Reactions of Dimesityldioxo-osmium(VI) with Donor Ligands; Reactions of $MO_2(2,4,6\text{-}Me_3C_6H_2)_2$, M = Os or Re, with Nitrogen Oxides. *X*-Ray Crystal Structures of $[2,4,6\text{-}Me_3C_6H_2N_2]^+[OsO_2(ONO_2)_2(2,4,6\text{-}Me_3C_6H_2)]^-$, $OsO(NBu^t)(2,4,6\text{-}Me_3C_6H_2)_2$, $OsO_3(NBu^t)$, and $ReO_3[N(2,4,6\text{-}Me_3C_6H_2)_2]$†

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The interaction of $OsO_2(mes)_2$(mes = $2,4,6\text{-}Me_3C_6H_2$), with pyridines, an isocyanide, and tertiary phosphines gives rise to complexes such as *trans*-OsO_2(bipy)$(mes)_2$(bipy = 2,2′-bipyridyl), *cis*-$OsO_2(2,6\text{-}Me_2C_6H_3NC)(mes)_2$, and *cis*-$OsO_2(PR_3)_2(mes)_2$. The oxoimido compound, $OsO(NBu^t)(mes)_2$, has been synthesised. The reactions of $MO_2(mes)_2$, M = Os or Re, with oxides of nitrogen, which involve oxygen transfer to the metal atom, have been studied. With NO, $ReO_2(mes)_2$ gives the dimesitylamido compound, $ReO_3[N(mes)_2]$, but $OsO_2(mes)_2$ is unreactive. The compound $ReO_2(mes)_2$ reacts with $NO_2(N_2O_4)$ quantitatively to give ReO_3(mes), nitromesitylene, and 2,4,6-trimethylbenzenediazonium nitrate, $OsO_2(mes)_2$ gives the salt $[(mes)N_2]^+$ $[OsO_2(ONO_2)_2(mes)]$ together with nitromesitylene and NO. The *X*-ray crystal structures of four compounds have been determined. In $[(mes)N_2][OsO_2(ONO_2)_2(mes)]$ the anion has a distorted trigonal-bipyramidal structure with equatorial oxo functions and the unidentate O-bonded nitrates axial. The compounds $OsO(NBu^t)(mes)_2$ and $OsO_3(NBu^t)$ are distorted tetrahedral with essentially linear, 4e imido ligands. The compound $ReO_3[N(mes)_2]$ is also distorted tetrahedral and in the solid state shows evidence of Re=O ··· Me(mes) interactions.

In previous papers a variety of oxo- and t-butylimido-compounds of osmium and of rhenium have been made and the structures of several determined by *X*-ray crystallography.[1–3]

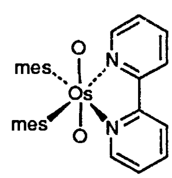
In this paper, reactions of $OsO_2(mes)_2$[1](mes = $2,4,6\text{-}Me_3C_6H_2$) with some donor ligands and the reaction of $MO_2(mes)_2$, M = Os or Re,[1] with NO and NO_2 are reported. An oxoimido compound, $OsO(NBu^t)(mes)_2$ has been made from $OsO_3(NBu^t)$. A relevant review of oxo and imido species has recently appeared.[4] Analytical and physical data for new compounds are given in Table 1 and n.m.r. data in Table 2.

Results and Discussion

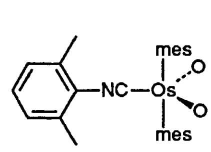
1. *Reactions of* $OsO_2(2,4,6\text{-}Me_3C_6H_2)_2$.—(*a*) With *pyridines*. The compound $OsO_2(mes)_2$ reacts with 2,2′-bipyridyl(bipy) and pyridines to give octahedral, 18-electron complexes. The bipyridyl compound *trans*-OsO_2(bipy)$(mes)_2$ is air stable and has a Os–O bond stretch at 857 cm^{-1} indicating the structure (I). With an excess of 4-t-butylpyridine a similar air-stable complex is formed but it is more soluble in Et_2O, tetrahydrofuran (thf), CH_2Cl_2, and $CHCl_3$ than is the bipy adduct. Again there is a single Os–O stretch at 871 cm^{-1} while the ^1H n.m.r. spectrum, like that of the bipy analogue, shows equivalence of mesityl, and also now of the pyridine, groups so that the structure is probably also similar to (I) rather than the isomer with *trans* mesityl groups. Pyridine itself gives a similar adduct according to i.r. and n.m.r. spectra but the solid readily loses pyridine.

The *trans*-dioxo grouping is that commonly formed for octahedral d^2 osmium.[5]

(*b*) 2,6-*Dimethylphenyl isocyanide*. Interaction of $OsO_2(mes)_2$ with excess of ligand in hexane leads to $OsO_2(2,6\text{-}Me_2C_6H_3NC)$-$(mes)_2$ which can be crystallised from Et_2O as orange plates. The



(I)



(II)

^1H n.m.r. spectrum together with two bands in the i.r. at 911 and 957 cm^{-1} indicate the five-co-ordinate structure (II) with equatorial OsO_2 groups.

No insertion of isocyanide into the Os–C bond of $OsO_2(mes)_2$ occurs, even at 110 °C in toluene for 2 d, and no insertion is evident with CO at 120 °C at 100 lbf in^{-2} ($\approx 6.895 \times 10^5$ Pa) in hexane for 1 week. The starting material $OsO_2(mes)_2$ is recovered.

(*c*) *Tertiary phosphines*. Although PMe_3, PMe_2Ph, and $PMePh_2$ give similar adducts, the crystals of the PMe_3 and PMe_2Ph compounds tend to lose phosphine; the adduct $OsO_2(PMePh_2)_2(mes)_2$ is quite stable. The ^1H n.m.r. spectra of the three complexes show that in solution at room temperature the PMe_3 is co-ordinated, but the PMe_2Ph complex is *ca.* 50% dissociated, while the $PMePh_2$ complex is *ca.* 90% dissociated. The dissociation is lower at low temperatures. The ^1H n.m.r.

† 2,4,6-Trimethylbenzenediazonium *cis*-bis(nitrato-κ*O*)dioxo(2,4,6-trimethylphenyl)osmate(VI); oxo(t-butylimido)bis(2,4,6-trimethylphenyl)osmium(VI), trioxo(t-butylimido)osmium(VIII), and [bis(2,4,6-trimethylphenyl)amido]trioxorhenium(VII).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical* and physical data for osmium and rhenium compounds

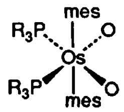
Compound	Colour	M.p.(°C)	Analytical data(%) C	H	N
$OsO_2(bipy)(mes)_2$	Orange	196	54.5 (54.5)	5.1 (4.9)	4.3 (4.5)
$OsO_2(4\text{-}Bu^tC_5H_4N)(mes)_2$	Red	161	59.3 (59.2)	6.8 (6.6)	3.8 (3.8)
$OsO_2(2,6\text{-}Me_2C_6H_3NC)(mes)_2$	Orange	130—132	54.6 (54.8)	5.2 (5.3)	2.3 (2.4)
$OsO_2(PMePh_2)_2(mes)_2$	Dark red	83—85	61.3 (61.4)	5.5 (5.6)	
$OsO(NBu^t)(mes)_2$	Dark green	163—165	51.4 (51.2)	6.0 (6.1)	2.8 (2.7)
$[(mes)N_2][OsO_2(ONO_2)_2(mes)]$	Brown	82 (decomp.)	35.2 (35.2)	3.6 (3.6)	9.0 (9.1)
$ReO_3(mes)$	Yellow	115	31.0 (30.5)	3.2 (3.1)	
$ReO_3[N(mes)_2]$	Orange	154 (decomp.)	44.5 (44.4)	4.5 (4.6)	3.0 (2.9)

* Calculated values in parentheses.

Table 2. Nuclear magnetic resonance (^1H) data [a]

Compound (Solvent)	δ, ^nJ(HH)	Assignment
$OsO_2(bipy)(mes)_2$ ($CDCl_3$)	8.85(dd), ^3J 7.0, ^4J 1.1	2 H $H^{6,6'}$ bipy
	8.28(dd), ^3J 8.0, ^4J 1.2	2 H $H^{3,3'}$ bipy
	8.00(m)	2 H $H^{4,4'}$ bipy
	7.48(m)	2 H $H^{5,5'}$ bipy
	7.05(s)	4 H C_6H_2
	2.46(s)	6 H p-CH_3
	2.39(s)	12 H o-CH_3
$OsO_2(4Bu^t\text{-}py)_2(mes)_2$ (C_6D_6)	8.55(dd), ^3J 5.0, ^4J 1.7	4 H o-C_5H_4N
	7.05(s)	4 H C_6H_2(mes)
	6.67(dd), ^3J 5.0, ^4J 1.7	4 H m-C_5H_4N
	2.73(s)	12 H o-CH_3(mes)
	2.36(s)	6 H p-CH_3(mes)
	0.86(s)	18 H Bu^t
$OsO_2(2,6\text{-}Me_2C_6H_3NC)(mes)_2$ (C_6D_6)	6.80(s)	4 H C_6H_2(mes)
	6.68(t), ^3J 7.0,	1 H p-C_6H_3
	6.51(d), ^3J 7.0	2 H m-C_6H_3
	2.47(s)	12 H o-CH_3(mes)
	2.28(s)	6 H p-CH_3(mes)
	1.99(s)	6 H o-CH_3
$OsO_2(PMePh_2)_2(mes)_2$ [b] (C_6D_6)	7.24(m), 6.99(m)	20 H PMePh_2
	6.85(s)	4 H C_6H_2(mes)
	2.55(s)	12 H o-CH_3(mes)
	2.29(s)	6 H p-CH_3(mes)
	2.14(m)[c], 1.72(m)	6 H P*Me*Ph_2
$OsO(NBu^t)(mes)_2$ ($CDCl_3$)	6.89(s)	4 H C_6H_2
	2.43(s)	6 H p-CH_3
	2.33(s)	12 H o-CH_3
	1.54(s)	9 H NBu^t
$[(mes)N_2][OsO_2(NO_3)_2(mes)]$ (CD_3CN)	7.39(s)	2 H $C_6H_2[(mes)N_2^+]$
	7.02(s)	2 H C_6H_2(mes)
	2.67(s)	6 H o-$CH_3[(mes)N_2^+]$
	2.62(s)	6 H o-CH_3(mes)
	2.49(s)	3 H p-$CH_3[(mes)N_2^+]$
	2.47(s)	3 H o-CH_3(mes)
$ReO_3(mes)$ (C_6D_6)	6.58(s)	2 H C_6H_2
	2.24(s)	6 H o-CH_3
	1.84(s)	3 H p-CH_3
$ReO_3[N(mes)_2]$ [c] (C_6D_6)	6.49(s)	4 H C_6H_2
	2.23(s)	12 H o-CH_3
	1.94(s)	6 H p-CH_3

[a] δ relative to $SiMe_4$ at 298 K, J in Hz. [b] $^{31}P\text{-}\{^1H\}(C_6D_6)$ 27.5(s) (complexed), -21.7(s) p.p.m. (free), see text. [c] See text and Figure 6 for variable-temperature spectra.



(III)

data together with i.r. data [ν(Os=O) 940, 955 cm^{-1}] for the solids support the structure **(III)** for the undissociated complexes.

Octahedral species with *cis*-OsO_2 groups are rare and the only one characterised by *X*-ray diffraction is the anion *cis*-$[OsO_2(O_2CMe\text{-}O)_2(O_2CMe\text{-}OO)]^-$;[6] the octahedral cation *cis*-$[OsO_2(bipy)_2]^{2+}$ has been characterised spectroscopically.[7]

2. *Synthesis of Bis(mesityl)oxo(t-butylimido)osmium*(VI).—The oxoimido complexes $OsO_3(NR)$, (R = 1-adamantyl or t-butyl), $OsO_2(NBu^t)_2$, $OsO(NBu^t)_3$, and $[OsO_3(NCMe_2CH_2CMe_3)]_2$dabco (dabcol = 4-diazabicyclo[2.2.2]octane), have been characterised,[8] and structural data are available on all except $OsO_3(NBu^t)$ which is described later. An oxoimidorhenium alkyl complex, $ReO[N(2,6\text{-}Pr^i{}_2C_6H_3)]_2(CH_2Bu^t)$, has been characterised spectroscopically.[9]

Interaction of $OsO_3(NBu^t)$[10] with two equivalents of $Mg(mes)_2$ in thf–Et_2O leads to the formation of both $OsO_2(mes)_2$ and $OsO(NBu^t)(mes)_2$, the latter in *ca.* 11% yield after chromatography on Kieselgel. The air-stable green crystals are very soluble in hexane and common organic solvents giving air-stable solutions. The i.r. spectrum has bands at 1 184 and 955 cm^{-1} that can be assigned as Os–N and Os–O stretches, respectively, by comparison with similar compounds.[11] The ^1H n.m.r. spectrum is in accord with the structure determined by *X*-ray crystallography (see below).

Attempts to prepare the corresponding *o*-tolyl derivative gave only the known $Os(o\text{-}MeC_6H_4)_4$.[12]

Due to electronegativity differences, the NBu^t ligand is a better π donor than oxo,[4] which implies that $OsO(NBu^t)(mes)_2$ should have a greater electron density on Os and hence should be more difficult to reduce but more easily oxidised than $OsO_2(mes)_2$. Cyclic voltammetry of the two compounds (Figure 1) and the potentials (Table 3) confirm this; the Os^V–Os^{IV} couple is irreversible in MeCN, probably due to the reactive nature of the solvent, although it is reversible in thf.

3. *Reactions of* $MO_2(mes)_2$, M = Os *or* Re *with* NO, N_2O_3, *and* N_2O_4.—These compounds, which differ only in that $ReO_2(mes)_2$ is paramagnetic with one unpaired electron, show completely different reactivity towards oxides of nitrogen. Thus, $ReO_2(mes)_2$ gives $ReO_3[N(mes)_2]$ with NO but $ReO_3(mes)$ with NO_2. The osmium analogue does not react with NO but with N_2O_3 and N_2O_4 gives the anion $[OsO_2(NO_3)_2(mes)]^-$ as its mesityl diazonium salt. We discuss first the reactions of $OsO_2(mes)_2$.

When $OsO_2(mes)_2$ in Et_2O is exposed to pure NO at room temperature there is no reaction and the complex can be recovered unchanged. However, if dry air (to give the approximate stoicheiometry N_2O_3) is admitted, there is immediate formation of a brown solid in yields *ca.* 80% based on osmium. The same solid is precipitated when an excess of NO_2–N_2O_4 (free from NO) is used, but the yield is considerably lower (*ca.* 47%); other products, notably nitromesitylene and NO (as N_2O_3), are formed as discussed below.

Crystallisation of the brown solid from tetrahydrofuran gives brown tablets of the salt $[(mes)N_2][OsO_2(ONO_2)_2(mes)]$. The crystal structure (see below) confirms the formulation; the i.r. spectrum has bands at 923 and 954 cm^{-1} [ν(*cis*-OsO_2)] with other bands for unidentate nitrate (1 531 and 1 265 cm^{-1}), and for ν(NN) of the diazonium group at 2 217 cm^{-1}. The presence

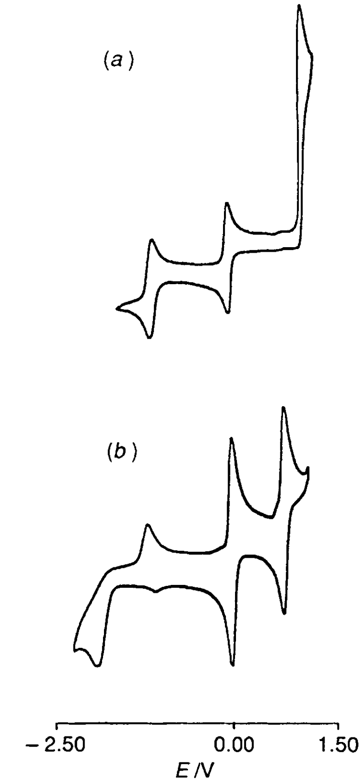


Figure 1. Cyclic voltammograms for $OsO_2(mes)_2$ (*a*) and $OsO(NBu^t)(mes)_2$ (*b*)

Table 3. Cyclic voltammetry[a]

Compound	$E_{\frac{1}{2}}$/V Os^V–Os^{VI}	$E_{\frac{1}{2}}$/V Os^{VI}–Os^{VII}
$OsO_2(mes)_2$	−1.28[b]	+1.16[c]
$OsO(NBu^t)(mes)_2$	−1.93[c]	+0.73[b]
	−1.89[b,d]	

[a] All values (V) referred to ferrocene-ferrocenium = 0.00(V). Sweep rate 100 mV s^{-1} in MeCN. 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. [b] Reversible. [c] Irreversible. [d] In tetrahydrofuran.

of the diazonium ion was also confirmed by standard chemical tests, *e.g.* reaction with aniline. Although the salt is stable in air as the solid, solutions in CH_2Cl_2 and thf are air and light sensitive, while $CHCl_3$ solutions decompose rapidly.

Following Frankland's discovery[13] of the reaction of NO with diethylzinc, there has been recent interest in these 'insertion' reactions of NO with transition-metal alkyls and aryls.[14] However, there has been little study of the reactions of N_2O_3 or NO_2–N_2O_4 and what has been done has been only with alkyls or aryls of main-group elements.[15,16]

Early studies by Bamberger[17] and by Kunz[18] on diarylmercury compounds established the reactions (1)—(3) leading to arylmercury nitrate and arenediazonium nitrate or

$$HgR_2 + 2N_2O_3 \longrightarrow Hg(R)(NO_3) + RN_2{}^+NO_3{}^- \quad (1)$$

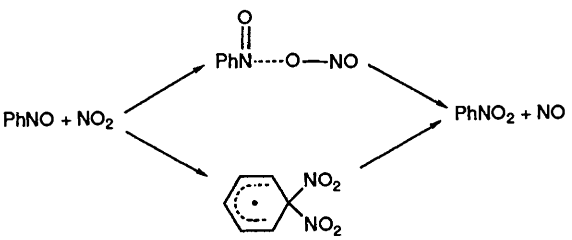
$$HgR_2 + N_2O_4 \longrightarrow Hg(R)(NO_3) + RNO \quad (2)$$

$$RNO + 2NO \longrightarrow RN_2{}^+NO_3{}^- \quad (3)$$

nitrosoarenes. The reaction (3) is considered[19] to proceed as in equation (4) for which there is supporting evidence. In more

$$RNO + 2NO \longrightarrow \underset{\displaystyle |\atop N\text{–}O}{RN}\text{–}O\text{–}NO \longrightarrow RN_2^+NO_3^- \quad (4)$$

recent detailed studies, nitrosobenzene has been shown to react with NO_2 (N_2O_4) to give nitrobenzene and NO by the routes suggested in equation (5).[20]



(5)

The overall stoicheiometry[20] with NO_2, owing to reaction (3) with the NO produced in equation (5) is as in equation (6).

$$3C_6H_5NO + 2NO_2 \longrightarrow 2C_6H_5NO_2 + C_6H_5N_2^+NO_3^- \quad (6)$$

Other studies on N_2O_4 reactions with organometallic compounds[15,16] include $PbEt_4$ and $PbPr^i_4$ which give alkylnitrato compounds, while $SnMe_4$[21] in ethyl acetate similarly gives $SnMe_2(NO_3)_2$ 'with vigorous gas evolution,' the nature of the gas being unspecified.

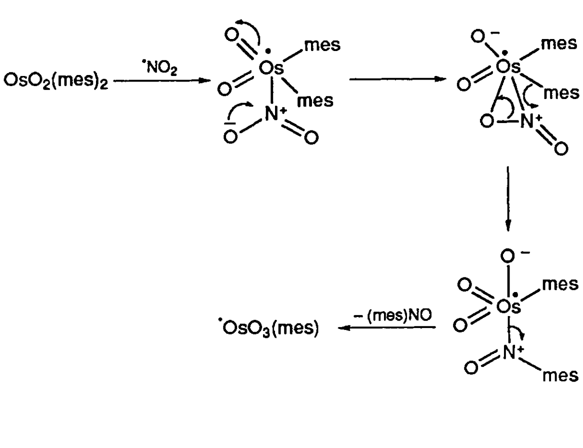
The relatively high yield of the diazonium salt in the reaction of $OsO_2(mes)_2$ with NO + O_2, *i.e.* N_2O_3, could indicate the stoicheiometry in equation (7) but the reaction with excess of

$$OsO_2(mes)_2 + 2N_2O_3 \longrightarrow [(mes)N_2]^+[OsO_2(NO_3)_2(mes)]^- \quad (7)$$

N_2O_4, which gives lower yields, is clearly more complex. The only other identifiable products from the reaction with NO_2 are $(mes)NO_2$ and NO (as blue N_2O_3 on condensation when removing the solvent Et_2O in vacuum). A stoicheiometric reaction with NO_2 would have required elimination of O_2 but mass spectrometric studies of the residual gas after cooling the system at *ca.* −130 °C show no oxygen to be present. There is also some brown unidentified material formed in the reaction.

Hence the conclusion is that in the NO_2 reaction reduction of NO_2 by $OsO_2(mes)_2$ takes place in what is clearly a complex way leading to $(mes)NO_2$, NO, and other products.

Since NO does not react with $OsO_2(mes)_2$ the initial attack on the compound is presumably by NO_2, as in equation (8).



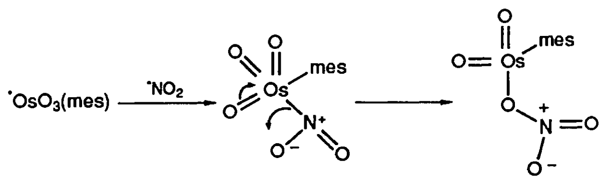
(8)

Support for this initial reaction comes from the essentially quantitative transfer of one oxygen atom from NO_2 to $Re^{VI}O_2(mes)_2$ to give $Re^{VII}O_3(mes)$[equation (9)]. The

$$ReO_2(mes)_2 + NO_2 \longrightarrow ReO_3(mes) + (mes)NO \quad (9)$$

difference from $OsO_2(mes)_2$ is that since $ReO_2(mes)_2$ is paramagnetic (1e), the resulting rhenium(VII) species, ReO_3-(mes), is diamagnetic, whereas that of Os^{VII}, $OsO_3(mes)$, would have a single unpaired electron and hence be reactive towards NO and/or NO_2.

The nitrosomesitylene formed in equations (8) and (9) will then react with NO or NO_2 according to equations (4)—(6) to give either 2,4,6-trimethylbenzenediazonium nitrate or nitromesitylene and NO. Hence in the osmium case, following equation (8), we have the reaction (4), *i.e.* (mes)NO + 2NO $\longrightarrow$ $[(mes)N_2]^+ + NO_3^-$ and the reaction of the tetrahedral osmium(VII) species with NO_2 [equation (10)]. This



(10)

reaction is followed by that in equation (11) where the neutral

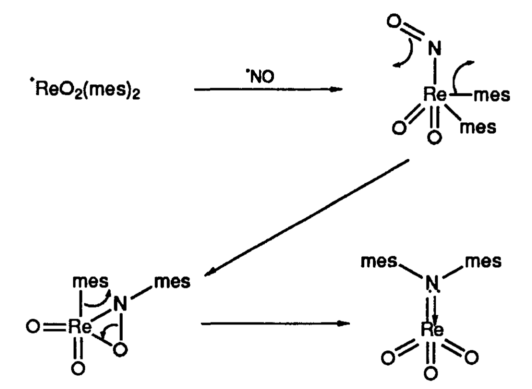
$$[(mes)N_2]^+NO_3^- + OsO_2(ONO_2)(mes) \longrightarrow [(mes)N_2]^+[OsO_2(ONO_2)_2(mes)]^- \quad (11)$$

four-co-ordinate osmium(VI) species further co-ordinates nitrate anion.The overall stoicheiometry thus corresponds to that in equation (7) for reaction with N_2O_3.

With pure NO_2 the initial attack must again be as in equation (8), but the (mes)NO will then react as in equation (5) to give $(mes)NO_2$ and NO, both of which are found. As noted above there are evidently other reactions leading to the as yet unidentified brown material; this could be some sort of osmium oxo nitrato complex formed by removal of the single mesityl group from $OsO_3(mes)$ or $OsO_2(NO_3)(mes)$.

The ion $[OsO_2(NO_3)_2(mes)]^-$ is one of the few known osmium nitrato complexes, which are rare and ill characterised.[22] It may be noted that $Mo^{VI}O_2(mes)_2$ gives only decomposition products with NO_2–N_2O_4, presumably since conversion into Mo^{VII} is impossible.

We now consider the reactions of the paramagnetic (1e) $ReO_2(mes)_2$ with NO and NO_2, which lead respectively to $ReO_3[N(mes)_2]$ and $ReO_3(mes)$ in essentially quantitative reactions; in the NO_2 reaction, $(mes)NO_2$ and $[(mes)N_2]^+$-NO_3^- are also formed. The reaction with NO is instantaneous at room temperature, and the formation of the amido species can be readily explained by oxygen-atom and mesityl-group migrations as in equation (12). There are well established precedents[14c] for oxygen transfer to metal from an intermediate with a co-ordinated η^2-RNO group in the studies of NO with paramagnetic alkyls such as $ReOMe_4$[23a] and $Nb(\eta^5\text{-}C_5H_5)_2$-$Me_2$[23b]; oxygen transfer also occurs with $Ti(\eta^5\text{-}C_5H_5)_2Ph$.[23b] In the present case, however, instead of elimination of RN as RN=NR[23b] a second aryl migration to the nitrogen atom occurs to give a dimesitylamido group. As far as we are aware, such a double migration has no precedent in NO chemistry.[14b,c] A migration of an acyl group to NBu^t in the thermal decomposition of the compound $Cr(NBu^t)_2[CO(mes)_2]$ has been invoked to account for the formation of the amide $NH(Bu^t)[CO(mes)]$.[24a] The only other example of a compound



(12)

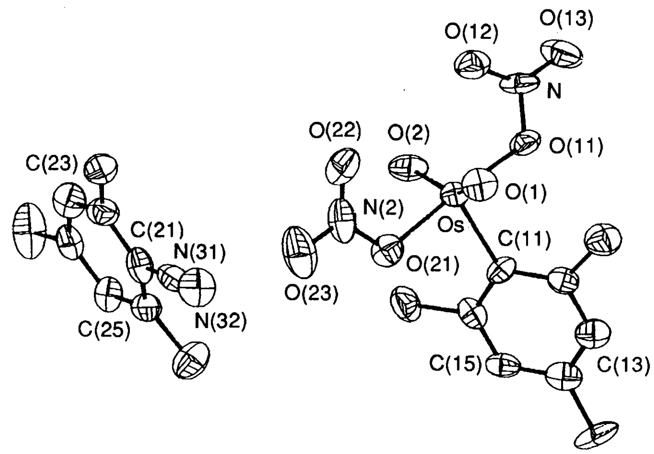
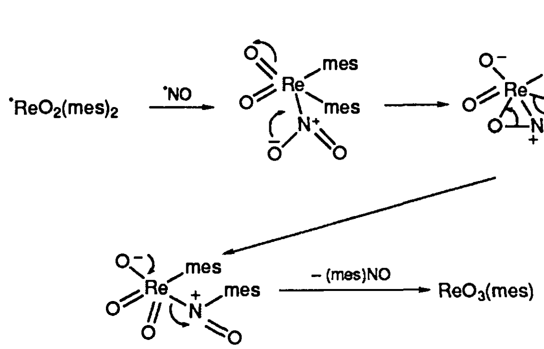


Figure 2. The structure of $[2,4,6\text{-}Me_3C_6H_2N_2][OsO_2(ONO_2)_2(2,4,6\text{-}Me_3C_6H_2)]$

of this type is $ReO_3(NPr^i_2)$[24b] which is thermally unstable but acts as a Lewis acid to give stable five-co-ordinate adducts such as $ReO_3(NPr^i_2)(py)$ (py = pyridine). The stability of the $N(mes)_2$ compound can be attributed to the steric bulk of the mesityl group. The spectroscopic data for the dimesitylamido compound are discussed later along with the *X*-ray study.

Finally, the reaction of $ReO_2(mes)_2$ with NO_2 to give $ReO_3(mes)$,[25,*] as noted above, may be assumed to give an initial diamagnetic intermediate in which intramolecular oxygen migrations, as in the osmium case, will then proceed as in equation (13), which is followed by reaction of (mes)NO and



(13)

* Reported during the course of these studies (see ref. 25). Mass, ^1H, and ^{13}C n.m.r. spectra for $ReO_3(mes)$ [very slightly contaminated by $ReO_2(mes)_2$] given by P. D. Savage (Ph.D. Thesis, University of London, 1987) are in agreement with those of Herrmann *et al.*,[25] as are the independent *X*-ray data of B. H-B. and M. B. H.

Table 4. Bond lengths (Å) and angles (°) for $[(mes)N_2][OsO_2(ONO_2)_2(mes)]$

C(11)–Os	2.053(13)	O(1)–Os	1.710(9)
O(2)–Os	1.718(10)	O(11)–Os	2.045(10)
O(21)–Os	2.040(10)	C(12)–C(11)	1.407(19)
C(16)–C(11)	1.430(17)	C(13)–C(12)	1.388(20)
C(121)–C(12)	1.523(22)	C(14)–C(13)	1.365(18)
C(15)–(C14)	1.402(17)	C(141)–C(14)	1.531(19)
C(16)–C(15)	1.369(15)	C(161)–C(16)	1.548(18)
N(1)–O(11)	1.327(12)	O(12)–N(1)	1.227(12)
O(13)–N(1)	1.188(14)	N(2)–O(21)	1.319(15)
O(22)–N(2)	1.193(16)	O(23)–N(2)	1.228(15)
N(32)–N(31)	1.116(15)	C(21)–N(31)	1.399(17)
C(22)–C(21)	1.413(17)	C(26)–C(21)	1.423(16)
C(23)–C(22)	1.361(18)	C(221)–C(22)	1.523(19)
C(24)–C(23)	1.417(24)	C(25)–C(24)	1.414(22)
C(241)–C(24)	1.492(23)	C(26)–C(25)	1.374(18)
C(261)–C(26)	1.509(19)		
O(1)–Os–C(11)	105.2(5)	O(2)–Os–C(11)	108.1(5)
O(2)–Os–O(1)	146.7(4)	O(11)–Os–C(11)	88.2(5)
O(11)–Os–O(1)	91.6(4)	O(11)–Os–O(2)	89.1(5)
O(21)–Os–C(11)	88.7(5)	O(21)–Os–O(1)	88.8(4)
O(21)–Os–O(2)	92.2(5)	O(21)–Os–O(11)	176.9(3)
C(12)–C(11)–Os	120.1(10)	C(16)–C(11)–Os	121.4(9)
C(16)–C(11)–C(12)	118.4(11)	C(13)–C(12)–C(11)	118.4(12)
C(121)–C(12)–C(11)	126.8(14)	C(121)–C(12)–C(13)	114.8(14)
C(14)–C(13)–C(12)	123.0(13)	C(15)–C(14)–C(13)	119.3(12)
C(141)–C(14)–C(13)	121.3(13)	C(141)–C(14)–C(15)	119.4(10)
C(16)–C(15)–C(14)	119.6(11)	C(15)–C(16)–C(11)	121.1(11)
C(161)–C(16)–C(11)	120.0(11)	C(161)–C(16)–C(15)	116.8(10)
N(1)–O(11)–Os	116.1(7)	O(12)–N(1)–O(11)	117.3(10)
O(13)–N(1)–O(11)	116.4(11)	O(13)–N(1)–O(12)	126.3(11)
N(2)–O(21)–Os	113.0(8)	O(22)–N(2)–O(21)	122.0(11)
O(23)–N(2)–O(21)	115.4(15)	O(23)–N(2)–O(22)	122.5(15)
C(21)–N(31)–N(32)	176.7(11)	C(22)–C(21)–N(31)	115.9(11)
C(26)–C(21)–N(31)	117.7(11)	C(26)–C(21)–C(22)	126.4(11)
C(23)–C(22)–C(21)	116.1(13)	C(221)–C(22)–C(21)	122.2(11)
C(221)–C(22)–C(23)	121.7(14)	C(24)–C(23)–C(22)	120.9(17)
C(25)–C(24)–C(23)	120.1(13)	C(241)–C(24)–C(23)	119.3(18)
C(241)–C(24)–C(25)	120.5(17)	C(26)–C(25)–C(24)	122.2(12)
C(25)–C(26)–C(21)	114.1(11)	C(261)–C(26)–C(21)	122.8(11)
C(261)–C(26)–C(25)	123.0(11)		
Non-bonded contacts			
O(23) ··· N(31)	3.001(19)	O(23) ··· N(32)	3.094(18)
N(32) ··· O(12a)	2.929(20)		

Symmetry operation: a = *x*, 1 + *y*,*z*.

excess of NO_2 to give $(mes)NO_2$ and $[(mes)N_2]^+NO_3^-$ according to the stoicheiometry of equation (6).

Crystal Structure Determinations.—Osmium compounds. The structures of the ions in $[(mes)N_2][OsO_2(ONO_2)_2(mes)]$ are shown in Figure 2 which also represents their true relative positions. Interactions between the anion and cation within the ion pair shown occur between O(23) and N(31) and N(32) and then between N(32) and O(12) of a second anion. Details are given in Table 4, which lists other relevant bond lengths and angles. The NN bond distance is similar to that in other diazonium salts[26] where the CNN group is also linear.

The anion has a distorted trigonal-bipyramidal structure with the two oxo functions equatorial and the two unidentate nitrates axial. The latter are oriented so that one of the non-bonding oxygens on each are positioned one each side of the O=Os=O group with O ··· Os distances of 2.88 and 2.89 Å, to give indications of very asymmetric bidentate co-ordination. The Os=O and Os–C(mes) distances in this five-co-ordinate

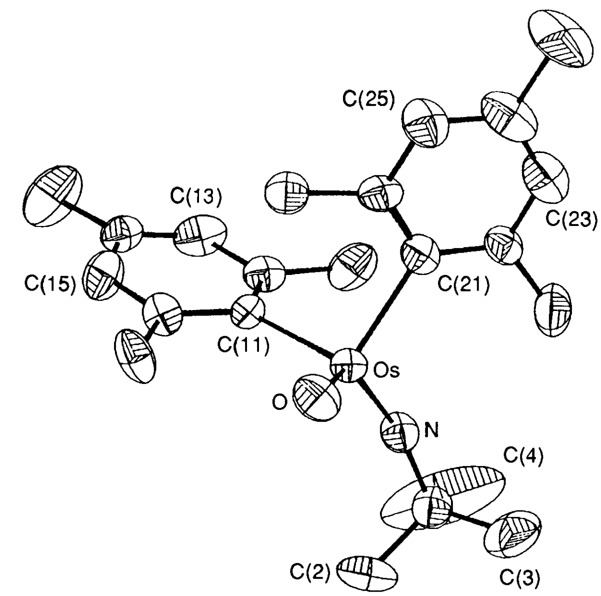


Figure 3. The structure of $OsO(NBu^t)(2,4,6\text{-}Me_3C_6H_2)_2$

Table 5. Bond lengths (Å) and angles (°) for $OsO(NBu^t)(mes)_2$

O–Os	1.739(12)	N–Os	1.731(12)
C(11)–Os	2.119(13)	C(21)–Os	2.161(14)
C(1)–N	1.437(17)	C(2)–C(1)	1.494(25)
C(3)–C(1)	1.538(27)	C(4)–C(1)	1.468(26)
C(12)–C(11)	1.412(17)	C(16)–C(11)	1.428(16)
C(13)–C(12)	1.387(19)	C(121)–C(12)	1.527(19)
C(14)–C(13)	1.353(19)	C(15)–C(14)	1.392(20)
C(141)–C(14)	1.455(20)	C(16)–C(15)	1.344(18)
C(161)–C(16)	1.536(18)	C(22)–C(21)	1.373(17)
C(26)–C(21)	1.390(18)	C(23)–C(22)	1.349(20)
C(221)–C(22)	1.528(21)	C(24)–C(23)	1.374(23)
C(25)–C(24)	1.373(21)	C(241)–C(24)	1.568(23)
C(26)–C(25)	1.394(19)	C(261)–C(26)	1.512(19)
N–Os–O	121.5(6)	C(11)–Os–O	112.2(5)
C(11)–Os–N	105.5(5)	C(21)–Os–O	103.4(5)
C(21)–Os–N	113.0(6)	C(21)–Os–C(11)	99.1(5)
C(1)–N–Os	161.0(9)	C(2)–C(1)–N	110.9(16)
C(3)–C(1)–N	109.3(13)	C(3)–C(1)–C(2)	110.9(20)
C(4)–C(1)–N	110.9(15)	C(4)–C(1)–C(2)	100.0(26)
C(4)–C(1)–C(3)	114.6(19)	C(12)–C(11)–Os	119.5(9)
C(16)–C(11)–Os	124.6(9)	C(116)–C(11)–C(12)	115.8(11)
C(13)–C(12)–C(11)	120.3(12)	C(121)–C(12)–C(11)	124.0(12)
C(121)–C(12)–C(13)	115.6(12)	C(14)–C(13)–C(12)	122.0(13)
C(15)–C(14)–C(13)	118.7(13)	C(141)–C(14)–C(13)	124.0(14)
C(141)–C(14)–C(15)	117.2(14)	C(16)–C(15)–C(14)	121.1(13)
C(15)–C(16)–C(11)	121.8(13)	C(161)–C(16)–C(11)	121.5(12)
C(161)–C(16)–C(15)	116.6(12)	C(22)–C(21)–Os	123.6(10)
C(26)–C(21)–Os	116.5(9)	C(26)–C(21)–C(22)	119.5(13)
C(23)–C(22)–C(21)	119.8(13)	C(221)–C(22)–C(21)	123.3(13)
C(221)–C(22)–C(23)	116.9(13)	C(24)–C(23)–C(22)	122.5(15)
C(25)–C(24)–C(23)	118.1(15)	C(241)–C(24)–C(23)	120.8(16)
C(241)–C(24)–C(25)	120.9(17)	C(26)–C(25)–C(24)	120.5(15)
C(25)–C(26)–C(21)	119.4(13)	C(261)–C(26)–C(21)	124.7(12)
C(261)–C(26)–C(25)	115.8(12)		

complex are very similar to the equivalent distances in the four-co-ordinate $OsO_2(mes)_2$.[1] The main distortion from trigonal-bipyramidal geometry occurs in the O=Os=O angle which has increased from the ideal 120 to 146.7(4)°. Considerable opening of this angle also occurred in the 'tetrahedral' $OsO_2(mes)_2$

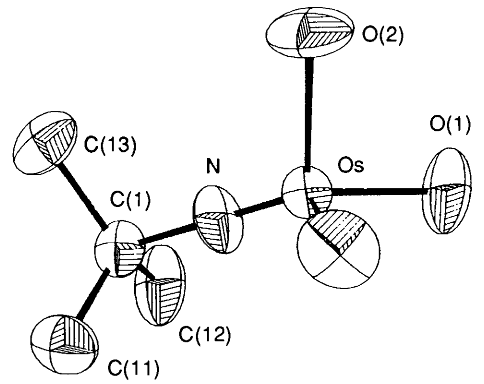


Figure 4. The structure of $OsO_3(NBu^t)$

Table 6. Bond lengths (Å) and angles (°) for $OsO_3(NBu^t)$

O(1)–Os	1.677(12)	O(2)–Os	1.693(10)
O(3)–Os	1.715(10)	N–Os	1.689(11)
C(1)–N	1.455(14)	C(11)–C(1)	1.502(15)
C(12)–C(1)	1.539(17)	C(13)–C(1)	1.510(14)
O(2)–Os–O(1)	107.5(5)	O(3)–Os–O(1)	109.9(5)
O(3)–Os–O(2)	110.4(6)	N–Os–O(1)	111.4(6)
N–Os–O(2)	109.2(5)	N–Os–O(3)	108.5(5)
C(1)–N–Os	175.7(7)	C(11)–C(1)–N	106.8(9)
C(12)–C(1)–N	106.8(10)	C(12)–C(1)–C(11)	111.8(9)
C(13)–C(1)–N	106.3(9)	C(13)–C(1)–C(11)	113.5(10)
C(13)–C(1)–C(12)	111.1(9)		

molecule, where the angle was 136.1(3)° and where some of the distortion was ascribed to the deforming effect of the filled non-bonding orbital in the diamagnetic d^2 complex.[1] A similar effect may be occurring here, although the influence of the 'non-bonded' nitrate oxygens mentioned above may also have to be taken into account.

A molecule of $OsO(NBu^t)(mes)_2$ is shown in Figure 3 and selected bond lengths and angles in Table 5. The metal co-ordination is, as expected, distorted tetrahedral, but the geometrical parameters provide some very interesting comparisons with those for $OsO_2(mes)_2$.[1] We first note that the Os–N–C(Bu^t) angle is 161(1)°; this value would still be taken to indicate a linear, 4e mode of bonding, analogous to an oxo function. As mentioned above, the imido ligand is stated to be a better π-donor ligand than oxo[4] and this seems to be borne out in the bond lengths where Os–N is marginally shorter than Os–O, in spite of the reverse relationship for covalent radii. However, both distances are somewhat longer than the Os=O distances in $OsO_2(mes)_2$, implying slightly weaker bonding. Most significantly, however, the O=Os=NR angle here is only 121.5(6)°, much smaller than in the dioxo compound. This, together with the slightly increased Os–C(mes) distances [2.12 and 2.16(1) compared with 2.05(1) Å in $OsO_2(mes)_2$] may be a result of the increased steric compression in the molecule arising out of the additional presence of the Bu^t group. On the other hand, the C(mes)–Os–C(mes)angle is slightly larger here [99.1(5) *vs.* 96.0(3)° in $OsO_2(mes)_2$] and this may be related electronically to the much reduced O=Os=N angle.

The molecular structure of $OsO_3(NBu^t)$ is shown in Figure 4; bond lengths and angles are given in Table 6. The structure is as expected with the metal co-ordination geometry close to tetrahedral and a linear 4e imido ligand. The slight spread of O–Os–N, O–Os–O angles is not systematic and the Os=N bond does not have any unique position in the geometry definition. Indeed, the Os–N bond length is not even the shortest metal–ligand bond (see Table 5).

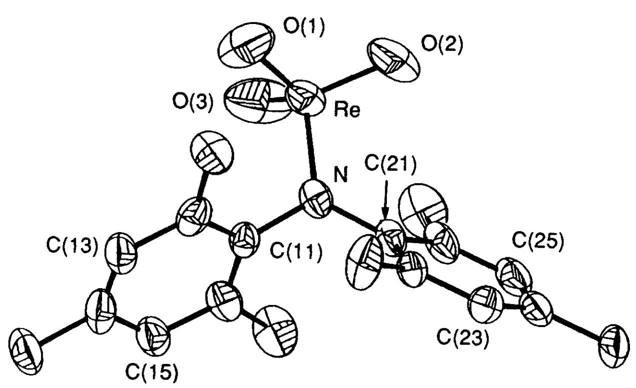


Figure 5. The structure of $ReO_3[N(mes)_2]$

Table 7. Bond lengths (Å) and angles (°) for $ReO_3[N(mes)_2]$

N–Re	1.909(10)	O(2)–Re	1.675(9)
O(3)–Re	1.695(10)	O(1)–Re	1.692(11)
C(11)–N	1.460(11)	C(21)–N	1.461(13)
C(12)–C(11)	1.399(13)	C(16)–C(11)	1.399(13)
C(13)–C(12)	1.429(13)	C(121)–C(12)	1.560(14)
C(14)–C(13)	1.361(13)	C(15)–C(14)	1.415(15)
C(141)–C(14)	1.507(14)	C(16)–C(15)	1.397(13)
C(161)–C(16)	1.523(15)	C(22)–C(21)	1.354(14)
C(26)–C(21)	1.419(12)	C(23)–C(22)	1.423(15)
C(221)–C(22)	1.519(14)	C(24)–C(23)	1.355(14)
C(25)–C(24)	1.369(15)	C(241)–C(24)	1.496(14)
C(26)–C(25)	1.406(15)	C(261)–C(26)	1.546(16)
O(2)–Re–N	107.4(5)	O(3)–Re–N	109.8(5)
O(3)–Re–O(2)	115.5(5)	O(1)–Re–N	110.6(5)
O(1)–Re–O(2)	108.8(6)	O(1)–Re–O(3)	104.7(6)
C(11)–N–Re	116.1(7)	C(21)–N–Re	122.8(6)
C(21)–N–C(11)	120.4(8)	C(12)–C(11)–N	119.4(9)
C(16)–C(11)–N	121.0(8)	C(16)–C(11)–C(12)	119.7(9)
C(13)–C(12)–C(11)	119.4(10)	C(121)–C(12)–C(11)	124.4(9)
C(121)–C(12)–C(13)	116.2(9)	C(14)–C(13)–C(12)	120.8(10)
C(15)–C(14)–C(13)	119.7(9)	C(141)–C(14)–C(13)	120.7(10)
C(141)–C(14)–C(15)	119.5(10)	C(16)–C(15)–C(14)	120.2(9)
C(15)–C(16)–C(11)	120.1(9)	C(161)–C(16)–C(11)	123.9(9)
C(161)–C(16)–C(15)	116.0(9)	C(22)–C(21)–N	119.5(8)
C(26)–C(21)–N	120.5(9)	C(26)–C(21)–C(22)	120.0(10)
C(23)–C(22)–C(21)	119.7(9)	C(221)–C(22)–C(21)	123.6(9)
C(221)–C(22)–C(23)	116.4(10)	C(24)–C(23)–C(22)	122.1(11)
C(25)–C(24)–C(23)	117.3(10)	C(241)–C(24)–C(23)	123.5(11)
C(241)–C(24)–C(25)	119.2(10)	C(26)–C(25)–C(24)	123.6(9)
C(25)–C(26)–C(21)	117.2(10)	C(261)–C(26)–C(21)	124.8(10)
C(261)–C(26)–C(25)	118.0(9)		

The molecular structure of $ReO_3[N(mes)_2]$ is shown in Figure 5, with bond lengths and angles in Table 7. The tetrahedral geometry at the Re atom is slightly distorted, with N–Re–O angles of 107.4–110.6(5)° and O–Re–O angles ranging from 104.7 to 115.5(6)°. The Re–O distances of 1.67—1.70(1) Å are equivalent within error and the Re–N distance of 1.91(1) Å indicates some Re–N multiple-bond character in spite of the presence of three oxo functions and thus a surfeit of electron density available for π bonding. The amido nitrogen is planar and the ligand itself is slightly asymmetrically bound [Re–N–C 116 and 122(1)°]. Detailed analysis of intramolecular non-bonded contacts shows a possible explanation for this. An *ortho* methyl carbon [C(121)] of one mesityl group makes a short contact of 2.82(1) Å with oxygen O(1). The likelihood that this is an attractive interaction is enhanced by the fact that the amido-ligand tilt is towards the interaction; *i.e.* the ligand is being pulled towards the oxygen atom on rhenium. Interaction of this sort has been noted previously[27] but with the α-hydrogen of the neopentyl group in $ReO_2(CH_2CMe_3)_2$ and of the type α-C–H • • • O=Re. The interaction with the methyl group in the present case arises because of the bending over of the mesityl of the amido group. There is no evidence for such interaction in our crystal structure determination of ReO_3(mes) and no comment was made on this by Herrmann *et al.*[25] No interaction has been reported also in the crystal structures of $ReO_2(CH_2CMe_3)_2$(Br)(py) and ReO_2[CHC(mes)](CH_2CMe_3).[28] To examine this point further we have explored the steric energy surface defined by all relevant single-bond torsions using the program EENY2. We first confirmed that on the basis of normal non-bonded potentials the O(1) • • • C(121) interaction is repulsive, but can easily be eliminated (and the total steric energy reduced) by torsion angle shifts. This is quite consistent with the interaction being attractive.

A further examination was made of possible sterically dependent ligand motions since solution n.m.r. studies (below) showed that all four *ortho*-methyl groups were equivalent. First, the amido-ligand co-ordination geometry was idealised, *i.e.* the two Re–N–C angles were equalised. Then, taking each of the three bonds Re–N, N–C(11), and N–C(21) in turn to define master torsions, stepwise rotations in these, followed by minimisations to adjust all remaining (steric) torsion angles, showed that free rotations were possible. The highest barriers occurred in the rotations about the N–C bonds, and these were of the order 105—126 kJ mol^{-1}. We are confident that such barriers are surmountable *via* small ligand tilts. Whilst these cannot be modelled reliably since molecular mechanics parametrisation of metal–ligand bonding is not well defined, the ligand tilt of *ca.* 4° in our complex, caused by what is almost certainly a fairly weak interaction, points to what is possible.

Although the *X*-ray structure indicates some interaction between a methyl group of a mesityl in the $N(mes)_2$ group with O=Re no such interaction is evident in solution from spectroscopic studies. The i.r. spectrum in hexane showed three bands at 972, 950, and 942 cm^{-1} respectively. The band at 950 cm^{-1} can be assigned as a mesityl vibration since a peak in a similar position is found in the spectrum of 2-bromomesitylene and appears also in the i.r. spectra of other transition-metal mesityl complexes and can be assigned as the out-of-plane C–H deformation vibration of the aromatic ring.[29] The bands at 972 and 942 cm^{-1} can be assigned as ν(Re=O) as expected for the local C_{3v} symmetry of the ReO_3 moiety.

Variable-temperature ^1H n.m.r. spectroscopy on dialkylamide complexes has indicated that there is restricted rotation about the M–N bond.[30] A representative set of spectra for $ReO_3[N(mes)_2]$ is shown in Figure 6. From these data standard calculations[31] indicate that the 'coalescence temperature' lies at some point between 203 and 213 K, giving a value of 39.6 ± 1.0 kJ mol^{-1} for the free energy of activation ($\Delta G^{\ddagger}$) and a rate constant (k) of approximately 480 s^{-1}. This value of $\Delta G^{\ddagger}$ is considerably less than that calculated from the crystal-structure calculations above. For this molecule, even though there may be hindered rotation about the Re–N bond attributable to 'lone pair' π donation by the N atom, it is not observed in the ^1H n.m.r. spectrum. This can be attributed to the very symmetrical nature of the amide ligand rendering the aryl groups equivalent even when rotation about the Re–N bond is frozen out. Thus, the free energy of activation calculated from the n.m.r. data is that for rotation about the N–C(mes) bond. This value of $\Delta G^{\ddagger}$ is consistent with values for the rotation about an N–C(aryl) bond, several of which have been calculated previously.[32]

Experimental

Microanalyses were by Imperial College Laboratories. Spectrometers: i.r., Perkin-Elmer 1720 (Fourier transform, spectra in

Figure 6. Variable-temperature ^1H n.m.r. spectra of $ReO_3[N(mes)_2]$ in CH_2Cl_2

Nujol mulls unless otherwise stated); n.mr., Bruker WM-250 and JEOL FX90Q (^{31}P, 36.21 MHz; data in p.p.m. relative to external 85% H_3PO_4; ^1H data relative to $SiMe_4$); mass, Kratos MS902, at 70 eV(1.12×10^{-17}J). Conductivity: Data Scientific PT1-18 conductivity meter. Melting points were determined in sealed capillaries and are uncorrected. The compounds $OsO_3(NBu^t)$[10] and $ReO_2(mes)_2$[1] were prepared as published; $OsO_2(mes)_2$[1] was prepared in 42% yield using an improved synthesis from OsO_4 with 2 equivalents rather than a large excess of dimesitylmagnesium in thf–Et_2O. Solvents were refluxed over sodium–benzophenone, except CH_2Cl_2 (calcium hydride), under nitrogen and distilled before use; all manipulations were carried out *in vacuo* or under purified argon or nitrogen.

Cylinder NO (British Oxygen Co.) was freed from any N_2O_4 by passing through a steel cylinder packed with powdered NaOH then a copper spiral tube cooled at −78 °C. Cylinder NO_2 (Cambrian Chemicals Ltd.) was purified by condensation after treatment with O_2 to remove any NO, and trap-to-trap distillation in vacuum.

There is some ambiguity in the assignment to M=O stretching frequencies due to other bands of variable intensity in the 850—950 cm^{-1} region such as the mesityl CH out of plane deformation noted above. We believe the bands listed are the M=O stretches but the assignment must be tentative in some cases.

(2,2′-Bipyridyl)dimesityldioxo-osmium(VI).—2,2′-Bipyridyl (0.034 g, 0.22 mmol) was added to a solution of $OsO_2(mes)_2$ (0.01 g, 0.22 mmol) in Et_2O (20 cm^3) to give immediately an orange precipitate. After stirring at room temperature for 2 h. the solvent was removed *in vacuo* and the orange residue extracted into warm Et_2O which was concentrated and cooled to −20 °C to give orange needles. Yield: 0.13g (96%). Mass spectrum (calculated values in parentheses): $[M - \text{bipy}]^+$, *m/z* 462 (462); $(\text{bipy})^+$ 156 (156). I.r.: 857vs, ν(Os=O); other 3 005m, 1 601m, 1 595m, 1 442s, 1 369s(sh), 1 314m, 1 157m, 1 061m, 1 019m, 910m, 848s, 763s, 739m, 650m, and 632m cm^{-1}.

Dimesityldioxobis(4-t-butylpyridine)osmium(VI).—To a solution of $OsO_2(mes)_2$ (0.1 g, 0.22 mmol) in Et_2O (20 cm^{-3}) at room temperature was added 4-t-butylpyridine (0.1 cm^3, 0.68 mmol) to give immediately a deep red solution. After stirring for 30 min the solvent was removed under vacuum and the residue washed with cold (−40 °C) hexane (5 cm^3) to remove excess of 4-t-butylpyridine. The residue was crystallised from Et_2O to afford red air-stable plates. Yield: 0.15g (93%). Mass spectrum: $[M - 2(4Bu^t\text{-py})]^+$, *m/z* 462 (462), $(4Bu^t\text{-py})^+$ 135 (135). I.r.: 871vs ν(Os=O); other 3 010m, 1 612vs, 1 548m, 1 496m, 1 417s, 1 278m, 1 225m, 1 069m, 1 012m, 958m, 862s, 853m, 846s, 833s, 829s, and 570m cm^{-1}.

The pyridine analogue was obtained similarly.

(2,6-Dimethylphenyl isocyanide)dimesityldioxo-osmium(VI).—The ligand 2,6-dimethylphenyl isocyanide (0.07 g, 0.53 mmol) was added to a solution of $OsO_2(mes)_2$ (0.1g, 0.22 mmol) in hexane to give an orange solid which was collected and crystallised from Et_2O to give air-stable, dark orange plates. Yield: 0.125g (96%). Mass spectrum: $[M - 2,6\text{-}Me_2C_6H_3NC]^+$ *m/z*, 462 (462), $(2,6\text{-}Me_2C_6H_3NC)^+$, 131 (131). I.r.: 957m, 911s ν(Os=O); other 3 006m, 2 179vs, 1 591m, 1 538m, 1 284s, 1 173s, 1 083m, 1 011s, 863vs, 849vs, 804m, 779vs, 708m, 645m, and 549m cm^{-1}.

Dimesitylbis(methyldiphenylphosphine)dioxo-osmium(VI).—Methyldiphenylphosphine (0.1 cm^3, 0.54 mmol) was added to a solution of $OsO_2(mes)_2$ (0.08g, 0.17 mmol) in Et_2O (20 cm^3) at −78 °C resulting in the immediate formation of a bright orange solution. After allowing the solution to reach room temperature, concentration and cooling afforded the air-stable product as deep red blocks. Yield: 0.13g (89%). Mass spectrum $[M - 2(PMePh_2)]^+$, *m/z* 462 (462), $(PMePh_2)^+$, 200 (200). I.r.: 955m, 940m, ν(Os=O); other 3 070m, 3 056m, 3 003m, 1 585m, 1 571m, 1 483m, 1 434s, 1 280m, 1 188m, 1 161m, 1 101m, 1 028m, 1 005m, 920m, 891vs, 885vs, 857vs, 849s, 744s, 712m, 697s, and 502m cm^{-1}.

The other phosphine adducts were prepared analogously.

Dimesityloxo-t-butylimido-osmium(VI).—To a solution of $OsO_3(NBu^t)$ (1.0 g, 3.23 mmol) in thf–Et_2O (2:1, 120 cm^3) at −78 °C was added dropwise, over a period of 1 h, a thf solution of dimesitylmagnesium (17.5 cm^3, of 0.37 mol dm^{-3} solution, 6.48 mmol). The resulting deep red-orange solution was slowly warmed to room temperature and stirred for a further 2 h. The solvents were removed *in vacuo* and hexane (150 cm^3) added to the residue. After stirring under a flow of oxygen overnight the dark green solution contained a brown solid. After filtration through Celite the solution was found to contain two components by t.l.c. (R_f 0.45, 0.25; CH_2Cl_2–hexane, 1:1); these were separated using CH_2Cl_2–hexane on Kieselgel-60. The first band eluted (R_f 0.45) was found to be $OsO_2(mes)_2$. Yield: 70 mg (5%). The second band was collected, evaporated, and crystallised from hexane to afford air-stable, dark green blocks. Yield: 0.18 g (11%). Mass spectrum: M^+, *m/z* 517 (517). I.r.:

Table 8. Crystal data, details of intensity measurement and structure refinement

Formula	$[(mes)N_2][OsO_2(ONO_2)_2(mes)]$	$OsO(NBu^t)(mes)_2$	$OsO_3(NBu^t)$	$ReO_3[N(mes)_2]$
M	612.594	515.68	309.32	487.578
System	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
a/Å	17.152(3)	11.065(1)	5.794(1)	9.182(3)
b/Å	7.742(2)	16.924(3)	18.442(2)	15.606(3)
c/Å	16.338(7)	14.173(2)	7.605(1)	13.761(2)
α/°	90	90	90	90
β/°	90	99.87(1)	109.02(1)	90.88(2)
γ/°	90	90	90	90
U/Å^3	2 196.54	2 614	768.25	1 756.91
Space group	$Pca2$	$P2_1/n$	$P2_1/c$	$P2_1/a$
Z	4	4	4	4
D_c/g cm^{-3}	1.85	1.310	2.673	1.838
μ/cm^{-1}	56.75	46.79	158.92	69.84
F(000)	1 196	1 016	560	944
Range h, k, l	0—17 0—18 0—8	0—13 0—20 −16 to 16	0—6 0—21 −9 to 9	−9 to 9 0—17 0—15
Total no. of reflections	1 563	5 024	1 537	2 663
No. of unique reflections	1 380	4 586	1 342	2 437
No. of reflections used [$F > 3\sigma(F)$]	1 288	3 309	1 089	2 060
No. of parameters	279	257	94	208
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF_o^2]$	0.005	0.0018 43	0.0008 83	0.004
Final R [= $\Sigma\Delta F/\|F_o\|$]	0.0276	0.0553	0.0353	0.0406
Final R' { = $[w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$}	0.0281	0.0602	0.0363	0.0455

Table 9. Fractional atomic co-ordinates ($\times 10^4$) for $[(mes)N_2][OsO_2(ONO_2)_2(mes)]$

Atom	x	y	z
Os	3 957.7(2)	10 239.4(5)	2 500.0
C(11)	3 772(7)	10 604(15)	3 729(7)
C(12)	4 387(7)	10 371(13)	4 289(8)
C(13)	4 248(7)	10 712(17)	5 110(8)
C(14)	3 544(6)	11 267(14)	5 398(8)
C(15)	2 918(6)	11 447(14)	4 853(6)
C(16)	3 029(6)	11 134(14)	4 037(7)
C(121)	5 215(10)	9 790(17)	4 092(10)
C(141)	3 427(8)	11 705(18)	6 304(8)
C(161)	2 308(6)	11 326(16)	3 473(8)
O(1)	4 877(4)	11 007(11)	2 322(4)
O(2)	3 138(5)	9 297(11)	2 092(6)
O(11)	4 377(4)	7 835(11)	2 771(4)
N(1)	4 620(6)	6 898(14)	2 140(6)
O(12)	4 548(4)	7 529(11)	1 455(5)
O(13)	4 897(7)	5 531(11)	2 297(5)
O(21)	3 537(4)	12 666(10)	2 297(4)
N(2)	3 539(5)	13 099(15)	1 516(8)
O(22)	3 784(6)	12 155(17)	999(6)
O(23)	3 268(7)	14 529(15)	1 359(10)
N(31)	2 603(7)	17 331(12)	300(6)
N(32)	3 174(6)	17 979(15)	409(7)
C(21)	1 882(6)	16 569(13)	121(7)
C(22)	1 782(6)	15 994(16)	−693(7)
C(23)	1 074(7)	15 304(17)	−877(13)
C(24)	469(8)	15 258(13)	−287(10)
C(25)	610(6)	15 832(18)	522(8)
C(26)	1 322(7)	16 471(14)	762(7)
C(221)	2 426(8)	16 146(18)	−1 331(7)
C(241)	−318(11)	14 614(21)	−529(14)
C(261)	1 504(6)	16 961(20)	1 635(8)

Table 10. Fractional atomic co-ordinates ($\times 10^4$) for $OsO(NBu^t)(mes)_2$

Atom	x	y	z
Os	1 154.4(4)	814.0(3)	2 640.9(3)
O	−233(9)	341(6)	2 672(7)
N	2 536(9)	312(7)	2 879(7)
C(1)	3 409(12)	−323(8)	3 050(10)
C(2)	3 081(42)	−972(13)	2 338(25)
C(3)	3 466(22)	−631(12)	4 078(16)
C(4)	4 598(22)	−83(18)	2 815(27)
C(11)	1 164(10)	1 407(7)	1 325(8)
C(12)	2 171(11)	1 890(7)	1 217(9)
C(13)	2 174(13)	2 304(8)	374(11)
C(14)	1 238(12)	2 253(8)	−376(10)
C(15)	274(14)	1 739(9)	−309(10)
C(16)	242(11)	1 321(8)	493(9)
C(21)	1 092(12)	1 829(8)	3 557(8)
C(22)	1 931(12)	1 966(8)	4 373(9)
C(23)	1 765(15)	2575(10)	4 951(10)
C(24)	743(15)	3 050(10)	4 785(11)
C(25)	−86(14)	2934(10)	3 958(10)
C(26)	67(11)	2 313(7)	3 344(9)
C(121)	3 262(13)	2 047(9)	2 014(11)
C(161)	−879(14)	786(10)	492(11)
C(141)	1 208(19)	2 666(12)	−1 280(13)
C(221)	3 082(16)	1 464(11)	4 669(11)
C(261)	−881(13)	2 258(9)	2 441(10)
C(241)	582(19)	3 748(15)	5 481(14)

1 184m, ν(Os=N), 955s, ν(Os=O); other 3 018m, 1 588m, 1 284m, 1 010s, 955s, 847s, 806m, and 574m cm^{-1}.

2,4,6-*Trimethylbenzenediazonium Mesitylbis(nitrato-κO)dioxo-osmate*(VI).—Nitric oxide was bubbled through a solution of $OsO_2(mes)_2$ (0.12 g, 0.26 mmol) for 1 h but no

Table 11. Fractional atomic co-ordinates (× 10^4) for $OsO_3(NBu^t)$

Atom	*x*	*y*	*z*
Os	126.6(7)	1 208.4(2)	1 121.0(5)
O(1)	2 948(17)	1 199(4)	964(13)
O(2)	−273(16)	416(5)	2 108(14)
O(3)	−174(20)	1 928(5)	2 460(12)
N	−2 020(17)	1 284(4)	−966(13)
C(1)	−3 893(19)	1 289(4)	−2 818(14)
C(11)	−5 326(23)	1 976(5)	−2 935(16)
C(12)	−2 560(23)	1 273(6)	−4 268(18)
C(13)	−5 392(21)	611(6)	−2 921(18)

Table 12. Fractional atomic co-ordinates (× 10^4) for $ReO_3[N(mes)_2]$

Atom	*x*	*y*	*z*
Re	2 238(1)	205.4(2)	248.3(2)
N	4 460(10)	−154(4)	2 623(5)
O(2)	1 931(10)	986(5)	3 295(6)
O(3)	1 834(12)	470(8)	1 309(6)
O(1)	951(10)	−615(6)	2 718(7)
C(11)	4 939(10)	−892(5)	2 039(6)
C(12)	4 323(11)	−1 703(6)	2 264(6)
C(13)	4 716(11)	−2 416(6)	1 660(6)
C(14)	5 688(12)	−2 315(6)	875(6)
C(15)	6 351(11)	−1 499(6)	666(6)
C(16)	5 984(11)	−796(5)	1 252(6)
C(121)	3 264(13)	−1 903(6)	3 170(7)
C(141)	6 128(14)	−3 071(7)	248(8)
C(161)	6 724(19)	56(6)	947(8)
C(21)	5 692(12)	348(5)	3 150(6)
C(22)	6 615(13)	−32(5)	3 853(7)
C(23)	7 776(12)	462(6)	4 391(7)
C(24)	7 993(12)	1 311(6)	4 230(7)
C(25)	7 057(13)	1 682(6)	3 512(8)
C(26)	5 911(12)	1 230(5)	2 939(7)
C(221)	6 385(14)	−954(5)	4 176(7)
C(241)	9 211(14)	1 846(7)	4 777(8)
C(261)	4 969(17)	1 727(6)	2 136(8)

evidence of reaction was observed. The solution in the closed flask was then injected with an amount of dry air calculated to react with the NO to give N_2O_3 when a brown solid rapidly appeared. After stirring for 1 h the solid was collected and crystallised from degassed thf to yield brown, air stable tablets. Yield: 0.13 g (81%). I.r.: 2 217s, ν(NN), 954m, 923m, ν(Os=O); other 3 006m, 1 591s, 1 531vs, 1 289s, 1 265s, 1 067m, 1 014m, 899s, 866m, 788m, 769m, 705m, 684m, and 565m cm^{-1}. Conductivity (MeCN): Λ_M = 108 ohm^{-1} cm^2 mol^{-1}.

The same product was obtained in *ca.* 47% yield by interaction of $OsO_2(mes)_2$ with pure NO_2. After collection of the precipitate, the ether was evaporated to leave a brown oil from which colourless crystals identified as nitromesitylene by n.m.r., i.r., and mass spectra {M^+, *m/z* 165 (165); $[M - OH]^+$, 148 (148)} and m.p. 42 °C (lit.,[33] 41—42 °C) were obtained. The ether collected in a trap was blue (N_2O_3) at −196 °C and on warming to room temperature became yellow-brown (NO_2 + NO). The brownish residual component after removal of $(mes)NO_2$ has no mesityl groups according to ^1H n.m.r. spectroscopy and was not investigated further.

Reaction of NO_2 *with* $ReO_2(mes)_2$; *Mesityltrioxorhenium*-(VII).—A stirred solution of $ReO_2(mes)_2$ (0.12 g, 0.26 mmol) in Et_2O (30 cm^3) at room temperature was exposed to excess of NO_2 gas. The initial, bright orange solution began to deposit a colourless solid {identified as $[(mes)N_2]^+NO_3^-$ by i.r. spectroscopy} after *ca.* 5 min. The solution was filtered and the solvent removed *in vacuo* to leave a yellow semi-solid residue. A solid-CO_2-cooled finger was inserted into the flask which was then placed under a static vacuum. Gentle warming of the residue gave colourless crystals on the cold-finger which were identified as nitromesitylene. The remaining dry yellow solid was crystallised from diethyl ether at −20 °C to afford $ReO_3(mes)$ as bright yellow blocks. Yield: 0.09 g (97%). Mass spectrum: M^+, ^{187}Re *m/z* 354 (354); ^{185}Re, 352 (352). I.r.: 986vs, 951vs ν(Re=O); other 3 053w, 1 592s, 1 535m, 1 287s, 1 246m, 1 030m, 883m, 850s, 589m, and 545m cm^{-1}.

Reaction of $ReO_2(mes)_2$ *with* NO; (*Dimesitylamido*)-*trioxorhenium*(VII).—Nitric oxide (11.0 cm^3, 0.45 mmol) was syringed through a septum into a stirred solution of $ReO_2(mes)_2$ (0.10g, 0.22 mmol) in toluene (30 cm^3). After 5 min the deep red solution became bright orange and 10 min later the solvent was removed *in vacuo*. The orange residue was extracted into hexane, which was filtered, concentrated, and cooled to −20 °C to give $ReO_3[N(mes)_2]$ as orange blocks. Yield: 0.10 g, (94%). Mass spectrum: M^+, ^{187}Re *m/z* 487 (487); ^{185}Re, 485 (485). I.r.: 972, 942 (hexane solution) ν(Re=O); 971vs, 934vs ν(Re=O; other 3 017m, 1 439s(sh), 1 202s, 1 187m, 1 148s, 1 025m, 958m, 908s, 851s, 816m, 594w, 569m, 557m, 544m, and 383s cm^{-1}.

X-*Ray Crystallography*.—Crystals of the complexes studied were sealed under argon in thin-walled glass capillaries. All *X*-ray measurements were made at room temperature using a Nonius CAD4 diffractometer and graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) following previously detailed procedures.[34] Intensity data were corrected for absorption on the basis of ψ-scan data[35] and subsequently using the DIFABS program.[36] Crystal data and collection details are given in Table 8. The structures were solved *via* standard heavy-atom procedures and refined by full-matrix least squares, with non-hydrogen atoms anisotropic and idealised hydrogens (AFIX in SHELX)[37] isotropic for the two imido complexes. No hydrogens were included in the diazonium or amido compounds. The weighting scheme $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ was introduced into the final stages of the refinements, with the parameter *g* being adjusted so as to give reasonably flat agreement analyses. All calculations were made on a DEC VAX 11/750 computer or on a T800 transputer hosted by an 80286ATPC. Final atomic co-ordinates are given in Tables 9—12.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

For the program EENY2 for steric energy surfaces see ref. 38.

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