Synthesis, Spectroscopy and Electrochemistry of Rhenium(v) Imido Complexes of Pyridine and a Comparative Study with Oxo and Nitrido Analogues; Crystal Structure of $[Re^V(NMe)(py)_3(OEt)Cl]ClO_4$ (py = pyridine)†

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A series of novel cationic methylimidorhenium(v) complexes, *trans*-$[Re^V(NMe)(py)_2(PPh_3)(OEt)Cl]^+$ **1**, *cis*-$[Re^V(NMe)(py)_2(PPh_3)(OEt)Cl]^+$ **2**, $[Re^V(NMe)(py)_3(OEt)Cl]^+$ **3** and $[Re^V(NMe)(4Me\text{-}py)_2(PPh_3)(OEt)Cl]^+$ **4** (py = pyridine) have been synthesized as their perchlorate salts. The crystal structure of **3** has been determined: monoclinic, space group $P2_1/c$, $a = 10.223(4)$, $b = 17.663(2)$, $c = 25.222(3)$ Å, $\beta = 90.70(2)°$ and $Z = 4$. The structure of **3** revealed an almost linear Re–N–Me geometry, consistent with a four-electron donor formulation for the methylimido unit. Spectroscopic studies on **1**–**4** and their nitrido and oxo analogues, $[Re^V(N)(py)_2(PPh_3)_2Cl]ClO_4$ **5** and $[Re^V(O)_2(py)_3(PPh_3)]ClO_4$ **6** all show low energy $(d_{xy}) \longrightarrow (d_{\pi^*})$ electronic absorption bands at 400–500 nm.

Recently, transition-metal–ligand multiply bonded species have attracted considerable attention and have been the subject of numerous studies. Recent work on oxo and nitrido d^2 rhenium(v) complexes by us and others showed that they exhibit interesting and rich photophysical behaviour.[1,2] In view of the isoelectronic π-donor nature of the imido to the oxo and nitrido moieties, a programme was launched to investigate the spectroscopy and electrochemistry of this class of compounds. Although a large number of rhenium(v) imido complexes are known,[3,4] they are mostly neutral species of type $[Re^V(NR')Cl_3(PR_3)]$ (R = alkyl or aryl).[3] To the best of our knowledge, there have been very few reports on cationic rhenium(v) imido and nitrido complexes of monodentate pyridine (py) or phosphine ligands[3d] despite the fact that a number of $[Re^V(O)_2(X\text{-}py)_4]^+$ species are known.[2a–e] Examples include $[Re^V(NMe)(MeNH_2)_4Cl]^{2+}$ [4a,b] and those which contain the phenylimido group with either a macrocycle or bidentate 2,2′-bipyridine as Co-ligand(s).[4c–f] Herein we report the synthesis, spectroscopy and electrochemistry of a series of novel cationic rhenium(v) methylimido pyridine phosphine complexes. The spectroscopic properties of these complexes and the crystal structure of $[Re^V(NMe)(py)_3(OEt)Cl]ClO_4$ are described and compared with oxo and nitrido analogues.

Experimental

Rhenium powder and potassium perrhenate(VII) were purchased from Johnson Matthey Ltd. 1,2-Dimethylhydrazine dihydrochloride was obtained from Aldrich Chemical Co. The complexes $[Re(NMe)Cl_3(PPh_3)_2]$,[3c] $[Re(N)Cl_2(PPh_3)_2]$[3b] and $[Re(O)_2I(PPh_3)_2]$[5] were prepared according to literature procedures except that $KReO_4$ was used in place of perrhenic acid in the preparation of $[Re(O)_2I(PPh_3)_2]$. Pyridine (Ajax, AR) was purified by distillation from KOH and stored over molecular sieves (4 Å). Acetonitrile was distilled over calcium hydride before use. All other reagents and solvents were of analytical grade and were used as received.

Synthesis of Rhenium Complexes.—All reactions were performed under strictly anhydrous and anaerobic conditions using standard Schlenk techniques under an atmosphere of nitrogen.

trans-$[Re^V(NMe)(py)_2(PPh_3)(OEt)Cl]ClO_4$ **1**. To a stirred suspension of $[Re(NMe)Cl_3(PPh_3)_2]$ (0.20 g, 0.24 mmol) in ethanol (30 cm^3) was added an excess of pyridine (0.19 g, 2.4 mmol). The reaction mixture was heated to reflux, causing the initial blue suspension to dissolve to give a reddish brown solution. Reflux was continued for 24 h. After cooling, the solution was filtered and the solvent removed on a rotary evaporator. The resulting reddish brown solid was then washed with diethyl ether, dried and recrystallized from ethanol–diethyl ether to afford reddish brown crystals of the complex. The perchlorate salt was obtained by metathesis of the chloride salt in ethanol using lithium perchlorate. Recrystallization of the crude perchlorate salt by vapour diffusion of diethyl ether into an acetonitrile solution of the complex gave **1** as reddish brown crystals. Yield: 60%. ^1H NMR (CD_3CN): δ 0.9 (t, 3 H, Me of OEt), 2.5 (d, 3 H, J_{P-H} 5.1 Hz, NMe), 4.0 (q, 2 H, OCH_2) and 7.1–8.4 (25 H, phenyl and pyridyl protons). Positive-ion FAB-MS: m/z 716 (M^+), 637 $\{(M - py)^+\}$, 592 $\{(M - py - OEt)^+\}$, 558 $\{(M - 2py)^+\}$, 513 $\{(M - 2py - OEt)^+\}$ and 454 $\{(M - PPh_3)^+\}$. UV/VIS (MeCN): λ/nm ($\varepsilon_{max}/dm^3\ mol^{-1}\ cm^{-1}$) 346 (5945) and 469 (315).

cis-$[Re^V(NMe)(py)_2(PPh_3)(OEt)Cl]ClO_4$ **2**. To a suspension of $[Re(NMe)Cl_3(PPh_3)_2]$ (0.20 g, 0.24 mmol) in ethanol (30 cm^3) was added an excess of pyridine (0.19 g, 2.4 mmol) and the reaction mixture was stirred for 24 h, after which the solvent was removed on a rotary evaporator. The reddish brown residue was washed with diethyl ether, dried and dissolved in ethanol (10 cm^3). Complex **2** was isolated as the perchlorate salt upon addition of lithium perchlorate. Recrystallization by vapour diffusion of diethyl ether into an acetonitrile solution of the complex gave **2** as reddish brown crystals. Yield: 85%. ^1H NMR (CD_3CN): δ 0.9 (t, 3 H, Me of OEt), 2.5 (d, 3 H, J_{P-H} 4.6 Hz, NMe), 3.5 (q, 2 H, OCH_2) and 7.3–8.4 (25 H, phenyl and pyridyl protons). Positive-ion FAB-MS: m/z 716 (M^+), 637 $\{(M - py)^+\}$, 592 $\{(M - py - OEt)^+\}$, 558 $\{(M - 2py)^+\}$ and 513 $\{(M - 2py - OEt)^+\}$. UV/VIS (MeCN): λ/nm ($\varepsilon_{max}/dm^3\ mol^{-1}\ cm^{-1}$) 327 (4480) and 478 (280).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

[Re^V(NMe)(py)$_3$(OEt)Cl]ClO$_4$ **3**. To a stirred suspension of [Re(NMe)Cl$_3$(PPh$_3$)$_2$] (0.20 g, 0.24 mmol) in ethanol (30 cm^3) was added an excess of pyridine (0.19 g, 2.4 mmol). The reaction mixture was heated to reflux, causing the initial blue suspension to dissolve to give a reddish brown solution. Reflux was continued for 24 h. After cooling, the solution was filtered and the solvent removed on a rotary evaporator. The resulting reddish brown solid was then washed with diethyl ether, dried and dissolved in ethanol. Upon addition of lithium perchlorate to the ethanolic solution, complex **1** was precipitated. Removal of **1** by filtration gave a filtrate which was then rotary evaporated to dryness. The solid residue was recrystallized by vapour diffusion of diethyl ether into an acetonitrile solution of the complex to yield purplish red crystals of **3**. Yield: 20%. ^{1}H NMR (CD$_3$OD): δ 1.2 (t, 3 H, Me of OEt), 3.1 (s, 3 H, NMe), 4.2 (q, 2 H, OCH$_2$) and 7.6–8.5 (15 H, pyridyl protons). Positive-ion FAB-MS: *m/z* 533 (M^+), 454 {(M − py)$^+$} and 409 {(M − py − OEt)$^+$}. UV/VIS (MeCN): λ/nm (ε$_{max}$/dm^3 mol^{-1}cm^{-1}) 355 (10 075) and 509 (1086).

[Re^V(NMe)(4Me-py)$_2$(PPh$_3$)(OEt)Cl]ClO$_4$ **4**. This was similarly prepared as for **1** except that 4-methylpyridine (0.22 g, 2.4 mmol) was used in place of pyridine. Yield: 85%. ^{1}H NMR (CD$_3$CN): δ 0.9 (t, 3 H, Me of OEt), 2.5 (d, 3 H, J_{PH} 4.9 Hz, NMe), 2.6 (s, 6 H, Me of 4Me-py), 4.0 (q, 2 H, OCH$_2$) and 7.1–8.2 (23 H, phenyl and pyridyl protons). Positive-ion FAB-MS: *m/z* 744 (M^+), 651 {(M − 4Me-py)$^+$}, 606 {(M − 4Me-py − OEt)$^+$}, 513 {[M − 2 (4Me-py) − OEt]$^+$}, 482 {(M − PPh$_3$)$^+$} and 437 {(M − PPh$_3$ − OEt)$^+$}. UV/VIS (MeCN): λ/nm (ε$_{max}$/dm^3 mol^{-1} cm^{-1}) 341 (7455) and 460 (310).

[Re^V(N)(py)$_2$(PPh$_3$)$_2$Cl]ClO$_4$ **5**. To a suspension of [Re(N)Cl$_2$(PPh$_3$)$_2$] (0.15 g, 0.19 mmol) in ethanol (10 cm^3) was added an excess of pyridine (3 cm^3, 37 mmol) and the reaction mixture was stirred for 0.5 h, during which the brick-red suspension turned into a clear orange-brown solution. This was filtered and upon addition of lithium perchlorate, orange-brown crystals of **5** were obtained after storing at 0 °C for 2 days. Yield: 60%. ^{1}H NMR (CD$_3$CN): δ 7.4–8.6 (40 H, phenyl and pyridyl protons). Positive-ion FAB-MS: *m/z* 918 (M^+), 839 {(M − py)$^+$}, 760 {(M − 2py)$^+$}, 656 {(M − PPh$_3$)$^+$}, 577 {(M − PPh$_3$ − py)$^+$} and 498 {(M − PPh$_3$ − 2py)$^+$}. UV/VIS (MeCN): λ/nm (ε$_{max}$/dm^3 mol^{-1} cm^{-1}) 342 (6905), 405 (sh) (2840).

[Re^V(O)$_2$(py)$_3$(PPh$_3$)]ClO$_4$ **6**. To a stirred suspension of [Re(NMe)Cl$_3$(PPh$_3$)$_2$] (0.30 g, 0.35 mmol) in ethanol–water (30 cm^3, 1 : 1 v/v) was added an excess of pyridine (0.28 g, 3.6 mmol) and the reaction mixture was then heated to reflux for 24 h to give an orange solution. This was cooled, filtered and the filtrate was evaporated to dryness. The brownish orange residue was washed with diethyl ether, dried and dissolved in ethanol, which was then filtered, followed by addition of lithium perchlorate to give yellow crystals of **6** upon storing at 0 °C for 2 days. Yield: 70%. ^{1}H NMR (CD$_3$CN): δ 7.4–9.0 (30 H, phenyl and pyridyl protons). Positive-ion FAB-MS: *m/z* 718 (M^+), 639 {(M − py)$^+$}, 560 {(M − 2 py)$^+$}, 481 {(M − 3 py)$^+$} and 456 {(M − PPh$_3$)$^+$}. UV/VIS (MeCN): λ/nm (ε$_{max}$/dm^3 mol^{-1} cm^{-1}) 337 (9985), 394 (sh) (830) and 463 (sh) (165).

Physical Measurements and Instrumentation.—UV/VIS spectra were obtained on a Milton Roy Spectronic 3000 diode array spectrophotometer, IR spectra as Nujol mulls on a Shimadzu IR-470 infrared spectrophotometer (4000–400 cm^{-1}), and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorometer. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. Proton NMR spectra were recorded on a JEOL JNM-GSX270 Fourier-transform NMR spectrometer with chemical shifts reported relative to SiMe$_4$. Positive-ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched DCR-3 pulsed Nd-YAG laser (10 Hz, G-resonator). Luminescence decay signals were recorded on a Tektronix model 2430 digital oscilloscope, and analysed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a 10 cm^3 roundbottom flask equipped with a sidearm 1 cm fluorescence cuvette and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze-pump-thaw cycles.

Crystal Structure Determination.—Crystals of **3** were obtained by the slow diffusion of diethyl ether into an acetonitrile solution of the complex.

Crystal data. 2(C$_{18}$H$_{23}$Cl$_2$N$_4$O$_5$Re), M_r = 1265.03, monoclinic, space group $P2_1/c$, a = 10.223(4), b = 17.663(2), c = 25.222(3) Å, β = 90.70(2)°, U = 4554.0(7) Å^3, Z = 4, D_c = 1.845 g cm^{-3}, μ(Mo-Kα) = 56.10 cm^{-1}, F(000) = 2464, T = 298 K. A crystal of dimensions 0.15 × 0.05 × 0.30 mm was used for data collection at 25 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using ω–2θ scan with ω-scan angles (0.65 + 0.35 tan θ)° at scan speeds of 1.37 to 8.24° min^{-1}. Intensity data (in the range of 2θ$_{max}$ = 43°; h 0–10, k 0–18; l −25 to 25, and three standard reflections measured after every 2 h showed no decay) were corrected for Lorentz and polarization effects and empirical absorption corrections based on the ψ-scan of four strong reflections (minimum and maximum transmission factors 0.342 and 1.000). Upon averaging the 5793 reflections, 5421 of which were uniquely measured, 5607 independent reflections were obtained (R_{int} = 0.031). 4123 Reflections with $I \geqslant 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined from systematic absences and the structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques[6] and refined by full-matrix least squares using the MSC-crystal structure package TEXSAN[7] on a Silicon Graphics Indy computer. All 60 non-hydrogen atoms were refined anisotropically and unrefined H atoms placed at calculated positions with thermal parameters 1.3 times that of the attached C atom. Convergence for 541 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.006F_o^2)^2]$ for 4123 reflections with $I \geqslant 3\sigma(I)$, was reached at R = 0.040 and R' = 0.043 with a goodness of fit of 2.61; $(\Delta/\sigma)_{max}$ = 0.04. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.30 and −0.99 e Å^{-3} respectively. Each asymmetric unit consists of two formula units of [C$_{18}$H$_{23}$ClN$_4$ORe]$^+$ClO$_4^-$. Atomic coordinates of non-hydrogen atoms are given in Table 1 and selected bond distances and angles in Table 2.

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

Results and Discussion

Reaction of [Re^V(NMe)Cl$_3$(PPh$_3$)$_2$] with pyridine or 4-methylpyridine in ethanol under reflux gave the respective imidorhenium(v) products, *trans*-[Re^V(NMe)(py)$_2$(PPh$_3$)(OEt)Cl]ClO$_4$ **1**, [Re^V(NMe)(py)$_3$(OEt)Cl]ClO$_4$ **3** and [Re^V(NMe)(4Me-py)$_2$(PPh$_3$)(OEt)Cl]ClO$_4$ **4**. If the reaction of [Re^V(NMe)Cl$_3$(PPh$_3$)$_2$] and pyridine was conducted at room temperature, only *cis*-[Re^V(NMe)(py)$_2$(PPh$_3$)(OEt)Cl]ClO$_4$ **2** was obtained. These findings were different from that reported by Leigh and co-workers[3d] where reaction of [Re^V(NMe)Cl$_3$(PPh$_3$)$_2$] with pyridine led only to [Re(NCH$_2$)Cl$_2$(py)(PPh$_3$)$_2$]. A similar reaction of [Re^V(N)Cl$_2$(PPh$_3$)$_2$] with pyridine in ethanol yielded [Re^V(N)(py)$_2$(PPh$_3$)$_2$Cl]ClO$_4$ **5**. On the other hand, reaction of [Re^V(NMe)Cl$_3$(PPh$_3$)$_2$] with pyridine in ethanol–water (1 : 1 v/v) afforded [Re^V(O)$_2$(py)$_3$(PPh$_3$)]ClO$_4$ **6** instead; all compounds were air stable. The newly synthesized complexes were characterized by ^{1}H NMR

Table 1 Atomic parameters for complex **3** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	0.201 88(5)	0.548 52(3)	0.118 21(2)	C(7)	0.140(2)	0.788 5(9)	0.144 0(7)
Re(2)	0.738 15(5)	0.190 41(3)	0.092 16(2)	C(8)	0.126(1)	0.714 2(7)	0.134 7(6)
Cl(1)	0.194 9(3)	0.414 7(2)	0.099 5(1)	C(9)	0.028(1)	0.570 4(7)	0.214 9(5)
Cl(2)	0.734 9(3)	0.325 8(2)	0.081 3(1)	C(10)	−0.077(1)	0.562 2(8)	0.248 1(5)
Cl(3)	0.267 1(3)	0.200 2(2)	0.365 1(1)	C(11)	−0.179(1)	0.518 8(8)	0.232 8(6)
Cl(4)	0.271 2(3)	0.031 0(2)	0.103 3(2)	C(12)	−0.176(1)	0.482 2(8)	0.185 1(7)
O(1)	0.302 2(8)	0.526 5(4)	0.181 2(3)	C(13)	−0.068(1)	0.491 8(7)	0.154 4(6)
O(2)	0.843 7(8)	0.205 9(4)	0.155 0(3)	C(14)	0.486(1)	0.510 6(7)	0.087 4(5)
O(3)	0.336(1)	0.249 6(8)	0.390 9(5)	C(15)	0.602(1)	0.516 8(8)	0.062 9(6)
O(4)	0.193(1)	0.170 8(7)	0.395 8(6)	C(16)	0.622(1)	0.571 6(8)	0.027 1(5)
O(5)	0.345(1)	0.149 1(6)	0.342 7(4)	C(17)	0.523(1)	0.623 3(8)	0.016 7(5)
O(6)	0.193(1)	0.238 0(6)	0.325 4(5)	C(18)	0.404(1)	0.614 5(7)	0.042 3(5)
O(7)	0.195(2)	−0.022 4(10)	0.080 3(7)	C(19)	0.852(2)	0.256 6(8)	0.198 3(6)
O(8)	0.345(1)	0.064(1)	0.069 0(7)	C(20)	0.984(2)	0.282(1)	0.208 8(7)
O(9)	0.203(2)	0.072(1)	0.120 0(7)	C(21)	0.561(2)	0.156 7(9)	−0.008 4(6)
O(10)	0.349(1)	0.000 0(7)	0.144 7(6)	C(22)	0.660(1)	0.023 9(7)	0.105 5(5)
N(1)	0.112 3(10)	0.573 8(5)	0.063 2(4)	C(23)	0.667(1)	−0.049 7(8)	0.119 4(6)
N(2)	0.223 0(9)	0.664 5(5)	0.141 1(4)	C(24)	0.784(2)	−0.076 6(7)	0.141 5(6)
N(3)	0.033 1(10)	0.535 3(5)	0.167 6(4)	C(25)	0.888(1)	−0.027 9(7)	0.146 4(6)
N(4)	0.385 0(9)	0.558 8(5)	0.077 5(4)	C(26)	0.871(1)	0.045 2(7)	0.130 4(5)
N(5)	0.645 7(10)	0.171 5(5)	0.035 9(4)	C(27)	0.469(1)	0.242 3(8)	0.130 2(5)
N(6)	0.758 3(10)	0.073 2(5)	0.110 6(4)	C(28)	0.363(1)	0.246 7(8)	0.163 3(7)
N(7)	0.571 1(9)	0.199 3(6)	0.144 0(4)	C(29)	0.360(1)	0.208 5(9)	0.209 7(6)
N(8)	0.916 4(9)	0.182 7(6)	0.048 5(4)	C(30)	0.464(1)	0.163 7(8)	0.222 7(5)
C(1)	0.305(2)	0.471 5(9)	0.222 5(6)	C(31)	0.570(1)	0.160 2(7)	0.189 1(5)
C(2)	0.439(2)	0.444 2(10)	0.234 3(7)	C(32)	0.930(1)	0.130 0(8)	0.011 4(6)
C(3)	0.032(2)	0.599 0(10)	0.020 1(6)	C(33)	1.041(1)	0.123 2(9)	−0.017 3(6)
C(4)	0.340(1)	0.692 1(7)	0.157 9(5)	C(34)	1.143(2)	0.172 5(10)	−0.008 1(6)
C(5)	0.359(1)	0.767 0(8)	0.168 9(6)	C(35)	1.129(1)	0.226 2(8)	0.028 8(6)
C(6)	0.259(2)	0.815 9(8)	0.162 1(7)	C(36)	1.017(1)	0.231 2(7)	0.056 4(5)

Table 2 Selected bond distances (Å) and angles (°) for complex **3** with e.s.d.s in parentheses

Re(1)–N(1)	1.71(1)	Re(2)–N(5)	1.73(1)
Re(1)–Cl(1)	2.411(3)	Re(2)–Cl(2)	2.407(3)
Re(1)–O(1)	1.922(8)	Re(2)–O(2)	1.926(8)
Re(1)–N(2)	2.139(9)	Re(2)–N(6)	2.13(1)
Re(1)–N(3)	2.15(1)	Re(2)–N(7)	2.17(1)
Re(1)–N(4)	2.153(9)	Re(2)–N(8)	2.146(9)
N(2)–Re(1)–N(3)	91.4(4)	N(6)–Re(2)–N(7)	90.9(4)
N(2)–Re(1)–N(4)	88.0(4)	N(6)–Re(2)–N(8)	88.1(4)
N(3)–Re(1)–Cl(1)	89.3(3)	N(7)–Re(2)–Cl(2)	89.1(3)
N(4)–Re(1)–Cl(1)	90.6(3)	N(8)–Re(2)–Cl(2)	91.0(3)
N(2)–Re(1)–Cl(1)	174.0(3)	N(6)–Re(2)–Cl(2)	172.3(3)
N(3)–Re(1)–N(4)	172.9(4)	N(7)–Re(2)–N(8)	173.8(4)
N(1)–Re(1)–N(2)	91.1(4)	N(5)–Re(2)–N(6)	92.5(4)
N(1)–Re(1)–N(3)	94.1(4)	N(5)–Re(2)–N(7)	94.8(4)
N(1)–Re(1)–N(4)	93.0(4)	N(5)–Re(2)–N(8)	91.4(4)
N(1)–Re(1)–Cl(1)	94.8(3)	N(5)–Re(2)–Cl(2)	95.2(3)
O(1)–Re(1)–N(2)	85.5(4)	O(2)–Re(2)–N(6)	84.5(4)
O(1)–Re(1)–N(3)	85.6(4)	O(2)–Re(2)–N(7)	86.0(4)
O(1)–Re(1)–N(4)	87.3(3)	O(2)–Re(2)–N(8)	87.8(4)
O(1)–Re(1)–Cl(1)	88.6(2)	O(2)–Re(2)–Cl(2)	87.8(2)
O(1)–Re(1)–N(1)	176.6(4)	O(2)–Re(2)–N(5)	176.9(4)
Re(1)–N(1)–C(3)	175(1)	Re(2)–N(5)–C(21)	176(1)
Re(1)–O(1)–C(1)	138.8(9)	Re(2)–O(2)–C(19)	138.7(8)

and IR spectroscopy, and by FAB-MS. The nitrido- and dioxorhenium(v) complexes **5** and **6** show intense IR absorption bands at 1093 and 809 cm^{-1}, respectively, assignable as the ν(Re≡N) and ν_{asym}(O=Re=O) stretches. IR absorptions corresponding to the ν(Re≡NMe) stretch have not been unambiguously assigned as is often the case found for similar complexes.[3a] Magnetic susceptibility measurements showed that they are diamagnetic, consistent with the $(d_{xy})^2$ ground-state electronic configuration. Complex **3** has also been crystallographically characterized.

Fig. 1 depicts a perspective view of the cation of **3** with atomic numbering. Each asymmetric unit is made up of two independent molecules. The molecule is essentially a distorted octahedron with the perchlorate ion being non-co-ordinating. The ethoxy group occupies a position *trans* to the methylimido moiety with a (Me)N–Re–O(Et) angle close to linearity [O(1)–Re(1)–N(1) 176.6(4), O(2)–Re(2)–N(5) 176.9(4)°]. The Re–O(Et) bond distances [Re(1)–O(1) 1.922(8), Re(2)–O(2) 1.926(8) Å] are slightly shorter than the standard Re–O single bond distance of 2.04 Å[8] and the Re–O–C angles of 138.7(8) and 138.8(9)° suggested little significant π-bonding interaction between the metal and the oxygen of the ethoxy group. The Re–N(Me) bond distance [Re(1)–N(1) 1.71(1), Re(2)–N(5) 1.73(1) Å] is slightly longer than that found in [Re^{V}(NMe)(MeNH$_2$)$_4$Cl]$^{2+}$ [1.694(11) Å][4b] and [Re(NMe)Cl$_3$(PEtPh$_2$)$_2$] [1.685(11) Å][3e] but is comparable to that found in the arylimido systems.[3a,f,g] The Re–N–C(Me) angle of 175(1), 176(1)° is in accordance with the Re≡NMe formulation where the methylimido acts as a four-electron donor to give an 18-electron species.

The electronic absorption spectra of complexes **1**–**6** in MeCN exhibit low-energy absorption bands in the region 330–500 nm. The occurrence of absorption bands at 337 (ε 9985) and 394 nm (ε 830 dm^3 mol^{-1} cm^{-1}) in **6** is quite similar to those found in *trans*-[Re^{V}(O)$_2$(py)$_4$]$^+$. With reference to previous spectroscopic works on d^2 *trans*-[Re^{V}(O)$_2$(py)$_4$]$^+$,[2a–e] it is likely that the more intense absorption at *ca.* 337 nm is metal-to-ligand charge transfer [d_{xy}(Re) $\longrightarrow$ π*(py) m.l.c.t.] in character and the lower intensity 394 nm band is assigned to a $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_\pi{}^*)^1$ singlet-singlet transition, with intensity stealing from the adjacent m.l.c.t. band ($d_\pi{}^* = d_{xz}, d_{yz}$ taking the O=Re=O bond axis as the *z* axis). The much weaker shoulder at *ca.* 463 nm (ε 165 dm^3 mol^{-1} cm^{-1}) is likely to be derived from a $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_\pi{}^*)^1$ singlet-triplet transition. For complexes **1**–**5**, the electronic absorption spectra are characterized in all cases by a relatively weak band at *ca.* 400–510 nm and a much more intense band at *ca.* 350 nm. With reference to

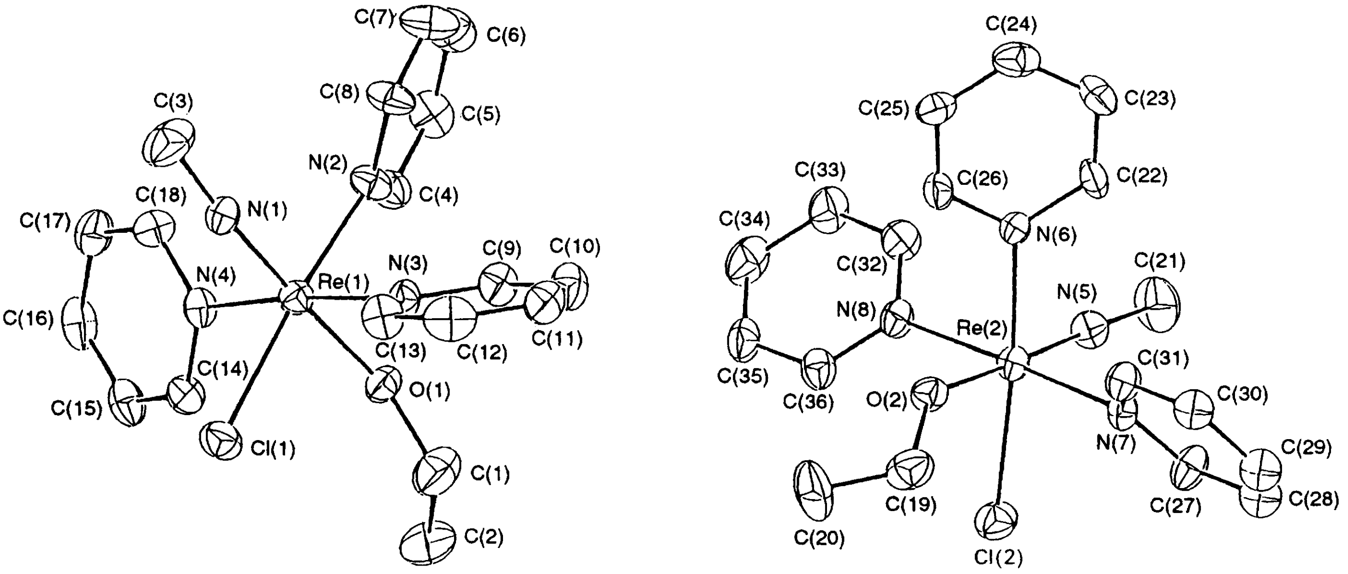

Fig. 1 Perspective drawing of the two crystallographically independent cations of **3** showing the atomic numbering scheme. Each asymmetric unit consists of two formula units of **3**. Thermal ellipsoids are at 50% probability level

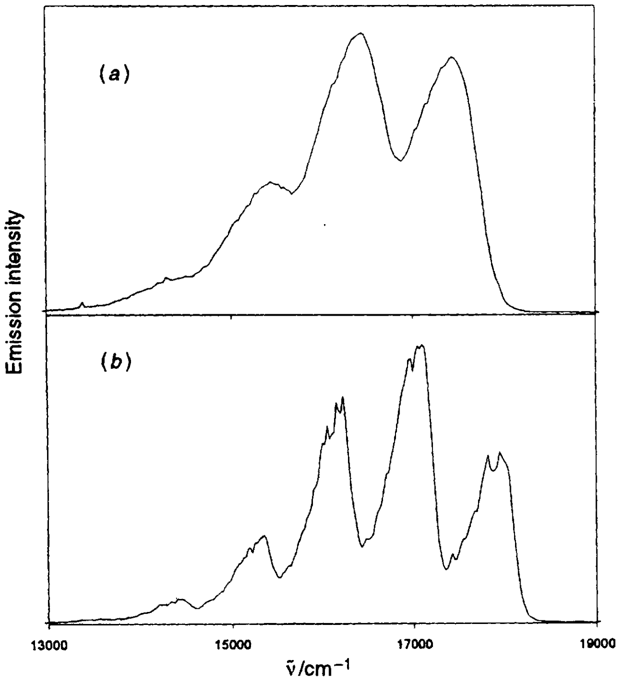

Fig. 2 Solid-state emission spectra of (*a*) complex **5** and (*b*) **6** at 77 K

Table 3 Photophysical data for complexes **5** and **6**

Complex	Medium (T/K)	λ_{em}/nm (τ_o/μs)
5	Solid (298)	604 (5.7 ± 0.5)
	Solid (77)	600
	MeCN	633 (0.65 ± 0.05)
6	Solid (298)	600 (31.7 ± 1.5)
	Solid (77)	600
	MeCN	610 (0.50 ± 0.05)

previous spectroscopic works on d^2 metal–ligand multiply bonded systems,[1,2,9] the relative insensitivity of the transition energies of the 400–500 nm bands in **1**–**5** probably suggested their origin as $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_\pi{}^*)^1$ transitions ($d_\pi{}^* = d_{xz}$, d_{yz} taking the Re–NMe bond axis to be the z axis). The slightly more intense absorption band at 350 nm is likely to be of a $[d_{xy}(\text{Re}) \longrightarrow \pi^*(\text{py})]$ m.l.c.t. transition origin.

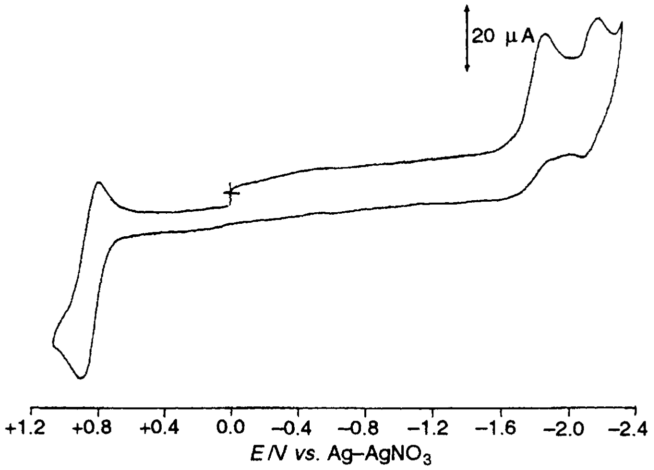

Fig. 3 Cyclic voltammogram of complex **3** in MeCN (0.1 mol dm^{-3} NBu_4PF_6). Working electrode, glassy carbon. Scan rate, 100 mV s^{-1}

Excitation of solid samples and MeCN solutions of complexes **5** and **6** at 350–400 nm at room temperature resulted in intense orange emission (Table 3). Well resolved vibronic structures have been observed in their 77 K solid-state emission spectra (Fig. 2) with vibrational progression spacings of *ca.* 1000 and 850 cm^{-1}, respectively, assigned as the Re≡N and Re=O stretches in the ground state. These are in good agreement with the observed Re≡N and Re=O stretches of *ca.* 1093 and 809 cm^{-1} in the IR spectra of **5** and **6**, respectively. The observation of bands at *ca.* 400–480 nm in their excitation spectra together with the observed lifetimes in the microsecond range suggest that the emissive state is likely to be derived from $(d_{xy})^1(d_\pi{}^*)^1$ triplets.

The cyclic voltammograms of **1**, **2** and **4** in MeCN (0.1 mol dm^{-3} NBu_4PF_6) all show a quasi-reversible one-electron oxidation couple at *ca.* +1.0 to +1.2 V *vs.* the ferrocenium–ferrocene couple. On the other hand, complex **3** displays a reversible one-electron oxidation couple at +0.8 V *vs.* ferrocenium–ferrocene, tentatively assigned to the Re^{VI}–Re^{V} couple (Fig. 3). The cathodic shift of the Re^{VI}–Re^{V} couple in **3** relative to **1** and **2** is in line with the replacement of a good π-acceptor PPh_3 ligand with an extra σ-donating pyridine in **3** which preferentially stabilizes the higher oxidation state. Similar quasi-reversible oxidation couples are observed in **5** and **6**, probably also metal-centred in nature although we cannot exclude the possibility of metal-perturbed phosphine ligand oxidation in complexes **1**, **2** and **4–6**. In all cases, only irreversible reduction waves are observable in the reductive scan.

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