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Reaction of α-halogenoester carbanions with cationic (η^6-arene) tricarbonylmanganese complexes

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Summary — The reaction of methyl 2-lithio 2-chloro and 2-lithio 2-bromopropanoate with cationic (arene)tricarbonylmanganese complexes affords the corresponding neutral (η^5-cyclohexadienyl) tricarbonyl complexes. Only one regioisomer is observed in the case of toluene and anisole complexes. The X-ray analysis of the complex due to the addition of methyl 2-lithio 2-chloropropanoate to the (benzene) manganese complex is reported.

(arene)tricarbonylmanganese / α-halogenoester carbanion / η^5-cyclohexadienyl / nucleophilic addition

Résumé — Réaction de carbanions d'α-halogénoesters avec des complexes (η^6-arène)tricarbonylmanganèse cationiques. Les 2-lithio 2-chloro et 2-lithio 2-bromo propanoate de méthyle réagissent avec les complexes cationiques d'(arène)tricarbonylmanganèse pour donner les complexes (η^5-cyclohexadiényl)tricarbonyl neutres correspondants. La formation d'un seul régioisomère est observée dans les cas des complexes du toluène et de l'anisole. La structure radiocristallographique du complexe dû à l'addition du 2-lithio 2-chloropropanoate de méthyle sur le complexe du (benzène)manganèse est décrite.

(arène)tricarbonylmanganèse / carbanion d'α-halogénoester / η^5-cyclohexadiényle / addition nucléophile

Introduction

The activation of arenes by coordination to transition metals provides a useful synthetic route to functionalized arenes [1]. The manganese mediated functionalization of arenes is particularly attractive because of the very high electrophilicity of the relevant complexes. A wide variety of nucleophiles add to the arene ring of these complexes such as ketone enolates and ester enolates [2–6], Grignard reagents [2, 6a, 6f, 6i], α-nitrile or α-nitro carbanions [6e, 6i, 7–9], diazo groups [10], carbenes [11], phosphates [12]. As it is well known that nucleophiles bearing substituents such as halogens, aryloxy, alkylthio groups at the carbanionic centers react rapidly with nitroarenes [13] which have also a highly electrophilic character, we were interested in studying the reactivity of such carbanions towards cationic arene-tricarbonyl complexes. Herein we report the full details of the syntheses of three new η^5-cyclohexadienyl complexes resulting from the addition of α-halogenoester carbanions to benzene and benzene-substituted tricarbonyl manganese cationic complexes and the X-ray analysis of one of them.

Results

We have shown that lithiated α-chloro and α-bromo ester carbanions (**2a**, **2b**) react with cationic (arene)tricarbonylmanganese complexes **1** to give, in very high yield, new neutral (cyclohexadienyl) tricarbonylmanganese complexes **3** by addition of the anion to the phenyl ring (fig 1).

The ^{1}H-NMR spectra of complexes **3** show the multiplicity of the H_6 proton (for example: t, J = 5.6 Hz in the case of **3a**) in agreement with an *endo* position of this hydrogen [14], in accordance with an *exo* addition of the nucleophile with respect to the metal atom. Two different signals for the diastereotopic H_1, H_5 and H_2, H_4 protons are observed: 3.19, 3.34 for **3a**, 3.13, 3.40 for **3d** and 5.01, 4.95 for **3a**, 4.93, 5.03 for **3d**, respectively. It is worth noting that the addition of **2a** to complexes **1b** and **1c** gives rise to the formation, in each case, of only one regioisomer (*meta* to the substituent) and 2 diastereoisomers in roughly the same ratio. Indeed, the resonance of the most deshielded proton (H_3) in **3c**, for example, appears as 2 doublets of doublets (4.96, dd, ^3J = 5.6 and ^4J = 2.3; 4.92, dd, ^3J = 5.6, ^4J = 2.3). This is clearly shown by ^{1}H- and ^{13}C-NMR

* Correspondence and reprints

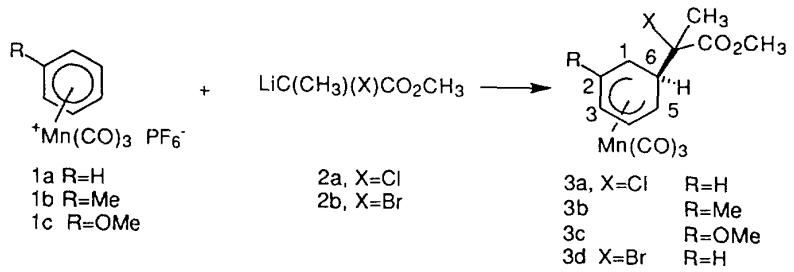


Fig 1.

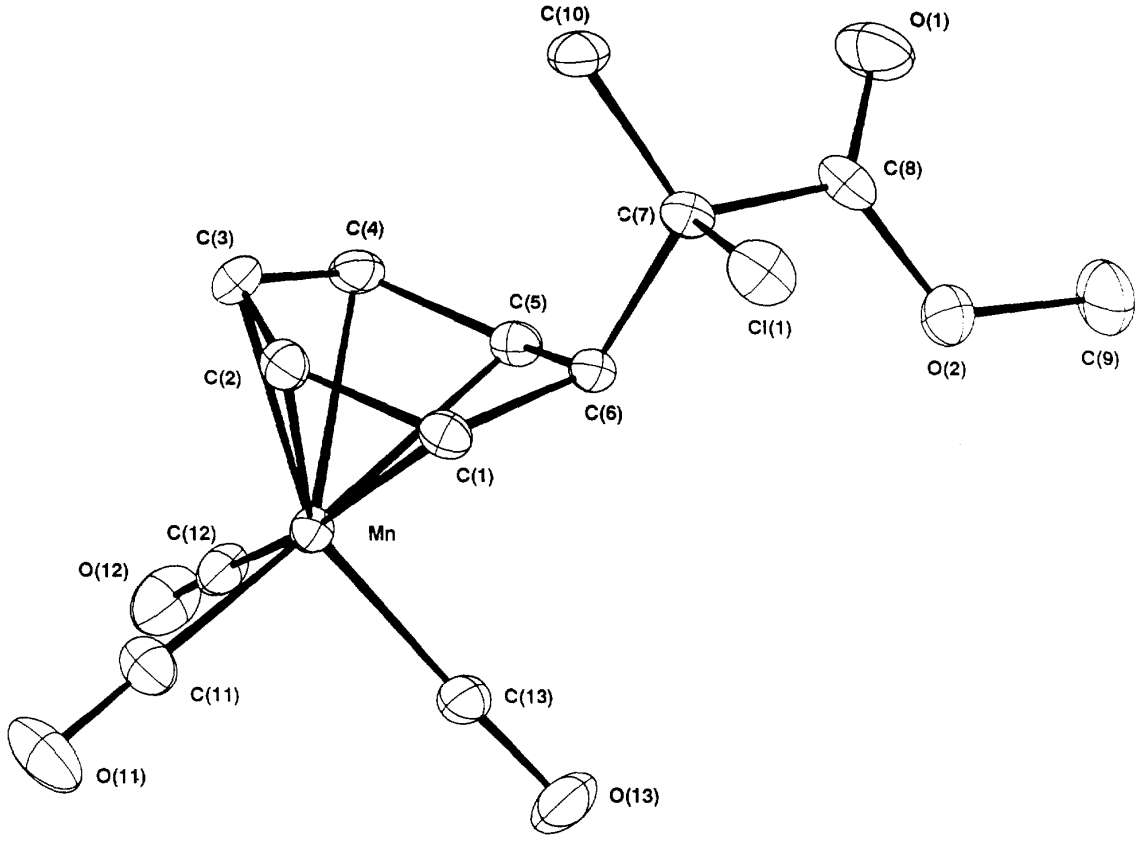


Fig 2. ORTEP view of complex **3a**.

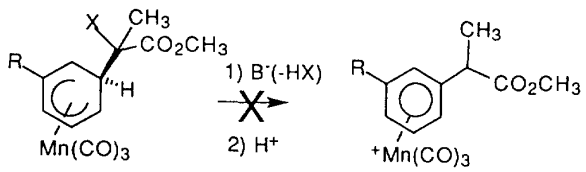
spectra (for example, methyl protons on C2 carbon exhibit two singlets at 1.32 and 1.35 ppm for **3b**).

Relatively few monometallic tricarbonylmanganese complexes having the same structure as complexes **3** have been structurally characterized [6f, 15]. Therefore, the structure determination of complex **3a** was undertaken to establish the coordination sphere around the manganese atom and to confirm the position of the nucleophilic substituent with respect to the metal atom.

As can be seen from the ORTEP view in figure 2, the cyclohexadienyl ring is nearly planar and folded about $C_1C_6C_5$ with an angle of 35°. The sp^3 C_6 carbon of the ring is eclipsed by a Mn–CO bond in agreement with other η^5-cyclohexadienyl complexes described in the literature. This compound represents the first structurally characterized example of an (η^5-cyclohexadienyl)tricarbonylmanganese complex substituted by an halogenoester.

Attempts to perform elimination of HX from complex **3a**, by using BuLi or NaH for example, did not succeed and the starting material alone was recovered (fig 3). The same observation was underlined in the case of (η^6-arene)tricarbonylchromium complexes which do not enter the vicarious nucleophilic substitution of hydrogen due to severe difficulties in HX elimination from (cyclohexadienyl)tricarbonylchromium complexes such as **4** [16] (fig 4).

In conclusion, α-halogenoester carbanions add very easily and in very high yield to cationic (η^6-arene)-



3a

Fig 3.

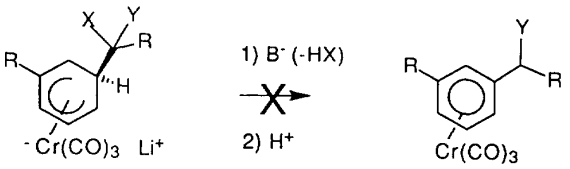


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Fig 4.

tricarbonylmanganese complexes. In the case of toluene and anisole complexes, this reaction is regioselective and only the formation of the *meta* isomer is observed. Studies of the oxidation of the complexes **3** to obtain the functionalized corresponding free arenes are in progress.

Experimental section

General

All reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl under dry nitrogen atmosphere and distilled just before use. ^{1}H- and ^{13}C-NMR spectra were acquired on Bruker AC 200 and 400 spectrometers, and chemical shifts were reported in parts per million downfield of Me_4Si. IR spectra were performed on a Perkin-Elmer 1420. Elemental analyses were performed by 'Le Service de Microanalyses de l'Université Pierre et Marie Curie'. Melting points were measured on a Reichert apparatus.

In a typical procedure, methyl chloropropanoate (0.9 mmol), dissolved in THF (10 mL) at −78 °C under nitrogen was added to a solution of $LiN(CH(CH_3)_2)_2$ (1.1 mmol) in THF (5 mL). The mixture was stirred during 5 min at −78 °C and the lithio derivative **2a** was added to the cationic complex **1a** (1.0 mmol) in suspension in THF (5 mL). After 10 min agitation under N_2, the reaction mixture was extracted with Et_2O. Solvents were removed under reduced pressure. The crude product was purified by flash chromatography on silica gel to give complex **3a**. Yellow crystals were obtained upon slow crystallization from diethyl ether/petroleum ether.

- *Complex* ***3a***

Yield: 97%; Fp: 84 °C.

IR (nujol): 2 020, 1 954, 1 912, 1 732 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): 5.68 (t, J = 5 Hz, 1H, H3); 5.01 (t, J = 5 Hz, 1H, H4); 4.95 (t, J = 5 Hz, 1H, H2); 3.74 (s, 3H, H9); 3.34 (m, 2H, H5 and H6); 3.19 (m, 1H, H1); 1.36 (s, 3H, H10).

^{13}C NMR ($CDCl_3$, 200 MHz): 220.0 ($Mn(CO)_3$); 170.1 (C8); 98.2 (C4); 97.9 (C2); 79.1 (C3); 71.9 (C7); 53.9 (C5); 53.1 (C1 and C9); 44.3 (C6); 23.4 (C10).

Anal calc for $C_{13}H_{12}ClMnO_5$: C, 46.08; H, 3.55. Found: C, 45.89; H, 3.58.

- *Complex* ***3b***

Yield: 91%; Fp: 110 °C.

IR (nujol): 2 020, 1 950, 1 920, 1 725 cm^{-1}.

^{1}H NMR (C_6D_6, 200 MHz): 4.65 (d, J = 6 Hz, 2H, H3, H3′); 4.17 (t, J = 6 Hz, 1H, H4); 4.10 (t, J = 6 Hz, 1H, H4′); 3.29 (t, J = 6 Hz, 1H, H6); 3.28 (t, J = 6 Hz, 1H, H6′); 3.18 (s, 6H, H9,H9′); 2.75 (m, 4H, H5, H5′, H1, H1′); 1.35 (s, 3H, CH3); 1.32 (s, 3H, CH3′); 1.13 (s, 3H, H10); 1.12 (s, 3H, H10′).

^{13}C NMR (C_3D_60, 200 MHz): 220.0 ($Mn(CO)_3$); 170.8 (C8); 115.15, 115.0 (C2, C2′); 98.4, 98.1 (C4, C4′); 81.53, 81.50 (C3, C3′); 73.1, 71.3 (C7, C7′); 56, 55.80, 55.47, 55.31 (C1, C1′, C5, C5′); 53.33 (C9); 46.77 (C6); 23.95, 22.36 (C10, C10′); 19.92 (CH3).

Anal calc for $C_{14}H_{14}ClMnO_5$: C, 47.69; H, 4.00. Found: C, 47.45; H, 3.90.

- *Complex* ***3c***

Yield: 82%; Fp: 92 °C.

IR (nujol): 2 015, 1 950, 1 915, 1 730 cm^{-1}.

Table I. X-ray experimental data.

Crystal data	
$[Mn(C_{10}H_{12}ClO_2)(CO)_3]$	Mo Kα radiation
M_r = 338.61	λ = 0.7107 Å
Triclinic	Cell parameters from 25 reflections
P−1	θ = 14–15°
a = 6.554(2) Å	μ = 10.85 cm^{-1}
b = 8.312(1) Å	T = 293(2) K
c = 13.538(5) Å	
α = 79.63(2)°	
β = 81.44(4)°	
γ = 89.57(1)°	
V = 717 Å^3	
Z = 2	
D_x = 1.568 g cm^{-3}	
Data collection	
Phillips PW 1100 diffractometer	2231 observed reflections ($I > 3\sigma(I)$)
ω/2θ scans	R_{int} = 0.0127
Absorption correction: DIFABS [19]	θ_{max} = 25°
Coefficient min = 0.86	h = −7 → 7
Coefficient max = 1.19	k = −9 → 9
2643 measured reflections	l = 0 → 16
2483 independent reflections	3 standard reflections
	Frequency: 60 min
	Decay: none
Refinement on F^2	
Refinement on F^2	$\Delta\rho_{max}$ = 0.34 e Å^{-3}
R = 0.0323	$\Delta\rho_{min}$ = −0.27 e Å^{-3}
R_w = 0.0341	Secondary extinction coefficient: 133 × 10^{-6}
S = 0.75	Atomic scattering factors from International Tables for X-ray Crystallography, Kynoch Press, Birmingham, England, 1974, Vol IV
2154 reflections	
219 parameters	
All H-atom parameters refined (one overall u[iso])	
w = 1	

Program used to solve and refine structure: CRYSTALS [17].
Program used for molecular graphics: CAMERON [18].

Table II. Selected bond lengths (Å) and angles (°) for complex **3a**.

Mn–C(11)	1.796(3)	C(11)–O(11)	1.148(4)
Mn–C(12)	1.803(3)	C(12)–O(12)	1.144(4)
Mn–C(13)	1.798(3)	C(13)–O(13)	1.144(4)
Mn–C(1)	2.229(3)	Mn–C(2)	2.139(3)
Mn–C(3)	2.125(3)	Mn–C(4)	2.140(3)
Mn–C(5)	2.215(3)	Cl(1)–C(7)	1.818(3)
C(1)–C(2)	1.382(4)	C(1)–C(6)	1.507(4)
C(2)–C(3)	1.412(4)	C(3)–C(4)	1.413(4)
C(4)–C(5)	1.389(4)	C(5)–C(6)	1.509(4)
C(6)–C(7)	1.556(4)	C(7)–C(8)	1.533(4)
C(7)–C(10)	1.531(4)	C(8)–O(1)	1.193(4)
C(8)–O(2)	1.322(4)	C(9)–0(2)	1.439(5)
C(11)–Mn–C(12)	86.8(2)	Mn–C(11)–O(11)	177.8(3)
C(11)–Mn–C(13)	94.1(2)	Mn–C(12)–O(12)	177.5(3)
C(12)–Mn–C(13)	93.2(2)	Mn–C(13)–O(13)	178.4(3)
C(11)–Mn–C(1)	104.1(1)	C(12)–Mn–C(1)	168.3(1)
C(13)–Mn–C(1)	90.3(1)	C(11)–Mn–C(2)	90.1(1)
C(12)–Mn–C(2)	141.2(1)	C(13)–Mn–C(2)	125.6(1)
C(11)–Mn–C(3)	105.3(1)	C(12)–Mn–C(3)	105.6(1)
C(13)–Mn–C(3)	153.5(1)	C(11)–Mn–C(4)	141.0(1)
C(12)–Mn–C(4)	90.4(1)	C(13)–Mn–C(4)	124.9(1)
C(11)–Mn–C(5)	168.0(1)(1)	C(12)–Mn–C(5)	104.5(1)
C(13)–Mn–C(5)	89.4(1)	C(2)–C(1)–C(6)	121.3(3)
C(1)–C(2)–C(3)	120.9(3)	C(2)–C(3)–C(4)	117.0(3)
C(3)–C(4)–C(5)	120.3(3)	C(4)–C(5)–C(6)	121.2(3)
C(1)–C(6)–C(5)	103.4(2)	C(1)–C(6)–C(7)	116.4(2)
C(5)–C(6)–C(7)	114.4(2)	Cl(1)–C(7)–C(6)	106.6(2)
Cl(1)–C(7)–C(8)	106.1(2)	C(6)–C(7)–C(8)	109.7(2)
Cl(1)–C(7)–C(10)	107.8(2)	C(6)–C(7)–C(10)	115.2(3)
C(8)–C(7)–C(10)	110.9(3)	C(7)–C(8)–O(1)	124.0(3)
C(7)–C(8)–O(2)	111.8(3)	O(1)–C(8)–O(2)	124.1(3)
C(8)–O(2)–C(9)	117.1(3)		

^{1}H NMR (C_6D_6, 400 MHz): 4.96 (dd, 1H, J = 5.6 Hz, J = 2.3 Hz, H3); 4.92 (dd, 1H, J = 5.6 Hz, J = 2.3 Hz, H3′); 4.25 (t, 1H, J = 5.6 Hz, H4); 4.21 (t, 1H, J = 5.6 Hz, H4′); 3.37 (t, 1H, J = 5.6 Hz, H6); 3.31 (t, 1H, J = 5.6 Hz, H6′); 3.19 (s, 3H, H9); 3.18 (s, 3H, H9′); 2.91 (m, 2H, H1 and H1′) 2.84 (s, 6H, OCH_3 and $OCH_{3'}$); 2.69 (t, 1H, J = 5.6 Hz, H5); 2.63 (t, 1H, J = 5.6 Hz, H5′); 1.15 (s, 3H, H10); 1.14 (s, 3H, H10′).

^{13}C NMR (C_6D_6) 400 MHz: 221.17 (Mn(CO)$_3$); 168.5, 168.4 (C9, C9′); 143.6, 143.4 (C2, C2′); 93.5, 93.3 (C4, C4′); 71.0, 70.8 (C7, C7′); 66.5, 66.1 (C3, C3′); 52.8 (OCH_3); 52.3 (C5, C5′); 51.2, 51.1 (C10, C10′); 46.3, 45.9 (C6, C6′); 38.5, 38.3 (C1, C1′); 22.3 (C8, C8′).

Anal calc for $C_{14}H_{14}ClMnO_6$: C, 45.57; H, 3.79. Found: C, 45.62; H, 3.81.

- *Complex* ***3d***

Yield: 94%; Fp: 108 °C.

IR (nujol): 2 015, 1 945, 1 921, 1 723 cm^{-1}.

^{1}H NMR ($CDCl_3$): 5.68 (tt, J = 5 Hz, J = 1 Hz, 1H, H3); 5.03 (tt, J = 5 Hz, J = 1 Hz, 1H, H4); 4.93 (tt, J = 5 Hz, J = 1 Hz, 1H, H2); 3.75 (s, 3H, H9); 3.55 (t, J = 5 Hz, 1H, H6); 3.40 (m, 1H, H5); 3.13 (m, 1H, H1); 1.47 (s, 3H, H10).

^{13}C NMR ($CDCl_3$): 221.9 (Mn(CO)$_3$); 170.4 (C8); 98.3 (C4); 98.0 (C2); 79.3 (C3); 63.4 (C7); 54.9 (C5); 54.6 (C1); 53.2 (C9); 45.8 (C6); 24.0 (C10).

Anal calc for $C_{13}H_{12}BrMnO_5$: C, 40.73; H, 3.13. Found: C, 40.26; H, 3.74.

X-ray determination for complex ***3a***

All experimental data are summarized in table I. Selected bond lengths (Å) and bond angles (°) are listed in table II. Fractional parameters, anisotropic thermal parameters, bond lengths and bond angles are available as supplementary material (tables S1–S5).

Supplementary material available

Supplementary material data have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication N° SUP 90457 (14 pages) and are available upon request from the Document Supply Centre.

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