COMMUNICATION

ChemComm
www.rsc.org/chemcomm

The seventeen- and eighteen-electron metallacarbaboranes $[1,1,1\text{-}(CO)_3\text{-}2\text{-}Ph\text{-}closo\text{-}1,2\text{-}MnCB_9H_9]^{n-}$ (n = 1, 2): a structurally characterized, redox-related pair

Shaowu Du,[a] Robert D. Farley,[b] Jeremy N. Harvey,[c] John C. Jeffery,[c] Jason A. Kautz,[a] John P. Maher,[c] Thomas D. McGrath,[a] Damien M. Murphy,[b] T. Riis-Johannessen[c] and F. Gordon A. Stone*[a]
[a] *Department of Chemistry and Biochemistry, Baylor University, Waco, Texas 76798-7348, USA. E-mail: gordon_stone@baylor.edu*
[b] *EPSRC National ENDOR Service, Cardiff University, Cardiff, UK CF10 3TB*
[c] *School of Chemistry, University of Bristol, Bristol, UK BS8 1TS*

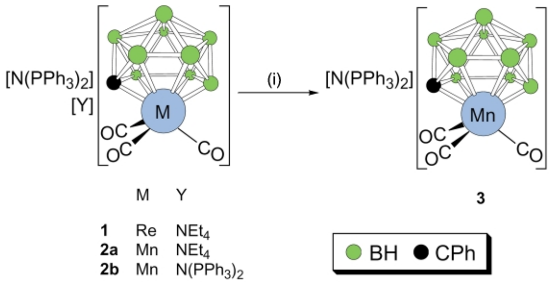
Received (in Cambridge, UK) 11th April 2003, Accepted 10th June 2003
First published as an Advance Article on the web 26th June 2003

An eleven-vertex manganese-monocarbaborane dianion, upon one-electron oxidation, gives a stable radical monoanion in which the unpaired electron is delocalized over the cluster.

Numerous transition-metal complexes are known that contain the cyclopentadienide anion $[C_5H_5]^-$, ranking it among the most important of ligands in organometallic chemistry.[1] Its isolobal carbaborane analogues, $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ and $[nido\text{-}7\text{-}CB_{10}H_{11}]^{3-}$, have been known for many years to behave similarly, acting as *pentahapto*, 6π-electron donor ligands to transition-element centres.[2,3] However, the resulting 12-vertex, icosahedral metallacarbaborane complexes, and in particular the one-carbon species, are far fewer in number: this relative scarcity is even greater when the sub-icosahedral derivatives are considered.[4] As part of an ongoing effort to redress these imbalances, we have discovered and now report the first eleven-vertex manganese-monocarbaborane complex and its unexpected conversion to a stable, seventeen-electron radical.

The new dianionic manganacarbaborane complex $[1,1,1\text{-}(CO)_3\text{-}2\text{-}Ph\text{-}closo\text{-}1,2\text{-}MnCB_9H_9]^{2-}$ was obtained from $[NEt_4][6\text{-}Ph\text{-}nido\text{-}6\text{-}CB_9H_{11}]$,[5] Bu^nLi and $[Mn(NCMe)_3(CO)_3][PF_6]$[6] in a manner parallel to that reported recently for the synthesis of the analogous rhenium species **1**,[7] and likewise was typically isolated as crystals of the mixed $[N(PPh_3)_2]^+[NEt_4]^+$ salt **2a** (Scheme 1).† The dianion shows a characteristic broad resonance at δ 51.8 in its $^{13}C\{^1H\}$ NMR spectrum, corresponding to the cage-carbon atom, along with a broad peak at δ 225.5 for the Mn-bound CO ligands. There are six $^{11}B\{^1H\}$ NMR signals between δ 36.1 and −28.3 in the ratio 1:1:1:2:2:2 (two coincide), consistent with the expected mirror-symmetric $\{closo\text{-}1,2\text{-}MnCB_9\}$ cluster architecture. Further confirmation of the latter was provided by an X-ray diffraction study on **2a**.‡ This established that the manganacarbaborane moiety consists of an $\{Mn(CO)_3\}$ fragment that is η^6-coordinated by the $\overline{CBBBBB}$ face of the $\{nido\text{-}CB_9\}$ ligand (see Fig. 1), very similar to the rhenacarbaborane of **1**.[7]

However, whereas the dianion of **1** undergoes two-electron oxidation reactions,[8] as do its 12-vertex analogues,[9] the dianion of compounds **2** under the same conditions loses only one electron. Thus, treatment of **2** with $HgCl_2$ in CH_2Cl_2, followed by column chromatography on silica, afforded the title monoanion as its $[N(PPh_3)_2]^+$ salt **3** (Scheme 1).† The increased stretching frequency of the three CO ligands in **3**, relative to **2**, was consistent with metal oxidation having occurred. Under such mild conditions it is unsurprising that a formal Mn^{III} species was not attained[10] and the absence of NMR signals further pointed to a paramagnetic Mn^{II} complex. Thus it appeared that an air-stable, seventeen-electron radical had been obtained.



Scheme 1 *Reagents and conditions*: i, **2a** with $HgCl_2$ in CH_2Cl_2.

The above, initially tentative formulation of the monoanionic product **3** was confirmed by an X-ray diffraction study,‡ which afforded the structure shown (Fig. 1). Overall, the manganacarbaborane moiety of **3** has a geometry closely similar to that of **2a**. However, relative to the precursor, there are further indicators of loss of electron density at manganese, namely significant lengthening of the Mn–CO distances and corresponding shortening of the C–O separations; the Mn vertex of **3** is also rather closer to the ligating carbaborane face. The $\{CB_9\}$ framework itself also exhibits some perturbation upon oxidation. There is slight overall lengthening of the average B–B and C–B distances and a modest enlargement of the ten-atom carbaborane "boat" (Fig. 1), as would be expected upon removal of an electron from a cluster bonding orbital. Indeed, since the cage lacks its full complement of skeletal electrons, it is more appropriately described as *hypercloso*.[11]

The EPR spectrum of compound **3** (CH_2Cl_2, 18 °C) shows a strong, six-line signal (g = 2.021, A = 4.2 mT) characteristic of a paramagnetic ^{55}Mn complex.[12] Although this spectrum shows

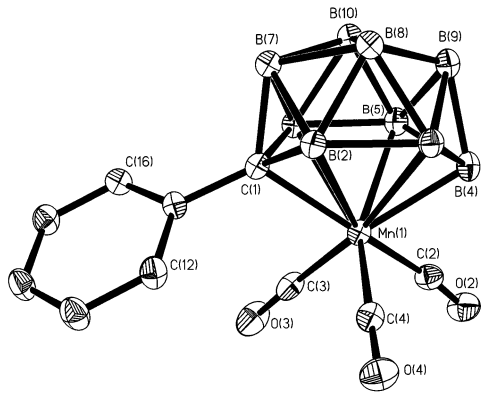


Fig. 1 Structure of the anion of **3** with crystallographic labeling scheme (thermal ellipsoids with 40% probability). Selected distances (Å) are: Mn(1)–C(1) 2.0508(18), Mn(1)–B(4) 2.109(2), Mn(1)–B(2,3,5,6) range 2.299(2)–2.335(2), Mn(1)–CO range 1.817(2)–1.858(2), C–O range 1.136(2)–1.146(2), C(1)···B(4) 3.510(3), B(2)···B(6) 2.654(3), B(3)···B(5) 2.680(3), B(7)···B(9) 2.945(3). The dianion of **2a** has a similar cluster architecture; selected distances (Å) are: Mn–C(1) 2.125(7), Mn–B(4) 2.118(8), Mn–B(2,3,5,6) range 2.354(8)–2.424(9), Mn–CO range 1.751(8)–1.788(8), C–O range 1.161(9)–1.181(9), C(1)···B(4) 3.464(11), B(2)···B(6) 2.575(12), B(3)···B(5) 2.647(12), B(7)···B(9) 2.897(13).

DOI: 10.1039/b304101h

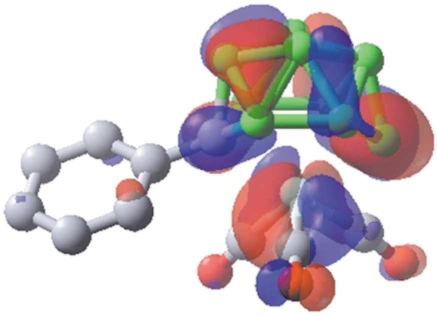


Fig. 2 The SOMO of **3** obtained from the DFT calculation.

no additional coupling to the cage hydrogens or borons, there is clear evidence of such interactions in the Q-band ENDOR at 10 K. The glassy X- and Q-band EPR spectra of the carbaborane, also at 10 K, reveal very little anisotropy in the rhombic g-tensor ($g_1 = 2.022$, $g_2 = 2.021$, $g_3 = 2.020$), whereas the A-tensor ($A_1 = 8.7$, $A_2 = -2.9$, $A_3 = 6.8$ mT) shows considerable anisotropy. At present the spectrum simulation, especially at Q-band, is rather poor and is complicated by g- and A-tensor axis non-coincidence effects, as observed previously in Mn^{II} complexes.[13] Notably, the g tensors for the latter species are appreciably different to that of **3**, perhaps suggesting that the unpaired electron in **3** is located largely in the carbaborane cage, with the metal centre still formally Mn^{I} rather than Mn^{II}. Contrary to this, however, is the relatively large observed ^{55}Mn hyperfine interaction, which indicates significant delocalization onto the manganese.

A DFT calculation[14] on the radical provided support for the above observations, and gave structural parameters that were in good agreement with those obtained from the X-ray diffraction study [max. deviation *ca*. 0.047 Å for Mn–B(3)]. The calculated SOMO (Fig. 2) reveals an antibonding interaction between the Mn centre and the carbaborane cage, consistent with the closer approach between these two upon oxidation. Moreover, the unpaired electron was found to be distributed over both the carbaborane cage and the $\{Mn(CO)_3\}$ moiety [Mulliken spin densities: Mn 0.37, $\{PhCB_9H_9\}$ 0.55, $\{(CO)_3\}$ 0.08], in accord with the spectroscopic results. This delocalization is likely a major contributor to the unusual stability of this radical, and complements the recently reported borane radical $[B_{12}Me_{12}]^{-\cdot}$ whose robustness may also be attributed to the substituent "sheath".[15] In the case of **3**, the metal centre may also play a role in enhancing stability. We continue to investigate the nature of these and related species and of the processes by which they are formed.

We thank the Robert A. Welch Foundation for support (Grant AA-1201) and the EPSRC for a studentship (T. Riis-Johannessen).

Notes and references

† **2**: Dark yellow microcrystals (1:1 mixture of **2a**, **2b** by integrated ^1H NMR); yield 73%. Anal. Calc. for $C_{54}H_{64}B_9MnN_2O_3P_2$ (**2a**): C, 64.7; H, 6.4; N, 2.8. Found: C, 64.9; H, 6.4; N, 2.8%; IR (CH_2Cl_2): ν_{max}(CO) 1967vs, 1886s, 1856s cm^{-1}. $^{11}B\{^1H\}$ NMR (115.5 MHz, CD_2Cl_2) δ 36.1 (1B), 10.1 (1B), −6.5 (3B), −25.8 (2B), −28.3 (2B).

3: Dark green microcrystals; yield 36% (not optimized). Anal. Calc. for $C_{46}H_{44}B_9MnNO_3P_2$: C, 63.3; H, 5.1; N, 1.6. Found: C, 63.3; H, 5.4; N, 1.6%; IR (CH_2Cl_2): ν_{max}(CO) 2028vs, 1985s, 1955m cm^{-1}.

‡ *Crystal data*: for both determinations: Lorentz, polarization and empirical absorption corrections; solution by direct methods and full-matrix least-squares refinement on all unique F^2 data (SHELXL97). **2a**: crystals from $(CH_3)_2CO$–petroleum ether (bp 40–60 °C) (20 °C); Enraf-Nonius CAD-4 diffractometer, Mo–Kα X-radiation (λ = 0.71073 Å); $C_{54}H_{64}B_9MnN_2O_3P_2$, M = 1003.24, monoclinic, a = 13.4979(9), b = 26.154(2), c = 15.1792(14) Å, β = 91.521(7)°, U = 5356.7(7) Å^3, T = 293(2) K, space group $P2_1/n$, Z = 4, μ(MoKα) = 0.351 mm^{-1}, 8652 reflections measured, 8303 unique (R_{int} = 0.0751), 4211 observed [$F > 4\sigma(F)$]. Final wR_2 (F^2) = 0.2466 (all data), R_1 [$F > 4\sigma(F)$] = 0.0827. **3**: Bruker Proteum CCD area-detector diffractometer, Cu–Kα X-radiation (λ = 1.54184 Å); crystals from CH_2Cl_2–toluene–petroleum ether (−30 °C); $C_{46}H_{44}B_9MnNO_3P_2$, M = 872.99, triclinic, a = 10.8998(1), b = 13.9049(1), c = 15.7182(2) Å, α = 85.196(1), β = 70.333(1), γ = 79.926(1)°, U = 2207.91(4) Å^3, T = 100(2) K, space group $P\bar{1}$, Z = 2, μ(CuKα) = 3.441 mm^{-1}, 17517 reflections measured, 7517 unique (R_{int} = 0.0279), 6672 observed. Final wR_2 (F^2) = 0.0995 (all data), R_1 [$F > 4\sigma(F)$] = 0.0366. CCDC 208486 and 208487. See http://www.rsc.org/suppdata/cc/b3/b304101h/ for crystallographic data in .cif or other electronic format.

1 C. Janiak and H. Schumann, *Adv. Organomet. Chem.*, 1991, **33**, 291.

2 M. F. Hawthorne, D. C. Young and P. A. Wegner, *J. Am. Chem. Soc.*, 1965, **87**, 1818.

3 D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer and L. J. Todd, *J. Am. Chem. Soc.*, 1967, **89**, 3342; W. H. Knoth, *J. Am. Chem. Soc.*, 1967, **89**, 3342.

4 R. N. Grimes, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995; vol. 1, ch. 9 and references cited therein.

5 T. Jelínek, M. Thornton-Pett and J. D. Kennedy, *Collect. Czech. Chem. Commun.*, 2002, **67**, 1035.See also: B. Brellochs, in *Contemporary Boron Chemistry*, ed. M. G. Davidson, A. K. Hughes, T. B. Marder and K. Wade, Royal Society of Chemistry, Cambridge, UK, 2000, p. 212.

6 R. H. Reiman and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1974, 808.

7 S. Du, J. A. Kautz, T. D. McGrath and F. G. A. Stone, *Organometallics*, 2003, **22**, 2842.

8 S. Du, J. A. Kautz, T. D. McGrath and F. G. A. Stone, unpublished results.

9 I. Blandford, J. C. Jeffery, P. A. Jelliss and F. G. A. Stone, *Organometallics*, 1998, **17**, 1402; S. Du, J. A. Kautz, T. D. McGrath and F. G. A. Stone, *Chem. Commun.*, 2002, 1004.

10 G. S. Girolami and R. J. Morris, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995; vol. 6, ch. 7 and references cited therein.

11 M. L. McKee, Z.-X. Wang and P. von R. Schleyer, *Inorg. Chem.*, 2000, **112**, 4781 and references cited therein.

12 R. Gross and W. Kaim, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 856.

13 R. D. Pike, A. L. Rieger and P. H. Rieger, *J. Chem. Soc., Faraday Trans.*, 1989, **85**, 3913; N. C. Brown, G. A. Carriedo, N. G. Connelly, F. J. Garcia Alonzo, I. C. Quarmby, A. L. Rieger, P. H. Rieger, V. Riera and M. Vivanco, *J. Chem. Soc., Dalton Trans.*, 1994, 3745.

14 The structure was optimized using unrestricted B3LYP theory, together with standard 6-31G* on all atoms except Mn, for which the Jaguar triple-ζ form of the standard Los Alamos ECP basis set (LACV3P) was used. Calculations used the Jaguar 4.1 program package (Schrödinger, Inc., Portland, OR, 1995–2002).

15 T. Peymann, C. B. Knobler and M. F. Hawthorne, *Chem. Commun.*, 1999, 2039.