Syntheses, Spectroscopy and X-Ray Crystal Structures of Luminescent Nitrido- and *trans*-Dioxo-rhenium(V) Complexes of Phosphines and Arsines†

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Reaction of [ReNCl$_2$(PPh$_3$)$_2$] and [ReO$_2$(PPh$_3$)$_2$I] with a variety of phosphines and arsines, L, yielded the respective complex cations [ReNL$_2$Cl]$^+$ and *trans*-[ReO$_2$L$_2$]$^+$. The X-ray crystal structures of [ReN(dpae)$_2$Cl]$^+$ and *trans*-[ReO$_2$(dadpe)$_2$]$^+$ [dpae = 1,2-bis(diphenylarsino)ethane, dadpe = 1-diphenylarsino-2-diphenylphosphinoethane] have been determined: [ReN(dpae)$_2$Cl]$^+$, monoclinic, space group *Cc*, $a = 10.362(2)$, $b = 22.823(5)$, $c = 21.363(6)$ Å, $\beta = 92.74(2)°$, $Z = 4$; *trans*-[ReO$_2$(dadpe)$_2$]$^+$, monoclinic, space group *Cc*, $a = 9.868(3)$, $b = 22.608(5)$, $c = 21.887(8)$ Å, $\beta = 91.87(3)°$, $Z = 4$. A Re≡N distance of 1.839(8) and Re=O distances of 1.785(8) and 1.766(8) Å have been measured. The [ReNL$_2$Cl]$^+$ and *trans*-[ReO$_2$L$_2$]$^+$ complexes exhibit intense ν(Re≡N) and ν_{asym}(ReO$_2$) stretches at 1043–1049 and 785–790 cm^{-1}, respectively. Excitation of solid samples of [ReNL$_2$Cl]ClO$_4$ and *trans*-[ReO$_2$L$_2$]ClO$_4$ at 350–380 nm at room temperature results in yellow-green and orange emission, respectively. Both [ReN(dppbz)$_2$Cl]$^+$ and [ReN(*R*-1,2-dppp)$_2$Cl]$^+$ [dppbz = 1,2-bis(diphenylphosphine)benzene, *R*-1,2-dppp = *R*-1,2-bis(diphenylphosphino)propane] exhibit intense long-lived room-temperature luminescence in fluid solutions. Concentration quenching has been observed for both [ReN(dppbz)$_2$Cl]$^+$ and [ReN(*R*-1,2-dppp)$_2$Cl]$^+$ in MeCN (0.1 mol dm^{-3} NBu$_4$PF$_6$) with self-quenching rate constants of *ca.* 5.7×10^7 and 3.2×10^8 dm^3 mol^{-1} s^{-1}, respectively, and inherent lifetimes of *ca.* 15 and 0.9 μs at infinite dilution. All the *trans*-[ReO$_2$L$_2$]$^+$ complexes exhibit room-temperature luminescence in MeCN. Cyclic voltammetric studies show that the [ReNL$_2$Cl]$^+$ complexes display an irreversible reduction couple at E_{pc} of *ca.* −2.1 to −2.4 and an irreversible oxidation couple at E_{pa} of *ca.* +1.4 to +1.7 V *vs.* ferrocene–ferrocenium in MeCN (0.1 mol dm^{-3} NBu$_4$PF$_6$). Irreversible reduction and oxidation couples are also observed for the *trans*-[ReO$_2$L$_2$]$^+$ species. A direct comparison of the photophysical and spectroscopic properties of [ReNL$_2$Cl]$^+$ and *trans*-[ReO$_2$L$_2$]$^+$ has been made.

Recently, there has been considerable interest in the spectroscopic as well as photophysical studies of luminescent metal-oxo complexes,[1] of which the *trans*-dioxorhenium(V) and osmium(VI) complexes of nitrogen-donor ligands are the most well studied. Studies on the isoelectronic nitrido complexes are less extensive and have been mainly confined to those of osmium(VI).[2] In this paper, we report on the syntheses, characterization and photophysical properties of a series of new nitrido- and *trans*-dioxo-rhenium(V) complexes of phosphine and arsine ligands, which provide a systematic direct comparison of the isoelectronic oxo and nitrido moieties with the same set of spectator ligands. The X-ray crystal structures of a nitrido and a *trans*-dioxo complex of rhenium(V) are described.

Experimental

Reagents and Materials.—Both rhenium powder and potassium perrhenate(VII) were purchased from Johnson Matthey Ltd. The complexes [ReNCl$_2$(PPh$_3$)$_2$],[3a] [ReN(dppe)$_2$Cl]Cl[3b] and [ReO$_2$(PPh$_3$)$_2$I][3c] were prepared according to literature procedures except that KReO$_4$ was used in place of perrhenic acid in the preparation of [ReO$_2$(PPh$_3$)$_2$I]. The ligands 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)benzene (dppbz), *R*-(+)-1,2-bis(diphenylphosphino)propane (*R*-1,2-dppp) and 1-diphenylarsino-2-diphenylphosphinoethane (dadpe) were obtained from Strem Chemicals, Inc.; 1,2-bis(diphenylarsino)ethane (dpae) was obtained from Aldrich Chemical Co. Tetra-*n*-butylammonium hexafluorophosphate (Aldrich) was recrystallized twice from absolute ethanol and vacuum dried before use. Both dichloromethane (AJAX, AR) and acetonitrile (Mallinckrodt, ChromAR) were distilled over calcium hydride before use. All other reagents and solvents were of analytical grade and were used as received.

Physical Measurements and Instrumentation.—The 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}), steady-state emission spectra on a Hitachi 650-60 fluorescence spectrophotometer. Phosphorus-31 NMR spectra were recorded on a JEOL JNM-GSX270 Fourier-transform NMR spectrometer with chemical shifts reported relative to H$_3$PO$_4$. Conductivity measurements were made using a Radiometer model CDH2 conductivity meter with 0.1 mol dm^{-3} KCl as calibrant. Magnetic susceptibility measurements were made using the Gouy method. Elemental analyses of the new complexes were performed either by the Butterworth Laboratories or the Shanghai Institute of Organic Chemistry, Academia Sinica.

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

Non-SI unit employed: eV ≈ 1.6×10^{-19} J.

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 round bottom 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. Concentration quenching experiments were monitored by time-resolved (lifetime) emission measurements in MeCN (0.1 mol dm^{-3} NBu_4PF_6) and data were treated by a Stern–Volmer fit as described by $\tau_0/\tau = 1 + k_q\tau_0[\mathrm{Re}]$, where τ_0 and τ are the respective excited-state lifetimes at infinite dilution and at various concentrations of the metal complex [Re], and k_q is the bimolecular self-quenching rate constant.

Cyclic voltammetric measurements were performed by using a Princeton Applied Research (PAR) universal programmer (model 175), potentiostat (model 173), and digital coulometer (model 179). The ferrocenium–ferrocene couple was used as the internal standard[4] in the electrochemical measurements in acetonitrile (0.1 mol dm^{-3} NBu_4PF_6). The working electrode was a glassy carbon (Atomergic Chemicals V25) electrode with a platinum foil acting as the counter electrode. Treatment of the electrode surfaces was as reported elsewhere.[5]

Syntheses of Rhenium Complexes.—$[ReNL_2Cl]Y$ (L = *dppe*, *dppbz*, *dpae*, *dadpe or* R-1,2-*dppp*; Y = Cl *or* ClO_4). These complexes were prepared by a method similar to that reported by Johnson.[3b] A suspension of $[ReNCl_2(PPh_3)_2]$ (0.2 g, 0.25 mmol) and L (0.55 mmol) in benzene (10 cm^3) was refluxed under an atmosphere of nitrogen for *ca.* 4 h during which the brick-red suspension turned yellow. The reaction mixture was then rotary evaporated to dryness. The yellow solid was then recrystallized from methanol–diethyl ether to give crystals of $[ReNL_2Cl]Cl$. The perchlorate salts were obtained by metathesis of the chloride salts in methanol using lithium perchlorate. Crystalline samples of $[ReNL_2Cl]ClO_4$ were obtained by recrystallization *via* diffusion of diethyl ether into an acetonitrile solution of the complex. An alternative procedure using methanol in place of benzene for the reaction of $[ReNCl_2(PPh_3)_2]$ and L followed by addition of $LiClO_4$ also afforded $[ReNL_2Cl]ClO_4$.

$[ReN(dppe)_2Cl]ClO_4$ (Found: C, 55.0; H, 4.2; Cl, 6.3; N, 1.1. Calc.: C, 55.2; H, 4.3; Cl, 6.3; N, 1.2%); IR (Nujol mull), $\nu(Re{\equiv}N)$ 1043 cm^{-1}; magnetic moment (at 298 K), μ_{eff} 0; UV/VIS (MeCN), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 221 (71 160), 239 (sh) (59 710), 269 (sh) (19 080), 307 (sh) (990) and 369 (250); ^{31}P NMR (MeCN), δ 27.89; molar conductivity (298 K) (in MeCN) 132 (in MeOH) 87 Ω^{-1} cm^2 mol^{-1}. $[ReN(dppbz)_2Cl]ClO_4\cdot MeCN$ (Found: C, 58.6; H, 4.0; N, 2.0. Calc.: C, 58.7; H, 4.1; N, 2.2%); IR (Nujol mull), $\nu(Re{\equiv}N)$ 1043 cm^{-1}; magnetic moment (at 298 K), μ_{eff} 0; UV/VIS (MeCN), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 221 (100 410), 244 (sh) (56 285), 269 (sh) (21 130), 278 (sh) (17 250), 287 (sh) (9640), 307 (sh) (1320), 360 (330), 427 (sh) (90) and 472 (sh) (60); ^{31}P NMR (MeCN), δ 33.38, (MeCN–MeOH 1 : 1 v/v) δ 33.23; molar conductivity (298 K) (in MeCN) 134 (in MeOH) 89 Ω^{-1} cm^2 mol^{-1}. $[ReN(dpae)_2Cl]ClO_4$ (Found: C, 47.8; H, 3.5; N, 1.0. Calc.: C, 47.8; H, 3.7; N, 1.1%); IR (Nujol mull), $\nu(Re{\equiv}N)$ 1044 cm^{-1}; magnetic moment (at 298 K), μ_{eff} 0; UV/VIS (MeCN), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 219 (74 850), 238 (sh) (59 610), 266 (sh) (18 490), 307 (sh) (750) and 372 (280). For $[ReN(dadpe)_2Cl]ClO_4$, both yellow and orange forms occur. Attempts to isolate pure forms of each isomer are difficult due to the relative ease of isomerization (Found: C, 50.9; H, 3.8; Cl, 5.8; N, 1.0. Calc.: C, 51.2; H, 4.0; Cl, 5.8; N, 1.2%); IR (Nujol mull), $\nu(Re{\equiv}N)$ 1043 cm^{-1}; magnetic moment (at 298 K), μ_{eff} 0; UV/VIS (MeCN), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 204 (116 400), 238 (sh) (57 010), 266 (sh) (19 800), 307 (sh) (900) and 372 (245); ^{31}P NMR (MeCN), δ 35.18, 36.84. $[ReN(\mathit{R}\text{-}1,2\text{-}dppp)_2Cl]ClO_4$ (Found: C, 55.7; H, 4.5; N, 1.1. Calc.: C, 55.9; H, 4.5; N, 1.2%); IR (Nujol mull), $\nu(Re{\equiv}N)$ 1049 cm^{-1}; magnetic moment (at 298 K), μ_{eff} 0; UV/VIS (MeCN), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 219 (70 890), 242 (sh) (56 420), 270 (sh) (20 850), 307 (sh) (945) and 374 (250); ^{31}P NMR (MeCN), δ 12.01 and 35.34.

$[ReO_2L_2]Y$ (L = *dppe*, *dppbz*, *dpae*, *dadpe or* R-1,2-*dppp*; Y = I *or* ClO_4). These complexes were prepared by a method similar to that reported by Brewer and Gray.[6] A suspension of $[ReO_2(PPh_3)_2I]$ (0.2 g, 0.23 mmol) and L (0.51 mmol) in methanol (10 cm^3) was refluxed for *ca.* 4 h during which the violet suspension turned to a clear yellow solution. The reaction mixture was then reduced in volume to afford yellow crystals of $[ReO_2L_2]I$, which were recrystallized from methanol–diethyl ether. The perchlorate salts were obtained by metathesis of the iodide salts in methanol using lithium perchlorate. Crystalline samples of $[ReO_2L_2]ClO_4$ were obtained by recrystallization *via* diffusion of diethyl ether into an acetonitrile solution of the complex.

$[ReO_2(dppe)_2]ClO_4\cdot H_2O$ (Found: C, 55.3; H, 4.2; Cl, 2.9. Calc.: C, 55.2; H, 4.5; Cl, 3.1%); IR (Nujol mull), $\nu_{asym}(Re{=}O)$ 784 cm^{-1}; magnetic moment (at 298 K), μ_{eff} 0; UV/VIS (MeCN), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 268 (42 615), 309 (sh) (2520) and 389 (sh) (207). $[ReO_2(dppbz)_2]ClO_4\cdot MeCN\cdot H_2O$ (Found: C, 58.6; H, 4.0; Cl, 2.6; N, 0.9. Calc.: C, 58.7; H, 4.2; Cl, 2.8; N, 1.1%); IR (Nujol mull), $\nu_{asym}(Re{=}O)$ 790 cm^{-1}; magnetic moment (at 298 K), μ_{eff} 0; UV/VIS (MeCN), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 240 (sh) (50 860), 270 (sh) (28 590), 290 (sh) (18 715) and 389 (sh) (235); ^{31}P NMR (MeCN), δ 15.45; molar conductivity (at 298 K) (in MeCN) 129, (in MeOH) 83 Ω^{-1} cm^2 mol^{-1}. $[ReO_2(dpae)_2]ClO_4\cdot H_2O$ (Found: C, 47.9; H, 3.5; Cl, 2.6. Calc.: C, 47.7; H, 3.8; Cl, 2.7%); IR (Nujol mull), $\nu_{asym}(Re{=}O)$ 786 cm^{-1}; magnetic moment (at 298 K), μ_{eff} 0; UV/VIS (MeCN), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 243 (sh) (41 040), 273 (52 890), 312 (sh) (2950) and 389 (sh) (295). $[ReO_2(dadpe)_2]ClO_4\cdot H_2O$ (Found: C, 51.4; H, 3.8; Cl, 2.7. Calc.: C, 51.2; H, 4.1; Cl, 2.9%); IR (Nujol mull), $\nu_{asym}(Re{=}O)$ 786 cm^{-1}; magnetic moment (at 298 K), μ_{eff} 0; UV/VIS (MeCN), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 244 (sh) (41 310), 270 (56 070), 312 (sh) (2670) and 395 (sh) (220); ^{31}P NMR (MeCN), δ 15.48 and 19.09. $[ReO_2(\mathit{R}\text{-}1,2\text{-}dppp)_2]ClO_4\cdot 2H_2O$ (Found: C, 55.2; H, 4.2; Cl, 2.7. Calc.: C, 55.0; H, 4.8; Cl, 3.0%); IR (Nujol mull), $\nu_{asym}(Re{=}O)$ 786 cm^{-1}; magnetic moment (at 298 K), μ_{eff} 0; UV/VIS (MeCN), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 273 (35 620), 312 (sh) (2540) and 400 (sh) (175).

Crystal Structure Determination.—$[ReN(dpae)_2Cl]ClO_4$. The complex $[ReN(dpae)_2Cl]ClO_4$ was recrystallized by vapour diffusion of diethyl ether into acetonitrile.

Crystal data. $C_{52}H_{48}As_4Cl_2NO_4Re$, M_r = 1307.8, monoclinic, space group *Cc*, *a* = 10.362(2), *b* = 22.823(5), *c* = 21.363(6) Å, β = 92.74(2)°, *U* = 5046(2) Å^3, *Z* = 4, D_c = 1.722 g cm^{-3}, *F*(000) = 2560, crystal dimensions = 0.30 × 0.50 × 0.50 mm. The intensity data were measured on a CAD-4 diffractometer using Mo-Kα radiation (λ = 0.7107 Å) using the ω–2θ scan mode at 297 K with $2\theta_{max}$ = 50°. Cell dimensions were obtained from 24 reflections with 2θ angles in the range 19.12–21.58°. 4698 Reflections were measured of which 3793 were observed $[I > 2.0\sigma(I)]$. Absorption corrections (μ = 38.8 cm^{-1}) were made according to ψ curves of three selected reflections. The minimum and maximum transmission factors are 0.77 and 1.00. The structure was solved by the Patterson method and refined by least squares. Full-matrix least-squares refinement on 576 parameters converged to yield agreement indices *R* = 0.033, *R'* = 0.020 and goodness of fit = 1.83; max. Δ/σ = 0.19; the residual $\Delta\rho < \pm 0.97$ e Å^{-3}; weights are based on counting statistics. Table 1 lists the atomic coordinates of non-hydrogen atoms. Selected bond distances and angles are summarized in Table 2. All the hydrogen atom parameters were calculated from the idealized geometry.

$[ReO_2(dadpe)_2]ClO_4$. The complex $[ReO_2(dadpe)_2]ClO_4$ was recrystallized by vapour diffusion of diethyl ether into acetonitrile.

Table 1 Atomic parameters for $[ReN(dpae)_2Cl]ClO_4$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Re	0.899 77	0.801 73(2)	0.846 39
As(1)	0.925 5(1)	0.703 0(1)	0.899 6(1)
As(2)	0.811 9(1)	0.827 6(1)	0.952 5(1)
As(3)	0.908 8(1)	0.902 9(1)	0.797 1(1)
As(4)	1.012 8(1)	0.775 1(1)	0.747 1(1)
Cl(5)	1.114 8(3)	0.834 4(1)	0.884 5(1)
N(6)	0.737 7(7)	0.781 4(3)	0.814 8(3)
C(1)	0.777 2(9)	0.700 5(4)	0.953 8(5)
C(2)	0.772 3(11)	0.752 6(4)	0.995 2(5)
C(3)	1.053 3(9)	0.901 0(4)	0.741 0(5)
C(4)	1.041 9(12)	0.846 6(5)	0.700 3(5)
C(11A)	1.077 1(8)	0.685 4(4)	0.953 0(4)
C(12A)	1.066 9(10)	0.654 0(5)	1.009 0(5)
C(13A)	1.175 6(11)	0.641 2(6)	1.044 8(5)
C(14A)	1.293 4(11)	0.659 3(5)	1.029 6(5)
C(15A)	1.304 5(10)	0.692 5(5)	0.975 4(5)
C(16A)	1.196 9(9)	0.705 2(4)	0.937 9(4)
C(11B)	0.894 3(10)	0.634 1(3)	0.848 1(5)
C(12B)	0.809 9(11)	0.636 2(4)	0.800 0(5)
C(13B)	0.787 0(12)	0.588 9(5)	0.759 3(6)
C(14B)	0.853 9(12)	0.538 6(5)	0.768 9(6)
C(15B)	0.939 8(12)	0.536 3(4)	0.817 4(6)
C(16B)	0.967 4(9)	0.582 4(4)	0.858 3(5)
C(21A)	0.907 7(9)	0.868 0(4)	1.018 2(4)
C(22A)	0.886 0(10)	0.857 3(5)	1.080 3(5)
C(23A)	0.950 9(11)	0.890 6(5)	1.126 4(5)
C(24A)	1.032 7(11)	0.934 0(5)	1.111 5(5)
C(25A)	1.057 3(12)	0.944 9(5)	1.050 0(5)
C(26A)	0.995 4(10)	0.911 1(4)	1.004 2(5)
C(21B)	0.650 7(9)	0.871 5(4)	0.951 1(5)
C(22B)	0.637 1(11)	0.923 6(5)	0.981 4(5)
C(23B)	0.524 5(12)	0.954 0(5)	0.980 0(6)
C(24B)	0.421 8(12)	0.929 6(6)	0.948 2(6)
C(25B)	0.428 4(11)	0.877 0(6)	0.914 9(7)
C(26B)	0.546 6(10)	0.848 9(5)	0.917 9(6)
C(31A)	0.769 7(9)	0.929 6(4)	0.742 9(4)
C(32A)	0.781 7(11)	0.978 3(5)	0.705 8(5)
C(33A)	0.680 8(12)	0.998 7(5)	0.667 5(6)
C(34A)	0.564 7(10)	0.969 3(5)	0.664 0(5)
C(35A)	0.545 2(9)	0.922 7(4)	0.698 7(6)
C(36A)	0.650 1(10)	0.903 6(4)	0.739 5(5)
C(31B)	0.942 6(9)	0.971 1(4)	0.847 7(5)
C(32B)	1.066 8(9)	0.992 2(4)	0.860 2(5)
C(33B)	1.088 0(10)	1.038 6(4)	0.900 4(5)
C(34B)	0.986 1(11)	1.064 2(4)	0.928 4(5)
C(35B)	0.861 1(11)	1.044 4(5)	0.914 5(5)
C(36B)	0.840 9(9)	0.996 9(4)	0.875 0(5)
C(41A)	0.921 9(11)	0.732 4(4)	0.681 7(5)
C(42A)	0.791 9(10)	0.737 3(5)	0.671 3(5)
C(43A)	0.727 7(11)	0.710 9(5)	0.620 1(6)
C(44A)	0.798 8(14)	0.677 1(6)	0.582 9(6)
C(45A)	0.924 6(14)	0.665 9(7)	0.592 1(7)
C(46A)	0.984 2(11)	0.697 3(6)	0.641 9(6)
C(41B)	1.176 8(9)	0.736 3(5)	0.758 7(5)
C(42B)	1.184 0(11)	0.676 2(5)	0.770 5(6)
C(43B)	1.300 5(15)	0.650 2(6)	0.783 3(7)
C(44B)	1.403 2(12)	0.685 2(6)	0.784 1(6)
C(45B)	1.410 2(13)	0.739 9(7)	0.769 5(8)
C(46B)	1.287 4(12)	0.766 5(6)	0.759 7(8)
Cl	0.242 3(3)	0.912 7(1)	0.585 9(1)
O(1)	0.306 8(7)	0.861 0(3)	0.605 6(3)
O(2)	0.241 0(7)	0.952 2(3)	0.636 0(4)
O(3)	0.114 9(7)	0.899 6(4)	0.566 0(4)
O(4)	0.304 9(7)	0.938 4(3)	0.535 5(3)

Table 2 Selected bond distances (Å) and angles (°) for $[ReN(dpae)_2Cl]^+$ with e.s.d.s in parentheses

Re–N(6)	1.839(8)	Re–Cl(5)	2.451(3)
Re–As(1)	2.532(1)	Re–As(2)	2.552(1)
Re–As(3)	2.541(1)	Re–As(4)	2.546(1)
As(1)–C(1)	1.968(10)	As(2)–C(2)	1.991(10)
As(3)–C(3)	1.962(9)	As(4)–C(4)	1.945(10)
As–C(Ph)	1.905(10)–1.946(10)		
As(1)–Re–As(2)	80.86(4)	As(3)–Re–As(4)	81.04(4)
As(1)–Re–As(3)	171.65(3)	As(2)–Re–As(4)	173.42(4)
As(1)–Re–As(4)	96.82(4)	As(2)–Re–As(3)	100.37(4)
Cl(5)–Re–N(6)	176.4(2)		
As–Re–N(6)	90.8(2)–97.4(2)		
As–Re–Cl(5)	79.07(7)–92.71(7)		

Crystal data. $C_{52}H_{48}As_2ClO_6P_2Re$, $M_r = 1202.4$, monoclinic, space group *Cc*, $a = 9.868(3)$, $b = 22.608(5)$, $c = 21.887(8)$ Å, $\beta = 91.87(3)°$, $U = 4880(3)$ Å^3, $Z = 4$, $D_c = 1.637$ g cm^{-3}, $F(000) = 2384$, crystal dimensions = 0.30 × 0.40 × 0.40 mm. The intensity data were measured on a CAD-4 diffractometer using Mo-Kα radiation ($\lambda = 0.7107$ Å) using the ω–2θ scan mode at 297 K with $2\theta_{max} = 45°$. Cell dimensions were obtained from 24 reflections with 2θ angles in the range 18.72–22.54°. 3409 Reflections were measured of which 2822 were observed [$I > 2.0\sigma(I)$]. Absorption corrections ($\mu = 33.1$ cm^{-1}) were made according to ψ curves of three selected reflections. The minimum and maximum transmission factors are 0.83 and 1.00. The structure was solved by the Patterson method and refined by least squares. Full-matrix least-squares refinement on 576 parameters converged to yield agreement indices $R = 0.034$, $R' = 0.024$ and goodness of fit = 1.63; max. $\Delta/\sigma = 0.34$; max. $\Delta\rho = 1.03$, min. $\Delta\rho = -0.75$ e Å^{-3}; weights are based on counting statistics. Table 3 lists the atomic coordinates of non-hydrogen atoms. Selected bond distances and angles are summarized in Table 4. All hydrogen atom parameters are from calculated values. There are partial disorders on the P and As sites; the final result is based on 80% of As plus 20% P for the As site and 80% P plus 20% As for the P site.

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

Results and Discussion

Reaction of $[ReNCl_2(PPh_3)_2]$ with the appropriate diphosphines or arsines afforded the complex cations $[ReNL_2Cl]^+$ in good yields, similar to that reported by Johnson.[3b] In the syntheses of the *trans*-$[ReO_2L_2]^+$ complexes, $[ReO_2(PPh_3)_2I]$ has proven to be a good starting material for complexes of the ReO_2^+ unit, as suggested by Brewer and Gray.[6] It seems that both $[ReNCl_2(PPh_3)_2]$ and $[ReO_2(PPh_3)_2I]$ are ideal starting materials for the general synthesis of the respective $Re^V{\equiv}N$ and $O{=}Re^V{=}O$ units.

Fig. 1 shows the perspective drawing of the $[ReN(dpae)_2Cl]^+$ cations. The molecule is essentially a distorted octahedron, with the perchlorate ions being non-co-ordinating. The As(1)–Re–As(2) and As(3)–Re–As(4) bond angles are 80.86(4) and 81.04(4)°, respectively, as would be required by the bite distance of the chelating ligand. The nitrido ligand is *trans* to the chloro group with a Cl–Re–N angle of 176.4(2)°. The nitrido group exerts a large *trans* labilizing effect on the Re–Cl bond [2.451(3) Å] which is longer than that for a normal Re–Cl bond though shorter than that reported for the *trans* Re–Cl bond in $[ReNCl_2(PEt_2Ph)_3]$.[7] The Re≡N bond distance of 1.839(8) Å is longer than that reported for other nitridorhenium(v) complexes such as $[ReNCl_2(PEt_2Ph)_3]$ [*d*(Re≡N) = 1.79 Å].[7] The shorter Re–Cl and the longer Re≡N bond distances than in $[ReNCl_2(PEt_2Ph)_3]$[7] may not be a genuine representation and may arise as a result of crystallographic effects.[8] The other bond distances and angles are normal.

Table 3 Atomic parameters for *trans*-[$ReO_2(dadpe)_2$]ClO_4 with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Re	0.951 38	0.798 13(3)	0.954 95
As(1)	0.843 9(2)	0.821 9(1)	1.056 8(1)
As(2)	1.059 4(2)	0.772 5(1)	0.854 5(1)
P(3)	0.962 0(3)	0.699 5(1)	1.002 6(1)
P(4)	0.958 8(3)	0.901 1(1)	0.904 8(1)
O(5)	1.114 8(9)	0.821 7(4)	0.982 6(4)
O(6)	0.786 6(8)	0.780 1(4)	0.927 0(3)
C(1)	0.800 0(13)	0.746 6(5)	1.093 4(6)
C(2)	1.100 5(18)	0.847 0(7)	0.816 7(7)
C(3)	0.811 6(13)	0.697 8(7)	1.051 1(5)
C(4)	1.113 4(15)	0.896 6(6)	0.859 5(6)
C(11A)	0.939 7(13)	0.861 8(6)	1.120 0(5)
C(12A)	1.038 0(14)	0.903 2(6)	1.105 7(6)
C(13A)	1.104 2(15)	0.937 2(7)	1.149 6(6)
C(14A)	1.072 8(16)	0.927 9(7)	1.208 5(7)
C(15A)	0.981 8(17)	0.885 6(8)	1.225 8(6)
C(16A)	0.916 5(15)	0.852 7(7)	1.182 0(6)
C(11B)	0.674 3(14)	0.862 9(6)	1.054 5(5)
C(12B)	0.564 0(14)	0.837 6(7)	1.021 8(7)
C(13B)	0.440 8(14)	0.864 0(8)	1.019 9(8)
C(14B)	0.423 3(16)	0.917 3(8)	1.047 8(7)
C(15B)	0.530 6(16)	0.946 6(7)	1.080 7(7)
C(16B)	0.654 6(14)	0.917 5(6)	1.080 9(6)
C(21A)	0.962 0(14)	0.735 1(6)	0.788 0(5)
C(22A)	1.025 3(15)	0.701 5(8)	0.744 5(6)
C(23A)	0.951 0(21)	0.677 5(8)	0.696 6(7)
C(24A)	0.814 3(18)	0.692 5(9)	0.689 7(6)
C(25A)	0.754 7(16)	0.722 8(8)	0.732 9(6)
C(26A)	0.825 1(15)	0.746 5(7)	0.781 3(6)
C(21B)	1.228 3(14)	0.728 4(6)	0.865 5(5)
C(22B)	1.347 6(16)	0.757 2(7)	0.874 1(7)
C(23B)	1.466 1(15)	0.723 3(8)	0.887 7(7)
C(24B)	1.456 5(16)	0.664 7(8)	0.893 9(7)
C(25B)	1.343 5(17)	0.637 1(8)	0.885 5(7)
C(26B)	1.222 8(15)	0.669 1(6)	0.871 7(6)
C(31A)	1.110 2(14)	0.683 8(6)	1.052 5(6)
C(32A)	1.098 7(16)	0.652 4(7)	1.107 4(6)
C(33A)	1.212 9(16)	0.641 7(8)	1.143 8(6)
C(34A)	1.334 6(15)	0.662 6(7)	1.127 2(7)
C(35A)	1.347 2(14)	0.692 9(7)	1.074 0(6)
C(36A)	1.235 5(13)	0.703 9(7)	1.038 0(5)
C(31B)	0.939 6(18)	0.635 9(5)	0.952 9(7)
C(32B)	1.004 2(13)	0.582 8(16)	0.962 0(6)
C(33B)	0.988 2(16)	0.535 3(6)	0.924 6(7)
C(34B)	0.902 8(16)	0.539 0(6)	0.875 3(7)
C(35B)	0.835 0(14)	0.593 2(7)	0.863 0(6)
C(36B)	0.854 8(14)	0.639 9(6)	0.902 0(6)
C(41A)	0.830 9(15)	0.925 3(6)	0.851 1(6)
C(42A)	0.705 4(17)	0.898 8(7)	0.851 0(6)
C(43A)	0.597 5(18)	0.917 6(8)	0.807 6(8)
C(44A)	0.620 7(18)	0.962 5(7)	0.769 8(7)
C(45A)	0.747 1(20)	0.987 4(9)	0.769 7(8)
C(46A)	0.849 6(17)	0.968 9(8)	0.811 0(7)
C(41B)	0.984 8(13)	0.964 9(5)	0.952 5(7)
C(42B)	0.882 8(13)	0.991 3(6)	0.981 1(5)
C(43B)	0.897 8(16)	1.037 0(6)	1.022 5(7)
C(44B)	1.025 3(17)	1.056 8(6)	1.035 1(6)
C(45B)	1.131 6(15)	1.033 8(6)	1.007 6(7)
C(46B)	1.106 3(16)	0.989 0(6)	0.965 2(6)
Cl	0.274 6(4)	0.914 4(2)	0.691 9(2)
O(1)	0.332 8(10)	0.940 7(5)	0.640 8(4)
O(2)	0.138 8(12)	0.901 8(6)	0.676 1(5)
O(3)	0.275 1(11)	0.954 1(5)	0.741 0(4)
O(4)	0.346 9(11)	0.862 1(5)	0.708 5(4)

Table 4 Selected bond distances (Å) and angles (°) for *trans*-[$ReO_2(dadpe)_2$]$^+$ with e.s.d.s in parentheses

Re–O(5)	1.785(8)	Re–O(6)	1.766(8)
Re–As(1)	2.557(2)	Re–As(2)	2.541(2)
Re–P(3)	2.463(3)	Re–P(4)	2.576(3)
As(1)–C(1)	1.94(1)	As(2)–C(2)	1.93(2)
P(3)–C(3)	1.85(1)	P(4)–C(4)	1.85(1)
As–C(Ph)	1.88(1)–1.95(1)		
P–C(Ph)	1.78(2)–1.83(1)		
O(5)–Re–O(6)	176.0(4)	P(3)–Re–P(4)	175.93(9)
As(1)–Re–As(2)	178.88(6)	As(2)–Re–P(4)	79.57(7)
As(1)–Re–P(3)	80.45(8)	As(2)–Re–P(3)	98.44(8)
As(1)–Re–P(4)	101.52(7)	As(1)–Re–O(6)	86.95(25)
As(1)–Re–O(5)	92.2(3)	As(2)–Re–O(6)	93.19(25)
As(2)–Re–O(5)	87.7(3)	P(3)–Re–O(6)	87.9(3)
P(3)–Re–O(5)	95.8(3)	P(4)–Re–O(6)	95.7(3)
P(4)–Re–O(5)	80.6(3)		

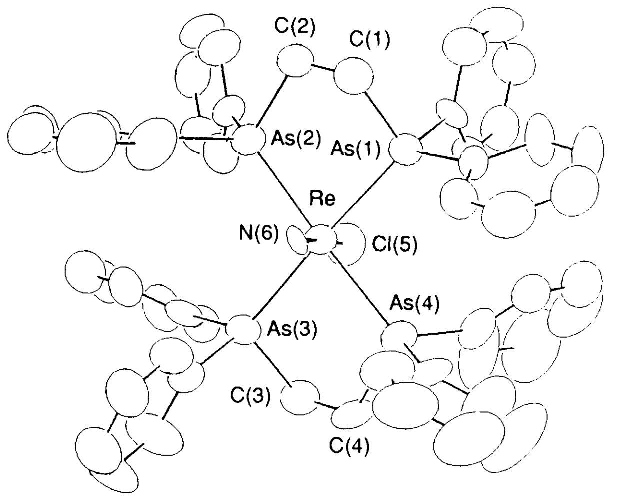

Fig. 1 A perspective drawing of the [ReN(dpae)$_2$Cl]$^+$ cation with atomic numbering

Fig. 2 shows the perspective drawing of the *trans*-[$ReO_2(dadpe)_2$]$^+$ cation. The cation is a distorted octahedron, with the perchlorate ions being non-co-ordinating. The As(1)–Re–As(2) and P(3)–Re–P(4) bond angles are almost linear, being 178.88(6) and 175.93(9)°, respectively. The P atoms on the two dadpe ligands are *trans* to each other, the same is true for the As atoms. The two oxo groups are *trans* to each other with a O(5)–Re–O(6) bond angle of 176.0(4)°. The Re=O bond distances are 1.785(8) and 1.766(8) Å, which are in the normal range for *trans*-dioxorhenium(v) complexes.[9] The other bond distances and angles are also normal.

All the nitridorhenium(v) and *trans*-dioxorhenium(v) complexes are air-stable solids. Magnetic susceptibility measurements show that they are diamagnetic, consistent with the $(d_{xy})^2$ ground-state electronic configuration in a C_{2v} and D_{2h} symmetry, respectively. A comparison between the IR absorption spectra of the corresponding nitrido- and dioxo-rhenium(v) complexes allows the assignment of the Re≡N and Re=O stretches to be made. All the nitridorhenium(v) complexes exhibit a strong IR absorption band at *ca.* 1043–1049 cm^{-1}, assignable as the Re≡N stretch. The observed stretching frequencies are comparable to those found for other nitridorhenium(v) complexes.[3a,b,10] All the *trans*-dioxorhenium(v) complexes are found to exhibit a strong IR absorption band at *ca.* 785–790 cm^{-1}, assignable to the ν_{asym}(Re=O) stretch, typical of the *trans*-ReO_2 unit.[9,11]

Both the nitrido and dioxo complexes are 1 : 1 electrolytes in acetonitrile and in methanol. The dissociation of the *trans*-

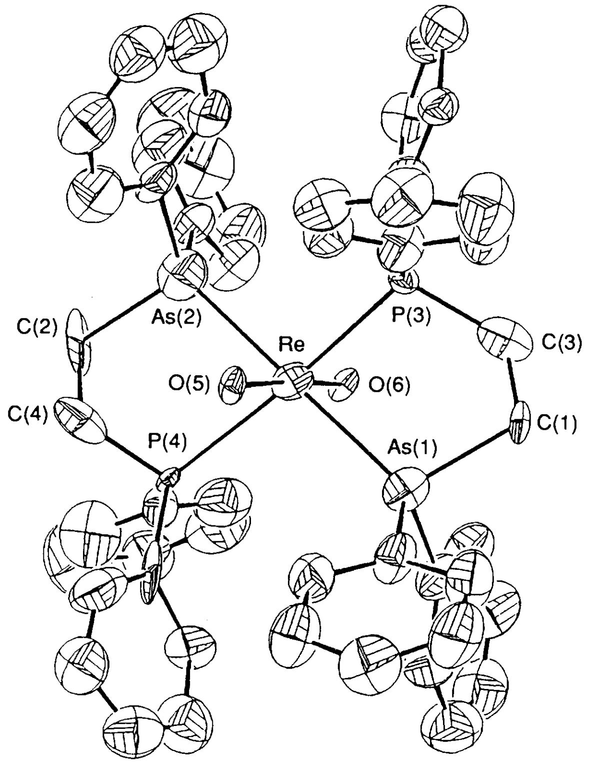

Fig. 2 A perspective drawing of the *trans*-[ReO$_2$(dadpe)$_2$]$^+$ cation with atomic numbering

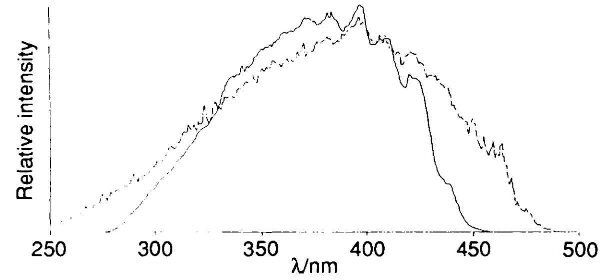

Fig. 3 Solid-state excitation spectra of (*a*) [ReN(*R*-1,2-dppp)$_2$Cl]ClO$_4$ (——) and (*b*) *trans*-[ReO$_2$(*R*-1,2-dppp)$_2$]ClO$_4$ (— — —) at 77 K

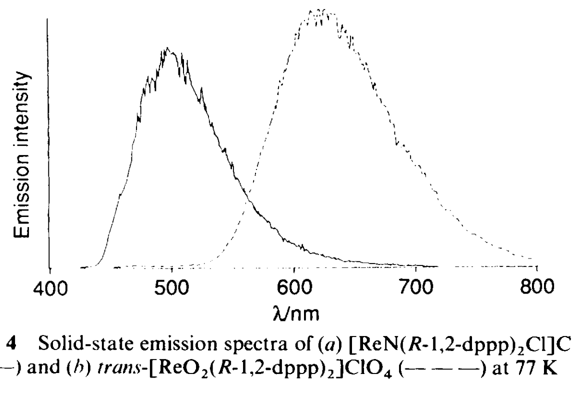

Fig. 4 Solid-state emission spectra of (*a*) [ReN(*R*-1,2-dppp)$_2$Cl]ClO$_4$ (——) and (*b*) *trans*-[ReO$_2$(*R*-1,2-dppp)$_2$]ClO$_4$ (— — —) at 77 K

chloro ligand in [Re^{V}NL$_2$Cl]$^+$ appears to be unimportant in both MeCN and MeOH, as evidenced from conductivity measurements and ^{31}P NMR spectroscopy. The presence of two ^{31}P NMR singlets for both [Re^{V}N(dadpe)$_2$Cl]$^+$ and *trans*-[Re^{V}O$_2$(dadpe)]$^+$ is consistent with the presence of two isomers, one with the As-donor atoms *trans* and the other *cis* to each other.

The UV/VIS absorption spectra of complexes [ReNL$_2$Cl]-ClO$_4$ in acetonitrile exhibit intense absorption bands in the region 220–300 nm and a weak absorption at *ca.* 360–375 nm ($\varepsilon \approx$ 250–330 dm^3 mol^{-1} cm^{-1}) with very weak shoulders in the region 400–550 nm ($\varepsilon < 100$). The large absorption coefficients observed for the bands at *ca.* 200–300 nm possibly suggest their origins as intraligand transition and ligand-to-metal charge-transfer transitions [$p_\pi(N^{3-}) \longrightarrow d_{\pi^*}(Re)$ and $p_\pi(Cl^-) \longrightarrow d_{\pi^*}(Re)$] where $d_{\pi^*} = d_{xz}, d_{yz}$. The relative insensitivity of the transition energies of these intense absorptions to the nature of the equatorial ligands probably rules out their assignment as metal-to-ligand charge-transfer transitions [$d_{xy} \longrightarrow \pi^*(L)$]. With reference to previous spectroscopic works on d^2 nitrido-osmium(VI) systems,[2] the energies of d orbitals of Re^V≡N complexes, assuming a C_{2v} symmetry are in the order, a_2 $(d_{xy}) < b_1$ $(d_{xz}) \approx b_2$ $(d_{yz}) < a_1(d_{x^2-y^2}) < a_1(d_{z^2})$. The weak absorptions in the low-energy region probably arise from transitions to excited states derived from spin triplets [$(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{yz})^1$ ($^1A_1 \longrightarrow {}^3B_1$) and $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{xz})^1$ ($^1A_1 \longrightarrow {}^3B_2$)].

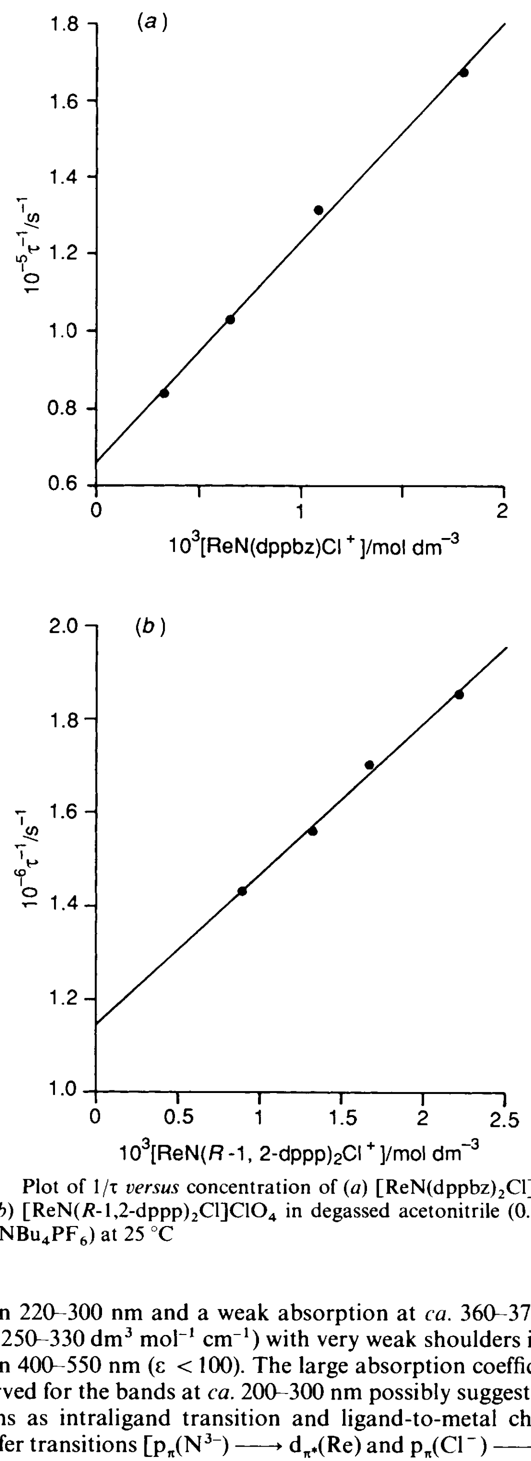

Fig. 5 Plot of $1/\tau$ *versus* concentration of (*a*) [ReN(dppbz)$_2$Cl]ClO$_4$ and (*b*) [ReN(*R*-1,2-dppp)$_2$Cl]ClO$_4$ in degassed acetonitrile (0.1 mol dm^{-3} NBu$_4$PF$_6$) at 25 °C

The UV/VIS absorption spectra of complexes *trans*-[ReO$_2$L$_2$]ClO$_4$ in acetonitrile are also dominated by intense absorptions in the high-energy region, which are likely to be intraligand and charge-transfer [$p_\pi(O^{2-}) \longrightarrow (d_{xz}, d_{yz})(Re^V)$]

Table 5 Photophysical data for complexes $[ReNL_2Cl]ClO_4$ (*a*) and *trans*-$[ReO_2L_2]ClO_4$ (*b*) at room temperature

(*a*) $[ReNL_2Cl]ClO_4$

L	λ_{em}/nm (τ_o/μs)
dppe	512 (2.0 ± 0.2)[a]
dppbz	514 (0.35 ± 0.05, 1.7 ± 0.2)[a]
	509 (10 ± 1)[b]
	509 (10 ± 1)[c]
	509[d]
dpae	500 (0.45 ± 0.05)[a]
dadpe	510 (0.50 ± 0.05, 2.7 ± 0.3)[a]
R-1,2-dppp	502 (9.5 ± 1.0)[a]
	520 (0.7 ± 0.1)[b]
	520 (0.7 ± 0.1)[c]
	519[d]

(*b*) *trans*-$[ReO_2L_2]ClO_4$

L	λ_{em}/nm (τ_o/μs)
dppe	613 (0.20 ± 0.2, 1.2 ± 0.2)[a]
	615 (0.8 ± 0.1)[b]
dppbz	607 (0.7 ± 0.1)[a]
	627 (1.0 ± 0.2)[b]
dpae	596 (1.5 ± 0.2)[a]
	627 (0.8 ± 0.1)[b]
dadpe	618 (0.20 ± 0.02, 1.4 ± 0.2)[a]
	630 (0.5 ± 0.1)[b]
R-1,2-dppp	613 (0.35 ± 0.05)[a]
	620 (0.7 ± 0.1)[b]

[a] Solid-state emission. Some show biexponential decays. [b] In degassed MeCN (0.1 mol dm^{-3} NBu_4PF_6). 0.65 mmol dm^{-3} = $[ReNL_2Cl]ClO_4$; 3.5 mmol dm^{-3} = $[ReO_2L_2]ClO_4$. The lifetimes measured for the dioxo species in MeCN are not very accurate due to the very weak emission signal detected. [c] In degassed MeOH–MeCN (1:1 v/v). [d] In degassed CH_2Cl_2.

Table 6 Cyclic voltammetric data for complexes $[ReNL_2Cl]ClO_4$ (*a*) and *trans*-$[ReO_2L_2]ClO_4$ (*b*) in acetonitrile (0.1 mol dm^{-3} NBu_4PF_6)[a]

(*a*) $[ReNL_2Cl]ClO_4$

L	E_{pc}/V[b]	E_{pa}/V[c]
dppe	−2.34	+1.55
dppbz	−2.26	+1.57
dpae	−2.21	+1.65
dadpe	−2.17	+1.51
R-1,2-dppp	−2.36	+1.45

(*b*) *trans*-$[ReO_2L_2]ClO_4$

L	E_{pc}/V[b]	E_{pa}/V[c]
dppe	−2.27	+1.33
	−2.39	
dppbz	−2.26	+1.43
	−2.37	
dpae	−2.13	+1.33
	−2.31	
dadpe	−2.44	+1.43
R-1,2-dppp	−2.26	+1.30
	−2.35	

[a] Working electrode, glassy carbon; scan rate; 100 mV s^{-1}; potentials quoted relative to the ferrocene–ferrocenium couple. [b] E_{pc} is the peak cathodic potential for the irreversible couple. [c] E_{pa} is the peak anodic potential for the irreversible couple.

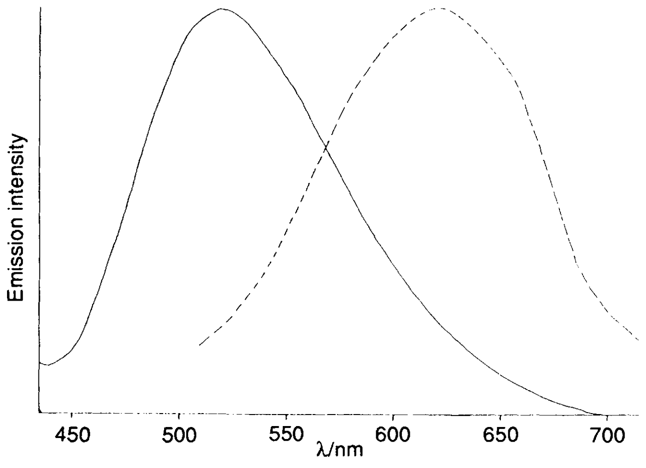

Fig. 6 Emission spectra of (*a*) $[ReN(R\text{-}1,2\text{-dppp})_2Cl]ClO_4$ (——) and (*b*) *trans*-$[ReO_2(R\text{-}1,2\text{-dppp})_2]ClO_4$ (— — —) in degassed acetonitrile at 25 °C

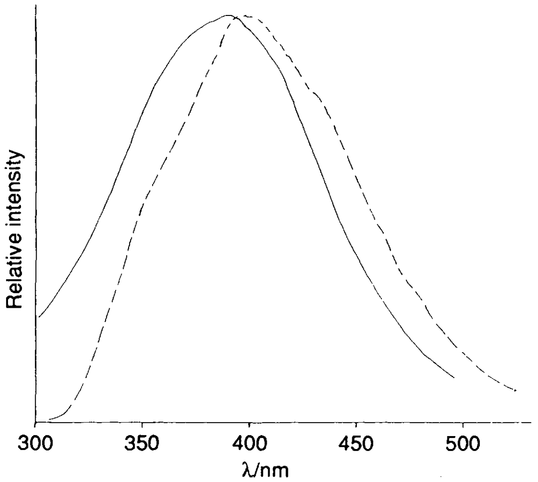

Fig. 7 Excitation spectra of (*a*) $[ReN(R\text{-}1,2\text{-dppp})_2Cl]ClO_4$ (——) and (*b*) *trans*-$[ReO_2(R\text{-}1,2\text{-dppp})_2]ClO_4$ (— — —) in degassed acetonitrile at 25 °C

transitions. With reference to previous spectroscopic works on d^2 *trans*-dioxorhenium(v) systems,[1a,b] the energies of d orbitals of $O{=}Re^V{=}O$ complexes, assuming a D_{2h} symmetry are in the order, b_{1g} (d_{xy}) < b_{2g} (d_{xz}) ≈ b_{3g} (d_{yz}) < a_g $(d_{x^2-y^2})$ < a_g (d_{z^2}). The very weak absorptions that tail into the 390–500 nm region are assigned as the $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{xz})^1$ $[^1A_g \longrightarrow {}^3B_{3g}]$ and $(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{yz})^1$ $[^1A_g \longrightarrow {}^3B_{2g}]$ transitions which are vibronically coupled to the $B_{1u}[ReO_2]$ stretching mode.

Excitation of solid samples of complexes $[ReNL_2Cl]ClO_4$ and *trans*-$[ReO_2L_2]ClO_4$ at 350–380 nm at room temperature results in yellow-green and orange emission, respectively. The solid-state excitation and emission spectra at 77 K are depicted in Figs. 3 and 4, respectively. Well resolved vibronic structures are observed in the solid-state excitation spectrum of $[Re(N)(R\text{-}1,2\text{-dppp})_2Cl]ClO_4$ at 77 K with a progression spacing of *ca.* 750–850 cm^{-1}. Similar progressions have been observed in the low-temperature absorption spectrum of $[OsNCl_4]^-$,[2a,b] suggestive of a weakened M≡N bond in the excited state. The photophysical data are summarized in Table 5. Both $[ReN(dppbz)_2Cl]^+$ and $[Re(N)(R\text{-}1,2\text{-dppp})_2Cl]^+$ exhibit intense long-lived room-temperature luminescence in fluid solutions while only a very weak emission at *ca.* 500 nm is detected in fluid solutions of $[ReN(dppe)_2Cl]^+$. Concentration quenching has been observed for both $[ReN(dppbz)_2Cl]^+$ and $[ReN(R\text{-}1,2\text{-dppp})_2Cl]^+$ in MeCN (0.1 mol dm^{-3} NBu_4PF_6) with self-quenching rate constants of *ca.* 5.7 × 10^7 and 3.2 × 10^8 dm^3 mol^{-1} s^{-1}, respectively, and inherent lifetimes of *ca.* 15 and 0.9 μs at infinite dilution (Fig. 5). A possible mechanism for self quenching would involve the coupling of two Re≡N units as suggested by Che *et al.*[2c] in the analogous $Os^{VI}{\equiv}N$ system. However, further studies have to be followed in order to elucidate the mechanism of concentration quenching. The much shorter excited-state lifetime of $[\mathrm{ReN(dppbz)_2Cl}]^+$ in the solid state than in acetonitrile is rather surprising. On the other hand, all the *trans*-$[\mathrm{ReO_2L_2}]^+$ complexes exhibit room-temperature luminescence in MeCN. The emission of these dioxo species is found to be completely quenched in MeOH, similar to that reported previously by Winkler and Gray,[1a,b] where interaction of the M=O unit with the OH group of the solvent has been suggested to provide an efficient relaxation pathway for the excited species. However, the lifetimes of both $[\mathrm{ReN(dppbz)_2Cl}]^+$ and $[\mathrm{ReN(}R\text{-1,2-dppp)}_2\mathrm{Cl}]^+$ are found to be rather insensitive on going from MeCN to MeOH. This may reflect a difference in the $\mathrm{p}K_\mathrm{a}$ values of the nitrido and oxo group. The room-temperature emission and excitation spectra of $[\mathrm{ReNL_2Cl}]^+$ and *trans*-$[\mathrm{ReO_2L_2}]^+$ in degassed acetonitrile are shown in Figs. 6 and 7, respectively. The excitation spectra of $[\mathrm{ReNL_2Cl}]^+$ show broad bands at *ca.* 390–410 nm. This together with the observed lifetime in the microsecond range suggest that the emissive state is likely to be derived from the $(\mathrm{d}_{xy})^1(\mathrm{d}_{xz})^1$ and $(\mathrm{d}_{xy})^1(\mathrm{d}_{yz})^1$ triplets. The excitation spectra of *trans*-$[\mathrm{ReO_2L_2}]^+$ show bands at *ca.* 400–440 nm, probably also derived from the $(\mathrm{d}_{xy})^1(\mathrm{d}_{xz})^1$ $[^3\mathrm{B}_{3\mathrm{g}}]$ and $(\mathrm{d}_{xy})^1(\mathrm{d}_{yz})^1$ $[^3\mathrm{B}_{2\mathrm{g}}]$ triplets assuming a D_{2h} symmetry. Similar assignments have also been made for other d^2 nitrido and dioxo systems [1,2] where the $(\mathrm{d}_{xy})^1(\mathrm{d}_{xz}, \mathrm{d}_{yz})^1$ triplet (^{3}E in C_{4v} and $^3\mathrm{E_g}$ in D_{4h} symmetry) is suggested to be the origin of the observed emission.

An interesting feature worth mentioning is that a comparison between the emission energies of the nitrido- and the *trans*-dioxo-rhenium(v) complexes shows that those of the former occur at higher energies than the latter. This probably indicates that the nitrido group is a better π donor ligand than the combination of two *trans* oxo groups, as has been suggested by various researchers.[12]

Cyclic voltammetric studies show that the $[\mathrm{ReNL_2Cl}]^+$ complexes display an irreversible reduction couple at E_pc of *ca.* −2.1 to −2.4 V and an irreversible oxidation couple at E_pa of *ca.* +1.4 to +1.7 V *vs.* ferrocene–ferrocenium in MeCN (0.1 mol dm^{-3} $\mathrm{NBu_4PF_6}$) (Table 6). Similarly, irreversible reduction and oxidation couples are observed for the *trans*-$[\mathrm{ReO_2L_2}]^+$ species (Table 6). The irreversible oxidation in both $[\mathrm{ReNL_2Cl}]^+$ and *trans*-$[\mathrm{ReO_2L_2}]^+$ is probably ligand-centred in nature. Assuming the reduction process to be metal-centred, a rough estimate of the excited-state reduction potential $E_\mathrm{f}[\mathrm{ReNL_2Cl}^{+*/0}]$ of *ca.* 0.8 V *vs.* the normal hydrogen electrode (NHE) can be made for L = dppbz [$E_{0-0} \approx 2.4$ eV, $E_\mathrm{pc} = -1.6$ V *vs.* NHE].

Conclusion

The nitridorhenium(v) complexes of phosphine and arsine ligands represent a new class of luminescent complexes.[*] By suitable design of the equatorial ligands and the systematic study of these nitrido and dioxo complexes, a direct comparison of their photophysical as well as spectroscopic properties can be made.

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[*] *Note added at proof:* Photophysical properties of nitridorhenium(v) complexes of diphosphine ligands have recently been reported.[13]