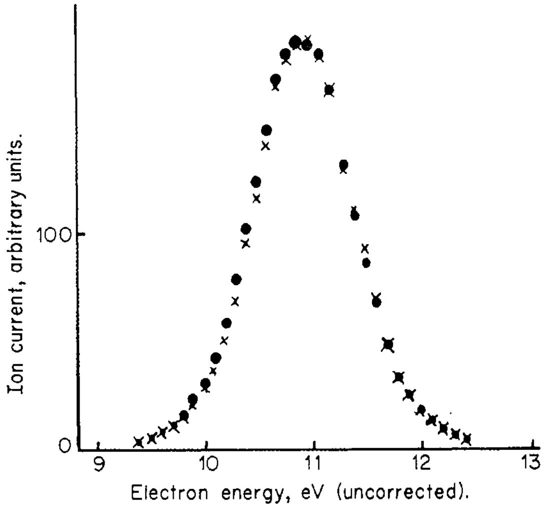

Figure 1.—Normalized ionization efficiency curves for SiF_3^- (crosses) and SiF_5^- (full circles).

to be 77 kcal mol^{-1}; this result, in conjunction with the value of −251 kcal mol^{-1} reported[8] for $\Delta H_f°(SiF_3)$, leads to $\Delta H_f°(SiF_3^-) = -328$ kcal mol^{-1}.

Since $\Delta H_5 \leq 0$ for the reaction to be observed then, since $\Delta H_f°(SiF_4) = -373$[9] and $\Delta H_f°(SiF_2) = -118$ kcal mol,$^{-1}$ [9] we deduce that $\Delta H_f°(SiF_5^-) \leq -583$ kcal mol^{-1}.

It is therefore apparent that this approach does yield information regarding the heats of formation of inorganic ions and other systems such as germanium tetrafluoride and phosphorus pentafluoride are being investigated.

Acknowledgment.—We thank the Science Research Council for a grant in support of this work.

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[9] "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich.

CONTRIBUTION NO. 2568 FROM THE
DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

An Improved Synthesis of 1,6-Dicarba-*closo*-decaborane(10)

BY PHILIP M. GARRETT, GARY S. DITTA,
AND M. F. HAWTHORNE

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The reported[1,2] syntheses of 1,6-dicarba-*closo*-decaborane(10), $1,6\text{-}B_8C_2H_{10}$, and its C-substituted derivatives were accomplished by the pyrolyses of 1,3-dicarba-*nido*-nonaborane(13), $1,3\text{-}B_7C_2H_{13}$, and its C-substituted derivatives in the presence of diborane. The yields were generally less than 40% and the C-phenyl derivative could not be obtained by this route (Table I). Moreover, the isolation of the pure product was quite laborious due to the presence of small amounts of by-product carboranes. We have recently reported representative derivative chemistry of the 1,6- and 1,10-$B_8C_2H_{10}$ carboranes[3] and we now wish to report a new and better route to the $1,6\text{-}B_8C_2H_{10}$ carborane and its C-substituted derivatives.

TABLE I

YIELD DATA FOR $1,6\text{-}B_8C_2H_{10}$ AND ITS C-MONOMETHYL, C,C′-DIMETHYL, AND C-MONOPHENYL DERIVATIVES

Compound	Yield,[a] %	Yield,[b] %
$1,6\text{-}B_8C_2H_{10}$	29	74[c]
$1,6\text{-}B_8C_2H_9(CH_3)$	33	86
$1,6\text{-}B_8C_2H_8(CH_3)_2$	41	85
$1,6\text{-}B_8C_2H_9(C_6H_5)$	Trace	81

[a] Prepared by pyrolysis of $B_7C_2H_{13}$ and its C-substituted derivatives in the presence of diborane.[1,2] [b] Prepared by hydroboration of $NaB_7C_2H_{12}$–$B_7C_2H_{13}$ and their C-substituted derivatives. [c] The yield was 82% when unreacted $B_7C_2H_{13}$ was recovered.

Treatment of a diethyl ether solution containing 1 mol each of $NaB_7C_2H_{12}$ and $B_7C_2H_{13}$ with 2 mol of diborane dissolved in tetrahydrofuran (THF) followed by addition of 2 mol of $B_7C_2H_{13}$ dissolved in diethyl ether and an additional 2 mol of diborane dissolved in THF gave $1,6\text{-}B_8C_2H_{10}$ in 74% yield. Its C-substituted derivatives could likewise be obtained in somewhat higher yields (Table I). In addition to $1,6\text{-}B_8C_2H_{10}$, the only other major product was sodium borohydride and consequently purification procedures were considerably easier than in the previous method. The crude C-monomethyl derivative was found to be an inseparable mixture of the 1-methyl and 6-methyl isomers of $1,6\text{-}B_8C_2H_{10}$ in a 2:1 abundance, respectively, which is the same ratio obtained by other routes.[2] The products were identified by their characteristic infrared and nuclear magnetic resonance spectra.[1,2] From preliminary results, not discussed here, the reaction path appears to be quite complex and its elucidation is currently underway.

Experimental Section

1,3-Dicarba-*nido*-nonaborane(13) and its C-substituted derivatives were prepared by literature methods.[1,4] Cylinder diborane was purchased from K & K Laboratories, Plainview, N. Y. The THF was distilled from lithium aluminum hydride prior to use. All other reagents were reagent grade and were used without further purification. All reactions were carried out under a nitrogen atmosphere.

Preparation of Diborane–THF Solution.—Diborane dissolves[5] in THF with formation of a weak Lewis acid–base complex which could be conveniently syringed in air. The apparatus, listed in its connected order, consisted of the cylinder of diborane, a nitrogen inlet with a T joint near the cylinder, an empty trap, a fritted-disk bubbler which was immersed in the THF, another empty trap, and finally two acetone traps in which undissolved diborane is destroyed. With the exception of the diborane

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[1] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 869 (1968).

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[3] P. M. Garrett, J. C. Smart, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 4707 (1969).

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[5] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 199.

cylinder, the apparatus was set up in a fume hood. Tygon tubing was employed and the THF was maintained at 0° during the diborane addition. After the system was thoroughly flushed with nitrogen, diborane was added without nitrogen until the first acetone trap, which contained ~200 ml of acetone, began to warm. At this point, depending on the rate of diborane addition, the solution contained 3–5 g of diborane/100 ml of the solution. Generally, after the first acetone trap began to warm, diborane addition was continued for an additional 10–20 min. The solution was most conveniently used when its concentration was between 4 and 6 g of diborane/100 ml of solution. The diborane–THF solution was then warmed to room temperature while the system was flushed with nitrogen. The fritted-disk bubbler was removed from the solution and it was replaced with a rubber septum. A known amount (~2 ml) was syringed into a 100-ml flask containing ~20 ml of water and which was connected to a 1-l. graduated cylinder filled with mineral oil. The hydrogen evolution was measured and the concentration of the solution was calculated as follows: grams of diborane per 100 ml of solution = (volume of H_2 (ml)/volume of diborane–THF solution used (ml))(0.0184), at 23° and 740 mm. *Caution! If the diborane–THF solution is permitted to become more concentrated than 8 g of diborane/100 ml of solution, the solution will be spontaneously flammable in air.* It is suggested that when the first acetone trap warms that the concentration be checked. If the concentration is too low, insert the fritted-disk bubbler, flush the system with nitrogen, and continue diborane addition. Diborane–THF solutions containing about 4 g of diborane/100 ml of solution cannot be stored for more than a few hours because at these high concentrations diborane reacts with THF to form *n*-butyl borate.

Preparation of 1,6-$B_8C_2H_{10}$.—This will be given as the general method. Into a 500-ml three-necked round-bottom flask equipped with a nitrogen inlet and a rubber septum were placed 5.0 g (4.42×10^{-2} mol) of $B_7C_2H_{13}$ and 75 ml of diethyl ether. After flushing the system with nitrogen, 0.90 g (2.25×10^{-2} mol) of 60% sodium hydride–mineral oil dispersion was slowly added as a solid. About 15 min after addition, the solution was cooled to 0° and 63 ml (2.5 g, 9.0×10^{-2} mol of diborane) of a 4.0 g of diborane/100 ml of the THF solution was added with a syringe over 5 min. The resulting slurry was stirred for 30 min. Into the slurry was then syringed 5.0 g of $B_7C_2H_{13}$ dissolved in 75 ml of diethyl ether followed by 63 ml of the above diborane–THF solution. The reaction mixture was stirred at 0° for 3 hr and then quickly filtered through a medium-fritted disk filter in air. The ether solvents were fractionated from the product under high vacuum using a vacuum-jacketed Vigreux column (1-in. diameter × 18 in.) which was topped with a sublimation apparatus. The cold finger of the sublimation apparatus was used to control the rate of evaporation of the solvents. After most of the solvent was evaporated, ~15 ml of *n*-pentane was condensed into the apparatus and the product was washed back into the flask. The resulting slurry was placed on a chromatography column packed with silica gel (2-in. diameter × 8 in.) and the product was eluted with *n*-pentane. The fraction containing the product was evaporated to dryness under high vacuum using the above Vigreux column–sublimation apparatus. The product was sublimed under high vacuum at room temperature to a −80° cold finger. The yield was 8.0 g or 74%, which was increased to 82% by washing the chromatography column with methylene chloride and isolating 1.0 g of unreacted $B_7C_2H_{13}$. *Caution! The $B_7C_2H_{13}$ recovered will often spontaneously inflame after being exposed to air for a few minutes.* It should be further purified before assuming that it is safe to store.

C-Monomethyl and C,C′-Dimethyl Derivatives of 1,6-$B_8C_2H_{10}$.—The C-monomethyl and C,C′-dimethyl derivatives of 1,6-$B_8C_2H_{10}$ were prepared by the procedure given for 1,6-$B_8C_2H_{10}$ and using $B_7C_2H_{12}(CH_3)$ and $B_7C_2H_{11}(CH_3)_2$, respectively, as starting materials. The procedure for the isolation of these two derivatives was somewhat different than for 1,6-$B_8C_2H_{10}$. After the chromatography step and evaporation of the pentane, the sublimation apparatus was replaced with an alembic distillation apparatus[6] and the product was distilled under high vacuum at room temperature and was collected at −80°. The yields of the crude C-monomethyl isomer mixture and of the C,C′-dimethyl derivatives were 86 and 85%, respectively, without recovery of unreacted starting carborane.

C-Monophenyl Derivative of 1,6-$B_8C_2H_{10}$.—The C-monophenyl derivative was prepared by the procedure given for 1,6-$B_8C_2H_{10}$ and using $B_7C_2H_{12}(C_6H_5)$ as starting material. The isolation of the product did not require use of the Vigreux column. The product was sublimed under high vacuum at 50° to a −80° cold finger. The yield of 1-(C_6H_5)-1,6-$B_8C_2H_{10}$ was 81%, without recovery of unreacted starting carborane.

Further Purification of 1,6-$B_8C_2H_{10}$ and Its C-Substituted Derivatives.—Because of very small amounts of air and thermally unstable impurities in the products isolated as described above, the 1,6-$B_8C_2H_{10}$ carborane and its C-substituted derivatives, with the exception of the C-phenyl derivative, should be passed under high vacuum through a column (1-in. diameter × 18 in.) heated at 300° and collected with a sublimation or alembic distillation apparatus. This purification step is necessary if the 1,6 isomer will be thermally rearranged to the 1,10 isomer in a sealed glass tube as described elsewhere.[1,2]

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INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401

Preparation and Characterization of Chlorotri(3-butenyl)phosphinorhodium(I)

BY PETER W. CLARK AND GEORGE E. HARTWELL

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Several transition metal complexes containing bidentate ligands in which one donor is a group V or VI atom and the other an olefin have been prepared, and a few reactions involving the olefin have been reported.[1,2] During an investigation of hydrogenation and hydroformylation mechanisms using ligands of the type $R_mP[(CH_2)_n—CH{=}CH_2]_{3-m}$, where $m = 0, 1,$ or 2 and $n = 0, 1, 2,$ or 3 with various platinum metals, we have prepared and characterized the novel trigonal bipyramidal compound $RhClP(CH_2CH_2CH{=}CH_2)_3$ which contains a tetradentate phosphine with three equivalent rhodium–olefin π bonds.

Experimental Section

Phosphorus trichloride (Matheson Coleman and Bell) and 4-bromo-1-butene (Pierce Chemical Co.) were used without further purification. The rhodium complexes $[Rh(CO)_2Cl]_2$ and $[Rh(C_2H_4)_2Cl]_2$ were prepared by the literature methods.[3,4] All solvents were dried before use.

The infrared spectra were recorded on a Perkin-Elmer 137 and a Perkin-Elmer 621 spectrometer and Raman spectra on a Cary 81 spectrometer using the He–Ne laser excitation at 6328 Å. Proton magnetic resonance spectra and the decoupled proton magnetic resonance spectra were obtained with a Varian HA100 spectrometer. The molecular weight was measured using a

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