

pentane was treated with 1.12 g (7.0 mmol) of bromine dissolved in pentane. The reaction mixture changed from yellow to orange to red; the infrared spectrum of the red solution showed absorptions for CH_3NCO (2320 (m), 2295 (vs), and 2260 (s) cm^{-1}) and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$ (2055 (vs) and 2015 (s) cm^{-1}). The $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3]\text{Br}$ was insoluble and was, therefore, not seen in the solution spectrum. Under reduced pressure, pentane and CH_3NCO were distilled from the mixture. The presence of the CH_3NCO in the distillate was further confirmed by addition of excess CH_3NH_2 to the solution to yield a white flaky precipitate of $(\text{CH}_3\text{NH})_2\text{CO}$. This was purified by sublimation under vacuum to give 0.13 g (1.48 mmol) of $(\text{CH}_3\text{NH})_2\text{CO}$, mp 99–100°. Its proton nmr spectrum in CDCl_3 showed a doublet at τ 7.25 ($J_{\text{HCNH}} = 5$ Hz) and a broad N–H absorption at τ 4.45 in a 3:1 intensity ratio.

The residue remaining after the pentane– CH_3NCO distillation was extracted with several aliquots of warm pentane; these were cooled at -20° to give 0.59 g (2.3 mmol) of red crystalline $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$, identified by its infrared spectrum. The pentane-insoluble residue was treated with excess NH_4PF_6 in 4 ml of water. The solid was filtered off and dried under vacuum. Several washings of the solid with ether removed additional $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$ (0.47 mmol) which had apparently formed from the reaction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3^+$ with Br^- in water. (In CH_2Cl_2 solvent, we have observed that this reaction does occur.) The remaining yellow powder (0.42 g, 1.20 mmol) was identified as $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3]\text{PF}_6$ by its infrared spectrum (2120 (s) and 2070 (vs, br) cm^{-1} in KBr).

Reaction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CONHC}_6\text{H}_{11}$ with I_2 .—This reaction was very similar to that given above and no attempt was made to determine product yields. To a suspension of 0.62 g (2.04 mmol) of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CONHC}_6\text{H}_{11}$ in 45 ml of hexane was added 0.52 g (2.04 mmol) of I_2 . On stirring at room temperature, the solution turned from yellow to black. The infrared spectrum of the solution showed absorptions for $\text{C}_6\text{H}_{11}\text{NCO}$ (2255 cm^{-1}) and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ (2040 (s) and 1998 (s) cm^{-1}).

The $\text{C}_6\text{H}_{11}\text{NCO}$ and solvent were distilled off under vacuum. On treatment with CH_3NH_2 , the white flaky $\text{C}_6\text{H}_{11}\text{NHC}(\text{O})\text{NHCH}_3$ (3330 (s), 2925 (m), 2850 (w), 1620 (vs), and 1580 (s) cm^{-1} in KBr) precipitated.

The black residue from the distillation was extracted with several 60-ml aliquots of warm pentane until the $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ was completely removed. The orange residue remaining consisted of a mixture of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3]\text{I}$ (2115 (s) and 2070 (vs) cm^{-1} in CH_2Cl_2) and $[\text{C}_6\text{H}_{11}\text{NH}_3]\text{I}$. The infrared spectrum of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3]\text{I}$ in CH_2Cl_2 changed with time to give $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$.

Reaction of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CONHC}_6\text{H}_{11}$ with HgCl_2 .—To an ether solution of 0.68 g (2.24 mmol) of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CONHC}_6\text{H}_{11}$ at -78° was added 0.62 g (2.30 mmol) of HgCl_2 . The mixture was warmed to near reflux with stirring, during which time a fine white material precipitated. After 1 hr the ether was removed at reduced pressure, leaving a pale yellow solid. The ether distillate contained $\text{C}_6\text{H}_{11}\text{NCO}$, which was identified by treating it with excess CH_3NH_2 to give $\text{C}_6\text{H}_{11}\text{NHC}(\text{O})\text{NHCH}_3$; its infrared spectrum in KBr pellet was identical with that reported in the previous section.

Approximately 60 mg of unreacted $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CONHC}_6\text{H}_{11}$ was extracted with hexane from the pale yellow solid. The hexane-insoluble residue in CH_2Cl_2 solution showed terminal C–O absorptions due to only $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3]\text{Cl}$ and $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$. The latter compound was extracted from the solid with 120 ml of warm ether. On reducing the volume to 60 ml and cooling at -20° overnight, 0.13 g (0.31 mmol) of yellow crystalline $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ separated from solution; its infrared spectrum in CH_2Cl_2 solution (2020 (s) and 1974 (s) cm^{-1}) was identical with that previously reported for this compound.¹⁰ Additional $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ was extracted with several 60-ml aliquots of warm ether until the ether was colorless. The residue (0.45 g) showed infrared absorptions (2120 (s) and 2060 (vs) cm^{-1}) characteristic of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3]\text{Cl}$; it also contained $[\text{C}_6\text{H}_{11}\text{NH}_3]\text{Cl}$.

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Chemical Studies of *closo*-1,5-Dicarbapentaborane(5)

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Since the discovery of the carborane $1,5\text{-C}_2\text{B}_3\text{H}_5$,¹ there has been virtually no further report of its chemical behavior. A generous gift of mixed light carboranes from Drs. R. E. Williams and J. Ditter (Chemical Systems, Inc., Santa Ana, Calif. 92705) has made it possible for us to isolate enough of this carborane for extensive laboratory studies.

The trigonal-bipyramidal structure of $\text{C}_2\text{B}_3\text{H}_5$ is such that the electron pair in the A_1 molecular orbital would be less delocalized, and the E-type orbitals would be constructed of more seriously bent atomic orbitals, than in larger carboranes. Thus only a seriously "strained" and thermodynamically unstable electronic situation seems possible. Indeed, the metastability of liquid $\text{C}_2\text{B}_3\text{H}_5$ is demonstrated by its slow room-temperature conversion to yellow-brown solids—possibly by the catalytic effect of impurities. Also, $\text{C}_2\text{B}_3\text{H}_5$, $\text{C}_2\text{B}_4\text{H}_6$, and $\text{C}_2\text{B}_5\text{H}_7$, passed as vapors at minimal pressure through a 13.56-Mc electrodeless discharge (in a quartz tube) or as solids bombarded by atomic hydrogen, are partially destroyed; forming only nonvolatile products. These range from pure white solids, which are partially soluble in or reactive to acetone or methanol, to brown glassy films inert to strong oxidizers. Thus even $\text{C}_2\text{B}_4\text{H}_6$ or $\text{C}_2\text{B}_5\text{H}_7$ must be regarded as metastable, although more enduring than $\text{C}_2\text{B}_3\text{H}_5$.

The kinetic stability of such carboranes may be ascribed to their cage structures and high electronic symmetry. The present results indicate that the $1,5\text{-C}_2\text{B}_3\text{H}_5$ skeleton becomes unstable when its electronic symmetry is seriously disturbed.

For example, a solid 1:1 trimethylamine adduct of $\text{C}_2\text{B}_3\text{H}_5$ exists at low temperatures, but when it begins to melt, there is rapid conversion to intractable polymeric material, with no formation of hydrogen or other volatiles. Similar instability appears when halogenation or NO_2 oxidation of $\text{C}_2\text{B}_3\text{H}_5$ is tried.

On the other hand, substitution derivatives lacking polarity seem stable. The suggested 2,3-dimethyl-1,5-dicarbapentaborane (5)² would be in this class, and the same argument applies to the methyl derivatives of $1,2\text{-C}_2\text{B}_3\text{H}_5$.^{2,3} The principle is more fully illustrated by our new B–B connected dicarbaborane $\text{C}_4\text{B}_6\text{H}_8$ and a B-1-propenyl derivative made from $1,5\text{-C}_2\text{B}_3\text{H}_5$ and propyne.

The Trimethylamine Adduct.—An electron-acceptor action (presumably through boron) is indicated by the clean formation of the adduct $\text{C}_2\text{B}_3\text{H}_5 \cdot \text{N}(\text{CH}_3)_3$ at -78° . In a stopcocked tube on the high-vacuum

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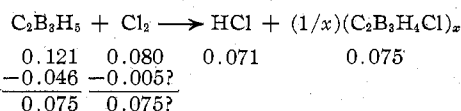
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manifold, this white solid compound showed the following dissociation pressures, in mm: 2.5 at -53° , 11.0 at -40° , 53.5 at -25.0° , and 86.0 at -20.0° , all conforming well to the equation $\log P = 12.188 - 2594/T$. These results could not have been affected by a slight irreversible conversion to a nonvolatile white solid, for both components were consumed equally by this very slow process, so that the vapor phase was always an equimolar mixture of $(\text{CH}_3)_3\text{N}$ and $\text{C}_2\text{B}_3\text{H}_5$. However, when a sample of the adduct began to melt in a very small sealed tube, conversion to the nonvolatile solid was very sudden and complete except for the equimolar amine-carborane mixture in the vapor phase; there was no volatile reaction product.

Assuming that $\text{N}(\text{CH}_3)_3$ was attached to an "electron-deficient" boron atom in $\text{C}_2\text{B}_3\text{H}_5$, the effect would be to concentrate the skeletal electrons toward the other cage atoms (especially boron), causing them to attack adjacent molecules in an electron-donor manner. No such reaction could occur in the vapor phase, where the adduct is not formed, and it would be slow in the solid phase because of rigid crystal geometry. Bases too weak to form an adduct would not cause the conversion; for example, methylphosphine failed to react with $\text{C}_2\text{B}_3\text{H}_5$ either at -78° or under 7 atm pressure at 50° .

Halogenation.—The action of 0.080 mmol of Cl_2 on 0.121 mmol of $\text{C}_2\text{B}_3\text{H}_5$ was tried by condensing both on a -196° cold finger, within a bulb attached to the high-vacuum system. The condensate was warmed first to -78° and then during 4 hr to 25° . An unreactive white solid formed on the surface of the cold finger. A trace of unused Cl_2 was removed by its action on Hg in a small closed tube. The infrared spectrum of the remaining gas showed only HCl and $\text{C}_2\text{B}_3\text{H}_5$; exposure to water now left pure $\text{C}_2\text{B}_3\text{H}_5$. The millimolar stoichiometry was as follows.

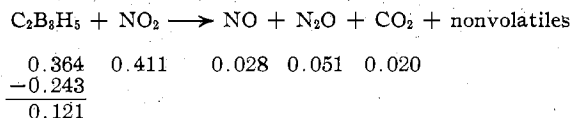


It appears that the expected product $\text{C}_2\text{B}_3\text{H}_4\text{Cl}$ converted to polymer as fast as it was formed; this result again would correlate with loss of electronic symmetry. The survival of a trace of Cl_2 despite the excess of $\text{C}_2\text{B}_3\text{H}_5$ could be ascribed to lack of reaction in the vapor phase; indeed, the polymer was found only on the cold finger.

An equimolar mixture of I_2 and $\text{C}_2\text{B}_3\text{H}_5$ required the presence of Al_2I_6 for partial reaction during 3 days at 85° ; the products were H_2 and a nonvolatile, viscous green liquid. Also, the dicarborene $\text{C}_4\text{B}_6\text{H}_8$ reacted during 3 hr with dissolved I_2 (purple) to give a similar green liquid. This liquid could have been a lower polymer than the chlorination product.

Nitrogen Dioxide Oxidation.—A mixture of NO_2 and $\text{C}_2\text{B}_3\text{H}_5$ in a reaction tube at 0.25 atm pressure (25°) was caused to undergo approximately a 50% reaction by repeated low-temperature condensation and re-warming. A trace of volatile product was suggested (with little certainty) by infrared peaks not easily assignable, but the quantity was too small for fuller study. The main product was an intractable, nonvolatile white solid. For complete consumption of the NO_2 , the remaining mixture of volatiles was left at

a pressure of 3 atm for 12 hr at 25° . The final reaction balance, in millimoles, was as follows.



From this, the empirical formula of the nonvolatile solid is calculated as $\text{C}_2\text{B}_3\text{H}_5\text{N}_{2.4}\text{O}_6$. Titration of the aqueous extract showed 0.06 mmol each of boric acid and a strong acid.

Spontaneous Polymerization of $\text{C}_2\text{B}_3\text{H}_5$.—Samples of liquid $\text{C}_2\text{B}_3\text{H}_5$ containing traces of C_2H_2 , C_2H_4 , C_3H_6 , and $\text{C}_2\text{B}_4\text{H}_6$ were stored for about 10 weeks in sealed Pyrex tubes at 25° . Some two-thirds of each sample then had converted to a buff-colored nonvolatile solid. The remaining volatiles now included $\text{C}_2\text{B}_3\text{H}_5$ and $\text{C}_2\text{B}_4\text{H}_6$ in a 3:1 ratio. Also found was a small yield of a colorless liquid having volatility 6.0 mm at 0° . Its vapor-phase molecular weight (121.2; calcd, 121.0) was confirmed by the mass spectrographic cutoff at m/e 122, corresponding to $\text{C}_4^{11}\text{B}_6\text{H}_8$. The 32.1-Mc ^{11}B nmr spectrum showed three equally intense peaks, interpreted by the aid of the proton spectrum as a singlet at +9.5 ppm and a doublet at 14.3 ppm ($J = 187$ cps), measured upfield from $(\text{CH}_3\text{O})_3\text{B}$. The 100-Mc proton spectrum showed the 1:1:1:1 quartet expected for the H-B units, at τ 7.1 ($J = 187$ cps) and a sharp singlet at τ 5.3. Both spectra confirm the structure as two trigonal-bipyramidal $\text{C}_2\text{B}_3\text{H}_4$ groups connected together by a B-B bond.

Pyrolytic Synthesis of the Double Carborane.—A sample of $\text{C}_2\text{B}_3\text{H}_5$ at 3 atm pressure in a sealed Pyrex tube, heated for 9 days at 165° , gave only a 1% yield of $\text{C}_4\text{B}_6\text{H}_8$. For better results, $\text{C}_2\text{B}_3\text{H}_5$ vapor was exposed to wall temperatures near 350° , with an internal cold finger to moderate the thermal effect and to sequester the pyrolysis product. A 9-hr run gave $\text{C}_4\text{B}_6\text{H}_8$ in 18% yield, based upon the consumed $\text{C}_2\text{B}_3\text{H}_5$. The yield of H_2 was 0.17 per $\text{C}_2\text{B}_3\text{H}_5$ destroyed, meaning that 0.82 of the destroyed $\text{C}_2\text{B}_3\text{H}_5$ yielded only 0.08H_2 . Hence it seems that most of the $\text{C}_2\text{B}_3\text{H}_5$ went to resin without loss of H_2 , while small amounts could have formed B-B linked chains of $\text{C}_2\text{B}_3\text{H}_5$ units. In fact, another volatile product (1-mg yield; vapor pressure ca. 1 mm at 25°) possibly was a three-cage chain: $\text{C}_2\text{B}_3\text{H}_4(\text{C}_2\text{B}_3\text{H}_3)\text{C}_2\text{B}_3\text{H}_4$.

The Propenyl Derivative.—A mixture of 1.0 mmol of C_3H_4 with 0.49 mmol of $\text{C}_2\text{B}_3\text{H}_5$, after 24 hr in a 40-ml sealed Pyrex tube at 165° , yielded 0.1 mmol of the new compound $\text{C}_2\text{B}_3\text{H}_4\text{C}_3\text{H}_5$, formally named *B-(cis-1-propenyl)-closo-1,5-dicarbapentaborane(5)*. This colorless liquid (volatility 15 mm at 22°) was isolated by high-vacuum fractional condensation at -65° . Its mass spectrum showed the expected group of parent ions corresponding to the statistical distribution of boron isotopes, with the cutoff at m/e 102, as calculated for $\text{C}_2^{11}\text{B}_3\text{H}_4\text{C}_3\text{H}_5$. Its 32.1-Mc ^{11}B nmr spectrum showed the expected doublet at +9.9 ppm ($J = 186$ cps) with a superposed singlet at +12.8 ppm (both measured upfield from methyl borate); the expected 2:1 intensity ratio could be inferred. The proton nmr spectrum showed the CH_3 group as a doublet of doublets at τ 2.9; $J_1 = 6.5$ cps; $J_2 = 1.3$ cps. J_1 is ascribed to splitting by the 2-CH proton, while J_2 must be

understood as due to a 1-CH proton trans to CH₃ in the propenyl group. Hence the CH₃ and C₂B₃H₄ groups are cis to each other. The CH protons in the propenyl group gave spectra difficult to resolve, but the carborane CH protons showed as a sharp peak at τ 4.6, scarcely shifted from C₂B₃H₅ itself.

The observed alkyne addition to C₂B₃H₅ is an unusual type of hydroboration: the first such reaction in which a C=C bond is retained in the product. The process seems to be more effective for propyne than for acetylene, for a mixture of 1.15 mmol of C₂B₃H₅ with 4 mmol of C₂H₂, after 16 hr in a 40-ml tube at 165°, showed only 5% destruction of the carborane (without H₂ formation), yielding 0.02 mmol of a product which was trapped out at -95° under high vacuum. Its infrared spectrum showed C-H and B-H bonds, and the mass spectrum had a parent ion cutoff at m/e 88, corresponding to C₂B₃H₄C₂H₃. Another such cutoff peak, at 114, could be ascribed to C₂B₃H₃(C₂H₃)₂; but we have not succeeded in obtaining either product in yields high enough for characterization. On a larger scale, any such products obviously would be interesting to polymer chemistry.

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A Nuclear Magnetic Resonance Study of the Ligand-Exchange Kinetics of Hexakis(trimethyl phosphite)aluminum(III) Ion in Mixed Solvents

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Recently data have been reported for the ligand-exchange kinetics of octahedral transition metal complexes in mixed solvents. Results have been reported for Ni(DMSO)₆²⁺ (DMSO = dimethyl sulfoxide) and Co(DMSO)₆²⁺ in DMSO-nitromethane and DMSO-methylene chloride,² Ni(DMF)₆²⁺ (DMF = *N,N*-dimethylformamide) in DMF-nitromethane,³ and Ni(3-picO)₆²⁺ in nitromethane-acetone.⁴ In all three studies, the kinetic exchange parameters were virtually independent of the composition of the solvent. Results of this type are of considerable aid in elucidating the mechanism of the reaction. Nitromethane appears to be the inert solvent of choice because it usually does not coordinate to the metal complex, a moderate number of metal complexes are soluble in this solvent, and it has a reasonable liquid range. To ascertain if

this conclusion is applicable to other metal ions we wish to report data for Al(TMP)₆³⁺ (TMP = trimethyl phosphite) in TMP-nitromethane mixed solvents. Previous studies for Al(H₂O)₆³⁺,⁵ Al(DMSO)₆³⁺,⁶ and Al(DMF)₆³⁺⁷ in pure solutions of the ligand have been reported.

Al(TMP)₆(ClO₄)₃ was prepared as previously described.⁸ *Anal.* Calcd for Al(TMP)₆(ClO₄)₃: C, 18.5; H, 4.7; Al, 2.3; Cl, 9.1; P, 15.9. Found: C, 18.5; H, 4.7; Al, 2.3; Cl, 9.1; P, 15.9. Karl Fisher analysis indicated less than 0.2% water. Nitromethane-*d*₃ was identical with that previously described.² Neither Al(DMF)₆(ClO₄)₃ nor Al(DMSO)₆(ClO₄)₃ is particularly soluble in nitromethane.

The proton nmr spectra were obtained on a Varian A-60 spectrometer equipped with a variable-temperature probe. The temperature was calculated by use of ethylene glycol either immediately before or after a spectrum was taken.

Infrared spectra were obtained on a Perkin-Elmer Model 521 spectrometer as Nujol mulls on CsI plates. The infrared spectra of TMP and Al(TMP)₆(ClO₄)₃ had P=O stretching frequencies at 1277 and 1248 cm⁻¹, respectively.⁸ The low-energy shift is indicative of coordination through the phosphoryl group.⁹

The methyl resonance of TMP is a doublet due to coupling with the phosphorus nucleus. The methyl doublet of coordinated TMP occurs 0.33 ppm downfield from the free ligand. The coupling constants for coordinated and free ligand are 11.2 and 11.4 ± 0.1 Hz.

Coordination numbers (*N*) for Al(TMP)₆³⁺ were obtained in CD₃NO₂-CHCl₃ (ethanol free), *N* = 5.9 ± 0.2, and in the above solvent mixture with excess TMP, *N* = 5.8 ± 0.2.

The exchange rates were measured in 0.10 and/or 0.13 *M* solutions of Al(TMP)₆³⁺ in pure TMP and in nitromethane-TMP mixed solvents of various compositions. The excess line widths at half-height ($\Delta\nu_B - \Delta\nu_B^0$) of the coordinated ligand as a function of temperature in pure TMP are summarized in Table I.

TABLE I
TEMPERATURE DEPENDENCE OF THE EXCESS LINE WIDTH
($\Delta\nu_B - \Delta\nu_B^0$) OF Al(TMP)₆³⁺ IN TMP

| [Al ³⁺], <i>M</i> | Temp, °K (±0.2°K) | $\Delta\nu_B - \Delta\nu_B^0$ (±0.2) | Temp, °K (±0.2°K) | $\Delta\nu_B - \Delta\nu_B^0$ (±0.2) |
|----------------------------------|----------------------|---|----------------------|---|
| 0.13 | 329.4 | 4.1 | 324.5 | 2.5 |
| | 326.7 | 3.0 | 323.3 | 2.2 |
| 0.10 | 330.9 | 4.7 | 324.0 | 2.4 |
| | 329.4 | 4.3 | 320.2 | 1.6 |
| | 327.0 | 3.5 | | |

The line width of the coordinated ligand was analyzed by using the equation

$$\pi\Delta\nu_B = 1/\tau_B + 1/T_{2B}^0 \quad (1)$$

where τ_B is the mean lifetime of a TMP molecule in the coordination sphere, $\Delta\nu_B$ is the observed line width of the bound ligand, and $1/T_{2B}^0$ ($1/T_{2B}^0 = \pi\Delta\nu_B^0$) is the relaxation rate of a bound TMP molecule in the absence of chemical exchange. Transition-state theory

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