

## PIRATE studies of dinuclear cyanoacetylide complexes

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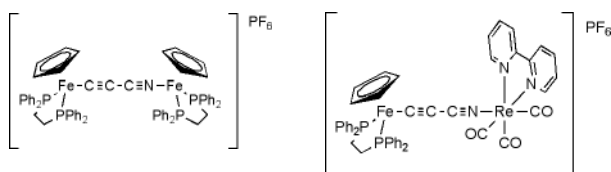
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### Introduction

Polynuclear systems in which some bridging ligand permits control over the spatial arrangement of the constituent metal centres and / or electronic interactions between them are of immense contemporary interest with a view to the construction of functional molecular structures.<sup>[1]</sup> The cyanide ligand,  $[\text{CN}]^-$ , is a classical example of a bridging ligand that has long been used in the assembly of polymetallic systems with interesting electronic, photochemical or magnetic properties. The ubiquitous  $[\text{CN}]^-$  ligand offers many useful structural and electronic properties, including cylindrical symmetry, a strong  $\sigma$ -bonding framework complimented by  $\pi$  and  $\pi^*$  orbitals of appropriate symmetry to interact with metal d orbitals, and a permanent dipole moment which can lead to directional electron transfer, coupled with a readily identifiable  $\nu(\text{C}\equiv\text{N})$  IR signature through which to monitor electronic and structural changes in the ligand. When used in combination, the structural and electronic properties of the cyanide ligand give rise to a wealth of fascinating chemistry.<sup>[2]</sup>

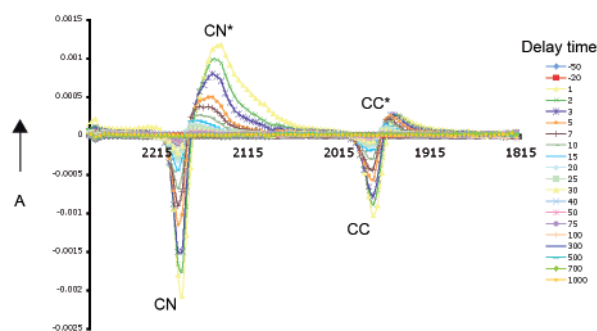
We have recently developed convenient synthetic routes to metal complexes featuring the *cyanoacetylide* ligand,  $[\text{C}\equiv\text{CC}\equiv\text{N}]^-$ , an extended analogue of the cyanide ligand which permits assembly of a diverse range of metal centres and supporting co-ligands.<sup>[3]</sup> The strong  $\nu(\text{C}\equiv\text{CC}\equiv\text{N})$  bands in the IR spectra of these species are convenient spectroscopic probes of the electronic structure of these complexes in both the ground and excited states.

We sought to exploit picosecond time-resolved infrared (ps-TRIR) methods to explore the excited state structures of bi-metallic cyanoacetylide complexes,<sup>[4]</sup> such as  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Fe}(\text{dppe})\text{Cp}\}]\text{PF}_6$ , and also those that feature an additional reporting ligand with a strong IR signature on one or both of the metal centres, such as  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]\text{PF}_6$ . The rhenium complex is particularly interesting as potential exists for photoexcitation into charge transfer excited states associated with the bpy ligand as well as the cyanoacetylide fragment. By correlating the shift in IR frequency of the metal localised reporting group with those of the  $\nu(\text{C}\equiv\text{CC}\equiv\text{N})$  bands we hoped to gain important experimental evidence for the contribution of the metal  $d\pi$ -system to the frontier orbitals of these fascinating materials.



### Results and discussion

The red coloured, homometallic iron complex  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Fe}(\text{dppe})\text{Cp}\}]\text{PF}_6$  features strong ground state IR bands at 2190 and 1984  $\text{cm}^{-1}$ . This complex features broad absorption bands centred near 260 ( $\epsilon$  10500  $\text{M}^{-1}\text{cm}^{-1}$ ), 310 ( $\epsilon$  12000  $\text{M}^{-1}\text{cm}^{-1}$ ) and 450 ( $\epsilon$  1200  $\text{M}^{-1}\text{cm}^{-1}$ ) nm. Following excitation at 400 nm, ps-TRIR spectroscopy revealed the transient to feature a very similar IR spectroscopic profile to that of the molecule in the ground state, with a small shift of both bands to smaller wavenumbers. The rapid decay of the transient over 50 ps implies little structural difference between the ground and excited states. Analysis of the kinetics of the decay reveals a longer lived ( $> 1$  ns) species, likely arising from ISC to the triplet excited state.



**Figure 1.** Difference TRIR spectra of  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Fe}(\text{dppe})\text{Cp}\}]\text{PF}_6$  in  $\text{CH}_2\text{Cl}_2$  measured after 400 nm excitation.

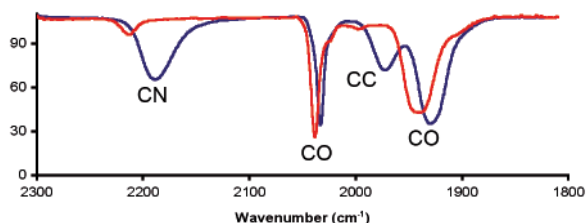
The complex  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Fe}(\text{dppe})\text{Cp}\}]\text{PF}_6$  undergoes two chemically and electrochemically reversible oxidations at +0.55 and +0.94 V vs SCE. Complimentary ground state IR spectroelectrochemical investigations reveal that the first oxidation causes a similar shift in the IR bands (2190, 1984 / 2188, 2065, 1862  $\text{cm}^{-1}$ ). Taken together it can be concluded that the HOMO of  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Fe}(\text{dppe})\text{Cp}\}]\text{PF}_6$  features appreciable ligand character and is not simply metal centred. Indeed, it is fascinating to compare the behaviour

of this cyanoacetylide complex with that of the isoelectronic buta-1,3-diyndiyl complex  $[\{\text{Cp}^*(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{C})\{\text{Fe}(\text{dppe})\text{Cp}^*\}]$  that offers rather heavily metal-centred HOMOs. This serves to illustrate the influence the change of a single atom within such a simple pair of linear bridging ligands can play on the electronic structure of the complexes that they form.

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) and NN (chelating -diimine donor ligand) playing a significant role in tuning the excited state nature (MLCT and/or LLCT), energy and luminescent properties of the complex.<sup>[5]</sup> In the ground state the complex  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]\text{PF}_6$  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 spectra of related mononuclear reference systems.

Thus, the broad band near 1920  $\text{cm}^{-1}$  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 2040  $\text{cm}^{-1}$  is assigned to the in-phase  $A'(1)$  vibration. The less intense bands at 1980 and 2190  $\text{cm}^{-1}$  are attributed to the  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{C}\equiv\text{N})$  modes of the cyanoacetylide ligand, respectively.

This compound undergoes both a reversible one-electron oxidation and one-electron reduction at a platinum electrode in  $\text{CH}_2\text{Cl}_2$ , which on the basis of IR spectroelectrochemical experiments can be assigned to a largely Fe centred oxidation and a bpy  $\pi^*$  localized reduction. For example, oxidation of  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]^+$  to  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]^{2+}$  results in very small (*ca.* +5 – 10  $\text{cm}^{-1}$ ) shifts in the  $\nu(\text{CO})$  bands indicates that oxidation causes only minor decrease in electron density at the rhenium centre. The  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{C}\equiv\text{N})$  bands show similarly small shifts to higher wavenumbers. The small positive shifts in the ligand stretching frequencies clearly indicate that the electron density removed on oxidation originates largely from the iron centre. A very similar anodic behaviour was also observed for the mononuclear reference  $[\text{FeCp}(\text{dppe})(\text{C}\equiv\text{CC}\equiv\text{N})]$ .

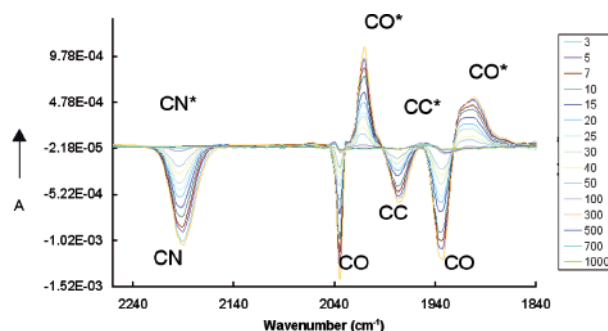


**Figure 2** The IR spectra of  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]\text{PF}_6$  ( $n = 1$  (blue), 2 (red)) collected spectroelectrochemically in an OTTE cell ( $\text{CH}_2\text{Cl}_2 / 0.3 \text{ M NBu}_4\text{PF}_6$ ).

In contrast, reduction of  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]\text{PF}_6$  causes a more significant shift in the  $\nu(\text{CO})$  bands to lower wavenumbers and consequently can be attributed to a bpy centred redox process.

The UV-vis absorption spectrum of  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]\text{PF}_6$  is characterized by broad, overlapping features centred near 370 ( $\epsilon$  7700  $\text{M}^{-1}\text{cm}^{-1}$ ) and 450 ( $\epsilon$  1600  $\text{M}^{-1}\text{cm}^{-1}$ ) nm. The ps-TRIR spectra of the heterobimetallic complex measured after excitation at 490 nm are shown in Figure 3. The transient, which has a lifetime  $\tau = 34$  ps determined from transient absorption spectroscopy at the University of Amsterdam, features significant shifts in the  $\nu(\text{CO})$  bands, whilst in marked contrast to the homobimetallic iron complex  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Fe}(\text{dppe})\text{Cp}\}]\text{PF}_6$ , the  $\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{C}\equiv\text{N})$  in the ground and excited states are almost coincident in the ground and excited states.

The shifts in  $\nu(\text{CO})$  band positions by some -20  $\text{cm}^{-1}$  following excitation at 490 nm are not consistent with a  $\text{Re}(\text{d})$ -to-bpy( $\pi^*$ ) MLCT process, but rather indicate a net increase in the electron density at the rhenium centre. Rather, this lowest energy excited state can be attributed to a charge-separated (CS) character, involving fast electron transfer from the donor  $\text{CpFe}(\text{d})$  moiety to the acceptor bpy( $\pi^*$ )Re site, mediated by the conjugated cyanoacetylide ligand. Excitation at shorter wavelengths (350 nm) gave rise to the more usual Re-to-bpy MLCT excited states, as evidenced by the characteristic shift in  $\nu(\text{CO})$  bands to larger wavenumbers.



**Figure 3.** Difference 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.

## Conclusions

The bimetallic iron complexes featuring the cyanoacetylide ligand differ significantly from the analogous buta-1,3-diyndiyl complexes, with the cyanoacetylide moiety making an appreciable contribution to the composition of the frontier orbitals of the complex, and participating in both the oxidation, evidenced by the significant shifts to lower wavenumbers in spectroelectrochemical and ps-TRIR experiments, respectively. In contrast, in  $[\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{Re}(\text{CO})_3(\text{bpy})\}]^+$  the introduction of the  $\text{Re}(\text{CO})_3(\text{bpy})$  system provides a low lying bpy centred LUMO, and largely decoupled the Fe,  $\text{C}\equiv\text{CC}\equiv\text{N}$  and Re fragments. A low-energy  $\{\text{CpFe}^{2+}\}(\text{C}\equiv\text{CC}\equiv\text{N})\text{Re}(\text{bpy}^{\cdot-})$  charge-separated (CS) state was identified from ps-TRIR experiments, the assignment of which is consistent with the electrochemical properties of this complex.

## References

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