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Structure of the Elusive Hydrido(methylcyclopentadienyl)dicarbonylmanganate(I) Anion, $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2H]^-$, as Determined by Single-Crystal X-ray Diffraction

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Summary: The reactive $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2H]^-$ *anion has been stabilized with the large counterion* $[K(18\text{-crown-6})]^+$, *and its structure has been determined by an X-ray diffraction study of a single crystal, which shows the unit cell to contain two inequivalent* $[K(18\text{-crown-6})][(\eta^5\text{-}C_5H_4Me))Mn(CO)_2H]$ *ion pairs. The anion adopts a three-legged piano-stool geometry in the crystal, with a* $C_5Mn(CO)_2$ *geometry very similar to that found in* $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$. *Salient bond distances (Å) and angles (deg) are as follows:* $Mn-H = 1.565(19)/1.54(2)$; $Mn\cdots K = 3.6186(11)/3.5874(11)$; $K\cdots H = 2.833(17)/2.771(19)$; $(O)C-Mn-C(O) = 89.83(11)/90.87(10)$; *and* $Mn\cdots H\cdots K = 107.2(6)/109.2(8)$. *The structure of* $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2H]^-$ *is compared with those reported for bridging hydride and σ-bond complexes derived from the* $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2]$ *moiety.*

Introduction

The complexes $[(\eta^5\text{-}C_5H_4R)Mn(CO)_3]$, where R = H (cymantrene; **1**), or Me (methylcymantrene; **2**), have proved to be remarkably versatile reagents in organometallic chemistry. The range and number of complexes formed from **1** and **2** is immense. In general, the synthetic methodology employed is photochemical, with in situ formation of the 16-electron intermediate $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2]$, as both **1** and **2** are thermally rather stable species.

Monoanionic (cyclopentadienyl)carbonylmetalates are valuable intermediates in organometallic synthesis.[1] They display characteristics typical of anionic metal complexes, undergoing ion-pairing and substitution reactions.[1−3] The cymantrene-derived anionic species $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2E]^-$ (where E = H, SiR_3, GeR_3, SnR_3) have been exploited as alternative synthons to the cymantrenes.[3,4] Furthermore, as the E group can be removed relatively easily (as E^+), it may be regarded as a "protecting group" for negative charge. Hence, these anionic derivatives can be viewed as precursors to dianionic metal complexes of the type $[(\eta^5\text{-}C_5H_4R)Mn(CO)_2]^{2-}$. The cymantrene derivative (R = H) has been isolated[5] but is extremely difficult to handle[6] and hence has limited utility. Such behavior is typical of dianionic metal complexes, for which there is a corresponding dearth of reports in the literature.

Monanionic species react with geminal dihalides, forming a wide range of species, including carbene complexes, as well the equivalent germyl, stannyl, and plumbyl derivatives.[7] An element−manganese double bond is formed in each of these cases by elimination, with the monoanionic species behaving as a synthetic equivalent to a dianionic metal complex. Bridged dinuclear species of the type $[\{(\eta^5\text{-}C_5H_4R)Mn(CO)_2\}_2X]$, where X = GeI^-,[8] $SnMe_2$,[9] $BNMe_2$, $BCMe_3$,[10] have also been reported as products of the reaction between these metal anions and the appropriate dihalide. These complexes are produced by elimination and the concomitant formation of an Mn−Mn bond.

Carbonyl hydride complexes have represented an area of intense research, due in part to their structural and spectroscopic variety, but also on account of the crucial role they play—or are suspected to play—in many metal-catalyzed reactions involving CO and H_2. These include such important industrial processes as the water-gas shift reaction, Fischer−Tropsch catalysis, hydroformylation, reductive carbonylation, and hydrogenation of alkenes.[11] However, simple carbonyl hydrides can be frustratingly difficult to isolate and pin down by standard structural techniques. Dimerization is a common problem with species of this sort; for example, $[CpFe(CO)_2H]$ (Cp = $\eta^5\text{-}C_5H_5$) is unstable with respect to decomposition to dihydrogen and $[\{CpFe(CO)_2\}_2]$[12] and, hence, has never been characterized structurally. The isoelectronic manganese anion $[Cp'Mn(CO)_2H]^-$ (**3**; Cp′ = $\eta^5\text{-}C_5H_4Me$) has been used to prepare a variety of

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novel species, including bridged boranes and stannanes. Borane σ-bonded complexes have also been reported: the reaction of **3** with ClB(pin) (pin = pinacol), ClB(cat) (cat = catechol), or ClB(Cy)$_2$ (Cy = cyclohexyl) produces an η^2-BH complex via nucleophilic substitution.[3] However, **3** has also eluded attempts to characterize it structurally, owing to its facile dimerization to the bridged hydride complex [{Cp′Mn(CO)$_2$}$_2$H]$^-$ (**4**), which has been characterized by X-ray crystallography on several occasions.[10,13,14] Most recently, Braunschweig and Ganter formed **4** through the reaction between (Me$_2$Si)$_2$NBCl$_2$ and [Cp′Mn(CO)$_2$H]$^-$ in the presence of TMEDA.[10] Earlier syntheses of **4** involved the reduction of [Cp′Mn(CO)$_2$(THF)] with NaBH$_4$ in the presence of a cryptand, with the Mn fragment dimerizing with the formation of an Mn−Mn bond supported by the bridging hydride.[14]

Results and Discussion

As part of a general study of the fragment [Cp′Mn(CO)$_2$], we have isolated and characterized by single-crystal X-ray diffraction the hydrido(methylcyclopentadienyl)dicarbonylmanganate(I) anion, [Cp′Mn(CO)$_2$H)]$^-$ (**3**). This was synthesized using the recently developed methodology of Braunschweig et al.,[10] in which [Cp′Mn(CO)$_2$(H)(SiMePh$_2$)] is treated with KBHEt$_3$ in THF. Our preparation involved addition of a small excess of 18-crown-6 to the reaction mixture. When the mixture was cooled to −40 °C, bright yellow crystals of [K(18-crown-6)][Cp′Mn(CO)$_2$H)] (**3′**) were obtained. The ^{1}H NMR spectrum of the reaction mixture (d_8-THF) showed a weak resonance at δ −27.30 ppm in addition to the main hydride resonance from **3′** at δ −12.20 ppm. This low-frequency resonance is characteristic of a bridging hydride—the corresponding resonance for **4** is reported at δ −27.48 ppm[10]—and indicates some dimerization still occurring as a byproduct of our synthesis.

A well-formed crystal of **3′** was studied by X-ray crystallography, which revealed two slightly different molecules in the unit cell (Figure 1). The geometry of the anion in each of these is a three-legged piano stool, with (O)C−Mn−C(O) and (O)C−Mn−H angles close to 90° for the two independent molecules in the unit cell. Thus, the geometry of the [(η^5-C$_5$)Mn(CO)$_2$] moiety does not differ significantly from that found for [CpMn(CO)$_3$].[15] The Mn−H distances of 1.565(19)/1.54(2) Å compare well with those determined by neutron diffraction for the neutral Mn(I) hydride complexes [HMn(CO)$_5$] (1.601(16) Å)[16] and [*cis*-HMn(CO)$_4$(PPh$_3$)] (1.573(2) Å),[17] and the K···H distances of 2.833(17)/2.771(19) Å are comparable with those determined for other transition-metal hydride anions which display electrostatic M−H···K interactions in the solid state.[18] The cation−anion packing in **3′** is dictated by a combination of this M−H···K interaction and the closest C−H(Cp′)···H−C(crown) van der Waals contact of 2.373 Å.

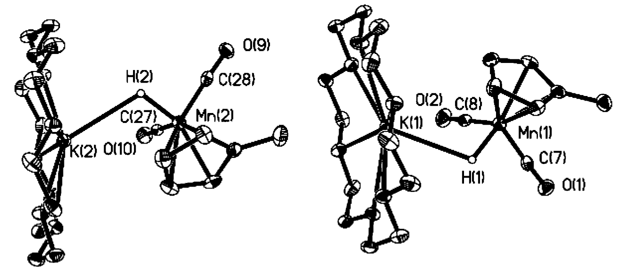
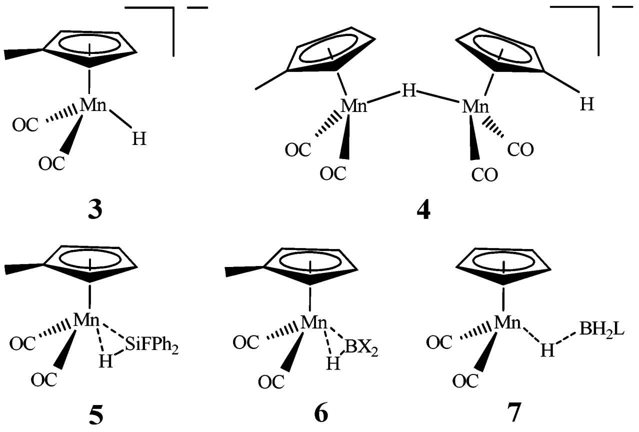


Figure 1. Molecular structure of [K(18-crown-6)][(η^5-C$_5$H$_4$-Me)Mn(CO)$_2$H] **3′** as determined by single-crystal X-ray diffraction at 133 K. Ellipsoids are drawn at the 50% probability level, and nonhydride hydrogen atoms are omitted for clarity. The structure contains two molecules of **3′** within the unit cell. Selected bond distances (Å) and angles (deg): Mn(1)−H(1) = 1.565(19), Mn(2)−H(2) = 1.54(2), Mn(1)−K(1) = 3.6186(11), Mn(2)−K(2) = 3.5874(11), K(1)−H(1) = 2.833(17), K(2)−H(2) = 2.771(19), Mn(1)−C(7) = 1.750(3), Mn(1)−C(8) = 1.745(3), Mn(2)−C(27) = 1.742(2), Mn(2)−C(28) = 1.747(2), C(7)−O(1) = 1.179(3), C(8)−O(2) = 1.182(3), C(27)−O(1) = 1.184(3), C(28)−O(9) = 1.183(3); Mn(1)−H(1)−K(1) = 107.2(6), Mn(2)−H(2)−K(2) = 109.2(8), C(7)−Mn(1)−C(8) = 89.83(11), C(27)−Mn(2)−C(28) = 90.87(10), C(7)−Mn(1)−H(1) = 89.2(8), C(8)−Mn(1)−H(1) = 93.3(7), C(27)−Mn(2)−H(2) = 92.0(7), C(28)−Mn(2)−H(2) = 90.8(8).

Chart 1



The structure of **3** thus deduced invites comparison with the dinuclear anion [{Cp′Mn(CO)$_2$}$_2$H]$^-$ (**4**), as well as with the silane and borane σ-bonded complexes [Cp′Mn(CO)$_2$(η^2-HSi(F)Ph$_2$)] (**5**),[19] [Cp′Mn(CO)$_2$(η^2-HBX$_2$)] (**6**),[3] and [CpMn(CO)$_2$(η^1-HB(H)$_2$L)] (**7**)[20] (Chart 1 and Table 1). The Mn−H distances in **3** and in **5**, [Cp′Mn(CO)$_2$(η^2-HBcat)] (**6a**), and [Cp′Mn(CO)$_2$(η^2-HBpin)] (**6b**) are equivalent within 3 esd's and are very similar to those of terminal hydrides in neutral Mn(I) complexes (q.v.). This is perhaps surprising, given the anionic nature of **3** and the apparent fractional Mn−H bond order in **5**, **6a**, and **6b**. The Mn−H−X angles are all close to 90° in the last three complexes and reveal the side-on H−X coordination characteristic of a synergic σ-bond interaction at Mn, in contrast to the significant flattening at H evident in the hydride-bridged species

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Table 1. Structural Parameters for Hydride and σ-Bond Complexes Containing the [CpMn(CO)$_2$] or [Cp′Mn(CO)$_2$] Fragment, As Determined by X-ray Diffraction

complex	*r*(Mn−H)/Å	∠Mn−H−X/deg	ref
[Cp′Mn(CO)$_2$H]$^-$ (**3**)	1.565(19)/ 1.54(2)		this work
[{Cp′Mn(CO)$_2$}$_2$H]$^-$ (**4**)	1.61(6)/ 1.59(6)	152(4)	10
[Cp′Mn(CO)$_2$(η^2-HSi(F)Ph$_2$)] (**5**)[a]	1.569(4)	88.2(2)	19
[Cp′Mn(CO)$_2$(η^2-HBcat)] (**6a**)	1.57(2)	93.2(7)	3
[Cp′Mn(CO)$_2$(η^2-HBpin)] (**6b**)	1.53(2)	93.2(9)	3
[Cp′Mn(CO)$_2$(η^2-HBCy$_2$)] (**6c**)	1.49(2)	105.7(9)	3
[CpMn(CO)$_2$(η^1-HB(H)$_2$NMe$_3$)] (**7a**)	1.65(4)	142(3)	20
[CpMn(CO)$_2$(η^1-HB(H)$_2$PMe$_3$)] (**7b**)	1.81(4)	129(3)	20

[a] Neutron diffraction structure.

4 and in the similar [{(CO)$_5$Cr}$_2$H]$^-$ anion (Cr−H−Cr = 158.9(6)°), as determined by neutron diffraction.[21] The borane−Lewis-base−adduct complexes [CpMn(CO)$_2$(η^1-HB(H)$_2$NMe$_3$)] (**7a**) and [CpMn(CO)$_2$(η^1-HB(H)$_2$PMe$_3$)] (**7b**) are a different story, however: here the borane ligand possess no suitable acceptor orbital, and the interaction is purely B−H→Mn σ-donation, with the Mn−H distance and Mn−H−B angles in **7a** and **7b** more reminiscent of those in the hydride-bridged anion **4**. The borane complex [Cp′Mn(CO)$_2$(η^2-HBCy$_2$)] (**6c**) is anomalous in these respects, with a Mn−H−B geometry suggesting an interaction intermediate between η^1 and η^2. Presumably the cyclohexyl ligands at the boron atom in **6c** render the vacant B$_{2p}$ orbital significantly higher in energy than do the alkoxy moieties in **6a** and **6b**, and the metal-to-ligand component of the σ-bond interaction is consequently less pronounced.

Experimental Section

All operations were carried out under an inert atmosphere using standard Schlenk or glovebox techniques, and solvents and other reagents were purified by standard techniques.[22] ^{1}H NMR spectra were recorded on a Bruker AV360 spectrometer operating at 360 MHz and referenced to the deuterated NMR solvent employed.

Synthesis of [K(18-crown-6)][Cp′Mn(CO)$_2$H] (3′).[10] A stirred solution of [Cp′Mn(CO)$_3$] (Aldrich; 5 g, 23 mmol) and HSiMePh$_2$ (Aldrich; 4.5 g, 23 mmol) in hexane (70 mL) was irradiated at room temperature with a medium-pressure mercury lamp for 8 h. The solution was then filtered into a clean Schlenk tube, and an equimolar amount of KBHEt$_3$ (Aldrich; 1 M, 23 mL) in THF was added. Immediate precipitation of a yellow powder occurred. The mixture was stirred for a further 2 h, and the solid K[Cp′Mn(CO)$_2$H] thus produced was collected by filtration and washed with hexane. A portion of K[Cp′Mn(CO)$_2$H] (0.8 g, 4 mmol) was then dissolved in THF (20 mL) and stirred for 20 min. To this was added a small excess of 18-crown-6 (1.3 g, 5 mmol), and the mixture was stirred for a further 2 h. The solution was then reduced in volume and stored overnight at −40 °C, whereupon yellow crystals of **3′** appeared. These were collected by filtration and washed.

^{1}H NMR (d_8-THF, δ in ppm): 4.2 (s, 4H, C$_5$*H*$_4$), 3.8 (s, 24H, crown *H*), 1.5 (s, 3H, C*H*$_3$), −12.2 (s, 1H, Mn*H*). Yield: 1.1 g; 55%.

Crystallographic Analysis of 3′. Yellow single crystals suitable for X-ray diffraction studies were obtained by cooling a solution of **3′** in THF to −40 °C. The crystal structure was solved and refined by direct methods using SHELX-97,[23] with the assistance of the program X-seed.[24] The hydride hydrogen atoms were located in the difference Fourier map and refined freely. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically.

Crystal data for **3′**: $C_{20}H_{33}KMnO_8$, $M_r = 495.50$, yellow block, $0.20 \times 0.20 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.4670(19)$ Å, $b = 13.707(3)$ Å, $c = 17.709(5)$ Å, $\alpha = 89.360(11)°$, $\beta = 88.989(11)°$, $\gamma = 89.096(15)°$, $V = 2297.2(9)$ Å^3, $Z = 4$, $D_c = 1.433$ g/cm^3, $F_{000} = 1044$, Nonius KappaCCD, Mo Kα radiation, $\lambda = 0.710\,73$ Å, $T = 133(2)$ K, $2\theta_{max} = 55.0°$, 13 775 reflections collected, 8962 unique reflections ($R_{int} = 0.0461$), final GOF = 0.977, R1 = 0.0412, and wR2 = 0.0683, *R* indices based on 6196 reflections with $I > 2\sigma(I)$ (refinement on F^2), 606 parameters, 0 restraints, *Lp* and absorption corrections applied, $\mu = 0.798$ mm^{-1}.

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Supporting Information Available: Tables of structural data for [K(18-crown-6)][Cp′Mn(CO)$_2$H] (**3′**); these data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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