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Cationic (η^6-Arene)tricarbonylmanganese Linked to Ferrocene Complexes

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Palladium-catalyzed Sonogashira coupling reactions of the neutral [η^5(1−5)-(1-chloro-4-methoxycyclohexa-2,4-dienyl)]tricarbonylmanganese(I) (**2**) and 2-bromo-5-{[η^5(1−5)-(4-methoxycyclohexa-2,4-dienyl]tricarbonylmanganese(I)}thiophene (**13**) with the ethynylferrocene derivative **5** give the dinuclear complexes 1-(ferrocenylethynyl)[η^5(1−5)-(4-methoxycyclohexa-2,4-dienyl)]tricarbonylmanganese(I) (**6**) and 2-(ferrocenylethynyl)-5-[η^5(1−5)-(4-methoxycyclohexa-2,4-dienyl)tricarbonylmanganese]thiophene (**10**). Similarly, condensation of **2** with 2-(ferrocenylethynyl)-5-ethynylthiophene (**18**) affords the dinuclear complex **19**. These complexes are valuable precursors, upon hydride abstraction, of the corresponding η^6-arene cations **7**, **11**, and **20**. The structure of one of them, 1-(ferrocenylethynyl)[η^6(1−6)-(4-methoxybenzene)]tricarbonylmanganese(I) tetrafluoroborate (**7**), has been investigated by X-ray diffraction.

Introduction

Organometallic chromophores have recently received increasing attention, motivated by the need to probe the properties of electron delocalization when the two end groups are linked with extended π conjugation. When they contain the main features donor−π system−acceptor, they offer a large diversity of tunable electronic behavior due to the size, nature, and redox ability of the transition-metal atoms,[1,2] which confer to them interesting properties: for example, optoelectronical and electrical applications.[3] A small number of heterobimetallic complexes with such a form have been described in the literature and usually contain, as end groups, metallocenyl derivatives (metal = Fe,[4] Ru,[5]) and Cr or W complexes.[6] As for conjugated dinuclear complexes containing cationic Mn complexes, to our knowledge, only two articles have been reported.[7a,b] The first complexes of type **A** (Figure 1) contain a cationic tricarbonyl(thiophene)manganese group linked to a ferrocene or to an (η^6-arene)tricarbonylchromium group by a conjugated double-bond system.[7a,b] Those of type **B** (Figure 1) have a cationic (η^6-arene)tricarbonylmanganese group conjugated with an (η^6-arene)tricarbon-

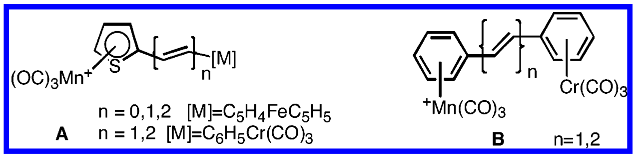

Figure 1. Dinuclear complexes containing cationic Mn complexes.

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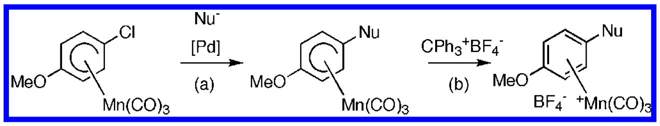
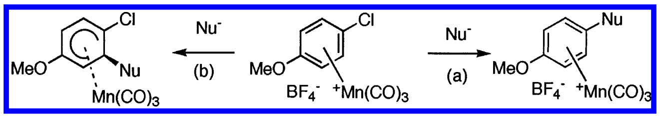
10.1021/om034168f CCC: $27.50

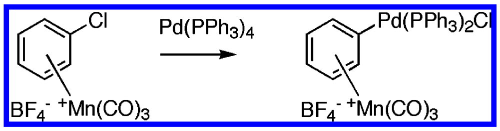
Scheme 1. Preparation of (Arene)tricarbonylmanganese Complexes via a Two-Step Procedure



Scheme 2. Reactivity of Chlorobenzene Complexes



Scheme 3. Formation of a Dinuclear Mn−Pd Complex



ylchromium entity.[7a] In both cases, the last step of the synthesis of the final complex consists of the coordination of the carbonylmanganese entity to the arene ring, a process which usually requires severe reaction conditions. An alternative procedure has used a transfer of an $Mn(CO)_3$ moiety, but the preparation of the transfer agent complex was found to be time consuming and in our hands proceeded only in moderate yield.[7a,c]

Here, we report an efficient synthesis of heterobimetallic complexes containing cationic (η^6-arene)$Mn(CO)_3^+$ complexes and a ferrocenyl entity via a two-step procedure that we have recently developed[8] in the case of mononuclear complexes (Scheme 1). The first step (a) involves a palladium-catalysis strategy for functionalization of (η^5-1-chlorocyclohexadienyl)$Mn(CO)_3$. This method preserves the methylene group and allows the second step (b): the rearomatization of the η^5 complex by hydride abstraction, which leads to new cationic (η^6-arene)$Mn(CO)_3^+$ complexes.

Results and Discussion

Ipso chloride substitution in (η^6-chloroarene)tricarbonylmanganese complexes allows a clean nucleophile introduction, but such a strategy is limited to amino, oxo, and thio derivatives (Scheme 2, path a; Nu = NR_2, OR, SR).[9] The main reaction for Mn complexes is the addition reaction, which leads to stable neutral (η^5-cyclohexadienyl)tricarbonylmanganese complexes (Scheme 2, path b),[10] whose reactivity has been described in several studies.[11]

Thus, the formation of a carbon−carbon bond is not possible by nucleophilic substitution starting from a cationic (η^6-chlorobenzene)tricarbonylmanganese derivative. Moreover, whereas the presence of the cationic electron-withdrawing tricarbonylmanganese entity activates the carbon−chlorine bond toward Pd(0) oxidative addition, no report of Pd-catalyzed carbon−carbon bond formation has been published to our knowledge. Indeed, we have shown[12] that although palladium inserts into the carbon−chlorine bond, the resulting bimetallic Mn/Pd complex is so stable that it did not give any further reaction (Scheme 3): no coupling reaction was observed.

Synthesis of Complex 7. Thus, to access the bimetallic target structures, we used as our starting material an η^5 complex, namely (η^5-1-chloro-4-methoxycyclohexadienyl)$Mn(CO)_3$ (**2**). This complex is easily accessible by employing the nucleophile addition chemistry described above, by regioselective hydride addition to (η^6-1-chloro-4-methoxybenzene)$Mn(CO)_3^+$ tetrafluoroborate (**1**) (Scheme 4).[8,9,11a,13,14] Functionalization of (η^5-chlorocyclohexadienyl)$Mn(CO)_3$ derivatives is efficient,[15] and C−O,[15d] C−N,[15d] C−S,[15d] C−P,[15d] and C−C[8,15a,b,d] bond formation are achieved by Pd-catalyzed reactions (Negishi, Sonogashira, and Stille reactions). An advantage of this strategy comes from the fact that neutral η^5 Mn complexes are stable and can be purified by silica gel column chromatography, in contrast to the cationic polar η^6-Mn structures. Ethynylferrocene **5** was prepared by classical methods in 80% yield by treating acetylferrocene (**3**) with $POCl_3$, DMF, and NaOAc. The resulting conjugated chloro aldehyde **4** was treated with

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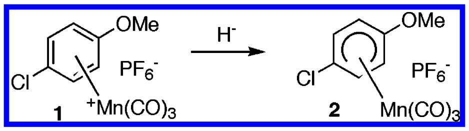
Scheme 4. Addition of Hydride to the Chloroarene Complex 1



Scheme 5. Preparation of the Dinuclear Complex 7

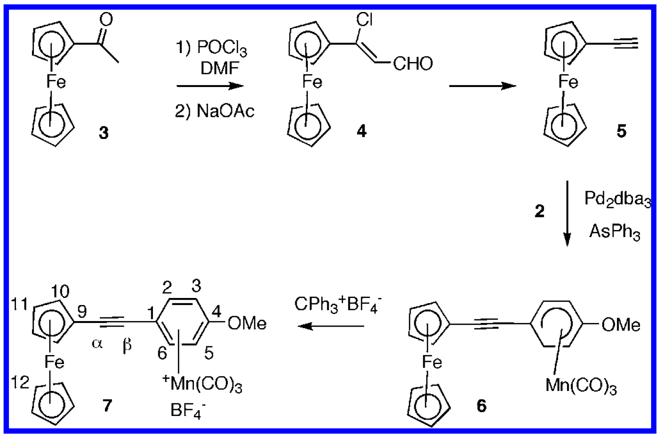


Table 1. Crystal Data for $C_{22}H_{16}BFeF_4MnO_4$[a]

formula	$C_{22}H_{16}BFeF_4MnO_4$
cryst class	orthorhombic
space group	$P2_1cn$
a (Å)	12.060(4)
b (Å)	12.829(4)
c (Å)	14.042(4)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2172(1)
Z	4
radiation type	Mo Kα
wavelength (Å)	0.710 690
density (g cm^{-3})	1.66
M_r	541.94
μ (cm^{-1})	13.10
temp (K)	295
size (mm)	0.20 × 0.20 × 0.30
color	dark red
shape	block
diffractometer	Enraf-Nonius Cad-4
scan type	$2\theta/\omega$
no. of rflns measd	2437
no of indep rflns	2413
θ(min,max)	1, 26.00
index ranges	
h	0−14
k	0−15
l	0−17
secondary extinction coeff	155
decay	0.02
refinement	on F
$R = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$	0.0699
$R_w = [\sum w(\|\|F_o\| - \|F_c\|\|)^2/\sum wF_o^2]^{1/2}$	0.0756
$\Delta\rho_{min}$ (e Å^{-3})	−0.58
$\Delta\rho_{max}$ e Å^{-3})	0.77
no. of rflns used	1547
$\sigma(I)$ limit	1.50
no. of params	250
goodness of fit	1.010

[a] Weighting scheme of the form $w = w'[1 - ((||F_o| - |F_c||)/6\sigma(F_o))^2]^2$ with $w'=1/\sum_r A_r T_r(X)$ with coefficients 2.90, 0.815, and 2.27 for a Chebychev series for which $X = F_c/F_c(\max)$.

1 N NaOH to afford ethynylferrocene **5** in 90% yield (Scheme 5).[16]

Ethynylferrocene **5** reacted with (η^5-1-chloro-4-methoxycyclohexadienyl)$Mn(CO)_3$ complex **2** in the presence of Pd_2dba_3 and $AsPh_3$ at 40 °C in NEt_3 for 22 h to afford **6** in 78% yield. This catalytic system has been proved to be the most efficient in the synthesis of alkyne-substituted (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes.[8] Triphenylcarbenium ion reagents are able to oxidize ferrocene to ferrocenium, but despite the presence of a ferrocenyl substituent in **6**, reaction with $CPh_3^+BF_4^-$ proceeded smoothly to deliver **7** in 92% yield (Scheme 5). The favored site of reaction is thus the neutral (cyclohexadienyl)manganese complex, and overall hydride abstraction occurs in preference to electron-transfer redox chemistry at iron. The mechanism of hydride abstraction from (cyclohexadienyl)manganese may involve an initial electron-transfer step followed by transfer of $H^\bullet$ to $Ph_3C^\bullet$.[17] Our results show that reaction at the organomanganese moiety is preferred over the possibility of ferrocene redox chemistry. Heck et al. reported also an hydride abstraction in the case of bimetallic sesquifulvalene complexes.[3e]

X-ray Analysis of Complex 7. Crystals of 1-(ferrocenylethynyl)[η^6-(4-methoxybenzene)]tricarbonylmanganese (**7**) were grown in a petroleum ether/acetone mixture. Two CAMERON views and some selected bond lengths are presented in Figures 2 and 3, and crystal data are reported in Table 1.

Three important features can be emphasized. First, the cation displays the well-known piano-stool conformation found in half-sandwich tricarbonyl complexes.[20] The conformation adopted by the $Mn(CO)_3$ entity is significant, because the η^6-arene is substituted by two electron-donating groups: the methoxy group and the ferrocenylacetylene. These effects compete and, in the solid state, the almost staggered conformation of the tripod shows a slightly dominant effect of the methoxy group. Indeed, the values of the torsion angles C(6)−C(100)−Mn−C(22), C(4)−C(100)−Mn−C(20) and C(2)−C(100)−Mn−C(21), C(100) being the center of the six-membered ring, are 17, 18, and 17°. This conclusion can be drawn because it is well reported in the case of substituted (η^6-arene)$Cr(CO)_3$ complexes that the conformation of the $Cr(CO)_3$ entity with respect to the arene

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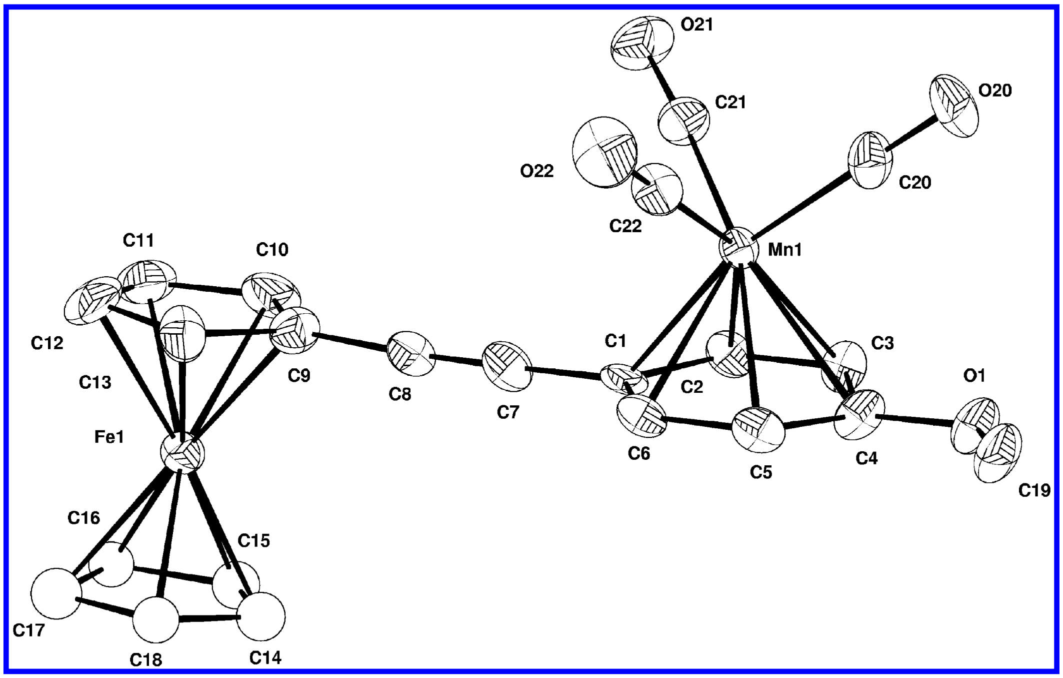


Figure 2. CAMERON view of the molecular structure of complex **7** ($C_{22}H_{16}BFeF_4MnO_4$). Selected bond lengths (Å): Mn−C1 = 2.207(12), Mn−C2 = 2.163(9), Mn−C3 = 2.168(13), Mn−C4 = 2.265(12), Mn−C5 = 2.182(13), Mn−C6 = 2.155(12), C1−C7 = 1.399(19), C7−C8 = 1.199(18), C8−C9 = 1.42(2), Mn−C20 = 1.803(14), C20−O20 = 1.135(16), C9−C10 = 1.48(2), C10−C11 = 1.39(2), C11−C12 = 1.36(3), C12−C13 = 1.40(3), C13−C9 = 1.41(2), Fe−C9 = 2.031(16), Fe−C10 = 2.052(17), Fe−C11 = 2.008(19), Fe−C12 = 2.042(16), Fe−C13 = 2.04(1).

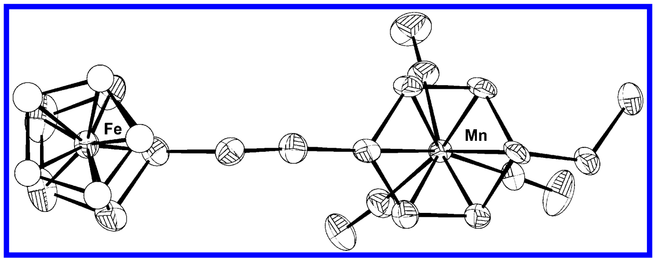
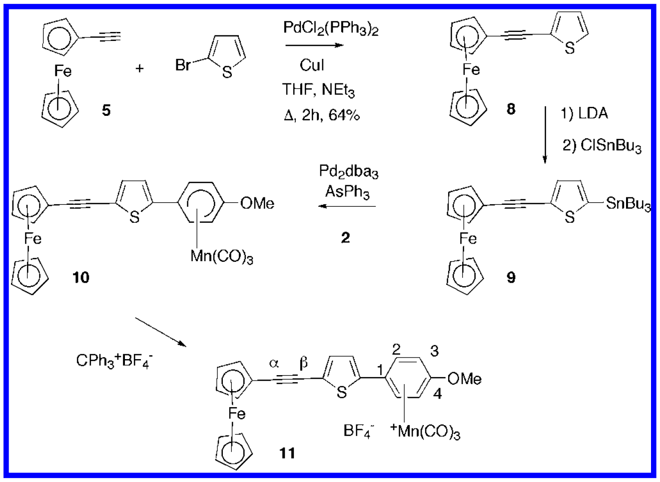


Figure 3. CAMERON view of the structure of complex **7** with the $Mn(CO)_3$ tripod projected onto the arene ring.

ring depends on the nature of the substituent.[10h] An electron-donating group, for example, favors the eclipsed conformation of the substituent by a Cr−CO bond. We observed a similar effect[21,22] in the case, for example, of (anisole)tricarbonylchromium substituted at the para position by the thiophenyl group,[21] where the corresponding torsion angles are 22, 22, and 23°. Second, the arene ring and C7 atom were found to be almost coplanar, as well as the Cp ring and C8 carbon atom. The methoxy group lies in the arene ring plane. The Mn−C(ring) bond lengths ranging from 2.15 to 2.27 Å (average 2.19 Å) are similar to the corresponding distances of other para-disubstituted (anisole)$Mn(CO)_3^+$ derivatives such as those substituted by a trimethylsilyl ynone or a thienyl ketone group.[8]

The arene, the Cp ring, and the triple bond are in the same plane. Therefore, an ideal overlap of the π system and a strong electronic coupling can be assumed in the solid state. The third point concerns the position of the Mn and Fe atoms: the structure shows clearly that the two metal atoms lie on the opposite faces of the conjugated system, probably for steric reasons. The antiperiplanar alignment of the two metal centers across the alkyne link is very pronounced. This is consistent with a high degree of orbital overlap through the extended π system. These data are remarkable, because dinuclear derivatives of comparable sesquifulvalene complexes all adopt a synperiplanar conformation.[3e]

Scheme 6. Preparation of the Dinuclear Complex 11



Synthesis of Complex 11. Two possible routes could be considered to prepare the heterodinuclear complex **11** which is homologated by a thienyl unit (Schemes 6 and 7). The first methodology involved a Sonogashira coupling with ethynylferrocene (**5**) and 2-bromothiophene in the presence of CuI, NEt_3, and $PdCl_2(PPh_3)_2$ (Scheme 6), which yielded the ferrocene derivative **8** in 64% yield. This compound was lithiated with lithium diisopropyl-

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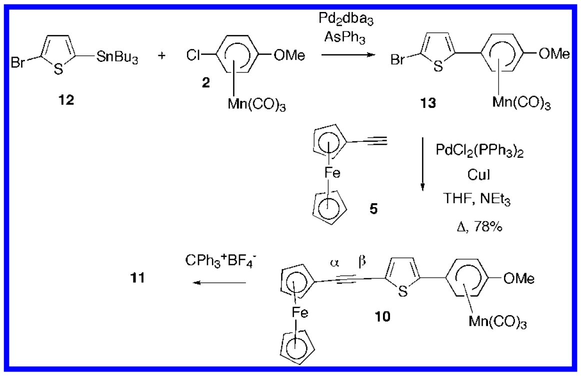
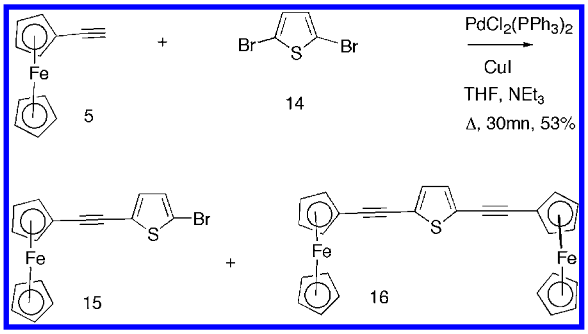
[21] Prim, D.; Tranchier, J. P.; Rose-Munch, F.; Rose, E. *Eur. J. Inorg. Chem.* **2000**, 901−905.

[22] In the case of chromium complexes, see: (a) Boutonnet, J. C.; Rose-Munch, F.; Rose, E.; Jeannin, Y.; Robert, Y. *J. Organomet. Chem.* **1985**, *297*, 185−191. (b) Rose-Munch, F.; Bellot, O.; Mignon, L.; Semra, A.; Robert, F.; Jeannin, Y. *J. Organomet. Chem.* **1991**, *402*, 1−16.

Scheme 7. Preparation of the Dinuclear Complex 11



Scheme 8. Preparation of the Mononuclear Complex 15



amide (LDA)[23] and treated with tributyltin chloride to give **9**, but all the attempts made to purify **9** by silica gel chromatography failed, due to a destannylation reaction affording the starting material **8**. Thus, the reaction mixture of **9** was reacted with the Mn complex **2** and afforded the dinuclear complex **10** in 25% yield for the two steps. Complex **10** reacted with triphenylcarbenium tetrafluoroborate, $CPh_3^+BF_4^-$, to deliver **11** quantitatively. No problem of stability during the reaction occurred.

A second method described in Scheme 7 was developed in order to increase the yield of preparation of **11**. Thus, a Stille reaction with the chloro Mn complex **2** and 2-(tributylstannyl)-5-bromothiophene **12** in the presence of Pd_2dba_3 and $AsPh_3$ delivered complex **13** in 48% yield. Then, a Sonogashira reaction with ethynylferrocene **5** and **13** delivered the expected complex **10** in 78% yield, showing the efficiency of this method in comparison with the first method.

Synthesis of Complex 20. We then turned our attention to the synthesis of **20**, containing a spacer homologated by a further triple bond. To achieve this goal, we undertook a Sonogashira reaction with ethynylferrocene **5** and 2,5-dibromothiophene **14**, and two compounds were obtained: the desired one, **15**, in 53% yield and the bis(ferrocene) derivative **16** as a byproduct (Scheme 8). Clearly, a competing reaction occurred between the two bromo derivatives **14** and **15**.

Nevertheless, using an excess of 2,5-dibromothiophene, it was possible to minimize the formation of the bis(ferrocene) derivative **16**. Moreover, the electron-donating ability of the ferrocenyl unit of complex **15** inhibits the oxidative addition of Pd into the C−Br bond of this complex with respect to the C−Br bond of the thiophene derivative **14**, avoiding the appearance of **16**. A second coupling reaction with (trimethylsilyl)acetylene and complex **15** afforded complex **17** almost quantitatively. This product was treated with NaOH in MeOH, yielding, again quantitatively, complex **18** (Scheme 9). Finally, a coupling reaction between **18** and the η^5-Mn complex **2** afforded in 48% yield the heterodinuclear complex **19**, from which hydrogen abstraction proceeded quantitatively, giving the dinuclear complex **20**.

Scheme 9. Preparation of the Dinuclear Complex 20

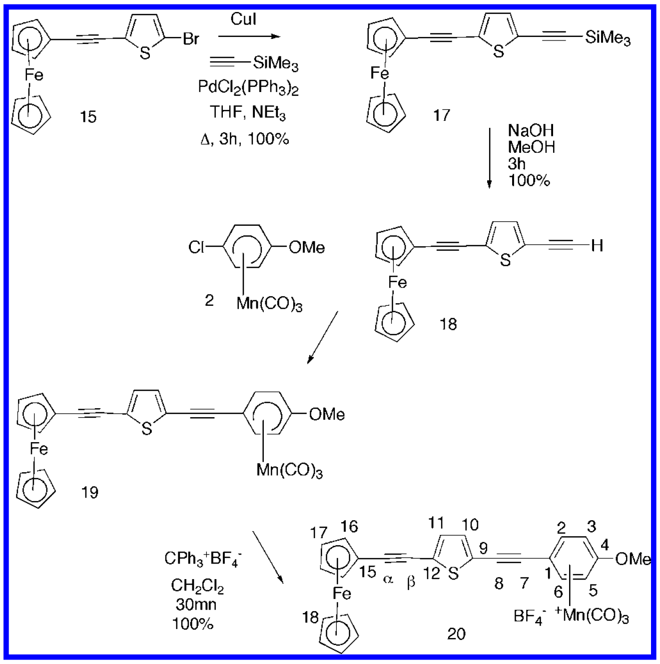


Table 2. Selected ^{1}H NMR Data (ppm)

	complex		
proton	7	11	20
H_2	7.35	7.58	7.43
H_3	6.62	6.63	6.63
$\delta(H_2) - \delta(H_3)$	0.73	0.95	0.80
C_5H_4 ($2H_a$)	4.46	4.39	4.39
C_5H_4 ($2H_b$)	4.64	4.58	4.57

NMR Spectroscopy. Selected ^{1}H NMR data, reported in Table 2, showed that for the six-membered-ring protons only H_2 protons are influenced by the nature of the spacer, with a maximum effect for the linker containing a triple bond and a thiophenyl unit (complex **11**). Indeed, the H_2 proton of **11** is the most deshielded and exhibits the largest difference of chemical shifts $\delta(H_2) - \delta(H_3) = 0.95$ ppm in comparison with **7** (0.73 ppm) and **20** (0.80 ppm). The chemical shifts of the C_5H_4 ring protons of **11** and **20** have roughly the same values (4.39 and 4.58 ppm for **11** and 4.39 and 4.57 ppm for **20**), but they are shielded with respect to those of **7** (4.46 and 4.64 ppm).

Selected ^{13}C NMR data are reported in Table 3. The carbonyl carbon resonance signals of complexes **7**, **11**, and **20** at 216.0, 216.0, and 215.7 ppm are not arranged according to decreasing donating ability[24] but present

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[23] Ewbank, P. C.; Nuding, G.; Suenaga, H.; McCullough, R. D.; Shinkai, S. *Tetrahedron Lett.* **2001**, *42*, 155−158.

[24] (a) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y.; *J. Am. Chem. Soc.* **1972**, *94*, 3406−3408. In the case of Cr complexes, see: (b) Van Meurs, F.; Baas, J. M. A.; Van Bekkum, H. *J. Organomet. Chem.* **1976**, *113*, 353−359.

Table 3. Selected ^{13}C NMR Data (ppm)

		complex[a]		
entry	carbon	**7**[e]	**11**[f]	**20**[g]
1	C_1	95.8	97.8	96.3
2	C_2	105.2	100.0	105.7
3	C_3	83.9	83.6	83.6
4	$\delta(C_2) - \delta(C_3)$	21.3	16.4	22.1
5	C_4	148.3	148.3	149.2
6	C_β[c]	91.8	101.5	86.8[h]
7	C_α[d]	77.8	77.7	77.9[i]
8	$\delta(C_\beta) - \delta(C_\alpha)$	14.0	23.8	11.7
9	Cp	70.8	*b*	70.6
10	CO	216.0	216.0	215.7

[a] [D$_6$]Me$_2$CO at 29.55 ppm. [b] 70−74 ppm, broad band. [c] C_β, alkyne carbon β to C_5H_4FeCp. [d] C_α, alkyne carbon α to C_5H_4FeCp. [e] For the atom numbering, see Scheme 5. [f] For the atom numbering, see Scheme 6. [g] For the atom numbering, see Scheme 9. [h] Or 77.9 or 85.6 or 89.6 ppm. [i] Or 85.6 or 86.8 or 89.6 ppm.

similar values and seem to be independent of the nature of the spacer (Table 3, entry 10). In fact, these signals appear at almost the same frequency as (4-methoxyanisole)tricarbonylmanganese(I) tetrafluoroborate (216.7 ppm)[11i] and (anisole)tricarbonylmanganese(I) tetrafluoroborate (216.2 ppm),[9a] whereas for an arene substituted by a withdrawing group, for example (phenylbenzoate)tricarbonylmanganese tetrafluoroborate, the carbonyl carbon resonance is at lower frequency: 213.0 ppm.[8,22] These last data are in good agreement with the fact that if the chemical shifts of the carbonyl carbon nuclei increase, the CO ligands should be deshielded with increasing electron richness of the metal center.[25]

Two important features, however, can be emphasized. First, the 100.0 ppm resonance of the C_2 carbon of complex **11** occurs at a lower value than those of complexes **7** and **20** (Table 3, entry 2). The overall shielding effect on this carbon is unexpected, suggesting a stronger electron donation of the spacer. The second point concerns the unexpected chemical shift of the carbon C_β (β to the ferrocenyl unit) of complex **11** at 101.5 ppm (Table 3, entry 6) with respect to the 91.8 ppm value of the carbon C_β of complex **7.** The carbons C_α of complexes **7** and **11** resonate at 77.8 and 77.9 ppm. The downfield shift of the C_β carbon (101.5 ppm for **11**) can be plausibly rationalized by a less efficient overall electronic back-donation. It is also significant that the largest difference of chemical shifts $\delta(C_\beta) - \delta(C_\alpha)$ (Table 3, entry 8) is observed in the case of complex **11**. This corresponds also to the largest difference of chemical shifts for the H_2 and H_3 protons of complex **11** (see Table 2), and since the ^{1}H and ^{13}C NMR data of complexes **7** and **20** are very similar, this reveals the unique role of the thiophene unit in **11**.

The ^{13}C NMR chemical shifts of Cp ligands are also often taken as a guide to the degree of cationic character of an FeCp moiety, and for complex **20**, the position of the Cp resonance is similar to that of complex **7**. The extent of electron donation from the ferrocene substituent should thus be similar in both cases. The electron donation is delocalized through the extended π system of **20**, attenuating the effect on the cationic metal complex (compared to the result in **7**). In **11**, the positive charge on the $Mn(CO)_3$ moiety is significantly less than in **20** because of the direct attachment of the thiophene substituent on the cationic arene complex. Thus, the alkynes serve as electronically conducting links, but a relatively small amount of charge delocalization occurs, while direct attachment of the π-excessive heterocycle causes substantial transfer of positive charge to the thiophene, but not onto the ferrocene.

IR Spectroscopy. Complexes **7**, **11**, and **20** present two CO stretching modes in accordance with the local symmetry C_{3v} due to the A_1 and E bands of the $Mn(CO)_3$ groups.[26] The lowest frequencies of the Mn−CO unit are observed in the case of complexes **7** and **11** at 2012 and 2077 cm^{-1} and at 2015 and 2073 cm^{-1} respectively, showing a better overall electron-donating influence of the 1-(ferrocenylethynyl)-(4-methoxybenzene)thiophene and 2-(ferrocenylethynyl-5-(4-methoxybenzene)thiophene units as compared to that of complex **20** (2024 and 2080 cm^{-1}) (see the Experimental Section). The ν_{as} E band of the vibrationally coupled Mn−CO stretching modes contains two degenerate antisymmetric modes and so is combined with the ν_s A_1 band in the ratio 2:1 to calculate an estimate of the overall band position that can be related to the degree of positive charge on the metal, and the extent of back-donation of electron density into the π^* antibonding orbital of each CO ligand. The values obtained in this way (weighted mean band positions: **7**, 2034 cm^{-1}; **11**, 2034 cm^{-1}; **20**, 2043 cm^{-1}) show that complex **20** has substantially more positive charge at the (arene)$Mn(CO)_3$ end than the other two compounds, which are quite similar to one another.

UV−Vis Spectroscopy. The electronic spectra were recorded in dichloromethane, chloroform, and acetonitrile. The longest wavelength absorptions of **7** at 470 nm (CH_3CN), 494 nm (CH_2Cl_2), and 493 nm ($CHCl_3$) have small extinction coefficients and are assigned to the metal to ligand charge transfer (MLCT) band arising from a charge transfer from the manganese center to the π- and σ-bound ligands.[4,27] The next band at 302 nm (CH_3CN), 310 nm (CH_2Cl_2), and 314 nm ($CHCl_3$) has an intense absorption and arises from intraligand (IL) transitions with a high oscillator strength to the most extent from $\pi-\pi^*$ transitions. These assignments are supported by the moderate negative solvatochromism of the MLCT band, which indicates that the electronic ground state is more polar than the first excited state (an increase in solvent polarity causes a hypsochromic shift).[28] This is also in agreement with the highly polar nature of the cationic (η^6-arene)tricarbonylmanganese complexes, which can be attributed to the dominant μ_z-dipole vector component directed from the arene to the manganese carbonyl tripod (Figure 4). The $\pi-\pi^*$ transition intraligand charge transfer (ILCT) detected along the μ_x-dipole axis are also shifted hypsochromically upon an increase in solvent polarity, which reflects the polarizability of **7**. A canonical resonance structure of the dinuclear complex **7** can be represented by a cumulene structure with a cationic iron atom and a neutral manganese atom (Figure 5).

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[25] In the case of Cr complexes, see ref 4b and: Müller, T. J. J.; Lindner, H. J. *Chem. Ber.* **1996**, *129*, 607−613.

[26] (a) Davison, G.; Riley, E. M. *Spectrochim. Acta* **1971**, *27A*, 1649. (b) Van Meurs, F.; Baas, J. M. A.; Van Bekkum, H. *J. Organomet. Chem.* **1976**, *113*, 353−359.

[27] Kanis, D. R.; Ratner, M. A.; Marks, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10338−10357.

[28] Paley, M. S.; Harris, J. M. *J. Org. Chem.* **1989**, *54*, 3774−3778.

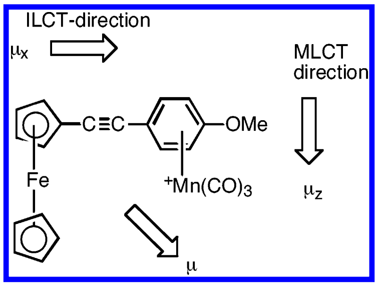

Figure 4. Additive nature of ground-state dipole vectors of carbonylmetal arenes with conjugated side chains.

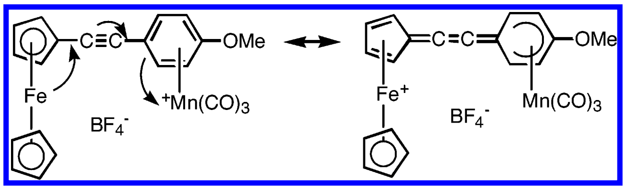

Figure 5. Mesomeric forms of complex **7**.

However, the X-ray structure data show clear alternating single- and triple-bond character in the three bonds of the link, thus reinforcing the assignment of an electronic ground state with alkyne, not cumulene, form. This crystal structure reveals that outward extension of the hapto-bound portions of the ligand to include contributions from *exo*-methylenecyclopentadiene (fulvene) and *exo*-methylenecyclohexadienyl bonding modes is not favored in the ground state, providing an illustration of the capacity of alkyne links to separate the charged and neutral metal complexes. The ILCT transitions and solvatochromic behavior observed in the UV spectrum, however, provide evidence for retained electronic communication through the π system.

The corresponding UV−vis bands for complex **11** (475 nm in CH_3CN, 481 nm in CH_2Cl_2, and 493 nm in $CHCl_3$) are similarly assigned to MLCT transitions and show similar solvatochromism with a significant shift between CH_3CN and the less polar chlorinated solvents. The degree of solvatochromism in the MLCT transitions of complex **20** was less pronounced (470 nm in CH_3CN, 480 nm in CH_2Cl_2, and 475 nm in $CHCl_3$). The ILCT transitions for the two complexes lie in the expected range (**11**, 344 nm in CH_3CN, 352 nm in CH_2Cl_2, and 352 nm in $CHCl_3$; **20**, 349 nm in CH_3CN, 359 nm in CH_2Cl_2, and 357 nm in $CHCl_3$).

Conclusion

We successfully developed a bimetallic Pd/Mn activation of carbon−chlorine bonds for the preparation of the first heterodinuclear Fe/Mn complexes involving a ferrocenyl unit conjugated to a cationic (η^6-arene)tricarbonylmanganese derivative. The (η^5-1-chlorocyclohexadienyl)tricarbonylmanganese starting material permits the creation of a carbon−carbon bond at the C_1 carbon. Despite the presence of a ferrocenyl group in the bimetallic complex, hydride abstraction by $CPh_3^+BF_4^-$ yields efficiently the corresponding cationic (η^6-arene)-tricarbonylmanganese complexes. These complexes have been studied in solution by different spectroscopic methods in order to explore the extent of electron transfer from one metal to the other and in the solid state by an X-ray structure of complex **7**, which provides further indications of pathways for delocalization of electron density through alkyne links. Alkyne links allow electronic communication but retain ground-state charge separation between the ends of the bimetallic molecule.

Experimental Section

All reactions and manipulations were routinely performed under a dry nitrogen atmosphere using Schlenk tube techniques. THF was dried over sodium benzophenone ketyl and distilled. Infrared spectra were measured on a Perkin-Elmer 1420 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on Bruker AC200 and AC400 spectrometers. Elemental analyses were performed by Le service de Microanalyses de l'Université Pierre et Marie Curie. UV−vis spectra were recorded on a UVIKON 923 spectrometer and mass spectra on a MALDI-TOF spectrometer. X-ray analysis: intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. Accurate cell dimensions and orientation matrixes were obtained from least-squares refinements of the setting angles of 25 well-defined reflections. No significant decay in the intensities of two standard reflections was observed during the course of the data collections. Crystal data, collection parameters, and other significant details are listed in the Supporting Information. The usual corrections for Lorentz and polarization effects were applied. Computations were performed by using CRYSTALS.[18a] Scattering factors and corrections for anomalous dispersion were taken from ref 18b. The structures were resolved by direct methods[19] and refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms, excluding the free BF_4^- anion. Hydrogen atoms were introduced in calculated positions, and only one overall isotropic displacement parameter was refined.

Preparation of 1-(ferrocenylethynyl)[η^5(1−5)-4-methoxycyclohexa-2,4-dienyl]tricarbonylmanganese (I) (6). Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$; 51 mg, 0.56 mmol), triphenylarsine (51 mg, 0.168 mmol), and ethynylferrocene (**5**;[16] 117 mg, 0.559 mmol) were introduced in a flask. (η^5-1-Chloro-4-methoxycyclohexa-2,4-dienyl)tricarbonylmanganese (**2**;[8] 158 mg, 0.559 mmol) was dissolved in NEt_3 (16 mL) and poured via a cannula into the flask. The reaction mixture was heated for 22 h at 40 °C with magnetic stirring. Filtration of the mixture on Celite and evaporation of the solution under reduced pressure gave a crude mixture which was purified on a silica gel chromatography column (petroleum ether/ether: 100/0 to 98/2). A red oil of **6** is obtained (198 mg, 0.434 mmol) in 78% yield. For $C_{21}H_{17}FeMnO_4$, $M_r = 455.7$. ^1H NMR (200 MHz, $CDCl_3$): δ 2.46 (d, $^2J = 12.5$ Hz, 1H, H_{6exo}), 2.94 (dd, $^2J = 12.5$ Hz, $^3J = 5$ Hz 1H, H_{6endo}), 3.05 (dd, $^3J = 6$, $^4J = 2.5$, 1H, H_5), 3.46 (s, 3H, OMe), 4.17 (m, 2H, C_5H_4), 4.20 (s, 5H, C_5H_5), 5.15 (d, $^3J = 5.5$, 1H, H_2), 5.75 (dd, $^3J = 5.5$, $^4J = 2.5$ Hz, 1H, H_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 32.1 (C_6), 36.1 (C_5), 49.4 (C_1), 54.4 (OMe), 65.1 (C_9), 67.4 (C_3), 68.8 (C_{10} or C_{11}), 70.1 (C_{12}), 71.4 (C_{10} or C_{11}), 85.2 (C_7 or C_8), 86.1 (C_7 or C_8), 96.3 (C_2), 143.2 (C_4), 222.6 (CO). UV (CH_3CN): λ 307 nm ($\epsilon = 10\,500$ L mol^{-1} cm^{-1}), λ 267 nm ($\epsilon = 13\,700$ L mol^{-1} cm^{-1}). UV (CH_2Cl_2): λ 311 nm ($\epsilon = 11\,600$ L mol^{-1} cm^{-1}), λ 274 nm ($\epsilon = 9547$ L mol^{-1} cm^{-1}). IR ($CHCl_3$): $\bar{\nu}$ 1951 cm^{-1} ($Mn(CO)_3$), 2018 cm^{-1} ($Mn(CO)_3$), 2201 cm^{-1} (CC). MS (MALDI-TOF, *m/z*): calcd for $C_{22}H_{17}FeMnO_4$, 455.98; found, 455.98 $[M]^+$.

Preparation of 1-(ferrocenylethynyl)[η^6(1−6)-4-methoxybenzene]tricarbonylmanganese(I) Tetrafluoroborate (7). Complex **6** was dissolved in dichloromethane (6 mL) (0.198 g, 0.434 mmol; 1 equiv). In another flask, triphenylcarbenium tetrafluoroborate, CPh_3BF_4 (172 mg, 0.521 mmol; 1.2 equiv), was dissolved in CH_2Cl_2 (5 mL). This solution was transferred via a cannula into the first flask and stirred for 1 h at room temperature with magnetic stirring. Freshly distilled Et_2O was added (40 mL): a precipitate formed. A red solid was recovered after filtration on a frit to afford **7** (216 mg, 0.399 mmol; 92%). Slow recrystallization from a petroleum ether/acetone mixture gave crystals (orthorhombic blocks, mp 143 °C) for an X-ray study. For $C_{22}H_{16}BF_4FeMnO_4$, $M_r = 541.8$. ^{1}H NMR (200 MHz, acetone-d_6): δ 4.23 (s, 3 H, OMe), 4.30 (s, 5 H, Cp), 4.46 (m, 2 H, H_{10} or H_{11}), 4.64 (m, 2 H, H_{10} or H_{11}), 6.62 (d, $^3J = 7.5$ Hz, 2 H, $H_{3,5}$), 7.35 (d, $^3J = 7.5$ Hz, 2 H, $H_{2,6}$). ^{13}C NMR (100 MHz, acetone-d_6): δ 58.8 (OMe), 61.7 (C_9), 70.8 (Cp), 70.9 (C_{10} or C_{11}), 72.8 (C_{10} or C_{11}), 77.8 (C_8), 83.9 ($C_{3,5}$), 91.8 (C_7), 95.8 (C_1), 105.2 ($C_{2,6}$), 148.3 (C_4), 216.0 (CO). UV (CH_3CN): λ 470 nm ($\epsilon = 1400$ L mol^{-1} cm^{-1}), λ 302 nm ($\epsilon =$ 11 700 L mol^{-1} cm^{-1}), λ 268 nm ($\epsilon = 14\,400$ L mol^{-1} cm^{-1}). UV (CH_2Cl_2): λ 494 nm ($\epsilon = 2000$ L mol^{-1} cm^{-1}), λ 310 nm ($\epsilon =$ 12 400 L mol^{-1} cm^{-1}), λ 269 nm ($\epsilon = 10\,500$ L mol^{-1} cm^{-1}). UV ($CHCl_3$): λ 493 nm ($\epsilon = 1800$ L mol^{-1} cm^{-1}), λ 314 nm ($\epsilon =$ 10 400 L mol^{-1} cm^{-1}), λ 272 nm ($\epsilon = 9400$ L mol^{-1} cm^{-1}). IR ($CHCl_3$): $\bar{\nu}$ 2012 cm^{-1} ($Mn(CO)_3^+$), 2077 cm^{-1} ($Mn(CO)_3^+$), 2213 cm^{-1} (CC). MS (MALDI-TOF, m/z): calcd for $C_{22}H_{16}FeMnO_4$, 454.98; found, 454.98 $[M - BF_4]^+$. Anal. Calcd for $C_{22}H_{16}BF_4FeMnO_4$: C, 48.76; H, 2.98; Found: C, 48.29; H, 3.11.

Synthesis of 2-(Ferrocenylethynyl)thiophene (8). Ethynylferrocene (**5**; 210 mg, 1 mmol; 1 equiv), *trans*-dichlorobis(triphenylphosphine)palladium ($PdCl_2(PPh_3)_2$; 35 mg, 0.05 mmol; 0.05 equiv), and copper(I) iodide (CuI; 10 mg, 0.05 mmol; 0.05 equiv) were dissolved in tetrahydrofuran (THF; 7 mL) and triethylamine (NEt_3; 7 mL). 2-Bromothiophene (0.107 mL, 1.1 mmol; 1.1 equiv) was added. The reaction mixture was heated for 2 h under reflux. The reaction mixture was cooled to room temperature and filtered on Celite. The solvents were removed under reduced pressure, and the residue was purified by silica gel chromatography column with petroleum ether. The orange solid **8** (185 mg, 0.634 mmol) was obtained in 64% yield and used without further purification for the next step. For $C_{16}H_{12}FeS$ $M_r = 291.9$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.23 (s, 5 H, Cp), 4.25 (m, 2 H, Cp), 4.49 (m, 2 H, Cp), 6.97 (dd, $^3J = 5$ Hz, $^3J = 3.5$ Hz, 1 H, H_4), 7.22 (m, 2 H, H_3 and H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.7 (C_5H_4 quat), 68.0 (C_5H_4), 69.0 (C_5H_5), 70.4 (C_5H_4), 77.7 (CC_{thio}), 91.3 (CC), 123.1 (C_2), 125.4 (C_3 or C_5), 126.0 (C_5 or C_3), 130.1 (C_4).

Synthesis of 2-(Ferrocenylethynyl)-5-(tributyltin)thiophene (9). In a flask a solution of diisopropylamine (0.124 mL, 0.873 mmol; 1.3 equiv) in THF (2 mL) was cooled to −78 °C, and then *n*-butyllithium (0.582 mL, 0.873 mmol; 1.3 equiv) was added and the mixture stirred for 15 min. In another flask, compound **8** (0.196 g, 0.671 mmol; 1 equiv) was dissolved in THF (4 mL) and cooled to −78 °C. Lithium diisopropylamide (LDA) was transferred into the other flask via a cannula. The reaction mixture was stirred for 1 h at −78 °C. Tributyltin chloride ($ClSnBu_3$; 0.200 mL, 0.738 mmol; 1 equiv) was added. The reaction mixture was stirred for 1 h at −78 °C and at room temperature for 1 h. The solution was extracted with Et_2O (20 mL) and distilled water (20 mL). The organic phase was washed twice with a saturated Na_2CO_3 solution (20 mL) and then with water (20 mL). The organic phase was dried over magnesium sulfate and filtered on Celite, and the solvents were removed under reduced pressure. The orange oil **9** was not purified because a carbon−tin cleavage occurred on silica gel column chromatography. For $C_{28}H_{38}FeSSn$ $M_r = 580.6$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.78−1.89 (m, 27 H, $Sn(Bu)_3$), 4.25 (m, 7 H, Cp and C_5H_4), 4.50 (m, 2 H, C_5H_4), 7.04 (d, $^3J = 3.5$ Hz, 1 H, H_3), 7.34 (d, $^3J = 3.5$ Hz, 1 H, H_4).

Synthesis of 2-(Ferrocenylethynyl)-5-[(η^5(1′−5′)-4′-methoxycyclohexa-2′,4′-dienyl)tricarbonylmanganese(I)]thiophene (10). Compound **9** used without purification was introduced into a flask (50 mL) with a water cooler. On the basis of the assumption that the yield of the preceding reaction was quantitative, triphenylarsine ($AsPh_3$; 39 mg, 0.127 mmol; 0.2 equiv) and tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$; 29 mg, 0.032 mmol; 0.05 equiv) were dissolved in DMF (5 mL). In another flask, (η^5-1-chloro-4-methoxycyclohexadienyl)tricarbonylmanganese (**2;** 0.179 mg, 0.634 mmol; 1 equiv) was dissolved in DMF (5 mL) and the solution was transferred via a cannula into the flask and stirred at room temperature for 15 h and for 1 h at room temperature. Distilled water (20 mL) and Et_2O (20 mL) were added. The organic phase was extracted three times with Et_2O (20 mL). The organic phases were washed five times with distilled water (20 mL), dried over magnesium sulfate, and filtered on Celite, and the solvents were evaporated under reduced pressure. The crude material was purified on a silica gel chromatography column with petroleum ether/Et_2O (100/0 to 98/2) as eluent, which afforded the orange compound **10** (0.086 g, 0.160 mmol; 25% in two steps). For $C_{26}H_{19}FeMnO_4S$ $M_r = 537.8$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.57 (d, $^2J = 12$ Hz, 1 H, $H_{6'exo}$), 3.14 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 1 H, $H_{5'}$), 3.23 (dd, $^2J = 12$ Hz, $^3J = 6$ Hz, 1 H, $H_{6'endo}$), 3.51 (s, 3 H, OMe), 4.23 (m, Cp or C_5H_4), 4.58 (m, 2 H, C_5H_4), 5.26 (d, $^3J = 5.5$ Hz, 1 H, $H_{2'}$), 5.79 (dd, $^3J = 5.5$ Hz, $^4J = 2$ Hz, 1 H, $H_{3'}$), 6.65 (d, $^3J = 3.5$ Hz, 1 H, H_{thio}), 7.00 (d, $J^3 = 3.5$ Hz, 1 H, H_{thio}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 30.3 ($C_{6'}$), 36.9 ($C_{5'}$), 54.5 (OMe), 62.2 ($C_{1'}$ or C_5H_4 quat), 64.7 (C_5H_4 quat or $C_{1'}$), 65.9 ($C_{3'}$), 69.1 (C_5H_4), 70.1 (Cp), 71.4 (C_5H_4), 78.9 (CC), 90.9 ($C_{2'}$), 93.7 (CC), 122.2 (C_3 or C_4), 123.1 ($C_{thio,quat}$), 131.9 (C_4 or C_3), 143.2 ($C_{4'}$), 146.6 ($C_{thio,quat}$), 222.0 (CO). UV (CH_3CN): λ 370 nm ($\epsilon = 16\,270$ L mol^{-1} cm^{-1}), λ 269 nm ($\epsilon = 14\,255$ L mol^{-1} cm^{-1}). UV (CH_2Cl_2): λ 377 nm ($\epsilon = 16\,100$ L mol^{-1} cm^{-1}), λ 265 nm ($\epsilon = 15\,900$ L mol^{-1} cm^{-1}). UV ($CHCl_3$): λ 377 nm ($\epsilon = 15\,600$ L mol^{-1} cm^{-1}), λ 265 nm ($\epsilon = 16\,400$ L mol^{-1} cm^{-1}). IR ($CHCl_3$): $\bar{\nu}$ 1943 cm^{-1} ($Mn(CO)_3$), 2017 cm^{-1} ($Mn(CO)_3$), 2208 cm^{-1} (CC).

Alternative Synthesis of 2-(Ferrocenylethynyl)-5-[η^5-(1′−5′)-(4′-methoxycyclohexa-2′,4′-dienyl)tricarbonylmanganese(I)]thiophene (10). In a flask, a solution of diisopropylamine (4 mL, 28.4 mmol; 1.1 equiv) in THF (15 mL) was cooled to −78 °C, *n*-butyllithium (17.75 mL, 28.4 mmol; 1.1 equiv) was added, and the solution was stirred for 15 min at −78 °C. In another flask, 2-bromothiophene (2.5 mL, 25.8 mmol; 1 equiv) in THF (15 mL) was cooled to −78 °C. LDA was transferred into the other flask via a cannula, and after the solution was stirred for 1 h, $ClSnBu_3$ was added (7.7 mL, 28.4 mmol; 1.1 equiv). The solution was stirred for 1 h at −78 °C and 1 h at room temperature. Et_2O (20 mL) and saturated Na_2CO_3 (20 mL) were added. The solution was extracted three times with saturated Na_2CO_3 (20 mL) and with water (20 mL). The organic phase was dried over magnesium sulfate, filtered on Celite, and evaporated under reduced pressure, giving 2-bromo-5-(tributylstannyl)thiophene (**12**) as a yellow liquid in quantitative yield (11.66 g, 25.82 mmol). For $C_{16}H_{29}BrSSn$ $M_r = 451.7$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.85−1.63 (m, 27 H, $Sn(Bu)_3$), 6.91 (d, $^3J = 3.5$ Hz, 1 H, H_2 or H_3), 7.13 (d, $^3J =$ 3.5 Hz, 1 H, H_2 or H_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 11.0 (Bu), 13.8 (Bu), 27.4 (Bu), 29.0 (Bu), 116.4 (C_1 or C_4), 131.0 (C_2 or C_3), 135.9 (C_2 or C_3), 139.6 (C_1 or C_4). In a flask (50 mL) was introduced (η^5-1-chloro-4-methoxycyclohexa-2,4-dienyl)tricarbonylmanganese (**2**; 0.282 mg, 1 mmol; 1 equiv), triphenylarsine ($AsPh_3$; 46 mg, 0.15 mmol; 0.15 equiv), and tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$; 46 mg, 0.05 mmol; 0.05 equiv) in DMF (5 mL). The mixture was heated for 10 min at 40 °C. In another flask, 2-bromo-5-(tributylstannyl)thiophene (**12;** 0.452 g, 1 mmol; 1 equiv) was dissolved in DMF (5 mL). The solution was transferred into the other flask via a cannula. The reaction mixture was heated to 40 °C for 1.5 h. After Et_2O (20 mL) and distilled water (20 mL) were added, the organic phase was recovered. The water phase was extracted four times with ethyl acetate. Organic phases were collected, washed with water, dried over $MgSO_4$, and evaporated under reduced pressure. Purification by silica gel column chromatography with petroleum ether as eluent gave the yellow solid 2-bromo-5-[η^5(1−5)-4-methoxycyclohexa-2,4-dienyl)tricarbonylmanganese]thiophene (**13**; 0.198 g, 0.484 mmol) in 48% yield. For $C_{14}H_{10}BrMnO_4S$ $M_r = 408.9$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54 (d, $^2J = 12$ Hz, 1 H, $H_{6'exo}$), 3.12 (dd, $^3J = 6$ Hz, $^4J = 2$ Hz, 1 H, $H_{5'}$), 3.18 (dd, $^2J = 12$ Hz, $^3J = 6$ Hz, 1 H, $H_{6'endo}$), 3.51 (s, 3 H, OMe), 5.17 (d, $^3J = 5.5$ Hz, 1 H,

$H_{2'}$), 5.77 (dd, $^3J = 5.5$ Hz, $^4J = 2$ Hz, 1 H, $H_{3'}$), 6.53 (d, $^3J = 3.5$ Hz, 1 H, H_{thio}), 6.85 (d, $^3J = 3.5$ Hz, 1 H, H_{thio}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 30.2 ($C_{6'}$), 36.8 ($C_{5'}$), 54.5 (OMe), 61.6 ($C_{1'}$), 65.7 (CH, $C_{3'}$), 90.8 ($C_{2'}$), 111.0 (C_5), 122.4 (C_3 or C_4), 130.5 (C_4 or C_3), 143.2 ($C_{4'}$), 147.5 (C_2), 222.5 (CO). IR ($CHCl_3$): $\bar{\nu}$ 1943 cm^{-1} ($Mn(CO)_3$), 2016 cm^{-1} ($Mn(CO)_3$). In a flask (50 mL), 2-bromo-5-[η^5(1−5)-4-methoxycyclohexa-2,4-dienyl)tricarbonylmanganese]thiophene (**13**; 0.198 g, 0.484 mmol; 1 equiv), *trans*-dichlorobis(triphenylphosphine)palladium ($PdCl_2(PPh_3)_2$; 17 mg, 0.024 mmol; 0.05 equiv), and copper(I) iodide (CuI; 5 mg, 0.024 mmol; 0.05 equiv) were dissolved in THF (2 mL) and triethylamine NEt_3 (5 mL). The reaction mixture was heated under reflux for 10 min. In another flask, ethynylferrocene (0.112 g, 0.532 mmol; 1.1 equiv) was dissolved in THF (3 mL). The solution was transferred via a cannula and stirred for 30 min. The solution was filtered on Celite and the solvent evaporated under reduced pressure. The residue was purified by silica gel column chromatography with a mixture of petroleum ether and ether (100/0 to 98/2). The orange powder **10** (0.203 g, 0.378 mmol) was obtained in 78% yield.

Synthesis of 2-(Ferrocenylethynyl)-5-{[η^6(1−6′)-(4′-methoxybenzene)]tricarbonylmanganese}thiophene Tetrafluoroborate (11). In a flask, **10** (0.198 g, 0.434 mmol; 1 equiv) was dissolved in dichloromethane (6 mL). In another flask, triphenylcarbenium tetrafluoroborate (CPh_3BF_4; 0.172 g, 0.521 mmol; 1.2 equiv) was dissolved in dichloromethane (5 mL). This solution was transferred into the first flask via a cannula and stirred for 30 min at room temperature. Freshly distilled diethyl ether (40 mL) was introduced into the medium, and an orange precipitate formed, affording **11** in 92% yield (216 mg, 0399 mmol). Mp: 129 °C. For $C_{26}H_{18}BF_4$-$FeMnO_4S$ $M_r = 536.99$. ^1H NMR (200 MHz, acetone-d_6): δ 4.22 (s, 3 H, OMe), 4.28 (s, 5 H, Cp), 4.39 (m, 2 H, C_5H_4), 4.57 (m, 2 H, C_5H_4), 6.63 (d, $^3J = 7.5$ Hz, 2 H, $H_{3,5}$), 7.35 (d, $^3J = 4$ Hz, 1 H, H_{thio}), 7.43 (d, $^3J = 7.5$ Hz, 2 H, $H_{2,6}$), 7.48 (d, $^3J = 4$ Hz, 1 H, H_{thio}). ^{13}C NMR (100 MHz, acetone-d_6): δ 58.9 (OMe), $70{-}74_{br}$ (C_p and C_5H_4) (CC), 83.6 ($C_{3,5}$), 97.8 (C_1), 100.0 ($C_{2,6}$), 101.5 (CC), 128.8 ($C_{thio\ quat}$), 130.0 (C_{thio}), 133.4 (C_{thio}), 134.3 ($C_{thio,quat}$), 148.7 (C_4), 216.0 (CO). UV (CH_2Cl_2): λ 269 nm (ϵ = 16 700 L mol^{-1} cm^{-1}), λ 352 nm (ϵ = 21 300 L mol^{-1} cm^{-1}), λ 481 nm (ϵ = 3400 L mol^{-1} cm^{-1}). UV ($CHCl_3$): λ 268 nm (ϵ = 17 000 L mol^{-1} cm^{-1}), λ 352 nm (ϵ = 20 800 L mol^{-1} cm^{-1}), λ 493 nm (ϵ = 3300 L mol^{-1} cm^{-1}). UV (CH_3CN): λ 270 nm (ϵ = 17 300 L mol^{-1} cm^{-1}), λ 344 nm (ϵ = 23 300 L mol^{-1} cm^{-1}), λ 475 nm (ϵ = 3100 L mol^{-1} cm^{-1}). IR ($CHCl_3$): $\bar{\nu}$ 2015 cm^{-1} ($Mn(CO)_3^+$), 2073 cm^{-1} ($Mn(CO)_3$), 2202 cm^{-1} (CC). IR (solid state): $\bar{\nu}$ 2020 cm^{-1} ($Mn(CO)_3^+$), 2068 cm^{-1} ($Mn(CO)_3^+$), 2360, 2341 cm^{-1} (CC). MS (MALDI-TOF, *m/z*): calcd for $C_{26}H_{18}FeMnO_4S$, 536.99; found, 536.96 $[M - BF_4]^+$. Anal. Calcd for $C_{26}H_{18}BF_4$-$FeMnO_4S$ ($M_r = 623.97$): C, 50.00; H, 2.91. Found: C, 49.31; H, 2.96.

Synthesis of 2-(Ferrocenylethynyl)-5-{[η^5(1′−5′)-(4′-methoxycyclohexa-2′,4′-dienyl)tricarbonylmanganese]ethynyl}thiophene (19). In a flask (50 mL) was added *trans*-dichlorobis(triphenylphosphine)palladium ($PdCl_2(PPh_3)_2$; 18 mg, 0.025 mmol; 0.05 equiv), and copper(I) iodide (CuI; 5 mg, 0.025 mmol; 0.05 equiv) was dissolved in THF (2 mL) and triethylamine NEt_3 (5 mL). 2,5-Dibromothiophene (**14**; 0.115 mL, 1 mmol; 2 equiv) was added and the reaction mixture heated under reflux for 10 min. In another flask, ethynylferrocene (**5**; 0.105 g, 0.5 mmol; 1 equiv) was dissolved in THF (3 mL) and transferred into the first flask via a cannula. The mixture was stirred for 30 min under reflux. Filtration on Celite and evaporation of the solvents under reduced pressure gave a residue which was purified by silica gel column chromatography (petroleum ether/ether: 100/0 to 90/0). A red powder of **15** was obtained (0.099 g, 0.267 mmol) in 53% yield. For $C_{16}H_{11}BrFeS$, $M_r = 370.8$. ^1H NMR (200 MHz, $CDCl_3$): δ 4.23 (s, 5 H, Cp), 4.25 (m, 2 H, C_5H_4), 4.48 (m, 2 H, C_5H_4), 6.91 (d, $^3J = 4$ Hz, 1 H, H_{thio}), 6.94 (d, $^3J = 4$ Hz, 1 H, H_{thio}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.2 ($C_{quat}C_5H_4$), 68.1 (C_5H_4), 69.0 (Cp), 70.4 (C_5H_4), 76.8 (CC), 92.6 (CC), 110.9 ($C_{thio,quat}$), 124.9 ($C_{thio,quat}$), 128.9 (C_{thio}), 130.6 (C_{thio}). The minor product **16** was obtained, but only a ^1H NMR spectrum of the crude material has been recorded. In a flask (50 mL), the bromothiophene **15** (0.210 g, 0.566 mmol; 1 equiv) and *trans*-dichlorobis(triphenylphosphine)palladium ($PdCl_2(PPh_3)_2$; 20 mg, 0.028 mmol; 0.05 equiv) and CuI (6 mg, 0.028 mmol; 0.05 equiv) were dissolved in THF (7 mL) and NEt_3 (7 mL). (Trimethylsilyl)acetylene (0.120 mL, 0.849 mmol; 1.5 equiv) was added and the reaction mixture heated under reflux with magnetic agitation for 3 h. The reaction mixture was filtered on Celite, and the solvents were evaporated under reduced pressure. The crude product was purified by silica gel column chromatography with petroleum ether as eluent. The orange solid **17** (0.220 g, 0.566 mmol) was obtained quantitatively. For $C_{21}H_{20}FeSSi$ $M_r = 388.0$. ^1H NMR (200 MHz, $CDCl_3$): δ 0.24 (s, 9 H, $Si(Me)_3$), 4.24 (s, 5 H, Cp), 4.25 (m, 2 H, C_5H_4), 4.49 (m, 2 H, C_5H_4), 7.01 (d, $^3J = 3.5$ Hz, 1 H, H_{thio}), 7.07 (d, $^3J = 3.5$ Hz, 1 H, H_{thio}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0 ($SiMe_3$), 64.4 (C_{quat} C_5H_4), 69.4 (C_5H_4), 70.3 (Cp), 71.7 (C_5H_4), 78.6 (CC), 93.7 (CC), 97.3 (CC), 99.8 (CC), 123.7 ($C_{thio,quat}$), 125.8 ($C_{thio,quat}$), 131.0 (C_{thio}), 132.7 (C_{thio}). Compound **17** (0.220 g, 0.566 mmol; 1 equiv) was dissolved in MeOH (15 mL). A solution of sodium hydroxide (0.670 mL, $c = 2$ N; 2.2 equiv) was then added. The reaction mixture was stirred at room temperature for 3 h and extracted with water and Et_2O. The organic phase was washed with a saturated solution of NaCl, dried over $MgSO_4$, and filtered on Celite. Evaporation of the solvents under reduced pressure afforded quantitatively the red oil **18** (0.179 g, 0.566 mmol). For $C_{28}H_{12}FeS$ $M_r = 315.9$. ^1H NMR (200 MHz, $CDCl_3$): δ 3.37 (s, 1 H, CCH), 4.25 (m, 7 H, Cp, C_5H_4), 4.51 (m, 2 H, C_5H_4), 7.04 (d, $^3J = 4$ Hz, 1 H, H_{thio}), 7.13 (d, $^3J = 4$ Hz, 1 H, H_{thio}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 64.2 (C_5H_4 C_{quat}), 69.3 (C_5H_4), 70.2 (Cp), 71.6 (C_5H_4), 78.3 (CC), 82.0 (CCH), 93.9 (CC), 122.3 ($C_{thio,quat}$), 126.1 ($C_{thio,quat}$), 130.8 (C_{thio}), 133.1 (C_{thio}). (η^5-1-Chloro-4-methoxycyclohexadienyl)tricarbonylmanganese (**2**; 0.134 mg, 0.472 mmol; 1 equiv), triphenylarsine ($AsPh_3$; 29 mg, 0.094 mmol; 0.20 equiv), and tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$; 22 mg, 0.024 mmol; 0.05 equiv) were introduced in a flask. NEt_3 (7 mL) was added. The reaction mixture was heated at 40 °C for 10 min. In another flask, the acetylene compound **18** (0.149 g, 0.472 mmol; 1 equiv) was dissolved in NEt_3 (8 mL). This solution was transferred into the first flask via a cannula. The reaction mixture was stirred for 2 h at 40 °C and filtered on Celite, and the solvents were evaporated under reduced pressure. A red oil was obtained, which was purified by silica gel column chromatography (petroleum ether/ether:100/0 to 90/10), giving compound **19** (0.128 g, 0.228 mmol) in 48% yield. For $C_{28}H_{19}FeMnO_4S$ $M_r = 561.8$. ^1H NMR (200 MHz, $CDCl_3$): δ 2.46 (d, $^2J = 13$ Hz, 1 H, H_{6exo}), 2.94 (dd, $^2J = 13$ Hz, $^3J = 6$ Hz, 1 H, H_{6endo}), 3.08 (dd, $^3J = 6$ Hz, $^4J = 2.5$ Hz, 1 H, H_5), 3.46 (s, 3 H, OMe), 4.23 (s, 5 H, H_{18}), 4.26 (m, 2 H, H_{16} or H_{17}), 4.48 (m, 2 H, H_{16} or H_{17}), 5.24 (d, $^3J = 6$ Hz, 1 H, H_2), 5.80 (dd, $^3J = 6$ Hz, $^4J = 2.5$ Hz, 1 H, H_3), 6.98 (d, $^3J = 4$ Hz, 1 H, H_{10} or H_{11}), 7.01 (d, $^3J = 4$ Hz, 1 H, H_{10} or H_{11}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 31.8 (C_6), 36.5 (C_5), 46.2 (C_1), 54.5 (OMe), 64.4 (C_{15}), 68.3 (C_3), 69.2 (C_{16} or C_{17}), 70.1 (C_{18}), 71.5 (C_{16} or C_{17}), 78.5 (CC), 78.9 (CC), 93.7 (CC), 94.8 (CC), 97.1 (C_2), 123.7 (C_9 or C_{12}), 125.3 (C_9 or C_{12}), 131.0 (C_{10} or C_{11}), 131.7 (C_{10} or C_{11}), 143.3 (C_4), 221.9 (CO). UV (CH_3CN): λ 355 nm (ϵ = 27 700 L mol^{-1} cm^{-1}), λ 264 nm (ϵ = 21 900 L mol^{-1} cm^{-1}). UV (CH_2Cl_2): λ 358 nm (ϵ = 27 000 L mol^{-1} cm^{-1}) UV ($CHCl_3$): λ 358 nm (ϵ = 26 900 L mol^{-1} cm^{-1}). IR ($CHCl_3$): $\bar{\nu}$ 1948 cm^{-1} ($Mn(CO)_3$), 2019 cm^{-1} ($Mn(CO)_3$). MS (MALDI-TOF, *m/z*): calcd for $C_{28}H_{19}FeMnO_4S$, 561.97; found, 561.97 $[M]^+$.

Synthesis of 2-(Ferrocenylethynyl)-5-{[(η^6(1′−6′)-4′-methoxyphenyl)tricarbonylmanganese]ethynyl}thiophene Tetrafluoroborate (20). Compound **19** (0.057 g, 0.102 mmol; 1 equiv) was dissolved in dichloromethane (5 mL) in a flask. In another flask triphenylcarbenium tetrafluoroborate (CPh_3BF_4; 0.034 g; 0.102 mmol; 1 equiv) was dissolved in dichloromethane (5 mL). This solution was transferred via a cannula into the first flask. The reaction mixture was stirred for 30 min, and freshly distilled Et_2O was added. An orange precipitate appeared and was collected by filtration to afford **20** (0.066 g, 0.102 mmol), obtained in quantitative yield. For $C_{28}H_{18}BF_4FeMnO_4S$ $M_r = 647.6$. Mp: 151 °C. ^1H NMR (200 MHz, acetone-d_6): $\delta = 4.24$ (s, 3 H, OMe), 4.28 (s, 5 H, Cp), 4.39 (m, 2 H, C_5H_4), 4.57 (m, 2 H, C_5H_4), 6.63 (d, $^3J = 7.5$ Hz, 2 H, $H_{3,5}$), 7.28 (d, $^3J = 4$ Hz, 1 H, H_{thio}), 7.43 (d, $^3J = 7.5$ Hz, 2 H, $H_{2,6}$), 7.48 (d, $^3J = 4$ Hz, 1 H, H_{thio}). ^{13}C NMR (100 MHz, acetone-d_6): δ 59.0 (OMe), 64.0 (C_{15}), 70.2 (C_5H_4), 70.6 (C_{18}), 72.1 (C_5H_4), 77.9 (CC), 83.6 ($C_{3,5}$), 85.6 (CC), 86.8 (CC), 89.6 (CC), 96.3 (C_1), 105.7 ($C_{2,6}$), 120.3 ($C_{thio,quat}$), 129.0 ($C_{thio,quat}$), 132.3 (C_{thio}), 136.3 (C_{thio}), 149.2 (C_4), 215.7 (CO). UV (CH_3CN): λ 470 nm ($\epsilon = 3100$ L mol^{-1} cm^{-1}), λ 349 nm ($\epsilon = 31\,400$ L mol^{-1} cm^{-1}), λ 260 nm ($\epsilon = 13\,400$). UV (CH_2Cl_2): λ 480 nm ($\epsilon = 4400$ L mol^{-1} cm^{-1}), λ 359 nm ($\epsilon = 27\,300$ L mol^{-1} cm^{-1}), λ 264 nm ($\epsilon = 23\,900$ L mol^{-1} cm^{-1}). UV ($CHCl_3$): λ 475 nm ($\epsilon = 3800$ L mol^{-1} cm^{-1}), λ 357 nm ($\epsilon = 28\,400$ L mol^{-1} cm^{-1}), λ 264 nm ($\epsilon = 24\,600$ L mol^{-1} cm^{-1}). IR ($CHCl_3$): $\bar{\nu}$ 2024 cm^{-1} ($Mn(CO)_3^+$), 2080 cm^{-1} ($Mn(CO)_3^+$), 2248, 2200 cm^{-1} (CC). MS (MALDI-TOF, *m*/*z*): calcd for $C_{28}H_{18}FeMnO_4S$, 560.97; found, 560.90 $[M - BF_4]^+$. Anal. Calcd for $C_{28}H_{18}BF_4FeMnO_4S$ ($M_r = 647.97$): C, 51.85; H, 2.80. Found: C, 51.71, H, 2.59.

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Supporting Information Available: Tables giving crystal data, atomic coordinates, and bond distances and angles and figures giving additional views of complex **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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