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Synthesis and reactivity of nitrido-rhenium and -osmium complexes with an oxygen tripod ligand

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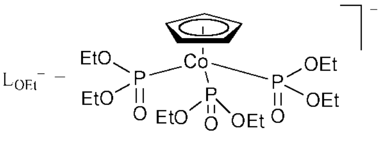
Interaction of [ReNCl$_3$(PPh$_3$)$_2$] or [ReOCl$_2$(PPh$_3$)$_3$] with NaL$_{OEt}$ (L$_{OEt}$ = [Co(η^5-C$_5$H$_5$){PO(OEt)$_2$}$_3$]) afforded [ReL$_{OEt}$N(PPh$_3$)Cl] **1** and [ReL$_{OEt}$OCl$_2$] **2**, respectively. Reaction of **1** with AgBF$_4$ gave the nitridorhenium(VI) complex [ReL$_{OEt}$N(PPh$_3$)Cl]BF$_4$ **1·**BF$_4$, which has a μ_{eff} of 1.8 μ_B. Treatment of **1** with MeOSO$_2$CF$_3$, PhCH$_2$Br or [Ph$_3$C]BF$_4$ afforded the respective organoimido species [ReL$_{OEt}$(NMe)(PPh$_3$)Cl][CF$_3$SO$_3$] **3**, [ReL$_{OEt}$(NCH$_2$Ph)-(PPh$_3$)Cl]Br **4**, and [ReL$_{OEt}$(NCPh$_3$)(PPh$_3$)Cl] **5**. Reaction of **1** with [Au(PPh$_3$)(CF$_3$SO$_3$)], [Ru(Et$_2$dtc)(PPh$_3$)$_2$-(CO)(CF$_3$SO$_3$)], or [ReMeO$_3$] yielded the bimetallic nitrido complexes [Au(PPh$_3$){NReL$_{OEt}$(PPh$_3$)Cl}][CF$_3$SO$_3$] **6**, [Ru(Et$_2$dtc)(PPh$_3$)(H$_2$O)(CO){NReL$_{OEt}$(PPh$_3$)Cl}][CF$_3$SO$_3$] **7** or [ReMeO$_3${NReL$_{OEt}$(PPh$_3$)Cl}] **8**, respectively. Treatment of [NBu$_4$^{n}][OsNCl$_4$] with NaL$_{OEt}$ gave [OsL$_{OEt}$NCl$_2$] **9**. The average Os–O, Os–Cl and Os–N distances in **9** are 2.066, 2.289 and 2.58(1) Å, respectively. Reaction of **9** with PPh$_3$ afforded the osmium(IV) phosphoran iminate species [OsL$_{OEt}$(NPPh$_3$)Cl$_2$] **10**, which has a μ_{eff} of 2.0 μ_B. The average Os–O, Os–Cl and Os–N distances in **10** are 2.099, 2.342, 1.893(5) Å, respectively, the Os–N–P angle being 137.5(3)°. The formal potentials of the L$_{OEt}$–Re and –Os complexes have been determined by cyclic voltammetry. On the basis of the Re^{VI}–Re^{V} formal potential, the π-donor strength was found to decrease in the order N^{3-} > [NAu(PPh$_3$)]$^{2-}$ > NMe^{2-}.

Introduction

Transition metal nitrido complexes are of interest because of their applications in metal-mediated nitrogen atom transfer reactions.[1–3] While early transition metal nitrides are basic and react with alkyl halides or Lewis acidic metal centres to give imido or μ-nitrido complexes, the late transition metal analogues exhibit electrophilic properties.[4] In an effort to understand the factors governing reactivity of metal nitrides, isoelectronic nitrido complexes of Re^V and Os^{VI} were synthesized and their reactivities compared. Of particular interest are complexes of Re and Os with Kläui's tripod ligand [Co(η^5-C$_5$H$_5$){PO(OEt)$_2$}$_3$] or L$_{OEt}$, which is known to stabilise metal ions in high oxidation states due to its π-donating capability.[5] It may be noted that while Ru–L$_{OEt}$ complexes are well documented,[5,6] there are few examples of the osmium congeners.[7] In this paper we report on the synthesis and crystal structures of nitrido complexes of Re^V and Os^{VI} with L$_{OEt}$ and their reactivity toward electrophiles and PPh$_3$.



Experimental

NMR Spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ^{1}H and ^{31}P, respectively. Chemical shifts (δ, ppm) are reported with reference to Si(CH$_3$)$_4$ (^{1}H) and H$_3$PO$_4$ (^{31}P). Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273A potentiostat. The working and reference electrodes were glassy carbon and Ag–AgNO$_3$ (0.1 M in acetonitrile), respectively. Potentials were reported with reference to the ferrocenium–ferrocene couple (Cp$_2$Fe$^{+/0}$). Elemental analyses were performed by Medac Ltd, Surrey, UK.

Materials

The compounds [ReN(PPh$_3$)$_2$Cl$_2$],[8] [ReO(PPh$_3$)$_2$Cl$_3$],[9] [NBu$_4$^{n}]-[OsNCl$_4$],[10] [Au(PPh$_3$)(CF$_3$SO$_3$)][11] and [ReMeO$_3$][12] were prepared according to the literature methods. The triflate compound [Ru(Et$_2$dtc)(PPh$_3$)$_2$(CO)(CF$_3$SO$_3$)] was synthesized by reaction of [Ru(Et$_2$dtc)(PPh$_3$)$_2$(CO)H] (Et$_2$dtc = *N*,*N*-diethyldithiocarbamate)[13] with triflic acid (CF$_3$SO$_3$H) as described elsewhere.[14] The compounds MeOSO$_2$CF$_3$, PhCH$_2$Br and [Ph$_3$C]BF$_4$ were obtained from Aldrich and used as received.

Preparations

[ReL$_{OEt}$N(PPh$_3$)Cl] 1. A mixture of [ReN(PPh$_3$)$_2$Cl$_2$] (0.71 g, 0.90 mmol) and NaL$_{OEt}$ (0.5 g, 0.896 mmol) in tetrahydrofuran (thf)–toluene (50 cm^3, 1 : 1) was heated at reflux overnight. The volatiles were removed *in vacuo* and the residue was washed with hexane. Recrystallisation from Et$_2$O–hexane afforded orange-red crystals, suitable for X-ray analysis (yield: 0.49 g, 54%). NMR (CDCl$_3$): ^{1}H, δ 0.77 (t, 3 H, CH$_3$), 1.02 (t, 3 H, CH$_3$), 1.18 (t, 3 H, CH$_3$), 1.30 (t, 3 H, CH$_3$), 1.36 (t, 3 H, CH$_3$), 1.37 (t, 3 H, CH$_3$), 2.71–2.93 (m, 2 H, OCH$_2$), 3.54–3.69 (m, 2 H, OCH$_2$), 3.97–4.05 (m, 2 H, OCH$_2$), 4.29–4.04 (m, 6 H, OCH$_2$), 4.99 (s, 5 H, C$_5$H$_5$) and 7.28–7.83 (m, 15 H, PPh$_3$); ^{31}P, δ 10.83 (s, PPh$_3$) and 109.1–110.5 (m, P(O)(OEt)$_2$). IR (cm^{-1}): 946 [ν(Re≡N)]. MS (FAB): *m*/*z* 1032 (M$^+$) (Found: C, 40.2; H, 4.91; N, 1.32. Calc. for C$_{35}$H$_{50}$ClCoNO$_9$P$_4$Re: C, 40.7; H, 4.84; N, 1.36%).

[ReL$_{OEt}$OCl$_2$] 2. A mixture of [ReO(PPh$_3$)$_2$Cl$_3$] (0.3 g, 0.361 mmol) and NaL$_{OEt}$ (0.15 g, 0.269 mmol) in thf–toluene (50 cm^3,

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1 : 1) was heated at reflux overnight. The volatiles were removed *in vacuo* and the residue was washed with hexane. Recrystallisation from ether–hexane afforded yellow crystals (yield: 0.10 g, 48%). Despite several attempts, we have not been able to obtain good carbon analysis for complex **2**. NMR (CDCl$_3$): ^{1}H, δ 1.26 (t, 6 H, CH$_3$), 1.31 (t, 6 H, CH$_3$), 1.33 (t, 6 H, CH$_3$), 4.07–4.30 (m, 12 H, OCH$_2$) and 5.14 (s, 5 H, C$_5$H$_5$); ^{31}P-{^{1}H}, δ 124.2 (m, P(O)(OEt)$_2$). MS (FAB): *m/z* 808 (M$^+$) (Found: C, 27.1; H, 4.32. Calc. for C$_{17}$H$_{35}$Cl$_2$CoO$_{10}$P$_3$Re: C, 25.3; H, 4.34%).

[ReL$_{OEt}$N(PPh$_3$)Cl]BF$_4$ 1·BF$_4$. To a solution of complex **1** (80 mg, 0.078 mmol) in CH$_2$Cl$_2$ (25 cm^3) was added AgBF$_4$ (24 mg, 0.088 mmol). The resulting mixture was stirred for 40 min and filtered. The solvent was pumped off and the residue extracted with CH$_2$Cl$_2$. Recrystallisation from CH$_2$Cl$_2$–Et$_2$O–hexane afforded brown crystals (109 mg, 53%). $\mu_{eff} = 1.7\ \mu_B$ (Found: C, 37.7; H, 4.48; N, 1.19. Calc. for C$_{35}$H$_{50}$BClCoF$_4$NO$_9$P$_4$Re: C, 37.5; H, 4.47; N, 1.25%).

[ReL$_{OEt}$(NMe)(PPh$_3$)Cl][CF$_3$SO$_3$] 3. To a solution of complex **1** (80 mg, 0.0784 mmol) in diethyl ether (20 cm^3) was added MeOSO$_2$CF$_3$ (0.02 ml, 0.14 mmol) at 0 °C under nitrogen. The resulting mixture was allowed to warm to room temperature and stirred for 1 d during which it changed from red to yellow. The solvent was pumped off and the residue extracted with CH$_2$Cl$_2$. Recrystallisation from CH$_2$Cl$_2$–Et$_2$O–hexane afforded yellow crystals (yield: 54 mg, 58%). NMR (CDCl$_3$): ^{1}H, δ 0.84 (t, 3 H, CH$_3$), 1.08 (t, 3 H, CH$_3$), 1.29–1.43 (t, overlapping, 12 H, CH$_3$), 1.95 (d, $^4J_{HP} = 4.92$ Hz, 3 H, NCH$_3$), 3.14–3.26 (m, 2 H, OCH$_2$), 3.52–3.58 (m, 2 H, OCH$_2$), 4.09–4.36 (m, 8 H, OCH$_2$), 5.11 (s, 5 H, C$_5$H$_5$) and 7.44–7.59 (m, 15 H, PPh$_3$); ^{31}P, δ −11.38 (s, PPh$_3$), 110.1, 119.5 and 124.0 (m, P(O)(OEt)$_2$). MS (FAB): *m/z* 1047, (M − CF$_3$SO$_3$ + 1)$^+$ (Found: C, 35.6; H, 4.34; N, 1.12. Calc. for C$_{37}$H$_{53}$ClCoF$_3$N$_{12}$P$_4$ReS$_2$·H$_2$O: C, 36.0; H, 4.62; N, 1.14%).

[ReL$_{OEt}$(NCH$_2$Ph)(PPh$_3$)Cl]Br 4. This was prepared similarly as for complex **3** from **1** (80 mg, 0.0775 mmol) and PhCH$_2$Br (0.02 cm^3, 0.078 mmol) Recrystallisation from CH$_2$Cl$_2$–Et$_2$O–hexane afforded yellow crystals (37 mg, 41%). NMR (CDCl$_3$): ^{1}H, δ 0.857 (t, 3 H, CH$_3$), 1.06 (t, 3 H, CH$_3$), 1.16 (t, 3 H, CH$_3$), 1.22 (t, 3 H, CH$_3$), 1.31 (t, 3 H, CH$_3$), 1.34 (t, 3 H, CH$_3$), 3.01–3.40 (m, 4 H, OCH$_2$), 3.53–3.87 (m, 4 H, OCH$_2$), 4.04–4.32 (m, 4 H, OCH$_2$), 5.13 (s, 5 H, C$_5$H$_5$) and 6.91–7.58 (m, 20 H, phenyl protons); ^{31}P-{^{1}H}, δ −12.6 (s, PPh$_3$) and 124.1 (m, P(O)(OEt)$_2$) (Found: C, 42.1; H, 4.98; N, 1.10. Calc. for C$_{42}$H$_{57}$BrClCoN$_9$P$_4$Re: C, 41.9; H, 4.74; N, 1.16%).

[ReL$_{OEt}$(NCPh$_3$)(PPh$_3$)Cl]BF$_4$ 5. This was prepared similarly as for complex **3** from **1** (94 mg, 0.091 mmol) and [CPh$_3$]BF$_4$ (30 mg, 0.09 mmol). Recrystallisation from CH$_2$Cl$_2$–Et$_2$O–hexane afforded yellow crystals (74 mg, 60%). NMR (CDCl$_3$): ^{1}H, δ 0.80 (t, 3 H, CH$_3$), 1.05 (t, 3 H, CH$_3$), 1.18–1.29 (t, overlapping, 9 H, CH$_3$), 1.34 (t, 3 H, CH$_3$), 2.35–2.42 (m, 2 H, OCH$_2$), 3.18–3.55 (m, 4 H, OCH$_2$), 3.89–4.34 (m, 6 H, OCH$_2$), 5.21 (s, 5 H, C$_5$H$_5$) and 6.92–7.33 (m, 30 H, phenyl protons). ^{31}P-{^{1}H}, δ −10.64 (s, PPh$_3$) and 119.9–124.5 (m, P(O)(OEt)$_2$); ^{19}F, δ −155.0 (BF$_4$). MS (FAB): *m/z* 1277, (M − BF$_4$ + 2)$^+$ (Found: C, 47.9; H, 4.86; N, 1.05. Calc. for C$_{54}$H$_{65}$BClCoF$_4$NO$_9$P$_4$Re: C, 47.6; H, 4.77; N, 1.03%).

[Au(PPh$_3$){NReL$_{OEt}$(PPh$_3$)Cl}][CF$_3$SO$_3$] 6. This was prepared as for complex **3** from **1** (130 mg, 0.126 mmol) and [Au(PPh$_3$)(CF$_3$SO$_3$)] (67 mg, 0.126 mmol) Recrystallisation from CH$_2$Cl$_2$–Et$_2$O–hexane afforded greenish yellow crystals (109 mg, 53%). NMR (CDCl$_3$): ^{1}H, δ 0.82 (t, 3 H, CH$_3$), 1.11 (t, 3 H, CH$_3$), 1.21 (t, overlapping, 6 H, CH$_3$), 1.29 (t, 3 H, CH$_3$), 1.34 (t, 3 H, CH$_3$), 2.90–3.11 (m, 2 H, OCH$_2$), 3.44–3.63 (m, 6 H, OCH$_2$), 4.05–4.39 (m, 4 H, OCH$_2$), 5.05 (s, 5 H, C$_5$H$_5$) and 6.91–7.58 (m, 30 H, phenyl protons); ^{31}P-{^{1}H}, δ −12.6 (s, RePPh$_3$), 30.3 (s, AuPPh$_3$) and 118.7–120.0 (m, P(O)(OEt)$_2$). IR (cm^{-1}): 953 [ν(Re=N–Au)]. MS (FAB): *m/z* 1492, (M − BF$_4$ + 1)$^+$ (Found: C, 39.2; H, 4.01; N, 0.84. Calc. for C$_{54}$H$_{65}$AuClCoF$_3$NO$_{12}$P$_5$ReS: C, 39.5; H, 3.96; N, 0.85%).

[Ru(Et$_2$dtc)(PPh$_3$)(H$_2$O)(CO){NReL$_{OEt}$(PPh$_3$)Cl}][CF$_3$SO$_3$] 7. This was prepared similarly as for complex **3** from **1** (100 mg, 0.097 mmol) and [Ru(Et$_2$dtc)(PPh$_3$)$_2$(CO)(CF$_3$SO$_3$)] (92 mg, 0.097 mmol). Recrystallisation from CH$_2$Cl$_2$–hexane afforded brown crystals (yield: 82 mg, 49%). NMR (CDCl$_3$): ^{1}H, δ 0.77 (t, 6 H, CH$_3$), 1.09 (t, 3 H, CH$_3$), 1.18–1.30 (overlapping t, 9 H, CH$_3$), 1.40 (t, 3 H, CH$_3$), 2.61–3.04 (overlapping NCH$_2$), 3.31–4.39 (m, 12 H, OCH$_2$), 4.39 (m, 12 H, OCH$_2$), 5.14 (s, 5 H, C$_5$H$_5$) and 7.10–7.48 (m, 30 H, phenyl protons); ^{31}P-{^{1}H}, δ 6.02 (s, RePPh$_3$), 43.3 (s, RuPPh$_3$) and 118.3–120.0 (m, PO(OEt)$_2$). IR (cm^{-1}): 1966 [ν(CO)]. MS (FAB): *m/z* 1572 (M$^+$ − CF$_3$SO$_3$) (Found: C, 41.13; H, 4.45; N, 1.55. Calc. for C$_{76}$H$_{90}$ClCoF$_3$N$_2$O$_{10}$P$_5$ReRuS$_2$: C, 41.01; H, 4.46; N, 1.62%).

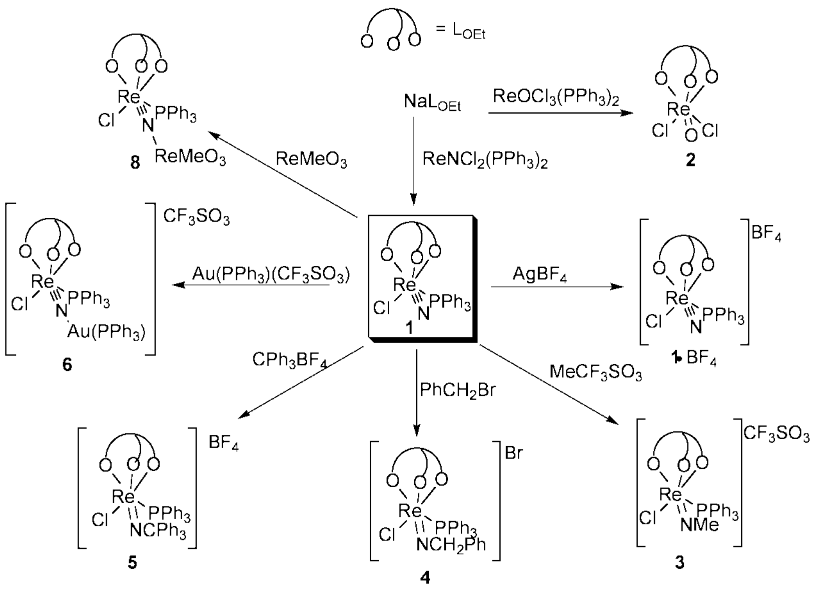
[ReMeO$_3${NReL$_{OEt}$(PPh$_3$)Cl}] 8. This was prepared similarly as for complex **3** from **1** (82 mg, 0.08 mmol) and [ReMeO$_3$] (20 mg, 0.08 mmol). The red product was recrystallised from CH$_2$Cl$_2$–hexane (yield: 50 mg, 50%). The complex was found to be unstable and decomposed to **1** and ReMeO$_3$ in solution, as reflected by NMR spectroscopy (see Results and discussion). Good analytical data were not obtained apparently because of dissociation of ReMeO$_3$ during recrystallisation. IR (cm^{-1}): 953 [ν(Re=N–Re)] and 920 [ν(Re=O)] (Found: C, 35.14; H, 4.55; N, 1.10. Calc. for C$_{36}$H$_{53}$ClCoNO$_9$P$_4$Re$_2$: C, 33.71; H, 4.14; N, 1.09%).

[OsL$_{OEt}$NCl$_2$] 9. A mixture of [NBu$^n{}_4$][OsNCl$_4$] (60 mg, 0.098 mmol) and NaL$_{OEt}$ (50 mg, 0.0896 mmol) in acetone (40 cm^3) was heated at reflux overnight. The volatiles were removed *in vacuo* and the residue was washed with hexane. Recrystallisation from CH$_2$Cl$_2$–hexane afforded deep red crystals, which are suitable for X-ray analysis (yield: 0.49 g, 54%). NMR (CDCl$_3$): ^{1}H, δ 1.21 (t, 6 H, CH$_3$), 1.33 (t, 6 H, CH$_3$), 1.35 (t, 6 H, CH$_3$), 3.99–4.06 (m, 4 H, OCH$_2$), 4.20–4.37 (m, 8 H, OCH$_2$) and 5.10 (s, 5 H, C$_5$H$_5$); ^{31}P-{^{1}H}, δ 109.9, 122.6–123.7 (m, P(O)(OEt)$_2$). MS (FAB): *m/z* 811, (M + 1)$^+$ (Found: C, 25.4; H, 4.39; N, 1.73. Calc. for C$_{17}$H$_{35}$Cl$_2$CoNO$_9$OsP$_3$: C, 25.2; H, 4.32; N, 1.73%).

[OsL$_{OEt}$(NPPh$_3$)Cl$_2$] 10. To a solution of complex **9** (50 mg, 0.062 mmol) in CH$_2$Cl$_2$ (25 cm^3) was added PPh$_3$ (20 mg, 0.076 mmol). The resulting mixture was stirred for 12 h, the solvent pumped off and the residue extracted with CH$_2$Cl$_2$. Recrystallisation from CH$_2$Cl$_2$–Et$_2$O–hexane afforded brown crystals, suitable for X-ray analysis (yield: 32 mg, 49%). $\mu_{eff} = 2.0\ \mu_B$ (Found: C, 39.2; H, 4.73; N, 1.29. Calc. for C$_{35}$H$_{50}$Cl$_2$CoN$_9$OsP$_4$: C, 39.2; H, 4.66; N, 1.31%).

X-Ray crystallography

A summary of pertinent crystallographic data and experimental details for complexes **1**, **9** and **10** is shown in Table 1. All data were collected on a MAR research image-plate diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator in the incident beam. The diffracted intensities were corrected for Lorentz-polarisation effects. For **1** the nitride and chloride were found to be twofold disordered. A model with occupancies of 0.7 and 0.3 for the two sites was used for refinement to give a reasonable set of thermal and positional parameters. In complex **9** the phosphorus atoms of the tripod ligand L$_{OEt}$ exhibit twofold positional disorder. A model with occupancies of 0.5 each gave the best results in terms of both *R* factor and positional parameters of the ligand. All structures were solved by direct



Scheme 1

methods and refined on *F* by a full-matrix least-squares analysis. Non-hydrogen atoms, except the disordered nitride and chloride of complex **1**, were refined anisotropically. Calculations were performed on a Silicon-Graphics computer, using the program package TEXSAN.[15] Hydrogen atoms were included and fixed in their idealised positions (C–H 0.95 Å). Selected bond lengths and angles for **1**, **9** and **10** are listed in Tables 2–4, respectively.

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Results and discussion

L$_{OEt}$Re complexes

The syntheses of L$_{OEt}$Re complexes are summarised in Scheme 1. Interaction of [ReNCl$_2$(PPh$_3$)$_2$] and [ReOCl$_3$(PPh$_3$)$_2$] with NaL$_{OEt}$ afforded air-stable [ReL$_{OEt}$N(PPh$_3$)Cl] **1** and [ReL$_{OEt}$OCl$_2$] **2**, respectively. The IR spectrum of **1** shows a peak at 946 cm^{-1}, which is tentatively assigned as ν(Re≡N). The ν(Re=O) for **2** was not assigned due to the presence of ligand bands in the region. X-Ray quality crystals of complex **1** were obtained by recrystallisation from CH$_2$Cl$_2$–hexane. However, the chloride and nitride in **1** were found to be twofold disordered. A model with site occupancies of 0.3 and 0.7 for the two sites was used for the refinement. Fig. 1 shows a perspective view of the molecule; selected bond lengths and angles are listed in Table 2. The Re–P and average Re–O distances were found to be 2.372(1) and 2.183 Å. Oxidation of **1** with AgBF$_4$ afforded [ReL$_{OEt}$N(PPh$_3$)Cl]BF$_4$ **1**·BF$_4$. The measured μ_{eff} of 1.8 μ_B is consistent with the formulation of Re^{VI}. Although the Re^{VI}–Re^{V} couple for **2** is reversible (see later section), no well defined products were obtained for oxidation of **2** with silver(I) salts. The nitride in **1** was found to be nucleophilic and react with electrophiles to give imidorhenium(V) complexes. Thus, treatment of **1** with MeOSO$_2$CF$_3$ afforded the methylimido complex [ReL$_{OEt}$(NMe)(PPh$_3$)Cl][CF$_3$SO$_3$] **3**. The *N*-methyl protons in **3** were found to couple with the phosphorus of PPh$_3$ and appear as a doublet at δ 1.95 ($^4J_{HP}$ = 4.92 Hz). Similarly interaction of **1** with PhCH$_2$Br or [Ph$_3$C]BF$_4$ gave the respective imido species [ReL$_{OEt}$(NCH$_2$Ph)(PPh$_3$)Cl]Br **4** or [ReL$_{OEt}$(NCPh$_3$)(PPh$_3$)Cl]BF$_4$ **5**. These imidorhenium(V) complexes are air stable in both the solid state and solution.

Bimetallic nitrido complexes containing L$_{OEt}$Re

Reaction of complex **1** with organometallic triflates afforded bimetallic nitrido complexes. Thus, **1** reacted with [Au(PPh$_3$)(CF$_3$SO$_3$)] to give [Au(PPh$_3$){NReL$_{OEt}$(PPh$_3$)Cl}][CF$_3$SO$_3$] **6**, isolated as an air-stable yellow solid. No reactions were found between **1** and [Ir(CO)(PPh$_3$)$_2$(CF$_3$SO$_3$)], which was prepared *in situ* from *trans*-[Ir(CO)(PPh$_3$)$_2$Cl] and Ag(CF$_3$SO$_3$), possibly because of steric reasons. The IR spectrum of **6** shows ν(Re=N–Au) at 953 cm^{-1}, which is higher than the ν(Re≡N) for **1**. Enhancement of the metal–nitride stretching frequency upon formation of μ-nitride bridges has also been observed for binuclear complexes of Os nitrides, *e.g.* in [Au(PPh$_3$)(NOsO$_3$)].[16] Reaction of **1** with [Ru(Et$_2$dtc)(PPh$_3$)$_2$(CO)(CF$_3$SO$_3$)],[14] which was prepared from [Ru(Et$_2$dtc)(PPh$_3$)$_2$(CO)H][13] and triflic acid, afforded [Ru(Et$_2$dtc)(PPh$_3$)(H$_2$O)(CO){NReL$_{OEt}$(PPh$_3$)Cl}][CF$_3$SO$_3$] **7**. One PPh$_3$ dissociated from Ru upon formation of **7** possibly due to steric congestion in the bimetallic complex. A preliminary diffraction study of **7** showed that the aqua ligand,

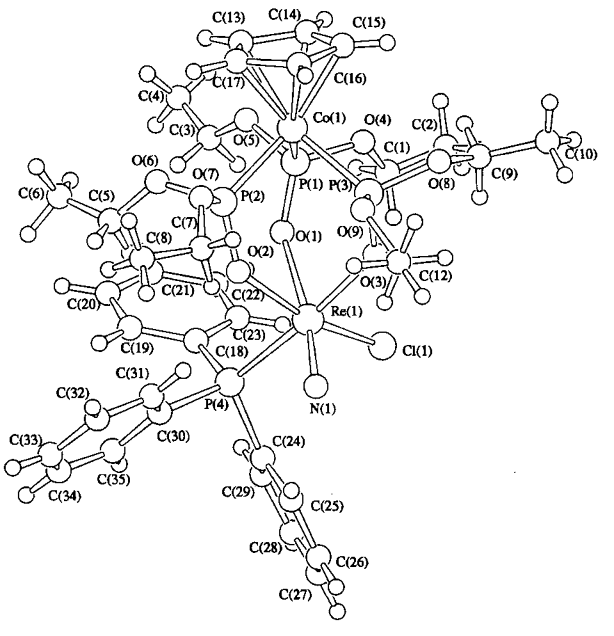

Fig. 1 Perspective view of [ReL$_{OEt}$N(PPh$_3$)Cl] **1**.

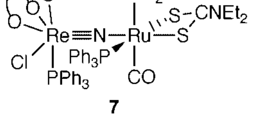

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Table 1 Crystallographic data and experimental details for [ReL$_{OEt}$N(PPh$_3$)Cl] **1**, [OsL$_{OEt}$NCl$_2$] **9** and [OsL$_{OEt}$(NPPh$_3$)Cl$_2$] **10**

	1	**9**	**10**
Empirical formula	$C_{35}H_{50}ClCoNO_9P_4Re$	$C_{17}H_{35}Cl_2CoNO_9OsP_3$	$C_{35}H_{50}Cl_2CoNO_9OsP_4$
M	1033.27	810.43	1072.72
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	14.031(1)	12.326(1)	18.414(2)
b/Å	14.582(1)	18.623(1)	12.214(3)
c/Å	20.993(2)	12.820(1)	19.449(1)
β/°	92.58(1)	94.49(2)	106.40(9)
V/Å^3	4290.8(4)	2933.8(4)	4196.3(6)
Z	4	4	4
D_{calc}/g cm^{-3}	1.599	1.835	1.513
T/K	298	298	298
μ/mm^{-1}	3.467	5.277	3.749
No. reflections measured	8244	5513	8165
No. reflections observed	5224	4088	6731
$R(F)$	0.042	0.056	0.035
R'	0.045	0.069	0.062

Table 2 Selected bond lengths (Å) and angles (°) for [ReL$_{OEt}$N(PPh$_3$)Cl] **1**

Re(1)–Cl(1)	2.292(3)	Re(1)–Cl(2)	2.216(6)
Re(1)–P(4)	2.372(1)	Re(1)–O(1)	2.251(3)
Re(1)–O(2)	2.179(4)	Re(1)–O(3)	2.115(3)
Re(1)–N(1)	1.795(8)	Re(1)–N(2)	1.97(2)
C(1)–Re(1)–Cl(2)	102.3(2)	Cl(1)–Re(1)–P(4)	89.54(8)
Cl(1)–Re(1)–O(1)	88.5(1)	Cl(1)–Re(1)–O(2)	165.5(1)
Cl(1)–Re(1)–O(3)	89.7(1)	Cl(1)–Re(1)–N(1)	101.8(2)
Cl(1)–Re(1)–N(2)	8.9(7)	Cl(2)–Re(1)–P(4)	99.4(2)
Cl(2)–Re(1)–O(1)	164.7(2)	Cl(2)–Re(1)–O(2)	90.8(2)
Cl(2)–Re(1)–O(3)	87.8(2)	Cl(2)–Re(1)–N(1)	12.6(3)
Cl(2)–Re(1)–N(2)	93.6(7)	P(4)–Re(1)–O(1)	91.32(9)
P(4)–Re(1)–O(2)	94.6(1)	P(4)–Re(1)–O(3)	172.7(1)
P(4)–Re(1)–N(1)	86.9(3)	P(4)–Re(1)–N(2)	89.3(7)
O(1)–Re(1)–O(2)	94.6(1)	O(1)–Re(1)–O(3)	81.4(1)
O(1)–Re(1)–N(1)	169.5(2)	O(1)–Re(1)–N(2)	97.4(7)
O(2)–Re(1)–O(3)	84.4(1)	O(2)–Re(1)–N(1)	92.3(2)
O(2)–Re(1)–N(2)	173.6(7)	O(3)–Re(1)–N(1)	100.4(3)
O(3)–Re(1)–N(2)	91.1(7)	N(1)–Re(1)–N(2)	92.9(7)

Table 3 Selected bond lengths (Å) and angles (°) for [OsL$_{OEt}$NCl$_2$] **9**

Os(1)–Cl(1)	2.300(4)	Os(1)–Cl(2)	2.277(7)
Os(1)–O(1)	2.022(8)	Os(1)–O(2)	2.159(8)
Os(1)–O(3)	2.017(8)	Os(1)–N(1)	1.58(1)
Cl(1)–Os(1)–Cl(4)	87.7(2)	Cl(1)–Os(1)–O(1)	167.7(4)
Cl(1)–Os(1)–O(2)	87.6(3)	Cl(1)–Os(1)–O(3)	89.1(3)
Cl(1)–Os(1)–N(1)	96.8(4)	Cl(2)–Os(1)–O(1)	90.4(3)
Cl(2)–Os(1)–O(2)	86.5(4)	Cl(2)–Os(1)–O(3)	166.0(4)
Cl(2)–Os(1)–N(1)	98.0(5)	O(1)–Os(1)–O(2)	80.1(5)
O(1)–Os(1)–O(3)	89.8(3)	O(1)–Os(1)–N(1)	95.6(6)
O(2)–Os(1)–O(3)	79.7(4)	O(2)–Os(1)–N(1)	173.8(4)
O(3)–Os(1)–N(1)	96.0(5)		

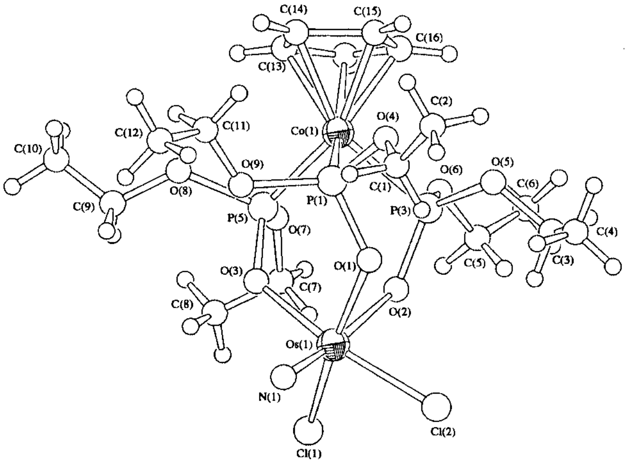

Fig. 2 Perspective view of [OsL$_{OEt}$NCl$_2$] **9**.

presumably derived from moisture in the solvent, is *trans* to the CO, and the nitride is *trans* to a sulfur of Et$_2$dtc as shown below.

Reaction of **1** with [ReMeO$_3$] afforded the adduct [ReMeO$_3${NReL$_{OEt}$(PPh$_3$)Cl}] **8**. While complex **8** is stable in the solid state, it decomposed readily to **1** and [ReMeO$_3$] in solution. The NMR spectrum of **8** in CDCl$_3$ only shows respective signals due to **1** and [ReMeO$_3$]. The IR Re=O stretching frequency for **8** of 920 cm^{-1} is lower than that for [ReMeO$_3$] (950 cm^{-1}),[17] indicating that the Re=O bonds are weakened upon adduct formation. Like **6**, the Re≡N stretching frequency for **8** (953 cm^{-1}) is higher than that for **1**.

L$_{OEt}$Os complexes

Interaction of [NBu$^n_4$][OsNCl$_4$] with NaL$_{OEt}$ in boiling acetone afforded [OsL$_{OEt}$NCl$_2$] **9**, isolated as air-stable deep red crystals. No reactions were found between [PPh$_4$]$_2$[OsO$_2$Cl$_4$][18] and NaL$_{OEt}$ possibly because of the preference of Os^{VI} for *trans*-O=Os=O geometry. The crystal structure of **9** has been determined and is shown in Fig. 2. Selected bond lengths and angles are listed in Table 3. The geometry around Os is essentially octahedral. The Os–N and average Os–Cl in **9** are 1.58(1) and 2.289 Å, respectively. The Os–O bond that is *trans* to the nitride (2.159(8) Å) is significantly longer than the other two Os–O bonds (average 2.039 Å), indicative of *trans* influence of the nitride. The IR Os–N stretching frequency was not assigned due to the presence of ligand bands in the 1000–1100 cm^{-1} region.

No alkylation occurred when complex **9** was treated with MeOSO$_2$CF$_3$, PhCH$_2$Br or [Ph$_3$C]BF$_4$, indicating that the osmium nitrido complex is less nucleophilic than the rhenium analogue **1**. In contrast to electrophilic *trans*-[OsN(tpy)Cl$_2$]$^+$ (tpy = 2,2′:6′,2″-terpyridine)[19] and [OsTpNCl$_2$] (Tp = hydridotris(pyrazol-1-yl)borate),[20] complex **9** does not react with nucleophiles such as NaN$_3$, Me$_3$NO and propylene sulfide. Reaction of **9** with PPh$_3$ in CH$_2$Cl$_2$ afforded the osmium(IV) phosphoraniminato complex [OsL$_{OEt}$(NPPh$_3$)Cl$_2$] **10**, which was characterised by X-ray diffraction. Fig. 3 shows a perspective view of **10**, selected bond lengths and angles are given in Table 4. The Os–N distance in **10** of 1.893(5) Å is comparable to that in *trans*-[Os(tpy)Cl$_2$(NPPh$_3$)]$^+$ (2.093(5) Å),[21] consistent with the formulation of a Os–N single bond. The P–N bond distance of 1.575(5) Å is similar to that in *trans*-[Os(tpy)Cl$_2$(NPPh$_3$)]$^+$ (1.618(5) Å)[21] and is typical for a P=N double bond. As expected, the average Os–Cl distance in **10** (2.342 Å) is

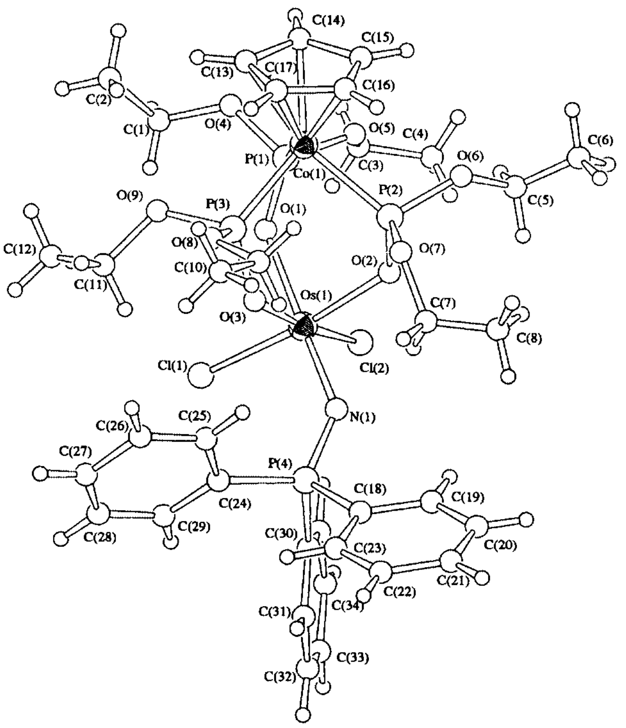

Fig. 3 Perspective view of [OsL$_{OEt}$(NPPh$_3$)Cl$_2$] **10**.

Table 4 Selected bond lengths (Å) and angles (°) for [OsL$_{OEt}$(NPPh$_3$)Cl$_2$] **10**

Os(1)–Cl(1)	2.338(2)	Os(1)–Cl(2)	2.346(2)
Os(1)–O(1)	2.110(4)	Os(1)–O(2)	2.097(4)
Os(1)–O(3)	2.090(4)	Os(1)–N(1)	1.893(5)
P(4)–N(1)	1.575(5)		
Cl(1)–Os(1)–Cl(2)	91.63(7)	Cl(1)–Os(1)–O(1)	87.7(1)
Cl(1)–Os(1)–O(2)	174.1(1)	Cl(1)–Os(1)–O(3)	91.9(1)
Cl(1)–Os(1)–N(1)	94.7(2)	Cl(2)–Os(1)–O(1)	89.7(1)
Cl(2)–Os(1)–O(2)	89.1(1)	Cl(2)–Os(1)–O(3)	173.8(1)
Cl(2)–Os(1)–N(1)	94.3(2)	O(1)–Os(1)–O(2)	86.4(2)
O(1)–Os(1)–O(3)	85.4(2)	O(1)–Os(1)–N(1)	175.2(2)
O(2)–Os(1)–O(3)	86.8(2)	O(2)–Os(1)–N(1)	91.1(2)
O(3)–Os(1)–N(1)	90.4(2)	Os(1)–N(1)–P(4)	137.5(3)

longer than that in **9**. Unlike most osmium(IV) phosphoran iminato complexes that contain linear Os–N=PR$_3$ moieties,[22] the Os–N–P linkage in **10** is bent with an angle of 137.5(3)°. The Os–N–P angle is slightly bigger than that in *trans*-[Os(tpy)Cl$_2$(NPPh$_3$)]$^+$ (132.5(3)°).[21] The measured magnetic moment for **10** of *ca.* 2.0 μ_B is different from the spin–only value for two unpaired electrons (2.83 μ_B) because of spin–orbit coupling.[21]

Electrochemistry

The formal potentials of the L$_{OEt}$–Re and –Os complexes have been determined by cyclic voltammetry and are summarised in Table 5. The cyclic voltammogram (CV) of **1** exhibits a reversible couple at −0.296 V *vs.* Cp$_2$Fe$^{+/0}$, which is assigned as the Re^{VI}–Re^{V} couple. Consistent with the assignment, the isolated rhenium(VI) complex **1**·BF$_4$ was reduced at the same potential. The Re^{VI}–Re^{V} potential for **2** (0.470 V) is more anodic than that for **1**, consistent with the higher π-donor strength of nitride compared with oxide. Oxidation of cationic imido complexes **3**–**5** is irreversible. The irreversible waves at 0.620, 0.705 and 0.557 V for complexes **3**–**5** are tentatively assigned as the respective Re^{VI}–Re^{V} oxidation. The dimetallic nitrido complexes **6** and **7** exhibit reversible Re^{VI}–Re^{V} couples at 0.161 and 0.08 V, respectively, which are higher than that for **1** but lower than those for **3**–**5**. On the basis of the Re^{VI}–Re^{V} potential for [ReL$_{OEt}$(X)(PPh$_3$)Cl], the π-donor strength of X is ranked in the order N^{3-} > [N{Au(PPh$_3$)}]$^{2-}$ > NR^{2-}. This trend is consistent with that found for [Os(X)O$_3$] [X = N, NBu^t or NAu(PPh$_3$)].[16] Complex **10** exhibits a reversible reduction at −0.718 V, which is tentatively assigned as the Os^{IV}–Os^{III} couple. The Os^{IV}–Os^{III} potential for **10** is less anodic than that for [Os(tpy)Cl$_2$(NPPh$_3$)]$^+$ (−0.27 V *vs.* standard calomel electrode),[21] indicative of the ability of the L$_{OEt}$ in stabilising Os in high oxidation states.

Table 5 Formal potentials ($E°$) for Re– and Os–L$_{OEt}$ complexes

Complex	$E°$[a]/V *vs.* Cp$_2$Fe$^{+/0}$
[ReL$_{OEt}$N(PPh$_3$)Cl]	−0.296
[ReL$_{OEt}$OCl$_2$]	0.470
[ReL$_{OEt}$(NMe)(PPh$_3$)Cl]$^+$	0.620[b]
[ReL$_{OEt}$(NCPh$_3$)(PPh$_3$)Cl]$^+$	0.705[b]
[ReL$_{OEt}$(NCH$_2$Ph)(PPh$_3$)Cl]$^+$	0.557[b]
[Au(PPh$_3$){NReL$_{OEt}$(PPh$_3$)Cl}]$^+$	0.161
[Ru(Et$_2$dtc)(PPh$_3$)(H$_2$O)(CO){NReL$_{OEt}$(PPh$_3$)Cl}]$^+$	0.080
[OsL$_{OEt}$(NPPh$_3$)Cl$_2$]	−0.718

[a] Potential measured in CH$_2$Cl$_2$ with 0.1 mol dm^{-3} [NBu$^n_4$]PF$_6$ as supporting electrolyte; scan rate = 100 mV s^{-1}. [b] Irreversible.

In summary, we have isolated the first nitrido complexes of Re^{V} and Os^{VI} with L$_{OEt}$. While the rhenium complex is nucleophilic and reacts with electrophiles to give imido or μ-nitrido complexes, the osmium analogue reacts with PPh$_3$ to give a phosphoraminatoosmium(IV) complex. On the basis of cyclic voltammetry, the π-donor strength for multiply bonded ligands is ranked in the order: N^{3-} > (NML$_n$)$^{2-}$ > NR^{2-} ≈ O^{2-}.

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