Addition of Carbenes to an Osmium(VI) Nitride Complex

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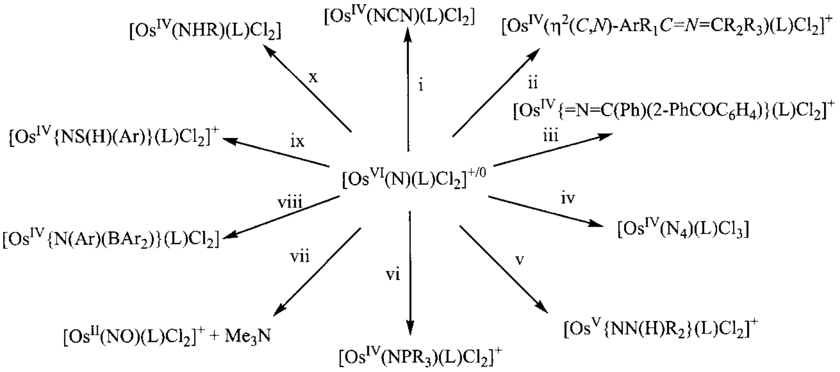
A series of osmium(VI) nitride complexes containing 8-quinolinolato ligands, $[Os^{VI}(N)(X\text{-}Q)_2Cl]$ (X = H, 5-Cl, 5-NO_2, 2-Me; **1a**–**d**), have been synthesized by reaction of HX-Q with $[nBu_4N][Os^{VI}(N)Cl_4]$ in the presence of 2,6-dimethylpyridine. The $\nu(Os{\equiv}N)$ stretches of these compounds occur at 1056–1075 cm^{-1}, and are within the range (1050–1120 cm^{-1}) found for most osmium nitride species. The structure of **1d** has been determined by X-ray crystallography. The osmium center adopts a distorted octahedral geometry, and the two quinolinolato ligands are *cis* to each other. The three N atoms are in a facial arrangement, and the Os≡N bond distance is 1.644(6) Å. Complex **1c** readily reacts with the carbene precursors bis(1,3-dialkylimidazolidin-2-ylidene) ($L^R{}_2$; R = Me, Et, or CH_2Ph) to produce the osmium(IV) azavinylidene species, $[Os^{IV}(N{=}L^R)(NO_2\text{-}Q)_2Cl]$, which are derived from the formal addition of the carbenes L^R to $Os^{VI}{\equiv}N$. The structure of $[Os^{IV}(N{=}L^{Et})(NO_2\text{-}Q)_2Cl]$ (**2b**) has been determined by X-ray crystallography. The osmium center has a distorted octahedral geometry in which the facial arrangement of the three N atoms is retained. The Os(1)–N(5) distance of 1.875(6) Å is rather long and, together with the rather acute Os(1)–N(5)–C(19) angle of 133.8(5)°, indicates that there is no significant multiple-bond character in the Os(1)–N(5) bond.

Introduction

Osmium(VI) nitride species containing nitrogen-based ligands, such as *cis*- and *trans*-$[Os^{VI}(N)(tpy)Cl_2]^+$ (tpy = 2,2′:6′,2′′-terpyridine), $[Os^{VI}(N)(tpm)Cl_2]^+$ [tpm = tris(1-pyrazolyl)methane], $[Os^{VI}(N)(Tp)Cl_2]$ [Tp^- = hydrotris(1-pyrazolyl)borate], and $[Os^{VI}(N)(bpy)Cl_3]$ (bpy = 2,2′-bipyridine), have been shown to exhibit novel electrophilic properties.[1–14] A variety of reagents such as phosphanes, amines, cyanide, azide, Grignard reagents, arylboranes, amine *N*-oxides, alkenes, and disubstituted benzenethiols have been reported to add to the nitride ligand.[1–14] These reactions are summarised in Scheme 1.



Scheme 1.Electrophilic reactions of osmium(VI) nitrido complexes: i) L = tpy, CN^-; ii) L = tpy, alkenes; iii) L = tpy, 1,3-diphenylisobenzofuran; iv) L = bpy, N_3^-; v) L = tpy/tpm, HNR_2 [R = Et, 1/2$(CH_2)_4O$, 1/2$(CH_2)_4CH_2$]; vi) L = tpy, PR_3; vii) L = tpy, Me_3NO; viii) L = Tp, arylboranes; ix) L = tpy, ArSH (Ar = 3,5-$Me_2C_6H_3$); x) L = Tp, RMgCl

We are interested in tuning the reactivities of these osmium(VI) nitride complexes by replacing tpy or Tp^- with other chelating ligands. We report here the synthesis of a series of new electrophilic osmium(VI) nitride complexes containing 8-quinolinolato ligands. These are the first examples of high-valent osmium complexes containing 8-qui-

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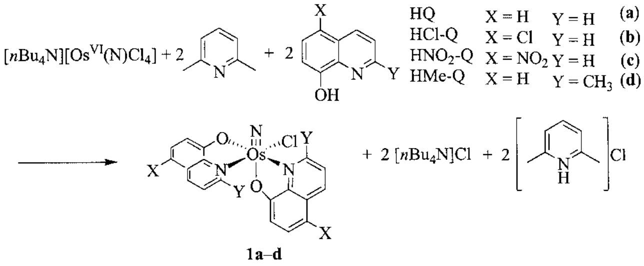
nolinolato ligands. We also report the reaction of the 5-nitro-8-quinolinolato complex with the carbene precursors bis(1,3-dialkylimidazolidin-2-ylidene) (L^R_2; R = Me, Et, or CH_2Ph) to produce (azavinylidene)osmium(IV) species that are derived from the formal addition of the carbenes L^R to $Os^{VI}{\equiv}N$. This is the first example of the addition of a carbene fragment to a nitride ligand, an important "missing" reaction for electrophilic metal nitride species.

Results and Discussion

Complexes **1a–d** were prepared in 55–65% yields from the reaction of $[nBu_4N][Os^{VI}(N)Cl_4]$ with the appropriate 8-hydroxyquinoline at room temperature in methanol in the presence of 2,6-dimethylpyridine, which functions as a mild base (Scheme 2).



Scheme 2. Preparation of osmium nitride complexes

These complexes are air-stable, diamagnetic, orange crystalline solids. They were characterized by ^1H NMR and IR spectroscopy, and elemental analysis (see Exp. Sect.). The ν(Os≡N) stretches of these complexes occur at 1056–1075 cm^{-1}, and are within the range (1050–1120 cm^{-1}) found for most osmium nitride species.[15–17] The assignment of the ν(Os≡N) stretches was supported by ^{15}N labeling. The structure of **1d** was determined by X-ray crystallography (Figure 1). The osmium center adopts a distorted octahedral geometry, and the two quinolinolato ligands are *cis* to each other. The three N atoms are in a facial arrangement. The Os≡N bond length of 1.644(6) Å is within the range (1.52–1.70 Å) found for other osmium nitride complexes.[3,17,18] The Os(1)–O(2) and Os(1)–O(1) bond lengths are 2.111(4) and 1.974(4) Å, respectively. The long Os(1)–O(2) distance reflects the rather large *trans* influence of the nitride ligand; it is assumed that **1a–c** also have the same configuration as **1d**. This is supported by their ^1H NMR spectra, which show that all four complexes have similar patterns.

The reaction of **1c** with bis(1,3-dialkylimidazolidin-2-ylidene) (L^R_2; R = Me, Et, or CH_2Ph) in CH_2Cl_2 under argon produces the (azavinylidene)osmium(IV) complexes **2a–c** as air-stable, dark-red, rod-shaped crystals in 40–46% yield (Scheme 3). However, no reaction occurs between L^R_2 and **1a**, **1b**, or **1d**.Complex **1c** is expected to be the most electrophilic among the four nitride species due to the presence of the electron-withdrawing nitro group in the 8-quinolinolato ligand.

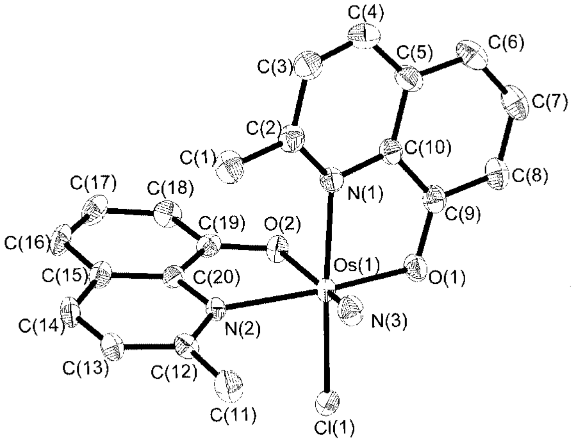
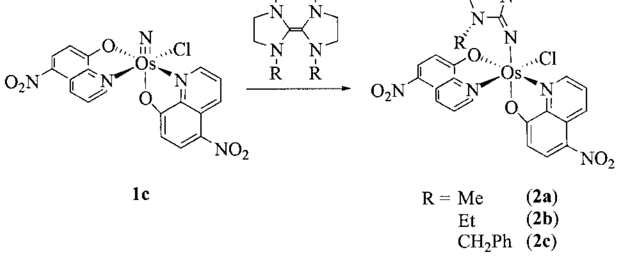


Figure 1.Molecular structure of **1d**



Scheme 3. Reaction of osmium nitride complex **1c** with L^R_2

The IR spectra (KBr) of the osmium(IV) complexes **2a–c** exhibit bands at around 2900 cm^{-1}, which correspond to the aliphatic C–H stretches of the alkyl groups on the imidazolin-2-ylidene ring. Complex **2b** has a room-temperature magnetic moment of 2.07 μ_B, which is consistent with its formulation as a d^4 Os^{IV} complex with a $d\pi_1^2\ d\pi_2^1\ d\pi_3^1$ electronic configuration. (Phosphoraniminato)osmium(IV) complexes have slightly lower magnetic moments of around 1.8 μ_B.[18,19] These magnetic moments are much lower than the spin-only value of 2.8 μ_B due to spin-orbit coupling.

The structure of **2b** was determined by X-ray crystallography (Figure 2). The osmium center has a distorted octahedral geometry in which the facial arrangement of the three N atoms is retained. The Os(1)–N(5) distance of 1.875(6) Å is within the range found for other (azavinylidene)osmium complexes (1.78–1.88 Å).[13,20] The Os(1)–N(5)–C(19) angle of 133.8(5)° is, however, the smallest among (azavinylidene)osmium complexes (152–176°).[13,20] The similar Os(1)–O(4) and Os(1)–O(1) distances [2.019(3) and 2.048(4) Å respectively] indicate that the *trans* influence of the azavinylidene ligand is negligible.

Complexes **2a–c** have extensive redox chemistry. Figure 3 displays the cyclic voltammogram of **2b** in CH_3CN (0.1 M $[nBu_4N][PF_6]$) recorded at a glassy-carbon working electrode. Three reversible waves appear at $E_{1/2}$ = +1.06 V (ΔE_p = 66 mV), +0.05 V (ΔE_p = 56 mV), and –0.95 V (ΔE_p = 64 mV) vs. ferrocenium/ferrocene (Fc^+/Fc), which are assigned to metal-centered $Os^{VI/V}$, $Os^{V/IV}$, and $Os^{IV/III}$ couples, respectively (Figure 3). There is also a quasi-reversible wave

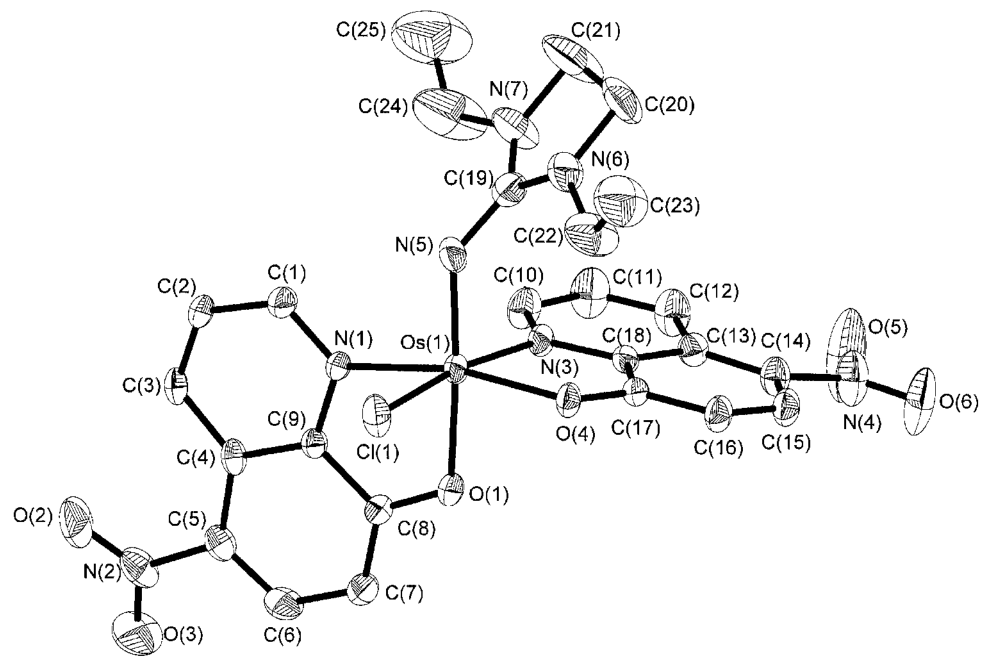


Figure 2. Molecular structure of **2b**

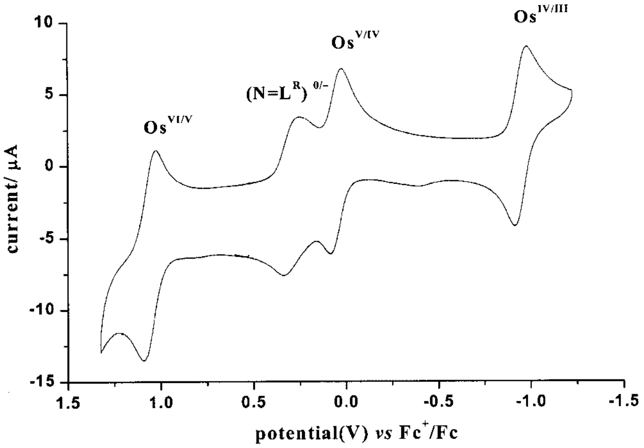


Figure 3. Cyclic voltammogram of $[Os^{IV}(N{=}L^{Et})(NO_2\text{-}Q)_2Cl]$ (**2b**) in CH_3CN (0.1 M $[nBu_4N][PF_6]$), scan rate = 100 mV s^{-1}

at $E_{1/2} = +0.29$ V ($\Delta E_p = 86$ mV), which is assigned to oxidation of the azavinylidene ligand, $(N{=}L^{Et})^- \rightarrow (N{=}L^{Et})$. The electrochemistry of **2b** is represented by Equation (1).

$$[Os^{VI}\{(N{=}L^{Et})^0\}(NO_2\text{-}Q)_2Cl]^{3+} \underset{-e}{\overset{+e}{\rightleftharpoons}} [Os^{V}\{(N{=}L^{Et})^0\}(NO_2\text{-}Q)_2Cl]^{2+} \underset{-e}{\overset{+e}{\rightleftharpoons}}$$

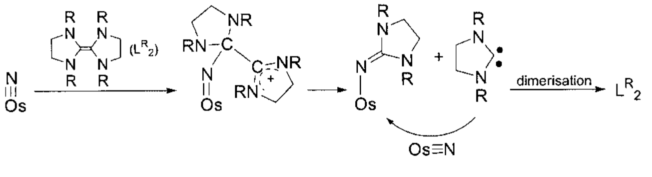
$$[Os^{IV}\{(N{=}L^{Et})\}(NO_2\text{-}Q)_2Cl] \underset{-e}{\overset{+e}{\rightleftharpoons}} [Os^{III}\{(N{=}L^{Et})\}(NO_2\text{-}Q)_2Cl] \quad (1)$$

Similar electrochemical behavior is found for **2a** and **2c**; the electrochemical data for **2a–c** are collected in Table 1. The $E_{1/2}$ of the quasi-reversible wave shifts from 0.29 V to 0.24 V on going from CH_3 or C_2H_5 to the more electron-rich CH_2Ph substituent, in accordance with its assignment as a ligand-centered redox couple.

Table 1. Electrochemical data for $[Os^{IV}(N{=}L^R)(NO_2\text{-}Q)_2Cl]$ (**2a**–**c**) in 0.1 M $[nBu_4N][PF_6]/CH_3CN$; scan rate = 100 mV s^{-1}; the errors in the potentials are typically 10 mV

	$E_{1/2}$ [V vs. Fc/Fc$^+$]			
	$Os^{VI/V}$	$(N = L^R)^{0/-}$	$Os^{V/IV}$	$Os^{IV/III}$
2a (R = Me)	1.06	0.29	0.06	–0.96
2b (R = Et)	1.06	0.29	0.05	–0.95
2c (R = CH_2Ph)	1.05	0.24	0.03	–1.01

The electron-rich alkenes L^R_2 are well-known carbene precursors; they react with a variety of transition-metal complexes to produce carbene complexes of the type $M{=}L^R$.[21,22] The work reported here, however, is the first example of the reaction of L^R_2 with a nitride complex that results in the formal addition of the carbene L^R to the nitride ligand. A similar, but much faster, reaction occurs between **1c** and the stable, commercially available carbene L^R (R = *tert*-butyl, 1,3-di-*tert*-butylimidazol-2-lylidene); however, in this case, attempts to purify the product have so far been unsuccessful. A proposed mechanism for the reaction of Os≡N with L^R_2, which is similar to that proposed for the formation of (carbene)metal compounds between metal complexes and L^R_2,[21] is shown in Scheme 4. It is generally believed that L^R_2 does not dissociate into the free carbene L^R prior to reaction with metal complexes. Hence, we suggest that L^R_2 reacts directly with Os≡N to produce the (azavinylidene)Os^{IV} compound.



Scheme 4. Proposed mechanism for the reaction of Os≡N with L^R_2

Conclusions

A series of osmium(VI) nitride complexes containing 8-quinolinolato ligands, $[Os^{VI}(N)(X\text{-}Q)_2Cl]$ (X = H, 5-Cl, 5-NO_2, 2-Me; **1a–d**), have been synthesized by reaction of HX-Q with $[nBu_4N][Os^{VI}(N)Cl_4]$ in the presence of 2,6-dimethylpyridine. Among these complexes **1c** is the most electrophilic, and it reacts readily with the carbene precursors bis(1,3-dialkylimidazolidin-2-ylidene) (L^R_2; R = Me, Et, or CH_2Ph) to produce a series of (azavinylidene)osmium(IV) species, $[Os^{IV}(N{=}L^R)(NO_2\text{-}Q)_2Cl]$, that are derived from the formal addition of the carbenes L^R to $Os^{VI}{\equiv}N$.

Experimental Section

Reagents and Physical Measurements: The complexes $[nBu_4N][Os^{VI}(N)Cl_4]$ and $[nBu_4N][Os^{VI}(^{15}N)Cl_4]$[23,24] and the electron-rich olefins bis(1,3-dialkylimidazolidin-2-ylidene)[25] were prepared by literature procedures. Acetonitrile was first heated to reflux in the presence of calcium hydride and then distilled under argon. Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized three times from boiling ethanol and dried in vacuo at 120 °C for 1 d before use. The 8-hydroxyquinoline ligands were purchased from Aldrich and were used as received. All other chemicals were of reagent grade and used without further purification. IR spectra were obtained from KBr discs with a Bomen MB-120 FTIR spectrophotometer. UV/Vis spectra were recorded with either a Perkin–Elmer Lamda 19 or a Shimadzu UV3100 spectrophotometer. ^1H NMR spectra were recorded with a Varian (300MHz) FT NMR spectrometer. The chemical shifts (δ, ppm) are reported relative to tetramethylsilane (TMS). Elemental analyses were performed with an Elementar Vario EL Analyzer. Cyclic voltammograms were obtained with a PAR model 273 potentiostat. A glassy-carbon disk working electrode and an $Ag/AgNO_3$ reference electrode were used. The supporting electrolyte was 0.1 M $[nBu_4N]PF_6$ in CH_3CN.

$[Os^{VI}(N)(Q)_2Cl]$ (1a): 8-Hydroxyquinoline (HQ; 50 mg, 0.34 mmol) was added to a solution of$[nBu_4N][Os^{VI}(N)Cl_4]$ (100 mg, 0.17 mmol) in 10 mL of methanol. After stirring for 15 min, 2,6-lutidine (0.5 mL) was added and the resulting orange solution was stirred for another 30 min. The orange solid was collected by filtration, washed with methanol, and dried in vacuo. Yield 47 mg (53%). $C_{18}H_{12}ClN_3O_2Os$ (528.01): calcd. C 40.95, H 2.27, N 7.96; found C 41.07, H 2.52, N 7.82. UV/Vis (DMF): λ_{max} = 266 nm (ε = 38700 $dm^3\,mol^{-1}\,cm^{-1}$), 340 (3790), 407 (6710). IR (KBr): $\tilde{\nu}$ = 1573 cm^{-1} (s), 1500 (s), 1464 (s), 1381 (s), 1319 (s), 1056 (w, OsN) [1025 (w, $Os^{15}N$)]. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 6.57 (d, 1 H), 7.27 (d, 1 H), 7.46 (t, 1 H), 7.61 (m, 3 H), 7.80 (t, 1 H), 7.94 (m, 1 H), 8.32 (d, 1 H), 8.73 (d, 1 H), 8.82 (d, 1 H), 9.25 (d, 1 H) ppm.

$[Os^{VI}(N)(Cl\text{-}Q)_2Cl]$ (1b): This complex was prepared by a procedure similar to that for **1a** using 5-chloro-8-hydroxyquinoline (61 mg, 0.34 mmol). Yield 58 mg (57%). $C_{18}H_{10}Cl_3N_3O_2Os$ (596.92): calcd. C 36.22, H 1.69, N 7.04; found: C, 35.89, H 1.86, N 6.83. UV/Vis (DMF): λ_{max} = 269 nm (ε = 13800 $dm^3\,mol^{-1}\,cm^{-1}$), 419 (3030). IR (KBr): $\tilde{\nu}$ = 1570 cm^{-1} (w), 1498 (s), 1457 (s), 1368 (s), 1302 (w), 1058 (w, OsN) [1027 (w, OsN^{15})]. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 6.58 (d, 1 H), 7.61 (d, 1 H), 7.63 (d, 1 H), 7.78 (m, 1 H), 8.54 (d, 1 H), 8.87 (m, 2 H), 8.37 (d, 1 H) ppm.

$[Os^{VI}(N)(NO_2\text{-}Q)_2Cl]$ (1c): This complex was prepared by a procedure similar to that for **1a** using 8-hydroxy-5-nitroquinoline (65 mg, 0.34 mmol). Yield 66 mg (63%). $C_{18}H_{10}ClN_5O_6Os$ (618.01): calcd. C 34.99, H 1.62, N 11.33; found: C, 35.17, H 1.86, N 10.97. UV/Vis (DMF): λ_{max} = 268 nm (ε = 9760 $dm^3\,mol^{-1}\,cm^{-1}$), 419 (8410). IR (KBr): $\tilde{\nu}$ = 1601 cm^{-1} (w), 1503 (s), 1462 (s), 1298 (vs), 1075 (w, OsN) [1040 (w, $Os^{15}N$)]. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 6.67 (d, 1 H), 7.75 (d, 1 H), 7.86 (m, 1 H), 8.27 (m, 1 H), 8.60 (d, 1 H), 8.82 (d, 1 H), 8.88 (d, 1 H), 9.48 (d, 1 H), 9.58 (m, 2 H) ppm.

$[Os^{VI}(N)(Me\text{-}Q)_2Cl]$ (1d): This orange complex was prepared by a procedure similar to that for **1a** using 8-hydroxy-5-methylquinoline (54 mg, 0.34 mmol). Yield 57 mg (60%). $C_{20}H_{16}ClN_3O_2Os$ (556.07): calcd. C 43.2, H 2.88, N 7.55; found: C, 43.43, H 3.24, N 7.34. UV/Vis (DMF): λ_{max} = 269 nm (ε = 14100 $dm^3\,mol^{-1}\,cm^{-1}$), 394 (2110). IR (KBr): $\tilde{\nu}$ = 1563 cm^{-1} (s), 1458 (s), 1324 (w), 1268 (w), 1056 (w, OsN) [1024 (w, $Os^{15}N$)]. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 2.15 (s, 3 H), 6.40 (d, 1 H), 7.15 (d, 1 H), 7.27 (t, 1 H), 7.50 (m, 3 H), 7.68 (t, 1 H), 8.00 (d, 1 H), 8.55 (m, 2 H) ppm.

$[Os^{IV}(N{=}L^{Me})(NO_2\text{-}Q)_2Cl]$ (2a): Complex **1c** (100 mg, 0.16 mmol) was added under argon to bis(1,3-dimethylimidazolidin-2-ylidene) L^{Me}_2 (31 mg, 0.16 mmol), in 15 mL of CH_2Cl_2, and the mixture was stirred for 24 h to give a red solution. After filtration, the solution was loaded onto a silica-gel column and eluted with acetone/CH_2Cl_2 (1:5). The red solid was recrystallized from CH_3CN/CH_3OH. Yield 49 mg (43%). $C_{23}H_{20}ClN_7O_6Os$ (716.16): calcd. C 38.57, H 2.82, N 13.69; found: C, 38.74, H 2.87, N 13.51. UV/Vis (CH_2Cl_2): λ_{max} = 254 nm (ε = 40300 $dm^3\,mol^{-1}\,cm^{-1}$), 301 (17400), 393 (16700), 449 (19800), 480 (19600). IR (KBr): $\tilde{\nu}$ = 3105 cm^{-1} (w, CH), 2878 (w, CH), 1593 (w), 1577 (w), 1559 (s), 1503 (s), 1450 (w), 1409 (w), 1286 (vs), 1186 (w), 1145 (w), 1102 (w), 1010 (w).

$[Os^{IV}(N{=}L^{Et})(NO_2\text{-}Q)_2Cl]$ (2b): This complex was prepared by a procedure similar to that for **2a**, using bis(1,3-diethylimidazolidin-2-ylidene) L^{Et}_2 (41 mg, 0.16 mmol). Crystals suitable for X-ray crystallography were obtained from acetonitrile/methanol. Yield 55 mg (46%). $C_{25}H_{24}ClN_7O_6Os$ (744.21): calcd. C 40.35, H 3.26, N 13.18; found C 40.27, H 3.18, N 12.95. UV/Vis (CH_2Cl_2): λ_{max} = 491 nm (ε = 38800 $dm^3\,mol^{-1}\,cm^{-1}$), 299 (30800), 393 (31000), 254 (72800). IR (KBr): $\tilde{\nu}$ = 2966 cm^{-1} (w), 2925 (w), 2869 (w, CH), 1596 (w), 1562 (w), 1503 (s), 1453 (w), 1288 (vs, NO), 1186 (w), 1145 (w), 1100 (w), 1009 (w).

$[Os^{IV}(N{=}L^{CH_2Ph})(NO_2\text{-}Q)_2Cl]$ (2c): The complex was prepared by a procedure similar to that for **2a**, using bis(1,3-dibenzylimidazolidin-2-ylidene), $L^{CH_2Ph}_2$ (81 mg, 0.16 mmol). Yield 49 mg (39%). $C_{35}H_{28}ClN_7O_6Os$ (868.32): calcd. C 48.41, H 3.26, N 11.29; found C 48.58, H 3.24, N 11.35. UV/Vis (CH_2Cl_2): λ_{max} = 253 nm (ε = 41800 $dm^3\,mol^{-1}\,cm^{-1}$), 296 (16900), 378 (17800), 496 (22800). IR (KBr): $\tilde{\nu}$ = 3105 cm^{-1} (w), 3060 (w, CH), 1601 (w), 1505 (s), 1299 (vs, NO), 1193 (w), 1148 (w), 1100 (w), 1071 (w).

X-ray Crystallographic Study: Intensity data were collected at ambient temperature using a Rigaku AFC7R diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) in the ω-scan mode. Details of the intensity data collection and crystal data are given in Table 2. Selected bond lengths and angles for **1d** and **2b**

are given in Table 3 and Table 4, respectively. The data were corrected for Lorentz and polarization effects. Absorption corrections by the ψ-scan method or an approximation by inter-image scaling were applied. The structures were resolved by direct methods (SIR92[26] or SHELXS-86[27]), and expanded using Fourier techniques (DIRDIF94[28]). Hydrogen atoms are included but not refined. All calculations were performed using the TeXsan[29] crystallographic software package from Molecular Structure Corporation. CCDC-226391 (**1d**) and -226392 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table 2. Summary of crystal data, details of data collection and solution and refinement parameters for **1d** and **2b**

	1d	**2b**
Empirical formula	$C_{20}H_{16}ClN_3O_2Os$	$C_{25}H_{24}ClN_7O_6Os$
M	556.02	744.1
Crystal color, habit	brown, plate	red, plate
Crystal size [mm]	0.25 × 0.22 × 0.04	0.48 × 0.10 × 0.03
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a [Å]	9.282(4)	14.154(2)
b [Å]	12.738(5)	13.267(2)
c [Å]	7.686(3)	15.1412(2)
α [°]	94.64(4)	–
β [°]	94.97(4)	110.46(1)
γ [°]	86.22(3)	–
Z	2	4
D_c [g cm^{-3}]	2.050	1.823
F(000)	532.00	1456.00
μ(Mo-K_α) [cm^{-1}]	72.43	48.52
Reflections collected	3381	17117
Unique reflections	3165	6415
R[a]	0.025	0.035
R_w[b]	0.034	0.029
Goodness of fit	1.27	1.09
Max. Δ/σ	0.00	0.00
No. of parameters	244	361
Max., min. residual density [e Å^{-3}]	0.72, –0.55	1.28, –0.56

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|)]^{1/2}$.

Table 3.Selected bond lengths [Å] and angles [°] for [Os^{VI}(N)(Me-Q)$_2$Cl] (**1d**)

Os(1)–N(1)	2.129(5)
Os(1)–N(2)	2.155(4)
Os(1)–N(3)	1.644(6)
Os(1)–O(1)	1.974(4)
Os(1)–O(2)	2.111(4)
Os(1)–Cl(1)	2.347(2)
N(3)–Os(1)–O(1)	103.7(2)
N(3)–Os(1)–O(2)	167.0(2)
N(3)–Os(1)–N(1)	91.1(2)
N(3)–Os(1)–N(2)	94.9(2)
N(3)–Os(1)–Cl(1)	100.7(2)
N(1)–Os(1)–O(1)	81.4(2)
N(2)–Os(1)–O(2)	76.8(2)

Table 4. Selected bond lengths [Å] and angles [°] for [Os(N=L^{Et})(NO$_2$-Q)$_2$Cl] (**2b**)

Os(1)–N(5)	1.875(6)
Os(1)–N(1)	2.083(4)
Os(1)–N(3)	2.059(5)
Os(1)–O(1)	2.048(4)
Os(1)–O(4)	2.019(3)
Os(1)–Cl(1)	2.365(2)
N(5)–C(19)	1.330(8)
N(5)–Os(1)–N(1)	96.0(2)
N(5)–Os(1)–N(3)	92.7(2)
N(5)–Os(1)–O(1)	173.2(2)
N(5)–Os(1)–O(4)	96.5(2)
N(5)–Os(1)–Cl(1)	91.5(2)
N(1)–Os(1)–O(1)	78.1(2)
N(3)–Os(1)–O(4)	79.7(2)
Os(1)–N(5)–C(19)	133.8(5)
N(7)–C(19)–N(6)	110.8(7)

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