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COMMUNICATION

Long Range Charge Transfer in Trimetallic Mixed-Valence Iron Complexes Mediated by Redox Non-Innocent Cyanoacetylide Ligands

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The reaction of $\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{dppe})\text{Cp}$ (**1**) with one-half equivalent of [*trans*- $\text{Fe}(\text{N}\equiv\text{CMe})_2(\text{dppx})_2][\text{BF}_4]_2$ ($\text{dppx} = \text{dppe}$ ($[\text{2}][\text{BF}_4]_2$) or dppm ($[\text{3}][\text{BF}_4]_2$)) affords trimetallic [*trans*- $\text{Fe}\{\text{N}\equiv\text{CC}\equiv\text{CFe}(\text{dppe})\text{Cp}\}_2(\text{dppx})_2][\text{BF}_4]_2$ ($\text{dppx} = \text{dppe}$ [$\text{4}][\text{BF}_4]_2$; $\text{dppx} = \text{dppm}$ [$\text{5}][\text{BF}_4]_2$). Both [$\text{4}][\text{BF}_4]_2$ and [$\text{5}][\text{BF}_4]_2$ undergo three, one-electron oxidation processes, arising from sequential oxidation of the two terminal $\text{Fe}(\text{C}\equiv\text{CR})(\text{dppe})\text{Cp}$ moieties and finally the central $\text{Fe}(\text{N}\equiv\text{CR})_2(\text{dppx})_2$ fragment. The redox products [$\text{4}^{\text{n}+}$ and [$\text{5}^{\text{n}+}$ ($\text{n} = 3, 4$) have been characterised by UV-vis-NIR and IR spectroelectrochemistry. The shifts in the characteristic $\nu(\text{C}\equiv\text{CC}\equiv\text{N})$ bands upon oxidation demonstrate not only the localised electronic structure of the trications, but also the redox non-innocence of the cyanoacetylide ligands. The trimetallic [formally $\text{Fe}(\text{II/II/III})$ mixed-valence] complexes [$\text{4}^{\text{3}+}$ and [$\text{5}^{\text{3}+}$ feature two distinct IVCT transitions, one associated with charge transfer from the central 18-electron $\{\text{Fe}(\text{N}\equiv\text{CR})_2(\text{dppx})_2\}^{2+}$ to terminal $\{\text{Fe}(\text{C}\equiv\text{CR})(\text{dppe})\text{Cp}\}^+$ moiety, and a lower energy transition involving charge transfer between the terminal Fe fragments which are separated by the redox active 9-atom, 10-bond $-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}\{\text{Fe}(\text{dppx})_2\}\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-$ bridge. The tetracationic complexes [$\text{4}^{\text{4}+}$ and [$\text{5}^{\text{4}+}$ generated by a further stepwise oxidation exhibit a single $\{\text{Fe}(\text{N}\equiv\text{CR})_2(\text{dppx})_2\}^{2+} \rightarrow \{\text{Fe}(\text{C}\equiv\text{CR})(\text{dppe})\text{Cp}\}^+$ IVCT transition.

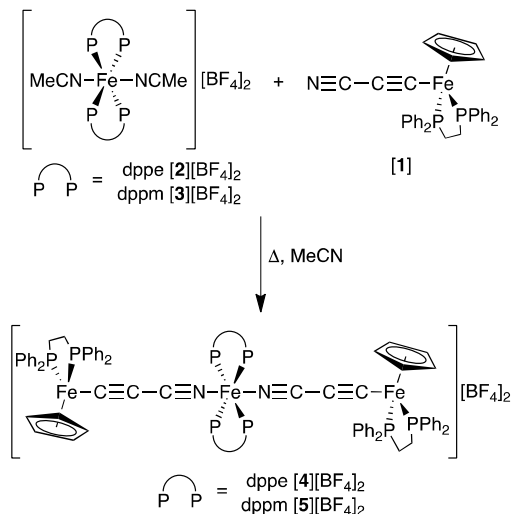
Cyanide-bridged bi- and polymetallic complexes have attracted attention for decades, a time frame extended considerably if one considers the early fascination with the colours of, and indirectly the $\text{Fe}(\text{II/III})$ IVCT processes in, Prussian Blue and its analogues. Whilst

most attention has focussed on cyanide-based framework materials and bimetallic complexes, the properties of discrete trimetallic compounds of the form $\text{M}-\text{C}\equiv\text{N}-\text{M}'-\text{N}\equiv\text{C}-\text{M}$ have also attracted interest. For example, recent investigations have shown that electronic interactions between the peripheral metal centres exist in $[(\text{py})_5\text{Ru}]-\text{C}\equiv\text{N}-[\text{Ru}(\text{py}')_4]-\text{N}\equiv\text{C}-[\text{Ru}(\text{py})_5]$ ($\text{py} = \text{pyridine}$, $\text{py}' = \text{pyridine}$, 4-methoxypyridine),¹ and magnetic interactions are present between the external iron centres in compounds such as $\text{Cp}(\text{dppe})\text{Fe}-\text{C}\equiv\text{N}-[\text{Ru}]-\text{N}\equiv\text{C}-\text{Fe}(\text{dppe})\text{Cp}$ ($\text{dppe} = 1,2$ -bis(diphenyl-phosphino)ethane, $[\text{Ru}] = \text{Ru}(2,2'$ -bipyridine)₂).² Although similar studies of complexes based on isoelectronic dicarbon bridging ligands, $-\text{C}\equiv\text{C}-$, and its valence isomers are rather more rare,^{3,5} longer polyynyl ligands $-(\text{C}\equiv\text{C})_n-$ have been used in the construction of some truly impressive linear polymetallic complexes,⁶⁻⁸ with computational and spectroscopic methods being used to demonstrate the presence of an extended $\dots\pi$ -d- $\pi\dots$ system along the molecular backbone.

Simple synthetic routes to complexes containing cyanoacetylide, $-\text{C}\equiv\text{CC}\equiv\text{N}$,^{9,11} and related cyanobutadiynyl, $-\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{N}$,¹² ligands have been established offering entry to systems with obvious structural and electronic relationships with both cyanide and polyynyl ligands. Cyanoacetylide ligands are not only of interest as novel conduits for the propagation of electronic and magnetic effects between remote metal centres,^{9,11} but also for the potential to realise a wide range of polymetallic complexes through synthetic strategies based on coordination driven self-assembly.

Complex $\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{dppe})\text{Cp}$ (**1**) can be prepared by reaction of $\text{Fe}(\text{C}\equiv\text{CLi})(\text{dppe})\text{Cp}$ with phenyl cyanate,¹⁰ or more conveniently by treatment of $[\text{Fe}(\text{C}\equiv\text{CH}_2)(\text{dppe})\text{Cp}]\text{PF}_6$ with 1-cyano-4-dimethylamino pyridinium tetrafluoroborate ($[\text{CAP}]\text{BF}_4$).^{12,13†} The reaction of **1** with one half-equivalent of $[\text{Fe}(\text{N}\equiv\text{CMe})_2(\text{dppe})_2][\text{BF}_4]_2$ ($[\text{2}][\text{BF}_4]_2$)¹⁴ or

$[\text{Fe}(\text{N}\equiv\text{CMe})_2(\text{dppm})_2][\text{BF}_4]_2$ ($[\mathbf{3}][\text{BF}_4]_2$)[†] in acetonitrile gave trimetallic $[\text{trans-Fe}\{\text{N}\equiv\text{CC}\equiv\text{Fe}(\text{dppe})\text{Cp}\}_2(\text{dppm})_2][\text{BF}_4]_2$ ($[\mathbf{4}][\text{BF}_4]_2$, khaki green, 95%) or $[\text{trans-Fe}\{\text{N}\equiv\text{CC}\equiv\text{Fe}(\text{dppm})\text{Cp}\}_2(\text{dppm})_2][\text{BF}_4]_2$ ($[\mathbf{5}][\text{BF}_4]_2$, brick red, 62%) as analytically pure precipitates (Scheme 1). A small red-shift in the lowest energy absorption band of $[\mathbf{4}][\text{BF}_4]_2$ relative to $[\mathbf{5}][\text{BF}_4]_2$ is apparently sufficient to lead to the difference in colour of these complexes.[†]



Scheme 1. Synthesis of the trimetallic iron compounds $[\mathbf{4}][\text{BF}_4]_2$ and $[\mathbf{5}][\text{BF}_4]_2$.

The electrochemical response of $[\mathbf{4}][\text{BF}_4]_2$ and $[\mathbf{5}][\text{BF}_4]_2$ in CH_2Cl_2 / 0.1 M NBu_4PF_6 was broadly similar, each exhibiting two, reversible one-electron oxidations and a third quasi-reversible process close to the limit of the accessible solvent window.[†] The $E_{1/2}$ values determined for the dppm-containing derivative $[\mathbf{5}][\text{BF}_4]_2$ ($E_{1/2}(1)$ –0.05; $E_{1/2}(2)$ 0.07; $E_{1/2}(3)$ 0.83 V) are slightly less positive than those of $[\mathbf{4}][\text{BF}_4]_2$ ($E_{1/2}(1)$ 0.02; $E_{1/2}(2)$ 0.15; $E_{1/2}(3)$ 0.92 V), which reflects the difference in electron donating properties of the dppm and dppe ligands at the central iron moiety. Comparison of the redox potentials with those of $\mathbf{1}$ (0.07 V vs $\text{FeCp}_2/[\text{FeCp}_2]^+$)¹⁰ and $[\mathbf{2}][\text{BF}_4]_2$ (+1.05 V vs $\text{FeCp}_2/[\text{FeCp}_2]^+$)¹⁵ permitted assignment of the first two redox processes in the trimetallic complexes to sequential oxidation of the peripheral $\text{Fe}(\text{C}\equiv\text{CR})(\text{dppe})\text{Cp}$ fragments, generating tricationic ($[\mathbf{4}]^{3+}$, $[\mathbf{5}]^{3+}$) and tetracationic ($[\mathbf{4}]^{4+}$, $[\mathbf{5}]^{4+}$) species, which would be classically regarded as $\text{Fe}(\text{II}/\text{II}/\text{III})$ and $\text{Fe}(\text{III}/\text{II}/\text{III})$ mixed valence complexes, respectively. The 120 mV difference in the redox potentials associated with the peripheral $\text{Fe}(\text{C}\equiv\text{CR})(\text{dppe})\text{Cp}$ fragments ($(E_{1/2}(1) - E_{1/2}(2))$) suggests that there is some through-bond and / or through space interaction between these moieties, which are estimated to be separated by *ca.* 15 Å.[†] The third quasi-reversible process is associated with the central iron moiety to give formally homo-valent $\text{Fe}(\text{III}/\text{III}/\text{III})$ compounds $[\mathbf{4}]^{5+}$ and $[\mathbf{5}]^{5+}$. In CH_2Cl_2 / 0.1M $\text{NBu}_4\text{BAR}^{\text{F}_4}$ ($\text{BAR}^{\text{F}_4} = \text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-}3,5\}_4$)¹⁶ small increases in $E_{1/2}(1)$ and $E_{1/2}(2)$ were observed in the case of both $[\mathbf{4}][\text{BF}_4]_2$ and $[\mathbf{5}][\text{BF}_4]_2$, although the difference between the first and second redox potentials is only modestly larger in the electrolyte solution containing the poorly ion-pairing $[\text{BAR}^{\text{F}_4}]^-$ anion ($|E_{1/2}(1) - E_{1/2}(2)| = 180$ mV) than in NBu_4PF_6 (120 mV). This suggests that Coulombic and ion-pairing effects only play a small role in stabilising the charge in the tricationic species: this result is perhaps unsurprising

and underlines the significance of through-bond contributions to the propagation of electronic information along the molecular backbone. The $E_{1/2}(3)$ redox couple associated with the central $\{\text{Fe}(\text{NCR})_2(\text{dppx})_2\}^{2+}$ fragment, which yields $[\mathbf{4}]^{5+}$ and $[\mathbf{5}]^{5+}$, is also sensitive to the ion-pairing interactions with the electrolyte, and moves beyond the accessible solvent window in $\text{NBu}_4\text{BAR}^{\text{F}_4}$ electrolyte solutions.

IR spectroelectrochemistry (CH_2Cl_2 / 0.1 M NBu_4PF_6)[†] was used to refine the proposed redox assignments and highlight the important role of the cyanoacetylide ligand in the initial redox processes. The two band $\nu(\text{C}\equiv\text{CC}\equiv\text{N})$ pattern observed initially for $[\mathbf{4}]^{2+}$ and $[\mathbf{5}]^{2+}$ splits into a superposition of $\nu(\text{C}\equiv\text{CC}\equiv\text{N})$ features associated with $\{\text{Cp}(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{M}^*\text{L}_n\}$ and $\{\text{Cp}(\text{dppe})\text{Fe}\}^+(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{M}^*\text{L}_n\}$ complexes on one-electron oxidation,⁹⁻¹¹ clearly supporting the notion of a ‘localised’ $[\{\text{Cp}(\text{dppe})\text{FeC}\equiv\text{CC}\equiv\text{N}\}^+ - \{\text{Fe}(\text{dppx})_2\}^{2+} - \{\text{N}\equiv\text{CC}\equiv\text{CFe}(\text{dppe})\text{Cp}\}]$ electronic structure in $[\mathbf{4}]^{3+}$ and $[\mathbf{5}]^{3+}$ (Table 1).[†] Although the oxidation processes are clearly not completely metal in character, with an appreciable degree of ligand contribution evidenced by the *ca.* 80 cm^{-1} shift in $\nu(\text{C}\equiv\text{CC}\equiv\text{N})$ frequencies upon oxidation, the general pattern is consistent with the formal $\text{Fe}(\text{II}/\text{II}/\text{III})$ mixed valence description, which is a useful if not particularly accurate way of describing the redox product.¹⁷ The ligand non-innocence also highlights the care that must be exercised in correlations between geometric separation of the metal centres and the real electron transfer distance. Further oxidation to the tetracations causes a loss in intensity of the IR features, and only a single band at 2138 ($[\mathbf{4}]^{4+}$) or 2151 ($[\mathbf{5}]^{4+}$) cm^{-1} is observed.

On one-electron oxidation to the trications $[\mathbf{4}]^{3+}$ and $[\mathbf{5}]^{3+}$, two new bands were observed in the NIR spectra ($[\mathbf{4}]^{3+}$ 5400 and 9350 cm^{-1} ; $[\mathbf{5}]^{3+}$ 5600 and 10300 cm^{-1}), which were better resolved in the case of $[\mathbf{5}]^{3+}$ (Figure 1). On further oxidation to $[\mathbf{4}]^{4+}$ and $[\mathbf{5}]^{4+}$ the lower energy band collapsed revealing an underlying pseudo- $\text{Fe}(\text{III})$ dd band (probably better described as a $\text{FeC}\equiv\text{C}$ $d\pi-d\pi$ transition given the contribution of the ligand fragment to the redox processes),¹⁸ and the higher energy absorption bands grew appreciably in intensity, but with negligible shift in energy.

Given the assignment of the first two oxidation processes to the peripheral $\text{Fe}(\text{C}\equiv\text{CR})(\text{dppe})\text{Cp}$ moieties, these NIR bands in the (formally) $\text{Fe}(\text{II}/\text{II}/\text{III})$ and $\text{Fe}(\text{III}/\text{II}/\text{III})$ mixed-valence complexes are attributed to two separate IVCT processes, the lower energy band corresponding to charge transfer between the distant $\text{Fe}(\text{C}\equiv\text{CR})(\text{dppe})\text{Cp}$ moieties (out-to-out) which is unique to the $\text{Fe}(\text{II}/\text{II}/\text{III})$ form, and the one at higher energy to charge transfer from the central iron(II) $\text{Fe}(\text{N}\equiv\text{CR})_2(\text{dppx})_2$ moiety to the peripheral $\{\text{Fe}(\text{C}\equiv\text{CR})(\text{dppe})\text{Cp}\}^+$ fragment(s). In keeping with this assignment, the energy of this latter ‘in-to-out’ IVCT process shifts to the red on replacement of the dppe ligands on the central iron atom ($[\mathbf{4}]^{3+}$) with dppm ($[\mathbf{5}]^{3+}$). Additional spectroelectrochemical investigation of $[\mathbf{4}][\text{BF}_4]_2$ in acetonitrile showed solvatochromic behaviour of these NIR bands, again consistent with the proposed IVCT character.[†]

The extraction of coupling information from the unique ‘out-to-out’ charge transfer processes in $[\mathbf{4}]^{3+}$ and $[\mathbf{5}]^{3+}$ is complicated by the redox non-innocent character of the iron cyanoacetylide metalloligands. However, taking the metal-metal distances as proxy for the electron transfer distance, and using the Hush relationships derived for the two-

state case¹⁹ with spectral parameters derived from Gaussian deconvolution,[†] coupling parameters H_{ab} can be estimated for [4]³⁺ (out-to-out 610 cm⁻¹, in-to-out 1845 cm⁻¹) and [5]³⁺ (out-to-out 665 cm⁻¹, in-to-out 1469 cm⁻¹). Despite the over-estimation of the electron transfer distance, these values compare well with analogous data from the trimetallic, cyanide-bridged complexes [(py)₅Ru]–C≡N–[Ru(py)₄]–N≡C–[Ru(py)₅] (H_{ab} = 700–800 cm⁻¹, 1100 cm⁻¹).¹

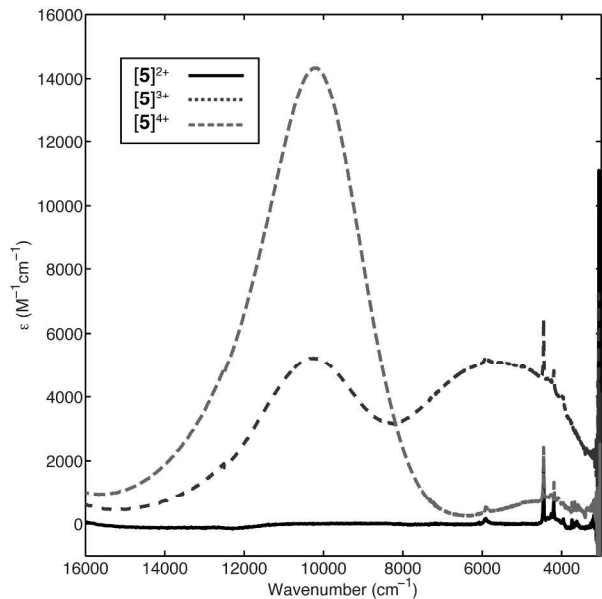


Figure 1. The NIR spectra of [5]ⁿ⁺ (n = 2, 3, 4) obtained spectroelectrochemically in CH₂Cl₂ / 0.1 M NBu₄PF₆.

	infrared (IR)		near infrared (NIR) [‡]	
	$\nu(\text{C}\equiv\text{C})$ / cm ⁻¹	$\nu(\text{C}\equiv\text{N})$ / cm ⁻¹	$\nu_{\text{max}}(\pi-\pi^*)$ / cm ⁻¹ (ϵ / M^{-1} cm ⁻¹)	$\nu_{\text{max}}(\text{MLCT})$ / cm ⁻¹ (ϵ / M^{-1} cm ⁻¹)
[4] ²⁺	1958s	2175vs	–	–
[4] ³⁺	1875s	2092s	5400 (7000)	9350 (3000)
	1957s	2154(sh)	[5500] ^{‡‡}	[9300] ^{‡‡}
[4] ⁴⁺		2177s	–	–
		2138m	–	9040 (12000)
[5] ²⁺	1963s	2177vs	–	–
[5] ³⁺	1902m	2111m	5600 (5000)	10300 (5000)
	1963vs	2155(sh)	–	–
		2180s	–	–
[5] ⁴⁺		2151m	–	10300 (14200)

Table 1. IR and NIR spectroscopic data obtained spectroelectrochemically in CH₂Cl₂ / 0.1 M NBu₄PF₆. Weak $d\pi-d\pi$ transitions: [4]⁴⁺ (5200 cm⁻¹ (1000 M⁻¹ cm⁻¹)); [5]⁴⁺ (4400 cm⁻¹ (800 M⁻¹ cm⁻¹)). [†]From the apparent NIR band centres. ^{‡‡}Data obtained in MeCN / 0.1 M NBu₄PF₆.

The effectiveness of the 9-atom, 10-bond –C≡C–N–Fe–N≡C–C≡C– bridge to promote interaction between remote metal centres, which is no doubt related to the redox-activity of the ligand fragment, is

comparable with cyanide-based M–C≡N–M'–N≡C–M type structures,¹ and highlights the great potential of the –C≡CC≡N moiety in the assembly of electro-optically active polymetallic structures.

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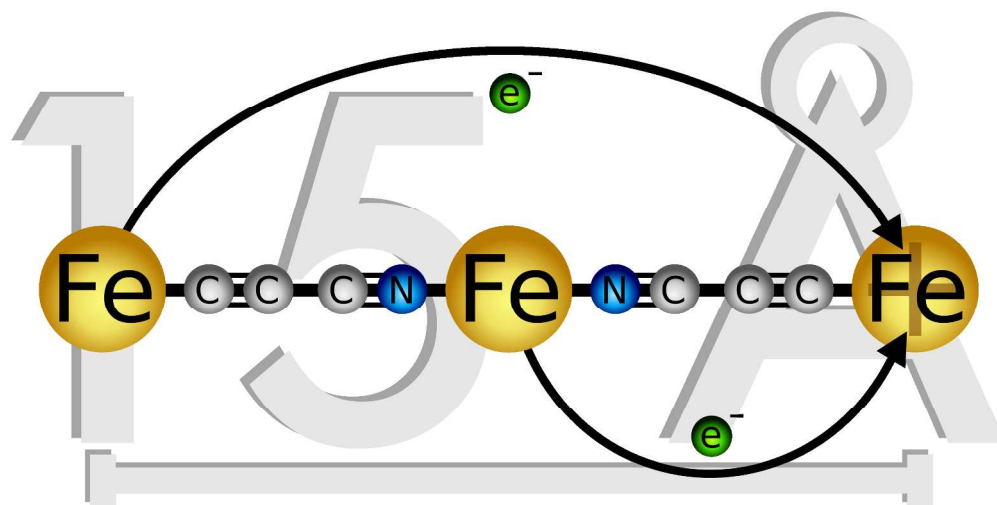
Notes and references

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[†] Electronic Supplementary Information (ESI) available: details of the preparation of [1][BF₄]₂, [3][BF₄]₂, [4][BF₄]₂ and [5][BF₄]₂; estimation of molecular length and Vis spectra of [4]²⁺ and [5]²⁺; UV-Vis-NIR and IR spectroelectrochemical details and spectral plots; Gaussian deconvolutions of the NIR spectra of [4]³⁺ and [5]³⁺; voltammetric details and CV plots; crystal structure analysis of [3][BF₄]₂ (CCDC-973687). See DOI: 10.1039/c000000x/

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A redox active 9-atom, 10-bond $\text{-C}\equiv\text{C-C}\equiv\text{N}\{\text{Fe}(\text{dppx})_2\}\text{N}\equiv\text{C-C}\equiv\text{C-}$ bridge is shown to be effective at promoting electron transfer between metal centres separated by some 15 Å.