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A Manganese(II) Allyl Complex: Synthesis, Structure, and Magnetic Properties of [Li(thf)$_4$][Mn{η^3-(Me$_3$Si)$_2$C$_3$H$_3$}{η^1-(Me$_3$Si)$_2$C$_3$H$_3$}$_2$]**

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The synthetic and structural organometallic chemistry of manganese(II) is atypical of organotransition metal chemistry due to the observation of essentially ionic C–Mn^{II} bonds, a property more commonly observed in organometallic compounds of the alkali and alkaline-earth metals.[1] Hence Mn^{II} forms no isolable complexes with neutral π-acidic ligands such as carbon monoxide, olefins, or arenes, but does form an extensive series of cyclopentadienide (Cp$^-$) complexes such as manganocene, [Cp$_2$Mn].[2] Despite the ubiquitous nature of the cyclopentadienide ligand in organomanganese(II) chemistry no examples of π coordination to an Mn^{II} center by other anionic ligands of the "-enide" family are known: attempts at preparing "open manganocenes" that contain a bis-(η^5-pentadienide)Mn arrangement, have only resulted in the formation of the unusual associated salts of general forumla [{(η^5-pentadienide)$_2$Mn^I}$_2${μ-Mn^{II}}].[3] Thus, we have sought to explore the capacity of the Mn^{II} ion for forming stable complexes with other π-bonded ligands of the -enide family.

Since π coordination of the sterically hindered allyl (or propenide) ligand [1,3-(Me$_3$Si)$_2$C$_3$H$_3$]$^-$ to a range of s-block metal cations has been observed, this ligand seemed the ideal candidate for use in the chemistry of the Mn^{II} ion.[4] Furthermore, the stability and crystalline properties of the [(η-Cp)$_3$M]$^-$ ions (M = Mn, Sn, Pb) suggested to us that the targeted synthesis of a tris(allyl)manganate anion would be prudent.[5] Thus we now report the synthesis and structure of [Mn{η^3-(Me$_3$Si)$_2$C$_3$H$_3$}{η^1-(Me$_3$Si)$_2$C$_3$H$_3$}$_2$][Li(thf)$_4$] ([**1**][Li(thf)$_4$]), which a subsequent X-ray crystallographic analysis revealed to contain both σ- and π-bonded [(Me$_3$Si)$_2$C$_3$H$_3$]$^-$ allyl ligands. The anion **1** is the first structurally authenticated example of π-allyl coordination to a manganese(II) center [Eq. (1)].

$$\mathrm{MnCl_2} + 3\,[\mathrm{Li}\{(\mathrm{Me_3Si})_2\mathrm{C_3H_3}\}] \xrightarrow[-2\,\mathrm{LiCl}]{\mathrm{thf}} [\mathbf{1}][\mathrm{Li(thf)_4}] \qquad (1)$$

The reaction between [Li{(Me$_3$Si)$_2$C$_3$H$_3$}] and MnCl$_2$ (3:1 equivalents) in thf solvent at −78 °C produced a dark red solution. Removal of thf followed by the addition of pentane afforded, on storage of a concentrated solution at 5 °C for

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several days, very air-sensitive, red-brown crystals of [**1**][Li(thf)$_4$] suitable for a single-crystal structure determination.[6]

The structure of the [Mn{η^3-(Me$_3$Si)$_2$C$_3$H$_3$}{η^1-(Me$_3$Si)$_2$C$_3$H$_3$}$_2$]$^-$ ion (**1**) contains an unsolvated Mn^{II} atom coordinated by one η^3- (or π-) and two η^1-bonded [(Me$_3$Si)$_2$C$_3$H$_3$]$^-$ ligands (Figure 1).

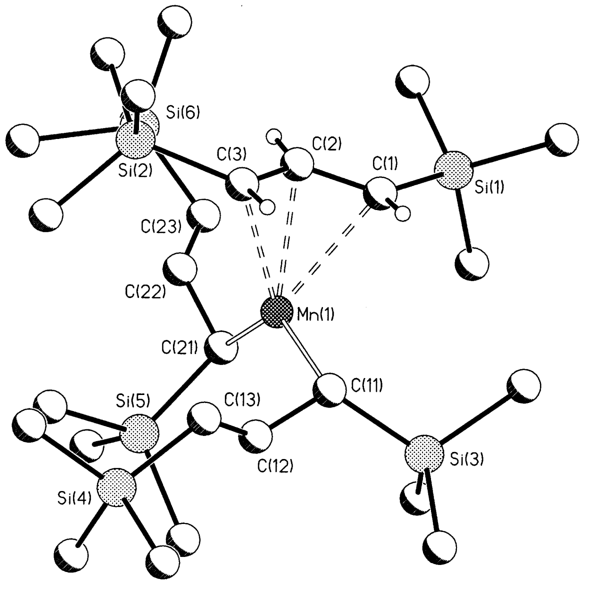

Figure 1. Molecular structure of the anion **1**. For clarity, only the η^3-allyl hydrogens are shown. The [Li(thf)$_4$]$^+$ cation has no remarkable structural features. Selected bond lengths [Å] and angles [°]: Mn(1)-C(1) 2.470(4), Mn(1)-C(2) 2.348(3), Mn(1)-C(3) 2.398 (4), C(1)-C(2) 1.390(5), C(2)-C(3) 1.400(5), Mn(1)-C(11) 2.184(4), C(11)-C(12) 1.460(5), C(12)-C(13) 1.337(5), Mn(1)-C(21) 2.187(4), C(21)-C(22) 1.487(5), C(22)-C(23) 1.314(6).

The C(2)-Mn(1)-C(11), C(2)-Mn(1)-C(21) and C(11)-Mn(1)-C(21) bond angles of 117.54(15), 110.81(14) and 131.05(14)°, respectively, show that Mn(1) resides in a distorted tetrahedral coordination environment. The Mn(1)–C(11) and Mn(1)–C(21) η^1 bond lengths are essentially identical at 2.184(4) and 2.187(4) Å, respectively, and are similar to the average C–Mn^{II} bond length of 2.185(10) Å observed in the structure of the related ion-contacted η^1-pentadienide complex [K{3-Me-1,5-(Me$_3$Si)$_2$C$_5$H$_4$}Mn].[7] The Mn(1)–C(1), Mn(1)–C(2), and Mn(1)-C(3) π bond lengths are 2.470(4), 2.348(3), and 2.398(4) Å, respectively, and indicate an appreciable degree of asymmetry in the Mn(1)–{η^3-(Me$_3$Si)$_2$C$_3$H$_3$} interaction, which probably arises as a consequence of the sterically congested coordination environment, although the influence of crystal-packing forces cannot be completely discounted.[8] Although no other examples of (η^3-allyl)manganese(II) complexes are presently known to enable structural comparisons, it is worthy of note that the lengths of the Mn(1)–C π bonds observed in the structure of **1** are similar to those commonly observed in the structures of high-spin manganocenes and the [(η^2-Cp)$_3$Mn]$^-$ ion.[2,5a] In contrast, however, the Mn(1)–C(η^3-allyl) distances in **1** are markedly longer than those of 2.10–2.28 Å observed in the structure of the Mn^I allyl complex [(η^3-pentadienyl)-Mn^I(dmpe)$_2$][9] (dmpe is 1,2-bis(dimethylphosphanyl)ethane) and also the mean Mn–C(η^5-Cp) distance of 2.157 Å observed in compounds of the type [Cp'Mn(CO)$_3$], in which Cp' is a substituted cyclopentadienyl derivative.[10] All allyl hydrogen atoms in **1** were located in the peak-difference map and allowed to refine freely: the C(1)-C(2)-C(3)-H(3) and C(3)-C(2)-C(1)-H(1) torsional angles are identical at 18(3)° and show that the terminal allyl hydrogen atoms are tilted away from Mn(1), whereas the C(2)–H(2) bond is tilted 9(1)° toward Mn(1). The significance of the bending of the allyl hydrogen atoms of the [(Me$_3$Si)$_2$C$_3$H$_3$]$^-$ ligand from the C(1)-C(2)-C(3) plane has been discussed for the structures of the related complexes [Ca{η^3-(Me$_3$Si)$_2$C$_3$H$_3$}$_2$(thf)$_2$][4a] and [{η^3-(Me$_3$Si)$_2$C$_3$H$_3$}Li(tmeda)] (tmeda is tetramethylethylenediamine),[4b] which display similar distortions relative to the calculated structure of the free [(Me$_3$Si)$_2$C$_3$H$_3$]$^-$ ion. Thus, in the structure of **1** H(1) and H(3) are oriented away from Mn(1) to reduce steric congestion and H(2) is oriented towards Mn(1) to improve the metal–ligand bonding. Theoretical investigations on the series of unsubstituted allyl–alkali-metal complexes [M(η^3-C$_3$H$_5$)] (M = Li–Cs) suggest that bending of the allyl hydrogen atoms as in **1** is common for ionic metal allyls[11] as it is for typical transition-metal allyls such as [Ni(η^3-C$_3$H$_5$)$_2$].[12]

Whereas allylmagnesium complexes usually contain η^1-bonded ligands,[13] for other s-block metals η^3-allyl bonding is normally observed:[4] the observation of both σ- and π-allyl bonding in **1** is, therefore, unique for an ionic metal allyl (resulting in a formal valence electron count of 13), although the square-planar allyl metallates [(η^3-C$_3$H$_5$)M(η^1-C$_3$H$_5$)$_2$]$^-$ (M = Ni, Pd) are structurally related to **1**.[14] It is possible that the lower hapticities of the η^1-allyl ligands allow a reduction in steric congestion in the coordination pocket that would otherwise arise from the voluminous Me$_3$Si substituents: on electrostatic grounds the 17 valence electron anion "[Mn{η^3-(Me$_3$Si)$_2$C$_3$H$_3$}$_3$]$^-$" (compare with [Cp$_2$Mn]) would be preferred, although in the absence of other [Mn^{II}(allyl)$_n$] complexes with which to compare the structure of **1** such assertions must be tentative.

Although solution-phase isotopic perturbation experiments have proved to be useful in rationalizing the structures of [Li(η^3-allyl)] fragments[15] the paramagnetism of [**1**][Li(thf)$_4$] has precluded similar attempts at corroborating the solid-state structure of the anion **1** by NMR spectroscopy. Indeed, the broad resonances and poor signal-to-noise ratio in the ^{1}H NMR spectrum of [**1**][Li(thf)$_4$] only confirm the various chemical environments.

The magnetic properties of [**1**][Li(thf)$_4$] were investigated by superconducting quantum interference device (SQUID) magnetometry in the temperature range 5–300 K and an applied field of 100G (see Supporting Information). Under these conditions the complex behaves as a Curie paramagnet: the effective magnetic moment, μ_{eff}, at the low-temperature limit of the experiment is 2.92 BM with the value steadily rising with temperature to 4.03 BM at 300 K. Attempts to model this behavior on the basis of zero-field splitting were not successful,[16] which is likely to indicate a low-spin/high-spin equilibrium between the S = 1/2 and S = 5/2 states of Mn^{II} within **1** as the temperature is raised. Our conclusion is similar to those reached regarding the magnetic properties of the $[(\eta^2\text{-Cp})_3Mn]^-$ ion and of "magnetically dilute" manganocenes.[5a,17]

In summary, we report the first allyl complex of manganese(II). The structure of the formally 13-electron $[Mn\{\eta^3\text{-}(Me_3Si)_2C_3H_3\}\{\eta^1\text{-}(Me_3Si)_2C_3H_3\}_2]^-$ ion provides a unique example of a manganese(II) "-enide" and the observation of both η^1- and η^3-allyl coordination to an Mn^{II} center is without precedent for an ionic metal allyl.

Experimental Section

A freshly prepared solution of $[\{(Me_3Si)_2C_3H_3\}Li]$ (8.6 mmol) in thf (20 ml) was added dropwise to a stirred suspension of $MnCl_2$ (0.36 g, 2.9 mmol) in thf (5 ml) at −78 °C. The resulting red/brown mixture was slowly warmed to room temperature and stirred (2 h). The thf was evaporated, replaced with pentane (20 ml) and the solution filtered (Celite, porosity 3). The filtrate was reduced in volume to about 2–3 ml and stored at +5 °C affording, after several days, red/brown plates of [**1**][Li(thf)$_4$] (1.10 g, 42 %), mp 60–62 °C. The extreme air-sensitivity of [**1**][Li(thf)$_4$] meant that accurate elemental analysis proved difficult to obtain: elemental analysis calcd (%) for $C_{43}H_{95}LiMnO_4Si_6$: C 56.97, H 10.56; found: C 54.95, H 10.31. ^1H NMR (C_6D_6, 300.15 MHz, 298 K), due to the paramagnetism of the anion **1** most resonances were broadened to the extent that ^nJ coupling patterns were obliterated and have been assigned tentatively: $\delta = 0.06$ (s, 18 H, Me_3Si), 0.21 (s, 18 H, Me_3Si), 0.37 (s, 18 H, Me_3Si), 1.67 (m, 16 H, thf CH_2CH_2), 2.76 (br, 2H η^1-allyl C-H), 3.61 (m, 16H thf CH_2OCH_2), 5.25, 5.97, 6.17, 6.45 ppm (br, m, η^3-allyl and vinyl C-H). IR (Nujol mull, KBr plates): $\tilde{\nu} = 3033.1$ (w, sh, allyl C−H stretch) 1036.2 cm^{-1} (m, sh, thf C−O stretch).

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[6] Crystal data for: [**1**][Li(thf)$_4$] $C_{43}H_{95}LiMnO_4Si_6$, $M_r = 906.61$, $T = 180(2)$ K, $\lambda = 0.71073$ Å, $\mu = 0.377$ mm^{-1} monoclinic, $P2_1/n$, $a = 11.97350(10)$, $b = 19.6810(2)$, $c = 25.3204(4)$ Å, $\beta = 97.9964(4)°$, $V = 5908.75(12)$ Å, $Z = 4$, $\rho_{calcd} = 1.019$ Mg m^{-3}. A total of 35776 reflections were collected of which 8149 were unique ($R_{int} = 0.0473$, 99.2 % completeness to $\theta = 23.00°$). The structure was solved by direct methods and refined by full-matrix least squares on F^2: $R1 = 0.0608$ and $wR2 = 0.1657$. CCDC-231180 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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