

# Di- $\mu$ -chloro-bis[(tetrahydrofuran- $\kappa$ O)-( $\eta^5$ -1,2,4-tri-*tert*-butylcyclopentadienyl)-manganese(II)] pentane solvate

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## Key indicators

Single-crystal X-ray study

$T = 150$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å

H-atom completeness 87%

Disorder in solvent or counterion

$R$  factor = 0.043

$wR$  factor = 0.054

Data-to-parameter ratio = 10.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $[\text{Mn}_2\text{Cl}_2(\text{C}_{17}\text{H}_{29})_2(\text{C}_4\text{H}_8\text{O})_2] \cdot \text{C}_5\text{H}_{12}$ , crystallizes as a centrosymmetric dimer with a chloro-bridged dimanganese center. The four-membered  $\text{Mn}_2\text{Cl}_2$  metallacycle is nearly square. The distorted tetrahedral coordination about each metal consists of one  $\text{C}_5\text{H}_2^t\text{Bu}_3$  ( $'''$ Cp) ligand, two chlorides and one O-coordinated tetrahydrofuran (THF) ligand. There is also one disordered molecule of pentane in the unit cell.

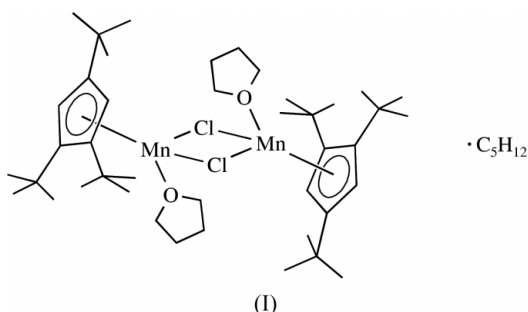
Received 6 May 2003

Accepted 10 June 2003

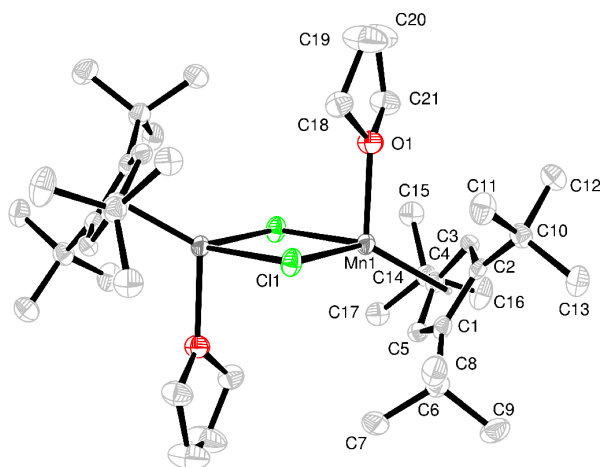
Online 24 June 2003

## Comment

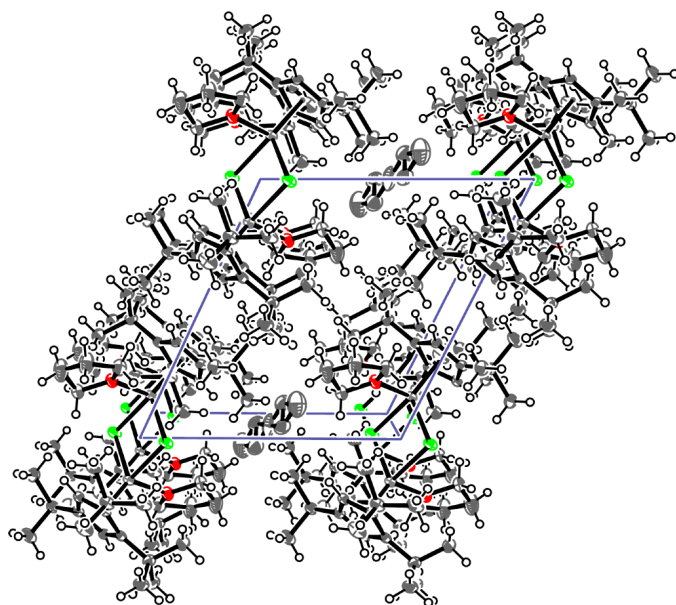
Complexes of the type  $(\text{C}_5\text{H}_{5-n}\text{R}_n)\text{MnCl}(L)$  are not well known in the literature. They have been proposed as reaction intermediates (Coffield *et al.*, 1957; Fischer & Breitschaft, 1966). Patents claim the use of  $(\text{C}_5\text{H}_{5-n}\text{R}_n)\text{MnX}$  in the synthesis of corresponding  $(\text{C}_5\text{H}_{5-n}\text{R}_n)\text{Mn}(\text{CO})_3$  molecules, useful to the fuel industry as anti-knock additives (Shapiro, 1959). Pioneering work was carried out by Köhler *et al.* (1984, 1987) using substituted cyclopentadienyl ligands. Sitzmann & Wolmershäuser (1995), Sitzmann (2001) and Sitzmann *et al.* (2003) were able to show that the introduction of steric bulk to the cyclopentadienyl ring significantly alters the reactivity of complexes containing main group elements, transition metals and lanthanides. This concept has been adopted by many other groups (Weber *et al.*, 2002; Werkema & Andersen, 2001; Harvey *et al.*, 2001; Schneider *et al.*, 1999; Schneider & Krüger, 1992; Eichhorn *et al.*, 2001). However, the synthetic potential of bulky cyclopentadienyl ligands in  $(\text{C}_5\text{H}_{5-n}\text{R}_n)\text{MnX}$  has not been previously explored.



Di- $\mu$ -chloro-bis[(tetrahydrofuran- $\kappa$ O)-( $\eta^5$ -1,2,4-tri-*tert*-butylcyclopentadienyl)manganese(II)] pentane solvate, (I), is a centrosymmetric dimer together with a solvent molecule. The manganese centers are bridged by chlorides forming a nearly square four-membered  $\text{Mn}_2\text{Cl}_2$  metallacycle. One  $\text{C}_5\text{H}_2^t\text{Bu}_3$  ( $'''$ Cp) ligand, two chlorides and one O-coordinated tetrahydrofuran (THF) molecule establish a distorted tetra-



**Figure 1**  
View of the structure of (I), with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms and the solvent molecule have been omitted.



**Figure 2**  
Packing diagram, viewed down the *a* axis of the unit cell.

hedral coordination sphere about each metal. The Mn—Cp (C1–C5) bond lengths are 2.449 (4), 2.490 (4), 2.431 (4), 2.444 (4) and 2.407 (4) Å, respectively. This deviation from ideal  $\eta^5$  coordination may be due to the relative *trans* influences of the chloride and THF. This trend agrees well with that observed in  $[(C_5H_4Me)Mn(PET_3)Cl]_2$ , (II) (Köhler *et al.*, 1984, 1987). Studies by Köhler *et al.* indicate that the Mn—Cp bond lengths are consistent with high-spin Mn<sup>II</sup>. The intramolecular Mn···Mn distance (3.57 Å) in compound (I) is similar to that in (II) (3.52 Å). This separation is too large for any significant bonding interaction, therefore each manganese center should be considered formally a 17-electron species. The unit cell contains one molecule of pentane. The central C atom sits on the inversion center at  $(\frac{1}{2}, \frac{1}{2}, 0)$ . The C atoms at the two and four positions each have 50% occupancy, and the terminal C atoms have full occupancy.

## Experimental

Colorless crystalline  $[(\eta^5-C_5H_2^tBu_3)Mn(Cl)(THF)]_2$  was obtained in roughly 30% yield from the reaction of equimolar amounts of  $Na(C_5H_2^tBu_3)$  and  $MnCl_2$  in tetrahydrofuran at room temperature, followed by extraction of the crude product with pentane and slow cooling to 243 K of a concentrated solution. The crystal was handled under a nitrogen atmosphere, mounted on a glass fiber with Paratone-N oil and cooled to 150 (1) K for data collection.

### Crystal data

$[Mn_2Cl_2(C_{17}H_{29})_2(C_4H_8O)_2] \cdot C_5H_{12}$	$Z = 1$
$M_r = 863.98$	$D_x = 1.189 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.6696$ (8) Å	Cell parameters from 3267 reflections
$b = 10.6803$ (8) Å	$\theta = 2.7\text{--}24.7^\circ$
$c = 12.414$ (1) Å	$\mu = 0.67 \text{ mm}^{-1}$
$\alpha = 65.563$ (1) $^\circ$	$T = 150.2 \text{ K}$
$\beta = 70.336$ (1) $^\circ$	Block, colorless
$\gamma = 86.995$ (1) $^\circ$	$0.28 \times 0.21 \times 0.19 \text{ mm}$
$V = 1206.5$ (1) Å <sup>3</sup>	

### Data collection

Bruker SMART 1K CCD diffractometer	3864 independent reflections
$\omega$ scans	2734 reflections with $I > 3\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{\text{int}} = 0.063$
$T_{\text{min}} = 0.685$ , $T_{\text{max}} = 0.881$	$\theta_{\text{max}} = 24.7^\circ$
6241 measured reflections	$h = 0 \rightarrow 12$
	$k = -12 \rightarrow 12$
	$l = -12 \rightarrow 14$

### Refinement

Refinement on $F$	250 parameters
$R = 0.043$	H-atom parameters constrained
$wR = 0.054$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.66$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
2734 reflections	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

Mn1—O1	2.202 (2)	Mn1—C1	2.457 (3)
Mn1—C5	2.406 (3)	Mn1—Cl1	2.4603 (8)
Mn1—C3	2.437 (3)	Mn1—C2	2.484 (3)
Mn1—C4	2.439 (3)	Mn1—Cl1 <sup>i</sup>	2.5013 (9)
O1—Mn1—Cl1	92.95 (6)	Cl1—Mn1—Cl1 <sup>i</sup>	88.17 (3)
O1—Mn1—Cl1 <sup>i</sup>	90.13 (6)	Mn1—Cl1—Mn1 <sup>i</sup>	91.83 (3)

Symmetry code: (i)  $-x, -y, 2 - z$ .

No H atoms for the disordered pentane were included in the refinement.

Data collection: *SMART* (Siemens, 1995–1999); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1993); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN*.

We thank Dr Allen G. Oliver, Dr Frederick J. Hollander and Alexandr Shafir for their assistance with data collection, solution and refinement. Professor Richard A. Andersen is acknowledged for helpful discussions.

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