Acknowledgment. The authors express their appreciation to Dr. P. M. Henry for helpful discussions, to Mr. O. W. Marks for help in the mathematical analysis, and to Mr. J. B. Forgie for his assistance in carrying out the experimental part of this study. This research was supported by the Advanced Research Projects Agency through the U. S. Army Research Office (Durham), Contract DA-31-124-ARO(D)-62.

Alan D. Craig, George A. Ward
Research Center, Hercules Inc.
Wilmington, Delaware 19899
Received July 15, 1966

The Direct Chlorination of Pentaborane(9)

Sir:

The previously unreported 1-chloropentaborane(9)[1] can be prepared in greater than 90% yields by the direct chlorination of pentaborane in the presence of aluminum chloride. In the absence of this catalyst 2-chloropentaborane[2] is by far the most predominant isomer, but so far the yields have not exceeded 30%.

In a typical experiment 6.5 mmoles of chlorine, 11.6 mmoles of pentaborane, about 1 g of aluminum chloride, and 13 ml of boron trichloride were condensed into a reaction flask on the vacuum line.[3] The flask was then sealed from the vacuum line and warmed from −108 to 0° over a 2-hr period and maintained at 0° for 18 hr. Separation of the reaction mixture by fractional condensation resulted in the isolation of 6.0 mmoles (92% based on chlorine) of 1-chloropentaborane. The mass spectrum of 1-chloropentaborane is almost identical with that of 2-chloropentaborane (some relative intensities are different). The ^{11}B nmr spectrum (32.1 Mc) is similar to that of other 1-halopentaboranes, consisting of a doublet at $\delta = 11.9$ ppm ($BF_3 \cdot O(C_2H_5)_2 = 0.0$), $J = 170 \pm 5$ cps, corresponding to B^{2-5}–H, and a singlet at $\delta = 29.3$ ppm corresponding to B^1–Cl with an area ratio of 4.0:1.0, respectively. The ^{1}H nmr spectrum (100 Mc) consists of a quartet of equally intense lines at τ 7.07, $J = 165 \pm 5$ cps, corresponding to the four identical terminal hydrogens bonded to ^{11}B, and a broad resonance at τ 11.27, corresponding to an equal number (area ratio 1.00 ± 0.03) of bridging hydrogens. The melting range of 1-chloropentaborane is 26–27° and its vapor pressure at 28° is 4.2 mm. The gas-phase infrared spectrum contains bands at: 2610 (s), 1840 (w), 1785 (w), 1610 (vw), 1435 (m), 1380 (m), 1200 (m), 1160 (m), 1065 (w), 905 (m), 855 (w), 765 (w), and 635 (m) cm^{-1}.

A similar reaction was attempted in the absence of aluminum chloride. In this case only traces of 1-chloropentaborane were observed, but a 15% yield of 2-chloropentaborane (based on chlorine) was obtained. Low-temperature liquid-phase reactions and low-pressure gas-phase reactions were carried out in an attempt to improve the yield of 2-chloropentaborane, but in all cases the yields have been between 10 and 30%.

A previous attempt to chlorinate pentaborane in the presence of aluminum chloride in carbon disulfide solution was reported[4] to yield "microquantities" of a chloropentaborane contaminated with carbon tetrachloride, and attempts to duplicate the reaction on a larger scale resulted in explosions.[5]

It appears that in the absence of a strong Lewis acid the chlorination of pentaborane is a radical reaction. By contrast, halogenations with bromine and iodine produce 1-halopentaboranes almost exclusively and in high yields. These reactions can be envisioned as occurring *via* heterolytic cleavage of the halogen followed by electrophilic displacement of a proton from the 1 position in pentaborane by the positive halogen. This is similar in concept to the chlorination in the presence of aluminum chloride, a strong heterolytic catalyst.

The assumption that the uncatalyzed chlorination of pentaborane is a radical reaction is supported by the following observations. First, when the bromination of pentaborane is carried out in the presence of strong ultraviolet irradiation, the reaction proceeds about 100 times faster than usual,[6] and the ratio of 2-bromo- to 1-bromopentaborane increases from the value 0.049 reported by Burg and Sandhu[7] to 1.2 (although the total yield of bromopentaboranes decreases to about 45%, based on bromine). Second, attempts to chlorinate pentaborane with ICl and ICl_3 resulted in the formation of 1-iodopentaborane, in both cases in greater than 90% yields. Further studies of the halogenation of pentaborane are in progress and will be reported shortly.

Acknowledgment. We wish to thank the National Science Foundation and the Wisconsin Alumni Research Foundation for support of this research.

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(1) All pentaboranes referred to in this communication are derivatives of pentaborane(9), B_5H_9.

(2) T. Onak and G. B. Dunks, *Inorg. Chem.*, **3**, 1060 (1964).

(3) R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(4) I. Shapiro and H. Landesman, *J. Chem. Phys.*, **33**, 1590 (1960).

(5) Pentaborane forms shock-sensitive mixtures with carbon tetrachloride: "Pentaborane," Callery Chemical Co. Technical Bulletin CT-1300, Oct 1, 1961, and references therein.

(6) L. H. Hall, V. V. Subbanna, and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 3969 (1964).

(7) A. B. Burg and J. S. Sandhu, *ibid.*, **87**, 3787 (1965).

Donald F. Gaines
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
Received July 25, 1966

$S = 1$ Ground State in Six-Coordinated Iron(II)

Sir:

We wish to report here on some results which demonstrate that $S = 1$ ground states may be stabilized in *six-coordinated* d^6 complex compounds. So far, triplet ground states have been assumed in d^6 configuration for square-planar iron(II) systems only, and even there not more than two examples were found.[1,2]

In what follows, the compounds $[Fe(phen)_2ox] \cdot 5H_2O$ (I) and $[Fe(phen)_2mal] \cdot 7H_2O$ (II), where phen = 1,10-phenanthroline, ox = oxalate, and mal = malonate, will be used as examples. Analogous results were obtained for the corresponding compounds where phenanthroline has been replaced by 4,7-dimethyl-1,10-phenanthroline or 2,2′-bipyridyl[3] as well as for $[Fe(phen)_2F_2] \cdot 4H_2O$.

Magnetic susceptibilities were measured repeatedly in an atmosphere of 400 μ pressure of nitrogen on 20- to

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(1) A. B. P. Lever, *J. Chem. Soc.*, 1821 (1965).

(2) J. Chatt and B. L. Shaw, *ibid.*, 285 (1961).

(3) The formulas of these compounds differ from those of the phenanthroline series in the amount of water of crystallization.