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COORDINATION CHEMISTRY OF PERHALOGENATED CYCLOPENTADIENES AND ALKYNES, XII. SYNTHESIS AND MOLECULAR STRUCTURE OF TRICARBONYL(TETRAKIS(TRIMETHYLSILYL)-CYCLOPENTADIENYL)MANGANESE

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NOTE

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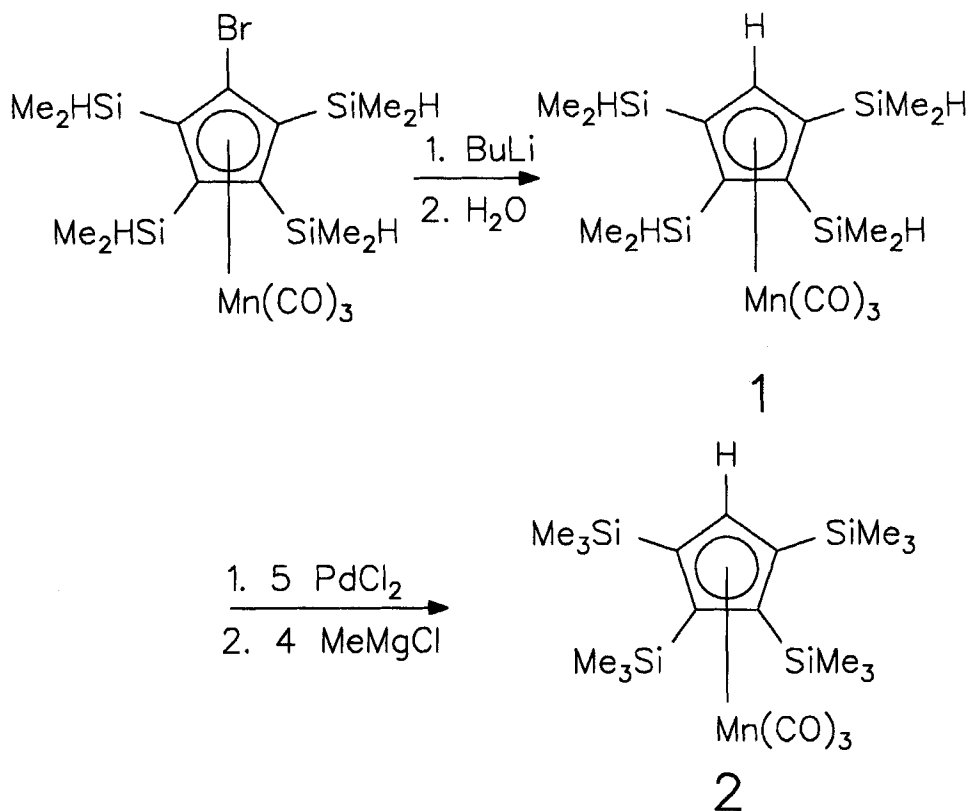
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KEYWORDS: Manganese complexes, silylated cyclopentadienyl ligands,
tetrakis(trimethylsilyl)cyclopentadienyl complex

Cyclopentadienyl complexes with two or three SiMe₃ substituents have found widespread synthetic applications: π -complexes of the main group elements¹ as well as of the f-group elements² can be stabilized, hexane-soluble cationic complexes can be prepared³ and the stereochemical effects of these bulky substituents have been examined.⁴ A certainly interesting extension of this work to higher silylated complexes was, however, so far not feasible due to the lack of synthetic procedures for the preparation of these ligands.⁵ Only recently, we have shown that up to five SiMe₂H substituents can be introduced into the cyclopentadienyl ligand of tricarbonyl(η^5 -cyclopentadienyl)manganese ("cymantrene") starting from [C₅Br₅]Mn(CO)₃ by a sequence of alternate bromine-lithium exchange reactions and electrophilic substitutions with SiMe₂HCl.⁶

[C₅(SiMe₂H)₄Br]Mn(CO)₃, obtained in high yield by this procedure, reacts in Et₂O at -78°C with butyl lithium, followed by hydrolysis with a few drops of water, to give [C₅(SiMe₂H)₄H]Mn(CO)₃ (**1**) in 85% isolated yield. *In situ* chlorination of the four Si-H functionalities can be achieved by stirring a benzene solution of **1** with five equivalents of PdCl₂ at room temp.,⁷ and careful addition of a 1.0 molar THF solution of MeMgCl yields [C₅(SiMe₃)₄H]Mn(CO)₃ (**2**) in about 50% isolated yield, (Scheme 1). This preparation is closely related to Sakurai's synthesis of [C₆(SiMe₃)₆] from [C₆(SiMe₂H)₆], although the reagents and conditions applied in the benzene system do not work here.⁸

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Scheme 1

At room temperature, $[\text{C}_5(\text{SiMe}_3)_4\text{H}]\text{Mn}(\text{CO})_3$ shows only two signals for the SiMe_3 groups in ^1H and the ^{13}C NMR spectra,[†] thus indicating the lack of substantial steric congestion in the complex. This result is rather surprising in the light of Okuda's observations with the $[\text{C}_5(\text{SiMe}_3)_3\text{H}_2]$ system. To obtain more information, a crystal structure determination was performed (Fig. 1).[‡]

The mean deviation in the cyclopentadienyl ring from the least-squares plane is only 0.0052 Å, but one of the silicon substituents (Si3) is shifted substantially away

[†] ^1H NMR (270 MHz, C_6D_6): $\delta = 0.303\text{s}$ [18H], 0.400s [18H], 5.426s [1H] ^{13}C NMR (68 MHz, C_6D_6): $\delta = 2.75, 4.48(\text{SiC}), 98.4, 109.5, 111.1$ (C_5R_5).

[‡] Crystal data for 2: $\text{C}_{20}\text{H}_{17}\text{MnO}_3\text{Si}_4$, $M = 492.8$, monoclinic, space group $P2_1/n$, $a = 11.458(5)$, $b = 16.624(6)$ Å, $c = 15.267(7)$ Å, $\beta = 105.61(3)^\circ$, $V = 2801(2)$ Å³, $T = 291$ K, $D_c = 1.169$ Mg/m³, $Z = 4$, $\mu(\text{MoK}\alpha) = 0.636$ mm⁻¹. Nicolet R3 diffractometer, $\text{MoK}\alpha$ radiation, graphite monochromator, ω -scan with variable scan speed, 2θ range 4–40°. Structure solution and refinement with SHELXTL PLUS 4.1/V, $R(F) = 0.044$, $R_w = 0.033$ for 2045 independent reflections ($|F| \geq 4\sigma(|F|)$). Full lists of crystallographic data, atomic positions, thermal parameters, bondlengths and angles and observed and calculated structure factors are available from the authors upon request.

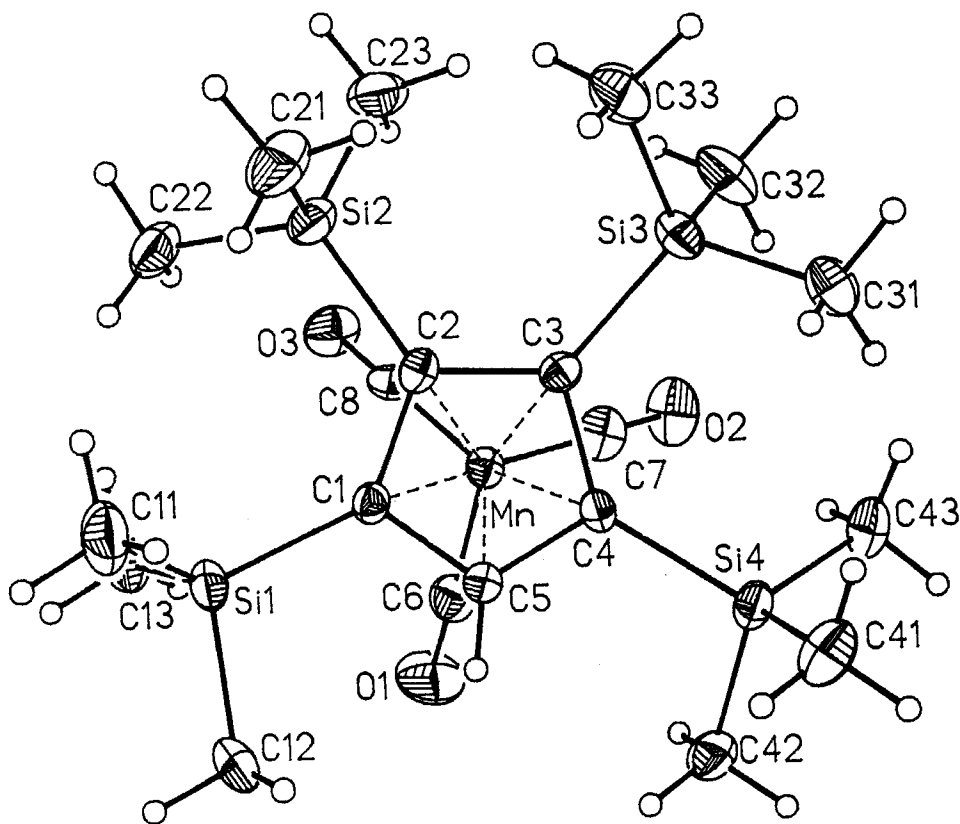


Figure 1 Molecular structure of **2** in the crystal. Thermal ellipsoids drawn at the 20% probability level.

from the $\text{Mn}(\text{CO})_3$ unit to the distal side of that plane (0.2895 Å), thus reducing the interaction with its two SiMe_3 neighbours. The C-C bond lengths range from 1.41(1) to 1.48(1) Å and are only slightly longer than in cymantrene complexes with no or smaller substituents. The main difference (over 10°) from an idealized geometry is observed in the bond angles C2-C1-Si1 and C3-C4-Si4. The two SiMe_3 groups next to the unsubstituted ring carbon atom are “pushed” towards the sterically least demanding substituent, the H-atom, thus avoiding too close a contact with the other two SiMe_3 groups. This effect, together with the displacement of Si3 mentioned above, allows the cyclopentadienyl ring to remain planar and act further as a η^5 ligand.

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