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Synthesis, Spectroscopy and Electrochemistry of Luminescent $[Re^VN\{Ph_2P(CH_2)_2PPh_2\}_2(MeCN)]^{2+}$

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

Treatment of $[Re^VN(dppe)_2Cl]ClO_4$ [dppe = 1,2-bis(diphenylphosphino)ethane] with $Ag(CF_3SO_3)$ in MeCN afforded $[Re^VN(dppe)_2(MeCN)][ClO_4]_2$ which showed rich photophysical behaviour; its luminescence quantum yield was greater by a factor of $>10^3$ than that of its chloro analogue $[Re^VN(dppe)_2Cl]^+$.

Recently, transition-metal–ligand multiply bonded species have attracted considerable attention and have been the subject of numerous studies.[1] In particular, the chemistry of metal nitrido species has attracted great attention owing to their potential role in nitrogen fixation reactions. Moreover, d^2 metal nitrido species are found to exhibit rich photophysical and photochemical behaviour.[2,3] In this communication, we report on the synthesis, characterization, photophysics and electrochemistry of a newly synthesized complex $[Re^VN(dppe)_2(MeCN)]^{2+}$ [dppe = 1,2-bis(diphenylphosphino)ethane]. The high luminescence quantum yield of $[Re^VN(dppe)_2(MeCN)]^{2+}$ relative to its chloro analogue, $[Re^VN(dppe)_2Cl]^+$ is also described.

Treatment of an acetonitrile solution (40 cm^3) of $[Re^VN(dppe)_2Cl]ClO_4$[2a,4] (250 mg, 0.2 mmol) with $Ag(CF_3SO_3)$ (150 mg, 0.6 mmol) at 70 °C under an atmosphere of nitrogen for 20 min, followed by filtration to remove the insoluble AgCl and subsequent addition of diethyl ether, afforded $[Re^VN(dppe)_2(MeCN)][ClO_4]_2$ in almost quantitative yield. Fluorescent yellow-green crystalline samples of $[Re^VN(dppe)_2(MeCN)][ClO_4]_2$ were obtained by recrystallization *via* diethyl ether diffusion into an acetonitrile solution of the complex. The identity of $[Re^VN(dppe)_2(MeCN)][ClO_4]_2$ has been confirmed by elemental analyses, IR, Raman and ^{31}P NMR spectroscopy and positive-ion fast atom bombardment (FAB) mass spectrometry.† The solution IR spectrum exhibits a sharp band of medium intensity at *ca.* 2265 cm^{-1}, typical of $\nu(C\equiv N)$ stretching. A comparison of the solid-state Raman spectra shows that the $\nu(Re\equiv N)$ stretch is shifted from 1044 cm^{-1} in $[Re^VN(dppe)_2Cl]^+$ to 1080 cm^{-1} in $[Re^VN(dppe)_2(MeCN)]^{2+}$, indicative of a stronger $Re\equiv N$ bond in the latter complex. This strengthening of the $Re\equiv N$ bond in $[Re^VN(dppe)_2(MeCN)]^{2+}$ could be attributed to a more effective $d_\pi(Re)–p_\pi(N)$ overlap due to removal of the $d_\pi–p_\pi$ overlap between the Re and Cl atoms upon replacing Cl by MeCN. The downfield shift of the ^{31}P NMR signal in $[Re^VN(dppe)_2(MeCN)]^{2+}$ (δ 39.0) relative to $[Re^VN(dppe)_2Cl]^+$ (δ 27.9)[2a] is in accord with the lower electron density at the Re centre in the former which withdraws electron density from the phosphorus donor atoms which are thus deshielded. The complex $[Re^VN(dppe)_2(MeCN)]^{2+}$ shows a strong positive-ion FAB mass spectrum with ion clusters observable in the region *m/z* 100–1200. The molecular ion M^+ is observed at *m/z* 1038 with additional prominent signals at *m/z* 997 $\{[M - MeCN]^+\}$ and 640 $\{[M - dppe]^+\}$.

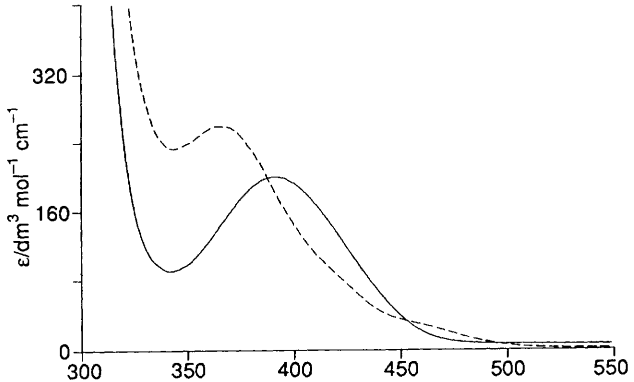

Fig. 1 Electronic absorption spectra of $[Re^VN(dppe)_2(MeCN)][ClO_4]_2$ (——) and $[Re^VN(dppe)_2Cl]ClO_4$ (– – –) in MeCN at 298 K

The electronic absorption spectrum of $[Re^VN(dppe)_2(MeCN)]^{2+}$ in MeCN at room temperature shows an absorption band at *ca.* 392 nm. With reference to previous spectroscopic work on d^2 metal nitrido systems,[2,3] the energies of the d orbitals of $Re^V\equiv N$ compounds, assuming 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 band at *ca.* 392 nm is derived from the $[(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{xz})^1]$ $(A_1 \longrightarrow B_2)$ and $[(d_{xy})^2 \longrightarrow (d_{xy})^1(d_{yz})^1]$ $(A_1 \longrightarrow B_1)$ transitions, which are both symmetry allowed. The red shift of the 392 nm band relative to the corresponding band at 369 nm in the chloro analogue, $[Re^VN(dppe)_2Cl]^+$ (Fig. 1), is in accord with the removal of the $d_\pi–p_\pi$ overlap between the Re and Cl atoms on replacing Cl by MeCN since such an overlap would raise the energies of the d_{xz} and d_{yz} orbitals. Addition of NBu_4Cl to an acetonitrile solution of $[Re^VN(dppe)_2(MeCN)]^{2+}$ regenerates $[Re^VN(dppe)_2Cl]^+$, characterized spectroscopically by the disappearance of the 392 nm band and the appearance of the 369 nm band.

Excitation of a solid sample of $[Re^VN(dppe)_2(MeCN)]^{2+}$ at

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† Characterizing data for $[Re^VN(dppe)_2(MeCN)][ClO_4]_2$ {Found: C, 51.55; H, 4.05; Cl, 4.90; N, 2.10. Calc. for $[Re^VN(dppe)_2(MeCN)][ClO_4]_2\cdot H_2O$: C, 51.70; H, 4.25; Cl, 5.65; N, 2.25%}. IR (Nujol mull): $\nu(C\equiv N)$ 2295, 2265, $\nu(Re\equiv N)$ 1072 cm^{-1}; IR (CH_2Cl_2): IR$\nu(C\equiv N)$ 2265, $\nu(Re\equiv N)$ 1072 cm^{-1}. Raman (solid sample): $\nu(C\equiv N)$ 2264, $\nu(Re\equiv N)$ 1080 cm^{-1}. Magnetic moment (at 298 K): $\mu_{eff} = 0$. UV/VIS (MeCN): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 224 (54 145), 243 (sh) (38 000), 268 (sh) (16 840), 392 (200). ^{31}P NMR (CD_3CN), δ 39.0. Molar conductivity (in MeCN at 298 K): 280 Ω^{-1} cm^2 mol^{-1}. Positive-ion FAB mass spectrum (glycerol–thioglycerol): *m/z* 1038 (M^+), 997 $\{[M - MeCN]^+\}$, 640 $\{[M - dppe]^+\}$.

Table 1 Photophysical data for nitridorhenium(v) complexes

Complex	Medium (T/K)	λ_{em}/nm(τ_o/µs)	φ_{lum}
$[Re^VN(dppe)_2(MeCN)]^{2+}$	Solid (298)	510 (18 ± 1)	
	Solid (77)	505	
	MeCN (298)	525 (2.1 ± 0.2)[a]	0.021[b]
$[Re^VN(dppe)_2Cl]^+$	Solid (298)	512 (2.0 ± 0.2)[c]	
	MeCN (298)	520 (0.10 ± 0.01)[d]	$\approx 10^{-5}$[b]

[a] In degassed MeCN (0.1 mol dm^{-3} NBu_4PF_6); [Re≡N] = 0.34 mmol dm^{-3}. [b] Measured according to literature method (ref. 5) using $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) as standard. [c] Ref. 2(*a*). [d] In degassed MeCN (0.1 mol dm^{-3} NBu_4PF_6); [Re≡N] = 3.6 mmol dm^{-3}.

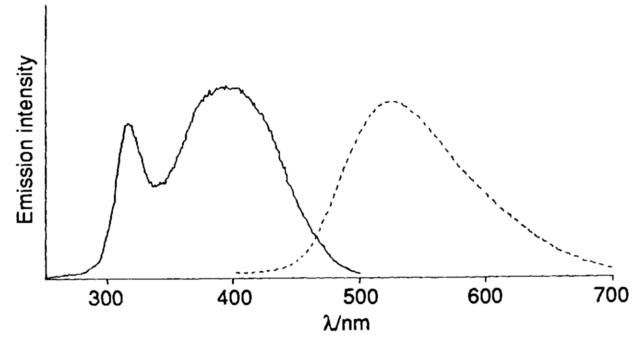

Fig. 2 Excitation (——) and emission (- - -) spectra of $[Re^VN(dppe)_2(MeCN)][ClO_4]_2$ in degassed MeCN at 298 K

$\lambda > 350$ nm at room temperature or at 77 K results in strong yellow-green emission; $[Re^VN(dppe)_2(MeCN)]^{2+}$ is also found to exhibit intense long-lived room-temperature luminescence in fluid solution (Fig. 2). The photophysical data are summarized in Table 1. The excitation spectrum shows broad bands at *ca.* 316 and 400 nm (Fig. 2). Given the long excited-state lifetime and our previous spectroscopic studies of d^2 metal nitrido systems,[2] 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. The excitation bands at *ca.* 316 and 400 nm are likely to be derived from the $^1[(d_{xy})^2] \longrightarrow {}^1[(d_{xy})^1(d_{\pi^*})^1]$ (singlet–singlet) and $^1[(d_{xy})^2] \longrightarrow {}^3[(d_{xy})^1(d_{\pi^*})^1]$ (singlet–triplet) transitions, respectively $[d_{\pi^*} = d_{xz}, d_{yz}]$. Unlike $[Re^VN(dppe)_2Cl]^+$ where the luminescence quantum yield (φ_{lum}) is very small ($\approx 10^{-5}$), the φ_{lum} value of 0.021 in $[Re^VN(dppe)_2(MeCN)]^{2+}$ is greater by a factor of $> 10^3$ over its chloro counterpart. It is interesting that the removal of the ligand-to-metal charge-transfer excited state $[p_\pi(Cl^-) \longrightarrow 5d_{\pi^*}(Re)]$ from $[Re^VN(dppe)_2Cl]^+$ in $[Re^VN(dppe)_2(MeCN)]^{2+}$ improves both the luminescence quantum yield and the radiative lifetime. Further studies to elucidate the mechanism of radiative enhancement are in progress, which should contribute to the future design of novel luminescent materials.

Cyclic voltammetric studies show that $[Re^VN(dppe)_2(MeCN)]^{2+}$ displays irreversible reduction couples at E_{pc} of *ca.* −2.26 and −1.67 V and an irreversible oxidation couple at E_{pa} of *ca.* +1.85 V *vs.* the ferrocenium–ferrocene couple in MeCN (0.1 mol dm^{-3} NBu_4PF_6). Addition of NBu_4Cl to an acetonitrile solution of $[Re^VN(dppe)_2(MeCN)]^{2+}$ gave a cyclic voltammogram identical to that of the chloro counterpart, $[Re^VN(dppe)_2Cl]^+$ (E_{pc} −2.34 V; E_{pa} +1.55 V *vs.* ferrocenium–ferrocene). It is likely that the reduction wave at *ca.* −1.67 V which is absent in the chloro analogue, corresponds to the reduction process $[Re^VN(dppe)_2(MeCN)]^{2+} + e^- \longrightarrow [Re^{IV}N(dppe)_2(MeCN)]^+$. The anodic shift of the $E^\circ[Re^V\text{–}Re^{IV}]$ couple in $[Re^VN(dppe)_2(MeCN)]^{2+}$ relative to $[Re^VN(dppe)_2Cl]^+$ is in accord with the stronger σ-donating ability of Cl^- over MeCN as well as the greater overall positive charge of $[Re^VN(dppe)_2(MeCN)]^{2+}$. The irreversible reduction and oxidation waves at *ca.* −2.26 and +1.85 V, respectively, are likely to be ligand centred in nature.

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