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Control over directional metal–metal charge transfer in cyanide-bridged dimanganese complexes: effects of μ-CN linkage isomerism and ancillary ligand set†

Kirsty M. Anderson, Neil G. Connelly, Estefania Llamas-Rey, A. Guy Orpen and Rowena L. Paul

School of Chemistry, University of Bristol, Bristol, UK BS8 1TS. E-mail: Neil.Connelly@bristol.ac.uk

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Synthesis and characterisation of cyano-bridged complexes of the form $[(\eta\text{-}C_5R_4Me)L(ON)Mn(\mu\text{-}XY)Mn(CO)_2L'(dppm)]^z$ (X,Y = C,N; z = 1–3) shows that systematic variation of the orientation of the CN bridge and the nature and geometric arrangement of the ancillary ligands affords control of the direction and energy of metal–metal charge transfer in the mixed valence dications.

While much of the current wide interest[1,2] in cyanide-bridged complexes centres on structural properties[1,3] deriving from the (usually linear) M(μ-CN)M′ unit, other important effects (optical,[4–6] magnetic,[1,7] *etc.*) depend on the facility with which intramolecular metal–metal charge transfer (MMCT) occurs in mixed valence complexes.

In order to understand more fully the nature of the MMCT process, and how its energy and direction (through the bridge) might be controlled, there is a need to prepare and study kinetically inert cyanide-bridged species, *i.e.* species in which linkage isomerisation, from M(μ-CN)M′ to M(μ-NC)M′, does not occur. Many systems, often constructed from classical coordination complex units, do isomerise.[1,8] However, by using low valent transition metal building blocks (*e.g.* organometallic or metal carbonyl units) we[9] and others[6,10] have isolated stable cyanide-bridged complexes and, in some cases, linkage isomers.[4,11–14]

Electrochemical studies[11,13,14] which probe the effects of linkage isomerism on redox potential are of particular relevance, especially those on the asymmetric species $\{(OC)_5Cr(\mu\text{-}CN)Fe(dppe)(\eta^5\text{-}C_5H_5)]$ and $[(OC)_5Cr(\mu\text{-}NC)Fe(dppe)(\eta^5\text{-}C_5H_5)]$ (each oxidised in two one-electron steps, at $E^{\circ\prime}_1$ and $E^{\circ\prime}_2$). These isomers show quite different redox behaviour, with $E^{\circ\prime}_1$ and $E^{\circ\prime}_2$ 0.28 and 0.97 V for the former and 0.46 and 0.91 V for the latter, $\Delta E^{\circ\prime}$ ($\Delta E^{\circ\prime} = E^{\circ\prime}_2 - E^{\circ\prime}_1$) is 0.68 and 0.45 V, respectively. The difference in $\Delta E^{\circ\prime}$ for the two neutral complexes implies different MMCT behaviour for the corresponding monocations $[(OC)_5Cr(\mu\text{-}CN)Fe(dppe)(\eta^5\text{-}C_5H_5)]^+$ and $\{(OC)_5Cr(\mu\text{-}NC)Fe(dppe)(\eta^5\text{-}C_5H_5)]^+$ although a direct comparison on the electronic properties of the two was not possible.[14]

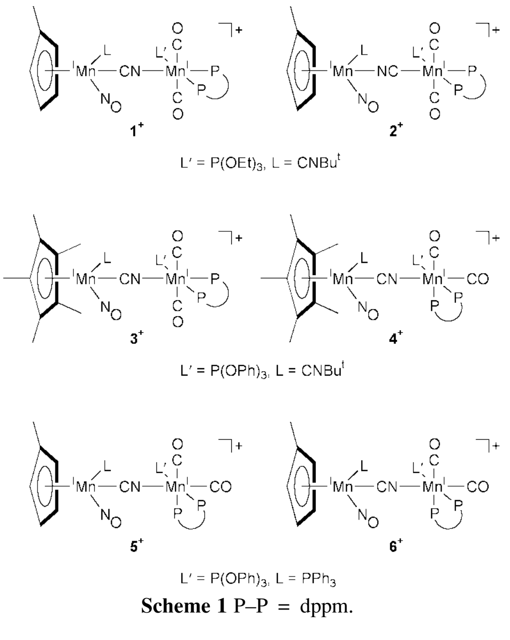
Here we describe a new and highly versatile series of stable cyanide-bridged linkage isomers, $[(\eta\text{-}C_5R_4Me)L(ON)Mn(\mu\text{-}XY)Mn(CO)_2L'(dppm)]^+$, in which the pseudo-tetrahedral unit $Mn^IX(NO)L(\eta\text{-}C_5R_4Me)$ (generalised as Mn_{tet}, R = H or Me) is joined to octahedral *cis*- or *trans*-$[Mn^IY(CO)_2L'(dppm)]$ (generalised as Mn_{oct}) by the bridge XY (X,Y = C,N). The potentials for, and order of, the sequential one-electron oxidations of the two metal centres in $Mn^I(\mu\text{-}XY)Mn^I$ to $Mn^I(\mu\text{-}XY)Mn^{II}$ and $Mn^{II}(\mu\text{-}XY)Mn^{II}$, vary not only with the orientation of the cyanide bridge but also with the cyclopentadienyl ring substituents R, the ancillary ligands L and L′ and the geometry of the $Mn(CO)_2$ unit (*cis* or *trans*) at Mn_{oct}. Thus, the energy and direction of MMCT within the Mn^IMn^{II} species $\{(\eta\text{-}C_5H_4Me)L(ON)Mn(\mu\text{-}XY)Mn(CO)_2L'(dppm)]^{2+}$ can be systematically controlled.

The complexes $[(\eta\text{-}C_5R_4Me)L(ON)Mn(\mu\text{-}XY)Mn(CO)_2L'(dppm)][PF_6]$ [X,Y = C,N; R = H or Me; L = PPh_3, $P(OPh)_3$ or $CNBu^t$; L′ = $P(OR')_3$ (R′ = Et or Ph); dppm = $Ph_2CH_2PPh_2$], with either *cis*- or *trans*-$Mn(CO)_2$ units, are prepared as their $[PF_6]^-$ salts by reacting $[Mn(CN)(CO)_2L'(dppm)]$ with $[MnI(NO)L(\eta\text{-}C_5R_4Me)]$ or $[MnBr(CO)_2L'(dppm)]$ with $[Mn(CN)(NO)L(\eta\text{-}C_5R_4Me)]$ in the presence of $TlPF_6$.‡ Representative examples are shown in Scheme 1 and Table S1 (ESI†).

The order in which the two Mn^I sites of the binuclear complexes are oxidised is indicated by cyclic voltammetry; assignment of each oxidation site is aided by observing the effects of altering the ancillary ligands L and L′ on redox potential (better donors L and L′ shift oxidation waves to less positive potentials) and noting that a *cis*-$[Mn^IY(CO)_2L'(dppm)]$ unit undergoes oxidative isomerisation, giving rise to an irreversible oxidation wave coupled with a reversible oxidation wave for the *trans* product.[15] The assignments based on cyclic voltammetry are supported by the results of IR spectroelectrochemistry (see below).

The effect of CN linkage isomerism on redox behaviour is demonstrated by $[(\eta\text{-}C_5H_4Me)(Bu^tNC)(ON)Mn(\mu\text{-}CN)Mn(CO)_2\{P(OEt)_3\}(dppm)$-*trans*$][PF_6]$ $\mathbf{1}^+[PF_6]^-$ and $[(\eta\text{-}C_5H_4Me)(Bu^tNC)(ON)Mn(\mu\text{-}NC)Mn(CO)_2\{P(OEt)_3\}(dppm)$-*trans*$][PF_6]$ $\mathbf{2}^+[PF_6]^-$, the X-ray structures of which are virtually identical; that of the cation $\mathbf{1}^+$ is shown in Fig. 1, together with important bond lengths and angles for the two isomers.§

Both $\mathbf{1}^+$ and $\mathbf{2}^+$ show two reversible oxidation waves in their cyclic voltammograms, IR spectroelectrochemistry¶ confirming that the first oxidation occurs at Mn_{oct} (Table 1). Thus, on electrolysis at $E_{applied}$ = 0.6 (for $\mathbf{1}^+$) or 0.75 V (for $\mathbf{2}^+$), ν(CO) increases by *ca.* 70–80 cm^{-1} while ν(NO) and $\nu(CNBu^t)$



Scheme 1 P–P = dppm.

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† Electronic supplementary information (ESI) available: Table S1: IR and electrochemical data. See http://www.rsc.org/suppdata/cc/b1/b104998b/

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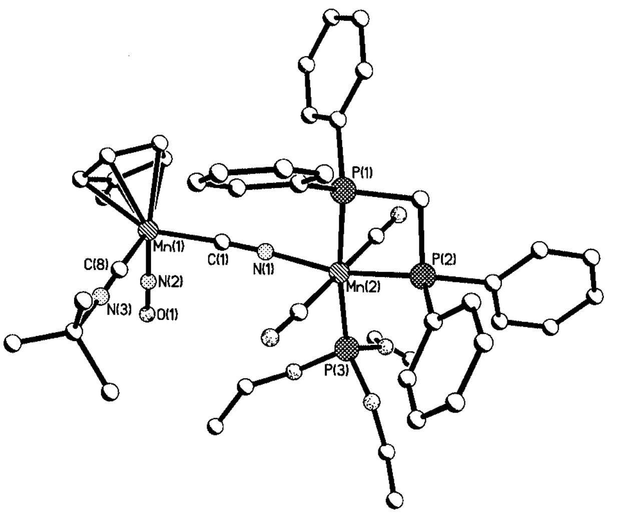

Fig. 1 Structure of the cation of [(η-C_5H_4Me)(Bu^tNC)(ON)Mn(μ-CN)Mn$(CO)_2$\{P$(OEt)_3$\}(dppm)][PF_6] **1**$^+$[PF_6]$^-$ (hydrogen atoms omitted for clarity); the structure of [(η-C_5H_4Me)(Bu^tNC)(ON)Mn(μ-NC)-Mn$(CO)_2$\{P$(OEt)_3$\}(dppm)][PF_6] **2**$^+$[PF_6]$^-$ is virtually identical. Important bond lengths (Å) and angles (°) for **1**$^+$: Mn_{tet}–CN 1.951(3), Mn_{oct}–NC 2.010(3), C–N 1.153(4), Mn_{tet}–NO 1.656(3), Mn_{tet}–$CNBu^t$ 1.916(4), Mn–P \{*trans* to P$(OEt)_3$\} 2.296(1), Mn–P (*trans* to $NCMn_{tet}$) 2.275(1); Mn_{tet}–C–N 176.9(3), Mn_{oct}–N–C 171.6(2). For **2**$^+$: Mn_{tet}–NC 1.968(3), Mn_{oct}–CN 1.955(3), C–N 1.151(4), Mn_{tet}–NO 1.665(3) Mn_{tet}–$CNBu^t$ 1.922(3), Mn–P \{*trans* to P$(OEt)_3$\} 2.283(1), Mn–P (*trans* to $CNMn_{tet}$) 2.290(1) Å; Mn_{tet}–N–C 173.6(2), Mn_{oct}–C–N 175.0(2).

increase by much smaller amounts (*ca.* 13–20 and 6–7 cm^{-1}, respectively), consistent with oxidation at the *trans*-Mn$(CO)_2$ terminus. [Further electrolysis of **1**$^{2+}$, at 1.45 V, results in increases in ν(CO), ν(NO) and ν($CNBu^t$) of 16, 101 and 62 cm^{-1}, this time consistent with oxidation at Mn_{tet} to give **1**$^{3+}$]. Thus, in the isomeric mixed valence dications **1**$^{2+}$ and **2**$^{2+}$, Mn^I to Mn^{II} MMCT occurs in the opposite sense with respect to the cyanide bridge, *i.e.* from Mn^I to CN to Mn^{II} in the former and from Mn^I to NC to Mn^{II} in the latter.

Cyanide bridge isomerisation leads to very different values of $\Delta E^{\circ\prime}$ for **1**$^+$ and **2**$^+$ (0.81 and 0.49 V respectively) and thence to a large difference in the MMCT band energy for the mono-oxidised complexes. Thus, UV–VIS spectroelectrochemistry¶ shows the growth of a MMCT absorption band at 890 nm on oxidation of **1**$^+$ to **1**$^{2+}$ and a similar band at 1360 nm on oxidation of **2**$^+$.

Further control of the direction (and energy) of MMCT is possible simply by varying the geometry (*cis* or *trans* dicarbonyl) of the Mn_{oct} unit. Thus, the positional isomers [(η-C_5Me_5)(Bu^tNC)(ON)Mn(μ-CN)Mn$(CO)_2$\{P$(OPh)_3$\}(dppm)-*trans*]$^+$ **3**$^+$ and [(η-C_5Me_5)(Bu^tNC)(ON)Mn(μ-CN)Mn$(CO)_2$-\{P$(OPh)_3$\}(dppm)-*cis*]$^+$ **4**$^+$ are first oxidised at Mn_{oct} and Mn_{tet} respectively, an assignment confirmed in the latter case by IR spectroelectrochemistry; electrolysis (E_{appl} = 1.0 V) leads to a large increase in enery for ν(NO) (94 cm^{-1}) and only a small increase in ν(CO) (Table S1, ESI†). Similar behaviour has been inferred from the CVs of [(η-C_5H_5)(dppe)Fe(μ-XY)(Mn$(CO)_2$-\{P$(OPh)_3$\}(dppm)][PF_6] (X, Y = C, N).[11]

Finally, the direction of MMCT can be controlled by varying the ligands L and L′. Thus, replacing PPh_3 at the *pseudo*-tetrahedral site of [(η-C_5H_4Me)(Ph_3P)(ON)Mn(μ-CN)Mn-$(CO)_2$\{P$(OPh)_3$\}(dppm)-*cis*]$^+$ **5**$^+$ by P$(OPh)_3$, giving [(η-C_5H_4Me)\{(PhO_3P)(ON)Mn(μ-CN)Mn$(CO)_2$\{P$(OPh)_3$\}-(dppm)- *cis*]$^+$ **6**$^+$, leads to the site of first oxidation changing from Mn_{tet} (first oxidation wave reversible) to Mn_{oct} [isomerisation of the *cis*-$Mn^I(CO)_2$ unit at the first oxidation step].

In summary, cyclic voltammetry and spectroelectrochemistry (IR and UV–VIS) on a range of stable linkage isomers shows that the order of oxidation of the two Mn^I sites in the Mn^I_{tet}(μ-XY)Mn^I_{oct} (X,Y = C,N) unit can be controlled by the orientation of XY, by the geometry at Mn^I_{oct} and by the ancillary ligands at either metal centre. In this way, the direction and energy of MMCT, from Mn^I to Mn^{II} through a cyanide bridge, may be systematically and selectively controlled.

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Notes and references

‡ All new complexes had satisfactory elemental analyses (C. H and N).

§ *Crystal data*: for **1**PF_6: (from CH_2Cl_2–*n*-hexane): $C_{48}H_{59}F_6Mn_2N_3O_7P_4$, M = 1137.74, triclinic, space group $P\bar{1}$ (no. 2), a = 11.077(4), b = 13.608(4), c = 19.195(3) Å, α = 103.00(3), β= 100.75(3), γ = 97.00(2)°, V = 2728.9(14) Å^3, Z = 2, μ = 0.65 mm^{-1}, $R1$ = 0.049. For **2**PF_6: (from CH_2Cl_2–*n*-hexane): $C_{48}H_{59}F_6Mn_2N_3O_7P_4$, M = 1137.74, triclinic, space group $P\bar{1}$ (no. 2), a = 11.092(2), b = 13.638(2), c = 19.076(4) Å, α = 102.98(1), β = 100.44(1), γ = 97.53(1)°, V = 2720.5(8) Å^3, Z = 2, μ = 0.652 mm^{-1}, $R1$ = 0.050. In each case an alternative model, with the C and N atoms of the CN bridge exchanged, was explored; there was no indication that the other linkage isomer was present in either crystal. CCDC reference numbers 166635 and 166636. See http://www.rsc.org/suppdata/cc/b1/b104998b/ for crystallographic data in CIF or other electronic format.

¶ UV–VIS spectroelectrochemistry was carried out in CH_2Cl_2 at 253 K, as described previously.[16] IR spectroelectrochemistry was carried out similarly, using a KBr microcavity cuvette, a Pt gauze working electrode and a Bruker IFS25 spectrometer. (Details will be described elsewhere.[17])

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