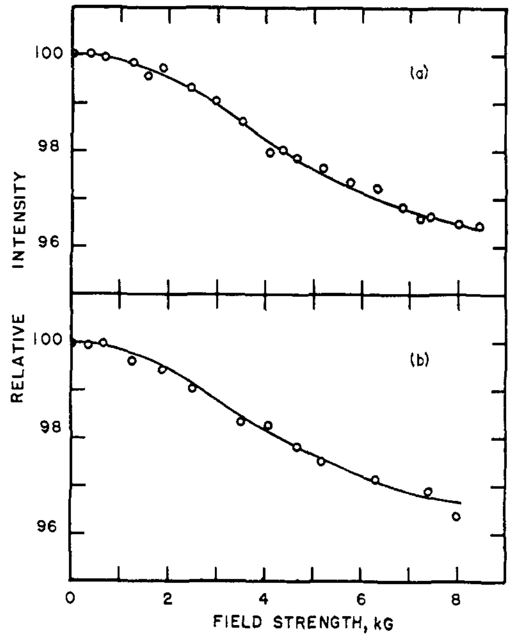

Figure 2. Magnetic field effect on delayed fluorescence from anthracene solutions in methylene chloride: (a) 3 × 10^{-4} *M*; (b) 8 × 10^{-5} *M*.

the rate constant by calculating a diffusion-limited constant for methylene chloride at 30°. Using the equation suggested by Osborne and Porter,[7] one obtains a value of 2.6 × 10^{10} l./(mole sec).

The results of these experiments are very relevant to the interpretation of the magnetic effects reported earlier on ECL emission from energy-deficient systems.[8] They permit one to give a coherent and plausible explanation of those effects in terms of the usually proposed mechanism involving triplet–triplet annihilations and in terms of experimentally confirmed field effects on steps included in that mechanism. One need only emphasize the importance of the radical-quenching steps toward controlling the ECL efficiency. The inhibition of those quenching steps would result in greater ECL efficiencies, hence greater intensities with increasing field. Clearly these experiments do not constitute a demonstration that the proposed mechanism for energy-deficient ECL is operative, but they are consistent with it.

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A Polyhedral Gallacarborane

Sir:

Although boron forms a considerable number and variety of electron-delocalized cage structures, including the boranes, carboranes, metalloboranes, and related systems, the remaining elements of group III have not been shown to form characterizable compounds of this type. In this report we describe the synthesis and characterization of the 1-methyl derivative of 1-galla-2,3-dicarba-*closo*-heptaborane(7) (I), for which we propose a structure in which a gallium atom is incorporated into a closed polyhedral system (Figure 1).

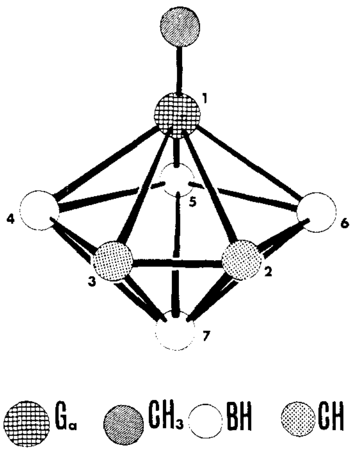

Figure 1. Proposed structure of $CH_3GaC_2B_4H_6$.

The reaction of 3 mmoles of trimethylgallium with 3 mmoles of 2,3-dicarba-*nido*-hexaborane(8) ($C_2B_4H_8$) in the gas phase at 215° produced gray solids, probably including gallium metal, and 50 mg of I ($\sim$20% yield based on $C_2B_4H_8$ consumed) plus a small quantity of trimethylboron. Following removal of the latter product by distillation at room temperature, pure I was obtained by sublimation at $\sim$50° *in vacuo*. At room temperature I is a slightly volatile, colorless crystalline solid, mp 33.5–34.5° (sealed tube), which survives at least brief exposure to air. The mass spectrum (Table I) is characteristic of a compact cage structure and contains a sharp cutoff at *m/e* 160, corresponding to the $^{12}C_3{}^{11}B_4{}^{71}Ga{}^{1}H_9{}^{+}$ parent ion. The fragmentation pattern is in close agreement with the spectrum calculated for $C_3B_4GaH_9$ based on natural isotope distributions and indicates very little hydrogen abstraction from the parent molecule in the mass spectrometer.

Table I. Partial Mass Spectrum of $CH_3GaC_2B_4H_6$

	Rel intensity	
m/e	Calcd[a]	Found
161	1.6	1.6
160	53.3	53.8
159	53.3	54.3
158	100.0	100.0
157	83.3	81.2
156	30.2	30.5
155	5.0	5.0
154	0.3	0.4

[a] Calculated from isotopic ratios $^{11}B/^{10}B$ = 4.0, $^{13}C/^{12}C$ = 0.011, and $^{71}Ga/^{69}Ga$ = 0.667.

The 32.1-MHz ^{11}B nmr spectrum (Figure 2) contains two partially overlapped doublets at low field and a third doublet at high field, whose relative areas indicate a 2:1:1 distribution of boron atoms with each bonded to a terminal hydrogen. The ^1H nmr spectrum in $CDCl_3$ solution contains resonances at τ 3.43 (area 2) and τ 9.83 (area 3) referenced to external tetramethylsilane, assigned to the cage CH and CH_3 groups, respectively. A quartet centered at τ 10.30 (J = 178 cps) of area 2 is attributed to the equivalent B(4)–H and B(6)–H groups,

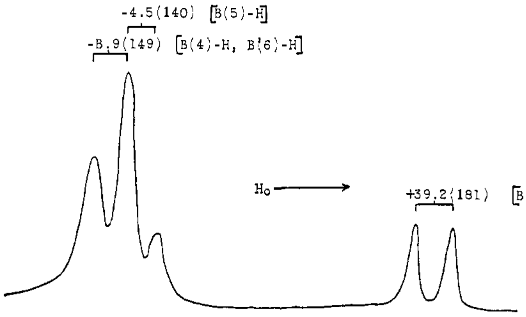

Figure 2. The 32.1-MHz ^{11}B nmr spectrum of *closo*-1-CH_3-1-$GaC_2B_4H_6$ ($CDCl_3$ solution). Chemical shifts are in ppm relative to $BF_3 \cdot O(C_2H_5)_2$, and coupling constants (cps) are given in parentheses.

but the expected B(5)–H and B(7)–H quartets of area 1 are not well defined and are partly obscured by the larger peaks. The infrared spectrum of I in $CDCl_3$ solution contains bands at 3050 (m), 2950 (s), 2905 (m), 2590 (vs), 1320 (m), 1283 (s), 1200 (s), 1023 (vs), 994 (vs), and 850 (m) cm^{-1}.

These data support the proposed structure but do not eliminate an alternate isomer in which the carbon atoms occupy nonadjacent equatorial positions, as in the *closo*-2,4-$C_2B_5H_7$ system.[1] However, the preparation of I from 2,3-$C_2B_4H_8$ under relatively mild conditions in what appears to be a simple insertion reaction[2] leads us to favor the adjacent carbon structure pending the results of an X-ray study to be undertaken shortly.

The synthesis and apparent stability of compound I suggests the possible existence of other cage compounds involving group III elements heavier than boron, and this possibility is currently under investigation.

Acknowledgment. This work was supported by the Office of Naval Research.

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A Small Carborane–Transition Metal Complex, (π-2-$CH_3C_3B_3H_5$)$Mn(CO)_3$

Sir:

The synthesis of π-bonded carborane–transition metal complexes analogous to the metallocenes has been an important recent development in boron chemistry. Most of the known compounds of this class are derived from the dicarbollide ion,[1] $C_2B_9H_{11}^{2-}$, or its isoelectronic analogs[2] such as $CB_{10}H_{11}^{3-}$, with the metal atom completing an icosahedral cage. A few nonicosahedral carborane complexes have been prepared,[3] of which the smallest to be reported[3b] is $(C_2B_6H_8)Mn(CO)_3^-$. The recently synthesized[4] tricarbahexaborate(1−) ion, $C_3B_3H_6^-$ (characterized as the 2,3- and 2,4-dimethyl derivatives), appeared a reasonable candidate for π coordination to transition metals, but our attempts to synthesize such complexes directly from the ions have so far been unsuccessful. However, the direct reaction of 2-methyltricarbahexaborane(7) with manganese carbonyl at 175–200° in a sealed tube gives a nearly quantitative yield of a product identified as (π-2-CH_3-$C_3B_3H_5$)$Mn(CO)_3$ (I), the proposed structure of which is presented in Figure 1.

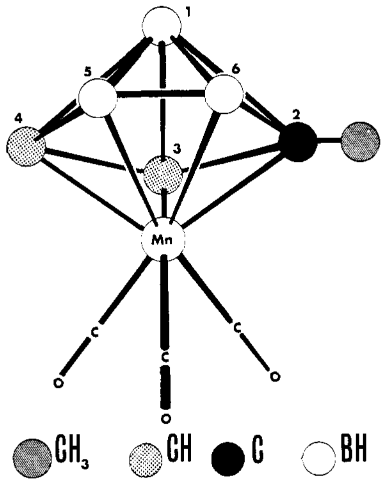

Figure 1. Proposed structure of $(CH_3C_3B_3H_5)Mn(CO)_3$.

$$CH_3C_3B_3H_6 + {}^1/_2Mn_2(CO)_{10} \longrightarrow (CH_3C_3B_3H_5)Mn(CO)_3 + 2CO + {}^1/_2H_2$$

Compound I, an isoelectronic analog of the known metallocene (π-C_5H_5)$Mn(CO)_3$,[5] is a slightly volatile, yellow-orange liquid which is easily distilled with mild heating in a vacuum system but is retained in a trap at 0°, thus allowing its easy separation from the much more volatile 2-$CH_3C_3B_3H_6$ starting material. The mass spectrum exhibits a sharp cutoff at *m/e* 228, corresponding to the $^{12}C_7{}^{11}B_3{}^{55}Mn{}^{16}O_3{}^1H_8{}^+$ ion, and the fragmentation pattern is consistent only with the presence of three boron atoms, as shown by calculated ^{11}B monoisotopic spectra. Peak groupings observed at *m/e* 200, 172, and 144 correspond to the successive loss of three CO groups from the parent ion, an effect also found in the mass spectrum of (π-C_5H_5)$Mn(CO)_3$.[6] The infrared spectrum of I (CCl_4 solution *vs.* CCl_4) contains two sharp, very strong CO stretching bands at 1956 and 2035 cm^{-1} (for comparison, (π-C_5H_5)$Mn(CO)_3$ in $CHCl_3$ solution exhibits CO absorbances[7] at 1939 and 2023 cm^{-1}, while the corresponding bands of (π-$CH_3C_5H_4$)$Mn(CO)_3$ are found[8] at 1940 and 2033

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