

The pure compound, recrystallized from hexane, had mp 121–122°: nmr δ (CCl₄) 3.86 (4 H, s), 1.28 (3 H, s), 1.17 (9 H, s) 0.93 (s, 2 H).

Further transformation of **14** by catalytic hydrogenation (Pd-on-charcoal, triethylamine), followed by refluxing with 2 *N* hydrochloric acid in methanol to (\pm)-D-homo-19-nor-testosterone **15**, mp 140.5–142°, undepressed on admixture with an authentic sample.²¹

It is apparent that α -hydroxymethyl ketones can be produced regiospecifically in high yields. They should prove valuable intermediates in synthesis.²²

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Four-Carbon Carboranes. Synthesis of Tetra-C-methyltetracarbadodecaborane(12) and Its Metallocarborane Derivatives

Sir:

Addition of two electrons to the icosahedral carborane C₂B₁₀H₁₂, a filled-shell electronic system, is expected to open or otherwise distort the polyhedral cage. Several isomeric C₂B₁₀H₁₂²⁻ ions and protonated C₂B₁₀H₁₃⁻ analogs are known,^{1–7} but the only X-ray determined structure⁸ is that of a C, C'-diphenyl derivative, (C₆H₅)₂C₂B₁₀H₁₁⁻, which is an icosahedral fragment containing a bridging C₆H₅CH group on the edge of the open face. The isoelectronic neutral species C₄B₈H₁₂ is unknown, and in fact the only previously reported carborane having four carbon atoms in the same cage is the C₄B₈H₈ system.^{9–11} We report here a new carborane, tetra-C-methyltetracarbadodecaborane (12), (CH₃)₄C₄B₈H₈ (I), a derivative of C₄B₈H₁₂, which exhibits structural dynamics of a type novel to carborane chemistry and also functions as a face-bonding ligand in metallocarborane formation. Compound I is a colorless, air-stable, sublimable crystalline solid, mp 138°, which has been obtained in 35–40% yield as an adjunct of the synthesis of the red bis(dicarbonylhexaboranyl)cobalt and -iron metallocarboranes [2,3-(CH₃)₂C₂B₄H₄]₂Co¹¹H and [2,3-(CH₃)₂C₂B₄H₄]₂Fe¹¹H₂ from Na⁺[2,3-(CH₃)₂C₂B₄H₅]⁻ and CoCl₂ or FeCl₂ in tetrahydrofuran (THF). The metal complexes *per se* are not directly germane to this report and will be de-

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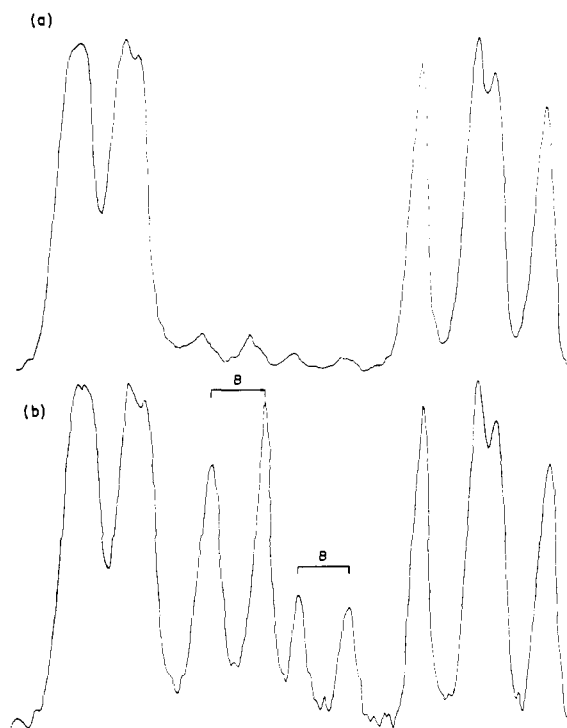


Figure 1. The 32.1-MHz ¹¹B nmr spectra of I in CCl₄ at ambient temperature: (a) 3 min after preparation of solution (large peaks are BH doublets of isomer A; small peaks in center are due to traces of isomer B (δ and J values given in text)), (b) same solution 12 min later (bracketed doublets are due to isomer B; the spectrum did not undergo further significant change other than slight increase in the area of the B resonances).

scribed elsewhere. We have determined that I forms *via* decomposition of the metal complexes and does not appear to be produced directly from the (CH₃)₂C₂B₄H₅⁻ ion.

The mass spectrum of I exhibits intense parent-group peaks with little cage fragmentation (calcd mass for ¹²C₈¹¹B₃¹H₂₀⁺, 204.2310; found, 204.2310); the ir spectrum contains strong CH₃ and BH stretching bands but has no appreciable B–H–B absorptions. The compound is thermally stable, but the isomer which is initially evident in solution and presumably exists in the solid state (A) undergoes reversible rearrangement in solution to a second isomer (B); an essentially solvent-independent equilibrium [B]/[A] ratio of ~ 0.5 (measured from ¹¹B and ¹H nmr peak areas) is reached within a few minutes at ambient temperature, and thereafter no further noticeable change occurs. The isomerization takes place in CCl₄, CH₂Cl₂, C₂H₅OH, THF, CH₃CN, CDCl₃, and C₆H₆ and is completely reversible, since on evaporation of the solvent followed by redissolving, the original nmr spectra (containing only A initially) are regenerated. The ¹¹B nmr spectrum of A in CCl₄ (Figure 1a) contains four B–H doublets of equal area of $\delta \sim -9.2$, ~ -8.4 , $+22.4$, and 29.5 ppm relative to BF₃·O(C₂H₅)₂ ($J = 155 \pm 20$ Hz); the two low-field doublets are heavily overlapped but distinguishable. On proton decoupling, all doublets collapse to singlet resonances. The ¹¹B spectrum of B (see Figure 1b) contains doublets at $\delta +2.4$ ($J = 150$ Hz) and $+11.0$ (148) with a 6:2 area ratio, which also collapse to singlets on decoupling; since the area 6 doublet is asymmetric (Figure 1b) and since in any case

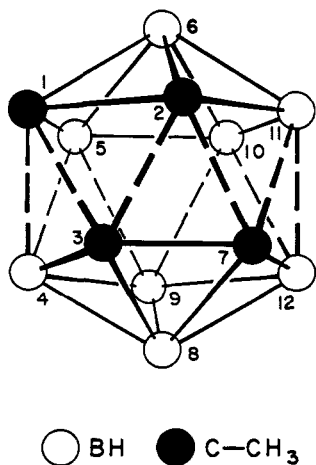


Figure 2. Possible structure for isomer B, formed by face-to-face fusion of two $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ units. Distortion from regular icosahedral symmetry is suggested by broken lines.

no reasonable structure would have six equivalent borons, this resonance is assumed to arise from superposition of signals of areas 4 and 2. The 100-MHz ^1H nmr spectrum of A in CCl_4 contains methyl resonances of equal area at $\delta -1.70$ and -1.62 ppm relative to $(\text{CH}_3)_4\text{Si}$, while the spectrum of B exhibits methyl peaks of equal area at $\delta -2.07$ and -2.01 .

The ^{11}B and ^1H nmr spectra of isomers A and B do not exhibit marked temperature dependence from -80 to $+20^\circ$, the primary effect on cooling being moderate peak broadening at low temperature. On heating the solution, the two CH_3 peaks in the proton nmr spectrum of B coalesce, collapsing at $+40^\circ$ to a singlet indicating equivalence of all four methyl groups; the proton spectrum of A, however, is basically unchanged at $+40^\circ$, as are the ^{11}B spectra of both A and B.

Unequivocal structure assignments for isomers A and B cannot be given at this time but some reasonable inferences can be made. A $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ cage is not expected to be a regular icosahedron (see above); however, the nmr data do not support a polyhedral-fragment structure like that of the isoelectronic $(\text{C}_6\text{H}_5)_2\text{C}_2\text{B}_{10}\text{H}_{11}^-$ ion previously described. The large range of ^{11}B nmr chemical shifts for isomer A suggests a relatively open structure, possibly consisting of two pyramidal $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ units linked at the edges^{12,13} (viable localized-bond valence structures based on Lipscomb's approach^{14,15} can be written for such a species). The simplicity and small range of the ^{11}B spectrum of B are consistent with a more compact icosahedral-like cage (Figure 2). Distortion from regular icosahedral geometry could occur *via* cooperative stretching of several bonds¹⁶ such that a high degree of symmetry is preserved, as required by the nmr spectra of B. The proposed structure of B is compatible with the observed nmr equivalence of the methyl groups at $+40^\circ$, since a fluxional rearrangement involving rela-

tive twisting of the two $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$ pyramids is readily visualized.

Compound I reacts readily with $\text{Mo}(\text{CO})_6$ in refluxing heptane, yielding the first known four-carbon metallocarborane system, $(\text{CO})_3\text{Mo}(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ (II). This complex, a dark green, air-stable crystalline solid, has been characterized from its mass spectrum (calcd for $^{12}\text{C}_{11}^{16}\text{O}_3^{100}\text{Mo}^{11}\text{B}_8^1\text{H}_{21}^+$ (protonated parent ion), 389.1321; found, 389.1311), the ^{11}B nmr spectrum, which contains resonances ($J = 162 \pm 6$ Hz) at $\delta -50.9$, -43.7 , -41.0 (asymmetric), and -29.5 , with relative areas 3:1:2:2, and the ^1H nmr spectrum, which exhibits methyl peaks of equal area at $\delta -1.45$, -1.88 , -1.99 , and -2.17 . The molecule satisfies the electronic requirements¹⁶⁻²⁰ ($2n + 2$ rule) for a closed 13-vertex polyhedron and is electronically analogous to the known $[(\text{CO})_3\text{MoC}_2\text{B}_{10}\text{H}_{12}]^{2-}$ dicarbon system.²¹ Since a number of possible structures have the total asymmetry indicated by the nmr spectra, an unambiguous assignment must await X-ray studies.

Compound II and its tungsten analog, similarly prepared, are the first metallocarboranes containing an electrically neutral carborane ligand. The ability of I, a formal six-electron donor, to function as an acceptor of metals may open the way of the preparation of heretofore inaccessible metallocarboranes of electron-poor transition metals such as vanadium and titanium or of metals in unusually low oxidation states. This and other implications of the present work are under investigation.

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Transition Metal Catalyzed Single Electron Transfer in Grignard Reagent Addition to Ketones

Sir:

Since 1968 evidence has been accumulating to indicate that Grignard reagent addition to ketones can proceed through a single electron transfer (SET) mechanism.¹ It is felt that the nature of the solvent, ketone, R group of the Grignard reagent, purity of magnesium used to prepare the Grignard reagent, and mode of preparation of the Grignard reagent are all influential

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