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Synthesis and redox properties of bis-ferrocenylethynyl derivatives of bis(dimethylphosphinoethane)manganese

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Paramagnetic Mn^{II} and Mn^{III} complexes containing two ferrocenylethynyl ligands were synthesized. Their redox reactions were studied by cyclic voltammetry and chemical methods. The structures of the resulting compounds were determined by IR, ^{1}H NMR, and ESR spectroscopy. The structure of the complex $[(FcC{\equiv}C)_2Mn(dmpe)_2]^+PF_6^-$ was established by X-ray diffraction analysis.

Key words: Mn^{II} and Mn^{III} paramagnetic complexes, ethynylferrocene, redox reactions, cyclic voltammetry, IR, ^{1}H NMR, and ESR spectra, X-ray diffraction analysis.

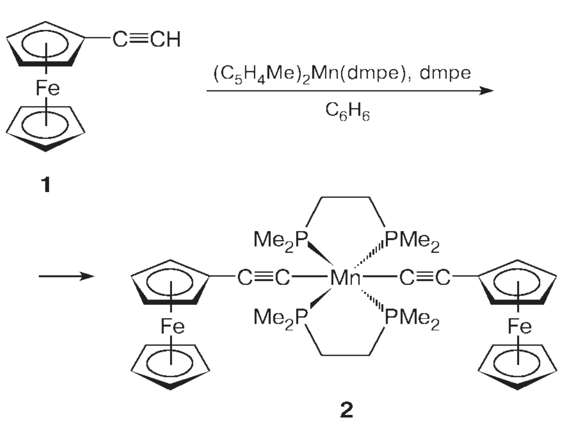
Previously, we have developed procedures for the preparation of the stable paramagnetic bis-alkynyl manganese complexes $(RC{\equiv}C)_2Mn(dmpe)_2$ (R = Ph or SiMe$_3$; dmpe = 1,2-bis(dimethylphosphino)ethane) by replacing bromine in MnBr$_2$ [1] or the cyclopentadienyl ligands in manganocenes[2] $(C_5H_4R)_2Mn$ (R = H or Me) with alkynyl groups in the presence of dmpe. We undertook the present study in order to extend these reactions to alk-1-ynes containing a transition metal atom in the substituents. Ferrocenylacetylene was used as such an alkyne.

Results and Discussion

We found that the reaction of ferrocenylacetylene **1** with the $(MeC_5H_4)_2Mn(dmpe)$ adduct in the presence of one equivalent of dmpe (the ratio was 2 : 1 : 1) was accompanied by the complete replacement of the MeC$_5$H$_4$ ligands to form bis-ferrocenylethynyl derivative of manganese(II) **2** (Scheme 1).

At ~20 °C, the reaction proceeded rather slowly and the conversion was completed in one week, whereas heating to 50—60 °C made it possible to reduce the reaction time to 10—12 h. It should be noted that this reaction proceeded more slowly than the analogous reactions with Me$_3$SiC≡CH and PhC≡CH studied by us previously[2] due, apparently, to the higher electron-donating ability of the ferrocenyl substituent. As a result, thermodynamically stable yellow-brown complex **2** was obtained in high yield (75%). However, this complex proved to be sensitive to atmospheric oxygen and other oxidizing reagents, particularly, upon storage in solutions. It is known[1,2] that the mononuclear manganese(II) complexes $(RC{\equiv}C)_2Mn(dmpe)_2$ (R = Ph or SiMe$_3$) are readily oxidized to form air-stable manganese(III) derivatives. The reactions of ferrocenium salts with compound **2** proceeded analogously to yield the stable violet cationic complex $[\mathbf{2}]^+PF_6^-$ in quantitative yield (Scheme 2).

Scheme 1



dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$

We synthesized complex **2** according to an alternative procedure based on the reactions of dmpe-containing manganese(II) dihalides MnX$_2$(dmpe)$_2$ (X = Cl or Br) with lithium ferrocenylacetylide. Although attempts to isolate the MnCl$_2$(dmpe)$_2$ complex in the individual form have failed,[3] the use of anhydrous MnCl$_2$ in the presence of dmpe allowed us to achieve the maximum yield of the final product. In this case, complex **2** was not isolated but was oxidized with Cp$_2$FeBF$_4$ to form the complex $[\mathbf{2}]^+BF_4^-$ (Scheme 3).

The compositions and the structures of compounds **2**, $[\mathbf{2}]^+PF_6^-$, and $[\mathbf{2}]^+BF_4^-$ were determined by elemental

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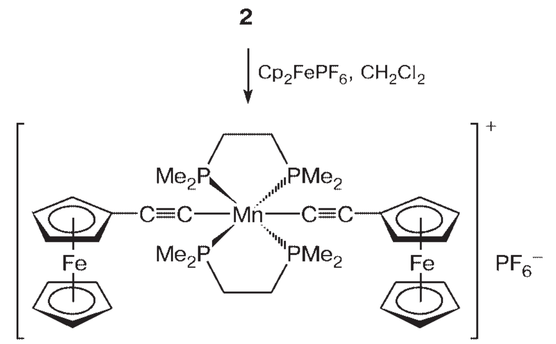
Scheme 2



$[\mathbf{2}]^+PF_6^-$

analysis and IR, ^{1}H NMR, and ESR spectroscopy. In addition, the structure of the complex $[\mathbf{2}]^+PF_6^-$ was established by X-ray diffraction analysis. The IR spectra of **2** and $[\mathbf{2}]^+BF_4^-$ each have one stretching vibration band of the triple bond at 2006 and 2026 cm^{-1}, respectively. These values are rather close to those found for the bis-phenylacetylide analogs,**[1,2]** the higher frequency belonging to the cationic complex. This may be associated with a decrease in back donation of the electron density to the acetylide ligand in the complexes with metals in higher oxidation states.

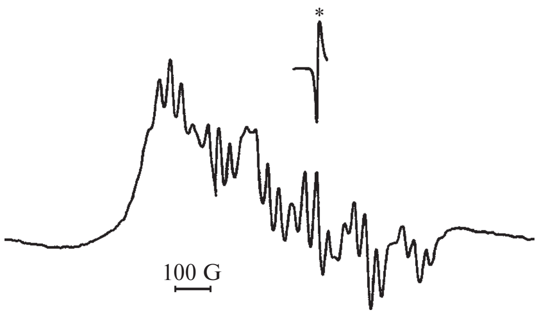
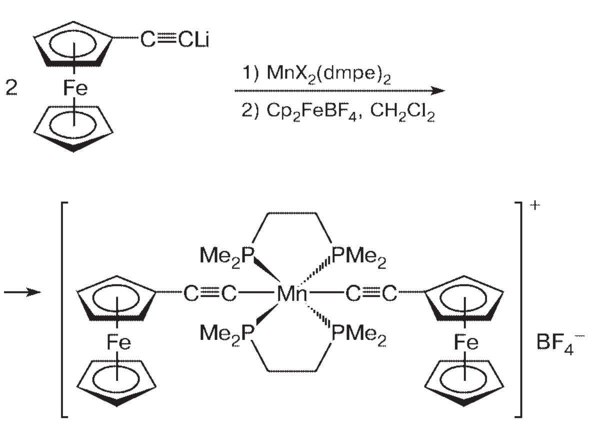


Fig. 1. ESR spectrum of complex **2** in toluene at 77 K (g = 2.0028). The standard is marked with an asterisk.

At liquid nitrogen temperature, the ESR spectrum of compound **2** in toluene has a well-resolved signal ($g \approx 2.038$), which is in agreement with the low-spin state of Mn^{II} (S = 1/2) in the axial ligand field (Fig. 1). This spectrum is very similar to that obtained for $(PhC{\equiv}C)_2Mn(dmpe)_2$.**[1]** The hyperfine structure results from interactions of the ^{55}Mn atom (I = 5/2, a = 125 Gs) with four equivalent ^{31}P atoms (I = 1/2, a = 27 Gs) (the a value was calculated between two limiting high-field signals). As expected, the corresponding Mn^{III} complex did not give ESR signals.

Scheme 3



$[\mathbf{2}]^+BF_4^-$

X = Cl, Br

The NMR spectra of paramagnetic compounds **2** and $\mathbf{2}^+$, like those of the mononuclear manganese complexes,**[1,2]** have signals for the methyl and methylene protons of the diphosphine ligands characteristic of Mn^{II} and Mn^{III} derivatives. As in the case of the phenyl analog, the chemical shifts for the protons in the substituted cyclopentadienyl ring of the ferrocenyl substituent alternate with each other, *viz.*, the signals for the α and β protons are shifted upfield and downfield, respectively. This is indicative of the π character of delocalization of the unpaired electron.**[4]** Therefore, it can be stated that the ^{1}H NMR spectra provide unambiguous evidence for the low-spin state of complexes **2** and $\mathbf{2}^+$ and, in addition, characterize the oxidation state of the manganese atom.

According to the X-ray diffraction data, two crystallographically independent molecules (A and B) of the complex $[\mathbf{2}]^+PF_6^-$ in the crystal (Fig. 2) have close geometric parameters (Table 1). The coordination environment about the manganese atom is an octahedron formed by two ferrocenylacetylide ligands in the *trans* positions and four phosphorus atoms located in the equatorial plane. The C≡C—Mn—C≡C chain is virtually linear and the Mn—P distances are close to the corresponding values in $[(PhC{\equiv}C)_2Mn(dmpe)_2]^+$.**[1]** Noteworthy is the unusual skewed arrangement of the ferrocene fragments, which are located at an angle of approximately 90° with respect to each other. In the structurally similar ruthenium complexes $(FcC{\equiv}C)_2Ru(P_2L_2)$,**[5—8]** the ferrocenyl substituents are always in the transoid positions regardless of the nature of the remaining ligands. Hence, unlike the ruthenium derivatives, the $[\mathbf{2}]^+PF_6^-$ molecule is noncentrosymmetrical due to which the latter would be expected to exhibit second-order nonlinear optical activity. However, the crystal packing is centrosymmetrical (the space group $P\bar{1}$). Hence, this effect cannot be manifested in single crystals of the complex $[\mathbf{2}]^+PF_6^-$ as well as in its solutions in which free rotation of the ferrocenyl substituents with respect to each other about the C—C bond is responsible for the absence of this effect.

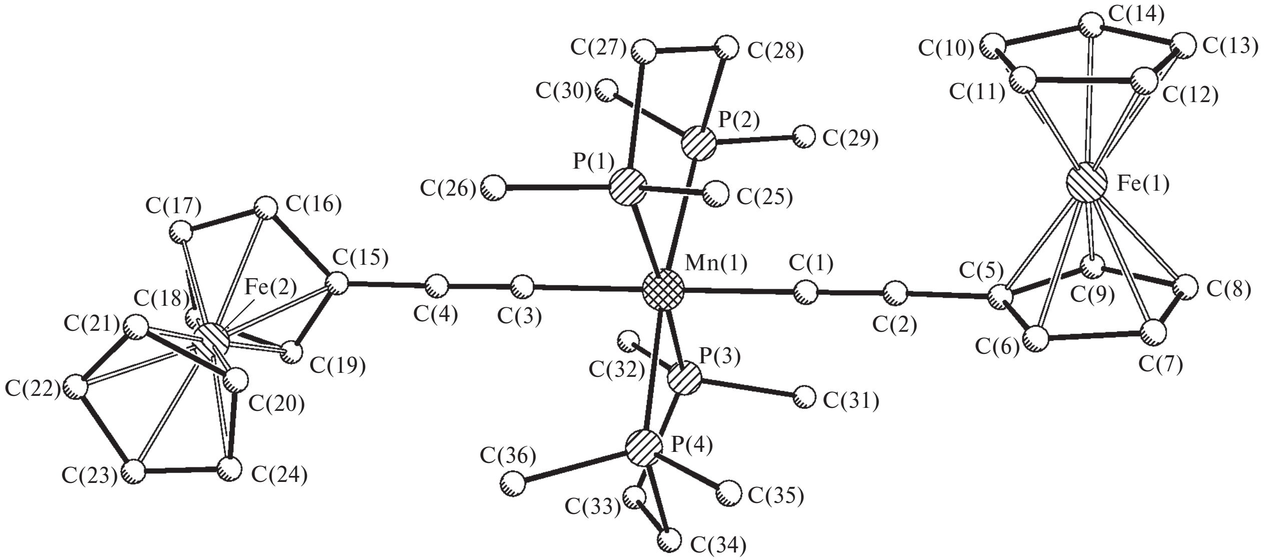


Fig. 2. Molecular structure of $[\mathbf{2}]^+PF_6^-$.

Electrochemistry of bis-ferrocenylacetylide complexes **2** was studied by cyclic voltammetry (CV) at ~20 °C. The cyclic voltammogram (Fig. 3) has three waves two of which ($E_{1/2}$ = −0.86 and 0.57 V) are reversible, and the third wave ($E_{1/2}$ = 0.76 V), although being reversible, possesses an anomalous cathodic peak. This is attributable to adsorption of the oxidation product on the electrode. Previously,[2] such adsorption has been observed in the case of binuclear manganese complexes. The first wave ($E_{1/2}$ = −0.86 V) is accounted for by oxidation of Mn^{II} to Mn^{III} because it is in the region of potentials close to those for $(RC{\equiv}C)_2Mn(dmpe)_2$.[1] At the same time, this wave is substantially shifted (by 0.16—0.17 V) to the negative region, which reflects the stronger donor properties of the ferrocenyl substituent compared to the phenyl and trimethysilyl groups. The remaining two waves at positive potentials correspond, apparently, to successive oxidation of the first and second iron atoms in the ferrocenylacetylide substituents (Scheme 4).

Table 1. Selected geometric parameters of two independent molecules (A and B) of the complex $[\mathbf{2}]^+PF_6^-$

Parameter	A	B
Bond	*d*/Å	
Mn(1)—C(1)	1.954(3)	1.953(3)
Mn(1)—C(3)	1.970(4)	1.955(3)
Mn(1)—P(1)	2.320(1)	2.308(1)
Mn(1)—P(2)	2.312(1)	2.314(1)
Mn(1)—P(3)	2.295(1)	2.316(1)
Mn(1)—P(4)	2.319(1)	2.308(1)
<Fe—C>	2.042	2.046
C(1)—C(2)	1.229(5)	1.212(4)
C(2)—C(5)	1.427(5)	1.428(5)
C(3)—C(4)	1.212(5)	1.224(5)
C(4)—C(15)	1.447(5)	1.424(5)
C(27)—C(28)	1.530(6)	1.516(6)
C(33)—C(34)	1.527(6)	1.527(6)
Fe—C	2.022(5)—2.065(3)	2.030(4)—2.074(3)
Bond angle	ω/deg	
C(1)—Mn(1)—C(3)	178.2(1)	177.6(1)
C(2)—C(1)—Mn(1)	173.7(3)	176.4(3)
C(1)—C(2)—C(5)	176.3(4)	174.8(4)
C(4)—C(3)—Mn(1)	178.3(3)	173.2(3)
C(3)—C(4)—C(15)	178.8(4)	177.3(4)

Scheme 4

$$Fe^{II}—Mn^{II}—Fe^{II} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} Fe^{II}—Mn^{III}—Fe^{II} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}$$

$$\rightleftharpoons Fe^{III}—Mn^{III}—Fe^{II} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} Fe^{III}—Mn^{III}—Fe^{III}$$

Due to the presence of the positively charged Mn atom in the bridge, the oxidation potentials of the Fe atoms are shifted to the positive region by 0.5—0.6 V.

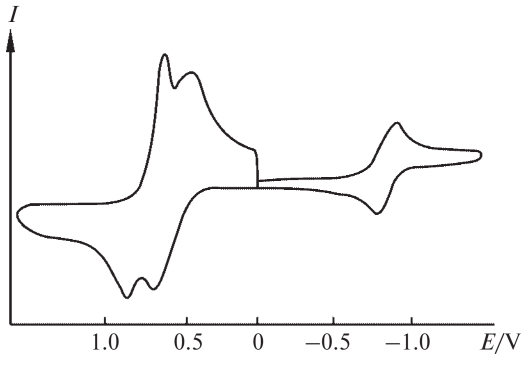


Fig. 3. Cyclic voltammogram of the complex $[\mathbf{2}]^+BF_4^-$ ($2 \cdot 10^{-3}$ mol L^{-1}) in the presence of Bu_4NPF_6 (0.1 mol L^{-1}) at a glassy-carbon electrode at $\upsilon = 0.2$ V s^{-1}.

The two last-mentioned redox processes are separated by 0.2 V, which indicates that two iron atoms interact with each other through a chain consisting of the cyclopentadienyl ligands, the triple bonds, and the Mn^{III} atom. This interaction is characterized by the equilibrium constant for the process shown in Scheme 5.

Scheme 5

$$\text{Fe}^{\text{II}}\text{—Mn}^{\text{III}}\text{—Fe}^{\text{II}} + \text{Fe}^{\text{III}}\text{—Mn}^{\text{III}}\text{—Fe}^{\text{III}} \overset{K_c}{\rightleftharpoons} \text{Fe}^{\text{II}}\text{—Mn}^{\text{III}}\text{—Fe}^{\text{III}}$$

The equilibrium constant (K_c), which was calculated according to the Nernst equation $\ln K_c = nF[\Delta E_{1/2}/(RT)]$, is $2.5 \cdot 10^3$. This value is close to the equilibrium constants for the bis-ferrocenylacetylide complexes of ruthenium with diphosphine ligands, *viz.*, with bis-diphenylphosphinomethane and bis-diphenylphosphinoethane.[5—7] It should be noted that complexes $\mathbf{2}^{n+}$ differ substantially from the $(\text{Fc—C}{\equiv}\text{C})_2\text{Ru}(\text{P}_2)_2$ derivatives[5—8] in that the Ru atom in the latter compounds contains 18 electrons, whereas oxidation begins with the iron atom and ends with the ruthenium atom. It should also be noted that this exchange in the complex $[\mathbf{2}]^+\text{BF}_4^-$ occurs through the 16-electron positively charged manganese atom containing two unpaired electrons, the conductivity through the Mn^{III}-containing bridge being virtually identical with that occurring through the bridge containing the Ru^{II} atom.

At the same time, the conductivities of the compound $[\mathbf{2}]^+\text{BF}_4^-$ and the ruthenium complexes[5—8] are higher than that of the $\text{Fc—C}{\equiv}\text{C—C}{\equiv}\text{C—Fc}$ complex,[9] which contains no metal atoms in the conducting bridge and which is characterized by the equilibrium constant of 52. Hence, it can be suggested that conjugated polymers containing organometallic fragments are, probably, better conductors than their hydrocarbon analogs.

Experimental

All reactions were carried out under an atmosphere of dry argon using anhydrous freshly distilled solvents and the Schlenk technique. Column chromatography was carried out with the use of aluminum oxide (Brockmann II).

The ^1H NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz). The IR spectra were measured on a Nicolet Magna 750 spectrometer (the resolution was 2 cm^{-1}) in KBr pellets, solutions in CH_2Cl_2, and Nujol mulls. The ESR spectra were recorded on a Varian E-12 spectrometer equipped with a double resonator (one resonator contained the sample under study and another resonator contained the reference sample with the g factor of 2.0028).

Electrochemical studies were carried out on a PI-50-1 potentiostat in CH_2Cl_2 in the presence of Bu_4NPF_6 (0.1 mol L^{-1}). A glassy-carbon electrode ($S = 2$ mm^2), a platinum plate, and a saturated calomel electrode were used as the working, auxiliary, and reference electrodes, respectively. The concentration of the compounds was $2 \cdot 10^{-3}$ mol L^{-1} and the rate of the potential scan (υ) was 0.2 V s^{-1}. The numbers of electrons involved in the reactions were estimated by comparing the observed peak currents with the currents of one-electron ferrocene/ferrocenium oxidation/reduction at the same concentrations.

The starting ethynylferrocene,[10] *trans*-bis[1,2-bis(dimethylphosphino)ethane]manganese dibromide,[3] and bis(methylcyclopentadienyl)-1,2-bis-(dimethylphosphino)ethanemanganese[11] were synthesized according to known procedures.

***trans*-Bis(ferrocenylethynyl)bis[bis(dimethylphosphino)ethane]manganese(II), $\mathbf{(FcC{\equiv}C)_2Mn(dmpe)_2}$ (2).** A solution of compound **1** (0.046 g, 0.22 mmol), $(\text{C}_5\text{H}_4\text{Me})_2\text{Mn(dmpe)}$ (0.039 g, 0.11 mmol), and dmpe (0.016 g, 0.11 mmol) in benzene (1 mL) was kept for 5 days. The crystals that precipitated were separated from the solution by decantation, washed with a minimum amount of benzene, and dried *in vacuo*. Brown crystals were obtained in a yield of 0.033 g (40%). The mother liquor was gradually diluted with hexane and kept at ~20 °C after which complex **2** was additionally obtained in a yield of 0.030 g. The total yield was 0.063 g (76%). Found (%): C, 55.46; H, 6.55. $\text{C}_{36}\text{H}_{50}\text{Fe}_2\text{MnP}_4$. Calculated (%): C, 55.91; H, 6.52. IR (Nujol mulls), ν/cm^{-1}: 2006 ($\text{C}{\equiv}\text{C}$). ^1H NMR (C_6D_6), δ: -14.90 (s, 24 H, PMe_2, $w_{1/2}$* = 309 Hz); -13.90 (s, 8 H, PCH_2); -4.20 (s, 4 H, α-C_5H_4, $w_{1/2} = 75$ Hz); 4.40 (s, 10 H, C_5H_5, $w_{1/2} = 24$ Hz); 10.90 (s, 4 H, β-C_5H_4, $w_{1/2} = 41$ Hz).

trans*-Bis(ferrocenylethynyl)bis[bis(dimethylphosphino)ethane]manganese(III) tetrafluoroborate, $\mathbf{[(FcC{\equiv}C)_2Mn(dmpe)_2]BF_4}$ ($\mathbf{[2]^+BF_4^-}$).** ***A. A solution of compound **1** (0.2 g, 0.952 mmol) in THF (5 mL) was cooled to -78 °C and then a 1.6 *M* BuLi solution in hexane (0.65 mL, 1.047 mmol) was added. The reaction mixture was stirred at this temperature for 1 h. Then a solution of $\text{MnCl}_2(\text{dmpe})_2$ in THF (5 mL), which was prepared from MnCl_2 (0.060 g, 0.476 mmol) and dmpe (0.16 mL, 0.952 mmol), was added and the reaction mixture was slowly warmed to ~20 °C and stirred for 2 h. The solvent was removed *in vacuo* and a solution of Cp_2FeBF_4 (0.116 g, 0.425 mmol) in CH_2Cl_2 (10 mL) was added to the residue. The mixture was stirred for 1 h after which the color of the solution changed from brown to violet. Then the solution was concentrated and the compound was reprecipitated with Et_2O. The yield was 0.307 g (75%). Found (%): C, 50.30; H, 5.96. $\text{C}_{36}\text{H}_{50}\text{BF}_4\text{Fe}_2\text{MnP}_4$. Calculated (%): C, 50.27; H, 5.86. IR (CH_2Cl_2), ν/cm^{-1}: 2024 ($\text{C}{\equiv}\text{C}$); (KBr), ν/cm^{-1}: 2026 ($\text{C}{\equiv}\text{C}$). ^1H NMR (CDCl_3), δ: -38.60 (s, 24 H, PMe_2, $w_{1/2} = 650$ Hz); -28.60 (s, 8 H, PCH_2, $w_{1/2} = 566$ Hz); -24.20 (s, 4 H, α-C_5H_4, $w_{1/2} = 125$ Hz); 1.70 (s, 10 H, C_5H_5, $w_{1/2} = 85$ Hz); 18.70 (s, 4 H, β-C_5H_4, $w_{1/2} = 130$ Hz).

B. A solution of compound **1** (0.139 g, 0.66 mmol) in THF (5 mL) was cooled to -78 °C and a 1.6 *M* BuLi solution (0.49 mL, 0.792 mmol) in hexane was added. The reaction mixture was stirred for 1 h. Then a solution of $\text{MnBr}_2(\text{dmpe})_2$ (0.170 g, 0.33 mmol) in THF (5 mL) was added. The reaction mixture was slowly warmed to ~20 °C and then stirred for 2 h. The solvent was distilled off *in vacuo* and a solution of Cp_2FeBF_4 (0.09 g, 0.33 mmol) in CH_2Cl_2 (10 mL) was added to the residue. The reaction mixture was stirred for 1 h after which the color of the solution changed from brown to violet. The solution was concentrated and the compound was reprecipitated with

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* $w_{1/2}$ is the width of the signal at the half-height.

Et_2O. The brown-violet precipitate that formed was chromatographed on a column with Al_2O_3 (elution with CH_2Cl_2 and then with a 5 : 1, CH_2Cl_2—MeOH mixture). The violet fraction was collected, the solutions were concentrated, and the compound was reprecipitated with Et_2O. The yield was 0.115 g (40%).

***trans*-Bis(ferrocenylethynyl)bis[bis(dimethylphosphino)ethane]manganese(III) hexafluorophosphate, $[(FcC{\equiv}C)_2Mn(dmpe)_2]PF_6$ ($[2]^+PF_6^-$).** Cp_2FePF_6 (0.0133 g, 0.0486 mmol) was added to a solution of compound **2** (0.0376 g, 0.0486 mmol) in CH_2Cl_2 (7 mL). The reaction mixture was stirred at ~20 °C for 1 h and then concentrated to the minimum volume. The compound was reprecipitated with Et_2O. The violet precipitate that formed was washed with Et_2O and dried. The complex was obtained in quantitative yield. Found (%): C, 47.24; H, 5.43. $C_{36}H_{50}F_6Fe_2MnP_5$. Calculated (%): C, 47.09; H, 5.49. IR (CH_2Cl_2), ν/cm^{-1}: 2023 (C≡C); 847 (PF_6). ^1H NMR (CD_2Cl_2), δ: −39.30 (s, 24 H, PMe_2, $w_{1/2}$ = 726 Hz); −28.90 (s, 8 H, PCH_2, $w_{1/2}$ = 790 Hz); −24.80 (s, 4 H, α-C_5H_4, $w_{1/2}$ = 168 Hz); 1.70 (s, 10 H, C_5H_5, $w_{1/2}$ = 50 Hz); 18.70 (s, 4 H, β-C_5H_4, $w_{1/2}$ = 98 Hz).

X-ray diffraction study of the complex $[2]^+PF_6^-$. Single crystals of the complex $[\mathbf{2}]^+PF_6^-$ suitable for X-ray diffraction study were prepared by crystallization from a CH_2Cl_2—Et_2O mixture. The crystals of $[C_{36}H_{50}P_4Fe_2Mn]PF_6$ are triclinic, space group $P\bar{1}$, at 110 K, a = 12.156(3), b = 14.084(3), c = 26.702(6) Å; α = 100.146(5), β = 90.949(5), γ = 115.597(6)°, V = 4036(2) Å^3, Z = 4, M = 918.25, d_{calc} = 1.511 g cm^{-3}, μ(Mo-Kα) = 12.69 cm^{-1}, F(000) = 1888. The intensities of 23412 independent reflections (R_{int} = 0.0388) were measured on an automated Bruker SMART 1000 CCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator, T = 110 K, $2\theta_{max}$ = 60°, the ω scan step was 0.3°, frames were exposed for 10 s). The X-ray data were processed using the SAINT program.[12] The empirical absorption correction was applied based on repeated measurements of the intensities of equivalent reflections (the SADABS program[13]). The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model. The final reliability factors were as follows: R_1 = 0.0676 (based on F for 13259 observed reflections with $I > 2\sigma(I)$) and wR_2 = 0.1823 (based on F^2 for all reflections) for 901 refinable parameters. All calculations were carried out using the SHELXTL-97 program package.[14]

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