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Polynuclear Metallacarborane−Hydrocarbon Assemblies: Metallacarborane Dendrimers[1]

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*Summary: The first dendrimers containing metallacarborane modules have been prepared and characterized. The acyl derivative nido-[η^5-$C_5H_4C(O)Cl$]Co(2,3-$Et_2C_2B_3H_5$) was treated with diaminobutane-dend-$(NH_2)_{16}$ (DAB-16) and Et_3N in CH_2Cl_2 to give the 16- and 32-cobalt metallodendrimers DAB-dend-[NHC(O)-C_5H_4Co(2,3-$Et_2C_2B_3H_5$)]$_{16}$ (**5**) and DAB-dend-[NHC(O)-C_5H_4Co(2,3-$Et_2C_2B_3H_5$)]$_{32}$ (**6**), which were isolated as air-stable yellow solids in 76% and 79% yields, respectively.*

The study of dendrimers[2] is well advanced since their first appearance 25 years ago.[3] Dendritic materials have attracted wide-ranging interest because of their actual or potential application in a broad spectrum of areas, including electrode coatings, nonlinear optical (NLO) materials, controlled artificial energy antennas (light harvesters), electrochemical biosensors, exoreceptors for molecular recognition, catalysis, biomedical applications, and organic electrical conductors. While most characterized dendrimers are purely organic in composition, attention has been increasingly directed to metal-containing systems,[4] particularly those containing electroactive metal centers.[4a] Transition metals with partially filled d shells may function as electrophores, chromophores, or active catalytic sites, with the metal center residing at the core (rarely), the interior branches, and/or the periphery of the molecule. The choice of transition-metal-containing units that are suitable for inclusion in dendritic systems is rapidly growing: known metallodendrimers incorporate ferrocenyl,[5] cobaltocenium,[5h,6] chromium carbonyl,[7] Co_2C_2,[8] and organoruthenium groups[9] and others.[4] Polyhedral metal−boron clusters afford an as yet unexplored potential for creating novel families of electronically tailorable metallodendrimers. Metallacarboranes seem especially promising for this role, given their well-established thermodynamic and redox stability, ease of modification via organosubstitution, and synthetic versatility.[10] Although dendrimers containing nonmetalated C_2B_{10} carborane cages have been prepared,[8b,9e,11] we know of none having metallaborane or metallacarborane cluster units. Here we report the synthesis and characterization of the first metallacarborane dendrimers.

As the metal-containing units of choice for attachment to poly(propyleneimine) dendrimers, 6- and 7-vertex CoC_2B_n (n = 3, 4) cobaltacarborane clusters were selected because of their relatively small, metallocene-like steric requirements and their well-established redox properties and synthetic tailorability.[12] Scheme 1 shows the conversion of CpCo(2,3-$Et_2C_2B_4H_4$) (**1**) to its Cp-substituted carboxylic acid and acyl derivatives [η^5-$C_5H_4C(O)R$]Co(2,3-$Et_2C_2B_4H_4$) (**2**, R = OH; **3**, R = Cl),

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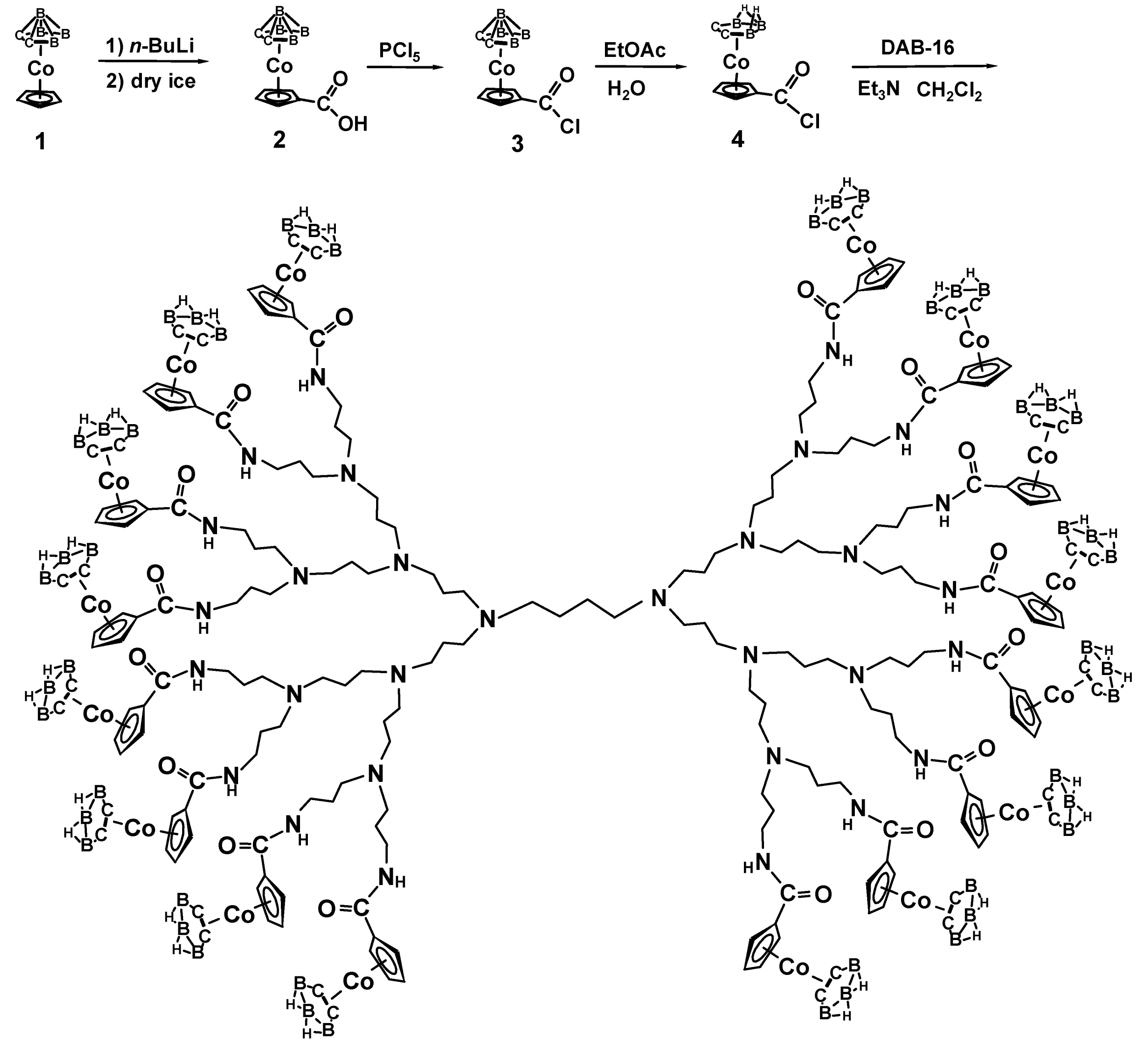
Scheme 1 [a]



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[a] Definitions: B = BH; carborane C = C$-$C$_2$H$_5$.

which were isolated as a red-orange solid and a red oil, respectively. Reaction of **3** with the polyamine diaminobutane-dend(NH$_2$)$_{16}$ (DAB-16) and Et$_3$N in CH$_2$Cl$_2$ gave products containing cobaltacarborane units at the dendrimer chain termini, but owing to partial decapping of the CoC$_2$B$_4$ clusters under the basic reaction conditions, mixtures containing varying numbers of CoC$_2$B$_3$ and CoC$_2$B$_4$ groups were obtained. To circumvent this problem, **3** was quantitatively decapped to generate the open-faced cobaltacarborane *nido*-[η^5-C$_5$H$_4$C(O)Cl]Co(2,3-Et$_2$C$_2$B$_3$H$_5$) (**4**), a red oil. Treatment of this compound with DAB-16 and Et$_3$N in CH$_2$Cl$_2$ afforded the desired 16-cobalt metallodendrimer DAB-*dend*-[NHC(O)-C$_5$H$_4$Co(2,3-Et$_2$C$_2$B$_3$H$_5$)]$_{16}$ (**5**), an air-stable yellow-orange solid, in 76% isolated yield. Similarly, the reaction of **4** with the fourth-generation dendrimer diaminobutane-dend(NH$_2$)$_{32}$ (DAB-32) and Et$_3$N gave the 32-cobalt metallodendrimer DAB-*dend*-[NHC(O)-C$_5$H$_4$Co(2,3-Et$_2$C$_2$B$_3$H$_5$)]$_{32}$ (**6**), an air-stable yellow solid, in 79% yield (Scheme 2).

Characterization of **5** and **6** is based on ^{1}H, ^{11}B, and ^{13}C NMR, IR, UV$-$visible, and matrix-assisted laser desorption ionization$-$time-of-flight mass spectroscopy, the last of which showed parent peaks at *m*/*e* 5998 for **3** and 12 139 for **4**, in both cases closely matching the calculated values (Supporting Information, Figure 3). In addition to the peak spread arising from the ^{10}B/^{11}B and ^{13}C/^{12}C isotopic abundances, the observation of lower mass peaks indicates fragmentation in the mass spectrometer as well as the presence of defective species having some unsubstituted chain termini; however, in both cases the fully substituted species exhibit by far the highest abundance. Both compounds exhibit slight air sensitivity in CHCl$_3$ solution but are stable indefinitely in CH$_2$Cl$_2$. Cyclic voltammetry on **5** in THF solution shows a single reduction process exhibiting features of chemical reversibility (Supporting Information, Figure 4a). The very negative potential values preclude measurement of the number of electrons involved in the cathodic process via controlled-potential coulometry, but the high ratio of current vs dendrimer concentration (6 $\times$ 10^{-5} mol dm^{-3}) strongly supports the assumption that the process involves the simultaneous one-electron reduction of all 16 cobalt centers, as has been observed in cobaltocenium dendrimers.[5h,6] The main cathodic process ($E^{\circ\prime} = -1.84$ V; $\Delta E_p = 130$ mV at 0.5 V s^{-1}) is

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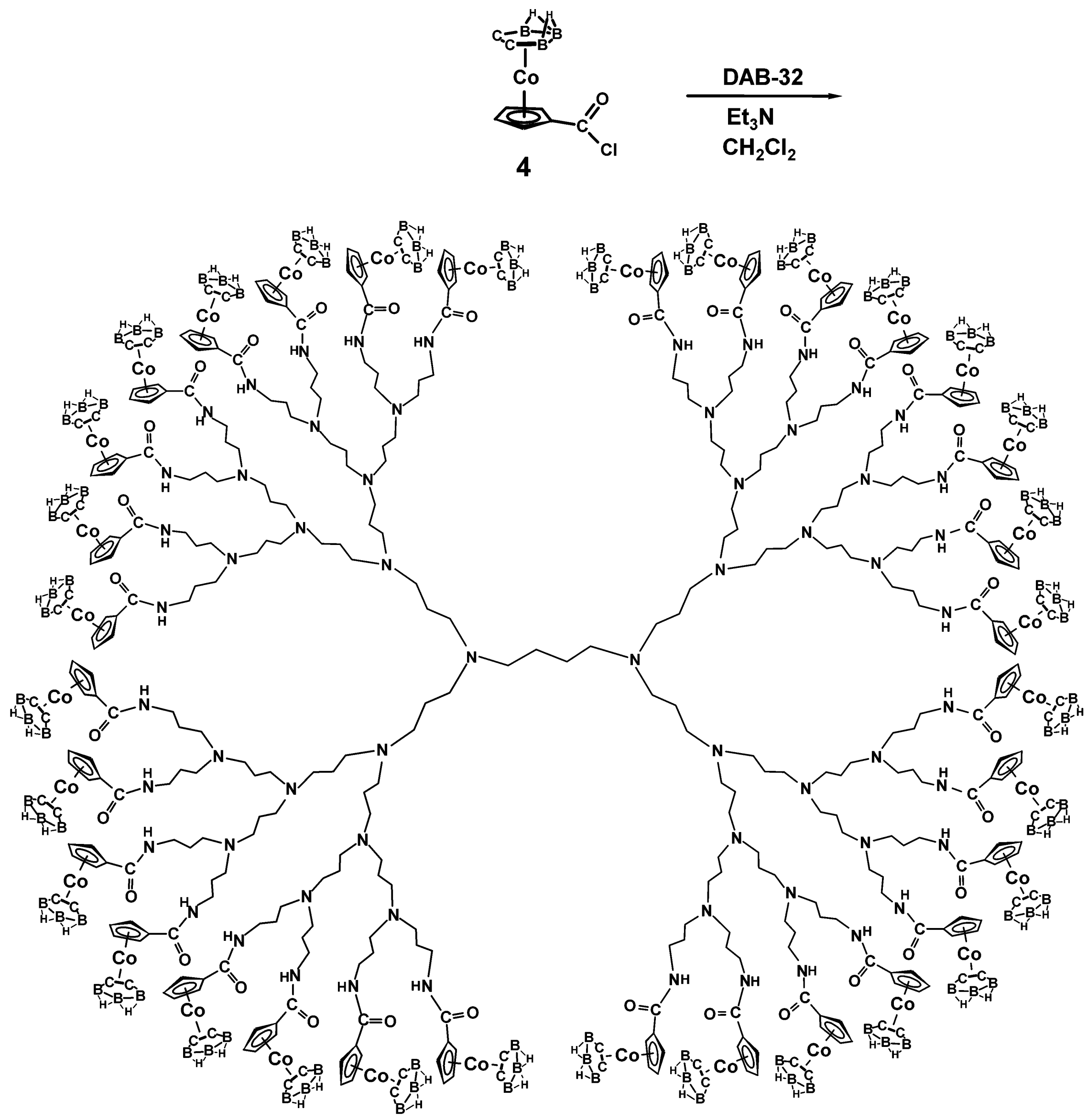
Scheme 2 [a]



[a] Definitions: B = BH; carborane C = C–C_2H_5.

followed by a minor peak ($E_p = -2.11$ V), the height of which linearly increases with the scan rate (rather than with the square root of the scan rate), indicating that it arises from electrode adsorption of **5** and not from chemical complications following the main reduction. However, such complications might be responsible for the observation that the peak-current ratio of the overall 16e reduction is slightly lower than unity ($i_{p,a}/i_{p,c} = 0.83$ regardless of scan rate), suggesting that the completely reduced dendrimer is stable, at least on the cyclic voltammetric time scale.

The 32-Co dendrimer **6** displays similar behavior (Supporting Information, Figure 4b); the analogous process ($E_p = -2.11$ V) following the main reduction ($E^{\circ\prime} = -1.87$ V, $\Delta E_p = 146$ mV) is even more marked than in **5** and exhibits the sharpened form typical of adsorption processes. To summarize, as is the case for most dendrimers containing redox active peripheral subunits, electronic interaction is not observed among the cobaltacarborane subunits.

The solubility and air stability of **5** and **6** are important attributes; moreover, they introduce to dendrimer science the new dimension of small-metallacarborane chemistry, opening possibilities for the design and construction of oligometallodendrimer- or polymetallodendrimer-based systems. The presence of multiple open C_2B_3 faces may be exploited via deprotonation of their B–H–B protons followed by introduction of organic substituents or stacking with transition-metal ions to form multidecker sandwich units.[12a] Such chemistry conceivably may lead to quite novel polydendritic architectures, such as three-dimensional networks linked by very stable $Co(C_2B_3)M(C_2B_3)Co$ multidecker sandwich bridges.

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Supporting Information Available: 500 MHz ^1H NMR spectra (Figure 1), 125.8 MHz ^{13}C NMR spectra (Figure 2), mass spectra (Figure 3), and cyclic voltammograms (Figure 4) for **5** and **6** and text giving synthetic details and spectroscopic data for compounds **2**–**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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