol) in 1,2-dichloroethane (10 cm^3) was added PPh$_4$I (0.23 g, 0.5 mmol) and the mixture refluxed (12 h) when the colour changed from orange-brown to green. After evaporation in vacuum the residue was extracted with hexane until the extracts were colourless (5 × 20 cm^3); the combined extracts were reduced in volume (10 cm^3) and cooled (−20 °C) to afford dark red dichroic prisms. Yield: *ca.* 60%. Mass spectrum: *m*/*z* 770 (*M* − Cl), 735 (*M* − 2Cl) and 664 (*M* − 2Cl − NBu^t). IR: 1231, 1200 (sh) and 1189 cm^{-1} (NBu^t). NMR: δ 1.84 (superimposed peaks, 27 H, NBu^t, bridging and terminal) and 1.40 (s, 18 H, terminal NBu^t).

X-Ray Crystallography.—Notwithstanding the air stability of some of the compounds, crystals used for X-ray work were sealed in thin-walled glass capillaries under argon. Unit-cell and intensity data for compounds **2**, **3** and **5** were obtained using a CAD4 diffractometer, following published procedures.[8] The intensity data were corrected for absorption using ψ-scan profiles. Data for compound **4** were obtained using an Enraf-Nonius FAST area detector diffractometer. Full details of the procedures used will be published separately, but the main features are summarised as follows.

With detector-to-crystal distance (d.e.t.) of 40 mm and a scanning angle ($= 2\theta_D$) of 18°, reflections were found in two 5° ω rotation regions separated by 90°. The orientation matrix and unit-cell dimensions were determined *via* the INDEX and REFINE procedures of the SADONL software (the 'small molecule' on-line version of MADNES[9]), using 250 reflections taken from both regions. Accurate values of d.e.t. and $2\theta_D$ were also determined by refinement as 40.55 mm and 17.95°. Intensity data corresponding to slightly more than one hemisphere of reciprocal space were recorded using two ω rotations of 100°, with a 90° φ shift, at χ = 0° and two further ω rotations of 70°, again with a φ shift of 90° at χ = 90° to record the cusp data. Throughout the data collection the ω step was 0.15° and the frame measuring time was 20 s. The structures were solved *via* the heavy-atom method and refined by least squares. Absorption corrections were applied at the isotropic refinement stage using the DIFABS[10] procedure. All atoms were refined anisotropically and no hydrogen atoms were included. Crystal data and further experimental details are summarised in Table 5. Final atomic coordinates are given in Tables 6–9.

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

Acknowledgements

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References

1 A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 269.
2 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., Wiley-Interscience, New York, 1978.
3 T. Behling, M. V. Capparelli, A. C. Skapski and G. Wilkinson, *Polyhedron*, 1982, **1**, 840 and refs. therein.
4 W. A. Nugent and J. H. Mayer, *Metal–Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988; R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401; K. Tatsumi and R. Hoffmann, *Inorg. Chem.*, 1980, **19**, 2656.
5 (*a*) A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 2753; (*b*) M. L. H. Green, G. Hogarth, P. C. Konidatis and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1990, 3781.
6 A. A. Danopoulos, B. Hussain-Bates, M. B. Hursthouse, W.-H. Leung and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1990, 1678.
7 A. A. Danopoulos, A. C. C. Wong, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 315.
8 R. A. Jones, K. M. A. Malik, M. B. Hursthouse and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.
9 MADNES VERSION 11-SEP-1989, J. W. Pflugrath and A. Messerschmidt, Distributed by Enraf-Nonius, Delft, 1989.
10 N. P. C. Walker and D. Stuart, *Acta Crystallogr., Sect A*, 1983, **39**, 158.

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