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

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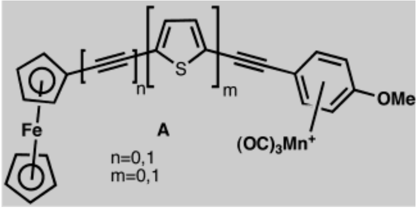
Palladium-catalyzed Sonogashira coupling reactions of the neutral [η^5(1−5)-1-ethynyl-4-methoxycyclohexa-2,4-dienyl]tricarbonylmanganese(I) (**4**) and (η^6-chlorobenzene)tricarbonylchromium (**5**) yields the dinuclear 1-[η^6- phenylethynyl]tricarbonylchromium−[η^5(1−5)-methoxycyclohexa-2,4-dienyl]tricarbonylmanganese complex **6**, which upon hydride abstraction affords the corresponding dinuclear diphenylacetylene η^6-Mn/η^6-Cr complex **7**. This study has been extended to the case of dinuclear η^6-Mn/η^6-Cr linked to different spacers comprising a thiophene, a triple bond, or a combination of them.

Introduction

The reactivity change that arises upon the complexation of an arene to tricarbonylchromium or -manganese fragments allows a variety of transformations to be carried out that are otherwise inaccessible.[1] Whereas (η^6-arene)tricarbonylchromium(0) complexes have been studied extensively and have a wide range of applications from their use in total synthesis[2] through their growing importance in the elaboration of polymetallic structures[3] with potential material science activity, isoelectronic cationic (η^6-arene)tricarbonylmanganese complexes[4] have been less developed for several reasons. First of all, the selective access to some substituted manganese(I) complexes, very important for further developments, remained unsolved until very recently.[4f] Second, whereas palladium-catalyzed coupling reactions in the field of chromium chemistry, defined as bimetallic Pd/Cr activation, are well known and are widely used,[1g,4k] only addition and substitution reactions at the π-system of manganese complexes were known up to 2001, when bimetallic Pd/Mn activation was developed.[4h−l] This discovery allowed us to develop a general strategy for unprecedented functionalization of cationic (η^6-arene)Mn complexes through the Pd-catalyzed reaction of (η^5-chlorocyclohexadienyl)Mn(CO)$_3$ complexes to obtain the first EWG-substituted[19] (η^6-arene)Mn(CO)$_3$ complexes, greatly expanding the scope of these complexes.[4k] This methodology was then successfully applied to the synthesis of heterobimetallic manganese−ferrocene complexes A.[3v] Now we report the synthesis of cationic (η^6-arene)Mn(CO)$_3$ tetrafluoroborate complexes connected to neutral (η^6-arene)Cr(CO)$_3$ as well as three X-ray



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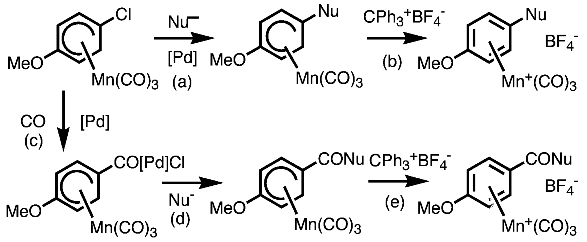
structures of mono- and dinuclear complexes **6**, **7**, and **22**, showing clearly that despite the presence of a (η^6-arene)Cr(CO)$_3$ group in the bimetallic complex, hydride abstraction by CPh$_3$$^+BF_4$$^-$ yields efficiently the corresponding cationic [(η^6-arene)Mn(CO)$_3$]$^+$ complexes. The results presented here establish the generality of the application of the new Mn/Pd activation approach to the synthesis of structures of this type.

Results and Discussion

The general strategy used for the functionalization of arene−Mn complexes consisted of a two-step synthesis in the case of (η^6-arene)tricarbonylmanganese mononuclear complexes.[4k] The first step involves a palladium-catalyzed strategy for functionalization of (η^5-chlorocyclohexadienyl)Mn(CO)$_3$ derivatives (path a), which preserves the CH$_2$ methylene group and allows the rearomatization (path b) of the η^5 complex by hydride abstraction, leading to original disubstituted (η^6-arene)-Mn(CO)$_3$$^+$ tetrafluoroborate complexes (Scheme 1). Thus, the palladium-catalyzed Stille reaction, amination, and etherification, thioetherification, and phosphorylation are successfully performed, giving *C*-(η^5-substituted-cyclohexadienyl)Mn(CO)$_3$ complexes and unprecedented N-, O-, S-, and P-substituted (η^5-cyclohexadienyl)Mn-(CO)$_3$ complexes using a nonelaborated Pd$_2$dba$_3$/AsPh$_3$ catalytic system. Exploiting the facile palladium-catalyzed ipso substitution of the chlorine atom in (η^5-chlorocyclohexadienyl)Mn(CO)$_3$, the reaction has been performed under a CO atmosphere (path c). The generated acylpalladate intermediate reacts with various nucleophiles, affording again unprecedented (η^5-electron-withdrawing-group-substituted-cyclohexadienyl)-Mn(CO)$_3$ complexes (path d). Thus, aryl, alkyl ketones, ynones, and enones, as well as carboxylic esters, thioesters, and amides are efficiently obtained after removal of the exo hydrogen.[1g,4k] We extended this study in the case of dinuclear Cr and Mn complexes by introducing, as nucleophiles, unsaturated groups which could be further linked to Cr complexes.

Scheme 1. Two-Step Synthesis of Cationic (arene)Mn(CO)$_3$ Complexes



Synthesis of 7. (η^5-1-chloro-4-methoxycyclohexa-2,4-dienyl)Mn(CO)$_3$ (**2**) is commonly prepared by regioselective hydride addition of LiAlH$_4$ to the cationic (η^6-1-chloro-4-methoxybenzene)Mn$^+$(CO)$_3$[4e,5,6] ortho to the chloride atom. The choice of this complex was intentional. Indeed, due to the electron-donating properties of the methoxy group of (η^6-1-chloro-4-methoxybenzene)-tricarbonylmanganese, addition is directed meta to the methoxy group. Furthermore, there is a synergic effect of the chlorine atom at the same position, explaining why no other isomer is detected by addition of an hydride.[1f] A Sonogashira palladium-catalyzed coupling reaction[7] of the chloro derivative **2**[4e] with (trimethylsilyl)acetylene turned out to be an efficient method for the preparation of the (trimethylsilyl)acetylene η^5-Mn-(CO)$_3$ complex **3** as an orange oil in 86% yield. Deprotection of the silylated alkyne with NaOH and MeOH in THF[3b] furnishes the acetylene complex **4** in quantitative yield as a pure yellow oil. The reaction of **4** with (chlorobenzene)tricarbonylchromium (**5**)[8] in the presence of 5 mol % of Pd$_2$dba$_3$, NEt$_3$, and AsPh$_3$ furnishes under mild conditions the dinuclear η^5-Mn/η^6-Cr complex **6** as an orange powder in 83% yield (Scheme 2). Rearomatization of this η^5 complex by hydride abstraction with CPh$_3$$^+BF_4$$^-$ affords an orange-red tetrafluoroborate of 1-(η^6-phenylethynyl)tricarbonylchromium-

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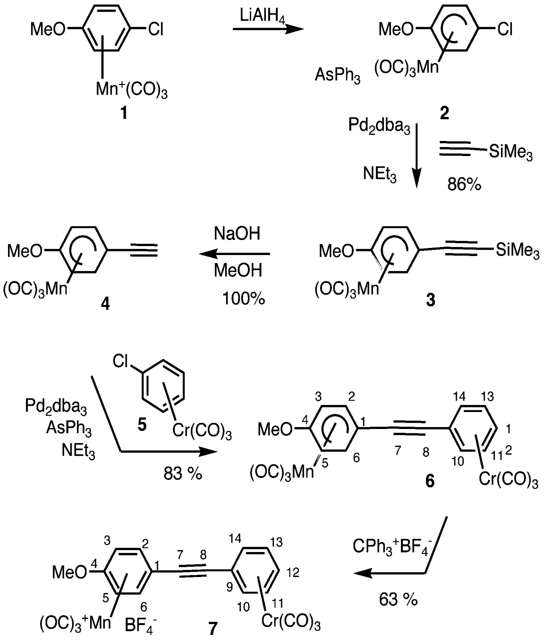
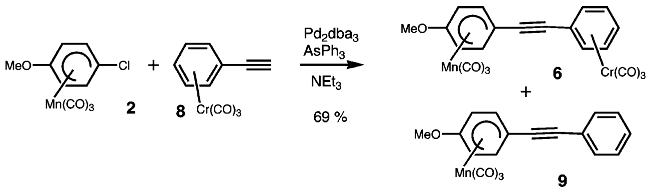
Scheme 2. Synthesis of Dinuclear Complex 7



Scheme 3. Alternative Synthesis of Complex 6



(0)−(η^6-4-methoxycyclohexa-2,4-dienyl)tricarbonylmanganese(I) (**7**) in 63% yield. An alternative route to the preparation of the heterodinuclear complex **6** could also be considered (Scheme 3). Indeed, a Sonogashira reaction with (η^6-phenylethynyl)tricarbonylchromium (**8**)[3b] and (η^5-cyclohexadienyl)tricarbonylmanganese complex **2** in the presence of Pd_2dba_3, $AsPh_3$ in NEt_3 yielded the dinuclear complex **6** in 69% yield but also the mononuclear complex **9** in 22% yield, which corresponds to the decoordination of the $Cr(CO)_3$ unit.

X-ray Analysis of Complex 6. Crystals of complex **6** were grown in a petroleum ether/acetone mixture. Three CAMERON views, some selected bond lengths, and crystal data are reported in Figures 1 and 2 and Tables 1 and 2.[9] Three important features can be emphasized. First, the η^5 structure of the coupling product is confirmed, showing, as usually described, five coplanar sp^2 carbons, while the remaining sp^3 carbon is located out of this plane away from the metal. The dihedral angle of 36° between [$C_1C_6C_5$] and [$C_1C_2C_3C_4C_5$] planes is in good agreement with literature data.[10] The Mn−C bond lengths ranging from 2.14 to 2.25 Å (average 2.19 Å) are similar to the corresponding distances of other methoxycyclohexadienyl−Mn complexes.[10] The Cr−C bond lengths range from 2.19 to 2.24 Å (average 2.20 Å). Second, the regioselectivity of the ipso process of the Pd-catalyzed reaction is clearly evidenced, the triple bond being linked to the arene carbon which originally bore the chlorine atom. The conformation of the $Mn(CO)_3$ tripod is such that the sp^3 carbon is eclipsed by one Mn−CO bond. Furthermore, the Cr arene ring, the cyclohexadienyl ring, and the C_7 and C_8 atoms were found to be almost coplanar. The dihedral angle between the [$C_1C_2C_3C_4C_5$] and [$C_9C_{10}C_{11}C_{12}C_{13}C_{14}$] planes is 20°. The Cr−C bond lengths range

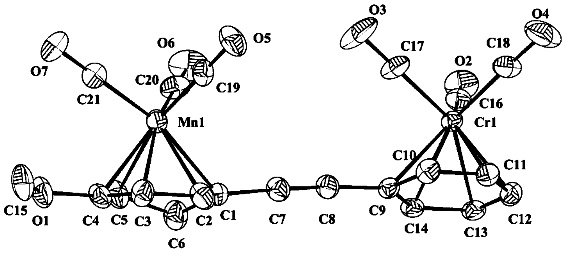


Figure 1. CAMERON view of the molecular structure of complex **6**.

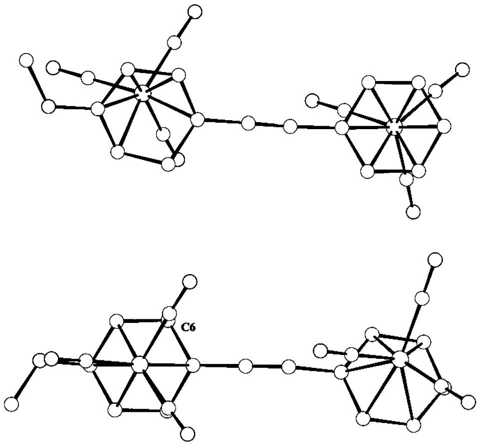


Figure 2. CAMERON views of the molecular structure of complex **6** with the $Cr(CO)_6$ tripod and the $Mn(CO)_3$ tripod projected onto the arene ring.

Table 1. Selected Bond Lengths (Å) of Complexes 6, 7, and 22

	6^b	7^b	22^c		6^b	7^b	22^c
$Mn-C_1$	2.21	2.20		γ(Mn)	0	−17	
$Mn-C_2$	2.25	2.16		$Cr-C_9$	2.24	2.21	2.20
$Mn-C_3$	2.16	2.17		$Cr-C_{10}$	2.21	2.22	2.20
$Mn-C_4$	2.18	2.24		$Cr-C_{11}$	2.20	2.22	2.22
$Mn-C_5$	2.14	2.16		$Cr-C_{12}$	2.20	2.23	2.20
$Mn-C_6$		2.17		$Cr-C_{13}$	2.19	2.21	2.21
C_1-C_7	1.43	1.42	1.45^a	$Cr-C_{14}$	2.23	2.17	2.22
C_7-C_8	1.17	1.20	1.19	α(Cr)	19	31	27
C_8-C_9	1.43	1.43	1.43	β(Cr)	19	25	26
α(Mn)	0	−16		γ(Cr)	18	29	29
β(Mn)	0	−15					

[a] $C_{18}-C_{19}$ = 1.43 Å; $C_{19}-C_{20}$ = 1.19 Å; $C_{20}-C_9$ = 1.44 Å; $C_{17}-C_{15}$ = 1.35 Å; $C_{15}-C_{16}$ = 1.40 Å; $C_{16}-C_{18}$ = 1.35 Å; $C_{17}-S$ = 1.72 Å; $C_{18}-S$ = 1.71 Å. [b] For the atom numbering, see Scheme 2. [c] For the atom numbering, see Scheme 6.

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Table 2. Crystal Data for Complexes 6 ($C_{21}H_{13}CrMnO_7$), 7 ($C_{21}H_{12}BCrF_4MnO_7$), and 22 ($C_{24}H_{14}CrO_4S$)

	6	**7**	**22**
formula	$C_{21}H_{13}Cr$-MnO_7	$C_{21}H_{12}BCrF_4$-MnO_7	$C_{24}H_{14}Cr$-O_4S
cryst class	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	14.774(5)	12.338(1)	12.367(3)
b (Å)	12.732(3)	12.704(1)	11.750(8)
c (Å)	21.413(6)	14.557(1)	14.778(6)
α (deg)	90	90	90
β (deg)	94.31(3)	90	104.46(3)
γ (deg)	90	90	90
V (Å^3)	2079(2)	4016(2)	2281.8(3)
Z	8	4	4
radiation type	Mo Kα		
wavelength (Å)	0.710 730		
density (Mg m^{-3})	1.60	1.66	1.44
M_r	484.25	570.05	450.44
μ (mm^{-1})	1.210	1.102	0.678
temp (K)	295	295	295
size (mm)	0.30 × 0.40 × 0.60	0.20 × 0.20 × 0.45	0.15 × 0.30 × 0.35
color	orange	red	pale orange
shape	parallelepiped	stick	plate
diffractometer type	Enraf-Nonius Mach-3		
scan type	$2\theta/\omega$		
no. of rflns measd	7713	2556	4041
no. of indep rflns	7052	2340	3849
R_{int}	0.0190	0.0	0.07
θ(min, max) (deg)	1, 25	1, 26	1, 25
h	0−17	0−15	0−14
k	0−15	0−15	0−13
l	−25 to +25	0−17	−17 to +17
refinement	on F		
R factor	0.045	0.056	0.0744
weighted R factor	0.054	0.064	0.0871
$\Delta\rho_{min}$ (e Å^{-3})	0.45	−0.50	−0.32
$\Delta\rho_{max}$ (e Å^{-3})	0.44	0.55	0.39
no. of rflns used	3313	1746	905
$\sigma(l)$ limit	3.00	1.50	3.00
no. of params	542	318	3.00
goodness of fit	1.161	1.096	1.114

from 2.19 to 2.24 Å (average 2.20 Å). The conformation of the Cr(CO)$_3$ tripod is slightly staggered with respect to the arene carbons. Indeed the dihedral angles α(Cr), β(Cr), and γ(Cr) between the projection of the Cr−CO bonds onto the arene ring and the Cr−C$_x$ bonds (C$_x$ = C$_9$, C$_{11}$, C$_{13}$) are respectively 19, 19, and 18°. Last, concerning the mutual position of the Mn and Cr atoms: the structure clearly shows that the two metal atoms lie on the same face of the conjugated system. These data are consistent with the structure of a comparable sesquifulvalene Cr complex, which adopts also a synperiplanar conformation.[11]

X-ray Analysis of Complex 7. Crystals of 1-[(η^6-phenylethynyl)tricarbonylchromium]−(η^6-4-methoxybenzene)tricarbonylmanganese tetrafluroborate (**7**) were grown in a pentane/acetone mixture at 0°C. Two CAMERON views, some selected bond lengths, and crystal data are reported in Figures 3 and 4 and in Tables 1 and 2.[9] The cation displays the well-known piano-stool conformation found in half-sandwich tricarbonyl complexes.[12] The Mn−C bond lengths ranging from 2.16 to 2.24 Å (average 2.18 Å) are slightly shorter than the corresponding distances for the complex (η^6-4-thiophenylcarbonylanisole)tricarbonylmanganese.[13] The conformation of the Mn(CO)$_3$ entity adopts an almost anti-eclipsed conformation with respect to the triple bond, the dihedral angles α(Mn), β(Mn), γ(Mn) being 16, 15, and 17°, whereas the conformation of the Cr(CO)$_3$ entity is almost staggered, the values of the torsion angles α-(Cr), β(Cr), γ(Cr) being 31, 25, and 29° (Table 1 and Figure 3). The conformation of the Mn(CO)$_3$ entity can be explained by the main role of the electron-donating methoxy group, whereas the conformation of the Cr(CO)$_3$ entity is unexpected, because it is not really influenced by the substitution of the triple bond. Similarly, the Cr−C bond lengths ranging from 2.17 to 2.23 Å (average 2.20 Å) are slightly shorter than the corresponding distances for the (η^6-4-thiophenylcarbonylanisole)tricarbonylchromium complex.[13] The arene rings and alkyne carbons were found to be almost coplanar. The dihedral angle between the two arene rings is only 6°. It is worth noting that the two metal atoms lie on the opposite faces of the conjugated system, probably for steric reasons. Thus, an interesting 180° rotation about the alkyne bond accompanied hydride abstraction of complex **6** (Figures 2 and 3).

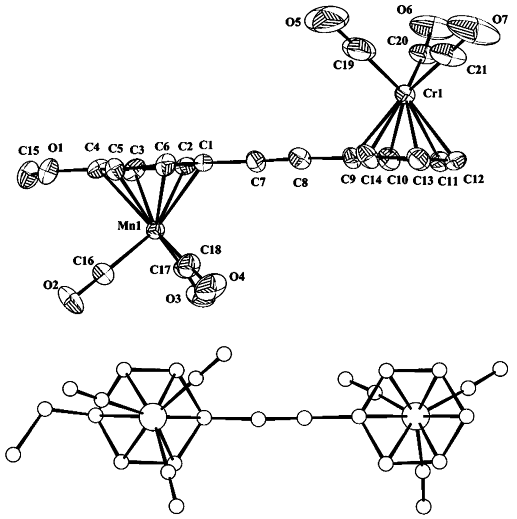

Figure 3. CAMERON views of the molecular structure of complex **7**.

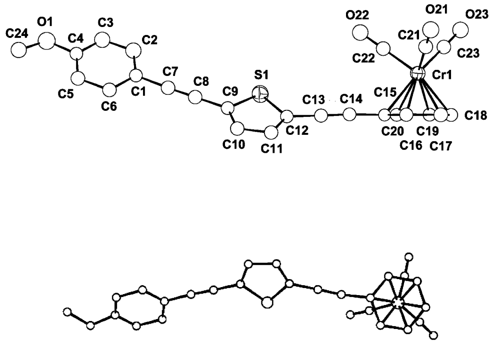

Figure 4. CAMERON views of the molecular structure of complex **22**.

Synthesis of Complex 13. We decided to increase the length of the spacer. For this reason, complex **13** homologated by a thienyl unit was prepared by following a two-step procedure (Scheme 4). The first step involved

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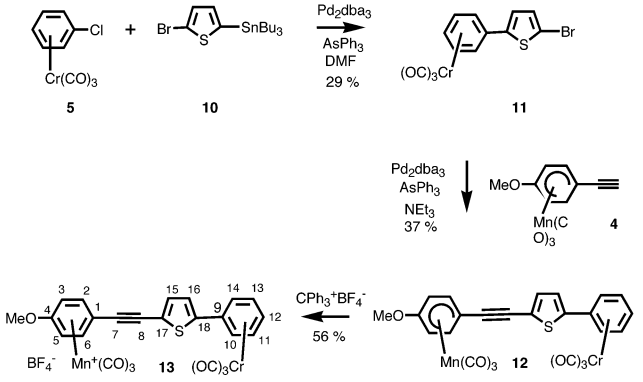
[11] Heck, J.; Dabeck, S.; Meyer-Friedrichsen, T.; Wong, H. *Coord. Chem. Rev.* **1999**, *190−192*, 1217−1254.

[12] Berndt, A. F.; Marsh, R. E. *Acta Crystallogr.* **1963**, *16*, 118−123.

[13] Prim, D.; Tranchier, J.-P.; Rose-Munch, F.; Rose, E.; Vaissermann, J. *Eur. J. Inorg. Chem.* **2000**, *5*, 901−905.

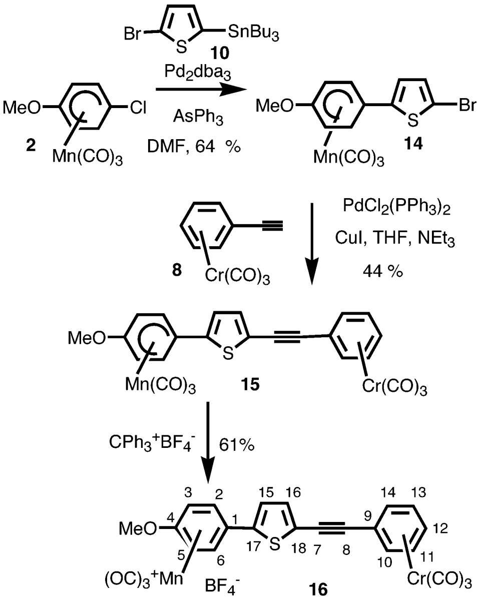
Scheme 4. Synthesis of Dinuclear Complex 13



a Stille coupling[14] with (chlorobenzene)tricarbonylchromium (**5**)[8] and 2-bromo-5-(tributylstannyl)thiophene (**10**) in the presence of Pd_2dba_3 and $AsPh_3$ in DMF, giving 2-bromo-5-[(η^6-phenyl)tricarbonylchromium]thiophene (**11**) in 29% yield. A Sonogashira coupling reaction of (η^5-1-ethynyl-4-methoxycyclohexa-2,4-dienyl)-$Mn(CO)_3$ (**4**) and **11** in the presence of $AsPh_3$, NEt_3, and $Pd_2(dba)_3$ afforded the binuclear η^5-Mn/η^6-Cr derivative **12** in 37% yield. Using $PdCl_2(PPh_3)_2$ and CuI as a catalytic system, this reaction was unsuccessful. Compound **12** reacted with triphenylcarbenium tetrafluoroborate to deliver the red-orange dinuclear complex **13** in 56% yield (Scheme 4).

Synthesis of Complex 16. Having in hand the dinuclear complex **13**, where the spacer between the η^6-Mn and the η^6-Cr entities is a triple bond and a thienyl residue, we undertook the synthesis of the dinuclear η^6-Mn/η^6-Cr species, where the spacer was in the reverse order. Thus, the Stille reaction of the complex (η^5-chlorocyclohexadienyl)tricarbonylmanganese (**2**) and the thienyltin derivative **10,** catalyzed by $Pd_2(dba)_3$, gave the (η^5-cyclohexadienyl)$Mn(CO)_3$ complex substituted by the bromothienyl unit **14** in 64% yield. A Sonogashira coupling reaction with the complex (η^6-ethynylbenzene)-tricarbonylchromium (**8**) in the presence of $PdCl_2(PPh_3)_2$ and CuI afforded the dinuclear complex **15** in 44% yield. Finally, the conjugated η^6-Mn/η^6-Cr dinuclear complex **16** was obtained in 61% yield by removal of the hydride of the CH_2 unit with $CPh_3^+BF_4^-$ (Scheme 5).

Scheme 5. Synthesis of Dinuclear Complex 16



Synthesis of Complex 20. We finally turned our attention to the synthesis of **20**, containing a spacer homologated by a further triple bond. To achieve this goal, we considered two possible routes to prepare the precursor compound **19**. The first methodology involved a Sonogashira coupling of the η^6-Cr complex **8** and 2,5-dibromothiophene **17**, which yielded the chromium complex **18** in 56% yield (Scheme 6). A second Sonogashira reaction of the η^5-Mn−alkyne **4** afforded the dinuclear η^5-Mn/η^6-Cr complex **19** in 25% yield. A second method was considered in order to increase the yield of **19**. Thus, a coupling with 2,5-dibromothiophene **17** and the alkyne derivative **4** in the presence of $PdCl_2(PPh_3)_2$ and CuI gave the mononuclear Mn complex **21** in 49% yield, which reacted with the alkyne **8**, liberating the dinuclear complex **19** in 80% yield. Hydride abstraction of **19** proceeded in 66% yield, affording the dinuclear complex **20**. The overall yield obtained for the preparation of complex **20** was 26%, instead of the 9% overall yield using the first method (Scheme 6). In the course of our attempts to obtain a crystal structure of the dinuclear complex **20**, we obtained, instead, crystals of the mononuclear complex **22**, where the $Cr(CO)_3$ is still coordinated to the arene ring but where the other end group was unexpectedly decoordinated. An ^1H NMR spectrum of the crystals showed that complexes **20** and **22** did not coexist.

X-ray Analysis of Complex 22. Crystals of 2-(4-methoxyphenylethynyl)-5-[(η^6-phenylethynyl)tricarbonylchromium]thiophene were grown in a pentane/acetone mixture at 0 °C. Two CAMERON views and some selected bond lengths and crystal data are reported in Figure 4 and Tables 1 and 2.[9] Two important features can be emphasized. First, the conformation of the Cr-$(CO)_3$ tripod with respect to the alkyne substituent is almost staggered. To our knowledge, in the literature, there is no other example of a phenylacetylene−$Cr(CO)_3$ complex presenting this conformation. Indeed, Müller et al. described an anti-eclipsed conformation of the $Cr(CO)_3$ tripod for the diphenylacetylene−$Cr(CO)_3$ complex with respect to the alkynyl moiety typical for arene complexes bearing electron-withdrawing substituents.[3c] The coordinated and the noncoordinated phenyl rings of **22** are mutually arranged with a large dihedral angle of 49°. The dihedral angles of the (η^6-arene)$Cr(CO)_3$ ring and the thienyl ring on one hand and of the free arene and the thienyl ring on the other hand are 39 and 10°, respectively. Therefore, the overlap of the π-system is not assumed in the solid state between the coordinated η^6-arene and the thienyl ring, whereas a good overlap of the π-system between the free arene and the thienyl ring occurs, showing an electronic coupling between them in the solid state.

NMR Spectroscopy. Selected ^1H NMR data, reported in Table 3, show that the H_2 protons of complexes **7**, **13**, **16**, and **20** are the most deshielded with respect to the H_3 protons, in good agreement with the electron-donating capability of the methoxy group. The large difference of chemical shifts $\delta(H_3) - \delta(H_2)$ is almost the same (around 0.85 ppm) for the three complexes **7**, **13**, and **20**, but this difference is larger for complex **16**. The

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(14) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508−524.

Scheme 6. Synthesis of Dinuclear Complex 20

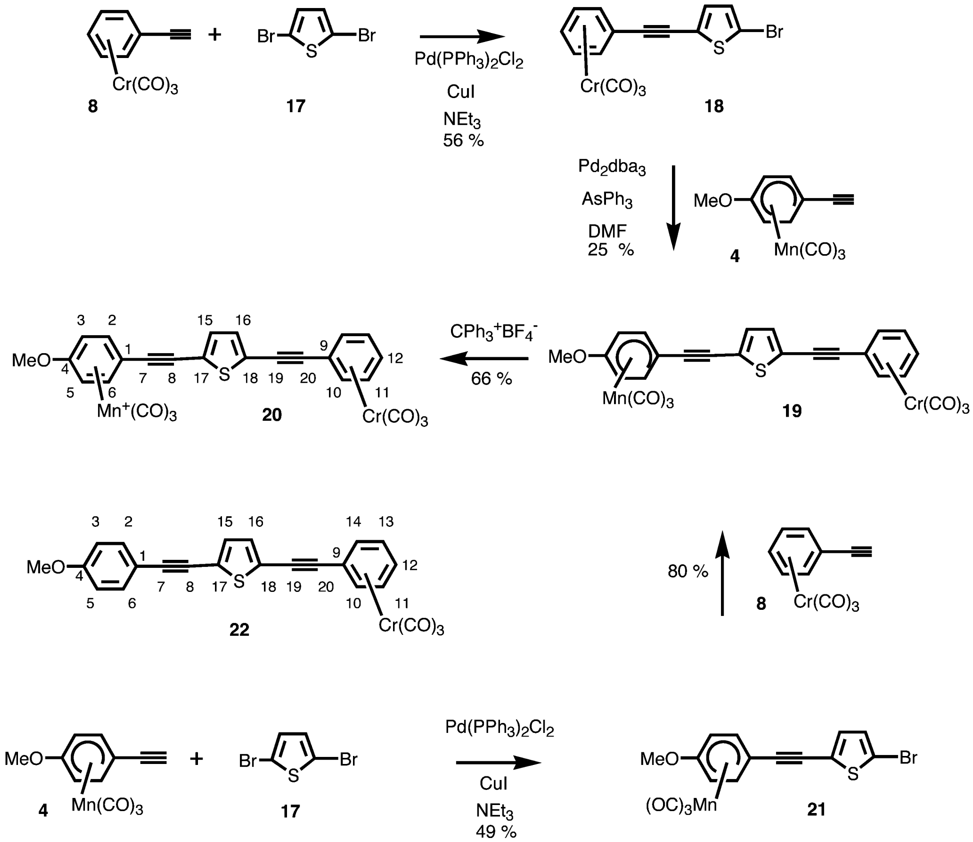

Table 3. ^{1}H NMR Data (ppm) of Complexes 7, 13, 16, and 20

	7	**13**	**16**	**20**
OMe	4.24	4.25	4.23	4.22
H_2	7.44^b	7.46^c	7.59^b	7.40^c
H_3	6.61^b	6.64^d	6.62^b	6.60^c
$\delta(H_2) - \delta(H_3)$	0.83	0.87^e	1.08^f	0.86^g
H_{10}	5.94^c	6.17^d	5.93^c	5.90^c
H_{11}	5.76^c	5.73−5.87^c	5.74^c	5.63−5.73^c
H_{12}	5.76^c	5.73−5.87^c	5.74^c	5.63−5.73^c
$\delta(H_{10}) - \delta(H_{11})$	0.18	0.37^e	0.19	0.22^g
H_{15}		7.51^{h,i}	7.48^{h,i}	7.40^{c,h}
H_{16}		7.57^{h,i}	7.92^{h,i}	7.53^{c,h}

[a] Me_2CO-d_6. [b] Doublet, $J = 7$ Hz. [c] Multiplet. [d] Doublet, $J = 8$ Hz. [e] ±0.07. [f] ±0.022. [g] ±0.06. [h] Or. [i] Doublet, $J = 4$ Hz.

Table 4. ^{1}H NMR Data (ppm)[a] of Complexes 6, 12, 15, and 19

	6	**12**	**15**	**19**
OMe	3.45	3.46	3.51	3.46
H_2	5.16−5.38^e	5.27^e	5.26−5.51^e	5.24−5.37^e
H_3	5.79^d	5.81^d	5.81^d	5.81^d
H_5	3.07^d	3.09^d	3.12−3.26^e	3.09^d
H_{6exo}	2.40^b	2.45^b	2.56^f	2.46^b
H_{6endo}	2.87^c	2.93^c	3.12−3.26^e	2.94^c
H_{10}	5.16−5.38^e	5.63^h	5.26−5.51^e	5.51^h
H_{11}	5.16−5.38^e	5.44^i	5.26−5.51^e	5.24−5.37^e
H_{12}	5.16−5.38^e	5.27^e	5.26−5.51^e	5.24−5.37^e
$\delta(H_{10}) - \delta(H_{11})$		0.19	−	−
H_{15}		7.06^e	6.67^g	7.00^g
H_{16}		7.06^e	7.10^g	7.11^g

[a] $CDCl_3$. [b] Doublet, $J = 13$ Hz. [c] Doublet of doublets, $J = 13$ and 6 Hz. [d] Doublet of doublets, $J = 6$ and 2 Hz. [e] Multiplet. [f] Doublet, $J = 11$ Hz. [g] Or doublet, $J = 4$ Hz. [h] Doublet, $J = 6$ Hz. [i] Triplet, $J = 6$ Hz.

difference of chemical shifts $\delta(H_{10}) - \delta(H_{11})$ is small at around 0.20 ppm, except for complex **13**, where the difference is almost twice as much (Table 3). The difference of chemical shifts $\delta(H_{10}) - \delta(H_{11})$ is almost the same for complexes **12** and **19** (Table 4) and complexes **7**, **16**, and **20** (0.18−0.22 ppm) (Table 3).

Selected ^{13}C NMR chemical shifts are reported in Tables 5 and 6. The manganese carbonyl carbon resonances of complexes **7**, **13**, **16**, and **20** present similar values (215.2−216.0 ppm).[15] Similarly the chromium carbonyl carbon resonances of these complexes present almost the same values (233.0−233.5 ppm), in good agreement with the same overall role of the residue which substitutes the Cr−arene ring. Similarly, the CrCO and MnCO carbon resonances of complexes **6**, **12**, **15**, and **19** are almost the same, respectively, in the range 231.3−232.4 ppm and 221.2−221.9 ppm (Table 6).

IR Spectroscopy. M−CO stretching modes in complexes **6**, **12**, **15**, and **19** and in **7**, **13**, **16**, and **20** present two CO stretching modes in accordance with the symmetry C_{3v} due to the A_1 and E bonds of the $Cr(CO)_3$ and the $Mn(CO)_3$ groups (Table 7).[16] The complexes **13** and **16** exhibit the lowest frequencies of the Cr−CO bonds at 1907 and 1908 cm^{-1}, whose spacer includes a triple

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(15) (a) (Dimethylaniline)tricarbonylchromium, δ(Cr−CO) 235.0 ppm in CH_2Cl_2: Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 360−369. (b) (Benzene)tricarbonylchromium, δ(Cr−CO) 233.3 ppm in CH_2Cl_2. (c) Methyl benzoate,[4k] δ(Cr−CO) 231.2 ppm in CH_2Cl_2. (d) (1,3-Dimethoxybenzene)tricarbonylmanganese hexafluorophosphate, 216.7 ppm (Mn−CO) in Me_2CO.-d_6. (Chlorobenzene)tricarbonylmanganese hexafluorophosphate, 214.9 ppm; (phenyl benzoate)tricarbonylmanganese, 213.0 ppm.[4e]

(16) (a) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975. (b) Van Meurs, F.; Baas, J. M. A.; Van Bekkum, H. *J. Organomet. Chem.* **1976**, *113*, 353−359.

Table 5. ^{13}C NMR Data (ppm)^{a} of Complexes 7, 13, 16, and 20

	7	13	16	20
OMe	59.1	58.5	59.0	59.2
C_1	101.3	101.6	101.2	92.4
C_2	106.7	105.2	100.7	106.1
C_3	83.6	83.1	83.6	83.8
C_4	149.8	148.7	149.2	149.6
C_7	86.8^{b}	86.2^{b}	89.5^{b}	86.4^{c}
C_8	88.1^{b}	88.9^{b}	93.1^{b}	86.7^{c}
C_{19}				89.3^{c}
C_{20}				89.8^{c}
C_9	81.1	91.5	81.4	81.6
C_{10}	93.4	92.1^{b}	93.6^{b}	93.7^{b}
C_{11}	97.4	93.7^{b}	97.0^{b}	97.0^{b}
C_{12}	94.4	93.5	94.1	94.0
C_{15}		125.9^{b}	130.1^{b}	134.7^{b}
C_{16}		136.3^{b}	135.7^{b}	136.5^{b}
C_{17}		129.2^{b}	126.2^{b}	122.8^{b}
C_{18}		133.0^{b}	129.5^{b}	126.5^{b}
Cr−CO	233.0	233.0	233.3	233.5
Mn−CO	215.6	215.2	216.0	215.8

^{a} Me_2CO-d_6. ^{b} Or. ^{c} Or.

Table 6. ^{13}C NMR Data (ppm)^{a} of Complexes 6, 12, 15, and 19

	6	12	15	19
OMe	54.5	54.5	54.4	54.5
C_1	43.6	45.6	60.5	45.3
C_2	97.9	97.2	91.5	97.3
C_3	68.8	68.5	66.3	68.5
C_4	143.4	143.3	143.1	143.3
C_5	36.6	36.6	37.0	36.6
C_6	31.6	31.8	30.2	31.7
C_7	81.6/91.1^{c}	78.5/96.1^{c}	83.1	78.3/95.9^{c}
C_8	81.6/91.1^{c}	78.5/96.1^{c}	83.1	78.3/95.9^{c}
C_{19}				82.6/89.4/89.8^{d}
C_{20}				82.6/89.4/89.8^{d}
C_9	*b*	102.5	89.9	82.6/89.4/89.8^{d}
C_{10}	91.9/94.6^{c}	90.2/92.3^{c}	91.3/94.5^{c}	91.3/94.7^{c}
C_{11}	91.9/94.6^{c}	90.2/92.3^{c}	91.3/94.5^{c}	91.3/94.7^{c}
C_{12}	90.3	91.0	90.7	90.9
C_{15}		124.8/132.5^{c}	121.9/134.2^{c}	131.6/133.2^{c}
C_{16}		124.8/132.5^{c}	121.9/134.2^{c}	131.6/133.2^{c}
C_{17}		124.4/140.5^{c}	120.1/149.0^{c}	122.4/125.9^{c}
C_{18}		124.4/140.5^{c}	120.1/149.0^{c}	122.4/125.9^{c}
Cr−CO	231.3	232.4	232.0	232.0
Mn−CO	221.2	221.7	221.9	221.8

^{a} $CDCl_3$. ^{b} Under another peak. ^{c} Or. ^{d} Or.

Table 7. IR Data (cm^{-1})^{a}

	ν(Cr−CO)	ν(Mn−CO)	ν(C≡C)
6	1911,^{b} 1976	1942, 2021	2211
12	1908, 1973	1948, 2019	2255
15	1915,^{c} 1976	1944, 2016	2208
19	1928,^{b} 1977	1953, 2019	2195, 2210
7	1911, 1977	2021,^{g} 2081	2230^{c}
13	1907,^{e} 1974	2018,^{d} 2079	2210
16	1908,^{c} 1977	2016, 2075	2207
20	1913, 1977	2036,^{f} 2080	2210

^{a} $CHCl_3$. ^{b} Very broad, ±10 cm^{-1}. ^{c} Broad. ^{d} Shoulder, 2028. ^{e} Shoulder, 1897. ^{f} Shoulder, 2026. ^{g} Shoulder, 2031.

bond and a thienyl residue but unexpectedly the lowest frequencies of the Mn−CO bonds at 2018 and 2016 cm^{-1}.

UV−Vis Spectroscopy. Most of the electronic spectra were recorded in $CHCl_3$, CH_2Cl_2, CH_3CN, and/or CH_3NO_2. The longest wavelength absorptions of **7** at 433 nm ($CHCl_3$), 443 nm (CH_2Cl_2), and 430 nm (CH_3CN) have small extinction coefficients and are assigned to the metal to ligand charge transfer (MLCT) band arising from a charge transition from the manganese center to the π- and σ-bound ligands.[17] The λ_{max} value is difficult to determine precisely, because in most cases, this band is a shoulder and the precision is not as accurate as those of the other bands. Thus, the precision of the λ_{max} value being at least ±10 cm^{-1} does not permit, at this stage, a conclusion about solvant chromaticity. The next bands at 328 nm (sh), 311 nm (sh) ($CHCl_3$), 311 nm (CH_2Cl_2), and 320 nm (sh) (CH_3CN) have an intense absorption and arise from intraligand (IL) transitions with a high oscillator strength to the most extent from π−π* transitions. A moderate positive solvatochromaticity of the MLCT band is observed, indicating that the electronic ground state is less polar than the first excited state; therefore, an increase in solvent polarity on going from CH_2Cl_2 to CH_3CN causes a slight hyperchromic shift (Table 8).[18]

Conclusion

We have successfully developed a versatile methodology based on a bimetallic Pd/Mn activation of the carbon−chloride bond for the preparation of the first neutral (η^5-cyclohexadienyl)Mn(CO)$_3$−(η^6-arene)Cr(CO)$_3$ derivatives. Hydride abstraction by $CPh_3^+BF_4^-$ gives rise to the formation of the first heterodinuclear (η^6-arene)Mn$^+$(CO)$_3$−(η^6-arene)Cr(CO)$_3$ complexes linked by a triple bond. 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 X-ray structures of complexes **6**, **7**, and **22**.

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. ^{1}H and ^{13}C{^{1}H} 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. In X-ray analyses, 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 intensity 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.[9a] Scattering factors and corrections for anomalous dispersion were taken from ref 9b. The structures were resolved by direct methods 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

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(17) Karris, D. R.; Ratner, M. A.; Marks, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10338−10357.

(18) Palez, M. S.; Harris, J. M. *J. Org. Chem.* **1989**, *54*, 3774−3778.

(19) Abbreviations used in this paper: TBAF = tetrabutylammonium fluoride, $Pd_2(dba)_3$ = palladium dibenzylideneacetone, $AsPh_3$ = triphenylarsine, CPh_3BF_4 = triphenylcarbenium tetrafluoroborate, EWG = electronwithdrawing group.

Table 8. UV–Vis Data (λ_{max}, nm (ϵ))

6	12	15	19	7	13	16	20
In $CHCl_3$							
		442 (7800)^c		433 (2300)^a	449 (3600)^a	456 (3200)^c	459 (3400)^c
		361 (17 200)^d		328 (7600)^a	341 (28 500)	343 (18 700)	353 (33 800)
				311 (9000)^a	263 (29 000)		263 (29 800)
				291 (10 200)			
In CH_2Cl_2							
418 (1515)^c	438 (5700)^a	439 (8500)^c	436 (9500)^a	443 (5500)^a	443 (4400)^a	452 (3700)^c	446 (7900)^c
312 (11 000)	345 (20 900)	362 (17 300)^d	351 (27 900)	311 (16 000)	341 (29 300)	342 (18 500)	351 (35 400)
	264 (26 100)			272 (19 700)	263 (28 600)	264 (23 000)	
In CH_3CN							
		436 (8800)^c		430 (2400)^a	436 (5100)^a	423 (4600)^c	433 (6600)^a
		362 (17 000)^d		320 (6800)^a	335 (29 400)	338 (19 000)	347 (39 500)
				270 (12 500)	265 (27 500)	265 (19 500)	265 (19 500)
In CH_3NO_2							
413 (3000)^a	439 (4800)^a	436 (8800)^c	436 (7300)^c				
378 (4200)	374 (17 000)	377 (16 100)	377 (23 300)				
370 (4500)	370 (18 700)	370 (16 000)	370 (24 200)				

[a] Shoulder. [b] Broad shoulder. [c] Broad maximum.

positions, and only one overall isotropic displacement parameter was refined.

Synthesis of (η^6-Ethynylbenzene)tricarbonylchromium(0)–(η^6-4-Methoxyphenyl)tricarbonylmanganese Tetrafluoroborate (7). (η^5-1-chloro-4-methoxycyclohexa-2,4-dienyl)Mn$(CO)_3$ (**2**;[5] 0.137 g, 0.485 mmol) was dissolved in NEt_3 (15 mL) and poured via a cannula into a 50 mL flask containing tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$; 0.044 g, 0.048 mmol), triphenylarsine ($AsPh_3$; 0.052 g, 0.170 mmol), and (trimethylsilyl)acetylene (0.075 mL, 0.533 mmol). The reaction mixture was magnetically stirred for 21 h at 40 °C. 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), giving the orange oil **3** (0.157 g) in 86% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.12 (s, 9H, Me), 2.35 (d, $J = 13$ Hz, 1H, H_{6exo}), 2.83 (dd, $J = 13$ and 6.5 Hz, 1H, H_{6endo}), 3.01 (dd, $J = 6.5$ and 2 Hz, 1H, H_5), 3.43 (s, 3H, OMe), 5.16 (d, $J = 6$ Hz, 1H, H_2), 5.72 (dd, $J = 6$ and 2 Hz, 1H, H_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.08 (C_9), 31.6 (C_6), 36.2 (C_5), 46.1 (C_1), 54.4 (OMe), 68.1 (C_3), 90.9 (C_7 or C_8), 97.6 (C_2), 106.1 (C_8 or C_7), 143.3 (C_4), 221.9 (CO–Mn). Anal. Calcd for $C_{15}H_{17}MnO_4Si$ ($M_r = 344.3$): C, 52.32; H, 4.98. Found: C, 52.05; H, 4.78. IR ($CHCl_3$): $\bar{\nu}$ 1938, 2025 cm^{-1} (CO–Mn), 2150 cm^{-1} (CC).

Complex **3** (0.165 g, 0.479 mmol) was dissolved in MeOH (13 mL) and treated with a solution of NaOH (2 M, 0.31 mL). The reaction mixture was stirred magnetically for 3 h at room temperature and extracted with diethyl ether and water saturated with NH_4Cl. The organic phase was dried over $MgSO_4$ and filtered on Celite. The solvents were evaporated under reduced pressure, giving the yellow oil **4** (0.130 g) in quantitative yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.36 (d, $J = 13$ Hz, 1H, H_{6exo}), 2.58 (s, 1H, H_8), 2.87 (ddd, $J = 13$, 6, and 1.5 Hz, 1H, H_{6endo}), 3.02 (dd, $J = 6$ and 2.5 Hz, 1H, H_5), 3.43 (s, 3H, OMe), 5.21 (dbr, $J = 6$ Hz, 1H, H_2), 5.76 (dd, $J = 6$ and 2.5 Hz, 1H, H_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 31.6 (C_6), 36.4 (C_5), 44.5 (C_1), 54.5 (OMe), 68.2 (C_3), 73.6 (C_8), 84.5 (C_7), 98.0 (C_2), 143.3 (C_4), 221.2 (CO–Mn). Anal. Calcd for $C_{12}H_9MnO_4$ ($M_r = 272.1$): C, 52.92; H, 3.33. Found: C, 52.93; H, 3.54. IR ($CHCl_3$): $\bar{\nu}$ 1938, 2025 cm^{-1} (CO–Mn), 2110 cm^{-1} (CC).

(Chlorobenzene)tricarbonylchromium[8] (0.051 g, 0.206 mmol) dissolved in NEt_3 (10 mL) was transferred via a cannula into a flask (50 mL) containing $Pd_2(dba)_3$ (0.028 g, 0.031 mmol), $AsPh_3$ (0.022 g, 0.072 mmol). The reaction mixture containing complex **4** (0.056 g, 0.206 mmol) dissolved in NEt_3 (8 mL) was added and stirred magnetically at 40 °C for 2 h, giving an orange solution which was filtered on Celite. Extraction with ether and water and then with a saturated solution of NH_4Cl gave a solution which was dried over $MgSO_4$ and evaporated under reduced pressure. The crude brown oil was purified on a silica gel chromatography column with the a petroleum ether/ether solution (80:20), giving the orange powder **6** (83 mg) in 83% yield. Anal. Calcd for $C_{21}H_{13}CrMnO_7$ ($M_r = 484.3$): C, 52.07; H, 2.69. Found: C, 52.05; H, 2.78. MS-ES$^+$: calcd m/z 349 (M + 1 − Cr$(CO)_3$); 348, (M − Cr$(CO)_3$).

Complex **6** can also be obtained in the following way. Complex **2** (0.111 g, 0.393 mmol) dissolved in NEt_3 (5 mL) was transferred via a cannula into a 50 mL flask containing $Pd_2(dba)_3$ (0.036 g, 0.039 mmol), $AsPh_3$ (0.042 g, 0.137 mmol), and (η^6-ethynylbenzene)tricarbonylchromium[8b,13] (**8**; 0.093 g, 0.393 mmol). The reaction mixture was stirred at 40 °C for 40 min and filtered on Celite. The solvent was evaporated under reduced pressure, and the crude product was purified on a silica gel chromatography column (petroleum ether/ether), giving **6** as an orange solid (0.131 g) in 69% yield.

Complex **6** (0.047 g; 0.097 mmol) was dissolved in CH_2Cl_2 (7 mL) and poured via a cannula into another flask containing CPh_3BF_4 (0.038 g, 0.116 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 15 min at room temperature, and half of the solvent was removed under reduced pressure. Precipitation of the product occurred by adding diethyl ether (20 mL), which was recovered by filtration, giving **7** (0.035 g, 63%). $C_{21}H_{12}BCrF_4MnO_7$: $M_r = 570.1$. MS-ES$^+$: m/z 483 (M − BF_4), 399 (M − BF_4 − 3CO), 371 (M − BF_4 − 4CO), 347 (M − BF_4 − Cr$(CO)_3$), 263 (M − BF_4 − Cr$(CO)_3$ − 3CO).

Synthesis of 2-[η^6-(4-methoxy-phenylethynyl)tricarbonylchromium]-5-phenyl-thiophene (13). $Pd_2(dba)_3$ (0.092 g, 0.1 mmol) and $AsPh_3$ (0.122 g, 0.4 mmol) were dissolved in DMF (25 mL). The solution was stirred at room temperature for 10 min and (η^6-chlorobenzene)tricarbonylchromium (0.497 g, 2 mmol) was added. 2-Bromo-5-(tributylstannyl)thiophene (0.561 mL, 2 mmol) was added; the reaction mixture became black after 19 h of stirring, and the reaction mixture was extracted with H_2O and diethyl ether. The organic solvents were dried over $MgSO_4$ and evaporated under reduced pressure, giving a brown red oil which was purified by two silica gel chromatography columns (petroleum ether/ether), giving **11** as a yellow powder (0.217 g) in 29% yield. $C_{13}H_7BrCrO_3S$: $M_r = 375.2$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.28 (m, 1H, H_4), 5.44 (t, $J = 6$ and 3 Hz, 2H, H_3, H_5), 5.59 (d, $J = 3$ Hz, 2H, H_2, H_6), 6.99 (s, 2H, H_8, H_9). IR ($CHCl_3$): $\bar{\nu}$ 1905, 1974 cm^{-1} (CO–Cr).

Complex **11** (0.155 g, 0.413 mmol) was dissolved in NEt_3 (27 mL) and transferred via a cannula into a flask (100 mL) containing $Pd_2(dba)_3$ (0.057 g, 0.062 mmol) and $AsPh_3$ (0.044 g, 0.145 mmol). The reaction mixture was stirred for 15 min at 40 °C. Then the cyclohexadienyl complex **4** (0.113 g, 0.413 mmol) dissolved in NEt_3 (15 mL) was slowly introduced. The reaction mixture was stirred at 40 °C for 4 h, and $Pd_2(dba)_3$ (0.038 g, 0.041 mmol) was introduced. The reaction mixture was stirred again magnetically for 20 h and filtered on Celite. Extraction of the mixture with Et_2O and a saturated solution of NH_4Cl gave an organic phase which was dried over $MgSO_4$ and filtered on Celite. Evaporation of the solvents under reduced pressure afforded a brown oil, which was purified on a silica gel chromatography column (petroleum ether/ether solution), affording complex **12** (0.086 g) in 37% yield. Anal. Calcd for $C_{25}H_{15}CrMnO_7S$ ($M_r = 566.4$): C, 53.01; H, 2.67. Found: C, 52.81; H, 2.51. MS-ES$^+$: m/z 566 (M), 565 (M − 1), 481 (M − 1 − 3CO), 429 (M − 1 − $Cr(CO)_3$), 345 (M − 1 − $Cr(CO)_3$ − 3CO).

Complex **12** (0.031 g, 0.055 mmol) in CH_2Cl_2 (9 mL) was treated with CPh_3BF_4 (0.029 g, 0.087 mmol) in CH_2Cl_2 (7 mL). The solution was stirred for 1 h at room temperature, half of the solvent was evaporated under reduced pressure, and Et_2O (20 mL) was added. A red-orange precipitate occurs. Filtration of this product, which was washed with ether, gave complex **13** (0.020 g) in 56% yield. Anal. Calcd for $C_{25}H_{14}BcrF_4MnO_7S$ ($M_r = 651.93$): C, 46.02; H, 2.16. Found: C, 45.73; H, 2.09. MS-ES$^+$: m/z 565 (M − BF_4), 481 (M − BF_4 − 3CO), 429 (M − BF_4 − $Cr(CO)_3$).

Synthesis of 2-[(η^6-4-Methoxyphenyl)tricarbonylmanganese]−5-[(η^6-Phenylethynyl)tricarbonylchromium]thiophene (16). Complex **14**[5] (0.180 g, 0.440 mmol), $PdCl_2(PPh_3)_2$ (0.0154 g, 0.022 mmol), CuI (0.0042 g, 0.022 mmol) in THF (2 mL), and NEt_3 (5 mL) were heated under reflux in a flask for 10 min, giving an orange solution. (η^6-Ethynylbenzene)tricarbonylchromium (**8**; 0.105 g, 0.440 mmol) in THF (5 mL) was added via a syringe. The reaction mixture was stirred magnetically under reflux for 4 h, became dark brown, and was then filtered on Celite. The solvents were evaporated under reduced pressure, giving a crude orange solid which was purified on a silica gel chromatography column (petroleum ether/ether), affording complex **15** (0.110 g) in 44% yield. Anal. Calcd for $C_{25}H_{15}CrMnO_7S$ ($M_r = 566.4$): C, 53.01; H, 2.67. Found: C, 52.83; H, 2.52.

Complex **15** (0.111 g, 0.196 mmol) in CH_2Cl_2 (5 mL) was stirred with CPh_3BF_4 (0.085 g, 0.267 mmol) under N_2 for 2 h. Half of the solvent was evaporated under reduced pressure, and Et_2O (20 mL) is added. A red-orange oil appeared. The oil was washed with Et_2O, giving complex **16** (0.078 g) in 61% yield as a red-orange oil. $C_{25}H_{14}BCrF_4MnO_7S$: $M_r = 652.2$. MS-ES$^+$: m/z 565 (M − BF_4), 481 (M − BF_4 − 3CO), 429 (M − BF_4 − $Cr(CO)_3$), 345 (M − BF_4 − $Cr(CO)_3$ − 3CO).

Synthesis of 2-[(η^6-4-Methoxyphenylethynyl)tricarbonylmanganese]−5-[(η^6-Phenylethynyl)tricarbonylchromium]thiophene (20). (Ethynylphenyl)tricarbonylchromium (**8**; 0.238 g, 1 mmol), $PdCl_2(PPh_3)_2$ (0.106 g, 0.15 mmol), CuI (0.028 g, 0.015 mmol), and 2,5-dibromothiophene (**17**; 0.338 mL, 3 mmol) were introduced in a flask containing NEt_3 (45 mL). The mixture was stirred magnetically under reflux for 5 h 30 min and filtered on Celite. The solvents were evaporated under reduced pressure, giving after chromatography on a silica gel column (petroleum ether/ether solution) the mononuclear complex **18** as an orange solid (0.223 g) in 56% yield. ^1H NMR (200 MHz, $CDCl_3$): δ 5.30−5.33 (m, 3H, H_3, H_4, H_5), 5.50 (d, $J = 6$ Hz, 2H, H_2, H_6), 6.95 (d, $J = 4$ Hz, 1H, H_{11}), 7.03 (d, $J = 4$ Hz, 1H, H_{10}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 81.6 (C_1), 88.9 (C_8), 90.0 (C_7), 90.9 (C_4), 91.3 (C_2, C_6), 94.7 (C_3, C_5), 114.6 (C_{12}), 128.5 (C_9), 130.3 (C_{10}), 133.6 (C_{11}), 231.9 (CO−Cr). Anal. Calcd for $C_{15}H_7BrCrO_3S$ ($M_r = 399.2$): C, 45.24; H, 1.77. Found: C, 44.89; H, 1.68.

Complex **18** (0.095 g, 0.235 mmol) in NEt_3 (13 mL) was transferred via a cannula under N_2 into a flask containing $Pd_2(dba)_3$ (0.021 g, 0.023 mmol) and $AsPh_3$ (0.025 g, 0.082 mmol). The mixture was magnetically stirred for 10 min at room temperature. Then another solution of complex **4** (0.064 g, 0.235 mmol) in NEt_3 (4 mL) was poured in this flask via a cannula, and the mixture was stirred for 3 h at 40 °C. Extraction with Et_2O and H_2O and then with NH_4Cl gave an organic phase which was dried over $MgSO_4$ and filtered on Celite. The resulting residue **19**, obtained after evaporation of the solvents under reduced pressure, was purified on a silica gel chromatography column (petroleum ether/ether mixture), giving an orange solid (0.035 g) in 25% yield. Anal. Calcd for $C_{27}H_{15}CrMnO_7S$ ($M_r = 590.4$): C, 54.92; H, 2.56. Found: C, 54.73; H, 2.43. MS-ES$^+$: m/z 591 (M + 1), 454 (M − $Cr(CO)_3$), 453 (M − 1 − $Cr(CO)_3$).

An alternative method for the preparation of complex **19** has been used by transferring a solution of complex **4** (0.255 g; 0.940 mmol) in THF (3 mL) via a cannula in a flask containing 2,5-dibromothiophene (**17;** 0.230 mL, 2 mmol), CuI (0.007 g, 0.05 mmol), $PdCl_2(PPh_3)_2$ (0.035 g, 0.05 mmol) in THF (2 mL), and NEt_3 (5 mL). The mixture was heated under reflux for 15 min and then filtered on Celite. The solvents were evaporated under reduced pressure, giving complex **21** (0.201 g) in 49% yield. ^1H NMR (200 MHz, $CDCl_3$): δ 2.44 (d, $J = 12$ Hz, 1H, H_{6exo}), 2.91 (dd, $J = 12$ and 6 Hz, 1H, H_{6endo}), 3.07 (dd, $J = 6$ and 2 Hz, 1H, H_5), 3.45 (s, 3H, OMe), 5.22 (d, $J = 6$ Hz, 1H, H_2), 5.79 (dd, $J = 6$ and 2 Hz, 1H, H_3), 6.88 (s, 2H, H_{10}, H_{11}). ^{13}C NMR (50 MHz, $CDCl_3$): δ 31.7 (C_6), 36.5 (C_5), 45.6 (C_1), 54.5 (OMe), 68.4 (C_3), 78.0 (C_7 or C_8), 95.2 (C_8 or C_7), 97.2 (C_2), 112.6 (C_9 or C_{12}), 125.1 (C_{12} or C_9), 130.1 (C_{10} or C_{11}), 132.1 (C_{11} or C_{10}), 143.3 (C_4), 221.6 (CO−Mn). Anal. Calcd for $C_{16}H_{10}BrMnO_4S$ ($M_r = 432.2$): C, 44.46; H, 2.33. Found: C, 44.31; H, 2.19.

To complex **21** (0.201 g, 0.46 mmol) in THF (2 mL), NEt_3 (5 mL), $PdCl_2(PPh_3)_2$ (0.016 g, 0.023 mmol), and CuI (0.004 g, 0.023 mmol) was transferred via a cannula the chromium complex **10** (0.109 g, 0.46 mmol) in THF (2 mL). The mixture was heated under reflux for 0.5 h and then filtered at room temperature on Celite. The yield was 40%; thus, we added $PdCl_2(PPh_3)_2$ (0.016 g, 0.023 mmol), CuI (0.004 g, 0.023 mmol), and complex **10** (0.109 g; 0.46 mmol) in THF (2 mL). The solvents were evaporated under reduced pressure, and the residue was purified on a silica gel chromatography column (petroleum ether/ether solution 1:1). Complex **19** (0.218 g) was obtained in 80% yield.

Complex **19** (0.109 g, 0.185 mmol) dissolved in CH_2Cl_2 (5 mL) was treated with CPh_3BF_4 (0.061 g, 0.185 mmol) in CH_2Cl_2 (8 mL). The solution was stirred magnetically for 15 min at room temperature. Half of the solvent was evaporated, and ether (20 mL) was added, giving a dark orange precipitate. The powder was filtered and washed with Et_2O, giving complex **20** (0.080 g) in 66% yield. For spectroscopic data, see Tables 3, 5, 7, and 8. MS-ES$^+$: m/z 589 (M − BF_4), 505 (M − BF_4 − 3CO), 453 (M − BF_4 − $Cr(CO)_3$). Anal. Calcd for $C_{27}H_{14}BCrF_4MnO_7S$ ($M_r = 675.93$): C, 47.93; H, 2.09. Found: C, 47.61; H, 2.01.

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Supporting Information Available: CIF files giving crystal data, atomic coordinates, and bond distances and angles for complexes **6**, **7**, and **22** and figures givingUV−visible spectra of dinuclear complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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