Synthesis and Reactivity of New Cyclomanganated (η^6-Arene)tricarbonylchromium Complexes

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(η^6-Arene)tricarbonylchromium complexes derived from *N*,*N*-dimethylbenzylamine or from benzyl methyl thioether undergo a cyclomanganation reaction when treated with $PhCH_2-Mn(CO)_5$ in boiling heptane. The manganation process is selective and involves solely aromatic C−H bond activation that yields bimetallic and trimetallic compounds, respectively, when compounds such as $[(\eta^6\text{-}C_6H_5CH_2R)Cr(CO)_3]$ (R = $N(CH_3)_2$, SCH_3) and the diamine $[\{\eta^6\text{-}C_6H_4\text{-}1,3\text{-}[CH_2N(CH_3)_2]\}Cr(CO)_3]$ are reacted. Cases of transmetalation reactions consisting of the transfer of a $Mn(CO)_4$ moiety from one aromatic ligand to another are observed with free aromatic ligands and with chromium π-complexed ligands. Two examples of bimetallic and trimetallic compounds, $[(2\text{-}\eta)\text{-}Mn\{[\eta^6\text{-}3,5\text{-}(CH_3O)_2\text{-}C_6H_2\text{-}CH_2N(CH_5)_2]Cr(CO)_3\}(CO)_4]$ (**2**) and $[(4\text{-}\eta{:}6\text{-}\eta)\text{-}\{Mn(CO)_4\}_2\{\{\eta^6\text{-}C_6H_2\text{-}1,3[CH_2N(CH_3)_2]_2\}Cr(CO)_3\}]$ (**6a**), respectively, were characterized by X-ray diffraction analysis. Both complexes bear distorted $Mn(CO)_4$ units with the ancillary amino ligand pointing away from the chromium.

Introduction

In the very wide field associated with intramolecular C−H activation, also referred to as the cyclometalation reaction,[1] the chemistry of cyclomanganated compounds is one of the most documented in the literature.[2] Several authors have studied the reaction between alkylpentacarbonylmanganese complexes, e.g. $R-Mn(CO)_5$, and various aromatic substrates bearing thioether, amino, or ketone functions.[2] Cyclomanganated complexes have been used intensively in the synthesis of various molecules of biological interest.[2c−e] However, even though widely applied and used, the cyclomanganation reaction has received less attention from a mechanistic point of view.[3]

We recently began a study of the title cyclomanganation reaction with benzylamine and pyridine derivatives and demonstrated that the regiochemistry of the manganation reaction could be influenced by the steric and the electronic effects of substituents located *ortho* to the manganation site.[4] We underlined the peculiar lability of cyclomanganated complexes such as tetracarbonyl{1-((dimethylamino)methyl-κN)-3,4-dimethoxyphenyl-κC^6}manganese[5] under thermal treatment.[4]

The Mn(I) center of $R-Mn(CO)_5$ may be seen as a nucleophilic agent in cyclomanganation reactions with regard to the electrophilic character of Pd(II), for example, in cyclopalladation reactions. Therefore, one may assume that the fate of the manganation process should be influenced by fluctuations in electron density at the aromatic carbon. In order to expand our investigations, we decided to undertake a study of the reactivity of a variety of (η^6-arene)tricarbonylchromium complexes which are known to possess an electrophilic arene ligand and acidic arene protons as compared to the corresponding free aromatics.[6] In 1973, Bruce and co-workers described the synthesis of the first cyclometalated (η^6-benzo[*h*]quinoline)tricarbonylchromium complex.[7a] Unfortunately, to the best of our knowledge, no further exploration of this class of polymetallic

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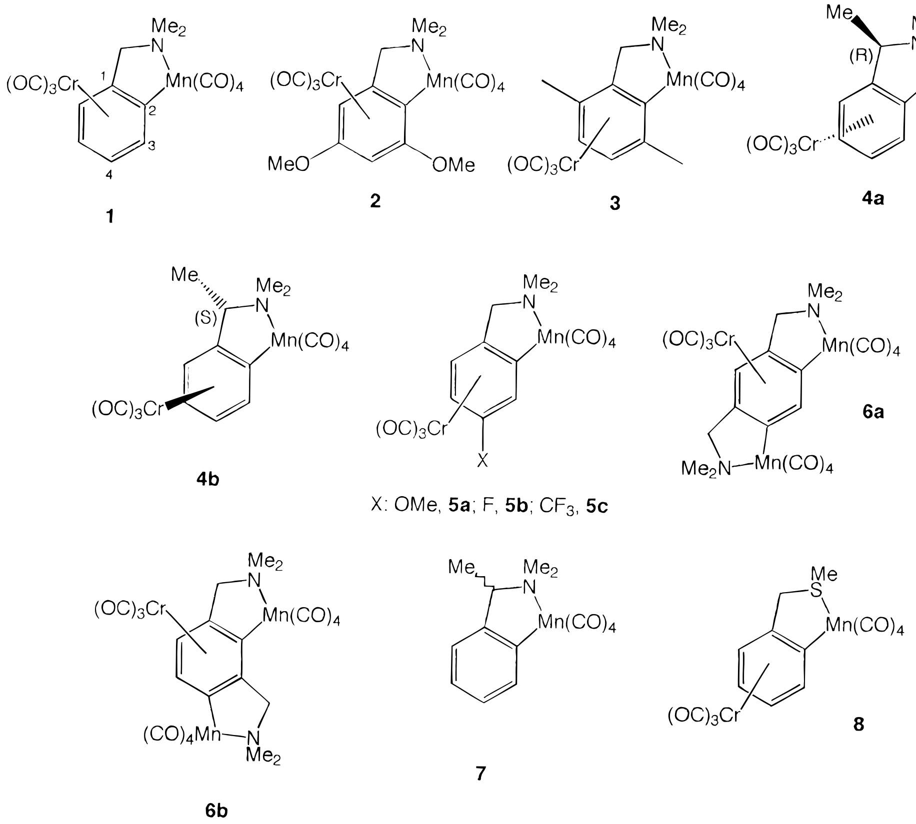
Chart 1

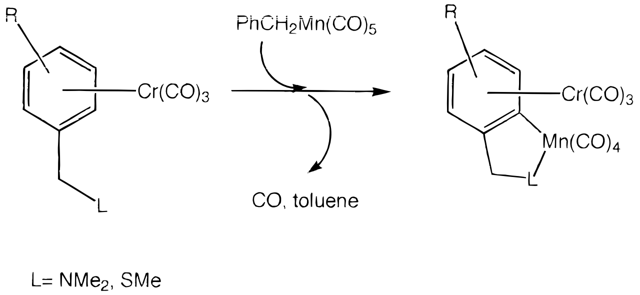


complexes was subsequently provided by the authors. Recently, a series of (η^6-acylaryl)tricarbonylchromium complexes have been reported to react with $PhCH_2-Mn(CO)_5$ and to yield small amounts of the corresponding bimetallic complexes.[7b] These derivatives of aromatic ketones were studied for their ability to react with unsaturated organic substrates, and the main point was made on the potential offered by the cyclomanganated complexes for the synthesis of optically active (η^6-arene)tricarbonylchromium complexes.[7b] Herein, we present our results on the synthesis and the reactivity of a series of cyclomanganated (η^6-arene)tricarbonylchromium complexes derived from benzylamine and from benzyl methyl thioether as well as our main findings about the relative lability of the tetracarbonylmanganese unit.

Results and Discussion

In order to perform cyclomanganation reactions, we chose to use $PhCH_2-Mn(CO)_5$, which has proven to be efficient and less prone to thermal decomposition than other alkyl derivatives.[4,8] The main compounds synthesized in this study are shown in Chart 1.[9]

Reaction of Benzylamine Derivatives with $PhCH_2-Mn(CO)_5$. The corresponding (η^6-arene)tricarbonylchromium complexes were prepared using the general method of Pauson and co-workers[10] and were treated with $PhCH_2-Mn(CO)_5$ in gently refluxing heptane for a period of time ranging from 3 to 8 h (eq 1).



(1)

The duration of the reaction was mainly determined by the decomposition of both alkylpentacarbonylmanganese and the cyclomanganated product. If careful heating was applied to the medium, the reaction mixture could withstand an overnight reflux with minor decomposition of the alkylmanganese starting compound. It is important to note that the reaction does not take place at lower temperatures in heptane. In no case was the decomposition of the (η^6-arene)tricarbonylchromium substrate observed. The manganation reaction is generally clean and the workup easy, since

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(9) According to IUPAC recommendations, the compounds described here can be named by following the "kappa convention" for chelate complexes (see ref 5, p 174). For example: **1**, tetracarbonyl {1-[(dimethylamino)methyl-κN]phenyl-κC^2}manganese(I); **6a**, {1,3-bis-[(dimethylamino)methyl-κN]phenyl-κC^4,κC^6}bis[tetracarbonylmanganese-(I)]. For purposes of clarity and consistency in the text the (dimethylamino)methyl group was assigned the 1-position on the arene ring.

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Table 1. Cyclomanganation of (η^6-arene)$Cr(CO)_3$ Complexes: Yields of Bimetallic Products

product	time (h)	yield (%)
1	5	80
2	4	100
3	6	15
4a (**4b**)	8 (3)	47 (51)

the bimetallic products often precipitate out of the solution as yellow amorphous powders. The bimetallic complexes, although slightly more polar than the nonmanganated substrates, can also be purified by chromatography on SiO_2 and by recrystallization from a nonpolar solvent.

The resulting manganated complexes are generally air-stable and can be stored for several months at room temperature in the solid state without undergoing decomposition. Table 1 presents some optimized yields for the cyclomanganation reaction. The yields of the transformations seem to be influenced by the solubility of the products. Complex **2** can be formed quantitatively during the reaction partly because it precipitates almost completely once it has been formed. This is not the case for **1**, **3**, **4a**, and **5a**, which are slightly soluble in heptane at 100 °C. Thus, they may undergo slight thermal decomposition by loss of CO and subsequent oxidation of Mn(I). However, the yields can be optimized by varying the amount of solvent and by adjusting the time of the reaction. The low yield recorded for **3** might be a consequence of the hindrance generated by the methyl group *ortho* to the $CH_2N(CH_3)_2$ moiety. Indeed, *ortho* substituents could restrict the rotation of the $CH_2N(CH_3)_2$ group and prevent the coordination of the manganese atom to the tertiary amine.[11] In contrast to the *meta*-methoxylated complex **2**, the methyl group of **3**, located at the *meta* position with respect to the $CH_2N(CH_3)_2$ fragment, may also prevent the manganese center from interacting with the hydrogen atom in the C−H activation step. We proposed previously that electrostatic interactions could favor the manganation of sites located *ortho* with respect to a methoxy substituent.[4] It is noteworthy that no metalation of the methyl group located *ortho* with respect to the CH_2NMe_2 moiety was detected.

We checked that $PhCH_2{-}Mn(CO)_5$ does not react at all with the benzylic hydrogens adjacent to the $N(CH_3)_2$ group of the (η^6-arene)tricarbonylchromium complexes studied here. Indeed, the cyclomanganation of the two *R* and *S* enantiomers of 1-[(η^6-phenyl)tricarbonylchromio]-1-(dimethylamino)ethane has been accomplished readily by reacting the corresponding substrates with $PhCH_2{-}Mn(CO)_5$ in refluxing heptane. Giving the possible lability of the benzylic hydrogen adjacent to the $N(CH_3)_2$ group, one could have expected a metalation accompanied with some degree of racemization.[12] The reaction is stereoselective. Complexes **4a** and **4b** are respectively the sole products that have been isolated. The structures of these two enantiomers have not yet been confirmed by X-ray diffraction analysis, but we may reasonably assume that in both cases the methyl group located at the asymmetric carbon is *exo* with respect to the $Cr(CO)_3$ moiety. A similar observation has been reported in the case of the stereoselective lithiation of similar chiral *N*,*N*-dimethylbenzylamine complexes which suggested that the $-CH(CH_3)N(CH_3)_2$ fragment may adopt exclusively a conformation that would minimize steric interactions with the $Cr(CO)_3$ fragment by placing the benzylic methyl group in a *anti* fashion with respect to the chromium.[13] This interpretation accounts reasonably for the formations of **4a** and **4b** presented herein. As we observed from circular dichroism (CD) experiments, the chiral information is not lost in the course of the reaction. A close comparison of the sign of the curves obtained for **4a** and **4b** with those of their respective precursors allows us to consider that the absolute configuration of the benzylic carbon is conserved in both cases during the metalation process.[14] The absence of racemization confirms the inertness of $PhCH_2{-}Mn(CO)_5$ toward activation of the benzylic positions bearing the endogenous amino ligand. Another side reaction has been reported for ferrocene derivatives and involves the metalation of a methyl group of the $CH_2N(CH_3)_2$ fragment.[15] In our case such a reaction was not observed.

The method of manganation presented here is by far more efficient and versatile than the one reported several years ago by Lotz and co-workers, who prepared two analogous complexes starting from lithiated (η^6-benzene)tricarbonylchromium and (η^6-fluorobenzene)-tricarbonylchromium complexes.[16]

Reaction of $PhCH_2{-}Mn(CO)_5$ with [(η^6-benzyl methyl thioether)$Cr(CO)_3$]. Complex **8**, which results from the thermal treatment of (η^6-benzyl methyl thioether)tricarbonylchromium with $PhCH_2{-}Mn(CO)_5$ in heptane, was isolated after purification by flash chromatography on silica gel. The former bright yellow complex is stable in the solid state and decomposes slowly when dissolved in humid organic solvents. Fast atom bombardment mass spectroscopy and elementary analysis gave satisfactory results.

Behavior of the "Pincer" Ligand−Tricarbonylchromium Complex toward Cyclomanganation. The free "pincer" ligand 1,3-bis((dimethylamino)methyl)-phenyl is an extremely powerful chelating agent which has been widely studied by van Koten and co-workers and which can undergo various metalation reactions resulting from the abstraction of a hydrogen or a halogen located mainly at the 2-position on the aromatic ring.[17] A sample of the pincer ligand was complexed in an η^6 fashion and isolated readily by following the method of Pauson and co-workers. The η^6-complexed ligand was treated with various amounts of $PhCH_2{-}Mn(CO)_5$ in refluxing heptane in order to shed light on the probability of chelating one manganese center with the two ancillary amino ligands (Scheme 1).

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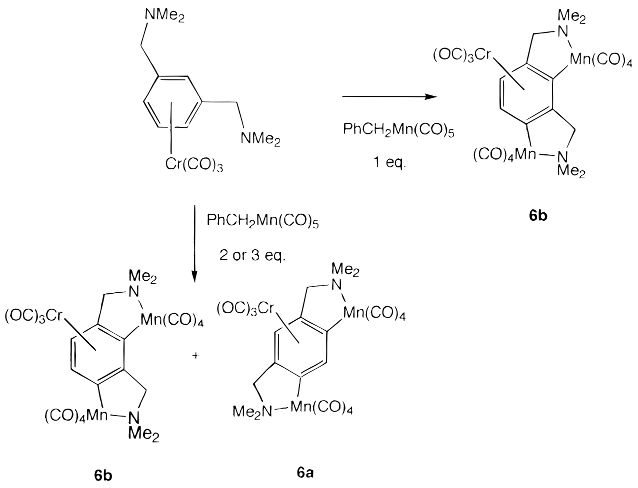
Scheme 1



None of our attempts to encapsulate one Mn(I) atom between the arms of the ligand led to the expected bimetallic species. According to FAB mass spectroscopy analyses only trimetallic species containing two Mn(CO)$_4$ fragments were formed with modest yields (Scheme 1). The reaction of an equimolar mixture of the pincer complex with PhCH$_2$−Mn(CO)$_5$ resulted in the precipitation of only one trimetallic isomer, complex **6b**. However, due to the modest yield in compound **6b** it is difficult to draw any definitive conclusions with regard to the apparent selectivity of the manganation reaction. If one assumes that some kind of isomerization process takes place between **6a** and **6b**, then factors such as the solubility should play an important role. These two compounds are only slightly soluble in nonpolar solvents such as heptane. The reaction carried out under similar conditions with 2 or 3 equiv of PhCH$_2$−Mn(CO)$_5$ led to mixtures of complexes **6a** and **6b** in respective ratios of 1:3.0 and 1:2.3. The two complexes were separated from the crude mixture by silica gel flash chromatography, and complex **6a** was recrystallized by the solvent diffusion method.

Spectroscopic Properties of Cyclomanganated (η^6-Arene)tricarbonylchromium Complexes. Infrared spectroscopy of cyclomanganated (η^6-arene)tricarbonylchromium complexes leads to the observation of composite spectra resulting from the overlap of intense CO bands of both the Mn(CO)$_4$ and the Cr(CO)$_3$ moieties. It is generally difficult to assign precisely the peaks observed in the region ranging from 1900 to 2000 cm^{-1}. In several cases a weak band at around 2080 cm^{-1} can be observed and assigned as the A band of the *cis*-chelated Mn(CO)$_4$ moiety. Furthermore, the typical carbonyl stretching E (or 2A′) band(s) related to the Cr(CO)$_3$ fragment[18,19] appears clearly in the region ranging from 1850 to 1890 cm^{-1}. From the IR data gathered in Table 2, we can ascertain that the Mn(CO)$_4$ moiety acts over the arene ring as an electron-donor substituent. A close comparison of the carbonyl stretching E (or 2A′) absorption wavenumber values of the substrates and of the corresponding manganated products suggests a greater flow of electron density from the metal-substituted arene to the chromium fragment, as was first proposed by Lotz and co-workers for analogous noncyclometalated complexes.[16] This is highlighted by the values of the parameter $\Delta\nu_E$ displayed in Table 2, which compare with the values reported for complexes bearing bulky electron-donating substituents such as *tert*-butyl.[18b] It is interesting to note that the absolute value of this parameter is about twice as large for the trimetallic complexes **6a** and **6b** than for bimetallic ones.

The proton NMR spectra of the manganated complexes presented in the present paper display the characteristic features generally observed for (η^6-arene)tricarbonylchromium complexes (Table 3).[20] The benzylic protons adjacent to a nitrogen- or sulfur-coordinated atom become diastereotopic upon manganation of the substrate. These protons appear, therefore, as two well-defined doublets that can be shifted as far as 1 ppm from each other. A strong deshielding is observed for the proton *ortho* with respect to the Mn(CO)$_4$. They usually appear, in C$_6$D$_6$, at the average value of 5.55 ppm, whereas the remaining aromatic proton signals are detected around 4.5 ppm. This important shift could be induced by the presence of an equatorial CO ligand of the Mn(CO)$_4$ moiety in the vicinity.

^{13}C NMR spectra display features similar to those reported by Lotz and co-workers for analogous complexes.[16] For instance, the *ipso* carbon bearing the manganese center appears at 122 ppm for **8**, 113 ppm for **5a**, and at 119 ppm for **1**. The ^{13}C NMR signal of the carbonyls of the Cr(CO)$_3$ fragment is generally deshielded by about 4 ppm upon manganation of the aromatic ring. This value is consistent with the electron-donor properties of Mn(CO)$_4$, deduced previously from IR experiments. The ^{13}C signals of the Mn(CO)$_4$ carbonyl ligands are weak and usually appear around 210 ppm.

Molecular Structures of Complexes 2 and 6a. Complexes **2** and **6a** are, to the best of our knowledge, the first reported examples of structurally characterized bimetallic and trimetallic cyclometalated (η^6-benzylamine)tricarbonylchromium derivatives. Tables 4 and 5 present respectively selected interatomic bond distances and bond angles.

Complex **2** crystallizes in the triclinic system, and the lattice belongs to the symmetry space group $P\bar{1}$. The arene ligand did not undergo any significant folding after the manganation. Furthermore, one can notice that the benzylic carbon remains in the mean plane of the arene. The two methoxy groups are found lying in

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Table 2. IR Data for Cyclomanganated Complexes and Respective Substrates (cm^{-1})

entry no.	product			starting material	
			E or 2A′	A_1E (or 2A′)	$\Delta\nu^a$
1	**1**	2080, 1990, 1953	1873	1969, 1889	16
2	**2**	2079, 1988, 1945	1863	1958, 1877	14
3	**3**	−, 1985, 1946	1861	1956, 1874	13
4	**4a**^{b}	2080, 1990, 1950	1869	1965, 1897, 1875^b	17
5	**5a**	2082, 1990, 1949	1865	1962, 1880	15
6	**6a**	2082, 2074, 1993, 1942	1861, 1845^b	1966, 1897	44
7	**6b**	2075, 1990, 1944	1856	1966, 1897	41
8	**8**	2084, 1997, 1956	1866	1968, 1890	24
9	**9**	2009, 1944, 1911	1872, 1851^b	1968, 1899	28

[a] $\Delta\nu = (\nu_H - \nu_{Mn})_{E\text{ or }A'} = (\nu_{E\text{ or }A'}$ of starting material) − ($\nu_{E\text{ or }A'}$ of product). [b] Determination of $\Delta\nu$ was done with average values of ν.

Table 3. ^{1}H NMR Data for Bimetallic Complexes

entry no.	compd	solvent	^{1}H NMR, δ (ppm)
1	**1**	C_6D_6	5.49 (d, H_3), 4.66 (t, H_5), 4.44 (m, H_4, H_6), 3.27 (d, $ArCH_2N$, $^1J = 15$ Hz), 2.00 (d, $\mathrm{ArC}H_2\mathrm{N}$, ^1J), 1.75 (s, 3H, $\mathrm{NC}H_3$), 1.37 (s, 3H, $\mathrm{NC}H_3$)
2	**2**	C_6D_6	4.83 (s, H_4), 4.46 (s, H_6), 3.72 (d, $\mathrm{ArC}H_2\mathrm{N}$, 1H, $^1J = 14$ Hz), 3.24 (s, 3H, $\mathrm{OC}H_3$), 3.18 (s, 3H, $\mathrm{OC}H_3$), 2.17 (d, 1H, ^1J), 1.89 (s, 3H, $\mathrm{NC}H_3$), 1.52 (s, 3H, $\mathrm{NC}H_3$)
3	**3**	C_6D_6	4.66 (d, 1H), 4.59 (d, 1H), 3.33 (d, 1H), 2.53 (d, 1H), 2.21 (s, 3H), 1.87 (s, 3H), 1.52 (s, 3H), 1.40 (s, 3H)
4	**4a,b**	C_6D_6	5.50 (d, H_3), 4.70 (t, H_5), 4.49 (t, H_4), 4.40 (d, H_6), 3.45 (q, 1H, $\mathrm{C}H\mathrm{CH}_3$), 1.77 (s, 3H, $\mathrm{NC}H_3$), 1.18 (s, 3H, $\mathrm{NC}H_3$), 0.33 (d, 3H, $\mathrm{CHC}H_3$)
5	**5a**	C_6D_6	5.60 (s, H_3), 4.93 (d, H_5), 4.78 (d, H_6), 3.18 (d, 1H, $\mathrm{ArC}H_2\mathrm{N}$), 3.11 (s, 3H, $\mathrm{OC}H_3$), 2.09 (d, 1H, $\mathrm{ArC}H_2\mathrm{N}$), 1.86 (s, 3H, $\mathrm{NC}H_3$), 1.47 (s, 3H, $\mathrm{NC}H_3$)
6	**6a**	C_3D_6O	6.48 (s, H_5), 5.66 (s, H_2), 4.03 (d, 2H, $\mathrm{ArC}H_2\mathrm{N}$), 4.34 (d, 2H, $\mathrm{ArC}H_2\mathrm{N}$), 2.95 (s, 6H, $\mathrm{NC}H_3$), 2.66 (s, 6H, $\mathrm{NC}H_3$)
7	**6b**	C_3D_6O	5.85 (d, H_5), 5.46 (d, H_6), 4.21 (d, 1H, $\mathrm{ArC}H_2\mathrm{N}$), 4.07 (d, 1H, $\mathrm{ArC}H_2\mathrm{N}$), 3.72 (d, 1H, $\mathrm{ArC}H_2\mathrm{N}$), 3.45 (d, 1H, $\mathrm{ArC}H_2\mathrm{N}$), 2.97 (s, 3H, $\mathrm{NC}H_3$), 2.96 (s, 3H, $\mathrm{NC}H_3$), 2.69 (s, 6H, $\mathrm{NC}H_3$)
8	**8**	$CDCl_3$	5.55 (m, 1H), 4.81 (t, 1H), 4.52 (m, 2H), 3.27 (d, 1H, $\mathrm{ArC}H_2\mathrm{S}$), 2.75 (1H, $\mathrm{ArC}H_2\mathrm{S}$), 1.52 (3H, $\mathrm{SC}H_3$)
9	**9**	C_6D_6	7.26−7.20 (m, 6H), 6.94−6.83 (m, 9H), 5.27 (d, H_3), 4.63 (d, H_5), 4.41 (d, H_6), 3.93 (t, H_4), 3.42 (d, $\mathrm{ArC}H_2\mathrm{S}$), 2.85 (d, $\mathrm{ArC}H_2\mathrm{S}$), 1.77 (s, 3H, $\mathrm{SC}H_3$)

Table 4. Selected Bond Distances (Å) for Compounds 2 and 6a

compd **2**		compd **6a**	
Mn−N1	2.156(2)	Mn1−C4	1.78(1)
Mn−C3	2.064(2)	Mn1−C5	1.87(1)
Mn−C12	1.849(2)	Mn1−C6	1.83(1)
Mn−C13	1.840(2)	Mn1−C7	1.87(1)
Mn−C14	1.857(2)	Mn1−N1	2.148(7)
Mn−C15	1.811(2)	Mn1−C10	2.061(8)
Cr−C2	2.212(2)	Mn2−C15	2.070(8)
Cr−C3	2.291(2)	Mn2−N2	2.160(7)
Cr−C6	2.248(2)	Mn2−C20	1.78(1)
Cr−C7	2.258(2)	Mn2−C21	1.85(1)
Cr−C8	2.241(2)	Mn2−C22	1.84(1)
Cr−C9	2.280(2)	Mn2−C23	1.85(1)
Cr−C16	1.824(2)	Cr−C1	1.84(1)
Cr−C17	1.833(2)	Cr−C2	1.83(1)
Cr−C18	1.831(2)	Cr−C3	1.83(1)
N1−C1	1.490(2)	Cr−C9	2.249(9)
Cl−C2	1.504(2)	Cr−C10	2.266(8)
C7−O1	1.362(2)	Cr−C13	2.226(8)
C7−O1	1.362(2)	Cr−C14	2.226(7)
C9−O2	1.361(2)	Cr−C15	2.299(8)
O1−C10	1.413(4)	Cr−C16	2.225(8)
O2−C11	1.434(3)	N1−C8	1.48(1)
C12−O3	1.128(3)	C8−C9	1.50(1)
C13−O4	1.139(3)	C14−C17	1.50(1)
C14−O5	1.136(3)	C15−C16	1.40(1)
C15−O6	1.139(3)	C17−N2	1.49(1)

Table 5. Selected Bond Angles (deg) for Compounds 2 and 6a

compd **2**		compd **6a**	
N1−Mn−C3	79.27(6)	C4−Mn1−C5	87.4(4)
N1−Mn−C12	95.73(9)	C4−Mn1−C6	91.9(4)
N1−Mn−C13	93.80(9)	C4−Mn1−C7	89.1(4)
N1−Mn−C14	90.28(9)	C4−Mn1−N1	172.7(4)
N1−Mn−C15	173.07(8)	C4−Mn1−C10	94.0(4)
C3−Mn−C12	85.89(8)	C5−Mn1−C6	94.1(4)
C3−Mn−C13	172.49(9)	C5−Mn1−C7	171.7(4)
C3−Mn−C14	91.91(8)	C21−Mn2−C22	94.2(4)
C3−Mn−C15	95.03(9)	C5−Mn1−C10	89.9(3)
C3−Cr−C18	97.78(8)	C22−Mn2−C23	90.8(4)
C12−Mn−C13	92.0(1)	C6−Mn1−C7	93.5(4)
C12−Mn−C14	173.1(1)	C8−N1−C11	107.0(7)
C12−Mn−C15	87.7(1)	C6−Mn1−N1	94.4(3)
C13−Mn−C14	91.0(1)	C8−N1−C12	108.4(8)
C13−Mn−C15	92.1(1)	C6−Mn1−C10	173.0(4)
C6−Cr−C17	104.99(9)	C11−N1−C12	107.4(7)
C14−Mn−C15	85.9(1)	C7−Mn1−N1	94.2(4)
C1−C2−C6	120.5(2)	N1−C8−C9	108.9(8)
C3−C2−C6	124.1(2)	C7−Mn1−C10	82.8(4)
C2−C3−C9	115.1(2)	C8−C9−C10	116.6(8)
C2−C6−C7	118.0(2)	N1−Mn1−C10	80.0(3)
C6−C7−C8	120.5(2)	C15−Mn2−N2	80.8(3)
C6−C7−O1	124.1(2)	C15−Mn2−C20	93.4(4)
C8−C7−O1	115.4(2)	C9−C10−C16	116.9(8)
C7−C8−C9	119.9(2)	C13−C14−C15	119.9(7)
C3−C9−C8	122.3(2)	C15−Mn2−C21	83.5(4)
C3−C9−O2	115.3(2)	C9−C13−C14	120.1(8)
C8−C9−O2	122.5(2)	C13−C14−C15	119.9(7)
C7−O1−C10	117.4(2)	C14−C15−C16	117.6(8)
N1−C1−C2	108.5(2)	C10−C16−C15	123.6(8)
C9−O2−C11	118.5(2)		
C1−C2−C3	115.3(2)		

the mean plane of the arene ring. The nitrogen atom bound to the manganese is pullsed out of the arene mean plane in a *trans* fashion with respect to the $Cr(CO)_3$ moiety. The bulkiness of $Mn(CO)_4$ not only induces a trivial "puckering" of the five-membered metallacycle but also induces an anti-eclipsed conformation to the $Cr(CO)_3$ tripod. The benzylic carbon is in the mean plane of the arene ligand. The axial benzylic hydrogen is proximal with respect to the $Cr(CO)_3$ moiety. The latter group adopts such a conformation in order to avoid steric interactions with the proximal carbonyl ligand of $Mn(CO)_4$. The plane defined by atoms C(13), Mn, and N(1) is not parallel to the mean plane of the aromatic ring. The $Mn(CO)_4$ moiety is twisted around the $Mn-C_{Ar}$ axis. The value of the torsion angle formed by C(9)−C(3)−Mn−C(15) amounts to 29.5°.

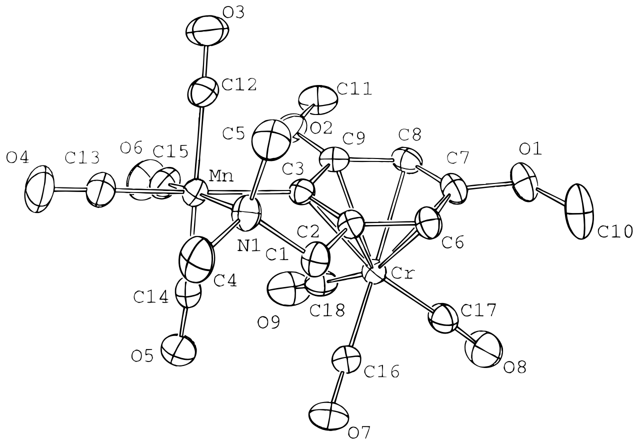


Figure 1. View of the molecular structure of **2**. Ellipsoids are scaled to enclose 30% of the electronic density. Hydrogen atoms are omitted.

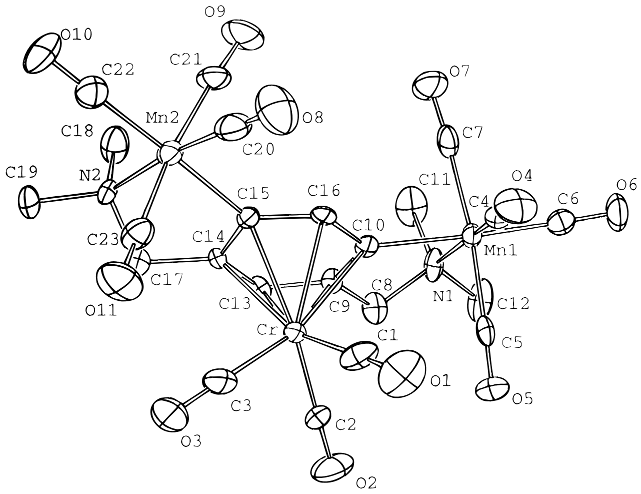


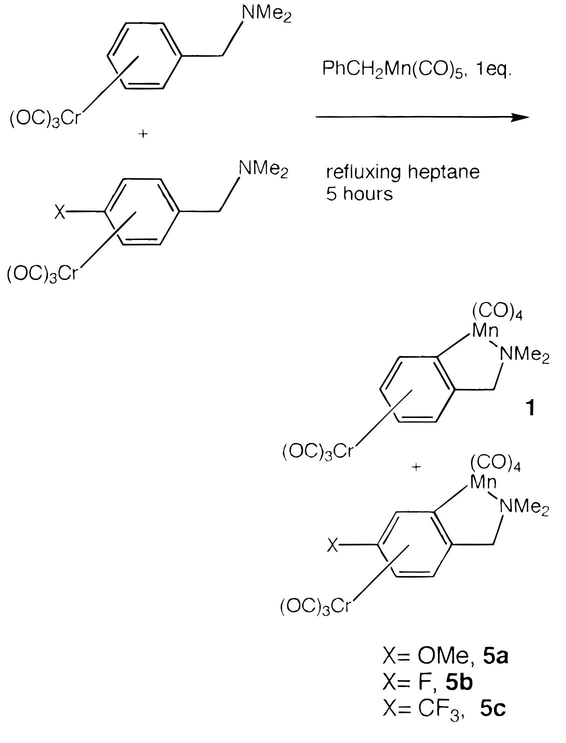
Figure 2. View of the molecular structure of **6a**. Ellipsoids are scaled to enclose 30% of the electronic density. Hydrogen atoms are omitted.

Close observation of the Mn(CO)$_4$ fragment reveals a distorted-octahedral geometry, as reported for other cyclomanganated complexes. In other terms, the proximal axial carbonyl ligand appears to be repelled by the Cr(CO)$_3$ tripod. The steric strain generated by the tetracarbonylmanganese moiety can be evaluated also from the slightly longer Cr−C(9) and Cr−C(3) bond distances of 2.28 and 2.29 Å, respectively, as compared to the mean value of 2.24 Å for the Cr−C$_{Ar}$ bonds in complex **2**.

The molecular structure of complex **6a** displays similar trends. It crystallizes in the monoclinic system, and the lattice fits the $P2_1/c$ symmetry group. In this crowded molecule the Cr(CO)$_3$ tripod adopts the predictable staggered conformation and the Mn(CO)$_4$ fragments appear as two distorted and twisted octahedral assemblies. The arene ring presents some signs of geometrical distortion, although they do not imply meaningful out-of-the-mean-plane folding. As compared with measurements for compound **2**, similar values of torsion angles are obtained for the angles defined by C(4)−Mn(1)−C(10)−C(16) (26.2°) and C(20)−Mn(2)−C(15)−C(16) (21.6°). The presence of two Mn(CO)$_4$ moieties on the arene ring does not influence the value of the C$_{Ar}$−Mn bond distance. Both C$_{Ar}$−Mn bond distances have values comparable to those reported herein for **2** and elsewhere for other mononuclear manganese complexes. In this polymetallic assembly the aromatic ring is shielded and covered by what one could consider as a "carbonyl blanket" made of the eight Mn- and three Cr-bonded carbonyl ligands (Figure 2).

Effect of Substituents on the Manganation of *para*-Substituted Dimethylbenzylamine Complexes. We were also interested in studying the substituent effects upon manganation of several *para*-substituted *N*,*N*-dimethylbenzylamine complexes. In these cases the cyclomanganation reaction should no doubt lead to one product metalated at the *meta* position with respect to the substituent. Furthermore, no steric effect could interfere and compete with the electronic effect of the substituent. Few reports address the effect of the substituent nature on the kinetics of the cyclomanganation reaction of free aromatics. The few studies carried out on *meta*- and *para*-substituted benzaldehyde, acetophenone, benzylamine, azobenzene, or phenylpyridine analogs reveal various substituent influences on the rate of the manganation reaction.[3] It was mainly established that a decrease in electron density on the arene ring should favor the cyclomanganation reaction. For instance, it was reported that electronegative or electron-withdrawing substituents such as fluorine would increase the metalation rate. We decided to carry out several competing cyclomanganation reactions by reacting equimolar mixtures of (η^6-*N*,*N*-dimethylbenzylamine)tricarbonylchromium, pentacarbonyl(phenylmethane-κC^1)manganese(I), and (η^6-4-X-*N*,*N*-dimethylbenzylamine)tricarbonylchromium (X = trifluoromethyl, fluoro, methoxy) (eq 2). The workup consisted of cooling the reaction mixture to −10 °C after 5 h of reaction at reflux temperature in heptane and solvent evaporation. The experiments were carried out in the presence of the internal reference 1,3,5-tri-*tert*-

Competing Metalation Reactions



(2)

Table 6

entry no.	complex	substituent	n_X/n_H	ln (n_Xn_H)	$\Delta\delta_{CO}$ (ppm)[a]	σ_m[b]	$\Delta\iota$[c]
1	**1**	H	1	0	0	0	0
2	**5b**	F	0.8(1)	−0.19(5)	−1.2	0.337	1.1
3	**5a**	OCH_3	0.62(3)	−0.47(5)	0.3	0.115	0.823
4	**5c**	CF_3	0.365(1)	−1.00(5)	−2.62	0.43	0.466

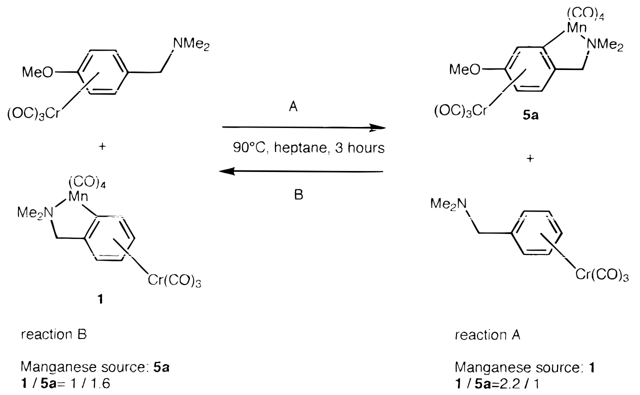
[a] See ref 22. [b] See ref 21. [c] See ref 23.

butylbenzene; conversions and n_X/n_H ratios were calculated from the ^{1}H NMR spectra of the crude mixtures. Details are given in the Experimental Section. For a given pair of substrates a series of experiments were performed at different concentrations. The former experiments allowed us to conclude that, within experimental error, concentration did not have a great influence on the value of the n_X/n_H ratio, which turned out to be mainly substituent dependent.

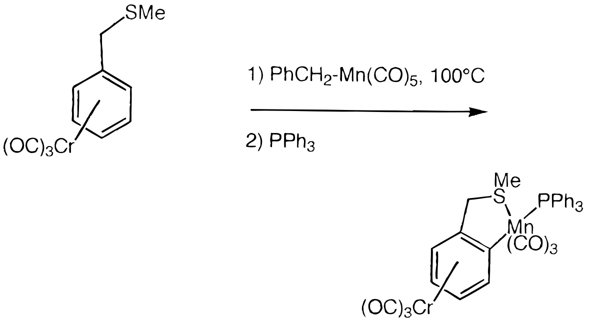
Table 6 presents the results obtained from the series of competition experiments carried out with complexes substituted with CF_3, OCH_3, and F. The data provided for H are expected extrapolations. The corresponding values of n_X/n_H ratios indicate that the cyclometalation occurs with some degree of selectivity at the (η^6-*N*,*N*-dimethylbenzylamine)Cr(CO)$_3$ unit and in the following order for *para*-substituted substrates: H > F > OCH_3 > CF_3. If we take into account all the data, no obvious correlation can be made either with the Hammett σ constants[21] or with the $\Delta\delta_{CO}$ parameter introduced by Fedorov and co-workers[22] or with the $\Delta\iota_X$ ($\Delta\iota_X = \iota_X - \iota_H$) parameter defined by Inamoto and co-workers, which is related to the inductive substituent effect parameter ι.[23] It is surprising that none of the substituted complexes undergo manganation more favorably than the *N*,*N*-dimethylbenzylamine complex. In a recent review dealing with the mechanistic aspects of several types of cyclometalation reactions, Ryabov predicted that it would be worthless trying to establish a correlation with Hammett parameters of substituents borne by the ligands undergoing the metalation.[24] The author underlined that the electronic properties of the substituent could affect both the reaction site and the metal center in the course of the reaction, thus rendering an interpretation of the results somewhat difficult.

We decided to investigate more closely the behavior of the title bimetallic complexes *versus* various species.

Scheme 2. "Mn(CO)$_4$" Transfer Reactions



Reactions with Carbon Monoxide and Phosphines. Solutions of complexes **1**, **2**, and **8** in tetrahydrofuran were separately submitted to a CO and ^{13}CO-enriched atmosphere at room temperature. We did not detect any trace of a carbonyl *cis*-migration product even after cooling the reaction medium below 0 °C. This contrasts dramatically with the results reported by Lotz and co-workers for a similar experiment conducted with pentacarbonyl{tricarbonyl(η^6-phenyl-κC^1)chromium}-manganese(I) that led to the production of the benzoyl derivative [(η^6-benzoyl-κC^7)tricarbonylchromio]pentacarbonylmanganese(I). Similarly, PPh_3 failed to induce the *cis* migration of CO ligands with both **1** and **8** and gave only the CO-displacement product **9** with the latter compound (eq 3).



9 (3)

Transfer of the Tetracarbonylmanganese Fragment. Ryabov reported that in some cases cyclopalladated complexes can undergo a transmetalation reaction.[25a] Bruce and co-workers pointed out that in some cases the Mn(CO)$_4$ moiety could be transfered efficiently from a dimanganated azobenzene complex to a "free" azobenzene molecule.[25b] Other authors reported similar results with acetophenone derivatives.[26] We undertook two control experiments in order to check whether or not complexes **1** and **5a** were able to interact somehow with their corresponding substrates.

In the first case, we reacted complex **1** with (η^6-4-methoxy-*N*,*N*-dimethylbenzylamine)tricarbonylchromium in heptane at 90 °C (Scheme 2).

In the second case, we reacted complex **5a** with (η^6-*N*,*N*-dimethylbenzylamine)tricarbonylchromium under the same conditions (Scheme 2).

Both experiments were run for 3.5 h with an internal reference. The reactions occurred with some decomposition and the formation of a brownish residue (20−35%). We observed from the proton NMR spectra of the respective crude mixtures the unexpected formation of

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(25) (a) Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252. (b) Bruce, M. I.; Lidell, M. J.; Snow, M. J.; Tiekink, E. R. T. *Aust. J. Chem.* **1988**, *41*, 1407.

(26) Robinson, N. P.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1992**, *430*, 79.

complex **5a** for the first experiment and the formation of complex **1** for the second experiment. This suggests that the tetracarbonylmanganese fragment underwent migration. For the first experiment the ratio of complex **1** relative to **5a** was 2.2:1. For the second experiment the ratio of complex **5a** relative to **1** was 1.6:1 (Scheme 2).

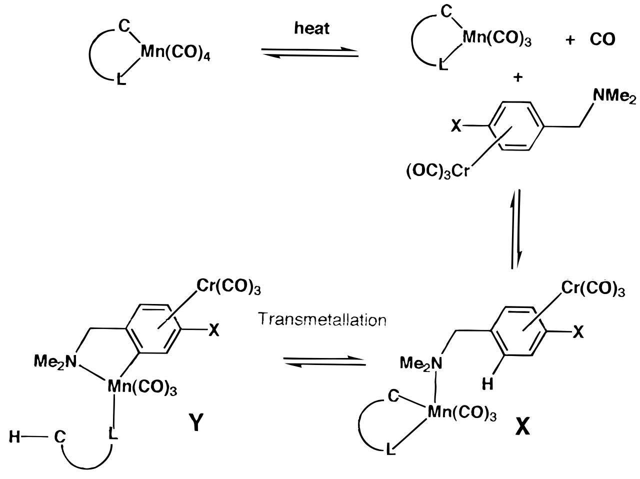
As a test for the inertness of the solvent in these “manganese transfer” reactions complex **1** was dissolved in toluene-d_8, which was chosen as a model of heptane. Although it seems very unlikely according to one reviewer, one could assume that cyclomanganated complexes undergo some manganese-exchange process with the deuterated solvent, which should yield a deuterium-enriched complex **1** upon thermal treatment. The solution of complex **1** was then heated at 110 °C in a sealed Schlenk tube for 3 h and analyzed by proton NMR at room temperature. Careful analyses of integrations and multiplicities indicated no relevant incorporation of deuterium by complex **1**. Therefore, this result suggests that the solvent does not play a preeminent role in the manganese-transfer reactions.

The lability of (η^6-aryl)tricarbonylchromium and aryltetracarbonylmanganese(I) complexes was confirmed by two additional experiments. We first reacted overnight at equimolar mixture of the benzylamine derivative tetracarbonyl{1-[(dimethylamino)methyl-κN]-phenyl-κC^2]manganese(I) with (η^6-*N*,*N*-dimethylbenzylamine)tricarbonylchromium in heptane at *ca.* 80 °C. This experiment allowed us to observe the formation of complex **1** in 60% yield. Similar experiments were carried out by reacting the chromium complex of *N*,*N*-dimethylbenzylamine with the *ortho*-manganated acetophenone complex. Heating the medium to 100 °C did not provide any trace of **1**. In a new experiment, raising the temperature to 130 °C resulted in the formation of very small amounts of compound **1** and large amounts of brownish decomposition products.

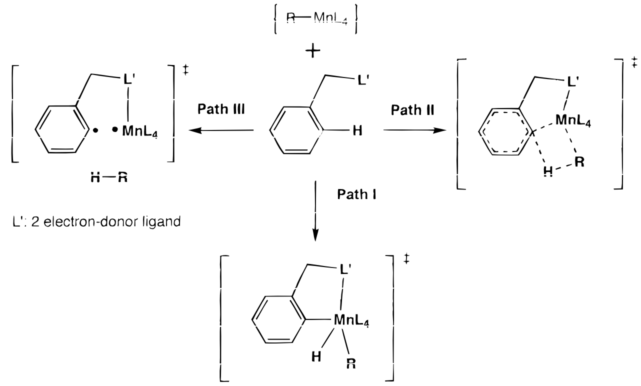
Additional experiments were then carried out separately with the two enantiomers of the *ortho*-manganated complex **7** and (η^6-*N*,*N*-dimethylbenzylamine)-tricarbonylchromium in order to check the possibility of transferring the chiral information borne by enantiomers of **7** through the formation of **1**, which then would possess planar chirality.[27] Qualitative circular dichroism experiments carried out in a region ranging from 210 to 500 nm did not reveal any optical activity for the two samples of **1** obtained respectively in 20% yield from reactions with the *S* enantiomer and with the *R* enantiomer of complex **7**.

Scheme 3 displays a possible mechanism for Mn(CO)$_4$ transfer reactions which accounts for the observations described above. The first step is the thermally promoted carbonyl ligand loss and the formation of an electron-deficent species which can coordinate any amino ligand present in the medium. The resulting transient species **X** may undergo an intramolecular transmetalation, yielding the species **Y** (Scheme 3). These two species can reasonably be considered as being in equilibrium. The species **Y** may then either coordinate carbon monoxide and yield the expected bimetallic complex.

Scheme 3



Scheme 4



The absence of asymmetric induction observed in the above experiment may be rationalized in terms of a large scrambling related to the lability of the Mn(CO)$_4$ moiety at the temperature required for the transmanganation to take place. It is possible that small amounts of chiral complex **1** form at the early stages of the reaction course. However, unavoidable interaction of these chiral species with unreacted (η^6-arene)tricarbonylchromium substrate, as depicted in Scheme 3, would eventually yield the racemic complex **1**.

The point that needs to be addressed in the scope of the cyclomanganation reaction is the nature of the intermediates involved in the C$_{Ar}$−H activation. Three types of mechanisms could reasonably account for the metalation of an aromatic carbon (Scheme 4).

The first one would entail a simple oxidative addition onto the manganese center that would lead to a very reactive hydrido−Mn(III) complex (path 1, Scheme 4).[2b] The latter species would form the final product *via* a reductive elimination of an alkane. The second mechanism would entail a multicentered process leading in a concerted manner to the metalated aromatic product (path 2, Scheme 4).[28] The third possible mechanism could involve a radical-mediated pathway within the manganation process (path 3, Scheme 4).[29] To date,

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(28) Bennett, R. L.; Bruce, M. I.; Stone, F. G. A. *J. Organomet. Chem.* **1975**, *94*, 65.

(29) In a comprehensive article dealing with the photochemistry of PhCH$_2$−Mn(CO)$_5$ Wrighton and a co-worker pointed out that photolysis of the former complex yields both CO loss and homolytic cleavage of the R−Mn bond: Young, K. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 157. For other leading references about the radical chemistry of alkyl- and arylmanganese complexes, see ref 2a.

none of these proposals can be ruled out. However, the "manganese transfer" reactions reported here must be taken into account in the overall process of cyclomanganation, since the cyclomanganated products can also take part in any of the stages of the manganation of an arene by $PhCH_2-Mn(CO)_5$.

Conclusion

We have demonstrated that several (η^6-arene)tricarbonylchromium complexes are suitable substrates for undergoing cyclomanganation reactions with $PhCH_2-Mn(CO)_5$. The reaction was shown to be mild and to be selectively directed toward the aromatic C−H bond located *ortho* with respect to the ancillary amino or thio ligand. Intrinsic steric bulk within the substrate could, however, lower the conversion rates. From the comparative study of the IR spectra of a series of substrates and cyclometalated products, we ascertained the electron-donating property of the chelated $Mn(CO)_4$ fragment. X-ray diffraction analyses of two polymetallic complexes indicate that metalation of (η^6-arene)tricarbonylchromium complexes by the sterically demanding $Mn(CO)_4$ group induces relevant structural distortions but no appreciable folding of the arene ligand. We have presented evidence that the $Mn(CO)_4$ moiety of a cyclometalated complex could in some cases migrate from its original chelating ligand to another one. The lability of the cyclometalated $[\{(\eta^6\text{-arene})Mn(CO)_4\}Cr(CO)_3]$ complexes such as those demonstrated here is unprecedented. In all cases presented herein, no evidence for exchange of the $Cr(CO)_3$ moiety has been found. We are now focusing our efforts on studying the synthetic potential of the bimetallic complexes reported herein, and we will pursue our investigation of the mechanistic issues of the cyclomanganation reaction.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere. Benzylpentacarbonylmanganese was prepared by following the literature procedure.[30] (η^6-Arene)tricarbonylchromium complexes were all prepared using the procedure of Pauson and co-workers, which consists of the thermal treatment of an aromatic substrate by $Cr(CO)_6$ in a mixture of 10% tetrahydrofuran in di-*n*-butyl ether. All experiments involving (η^6-arene)tricarbonylchromium complexes were always protected from exposure to light and oxygen. N-Methylation of racemic and optically active benzylamine derivatives was performed by using the procedure of van Koten and co-workers.[31] The two *R* and *S* enantiomers of complex **7** were successfully synthesized from chiral 1-(phenylamino)ethane derivatives commercially available from Aldrich Chemical Co. and Lancaster in ca. 97% optical purity. Tetrahydrofuran (THF), di-*n*-butyl ether (DBE), diethyl ether, hexane, and heptane were dried over sodium benzophenone ketyl under a dry nitrogen atmosphere and distilled prior to use. Before NMR experiments were performed, NMR solvents and tubes were purged with dry nitrogen to remove oxygen. Products were separated by flash chromatography on a silica gel column (60 μm) under an atmosphere of dry nitrogen gas. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker AC 300 (resonance frequencies 300 MHz for ^{1}H and 75 MHz for ^{13}C) spectrometer, and chemical shifts are reported in parts per million downfield of Me_4Si. ^{1}H NMR spectra were referenced against the residual ^{1}H impurity of the deuterated solvent (δ ppm) 7.15 (C_6D_6), 7.24 ($CDCl_3$), 2.05 ($(CD_3)_2CO$)), and ^{13}C NMR spectra were referenced against the ^{13}C resonance of the solvent (δ 128.0 (C_6D_6), 77.1 ($CDCl_3$), 29.8, 206.0 ($(CD_3)_2CO$)). Infrared spectra (reported in cm^{-1}) were measured on a Bruker IFS 66 FT spectrometer. Specific rotations [α] were determined for complexes (*S*)-**7** and (*R*)-**7** at 20 °C in a 10 cm length cell at the wavelength of the sodium D band (589 nm), and rotation angles were measured in grad. Mass spectra and high-resolution MS were performed at the "Service de Spectrométrie de Masse de l'Université Louis Pasteur" by using the positive ion fast atom bombardment method. Elemental analyses (reported in percent mass) were performed at the "Service Central d'Analyses du CNRS" at Vernaison, France. Circular dichroism measurements were carried out at the "Ecole Supérieure de Biotechnologies de Strasbourg", Strasbourg, France.

General Procedure for the Preparation of (η^6-Arene)tricarbonylchromium Complexes. In a 1:10 mixture of tetrahydrofuran and di-*n*-butyl ether were dissolved an amount of hexacarbonylchromium and a slight excess of arene. The resulting solution was brought to reflux for several hours under an atmosphere of nitrogen until traces of chromium oxide began to appear in the reaction medium. At this stage the color of the reaction medium was yellow to orange. The solution was cooled to room temperature and filtered over Celite, and both the solvents and the unreacted $Cr(CO)_6$ were removed under vacuum. The crude oily residue was then redissolved in dry diethyl ether and the solution mixed with silica gel. The solvent was removed under reduced pressure, and the resulting coated silica gel was loaded on the top of a silica gel column packed in dry and degassed hexane. The unreacted arene ligand was eluted first with Et_2O/hexane (1:9). The (η^6-arene)tricarbonylchromium complex was often eluted with a pure polar solvent such as diethyl ether, acetone, or dichloromethane. The solvent was then evaporated under reduced pressure and the complex recrystallized from dry pentane or hexane.

Preparation of $[\{\eta^6\text{-}C_6H_5CH_2N(CH_3)_2\}Cr(CO)_3]$: $Cr(CO)_6$ (4.4 g, 20 mmol), *N,N*-dimethylbenzylamine (3.0 g, 30 mmol), THF (10 mL), DBE (90 mL); reflux for 48 h;[32] chromatography on SiO_2/Et_2O; 29% yield (1.6 g). IR $\nu(CH_2Cl_2)$: 1968.9, 1888.9. ^{1}H NMR ($CDCl_3$): δ 5.35 (m, 4H), 5.25 (m, 1H), 3.14 (s, 2H), 2.27 (s, 6H, N*Me*$_2$). ^{13}C NMR ($CDCl_3$): δ 45.3, 62.9, 91.4, 93.2, 93.9, 108.6, 232.9.

Preparation of $[\{\eta^6\text{-}3,5\text{-}(CH_3O)_2\text{-}C_6H_3CH_2N(CH_3)_2\}Cr(CO)_3]$: $Cr(CO)_6$ (2.5 g, 15 mmol), *N,N*-dimethyl-3,5-dimethoxybenzylamine (1.5 g, 20 mmol), THF (8 mL), DBE (60 mL); reflux for 48 h; 666 mg, 9.4% yield. IR $\nu(CH_2Cl_2)$: 1958.0, 1877.0. ^{1}H NMR ($CDCl_3$): δ 5.13 (s), 4.86 (s), 3.78 (s), 3.72 (s), 2.30 (s). ^{13}C NMR ($CDCl_3$): δ 45.4, 55.8, 63.6, 68.7, 75.4, 101.0, 107.3, 108.2, 143.6, 161.0, 233.6. MS (FAB): *m/e* 331.1 $(M)^+$, 275.1 $(M - 2CO)^+$, 247.1 $(M - 3CO)^+$, 194.1 $(M - Cr(CO)_3)^+$.

Preparation of $[\{\eta^6\text{-}3,6\text{-}(CH_3)_2\text{-}C_6H_3CH_2N(CH_3)_2\}Cr(CO)_3]$: $Cr(CO)_6$ (3.3 g, 15 mmol), *N,N*-dimethyl-3,6-dimethylbenzylamine (4.9 g, 30 mmol), THF (15 mL), DBE (150 mL); reflux for 48 h; chromatography on SiO_2/Et_2O; yield 58.4% (2.62 g). Anal. Calcd for $C_{14}H_{18}CrNO_3$: C, 55.99; H, 6.04; N, 4.66. Found: C, 56.24; H, 5.86; N, 4.77. IR $\nu(CH_2Cl_2)$: 1874, 1956. ^{1}H NMR (C_6D_6): δ 1.63 (s, 3H), 1.79 (s, 3H), 1.95 (s, 6H), 2.56 (d, 1H, $ArCH_2N$), 3.22 (d, 1H, $ArCH_2N$), 4.47 (dd, H_4, $^4J = 1.2$ Hz), 4.63 (d, H_5), 4.91 (d, H_2, $^4J = 1.2$). ^{13}C NMR (C_6D_6): δ 17.8, 19.8, 45.1, 60.9, 93.1, 96.0, 96.7, 106.5, 107.0, 108.4, 234.3.

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[30] Bruce, M. I.; Liddell, M. I.; Pain, G. N. *Inorg. Synth.* **1989**, *26*, 172.

[31] van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021.

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Preparation of $[\{\eta^6\text{-4-}CH_3O\text{-}C_6H_4CH_2N(CH_3)_2\}Cr(CO)_3]$:[33] $Cr(CO)_6$ (3.0 g, 13.6 mmol), 4-methoxy-*N*,*N*-dimethylbenzylamine (3.4 g, 20.4 mmol), THF (10 mL), DBE (150 mL); reflux for 40 h; chromatography over SiO_2/acetone; yield 51.0% (2.1 g). ^1H NMR (C_6D_6): δ 1.93 (s, NMe_2), 2.66 (s, 2H, $ArCH_2N$), 2.92 (s, OMe), 4.43 (d, 2H), 5.01 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 45.1, 55.8, 62.0, 78.1, 96.4, 101.2, 142.7, 233.1.

Preparation of $[\{\eta^6\text{-4-}CF_3\text{-}C_6H_4CH_2N(CH_3)_2\}Cr(CO)_3]$: $Cr(CO)_6$ (3.11 g, 15 mmol), 4-(trifluoromethyl)-*N*,*N*-dimethylbenzylamine (1.9 g, 10 mmol), THF (10 mL), DBE (80 mL); reflux for 24 h; chromatography over SiO_2/acetone; yield 7% (250 mg). ^1H NMR (C_6D_6): δ 1.84 (s, 6H, N−CH_3), 2.70 (s, 2H), 4.42 (d, 2H), 4.94 (d, 2H). ^{13}C NMR (C_6D_6): δ 45.5, 62.5, 89.6, 90.1, 102.3, 230.2.

Preparation of $[\{\eta^6\text{-4-F-}C_6H_4CH_2N(CH_3)_2\}Cr(CO))_3]$:[33] $Cr(CO)_6$ (1.45 g, 6.6 mmol), 4-fluoro-*N*,*N*-dimethylbenzylamine (841 mg, 5.5 mmol), THF (5 mL), DBE (70 mL); reflux for 24 h; chromatography over SiO_2/acetone; yield 15% (250 mg). ^1H NMR ($CDCl_3$): δ 2.25 (s, 6H), 3.00 (s, 2H), 5.37 (m, 2H), 5.51 (m, 2 H). ^{13}C NMR (C_6D_6): δ 45.1, 61.8, 79.2, 94.2, 102.8, 231.6.

Preparation of $[\{\eta^6\text{-1,3-}[CH_2N(CH_3)_2]_2C_6H_4\}Cr(CO)_3]$: $Cr(CO)_6$ (3 g, 13.6 mmol), 1,3-bis[(dimethylamino)methyl]benzene (6.05 g, 27.2 mmol), THF (7 mL), DBE (140 mL); reflux for 48 h; chromatography on SiO_2/acetone; yield 33.5% (1.63 g). Anal. Calcd for $C_{15}H_{20}CrN_2O_3$: C, 54.87; H, 6.14; N, 8.53. Found: C, 55.03; H, 6.39; N, 8.42. IR $\nu(CH_2Cl_2)$: 1897.0, 1966.1. ^1H NMR (C_6D_6): δ 1.93 (s, 6H), 2.85 (s, 4H), 4.65 (m, 3H), 5.10 (s, 1H). ^{13}C NMR (C_6D_6): 45.0, 62.6, 92.5, 93.4, 95.2, 109.3, 233.6.

Preparation of $[(\eta^6\text{-}C_6H_5CH_2SCH_3)Cr(CO)_3]$: $Cr(CO)_6$ (2.4 g, 11 mmol), benzyl methyl thioether dried over Al_2O_3 grade I (3 g, 22 mmol), THF (10 mL), DBE (150 mL); reflux for 45 h; chromatography on SiO_2/1:1 hexane/Et_2O; yield 69% (2.06 g). Anal. Calcd for $C_{11}H_{10}CrO_3S$: C, 48.81; H, 3.65. Found: C, 48.00; H, 3.42. IR $\nu(CH_2Cl_2)$: 1890.0, 1968.0. ^1H NMR (C_6D_6): δ 1.55 (s, 3H), 2.75 (s, 2H), 4.26−4.44 (m, 5H). ^{13}C NMR (C_6D_6): 15.1, 37.7, 90.5, 92.7, 93.1, 233.2.

Preparation of $[\{\eta^6\text{-}(S)\text{-}C_6H_5CH(CH_3)N(CH_3)_2\}Cr(CO)_3]$: $Cr(CO)_6$ (1.5 g, 0.00682 mol), (*S*)-α-methyl-*N*,*N*-dimethylbenzylamine (2.0 g, 0.0136 mol), THF (15 mL), DBE (150 mL); reflux for 24 h; chromatography over SiO_2/Et_2O; yield 58.5% (1.14 g), IR $\nu(CH_2Cl_2)$: 1875.0, 1897.0, 1965. UV−vis (CH_2Cl_2): 230, 255 (sh), 316 nm. ^1H NMR (C_6D_6): δ 0.97 (d, 3H), 1.86 (s, 6H), 3.13 (d, 1H), 4.48 (m, 3H), 4.67 (d, 1H), 4.89 (d, 1H). ^{13}C NMR (C_6D_6): δ 12.2, 40.6, 61.5, 91.6, 91.9, 93.0, 95.7, 112.6, 233.6.

Preparation of $[\{\eta^6\text{-}(R)\text{-}C_6H_5CH(CH_3)N(CH_3)_2\}Cr(CO)_3]$: $Cr(CO)_6$ (2.95 g, 13.4 mmol), (*R*)-α-methyl-*N*,*N*-dimethylbenzylamine (4 g, 26.8 mmol), THF (10 mL), DBE (150 mL); reflux for 48 h; chromatography over SiO_2/Et_2O; yield 47.3% (1.8 g).

Complexes (*S*)-7 and (*R*)-7. IR $\nu(CH_2Cl_2)$: 2067.3, 1973.8, 1930.4. ^1H NMR (C_6D_6): δ 0.64 (d, CH_3, 3H), 1.51 (s, CH_3, 3H), 2.06 (s, CH_3, 3H), 3.36 (q, 1H), 6.75 (d, 1H), 7.07 (t, 1H), 7.16 (m, 1H), 8.01 (d, 1H). High-resolution MS (FAB+) found (calcd) for $C_{12}H_{14}NO_4Mn$: 315.0300 (315.0303). Specific rotation for (*R*)-**7**: $[\alpha]_D$(MeOH, 20 °C, 3.19×10^{-3} g mL^{-1}) = −135 grad. Specific rotation for (*S*)-**7**: $[\alpha]_D$(MeOH, 20 °C, 2.18×10^{-3} g mL^{-1}) = +129 grad.

General Procedure for the Cyclomanganation of (η^6-Arene)tricarbonylchromium Complexes. A mixture of the starting (η^6-arene)$Cr(CO)_3$ complex and $PhCH_2-Mn(CO)_5$ was dissolved in a minimum volume (10 mL) of dry heptane and gently stirred at the boiling temperature of the solvent. The reaction was stopped when signs of manganese decomposition appeared. The reaction mixture was then cooled to −10 °C and filtered. The solid residue was washed three times with 20 mL of dry hexane and dried under vacuum. The solid was dissolved in a small volume of dry diethyl ether or acetone and filtered over Celite to remove the insoluble particles. The filtrate was concentrated to ca. 5 mL and the product precipitated by addition of hexane. The yellow amorphous compound can be stored for several weeks in a cool and dark place without undergoing decomposition. If necessary, mixtures of manganated complexes can be separated by silica gel chromatography under an inert and dry atmosphere.

Complex 1: $[\{\eta^6\text{-}C_6H_5CH_2N(CH_3)_2\}Cr(CO)_3]$ (360 mg, 1.3 mmol), $PhCH_2-Mn(CO)_5$ (0.42 g, 1.4 mmol), heptane (40 mL); reflux 5 h. Complex **1** was obtained in 80% yield (0.46 g). Anal. Calcd for $C_{16}H_{12}CrMnNO_7$: C, 44.27; N, 3.23; H, 2.76; Mn, 12.65. Found: C, 44.06; N, 3.25; H, 2.98; Mn, 13.80.

Complex 2. Anal. Calcd for $C_{18}H_{16}CrMnNO_9$: C, 43.49; N, 2.82; H, 3.22; Mn, 11.05. Found: C, 43.11; N, 3.07; H, 3.18; Mn, 12.50.

Complex 3: $[\{\eta^6\text{-3-}CH_3\text{-6-}CH_3\text{-}C_6H_3CH_2N(CH_3)_2\}Cr(CO)_3]$ (0.3 g, 1 mmol), $PhCH_2-Mn(CO)_5$ (0.29 g, 1 mmol), heptane (20 mL); reflux for 6 h. Complex **3** was obtained in 15% yield (0.073 g). Anal. Calcd for $C_{18}H_{17}CrMnO_7$: C, 46.36; H, 3.67. Found: C, 44.56; H, 3.36.

Complex 4b: (*R*)-$[\{\eta^6\text{-}C_6H_5CH(CH_3)N(CH_3)_2\}Cr(CO)_3]$ (0.29 g, 1.02 mmol), $PhCH_2-Mn(CO)_5$ (0.29 g, 1.02 mmol), heptane (25 mL); reflux for 6 h. Complex **4b** was obtained in 51% yield (0.24 g). Anal. Calcd for $C_{17}H_{14}CrMnNO_7$: C, 45.25; H, 3.13; N, 3.10. Found: C, 45.34; H, 3.30; N, 2.99. UV−vis λ(heptane/Et_2O): 213.8 ($\epsilon = 5.6 \times 10^6$ mol^{-1} L m^{-1}), 324.1 ($\epsilon = 4.2 \times 10^6$) nm. Circular dichroism λ(heptane/Et_2O): max 292.3, 294.4 nm. ^{13}C NMR (C_6D_6): δ 8.8, 47.0, 52.6, 91.0, 91.9, 92.3, 105.8, 210 (m, Mn−CO), 235.8 (Cr−CO).

Complex 5a: $[\{\eta^6\text{-4-}CH_3O\text{-}C_6H_4CH_2N(CH_3)_2\}Cr(CO)_3]$ (0.15 g, 0.5 mmol), $PhCH_2-Mn(CO)_5$ (0.14 g, 0.5 mmol), heptane (20 mL); reflux for 7 h. Complex **5a** was obtained in 52% yield (0.12 g). ^{13}C NMR (C_6D_6): δ 55.4, 55.8, 72.7, 81.6, 89.8, 91.7, 112.9, 141.1, 210 (m), 235.7. High-resolution MS (FAB+): found (calculated) for $C_{17}H_{14}NO_8CrMn$, 466.950 40 (466.950 50).

Complex 5c. IR $\nu_{CO}(CH_2Cl_2)$: 2083.6, 1993.7, 1965.4, 1952.7, 1896.1. ^1H NMR (C_6D_6): δ 6.18 (s, 1H), 5.13 (d, 1H), 4.21 (d, 1H), 3.25 (d, 1H, ^2J = 14 Hz), 1.96 (d, 1H, ^2J = 14 Hz), 1.69 (s, 3H, N−CH_3), 1.28 (s, 3H, N−CH_3). MS (FAB+): 505.0 $(M)^+$, 449.0 $(M - 2CO)^+$, 421.0 $(M - 3CO)^+$, 393.0 $(M - 4CO)^+$, 365.0 $(M - 5CO)^+$, 307.1.

Complexes 6a and 6b: $[\{\eta^6\text{-1,3-}\{CH_2N(CH_3)_2\}_2\text{-}C_6H_4\}Cr(CO)_3]$ (0.1 g, 0.28 mmol), $PhCH_2-Mn(CO)_5$ (0.24 g, 0.84 mmol), heptane (15 mL); reflux 6 h. The crude mixture was analyzed by ^1H NMR and chromatographed over SiO_2. Complex **6b** was first eluted with a 50/50 mixture of CH_2Cl_2 and hexane (0.026 g, 14.7%), followed by **6a** (pure CH_2Cl_2, 0.011 g, 6.4%). Complex **6b**: ^{13}C NMR (CD_2Cl_2) δ, 56.5, 57.4 (m), 74.9, 78.7, 94.0, 105.0, 118.0, 133 (m), 212.0 (m), 238.5; Ms (FAB+) *m*/*e* 660 $(M - CO)^+$, 633 $(M - 2CO)^+$, 495 $(M - Mn(CO)_4 - CO)^+$, 467 $(M - Mn(CO)_4 - 2CO)^+$. Complex **6a**: high-resolution MS (FAB+) found (calcd) for $C_{23}H_{18}N_2CrMn_2$ 659.9084 (659.9077).

Complex 8: $[(\eta^6\text{-}C_6H_5CH_2SCH_3)Cr(CO)_3]$ (0.2 g, 0.73 mmol), $PhCH_2-Mn(CO)_5$ (0.21 g, 0.74 mmol), heptane (20 mL); reflux 3 h. Silica was added to the reaction medium and the solvent evaporated under reduced pressure. The resulting powder was loaded on the top of a SiO_2 column and complex **8** eluted with pure Et_2O (0.13 g, 40% yield). ^{13}C NMR (C_3D_6O): δ 23.7, 50.1, 91.5, 92.9, 95.8, 109.9, 122.0, 218.0 (m), 236.4. MS (FAB): *m*/*e* 439.9 $(M)^+$, 383.9 $(M - 2CO)^-$, 355.9 $(M - 3CO)^+$, 327.9 $(M - 4CO)^+$, 299.9 $(M - 5CO)^+$. Anal. Calcd for $C_{15}H_9CrMnO_7S$: C, 40.81; H, 2.04. Found: C, 40.67; H, 2.16.

Competing Metalation Reactions. The two (η^6-arene)tricarbonylchromium complexes were loaded in equal amounts in a Schlenk vessel containing 0.5 equiv of $PhCH_2-Mn(CO)_5$ per chromium. 1,3,5-Tris-*tert*-butylbenzene was added to this mixture. Dried and degassed heptane was then added and the suspension vigorously stirred. The mixture was heated to reflux for 5 h and cooled to −10 °C. The solvent was then removed under vacuum and the crude residue analyzed by

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[33] Gilday, J. P.; Negri, J. T.; Widdowson, D. A. *Tetrahedron* **1989**, *45*, 4605.

proton NMR. Ratios n_X/n_H were calculated from the relative integrals of the signal of the aromatic protons located *ortho* to the manganese atom. These signals appear at the following chemical shifts in C_6D_6: **1**, 5.49 ppm; **5a**, 5.58 ppm; **5b**, 5.70 ppm; **5c**, 6.18 ppm. For a given complex, the integrals of these signals were measured and found consistent with those of the methyls of the $N(CH_3)_2$ moiety.

Manganese(I) Transfer Reactions. General Procedure. The two complexes were dissolved in dry heptane under an N_2 atmosphere. The mixture was then heated to 90 °C for several hours. The medium was cooled to −10 °C and the solvent evaporated under reduced pressure.

Reaction of 5a with $[\{\eta^6\text{-}C_6H_5CH_2N(CH_3)_2\}Cr(CO)_3]$: 5a (0.035 g, 0.075 mmol), $[\{\eta^6\text{-}C_6H_5CH_2N(CH_3)_2\}Cr(CO)_3]$ (0.020 g, 0.075 mmol), heptane (10 mL), 1,3,6-(t-Bu)$_3C_6H_3$ (0.026 g, 0.106 mmol). The mixture was heated to 90 °C for 4 h. The solvent was evaporated and the crude mixture analyzed by ^1H NMR. Careful analysis of the spectrum indicated the formation of complex **1** and a 35% loss in Mn(I). Compounds **5a** and **1** were formed in a ratio of 1.62:1.

Reaction of 1 with $[\{\eta^6\text{-}4\text{-OMe-}C_6H_5CH_2N(CH_3)_2\}Cr(CO)_3]$: 1 (0.040 g, 0.091 mmol), $[\{\eta^6\text{-}4\text{-OMe-}C_6H_5CH_2N(CH_3)_2\}Cr(CO)_3]$ (0.027 g, 0.091 mmol), heptane (10 mL), 1,3,6-(t-Bu)$_3C_6H_3$ (0.01 g, 0.0406 mmol). The mixture was heated to 90 °C for 4 h. The solvent was evaporated and the crude mixture analyzed by ^1H NMR. The analysis of the spectrum indicates 21% loss of Mn(I) and the formation of complex **5a**. Compounds **1** and **5a** were formed in a ratio of 2.16:1.

Reaction of $[(2\text{-}\eta)\text{-}Mn\{C_6H_4CH_2N(CH_3)_3\}(CO)_4]$ with $[\{\eta^6\text{-}C_6H_5CH_2N(CH_3)_3\}Cr(CO)_3]$: $[(2\text{-}\eta)\text{-}Mn\{C_6H_4CH_2N(CH_3)_3\}(CO)_4]$ (0.37 g, 1.22 mmol), $[\{\eta^6\text{-}C_6H_5CH_2N(CH_3)_3\}Cr(CO)_3]$ (0.3 g, 1.12 mmol), heptane (30 mL). The solution was heated to 80 °C overnight. The reaction mixture was stripped of solvent, and the crude mixture was analyzed by ^1H NMR. Complex **1** was recovered in 60% yield.

Reaction of $[\{\eta^6\text{-}C_6H_5CH_2N(CH_3)_3\}Cr(CO)_3]$ with (*R*)-7: $[\{\eta^6\text{-}C_6H_5CH_2N(CH_3)_3\}Cr(CO)_3]$ ().27 g, 1 mmol), **(*R*)-7** (315 mg, 1 mmol), heptane (15 mL). The reaction mixture was heated overnight to 80 °C. The solution was stripped of solvent and the residue washed with hexane, redissolved in Et_2O, and filtered over Celite. Solvents were removed over reduced pressure, and complex **1** was recovered in 22% yield (0.1 g).

Formation of Complex 9. $[(\eta^6\text{-}C_6H_5CH_2SCH_3)Cr(CO)_3]$ (0.195 g, 0.71 mmol) was reacted with $PhCH_2{-}Mn(CO)_5$ (0.2 g, 0.71 mmol) in refluxing heptane (20 mL) for 2 h. The mixture was cooled to room temperature and added with PPh_3 (0.19 g, 0.7 mmol). The solution was heated again to reflux of solvents, and a yellow solid precipitated out of the solution. The pale yellow solid was recovered after filtration in 56% yield (0.27 g). ^{13}C NMR (C_6D_6): δ 22.8, 49.3, 89.1, 90.3, 92.9, 108.5, 127.0−133.0 (m), 214.2 (m), 223.4 (m), 236.3. ^{31}P NMR (C_6D_6): δ, 57.0. MS (FAB+): *m/e* 673.8 $(M)^+$, 589.9 $(M - 3CO)^+$, 505.9 $(M - 6CO)^+$, 355.8, 317.0, 263.0.

Radiocrystallographic Determination of the Molecular Structures of Compounds 2 and 6a (See Table 4 for Acquisition Parameters). Collection of the X-ray Data and Structure Determination for 6a and 2. For both structures data were collected on a Enraf-Nonius CAD4-F diffractometer using Mo Kα graphite-monochromated radiation ($\lambda = 0.7107$ Å, room temperature, $\theta/2\theta$ scans). Absorption corrections derived from the ψ scans of four reflections were applied. The structures were solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors ($d_{C-H} = 0.95$ Å, $B_H = 1.3B_{equiv}$ for the atom to which it was attached). Non-hydrogen atoms were refined anisotropically. For all computations the Enraf-Nonius Molen package was used.[34]

Crystal Data for 2: yellow crystals, crystal dimensions 0.40 × 0.35 × 0.25 mm^3, $C_{18}H_{16}NO_9CrMn$, $M_r = 497.3$, triclinic, space group $P\bar{1}$, $a = 8.132(2)$ Å, $b = 10.225(3)$ Å, $c = 13.112(3)$ Å, $\alpha = 79.47(2)°$, $\beta = 86.13(2)°$, $\gamma = 75.73(2)°$, $V = 1038.5$ Å^3, $Z = 2$, $D_c = 1.590$ g cm^{-3}, μ(Mo Kα) = 11.414 cm^{-1}. A total of 6351 reflections was collected: $4° < 2\theta < 58°$; 4345 reflections having $I > 3\sigma(I)$; transmission factors 0.76/1.00; 271 parameters. Final results: $R(F) = 0.033$, $R_w(F) = 0.052$, GOF = 1.100, maximum residual electronic density 0.08 e Å^{-3}. Atomic coordinates with their estimated standard deviations corresponding to the final least-squares refinement are given in the Supporting Information.

Crystal Data for 6a: yellow crystals, crystal dimensions 0.38 × 0.24 × 0.20 mm^3, $C_{23}H_{18}N_2O_{11}CrMn_2$, $M_r = 660.3$, monoclinic, space group $P2_1/c$, $a = 17.520(5)$ Å, $b = 10.621(3)$ Å, $c = 15.059(4)$ Å, $\beta = 105.47(2)°$, $V = 2700.7$ Å^3, $Z = 4$, $D_c = 1.624$ g cm^{-3}, μ(Mo Kα), = 13.281 cm^{-1}. A total of 5936 reflections was collected: $4° < 2\theta < 52°$; 1841 reflections having $I > 3\sigma(I)$; transmission factors 0.91/1.00; 352 parameters. Final results: $R(F) = 0.045$, $R_w(F) = 0.049$, GOF = 1.001, maximum residual electronic density 0.11 e Å^{-3}. Atomic coordinates with their estimated standard deviations corresponding to the final least-squares refinement are given in the Supporting Information.

Complete atom coordinates, thermal parameters, and bond lengths and angles for both structures have been deposited at the Cambridge Crystallographic Data Centre.

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Supporting Information Available: Tables giving complete crystallographic data for complexes **2** and **6a** and a figure showing circular dichroism curves obtained for complexes **4a** and **4b** (20 pages). Ordering information is given on any current masthead page.

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[34] Fair, C. K. In *MOLEN: An Interactive Intelligent System for Crystal Structure Analysis*; Nonius: Delft, The Netherlands, 1990.