to noise ratio was poor and a second peak may not have been observed (see below).

At −55 °C, the Cp protons give rise to two peaks δ 4.95 and 4.94, while the remaining peaks in the ^{1}H NMR spectrum are invariant with temperature. A "windshield wiper" motion is common for σ,π-complexes similar to 3.[21-24] The anion in [Cp$_2$Mo$_2$(CO)$_4$(μ-CCPh)][PPN] (4) was also observed to be fluxional and showed four resonances due to CO carbon atoms at −60 °C that coalesce to two peaks at room temperature.[15]

The observation that the diasteriotopic methylene protons in 3 are not interchanged on the NMR time scale places additional restraints on the fluxional process; namely, a time-average mirror plane containing the μ-acetylide cannot be generated. Hence, the Cp groups must be related by a time average C_2 axis in the high temperature limit. The process shown in Scheme II generates such an axis wherein the two Cp group environments are interchanged, the carbonyl group environments are interchanged pairwise (a = c, b = d), but enantiomers are not interchanged so that $A \neq B$ (the AB quartet is preserved). The "cis–cis" isomerization common to CpM(CO)$_2$XY species[25] that would cause all CO group environments to become equivalent must have higher activation energy than the process shown in Scheme II. A cis–cis isomerization in a dimeric structure, e.g. 3, would also cause the interconversion of enantiomers and the collapse of the AB quartet.[26]

The solid-state structure of the anion in 3 is very similar to that in 4. Thus, the Mo1–Mo2 distance, 3.127 (1) Å, is appropriate for a Mo–Mo single bond, the Mo1–C5 distance, 2.03 (1) Å, approaches the value expected for a Mo=C double bond, while the Mo2–C5,C6 distances of 2.28 (1) and 2.32 (1) Å are normal for Mo bonded to a π-system. The C5–C6 distance (1.26 (1) Å) is only slightly longer than that in free acetylenes (ca. 1.18 Å).[27] These values compare well with those found for 4.[15]

An interesting feature of the structure of 3 is the cation–anion interaction and the packing arrangement. The sodium ion is encapsulated in the 15-crown-5 ring but forms two addition bonds to the oxygen atoms of one of the carbonyl groups (O4) and the methoxy group (O5) (Figure 2). The average of the Na–O (crown) distances is 2.465 ± 0.046 Å (range 2.54 (1)–2.41 (1)). The Na–O bond lengths to the carbonyl and methoxy oxygen atoms are 2.46 (1) and 2.56 (1) Å, respectively. Several structures of metal carbonyl anions with Na(crown)$^+$, K(crown)$^+$, or Na(crypt)$^+$ counterions have been determined.[28-30] Coordination of a carbonyl oxygen to the alkali metal ion is not unusual in these structures, but in most cases, bonds are formed from both sides of the crown ring rather than in a chelate-type structure as found here.[29,30] The Na–O bond distances determined here fall within the range of distances found in previous work.[28-30]

Interest in solid-state materials based on organometallic compounds has spurred new work on the extended structures of ionic organometallics. Braga and Grepioni found that large cluster anions form columnar stacks around which the cations form a sheath.[31] As Figure 3 shows, the dimolybdenum anions of 3 crystallized in a 2-dimensional sheet parallel with the 011 planes, and the Na(crown)$^+$ cations are layered on either side of the anion sheet. Apparently, the negative charge in the large anions is sufficiently delocalized that their packing more closely resembles that of neutral complexes, and the result is a structure featuring layers of alternating charge.

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Supplementary Material Available: Tables of crystallographic statistics, positional coordinates, thermal parameters, and bond lengths and angles (5 pages). Ordering information is given on any current masthead page.

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Carbon–Hydrogen Coupling Constants (J(^{13}C–^{1}H)) in Icosahedral Carboranes[1]

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Summary: Carbon–hydrogen coupling constants (J(^{13}C–^{1}H)) are measured for *o*-carborane, *m*-carborane, *p*-carborane, and various carbon- and boron-substituted *o*-carboranes. The values cluster about 190 Hz, implying approximately 38% s character in the C–H bond, or a hybridization of roughly sp$^{1.6}$.

Although the structures and bonding of the icosahedral carboranes have been reviewed many times,[2] little attention has been paid to a technique available for determining the hybridization at the hexacoordinate carbons, mea-

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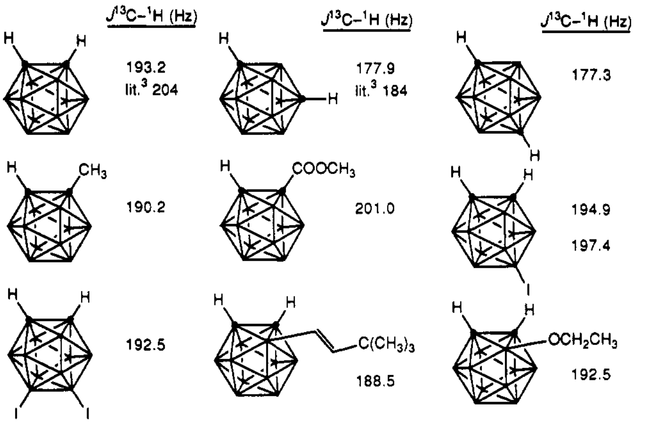
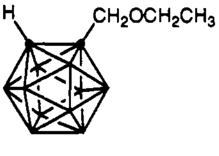
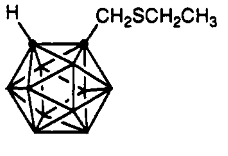
Chart I



surement of the ^{13}C–^{1}H coupling constant. In 1969, values of 204 and 184 Hz were reported for the ^{13}C–^{1}H coupling constants of *o*- and *m*-carborane by accumulating successive runs at natural abundance.[3] Nearly a decade later, these values were collected along with more precise coupling constants for two new compounds 1 and 2.[4]

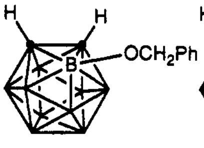


1, 196.8 Hz[4]

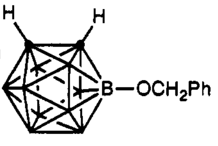


2, 193.2 Hz[4]

Two molecules in which B_3 or B_4 was substituted (3 and 4) appeared from the Zakharkin group in 1976.[5] Only one



3, 142 Hz[5] (!!)



4, 192 Hz[5] (?)

value was reported for 4, which seems strange as two must exist, and 3 apparently had a $J(^{13}C–^1H)$ value some 50 Hz lower than the other compounds. Application of the relationship % s character = $0.2J(^{13}C–H)$ leads to a hybridization for 3 of $sp^{2.5}$, not $sp^{1.6}$ as in the other three cases.

As we had a number of differently substituted icosahedral compounds in hand, it seemed worthwhile to determine better values for the parent compounds, to provide some numbers for new structural types, and to attempt to resolve the question of the "odd" value of 142 Hz for 3—is there something special about substitution by oxygen at B_3 that dramatically changes the bonding?

The two parent compounds *o*- and *m*-carborane have similar coupling constants, and the numbers reported earlier were within about 5% of the correct values (Chart I). The coupling constant of *p*-carborane is reported here for the first time and is very similar to that for the meta compound. Examination of compounds substituted at carbon or boron shows that neither adjacent nor remote "para" substitution has a substantial effect on the value of *J*. In particular, there is no noticable "antipodal effect".[2]

We find that substitution by oxygen at B_3 does not lead to a reduced value for *J*, as 3-ethoxy-*o*-carborane has a coupling constant of 192.5 Hz, far from the 142 Hz reported for 3[5] and squarely in the "normal" range. There is no remarkable "oxygen" effect.[6]

Experimental Section

Compounds. The parent compounds are commercially available, and the substituted compounds 1-carbomethoxy-*o*-carborane,[7] 3-methoxy-*o*-carborane,[8] 9-iodo-*o*-carborane,[9] and 9,12-diiodo-*o*-carborane[9] are known. The remaining compound emerges from our work on *o*-carboranylcarbenes.[10]

(1*E*)-3,3-Dimethyl-1-buten-1-yldibromoborane–Dimethyl Sulfide. Brown's procedure[11] was followed exactly. To a solution of 4.2 g (51 mmol) of 3,3-dimethylbutyne in 15 mL of CH_2Cl_2 maintained at 10–15 °C was added dropwise a solution containing 6.4 mL (50 mmol) of $HBBr_2{\cdot}SMe_2$ in 10 mL of CH_2Cl_2. After completion of the addition of the $HBBr_2{\cdot}SMe_2$ solution, the cold bath was removed; the reaction mixture was warmed to room temperature and then stirred for 1 h. The solvent was removed under vacuum to give the crude product, which was used for the next step without further purification. ^{1}H NMR ($CDCl_3$): δ 6.21 (d, 1 H), 5.53 (d, 1 H), 2.35 (s, 6 H), 1.05 (s, 9 H).

3-(3′,3′-Dimethylbutenyl)-*o*-carborane. To the flask containing ether and $(B_9C_2H_{11})^{2-}$, made from 8.7 g (45 mmol) of $[Me_3NH][B_9C_2H_{12}]$,[12] was added dropwise the borane made as above in 80 mL of dimethyl sulfide. The reaction mixture was kept at 0 °C during the addition. After the addition was finished, the reaction mixture was stirred at 40 °C for an additional 12 h. Then it was cooled to room temperature and quenched with 10 mL of water. The organic layer was then washed with 5% aqueous NaOH (3 × 10 mL) followed by water (2 × 10 mL) and dried over $MgSO_4$. The solution was filtered, and the solvent was removed under vacuum. The crude product was chromatographed (silica gel/hexanes) to produce 8.3 g of a waxy solid (81% yield), mp 35–40 °C. ^{1}H NMR ($CDCl_3$): δ 6.23 (d, 1 H), 5.46 (d, 1 H), 3.48 (br s, 2 H), 1.01 (s, 9 H), 3.10–1.10 (m, 9 cage H). ^{13}C NMR ($CDCl_3$): δ 159.9 (d), 57.2 (d, 2 C), 35.5 (s), 29.6 (q, 3 C). IR ($CHCl_3$, cm^{-1}): 3088 (w), 2961 (m), 2594 (s), 1631 (w). MS: *m/e* 228 (46), 227 (95), 226 (M$^+$, 97), 210, (100), 209 (99), 194 (56), 180 (32). HRMS: calcd for $^{11}B_8{}^{10}B_2C_8H_{22}$ 226.2725, found 226.2743. Anal. Calcd for $B_{10}C_8H_{22}$: C, 42.48; H, 9.73. Found: C, 42.57; H, 9.61.

NMR Spectroscopy. Spectra were obtained on a General Electric QE-300 spectrometer operated at 75.48 MHz with signals referenced to TMS in $CDCl_3$ solvent. Values did not differ significantly when repeated on different samples or when measured on a JEOL GSX 500 spectrometer operated at 125.77 MHz.

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