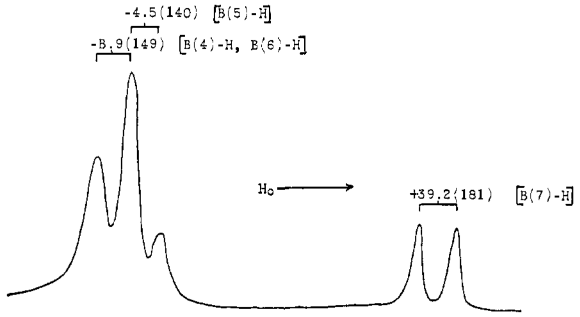

Figure 2. The 32.1-MHz ^{11}B nmr spectrum of *closo*-1-CH_3-1-$GaC_2B_4H_6$ ($CDCl_3$ solution). Chemical shifts are in ppm relative to $BF_3 \cdot O(C_2H_5)_2$, and coupling constants (cps) are given in parentheses.

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.

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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.

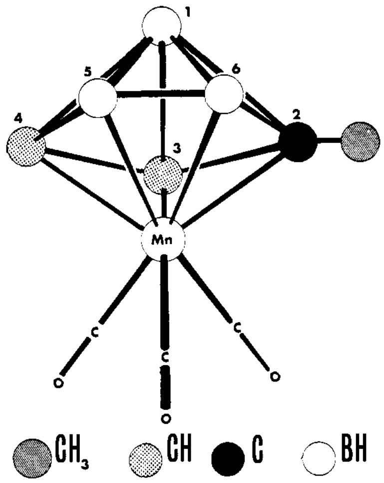

Figure 1. Proposed structure of $(CH_3C_3B_3H_5)Mn(CO)_3$.

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

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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cm^{-1}). Also present in the spectrum of I are absorptions at 2590 (s, BH stretch), 635 (s), and 670 (s) cm^{-1} and a CH_3 stretch (mw) at 2930 cm^{-1}, the remaining bands being broad and not well resolved.

The 32.1-MHz ^{11}B nmr spectrum of pure liquid I consists of two overlapping doublets at low field plus a high-field doublet, all of equal area (δ −7.4 ppm relative to $BF_3 \cdot O(C_2H_5)_2$, J = 140 cps; δ −1.0, $J \approx 140$; δ +132, J = 195). By analogy with the spectra of parent 2,3,4-$C_3B_3H_7$[9] and its methyl derivatives,[10] the high-field resonance is attributed to the apex B(1)–H group while the low-field doublets are assigned to the nonequivalent B(5)–H and B(6)–H groups. Interpretation of the very large chemical shift of the B(1)–H resonance will not be attempted here except to note that B(1) is the only cage atom not bonded to the metal (a unique situation among known carborane–transition metal complexes). Chemical shifts of several hundred parts per million have been observed in the ^{11}B spectra of paramagnetic iron(III) dicarbollyl complexes,[1b] but such effects have not been reported for diamagnetic carborane–metal π complexes.

The ^1H nmr spectrum of pure I is similar to that of 2-$CH_3C_3B_3H_6$[10] and exhibits single resonances at τ 4.60, 6.80, and 8.94 (relative to external tetramethylsilane) with relative areas of approximately 1:1:3, assigned to C(3)–H, C(4)–H, and CH_3, respectively. The expected quartets arising from three nonequivalent B–H groups are too weak to be clearly identified.

The proposed structure is strongly indicated by the spectroscopic data, volatility, and conditions of synthesis, but an X-ray structure determination is clearly desirable and is planned for the near future. It seems likely that additional transition metal complexes of the small *nido*-carboranes can be prepared, and further studies in this area are in progress.

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

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Heats of Formation of Potassium Perbromate and of the Perbromate Ion, and the Potential of the BrO_3^-–BrO_4^- Electrode

Sir:

The preparation of perbromates by various methods was recently reported.[1,2] There has been some speculation on whether thermodynamic or kinetic effects make it necessary to use extreme oxidizing conditions in preparing bromine in its highest oxidation state.[2] In order to shed further light on this problem, this communication reports the results of our preliminary studies of the heats of formation of potassium perbromate and the perbromate ion.

Potassium perbromate was prepared by a method described elsewhere[2] and repeatedly recrystallized from conductance water before being dried to constant weight at 105° and stored in a desiccator over anhydrous phosphorus pentoxide. The purity of the compound was confirmed by elemental analysis (*Anal.* Calcd: K, 21.37; Br, 43.66; O, 34.97. Found: K, 21.27; Br, 43.67; O, 35.06), determination of oxidizing power (7.98 equiv/mole when reduced to bromide), and comparison of infrared and laser–Raman spectra.[2]

The heat of decomposition of potassium perbromate was determined in an oxygen bomb calorimeter (Parr Instrument Co., Moline, Ill., Catalog No. 1300) equipped with an 18–31° calorimetric thermometer readable to ±0.002° and certified by the National Bureau of Standards. The energy equivalent of the calorimeter was determined in the usual way with 1.00 ml of water in the bomb at 25° and 30.0 atm of oxygen pressure by combustion of benzoic acid pellets, and was found to be −2414.9 ± 12.3 cal/deg. Parr 45C10 standard fuse wire was used to ignite each sample.

Three determinations of the heat of combustion of mineral oil (York Pharmacal Co., Brookfield, Mo.) gave an average value of −11,006 ± 2 cal/g. The bomb was flushed twice with oxygen at 20 atm before filling to a final pressure of 30.0 atm for each calorimetric run. Under these conditions there was no need for a nitric acid correction of the data.

Four measurements have been done to determine the heat of decomposition of crystalline potassium perbromate. Mineral oil was mixed with the $KBrO_4$ in the sample cup of the calorimeter. Experimental conditions were identical with those described for the combustion of the oil. In each case the ignition was violent enough to be audible throughout the room. After each run the bomb washings were collected and aliquots titrated with standard silver nitrate solution at a silver billet electrode to obtain a bromide balance.

It was found that conversions to bromide averaged 96.0% and ranged from 93.0 to 98.5%. It has been shown[2] that while both bromate and perbromate are reduced to bromine by 12 m HBr, only bromate is reduced by dilute HBr. Adjustment of the pH and the addition of excess KI allows the determination of bromate and perbromate by titration with standard thiosulfate solution. Aliquots of bomb washings treated in this way gave a total bromine balance that agreed within 1–2% with that known from the initial weight of $KBrO_4$.

If it is assumed that the present value for the heat of formation of $KBrO_4$(c) is correct, then the heat of decomposition of $KBrO_4$(c) to $KBrO_3$(c) would be −9.7 kcal. This reaction could contribute 2 or 3 cal to the heat of the 93.0% complete reaction. This would introduce a maximum error of 1.5% for this enthalpy value which is the least exact in the series. This error is small compared with the experimental uncertainty of all the measurements which was calculated to be 2.16 kcal/mole at the 95% confidence level,[3] or 9.01% for this individual result.

The bromine balance error was therefore ignored in subsequent data calculations, but was accounted for in computing over-all experimental uncertainty, which was taken as the product of the measurement uncertainty and the uncertainty in the bromine balance.

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