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# NOTE

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

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Cyclopentadienyl complexes with two or three $SiMe_3$ substitutents have found widespread synthetic applications: $\pi$-complexes of the main group elements[1] as well as of the f-group elements[2] can be stabilized, hexane-soluble cationic complexes can be prepared[3] 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 $SiMe_2H$ substituents can be introduced into the cyclopentadienyl ligand of tricarbonyl($\eta^5$-cyclopentadienyl)manganese ("cymantrene") starting from $[C_5Br_5]Mn(CO)_3$ by a sequence of alternate bromine-lithium exchange reactions and electrophilic substitutions with $SiMe_2HCl$.[6]

$[C_5(SiMe_2H)_4Br]Mn(CO)_3$, obtained in high yield by this procedure, reacts in $Et_2O$ at $-78°C$ with butyl lithium, followed by hydrolysis with a few drops of water, to give $[C_5(SiMe_2H)_4H]Mn(CO)_3$ (**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 $PdCl_2$ at room temp.,[7] and careful addition of a 1.0 molar THF solution of MeMgCl yields $[C_5(SiMe_3)_4H]Mn(CO)_3$ (**2**) in about 50% isolated yield, (Scheme 1). This preparation is closely related to Sakurai's synthesis of $[C_6(SiMe_3)_6]$ from $[C_6(SiMe_2H)_6]$, although the reagents and conditions applied in the benzene system do not work here.[8]

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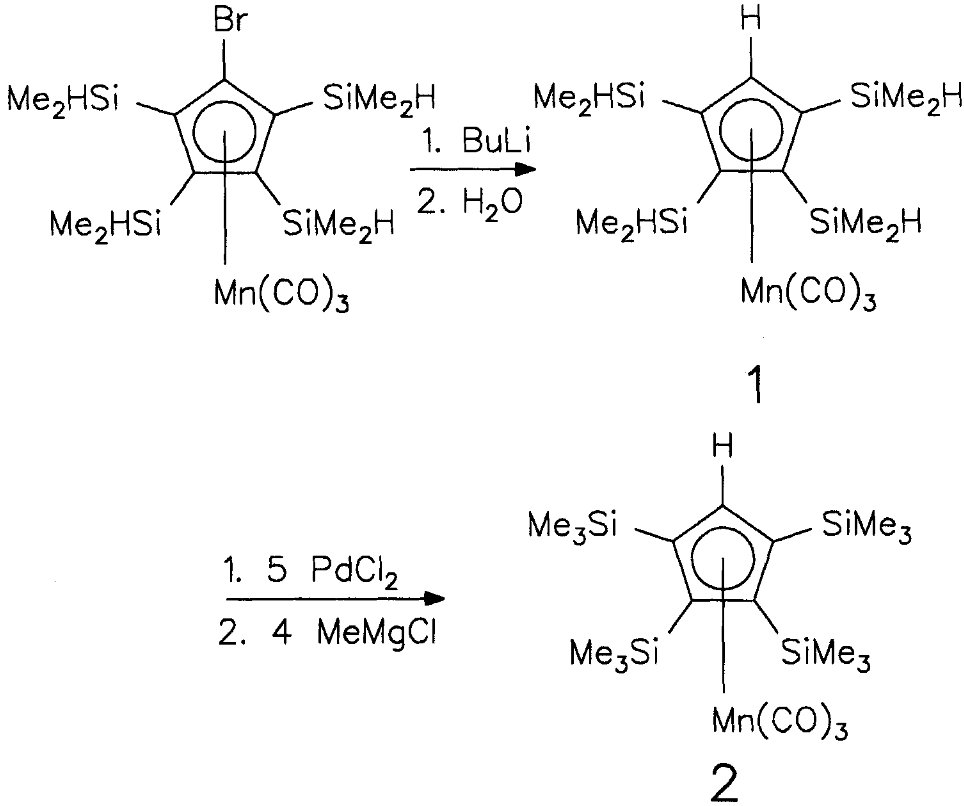


**Scheme 1**

At room temperature, $[C_5(SiMe_3)_4H]Mn(CO)_3$ 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 $[C_5(SiMe_3)_3H_2]$ 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 substitutents (Si3) is shifted substantially away

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

‡ *Crystal data for* **2:** $C_{20}H_{37}MnO_3Si_4$, $M$ = 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)°, $V$ = 2801(2) Å$^3$, $T$ = 291 K, $D_c$ = 1.169 Mg/m$^3$, $Z$ = 4, $\mu(MoK_\alpha)$ = 0.636 mm$^{-1}$. Nicolet R3 diffractometer, $MoK_\alpha$ radiation, graphite monochromator, $\omega$-scan with variable scan speed, 2$\Theta$ 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.

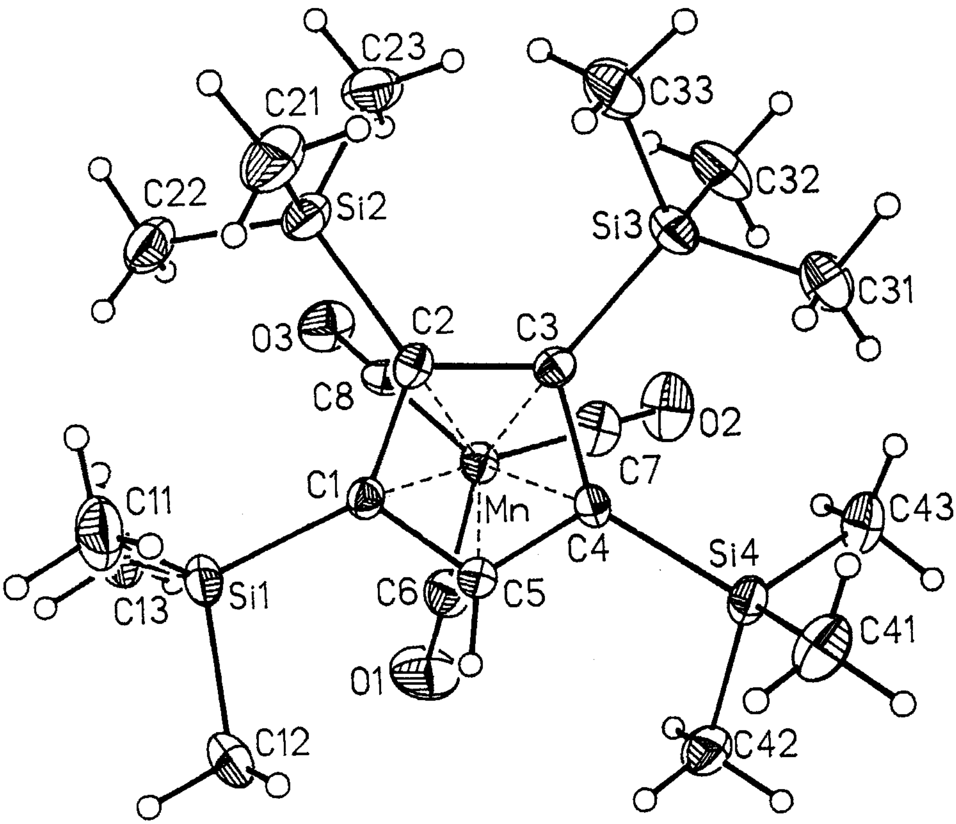


**Figure 1** Molecular structure of **2** in the crystal. Thermal ellipsoids drawn at the 20% probability level.

from the $Mn(CO)_3$ 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 substitutents. 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 $\eta^5$ ligand.

## *Acknowledgements*

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