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(Chloromethyl)pentacarbonylmanganese(I); a crystal structure with a non-crystallographic centre of symmetry.

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Running title: (Chloromethyl)pentacarbonylmanganese(I)

Abstract

There are two molecules in the asymmetric unit of the $P2_1/c$ unit cell $\text{ClCH}_2\text{Mn}(\text{CO})_5$, the first halomethyl complex of manganese to be structurally determined. The molecules are crystallographically independent, despite an apparent local centre of symmetry. The average bond parameters include $\text{Mn-C}_{\text{alkyl}}$ 2.128(8) Å, C-Cl 1.811(8) Å and Mn-C-Cl 116.7(4)°.

Keywords: Chloromethyl, manganese carbonyl, crystal structure, non-crystallographic symmetry

Introduction.

Haloalkyl complexes of transition metals ClCH_2ML_n are useful in the synthesis of other derivatives and are of interest as substrates for α -elimination of CH_2 fragments, and for preparations of methylene compounds [1]. Structures of ClCH_2 derivatives of chromium [2] iron [3] cobalt [4] and zinc [5] have been reported for the 3d elements, but none previously for manganese. Only four earlier X-ray structures of ClCH_2 derivatives of metal carbonyls have appeared, namely $\text{ClCH}_2\text{Co}(\text{CO})_3\text{PPh}_3$ [4a], $\text{ClCH}_2\text{CoCp}(\text{CO})\text{Cl}$ [4b], $\text{ClCH}_2\text{FeCl}(\text{CO})_2(\text{PEt}_3)_2$ [3] and $\text{ClCH}_2\text{IrCp}^*(\text{CO})_2$ [6].

Experimental.

Preparation: Triethanolamine (0.34 g, 2.3 mmol) and triethylamine (*ca* 1 mL, excess) were added to a cooled (0°C) dichloromethane solution (15 mL) of $\text{Cl}_3\text{SiMn}(\text{CO})_5$ (0.75 g, 2.27 mmol). The mixture was allowed to warm to room temperature and stirred for 18 h. The solvent was evaporated quickly under vacuum, and the residue was extracted with diethylether. The solvent was removed from the

filtered extract and the residue sublimed without heating, under a static vacuum, on to a cold finger. Transparent, well-formed crystals were produced and identified by the X-ray structure determination as $\text{ClCH}_2\text{Mn}(\text{CO})_5$ (**1**) (0.036 g, 7%). Infrared spectrum: $\nu(\text{CO})$ (hexane, cm^{-1}) 2120w, 2024s,br, 2001s. $^1\text{H NMR}$ (CDCl_3) δ 3.58 (CH_2).

Structure determination: Suitable crystals of **1** were obtained by sealing a small amount of sample in an evacuated glass ampoule (ca 0.5 mL) and allowing crystals to grow by sublimation – body heat was sufficient to cause the crystals to sublime from one end of the ampoule to the other. Crystal data are summarised in Table 1. Data were collected on a Siemens P4 diffractometer and processed using standard software. The structure was solved with SHELXS-97 and refined (on F^2) using SHELXL-97 [7]. All non-hydrogen atoms were treated anisotropically and CH_2 hydrogen atoms were included with a riding model with $d(\text{C-H})$ 0.99 Å, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$. ORTEP-3 was used for the Figure [8].

Results and Discussion.

In an attempt to prepare a silatrane derivative of $\text{Mn}(\text{CO})_5$, triethanolamine was reacted with $\text{Cl}_3\text{SiMn}(\text{CO})_5$ in CH_2Cl_2 with excess Et_3N present. However the only tractable species isolated was $\text{ClCH}_2\text{Mn}(\text{CO})_5$, in somewhat low yields (Scheme 1). Presumably the ClCH_2 ligand is derived from the solvent, by nucleophilic attack of $[\text{Mn}(\text{CO})_5]^-$ generated *in situ* from cleavage of the Si-Mn bond by the amine. A more rational synthesis of **1** from ClCH_2I and pre-formed $[\text{Mn}(\text{CO})_5]^-$ is available [9]. $\text{ClCH}_2\text{Mn}(\text{CO})_5$ is surprisingly very volatile, so required X-ray data collection at low temperature, 158(2) K. It forms beautiful diamond-like crystals by vacuum sublimation with very mild warming.

The X-ray crystal structure determination of **1** revealed two crystallographically independent molecules in the asymmetric unit (see below for a detailed analysis of the relationship between the two molecules). The structure is shown in Figure 1 for one of the molecules (the other does not differ significantly). There is the expected pseudo-octahedral coordination around the Mn atom. The average Mn-C bond to the alkyl group is 2.128(8) Å, longer than the corresponding distance in ClCH₂Co(CO)₃(PPh₃) of 2.022(3) Å [4], as expected for the larger manganese atom; the M-C-Cl angles for the two are 117.0(4) and 116.4° respectively. Only limited comparisons with simpler RMn(CO)₅ molecules are possible because of a paucity of data for examples where R is bonded through an sp³ carbon atom; attempts to define the parent CH₃Mn(CO)₅ were thwarted by disorder [10]. However the Mn-C bond length of 2.128(8) Å is shorter than those in PhOOCCH=CHCH₂Mn(CO)₅ (2.214 Å [11]) or 1,2-C₆H₄[C₂H₄Mn(CO)₅]₂ (2.196 Å [12]), and similar to that in (PhO)₂CHMn(CO)₅ (2.141 Å [13]), which are also bonded through sp³ carbon atoms.

In ClCH₂Mn(CO)₅ the average Mn-C_{axial} distance (*trans* to ClCH₂ group) of 1.847(9) Å is shorter than the average Mn-C_{equatorial} distance of 1.864(9) Å, as expected *trans* to a non- π -accepting alkyl ligand. The average C-Cl distance of 1.811(8) Å is normal for a Cl-C(sp³) bond. There is therefore no indication of any η^2 contribution towards the bonding, of the type analysed for XCH₂ substituents by Siegbahn [14], presumably because the manganese atom has already achieved an eighteen-electron configuration.

The equatorial carbonyl groups are bent towards the alkyl group, so that the average C-Mn-C_{equatorial} angle is 86.2(4)°. This 'umbrella' effect is well established [15].

A careful examination of the two independent molecules in the asymmetric unit revealed an apparent relationship, which raised the possibility of a mis-assigned space group [16] so a more detailed analysis was carried out. The corresponding atoms from the two molecules showed them to be closely related as x, y, z and $1/2-x, 3/4-y, -z$, which is not a crystallographic relationship between coordinates in $P2_1/c$ but does correspond to an apparent centre of symmetry at $1/4; 3/8; 0$. This is a non-crystallographic or local centre of symmetry, but it is not unusual to find such local centres. For example Marsh et al. have found several structures, having space group $Pca2_1$ or $Pna2_1$ with more than one molecule in the asymmetric unit, containing local centres of symmetry [17], and Dalhus and Henrik report another example, also in $Pca2_1$ [18]. A situation similar to that observed for **1** was reported for 2-methylpyrazine [19] which crystallizes in the tetragonal space group $I-4$ with two independent molecules in the asymmetric unit. The two molecules are approximately related as x, y, z and $1/2-x, y, -1/4+z$; which is not a crystallographic symmetry operation. However 2-methylpyrazine crystallizes as twinned crystals with a twin law $R = (010, 100, 00-1)$, i.e. the two twin domains are related by a two-fold axis along $[110]$. The R factors using standard refinement methods (i.e. without twin) were $wR_2=0.272, R_1=0.104$, but with the introduction of the twin law the R factors dropped to $wR_2=0.0676, R_1= 0.0271$ [19].

Considering that in the crystals of **1** investigated in the present paper a^* and c^* are nearly equal it is possible that twinning by merohedry may also be present here, that there are two domains with two reciprocal lattices exactly coincident. Thus we tried a twin-refinement with the original cell parameters and space group $P2_1/c$ using the twin law $R=(0\ 0\ 1, 0\ -1\ 0, 1\ 0\ 0)$, covering the situation where the two domains (if they existed) would be related by a two-fold axis along $[101]$. However, the batch

scale factor refined to 0.0048, suggesting that a second twin-domain does not exist. We also attempted a second twin-refinement with the original cell parameters and space group $P2_1/c$ using the twin law $R=(0\ 0\ 1, 0\ -1\ 0, 1\ 0\ 0)$, for the case where the two domains would be related by a two-fold axis along $[-101]$; again the batch scale factor refined to 0.0048. Other more complicated twin refinements were examined without success. It is noted that the reflections are very strong when $h = \text{odd}$ and $k = 2, 6, 10, 14\dots$ or when $h = \text{even}$ and $k = 4, 8, 12, 16$, but this behaviour is completely explained by the presence of the two independent molecules related by the non-crystallographic center at $1/4; 3/8; 0$. The situation in $(h0l)$ is more complicated because the reflections with $h+l = 2n+1$ are weak, which may suggest an n -glide, however there are 10 $h0l$ reflections (but not strong) with $h+l = 2n+1$ and with $I > 3\sigma(I)$, so this unusual systematic extinction in $P2_1/c$ is not significant. We therefore conclude that the refinement reported here is correct in $P2_1/c$, with $Z' = 2$.

Supplementary material

CCDC 673810 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Rd, Cambridge CB2 1EZ, UK; email: deposit@ccdc.cam.ac.uk.

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Table 1. Crystal data and structure refinement details for **1**.

Molecular formula	C ₆ H ₂ ClMnO ₅
Formula weight	244.47
Temperature	158(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 ₁ /c
Unit cell dimensions	
a (Å)	11.265(4)
b (Å)	14.167(14)
c (Å)	11.715(3)
β (°)	111.36(1)
Volume (Å ³)	1741.2(18)
Z	8
Density (calc.) g cm ⁻³	1.865
Absorption coefficient (mm ⁻¹)	1.806
F(000)	960
Crystal size (mm ³)	0.46 x 0.42 x 0.35
θ range for data collection (°)	2.4 to 25.0 deg.
Reflections collected	3384
Unique reflections	3018 [R(int) = 0.0881]
Completeness to θ = 26.31	98.4 %
Absorption correction	psi-scan
Max. and min. transmission	0.571 and 0.490
Data / restraints / parameters	3081 / 0 / 235

Goodness-of-fit on F^2	1.038
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0640$, $wR_2 = 0.1458$
R indices (all data)	$R_1 = 0.1048$, $wR_2 = 0.1545$
Largest diff. features ($e \text{ \AA}^{-3}$)	0.71 and -1.32

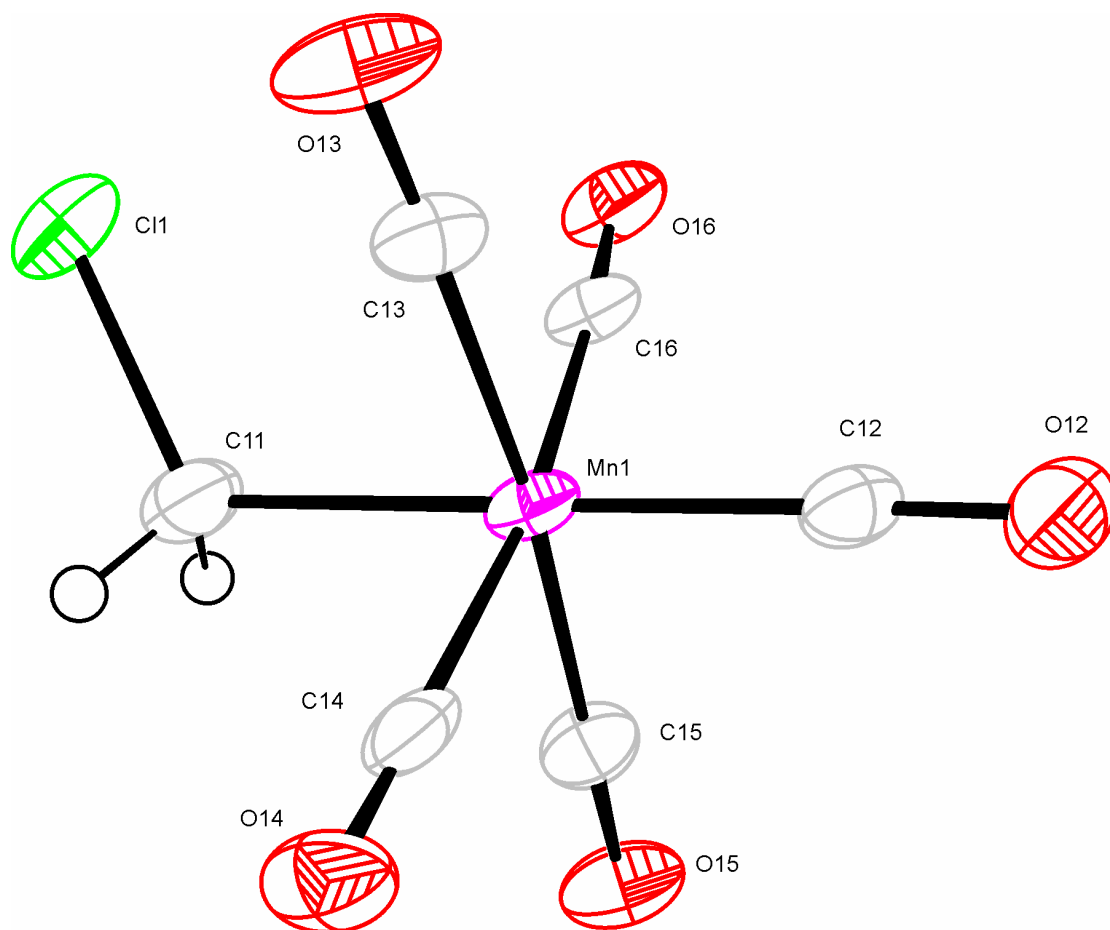
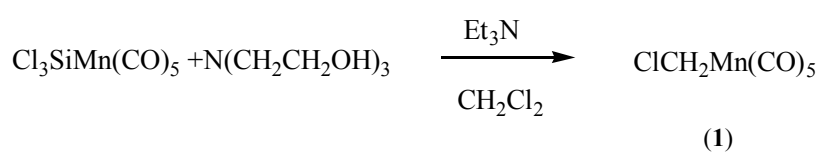


Figure 1. The structure of molecule 1 of ClCH₂Mn(CO)₅, with ellipsoids plotted at the 50% level.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

	Molecule 1	Molecule 2
Mn1-C1	2.125(10)	2.130(10)
Mn1-C2	1.836(10)	1.856(11)
Mn1-C3	1.864(9)	1.855(8)
Mn1-C4	1.883(9)	1.861(9)
Mn1-C5	1.843(9)	1.849(9)
Mn1-C6	1.862(8)	1.893(9)
C1-C11	1.806(8)	1.817(8)
Mn1-C1-C11	117.0(4)	116.4(4)

**Scheme 1**