Syntheses, Spectroscopy and Electrochemistry of Nitridorhenium(V) Organometallics. X-Ray Crystal Structure of $[Re^{V}NMe_2(PPh_3)_2]$

Vivian Wing-Wah Yam,* Kwok-Kwong Tam and Ting-Fong Lai
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

Treatment of $[Re^{V}NCl_2(PPh_3)_2]$ with LiR gives the complexes $[Re^{V}NR_2(PPh_3)_2]$ (R = Me, $C{\equiv}CBu^t$, Ph or C_6H_4Me-*p*) which show rich photophysical behaviour; the crystal structure of $[Re^{V}NMe_2(PPh_3)_2]$ exhibits a $Re{\equiv}N$ distance of 1.641 (4) Å.

The spectroscopy and photophysics of d^2 metal–ligand multiply bonded species, particularly those of the oxo- and nitrido-ligands, have attracted considerable attention in recent years.[1,2] However, most studies have been confined to the Werner-type complexes, with relatively less attention focused on the organometallic analogues. In this contribution we report on the syntheses, spectroscopy and electrochemistry of a series of organorhenium(V) nitrido complexes. The X-ray crystal structure of the methylrhenium complex $[Re^{V}NMe_2(PPh_3)_2]$ **1** has also been determined.

Treatment of a suspension of $[Re^{V}NCl_2(PPh_3)_2]$ with 2.1 equivalents of $LiC{\equiv}CBu^t$ in toluene under nitrogen at room temperature for 3 h gave $[Re^{V}N(C{\equiv}CBu^t)_2(PPh_3)_2]$ **2**, isolated as air-stable orange microcrystals (yield 70–75%). The phenyl and *p*-tolyl analogues $[Re^{V}NPh_2(PPh_3)_2]$ **3** and $[Re^{V}N(C_6H_4Me\text{-}p)_2(PPh_3)_2]$ **4** were prepared similarly from the respective aryllithium compounds and isolated as orange and reddish orange air-stable microcrystals, respectively; see also the method of Chatt *et al.*[3] Although previous attempts to obtain the methylrhenium derivative did not yield **1**,[3] we found that by heating a suspension of $[Re^{V}NCl_2(PPh_3)_2]$ with 2.1 equivalents of LiMe in toluene under nitrogen at *ca.* 70 °C for 24 h **1** was formed as reddish orange microcrystals (yield 40%) and its crystal structure has been determined (Fig. 1).[†] The structure of **1** resembles that of the chloro analogue $[Re^{V}NCl_2(PPh_3)_2]$ in having a distorted trigonal-bipyramidal geometry, with an $Re{\equiv}N$ distance of 1.641(4) Å which is slightly longer than that for $[Re^{V}NCl_2(PPh_3)_2]$ [1.602(9) Å].[6] This could be attributed to the strong σ-donating effect of the methyl groups which would lower the nitrogen–rhenium p_π–d_π overlap. The almost *trans* arrangement of the two phosphorus atoms is consistent with the observation of a singlet in the ^{31}P NMR spectrum at δ 44.59 (relative to H_3PO_4). However, for compound **2** the absence of a $\nu(C{\equiv}C)$ stretch in the IR spectrum might suggest a *trans* arrangement of the $C{\equiv}CBu^t$ groups rather than the triphenylphosphines, since both would give a singlet in the ^{31}P NMR spectrum. All compounds **1**–**4** show an intense $\nu(Re{\equiv}N)$ stretch at *ca.* 1065–1080 cm^{-1}.[‡]

The electronic absorption spectra of **1**–**4** in toluene at room temperature show absorption bands in the 400–550 nm region, with those of **2**, **3** and **4** being vibronically structured with progressional spacings of *ca.* 800–920 cm^{-1}. Similar progressions have been observed in the low-temperature absorption spectrum of $[Os^{VI}NCl_4]^-$,[2a,b] suggestive of a weakened $M{\equiv}N$ bond in the excited state. The UV/VIS spectral data are collected in Table 1. With reference to previous spectroscopic studies on d^2 metal–nitrido systems,[2] the energies of d orbitals of $Re^{V}{\equiv}N$ compounds, assuming a C_{2v} symmetry, are in the order $a_2(d_{xy}) < b_1(d_{xz}) \approx b_2(d_{yz}) < a_1(d_{x^2-y^2}) < a_1(d_{z^2})$. It is likely that the low-energy absorption bands at *ca.* 430–550 nm are derived from $[(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{xz})^1]$ $(A_1 \longrightarrow B_2)$ and $[(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{yz})^1]$ $(A_1 \longrightarrow B_1)$ transitions, which are symmetry allowed.

Excitation of solid samples of **1**–**4** at λ > 400 nm at room temperature and at 77 K results in red emission. The solid-state emission spectrum of **2** at 77 K is shown in Fig. 2. The excitation spectra of **1**–**4** show broad bands at *ca.* 450–550 nm. The photophysical data are summarized in Table 1. Compound **2** is also found to exhibit room-temperature luminescence in fluid solution (Fig. 2). This is the first example of an organo-

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[†] *Crystal data.* $C_{38}H_{36}NP_2Re$, *M* = 754.86, crystal dimensions 0.05 × 0.18 × 0.18 mm, monoclinic, space group *C*2/*c*, *a* = 24.141(5), *b* = 9.632(3), *c* = 15.727(4) Å, β = 116.12(2), *U* = 3283.5(3.4) $Å^3$, *Z* = 4, D_c = 1.527 g cm^{-3}, *F*(000) = 1504, μ(Mo-Kα) = 38.72 cm^{-1}, 191 parameters, 6834 data measured, no. of data used in calculation 2600 $[I > 1.5\sigma(I)]$, *R* = 0.019, *R'* = 0.027, $w = 4F_o^2/[\sigma^2(F_o)^2 + (0.04F_o^2)^2]$. The maximum and minimum residues in the final Δ*F* synthesis were 0.370 and −0.207 e $Å^{-3}$ respectively. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å) at 297 K to $2\theta_{max} = 52°$. Intensity data were corrected for Lorentz, polarization and absorption effects. Atomic scattering factors were taken from ref. 4. Calculations were carried out on a MicroVax II computer using the Enraf-Nonius SDP package.[5] The rhenium atom was located from a Patterson synthesis and all other non-hydrogen atoms from subsequent Fourier maps. Refinement was by full-matrix least squares. All non-hydrogen atoms were refined anisotopically. The methyl hydrogen atoms were omitted while the other hydrogen atoms at calculated positions were included in the structure factor calculation. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

[‡] For **1**, Found: C, 59.65; H, 4.60; N, 1.70. Calc. for **1**·$0.5H_2O$: C, 59.75; H, 4.90; N, 1.85%; IR (Nujol mull, cm^{-1}), $\nu(Re{\equiv}N)$ 1077; ^1H NMR (C_6D_6, relative to $SiMe_4$), δ 1.6 [t, *J*(HP) 7.0 Hz, 6 H, Me], 7.0 (m, 18 H, aryl protons *m* and *p* to P), 8.0 (m, 12 H, aryl protons *o* to P); ^{31}P NMR (toluene, relative to H_3PO_4), δ 44.59 (s). For **2**, Found: C, 64.60; H, 5.15; N, 1.45. Calc. for **2**: C, 65.00; H, 5.45; N, 1.60%; IR (Nujol mull, cm^{-1}), $\nu(Re{\equiv}N)$ 1080; ^1H NMR (C_6D_6, relative to $SiMe_4$), δ 0.9 (s, 18 H, Bu^t), 7.0 (m, 18 H, aryl protons *m* and *p* to P), 8.1 (m, 12 H, aryl protons *o* to P); ^{31}P NMR (toluene, relative to H_3PO_4), δ 34.62 (s). For **3**, Found: C, 66.00; H, 4.50; N, 1.40. Calc. for **3**: C, 65.60; H, 4.60; N, 1.60%; IR (Nujol mull, cm^{-1}), $\nu(Re{\equiv}N)$ 1065; ^1H NMR (C_6D_6, relative to $SiMe_4$), δ 6.8 (m, 10 H, Ph), 7.0 (m, 18 H, aryl protons *m* and *p* to P), 7.7 (m, 12 H, aryl protons *o* to P); ^{31}P NMR (toluene, relative to H_3PO_4), δ 32.13 (s). For **4**, Found: C, 68.35; H, 5.10; N, 1.30. Calc. for **4**·$C_6H_5CH_3$: C, 68.50; H, 5.25; N, 1.40%; IR (Nujol mull, cm^{-1}), $\nu(Re{\equiv}N)$ 1070; ^1H NMR (C_6D_6, relative to $SiMe_4$), δ 2.2 (s, 6 H, Me), 6.7 (m, 8 H, tolyl protons), 7.0 (m, 18 H, aryl protons *m* and *p* to P), 7.7 (m, 12 H, aryl protons *o* to P); ^{31}P NMR (CH_2Cl_2, relative to H_3PO_4), δ 31.86 (s).

Table 1 Photophysical and cyclic voltammetric data for compounds **1**–**4** at 298 K

Compound	Absorption λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	Emission λ/nm (τ_o/μs)	E_f(Re^{VI}–Re^V)^a/V
1	344 (3230), 431 (sh) (655)	680^b	−0.06
2	337 (1375), 458 (430)	720 (6.5)^b	+0.03
		715^c	
		809^d	
3	322 (sh) (5730), 363 (sh) (2120), 481 (1195)	640^b	−0.02
4	325 (sh) (4690), 366 (sh) (1865), 489 (1130)	650^b	−0.18

[a] In CH_2Cl_2 (0.1 mol dm^{-3} NBu$^n{}_4$PF$_6$); working electrode, glassy carbon; scan rate, 100 mV s^{-1}; potentials quoted relative to ferrocene–ferrocenium couple. [b] Solid-state emission. [c] Solid-state emission at 77 K. [d] In degassed benzene.

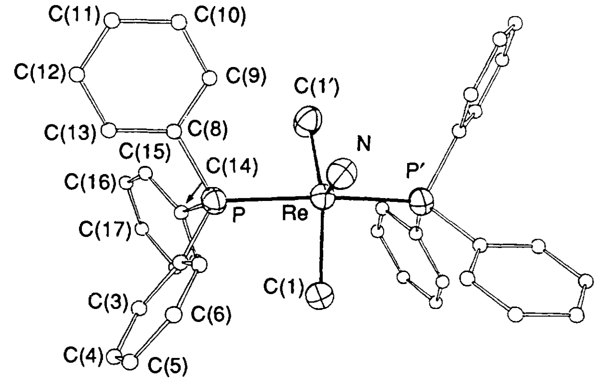

Fig. 1 Perspective drawing of [Re^{V}NMe$_2$(PPh$_3$)$_2$] **1** showing the atom numbering scheme. Selected bond distances (Å) and angles (°): Re–N 1.641(4), Re–P 2.4170(9), Re–C(1) 2.188(3), P–Re–P′ 163.79(2), P–Re–N 98.11(3), P–Re–C(1) 87.0(2), N–Re–C(1) 111.3(1), C(1)–Re–C(1′) 137.5(1). The Re–N bond lies on a crystallographic two-fold axis and the molecule possesses a two-fold symmetry; P′ and C(1′) are related to P and C(1) by symmetry operation: $-x, y, \frac{1}{2} - z$. Thermal ellipsoids are at 50% probability level. For clarity phenyl carbon atoms are given arbitrary radius and hydrogen atoms are omitted

rhenium(v) nitrido species to exhibit fluid solution luminescence at room temperature. The emissive state is likely to be derived from the $(d_{xy})^1(d_{xz})^1(^3B_2)$ and $(d_{xy})^1(d_{yz})^1(^3B_1)$ triplets assuming a C_{2v} symmetry. Similar assignments have also been made for other d^2 nitrido and dioxo systems.[1,2]

Cyclic voltammetric studies show that **1**–**4** display a quasi-reversible one-electron oxidation couple at −0.18 to +0.03 V and an irreversible oxidation couple at > +1.0 V *vs.* ferrocene–ferrocenium in CH_2Cl_2 (0.1 mol dm^{-3} NBu$^n{}_4$PF$_6$) (Table 1). No reduction couples were observed up to −2.50 V. The quasi-reversible oxidation is assigned to the Re^{VI}–Re^V couple, with **4** being the most easily oxidized and **2** the least. This is consistent with the order of σ-donating ability of the organo moieties. The presence of empty π* orbitals in the *tert*-butylacetylide groups also contributes to the observation of a relatively more anodic E_f(Re^{VI}–Re^V) value for **2**. The relative ease of oxidizing Re^V to Re^{VI} in the uncharged **1**–**4** compared to the positively charged species [Re^{V}N(L-L)$_2$Cl]$^+$ (L-L = bidentate phosphine or arsine)[2f,g] could be partially attributed to the charge effect. Moreover, the introduction of organo functionalities inevitably stabilizes the more electron-deficient d^1 rhenium(vi) species. An excited-state reduction potential E_f(Re^{VI}–Re^{V*}) of *ca.* −1.52 V *vs.* the normal hydrogen electrode has been estimated for **4** ($E_{0-0} \approx 3.2 \times 10^{-19}$ J). Unlike the non-organo complex [Re^{V}N(dppbz)$_2$Cl]$^{+*}$ [dppbz = 1,2-bis(diphenylphosphino)benzene][2f] which is an oxidant and [Re^{V}N(dmpe)$_2$Cl]$^{+*}$ [dmpe = 1,2-bis(dimethylphosphino)ethane][2g] which is a weak reductant, **2** is a strong reducing agent in the excited state, indicating the wide capabilities and effectiveness of tuning photophysical properties *via* the introduction of organo functionalities.

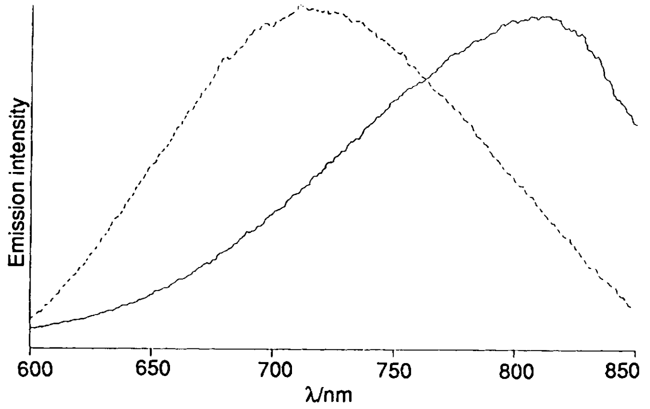

Fig. 2 Corrected emission spectra of [Re^{V}N(C≡CBu^t)$_2$(PPh$_3$)$_2$] **2** in the solid state at 77 K (······) and in degassed benzene at 298 K (——)

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