

# 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  $\{[\text{Cp}(\text{dppe})\text{Fe}-(\mu\text{-C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]\text{PF}_6$  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.<sup>1</sup> In this regard, the ubiquitous cyanide ligand,  $[\text{CN}]^-$ , offers many useful structural and electronic properties, including cylindrical symmetry and a strong  $\sigma$ -bonding framework complemented by  $\pi$  and  $\pi^*$  orbitals of appropriate symmetry to interact with metal d orbitals. Cyanide 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  $\nu(\text{C}\equiv\text{N})$  IR signature.<sup>2</sup> When employed as a bridging ligand in the assembly of polynuclear systems, the structural and electronic properties of the cyanide ligand give rise to compounds with a wealth of interesting electronic, photochemical or magnetic properties.<sup>3</sup> In turn, this leads to a considerable interest in new cyanometallate building blocks.<sup>4</sup>

Convenient synthetic routes to metal complexes featuring the *cyanoacetylide* ligand,  $[\text{C}\equiv\text{CC}\equiv\text{N}]^-$ , including bridging examples, have been developed,<sup>5</sup> 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,<sup>3</sup> the introduction of a new cyanide-like ligand offers a wealth of possibilities for study. The iso-electronic

relationship between  $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{N}\{\text{M}'\text{L}_n\}^+$  and “all-carbon” buta-1,3-diyndiyl complexes  $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{M}'\text{L}_n\}$  is also worthy of mention.<sup>6</sup>

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  $[\{\text{Cp}(\text{dppe})\text{Fe}-(\mu\text{-C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]\text{PF}_6$  (**[3]PF<sub>6</sub>**). By correlating the shift in  $\nu(\text{CO})$ <sup>7</sup> and  $\nu(\text{C}\equiv\text{CC}\equiv\text{N})$ <sup>5</sup> 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  $\text{Re}(\text{CO})_3(\text{bpy})$  offers the potential for direct monitoring of the excited state behaviour of **[3]**<sup>+</sup>, as photoexcitation into charge transfer excited states associated with the bpy ligand results in well-characterised shifts in the  $\nu(\text{CO})$  pattern. The photochemistry and excited state properties of rhenium complexes of general form  $[\text{ReX}(\text{CO})_3(\text{NN})]$  have been studied in extensive detail, with the ligands X (halide, pseudo halide, or other donor) and NN (chelating  $\alpha$ -diimine ligand) both playing a significant role in tuning the excited state nature (MLCT and/or XLCT), energy and luminescent properties of the complex.<sup>8</sup>

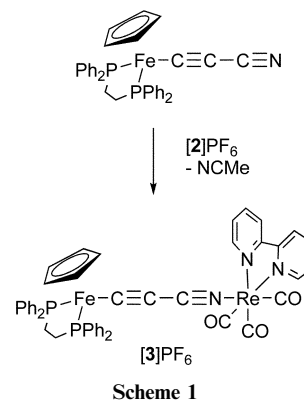
Reaction of  $[\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{dppe})\text{Cp}]$  (**1**) with  $[\text{Re}(\text{NCMe})(\text{CO})_3(\text{bpy})]\text{PF}_6$  (**[2]PF<sub>6</sub>**) gave the yellow heterobimetallic complex **[3]PF<sub>6</sub>** (Scheme 1). In the ground state, **[3]PF<sub>6</sub>** offers a rich series of  $\nu(\text{C}\equiv\text{C})$ ,  $\nu(\text{C}\equiv\text{N})$  and  $\nu(\text{CO})$  bands between 1900–2250  $\text{cm}^{-1}$ , 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  $\text{cm}^{-1}$  is assigned to the unresolved out-of-phase A'(2) and equatorial A''  $\nu(\text{CO})$  vibrations, whilst the sharper  $\nu(\text{CO})$  band near 2035  $\text{cm}^{-1}$  is

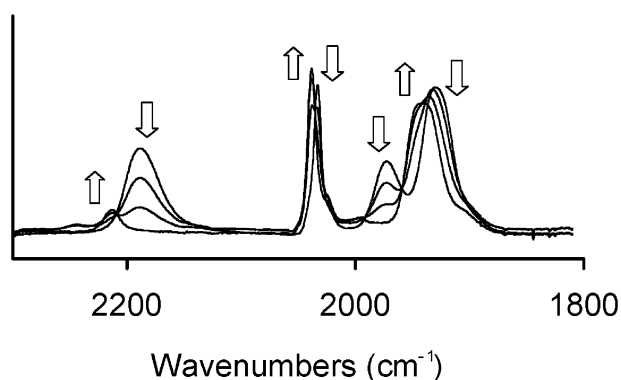
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† Electronic supplementary information (ESI) available: Synthetic procedures for **[3]PF<sub>6</sub>** and **[3]BF<sub>4</sub>**, and representative CV plot, observed and calculated vibrational frequencies, computational details, including TD-DFT results and tables of bond lengths, orbital energies and orbital composition for **[3-H]**<sup>+</sup>, and brief description of the disorder model used in the refinement of the structure **[3]BF<sub>4</sub>**. 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  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]^{n+}$  ( $n = 1, 2$ ) collected spectroelectrochemically in an OTTLE cell ( $\text{CH}_2\text{Cl}_2/0.1 \text{ M NBu}_4\text{PF}_6$ ). The arrows show the trends on the anodic cycle.

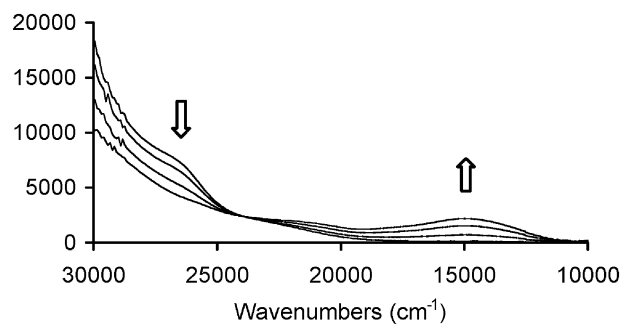
assigned to the in-phase  $A'(1)$  vibration. The bands at 1970 and 2190  $\text{cm}^{-1}$  are attributed to the coupled  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{C}\equiv\text{N})$  modes of the cyanoacetylide ligand, respectively (*cf.* **1**  $\nu(\text{C}\equiv\text{C}/\text{C}\equiv\text{N})$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

Compound **[3]PF<sub>6</sub>** undergoes reversible one-electron oxidation ( $E_{1/2} = +0.23 \text{ V vs. ferrocene/ferrocenium}$ ;  $I_c/I_a = 1$ ) and irreversible one-electron reduction ( $E_{1/2} = -1.67 \text{ V}$ ;  $I_c/I_a < 0.37$  at  $\nu \leq 100 \text{ mV s}^{-1}$ ) 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  $\pi^*(\text{bpy})$  localized reduction (see below). The reduction becomes more chemically reversible below 270 K.

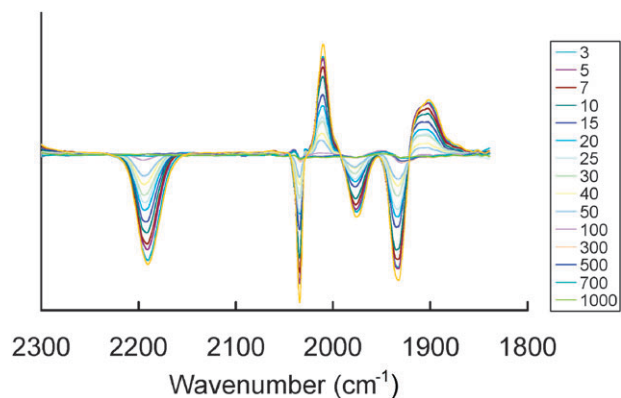
The oxidation of **[3]PF<sub>6</sub>** results in a small (5–10  $\text{cm}^{-1}$ ) increase in the  $\nu(\text{CO})$  wavenumbers, pointing to only a minor decrease in electron density at the rhenium centre (Fig. 1).

The  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{C}\equiv\text{N})$  bands also show relatively small shifts (*ca.* 30  $\text{cm}^{-1}$ ) 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]PF<sub>6</sub>** in  $\text{CH}_2\text{Cl}_2$  results in cleavage of the axial Re–NCCC bond, affording **1** ( $\nu(\text{C}\equiv\text{C}/\text{C}\equiv\text{N})$  at 1994/2175  $\text{cm}^{-1}$ ) and two unidentified  $[\text{ReL}(\text{CO})_3(\text{bpy})]$  species ( $A'(1)$   $\nu(\text{CO})$  at 2024 and 2007  $\text{cm}^{-1}$ ).

The UV-Vis absorption spectrum of **[3]PF<sub>6</sub>** is characterized by broad, overlapping features centred near 27000  $\text{cm}^{-1}$  ( $\epsilon = 7700 \text{ M}^{-1}\text{cm}^{-1}$ ) and 22200  $\text{cm}^{-1}$  ( $\epsilon = 1600 \text{ M}^{-1}\text{cm}^{-1}$ ). The oxidation of **[3]PF<sub>6</sub>** gives rise to a new absorption band from **[3]<sup>2+</sup>** at 15000  $\text{cm}^{-1}$  ( $\epsilon = 2000 \text{ M}^{-1}\text{cm}^{-1}$ ), assigned to a  $\text{Re} \rightarrow \text{Fe}$  charge transfer band (Fig. 2). With a view to probing the low energy excitation processes in more detail, ps-TRIR spectroscopy was employed.<sup>9</sup> The ps-TRIR spectra of **[3]PF<sub>6</sub>** measured after excitation at 490 nm are shown in Fig. 3. In the transient, the  $\nu(\text{CO})$  bands shift to smaller wavenumbers by *ca.* 20  $\text{cm}^{-1}$ , consistent with one-electron reduction of the bpy ligand. In contrast, the  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{C}\equiv\text{N})$  bands in the ground and excited states are almost coincident. Analysis of the ps-TRIR spectra yields a transient decay lifetime of  $\sim 30 \text{ ps}$ , consistent with the lifetime of  $30 \pm 4 \text{ ps}$  determined



**Fig. 2** The UV-Vis spectroelectrochemical conversion of  $[\mathbf{3}]^{n+}$  ( $n = 1, 2$ ) in an OTTLE cell ( $\text{CH}_2\text{Cl}_2/0.1 \text{ M NBu}_4\text{PF}_6$ ). The arrows show the trends on the anodic cycle.

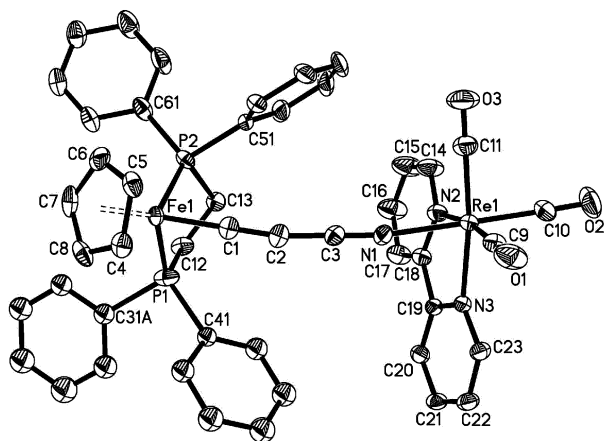


**Fig. 3** Difference ps-TRIR spectra of  $[\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]\text{PF}_6$  in  $\text{CH}_2\text{Cl}_2$  measured after 490 nm excitation. The legend shows the delay times (ps) for each spectral acquisition.

from transient absorption (TA) spectroscopy ( $\lambda_{\text{ex}} = 460 \text{ nm}$ ). 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.<sup>10</sup> 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  $\text{Re}(\text{d})\text{-to-bpy}(\pi^*)$  MLCT transition. Instead, the lowest energy excited state can be attributed charge-separated (CS) character, involving fast electron transfer from the donor  $\text{CpFe}(\text{d})$  moiety to the acceptor  $\text{bpy}(\pi^*)\text{Re}$  site, mediated by the conjugated cyanoacetylide ligand.

Electronic structure calculations were also undertaken to support these observations using the simplified model  $[\{\text{Cp}(\text{dHpe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3\text{bpy}\}]^+ [\mathbf{3}\text{-H}]^+$  (dHpe = 1,2-diphosphinoethane). The geometry of  $[\mathbf{3}\text{-H}]^+$  is in good agreement with the structure of the cation in **[3]BF<sub>4</sub>** (Fig. 4),<sup>‡</sup> and vibrational frequency calculations based on the optimized geometry of  $[\mathbf{3}\text{-H}]^+$  are in good agreement with the IR spectrum of **[3]PF<sub>6</sub>**, which gives confidence in the accuracy of the models (calculated values:  $[\mathbf{3}\text{-H}]^+$   $\nu(\text{C}\equiv\text{N})$  2204,  $\nu(\text{C}\equiv\text{C})$  1980,  $\nu(\text{CO})$  2016, 1941, 1934  $\text{cm}^{-1}$ ).

The HOMO in  $[\mathbf{3}\text{-H}]^+$  has the same general composition as  $\text{d}^6/\text{d}^6$  bimetallic butadiynyl bridged complexes,<sup>6</sup> and is derived from the out-of-phase mixing of the  $\text{Fe}(\text{d})$ ,  $\text{C}\equiv\text{C}$  and  $\text{C}\equiv\text{N}$  ( $\pi$ ) and  $\text{Re}(\text{d})$  orbitals (Fig. 5). The HOMO is largely (40%) Fe in character, admixed with appreciable

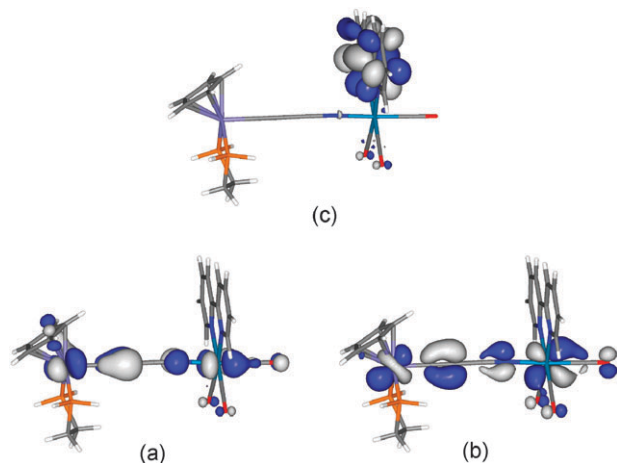


**Fig. 4** A plot (50% ellipsoids) of the cation  $[(\text{Cp}(\text{dppe})\text{Fe})-(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]^+$  from  $[\mathbf{3}]\text{BF}_4$ . Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Fe(1)–P(1) 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  $\text{C}\equiv\text{CC}\equiv\text{N}$  (27%) and Re (15%) fragments. The HOMO-1, which is approximately orthogonal to the HOMO, is similarly comprised. The bpy  $\pi^*$  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  $[\mathbf{3}\text{-H}]^+$ , a band with significant (HOMO-1)  $\rightarrow$  LUMO (Fe-to-bpy  $\pi^*$ ) character and reasonable intensity ( $f = 0.0492$ ) is calculated at 461 nm ( $21\,700\text{ cm}^{-1}$ ). A predominantly Re-to-bpy MLCT is calculated at shorter wavelengths 409 nm ( $24\,400\text{ cm}^{-1}$ ,  $f = 0.0016$ ). At shorter wavelengths, a series of transitions associated with the Fe(dHpe)Cp fragment can be identified.

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



**Fig. 5** The (a) HOMO (b) HOMO-1 (c) LUMO of  $[\mathbf{3}\text{-H}]^+$ .

ps-TRIR spectroscopy. Given the appreciable Fe character in these high lying orbitals, the photoproduct can be described as a  $\{\text{CpFe}^+\}(\text{C}\equiv\text{CC}\equiv\text{N})\text{Re}(\text{bpy}^{\bullet-})$  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  $\pi$ -orbital structure similar to that of both cyanide and buta-1,3-diyndiyl, and is therefore appropriate for use as a  $\pi$ -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  $[\mathbf{3}]\text{BF}_4$ :  $\text{C}_{47}\text{H}_{37}\text{FeN}_3\text{O}_3\text{P}_2\text{Re BF}_4$ ,  $M = 1082.60$ , monoclinic, space group  $P2_1/c$ (no.14),  $a = 10.9091(2)$ ,  $b = 32.1612(6)$ ,  $c = 12.9704(2)$  Å,  $\beta = 106.00(1)^\circ$ ,  $U = 4374.38(22)$  Å<sup>3</sup>,  $F(000) = 2144$ ,  $Z = 4$ ,  $D_c = 1.644\text{ mg m}^{-3}$ ,  $\mu = 3.232\text{ mm}^{-1}$  (Mo-K $\alpha$ ,  $\lambda = 0.71073$  Å),  $T = 120.0(1)$  K. 58 630 reflections were collected yielding 12 770 unique data ( $R_{\text{merg}} = 0.0249$ ). Final  $wR_2(F^2) = 0.0723$  for all data (507 refined parameters), conventional  $R_1(F) = 0.0303$  for 11 686 reflections with  $I \geq 2\sigma$ , 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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