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Nitrido-ruthenium(VI) and -osmium(VI) complexes containing chelating multianionic (N, O) ligands. Synthesis, crystal structures and reactions with triphenylphosphine

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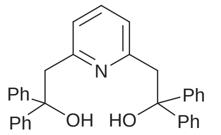
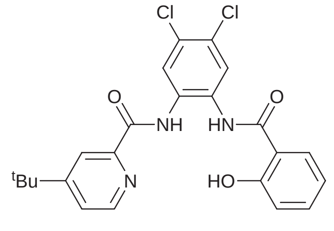
A series of nitrido-ruthenium(VI) and -osmium(VI) complexes containing chelating di-, tri- and tetra-anionic ligands was synthesized by ligand substitution reaction in methanol under room conditions in the presence of 2,6-dimethylpyridine. All the newly prepared complexes are air-stable diamagnetic solids. The crystal structures of seven complexes have been established by X-ray crystallography. The $Ru\equiv N$ (1.615–1.594 Å) and the $Os\equiv N$ (1.612–1.621 Å) bond distances are rather insensitive to the electron-donating power of the auxiliary ligands. All the nitridoruthenium(VI) complexes react spontaneously with triphenylphosphine, and the intermediate $[Ru^{IV}(N{=}PPh_3)L^1(py)Cl]$ has been isolated and characterized spectroscopically for the reaction with $[Ru^{VI}N(L^1)Cl]$. However, for those nitridoruthenium(VI) complexes bearing the tri- $(L^2)^{3-}$ and tetra-anionic $(L^{3,4})^{4-}$ ligands, the phosphiniminato-ruthenium(IV) intermediate undergoes further reaction with pyrazole to generate a bis(pyrazole)ruthenium(IV) complex as the product.

Introduction

The study of metal–ligand multiple bonded (M=X) complexes has received considerable attention.[1] Of our particular interest is the chemistry of high-valent oxo-, nitrido- and imido-ruthenium and -osmium complexes, and their reactivities toward organic substrates.[2] While high-valent nitrido-osmium(VI) complexes of some amine and/or polypyridyl ligands are known to exhibit interesting photochemistry[3] and electrochemistry,[4,5] related studies on the ruthenium(VI) analogues are sparse in the literature. Electrochemical studies revealed that high-valent oxoruthenium(VI) complexes are at least 500 mV more oxidizing than their osmium(VI) counterparts;[2,6] therefore, it is discernible that high-valent nitrido-ruthenium(VI) complexes could be rather electrophilic and reactive. Indeed, a $N\equiv Ru$ species has been postulated to be the active intermediate in the oxidation of bound ammonia to nitrite.[7] Herein we describe synthetic and structural studies of some nitrido-ruthenium(VI) and -osmium(VI) complexes containing chelating multianionic N, O ligands. Some of them have been characterized by X-ray crystallography, and their nitrogen atom transfer reactions to triphenylphosphine have also been examined.



H_2L^1



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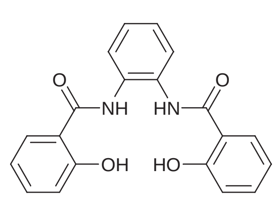

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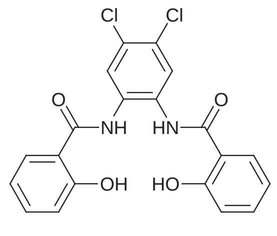

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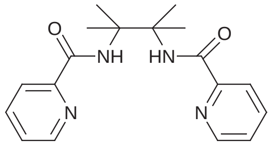


H_2L^5

Experimental

Materials

All solvents were purified by the standard methods before use. The compounds $[NBu^n_4][Ru^{VI}NCl_4]$,[8] 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridine (H_2L^1)[9] and 1,2-bis(2-hydroxybenzamido)benzene[10] (H_4L^3) were prepared according to the reported procedures.

Physical measurements

Infrared spectra were recorded as Nujol mulls on a Nicolet model 20 FXC FT-IR spectrometer, fast atom bombardment (FAB) mass spectra on a Finnigan MAT 95 mass spectrometer using 3-nitrobenzyl alcohol as matrix, electrospray (ES) mass spectra on a Finnigan LCQ mass spectrometer and NMR spectra using Bruker DPX 300 and 500 pulsed Fourier transform instruments. Cyclic voltammetric measurements were conducted using a Princeton Applied Research model 273 potentiostat with a glassy carbon electrode and Ag–$AgNO_3$ (0.1 mol dm^{-3} in MeCN) as the reference electrode, and the deaerated dichloromethane solutions in 0.10 M tetra-*n*-butylammonium hexafluorophosphate containing the sample complexes were scanned under an argon atmosphere. Elemental analyses were performed by Butterworth Co. Ltd., UK.

X-Ray crystallography

X-Ray diffraction data were collected on either a Rigaku

AFC7R or MAR diffractometer using graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) at 301 K. Intensity data were corrected for Lorentz-polarization effects, and the structures were solved by the Patterson method and expanded by Fourier methods (PATTY).[11] Structure refinements were performed by full-matrix least squares using the software package TEXSAN[12] on a Silicon Graphics Indy computer. For complexes **3a**, **3b** and **4a**, disorder in the terminal carbon atoms of one of the *n*-butyl groups of the [NBu$^n{}_4$]$^+$ cation was treated by assigning occupation numbers of *ca.* 0.5 to the disordered carbon atoms: 0.5 each to C(36) and C(37) in **3a**, as well as to C(36) and C(36′) in **3b**; 0.55 and 0.45 to C(36) and C(36′) in **4a**, where the thermal parameters of these disordered carbon atoms are comparable. For structures **5a** and **5b** the NH protons were located in the Fourier difference syntheses and their positional parameters included in the least squares refinement.

CCDC reference number 186/1097.

See http://www.rsc.org/suppdata/dt/1998/3183/ for crystallographic files in .cif format.

Ligand syntheses

1-(4-*tert*-Butylpyridine-2-carboxamido)-4,5-dichloro-2-(2-hydroxybenzamido)benzene (H_3L^2).[10] To a stirred anhydrous 1,4-dioxane (60 cm^3) solution of *N*-(2-amino-4,5-dichlorophenyl)-4-*tert*-butylpyridine-2-carboxamide (3.0 g, 8.9 mmol) was slowly added *O*-acetylsalicyloyl chloride (1.8 g, 9.0 mmol). After the mixture was stirred for 12 h water (*ca.* 100 cm^3) was added cautiously to the solution with stirring, and the resulting white precipitate was collected by filtration and washed with water. The solid was redissolved in 1,4-dioxane (50 cm^3), and concentrated hydrochloric acid (15 cm^3) added; the mixture was stirred for 12 h. The reaction mixture was treated by dropwise addition of water (*ca.* 100 cm^3) to induce precipitation of the product, and the solid was then collected on a frit and washed with water. The crude product was recrystallized from acetone. Yield: 2.4 g, 59%. IR (Nujol, cm^{-1}) 3275 (ν_{OH}), 3111 (ν_{NH}), 2846, 1667 ($\nu_{C=O}$) and 1645 ($\nu_{C=O}$). ^{1}H NMR (300 MHz, 298 K, CDCl$_3$) δ 1.38 (s, 9 H), 6.92 (m, 1 H), 7.00 (dd, 1 H, $J = 8.4$, 1.0), 7.43 (m, 1 H), 7.5 (dd, 1 H, $J = 5.2$, 1.9), 7.54 (s, 1 H), 7.75 (dd, 1 H, $J = 8.0$, 1.3), 8.02 (s, 1 H), 8.31 (d, 1 H, $J = 1.6$), 8.50 (dd, 1 H, $J = 5.2$, 0.5 Hz), 10.12 (s, 1 H), 10.32 (s, 1 H) and 12.05 (s, 1 H). ^{13}C NMR (75.47 MHz, 298 K, CDCl$_3$) δ 30.49, 35.24, 114.24, 118.67, 119.02, 119.90, 124.37, 124.61, 125.37, 126.38, 127.93, 129.32, 129.73, 130.32, 134.78, 147.93, 148.45, 162.19, 162.70, 164.28 and 168.72. MS *m*/*z* 458 (M^+) (Found: C, 60.18; H, 4.58; N, 9.23. Calc. for $C_{23}H_{21}Cl_2N_3O_3$: C, 60.27; H, 4.62; N, 9.17%).

1,2-Dichloro-4,5-bis(2-hydroxybenzamido)benzene (H_4L^4). A similar procedure was employed as for the preparation of H_3L^2. Yield: 1.8 g, 76%. IR (Nujol, cm^{-1}) 3280 (ν_{OH}), 3100 (ν_{NH}), 2880, 1650 ($\nu_{C=O}$). ^{1}H NMR [300 MHz, 298 K, (CD$_3$)$_2$CO] δ 6.96 (d, 4 H, $J = 7.9$), 7.47 (dt, 2 H, $J = 7.9$, 1.4), 8.02 (dd, 2 H, $J = 8.4$, 1.6 Hz), 8.14 (m, 2 H), 10.15 (s, 2 H) and 11.49 (s, 2 H). ^{13}C NMR [75.47 MHz, 298 K, (CD$_3$)$_2$CO] δ 116.61, 118.46, 120.37, 127.74, 129.19, 129.63, 131.76, 135.45, 160.65 and 168.62. MS *m*/*z* 417 (M^+) (Found: C, 57.49; H, 3.29; N, 6.81. Calc. for $C_{20}H_{14}Cl_2N_2O_4$: C, 57.57; H, 3.38; N, 6.71%).

2,3-Dimethyl-2,3-bis(pyridine-2-carboxamido)butane (H_2L^5). Pyridine-2-carboxylic acid (1.06 g, 8.17 mmol) was added to neat SOCl$_2$ (*ca.* 10 cm^3), and the mixture refluxed for 3 h. An excess of SOCl$_2$ was removed by vacuum evaporation. The solid residue was redissolved in dichloromethane (30 cm^3), and the solution added dropwise to another dichloromethane solution (30 cm^3) of 2,3-diamino-2,3-dimethylbutane (0.5 g, 4.31 mmol) and triethylamine (*ca.* 3 cm^3). The mixture was allowed to stand overnight with stirring. Removal of solvent under vacuum left an oily substance. The crude product was purified on a silica gel column using diethyl ether–light petroleum (bp 40–60 °C) (9:2 v/v) as the eluent. The product was obtained as a white solid. Yield: 0.85 g, 60%. IR (Nujol, cm^{-1}) 3100 (ν_{NH}), 3000, 2890, 1680 ($\nu_{C=O}$). ^{1}H NMR (300 MHz, 298 K, CDCl$_3$) δ 1.69 (s, 12 H), 7.39 (t, 2 H, $J = 6.1$), 7.82 (t, 2 H, $J = 7.7$), 8.18 (d, 2 H, $J = 7.7$), 8.57 (d, 2 H, $J = 3.8$ Hz) and 8.91 (s, 2 H). ^{13}C NMR (75.47 MHz, 298 K, CDCl$_3$) δ 22.34, 60.68, 121.80, 124.61, 125.82, 137.19, 147.96, 150.91 and 164.25. MS *m*/*z* 326 (M^+) (Found: C, 66.31; H, 6.82; N, 17.12. Calc. for $C_{18}H_{22}N_4O_2$: C, 66.24; H, 6.79; N, 17.17%).

Syntheses of nitrido-ruthenium(VI) and -osmium(VI) complexes

[Ru^{VI}N(L^1)Cl] 1. To a stirred solution of H_2L^1 (1 g, 2.1 mmol) and 2,6-dimethylpyridine (0.5 cm^3) in anhydrous chloroform (10 cm^3) was added a methanolic solution (30 cm^3) of [NBu$^n{}_4$][Ru^{VI}NCl$_4$] (1 g, 2.0 mmol) and the mixture stirred for 2 h. The purple precipitate formed was collected by filtration, and washed first with chloroform then with diethyl ether. The product was dried on a frit by vacuum suction. Yield: 0.46 g, 37% (Found: C, 63.70; H, 4.25; N, 4.45. Calc. for $C_{33}H_{27}ClN_2O_2Ru$: C, 63.92; H, 4.39; N, 4.52%); IR (Nujol, cm^{-1}) 3060, 2922, 1600, 1573 and 1025. ^{1}H NMR (300 MHz, 298 K, CDCl$_3$) δ 3.75 (d, 2 H, $J = 14.8$), 4.55 (d, 2 H, $J = 14.8$ Hz) and 6.9–8.2 (m, 23 H). FAB MS *m*/*z* 585 ($M^+ - Cl$) and 570 ($M^+ - Cl - N$).

[M^{VI}N(L^2)] 2 (M = Ru a or Os b). To a methanolic solution (30 cm^3) of [NBu$^n{}_4$][M^{VI}(N)Cl$_4$] (0.2 g, 0.4 mmol) were added H_3L^2 (0.13 g, 0.4 mmol) in chloroform (10 cm^3) and 2,6-dimethylpyridine (*ca.* 0.5 cm^{-3}). The mixture was stirred for 2 h and a brown precipitate gradually deposited. The brown solid was collected, washed with acetone, and then dried *in vacuo*. For **2a**: yield 0.10 g (56%) (Found: C, 48.36; H, 3.04; N, 9.76. Calc. for $C_{23}H_{18}Cl_2N_4O_3Ru$: C, 48.43; H, 3.18; N, 9.82%); IR (Nujol, cm^{-1}) 2890, 1680 ($\nu_{C=O}$), 1620 ($\nu_{C=O}$) and 1102; ^{1}H NMR [300 MHz, 298 K, (CD$_3$)$_2$SO] δ 1.51 (s, 9 H), 6.94 (t, 1 H, $J = 7.2$), 7.24 (d, 1 H, $J = 7.5$), 7.42 (t, 1 H, $J = 6.7$), 8.29 (m, 3 H), 8.69 (s, 1 H) and 9.30 (d, 2 H, $J = 5.7$ Hz); FAB MS *m*/*z* 571 ($M^+ + 1$) and 558 ($M^+ - N$). For **2b**: yield 0.19 g (72%) (Found: C, 41.66; H, 2.65; N, 8.44. Calc. for $C_{23}H_{18}Cl_2N_4O_3Os$: C, 41.89; H, 2.75; N, 8.49%). IR (Nujol, cm^{-1}) 2890, 1690 ($\nu_{C=O}$), 1620 ($\nu_{C=O}$) and 1068; ^{1}H NMR [300 MHz, 298 K, (CD$_3$)$_2$SO] δ 1.45 (s, 9 H), 6.93 (m, 1 H), 7.23 (d, 1 H, $J = 8.1$), 7.43 (m, 1 H), 8.23 (dd, 1 H, $J = 8.1$, 1.5), 8.29 (d, 2 H, $J = 2.6$ Hz), 8.66 (s, 1 H), 9.21 (s, 1 H) and 9.27 (m, 1 H); FAB MS *m*/*z* 661 ($M^+ + 1$).

[NBu$^n{}_4$][M^{VI}N(L^3)] 3 (M = Ru a or Os b). To a stirred methanolic solution (10 cm^3) of [NBu$^n{}_4$][M^{VI}NCl$_4$] (0.5 g, 1.0 mmol) was added H_4L^3 (0.35 g, 1.0 mmol) and 2,6-dimethylpyridine (*ca.* 0.5 cm^3), and the mixture was stirred for 1 d. Solvent evaporation by vacuum left an oily residue, which was chromatographed on an alumina column (activity 90, neutral) using chloroform as the eluent. The orange (Ru) or yellow (Os) band was collected in one portion and concentrated to *ca.* 2 cm^3 by rotary evaporation. Addition of diethyl ether to the red solution led to isolation of the complex as orange or yellow prism-shaped crystals. The crystalline solid was collected on a frit and dried *in vacuo*. For **3a**: yield 0.3 g (43%) (Found: C, 61.52; H, 6.76; N, 7.76. Calc. for $C_{36}H_{48}N_4O_4Ru$: C, 61.61; H, 6.89; N, 7.98%); IR (Nujol, cm^{-1}) 3066, 2850, 1615 ($\nu_{C=O}$), 1580 and 1073; ^{1}H NMR (300 MHz, 298 K, CDCl$_3$) δ 0.78 (t, 12 H, $J = 7.0$), 1.13 (m, 16 H), 2.63 (m, 8 H), 6.91 (m, 2 H), 6.99 (m, 2 H), 7.27 (d, 2 H, $J = 6.9$), 7.36 (m, 2 H), 8.20 (dd, 2 H, $J = 7.9$, 1.6 Hz) and 8.89 (m, 2 H); FAB MS (negative) *m*/*z* 460 (M^-). For **3b**: yield 0.54 g (68%) (Found: C, 54.48; H, 6.19; N, 7.22. Calc. for $C_{36}H_{48}N_4O_4Os$: C, 54.66; H, 6.12; N, 7.08%); IR (Nujol, cm^{-1}) 3064, 2580, 1625 ($\nu_{C=O}$), 1595 and 1108; ^{1}H NMR (300 MHz, 298 K, CDCl$_3$) δ 0.80 (t, 12 H, $J = 7.0$), 1.15

(m, 16 H), 2.63 (m, 8 H), 6.97 (m, 4 H), 7.36 (m, 4 H), 8.27 (d, 2 H, $J = 7.8$) and 8.97 (dd, 2 H, $J = 6.3$, 3.5 Hz); FAB MS (negative) m/z 548 (M^-).

$[NBu^n{}_4][M^{VI}N(L^4)]$ 4 (M = Ru a or Os b). The complexes were synthesized in a manner similar to that for **3**. For **4a**: yield 0.14 g, 53% (Found: C, 56.03; H, 6.06; N, 7.32. Calc. for $C_{36}H_{46}Cl_2N_4O_4Ru$: C, 56.10; H, 6.02; N, 7.27%); IR (Nujol, cm^{-1}) 3020, 2965, 2870, 1600 and 1010; ^1H NMR (300 MHz, 298 K, $CDCl_3$) δ 0.84 (t, 12 H, $J = 7.1$), 1.18 (m, 8 H), 1.32 (m, 8 H), 2.80 (m, 8 H), 6.93 (m, 2 H), 7.28 (d, 2 H, $J = 9.2$), 7.35 (m, 2 H), 8.19 (d, 2 H, $J = 7.9$ Hz) and 9.21 (s, 2 H); FAB MS (negative) m/z 528 (M^-). For **4b**: yield 0.66 g (77%) (Found: C, 50.33; H, 5.23; N, 6.67. Calc. for $C_{36}H_{46}Cl_2N_4O_4Os$: C, 50.28; H, 5.39; N, 6.52%); IR (Nujol, cm^{-1}) 3020, 2990, 2850, 1600($\nu_{C=O}$) and 1110; ^1H NMR (300 MHz, 298 K, $CDCl_3$) δ 0.85 (t, 12 H, $J = 7.1$), 1.19 (m, 8 H), 1.32 (m, 8 H), 2.76 (m, 8 H), 6.95 (m, 2 H), 7.37 (m, 4 H), 8.26 (dd, 2 H, $J = 8.0$, 1.5 Hz) and 9.28 (s, 2 H); FAB MS (negative) m/z 617 (M^-).

$[M^{VI}N(H_2L^5)Cl_3]$ 5 (M = Ru a or Os b]. To a stirred solution of $[NBu^n{}_4][M^{VI}(N)Cl_4]$ (0.5 g, 1.0 mmol) in methanol (10 cm^3) were added H_2L^5 (0.326 g, 1.0 mmol) in chloroform (5 cm^3) and a few drops of 2,6-dimethylpyridine and stirred for 3 h. The pink solid formed was collected, washed with methanol and dried *in vacuo*. For **5a**: yield 0.21 g (38%) (Found: C, 39.36; H, 4.22; N, 12.62. Calc. for $C_{18}H_{22}Cl_3N_5O_2Ru$: C, 39.46; H, 4.05; N, 12.78%); IR (Nujol, cm^{-1}) 3320 (ν_{NH}), 2950, 1650 ($\nu_{C=O}$), 1640 ($\nu_{C=O}$) and 1067; ^1H NMR (300 MHz, 298 K, $CDCl_3$) δ 1.53 (s, 6 H), 1.61 (s, 6 H), 7.53 (t, 1 H, $J = 6.0$), 7.92 (m, 2 H), 8.20 (d, 1 H, $J = 7.9$), 8.42 (t, 1 H, $J = 7.3$), 8.54 (s, 1 H), 8.59 (d, 1 H, $J = 4.4$), 8.78 (d, 1 H, $J = 7.9$), 9.27 (d, 1 H, $J = 7.1$ Hz) and 11.40 (s, 1 H); FAB MS m/z 512 ($M^+ - Cl$). For **5b**: yield 0.35 g (55%) (Found: C, 33.77; H, 3.55; N, 10.83. Calc. for $C_{18}H_{22}Cl_3N_5O_2Os$: C, 33.94; H, 3.48; N, 10.99%); IR (Nujol, cm^{-1}) 3320 (ν_{NH}), 2950, 1660 ($\nu_{C=O}$), 1640 ($\nu_{C=O}$) and 1112; ^1H NMR (300 MHz, 298 K, $CDCl_3$) δ 1.52 (s, 6 H), 1.62 (s, 6 H), 7.54 (dd, 1 H, $J = 7.1$, 4.7), 7.87 (t, 1 H, $J = 6.5$), 7.95 (dt, 1 H, $J = 7.8$, 1.4), 8.21 (d, 1 H, $J = 7.8$), 8.31 (t, 1 H, $J = 7.8$), 8.57 (s, 1 H), 8.60 (d, 1 H, $J = 4.4$), 8.82 (d, 1 H, $J = 8.0$), 9.15 (d, 1 H, $J = 5.4$ Hz) and 11.63 (s, 1 H); FAB MS m/z 637 (M^+) and 602 ($M^+ - Cl$).

Reactions with triphenylphosphine

$[Ru^{IV}(NPPh_3)L^1(py)Cl]$. Triphenylphosphine (42 mg, 0.16 mmol) was added under an argon atmosphere to a dichloromethane solution (20 cm^3) of complex **1** (100 mg, 0.16 mmol) and pyridine (1 cm^3) with stirring. An instantaneous change from yellow-orange to a dark green solution occurred; this was stirred for 1 h and the solvent removed by rotary evaporation. The green residue was then loaded on an alumina column and eluted with chloroform, the green band being collected in one fraction. After solvent evaporation a green solid was obtained. Yield: 90 mg (58%) (Found: C, 69.88; H, 4.75; N, 4.55. Calc. for $C_{56}H_{47}ClN_3O_2PRu$: C, 69.95; H, 4.93; N, 4.37%); IR (Nujol, cm^{-1}) 2850, 1650 ($\nu_{C=O}$), 1605 and 1160 ($\nu_{N=P}$). ^1H NMR (300 MHz, 298 K, $CDCl_3$) δ 3.32 (d, 2 H, $J = 14.6$), 4.90 (d, 2 H, $J = 14.6$ Hz) and 6.90–7.90 (m, 38 H). ^{31}P NMR (202.48 MHz, 298 K, $CDCl_3$) δ +66.41. FAB MS m/z 926 (M^+).

$[NBu^n{}_4][Ru^{IV}L(Hpz)(pz)]$ (L = L^3 or L^4). A light orange acetonitrile solution containing the nitridoruthenium complex **3a** or **4a** (100 mg, 0.13 mmol) and pyrazole (Hpz, 198 mg, 0.26 mmol) was treated with triphenylphosphine (34 mg, 0.13 mmol) under an argon atmosphere; an instantaneous change to dark green occurred. The reaction mixture was stirred for 15 min and then rotary evaporated to dryness to leave a dark green solid. The solid was extracted by diethyl ether (3 × 20 cm^3), and the combined organic extracts were evaporated to dryness to leave $HN{=}PPh_3$ as a white solid [EI MS 277 (M^+); ^{31}P NMR δ +30.1]. The dark green residue was recrystallized by slow diffusion of diethyl ether into its acetonitrile solution, and a dark green microcrystalline solid was collected by filtration. For $[NBu^n{}_4][Ru^{IV}L^3(Hpz)(pz)]$: yield 80 mg (76%) (Found: C, 61.11; H, 6.66; N, 11.89. Calc. for $C_{42}H_{55}N_7O_4Ru$: C, 61.29; H, 6.74; N, 11.91%); IR (Nujol, cm^{-1}) 2925, 1595 ($\nu_{C=O}$) and 1460; ES MS (negative) m/z 581 (M^-). For $[NBu^n{}_4][Ru^{IV}L^4(Hpz)(pz)]$: yield 96 mg (83%) (Found: C, 56.45; H, 5.88; N, 10.78. Calc. for $C_{42}H_{53}Cl_2N_7O_4Ru$: C, 56.56; H, 5.99; N, 10.99%); IR (Nujol, cm^{-1}) 2930, 1600 ($\nu_{C=O}$) and 1460; ES MS (negative) m/z 649 (M^-).

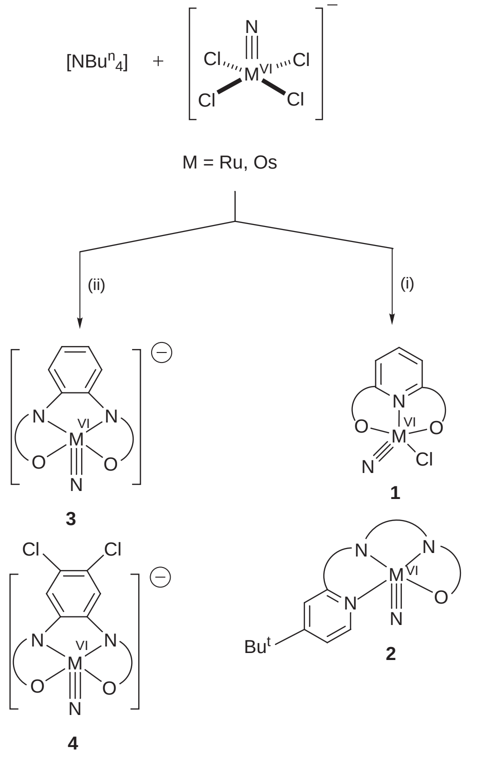
$[Ru^{IV}L^2(Hpz)(pz)]$. A round-bottom flask (25 cm^3) was charged with complex **2a** (100 mg, 0.17 mmol), pyrazole (198 mg, 0.35 mmol), triphenylphosphine (46 mg, 0.17 mmol) and dichloromethane (10 cm^3). The orange-brown suspension was stirred for 0.5 h, and a homogeneous dark brown solution resulted. After complete removal of solvent by rotary evaporation a brown solid was isolated. The solid residue was extracted by diethyl ether (3 × 20 cm^3), and the combined organic extracts were evaporated to dryness to leave $HN{=}PPh_3$ as a white residue [EI MS $m/z = 277$ (M^+); ^{31}P NMR δ +30.1]. The remaining brown solid was recrystallized by slow diffusion of diethyl ether into its chloroform solution, and a brown microcrystalline solid was isolated by filtration. Yield: 100 mg, 88% (Found: C, 50.25; H, 3.45; N, 14.32. Calc. for $C_{29}H_{25}Cl_2N_7O_3Ru$: C, 50.37; H, 3.64; N, 14.18%); IR (Nujol, cm^{-1}) 2850, 1680 ($\nu_{C=O}$), 1630 ($\nu_{C=O}$) and 1460. FAB MS m/z 693 ($M^+ + 1$).

Results and discussion

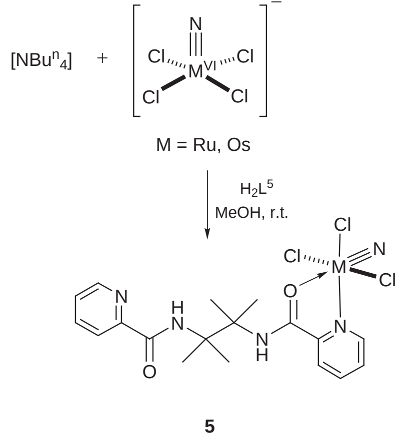
Synthesis and spectral characterization

Multianionic chelating ligands are strong σ donors capable of stabilizing metal ions in high oxidation states. Notable examples are complexes of Cu^{III}, Mn^V and Fe^{IV} which are readily attainable by using tetraanionic amide ligands.[13] In this work we have prepared a series of auxiliary (N, O) ligands, H_2L^1, H_3L^2 and $H_4L^{3,4}$, with different electronic charges upon deprotonation of the amide and hydroxyl groups. The H_2L^1 ligand was first reported by Berg and Holm,[9] and its high-valent dioxo- and nitrido-osmium(VI),[14] oxo-[9] and bis(imido)-molybdenum(VI)[15] derivatives have been prepared and structurally characterized. On the contrary, the use of tetradentate trianionic ligands to support high-valent metal centres has received relatively less attention, a noteworthy example being the preparation of an iron(IV) metallocorrole complex by Vogel *et al.*[16] The H_3L^2 ligand was prepared by the method developed by Kabanos and co-workers.[10,17] The presence of a *tert*-butyl substituent rendered the ligand more soluble in organic solvents. We are interested to examine the effect of the electron-donating strength (in terms of formal anionic charge) of the auxiliary ligands on the M≡N functions, especially on its electrophilicity. We envisaged that the increase in σ donation from the ligand would promote the electron density at the metal centre; as a result the electrophilicity of the nitrido ligand would be reduced.[1]

Several methods are known for the preparation of high-valent terminal nitrido-ruthenium(VI) and -osmium(VI) complexes: (1) oxidative deprotonation of co-ordinated amines,[3a] (2) thermal decomposition of azidoosmium complexes,[8,18] and recently (3) reduction of nitrosyl complexes.[19] A synthetic route based on the ligand substitution reactions of $[M^{VI}NCl_4]^-$ provides the easiest entry to our target complexes, and similar methods had previously been exploited by Shapley and co-workers[20] for the preparation of nitrido-ruthenium(VI) and -osmium(VI) bearing anionic N, S, O or carboxylate ligands. Treatment of $[NBu^n{}_4][M^{VI}NCl_4]$ with H_nL^{1-4} ($n = 1$–4) in methanol–chloroform (5:1 v/v) with a few drops of 2,6-dimethylpyridine (acting as a base) affords the desired nitrido-



Scheme 1 (i) For H_2L^1 and H_3L^2, 2,6-dimethylpyridine, MeOH–CHCl$_3$, room temperature (r.t.); (ii) for H_4L^3 and H_4L^4, 2,6-dimethylpyridine, MeOH, r.t.



Scheme 2

metal complexes in moderate to good yields (Scheme 1). However, this method is apparently limited to those ligands bearing OH groups, for example a pyridine amide ligand (H_2L^5) lacking any OH groups failed to effect metal encapsulations, instead pyridyl nitrido-ruthenium(VI) and -osmium(VI) adducts $[M^{VI}N(H_2L^5)Cl_3]$ **5a** and **5b** were produced (Scheme 2). Complexes **1**, **2a**, **2b** and **5a**, **5b** were isolated as insoluble solids in good purities as revealed by ^1H NMR spectroscopy. Analytically pure samples of **3a**, **3b** and **4a**, **4b** were obtained after purification by column chromatography on alumina using chloroform as the eluent. Good quality crystals were grown by slow diffusion of diethyl ether into dichloromethane or chloroform solutions.

All the nitrido complexes prepared in this work are diamagnetic solids, consistent with the formulation of a singlet $(d_{xy})^2$ electronic ground state (taking the M≡N axis as the *z* direction). Their infrared spectra do not show any NH and/or OH stretches, suggesting that the chelating ligands are in completely deprotonated forms. However the M≡N stretches cannot be unequivocally assigned because of extensive overlap with the ligand absorptions in the same spectral region. Their UV/VIS spectra are featureless and dominated by intense absorption(s) at $\lambda < 250$ nm. Complexes **1**, **3a**, **3b** and **4a**, **4b** show similar ^1H NMR spectral patterns to those of their respective unbound ligands, suggesting that the mirror symmetry of the chelating ligands is retained after co-ordination. For **3** and **4** the aromatic protons on the ligands are downfield-shifted relative to the unbound states probably due to inductive withdrawal of electrons by the electrophilic metal centre. All the ^1H NMR spectra of the nitridometal complexes show no amido and phenolic proton absorptions, consistent with the infrared results that the ligands are in their deprotonated forms. The ^1H NMR spectra of the ruthenium and the analogous osmium complexes revealed similar patterns implying an isostructural relationship.

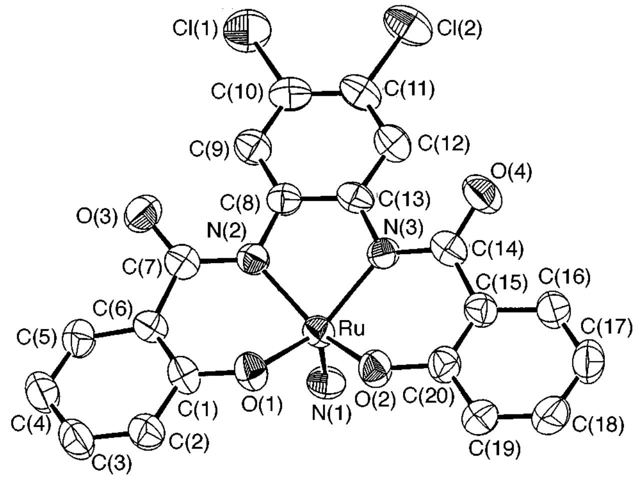


Fig. 1 Perspective view of $[Ru^{VI}N(L^4)]^-$ **4a**.

Structural studies of the nitrido-ruthenium and -osmium complexes

The crystal structures of some nitrido-ruthenium(VI) (**1**, **3a**, **4a** and **5a**) and -osmium(VI) (**2b**, **3b** and **5b**) complexes were determined by single-crystal X-ray diffraction method. The crystal data, selected bond distances and angles are listed in Tables 1 and 2 respectively. All the nitridometal complexes prepared in this work are five-co-ordinated (except **5a** and **5b**); this can be ascribed to the strong *trans* effect exerted by the nitride (N^{3-}) ligand.

As revealed by X-ray crystal analysis, complexes **3a** and **4a** are isostructural, and for illustration a perspective view of **4a** is shown in Fig. 1. Both complexes adopt a distorted square pyramidal co-ordination with the terminal nitride ligand in the apical position. The metal centre is slightly elevated by ≈0.58 Å from the mean equatorial plane consisting of the four N- and O-donor atoms; a similar structural feature has been found for some other nitridometal complexes.[21] The Ru^{VI}–N (amide) bond distances for **3a** and **4a** are in a range of 1.991(6)–2.006(3) Å, significantly shorter than the Ru^{II}–N(sp^3) {2.144(4) Å in $[Ru(NH_3)_6]I_2$},[22] Ru^{III}–N(sp^3) {2.104–2.117 Å in *cis*-$[Ru^{III}([14]aneN_4)Cl_2]Cl$}[23] and Ru^{IV}–N(sp^3) {2.085–2.141(5) Å in *trans*-$[Ru^{IV}(tmc)O(MeCN)][PF_6]_2$}[24] ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane, tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) distances involving saturated amine ligands, but the values are close to those [1.987(5)–2.044(5) Å] of $[Ru^{IV}(chbae)(PPh_3)(py)]$[25] [chbae = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane tetraanion].

Complexes **5a** and **5b** are six-co-ordinated and isostructural; the metal atoms adopt a distorted octahedral co-ordination where the pyridine amide ligand (H_2L^5) binds to the M≡N moiety in a bidentate fashion *via* the pyridyl nitrogen and the carbonyl oxygen atoms. The carbonyl oxygen atom is opposite to the N^{3-} ligand. The Ru≡N and Os≡N distances are found to be 1.598(3) and 1.612(5) Å respectively.

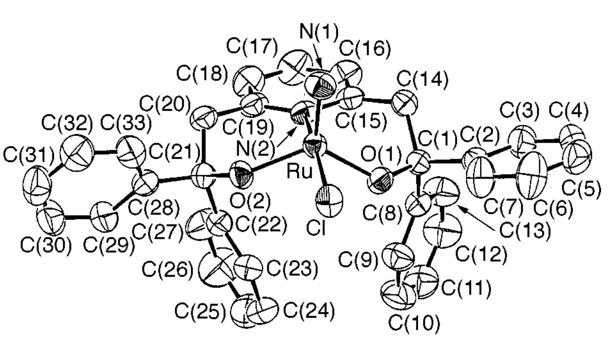


Fig. 2 Perspective view of [Ru^{VI}N(L^1)Cl] **1**.

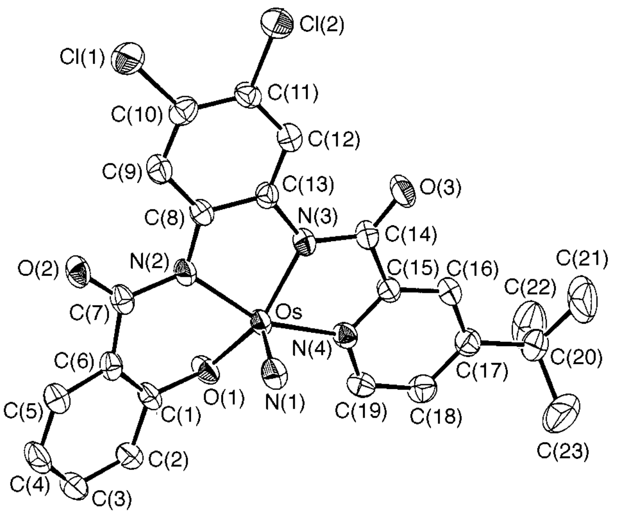
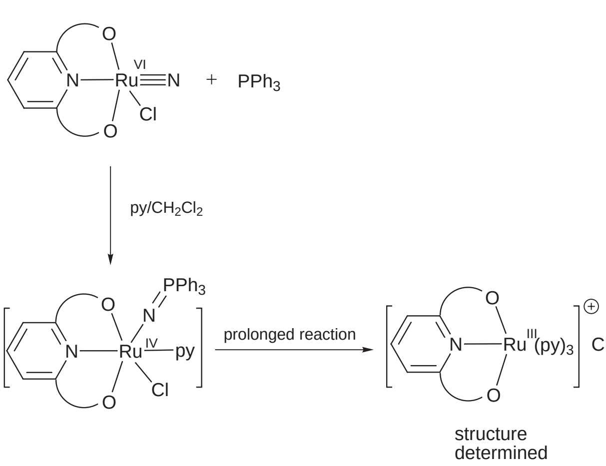


Fig. 3 Perspective view of [Os^{VI}N(L^3)] **2b**.

The structure of complex **1** (Fig. 2) is again isostructural to the osmium(VI) analogue [Os^{VI}N(L^1)Cl] reported earlier,[14] and the co-ordination polyhedron around the metal atom can be described as distorted trigonal bipyramidal with the N(1), O(1) and O(2) atoms on the trigonal plane. The N(2)–Ru–Cl(1) axis significantly deviates from linearity [167.0(1)°]. The respective N(1)–Ru–O(1), O(1)–Ru–O(2) and N(1)–Ru–O(2) bond angles are 117.7(2), 129.2(1) and 112.4(2)°, and the two six-membered chelate rings are in a *gauche* conformation. The trigonal plane defined by the Ru, N(1), O(1) and O(2) atoms is a near isosceles triangle. The Ru–O(1) and the Ru–O(2) bond distances are 1.902(3) and 1.921(3) Å respectively, comparable to those [2.007(3) and 1.897(3) Å] found in [NPr$_4$][Ru^{V}O(phab)][26] [phab = 1,2-bis(2-hydroxy-2,2-diphenylethanamido)benzene tetraanion]. The Ru≡N distance of 1.615(4) Å is close to that found in the tetraanionic (L^3)$^{4-}$ [1.594(4) Å] and (L^4)$^{4-}$ [1.609(6) Å] analogues. On the other hand the alkoxide (O$^-$) and amide (N$^-$) donor atoms of the L^3 and L^4 tetraanions are regarded as considerably more basic than the chloride ligand; notwithstanding, these Ru≡N distances are comparable to those found for [Ru^{VI}N(H$_2$L^5)Cl$_3$] **5a** [Ru≡N 1.598(3) Å], [Ru^{VI}NCl$_4$]$^-$ (Ru≡N 1.570 Å)[22] and [Ru^{VI}NMe$_4$]$^-$ (Ru≡N 1.58 Å).[27]

Although we could not obtain crystals of [Ru^{VI}N(L^2)] **2a** suitable for X-ray crystal analysis, the molecular structure of the osmium(VI) analogue **2b** has been determined. As shown in Fig. 3, complex **2b** is five-co-ordinated and exhibits distorted square pyramidal co-ordination at the osmium centre; the Os≡N bond distance was found to be 1.621(4) Å. Similar insensitivity of the Os≡N bond distances to the number of anionic donor atoms is also observed for the isostructural nitridoosmium(VI) analogues [Os^{VI}N(L^1)Cl] [1.634(5) Å],[22] [NBu$^n_4$][Os^{VI}N(L^3)] **3b** [1.618(7) Å], [Os^{VI}N(H$_2$L^5)Cl$_3$] **5b** [1.612(5) Å] and [Os^{VI}NCl$_5$]$^{2-}$ (1.614 Å).[28] Unlike the oxoruthenium(IV) systems, the O=Ru bond strength is sensitive to the electron-donating power of, as well as the presence of π unsaturation in, equatorial macrocyclic amine ligands.[24] The Os–O(1) (2.010 Å) and Os–N (amide) (2.004 and 1.962 Å) distances are comparable to those for [NBu$^n_4$][Os^{VI}N(L^3)] **3b** [Os–O 1.97 Å, Os–N (amide) 2.010 and 2.011 Å]. The Os–N (py) distance (2.088 Å) is also close to the reported value (2.119 Å) for [Os^{VI}N(L^1)Cl].[14]



Scheme 3

Nitrogen-atom transfer reactions of nitridoruthenium to PPh$_3$

To examine the possible influence of the electron-donating power of the auxiliary ligands on the electrophilicity of the Ru≡N function, triphenylphosphine was used as a nucleophile to effect a series of nitrogen atom transfer reactions. When [Ru^{VI}N(L^1)Cl] was treated with a stoichiometric amount of PPh$_3$ in dry dichloromethane–pyridine (20 : 1) an instantaneous change from a yellow orange to dark green solution occurred (Scheme 3). After column chromatography on alumina a green solid was isolated. The IR spectrum of the green compound revealed a strong absorption peak at 1106 cm^{-1} which is conspicuously absent from the spectrum of complex **1**. According to related studies this could be assigned as a N=P stretch.[29] The ^{31}P NMR spectrum of the compound showed a singlet at δ +66.4 *vs.* 85% H$_3$PO$_4$, which is close to other reported values for a phosphiniminate co-ordinated to a metal centre.[30] With the aid of mass spectroscopy ($M^+ - \mathrm{Cl}$ $m/z = 926$), ^{1}H NMR and elemental analysis, the green solid can be formulated as [Ru^{IV}(N=PPh$_3$)L^1(py)Cl]. When the triphenylphosphine reduction was monitored by ^{31}P NMR spectroscopy in a CD$_2$Cl$_2$–C$_5$D$_5$N mixture [Ru^{IV}(N=PPh$_3$)L^1(py)Cl] (^{31}P = δ +66.4) was formed instantaneously upon mixing the reactants, no absorption (δ −3.5) corresponding to free PPh$_3$ being detected indicates that all PPh$_3$ was consumed on the NMR timescale. However, on prolonged standing (14 h) of the reaction mixture the ^{31}P NMR spectrum revealed only a singlet at δ +30.1 (Ph$_3$P=NH) and the complex [Ru^{III}L^1(py)$_3$]Cl was isolated and characterized by spectroscopic as well as X-ray crystallographic means.[31]

Likewise complexes **2a**, **3a** and **4a** undergo facile reactions with triphenylphosphine, however we were unable to isolate analytically pure ruthenium(IV) phosphiniminato complexes when CH$_2$Cl$_2$–pyridine (20 : 1) was employed as the reaction medium (Scheme 4). The ^{31}P NMR spectra recorded for their reactions with PPh$_3$ in CD$_2$Cl$_2$–C$_5$D$_5$N mixture revealed a weak singlet absorption at δ +30.1 (Ph$_3$P=NH) only, and yet no free PPh$_3$ was detected. When the triphenylphosphine reductions were carried out using CH$_2$Cl$_2$ (**2a**) or MeCN (**3a** and **4a**) as solvent in the presence of an excess of pyrazole (Hpz) (10 equivalents *vs.* Ru≡N) some green crystalline solids were obtained by addition of diethyl ether (>76% isolated yield). The product complexes are paramagnetic solids with $\mu_{\mathrm{eff}} = 2.9$ μ_B ($\mu_B = 9.27 \times 10^{-24}$ J T^{-1}) consistent with a ground state electronic configuration with two unpaired electrons ($S = 1$)

Table 1 Crystallographic data for the nitrido-ruthenium(VI) and -osmium(VI) complexes

	1	**2b**	**3a**	**4a**·CHCl$_3$	**3b**	**5a**	**5b**
Formula	$C_{33}H_{27}ClN_2O_2Ru$	$C_{23}H_{18}Cl_2N_4O_3Os$	$C_{36}H_{48}N_4O_4Ru$	$C_{37}H_{47}Cl_5N_4O_4Ru$	$C_{36}H_{48}N_4O_4Os$	$C_{18}H_{22}Cl_3N_5O_2Ru$	$C_{18}H_{22}Cl_3N_5O_2Os$
M	620.11	659.53	701.87	890.14	791	546.83	635.96
Crystal symmetry	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$Pbca$ (no. 61)	$P\bar{1}$ (no. 2)	$Pbca$ (no. 61)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	9.609(7)	14.107(2)	15.346(3)	12.074(2)	19.816(2)	11.817(2)	11.825(2)
b/Å	18.444(7)	10.225(1)	19.721(3)	13.118(2)	22.746(4)	10.165(2)	10.276(4)
c/Å	16.099(8)	15.216(9)	22.744(4)	13.648(2)	15.430(2)	19.091(3)	19.011(1)
α/°				75.65(2)			
β/°	104.56(5)	91.581(7)		84.14(2)		100.72(2)	100.952(7)
γ/°				86.46(2)			
U/Å^3	2761(2)	2194.0(4)	6883(1)	2081.8(6)	6955(1)	2254.3(8)	2267.9(8)
Z	4	4	8	2	8	4	4
Diffractometer	Rigaku AFC7R	Rigaku AFC7R	MAR	MAR	Rigaku AFC7R	MAR	Rigaku AFC7R
D_c/g cm^{-3}	1.491	1.997	1.354	1.420	1.511	1.611	1.862
No. collected data	5355	4051	53014	28929	6753	20165	4464
No. unique data	5040	3884	7048	5737	6753	4128	4247
No. data used	3454	3223	3902	3695	3047	2986	2944
No. parameters	352	298	405	458	405	265	265
μ(Mo-Kα)/cm^{-1}	6.98	60.87	4.99	7.39	37.08	10.74	59.96
F(000)	1264	1272	2944	916	3200	1100	1228
R	0.041	0.020	0.042	0.056	0.031	0.032	0.028
R'	0.046	0.028	0.056	0.076	0.041	0.046	0.030
Goodness of fit	1.80	1.39	2.14	1.52	1.29	2.24	1.33

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ where $w = 4F_o^2/\sigma^2(F_o^2)$.

Table 2 Selected bond distances (Å) and angles (°) for the ruthenium(VI) and osmium(VI) nitrido complexes

Complex **1**

Ru–N(1)	1.615(4)	N(1)–Ru–N(2)	95.3(2)
Ru–N(2)	2.125(4)	O(1)–Ru–O(2)	129.2(1)
Ru–O(1)	1.902(3)	N(1)–Ru–O(1)	117.7(2)
Ru–O(2)	1.921(3)	N(1)–Ru–O(2)	112.4(2)
Ru–Cl	2.366(1)	O(1)–Ru–O(2)	129.2(1)
		N(2)–Ru–Cl	167.0(1)

Complex **2b**

Os–N(1)	1.621(4)	N(1)–Os–N(2)	104.0(2)
Os–N(2)	2.004(3)	N(1)–Os–N(3)	107.4(2)
Os–N(3)	1.962(3)	N(1)–Os–N(4)	98.2(1)
Os–N(4)	2.088(3)	N(1)–Os–O(1)	105.4(2)
Os–O(1)	2.010(3)	N(2)–Os–N(4)	154.7(1)
		O(1)–Os–N(3)	147.2(1)

Complex **3a**[a]

Ru–N(1)	1.594(4)	N(1)–Ru–N(2)	105.8(2)
Ru–N(2)	2.006(3)	N(1)–Ru–N(3)	106.0(2)
Ru–N(3)	1.992(4)	N(1)–Ru–O(1)	108.4(2)
Ru–O(1)	1.956(3)	N(1)–Ru–O(2)	108.0(1)
Ru–O(2)	1.957(3)	N(2)–Ru–O(2)	146.2(1)
		O(1)–Ru–N(3)	145.6(1)

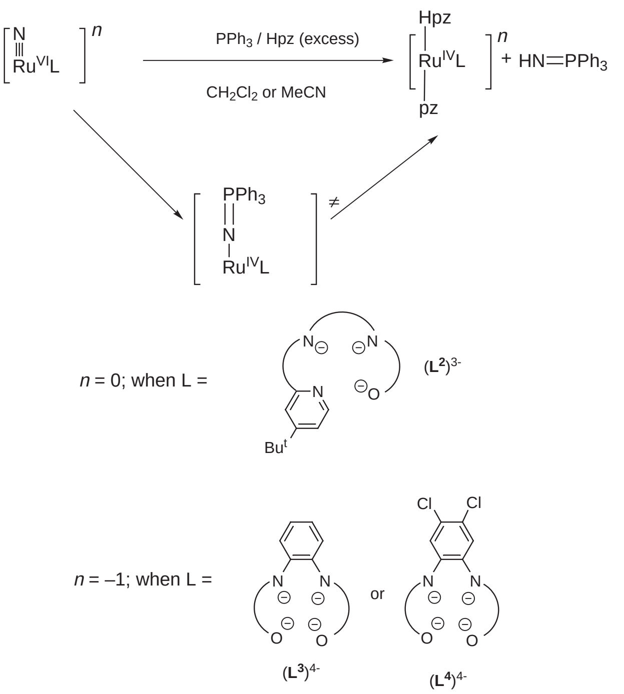
Complex **4a**

Ru–N(1)	1.609(6)	N(1)–Ru–N(2)	105.8(3)
Ru–N(2)	1.991(5)	N(1)–Ru–N(3)	106.8(3)
Ru–N(3)	1.992(6)	N(1)–Ru–O(1)	108.3(3)
Ru–O(1)	1.960(4)	N(1)–Ru–O(2)	107.3(3)
Ru–O(2)	1.955(5)	N(2)–Ru–O(2)	146.9(2)
		O(1)–Ru–N(3)	144.9(2)

Complex **3b**[a]

Os–N(1)	1.618(7)	N(1)–Os–N(2)	107.0(3)
Os–N(2)	2.011(6)	N(1)–Os–N(3)	106.1(3)
Os–N(3)	2.010(6)	N(1)–Os–O(1)	109.0(3)
Os–O(1)	1.969(5)	N(1)–Os–O(2)	107.4(3)
Os–O(2)	1.977(5)	N(2)–Os–O(2)	145.5(2)
		O(1)–Os–N(3)	144.9(2)

[a] Same atom labelling scheme is adopted.



Scheme 4

indicating that the ruthenium centre is in the +4 oxidation state. According to the mass spectroscopic analyses, molecular ion peaks at m/z = 693 (M^+ + 1), 581 (M^-) and 649 (M^-), these green solids could be formulated as $[Ru^{IV}L^2(Hpz)(pz)]$, $[Ru^{IV}L^3(Hpz)(pz)]^-$ and $[Ru^{IV}L^4(Hpz)(pz)]^-$ respectively. The cyclic voltammogram of $[NBu_4][Ru^{IV}L^4(Hpz)(pz)]$ in 0.1 mol dm^{-3} NBu_4PF_4 (CH_2Cl_2) showed three quasi-reversible couples at +0.8, +0.04 and −1.24 V *vs.* Ag–AgNO$_3$.

All the triphenylphosphine reductions of the nitridoruthenium complexes take place spontaneously. When the reaction with $[NBu^n_4][Ru^{VI}N(L^4)]$ was monitored by UV/VIS spectroscopy immediately after mixing of the reactants a new species exhibiting an absorption band at 551 nm was generated. This species slowly converted into $[NBu^n_4][Ru^{IV}L^4(Hpz)(pz)]$ (over 12 h) manifested by the gradual decay of the 551 nm band, suggesting that the putative $Ru^{IV}(N{=}PPh_3)$ species is unstable toward subsequent ligand substitution. The failure to observe the ruthenium(IV) intermediate by ^{31}P NMR spectroscopy could be ascribed to the paramagnetic nature of the molecule.

Despite previous reports that $[Os^{VI}N(terpy)Cl_2]Cl$ will also react with PPh_3 to give $[Os^{IV}(N{=}PPh_3)(terpy)Cl_2]Cl$ (terpy = 2,2′:6′,2″-terpyridine),[32] the analogous reaction of $[NBu^n_4][Os^{VI}N(L^4)]$ was found to be sluggish. This observation is consistent with the findings from related studies on the oxo-ruthenium(VI) and -osmium(VI) complexes that high-valent ruthenium is a stronger oxidant than its osmium counterpart.[2,6] A ^{31}P NMR spectrum recorded after 12 h of reaction revealed that the mixture contained largely unchanged PPh_3 (δ −3.5).

Conclusion

A series of nitrido-ruthenium(VI) and -osmium(VI) complexes containing di-, tri- and tetra-anionic ligands was prepared *via* ligand substitution reactions. The M≡N bond distance is invariant to the electron-donating power of the auxiliary ligands. All the nitridoruthenium(VI) complexes react readily with triphenylphosphine, and the intermediate $[Ru^{IV}(N{=}PPh_3)(L^1)(py)Cl]$ can be isolated and characterized spectroscopically for the reaction with $[Ru^{VI}N(L^1)Cl]$. However, for those nitridoruthenium complexes bearing the tri- $(L^2)^{3-}$ and tetra-anionic $(L^{3,4})^{4-}$ ligands the phosphiniminatoruthenium(IV) intermediate undergoes further reaction with pyrazole to generate a bis(pyrazole)ruthenium(IV) complex as the product.

Acknowledgements

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