Trinuclear, Mixed-Valence, Zwitterionic, and Sandwiched Manganacarborane: A Novel "Butterfly" Cluster

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The most stable oxidation state of manganese is 2+, and a number of Mn^{II} complexes are now known. The majority of Mn^{II} complexes exhibit certain unique electronic properties due to a high-spin d^5 configuration.[1] One important class of such species is the sandwiched π-complex manganocene, $(\eta^5\text{-}C_5H_5)_2Mn$; the methyl and pentamethyl derivatives of the manganocene $(\eta^5\text{-}C_5H_4(Me))_2Mn$ and $(\eta^5\text{-}C_5Me_5)_2Mn$, are also known.[2-4] However, most of the reported manganacarborane complexes are half-sandwiched closo species with $Mn(R_3P)_x(CO)_{3-x}$ (R = alkyl or aryl group; x = 0, 1, or 2) occupying a vertex of either an icosahedron or its lower homologues.[5] The only known sandwiched manganacarboranes to date have been the anionic species $[4,4'\text{-}Mn^{II}(1,6\text{-}C_2B_{10}H_{12})_2]^{2-}$ and Mn^{IV} complexes of the formula $[Mn(CB_{10}H_{11})_2]^{2-}$, for which no crystal structures have been reported.[6,7] We report herein the synthesis and X-ray crystal structure of a zwitterionic manganese sandwich complex $\{[Li^+(THF)][Li^+(TMEDA)]_2\}\{$*commo*-$Mn_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_4\}^{3-}$ (**1**). To the best of our knowledge, compound **1** represents the first sandwiched mixed-valence, and trinuclear "butterfly" cluster complex of any organometallic system known to date.

Treatment of the double salt $Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ (**2**)[8] with anhydrous $MnCl_2$ in a molar ratio of 2:1 in dry tetrahydrofuran (THF) produced the *closo*-carborane $1,2\text{-}(SiMe_3)_2\text{-}1,2\text{-}C_2B_4H_4$ (**3**)[9] and a waxy solid that is a mixture of product (**1**) and the precursor (**2**) as shown in eq 1. This solid was then dissolved in a solution mixture of hexane, THF, and *N,N*-tetramethylethylenediamine (TMEDA) to isolate fairly air stable, dark red crystals of **1** in 93% yield.[10]

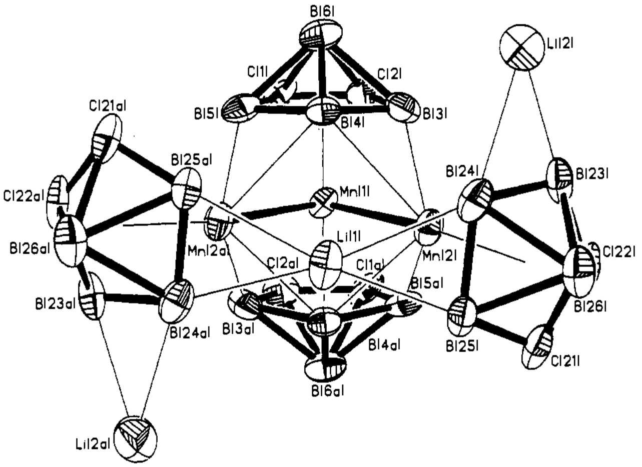

Figure 1. Thermal ellipsoid diagram of selected cage atoms that form a "butterfly" cluster of **1** drawn at the 40% probability level. Pertinent distances (Å), angles, and dihedral angles (deg): Mn(1)-Mn(2), 2.682 (2); Mn(2)-Mn(2a), 3.283 (2); Mn(1)-C(1), 2.155 (10); Mn(1)-C(2), 2.170 (10); Mn(1)-B(3), 2.163 (12); Mn(1)-B(4), 2.249 (11); Mn(1)-B(5), 2.183 (11); Mn(1)-(C_2B_3 centroid 1), 1.708; Mn(2)-B(3), 2.445 (12); Mn(2)-B(4), 2.518 (11); Mn(2a)-B(4), 2.436 (12); Mn(2a)-B(5), 2.371 (12); Mn(2)-C(21), 2.679 (10); Mn(2)-C(22), 2.582 (10); Mn(2)-B(23), 2.393 (13); Mn(2)-B(24), 2.398 (11); Mn(2)-B(25), 2.507 (11); Mn(2)-(C_2B_3 centroid 2), 2.125; Li(1)-B(24), 2.462 (15); Li(1)-B(25), 2.333 (13); Li(1)-O(40), 1.894 (25); Li(2)-B(23), 2.237 (23); Li(2)-B(24), 2.273 (25); Li(2)-N(50), 2.065 (27); Li(2)-N(51), 2.044 (22); Mn(2)-Mn(1)-Mn(2a), 75.5 (1); centroid 1[C(1) to B(5)]-Mn(1)-centroid 1a[C(1a) to B(5a)], 177.6; Mn(2)-Mn(1)-centroid 1, 90.5; Mn(2)-Mn(1)-centroid 1a, 87.6; Mn(1)-Mn(2)-centroid 2[C(21) to B(25)], 174.9; plane 1[Mn(2), Mn(1), Mn(2a)]-plane 2[C(1) to B(5)], 2.4; plane 1-plane 2a, 2.4; plane 2-plane 2a, 1.7; plane 1-plane 3[C(21) to B(25)], 86.8; plane 2-plane 3, 87.4; plane 2a-plane 3, 88.8; plane 3-plane 3a, 69.0.

$$
\begin{aligned}
&9Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2C_2B_4H_4]^{2-}\ (\mathbf{2}) + \\
&6MnCl_2 \xrightarrow[\text{2. hexane/THF/TMEDA}]{\text{1. THF, 0°C, 1 h, and 25°C, 24 h}} 3LiCl + 9NaCl + \\
&2\{[Li^+(THF)][Li^+(TMEDA)]_2\}\text{-} \\
&\{commo\text{-}Mn_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_4\}^{3-}\ (\mathbf{1}) + \\
&closo\text{-}1,2\text{-}(SiMe_3)_2\text{-}1,2\text{-}C_2B_4H_4\ (\mathbf{3}) \qquad (1)
\end{aligned}
$$

The paramagnetism of **1** precluded obtaining useful NMR data. However, the IR spectrum[11] indicated the presence of a hetero-

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(1) (a) Treichel, P. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4, Chapter 29, pp 1-159. (b) Chiswell, B.; McKenzie, E. D.; Lindoy, L. F. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 4, Chapter 41, pp 1-122. (c) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; Chapter 18-D-2 and references therein.

(2) Wilkinson, G.; Cotton, F. A.; Birmingham, J. M. *J. Inorg. Nucl. Chem.* **1956**, *2*, 95.

(3) Robbins, J. L.; Edelstein, N. M.; Cooper, S. R.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3853.

(4) (a) Bünder, W.; Weiss, E. *Z. Naturforsch., B* **1978**, *33*, 1235. (b) Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 892. (c) Haaland, A. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 267. (d) Almenningen, A.; Haaland, A.; Samdal, S. *J. Organomet. Chem.* **1978**, *149*, 219.

(5) (a) Hawthorne, M. F.; Andrews, T. D. *J. Am. Chem. Soc.* **1965**, *87*, 2496. (b) Hawthorne, M. F.; Pitts, A. D. *J. Am. Chem. Soc.* **1967**, *89*, 7115. (c) George, A. D.; Hawthorne, M. F. *Inorg. Chem.* **1969**, *8*, 1801. (d) Hollander, F. J.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1973**, *12*, 2262. (e) Matteson, D. S.; Grunzinger, R. E., Jr. *Inorg. Chem.* **1974**, *13*, 671. (f) Little, J. L.; Welcker, P. S.; Loy, N. J.; Todd, L. J. *Inorg. Chem.* **1970**, *9*, 63. (g) Howard, J. W.; Grimes, R. N. *J. Am. Chem. Soc.* **1969**, *91*, 6499. (h) Howard, J. W.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 263. (i) Zakharkin, L. I.; L'vov, A. I. *Zh. Obshch. Khim.* **1971**, *41*, 1880. (j) Young, D. A. T.; Paxson, T. E.; Hawthorne, M. F. *Inorg. Chem.* **1971**, *10*, 786. (k) Hyatt, D. E.; Little, J. L.; Moran, J. T.; Scholer, F. R.; Todd, L. J. *J. Am. Chem. Soc.* **1967**, *89*, 3342. (l) Zakharkin, L. I.; Ol'shevskaya, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 2296. (m) Cowie, J.; Hamilton, E. J. M.; Laurie, J. C. V.; Welch, A. J. *J. Organomet. Chem.* **1990**, *394*, 1. (n) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.

(6) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1976**, *15*, 2872.

(7) Knoth, W. H. *Inorg. Chem.* **1971**, *10*, 598.

(8) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 4600. Barreto, R. D.; Hosmane, N. S. *Inorg. Synth.*, in press.

(9) Hosmane, N. S.; Barreto, R. D.; Tolle, M. A.; Alexander, J. J.; Quintana, W.; Siriwardane, U.; Shore, S. G.; Williams, R. E. *Inorg. Chem.* **1990**, *29*, 1698.

(10) A 10.0-mmol sample of $Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ (**2**) was allowed to react with 5.0 mmol of anhydrous manganese(II) chloride (0.63 g) in dry THF (30 mL) at 0 °C for 1 h and then at room temperature for 24 h, during which time the solution became turbid and its color turned to dark red. The solution was then filtered through a frit in vacuo, and THF and other volatiles were removed from the filtrate by vacuum distillation to collect a waxy solid, to which 50 mL of hexane and a minimum quantity of freshly distilled and dried THF and TMEDA (~4 mL) was added in order to dissolve the solid. The resultant dark red solution was left standing overnight, during which time the dark red crystals appeared inside the flask. These crystals were then separated by vacuum filtration, washed repeatedly with a minimum quantity of anhydrous pentane, dried in vacuo overnight, and later identified as $\{[Li^+(THF)][Li^+(TMEDA)]_2\}\{$*commo*-$Mn_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_4\}^{3-}$ (**1**) (2.1 g, 1.67 mmol; 92.5% yield based on $MnCl_2$ consumed; mp 252 °C dec; reasonably air stable; moderately soluble in polar organic solvents). The solvent THF and the volatile product, contained in the first filtrate, were fractionated in vacuo to collect the *closo*-carborane $1,2\text{-}(SiMe_3)_2\text{-}1,2\text{-}C_2B_4H_4$ (**3**) (0.181 g, 0.83 mmol) and the solvent THF in traps held at −45 and −196 °C, respectively. After removal of all the solvents in vacuo from the second filtrate, 2.4 mmol of the unreacted precursor $Na^+(THF)Li^+[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$ (**2**) was recovered.

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carborane complex, and the microanalytical data suggested its molecular formula as $C_{48}H_{128}N_4OB_{16}Si_8Li_3Mn_3$.[11] The crystal structure (see Figure 1) reveals that complex **1** has a 2-fold symmetry in which the rotation axis, parallel to *b*, passes through the atoms Mn(1), Li(1), and O(40) and bisects the angle Mn(2)-Mn(1)-Mn(2a) (plane 1).[12] Although the three Mn atoms form a central plane with the Mn-Mn distance of 2.682 (2) Å, the Mn(2)-Mn(2a) distance of 3.283 (2) Å and the Mn(2)-Mn(1)-Mn(2a) angle of 75.5 (1)° indicate that no direct bonding exists between the two terminal Mn atoms. However, the central manganese atom [Mn(1)] adopts an essentially η^5-bonding posture with respect to each of the C_2B_3 faces (plane 2), with the metal to cage distances ranging from 2.155 to 2.249 Å, which are significantly shorter than the Mn-η^5-carbon distance of 2.42 Å in the high-spin, polymeric, zigzag structure of $Mn(C_5H_5)_2$[4a,c] and slightly longer than those found in the low-spin, monomeric structure of $Mn(C_5Me_5)_2$.[4b]

The "butterfly" geometry of **1** is primarily due to bondings of the terminal manganese atoms to two adjacent borons of each of the central carborane ligands [Mn(2 or 2a)-B = 2.37-2.52 Å] as well as to the planar pentagonal faces (plane 3) of the terminal carborane ligands [Mn(2 or 2a)-Cnt(2) = 2.125 Å], each of which makes dihedral angles of 86.8° and 87.4° to the planes formed by the three Mn atoms and the C(1), C(2), B(3), B(4), and B(5) atoms of the central ligands, respectively (see Figure 1). Thus, compound **1** distinguishes itself from other structurally characterized trinuclear π-complex cluster systems such as $(\eta^5\text{-}C_5H_5)_3Mn_3(\mu_3\text{-}NO)(\mu_2\text{-}NO)_3$,[13] $[(\eta^5\text{-}C_5H_5)_3Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3]^+$,[14] and $[\{(C_2B_9H_9)(\text{4-methylisonicotinate})\}_3Cu_3(\mu\text{-}H)_3]$,[15] all of which are based on an equilateral triangle of metal atoms. The bridging of two terminal carborane ligands by the Li^+(THF) moiety and bonding of each of the Li^+(TMEDA) groups to two adjacent borons of the respective cages form a zwitterionic cluster of **1** (see Figure S1, supplementary material). Since each carborane ligand bears a 2- charge and three Li^+ cations are present, the total formal oxidation states of three Mn atoms in **1** would be 5+. Because of a 2-fold symmetry, mentioned above,[12] it is expected that the two terminal Mn atoms would be identical and, therefore, would formally be in an oxidation state of either 2+ or 1+. Accordingly, the oxidation state of 1+ or 3+ could be assigned to the central metal Mn(1). In order to obtain more information regarding the oxidation states of the metals, magnetic measurements on a powdered sample of **1** were undertaken.

The magnetic susceptibility of **1** was measured in the temperature range 15-300 K using the Faraday method.[16] The room temperature effective magnetic moment of 8.3 μ_B for **1** is significantly less than the calculated spin-only value of 9.7 μ_B for the high-spin $Mn(II)_{terminal}$-$Mn(I)_{central}$-$Mn(II)_{terminal}$ trimer system. Therefore, it is most likely that cluster **1** consists of a trimer in which the central Mn could be formally in a 3+ oxidation state and bonded to two terminal Mn(I) atoms. The shorter Mn(1)-C_2B_3 cent(1) distance (1.708 Å) when compared to that of Mn(2)-C_2B_3 cent(2) (2.125 Å) strongly supports the assignment that **1** is a high-spin complex of the Mn(I)-Mn(III)-Mn(I) trimer system. Nevertheless, the magnetic moment decreases monotonically with decreasing temperature and reaches 6.2 μ_B at 15 K, indicating that a significant antiferromagnetic coupling exists between central Mn(1) and terminal Mn(2 or 2a) atoms. A significantly long distance of 3.283 (2) Å between the two terminal manganese atoms rules out the possibility of a direct coupling between Mn(2) and Mn(2a). There was no signal in the X-band EPR spectrum of **1** at room temperature.

The low-temperature EPR spectral measurements and theoretical expressions for the antiferromagnetic interactions of **1** are in progress. Investigations of the reaction chemistry of the zwitterionic **1** and other related sandwich cluster complexes are also currently underway in our laboratories.

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Supplementary Material Available: Structural details for **1** including tables of positional and thermal parameters, selected bond distances, bond angles, and torsion angles, and Figure S1 (11 pages); listing of observed and calculated structure factors for **1** (10 pages). Ordering information is given on any current masthead page.

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(11) IR (cm^{-1}; C_6D_6 vs C_6D_6): 2960 (ms), 2899 (w), 2840 (w) [ν(CH)], 2520 (s), 2455 (s) [ν(BH)], 2260 (s), 1455 (s) [$\delta(CH)_{asym}$], 1330 (s), 1245 (vs) [$\delta(CH)_{sym}$], 1180 (s), 1160 (s), 835 (vvs, br) [ρ(CH)], 750 (mw), 625 (w). Anal. Calcd for $C_{48}H_{128}N_4OB_{16}Si_8Li_3Mn_3$: C, 42.37; H, 9.48; N, 4.12; Si, 16.51; Mn, 12.11. Found: C, 43.64; H, 9.36; N, 4.25; Si, 16.66; Mn, 11.77.

(12) $C_{48}H_{128}N_4OB_{16}Si_8Li_3Mn_3$: fw, 1360.85. A data set was collected at 210 K on a dark brown platelike crystal of monoclinic space group *C*2/*c* with the following unit cell parameters: $a = 16.917$ (6) Å, $b = 23.925$ (10) Å, $c = 20.585$ (8) Å, $\beta = 97.05$ (3)°, $V = 8269$ (5) Å^3, $Z = 4$, and $D_{calcd} = 1.093$ g/cm^3, $\mu = 0.619$ mm^{-1}. Of 4801 data collected using a Nicolet R3m/V diffractometer (Mo Kα; 2θ, 3.5-42.0°), 2763 reflections were considered as observed [$I > 3.0\sigma(I)$]. Compound **1** has a 2-fold symmetry in which the rotation axis, parallel to *b*, passes through the atoms Mn(1), Li(1), and O(40) and bisects the angle Mn(2)-Mn(1)-Mn(2a) (see Table I, supplementary material, for atomic coordinates). Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by the heavy-atom methods stored in the program package SHELXTL-PLUS (Sheldrick, G. M. *Structure Determination Software Programs*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990). All non-H atoms were refined anisotropically. The exo-cage Si-C bond distances of the two disordered $SiMe_3$ groups [Si(1)-Me_3 and Si(2)-Me_3] were constrained during the refinements. Cage H atoms were located in difference Fourier maps, and methyl and methylene H atoms, except for those in the disordered methyl groups, were calculated. The final refinement converged at $R = 0.076$, $wR = 0.099$, and GOF = 2.08 for observed reflections. Maximum and minumum residual electron densities are 0.84 and -0.56 e/Å^3, respectively.

(13) Elder, R. C. *Inorg. Chem.* **1974**, *13*, 1037.

(14) Vergamini, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6327.

(15) Kang, H. C.; Do, Y.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1988**, *27*, 1716.

(16) Dobson, J. C.; Helms, J. H.; Doppelt, P.; Sullivan, B. P.; Hatfield, W. E.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 2200.

An Unprecedented Rapid and Direct Br^+ Transfer from the Bromonium Ion of Adamantylideneadamantane to Acceptor Olefins

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Adamantylideneadamantane (Ad=Ad) is unique among presently investigated olefins in that its structure absolutely impedes the progress of Br_2 addition beyond the stage of bromonium ion (I) formation.[1,2] In halogenated hydrocarbons, an equilibrium

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(1) Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907.

(2) Ślebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.

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