Facile photoinduced charge separation through a cyanoacetylide bridge in a heterobimetallic Fe(II)–Re(I) complex⁺

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Photoinduced Fe-to-bpy charge transfer in [{Cp(dppe)Fe}-(μ -C \equiv CC \equiv N){Re(CO)₃(bpy)}]PF₆ has been observed by ps-TRIR spectroscopy, supported by UV-Vis/IR spectroelectrochemistry and DFT calculations.

Polynuclear systems in which some bridging ligand permits control over the spatial arrangement of the constituent metal centres and electronic interactions between them are of immense contemporary interest with a view to the construction of functional molecular structures.¹ In this regard, the ubiquitous cyanide ligand, [CN]⁻, offers many useful structural and electronic properties, including cylindrical symmetry and a strong σ -bonding framework complemented by π and π^* orbitals of appropriate symmetry to interact with metal d orbitals. Cvanide also has a permanent dipole moment suited for promotion of directional electron transfer. The electronic and physical structure of the ligand can be monitored readily through the ν (C \equiv N) IR signature.² When employed as a bridging ligand in the assembly of polymetallic systems, the structural and electronic properties of the cyanide ligand give rise to compounds with a wealth of interesting electronic, photochemical or magnetic properties.³ In turn, this leads to a considerable interest in new cyanometallate building blocks.4

Convenient synthetic routes to metal complexes featuring the *cyanoacetylide* ligand, $[C \equiv CC \equiv N]^-$, including bridging examples, have been developed,⁵ and studies of the electronic characteristics of metal compounds featuring this "extended" cyanide-like ligand are now possible. Given the numerous interesting physical properties associated with cyanide complexes,³ the introduction of a new cyanide-like ligand offers a wealth of possibilities for study. The iso-electronic relationship between $\{ML_n\}C \equiv CC \equiv N\{M'L_n\}^+$ and "all-carbon" buta-1,3-diyndiyl complexes $\{ML_n\}C \equiv CC \equiv C\{M'L_n\}$ is also worthy of mention.⁶

With a view to exploring the capacity of the cyanoacetylide fragment to mediate electronic effects between remote metal centres we have prepared the heterometallic complex $[{Cp(dppe)Fe}(\mu-C \equiv CC \equiv N){Re(CO)_3(bpy)}]PF_6$ ([3]PF₆). By correlating the shift in $\nu(CO)^7$ and $\nu(C \equiv CC \equiv N)^5$ bands with changes in oxidation state, important evidence for the contribution of the metal $d\pi$ -system to the frontier orbitals of these fascinating materials is obtained. Furthermore, the rhenium fragment Re(CO)₃(bpy) offers the potential for direct monitoring of the excited state behaviour of $[3]^+$, as photoexcitation into charge transfer excited states associated with the bpv ligand results in well-characterised shifts in the ν (CO) pattern. The photochemistry and excited state properties of rhenium complexes of general form [ReX(CO)₃(NN)] have been studied in extensive detail, with the ligands X (halide, pseudo halide, or other donor) and NN (chelating *α*-diimine ligand) both playing a significant role in tuning the excited state nature (MLCT and/or XLCT), energy and luminescent properties of the complex.⁸

Reaction of [Fe(C \equiv CC \equiv N)(dppe)Cp] (1) with [Re(NCMe)-(CO)₃(bpy)]PF₆ ([2]PF₆) gave the yellow heterobimetallic complex [3]PF₆ (Scheme 1). In the ground state, [3]PF₆ offers a rich series of ν (C \equiv C), ν (C \equiv N) and ν (CO) bands between 1900–2250 cm⁻¹, which can readily be assigned by comparison with the IR spectra of related mononuclear reference systems and DFT calculations (see below). Thus, the broad band near 1930 cm⁻¹ is assigned to the unresolved out-of-phase A'(2) and equatorial A" ν (CO) vibrations, whilst the sharper ν (CO) band near 2035 cm⁻¹ is



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[†] Electronic supplementary information (ESI) available: Synthetic procedures for [3]PF₆ and [3]BF₄, and representative CV plot, observed and calculated vibrational frequencies, computational details, including TD-DFT results and tables of bond lengths, orbital energies and orbital composition for [3-H]⁺, and brief description of the disorder model used in the refinement of the structure [3]BF₄. CCDC reference number 693768. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811357b



Fig. 1 The IR spectra of $[{Cp(dppe)Fe}(C \equiv CC \equiv N){Re(CO)_{3^-}}(bpy)]^{n^+}$ (n = 1, 2) collected spectroelectrochemically in an OTTLE cell (CH₂Cl₂/0.1 M NBu₄PF₆). The arrows the trends on the anodic cycle.

assigned to the in-phase A'(1) vibration. The bands at 1970 and 2190 cm⁻¹ are attributed to the coupled $\nu(C \equiv C)$ and $\nu(C \equiv N)$ modes of the cyanoacetylide ligand, respectively (*cf.* 1 $\nu(C \equiv C/C \equiv N)$ 1991/2174 cm⁻¹).

Compound [3]PF₆ undergoes reversible one-electron oxidation ($E_{1/2} = +0.23$ V vs. ferrocene/ferrocenium; $I_c/I_a = 1$) and irreversible one-electron reduction ($E_{1/2} = -1.67$ V; $I_c/I_a < 0.37$ at $\nu \le 100$ mV s⁻¹) on a cyclic voltammetric scan at a platinum microelectrode in tetrahydrofuran (thf) at 293 K, which on the basis of IR spectroelectrochemical experiments can be assigned to a largely Fe centred oxidation and a $\pi^*(bpy)$ localized reduction (see below). The reduction becomes more chemically reversible below 270 K.

The oxidation of [3]PF₆ results in a small (5–10 cm⁻¹) increase in the ν (CO) wavenumbers, pointing to only a minor decrease in electron density at the rhenium centre (Fig. 1).

The $\nu(C \equiv C)$ and $\nu(C \equiv N)$ bands also show relatively small shifts (*ca.* 30 cm⁻¹) to higher wavenumbers. The limited positive shifts in the ligand stretching frequencies clearly indicate that the electron density removed on oxidation originates largely from the iron centre, with a minor contribution from the cyanoacetylide ligand and Re based orbitals. At 293 K the bpy-localised reduction of [3]PF₆ in CH₂Cl₂ results in cleavage of the axial Re–NCCC bond, affording 1 ($\nu(C \equiv C/C \equiv N)$ at 1994/2175 cm⁻¹) and two unidentified [ReL(CO)₃(bpy)] species (A'(1) $\nu(CO)$ at 2024 and 2007 cm⁻¹).

The UV-Vis absorption spectrum of [3]PF₆ is characterized by broad, overlapping features centred near 27000 cm⁻¹ ($\varepsilon = 7700 \text{ M}^{-1}\text{cm}^{-1}$) and 22200 cm⁻¹ ($\varepsilon = 1600 \text{ M}^{-1}\text{cm}^{-1}$). The oxidation of [3]PF₆ gives rise to a new absorption band from [3]²⁺ at 15000 cm⁻¹ ($\varepsilon = 2000 \text{ M}^{-1}\text{cm}^{-1}$), assigned to a Re \rightarrow Fe charge transfer band (Fig. 2). With a view to probing the low energy excitation processes in more detail, ps-TRIR spectroscopy was employed.⁹ The ps-TRIR spectra of [3]PF₆ measured after excitation at 490 nm are shown in Fig. 3. In the transient, the ν (CO) bands shift to smaller wavenumbers by *ca*. 20 cm⁻¹, consistent with one-electron reduction of the bpy ligand. In contrast, the ν (C \equiv C) and ν (C \equiv N) bands in the ground and excited states are almost coincident. Analysis of the ps-TRIR spectra yields a transient decay lifetime of ~30 ps, consistent with the lifetime of 30 ± 4 ps determined



Fig. 2 The UV-Vis spectroelectrochemical conversion of $[3]^{n+1}$ (n = 1, 2) in an OTTLE cell (CH₂Cl₂/0.1 M NBu₄PF₆). The arrows show the trends on the anodic cycle.



Fig. 3 Difference ps-TRIR spectra of $[Cp(dppe)Fe\}(C \equiv CC \equiv N)$ -{Re(CO)₃(bpy)}]PF₆ in CH₂Cl₂ measured after 490 nm excitation. The legend shows the delay times (ps) for each spectral acquisition.

from transient absorption (TA) spectroscopy ($\lambda_{ex} = 460$ nm). The initial TA spectrum shows a prominent band at *ca*. 500 nm and a weak broad absorption rising between 650–800 nm, which can safely be assigned to IL transitions of the bpy radical anion.¹⁰ These observations indicate a net increase in the electron density at the rhenium-bpy centre and are not consistent with the 460–490 nm excitation into a Re(d)-to-bpy(π^*) MLCT transition. Instead, the lowest energy excited state can be attributed charge-separated (CS) character, involving fast electron transfer from the donor CpFe(d) moiety to the acceptor bpy(π^*)Re site, mediated by the conjugated cyanoacetylide ligand.

Electronic structure calculations were also undertaken to support these observations using the simplified model [{Cp(dHpe)Fe}(C \equiv CC \equiv N){Re(CO)₃bpy}]⁺ [**3-H**]⁺ (dHpe = 1,2-diphosphinoethane). The geometry of [**3-H**]⁺ is in good agreement with the structure of the cation in [**3**]BF₄ (Fig. 4),‡ and vibrational frequency calculations based on the optimized geometry of [**3-H**]⁺ are in good agreement with the IR spectrum of [**3**]PF₆, which gives confidence in the accuracy of the models (calculated values: [**3-H**]⁺ ν (C \equiv N) 2204, ν (C \equiv C) 1980, ν (CO) 2016, 1941, 1934 cm⁻¹).

The HOMO in [**3-H**]⁺ has the same general composition as d^6/d^6 bimetallic butadiyndiyl bridged complexes,⁶ and is derived from the out-of-phase mixing of the Fe(d), C \equiv C and C \equiv N (π) and Re(d) orbitals (Fig. 5). The HOMO is largely (40%) Fe in character, admixed with appreciable



Fig. 4 A plot (50% ellipsoids) of the cation [{Cp(dppe)Fe}-(C \equiv CC \equiv N){Re(CO)₃(bpy)}]⁺ from [3]BF₄. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1)–P(1) 2.1803(8); Fe(1)–P(2) 2.2033(7); Fe(1)–C(1) 1.828(3); C(1)–C(2) 1.235(4); C(2)–C(3) 1.348(4); C(3)–N(1) 1.161(3); N(1)–Re(1) 2.120(2); Re(1)–N(2) 2.180(2); Re(1)–N(3) 2.172(2); P(1)–Fe(1)–P(2) 87.59(3); Fe(1)–C(1)–C(2) 177.9(2); C(1)–C(2)–C(3) 170.1(3); C(2)–C(3)–N(1) 179.6(3); C(3)–N(1)–Re(1) 169.2(2).

contributions from the C \equiv CC \equiv N (27%) and Re (15%) fragments. The HOMO-1, which is approximately orthogonal to the HOMO, is similarly comprised. The bpy π^* system makes up the LUMO, and is well separated from the other frontier orbitals.

TD-DFT calculations support the interpretation of the photochemical results. In [**3-H**]⁺, a band with significant (HOMO-1) \rightarrow LUMO (Fe-to-bpy π^*) character and reasonable intensity (f = 0.0492) is calculated at 461 nm (21 700 cm⁻¹). A predominantly Re-to-bpy MLCT is calculated at shorter wavelengths 409 nm (24 400 cm⁻¹, f = 0.0016). At shorter wavelengths, a series of transitions associated with the Fe(dHpe)Cp fragment can be identified.

In conclusion, mixing of Fe, $C \equiv CC \equiv N$ and Re character in the high lying occupied orbitals allows a new low energy $d\pi d - \pi^*(bpy)$ transition, which has been characterized by



Fig. 5 The (a) HOMO (b) HOMO-1 (c) LUMO of $[3-H]^+$.

ps-TRIR spectroscopy. Given the appreciable Fe character in these high lying orbitals, the photoproduct can be described as a {CpFe^{•+}}(C \equiv CC \equiv N)Re(bpy^{•-}) CS state. This description is consistent with the spectroscopic properties of the complex upon one-electron electrochemical oxidation and reduction. The cyanoacetylide ligand offers a π -orbital structure similar to that of both cyanide and buta-1,3-diyndiyl, and is therefore appropriate for use as a π -donating bridging ligand. With the development of convenient synthetic routes to complexes featuring this fragment, there is considerable scope for the development of the "cyanide-like" cyanoacetylide ligand as a bridging ligand in inorganic systems. The fascinating potential of cyanoacetylide ligand to act as a mediating unit for magnetic effects is high on a long list of future studies.

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Notes and references

‡ Crystal data for [3]BF₄: C₄₇H₃₇FeN₃O₃P₂Re BF₄, M = 1082.60, monoclinic, space group $P2_1/c(\text{no.14})$, a = 10.9091(2), b = 32.1612(6), c = 12.9704(2) Å, $\beta = 106.00(1)^\circ$, U = 4374.38(22) Å³, F(000) = 2144, Z = 4, $D_c = 1.644$ mg m⁻³, $\mu = 3.232$ mm⁻¹ (Mo-Kα, $\lambda = 0.71073$ Å), T = 120.0(1) K. 58 630 reflections were collected yielding 12770 unique data ($R_{\text{merg}} = 0.0249$). Final $wR_2(F^2) = 0.0.723$ for all data (507 refined parameters), conventional $R_1(F) = 0.0303$ for 11686 reflections with $I ≥ 2\sigma$, GOF = 1.033. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC number 693768.†

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