Studies on Transition-metal Oxo and Nitrido Complexes. Part 8.[1] Reactions of Osmium Oxo-imido Complexes with Alkenes†

William P. Griffith,* Neil T. McManus, and Andrew D. White
Inorganic Chemistry Research Laboratories, Imperial College, London SW7 2AY

Reaction of $[OsO_3(NR)]$ [R = Bu^t, t-pentyl, adamant-1-yl (Ad), or 1,1,3,3-tetramethylbutyl (C_8H_{17})] and of $[OsO_2(NBu^t)_2]$ with alkenes R′ yields alkanolaminato and diaminato complexes of stoicheiometries $[\{OsO_2(OR'NR)\}_2]$ and $[OsO_2(NBu^tR'NBu^t)]$ respectively. The adducts $[OsO_3(NR)L]$ (R = Bu^t, t-pentyl, or C_8H_{17}; L = quinuclidine) and $[\{OsO_3(NR)\}_2L']$ {R = Bu^t or C_8H_{17}, L′ = 1,4-diazabicyclo[2.2.2]octane (dabo) or 1,3,5,7-tetra-azatricyclo[3.3.1.1^{3,7}]decane; R = t-pentyl, L′ = dabo} react with alkenes R′ to give $[OsO_2(OR'NR)L]$ and $[\{OsO_2(OR'NR)\}_2L']$. The structures of these complexes are discussed.

It has long been known[2] that osmium tetraoxide (OsO_4) reacts with alkenes R′ to give oxo-osmium 'monoesters,' now known to be oxo-bridged diolato dimers $[Os_2O_4(OR'O)_2]$ (I);[3] on hydrolysis these give *cis* diols.[2,4] Osmium(VIII) oxo(alkylimido) complexes $[OsO_3(NR)]$[5] will also react with alkenes to give unidentified species assumed to be monomeric alkanolaminato complexes.[6] On hydrolysis these give 2-aminoalcohols (HO)R′-(NHR):[6,7] such reactions can be rendered catalytic with secondary oxidants such as chloramine-T[8] or *N*-argentio-*N*-chlorocarbamates.[9] Reaction of $[OsO_2(NR)_2]$ or of $[OsO(NR)_3]$ with alkenes R′ gives 1,2-diamines, (NHR)R′(NHR).[10]

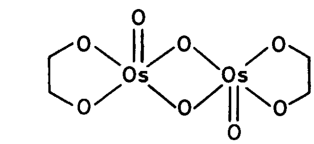
In this work we investigate the nature of the osmium-containing complexes formed from $[OsO_3(NR)]$ and alkenes, the formation of adducts of $[OsO_3(NR)]$ with bridgehead amines and the reactions of these adducts with alkenes. We have briefly reported the *X*-ray crystal structure of the complex formed from $[OsO_3(NBu^t)]$ and isobutylene,[11] $[\{OsO_2(OCMe_2CH_2NBu^t)\}_2]$, and of the adduct $[\{OsO_3(NC_8H_{17})\}_2(dabo)]$ (C_8H_{17} = 1,1,3,3-tetramethylbutyl, dabo = 1,4-diazabicyclo[2.2.2]octane).[12]

Results and Discussion

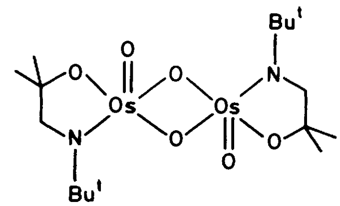
A. Alkanolaminato Oxo-osmium(VI) *Complexes*, $[\{OsO_2(OR'NR)\}_2]$.—The known oxo-imido osmium(VIII) complexes are $[OsO_3(NR)]$ [R = Bu^t,[5,6,7,10] t-pentyl (C_5H_{11}),[7,10] adamant-1-yl‡ (Ad),[6,7] or C_8H_{17}[5]], $[OsO_2(NR^1)(NR^2)]$ ($R^1 = R^2$ = Bu^t or Ad; $R^1 = C_5H_{11}$, R^2 = Ad),[10] and $[OsO(NR^1)_2(NR^2)]$ ($R^1 = R^2$ = Bu^t; R^1 = Bu^t, R^2 = Ad).[10]

In this part of the work, concerned with the nature of the inorganic products of the reaction of $[OsO_3(NR)]$ with alkenes, we have mainly used the NBu^t and NC_8H_{17} complexes. The alkenes used were ethylene, propylene, isobutylene (CMe_2CH_2), acrylonitrile (CH_2CHCN), fumaronitrile [$(CHCN)_2$], methyl methacrylate ($CH_2CMeCOOMe$), methyl acrylate ($CH_2CHCOOMe$), and both dimethyl and diethyl fumarates, $(CHCOOR)_2$. A representative list of products with analytical and spectroscopic data is given in the Table.

Our preliminary *X*-ray study on $[\{OsO_2(OCMe_2CH_2NBu^t)\}_2]$ (3)[11] shows this to have structure (II), very similar to that found[3,13] for the diolato 'monoester' $[Os_2O_4(OC_2Me_4O)_2]$ formed from OsO_4 and tetramethylethylene, see structure of (I). Like (I) the monoester has an *anti* configuration with square-based pyramidal osmium(VI) atoms linked by a planar Os_2O_2 bridge (mean Os–O bridge distance 1.92 Å); the axial Os=O distance is 1.67 Å and the Os–N distance 1.91 Å.[11] Molecular weight data obtained cryoscopically in benzene for this complex and for complex (6) show that both are dimers in solution, as is also the case for the diolato complexes $[Os_2O_4(OR'O)_2]$.[3] Mass spectral (electron impact) data however gave parent ion and breakdown patterns for mononuclear species $[OsO_2(OR'NR)]$ so presumably the Os_2O_2 bridge is cleaved under such conditions.



(I)



(II)

Spectroscopic data.—In the Table we list i.r. and Raman data for the solids and some solutions in the 950—650 cm^{-1} regions where we know from previous studies[3] that Os=O and Os_2O_2(bridge) stretches occur. Bands in these regions are found for all these complexes irrespective of the nature of R′, so we assign the 950 cm^{-1} bands to ν(Os=O) and those near 650 cm^{-1} to an asymmetric ring stretch ν(Os_2O_2). In solution the bands are little shifted in the Raman or i.r. spectra. The ESCA (electron spectroscopy for chemical analysis) data give binding energies typical of osmium(VI) complexes (see section *D* below).

In the Experimental section we list ^{1}H n.m.r. data for complexes (2), (3), (5), (6), and (8) with suggested assignments. We assign shifts for protons adjacent to nitrogen (CH_n–N, n = 1 or 2) in the alkanolaminato ring at lower frequencies than for those adjacent to oxygen (CH_n–O) on the basis of normal shielding arguments for organic molecules.

It is noticeable from the ^{1}H n.m.r. spectra of complexes formed from asymmetric alkenes [*viz*. complexes (3), (5), (6), and (8) formed from isobutylene, methyl acrylate, and methyl

† *Non-S.I. unit employed*: eV ≈ 1.60 × 10^{-19} J.
‡ Adamantane = tricyclo[3.3.1.1^{3,7}]decane.

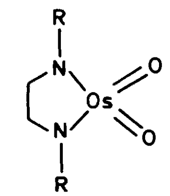
Table. Analytical and spectroscopic data

Complex	Analyses[a] C	H	N	Vibrational spectra[b] (cm^{-1}) ν(OsO)	ν(Os_2O_2) or ν(OsN)	ESCA Binding energies (eV)
(*a*) Imido and alkanolaminato						
(**1**) $[OsO_3(NC_{18}H_{17})]$	26.4 (26.3)	4.6 (4.7)	3.8 (3.8)	927s, 916vs *922vs, 914s, 906s* (924m, 914s) *(924p, 918dp)*	1 207s *1 206w* (1 203) *(1 210w)*	
(**2**) $[\{OsO_2(OC_2H_4NBu^t)\}_2]$	20.9 (21.4)	3.6 (3.9)	3.9 (4.2)	960s	650m	
(**3**) $[\{OsO_2(OCMe_2CH_2NBu^t)\}_2]$[c]	26.5 (26.3)	4.7 (4.7)	3.7 (3.8)	960s	660m	
(**4**) $[\{OsO_2(OCHMeCH_2NBu^t)\}_2]$	24.5 (23.9)	4.3 (4.3)	3.6 (4.0)	939s *934s*	680m	
(**5**) $[\{OsO_2[OCH(COOMe)CH_2NBu^t]\}_2]$	24.5 (24.4)	3.8 (3.8)	3.3 (3.6)	955s	667m	52.1, 54.8
(**6**) $[\{OsO_2[OCMe(COOMe)CH_2NBu^t]\}_2]$[c]	26.6 (26.4)	4.2 (4.1)	3.3 (3.4)	958s	671m	52.3, 55.0
(**7**) $[\{OsO_2(OC_6H_{10}NBu^t)\}_2]$	29.5 (30.6)	4.9 (4.9)	3.4 (3.6)	977s *971s*	679m	52.1, 54.9
(**8**) $[\{OsO_2(OCMe_2CH_2NC_5H_{11})\}_2]$	29.0 (28.5)	5.0 (5.0)	3.7 (3.7)	*925s*		
(*b*) Diaminato						
(**9**) $[OsO_2\{NBu^t(CHCN)_2NBu^t\}]$	31.6 (32.6)	4.2 (4.6)	11.7 (12.7)	930w, 905s, 896vs (930w, 916vs) *901s*		52.0, 54.7
(*c*) Adducts and their esters						
(**10**) $[OsO_3(NC_8H_{17})(qncd)]$	37.7 (37.8)	6.3 (6.3)	5.8 (5.9)	885s, 870s	1 210vs	
(**11**) $[\{OsO_3(NC_8H_{17})\}_2(tatd)]$	31.4 (30.3)	5.2 (5.3)	9.6 (9.7)	880s, 875s	1 212vs	
(**12**) $[\{OsO_3(NC_8H_{17})\}_2(dabo)]$[c]	31.5 (31.3)	5.5 (5.5)	6.6 (6.7)	883m, 875vs, 845s *887s, 878m, 850w* (924s, 914s, 880m, 873s) *(929s, 912m, 889s, 878w)*	1 167s *1 174m* (1 210, 1 170) *(1 204w, 1 170w)*	53.0, 55.7
(**13**) $[OsO_2\{O(CHCOOMe)_2NBu^t\}(qncd)]$	35.6 (36.4)	5.3 (5.4)	4.8 (5.0)	900s, 864s *896s, 862m* *(891p, 859w)*		51.8, 54.5
(**14**) $[\{OsO_2[O(CHCOOMe)_2NBu^t]\}_2(dabo)]$	31.9 (30.9)	4.5 (4.6)	5.5 (5.5)	900s, 863s *897s, 861m*		
(**15**) $[\{OsO_2[O(CHCOOMe)_2NBu^t]\}(tatd)]$	33.4 (32.4)	4.9 (4.9)	12.9 (11.8)	894s, 850m *(895vs, 861m)*		
(**16**) $[OsO_2(OC_6H_{10}NBu^t)(qncd)]$	39.6 (40.6)	6.4 (6.4)	5.1 (5.6)	890vs, 850m *894vs, 856w* *897p, 860w*		51.8, 54.5
(**17**) $[OsO_2\{O(CHCOOMe)_2NAd\}(qncd)]$	42.8 (43.9)	5.6 (5.6)	4.2 (4.4)	889s, 865m (859s) *888s, 961m* *(894p, 859w)*		

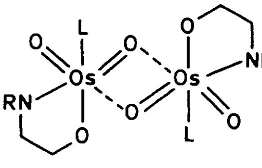
[a] Calculated analyses in parentheses. [b] Data on solids (solutions in parentheses: toluene for i.r. and CCl_4 for Raman); Raman data in italic (p = polarised, dp = depolarised). [c] Molecular weights in benzene (calculated values in parentheses): complex (**3**), 770 (734); (**6**), 860 (814); (**12**), 488 (841).

methacrylate] that these have added to the osmium so that their CH_2 groups are exclusively attached to the NR group, irrespective of whether the alkenes bear electron-withdrawing (COOMe) or electron-donating (Me) groups. This selectivity must be a direct consequence of the steric constraints imposed by the bulky alkyl groups (R) at the nitrogen atom.

B. Diaminato Oxo-osmium(VI) *Complexes*, $[OsO_2(NRR'NR)]$.—Sharpless and co-workers[10] have shown that such species are formed by reaction of $[OsO_2(NBu^t)_2]$ with dimethyl- and diethyl-fumarate, the complex formed with the latter being monomeric in benzene; structure (**III**) was proposed for these species. We have confirmed that these two complexes



(III)



(IV)

are monomeric and have made the new species $[OsO_2\{N\text{-}Bu^t(CHCN)_2NBu^t\}]$ (9) from fumaronitrile and $[OsO_2(NBu^t)_2]$. The Raman and i.r. spectra of (9) are similar in the solid state and, in the case of the i.r. spectrum, of the solution in toluene; this suggests that there is no change in structure from solid to solution. The presence of ν(OsO) bands near 900 cm^{-1} is characteristic of *cis*-dioxo complexes[14] and supports structure (III). The monomeric nature of these complexes has interesting implications for the mechanism of the OsO_4–alkene reaction: it has been suggested that the existence of a monomeric diolato intermediate $OsO_2(OR'O)$, analogous to (III), is unlikely because of the strain on the diolato ring for such a tetrahedral structure.[15]

C. Adducts of $[OsO_3(NR)]$ *with Bridgehead Amines.*—We have shown in earlier work that OsO_4 will form adducts of the type $[OsO_4L]$ (*e.g.* with L = quinuclidine, qncd) and $[(OsO_4)_2L']$ {*e.g.* with L′ = 1,3,5,7-tetra-azatricyclo-$[3.3.1.1^{3,7}]$decane (tatd) and with 1,4-diazabicyclo[2.2.2]octane (dabo)}[16] and reported the *X*-ray crystal structures of $[OsO_4(qncd)]$ and of $[(OsO_4)_2(tatd)]$.[17] It has recently been shown that $[OsO_3(NBu^t)]$ will form adducts $[OsO_3(NBu^t)L]$ with quinuclidine and with substituted quinuclidines,[18] and $[\{OsO_3(NBu^t)\}_2L']$ (L′ = tatd or dabo).

We have also prepared the new adducts $[OsO_3(NC_8H_{17})(qncd)]$ (10), $[\{OsO_3(NC_8H_{17})\}_2(tatd)]$ (11), and $[\{OsO_3(NC_8H_{17})\}_2(dabo)]$ (12), as well as the known corresponding species with $[OsO_3(NBu^t)]$, and reported the *X*-ray crystal structure of (12).[12] This has a symmetrical structure with the amine bridging two $OsO_3(NC_8H_{17})$ units. As in $[OsO_4(qncd)]$ and in $[(OsO_4)_2(tatd)]$[17] there is trigonal-bipyramidal coordination about the osmium with the oxo ligands in the equatorial positions (mean Os=O distance 1.71 Å, similar to the 1.706 Å found in the OsO_4 adducts).[17] The axial positions are occupied by the NC_8H_{17} nitrogen atoms {Os–N 1.73 Å, comparable with the 1.697 Å found for Os–N in $[OsO_3(NAd)]$[19]} and a long bond to the amine (Os–N 2.42 Å). This is slightly longer than the 2.37 Å observed in $[OsO_4(qncd)]$ and $[(OsO_4)_2(tatd)]$, perhaps reflecting a greater *trans*-weakening influence of the imido ligand as compared with the oxo ligand.

Vibrational spectra of these complexes in the solid state are similar in the ν(OsO) stretching region to those of the OsO_4 adducts, as expected in view of the structural similarities and the local C_{3v} symmetry about the osmium atoms. The Raman and i.r. spectra of solutions of the diazabicyclo[2.2.2]octane complex (12), however, also have bands characteristic of free $[OsO_3(NC_8H_{17})]$ in the ν(OsN) and ν(OsO) regions, so it appears that dissociation to $[OsO_3(NC_8H_{17})]$ and $[OsO_3(NC_8H_{17})(dabo)]$ occurs. The low molecular weight of the complex in benzene also indicates dissociation: the osmium tetraoxide analogue $[(OsO_4)_2(dabo)]$ shows no such dissociation, however.[16]

Attempts to prepare similar adducts of $[OsO_2(NBu^t)_2]$ were unsuccessful; it is unlikely that $[OsO_2(NR)_2L]$ or $[\{OsO_2(NR)_2\}_2L]$ species would exist for steric reasons, since at least one bulky NR ligand would necessarily have to lie in an equatorial position of the trigonal bipyramid *cis* to the amine. Attempts to make $[OsO_3(NR)(py)]$ (py = pyridine) were also unsuccessful, the main product being $[Os_2O_6(py)_4]$.

D. Reactions of $[\{OsO_3(NR)\}_nL]$ *with Alkenes.*—We have shown that $[OsO_4L]$ (L = quinuclidine, isoquinoline, or phthalazine) react with alkenes R′ to give green esters $[\{OsO_2(ORO')L\}_2]$[20] and have reported the *X*-ray crystal structure of the ester derived from cyclohexene, $[\{OsO_2(o\text{-}OC_6H_{10}O)(qncd)\}_2]$.[20,21] The 2:1 adducts $[(OsO_4)_2L']$ (L′ = tatd or dabo) similarly reacted with alkenes R′ to give $[OsO_2(OR'O)(tatd)]$ in the case of tatd and $[\{OsO_2(OR'O)\}_2(dabo)]$ in the case of 1,4-diazabicyclo[2.2.2]octane.[16] We seek here to elucidate the nature of the species formed by reaction of $[OsO_3(NR)L]$ and $[\{OsO_3(NR)\}_2L]$ with alkenes.

We find, not unexpectedly, that these reactions give products apparently analogous to those found for the OsO_4 adducts, though we have not yet succeeded in obtaining suitable crystals for *X*-ray study. The quinuclidine adducts $[OsO_3(NR)(qncd)]$ (R = Bu^t, C_5H_{11}, C_8H_{17}, or Ad) yield dark green complexes of stoicheiometry $[OsO_2(OR'NR)(qncd)]$. Their colour and the fact that their i.r. and Raman spectra show two bands in the ν(OsO) region near 880 cm^{-1} just as do the corresponding oxo species $[OsO_2(OR'O)(qncd)]$ suggests similar structures for both.

Our *X*-ray study on the cyclohexanediolato complex $[OsO_2(o\text{-}OC_6H_{10}O)(qncd)]$ showed this to be dimeric with an asymmetric Os_2O_2 bridge,[21] and we tentatively suggest an analogous structure, (IV), for the present species. They are too insoluble for reliable molecular weight studies to be obtained, but the similarity of the i.r. and Raman spectra of the solid complexes (13), (16), and (17) with those of their solutions suggests little change in structure from solid to solution. In the case of the tatd adducts $[\{OsO_3(NR)\}_2(tatd)]$ (R = Bu^t or C_8H_{17}) reactions with alkenes R′ gave green products of stoicheiometry $[\{OsO_2(OR'NR)\}(tatd)]$ as was the case with the corresponding reactions with $[(OsO_4)_2(tatd)]$.[16] Thus, reaction of $[\{OsO_3(NBu^t)\}_2(tatd)]$ with dimethyl fumarate gives a 48% yield of $[OsO_2\{O(CHCOOMe)_2NBu^t\}(tatd)]$, increased to 90% by addition of excess tatd suggesting that dissociation of the initial adduct to a 1:1 complex initially occurs. With dabo, on the other hand, the bridging role of the ligand in the adduct is apparently retained in the products with alkenes; thus, $[\{OsO_3(NBu^t)\}_2(dabo)]$ reacts with dimethyl fumarate to give $[\{OsO_2[O(CHCOOMe)_2NBu^t]\}_2(dabo)]$ (14) and a similar situation is observed for reactions of $[(OsO_4)_2(dabo)]$ with alkenes.[16]

In the Experimental section we list full ^1H n.m.r. data for three of the complexes (13)—(15); as with the alkanolaminato esters it appears that the methylene groups are adjacent to the bulky imido groups.

ESCA Data.—In the Table we report $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ binding energies for a number of the complexes described in the paper; it is known that such binding energies are indicative of the oxidation state of the osmium atom.[22,23] Although the $[OsO_3(NR)]$ species were too volatile for such studies the bis(imido) complex $[OsO_2(NBu^t)_2]$ gave high binding energies as expected for osmium(VIII), as was the case for the adducts $[\{OsO_3(NC_8H_{17})\}_2L']$ (L′ = tatd or dabo). All the other complexes listed in the Table are formally of osmium(VI) and indeed show lower binding energies, typically $4f_{\frac{7}{2}}$ and $4f_{\frac{5}{2}}$ of 52.0 and 55.0 eV respectively. We have found values of 52.3 and 55.0 eV for *trans*-$K_2[Os^{VI}O_2(OH)_4]$ and of 53.0 and 55.8 eV for the osmium(VII) complex $[PPh_4][OsO_4]$, analogous to $[AsPh_4][OsO_4]$ recently reported.[24]

Experimental

The complexes $[OsO_3(NR)]$ (R = Bu^t,[10] C_5H_{11},[10] Ad,[6] or C_8H_{17}[5]) and $[OsO_2(NBu^t)_2]$[10] were made as in the literature and gave satisfactory elemental analyses; data for $[OsO_3(NC_8H_{17})]$ only are listed in the Table since spectroscopic data for it are not available in the literature.

For the alkanolaminato species $[\{OsO_2(OR'NR)\}_2]$ the preparation of the isobutylene complex $[\{OsO_2(OCMe_2CH_2NBu^t)\}_2]$ is typical for one involving a gaseous alkene, while that for the methyl methacrylate complex $[\{OsO_2[OCMe(COOMe)CH_2NBu^t]\}_2]$ is typical for one involving a liquid alkene.

$[\{OsO_2(OCMe_2CH_2NBu^t)\}_2]$ (**3**).—A solution of $[OsO_3(NBu^t)]$ (0.15 g, 0.48 mmol) in diethyl ether (3 cm^3) was stirred under an atmosphere of isobutylene for 4 h. The resulting red-brown solid was filtered off and dried *in vacuo*. A further crop of solid was obtained by reducing the volume of solvent.

$[\{OsO_2[OCMe(COOMe)CH_2NBu^t]\}_2]$ (**6**).—To $[OsO_3(NBu^t)]$ (0.14 g, 0.4 mmol) in diethyl ether was added methyl methacrylate (0.06 g, 0.4 mmol) and the mixture stirred at room temperature for 15 h. The deep red product was filtered off and air-dried.

The known diaminato complexes $[OsO_2\{NBu^t(CHCOOR)_2NBu^t\}]$ (R = Me or Et) were made as in the literature;[10] we found however that the use of diethyl ether as solvent eliminates the need for t.l.c. separation. The complex $[OsO_2\{NBu^t(CHCN)_2NBu^t\}]$ (**9**) was made from $[OsO_2(NBu^t)_2]$ (0.16 g, 0.44 mmol) in diethyl ether (3 cm^3) with fumaronitrile (0.03 g, 0.38 mmol); it is deep red.

For the adducts $[OsO_3(NR)(qncd)]$ and $[\{OsO_3(NR)\}_2L']$ (L′ = tatd or dabo) the preparation of the adducts with R = C_8H_{17} are typical.

$[\{OsO_3(NC_8H_{17})\}_2(dabo)]$ (**12**).— To $[OsO_3(NC_8H_{17})]$ (0.1 g, 0.3 mmol) in diethyl ether (3 cm^3) was added 1,4-diazabicyclo[2.2.2]octane (0.015 g, 0.14 mmol). The bright orange solid was filtered off and air-dried.

The adduct with quinuclidine is more soluble and for this addition of light petroleum (b.p. 40–60 °C; 4 cm^3) is necessary.

The alkanolaminato ester adducts $[OsO_2(OR'NR)(qncd)]$ and $[\{OsO_2(OR'NR)\}_2L']$ (L′ = tatd or dabo) were made by methods of which the following is typical.

$[OsO_2(OC_6H_{10}NBu^t)(qncd)]$ (**16**).—To a solution of $[OsO_3(NBu^t)(qncd)]$, generated *in situ* by stirring a mixture of $[OsO_3(NBu^t)]$ (0.15 g, 0.5 mmol) and quinuclidine (0.06 g, 0.5 mmol) in diethyl ether (5 cm^3) for 20 min was added a slight excess of cyclohexene (0.05 g, 0.7 mmol). The mixture was stirred at room temperature for 12 h, cooled to −20 °C and the dark green solid filtered off.

*Hydrogen-*1 *N.M.R. Spectra.*—We report here a detailed list of the ^1H spectra, measured in C^2HCl_3, of five alkanolaminato and three alkanolaminato ester adducts. Chemical shifts (δ/p.p.m. relative to $SiMe_4$, with integrals and assignments in parentheses) are listed.

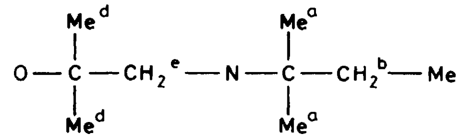
$[\{OsO_2(OC_2H_4NBu^t)\}_2]$ (**2**). 1.56 (s, 9 H, NBu^t), 4.20 (s, 1 H, CH′–N), 4.26 (s, 1 H, CH″–N), 4.52 (br s, 2 H, CH_2–O).

$[\{OsO_2(OCMe_2CH_2NBu^t)\}_2]$ (**3**). 1.44 (s, 6 H, Me_2C–O), 1.52 (s, 9 H, NBu^t), 4.02 (br s, 2 H, CH_2–N).

$[\{OsO_2[OCH(COOMe)CH_2NBu^t]\}_2]$ (**5**). 1.51 (s, 9 H, NBu^t), 3.67 (s, 3 H, $COOCH_3$), 4.45 (br s, 2 H, CH_2–N), 5.09 (br s, 1 H, CH–O).

$[\{OsO_2[OCMe(COOMe)CH_2NBu^t]\}_2]$ (**6**). 1.51 (s, 9 H, NBu^t), 1.84 (s, 3 H, CH_3–C–O), 3.68 (s, 3 H, $COOCH_3$), 4.21 (br s, 2 H, CH_2–N).

$[\{OsO_2(OCMe_2CH_2NC_5H_{11})\}_2]$ (**8**). 0.81 (t, *J* = 7 Hz, 3 H, $CH_3{}^c$), 1.48 (s, 6 H, N–$CMe_2{}^a$), 1.52 (s, 6 H, $Me_2{}^d$–C–O), 1.91 (q, *J* = 7 Hz, 2 H, –$CH_2{}^b$), 4.05 (br s, 2 H, $CH_2{}^e$–N). The atom numbering is shown below.



$[OsO_2\{O(CHCOOMe)_2NBu^t\}(qncd)]$ (**13**). 1.14 (s, 9 H, NBu^t), 1.65 (br s, 6 H, $CH_2{}^b$) 1.93 (br m, 1 H, CH^c), 3.08 (br m, 6 H, $CH_2{}^a$), 3.67 (s, 6 H, $COOCH_3$), 4.02 (s, 1 H, HC–N), 4.43 (s, 1 H, HC–O). The atom numbering for qncd is $N(CH_2{}^a)_3(CH_2{}^b)_3CH^c$.

$[\{OsO_2[O(CHCOOMe)_2NBu^t]\}_2(dabo)]$ (**14**). 1.17 (s, 9 H, NBu^t), 3.16 (s, 6 H, $CH_2{}^a$), 3.68 (s, 3 H, $COOCH_3$), 3.70 (s, 3 H, $COOCH_3$), 4.05 (s, 1 H, HC–N), 4.49 (s, 1 H, HC–O); $CH_2{}^a$ are the protons of $N_2C_6H_{12}$.

$[OsO_2\{O(CHCOOMe)_2NBu^t\}(tatd)]$ (**15**). 1.21 (s, 9 H, NBu^t), 3.71 (s, 3 H, $COOCH_3$), 3.72 (s, 3 H, $COOCH_3$), 4.11 (s, 1 H, HC–N), 4.52 (s, 1 H, HC–O), 4.71 (br s, 12 H, $CH_2{}^a$); $CH_2{}^a$ are the protons of $N_4C_6H_{12}$.

Infrared spectra were measured on a Perkin-Elmer 683 instrument as liquid paraffin mulls between caesium iodide plates, and Raman spectra as spinning discs in a KBr base using a Spex Ramalog 5 instrument with a krypton-ion laser with 6 147 Å or 5 682 Å excitation for red and yellow samples and 5 308 Å for green samples. ^1H N.m.r spectra were measured on a JEOL FX 90Q spectrometer. ESCA spectra were measured on a V.G. Escalab Mark II instrument at 10^{-9} Torr (*ca.* 1.33×10^{-7} Pa) with data collected at a pass energy of 20 eV and ultimate resolution of 0.7 eV. Samples were run as pressed discs on indium foil, correction being made for sample charging. Microanalyses were performed by Mr. K. Jones of the Microanalytical Department.

Acknowledgements

We thank the S.E.R.C. for a postdoctoral fellowship to one of us (N. T. M.) and for a CASE studentship with British Petroleum (to A. D. W.). We thank Professor S. V. Ley for helpful discussions, Dr. M. Morris for ESCA measurements, and Johnson-Matthey for the loan of platinum metals in the early stages of this work.

References

1 Part 7, M. J. Wright and W. P. Griffith, *Transition Met. Chem.*, 1982, **7**, 53.
2 R. Criegee, *Annalen*, 1936, **522**, 75; R. Criegee, B. Marchand, and H. Wannowius, *Annalen*, 1942, **550**, 99.
3 R. J. Collin, J. Jones, and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1974, 1094.
4 M. Schröder, *Chem. Rev.*, 1980, **80**, 187.
5 N. A. Milas and M. I. Iliopulos, *J. Am. Chem. Soc.*, 1959, **81**, 6089.
6 D. W. Patrick, L. K. Truesdale, S. A. Biller, and K. B. Sharpless, *J. Am. Chem. Soc.*, 1975, **97**, 2305.

7 D. W. Patrick, L. K. Truesdale, S. A. Biller, and K. B. Sharpless, *J. Org. Chem.*, 1978, **43**, 2628.
8 E. Herranz and K. B. Sharpless. *J. Org. Chem.*, 1976, **41**, 177; 1978, **43**, 2544.
9 E. Herranz, S. A. Biller, and K. B. Sharpless, *J. Am. Chem. Soc.*, 1978, **100**, 3596.
10 A. O. Chong, K. Oshima, and K. B. Sharpless, *J. Am. Chem. Soc.*, 1977, **99**, 3420.
11 W. P. Griffith, N. T. McManus, A. C. Skapski, and A. J. Nielson, *Inorg. Chim. Acta*, 1985, **103**, L5.
12 W. P. Griffith, N. T. McManus, A. C. Skapski, and A. D. White, *Inorg. Chim. Acta*, 1985, **105**, 11.
13 R. J. Collin, W. P. Griffith, F. L. Phillips, and A. C. Skapski, *Biochim. Biophys. Acta*, 1974, **354**, 152; F. L. Phillips and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1975, 2586.
14 W. P. Griffith, *J. Chem. Soc. A*, 1969, 211.
15 K. B. Sharpless, A. Y. Tetranishi, and J-E. Backvall, *J. Am. Chem. Soc.*, 1977, **99**, 3120.
16 M. J. Cleare, P. C. Hydes, W. P. Griffith, and M. J. Wright, *J. Chem. Soc., Dalton Trans.*, 1977, 941.
17 W. P. Griffith, A. C. Skapski, K. A. Woode, and M. J. Wright, *Inorg. Chim. Acta*, 1978, **31**, L413.
18 S. G. Hentges and K. B. Sharpless, *J. Org. Chem.*, 1980, **45**, 2257.
19 W. A. Nugent, R. L. Harlow, and R. J. McKinney, *J. Am. Chem. Soc.*, 1979, **101**, 7265.
20 M. Schröder, A. J. Nielson, and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1979, 1607.
21 B. A. Cartwright, W. P. Griffith, M. Schröder, and A. C. Skapski, *J. Chem. Soc., Chem. Commun.*, 1978, 853.
22 D. J. Salmon and R. A. Walton, *Inorg. Chem.*, 1978, **17**, 2379.
23 J. P. Hall and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1980, 2410.
24 E. Bilger, J. Pebler, R. Weber, and K. Dehnicke, *Z. Naturforsch., Teil B*, 1984, **39**, 259.

Received 12th July 1985; *Paper* 5/1180