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Synthesis and Oxidation of Cationic Heterobinuclear Cyanide-Bridged Complexes of Manganese and Iron

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Several heterobinuclear cyanide-bridged cationic complexes of the type $[LnM_1-CN-M_2Ln]^+$, where LnM_1 and LnM_2 are the fragments $Fe(C_5H_5)(dppe)$ or *cis*- or *trans*-$Mn(CO)_2(L-L)L$ [L-L = dppm, dppe; L = $P(OPh)_3$, PEt_3; dppe = $Ph_2P(CH_2CH_2)PPh_2$; dppm = $Ph_2P(CH_2)PPh_2$], have been prepared as hexafluorophosphate salts by reacting the appropriate mononuclear complexes LnM_1-CN and $X-M_2Ln$ (X = Br, I) in the presence of $TlPF_6$ or $(NH_4)PF_6$ as halogen abstractors. The oxidation of these compounds have been studied electrochemically by cyclic voltammetry and chemically by infrared spectroscopy. The results indicated that the first oxidation of the cations affects the Fe or Mn fragment depending on its position relative to the cyanide bridge and the stereochemistry (cis or trans) of the dicarbonyl fragments. When the oxidation affects a *cis*-$Mn(CO)_2(L-L)L$ moiety, a very rapid isomerization to the trans form is observed and, in the case of the *cis*-dicarbonyl complexes $[(C_5H_5)(dppe)Fe-CN-Mn(CO)_2(L-L)L]^+$, the first oxidation takes place at Fe but is followed by electron transfer to Mn with concomitant isomerization to the *trans*-dicarbonyl form.

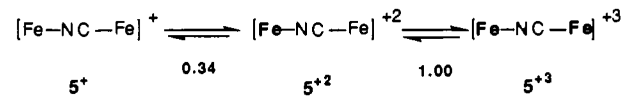
Introduction

The electrochemical behavior of binuclear ligand-bridged complexes may be useful for understanding inner-sphere redox reaction mechanisms and other electron-transfer processes.[1] In earlier studies,[2] we have found that a complex of the type $[L(L-L)(CO)_2Mn-CN-Mn(CO)_2(L-L)'L']^+$, where L-L is a diphosphine and L a phosphite or a phosphine, undergoes two one-electron oxidations and that the first one may occur on either side of the cyanide bridge depending on the ligands L-L and L and on the stereochemistry (cis or trans) of the carbonyl ligands. The oxidation of a *trans*-dicarbonyl fragment occurs at potentials much lower than those of the cis ones, and with retention of the stereochemistry, while the oxidation of a *cis*-dicarbonyl promotes a rapid isomerization to the trans form. In certain cases, however, the oxidation occurs at one *trans*-$Mn(CO)_2$ center but is followed by an intramolecular electron transfer that causes the isomerization (from cis to trans) of the fragment at the other side of the bridge. This happens when the *trans*-$Mn(CO)_2$ moiety that is oxidized first is electron poorer than the *trans*-$Mn(CO)_2$ fragment formed after the isomerization of the cis form at the other side of the bridge. The results also indicated that the effect is favored when the difference between the electron richness of these two *trans*-dicarbonyl moieties is large. Assuming that this might be a general process, we have now extended these studies to other cyanide-bridged binuclear complexes containing one $Mn(CO)_2(L-L)L$ group and a metal-ligand fragment of a different metal. We first chose the fragment $Fe(C_5H_5)(dppe)$, because, on the basis of the data in the literature,[3] it has an electron richness not very different from that of the manganese dicarbonyl fragments and is intermediate between those of a *cis*- and *trans*-$Mn(CO)_2(L-L)L$ group.

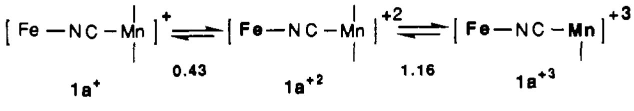
Results and Discussion

Synthesis and Characterization of the Binuclear Cyanide-Bridged Complexes. Similar to other binuclear manganese complexes with a bridging cyanide ligand reported earlier,[2,4] the hexafluorophosphate salts of the heterobinuclear cations $1a^+$ and $2a^+$ (Figure 1) were prepared from *trans*- or *cis*-$Mn(CN)(CO)_2(dppm)[P(OPh)_3]$ (dppm = $Ph_2PCH_2PPh_2$) and $FeI(C_5H_5)(dppe)$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in methylene chloride (CH_2Cl_2) in the presence of thallium(I) hexafluorophosphate. (*Caution*! Thallous salts are very poisonous[5] and should be handled with precautions.)

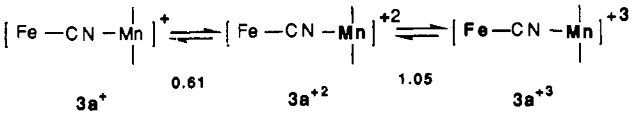
Scheme I



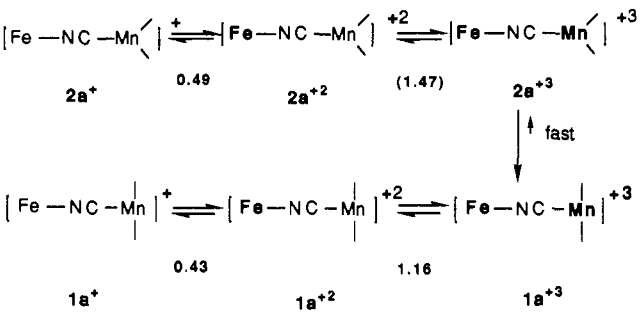
Scheme II



Scheme III



Scheme IV[a]



[a] The value in parentheses is a peak oxidation potential.

In the case of $2a^+$, the preparation using ammonium hexafluorophosphate in methanol was also successful. Their isomers $3a^+$ and $4a^+$ were also prepared as PF_6^- salts by the same method using $Fe(CN)(C_5H_5)(dppe)$ and *trans*- or *cis*-$MnBr(CO)_2(dppm)[P(OPh)_3]$. The hexafluorophosphate of the analogous cation $4b^+$, having the fragment *cis*-$Mn(CO)_2(dppe)(PEt_3)$, could also be obtained from the mononuclear complexes *cis*-$MnBr(CO)_2(dppe)(PEt_3)$ and $Fe(CN)(C_5H_5)(dppe)$, but our attempts to prepare the isomeric complex $2b^+$ by the same method resulted in a mixture of the desired product, the starting mononuclear cyanide dicarbonyl, some of the hexafluorophosphate of the diiron cation 5^+, and other products. On the other hand, the cation $3b^+$ (and its FeNCMn isomer) could not be generated by this procedure because the necessary complexes *trans*-$MnX(CO)_2(dppe)(PEt_3)$ isomerize very rapidly in solution to their *cis*-dicarbonyl forms. The hexafluorophosphate of the diiron cyan-

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(1) For example: Atwood, J. D. *Inorganic Reaction Mechanisms*; Brooks Cole: Monterey, CA, 1985; Chapter 8, p 287. Richardson, D. E. *Comments Inorg. Chem.* **1985**, *3*, 367. Burdett, J. K. *Comments Inorg. Chem.* **1981**, *1*, 85. Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 8.

(2) Carriedo, G. A.; Connelly, N. G.; Crespo, C.; Quarmby, I. C.; Riera, V. *J. Chem. Soc., Chem. Commun.* **1987**, 1806. Connelly, N. G.; Quarmby, I. C.; Worth, G. H.; Carriedo, G. A.; Crespo, C.; Riera, V. *J. Chem. Soc., Dalton Trans.* **1991**, 315.

(3) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1.

(4) Carriedo, G. A.; Crespo, M. C.; Riera, V.; Valin, M. L.; Moreiras, D.; Solans, X. *Inorg. Chim. Acta* **1986**, *121*, 191.

(5) Manzo, L.; Sabbioni, E. In *Handbook on Toxicity of Inorganic Compounds*; Seiler, H. G., Siger, H., Sigel, A., Eds.; Marcel Dekker: New York, 1988; p 677.

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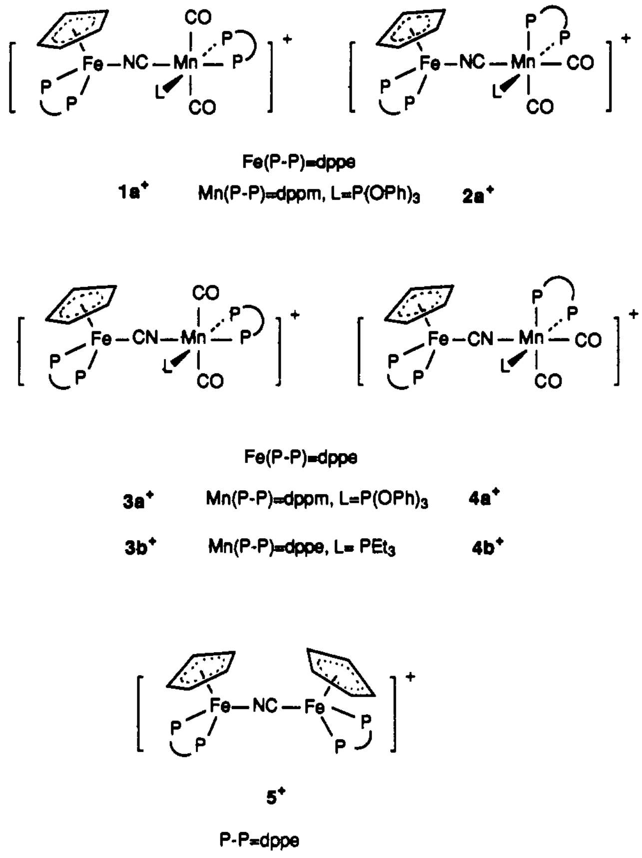
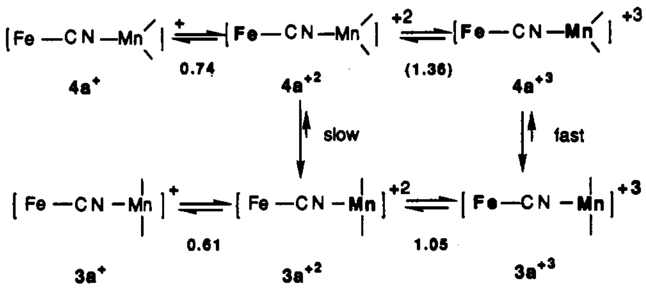


Figure 1.

Scheme V[a]



[a] The value in parentheses is a peak oxidation potential.

ide-bridged cation 5^+, which is analogous to the known diruthenium and iron–ruthenium complexes,[6] was prepared by reacting $Fe(CN)(C_5H_5)(dppe)$ and $FeI(C_5H_5)(dppe)$ with $(NH_4)PF_6$ in methanol or with $TlPF_6$ in CH_2Cl_2.

All new complexes were characterized by the analytical and spectroscopic data given in the Experimental Section. All compounds had the expected infrared (IR) absorptions at 840 cm^{-1} (PF_6^-) and ca. 1100 cm^{-1} (C_5H_5) and the heptet in the ^{31}P NMR spectra at −144 ppm (J(PF) = 710 Hz) corresponding to the PF_6^- anion. In some cases, the preparation of very pure samples required several recrystallizations.

Oxidation of the Binuclear Complexes. The oxidations of the cationic complexes 1^+ to 5^+ were explored by IR spectroscopy and cyclic voltammetry. Although a complete electrochemical study was not undertaken, the data obtained from these two techniques in combination with the information obtained earlier for related dimanganese cationic complexes were sufficient to characterize the oxidation processes and their consequences. The results are described in Schemes I–VI. In these schemes the bold metal atoms are the ones being oxidized. A summary of the half-wave potentials is given in Table I. In Table II are given some relevant IR data.

Scheme VI

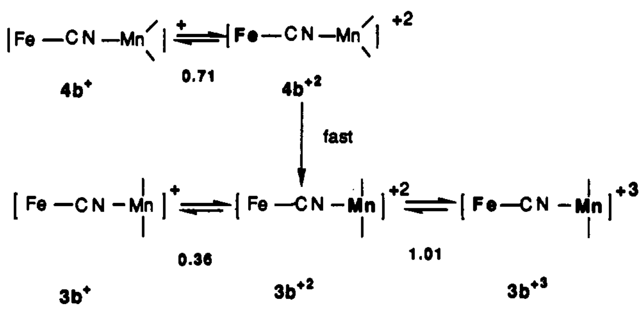


Table I. Cyclic Voltammetric Half-Wave Potentials (V)[a]

cation	$E_{1/2}(1)$	$E_{1/2}(2)$	cation	$E_{1/2}(1)$	$E_{1/2}(2)$
$1a^+$	0.43	1.16	$4a^+$	0.74	1.36[c]
$2a^+$	0.49	1.47[c]	$4b^+$	0.71[d]	
$3a^+$	0.61	1.05	5^+	0.34	1.00
$3b^+$	0.36[b]	1.01[b]			

[a] Measured in methylene chloride with reference to the SCE. [b] Measured in the CV of $4b^+$ and in that of (impure) $3b^{2+}$. [c] Irreversible; the potential given is the oxidation peak potential. [d] Estimated from $^1/_2\Delta E_p$ of the reversible second wave.

Table II. IR Data for the Binuclear Cations (cm^{-1})[a]

cation	ν(CN)	ν(CO)	
$1a^+$	2091 w	2015 vw	1933 s
$1a^{2+}$	2002 m	2047 m	1946 s
$2a^+$		1974 s	1918 s
$2a^{2+}$	2050 w	1974 s	1936 m
$3a^+$	2077 w	2017 vw	1926 s
$3a^{2+}$			2002 s
$3b^+$	2062 w		1890 s
$3b^{2+}$	2004 m		1972 s
$4a^+$	2062 m	1969 s	1904 s
$4a^{2+}$		1970 s	1921 s
$4b^+$	2053 m	1939 s	1871 s
5^+	2069 w		
5^{2+}	1994 s		

[a] Measured in CH_2Cl_2.

Oxidation of the Diiron Complex 5^+. The cyclic voltammograms (CV) of the PF_6^- salt of 5^+ in methylene chloride showed two diffusion-controlled ($i/v^{1/2}$ constant in the range 50–500 mV s^{-1}) chemically reversible (i_c/i_a = 1) oxidation waves (Table I). Considering the case of the dimanganese complex $[\{trans\text{-}Mn(CO)_2(dppm)[P(OPh)_3]\}_2(\mu\text{-}CN)]^+$ (6^+), we assumed that the first oxidation occurs at the electron richer N-bonded Fe moiety (see Scheme I).

The chemical oxidation using p-tolyldiazonium hexafluorophosphate or $[Fe(C_5H_5)_2]PF_6$ in methylene chloride gave the PF_6^- salt of the dication 5^{2+}, which could be isolated as a stable gray-green solid (the molar conductivity in a 5×10^{-4} M acetone solution was 189 Ω^{-1} cm^2 mol^{-1}, which corresponds to a 2:1 electrolyte[7]). The μ-CN stretching IR band of 5^{2+} was much more intense and 75 cm^{-1} lower in frequency than that of 5^+, while the CV's of both cationic complexes were identical. Thus, the latter cation was regenerated by reduction of 5^{2+} with aqueous hydrazine. (*Caution*! Hydrazine is a suspected cancer agent.) Further oxidation of the dication using $NOPF_6$ resulted in decomposition.

Oxidation of the Complexes Containing the Fragment *trans*-$Mn(CO)_2(dppm)[P(OPh)_3)]$, $1a^+$ and $3a^+$. The CV's of the hexafluorophosphate salts of these two cations showed two one-electron diffusion-controlled oxidation waves with i_c/i_a about 0.9.

In the case of $1a^+$ (Scheme II), the first oxidation ($E_{1/2}$ = 0.43 V), which gives the dication $1a^{2+}$, occurs at the Fe center, and

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(6) Baird, G. J.; Davis, S. G.; Moon, S. D.; Simpson, S. J.; Jones, R. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1479. Mishra, A.; Agarwala, U. C. *Inorg. Chim. Acta* **1990**, *170*, 209.

(7) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

the second one ($E_{1/2}$ = 1.16 V) occurs at the Mn center to give the trication. It should be noticed that if the first oxidation would have occurred at manganese, $E_{1/2}$ of the first wave would have been of the order of 0.85 V, which is the value corresponding to a C-bonded *trans*-Mn(CO)$_2$(dppm)[P(OPh)$_3$] fragment[2] in a Mn$_2$(μ-CN) complex. This interpretation is in accord with the result of the chemical oxidation of **1a**$^+$, which reacted with ferrocenium hexafluorophosphate in methylene chloride to generate the blue dication **1a**$^{2+}$, having in the IR spectrum one medium-intensity ν(CN) absorption and two carbonyl bands (Table II), one of medium intensity and one very strong. The latter (at 1946 cm^{-1}) is only 13 cm^{-1} higher in frequency than the strong band (asymmetric vibration mode) of the starting monocation. The oxidation of the manganese carbonyl center would have increased the frequency of the asymmetric carbonyl vibration by 70 cm^{-1}. It should be noted that in this case the two absorptions at higher frequencies might not correspond to pure ν(CN) or ν(CO) vibrations, because of the possibility of the coupling between the two vibrators, which could also explain the increase of the intensity of both bands. The hexafluorophosphate salt of the cation **1a**$^{2+}$ (which can be reconverted to **1a**$^+$ by reduction with aqueous hydrazine) is stable, but our attempts to obtain analytically pure samples were unsuccessful. On the other hand, the oxidation of **1a**$^+$ with 2 equiv of the stronger oxidant nitrosyl tetrafluoroborate, (NO)BF$_4$, resulted in decomposition with formation of the cationic mononuclear complex *trans*-{Mn(CN)(CO)$_2$(dppm)[P(OPh)$_3$]}$^+$, as well as the also known N-protonated dication,[8] as revealed by their ν(CN) absorptions.

Contrary to **1a**$^+$, its coordination isomer **3a**$^+$ is oxidized first at the manganese site and second at the Fe site to give the very unstable trication **3a**$^{3+}$ (Scheme III). This was evidenced by adding *p*-tolyldiazonium hexafluorophosphate to **3a**$^+$ in methylene chloride, which generated the red-violet dication **3a**$^{2+}$ (note that the dication **1a**$^{2+}$ is blue). The IR spectrum of **3a**$^{2+}$ showed a single strong absorption at 2002 cm^{-1}, which is 73 cm^{-1} higher in frequency than that of the starting monocation. This carbonyl stretching frequency (which is 1998 cm^{-1} if generated with nitrosyl tetrafluoroborate and shifts to 2002 cm^{-1} upon addition of excess PF$_6^-$ anion) is close to that of other N-bonded *trans*-Mn^{II}(CO)$_2$(dppm)[P(OPh)$_3$] fragments.[2] The observation that the first oxidation of **3a**$^+$ occurs at manganese is consistent with the $E_{1/2}$ value of the first oxidation wave in the CV (0.61 V). This value, which is very similar to that of the corresponding dimanganese cation **6**$^+$, is lower than the potential required to oxidize the C-bonded Fe(C$_5$H$_5$)(dppe) fragment, which, as shown below for **4a**$^+$ and **4b**$^+$, is about 0.7 V. The cation **3a**$^{2+}$ could be reduced back to **3a**$^+$ with aqueous hydrazine but could not be isolated as the pure hexafluorophosphate salt. In solution in the absence of excess oxidant, this dication decomposed with formation of the monocationic *cis*-dicarbonyl **4a**$^+$, which was recovered in ca. 50% yield. However, **3a**$^+$ could not be isomerized to **4a**$^+$ by catalytic amounts of an oxidant, which would have been reminiscent of the trans–cis isomerizations of mononuclear dicarbonyl manganese complexes.[9] We observed that adding small amounts of *p*-tolyldiazonium hexafluorophosphate to a solution of **3a**$^+$ resulted in the formation of some **3a**$^{2+}$ and subsequently of **4a**$^+$, but after some time the dication disappeared from the solution and the isomerization did not proceed further.

Oxidation of the Complexes Containing the Fragment *cis*-Mn(CO)$_2$(L-L)L, 2a$^+$, 4a$^+$, and 4b$^+$. The results obtained by cyclic voltammetry and IR spectroscopy for these complexes clearly indicated that in both cases the first oxidation occurs at the Fe center and the second at the manganese. This is reasonable because the $E_{1/2}$ values for the oxidations of the *cis*-Mn(CO)$_2$ fragments are ca. 1.2 V when they are bonded to the N-side of the CN bridge and even higher when they are C-bonded.[2]

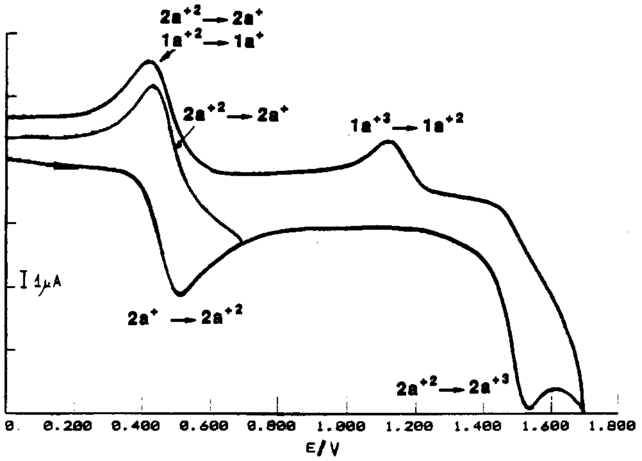

Figure 2. Cyclic voltammogram of **2a**$^+$ at 50 mV s^{-1}, from 0 to 1.7 V and from 0 to 0.7 V.

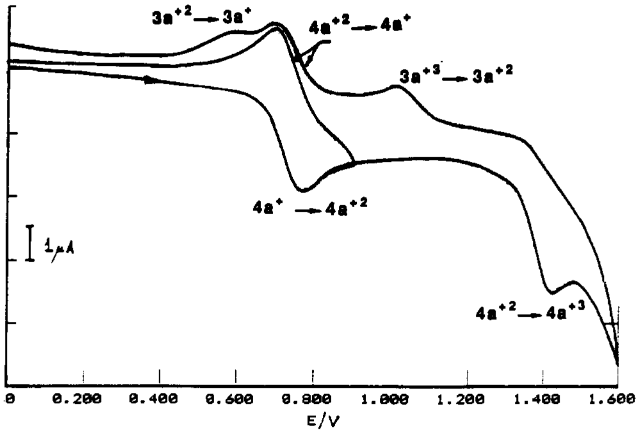

Figure 3. Cyclic voltammogram of **4a**$^+$ at 50 mV s^{-1}, from 0 to 1.6 V and from 0 to 0.9 V.

As might be expected from the previous studies,[2] the second oxidation of **2a**$^+$ and **4a**$^+$ is followed by a rapid isomerization to the *trans*-dicarbonyl forms (Schemes IV and V). Thus, the CV's of both complexes (Figures 2 and 3) showed two oxidation waves, the second of which was totally irreversible even at high scan rates, and two product waves, which corresponded to their isomers **1a**$^+$ and **3a**$^+$, respectively. In the case of **2a**$^+$, the reduction peak of the first wave is broad because of the proximity of the first oxidation potentials of **2a**$^+$ and the product of its second oxidation **1a**$^+$ (the relatively small intensity of the peaks of **1a**$^+$ in the CV of **2a**$^+$ may be due more to the instability of the trication than to the rate of the cis to trans isomerization process, which is fast). The product waves were not observed in the voltammograms when the potential ranges scanned were insufficient to produce the second oxidation (Figures 2 and 3).

The chemical oxidation of **2a**$^+$ with the *p*-tolyldiazonium ion in methylene chloride led to the blue dication **2a**$^{2+}$, which was isolated as the hexafluorophosphate salt. However, the IR spectrum in solution of the product always showed the presence of some **2a**$^+$. Further oxidation (2 equiv of nitrosyl tetrafluoroborate) followed by reduction with aqueous hydrazine led to **1a**$^+$ among some mononuclear decomposition products. The dication **2a**$^{2+}$ is stable (even for some time in solution under air) but reacts very quickly with chloride ions, liberating *cis*-Mn(CN)(CO)$_2$(dppm)[P(OPh)$_3$].

The chemical oxidation of **4a**$^+$ required nitrosyl tetrafluoroborate and gave initially the blue dication **4a**$^{2+}$ [ν(CO) absorptions at 1970 s, and 1921 s cm^{-1}]. However, this cation isomerized in solution to the violet (also unstable) isomer **3a**$^{2+}$ (see Scheme V). It seems that this isomerization is not fast enough to affect the shape of the CV of **4a**$^+$ to a significant extent. This isomerization is equivalent to that observed previously for dimanganese cyanide-bridged complexes[2] and likely occurs by an intramolecular

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(8) Connelly, N. G.; Hassard, K. A.; Dunne, B. J.; Orpen, A. G.; Raven, S. J.; Carriedo, G. A.; Riera, V. *J. Chem. Soc., Dalton Trans.* **1988**, 1623.

(9) Connelly, N. G.; Raven, S. J.; Carriedo, G. A.; Riera, V. *J. Chem. Soc., Chem. Commun.* **1986**, 992.

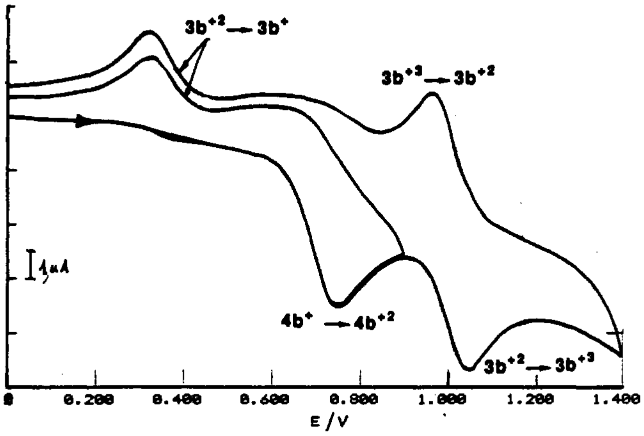
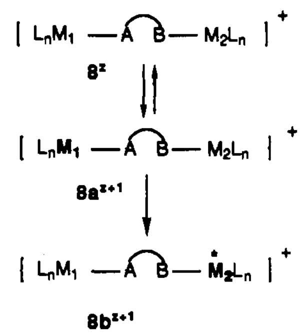


Figure 4. Cyclic voltammogram of **4b**$^+$ at 50 mV s^{-1}, from 0 to 1.4 V and from 0 to 0.9 V.

electron transfer from Mn to Fe through the CN bridge. Therefore, this process should be favored by electron richer $Mn(CO)_2(L\text{-}L)L$ fragments.[2] In accord with this expectation, the CV of the cation **4b**$^+$ (Figure 4), analogous to **4a**$^+$, but having PEt_3 and dppe ligands,[10] very closely resembled that of the trans-CN cis dimanganese complex[2] $\{[(PhO)_3P](dppm)(CO)_2Mn\text{-}CN\text{-}Mn(CO)_2(dppe)(PEt_3)\}^+$ (**7**$^+$) and can be interpreted by Scheme VI. Thus, the first oxidation (which occurs at Fe^{II}) is irreversible, and the second oxidation wave corresponds to the cation **3b**$^{2+}$ and not to **4b**$^{2+}$. Note that the $E_{1/2}$ values are consistent with the results discussed so far. Thus, the cations **4**$^+$ are both oxidized at Fe first at very close potentials, while the cations **3**$^+$ are both oxidized at manganese first, and therefore the change in the ligands is reflected in a change in the first oxidation potential, while the second remains almost constant.

The chemical oxidation of **4b**$^+$, which occurred not only with NO^+ but also with the *p*-tolyldiazonium ion (because of the isomerization of the dication), led to the hexafluorophosphate salt of **3b**$^{2+}$ as a brown solid, which was not obtained pure. The IR spectrum of this cation showed one strong carbonyl absorption at 1972 cm^{-1} and a medium-intensity cyanide band at 2004 cm^{-1} (58 cm^{-1} lower in frequency and more intense than that of **3b**$^+$). The reduction of **3b**$^{2+}$ with aqueous hydrazine led to the *trans*-dicarbonyl **3b**$^+$ (ν(CO) at 1890 cm^{-1}), but, as in the case of other mononuclear manganese(I) dicarbonyl derivatives, this cation isomerized in solution to the cis form **4b**$^+$ (see ref 12). In accord with Scheme VI, the CV of the hexafluorophosphate of **3b**$^{2+}$ in methylene chloride showed the waves with $E_{1/2}$ at 0.36 and 1.01 V that appeared as product waves in the CV of **4b**$^+$ (for the N-bonded $Mn(CO)_2(dppe)(PEt_3)$ fragment[2] $E_{1/2}$ is 0.38 V).

Scheme VII



The fact that the isomerization process in Scheme VI is much faster than the analogous one in Scheme V can be understood by considering that in the starting binuclear monocation **4b**$^+$ the two metal centers involved are closer in electron richness than those of **4a**$^+$. This effect makes more accessible the higher energy form of the corresponding mixed-valence dication (the one having the Mn center oxidized) which is very likely the form in which the isomerization takes place.

Conclusions. From the observations outlined above it could be inferred that the isomerization with electron transfer of the type described in Schemes V and VI might be a general one. Thus, given a generic binuclear complex **8**^{z} (Scheme VII), if the oxidation potential of the fragment M_1-A is lower than that of M_2-B, the complex will be oxidized at M_1 first, to give **8a**$^{z+1}$. However, if the fragment M_2 has another isomeric form, M_2*, and the oxidation potential of B-M_2* is lower than that of M_1-A, the isomerization of **8a**$^{z+1}$ to **8b**$^{z+1}$ could take place, provided that the A–B bridge allows some electron transfer and that the kinetic factors are favorable. Moreover, the process would be faster, the smaller the difference in electron richness (as measured by the redox potentials) of the M_1-A and M_2-B fragments.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere with standard Schlenk techniques. IR spectra were recorded on a Perkin-Elmer FT 1720-X spectrometer, and the frequencies are given in cm^{-1}. NMR spectra were recorded on a Bruker AC-300 instrument. Chemical shifts are given in δ relative to TMS (^{1}H) or 85% H_3PO_4 (^{31}P, proton decoupled), downfield positive to the reference; *J* values are given in hertz. Elemental analyses were performed with a Perkin-Elmer 240 microanalyzer. The discrepancies observed in some of the N data can be due to the small amount of this element present in the compounds. Molar conductivities (Λ) were measured in 5×10^{-4} M solution in acetone and are given in Ω^{-1} cm^2 mol^{-1}. The cyclic voltammetric measurements were made by using INELECSA PDC 1212 (Universidad de Sevilla, Spain) and PAR M273 instruments. The auxiliary electrode was a platinum wire, and the working electrode was a platinum bead. The reference was an aqueous saturated calomel electrode separated from the solution by a fine-porosity frit and an agar–agar bridge saturated with KCl. Solutions were 0.5×10^{-3} M in the complex and 0.1 M in $(NBu_4)PF_6$ as supporting electrolyte. Under the same experimental conditions, $E_{1/2}$ for the ferrocene–ferrocenium couple was 0.46 V with peak separations of about 80 mV.

The compounds *cis*- and *trans*-$MnX(CO)_2(dppm)[P(OPh)_3]$ (X = Br,[13] CN[14]) and *cis*-$MnX(CO)_2(dppe)(PEt_3)$[2] were prepared as previously reported. $Fe(CN)(dppe)(C_5H_5)$ and $FeI(dppe)(C_5H_5)$ were prepared as described in the literature.[15] The latter compound could also be synthesized by the method given below.

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(10) The use of dppe instead of dppm in the PEt_3 complex was necessary for synthetic reasons because the tricarbonyl *fac*-$MnBr(CO)_3(dppm)$ reacts with PEt_3 to give the expected dicarbonyl only in poor yield. However, as stated in ref 8, the effect on $E_{1/2}$ of replacing dppm by dppe in this dicarbonyl is minimal.

(11) This is assumed because the potential of the first oxidation of the trans-CN cis complex **7**$^+$, which occurs at the *trans*-$Mn(CO)_2(dppm)[P(OPh)_3]$ fragment, is 0.83 V, indicating that the potential for an N-bonded *cis*-$Mn(CO)_2(dppe)(PEt_3)$ fragment should be higher (although probably not much higher) than this value, and therefore higher than 0.71 V.

(12) It should be mentioned that the data obtained for the binuclear complexes **4b**$^+$ and **3b**$^+$ are not very different from those corresponding to the mononuclear compounds *cis*- and *trans*-$Mn(CN)(CO)_2(dppe)(PEt_3)$. The cis neutral complex (which is pale yellow) has IR absorptions (cm^{-1}) at 2091 w (CN) and 1937 s and 1874 s (CO). The oxidation with the diazonium salt in methylene chloride gave first a deep yellow cis cation with IR bands at 2018 w (CN) and 1946 (s) and 1890 (CO) (this intermediate was not characterized; the cis dicarbonyl oxidized form of the starting complex seems to be unlikely because it should be too unstable to be observed as indicated by the cyclic voltammetric data below) and after 30 min a pink trans cation with IR absorptions at 2108 w (CN) and 1971 s (CO), which after reduction gave the neutral complex *trans*-$Mn(CN)(CO)_2(dppe)(PEt_3)$ (a strong carbonyl absorption at 1890 cm^{-1}), which in solution isomerized to the starting cis form. The CV of this latter complex[2] showed an irreversible wave with $E_p(ox) = 0.77$ V and a product wave corresponding to the trans form at $E_{1/2} = 0.32$ V. The spectroscopic similarities in the ν(CO) region are, however, not surprising, especially in the cases of the *trans*-dicarbonyl forms, the frequencies of which are not very sensitive to the rest of the ligands.

(13) Bombin, F.; Carriedo, G. A.; Miguel, J. A.; Riera, V. *J. Chem. Soc., Dalton Trans.* **1981**, 2049.

(14) Carriedo, G. A.; Crespo, M. C.; Riera, V.; Sanchez, M. G.; Valin, M. L.; Moreiras, D.; Solans, X. *J. Organomet. Chem.* **1986**, *302*, 47. The procedure described in this reference can be improved by washing the reaction product with aqueous sodium thiosulfate before isolation, in order to remove AgCN coordinated to the desired manganese cyanide complex.

(15) Treichel, P. M.; Molzahn, D. C. *Synth. React. Met.-Org. Chem.* **1979**, *9*, 21.

Some of the reactions described below were difficult to follow by IR spectroscopy due to the proximity of the bands of the starting and final materials. On the other hand, because of the inhomogeneity of the reaction conditions, the simple scaling up of the synthetic procedure occasionally led to impure samples and fluctuations in the yields. Therefore checking the compounds by ^{31}P NMR spectroscopy is always necessary.

FeI(dppe)(C_5H_5). A water-cooled solution of FeI(CO)$_2$(C_5H_5) (0.37 g, 1.2 mmol) and dppe (0.49 g, 1.2 mmol) in toluene (20 mL) was irradiated with UV light for 4 h. The resulting mixture was filtered through Celite, and the solvent was evaporated to dryness under vacuum. The black residue was dissolved in CH_2Cl_2, and the solution was chromatographed on alumina, collecting a nearly black fraction. The resulting solution was concentrated and mixed with hexane, and the mixture was cooled in a freezer to give black crystals (0.35 g, 45%).

***trans*-{(C_5H_5)(dppe)Fe–NC–Mn(CO)$_2$(dppm)[P(OPh)$_3$]}PF$_6$.** To a solution of the complexes *trans*-Mn(CN)(CO)$_2$(dppm)[P(OPh)$_3$] (0.165 g, 0.193 mmol) and FeI(dppe)(C_5H_5) (0.129 g, 0.193 mmol) in methylene chloride (15 mL) was added solid TlPF$_6$ (0.1 g, 0.29 mmol), and the mixture was stirred at room temperature for 5 h, after which it was filtered through Celite and the solvent was evaporated to give a red solid, which was washed several times with diethyl ether and recrystallized from methylene chloride–diethyl ether. Yield: 81% (0.23 g). Anal. Calcd for $C_{77}H_{66}FeMnNP_6O_5F_6$: C, 61.8; H, 4.4; N, 0.9. Found: C, 62.1; H, 4.5; N, 0.9. IR (CH_2Cl_2): 2091 w (CN), 2015 vw, 1933 s (CO). Molar conductivity: 120. ^{1}H NMR ($CDCl_3$): 6.5–8.0 (C_6H_5, m, br, 55 H), 4.42 (PCH_2P, t, 2 H), 4.02 (C_5H_5, s, 5 H), 2.38, 2.05 (PCH_2CH_2P, m, 4 H). ^{31}P NMR ($CDCl_3$): 169.8 [P(OPh)$_3$, br, 1 P], 96.9 (dppe, s, 2 P), 32.8 (dppm, m, br, 1 P), 27.8 (dppm, m, br, 1 P).

***cis*-{(C_5H_5)(dppe)Fe–NC–Mn(CO)$_2$(dppm)[P(OPh)$_3$]}PF$_6$.** To a solution of the complexes *cis*-Mn(CN)(CO)$_2$(dppm)[P(OPh)$_3$] (0.1 g, 0.12 mmol) and FeI(dppe)(C_5H_5) (0.09 g, 0.14 mmol) in methanol (10 mL) was added solid (NH_4)PF$_6$ (0.1 g, 0.6 mmol), and the mixture was stirred at room temperature for 5–6 h, after which it was filtered through Celite and the solvent was evaporated to give a red residue. This solid was dissolved in methylene chloride, and to the solution was added sufficient diethyl ether to form a precipitate, which was dried in vacuo. Yield: 70% (0.11 g). The product (which occasionally contained some of the starting cyanide manganese complex) was recrystallized by cooling a nearly saturated solution in methylene chloride–ethanol. Further purification was from methylene chloride–diethyl ether. The compound can also be prepared from TlPF$_6$ in CH_2Cl_2. The reaction time was 2 days, and the product had to be separated from unreacted mononuclear manganese cyanide complex. Anal. Calcd for $C_{77}H_{66}FeMnNP_6O_5F_6$: C, 61.8; H, 4.4; N, 0.9. Found: C, 62.1; H, 4.5; N, 1.0. IR (CH_2Cl_2): 2050 vw (CN), 1974 s, 1918 s (CO). Molar conductivity: 140. ^{1}H NMR (Cl_2CD_2): 6.7–8.0 (C_6H_5, m, br, 55 H), 4.5 (PCH_2P, m, vbr), 4.1 (C_5H_5, s, br, 5 H), 3.4 (PCH_2P, m, 2 H), 2.4–1.6 (PCH_2CH_2P, m, br, 4 H). ^{31}P NMR ($CDCl_3$): 167.5 [P(OPh$_3$), m, 1 P], 94.9 (dppe, AB, *J*(AB) = 30.4, 2 P), 27.7, 16.4 (dppm, ABX, *J*(AB) = 45.5, *J*(AX) = 81.2, *J*(BX) = 72.2, 2 P).

***trans*-{(C_5H_5)(dppe)Fe–CN–Mn(CO)$_2$(dppm)[P(OPh)$_3$]}PF$_6$.** To a solution of the complexes *trans*-MnBr(CO)$_2$(dppm)[P(OPh)$_3$] (0.193 g, 0.21 mmol) and Fe(CN)(dppe)(C_5H_5) (0.117 g, 0.22 mmol) in methylene chloride (25 mL) was added solid TlPF$_6$ (0.1 g, 0.29 mmol), and the mixture was stirred at room temperature for 3 days, after which it was filtered through Celite and the solvent was evaporated under vacuum. Yield: 80% (0.28 g). Anal. Calcd for $C_{77}H_{66}FeMnNP_6O_5F_6$: C, 61.8; H, 4.4; N, 0.9. Found: C, 61.7; H, 4.6; N, 0.7. IR (CH_2Cl_2): 2077 w (CN), 2017 vw, 1926 s (CO). Molar conductivity: 130. ^{1}H NMR ($CDCl_3$): 6.5–7.8 (C_5H_5, m, br, 55 H), 4.27 (PCH_2P, t, 2 H), 4.00 (C_5H_5, s, 5 H), 2.30, 2.02 (PCH_2CH_2P, m, 4 H). ^{31}P NMR ($CDCl_3$): 168.6 [P(OPh$_3$), m, XAB, 1 P], 102.1 (dppe, s 2 P), 45.8, 21.8 (dppm, ABX, *J*(AB) = 27, *J*(AX) = 53, *J*(BX) = 65, 2 P).

***cis*-{(C_5H_5)(dppe)Fe–CN–Mn(CO)$_2$(dppm)[P(OPh)$_3$]}PF$_6$.** To a solution of the complexes *cis*-MnBr(CO)$_2$(dppm)[P(OPh)$_3$] (0.61 g, 0.69 mmol) and Fe(CN)(dppe)(C_5H_5) (0.37 g, 069 mmol) in methylene chloride (30 mL) was added solid TlPF$_6$ (0.3 g, 0.87 mmol), and the mixture was stirred at room temperature for 9 days in the absence of light. The mixture was then filtered through Celite, and the solvent was evaporated under vacuum. The resulting orange oil was redissolved in 20 mL of methylene chloride, and the solution was chromatographed on Florisil with neat methylene chloride as eluent. The unreacted mononuclear manganese bromo carbonyl complex was eluted first, followed by a pale yellow band of the desired product. The resulting solution was evaporated in vacuo to give a dark yellow solid. Yield: 25% (0.23 g). Anal. Calcd for $C_{77}H_{66}FeMnNP_6O_5F_6$: C, 61.8; H, 4.4; N, 0.9. Found: C, 62.7; H, 4.3; N, 0.9. IR (CH_2Cl_2): 2062 w (CN), 1969 s, 1904 s (CO). Molar conductivity: 121. ^{1}H NMR ($CDCl_3$): 6.5–8.1 (C_5H_5, m, br, 55 H), 4.6–4.9 (PCH_2P, m, 2 H), 4.11 (C_5H_5, s, br, 5 H), 1.8–2.2 (PCH_2CH_2P, m, 4 H). ^{31}P NMR ($CDCl_3$): 162.4 [P(OPh)$_3$, br, 1 P], 99.4 (dppe, s, 2 P), 23.6 (dppm, m, br, 1 P), 9.6 (dppm, m, br, 1 P). ^{31}P NMR at −70 °C: 162.9 (br), 100.0 (AB, *J*(AB) = 29), 23.3, 9.7 (ABX, *J*(AB) = 43, *J*(AX) = 118, *J*(BX) = 78).

***cis*-[(C_5H_5)(dppe)Fe–CN–Mn(CO)$_2$(dppe)(PEt$_3$)]PF$_6$.** To a solution of the complexes *cis*-MnBr(CO)$_2$(dppe)(PEt$_3$) (0.13 g, 0.19 mmol) and Fe(CN)(dppe)(C_5H_5) (0.11 g, 0.2 mmol) in methylene chloride (20 mL) was added solid TlPF$_6$ (0.13 g, 0.3 mmol), and the mixture was stirred at room temperature for ca. 2 days in the absence of light. This reaction must be monitored carefully by IR spectroscopy until the ν(CN) and ν(CO) absorptions change from 2064 w and 1930 s, 1854 s to respectively 2053 w and 1939 s, 1871 s cm^{-1}. The mixture was filtered through Celite, and the solution was concentrated to ca. 5 mL. Addition of diethyl ether afforded a yellow solid, which was washed twice with diethyl ether and dried in vacuo. Yield: 83% (0.2 g). Anal. Calcd for $C_{66}H_{68}FeMnNP_6O_2F_6$: C, 60.1; H, 5.2; N, 1.1. Found: C, 60.0; H, 5.3; N, 1.3. IR (CH_2Cl_2): 2053 m (CN), 1939 s, 1871 s (CO). Molar conductivity: 135. ^{1}H NMR ($CDCl_3$): 6.7–7.8 (C_5H_5, m, br, 40 H), 4.22 (C_5H_5, s, 5 H), 2.7, 2.0 (PCH_2CH_2P, m, 8 H), 1.48 (PCH_2-, m, 6 H), 0.82 (CH_3P, m, 9 H). ^{31}P NMR ($CDCl_3$): 98.1 (dppe-Fe, s, 2 P), 73.9 (dppe–Mn m, br, 1 P), 57.9 (dppe–Mn, m, br, 1 P), 38.4 (PEt$_3$, m, br, 1 P). [^{31}P NMR for the trans isomer **3b**$^+$: 104.8 (dppe–Fe), 88.0, 80.6 (dppe–Mn), 41.4 (PEt$_3$).]

[(C_5H_5)(dppe)Fe–CN–Fe(dppe)(C_5H_5)]PF$_6$. A mixture of FeI(dppe)(C_5H_5) (0.11 g, 0.17 mmol), Fe(CN)(dppe)(C_5H_5) (0.09 g, 0.16 mmol), and solid (NH_4)PF$_6$ (0.10 g, 0.61 mmol) in methanol (15 mL) was stirred for 6 h at room temperature and filtered through Celite. The solvent was evaporated under vacuum, and the red residue was washed several times with diethyl ether. The product was dissolved in methylene chloride, and the solution was filtered and concentrated. Addition of diethyl ether gave a red-brown precipitate, which was washed with ether and dried in vacuo. Yield: 79% (0.11 g). The compound was recrystallized from methylene chloride–diethyl ether as red microcrystals. Anal. Calcd for $C_{63}H_{58}Fe_2NP_5F_6$: C, 62.5; H, 4.8; N, 1.2. Found: C, 62.8; H, 4.9; N, 1.2. IR (CH_2Cl_2): 2069 m (CN). Molar conductivity: 125. ^{1}H NMR (acetone-d_6): 6.8–8.2 (C_6H_5, m, br, 40 H), 3.93 (C_5H_5, s, 5 H), 4.01 (C_5H_5, s, 5 H); the signals of the PCH_2CH_2P protons were not clearly observed in this solvent. ^{31}P NMR (acetone-d_6): 103.7 (dppe–Fe–CN, s, 2 P), 99.9 (dppe–Fe–NC, m, br, 2 P) (100.4 and 96.7 in CD_2Cl_2).

***cis*-{(C_5H_5)(dppe)Fe–NC–Mn(CO)$_2$(dppm)[P(OPh)$_3$]}[PF$_6$]$_2$.** The complex *trans*-{(C_5H_5)(dppe)Fe–NC–Mn(CO)$_2$(dppm)[P(OPh)$_3$]}PF$_6$ (0.19 g, 0.128 mmol) and the salt ($N_2C_6H_4$-4-CH_3)PF$_6$ (0.042 g, 0.16 mmol) were stirred in methylene chloride (15 mL) for 1 h. The resulting solution was filtered through Celite and concentrated in vacuo. Addition of *n*-hexane gave a green-black crystalline precipitate, which was recrystallized from methylene chloride–hexane. Yield: 80% (0.17 g). Anal. Calcd for $C_{77}H_{66}FeMnNO_5P_7F_{12}$: C, 56.3; H, 4.0; N, 0.9. Found: C, 57.0; H, 4.3; N, 1.2. IR (CH_2Cl_2): 2050 w (CN), 1974 s, 1936 m (CO). Molar conductivity: 228.

[(C_5H_5)(dppe)Fe–CN–Fe(dppe)(C_5H_5)][PF$_6$]$_2$. The complex [(C_5H_5)(dppe)Fe–CN–Fe(dppe)(C_5H_5)]PF$_6$ (0.12 g, 0.09 mmol) and the salt ($N_2C_6H_4$-4-CH_3)PF$_6$ (0.028 g, 0.10 mmol) were stirred in methylene chloride (15 mL) for 0.5 h. The resulting solution was filtered through Celite and concentrated in vacuo to ca. 5 mL. Addition of diethyl ether gave a dark gray solid, which was washed with diethyl ether and dried in vacuo. Yield: 76% (0.13 g). The product was recrystallized from methylene chloride–diethyl ether. Using ferrocenium hexafluorophosphate as the oxidant led to almost identical results. Anal. Calcd for $C_{63}H_{58}FeMnNP_6F_{12}\cdot CH_2Cl_2$: C, 53.4; H, 4.2; N, 1.0. Found: C, 53.5; H, 4.3; N, 1.1. IR (CH_2Cl_2): 1994 m (CN). Molar conductivity: 189.

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