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Cyclomanganated (η^6-arene)tricarbonylchromium complexes: synthesis and reactivity

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Abstract

The cyclomanganation of (η^6-arene)tricarbonylchromium complexes by reaction with benzylpentacarbonylmanganese affords new bimetallic compounds. The mechanism of the manganation as well as other underlying aspects of the reactivity of cyclomanganated complexes are addressed in this report. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Chromium; Manganese; Carbonyl; Cyclometallation

1. Introduction

Organometallic materials bearing more than one metal center increasingly draw the interest of synthetical organometallic chemists [1]. We began recently to study the orthometallation reactions of (η^6-arene)tricarbonylchromium complexes by softer ways than the well known lithiation method [2]. Indeed it is well established that in such chromium(0) complexes the arene ligand bears a decreased electron density due to a charge transfer towards the $Cr(CO)_3$ moiety [3]. The latter bulky fragment behaves somewhat like an electron withdrawing substituent; it enables mainly reactions such as aromatic nucleophilic substitutions [4], metallation at the arene ring [5] and at the benzylic positions [6], and provides an outstanding stereochemical control due to the fact that one side of the arene is occupied by the carbonyl–metal tripod. The lithiation of (η^6-arene)tricarbonylchromium complexes by abstraction of an aromatic proton is easier than for aromatics. It is generally carried out at temperatures between −78 and −30°C. The corresponding lithio complexes readily react with electrophiles but cannot be isolated in a pure state due to their temperature sensitivity [7]. Other metallated arenetricarbonylchromium complexes have been prepared by transmetallation and replacement of lithium by manganese(I) [8], titanium(IV) [9], gold(I), copper(I) [10] centers, by ligand exchange reactions for the synthesis of a mercurated arenetricarbonylchromium complex [11] or by an oxidative-addition of Pd(0) complexes to chloroarenetricarbonylchromium complexes [12]. When we started our study no recent examples of metallation of (η^6-arene)tricarbonylchromium complexes via C–H activation were reported. Therefore, we decided to probe the feasibility of such metallation with (η^6-arene)tricarbonylchromium substrates and to take as a model the orthomanganation reaction promoted by compounds, such as $R-Mn(CO)_5$, when they are opposed to aromatics bearing endogenous ligands [13]. Herein we present a survey of our research encompassing both published [14] and recent results.

2. Results and discussion

2.1. Cyclomanganation of (η^6-arene)tricarbonylchromium complexes

The orthomanganation of aromatic compounds is a known reaction that has been intensively studied [15]. The thermolysis of alkylpentacarbonylmanganese compounds in the presence of various types of aromatic

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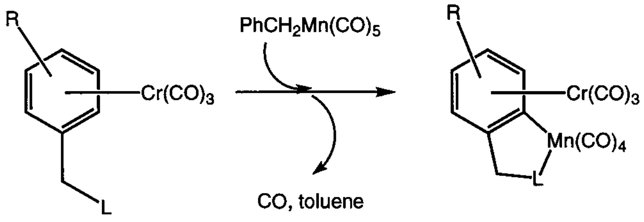
substrates yields selectively the corresponding orthometallated cyclomanganated product. Those deriving from aromatic ketones or aldehydes found some interesting applications in organic synthesis [16]. Indeed photochemical or chemical activation of the cyclomanganated complexes in presence of either an alkene, an alkyne or sulfurdioxide may yield either indanol derivatives or aromatic sulfonates [17]. Similar reactions have been reported recently also with cyclomanganated (η^6-acetophenone)tricarbonylchromium derivatives [18]. This abundance of applications reported for the manganese complexes of aromatic ketones and aldehydes contrasts dramatically with the absolute absence of similar reports in the cases of the complexes of benzylamine and phenylpyridine derivatives for instance. We thus decided to focus our study of the cyclomanganation reaction on benzylamine [14] and phenylpyridine $Cr(CO)_3$ derivatives with the wish that these derivatives will display a peculiar reactivity.



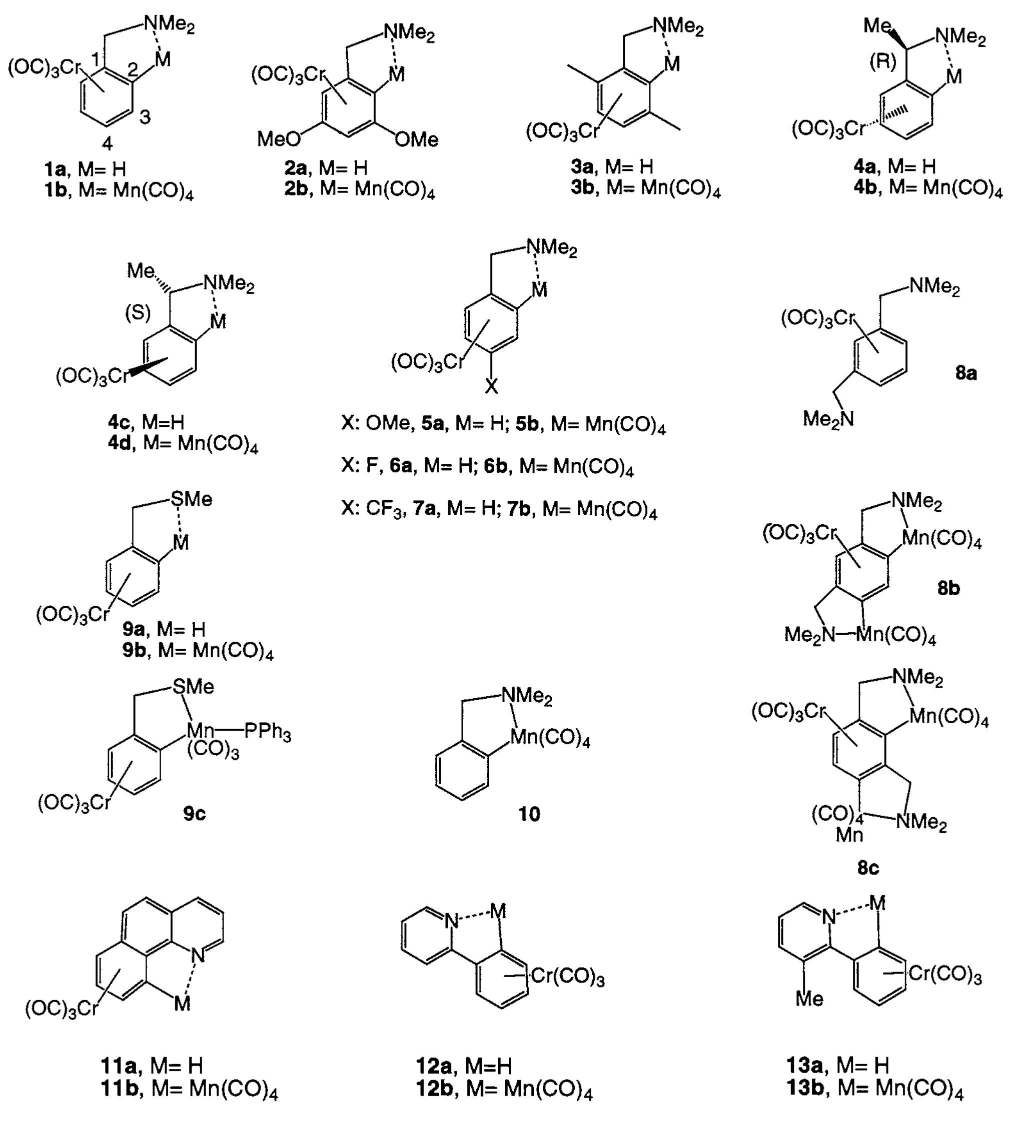


Chart I

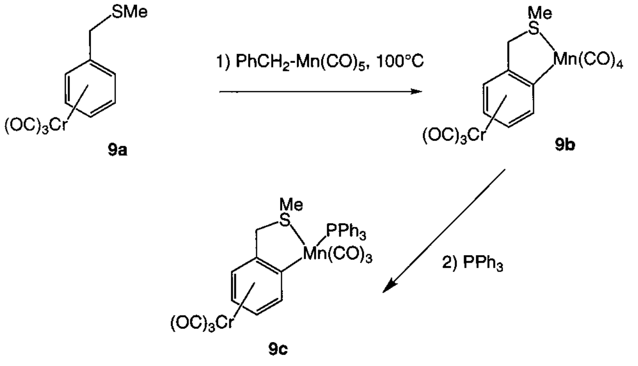
Table 1
Cyclomanganation of (η^6-arene)$Cr(CO)_3$ complexes (yields in bimetallic products)

Product	Time (h)	Yield (%)
1b	5	80
2b	4	100
3b	6	15
4b (d)	8(3)	47 (51)
11b	4	58
12b	8	83
13b	5	86

The corresponding (η^6-arene)tricarbonylchromium substrates (Chart I) were prepared using the general method of Pauson and Mahaffy [19] and were treated with $PhCH_2Mn(CO)_5$ in gently refluxing heptane for a period of time ranging from 3 to 8 h (Eq. 1) [14]. The duration of the reaction was mainly determined by the decomposition of both the 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. The manganation reaction is generally clean and the workup easy since the bimetallic products often precipitate out of the solution as yellow or orange amorphous powders. The compounds described in the present paper are displayed in Chart I. Table 1 presents the yields of formation of benzylamine and aryl-2-pyridine based bi-nuclear complexes that range between 15 (**3b**) and 100% (**2b**).

Far from being mainly dependent on the nature of the aromatic substrate (except for substrates in which the metallation site is hindered such as for **3a**) the manganation reaction seems to be also influenced by the solutility of the bimetallic product in the solvent used for this reaction. In an attempt to establish the effect of various substituents of the coordinated arene on the relative rate of cyclomanganation we undertook a systematic study reacting equimolar mixtures of $PhCH_2Mn(CO)_5$, **1a** and alternatively **5a**, **6a** and **7a** [14]. Unfortunately, no consistent correlation could be established neither with the Hammett σ constants [20] or with the $\Delta\delta_{CO}$ parameter introduced by Fedorov and co-workers [21] or with the $\Delta\iota_X$ ($\Delta\iota_X = \iota_X - \iota_H$) parameter defined by Inamoto and co-workers and which is related to the inductive substituent effect parameter ι [22].

The double metallation of ligand **8a** can be achieved also giving rise to mixtures of **8b** and **8c** [14]. A thioether such as **9a** also affords a cyclomanganated product **9b** that can be further modified by substitution of a CO ligand by triphenylphosphine to give **9c** (Scheme 1) [14].



Scheme 1.

2.2. Infrared spectroscopy of the new bimetallic compounds

IR spectroscopy has proved to be a useful tool for the interpretation of the electronic effects of organic substituents located on the complexed aromatic ligands of (η^6-arene)$Cr(CO)_3$ complexes. Indeed bathochromic shifts of the carbonyl ligand absorption bands are observable when the substitution pattern is modified on the complexed arene. To estimate the relative electronic effect of a given organic substituent, van Meurs and co-workers [23] calculated a $\Delta\nu_R$ parameter that corresponds to the shift underwent by either the A_1 or E-mode band upon change on the substitution pattern [24]. In short terms, the value and the sign of this parameter would inform on the electron-donating (negative value) or electron-accepting (positive value) nature of the substituent R. We therefore decided to apply this treatment to our compounds in order to establish the role of the $Mn(CO)_4$ moiety.

IR spectroscopy of cyclomanganated (η^6-arene) $Cr(CO)_3$ 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}. However, the typical carbonyl stretching E (or 2A′) band(s) related to the $Cr(CO)_3$ fragment [25,26] appears in the region ranging from 1850 to 1890 cm^{-1}. From the IR data gathered in Table 2 (entries 1–12), we can assume that the $Mn(CO)_4$ moiety acts over the arene ring as an electron-donating substituent. Comparison of the carbonyl stretching E (or 2A′) absorption wavenumbers values of the substrates and the corresponding manganated products suggests indeed 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 non-cyclometallated complexes [8]. This is highlighted by the negative values of the parameter $\Delta\nu_M$ calculated for the E-mode carbonyl absorption bands (Table 2).

Data extracted from other reports [8,9,12,18,27] (entries 13–21) and related to other metallated (η^6-

Table 2
IR data for metallated (η^6-arene)tricarbonylchromium complexes and their non-metallated analogues (values measured in CH_2Cl_2 solutions (cm^{-1}) unless otherwise stated)

Entry	Metallated complex		E or 2A′	Non-metallated complex	A_1E (or 2A′)	$(\Delta\nu_M)_E$ [a]
1	**1b**	2080, 1990, 1953	1873	**1a**	1969, 1889	−16
2	**2b**	2079, 1988, 1945	1863	**2b**	1958, 1877	−14
3	**3b**	1985, 1946	1861	**3a**	1956, 1874	−13
4	**4b (d)**	2080, 1990, 1950	1869	**4a (c)**	1965, 1897,1875 [b]	−17
5	**5b**	2082, 1990, 1949	1865	**5a**	1962, 1880	−15
6	**8b**	2082, 2074, 1993, 1942	1861, 1845 [b]	**8a**	1966, 1897	−44
7	**8c**	2075, 1990, 1944	1856	**8a**	1966, 1897	−41
8	**9b**	2084, 1997, 1956	1866	**9a**	1968, 1890	−24
9	**9c**	2009, 1944, 1911	1872, 1851 [b]	**9a**	1968, 1899	−28
10	**11b**	2086, 2005, 1989,1949	1877	**11a**	1964, 1889	−11
11	**12b**	2086, 2006, 1988, 1954	1881	**12a**	1970, 1895	−14
12	**13b**	2085, 2005, 1986, 1952	1878	**13a**	1969, 1894	−15
13	**14b**[c]	1947	1867	**14a**[c]	1971, 1874, 1860[b]	0[d]
14	**15**[c]	1953	1882, 1860[b]	**14a**[c]		4[d]
15	**16**[c]	1947	1867	**14a**[c]		0[d]
16	**17**[c]	1940	1860, 1840[b]	**14a**[c]		−17[d]
17	**18**	1952	1872	**14a**	1970, 1891	−19[e]
18	**19**	1951	1878	**14a**		−13[e]
19	**20b**	2093, 2010, 1965, 1937	1894, 1866[b]	**20a**	1965, 1903	−23[f]
20	**21**	2090, 2075, 2027, 2006, 1983, 1953	1877	**14a**		−14[g]
21	**22**	2098, 2084, 2014, 1989, 1973, 1951	1868	**14a**		−23[g]

a $(\Delta\nu_M)_E = (\nu_M - \nu_H)_{E \text{ or } A'} = \nu_{E \text{ or } A'}$ of metallated complex $- \nu_{E \text{ or } A'}$ of corresponding non-metallated complex.
[b] Determination of $\Delta\nu$ was done with average values of ν.
[c] KBr pellet; see ref [27]. See refs.: [d] [12], [e] [9], [f] [18] and [g] [8].

arene)tricarbonylchromium complexes (Chart II) suggest that even when the metal-substituent is a Ti(IV) or a Pd(II) center (entries 17 and 16, respectively, Table 2) the electron flow is more likely to be directed from the metal-substituent towards the chromiumtricarbonyl tripod ($\Delta\nu_E < 0$ cm^{-1}). Only data of compounds **15**, **14b** and **16** suggest either slight electron density transfer from the Cr(0) to the Pd(II) center ($\Delta\nu_E > 0$ cm^{-1}, Table 2, entry 14) or no transfer at all ($\Delta\nu_E = 0$ cm^{-1}, Table 2, entries 13 and 15) what would be consistent at a first approximation given the generally accepted electrophilic character of Pd(II) complexes. Although the $\Delta\nu$ parameter gives consistent values for organic arene substituents caution must be taken for the interpretation of $\Delta\nu_M$ values. Additional information on the actual electronic effect of the metal substituents treated here can be obtained from the evaluation of the force constant, k (in mdyne Å^{-1}), of the carbonyl C–O bonds related to the $Cr(CO)_3$ fragment. For this to be carried out one must have the exact frequencies of the A_1 and E-mode absorption bands. Because of the overlap of $Mn(CO)_4$ absorption bands with those produced by $Cr(CO)_3$ it was not possible to assign clearly the absorption band corresponding to the A_1-mode of the $Cr(CO)_3$ tripod of our compounds. Consequently, this problem precluded an exact calculation of k. However, on the basis of data published by other authors we calculated the values of k_M and Δk_{CO} by following the Cotton-Kraihanzel approximation [28] (Table 3) for palladium(II) compounds **14b**, **15**, **16**, **17**, for a titanium(IV) compound **18**, for a gold(I) compound **19** and for manganese(I) compounds **21** and **22** (Chart II). The data listed in Table 3 indicate clearly that in all cases the force constant is decreased upon metallation of the reference arene ligand (**14a**). The negative values obtained for Δk_{CO} compare well with those correlated to electron-donating effects of classical organic substituents.

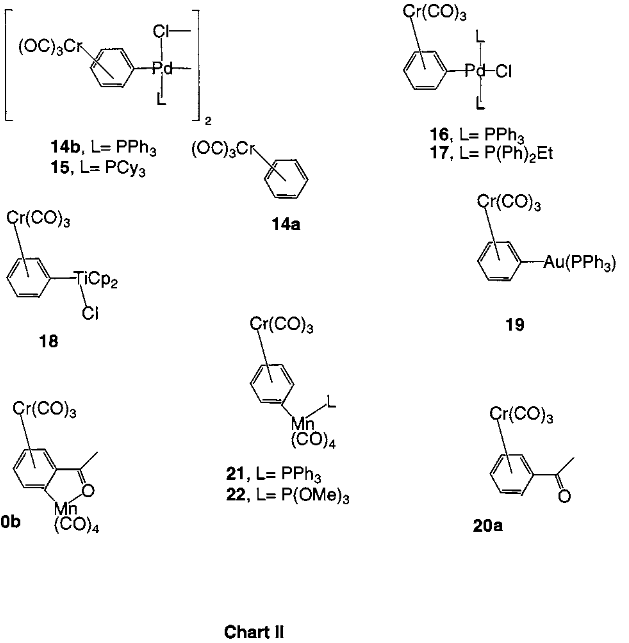


Chart II

2.3. *Clues for the mechanism of the cyclomanganation reaction*

The cyclomanganation reaction proceeds via activation of an aromatic carbon to hydrogen bond. The actual process of this reaction has not yet been completely elucidated. However, we brought recently the evidence that to some extent the manganation of an aromatic compound upon thermal treatment with an alkylpentacarbonylmanganese complex is a reversible process [29].

2.3.1. *Stereoselective cyclomanganation of **4a** [14]*

The separate cyclomanganation of compounds *(*R)-**4a** and (*S*)-**4c**, both respective enantiomers, is a stereoselective reaction that affords optically active bimetallic products with an apparent 100% diastereomeric yield according to ^{1}H-NMR analyses. Comparative optical circular dichroism measurements (CD) carried out on **4b** and **4d** provided additional evidences that the reaction was stereoselective and furthermore that no racemization took place (Fig. 1). This stereoselectivity reflects the importance of the stereochemical control initiated by the $Cr(CO)_3$ tripod. Although we have not yet been able to confirm the exact structures of **4b** and **4d**, it is very likely in both cases that the methyl group attached to the benzylic carbon is anti with respect to the $Cr(CO)_3$ tripod. This suggested to us that the manganation reaction could be reversible and that steric interactions within the reaction intermediates could lead to the less hindered and more thermodynamically stable isomer, e.g. **4b** or **4d** (Scheme 2). In this case a reversible metallation entails the lability of the $Mn(CO)_4$ moiety.

2.3.2. *Intrinsic lability of the $Mn(CO)_4$ moiety*

Bruce and co-workers pointed out that in some cases the $Mn(CO)_4$ moiety could be transferred efficiently from a dimanganated azobenzene complex to a 'free' azobenzene molecule [30]. Other authors reported similar results with acetophenone derivatives [31]. We undertook two control experiments in order to check whether or not complexes **1b** or **5b** were able to interact somehow with their corresponding substrates [14].

Table 3
List of carbonyl C–O bonds force constants related to the $Cr(CO)_3$ moiety of selected (η^6-arene)tricarbonyl complexes

Metallated complex	k^a_M	Reference complex	k^a_H	$\Delta k^{a,b}_{CO}$
14b	14.46	c	14.61	−0.15
15	14.56	c		−0.05
16	14.48	c		−0.13
17	14.28	c		−0.33
18	14.56	d	14.85	−0.29
19	14.62	d		−0.23
21	14.78	d		−0.07
22	14.63	d		−0.22

[a] In (mdyne Å^{-1}). [b] $\Delta k_{CO} = k_M - k_H$. [c] **14a** in KBr. [d] **14a** in CH_2Cl_2.

On the one hand, we reacted complex **1b** with **5a** in heptane at 90 °C (Scheme 3). On the other hand, we reacted complex **5b** with **1a** under the same conditions (Scheme 3).

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 (corresponding to ca. 20–35% of the total manganese amount). We observed in the proton NMR spectra of the respective crude mixtures the unexpected formation of complex **5b** for the first experiment and the formation of complex **1b** for the second experiment. This suggests that the tetracarbonylmanganese fragment underwent migration. For the first experiment the ratio of complex **1b** relatively to **5b** was 2.2:1. For the second experiment the ratio of complex **5b** relatively to **1b** was 1.6:1 (Scheme 3).

The lability of [(η^6-aryl)tricarbonylchromium]- and aryl-tetracarbonylmanganese(I) complexes was confirmed by two additional sets of experiments.

Firstly, we reacted overnight an equimolar mixture of the benzylamine derivative **10** with **1a** in heptane at ca. 80°C. This experiment allowed us to observe the formation of complex **1b** in 60% yield.

Secondly, two comparative experiments were undertaken to compare the strength of chelation of a benzylamine-type ligand with respect to a 2-phenylpyridine-type one. For instance two experiments were done following identical conditions by reacting **12b** with **1a** (reaction B, Scheme 4) and **12a** with **1b** (reaction A, Scheme 4) in presence of an internal reference (Scheme 4). For the first experiment, the ^{1}H-NMR spectrum of the crude mixture did not reveal any new product. In contrast, the second experiment lead to the formation of **12b** in 62% yield and the generation of **1a** in 97.5% yield. This result implies that among all the manganese borne by **1b** and released during the reaction, roughly two-thirds were actually transferred to form **12b** and about one-third were lost in a decomposition process generating carbon monoxide and manganese-containing solid residues.

2.3.3. *A possible mechanism for the transfer of the $Mn(CO)_4$ moiety*

Scheme 5 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 deficient species **A** which can coordinate any ligand present in the medium. The resulting transient species **B** may undergo an intramolecular

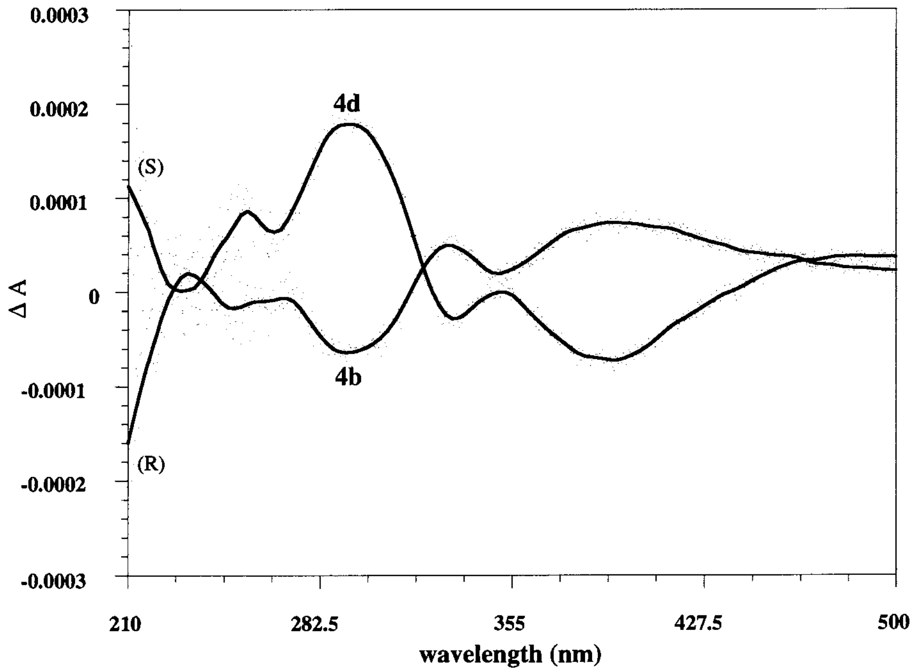
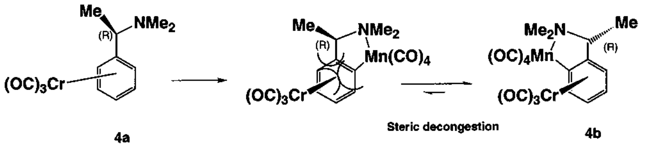


Fig. 1. Optical circular dichroïsm spectra [ΔA vs. λ (nm)] of compounds **4b** and **4d** measured in heptane (see ref. [14]).

transmetallation yielding the species **C** (Scheme 5). These two species can reasonably be considered as being in equilibrium. The species **C** may then coordinate carbon monoxide generated by the partial decomposition of aryltricarbonylmanganese species and eventually yield the expected bimetallic product.

3. Conclusion

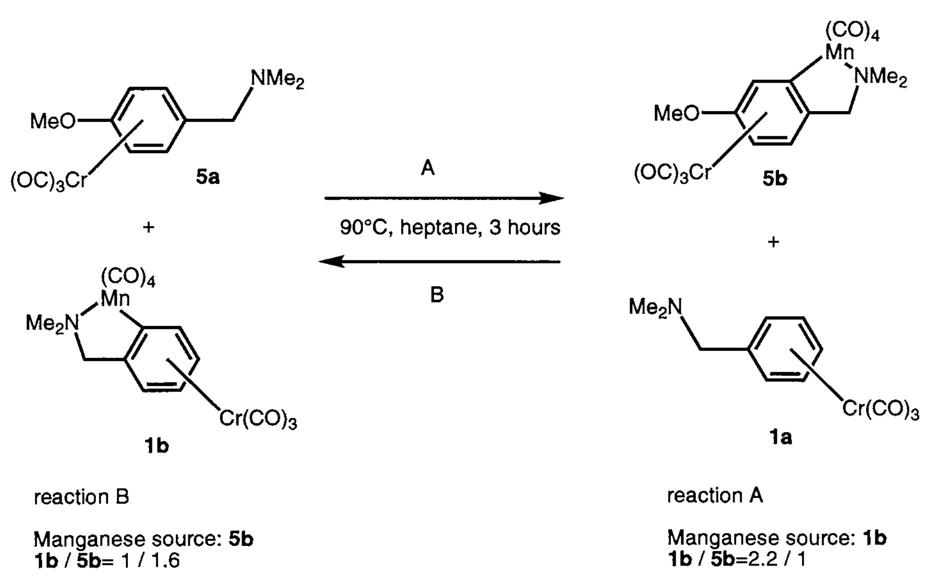
Investigation on the mechanism of the cyclomanganation reaction still focuses the interest of chemists. In a recent report, it has been demonstrated that in the overall process encompassing coordination of the ligand to the manganese(I) center and the C–H activation step, kinetic data provide evidence for a reaction mechanism with no defined rate limiting step [32]. Our results on the lability of the $Mn(CO)_4$ moiety bring additional elements for the understanding of this complex reaction. It is now clear that the exchange of coordinated $Mn(CO)_4$ fragments from ligand to ligand is a process that may take place in the reaction between alkylpentacarbonylmanganese and aromatic substrates. We demonstrated that the cyclomanganation of (η^6-arene)tricarbonylchromium complexes can be achieved readily providing thus new bimetallic substrates for further investigations. Hence, we will concentrate our future efforts in the study of new applications of cyclomanganated aromatics in organometallic synthesis that do not imply the irreversible loss of the Mn(I) center [33].



Scheme 2.

4. Experimental section

All reactions were performed under a dry nitrogen atmosphere. Products were separated by flash chromatography on silica gel (Aldrich, 60 µm) under a dry nitrogen atmosphere. Before NMR experiments were performed, NMR solvents and tubes were purged with dry nitrogen to remove oxygen. All ^{1}H- and ^{13}C-NMR spectra were recorded at ambient temperature on Bruker AC 300 and DRX 500 spectrometers (resonance frequencies 300 and 500 MHz for ^{1}H and 75 and 125 MHz for ^{13}C). Chemical shifts are reported in ppm downfield of Me_4Si. Coupling constants are reported in Hz. IR spectra (reported in cm^{-1}) were measured on a Perkin-Elmer 1600 Fourier transform spectrometer (Table 2). Elemental analyses (reported in percent mass) were performed at the 'Service Central d'Analyses du CNRS' at Vernaison, France and at the 'Service de Microanalyse de l'Université Louis Pasteur' at Strasbourg, France. Melting points were measured on a Büchi apparatus. Optical circular dichroism measurements were carried out in heptane with a ISA Jobin-



Scheme 3.

Yvon CD6 instrument. Benzylpentacarbonylmanganese was prepared by following the literature procedure [34]. (η^6-Arene)tricarbonylchromium complexes were prepared using the procedure of Pauson and Mahaffy which consists of the thermal treatment of the corresponding organic substrate by $Cr(CO)_6$ in a mixture of 10% THF in *n*-dibutylether. All experiments involving (η^6-arene)tricarbonylchromium complexes were always protected from exposure to light. Complexes **11a** [35] and **11b** have already been reported in literature. Herein we present an improved synthesis of **11b** [36].

4.1. General procedure for the preparation of (η^6-arene)tricarbonylchromium complexes

In a 1:10 mixture of THF and DBE were dissolved an amount of arene and a slight excess of hexacarbonylchromium. The resulting solution was brought to reflux for several hours under a dry nitrogen atmosphere until traces of chromium oxide appeared. After being cooled to room temperature, the solution was filtered over Celite and both solvents and hexacarbonylchromium were removed under vacuum. The crude oil was redissolved in dichloromethane and silica was added. The solvent was removed 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 was eluted first, followed by the (η^6-arene)tricarbonylchromium complex. The solvent was then evaporated under reduced pressure and the complex recrystallized from dry hexane.

*4.1.1. Preparation of **11a***

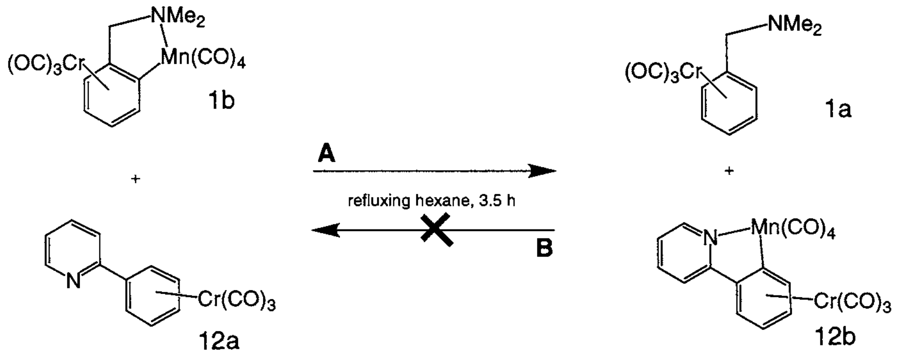
The reactants, conditions, and results follow: $Cr(CO)_6$ (3.0 g, 13.5 mmol), benzo[h]quinoline (2.0 g, 11.2 mmol), THF (7 ml), DBE (70 ml); reflux for 38 h; chromatography on SiO_2, hexane/CH_2Cl_2(3:7); 36% yield (1.25 g) of air stable, orange complex **11a**. ^{1}H-NMR (C_6D_6): δ 8.61 (dd, 1H, $^3J=4.4$, $^1J=1.83$), 7.37–7.33 (m, 1H), 6.82–6.72 (m, 4H), 5.13–5.10 (m, 1H), 4.72–4.69 (m, 2H).

*4.1.2. Preparation of **12a***

The reactants, conditions, and results follow: $Cr(CO)_6$ (10.6 g, 48.3 mmol), 2-phenylpyridine (5.0 g, 32.2 mmol), THF (13 ml), DBE (130 ml); reflux for 71 h; chromatography on SiO_2, hexane/dichloromethane (3:7); 84% yield (7.9 g) of air stable, crystalline, orange–yellow complex **12a**. F.p.: 121–122°C. ^{1}H-NMR (C_6D_6): 8.31 (d, 1H, $J=4.4$), 7.00 (t, 1H, $J=7.6$), 6.91 (d, 1H, $J=8.0$), 6.55 (t, 1H, $J=5.9$), 5.75 (d, 2H, $J=6.3$), 4.60 (t, 2H, $J=5.5$), 4.49 (m, 1H); ^{1}H-NMR ($CDCl_3$): 8.61 (d, 1H, $J=4.0$), 7.76 (t, 1H, $J=7.6$), 7.56 (d, 1H, $J=8.2$), 7.26 (m, 1H), 6.18 (d, 2H, $J=6.1$), 5.53–5.41 (m, 3H). ^{13}C-NMR($CDCl_3$): 232.5, 153.6, 149.5, 136.8, 123.4, 119.9, 105.5, 92.3, 92.1, 91.8. Anal. Found: C, 57.76; H, 3.18; N, 4.66. $C_{14}H_9NO_3Cr$ Calc.: C, 57.73; H, 3.09; N, 4.81%.

*4.1.3. Preparation of **13a***

The reactants, conditions, and results follow: $Cr(CO)_6$ (2.1 g, 9.4 mmol), 3-methyl, 2-phenylpyridine (1.1 g, 6.3 mmol), THF (7 ml), DBE (70 ml); reflux for 43 h; chromatography on SiO_2, hexane/dichloromethane (2:8); 80% yield (1.5 g) of air stable,



Scheme 4.

crystalline, orange–yellow complex **13a**. F.p.: 106–108°C. ^{1}H-NMR (C_6D_6): δ 8.31 (d, 1H, $J=3.8$), 6.82 (d, 1H, $J=7.7$), 6.54 (m, 1H), 5.41 (d, 2H, $J=6.3$), 4.55 (t, 2H, $J=5.8$), 4.47 (m, 1H), 2.03 (s, 3H); ^{1}H-NMR ($CDCl_3$): 8.51 (d, 1H, $J=4.3$), 7.55 (d, 1H, $J=7.6$), 7.23–7.19 (m, 1H), 5.85 (d, 2H, $J=7.0$), 5.48–5.40 (m, 3H), 2.57 (s, 3H). ^{13}C-NMR($CDCl_3$): 232.7, 152.2, 147.0, 139.5, 131.0, 123.1, 109.6, 94.8, 91.8, 20.3. Anal. Found: C, 59.27; H, 3.63; N, 4.52. $C_{15}H_{11}NO_3Cr$ Calc.: C, 59.02; H, 3.61; N, 4.59%.

4.2. General procedure for the cyclomanganation of (η^6-arene)tricarbonylchromium complexes

A mixture of (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 mixture was redissolved in dichloromethane and silica was added. The solvent was removed and the resulting coated silica gel was loaded on the top of a silica gel column packed in dry and degassed hexane.

4.2.1. Complex 11b

The reactants, conditions, and results follow: **11b** (0.13 g, 0.4 mmol), $PhCH_2$–$Mn(CO)_5$ (0.12 g, 0.4 mmol), heptane (10 ml); reflux 4 h; chromatography on SiO_2, hexane/diethylether (5:5) 58% yield (0.12 g) of air stable, crystalline, red complex **11b**. ^{1}H-NMR (C_6D_6): δ 8.07 (t, 1H), 6.96 (m, 1H), 6.65 (d, 1H), 6.40 (d, 1H), 6.30 (m, 1H), 6.07 (d, 1H), 5.33 (d, 1H), 4.64 (t, 1H).

4.2.2. Complex 12b

The reactants, conditions, and results follow: **12a** (1.23 g, 4.2 mmol), $PhCH_2$–$Mn(CO)_5$ (1.21 g, 4.2 mmol), heptane (10 ml); reflux 8 h; chromatography on SiO_2, dichloromethane; 83% yield (1.59 g) of air stable, amorphous, red–orange complex **12b**. F.p.: 150–155°C (decomp.). ^{1}H-NMR (C_6D_6): δ 7.89 (d,1H, $J=5.52$), 6.72 (t, 1H, $J=7.89$), 6.58 (d, 1H, 8.07), 6.02 (t, 1H, $J=6.61$), 5.90 (d, 1H, $J=6.27$), 4.86–4.77 (m, 2H), 4.58 (t, 1H, $J=6.06$). ^{13}C-NMR (CD_2Cl_2): 235.7 (Cr–*C*O), 219.4 (Mn–*C*O), 212.5 (Mn–*C*O), 211.6 (Mn–*C*O), 210.8 (Mn–*C*O), 165.1, 154.8, 139.1, 137.9, 124.7, 120.8, 114.1, 107.0, 94.8, 92.5, 88.5. Anal. Found: C, 47.39; H, 1.77; N, 3.08. $C_{18}H_8NO_7CrMn$ Calc.: C, 47.26; H, 1.75; N, 3.06%.

4.2.3. Complex 13b

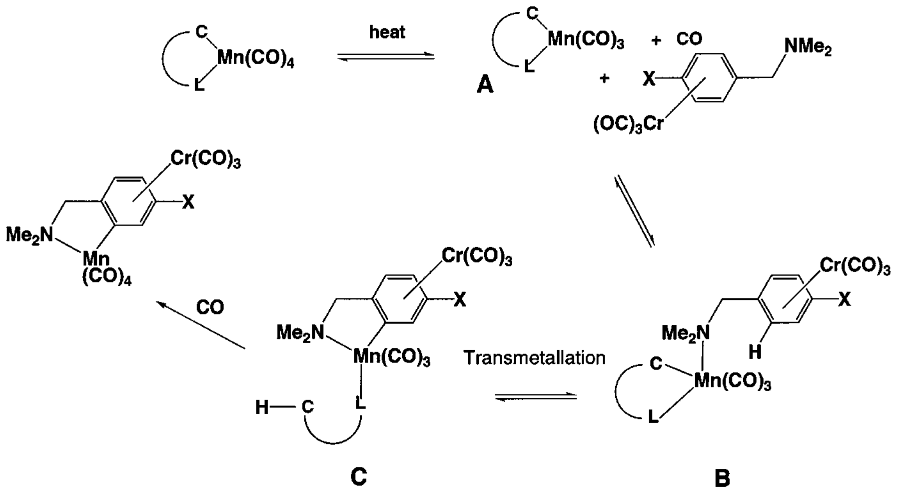
The reactants, conditions, and results follow: **13a** (0.82 g, 2.6 mmol), $PhCH_2$–$Mn(CO)_5$ (0.76 g, 2.65 mmol), heptane (17 ml); reflux 5 h; chromatography on SiO_2, hexane/dichloromethane (2:8); 86% yield (1.07 g) of air stable, crystalline, red–orange complex **13b**. Fp.: 140–145°C (decomp.). ^{1}H-NMR ($CDCl_3$): δ 8.69 (d, 1H, $J=5.22$), 7.66 (d, 1H, $J=7.68$), 7.15 (t, 1H, $J=6.45$), 6.14 (d, 1H, $J=6.03$), 6.00 (d, 1H, $J=6.87$), 5.54 (t, 1H, $J=6.18$), 5.35 (t, 1H, $J=5.91$), 2.72 (s, 3H). ^{13}C-NMR (CD_2Cl_2): 235.7 (Cr–*C*O), 219.3 (Mn–*C*O), 212.1 (Mn–*C*O), 211.8 (Mn–*C*O), 210.9 (Mn–*C*O), 163.2, 152.9, 143.3, 141.0, 134.4, 123.8, 115.3, 107.6, 94.6, 93.1, 92.2, 22.8. Anal. Found: C, 48.62; H, 2.13; N, 2.99. $C_{19}H_{10}NO_7MnCr$ Calc.: 48.41; H, 2.12; N, 2.97%.

4.3. General procedure for $Mn(CO)_4$ transfer reactions

The two complexes were dissolved in dry heptane under an N_2 atmosphere with 1,3,5-tris-*tert*-butylbenzene as a reference. The mixture was heated to 100°C for 3 h. The solvent was then removed under vacuum and the crude residue analyzed by proton NMR.

4.3.1. Reaction of 1a with 12b

A total of 150.2 mg (0.33 mmol) of **12b**, 89.1 mg (0.33 mmol) of **1a**, 22.2 mg (0.09 mmol) of 1,3,5-tris-*tert*-butylbenzene and 10 ml of heptane were reacted together. ^{1}H-NMR of the crude mixture showed no evidence for the $Mn(CO)_4$ moiety transfer: no doublets consistent with the benzylic $-CH_2-$ protons of **1a** appeared.



Scheme 5.

4.3.2. Reaction of **1b** with **12a**

A total of 155.5 mg (0.36 mmol) of **1b**, 103.5 mg, (0.36 mmol) of **12a**, 27.3 mg (0.111 mmol) of 1,3,5-tris-*tert*-butylbenzene and 10 ml of heptane were used. Yields for **1a** and **12b** were calculated by analysis of the ^{1}H-NMR peak integrations of the signals of **1a**, **12b** and 1,3,5-tris-*tert*-butylbenzene of the crude mixture. **1a**, 97.4% yield; **12b**, 62.0% yield.

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