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Study of η^5 -(1-chloro-4-methylcyclohexadienyl) and η^5 -(1-methyl-4-chlorocyclohexadienyl)tricarbonylmanganese complexes in solution and in the solid state

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Abstract

The spectroscopic studies of neutral η^5 -(1-chloro-4-methylcyclohexadienyl) and η^5 -(1-methyl-4-chlorocyclohexadienyl) tricarbonylmanganese complexes have been realized in solution by ¹H NMR spectroscopy as well as in the solid state. The structures showed a dihedral angle of the sp³ carbon of 33.2° and 36.6° with respect to the cyclohexadienyl ring. **To cite this article:** F. Rose-Munch et al., C. R. Chimie 6 (2003).

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Résumé

Les études spectroscopiques des complexes neutres du η^5 -(1-chloro-4-méthyl-cyclohexadiényl) et du η^5 -(1-méthyl-4-chloro-cyclohexadiényl)tricarbonyl manganèse ont été réalisées en particulier en solution par RMN ¹H et à l'état solide par radiocristallographie. Ces structures montrent un angle dièdre de 33,2° et de 36,6° du carbone sp³ par rapport au plan du cyclohexadiényle. **Pour citer cet article :** F. Rose-Munch et al., C. R. Chimie 6 (2003).

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Keywords: arenetricarbonylchromium complexes; arenetricarbonylmanganese complexes; arene; hydride; chromium; manganese

Mots clés : complexes arènetricarbonylchrome ; complexes arènetricarbonylmanganèse ; arène ; hydrure ; chrome ; manganèse

1. Introduction

Although known since 1957, cationic η^6 -(arene)tricarbonylmanganese complexes [1–4] have

received little attention in comparison with the isoelectronic neutral η^6 -(arene)tricarbonylchromium derivatives [5–8], which have been widely used in organic synthesis. The main feature of cationic manganese complexes is their high electrophilic properties which allowed addition reactions of nucleophiles such as,

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inter alia, hydrides [9–14], to the coordinated arenes, leading to the formation of stable η^5 -(cyclohexadienyl) $\text{Mn}(\text{CO})_3$ complexes. The high solubility and the ‘non-charged’ nature of these last complexes gave them some interesting properties that were used in different fields. At first, they have been proved to be useful for the purification of η^6 -(halogenoarene) $\text{Mn}^+(\text{CO})_3$ complexes, which are difficult to obtain in a pure form after coordination of the corresponding arenes to the $\text{Mn}(\text{CO})_3$ entity. Indeed, it has been well reported that complexation of bromobenzene, for example, suffered rather extensive loss of bromine and yielded a mixture of cationic bromobenzene and benzene complexes **1** and **2** (Fig. 1) [15, 16]. Thus, reaction of this mixture of complexes **1** and **2** with an hydride source afforded a mixture of neutral η^5 -(bromocyclohexadienyl) and η^5 -(cyclohexadienyl) $\text{Mn}(\text{CO})_3$ **3** and **4** that could easily be separated by silica gel chromatography column. Hydride abstraction by $\text{CPh}_3^+ \text{PF}_6^-$ from complex **3** gave the pure bromobenzene complex **1** (Fig. 1). Another source of difficulty to obtain η^6 -(halogenoarene) in a pure state comes from the problem due to their reactivity with polar solvents [16] and attempts to recrystallise the crude material from acetone–ethanol are frustrated by the reaction of the halogenoarene complex with EtOH, giving the ethoxybenzene complex. Only a relatively few studies about the reactivity of the neutral η^5 -Mn complexes were developed and involved attack at the terminus of the π -system leading to the formation of cyclohexadienes [4, 17] after an oxidative process. As far as we are concerned, we have used the anionic chromium complex **6** as a hydride donor towards cationic benzene Mn complex **2**, thus demonstrating not

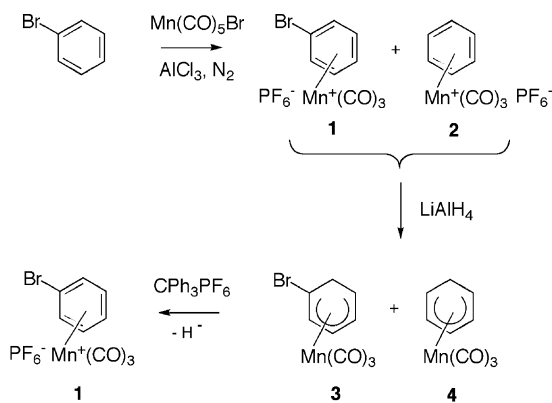


Fig. 1. Complexation of bromobenzene to $\text{Mn}(\text{CO})_3$ entity.

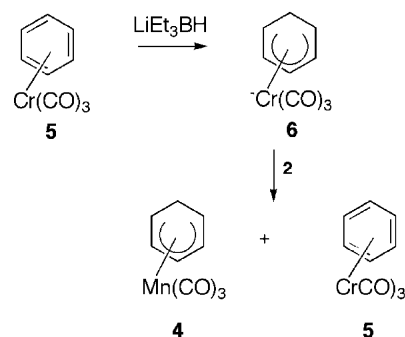


Fig. 2. Easy hydride addition to Mn complexes.

only the easy hydride addition to Mn complexes, but also the reversibility of hydride addition in the case of η^6 -(benzene) $\text{Cr}(\text{CO})_3$ complex. Indeed, hydride H^- was trapped with cationic η^6 -(benzene) $\text{Mn}^+(\text{CO})_3$ **2** to give the neutral η^5 -Mn complex **4** and the η^6 -Cr complex **5** (Fig. 2) [18]. We also described the first *cine* and *tele* nucleophilic substitutions of η^5 -(halogenocyclohexadienyl) $\text{Mn}(\text{CO})_3$ complexes after treatment with hydrides and a proton source [19]. Finally, very recently, we showed that η^5 -Mn complexes [19–23] could represent key building blocks for the synthesis of a new generation of electron-withdrawing group substituted η^6 -(arene) $\text{Mn}^+(\text{CO})_3$ complexes, via palladium-catalyzed reactions (Fig. 3) [24, 25]. Indeed, Pd-catalyzed reactions of complex **7** in the presence of AsPh_3 efficiently afforded the corresponding η^5 -Mn derivatives **8** substituted by carbon, oxygen, nitrogen, sulphur and phosphorous nucleophiles or η^5 complexes **9** under CO atmosphere. Removal of the exo-hydrogen with CPh_3BF_4 yielded the η^6 -complexes **10** or **11**. In the course of these studies, using differently substituted η^5 -(halogenocyclohexadienyl) $\text{Mn}(\text{CO})_3$ complexes as starting material, we prepared the two regioisomer chloro complexes **13** and **14**. In this paper, we describe their structures in solution by means of NMR spectroscopy and in the solid state by means of X-ray analysis.

2. Results and discussion

Addition of LiAlH_4 to *p*-chlorotoluene tricarbonyl-manganese complex **12** gave a 65:35 mixture of 1-chloro and 4-chloro complexes **13** and **14** in 90% yield [19, 26] Other hydride sources have been described in the literature, for example: LiEt_3BH , $\text{LiB}(i-$

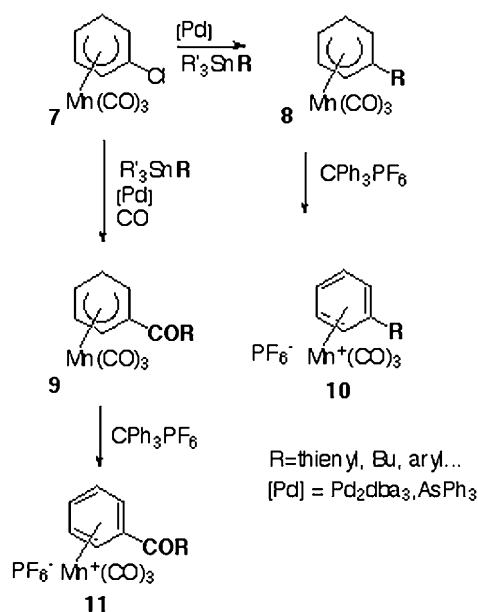


Fig. 3. Palladium-catalyzed reactions applied to the syntheses of new Mn complexes.

PrO_3H [9], KBH_4 , KBEt_3H , $\text{KB}(i\text{-PrO})_3\text{H}$, $\text{LiB}[\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5]_3\text{H}$ [10], Bu_4NBH_4 [11], NaBH_4 [14]. This confirms that the major isomer **13** corresponds to an addition of the hydride *ortho* to the chloride group in harmony with the inductive effect predominating over the mesomeric effect for chloride atom (Fig. 4).

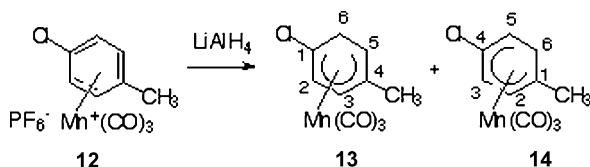


Fig. 4. Synthesis of complexes **13** and **14**.

2.1. ^1H NMR study

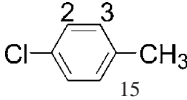
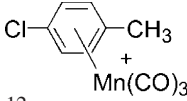
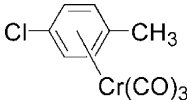
The chemical shifts of protons of *para*-chlorotoluene **15** are given in Table 1, entry 1, as well as those of the Mn and Cr corresponding complexes **12** and **16** (entries 2 and 5). The shielding of each proton $\Delta\delta_1 = \delta - \delta'$ (difference in chemical shift between $\text{H}_{2,6}$ of complex **15** and the same protons in **12**) and $\Delta\delta_2 = \delta - \delta''$ (difference in chemical shift between $\text{H}_{2,6}$ of complex **15** and the same protons in **16**) is calculated in entries 3 and 6 and the difference of chemical shifts $\delta_{\text{H3}} - \delta_{\text{H2}}$ is reported in column 5. These data are in a good

agreement with other ^1H NMR data comparing arene Cr and arene Mn complexes [27]. The chemical shifts of the cationic η^6 -Mn complexes resonated at higher frequencies than the corresponding neutral η^6 -Cr complexes. The H_2 and H_6 protons *ortho* to the chloride atom resonated in each case at the highest frequency (Table 1, entries 1, 2, 5). The difference of chemical shifts $\delta_{\text{H3}} - \delta_{\text{H2}}$ is amplified in the case of Cr and Mn complexes (0.22 and 0.23 ppm) (entries 2 and 5) with respect to the free arene: 0.09 ppm in $\text{Me}_2\text{CO}-d_6$ for example (column 5). The shielding effects due to the complexation $\Delta\delta_1$ and $\Delta\delta_2$ are smaller for the H_2 and H_6 protons (0.10 and 1.36 ppm) than for the H_3 and H_5 protons (0.18 and 1.50 ppm) (Table 1, entries 3 and 6). We did not try to predict the regioselectivity of the addition of an anion to complex **12** because it is well preceded in the literature [28] that regioselectivities of nucleophilic additions are strongly dependent upon the substituent of the ring, the reaction medium and the nature of the nucleophile. It is pointed out that “the effect of substituent on the regioselectivity seems to be very complex” and that addition of nucleophiles can even proceed with inversion of regioselectivity by changing the nature of the solvent. Nevertheless, in our case, it was not surprising to observe a major addition of the hydride to the C2 carbon *ortho* to the chloride atom because there is a synergic effect of the methyl and the chloro groups. Indeed the methyl moiety activates the *meta* position and the chloro moiety activates the *ortho* position. Selected ^1H NMR chemical shifts of η^5 -cyclohexadienyl complexes **13** and **14** are given Table 2 in C_6D_6 and in CDCl_3 showing clearly an increasing sp^2 character from H_5 to H_2 and to H_3 protons. In complex **14**, an unexpected high value, difficult to explain, was observed for the difference $\delta_3 - \delta_2$ in the range 1.3–1.7 ppm, whereas the H_3 and H_2 positions seem relatively similar for complex **13** ($\delta_3 - \delta_2$ in the range 0.10–0.52 ppm). A characteristic $^1J_{\text{gem}}$ of 12–14 Hz is observed for the H_6 hydrogens: the $\text{H}_{6\text{exo}}$ hydrogen is coupled only with the $\text{H}_{6\text{endo}}$ hydrogen because the first one is almost perpendicular to the cyclohexadienyl moiety whereas $\text{H}_{6\text{endo}}$ is usually a doublet of doublet $J = 5\text{--}6$ and $J = 12\text{--}14$ Hz.

2.2. X-ray structures of complexes **13** and **14**

Fig. 5 shows two Cameron views of complex **13**, the first one corresponding to the projection of the tricar-

Table 1
Selected ^1H NMR data of complexes **12** and **16**.



Entry	Arene	$\text{H}_{2,6}^{\text{a}}$	$\text{H}_{3,5}^{\text{a}}$	$\delta_{\text{H}_3} - \delta_{\text{H}_2}^{\text{a}}$
1		δ 7.26 ^{b,c,f} δ 7.26 ^{d,f}	7.17 ^{b, c, f} 7.17 ^{d, f}	0.09 0.09
2		δ' 7.16 ^{b, c, f}	6.94 ^{b, c, f} 6.48 ^{d, e}	0.22
3	$\Delta \delta_1^{\text{b}} = \delta - \delta'$	δ' 6.66 ^{d,e} 0.10	0.18	0.18
4	$\Delta \delta_1^{\text{d}}$	0.60	0.69	
5		δ'' 5.90 ^{b, c, f} δ'' 5.77 ^{d,f}	5.67 ^{b, c, f} 5.54 ^{d, f}	0.23 0.23
6	$\Delta \delta_2^{\text{b}} = \delta - \delta''$	1.36	1.50	
7	$\Delta \delta_2^{\text{d}}$		1.49	1.63

^a ppm; ^b Me₂CO-d₆; ^c d, $J=8\text{Hz}$; ^d CD₃CN; ^e [12]; ^f this work.

bonylmanganese tripod on the cyclohexadienyl plane. The dienyl carbon atoms C1, C2, C3, C4 and C5 define a nearly perfect plane (maximum deviation 0.06 Å). The cyclohexadienyl ring is folded about C1–C5 with a dihedral angle of 33.2°. The carbon–carbon bond distances in the cyclohexadienyl ring (except the 1.369 Å value for C1–C2 bond that shows a greater double-bond character) are not significantly different from each other and can be compared with the 1.391 and 1.417 Å extreme values described in the case of tricarbonyl 6-phenyl, η^5 -(1,2,3,4,5-cyclohexadienyl)manganese complex [29] or the 1.41 Å average value of the tricarbonyl η^5 -(cyclohexadienyl)manganese complex

[30]. In each case, the mean carbon–carbon bond length is less than the value of 1.43 Å for the carbon–carbon distance in π -cyclopentadienyl systems, indicating that carbon–carbon bond of complexed π -dienyl system are stronger than those in the corresponding π -cyclopentadienyl case. The central atom C3 of the dienyl system is only 2.137(5) Å from manganese ion, whereas the intermediate carbon atoms C2 and C4 and the terminal atoms C1 and C5 are 2.245(7) and 2.157(5) Å and 2.197(5) and 2.183(5) Å from the metal atom, respectively. The carbon–carbon distances in the bent back portion are normal single bond lengths 1.470(8) and 1.463(8) Å. The C10–O3 bond eclipses

Table 2
Selected ^1H NMR data of complexes **13** and **14**.

complexes	H_2	H_3	$\delta_3 - \delta_2$	H_5	$\delta_5 - \delta_3$	H_{endo}	H_{exo}
	4.48 ^a	4.58 ^a	0.10 ^a	2.29 ^a	2.28 ^a	2.73 ^a	2.07 ^a
	5.00 ^b	5.52 ^b	0.52 ^b	3.09 ^b	3.43 ^b	3.02 ^b	2.62 ^b
	3.58 ^a	5.30 ^a	1.72 ^a	2.60 ^a	2.69 ^a	2.60 ^a	2.03 ^a
	4.60 ^b	5.91 ^b	1.31 ^b	3.07 ^b	2.84 ^b	2.36 ^b	2.66 ^b

^a C₆D₆; ^b CDCl₃.

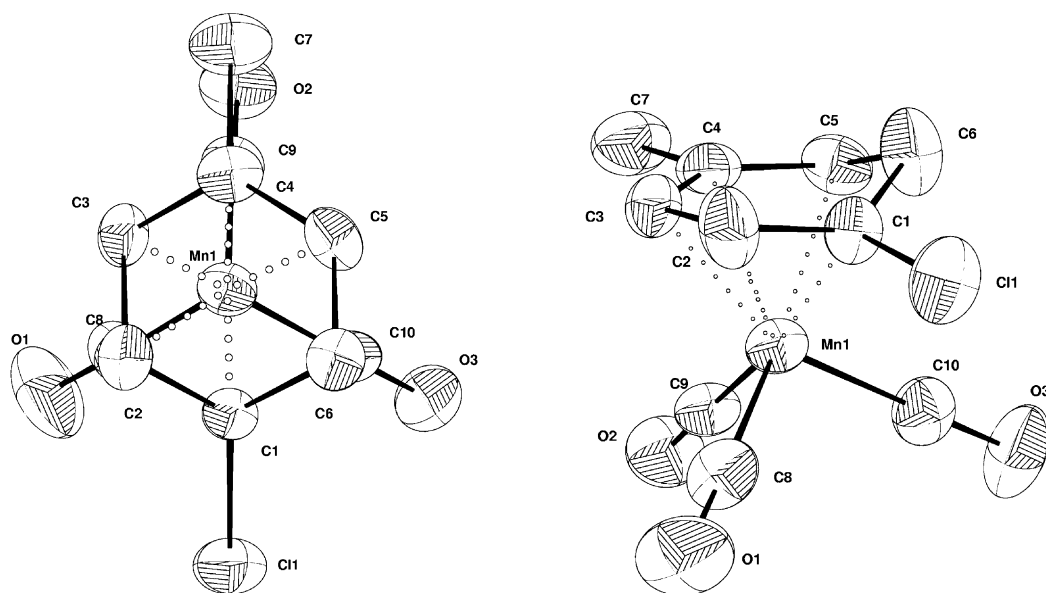


Fig. 5. Cameron views of complex **13** (C_7H_8Cl)Mn(CO)₃ with the thermal ellipsoids at the 50% probability level.

the saturated carbon C6 and the carbon-chloride bond is anti-eclipsed with respect to the projection of the Mn(CO)₃ tripod (Fig. 5).

Fig. 6 shows two Cameron views of complex **14**, the first one corresponding to the projection of the tricarbonylmanganese tripod on the cyclohexadienyl plane. The five unsaturated carbon atoms of the cyclohexadienyl ring are almost coplanar (maximum deviation

0.03 Å) while the remaining atom C6 lies in the C1 C6 C5 plane, which makes a 36.6° angle with the other plane. This value can be compared with the dihedral angle of 42.5° found by Churchill and Scholer [30] in the case of tricarbonyl- η^5 -(1,2,3,4,5-cyclohexadienyl)manganese complex, with the dihedral angle of 36.5(5)° found by Sweigart et al. for the tricarbonyl 6-phenyl, η^5 -(1,2,3,4,5-cyclohexadienyl)manganese

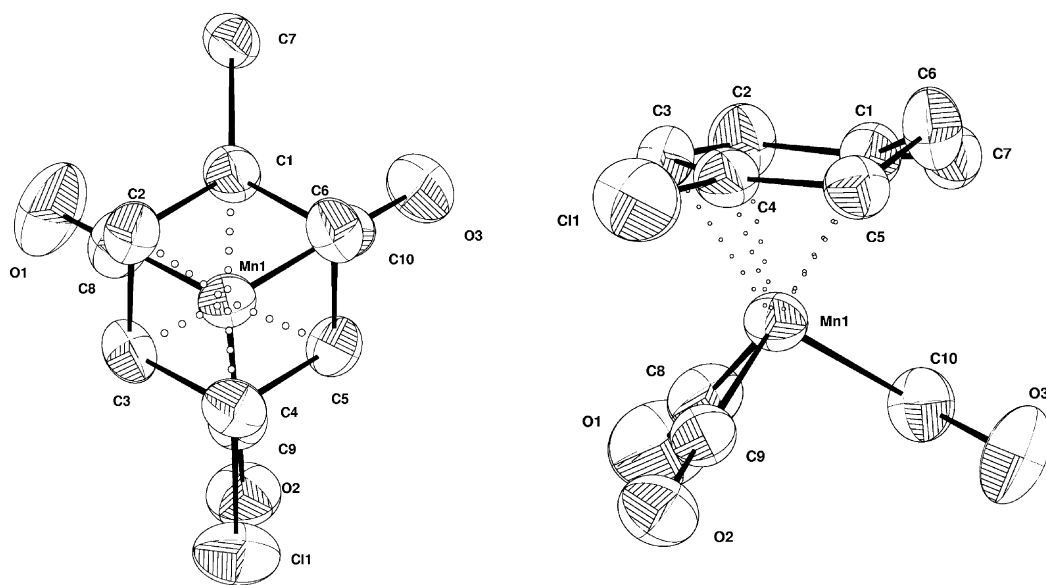


Fig. 6. Cameron views of complex **14** (C_7H_8Cl)Mn(CO)₃ with the thermal ellipsoids at the 50% probability level.

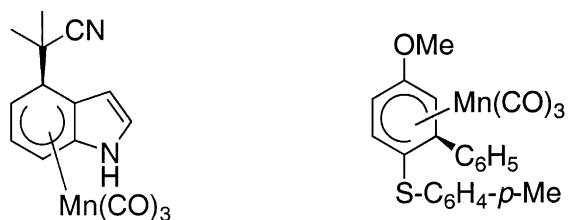


Fig. 7. Two examples of η^5 -(cyclohexadienyl) $\text{Mn}(\text{CO})_3$ complexes **17** and **18**, described in the literature.

complex [29], with the $42.2(3)^\circ$ value found by Chung et al., for the tricarbonyl 1- $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si}$, 6-phenyl, η^5 -(1,2,3,4,5-cyclohexadienyl) manganese complex [28] and with the 37° value found recently with respect to the (exo- η^5 - C_{10}H_8) $\text{Mn}(\text{CO})_3$ complex [31]. However, it is fairly different from the dihedral angle of 29.6° in the case of the tricarbonyl 4-isobutyronitrile, η^5 -(3a,5,6,7,7a-indenyl) manganese complex **17** [32] and with the dihedral angle of 25.5° for complex **18** (Fig. 7) that we recently prepared [21]. C10–O3 bond eclipses the sp^3 carbon C6. The carbon–carbon bond distances in the cyclohexadienyl ring are not significantly different from each other, indicating the delocalization of electrons in this portion of the ring and are also similar to those described in the literature [29, 30]. Nevertheless, the bond distances C1–C2 (1.379 Å) and C4–C5 (1.392 Å) are slightly shorter than the C2–C3 (1.402 Å) and C3–C4 (1.414 Å) bond lengths. The carbon–carbon lengths in the bent back portion are those of single bonds: 1.469(7) and 1.488(7). The metal–carbon distances in the cyclohexadienyl ring show a normal pattern in which the metal atom is closer to the C3 carbon atom and further from the substituted C1 carbon atom. Indeed, the central atom C3 is only 2.125(5) from the manganese ion, the intermediate carbon atoms C2 and C4 are 2.210(5) and 2.129(4) from the manganese and the terminal atoms C1 and C5 are 2.259(4) and 2.191(4) from the metal. The carbon–chloride bond is eclipsed by the Mn–C9–O2 bond (Fig. 6).

3. Experimental section

3.1. Synthesis of complexes 13 and 14

$(\text{C}_7\text{H}_8\text{Cl})\text{Mn}(\text{CO})_3$ were synthesized and fully characterized as previously described [16, 19].

Crystals of **13** and **14** were obtained by slow cooling of a pentane solution at 20°C . A crystal (plate) of each

of them of dimensions $0.1 \times 0.38 \times 0.56$ mm and $0.16 \times 0.5 \times 0.7$ mm, respectively, was mounted in a glass capillary under nitrogen.

3.2. Crystallography

Selected crystals were set up on an Enraf Nonius CAD4 diffractometer. Accurate unit cell dimensions and crystal orientation matrices together with their estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 reflections. For both compounds, two standard reflections were monitored periodically; no intensity decay occurred during any of the data collections. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections were applied (CARSPECIAUX 121/P “symbol” Scan). Crystallographic data and other pertinent information are summarized in Table 3.

3.3. Structure solution and refinement

For the two compounds, the observed systematic absences are, $h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$, and the space group is then $P2_1/n$. Computations were performed by using PC version of CRYSTALS [33]. Scattering factors for all atoms were as incorporated in CRYSTALS.

Structures were solved by direct method [34]. All remaining non-hydrogen atoms were found by electron density map calculations. Their atomic coordinates were refined, and they were affected isotropic then anisotropic displacement factors.

At this stage, hydrogen atoms were located on a difference electron density map; their coordinates were refined with an overall isotropic displacement factor. Least-square refinement was carried out by minimising the function $\sum w (|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The criteria for a satisfactory complete analysis were the ratios of the rms shift to standard deviation being less than 0.02 and no significant features in the final difference map.

The molecular geometry and the atom numbering scheme of compounds 13 and 14 are shown in Figs. 5 and 6 produced by the program CAMERON [35] included in the CRYSTALS crystallographic program system.

Table 3
Crystal data of complexes **13** and **14**.

Formula	(C ₇ H ₈ Cl)Mn(CO) ₃ compound 13	(C ₇ H ₈ Cl)Mn(CO) ₃ compound 14
Chemical formula weight	266.6	266.6
Crystal system	monoclinic	monoclinic
Space group	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> (Å)	7.400(2)	7.390(4)
<i>b</i> (Å)	14.368(4)	14.464(6)
<i>c</i> (Å)	10.153(3)	13.133(4)
β (°)	98.23(2)	98.57(4)
<i>V</i> (Å ³)	1068(4)	1071(6)
<i>Z</i>	4	4
<i>d</i> calc (g cm ⁻³)	1.658	1.653
λ (MoK α) (Å)	0.71069	0.71069
μ (MoK α) (cm ⁻¹)	14.2	14.2
Number of reflections for lattice parameters	25	25
Range for lattice parameters (°)	14–15	14–15
Temperature (K)	295	295
Collection method	ω 2 θ	ω 2 θ
Absorption corrected by	ψ scan	ψ scan
Correction (min/max)	0.55/1	0.58/1
Number of reflections collected	2073	2069
Number of unique reflections	1870	1872
Number of reflections with <i>I</i> > 3 σ (<i>I</i>)	1116	1352
2 θ range (°)	3 to 50	3 to 50
$R = \Sigma(F_o - F_c) / \Sigma F_o $	0.0426	0.0436
$R_w = [\Sigma w (F_o - F_c)^2 / \Sigma w F_o ^2]^{1/2}$	0.0505	0.0495
$S = [\Sigma w (F_o - F_c)^2 / (m - n)]^{1/2}$	1.13	1.18
Number of parameters refined	161	161
Weighting scheme	$w = w' [1 - \{\Delta F / 6 \sigma(F)\}^2]^{a,b}$	$w = w' [1 - \{\Delta F / 6 \sigma(F)\}^2]^{a,b}$
(Δ / σ)	< 0.02	0.02

^a $w' = 1 / \Sigma_1^n \text{Ar Tr}(x)$, where *n* is the number (3) of coefficients Ar, for a Chebyshev serie, for which *x* is *F_o/F_o(max)*.

^b J.R. Carruthers, D.J. Watkin (Chebychev Weighting), Acta Crystallogr. A 35 (1979) 698–699.

Supplementary material

All crystallographic data have been sent in electronic format to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK as cif files Nos. CCDC 200287 and 200288. They can be obtained by contacting the CCDC [Fax : (internat.) 44–1223/336–033 ; E-mail : deposit@ccdc.cam.ac.uk].

Acknowledgements

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