Oxo-, Nitrido- and Imido-osmium(VI) Complexes with a Sterically Bulky Chelating Alkoxide Ligand[‡]

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The synthesis and characterization of dioxoosmium(VI) complexes *cis*-$[OsO_2L]$ and *trans*-$[OsO_2L']$ (L′ = NH_2Bu^t, pyridine or 4-*tert*-butylpyridine), the nitrido complex [OsN(L)Cl], and imido complexes $[OsL(NCOCF_3)Cl(O_2CCF_3)]$ and $[OsL(NPh)_2]$ [H_2L = 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridine] are described. The crystal structures of [OsN(L)Cl] and $[OsO_2L(NH_2Bu^t)]\cdot 0.5C_6H_{14}$ have been determined: the Os≡N and average Os=O bond distances are 1.634(5) and 1.741(5) Å, respectively.

Sterically bulky alkoxide ligands play an important role in the development of new homogeneous catalysts. These ligands are capable of generating co-ordinatively unsaturated high-valent metal ions, whose chemistry differs significantly from that of classical rhodium(I) and iridium(I) complexes. In an attempt to investigate the chemistry of high-valent osmium alkoxide complexes, we focused on the ligand 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridine (H_2L) which was first prepared by Berg and Holm.[1] Unlike other alkoxide ligands such as R_3SiO^-, H_2L possesses a pyridyl functional group which would facilitate co-ordination to transition-metal ions. Herein are described the synthesis and chemical properties of osmium(VI) oxo, nitrido and imido complexes of H_2L.

Experimental

Reagents and Materials.—The ligand H_2L (ref. 1) and the complexes $K_2[OsO_2(OH)_4]$[2] and $[NBu_4][OsNCl_4]$[3] were prepared by published procedures.

Physical Measurements and Instrumentation.—Electronic absorption spectra were recorded with a Milton Roy Spectronic 3000 Array spectrophotometer, infrared spectra using a Nicolet-20 SXC FT-IR spectrometer, and ^1H NMR spectra on a JEOL model FX-90Q (90 MHz) or JNM-GSX 270 FT spectrometer (270 MHz). Chemical shifts (δ) are reported relative to tetramethylsilane. Elemental analyses of the new complexes were performed by Butterworth Laboratories.

Synthesis.—[2,6-*Bis*(2-*hydroxy*-2,2-*diphenylethyl*)*pyridinato*-(2 –)]*chloronitridoosmium*(VI) [OsN(L)Cl] **1**. To a solution of H_2L (0.3 g) in methanol (25 cm^3) was added $[NBu_4][OsNCl_4]$ (0.25 g). The mixture was stirred at 60–70 °C for 1 h. A red-brown solid was obtained, which was washed with methanol. Recrystallization from dichloromethane–diethyl ether gave reddish purple prisms (Found: C, 55.60; H, 3.45; N, 3.55. Calc. for $C_{33}H_{27}ClN_2O_2Os$: C, 55.90; H, 3.85; N, 3.95%). IR (KBr): 1001, 1017, 1024 and 1049 cm^{-1}. ^1H NMR (270 MHz, CD_2Cl_2): δ 3.88–4.22 (m, CH_2, 4 H) and 7.41–7.44 (m, H of phenyl and pyridine, 23 H). UV/VIS ($CHCl_3$): λ_{max}/nm (log ε) 243 (3.75), 256 (3.53) (sh), 368 (1.97) and 519 (2.17).

[2,6-*Bis*(2-*hydroxy*-2,2-*diphenylethyl*)*pyridinato*(2 –)]-*chloro*(*trifluoroacetato*)(*trifluoroacetylimido*)*osmium*(VI) $[OsL(NCOCF_3)Cl(O_2CCF_3)]$ **2**. A dichloromethane solution of complex **1** (0.2 g in 50 cm^3) was treated with trifluoroacetic anhydride (1 cm^3) and glacial acetic acid (0.1 cm^3) and then refluxed with stirring for 16 h. The solution was filtered and evaporated under vacuum to give an oily residue. Addition of heptane afforded a brown precipitate, which was recrystallized from acetone–diethyl ether to yield an analytically pure product (Found: C, 48.15; H, 2.90; N, 3.05. Calc. for $C_{37}H_{27}ClF_6N_2O_5Os$: C, 48.35; H, 2.95; N, 3.05%). IR (Nujol): ν(Os=N) 1197, ν(C=O) 1672, 1719 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 3.81–4.40 (m, CH_2, 4 H) and 7.07–7.50 (m, H of phenyl and pyridine, 23 H). UV/VIS ($CHCl_3$): λ_{max}/nm (log ε) 244 (4.10) and 373 (3.08) (sh).

[2,6-*Bis*(2-*hydroxy*-2,2-*diphenylethyl*)*pyridinato*(2 –)]*dioxoosmium*(VI) $[OsO_2L]$ **3**. A solution of H_2L (0.3 g) and $K_2[OsO_2(OH)_4]$ (0.3 g) in methanol (50 cm^3) was stirred at 50–60 °C for 0.5 h. The colour gradually changed from green to red-brown, and a red-brown precipitate was slowly formed. The precipitate was filtered off, washed with methanol and recrystallized from dichloromethane–methanol to give an analytically pure product (Found: C, 57.55; H, 3.80; N, 1.95. Calc. for $C_{33}H_{27}NO_4Os$: C, 57.30; H, 3.95; N, 2.00%). IR (KBr): ν(Os=O) 823, 817 and 803 cm^{-1}. ^1H NMR [90 MHz, $(CD_3)_2SO$]: δ 4.47 (s, CH_2, 4 H) and 6.8–7.6 (m, H of phenyl and pyridine, 23 H). UV/VIS ($CHCl_3$): λ_{max}/nm (log ε) 243 (3.92), 271 (3.87), 367 (3.22) (sh) and 516 (2.74) (sh).

[2,6-*Bis*(2-*hydroxy*-2,2-*diphenylethyl*)*pyridinato*(2 –)]*di*(*phenylimido*)*osmium*(VI) $[OsL(NPh)_2]$ **4**. To a refluxing suspension of complex **3** (0.2 g) in dry toluene (30 cm^3) was added excess of phenyl isocyanate. A dark brown colour appeared immediately. The mixture was refluxed with stirring for 0.5 h, and then evaporated under vacuum to remove the volatile components. Addition of heptane gave a dark brown precipitate, which was collected and purified by chromatography on an alumina column with $CHCl_3$ as the eluent (Found: C, 64.55; H, 4.20; N, 4.90. Calc. for $C_{45}H_{37}N_3O_2Os$: C, 64.20; H, 4.45; N, 5.00%). IR (Nujol): ν(Os=N) 1233 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 4.05–4.45 (m, CH_2, 4 H) and 6.91–7.98 (m, H of phenyl and pyridine, 33 H). UV/VIS (MeCN): λ_{max}/nm (log ε) 224 (4.26), 255 (4.29), 356 (3.61) (sh) and 482 (3.29) (sh).

[2,6-*Bis*(2-*hydroxy*-2,2-*diphenylethyl*)*pyridinato*(2 –)](tert-*butylamine*)*dioxoosmium*(VI)$[OsO_2L(NH_2Bu^t)]$ **5**. A chloroform solution (50 cm^3) of complex **3** (0.1 g) and *tert*-butylamine (0.5 cm^3) was refluxed for 2.5 h to give a brown solution, which was

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[‡] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

filtered and concentrated to *ca.* 10 cm^3. Upon slow diffusion of hexane into the solution orange prisms were obtained (Found: C, 58.00; H, 4.95; N, 3.55. Calc. for $C_{37}H_{38}N_2O_4Os$: C, 58.10; H, 5.00; N, 3.65%). IR (Nujol): ν(Os=O) 829, ν(NH) 3268, 3210 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.60 (s, CH_3, 9 H), 4.12–4.44 (br, CH_2, 4 H), 5.39 (br, NH_2, 2 H) and 7.09–7.55 (m, H of phenyl and pyridine, 23 H). UV/VIS ($CHCl_3$): λ_{max}/nm (log ε) 243 (4.02), 277 (3.80) (sh), 320 (3.57) (sh) and 362 (3.10) (sh).

[2,6-*Bis*(2-*hydroxy*-2,2-*diphenylethyl*)*pyridinato*(2 –)]-*dioxo*-(*pyridine*)*osmium*(VI) $[OsO_2L(py)]$ **6**. To a solution of complex **3** (0.1 g) in chloroform (20 cm^3) was added dried pyridine (0.5 cm^3). The mixture was refluxed for 3 h, then cooled and filtered. The solvent was distilled off and the residue was treated with diethyl ether. The red-brown precipitate obtained was collected, washed with diethyl ether, and dried (Found: C, 59.20; H, 4.20; N, 3.65. Calc. for $C_{38}H_{32}N_2O_4Os$: C, 59.20; H, 4.20; N, 3.65%). IR (Nujol): ν(Os=O) 833 cm^{-1}. UV/VIS ($CHCl_3$): λ_{max}/nm (log ε) 243 (4.09), 259 (3.85) (sh), 262 (4.05) (sh) and 367 (2.91) (sh).

[2,6-*Bis*(2-*hydroxy*-2,2-*diphenylethyl*)*pyridinato*(2 –)](4-tert-*butylpyridine*)*dioxoosmium*(VI) **7**. This complex was prepared by the same procedure as for **6** using 4-*tert*-butylpyridine (Found: C, 60.85; H, 4.85; N, 3.40. Calc. for $C_{42}H_{40}N_2O_4Os$: C, 61.00; H, 4.90; N, 3.40%). IR (Nujol): ν(Os=O) 834 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.35 (s, CH_3, 9 H), 4.19–4.68 (br, CH_2, 4 H) and 7.09–7.60 (m, H of phenyl and pyridine, 28 H). UV/VIS ($CHCl_3$): λ_{max}/nm (log ε) 245 (4.00), 264 (3.98) (sh), 298 (3.86) (sh) and 365 (3.26) (sh).

X-Ray Structure Determinations.—Crystal data. Complex **1**, $C_{33}H_{27}ClN_2O_2Os$, M = 709.24, space group $P2_1/n$, monoclinic, a = 9.672(1), b = 18.406(4), c = 16.026(3) Å, β = 104.83(1)°, U = 2758.0(8) Å^3, D_c = 1.708 g cm^{-3}, Z = 4, F(000) = 1392, μ(Mo-Kα) = 47.6 cm^{-1}, dimensions 0.06 × 0.16 × 0.24 mm.

Complex $\mathbf{5}\cdot 0.5C_6H_{14}$ crystallized as orange prisms from chloroform–hexane, $C_{40}H_{45}N_2O_4Os$, M = 808.00 (containing 0.5 C_6H_{14}), space group $P2_1/n$, monoclinic, a = 12.437(3), b = 20.151(9), c = 13.783(2) Å, β = 92.70(2)°, U = 3450(2) Å^3, D_c = 1.556 g cm^{-3}, Z = 4, F(000) = 1628, μ(Mo-Kα) = 37.39 cm^{-1}, dimensions 0.08 × 0.12 × 0.20 mm.

Intensities (h, $\pm k$, $\pm l$; 4845, 6066 unique data for complexes **1** and **5** respectively) were measured at 21 °C on a Nicolet R3m/V four-circle diffractometer (graphite-monochromatized Mo-Kα radiation, λ = 0.710 73 Å) using the ω–2θ variable scan (2.00–15.63° min^{-1} for **1**, 1.50–12.34° min^{-1} for **5**) technique in the bisecting mode up to $2\theta_{max}$ = 50°. The raw data were processed with the profile-fitting procedures of Diamond[4] and corrected for absorption using ψ-scan data.[5]

For each complex the osmium atom was located from a Patterson map, and the coordinates of the other non-hydrogen atoms were derived from successive Fourier difference syntheses. All non-hydrogen atoms were subjected to anisotropic refinement. The H atoms were generated geometrically (C–H bonds fixed at 0.96 Å) and assigned the same isotropic thermal parameter of 0.08 Å^2. In complex **5** the hexane molecule exhibiting two-fold disorder was modelled by six carbon atoms of half site occupancy.

All computations were performed using the SHELXTL-PLUS program package[6] on a DEC MicroVAX-II computer. Analytical expressions of neutral atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[7] For complex **1**, convergence for 3376 observed data ($|F_o| \geqslant 6\sigma|F_o|$) and 352 variables was reached at R = 0.029, R' = 0.031 and S = 1.105 with the weighting scheme $w = [\sigma^2(F_o) + 0.0002|F_o|^2]^{-1}$. The final Fourier difference map showed residual extrema in the range +1.23 to −0.64 e Å^{-3}. For complex **5**, convergence for 3814 observed data ($|F_o| \geqslant 6\sigma|F_o|$) and 423 variables was reached at R = 0.032, R' = 0.037 and S = 1.167 with the weighting scheme $w = [\sigma^2(F_o) + 0.0003|F_o|^2]^{-1}$. The final Fourier difference map showed residual extrema in the range +1.11 to −0.59 e Å^{-3}.

Atomic coordinates of the non-hydrogen atoms and selected bond distances and angles for complex **1** are listed in Tables 1 and 2 respectively. The corresponding values for complex **5** are listed in Tables 3 and 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis and Characterization.—The ligands. According to the procedure by Berg and Holm,[1] 2,6-dimethylpyridine was used as the starting material for the ligand synthesis. Two sequential steps of lithiation and subsequent reaction with benzophenone afforded the ligand H_2L in moderate yield. We have found that another compound, 2-(2-hydroxy-2,2-diphenylethyl)-6-methylpyridine was the major product of the reaction if the concentration of butyllithium used was inadvertently reduced. This compound has been mentioned in the literature.[8] Its well resolved ^{1}H NMR spectrum (90 MHz, $CDCl_3$) shows peaks at δ 8.11 (br, OH, 1 H), 7.52–6.81 (m, H of phenyl and pyridine, 13 H), 3.64 (s, CH_2, 2 H) and 2.43 (s, CH_3, 3 H).

The nitrido- and imido-osmium(VI) *complexes.* Reaction of $[NBu_4][OsNCl_4]$ with H_2L in methanol readily afforded complex **1**. Since the IR spectrum of **1** is little different from that of H_2L or **3**, it is likely that the Os≡N stretch occurs at a similar frequency to that of the ligand stretches.

Treatment of complex **1** with trifluoroacetic anhydride in the presence of a small amount of glacial acetic acid in dry dichloromethane gave the imido complex $[OsL(NCOCF_3)Cl(O_2CCF_3)]$ **2**. It exhibits an intense IR band at 1197 cm^{-1}, which is absent in the spectrum of H_2L or **3**. This band falls in the range of Os=NR vibrations[9] and can be reasonably considered as characteristic of the imido ligand. The ν(C=O) stretches of the trifluoroacetate and trifluoroacetylimide groups were observed at 1672 and 1719 cm^{-1} respectively. Formation of a trifluoroacetylimidometal complex from the reaction of a nitrido metal complex with trifluoroacetic anhydride was first reported by Groves and Takahashi.[10] However, in their case the trifluoroacetylimidomanganese(V) complex was a reactive intermediate and has not been isolated.

Reaction of $[OsO_2L]$ **3** (see below) with phenyl isocyanate in dry toluene led to the formation of the phenylimido complex $[OsL(NPh)_2]$ **4**. A reaction of this kind was suggested to proceed *via* oxo/imido exchange.[9] The IR spectrum of **4** shows a new intense band at 1233 cm^{-1}, which could be ascribed to the Os=N–Ph vibration.

Complexes **1**–**7** are all air-stable solids, which give well resolved ^{1}H NMR spectra showing the methylene, phenyl and pyridyl proton resonances of the alkoxide ligand at normal positions. This indicates the diamagnetic nature of the osmium complexes, in accordance with the low-spin d^2 electronic configuration of Os^{VI}.

The dioxoosmium(VI) *complexes.* Our earlier studies showed that reaction of $K_2[OsO_2(OH)_4]$ with macrocyclic amines did not yield the desired dioxo(macrocyclic amine)osmium(VI) complexes.[11] However, in this work, treatment of $K_2[OsO_2(OH)_4]$ with the diol ligand in methanol afforded **3** within half an hour. Since the IR spectrum of **3** shows three very intense bands in the region 800–900 cm^{-1} it is likely to be a five-co-ordinate *cis*-dioxo species. Very few *cis*-dioxoosmium(VI) complexes are known.[12] Similar reaction of $[MoO_2(acac)_2]$ (acac = acetylacetonate) with H_2L in methanol gave a *cis*-dioxomolybdenum(VI) complex.[1]

Complex **3** reacts readily with nitrogen bases, such as *tert*-butylamine, pyridine and *tert*-butylpyridine in chloroform to give six-co-ordinated dioxoosmium(VI) complexes. The IR spectrum of **5** shows sharp N–H stretching bands at 3268 and 3210 cm^{-1}. As expected for the *trans*-dioxo configuration, only one intense $\nu(OsO_2)$ stretch was observed for **5**–**7** at nearly the same frequency as those observed for dioxoosmium(VI) esters.[13]

Table 1 Atomic coordinates (× 10^5 for Os, × 10^4 for other atoms) of [OsN(L)Cl] **1**

Atom	*x*	*y*	*z*
Os	19 015(3)	15 943(1)	35 602(2)
Cl	1 154(2)	2 768(1)	3 837(1)
O(1)	2 997(4)	2 122(2)	2 904(3)
O(2)	−109(4)	1 405(2)	3 313(3)
N(1)	2 836(6)	1 396(3)	4 535(4)
N(2)	2 172(5)	579(3)	3 000(3)
C(1)	3 511(7)	1 813(3)	2 222(4)
C(2)	2 255(7)	1 752(4)	1 407(4)
C(3)	2 261(9)	1 260(5)	746(5)
C(4)	1 125(10)	1 231(6)	36(6)
C(5)	−8(10)	1 684(6)	−52(6)
C(6)	−44(8)	2 163(5)	582(6)
C(7)	1 087(8)	2 208(4)	1 316(5)
C(8)	4 709(7)	2 320(4)	2 097(5)
C(9)	4 896(8)	2 490(4)	1 297(5)
C(10)	6 049(10)	2 896(5)	1 210(7)
C(11)	7 059(10)	3 124(4)	1 926(7)
C(12)	6 873(9)	2 974(4)	2 731(6)
C(13)	5 708(8)	2 578(4)	2 821(5)
C(14)	4 213(7)	1 080(4)	2 526(5)
C(15)	3 228(7)	468(3)	2 579(4)
C(16)	3 392(8)	−211(4)	2 248(5)
C(17)	2 504(8)	−771(4)	2 322(5)
C(18)	1 458(8)	−659(3)	2 751(4)
C(19)	1 313(7)	13(3)	3 096(4)
C(20)	262(7)	122(3)	3 613(4)
C(21)	−835(7)	728(3)	3 275(4)
C(22)	−1 729(7)	600(3)	2 347(4)
C(23)	−2 271(8)	−74(4)	2 064(5)
C(24)	−3 100(9)	−172(5)	1 238(5)
C(25)	−3 368(8)	399(5)	677(5)
C(26)	−2 851(9)	1 079(5)	940(5)
C(27)	−2 040(8)	1 175(4)	1 784(5)
C(28)	−1 823(6)	795(3)	3 894(4)
C(29)	−1 932(8)	1 445(4)	4 305(5)
C(30)	−2 809(9)	1 512(5)	4 851(6)
C(31)	−3 557(8)	947(5)	5 020(5)
C(32)	−3 453(7)	287(5)	4 637(5)
C(33)	−2 596(8)	211(4)	4 070(5)

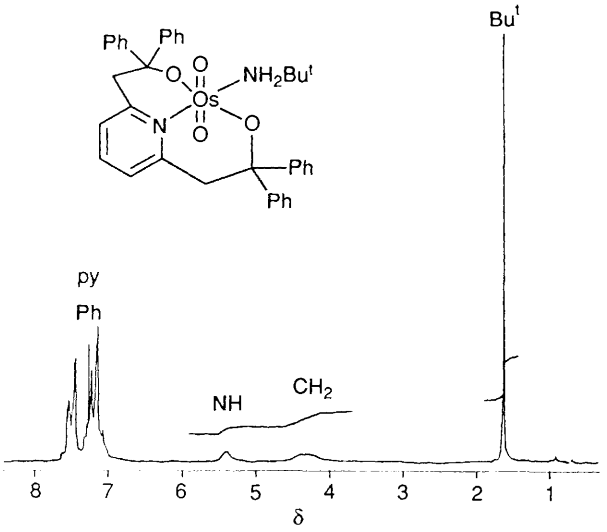

Fig. 1 Proton NMR spectrum of $[OsO_2L(NH_2Bu^t)]$ **5** (90 MHz, $CDCl_3$, $SiMe_4$ reference)

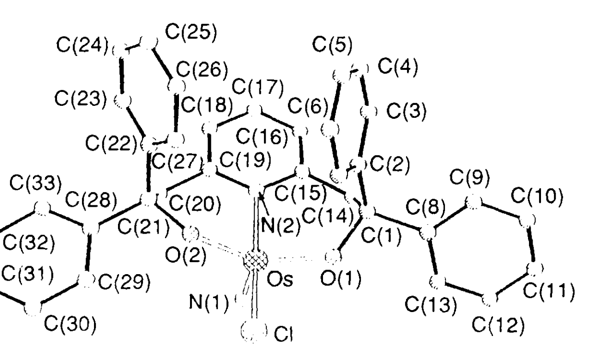

Fig. 2 A perspective view of [OsN(L)Cl] **1** with the atom labelling scheme

The dioxoosmium(VI) complexes **3** and **5**–**7** also give well resolved ^1H NMR spectra. A typical spectrum of **5** is shown in Fig. 1. The phenyl and pyridyl proton resonances of the alkoxide ligand and the *tert*-butyl proton resonances of the co-ordinated NH_2Bu^t are normal. The methylene protons unexpectedly give a broad peak like the amino protons.

Table 2 Bond lengths (Å) and angles (°) of [OsN(L)Cl] **1**

Os–Cl	2.356(2)	Os–O(1)	1.933(5)
Os–O(2)	1.915(4)	Os–N(1)	1.634(5)
Os–N(2)	2.119(5)		
Cl–Os–O(1)	83.1(1)	Cl–Os–O(2)	82.1(1)
O(1)–Os–O(2)	130.4(2)	Cl–Os–N(1)	98.4(2)
O(1)–Os–N(1)	112.7(2)	O(2)–Os–N(1)	116.2(3)
Cl–Os–N(2)	165.0(1)	O(1)–Os–N(2)	93.9(2)
O(2)–Os–N(2)	88.9(2)	N(1)–Os–N(2)	96.3(2)
Os–O(1)–C(1)	124.3(4)	Os–O(2)–C(21)	129.2(4)
Os–N(2)–C(15)	121.7(4)	Os–N(2)–C(19)	118.7(4)
C(15)–N(2)–C(19)	119.5(5)		

X-Ray Structural Determinations.—A perspective drawing of the molecular structure of complex **1** with the atomic numbering scheme is shown in Fig. 2. The co-ordination polyhedron around the osmium atom can be described as a distorted trigonal bipyramid with the chlorine atom and the nitrogen atom of the pyridine ring occupying the axial positions [Cl–Os–N(2) 165.0(1)°]. The molecule possesses approximate C_s symmetry with a pseudo-mirror plane passing through the atoms Os, Cl, N(1), N(2) and C(17). The two six-membered chelate rings are in the *gauche* conformation. The crystal structure consists of a packing of discrete molecules with normal van der Waals separations.

The measured Os–N(1) distance of 1.634(5) Å is comparable to those values found in other nitridoosmium(VI) complexes.[14] The Os–Cl bond distance [2.356(2) Å] is similar to that found in $[OsNCl_4]^-$ [14d] and $K_2[OsNCl_5]$.[14e]

X-Ray analysis revealed that $[OsO_2L(NH_2Bu^t)]$ **5** contains cocrystallized hexane in a 2:1 molar ratio. A perspective view of the molecular structure with the atomic numbering scheme is shown in Fig. 3. The co-ordination polyhedron around the osmium atom can be described as a distorted octahedron with two nitrogen atoms *trans* to each other in a *trans*-dioxo configuration. This is very different from the structure of $[MoO_2L(Me_2SO)]$ in which the two oxo ligands are *cis* to each other.[1] The two six-membered chelate rings in this complex are in the *gauche* conformation. The crystal structure consists of a packing of discrete complex and solvent molecules with normal van der Waals separations.

The Os–O(3) and Os–O(4) bond lengths are 1.733(5) and 1.749(4) Å respectively, which are similar to the Os=O distances found in $[OsO_2(en)_2]^{2+}$ (en = 1,2-diaminoethane)[15a] and dioxo[1,1,2,2-tetramethyl-*N*,*N*′-ethylenebis(3-*tert*-butyl salicyli-

Table 3 Atomic coordinates (× 10^5 for Os, × 10^4 for other atoms) of $[\mathrm{OsO_2L(NH_2Bu^t)}]\cdot0.5\mathrm{C_6H_{14}}$ **5**

Atom	*x*	*y*	*z*
Os	46 032(1)	49 503(1)	29 608(1)
O(1)	4 985(4)	3 985(2)	2 918(3)
O(2)	4 064(4)	5 876(2)	3 192(3)
O(3)	3 608(4)	4 842(2)	2 052(3)
O(4)	5 613(4)	5 081(2)	3 868(3)
N(1)	5 663(4)	5 237(3)	1 889(4)
C(1)	5 715(6)	3 735(3)	2 258(5)
C(2)	6 885(6)	3 787(3)	2 687(6)
C(3)	7 036(7)	3 777(4)	3 675(6)
C(4)	8 076(8)	3 724(4)	4 093(7)
C(5)	8 938(8)	3 685(5)	3 518(9)
C(6)	8 786(8)	3 720(5)	2 520(9)
C(7)	7 757(7)	3 773(4)	2 120(7)
C(8)	5 423(6)	2 998(3)	2 092(5)
C(9)	6 148(7)	2 482(3)	2 204(5)
C(10)	5 845(8)	1 841(4)	2 041(6)
C(11)	4 814(8)	1 685(4)	1 761(6)
C(12)	4 053(7)	2 189(4)	1 647(6)
C(13)	4 367(7)	2 837(4)	1 829(6)
C(14)	5 553(7)	4 089(3)	1 263(5)
C(15)	5 928(6)	4 791(3)	1 202(5)
C(16)	6 536(6)	4 992(4)	419(5)
C(17)	6 873(7)	5 638(4)	365(6)
C(18)	6 633(6)	6 078(4)	1 080(6)
C(19)	6 020(6)	5 871(3)	1 843(5)
C(20)	5 763(6)	6 344(3)	2 647(5)
C(21)	4 528(6)	6 449(3)	2 796(5)
C(22)	4 448(6)	6 997(3)	3 572(5)
C(23)	4 840(7)	6 867(4)	4 501(6)
C(24)	4 787(7)	7 334(5)	5 244(6)
C(25)	4 310(8)	7 919(4)	5 052(6)
C(26)	3 891(8)	8 063(4)	4 142(6)
C(27)	3 963(7)	7 601(3)	3 406(6)
C(28)	3 941(6)	6 656(3)	1 849(5)
C(29)	2 901(7)	6 446(4)	1 638(6)
C(30)	2 309(7)	6 684(4)	835(6)
C(31)	2 756(8)	7 133(4)	232(6)
C(32)	3 790(8)	7 342(4)	403(6)
C(33)	4 391(7)	7 113(3)	1 204(5)
N(2)	3 614(5)	4 631(3)	4 098(4)
C(34)	2 457(6)	4 444(3)	4 023(5)
C(35)	1 844(7)	5 053(4)	3 645(7)
C(36)	2 131(7)	4 258(4)	5 044(5)
C(37)	2 309(7)	3 855(4)	3 347(6)
C(38)*	5 590(10)	−127(12)	4 906(12)
C(39)	5 687(14)	123(14)	3 853(12)
C(40)	4 572(16)	444(13)	3 684(15)
C(41)	4 629(15)	−267(9)	4 768(10)
C(42)	4 443(14)	−27(12)	3 737(10)
C(43)	5 465(15)	273(11)	3 354(13)

* The two-fold disordered solvent molecule, hexane, was treated as C(38)–C(40) and C(41)–C(43), each of half site occupancy.

Table 4 Selected bond lengths (Å) and angles (°) of $[\mathrm{OsO_2L(NH_2Bu^t)}]$

Os–O(1)	2.004(4)	Os–O(2)	2.012(4)
Os–O(3)	1.733(5)	Os–O(4)	1.749(4)
Os–N(1)	2.106(5)	Os–N(2)	2.136(6)
N(2)–C(34)	1.486(9)		
O(1)–Os–O(2)	170.2(2)	O(1)–Os–O(3)	91.1(2)
O(2)–Os–O(3)	89.9(2)	O(1)–Os–O(4)	90.2(2)
O(2)–Os–O(4)	88.9(2)	O(3)–Os–O(4)	178.5(2)
O(1)–Os–N(1)	95.1(2)	O(2)–Os–N(1)	94.7(2)
O(3)–Os–N(1)	88.7(2)	O(4)–Os–N(1)	90.5(2)
O(1)–Os–N(2)	82.8(2)	O(2)–Os–N(2)	87.4(2)
O(3)–Os–N(2)	94.4(2)	O(4)–Os–N(2)	86.6(2)
N(1)–Os–N(2)	176.3(2)	Os–N(2)–C(34)	128.0(4)

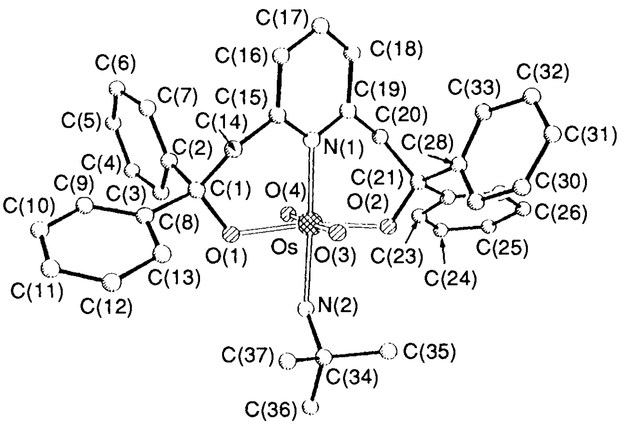

Fig. 3 A perspective view of $[\mathrm{OsO_2L(NH_2Bu^t)}]$ **5** with the atom labelling scheme

deneiminato)]osmium(IV).[15b] The Os–N(2) bond length of 2.136(6) Å is significantly longer than the Os–N distances [1.710(8) and 1.719(8) Å] in bis(*tert*-butylimido)dioxoosmium,[16] indicating that the ligand composed of N(2) and C(34)–C(37) is a *tert*-butylamine rather than a *tert*-butylimido group. The Os–O(1) and Os–O(2) bond distances [2.004(4) and 2.012(4) Å respectively] are comparable to the Os–O single bond length (2.03 Å) found in $\mathrm{K_2[OsO_2(OH)_4]}$.[17] Atoms O(1) and O(2) are *trans* to each other with the O(1)–Os–O(2) axis deviating slightly from linearity [170.2(2)°].

Electrochemistry and Reactivities.—In acetonitrile complexes **1** and **5** undergo irreversible electrochemical oxidation at potentials of 1.76 and 1.4 V *vs.* Ag–$\mathrm{AgNO_3}$ (0.1 mol $\mathrm{dm^{-3}}$) respectively. All the newly prepared oxo-, nitrido- and imido-osmium complexes are unreactive towards alkenes. However, **1** reacted with $\mathrm{PPh_3}$ in refluxing acetonitrile to give O=$\mathrm{PPh_3}$.

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