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 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(η⁵-cyclopentadienyl)manganese ("cymantrane") starting from [C₅Br₅]Mn(CO)₃ by a sequence of alternate bromine-lithium exchange reactions and electrophilic substitutions with SiMe₂HCl.⁶

[C₅(SiMe₃H)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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At room temperature, \([\text{C}_5(\text{SiMe}_3)_4\text{H}]\text{Mn(CO)}_3\) shows only two signals for the SiMe\(_3\) groups in \(^1\text{H}\) and the \(^{13}\text{C}\) NMR spectra,\(^\dagger\) 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).\(^\ddagger\)

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

\(^{\dagger}\) \(^1\text{H}\) NMR (270 MHz, C\(_6\)D\(_6\)); \(\delta = 0.303\) s [18H], 0.400 s [18H], 5.426 s [1H] \(^{13}\text{C}\) NMR (68 MHz, C\(_6\)D\(_6\)); \(\delta = 2.75, 4.48(\text{SiC}), 98.4, 109.5, 111.1 (\text{C}_3R_3)\).

\(^\ddagger\) Crystal data for 2: \(\text{C}_{20}\text{H}_{32}\text{MnO}_3\text{Si}_4\); \(M = 492.8\), monoclinic, space group \(P2_1/n\), \(a = 11.458(5)\), \(b = 16.624(6)\) Å, \(c = 15.267(7)\) Å, \(\beta = 105.61(3)^\circ\), \(V = 2801(2)\) Å\(^3\), \(T = 291\) K, \(D_e = 1.169\) Mg/m\(^3\), \(Z = 4\), \(\mu(\text{MoK}α) = 0.636\) mm\(^{-1}\). Nicolet R3 diffractometer, MoK\(_α\) radiation, graphite monochromator, \(ω\)-scan with variable scan speed, 2\(θ\) range 4-40\(^o\). Structure solution and refinement with SHELXTL PLUS 4.1k, \(R(F) = 0.044\), \(R_w = 0.033\) 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.
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 η$^5$ ligand.

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References