

The effect of μ -CN linkage isomerism and ancillary ligand set on directional metal–metal charge-transfer in cyanide-bridged dimanganese complexes†‡

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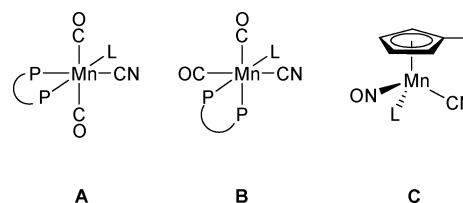
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The reaction of $[\text{Mn}(\text{CN})\text{L}'(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]$ with *cis*- or *trans*- $[\text{MnBrL}(\text{CO})_2(\text{dppm})]$, in the presence of $\text{Ti}[\text{PF}_6]$, gives homobinuclear cyanomanganese(I) complexes *cis*- or *trans*- $[(\text{dppm})(\text{CO})_2\text{LMn}(\mu\text{-NC})\text{MnL}'(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]^+$, linkage isomers of which, *cis*- or *trans*- $[(\text{dppm})(\text{CO})_2\text{LMn}(\mu\text{-CN})\text{MnL}'(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]^+$, are synthesised by reacting *cis*- or *trans*- $[\text{Mn}(\text{CN})\text{L}(\text{CO})_2(\text{dppm})]$ with $[\text{MnIL}'(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]$ in the presence of $\text{Ti}[\text{PF}_6]$. X-Ray structural studies on the isomers *trans*- $[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ and *trans*- $[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-CN})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ show nearly identical molecular structures whereas *cis*- $[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}\{ \text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ and *cis*- $[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-CN})\text{Mn}\{ \text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ differ, effectively in the *N*- and *C*-coordination respectively of two different optical isomers of the *pseudo*-tetrahedral units $(\text{NC})\text{Mn}\{ \text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})$ and $(\text{CN})\text{Mn}\{ \text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})$ to the octahedral manganese centre. Electrochemical and spectroscopic studies on $[(\text{dppm})(\text{CO})_2\text{LMn}(\mu\text{-XY})\text{MnL}'(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]^+$ show that systematic variation of the ligands L and L', of the cyclopentadienyl ring substituents R, and of the μ -CN orientation (XY = CN or NC) allows control of the order of oxidation of the two metal centres and hence the direction and energy of metal–metal charge-transfer (MMCT) through the cyanide bridge in the mixed-valence dications. Chemical one-electron oxidation of *cis*- or *trans*- $[(\text{dppm})(\text{CO})_2\text{LMn}(\mu\text{-NC})\text{MnL}'(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]^+$ with $[\text{NO}][\text{PF}_6]$ gives the mixed-valence dications *trans*- $[(\text{dppm})(\text{CO})_2\text{LMn}^{\text{II}}(\mu\text{-NC})\text{MnL}'(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]^{2+}$ which show solvatochromic absorptions in the electronic spectrum, assigned to optically induced Mn(I)-to-Mn(II) electron transfer *via* the cyanide bridge.

Introduction

In our studies of the construction and properties of cyanide-bridged complexes containing redox-active units such as A–C (Scheme 1) we have previously investigated two series of complexes in which linking two of the same or very similar mononuclear units (*i.e.* two of the octahedral units, A and/or B, or two of the tetrahedral units, C) gives linkage isomers (due to the asymmetry of the cyanide bridge), *i.e.* $[(\text{L-L})\text{LMn}(\mu\text{-CN})\text{MnL}'(\text{NO})(\text{L}'\text{-L}')][\text{PF}_6]$ {L or L' = $\text{P}(\text{OPh})_3$, $\text{P}(\text{OEt})_3$ or PET_3 ; L-L or L'-L' = dppm or dppe}^{1,2} and $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{NO})\text{LMn}(\mu\text{-CN})\text{MnL}'(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})][\text{PF}_6]$ (L or L' = PPh_3 , CNBu^t or CNXyl).³ Varying the ancillary ligands at each metal centre then allows fine tuning of the energy of intramolecular metal–metal charge-transfer (MMCT) and thence electronic properties such as solvatochromism.

We now give details⁴ of a third series of complexes, $[(\text{dppm})(\text{CO})_2\text{LMn}(\mu\text{-XY})\text{MnL}'(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]^+$ (XY = CN



Scheme 1 P–P = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ = dppm.

or NC) in which one octahedral unit (based on A or B) and one *pseudo*-tetrahedral unit (based on C) are linked. The order of one-electron oxidation of the two metal centres in the monocations, and hence the direction and energy of metal–metal charge-transfer (MMCT) in the corresponding mixed-valence dications, can be controlled by the systematic variation of the ligands at either manganese atom, the *cis* or *trans* arrangement of the $\text{Mn}(\text{CO})_2$ fragment, the substitution pattern in the $\eta^5\text{-C}_5\text{R}_4\text{Me}$ ring, and the orientation of the cyanide bridge.

Results and discussion

The synthesis and spectroscopic characterisation of linkage isomers

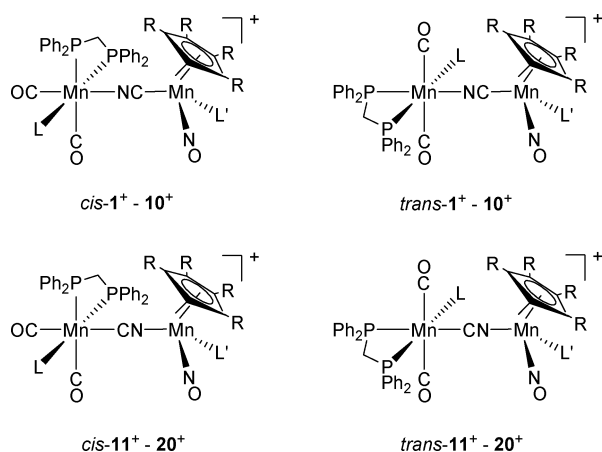
The room temperature reaction of the *pseudo*-tetrahedral cyanomanganese complexes $[\text{Mn}(\text{CN})\text{L}'(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]$

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{R = H, L' = PPh₃, P(OPh)₃, CNBu^t or CNXyl; R = Me, L = CNBu^t} with octahedral *cis*- or *trans*-[MnBrL(CO)₂(dppm)] {L = P(OPh)₃ or P(OEt)₃} in the presence of Ti[PF₆] in CH₂Cl₂ gave orange or red solutions from which *cis*- or *trans*-[(dppm)(CO)₂LMn(μ-NC)MnL'(NO)(η⁵-C₅R₄Me)][PF₆]⁺[PF₆]⁻–¹⁰⁺[PF₆]⁻ (Scheme 2) were isolated as yellow to red microcrystalline solids. In some cases, the attempted synthesis of *trans*-Mn(CO)₂ complexes gave inseparable mixtures of *cis*- and *trans*-Mn(CO)₂ isomers, necessitating an alternative preparative route. Thus, for example, *trans*-7⁺ was synthesised by one-electron oxidation of *cis*-7⁺ with [NO][PF₆] and *in situ* reduction with N₂H₄·xH₂O of the dication, *trans*-7²⁺, formed by redox-induced *cis*–*trans* isomerisation.⁵



Scheme 2 Complexes *cis*- and *trans*-1⁺–20⁺ (*cis* or *trans* refers to the relative arrangement of the two carbonyl ligands at the octahedral manganese centre).

The linkage isomers of 1⁺–10⁺, *i.e.* *cis*- and *trans*-[(dppm)(CO)₂LMn(μ-CN)MnL'(NO)(η⁵-C₅R₄Me)][PF₆]⁺ 11⁺[PF₆]⁻–20⁺[PF₆]⁻ (Scheme 2), were synthesised by the room temperature reaction of the octahedral cyanomanganese ligands *cis*- or *trans*-[Mn(CN)L(CO)₂(dppm)] {L = P(OPh)₃ or P(OEt)₃} with the *pseudo*-tetrahedral iodide complexes [MnIL'(NO)(η⁵-C₅R₄Me)] {R = H, L' = PPh₃, P(OPh)₃, CNBu^t or CNXyl; R = Me, L' = CNBu^t} in the presence of Ti[PF₆] in CH₂Cl₂. Alternatively, *cis*-15⁺ and *cis*- and *trans*-[(dppm)(CO)₂{(RO)₃P}Mn(μ-CN)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)]⁺ (R = Ph 19⁺ or Et 20⁺) were synthesised by the reaction of *cis*-[Mn(CN){P(OR)₃}(CO)₂(dppm)] with [Mn(CO)L(NO)(η⁵-C₅H₄Me)][PF₆] (L = PPh₃ or CNBu^t) in the presence of Me₃NO. Analytical data for *cis*- and *trans*-1⁺[PF₆]⁻–20⁺[PF₆]⁻ are given in Table 1.

In CH₂Cl₂ the IR spectra (Table 1) of 1⁺–20⁺ show increases in ν(CN) of 20–30 cm⁻¹ compared with the mononuclear cyanomanganese precursors [Mn(CN)L'(NO)(η⁵-C₅R₄Me)] and [Mn(CN)L(CO)₂(dppm)]. Though such shifts to higher energy have been usually attributed to the kinematic effect of constraining the CN motion by *N*-coordination to a second metal fragment,⁶ a recent theoretical study⁷ has shown this factor to be rather less important than others such as σ-bonding and cation charge.

The number of carbonyl stretching bands observed for [(dppm)(CO)₂LMn(μ-XY)MnL'(NO)(η⁵-C₅R₄Me)]⁺ 1⁺–20⁺ depends on the geometry of the Mn(CO)₂ unit; two are observed for *cis*-Mn(CO)₂ and one for *trans*-Mn(CO)₂ species (with a very

weak second band observed at higher energy for the symmetry forbidden A-mode). This, and the observation of redox-induced *cis*–*trans* isomerisation on oxidation,⁵ provides a useful diagnostic tool for identifying the order of oxidation of the two redox-active centres in 1⁺–20⁺.

The IR spectra show not only that linkage isomers such as 1⁺ and 11⁺ are distinguishable but also that they are stable to isomerisation (*cf.* the more ready isomerisation of species such as [(Ph₃P)Au(μ-CN)RhCl₂(PMe₂Ph)₃]⁺ and [(OC)₅W(μ-NC)Cu(PPh₃)₃] to [(Ph₃P)Au(μ-NC)RhCl₂(PMe₂Ph)₃]⁺⁸ and [(OC)₅W(μ-CN)Cu(PPh₃)₃]⁹ respectively). In general, the ν(NO) band appears at approximately 10 cm⁻¹ higher energy when the *pseudo*-tetrahedral Mn centre is bound to the better π-accepting C-end of the bridging cyanide {compare ν(NO) = 1742 cm⁻¹ for *cis*-1⁺ with ν(NO) = 1734 cm⁻¹ for the linkage isomer *cis*-11⁺}. Conversely, the ν(CO) bands appear at lower energy when the octahedral centre is bound to the better σ-donating N-end of the bridge. {Compare ν(CO) = 1971, 1905 cm⁻¹ for *cis*-1⁺ with ν(CO) = 1974, 1920 cm⁻¹ for *cis*-11⁺}.}

The X-ray structures of *cis*-2⁺, *trans*-7⁺, *cis*-8⁺, *cis*-9⁺, *cis*-12⁺ and *trans*-17⁺

As far as we are aware, only two pairs of stable dinuclear complexes showing cyanide–isocyanide linkage isomerism have been previously structurally characterised, namely [(H₃N)₅Co(μ-XY)Co(CN)₅] (XY = CN and NC)¹⁰ and [(OC)₅Cr(μ-XY)Fe(dppe)(η⁵-C₅H₅)] (XY = CN and NC).¹¹ Structural analyses of two pairs of the new linkage isomers, namely *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-XY)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)]⁺ (XY = NC, *trans*-7⁺; XY = CN, *trans*-17⁺), and *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-XY)Mn{P(OPh)₃}(NO)(η⁵-C₅H₄Me)]⁺ (XY = NC, *cis*-2⁺; XY = CN, *cis*-12⁺) were therefore carried out in order to investigate possible changes arising from μ-CN isomerism.

The structures of the cations *trans*-17⁺ (also representative of *trans*-7⁺, see below), *cis*-2⁺ and *cis*-12⁺ are shown in Fig. 1–3 respectively; selected bond lengths and angles are given in Table 2 (for *trans*-7⁺ and *trans*-17⁺) and Table 3 (for *cis*-2⁺ and for the two crystallographically independent units of *cis*-12⁺). Dinuclear complexes containing the cyanomanganese ligands [Mn(CN)(CNXyl)(NO)(η⁵-C₅H₄Me)] and [Mn(CN)(CNBu^t)(NO)(η⁵-C₅Me₅)], namely *cis*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNXyl)(NO)(η⁵-C₅H₄Me)]⁺ *cis*-8⁺ (Fig. 4) and *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅Me₅)]⁺ *cis*-9⁺ (Fig. 5), have also been structurally characterised. Selected bond lengths and angles are given in Table 4.

Each of the cations *trans*-7⁺, *trans*-17⁺, *cis*-2⁺, *cis*-12⁺, *cis*-8⁺ and *cis*-9⁺ contains two manganese centres linked by a nearly linear Mn–CN–Mn bridge, with Mn–C–N and C–N–Mn angles ranging from 171.6 to 179.1°. The geometries of the [MnXL(CO)₂(dppm)] and [MnYL(NO)(η⁵-C₅R₄Me)] fragments are octahedral and *pseudo*-tetrahedral respectively (from now on designated as Mn_{oct} and Mn_{tet}).

For a given pair of linkage isomers, the Mn–CN bond length appears shorter than Mn–NC *cf.* Mn_{tet}–CN = 1.951(3) Å in *trans*-7⁺ *vs.* Mn_{tet}–NC = 1.968(3) Å in *trans*-17⁺, and CN–Mn_{oct} = 2.010(3) Å in *trans*-7⁺ *vs.* NC–Mn_{oct} = 1.955(3) Å in *trans*-17⁺, indicating the better π-accepting ability of a C-donor fragment.

Table 1 Analytical and IR spectroscopic data for *cis*- and *trans*-[(dppm)(CO)₂LMn(μ-XY)MnL'(NO)(η⁵-C₅R₄Me)][PF₆]

Complex ^a	XY	L	L'	R	Colour	Yield (%)	Analysis (%) ^b			IR ^c /cm ⁻¹			
							C	H	N	ν(CNR)	ν(CN)	ν(CO)	ν(NO)
<i>cis</i> -1 ⁺	NC	P(OPh) ₃	PPh ₃	H	Orange	63	59.7 (59.9)	4.4 (4.2)	2.0 (2.0)	—	2109w	1971, 1905	1742
<i>trans</i> -1 ⁺	NC	P(OPh) ₃	PPh ₃	H	Orange	68	59.6 (59.9)	4.1 (4.2)	2.2 (2.0)	—	2116w	2018w, 1930	1741
<i>cis</i> -2 ⁺	NC	P(OPh) ₃	P(OPh) ₃	H	Orange	62	58.0 (58.0)	3.6 (4.1)	2.2 (1.9)	—	2127w	1971, 1905	1763
<i>trans</i> -2 ⁺	NC	P(OPh) ₃	P(OPh) ₃	H	Orange	59	58.0 (58.0)	4.2 (4.1)	2.2 (1.9)	—	2127w	2018w, 1930	1763
<i>cis</i> -3 ⁺	NC	P(OPh) ₃	CNBu ^t	H	Orange	71	56.4 (55.9)	4.7 (4.4)	3.6 (3.4)	2168m	2130w	1971, 1908	1764
<i>trans</i> -3 ⁺	NC	P(OPh) ₃	CNBu ^t	H	Orange	45	55.6 (55.9)	4.4 (4.4)	3.6 (3.4)	2167m	2132w	2020w, 1932	1762
<i>cis</i> -4 ⁺	NC	P(OPh) ₃	CNXyl	H	Orange	75	57.9 (57.6)	4.3 (4.2)	3.3 (3.3)	2147m	2130w	1970, 1908	1766
<i>trans</i> -4 ⁺	NC	P(OPh) ₃	CNXyl	H	Orange	54	57.9 (57.6)	4.3 (4.2)	3.2 (3.3)	2146m	2132w	2019w, 1932	1765
<i>cis</i> -5 ⁺	NC	P(OEt) ₃	PPh ₃	H	Orange	66	55.1 (55.3)	4.7 (4.7)	2.5 (2.2)	—	2102w	1959, 1894	1743
<i>trans</i> -5 ⁺	NC	P(OEt) ₃	PPh ₃	H	Orange	59	55.5 (55.3)	4.6 (4.7)	2.3 (2.2)	—	2113w	2010w, 1915	1742
<i>cis</i> -6 ⁺	NC	P(OEt) ₃	P(OPh) ₃	H	Orange	70	53.2 (53.3)	4.3 (4.6)	2.1 (2.1)	—	2127w	1958, 1894	1763
<i>trans</i> -6 ⁺	NC	P(OEt) ₃	P(OPh) ₃	H	Orange	55	53.8 (53.3)	4.6 (4.6)	2.2 (2.1)	—	2124w	2010w, 1915	1764
<i>cis</i> -7 ⁺	NC	P(OEt) ₃	CNBu ^t	H	Red	38	50.2 (50.1)	4.7 (5.0)	3.7 (3.9)	2168m	2133w	1958, 1894	1762
<i>trans</i> -7 ⁺	NC	P(OEt) ₃	CNBu ^t	H	Yellow	73	50.4 (50.1)	4.8 (5.0)	3.9 (3.9)	2168m	2132w	2010w, 1916	1763
<i>cis</i> -8 ⁺	NC	P(OEt) ₃	CNXyl	H	Red	67	51.8 (52.2)	4.7 (4.7)	3.3 (3.7)	2145m	2132w	1958, 1894	1766
<i>trans</i> -8 ⁺	NC	P(OEt) ₃	CNXyl	H	Orange	54	51.7 (52.2)	4.6 (4.7)	3.5 (3.7)	2146m	2131w	2010w, 1916	1766
<i>cis</i> -9 ⁺	NC	P(OPh) ₃	CNBu ^t	Me	Orange	72	54.8 (54.6) ^d	4.8 (4.7)	3.3 (3.1)	2152m	2121w	1970, 1905	1742
<i>trans</i> -9 ⁺	NC	P(OPh) ₃	CNBu ^t	Me	Orange	48	56.8 (57.2)	4.7 (4.8)	2.9 (3.3)	2154m	2123w	2021w, 1931	1740
<i>cis</i> -10 ⁺	NC	P(OEt) ₃	CNBu ^t	Me	Red	55	51.5 (51.8)	5.6 (5.4)	3.6 (3.7)	2154m	2118w	1958, 1894	1741
<i>trans</i> -10 ⁺	NC	P(OEt) ₃	CNBu ^t	Me	Orange	30	52.1 (51.8)	5.5 (5.4)	4.1 (3.7)	2153m	2120w	2009w, 1914	1740
<i>cis</i> -11 ⁺	CN	P(OPh) ₃	PPh ₃	H	Green	47	59.7 (59.9)	4.4 (4.2)	2.3 (2.0)	—	2104w	1974, 1920	1734
<i>trans</i> -11 ⁺	CN	P(OPh) ₃	PPh ₃	H	Green	31	59.8 (59.9)	4.1 (4.2)	1.9 (2.0)	—	2081w	2016w, 1936	1735
<i>cis</i> -12 ⁺	CN	P(OPh) ₃	P(OPh) ₃	H	Pink	56	57.9 (58.0)	3.6 (4.1)	2.4 (1.9)	—	2121w	1973, 1920	1756
<i>trans</i> -12 ⁺	CN	P(OPh) ₃	P(OPh) ₃	H	Brown	45	58.0 (58.0)	4.1 (4.1)	2.2 (1.9)	—	2103w	2015w, 1935	1756
<i>cis</i> -13 ⁺	CN	P(OPh) ₃	CNBu ^t	H	Pink	81	55.7 (55.9)	4.5 (4.4)	3.4 (3.4)	2171m	2128w	1975, 1922	1758
<i>trans</i> -13 ⁺	CN	P(OPh) ₃	CNBu ^t	H	Green	74	56.0 (55.9)	4.4 (4.4)	3.4 (3.4)	2172m	2111w	2015w, 1936	1757
<i>cis</i> -14 ⁺	CN	P(OPh) ₃	CNXyl	H	Purple	62	57.6 (57.6)	4.4 (4.2)	3.3 (3.3)	2147m	2132sh	1974, 1922	1761
<i>trans</i> -14 ⁺	CN	P(OPh) ₃	CNXyl	H	Black	53	57.5 (57.6)	4.1 (4.2)	3.2 (3.3)	2147m	2111w	2017w, 1936	1760
<i>cis</i> -15 ⁺	CN	P(OEt) ₃	PPh ₃	H	Green	44	55.1 (55.3)	4.9 (4.7)	2.2 (2.2)	—	2099w	1963, 1908	1736
<i>trans</i> -15 ⁺	CN	P(OEt) ₃	PPh ₃	H	Green	28	54.8 (55.3)	4.4 (4.7)	2.2 (2.2)	—	2088w	2006w, 1921	1734
<i>cis</i> -16 ⁺	CN	P(OEt) ₃	P(OPh) ₃	H	Red	44	53.2 (53.3)	4.3 (4.6)	2.1 (2.1)	—	2113w	1962, 1906	1758
<i>trans</i> -16 ⁺	CN	P(OEt) ₃	P(OPh) ₃	H	Brown	40	53.0 (53.3)	4.6 (4.6)	2.3 (2.1)	—	2096w	2006w, 1922	1757
<i>cis</i> -17 ⁺	CN	P(OEt) ₃	CNBu ^t	H	Pink	70	49.6 (50.1)	5.1 (5.0)	3.8 (3.9)	2172m	2123w	1962, 1907	1758
<i>trans</i> -17 ⁺	CN	P(OEt) ₃	CNBu ^t	H	Green	66	50.4 (50.1)	5.0 (5.0)	3.8 (3.9)	2172m	2106w	2007w, 1921	1757
<i>cis</i> -18 ⁺	CN	P(OEt) ₃	CNXyl	H	Pink	40	51.7 (52.2)	4.6 (4.7)	3.5 (3.7)	2145m	2128sh	1962, 1907	1761
<i>trans</i> -18 ⁺	CN	P(OEt) ₃	CNXyl	H	Green	34	51.7 (52.2)	4.7 (4.7)	3.3 (3.7)	2146m	2105w	2006w, 1921	1760
<i>cis</i> -19 ⁺	CN	P(OPh) ₃	CNBu ^t	Me	Green	55	57.0 (57.2)	4.8 (4.8)	3.0 (3.3)	2158m	2114w	1969, 1903	1735
<i>trans</i> -19 ⁺	CN	P(OPh) ₃	CNBu ^t	Me	Brown	56	57.4 (57.2)	4.7 (4.8)	3.1 (3.3)	2157m	2113w	2015w, 1928	1733
<i>cis</i> -20 ⁺	CN	P(OEt) ₃	CNBu ^t	Me	Pink	68	51.2 (51.8)	5.6 (5.4)	4.1 (3.7)	2158m	2113w	1961, 1906	1734
<i>trans</i> -20 ⁺	CN	P(OEt) ₃	CNBu ^t	Me	Brown	45	51.4 (51.8)	5.5 (5.4)	3.9 (3.7)	2157m	2111w	2004w, 1920	1733

^a Isolated as [PF₆]⁻ salts. ^b Calculated values in parentheses. ^c Strong absorptions in CH₂Cl₂ unless stated otherwise; sh = shoulder, m = medium, w = weak. ^d Analysed as a 1 : 1 CH₂Cl₂ solvate.

Table 2 Selected bond lengths (Å) and angles (°) for *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)]⁺ *trans*-7⁺ and *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-CN)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)]⁺ *trans*-17⁺

	<i>trans</i> -7 ⁺	<i>trans</i> -17 ⁺		<i>trans</i> -7 ⁺	<i>trans</i> -17 ⁺
Mn(1)–C(1)	1.951(3)	—	Mn(1)–C(1)–N(1)	176.9(3)	—
Mn(1)–N(1)	—	1.968(3)	Mn(1)–N(1)–C(1)	—	173.6(2)
Mn(2)–N(1)	2.010(3)	—	Mn(2)–N(1)–C(1)	171.6(2)	—
Mn(2)–C(1)	—	1.955(3)	Mn(2)–C(1)–N(1)	—	175.0(2)
C(1)–N(1)	1.153(4)	1.151(4)	N(1)–Mn(1)–C(1)	96.3(2)	—
Mn(1)–N(2)	1.656(3)	1.655(3)	N(1)–Mn(1)–N(2)	—	98.3(1)
Mn(1)–C(8)	1.916(4)	1.922(3)	C(1)–Mn(1)–C(8)	88.6(1)	—
N(2)–O(1)	1.171(4)	1.176(3)	C(8)–Mn(1)–N(1)	—	89.4(1)
C(8)–N(3)	1.150(4)	1.151(4)	Mn(1)–N(2)–O(1)	175.9(3)	174.4(3)
Mn(2)–P(1)	2.296(1)	2.283(9)	C(8)–Mn(1)–N(2)	96.1(2)	95.8(1)
Mn(2)–P(2)	2.275(1)	2.290(9)	P(1)–Mn(2)–P(2)	72.5(1)	72.2(3)
Mn(2)–P(3)	2.211(1)	2.205(10)	P(2)–Mn(2)–P(3)	100.4(1)	100.8(3)
Mn(2)–C(14)	1.839(3)	1.829(3)	P(1)–Mn(2)–P(3)	172.8(1)	172.9(4)
Mn(2)–C(13)	1.834(3)	1.827(3)	N(1)–Mn(2)–P(2)	165.3(1)	—
C(14)–O(3)	1.146(4)	1.147(3)	C(1)–Mn(2)–P(2)	—	164.8(8)
C(13)–O(2)	1.147(4)	1.149(3)	C(14)–Mn(2)–C(13)	178.7(1)	176.5(1)
			Mn(2)–C(14)–O(3)	177.3(3)	176.6(3)
Mn(1)···Mn(2)	5.096	5.058	Mn(2)–C(13)–O(2)	179.1(3)	179.7(3)

Table 3 Selected bond lengths (Å) and angles (°) for *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn{P(OPh)₃}(NO)(η⁵-C₅H₄Me)]⁺ *cis*-2⁺ and *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-CN)Mn{P(OPh)₃}(NO)(η⁵-C₅H₄Me)]⁺ *cis*-12⁺

	<i>cis</i> -2 ⁺	<i>cis</i> -12 ⁺ ^a		<i>cis</i> -2 ⁺	<i>cis</i> -12 ⁺ ^a
Mn(1)–C(1)	—	1.960(8)	Mn(1)–C(1)–N(1)	—	178.7(6)
Mn(1)–C(1)′	—	1.994(7)	Mn(1)–C(1)–N(1)′	—	179.0(6)
Mn(1)–N(1)	2.033(14)	—	Mn(1)–N(1)–C(1)	175.8(13)	—
Mn(2)–N(1)	—	1.927(6)	Mn(2)–N(1)–C(1)	—	173.4(6)
Mn(2)–N(1)′	—	1.935(6)	Mn(2)–N(1)′–C(1)′	—	176.7(6)
Mn(2)–C(1)	1.912(17)	—	Mn(2)–C(1)–N(1)	171.1(15)	—
C(1)–N(1)	1.184(16)	1.180(7)	P(4)–Mn(2)–N(1)	—	86.06(17)
C(1)′–N(1)′	—	1.147(7)	P(4)–Mn(2)–N(1)′	—	86.16(15)
Mn(2)–N(2)	1.637(17)	1.612(8)	P(4)–Mn(2)–C(1)	87.9(5)	—
Mn(2)–N(2)′	—	1.631(7)	N(2)–Mn(2)–N(1)	—	98.9(3)
Mn(2)–P(4)	2.198(6)	2.218(2)	N(2)–Mn(2)–N(1)′	—	100.6(3)
Mn(2)–P(4)′	—	2.204(2)	N(2)–Mn(2)–C(1)	96.6(7)	—
N(2)–O(1)	1.218(17)	1.210(8)	C(1)–Mn(1)–P(2)	—	86.38(19)
N(2)′–O(1)′	—	1.192(7)	C(1)′–Mn(1)–P(2)′	—	87.54(18)
Mn(1)–P(1)	2.285(6)	2.324(2)	N(1)–Mn(1)–P(2)	88.2(4)	—
Mn(1)–P(1)′	—	2.348(2)	Mn(2)–N(2)–O(1)	172.7(14)	171.1(6)
Mn(1)–P(2)	2.340(6)	2.293(2)	Mn(2)–N(2)–O(1)′	—	173.7(6)
Mn(1)–P(2)′	—	2.285(2)	P(4)–Mn(2)–N(2)	94.2(5)	98.6(2)
Mn(1)–P(3)	2.207(6)	2.197(2)	P(4)–Mn(2)–N(2)′	—	95.0(2)
Mn(1)–P(3)′	—	2.208(2)	P(1)–Mn(1)–P(2)	72.9(2)	72.35(7)
Mn(1)–C(2)	1.753(19)	1.795(8)	P(1)–Mn(1)–P(2)′	—	72.41(7)
Mn(1)–C(2)′	—	1.814(7)	P(2)–Mn(1)–P(3)	96.1(2)	167.05(8)
Mn(1)–C(3)	1.727(17)	1.798(7)	P(2)–Mn(1)–P(3)′	—	171.48(8)
Mn(1)–C(3)′	—	1.785(7)	P(1)–Mn(1)–P(3)	168.7(2)	94.94(8)
C(2)–O(2)	1.197(18)	1.133(7)	P(1)–Mn(1)–P(3)′	—	99.42(8)
C(2)′–O(2)′	—	1.170(7)	C(2)–Mn(1)–C(3)	86.8(8)	89.7(3)
C(3)–O(3)	1.199(16)	1.154(7)	C(2)–Mn(1)–C(3)′	—	88.3(3)
C(3)′–O(3)′	—	1.161(7)	Mn(1)–C(2)–O(2)	175.3(17)	177.9(7)
Mn(1) ... Mn(2)	5.109	5.059	Mn(1)–C(2)–O(2)′	—	174.2(6)
Mn(1)′ ... Mn(2)′	—	5.073	Mn(1)–C(3)–O(3)	175.5(14)	175.6(5)
			Mn(1)–C(3)–O(3)′	—	178.1(6)

^a There are two independent molecules in the asymmetric unit. Equivalent atoms for the second are distinguished from the first by primes.

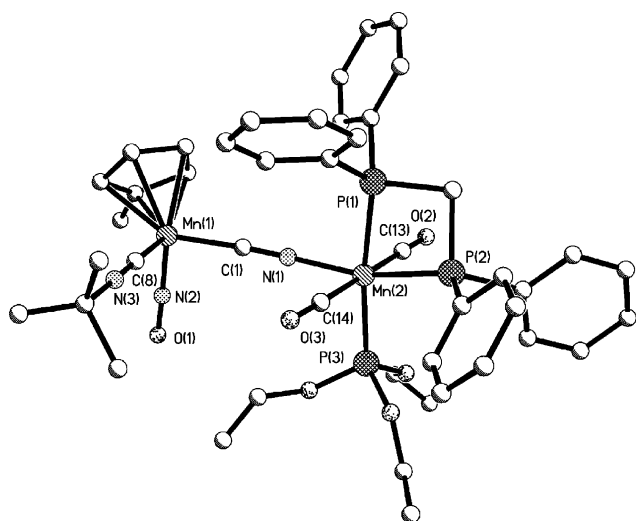


Fig. 1 The structure of *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-CN)Mn(CNBu)(NO)(η⁵-C₅H₄Me)]⁺ *trans*-17⁺. The hydrogen atoms have been omitted for clarity.

The μ-CN bond lengths are in the range 1.15–1.18 Å, similar to those in other cyanide-bridged complexes.¹²

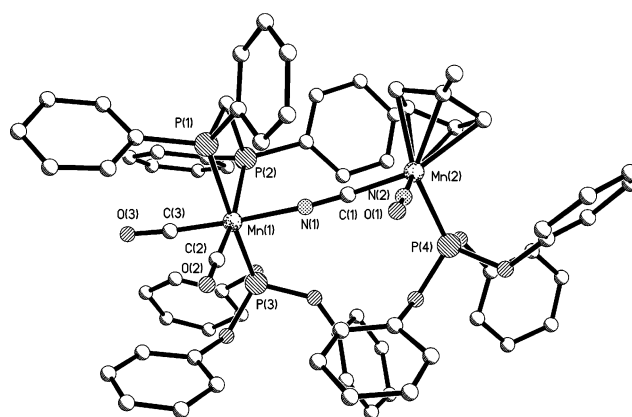


Fig. 2 The structure of *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn{P(OPh)₃}(NO)(η⁵-C₅H₄Me)]⁺ *cis*-2⁺. Hydrogen atoms have been omitted for clarity.

As found in the other structurally characterised linkage isomers noted above,^{10,11} the molecular structures of *trans*-7⁺ and *trans*-17⁺ are very similar. (They are crystallographically isostructural.) By contrast, those of *cis*-2⁺ and *cis*-12⁺ are rather different, at least in the solid state. Thus, the torsion angle, τ , formed by the two Mn–P(OPh)₃ vectors (*i.e.* P–Mn–XY–Mn–P with the

Table 4 Selected bond lengths (Å) and angles (°) for *cis*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNXyl)(NO)(η⁵-C₅H₄Me)]⁺ *cis*-8⁺ and *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅Me₅)]⁺ *cis*-9⁺

	<i>cis</i> -8 ⁺	<i>cis</i> -9 ⁺		<i>cis</i> -8 ⁺	<i>cis</i> -9 ⁺
Mn(1)–C(1)	1.951(5)	1.938(9)	Mn(1)–C(1)–N(1)	177.0(5)	176.6(7)
Mn(2)–N(1)	2.012(4)	1.996(7)	Mn(2)–N(1)–C(1)	176.3(4)	176.0(6)
C(1)–N(1)	1.157(5)	1.161(9)	Mn(1)–N(2)–O(2)	176.5(4)	173.8(10)
Mn(1)–N(2)	1.653(5)	1.629(10)	C(42)–Mn(1)–N(2)	96.2(2)	97.2(5)
Mn(1)–C(42)	1.892(6)	1.883(10)	N(2)–Mn(1)–C(1)	96.2(2)	99.7(4)
N(2)–O(1)	1.182(5)	1.179(12)	C(42)–Mn(1)–C(1)	91.5(2)	90.5(3)
C(42)–N(3)	1.158(6)	1.150(10)	P(1)–Mn(2)–P(2)	72.3(1)	70.7(1)
Mn(2)–P(1)	2.298(2)	2.303(2)	P(2)–Mn(2)–P(3)	98.9(1)	97.7(1)
Mn(2)–P(2)	2.358(2)	2.352(2)	P(3)–Mn(2)–P(1)	170.9(1)	168.0(1)
Mn(2)–P(3)	2.224(2)	2.202(3)	N(1)–Mn(2)–P(2)	84.8(1)	84.8(2)
Mn(2)–C(2)	1.806(8)	1.791(9)	C(2)–Mn(2)–C(3)	89.8(2)	88.7(4)
Mn(2)–C(3)	1.777(5)	1.742(9)	Mn(2)–C(2)–O(2)	177.8(5)	174.9(7)
C(2)–O(2)	1.159(7)	1.153(9)	Mn(2)–C(3)–O(3)	178.8(5)	176.2(1)
C(3)–O(3)	1.162(5)	1.164(10)			
Mn(1)...Mn(2)	5.114	5.086			

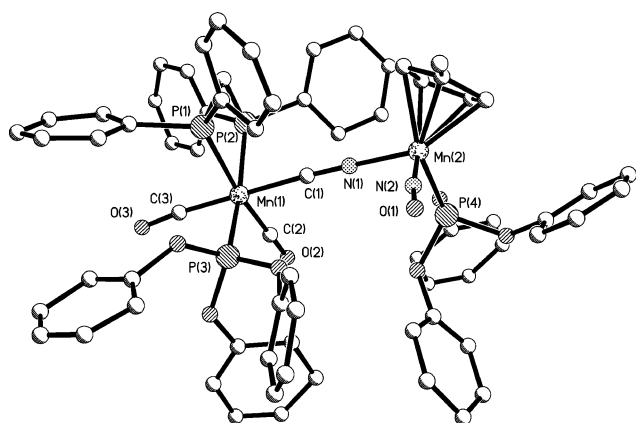


Fig. 3 The structure of *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn{P(OPh)₃}(NO)(η⁵-C₅H₄Me)]⁺ *cis*-12⁺. Hydrogen atoms have been omitted for clarity.

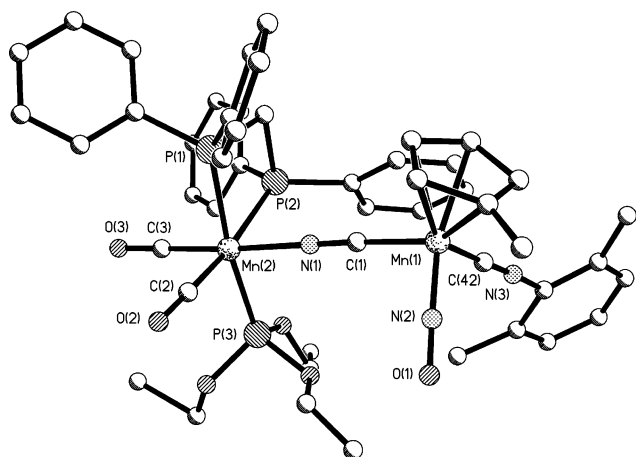


Fig. 4 The structure of *cis*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNXyl)(NO)(η⁵-C₅H₄Me)]⁺ *cis*-8⁺. Hydrogen atoms have been omitted for clarity.

Mn–XY–Mn backbone assumed to be linear) is 13.2° for *cis*-2⁺ and 86.1 and 76.2° for the two independent units of *cis*-12⁺ respectively. Formally, this appears to be the result of *N*- and *C*-coordination respectively of two different optical iso-

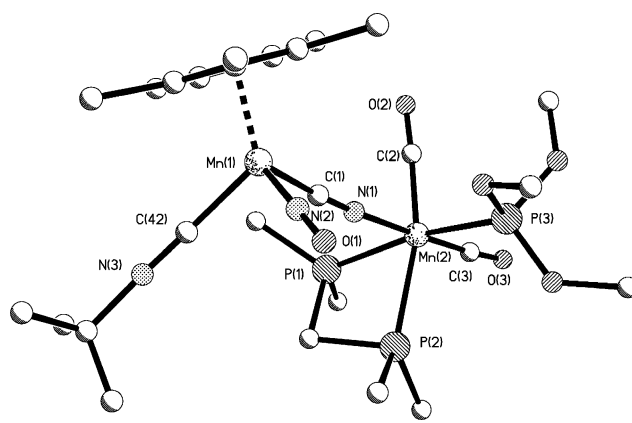


Fig. 5 The structure of *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅Me₅)]⁺ *cis*-9⁺. Hydrogen atoms and all but the *ipso* carbons of the phenyl rings of dppm have been omitted for clarity.

mers of the *pseudo*-tetrahedral units (NC)Mn{P(OPh)₃}(NO)(η⁵-C₅H₄Me) and (CN)Mn{P(OPh)₃}(NO)(η⁵-C₅H₄Me) to the octahedral manganese centre, *i.e.* *cis*-2⁺ and *cis*-12⁺ are different diastereoisomers. (Each of *cis*-1⁺ to *cis*-20⁺ can exist as diastereoisomers although in no case has evidence been found for the co-existence of two such isomers, *e.g.* by IR spectroscopy.)

The structural analysis of *cis*-9⁺ is the first of a complex containing the *N*-donor cyanomanganese ligand [Mn(CN)(CNBu^t)(NO)(η⁵-C₅Me₅)] the estimated cone angle of which, θ, (106°) is larger than that of [Mn(CN)(CNBu^t)(NO)(η⁵-C₅H₄Me)] (θ = 57°) due to the increased methylation on the cyclopentadienyl ring. Thus, the structure of *cis*-9⁺ differs from those of the other *cis* complexes, *cis*-2⁺, *cis*-8⁺ and *cis*-12⁺, in the relative arrangement of the metal fragments. In the less sterically hindered complexes, such as *cis*-8⁺, the η⁵-C₅H₄Me ring and the dppm ligand are *syn* relative to each other (Fig. 4). However, in complex *cis*-9⁺ the bulky η⁵-C₅Me₅ and dppm ligands are positioned *anti* to each other (Fig. 5).

Electrochemical studies

The cyclic voltammograms (CVs) of 1⁺–20⁺ each show two oxidation waves (Table 5) in CH₂Cl₂ at a platinum electrode,

Table 5 Electrochemical data^a for *cis*- and *trans*-[(dppm)(CO)₂LMn(μ-XY)MnL'(NO)(η⁵-C₅R₄Me)][PF₆]

Complex	L	L'	R	XY	Process (<i>E</i> ^{o'} /V) ^b		
					+ → 2+	2+ → 3+	Δ <i>E</i> ^{o'} ^c /V
<i>cis</i> -1 ⁺	P(OPh) ₃	PPh ₃	H	NC	1.03	1.54(I) (0.70, 1.36) ^d	—
<i>trans</i> -1 ⁺	P(OPh) ₃	PPh ₃	H	NC	0.68	1.35	0.67
<i>cis</i> -2 ⁺	P(OPh) ₃	P(OPh) ₃	H	NC	1.24(I) (0.73)	(1.60)	—
<i>trans</i> -2 ⁺	P(OPh) ₃	P(OPh) ₃	H	NC	0.73	1.61	0.88
<i>cis</i> -3 ⁺	P(OPh) ₃	CNBu ^t	H	NC	1.20(I) (0.73)	(1.43)	—
<i>trans</i> -3 ⁺	P(OPh) ₃	CNBu ^t	H	NC	0.72	1.45	0.73
<i>cis</i> -4 ⁺	P(OPh) ₃	CNXyl	H	NC	1.26(I) (0.72)	(1.51)	—
<i>trans</i> -4 ⁺	P(OPh) ₃	CNXyl	H	NC	0.74	1.47	0.73
<i>cis</i> -5 ⁺	P(OEt) ₃	PPh ₃	H	NC	1.02(I) (0.54)	(1.34)	—
<i>trans</i> -5 ⁺	P(OEt) ₃	PPh ₃	H	NC	0.53	1.31	0.78
<i>cis</i> -6 ⁺	P(OEt) ₃	P(OPh) ₃	H	NC	1.09(I) (0.55)	(1.56)	—
<i>trans</i> -6 ⁺	P(OEt) ₃	P(OPh) ₃	H	NC	0.57	1.55	0.98
<i>cis</i> -7 ⁺	P(OEt) ₃	CNBu ^t	H	NC	1.06(I) (0.54)	(1.36)	—
<i>trans</i> -7 ⁺	P(OEt) ₃	CNBu ^t	H	NC	0.55	1.36	0.81
<i>cis</i> -8 ⁺	P(OEt) ₃	CNXyl	H	NC	1.11(I) (0.56)	(1.44)	—
<i>trans</i> -8 ⁺	P(OEt) ₃	CNXyl	H	NC	0.55	1.43	0.88
<i>cis</i> -9 ⁺	P(OPh) ₃	CNBu ^t	Me	NC	0.99	1.51(I) (0.64, 1.25) ^d	—
<i>trans</i> -9 ⁺	P(OPh) ₃	CNBu ^t	Me	NC	0.67	1.28	0.61
<i>cis</i> -10 ⁺	P(OEt) ₃	CNBu ^t	Me	NC	0.99(I) (0.50)	(1.30)	—
<i>trans</i> -10 ⁺	P(OEt) ₃	CNBu ^t	Me	NC	0.51	1.32	0.81
<i>cis</i> -11 ⁺	P(OPh) ₃	PPh ₃	H	CN	0.84	1.65(I) (1.28)	—
<i>trans</i> -11 ⁺	P(OPh) ₃	PPh ₃	H	CN	0.76	1.31	0.55
<i>cis</i> -12 ⁺	P(OPh) ₃	P(OPh) ₃	H	CN	1.08	1.65(I) (1.40)	—
<i>trans</i> -12 ⁺	P(OPh) ₃	P(OPh) ₃	H	CN	0.90	1.42	0.52
<i>cis</i> -13 ⁺	P(OPh) ₃	CNBu ^t	H	CN	1.01	1.58(I) (1.39)	—
<i>trans</i> -13 ⁺	P(OPh) ₃	CNBu ^t	H	CN	0.87	1.28	0.41
<i>cis</i> -14 ⁺	P(OPh) ₃	CNXyl	H	CN	1.07	1.56(I) (1.39)	—
<i>trans</i> -14 ⁺	P(OPh) ₃	CNXyl	H	CN	0.92	1.33	0.41
<i>cis</i> -15 ⁺	P(OEt) ₃	PPh ₃	H	CN	0.79	1.44(I) (1.22)	—
<i>trans</i> -15 ⁺	P(OEt) ₃	PPh ₃	H	CN	0.69	1.19	0.50
<i>cis</i> -16 ⁺	P(OEt) ₃	P(OPh) ₃	H	CN	1.06(I) (0.73)	1.42	—
<i>trans</i> -16 ⁺	P(OEt) ₃	P(OPh) ₃	H	CN	0.77	1.36	0.59
<i>cis</i> -17 ⁺	P(OEt) ₃	CNBu ^t	H	CN	0.98 (0.72)	1.39(I) (1.21)	—
<i>trans</i> -17 ⁺	P(OEt) ₃	CNBu ^t	H	CN	0.72	1.21	0.49
<i>cis</i> -18 ⁺	P(OEt) ₃	CNXyl	H	CN	1.05(I) (0.74)	1.31	—
<i>trans</i> -18 ⁺	P(OEt) ₃	CNXyl	H	CN	0.75	1.31	0.56
<i>cis</i> -19 ⁺	P(OPh) ₃	CNBu ^t	Me	CN	0.75	1.57(I) (1.34)	—
<i>trans</i> -19 ⁺	P(OPh) ₃	CNBu ^t	Me	CN	0.88	1.20	0.32
<i>cis</i> -20 ⁺	P(OEt) ₃	CNBu ^t	Me	CN	0.78	1.41(I) (1.21)	—
<i>trans</i> -20 ⁺	P(OEt) ₃	CNBu ^t	Me	CN	0.70	1.18	0.48

^a At a Pt electrode in CH₂Cl₂, with potentials relative to the saturated calomel electrode, calibrated vs. the [Fe(η⁵-C₅Me₅)₂]⁺/[Fe(η⁵-C₅Me₅)₂] couple (at −0.08 V). ^b For an irreversible (I) process, the oxidation peak potential, (*E*_p)_{ox}, is given at a scan rate of 200 mV s^{−1}. Potentials for associated reversible product waves are given in parentheses. ^c Δ*E*^{o'} is the difference between the potentials for the two reversible oxidation waves (of the *trans*⁺ isomers only).

^d The two product waves, observed only after scanning the second, irreversible, oxidation wave, are due to the *trans*-dication/*trans*-monocation and *trans*-trication/*trans*-dication couples respectively.

corresponding to the sequential oxidation of the two metal centres. Generally, the waves are reversible on the cyclic voltammetry timescale when the coordination geometry of the manganese centre is *pseudo*-tetrahedral or *trans*-dicarbonyl octahedral. However, they are irreversible when a *cis*-dicarbonyl unit is oxidised due to the redox-induced *cis*–*trans* isomerisation of the Mn^{II}(CO)₂ fragment.⁵ In these cases, the irreversible oxidation wave is coupled to a reversible product wave, at a more negative potential.

The occurrence of an irreversible oxidation wave for *cis*-[(dppm)(CO)₂LMn(μ-XY)Mn(NO)L'(η⁵-C₅R₄Me)]⁺ therefore allows the identification of which manganese centre is oxidised first (aided by comparing the individual redox potentials with those of the corresponding mononuclear units and noting the effects of altering the ligands L and L' or the extent of ring methylation in η⁵-C₅R₄Me). As noted previously,³ increased ring methylation in [Mn(CN)(CNBu^t)(NO)(η⁵-C₅R₄Me)], from η⁵-C₅H₄Me to η⁵-

C₅Me₅, lowers the oxidation potential by 210 mV; better donors L and L' shift oxidation waves to less positive potentials, *e.g.* the oxidation potential of [Mn(CN)L'(NO)(η⁵-C₅H₄Me)] decreases from 1.11 V (L' = CNXyl) to 0.85 V (L' = PPh₃) and that of *trans*-[Mn(CN)L(CO)₂(dppm)] decreases from 0.64 V {L = P(OPh)₃} to 0.50 V {L = P(OEt)₃}.

The variation of the orientation of the cyanide bridge, of the ligands L and L', of the extent of ring methylation in the η⁵-C₅R₄Me group, and the *cis* or *trans* orientation of the Mn(CO)₂ fragment all affect the order in which the metal centres in *cis*-[(dppm)(CO)₂LMn(μ-XY)Mn(NO)L'(η⁵-C₅R₄Me)]⁺ are oxidised. This, in turn, leads to control of the direction and energy of metal–metal charge-transfer in the corresponding dications (see below).

The CV of *cis*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn-{P(OPh)₃}(NO)(η⁵-C₅H₄Me)]⁺ *cis*-6⁺ [Fig. 6(a)] shows one irreversible oxidation wave at 1.09 V followed by a reversible

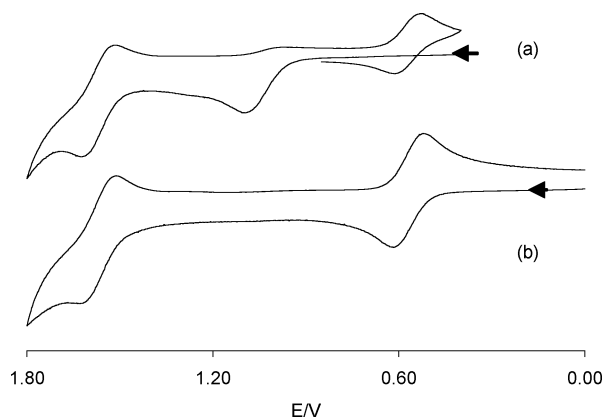


Fig. 6 The CVs in CH_2Cl_2 of (a) $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$, cis-6^+ , from 0.30 to 1.80 to 0.40 to 0.85 V, and (b) $\text{trans}-[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$, trans-6^+ , from 0.0 to 1.80 V at a scan rate of 200 mV s^{-1} .

product oxidation wave at 1.56 V, and a product reduction wave, at 0.52 V, which a subsequent scan shows to be reversible and centred at 0.55 V. Thus, the first step is oxidation at the $\text{cis-Mn}(\text{CO})_2$ site; the two product waves appear at potentials identical to those of trans-6^+ [Fig. 6(b)], confirming that after oxidation at the N -bound $\text{cis-Mn}(\text{CO})_2$ unit, cis-6^{2+} rapidly isomerises to trans-6^{2+} .

The CV of $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ cis-2^+ [Fig. 7(a)] is very similar to that of cis-6^+ , showing one irreversible process at 1.24 V {oxidation at the $\text{cis-Mn}(\text{CO})_2$ site}, and two reversible product waves at 1.60 and 0.73 V corresponding to the $\text{trans-2}^{3+}/\text{trans-2}^{2+}$ and $\text{trans-2}^{2+}/\text{trans-2}^+$ couples for the product of

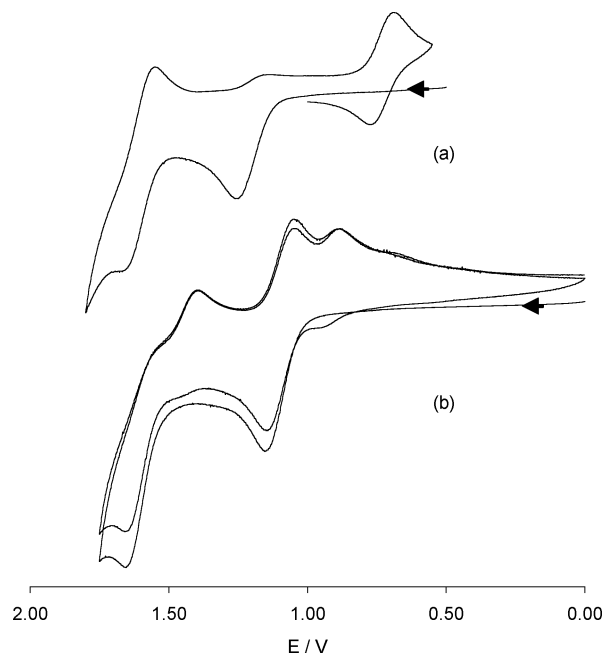
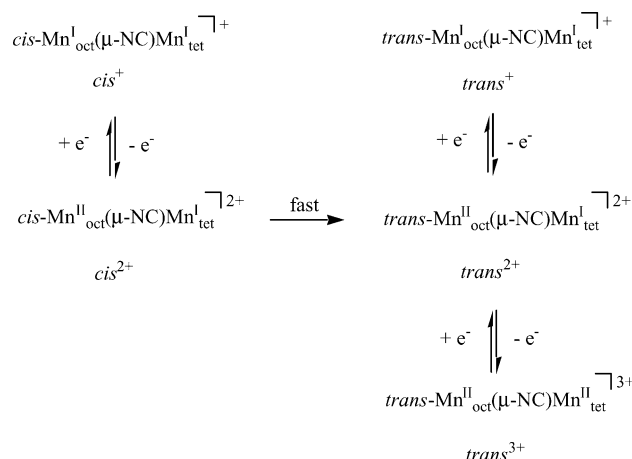
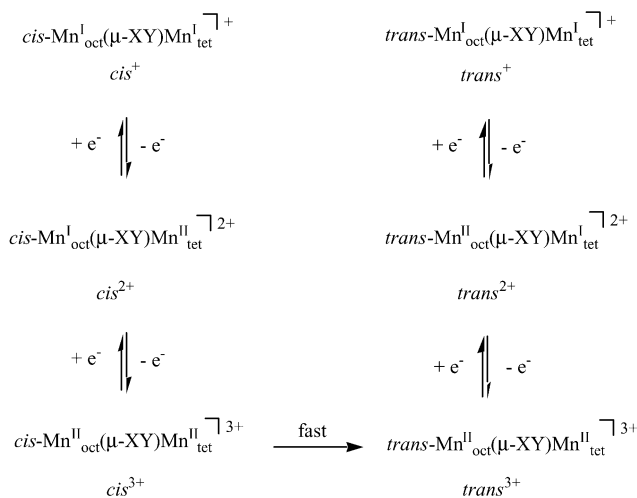


Fig. 7 The CVs in CH_2Cl_2 of $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-XY})\text{Mn}\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ (a) $\text{XY} = \text{NC}$, cis-2^+ , from 0.50 to 1.80 to 0.50 to 0.90 V, and (b) $\text{XY} = \text{CN}$, cis-12^+ , from 0.0 to 1.80 V, multiple scan, at a scan rate of 200 mV s^{-1} .

oxidative isomerisation. However, the CV of its linkage isomer $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-CN})\text{Mn}\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ cis-12^+ [Fig. 7(b)] shows the first process to be reversible and therefore related to the oxidation of Mn_{tet} . The second oxidation process is irreversible with associated product waves identical to those of trans-12^+ . Changing the orientation of the cyanide bridge from $\text{Mn}_{\text{oct}}\text{-NC-Mn}_{\text{tet}}$ (in cis-2^+) to $\text{Mn}_{\text{oct}}\text{-CN-Mn}_{\text{tet}}$ in (cis-12^+) therefore reverses the order in which the metal centres oxidise. The overall electrochemical behaviour of cis-2^+ and cis-12^+ is summarised in Schemes 3 and 4 respectively.



Scheme 3 The oxidation of $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{MnL}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ {L = $\text{P}(\text{OPh})_3$, cis-2^+ or CNBu^t , cis-3^+ }.



Scheme 4 The oxidation of $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-XY})\text{MnL}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ {XY = NC, L = CNBu^t , R = Me, cis-9^+ ; XY = CN, L = $\text{P}(\text{OPh})_3$, R = H, cis-12^+ }.

Complexes $[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-CN})\text{Mn}\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ cis-12^+ and $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-CN})\text{Mn}\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ cis-16^+ provide an example of the effect of varying L, the ligand at $\text{cis-Mn}_{\text{oct}}$. Although they differ only in the replacement of L = $\text{P}(\text{OPh})_3$ in cis-12^+ by L = $\text{P}(\text{OEt})_3$ in cis-16^+ their electrochemistry is very different. The CV of cis-16^+ (Fig. 8) shows an irreversible oxidation wave at 1.06 V, corresponding to the oxidation of the octahedral metal centre, and

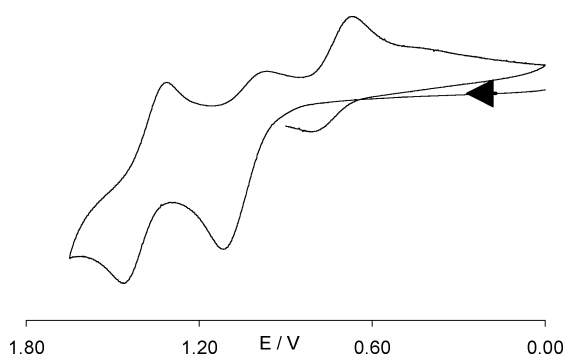


Fig. 8 The CV in CH_2Cl_2 of $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}-(\mu\text{-CN})\text{Mn}\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ cis-16^+ from 0.0 to 1.65 to 0.0 to 0.90 V at a scan rate of 200 mV s^{-1} .

two product waves at 1.42 and 0.73 V, identical to those of trans-16^+ . Thus, changing the phosphite, L, to a better donor leads to the site of first oxidation changing from Mn_{tet} (first oxidation wave reversible) to $\text{cis-Mn}_{\text{oct}}$ (first oxidation wave irreversible).

By contrast, the complexes $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}-(\mu\text{-NC})\text{Mn}(\text{PPh}_3)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ cis-1^+ and $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ cis-2^+ provide an example of how the ligand L' at Mn_{tet} influences the order of oxidation. In the CV of cis-1^+ [Fig. 9(a)] the first wave is reversible and therefore associated with oxidation at Mn_{tet} . However, on changing PPh_3 (in cis-1^+) for the better π -acceptor P(OPh)_3 (in cis-2^+) the first wave becomes irreversible [Fig. 9(b)] indicating oxidation at $\text{cis-Mn}_{\text{oct}}$.

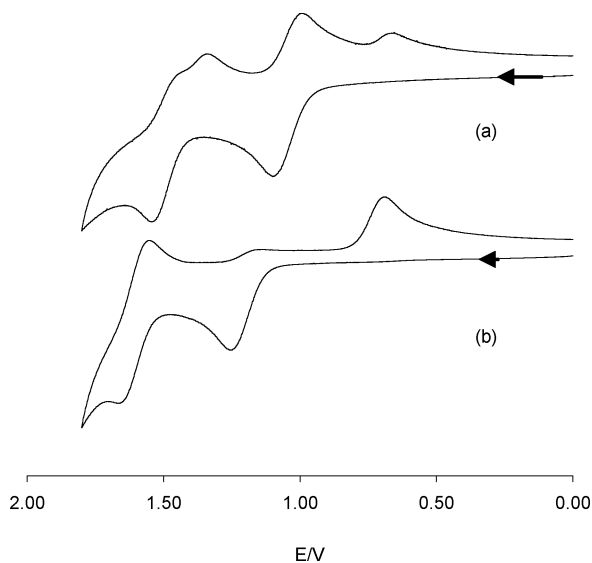


Fig. 9 The CVs in CH_2Cl_2 of $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}-(\mu\text{-NC})\text{MnL}'(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ (a) $\text{L}' = \text{PPh}_3$, cis-1^+ , and (b) $\text{L}' = \text{P(OPh)}_3$, cis-2^+ from 0.0 to 1.8 V.

Finally, $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ cis-3^+ and $\text{cis}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{Me}_5)]^+$ cis-9^+ show how the extent of methylation of the $\eta^5\text{-C}_5\text{R}_4\text{Me}$ group influences the order in which the metal centres are oxidised. The first wave in the CV of cis-3^+ is irreversible and therefore associated with the oxidation

of $\text{cis-Mn}_{\text{oct}}$; the two reversible product waves correspond to the $\text{trans-3}^{3+}/\text{trans-3}^{2+}$ and $\text{trans-3}^{2+}/\text{trans-3}^{1+}$ couples. However, the increased ring methylation in the $\eta^5\text{-C}_5\text{Me}_5$ complex cis-9^+ increases the electron density at Mn_{tet} which is then the first oxidation site; the first oxidation wave is reversible and the second irreversible (oxidation at $\text{cis-Mn}_{\text{oct}}$). The electrochemical behaviour of cis-3^+ is described by Scheme 3 and that of cis-9^+ by Scheme 4.

In the absence of redox-induced isomerisation, the order of oxidation of the two metal centres in $\text{trans-1}^+ \text{--} \text{20}^+$ can only be assigned by comparing the potentials for the two reversible oxidation waves with those of mononuclear precursors (and related complexes) and by observing the shifts in each oxidation wave as the ligands on each centre are altered.

The first oxidation of $\text{trans}-[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ trans-7^+ occurs at 0.55 V. Since the oxidation potential of the mononuclear cyanomanganese ligand $[\text{Mn}(\text{CN})(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ occurs at ca. 1.0 V, and the potential will increase when this ligand is *N*-coordinated to a second metal, the process at 0.55 V must be related to the oxidation of $\text{trans-Mn}_{\text{oct}}$ in trans-7^+ . The second wave, associated with the oxidation of Mn_{tet} , is centred at 1.36 V which compares well with that of the mononuclear complex $[\text{Mn}(\text{CNBu}^t)_2(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ ($E^\circ = 1.45 \text{ V}$).³ (In this case, the assignment of the order of oxidation for trans-7^+ has been confirmed chemically and spectroscopically—see below.)

By contrast, the first oxidation wave of the linkage isomer of trans-7^+ , i.e. $\text{trans}-[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-CN})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ trans-17^+ , occurs at 0.72 V, which compares well with the oxidation potential of mononuclear $\text{trans}-[\text{Mn}(\text{CN})\{\text{P}(\text{OEt})_3\}(\text{CO})_2(\text{dppm})]$ ($E^\circ = 0.50 \text{ V}$),¹ indicating oxidation at Mn_{oct} . The potential for the second process for trans-17^+ (1.21 V) compares with that of $[\text{Mn}(\text{CNBu}^t)(\text{NCMe})(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ ($E^\circ = 1.23 \text{ V}$).³

Thus, although in each case Mn_{oct} is oxidised first, reversal of the cyanide bridge leads to a different route for MMCT from $\text{Mn}(\text{I})$ to $\text{Mn}(\text{II})$ in the resulting dication, i.e. *via C* then *N* in trans-7^{2+} but from *N* to *C* in trans-17^{2+} .

A comparison of $\text{trans}-[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-CN})\text{MnL}'(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ [$\text{L}' = \text{PPh}_3$ trans-15^+ , P(OPh)_3 trans-16^+ , CNBu^t trans-17^+ or CNXyl trans-18^+] shows that the first oxidation potential (Table 5) is relatively unchanged while the second decreases in the order $\text{P(OPh)}_3 > \text{CNXyl} > \text{CNBu}^t > \text{PPh}_3$. Thus, the first oxidation occurs at the *C*-bound octahedral centre. Indeed, further comparisons indicate that the first oxidation for all of $\text{trans-1}^+ \text{--} \text{20}^+$ occurs at Mn_{oct} , i.e. the order of oxidation of the two metal centres is independent of L, L' and R as well as the $\mu\text{-CN}$ orientation (in marked contrast to the *cis* isomers described above).

This therefore shows that the *cis* or *trans* arrangement of the $\text{Mn}(\text{CO})_2$ fragment can also alter the oxidation order, as shown above for *cis*- and $\text{trans}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{Me}_5)]^+$, *cis-9*⁺ and trans-9^+ , and *cis*- and $\text{trans}-[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-CN})\text{Mn}\{\text{P}(\text{OPh})_3\}(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$, *cis-12*⁺ and trans-12^+ . To underline this point, the order of oxidation of the metal centres for both *9*⁺ and *12*⁺ is described by Scheme 4. The first oxidation in the *cis* complexes occurs at Mn_{tet} and the second at Mn_{oct} . However, after isomerisation the first site to be reduced is Mn_{tet} , i.e. the order

Table 6 Analytical data for *trans*-[(dppm)(CO)₂LMn(μ-NC)MnL'(NO)(η⁵-C₅R₄Me)][PF₆]₂

Complex ^a	L	L'	R	Yield (%)	Analysis (%) ^b			IR ^c /cm ⁻¹			
					C	H	N	ν(CNR)	ν(CN)	ν(CO)	ν(NO)
<i>trans</i> -1 ²⁺	P(OPh) ₃	PPh ₃	H	67	50.1 (50.3)	3.8 (3.7)	1.7 (1.8)	—	2052ms	2068 w.sh, 1999	1752
<i>trans</i> -2 ²⁺	P(OPh) ₃	P(OPh) ₃	H	56	51.7 (51.8) ^d	3.7 (3.7)	1.7 (1.7)	—	2077m	2067m, 2002	1772
<i>trans</i> -3 ²⁺	P(OPh) ₃	CNBu ^t	H	75	48.8 (50.0)	3.5 (3.9)	3.3 (3.1)	2177	2081 m	2069 m, 2005	1774
<i>trans</i> -4 ²⁺	P(OPh) ₃	CNXYl	H	70	51.2 (51.7)	4.0 (3.8)	2.5 (3.0)	2154	2085m	2072m.sh, 2006	1777
<i>trans</i> -5 ²⁺	P(OEt) ₃	PPh ₃	H	35	49.9 (49.6)	3.9 (4.2)	2.2 (2.0)	—	2054ms	2065 m.sh, 1992	1752
<i>trans</i> -6 ²⁺	P(OEt) ₃	P(OPh) ₃	H	77	47.7 (48.0)	4.2 (4.1)	1.8 (1.9)	—	2079m	2065sh, 1995	1773
<i>trans</i> -7 ²⁺	P(OEt) ₃	CNBu ^t	H	79	44.5 (44.1)	4.4 (4.4)	2.9 (3.4)	2176	2084m	2069sh, 1997	1774
<i>trans</i> -8 ²⁺	P(OEt) ₃	CNXYl	H	62	44.2 (44.4)	4.3 (4.1)	2.7 (3.1)	2153	2088m	2071w.sh, 1996	1776
<i>trans</i> -9 ²⁺	P(OPh) ₃	CNBu ^t	Me	54	45.7 (46.0) ^e	4.5 (4.8)	3.2 (3.3)	2162	2058	2000	1755
<i>trans</i> -10 ²⁺	P(OEt) ₃	CNBu ^t	Me	48	51.4 (51.4)	4.5 (4.3)	2.9 (3.0)	2163	2060m	2072m, 1994	1755

^a Isolated as [PF₆]⁻ salts. ^b Calculated values in parentheses. ^c Strong absorptions in CH₂Cl₂, unless otherwise stated; w = weak, m = medium, sh = shoulder. ^d Analysed as a 2 : 1 CH₂Cl₂ solvate. ^e Analysed as a 1 : 1 CH₂Cl₂ solvate.

of oxidation of the monocation is not the reverse of the order of reduction of the trication.

Finally, the different redox behaviour for linkage isomers reflects the σ-donor and π-acceptor properties of the cyanide ligand. Thus, for a pair of linkage isomers in *trans*-1⁺–20⁺, that with the more electron-rich fragment bound to the N atom is approximately 0.2 V easier to oxidise than that bound to C (cf. $E_1^{o'} = 0.55$ V for *trans*-7⁺ and 0.72 V for *trans*-17⁺). When the second process is detectable by cyclic voltammetry, the difference in oxidation potentials, $\Delta E^{o'}$ ($\Delta E^{o'} = E_2^{o'} - E_1^{o'}$) also varies for linkage isomers, being 0.81 and 0.49 V for *trans*-7⁺ and *trans*-17⁺ respectively as a representative example. The consequences for the electronic spectra of the mixed valence dications *trans*-[(dppm)(CO)₂LMn(μ-XY)MnL'(NO)(η⁵-C₅R₄Me)]²⁺ are noted below.

The synthesis and characterisation of the mixed valence dications 1²⁺–20²⁺

With the exceptions of *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn(PPh₃)(NO)(η⁵-C₅H₄Me)]⁺ *cis*-1⁺ and *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅Me₅)]⁺ *cis*-9⁺, all of the *cis* and *trans* isomers of [(dppm)(CO)₂LMn(μ-NC)MnL'(NO)(η⁵-C₅R₄Me)]⁺ 1⁺–10⁺ react with the one-electron oxidant [NO][PF₆] to form the corresponding dications *trans*-1²⁺–20²⁺. (The oxidation of *cis*-1⁺ and *cis*-9⁺, at C-bound Mn_{1et}, gave dications which are not stable at room temperature although spectroelectrochemistry at –30 °C provides evidence for *cis*-9²⁺ at lower temperatures—see below.) By contrast, chemical one-electron oxidation of the linkage isomers [(dppm)(CO)₂LMn(μ-CN)MnL'(NO)(η⁵-C₅R₄Me)]⁺ 11⁺–20⁺ with [Fe(η⁵-C₅H₅)(η⁵-C₅H₄COMe)][PF₆], [NO][PF₆] or [N(C₆H₄Br-*p*)₃][SbCl₆] led to decomposition even at low temperature (although, again, low temperature spectroelectrochemistry suggests some stability for *trans*-17²⁺).

The most convenient route to the purple mixed-valence salts *trans*-1²⁺–10²⁺2[PF₆]⁻ involves treatment of *trans*-[(dppm)(CO)₂LMn(μ-NC)MnL'(NO)(η⁵-C₅R₄Me)]⁺ *trans*-1⁺–10⁺ in CH₂Cl₂ with one equivalent of [NO][PF₆]. The solid products decompose significantly within 4 weeks, even when stored under argon at –20 °C, to a mixture containing the *cis* and *trans* monocations; they are soluble in polar solvents such as CH₂Cl₂, CHCl₃, thf, acetone and dmf, giving very air-sensitive

solutions. Nevertheless, *trans*-1²⁺–10²⁺2[PF₆]⁻ were characterised by elemental analysis (Table 6), cyclic voltammetry (each dication shows one oxidation and one reduction wave at potentials identical to those of the two oxidation waves of the corresponding monocation *trans*-1⁺–10⁺) and IR spectroscopy (Table 6).

Each dication, *trans*-1²⁺–10²⁺, shows two IR carbonyl bands of different intensity. The stronger absorption is shifted to higher wavenumber with respect to that of the corresponding monocation by ca. 80 cm⁻¹; the second absorption, assigned to the symmetric stretch of the *trans*-Mn(CO)₂ fragment, is also shifted (by ca. 60 cm⁻¹) but, more significantly, it is more intense when compared to that of the monocations. Similar behaviour has been found on one-electron oxidation of species such as [(H₃N)₅Ru^{II}(μ-NC)Mn^I(CO)₂{P(OPh)₃}(dppm)-*trans*)]²⁺, with the increased intensity of the symmetric stretch resulting from coupling with the cyanide stretching vibration.¹³

The absorptions corresponding to the nitrosyl and, when present, isocyanide ligands are also shifted to higher wavenumber with respect to the monocations, but by only ca. 10 cm⁻¹. Thus, the larger energy shift in the carbonyl bands confirms that oxidation of the *trans* monocations occurs at Mn_{1et} which also leads to a lower energy bridging cyanide band (decreased by ca. 40 cm⁻¹ with respect to that of the monocations).

Addition of one equivalent of [NO][PF₆] to a solution of the dication *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅Me₅)]²⁺ *trans*-10²⁺ led to the formation of a complex showing ν(CNR) and ν(NO) shifted by ca. 70 cm⁻¹ to higher wavenumbers and ν(CO) shifted to higher energy by 10 cm⁻¹, suggesting oxidation at C-bound Mn_{1et} and some stability for *trans*-10³⁺. However, this trication could not be isolated.

Although only *trans*-1²⁺–10²⁺ proved isolable, other less stable dications (and one trication) were characterised in solution by low temperature IR spectroelectrochemistry, i.e. on *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-XY)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)]⁺ (XY = NC, *trans*-7⁺; XY = CN, *trans*-17⁺) and *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅Me₅)]⁺ *cis*-9⁺.

Electrolysis of *trans*-7⁺ at an applied potential, E_{app} , of 0.6 V (vs. a Ag wire electrode) at –30 °C in CH₂Cl₂, resulted in the ν(CO) band at 1914 cm⁻¹ collapsing and a new band forming at 1998 cm⁻¹. Increases of ca. 13 cm⁻¹ and 8 cm⁻¹ were observed

for $\nu(\text{NO})$ and $\nu(\text{CNR})$ respectively; the $\nu(\text{CN})$ band decreased in energy by 48 cm^{-1} and became more intense. Thus, the shifts in all of the bands are consistent with oxidation at the *N*-bound *trans*- $\text{Mn}(\text{CO})_2$ centre, generating *trans*- $[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^{2+}$ *trans*- 7^{2+} (cf. the isolated salt *trans*- $7^{2+}2[\text{PF}_6]^-$, see above).

Increasing E_{app} to 1.45 V resulted in increases in energy for $\nu(\text{CO})$, $\nu(\text{NO})$ and $\nu(\text{CNR})$ of 16, 101 and 62 cm^{-1} respectively, this time consistent with oxidation at the *C*-bound manganese centre and the generation of *trans*- 7^{3+} . Lowering E_{app} to 0.6 V and then to 0.0 V regenerated *trans*- 7^{2+} and *trans*- 7^+ respectively, with the intensities of the corresponding IR bands greater than 85% of those observed in the forward process. Thus, the trication *trans*- 7^{3+} and the dication *trans*- 7^{2+} appear to be stable in CH_2Cl_2 at -30°C .

Electrolysis at 0.72 V of *trans*- 17^+ , the linkage isomer of *trans*- 7^+ , at -30°C in CH_2Cl_2 , resulted in a large increase in the energy of the carbonyl bands, while $\nu(\text{NO})$ and $\nu(\text{CNR})$ move to higher energy by only 8 and 12 cm^{-1} . Thus, oxidation at Mn_{oct} , as proposed on the basis of cyclic voltammetry, gave *trans*- $[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-CN})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^{2+}$ *trans*- 17^{2+} . Lowering E_{app} to 0.0 V regenerated *trans*- 17^+ , confirming that the dication *trans*- 17^{2+} is stable at -30°C (although not isolable at room temperature). By contrast, increasing E_{app} to 1.21 V to generate *trans*- 17^{3+} resulted in sample decomposition.

Cyclic voltammetry of *cis*- $[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{PPh}_3)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^+$ *cis*- 1^+ and *cis*- $[(\text{dppm})(\text{CO})_2\{(\text{PhO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{Me}_5)]^+$ *cis*- 9^+ indicated reversible one-electron oxidation at Mn_{oct} but chemical oxidation at room temperature led to sample decomposition. However, at -30°C IR spectroelectrochemistry of *cis*- 9^+ , at $E_{\text{app}} = 1.0\text{ V}$, led to an increase in energy for $\nu(\text{NO})$ and $\nu(\text{CNR})$ of 94 and 69 cm^{-1} , but only a small increase for one of the $\nu(\text{CO})$ bands. Thus, the formation of *cis*- 9^{2+} again confirmed the assignment made on the basis of cyclic voltammetry. Lowering E_{app} to 0.0 V regenerated *cis*- 9^+ , with the intensities of the bands greater than 90% of those observed in the forward process, indicating stability of the dication *cis*- 9^{2+} in CH_2Cl_2 at -30°C .

The electronic spectra of the mixed valence dications *trans*- 1^{2+} – 10^{2+}

The electronic spectra of *trans*- 1^+ – 10^+ and the mononuclear cyanomanganese(I) precursors $[\text{Mn}(\text{CN})\text{L}(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]$ and *trans*- $[\text{MnBrL}(\text{CO})_2(\text{dppm})]$ show no absorptions above 400 nm. However, the dications *trans*- 1^{2+} – 10^{2+} show two distinct absorptions in CH_2Cl_2 , one in the visible or near-IR region and a second weaker band at higher energy (Table 7), e.g. *trans*- 3^{2+} shows absorptions at 504 nm ($\epsilon = 1061\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) and 972 nm ($\epsilon = 2633\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$). The lower energy bands are assigned to optically induced metal–metal charge-transfer (MMCT) from Mn(I) to Mn(II) centre *via* the cyanide bridge as they are solvatochromic (see below); the higher energy bands are essentially unaffected by the solvent.

A comparison of the electronic spectral data for *trans*- 1^{2+} – 10^{2+} shows that the energy of the MMCT band varies with the ligands at the two manganese centres. Fig. 10 shows the spectra of *trans*- $[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]^{2+}$ ($\text{R} = \text{H}$, *trans*- 7^{2+} ; $\text{R} = \text{Me}$, *trans*- 10^{2+}). The higher

Table 7 Electronic spectroscopic data for *trans*- $[(\text{dppm})(\text{CO})_2\text{LMn}(\mu\text{-NC})\text{MnL}'(\text{NO})(\eta^5\text{-C}_5\text{R}_4\text{Me})]^{2+}$ in CH_2Cl_2

Complex	L	L'	R	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$)
<i>trans</i> - 1^{2+}	P(OPh) ₃	PPh ₃	H	501 (990), 1100 (3350)
<i>trans</i> - 2^{2+}	P(OPh) ₃	P(OPh) ₃	H	503 (— ^a), 852 (2930)
<i>trans</i> - 3^{2+}	P(OPh) ₃	CNBu ^t	H	504 (1061), 972 (2633)
<i>trans</i> - 4^{2+}	P(OPh) ₃	CNXyl	H	504 (1078), 948 (2096)
<i>trans</i> - 5^{2+}	P(OEt) ₃	PPh ₃	H	500 (1135), 1004 (2523)
<i>trans</i> - 6^{2+}	P(OEt) ₃	P(OPh) ₃	H	464 (— ^a), 811 (2909)
<i>trans</i> - 7^{2+}	P(OEt) ₃	CNBu ^t	H	488 (1490), 877 (2685)
<i>trans</i> - 8^{2+}	P(OEt) ₃	CNXyl	H	500 (1148), 856 (1409)
<i>trans</i> - 9^{2+}	P(OPh) ₃	CNBu ^t	Me	504 (1236), 1180 (2955)
<i>trans</i> - 10^{2+}	P(OEt) ₃	CNBu ^t	Me	499 (1310), 1021 (3460)

^a Not determined due to ill-defined bands.

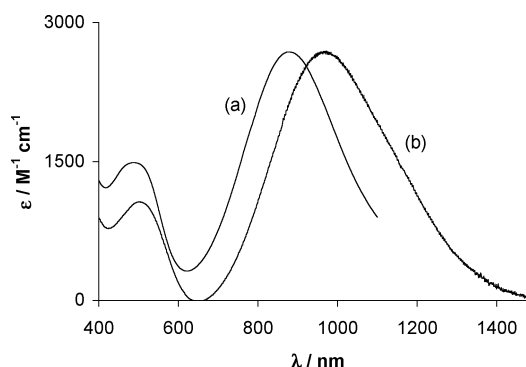


Fig. 10 The electronic spectra of (a) *trans*- $[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^{2+}$ *trans*- 7^{2+} and (b) *trans*- $[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}(\mu\text{-NC})\text{Mn}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{Me}_5)]^{2+}$ *trans*- 10^{2+} in CH_2Cl_2 .

value of λ_{max} (1021 nm) for *trans*- 10^{2+} indicates relatively facile Mn(I) to Mn(II) MMCT compared with *trans*- 7^{2+} (877 nm).

The electronic spectra of the air-sensitive dications *trans*- 7^{2+} and *trans*- 17^{2+} were further studied by *in situ* spectroelectrochemical oxidation of the corresponding monocations *trans*- 7^+ and *trans*- 17^+ in CH_2Cl_2 at -30°C . In addition, this technique was used to monitor the second oxidation step, to the trications *trans*- $[(\text{dppm})(\text{CO})_2\{(\text{EtO})_3\text{P}\}\text{Mn}^{\text{II}}(\mu\text{-XY})\text{Mn}^{\text{II}}(\text{CNBu}^t)(\text{NO})(\eta^5\text{-C}_5\text{H}_4\text{Me})]^{3+}$ ($\text{XY} = \text{NC}$, *trans*- 7^{3+} ; $\text{XY} = \text{CN}$, *trans*- 17^{3+}). As E_{app} is increased from 0.0 to 0.6 V (vs. a Ag/AgCl electrode) the dication *trans*- 7^{2+} is generated from *trans*- 7^+ . The octahedral Mn(I) site is oxidised to Mn(II) and the weak absorption at 370 nm loses intensity. More obviously, a MMCT band appears at ca. 890 nm, as observed for the isolated dication *trans*- 7^{2+} . A second, less intense band appears at 493 nm. Isosbestic points at 317 and 412 nm suggest that *trans*- 7^+ and *trans*- 7^{2+} are the only absorbing species in solution.

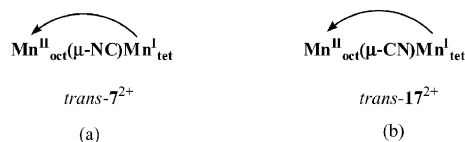
Increasing E_{app} past the E^{O} value for the second oxidation step (1.36 V) causes the MMCT band to collapse as the intermetallic interaction is switched off. Lowering E_{app} to 0.6 V regenerates *trans*- 7^{2+} with the intensity of the corresponding MMCT band greater than 90% of that observed in the forward process. As shown by IR spectroelectrochemistry, *trans*- 7^{3+} and *trans*- 7^{2+} appear to be stable in CH_2Cl_2 at -30°C .

The linkage isomer of *trans*- 7^+ , i.e. *trans*- 17^+ , shows no significant absorptions above 220 nm. However, as E_{app} is increased

from 0.0 to 0.7 V, and the dication *trans*-**17**²⁺ is generated, Mn_{oct} is oxidised and a broad MMCT band appears at 1354 nm (with a shoulder towards lower wavelength). A second band, significantly weaker, is observed at 537 nm; two isosbestic points are observed at 305 and 408 nm. The lower energy of the MMCT band for *trans*-**17**²⁺, cf. that of *trans*-**7**²⁺, indicates that electron transfer from Mn(I) to Mn(II) in Mn^{II}_{oct}–CN–Mn^I_{tet} (in *trans*-**17**²⁺) is easier than from Mn(I) to Mn(II) in Mn^{II}_{oct}–NC–Mn^I_{tet} (of *trans*-**7**²⁺).

Although the effect of the bridging ligand on the extent of intermetallic interaction in mixed-valence complexes has been frequently studied, no such study has been made with respect to cyanide–isocyanide isomerism in dinuclear complexes. Indirect effects of the cyanide orientation have been recorded during the spontaneous isomerisation of [(pc)Fe{(μ-CN)Fe(dppe)(η⁵-C₅H₅)₂}]⁺ (pc = phthalocyaninate) to [(pc)Fe{(μ-NC)Fe(dppe)(η⁵-C₅H₅)₂}]⁺,¹⁴ in which the near-IR spectrum shows a change in the wavelength of the MMCT band from 1293 to 2150 nm. Therefore, the effect of cyanide orientation on the energy of the MMCT band has been studied in *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn^{II}(μ-XY)Mn^I(CNBu^t)(NO)(η⁵-C₅H₄Me)]²⁺ (XY = NC, *trans*-**7**²⁺; XY = CN, *trans*-**17**²⁺) as a representative example.

As shown by CV and IR spectroelectrochemistry, the first oxidation of *trans*-**7**⁺ and *trans*-**17**⁺ occurs at Mn_{oct}. Therefore, MMCT in the mixed-valence species *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn^{II}(μ-XY)Mn^I(CNBu^t)(NO)(η⁵-C₅H₄Me)]²⁺ will take place in the same direction, from Mn_{tet} to Mn_{oct}, but across a bridging cyanide in two different orientations, i.e. from Mn(I) to CN to Mn(II) in *trans*-**7**²⁺ and from Mn(I) to NC to Mn(II) in *trans*-**17**²⁺ (Scheme 5).



Scheme 5 The direction of MMCT in the mixed-valence complexes (a) *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)]²⁺ *trans*-**7**²⁺ and (b) *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-CN)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)]²⁺ *trans*-**17**²⁺.

Hush theory¹⁵ relates the energy of the MMCT band, E_{op} , to the ground state free energy difference, ΔG° , and the reorganisation energy, χ , according to eqn (1). In addition, $\Delta G^\circ = -nF\Delta E^\circ$, where ΔE° is the difference between the potentials for the two redox processes.

$$E_{\text{op}} = \Delta G^\circ + \chi = -nF\Delta E^\circ \quad (1)$$

A plot of the energy of the MMCT band, E_{op} in cm⁻¹, against ΔE° for *trans*-**1**²⁺–**10**²⁺ and *trans*-**17**²⁺ (obtained by electronic

spectroelectrochemistry) (Fig. 11) is approximately linear ($R^2 = 0.86$); as ΔE° decreases, the Mn(I) to Mn(II) electron transfer becomes generally more favourable and thus the MMCT band energy decreases. Such a relationship has also been found for the trinuclear complexes [(pc)Fe{(μ-XY)Ru(PPh₃)₂(η⁵-C₅H₅)₂}] and [(pc)Fe{(μ-XY)Fe(dppe)(η⁵-C₅H₅)₂}] (XY = CN or NC).¹⁴

Although the MMCT band for *trans*-[(dppm)(CO)₂LMn(μ-NC)MnL'(NO)(η⁵-C₅R₄Me)]²⁺ *trans*-**1**²⁺–**10**²⁺ is solvatochromic, it is rather weakly so. (Data for *trans*-**2**²⁺ in four solvents are given in Table 8; those for *trans*-**4**²⁺, *trans*-**6**²⁺–**8**²⁺ and *trans*-**10**²⁺ are given as ESI†.) This behaviour contrasts markedly with the pronounced solvatochromism exhibited by [X₃Fe^{III}–(μ-NC)Mn^I(CO)₂L(dppm)-*trans*)]¹⁶ and [(H₃N)₅Ru^{III}(μ-NC)Mn^I(CO)₂L(dppm)-*trans*)]³⁺.¹³ For example, *trans*-[(dppm)(CO)₂{(PhO)₃P}Mn^{II}(μ-NC)Mn^I{P(OPh)₃}(NO)(η⁵-C₅H₄Me)]²⁺ *trans*-**2**²⁺ shows MMCT bands at 848, 852 and 870 nm in MeCN, CH₂Cl₂ and thf respectively, an overall shift of only ca. 20 nm. By contrast, the MMCT band of *trans*-[(H₃N)₅Ru^{III}(μ-NC)Mn^I(CO)₂{P(OPh)₃}(dppm)-*trans*)]³⁺ occurs at 963, 1134 and 946 nm in the same solvents, the overall difference of ca. 190 nm resulting from variable hydrogen bonding of the solvent with the Ru^{III}(NH₃)₅ group. Such hydrogen bonding is likely to be much less significant for *trans*-[(dppm)(CO)₂LMn(μ-NC)MnL'(NO)(η⁵-C₅R₄Me)]²⁺.

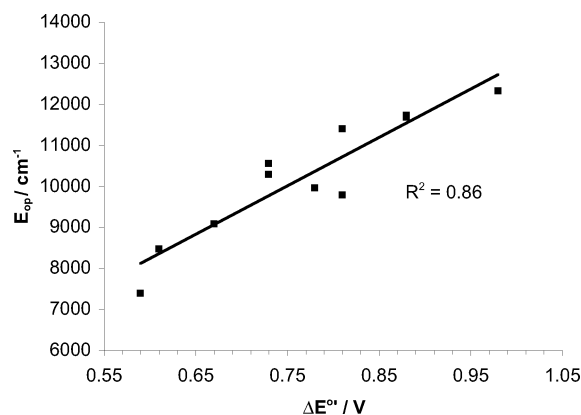


Fig. 11 Plot of ΔE° vs. E_{op} for *trans*-**1**²⁺–**10**²⁺ and *trans*-**17**²⁺.

For mixed-valence species the magnitude of the intermetallic interaction can be expressed in terms of the coupling parameter J , in units of cm⁻¹, or the degree of electron delocalisation, a^2 [eqn (2) and (3)].

$$J = 2.05 \times 10^{-2} [\varepsilon \times \nu_{1/2} \times E]^{1/2} \times r^{-1} \text{ (cm}^{-1}\text{)} \quad (2)$$

$$a^2 = 4.24 \times 10^{-4} [(\varepsilon \times \nu_{1/2}) / (E \times r^2)] \text{ (%) } \quad (3)$$

Table 8 Metal–metal charge-transfer data for *trans*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn{P(OPh)₃}(NO)(η⁵-C₅H₄Me)]²⁺ *trans*-**2**²⁺

Solvent	DN ^a	λ_{max} / nm	E / cm ⁻¹	ε / dm ³ mol ⁻¹ cm ⁻¹	$\nu_{1/2}$ / cm ⁻¹	J / cm ⁻¹	a^2 (%)
CH ₂ Cl ₂	1.0	852	11737	2930	3530	1403	1.43
MeCN	14.1	848	11792	2550	3501	1302	1.22
acetone	17.0	855	11692	2834	3650	1395	1.42
thf	20.0	870	11494	2725	3642	1355	1.39

^a DN = Gutmann donor number.

Here, ϵ is the extinction coefficient for the MMCT band in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, $\nu_{1/2}$ is the width of the band at half-height in cm^{-1} , E is the energy of the band maximum in cm^{-1} and r is the metal-metal separation in Å.

Values of J and a^2 for *trans*-**2**²⁺ are given in Table 8, and for *trans*-**4**²⁺, *trans*-**6**²⁺-**8**²⁺ and *trans*-**10**²⁺ in the ESI.† (The value of $r = 5.110$ Å, the metal-metal separation along the Mn–C–N–Mn linkage, was calculated from the X-ray structure of *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)]⁺ *trans*-**7**⁺. The through space distance is insignificantly different, at 5.096 Å.)

The values of J for *trans*-**1**²⁺–**10**²⁺ in CH₂Cl₂ vary only modestly, ranging from 1513 cm^{-1} for *trans*-**6**²⁺ to 967 cm^{-1} for *trans*-**8**²⁺, and are generally smaller than those of other mixed-valence complexes containing cyanomanganese ligands, such as [(H₃N)₅Ru(μ-NC)MnL'(NO)(η⁵-C₅H₄Me)]³⁺ {L' = PPh₃ or P(OPh)₃}¹³ or [X₃Fe(μ-NC)MnL_x] {L_x = *cis*- or *trans*-(CO)₂{P(OR)₃}(dppm); R = OPh or OEt}.¹⁶ The computed values of a^2 , the degree of delocalisation, are consistent with the assignment of *trans*-**1**²⁺–**10**²⁺ as Class II mixed-valence complexes.

Conclusions

The reaction of cyanomanganese complexes [Mn(CN)L'(NO)(η⁵-C₅R₄Me)] with *cis*- or *trans*-[MnBrL(CO)₂(dppm)] in the presence of Ti[PF₆]₃ gives homobinuclear cyanomanganese(i) species of the general formula *cis*- or *trans*-[(dppm)(CO)₂LMn(μ-NC)MnL'(NO)(η⁵-C₅R₄Me)]⁺ **1**⁺–**10**⁺. The linkage isomers of **1**⁺–**10**⁺, namely *cis*- or *trans*-[(dppm)(CO)₂LMn(μ-CN)-MnL'(NO)(η⁵-C₅R₄Me)]⁺ **11**⁺–**20**⁺, were synthesised by reacting the cyanomanganese ligands *cis*- or *trans*-[Mn(CN)L(CO)₂(dppm)] with [MnIL'(NO)(η⁵-C₅R₄Me)] in the presence of Ti[PF₆]₃.

The linkage isomers *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)]⁺ *trans*-**7**⁺ and *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-CN)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)]⁺ *trans*-**17**⁺ are isostructural but *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn{P(OPh)₃}(NO)(η⁵-C₅H₄Me)]⁺ *cis*-**2**⁺ and *cis*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-CN)Mn{P(OPh)₃}(NO)(η⁵-C₅H₄Me)]⁺ *cis*-**12**⁺ differ by coordination of two different optical isomers of the *pseudo*-tetrahedral unit.

The cations *cis*- and *trans*-**1**⁺–**20**⁺ undergo sequential oxidation of the two Mn(i) centres to Mn(ii); the redox-induced isomerisation observed for units containing the *cis*-Mn(CO)₂ fragment allows assignment of the order of oxidation of the *cis* isomers. This order may be controlled by systematic variation of the ligands L and L', the substituents on the cyclopentadienyl ring and the μ-CN orientation.

One-electron oxidation of *trans*-[(dppm)(CO)₂LMnⁱ(μ-NC)MnⁱL'(NO)(η⁵-C₅R₄Me)]⁺ *trans*-**1**⁺–**10**⁺ with [NO][PF₆]₃ in CH₂Cl₂ forms the dications *trans*-**1**²⁺–**10**²⁺ which are also obtained by oxidising *cis*-[(dppm)(CO)₂LMnⁱ(μ-NC)MnⁱL'(NO)(η⁵-C₅R₄Me)]⁺ *cis*-**1**⁺–**10**⁺ by *cis*–*trans* isomerisation at the octahedral Mn(CO)₂ site.

The dications show weakly solvatochromic MMCT bands consistent with Class II mixed-valency. The energy of these bands is affected by the orientation of the cyanide bridge such that electron transfer from Mn(i) to Mn(ii) through the unit Mnⁱⁱ(μ-NC)Mnⁱ in *trans*-[(dppm)(CO)₂{(EtO)₃P}Mnⁱⁱ(μ-NC)Mnⁱ-

(CNBu^t)(NO)(η⁵-C₅H₄Me)]²⁺ *trans*-**7**²⁺ occurs at higher energy than through the Mnⁱⁱ(μ-CN)Mnⁱ in the linkage isomer *trans*-[(dppm)(CO)₂{(EtO)₃P}Mnⁱⁱ(μ-CN)Mnⁱ(CNBu^t)(NO)(η⁵-C₅H₄Me)]²⁺ *trans*-**17**²⁺.

Experimental

The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry nitrogen using dried and deoxygenated solvents purified either by distillation or by using Anhydrous Engineering double alumina or alumina–copper catalyst drying columns. Reactions were monitored by IR spectroscopy where necessary. Unless stated otherwise, complexes were purified using a mixture of two solvents. The impure solid was dissolved in the more polar solvent, the resulting solution was filtered and then treated with the second solvent, and the mixture was reduced in volume *in vacuo* to induce precipitation. Unless otherwise stated, complexes are stable under nitrogen and dissolve in polar solvents such as CH₂Cl₂, thf and acetone to give moderately air-stable solutions.

The compounds *trans*- and *cis*-[Mn(CN)(CO)₂L(dppm)] {L = P(OEt)₃¹ and P(OPh)₃}¹⁷ and [MnBr(CO)₂L(dppm)] {L = P(OEt)₃¹ and P(OPh)₃}¹⁸ [Mn(CO)(PPh₃)(NO)(η⁵-C₅H₄Me)][PF₆]₃¹⁹ [Mn(CN)(PR₃)(NO)(η⁵-C₅H₄Me)] (R = Ph and OPh)^{20,21} [Fe(η⁵-C₅H₅)₂][PF₆]₂²² and [Fe(η⁵-C₅H₅)(η⁵-C₅H₄COMe)][PF₆]₂²² were prepared by published methods. The compounds [NO][PF₆]₃, CNXyl and CNBu^t were purchased from Aldrich and Ti[PF₆]₃ was purchased from Strem Chemicals.

IR spectra were recorded on a Nicolet 5ZDX FT spectrometer. Electrochemical studies were carried out using an EG&G Model 273A potentiostat linked to a computer using EG&G Model 270 Research Electrochemistry software in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire and the working electrode a platinum disc (1.6 mm diameter). The reference was an aqueous saturated calomel electrode separated from the test solution by a fine porosity frit and an agar bridge saturated with KCl. Solutions were 5.0 × 10^{−4} or 1.0 × 10^{−3} mol dm^{−3} in the test compound and 0.1 mol dm^{−3} in [NBu₄]⁺[PF₆][−] as the supporting electrolyte with CH₂Cl₂ as the solvent. Under these conditions, E° for the one-electron oxidation of [Fe(η⁵-C₅Me₅)₂], added to the test solutions as an internal calibrant, is −0.08 V. UV-visible spectra were recorded on a Perkin Elmer Lambda 2 spectrometer using 1.0 cm path length quartz cells. UV-visible-near-IR spectra were recorded on a Perkin Elmer Lambda 19 spectrometer using 0.1 cm path length quartz cells. UV-visible-near-IR spectroelectrochemical measurements were made using an EG&G model 273A potentiostat in conjunction with a three-electrode system fitted to the Perkin Elmer Lambda 19 spectrometer. IR spectroelectrochemical measurements were made in conjunction with a three-electrode system fitted to a Bruker IFS25 Spectrometer.

Microanalyses were carried out by the staff of the Microanalysis Service of the School of Chemistry, University of Bristol.

Syntheses

cis-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn(PPh₃)(NO)(η⁵-C₅H₄Me)][PF₆]₃ *cis*-**1**⁺[PF₆]₃[−]. To a stirred solution of [Mn(CN)(PPh₃)(NO)(η⁵-C₅H₄Me)] (67 mg, 0.15 mmol) and *cis*-[MnBr(CO)₂{P(OPh)₃}(dppm)] (130 mg, 0.15 mmol) in CH₂Cl₂

(20 cm³) was added Ti[PF₆] (54 mg, 0.15 mmol). After 24 h the orange solution was filtered through Celite and evaporated to dryness *in vacuo*. After washing the product with toluene (2 × 10 cm³), the orange residue was purified using CH₂Cl₂–*n*-hexane to give an orange crystalline solid, yield 129 mg (63%).

The complexes *cis*-2⁺[PF₆][−]–*cis*-8⁺[PF₆][−] were prepared similarly, although the reaction times varied from 24 h to 72 h. Complexes *trans*-1⁺[PF₆][−]–*trans*-6⁺[PF₆][−], *trans*-9⁺[PF₆][−] and *trans*-10⁺[PF₆][−] were prepared similarly by using *trans*-[MnBr(CO)₂{P(OR)₃}(dppm)].

cis-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅Me₅)] [PF₆][−] *cis*-9⁺[PF₆][−]. To a stirred solution of [Mn(CN)(CNBu^t)(NO)(η⁵-C₅Me₅)] (26 mg, 0.08 mmol) and *cis*-[MnBr(CO)₂{P(OPh)₃}(dppm)] (70 mg, 0.08 mmol) in CH₂Cl₂ (15 cm³) was added Ti[PF₆] (31 mg, 0.09 mmol). After 24 h the orange solution was filtered through Celite and the volume of the solution reduced to *ca.* 5 cm³. After adding *n*-hexane (5 cm³) the volume of the solution was reduced *in vacuo* to leave an orange solid, yield 72 mg (72%).

The complex *cis*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅Me₅)] [PF₆][−] *cis*-10⁺[PF₆][−] was prepared similarly as a red solid.

trans-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNXyl)(NO)(η⁵-C₅H₄Me)] [PF₆][−] *trans*-8⁺[PF₆][−]. To a stirred solution of *cis*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNXyl)(NO)(η⁵-C₅H₄Me)] [PF₆][−] *cis*-8⁺[PF₆][−] (100 mg, 0.09 mmol) in CH₂Cl₂ (15 cm³) was added [NO][PF₆][−] (17 mg, 0.10 mmol). After 15 min, N₂H₄·xH₂O (0.3 cm³) was added to the purple solution. The resulting orange solution was stirred for 15 min in the presence of MgSO₄ and then filtered through Celite. Addition of *n*-hexane (15 cm³) induced precipitation of a solid which was purified using CH₂Cl₂–*n*-hexane to give a crystalline orange solid, yield 54 mg (54%).

The complex *trans*-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-NC)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)] [PF₆][−] *trans*-7⁺[PF₆][−] was prepared similarly as a yellow solid.

cis-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-CN)Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)] [PF₆][−] *cis*-17⁺[PF₆][−]. To a stirred solution of *cis*-[Mn(CN)(CO)₂{P(OEt)₃}(dppm)] (200 mg, 0.29 mmol) and [Mn(CNBu^t)(NO)(η⁵-C₅H₄Me)] (109 mg, 0.29 mmol) in CH₂Cl₂ (15 cm³) was added Ti[PF₆] (112 mg, 0.32 mmol). After 50 min the red solution was filtered through Celite and the volume of the filtrate reduced to *ca.* 5 cm³. After adding *n*-hexane (5 cm³) the volume of the solution was reduced *in vacuo* to induce precipitation of a pink solid which was thoroughly washed with diethyl ether (3 × 10 cm³), yield 220 mg (70%).

The complexes *cis*- or *trans*-11⁺[PF₆][−]–18⁺[PF₆][−], except *cis*-15⁺[PF₆][−], were prepared similarly with the following modifications: *trans*-17⁺[PF₆][−] and *trans*-18⁺[PF₆][−] were purified using CH₂Cl₂–*n*-hexane; the reaction time for *cis*-11⁺[PF₆][−] was 2 h.

cis-[(dppm)(CO)₂{(EtO)₃P}Mn(μ-CN)Mn(PPh₃)(NO)(η⁵-C₅H₄Me)] [PF₆][−] *cis*-15⁺[PF₆][−]. To a stirred solution of *cis*-[Mn(CN)(CO)₂{P(OEt)₃}(dppm)] (150 mg, 0.22 mmol) and [Mn(CO)(PPh₃)(NO)(η⁵-C₅H₄Me)] (130 mg, 0.22 mmol) in CH₂Cl₂ (25 cm³) was added Me₃NO (16 mg, 0.22 mmol). After 45 min the green solution was filtered through Celite and the

Table 9 Crystal and refinement data for cyanide-bridged manganese complexes

Compound	Formula	<i>M</i>	Crystal system	Space group (no.)	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	<i>a</i> /°	<i>b</i> /°	<i>γ</i> /°	<i>U</i> /Å ³	<i>Z</i>	μ/mm ^{−1}	Reflections collected	Independent reflections (<i>R</i> _{int})	Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ , <i>wR</i> ₂
<i>trans</i> -7 ⁺ [PF ₆] [−] ·Me ₃ CO	C ₄₈ H ₅₉ F ₆ Mn ₂ N ₃ O ₇ P ₄	1137.74	Triclinic	<i>P</i> 1 (2)	11.077(4)	13.608(4)	19.195(3)	103.00(3)	100.75(3)	97.00(2)	2728.9(14)	2	0.650	23701	9579 (0.0225)	0.0486, 0.1230	
<i>trans</i> -17 ⁺ [PF ₆] [−] ·Me ₃ CO	C ₄₈ H ₅₉ F ₆ Mn ₂ N ₃ O ₇ P ₄	1137.74	Triclinic	<i>P</i> 1 (2)	11.091(15)	13.638(2)	19.076(4)	102.981(2)	100.441(2)	97.525(1)	2720.5(8)	2	0.652	28916	12399 (0.0381)	0.0496, 0.1210	
<i>cis</i> -12 ⁺ [PF ₆] [−]	C ₇₀ H ₅₉ F ₆ Mn ₂ N ₃ O ₉ P ₅	1450.92	Orthorhombic	<i>P</i> ca2(1) (29)	34.821(3)	11.161 (1)	37.628(3)	90	90	90	14624(2)	8	0.524	89374	31246 (0.1414)	0.0707, 0.1182	
<i>cis</i> -2 ⁺ [PF ₆] [−]	C ₇₀ H ₅₉ F ₆ Mn ₂ N ₃ O ₉ P ₅	1450.92	Monoclinic	<i>P</i> 2(1)/ <i>c</i> (14)	18.98(3)	11.234(17)	31.52(4)	90	94.01(15)	90	6703(15)	4	0.571	35220	11793 (0.6332)	0.1160, 0.1801	
<i>cis</i> -8 ⁺ [PF ₆] [−] ·1.5CH ₂ Cl ₂	C _{90.5} H ₆₃ Cl ₃ F ₆ Mn ₂ N ₃ O ₆ P ₄	1255.09	Triclinic	<i>P</i> 1 (2)	9.9087(6)	12.8321(8)	22.7982(14)	86.824(1)	86.597(1)	79.134(1)	2838.9(3)	2	0.767	24825	9978 (0.0563)	0.0571, 0.1368	
<i>cis</i> -9 ⁺ [PF ₆] [−] ·CH ₂ Cl ₂	C ₉₂ H ₆₃ Cl ₂ F ₆ Mn ₂ N ₃ O ₆ P ₄	1364.81	Triclinic	<i>P</i> 1 (2)	13.651(2)	14.574(3)	18.143(3)	68.629(3)	79.220(3)	71.517(3)	3177.5(9)	2	0.652	27758	11185 (0.1009)	0.0820, 0.1866	

volume reduced *in vacuo* to ca. 15 cm³. After adding toluene (30 cm³) the volume of the solution was reduced *in vacuo* to induce precipitation of a green solid which was thoroughly washed with *n*-hexane (3 × 10 cm³), yield 122 mg (44%).

The complexes *cis*-19⁺[PF₆][−], *trans*-19⁺[PF₆][−], *cis*-20⁺[PF₆][−] and *trans*-20⁺[PF₆][−] were prepared similarly.

trans-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn(PPh₃)(NO)(η⁵-C₅H₄Me)][PF₆]₂ *trans*-1²⁺2[PF₆][−]. To a stirred solution of *trans*-[(dppm)(CO)₂{(PhO)₃P}Mn(μ-NC)Mn(PPh₃)(NO)(η⁵-C₅H₄Me)][PF₆] *trans*-1⁺[PF₆][−] (150 mg, 0.133 mmol) in CH₂Cl₂ (20 cm³) was added [NO][PF₆] (26 mg, 0.146 mmol). After 50 min the resulting purple solution was filtered through Celite, *n*-Hexane (20 cm³) was added and the volume of the solution was reduced *in vacuo* to induce precipitation of a purple solid which was washed with *n*-hexane–Et₂O (1 : 1) (20 cm³) and dried *in vacuo*, yield 93 mg (55%).

The complexes *trans*-2²⁺2[PF₆][−]–10²⁺2[PF₆][−] were prepared similarly as purple solids.

Crystal structure determinations of *cis*-2⁺[PF₆][−], *trans*-7⁺[PF₆][−]·Me₂CO, *cis*-8⁺[PF₆][−]·1.5CH₂Cl₂, *cis*-9⁺[PF₆][−]·CH₂Cl₂, *cis*-12⁺[PF₆][−] and *trans*-17⁺[PF₆][−]·Me₂CO

Crystals suitable for X-ray diffraction study were grown as follows: orange-red crystals of *cis*-2⁺[PF₆][−], *cis*-8⁺[PF₆][−]·1.5CH₂Cl₂, *cis*-9⁺[PF₆][−]·CH₂Cl₂ and *cis*-12⁺[PF₆][−], slow diffusion of *n*-hexane into a concentrated CH₂Cl₂ solution of the complex at −20 °C; orange-red crystals of *trans*-7⁺[PF₆][−]·Me₂CO and dark green crystals of *trans*-17⁺[PF₆][−]·Me₂CO, slow diffusion of diethyl ether into an acetone solution of the salt at −20 °C.

Crystals of *trans*-7⁺[PF₆][−] and *trans*-17⁺[PF₆][−] both contain one molecule of acetone per asymmetric unit, whilst that of *cis*-8⁺[PF₆][−] contains 1.5 equivalents of CH₂Cl₂ per asymmetric unit and that of *cis*-9⁺[PF₆][−] contains one molecule of CH₂Cl₂ per asymmetric unit. The Bu^t group of *trans*-7⁺ is rotationally disordered over two positions in an approximately 3 : 1 ratio, and two of the ethyl groups of the P(OEt)₃ ligand of *cis*-8⁺ are each disordered over two positions in a 1 : 1 ratio. The structure of *cis*-9⁺ contains two disordered phenyl rings belonging to the dppm ligand, and two disordered OPh groups on the P(OPh)₃ ligand. The orientation of the cyanide bridges in all structures was assigned on the basis of the best agreement for the thermal parameters and occupancy factors for the C and N atoms after refinement in two alternative models in which the C and N atoms were exchanged.

For *cis*-12⁺, the crystal also contained disordered solvent molecules which could not be resolved. This was modelled using the programme SQUEEZE,²³ which found the unit cell to contain four voids of 243 Å³, each containing 52 electrons, and four voids of 263 Å³ each containing 48 electrons. This is believed to be due to the presence of highly disordered CH₂Cl₂ molecules located within these voids.

Many of the details of the structure analyses are listed in Table 9. CCDC reference numbers 166635, 166636, 644601–644604.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b705975b

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