Carbonyl–metal fragment insertion into eight-vertex [*closo*-1-CB_7H_8]$^-$. Facile synthesis of ten-vertex metalladicarbollide complexes [2,2,2-$(CO)_3$-1-OH-*closo*-2,1,10-$MC_2B_7H_8$]$^{n-}$ {M = Fe, Ru (n = 0), Mn, Re (n = 1)}

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Received (in CAMBS) 1st June 2006, Accepted 12th June 2006
First published as an Advance Article on the web 5th July 2006
DOI: 10.1039/b607768d

Insertion of {$M(CO)_4$} fragments (M = Fe, Ru, Mn, Re) into the eight-vertex monocarborane anion [*closo*-1-CB_7H_8]$^-$ affords ten-vertex metal–dicarbollide complexes.

For almost four decades the di- and tri-anionic carbollide ligands [*nido*-$C_2B_9H_{11}$]$^{2-}$ and [*nido*-$CB_{10}H_{11}$]$^{3-}$ when forming complexes with transition metals have been the subject of comparisons with the ubiquitous cyclopentadienide ligand [C_5H_5]$^-$, since all three are isolobal and can act as pentahapto, 6π-electron donors.[1,2] Until recently, the resulting 12-vertex metal–carbollide complexes have been primarily those of the [*nido*-$C_2B_9H_{11}$]$^{2-}$ ligand, these far outnumbering species with eleven vertices or fewer.[3] However, advances in the synthesis of intermediate-sized monocarboranes[4] initiated by Brellochs[5] are fueling a multi-pronged expansion in the chemistry of the smaller metallacarbollides, enabling for example the synthesis of several nine- and ten-vertex iron–monocarbollide species.[6] In attempting to identify a minor by-product formed in one of these systems we discovered that the species was in fact a ten-vertex iron–dicarbollide cluster in which one of the cage carbon atoms carried an OH substituent. Moreover, by modifying the reaction conditions this compound, as well as corresponding ruthenium, manganese and rhenium species, could all be prepared in good yields, as we now report.

Recently it was shown[6a] that two {$Fe(CO)_3$} fragments successively insert into the eight-vertex carborane anion [*closo*-1-CB_7H_8]$^-$ to yield the nine- and ten-vertex anionic complexes [7,7,7-$(CO)_3$-*closo*-7,1-$FeCB_7H_8$]$^-$ (**1**) and then [6,6,6,10,10,10-$(CO)_6$-*closo*-6,10,1-$Fe_2CB_7H_8$]$^-$ (**2**), respectively, upon heating salts of the carborane with excess [$Fe_3(CO)_{12}$] or [$Fe(CO)_5$] in refluxing thf (tetrahydrofuran). The latter reaction always yielded small amounts (up to *ca.* 5%) of a by-product, which has now been identified as the neutral ferradicarbollide complex [2,2,2-$(CO)_3$-1-OH-*closo*-2,1,10-$FeC_2B_7H_8$] (**3a**).† Yields of **3a** improved to 62% when [$Fe_2(CO)_9$] was used as the iron reagent, but the rather acidic cage–OH unit made purification difficult. Accordingly, addition of PEt_3 and Me_3NO to the crude product resulted in rapid CO substitution and formation of [2,2-$(CO)_2$-1-OH-2-PEt_3-*closo*-2,1,10-$FeC_2B_7H_8$] (**3b**)† for which the greater cluster electron density destabilizes the conjugate base and so renders the species far less acidic. Compound **3b** was then easily isolated by column chromatography on silica and initially identified by an X-ray diffraction study (Fig. 1).‡ The cluster consists of an {$Fe(CO)_2(PEt_3)$} moiety that is η^5-coordinated to the open face of a {*nido*-1,9-C_2B_7} carborane ligand. To our knowledge the parent carborane of this ligand remains unknown. However, there have been a few reports of (non-hydroxylated) cobalt complexes analogous to compounds **3**, obtained from {*arachno*-C_2B_7} precursors or by degradation of species of higher nuclearity.[7] Notably, the thermodynamically preferred[3,7c,8] *para* dispositions of the two cage-carbon atoms in those {*closo*-2,1,10-CoC_2B_7} systems were typically achieved by thermal rearrangement at high temperatures. In the compounds described herein, much milder conditions afford the same respective arrangement of metal and

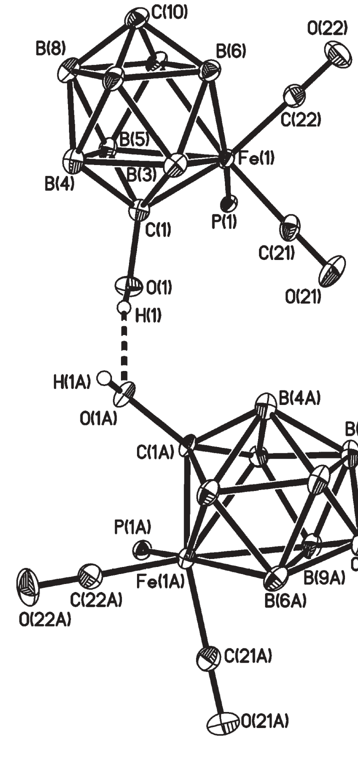

Fig. 1 The hydrogen bonded pair of crystallographically independent molecules of **3b** (thermal ellipsoids at 40% probability). Selected distances (Å) and angles (°) are: Fe(1)–C(1) 1.966(3), Fe(1)–B(3) 2.198(3), Fe(1)–B(5) 2.204(3), Fe(1)–B(6) 2.176(3), Fe(1)–B(9) 2.180(3), C(1)–O(1) 1.391(3), H(1)···O(1A) 2.09, O(1)···O(1A) 2.896(3); O(1)–C(1)–Fe(1) 123.19(18), O(1)–H(1)···O(1A) 160.6.

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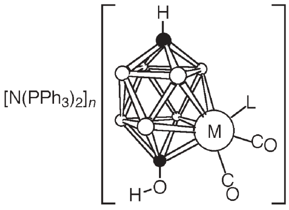

	n	M	L
3a	0	Fe	CO
3b	0	Fe	PEt_3
4	0	Ru	CO
5	1	Mn	CO
6	1	Re	CO

○ BH ● C

Chart 1

carbon vertices. A general structure for compounds **3–6** is presented in Chart 1.

The five-atom belt bonded to iron has a pronounced envelope shape, as required by the cluster architecture, but cage···Fe distances are otherwise within normal ranges.[3] Internuclear distances confirmed that the atom at the 1-position was indeed carbon rather than boron. An additional notable feature of the crystal structure is that the compound crystallizes with two crystallographically independent molecules that form hydrogen bonded pairs. Although the hydroxyl hydrogens could be located in Fourier difference maps their positions could not sensibly be refined. Notably, though, the "rotating model" used in their refinement placed these atoms very close to where they are found in difference maps. The donor···acceptor (O···O) distance is 2.896(3) Å, so the O–H···O interaction is relatively weak[9] but nevertheless is apparently sufficient to produce the observed crystal packing.

Both of compounds **3** show four signals in their $^{11}B\{^1H\}$ NMR spectra, in the ratio 1 : 2 : 2 : 2, consistent with molecular mirror symmetry and in the range expected for a dicarbametallaborane.[10] In addition, the cage-carbon atom bearing the OH group resonates in $^{13}C\{^1H\}$ NMR spectra at δ 177.3 (**3a**) and 184.5 (**3b**), far downfield from the cluster {CH} vertex [δ 80.4 (**3a**) and 78.5 (**3b**)], as is to be expected. The same spectra show a single resonance for the Fe-bound CO ligands (δ 204.3) in **3a**, with a doublet [δ 211.0; $J(PC)$ = 25 Hz] for those in **3b**.

When $[Mn_2(CO)_{10}]$ was similarly treated with $[NBu^n{}_4]$[*closo*-1-CB_7H_8] in refluxing thf, ^{11}B NMR analysis of the product mixture indicated slow (48 h) formation of an analogue of **3a**. It was subsequently discovered that the same species is rapidly formed (2 h) by irradiation (Hg vapour arc lamp) of the same reagent mixture at room temperature. Moreover, although attempts to prepare the related ruthenium and rhenium species by thermal reaction in thf between $[NBu^n{}_4]$[*closo*-1-CB_7H_8] and $[Ru_3(CO)_{12}]$ or $[Re_2(CO)_{10}]$ failed, the photochemical route was successful. Formation of the ruthenadicarbollide complex [2,2,2-$(CO)_3$-1-OH-*closo*-2,1,10-$RuC_2B_7H_8$] (**4**)† is accompanied by apparent ruthenium analogues of the anionic complexes **1** and **2** but is readily separated from the latter two by column chromatography on silica gel, the anionic species being isolated as $[N(PPh_3)_2]^+$ salts.[11] Similarly, addition of $[N(PPh_3)_2]Cl$ to the manganese or rhenium reaction mixtures and column chromatography on silica afforded the corresponding metalladicarbollide salts $[N(PPh_3)_2]$[2,2,2-$(CO)_3$-1-OH-*closo*-2,1,10-$MC_2B_7H_8$] [M = Mn (**5**), Re (**6**)].†

The identities of compounds **4–6** were confirmed by their spectroscopic data and by X-ray diffraction studies (see Fig. 2).‡ As with compounds **3**, all three show four $^{11}B\{^1H\}$ NMR signals in the ratio 1 : 2 : 2 : 2, whilst their $^{13}C\{^1H\}$ NMR spectra display characteristic broad resonances at δ 180.7 (**4**), 180.2 (**5**) and 168.6 (**6**) for the cage {COH} unit and at δ 81.8 (**4**), 75.0 (**5**) and 88.1 (**6**) for the cluster {CH} vertex. Signals at δ 190.8, 226.0 (br) and 201.8 in the same spectra are typical for the metal-bound CO ligands in **4**, **5** and **6**, respectively.

It has been reported previously that Na[*nido*-$B_{10}H_{13}$] reacts with $[M(CO)_6]$ (M = Cr, Mo or W) under photochemical conditions to form [2,2,2,2-$(CO)_4$-1-(OH)-*closo*-2,1-$MCB_{10}H_{10}]^-$ derivatives,[12] a transformation that involves carbon vertex incorporation *via* insertion of a carbonyl into the [*nido*-$B_{10}H_{13}]^-$ anion, ultimately to afford a metal complex containing the monocarbollide ligand {7-OH-*nido*-7-$CB_{10}H_{10}$}. Carbonyl insertion has also been invoked in the formation of iridacarbollides from $[IrCl(CO)(PPh_3)_2]$ and [*closo*-$B_{10}H_{10}]^{2-}$ although this system is substantially more complex.[13] The synthesis of dicarbon carboranes related to that found in compounds **3–6** has traditionally involved insertion of an acetylene into a borane substrate, followed by boron atom removal as necessary to achieve the correct vertex count.[14] In contrast, insertion of a single carbon atom using cyanide anion, organic cyanides/isocyanides or aldehydes has been the typical synthetic route to mono- and tri-carbon carboranes from boranes and dicarboranes, respectively.[4,5,14,15] It has been shown recently, however, that double carbon atom insertion is possible by

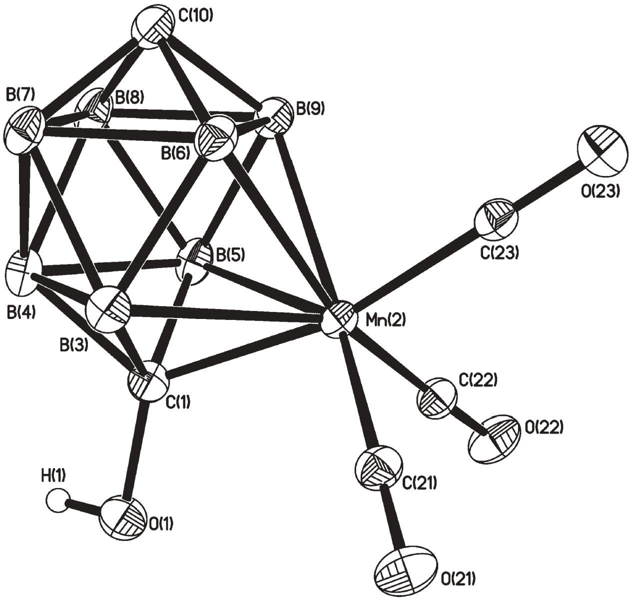

Fig. 2 Structure of the anion of **5** (thermal ellipsoids at 40% probability); that of **6**, and the three crystallographically independent neutral molecules of **4**, are very similar. Selected distances (Å) and angles (°) are as follows. For one of the independent molecules of **4**: Ru(2)–C(1) 2.082(3), Ru(2)–B(3) 2.298(3), Ru(2)–B(5) 2.307(3), Ru(2)–B(6) 2.282(3), Ru(2)–B(9) 2.300(3), C(1)–O(1) 1.401(3); O(1)–C(1)–Ru(2) 120.9(2). For **5**: Mn(2)–C(1) 1.994(2), Mn(2)–B(3) 2.238(2), Mn(2)–B(5) 2.244(2), Mn(2)–B(6) 2.205(2), Mn(2)–B(9) 2.211(2), C(1)–O(1) 1.399(2); O(1)–C(1)–Mn(2) 121.97(14). For **6**: Re(1)–C(1) 2.112(3), Re(1)–B(3) 2.397(4), Re(1)–B(5) 2.387(4), Re(1)–B(6) 2.345(5), Re(1)–B(9) 2.340(5), C(1)–O(1) 1.405(4); O(1)–C(1)–Re(1) 119.7(2).

successive aldehyde addition to a borane substrate, the reaction giving first a mono- and then a di-carborane.[5,16] To our knowledge, the introduction of a carbon atom into the smaller monocarborane cages *via* carbonyl insertion has not previously been demonstrated.

The mechanism of formation of compounds **3a** and **4–6** is presently unclear. Moreover, reactions with the iron or ruthenium carbonyl reagents may proceed differently from those with manganese and rhenium carbonyls. Nevertheless, it seems likely that the pathway involves initial interaction between the carborane and a metal–carbonyl fragment, so as to bring a metal-ligated CO group into close proximity with the cage, thus activating the carbonyl towards cluster insertion. Protonation of a metal–carbonyl group, yielding an alkylidyne–metal fragment that then inserts into the cluster, is one attractive mechanistic possibility for which there is some prior evidence.[17] Notably, moreover, in at least one of the present systems the deliberate addition of traces of H_2O to the reaction mixture improves the yield of metalladicarbollide, consistent with the proposal of an M–CO protonation step. We are at present continuing to investigate the mechanisms of these reactions and to examine for similar behaviour with other metal reagents. In addition, the pendant OH group in these new compounds provides a reactive centre for appending other functional organic moieties to the cluster[18] *via* relatively simple transformations, an avenue with considerable potential that we are actively pursuing.

We thank the Robert A. Welch Foundation for support (Grant AA-0006) and the National Science Foundation Major Research Instrumentation Program (Grant CHE-0321214) for funds to purchase the Bruker-Nonius X8 APEX diffractometer.

Notes and references

† Satisfactory microanalyses were obtained for all compounds. For **3a**: yellow microcrystals; yield 62%. IR (CH_2Cl_2): ν_{max}(CO) 2092 s, 2042 s cm^{-1}. δ_H (360.1 MHz, 298 K, CD_2Cl_2) 6.16 (br s, 1H, cage CH), 3.68 (br, 1H, cage COH); δ_C (90.6 MHz, 298 K, CD_2Cl_2) 204.3 (Fe–CO), 177.3 (br, cage COH), 80.4 (br, cage CH); δ_B (115.5 MHz, 298 K, CD_2Cl_2, unit integral except where indicated) 14.5, −0.3 (2B), −15.7 (2B), −22.1 (2B). For **3b**: yellow crystals; yield 61%. IR (CH_2Cl_2): ν_{max}(CO) 2019 s, 1971 s cm^{-1}. δ_H 6.00 (br s, 1H, cage CH), 3.69 (br, 1H, COH); δ_C 211.0 (d, J(PC) = 25 Hz, Fe–CO), 184.5 (br, cage COH), 78.5 (br, cage CH); δ_B 8.3, −1.0 (2B), −17.4 (2B), −22.4 (2B); δ_P (145.8 MHz, 298 K, CD_2Cl_2) 54.8. For **4**: colourless crystals; yield 39% (not optimised). IR (CH_2Cl_2): ν_{max}(CO) 2105 s, 2051 s cm^{-1}. δ_H 6.40 (br s, 1H, cage CH), 5.95 (br, 1H, cage COH); δ_C 190.8 (Ru–CO), 180.7 (br, cage COH), 81.8 (br, cage CH); δ_B 11.6, −2.4 (2B), −15.5 (2B), −23.0 (2B). For **5**: yellow crystals; yield 87%. IR (CH_2Cl_2): ν_{max}(CO) 1991 s, 1903 s cm^{-1}. δ_H 5.64 (br s, 1H, cage CH), 4.89 (s, 1H, COH); δ_C 226.0 (br, Mn–CO), 180.2 (br, cage COH), 75.0 (br, cage CH); δ_B 1.4, −4.8 (2B), −18.0 (2B), −23.8 (2B). For **6**: yellow crystals; yield 63%. IR (CH_2Cl_2): ν_{max}(CO) 1996 s, 1904 s cm^{-1}. δ_H 6.83 (br, 1H, cage CH), 5.79 (br, 1H, cage COH); δ_C 201.8 (Re–CO), 168.6 (cage COH), 88.1 (br, cage CH); δ_B −5.2, −12.3 (2B), −20.1 (2B), −22.5 (2B).

‡ *Crystal data*. For all determinations: Bruker-Nonius X8 Apex CCD diffractometer, Mo Kα X-radiation, T = 110(2) K. For **3b**: $C_{10}H_{24}B_7FeO_3P$, M_r = 354.78, monoclinic, $P2_1/n$, a = 19.121(11), b = 9.018(5), c = 20.973(11) Å, β = 103.516(18)°, V = 3516(3) $Å^3$, Z = 8 (2 independents), μ = 0.950 mm^{-1}, $F(000)$ = 1472. 46927 reflections collected to θ_{max} = 27.66°, 8146 unique (R_{int} = 0.0791), R_1 = 0.0739, wR_2 = 0.1114 for refinement on all F^2 data. For **4**: $C_5H_9B_7O_4Ru$, M_r = 309.86, triclinic, $P\bar{1}$, a = 7.6548(7), b = 11.6193(12), c = 19.6123(19) Å, α = 93.716(5), β = 98.033(5), γ = 90.739(5)°, V = 1723.2(3) $Å^3$, Z = 6 (3 independents), μ = 1.351 mm^{-1}, $F(000)$ = 900. 27098 reflections collected to θ_{max} = 28.08°, 8204 unique (R_{int} = 0.0471), R_1 = 0.0456, wR_2 = 0.0730 for refinement on all F^2 data. The ruthenacarbollides form hydrogen bonded helices that extend along the crystallographic a direction, as will be discussed elsewhere.[11] For **5**: $C_{41}H_{39}B_7MnNO_4P_2$, M_r = 802.28, monoclinic, $P2_1/n$, a = 14.972(2), b = 15.004(3), c = 17.410(3) Å, β = 95.022(6)°, V = 3895.9(11) $Å^3$, Z = 4, μ = 0.465 mm^{-1}, $F(000)$ = 1656. 45746 reflections collected to θ_{max} = 29.67°, 10928 unique (R_{int} = 0.0476), R_1 = 0.0611, wR_2 = 0.1143 for refinement on all F^2 data. For **6**: $C_{41}H_{39}B_7NO_4P_2Re$, M_r = 933.54, monoclinic, $P2_1/n$, a = 15.098(3), b = 15.289(3), c = 17.297(4) Å, β = 98.085(9)°, V = 3953.1(14) $Å^3$, Z = 4, μ = 3.199 mm^{-1}, $F(000)$ = 1856. 44201 reflections collected to θ_{max} = 29.69°, 10667 unique (R_{int} = 0.0673), R_1 = 0.0645, wR_2 = 0.0720 for refinement on all F^2 data. CCDC 609673–609676 for **3b**, **4**, **5** and **6**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607768d

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