The decomposition of the isopropylamine–nitric oxide product in the presence of oxygen gave several decomposition products. Water and isopropylamine were definitely identified as products. Qualitative indications were obtained for the presence of an olefin, a nitrite, and an alcohol. Some of these products can be accounted for if it is considered that some of the addition compound decomposes into starting materials (isopropylamine and nitric oxide). The nitric oxide is oxidized by oxygen to nitrogen dioxide, and a mixture of NO and NO_2 in the presence of moisture forms some nitrous acid. The nitrous acid can then form an isopropylammonium diazonium compound which is unstable and will decompose to an alcohol, an olefin, and nitrogen. Water can be accounted for as one of the products of decomposition of isopropylammonium nitrite.[13]

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(13) P. Neogi, *Proc. Chem. Soc.*, **27**, 242 (1911).

CONTRIBUTION FROM THE REACTION MOTORS DIVISION,
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Reaction of Decaborane and Its Derivatives. II. Addition Reactions of 6,9-Bis(acetonitrile)decaborane with Hydrazine

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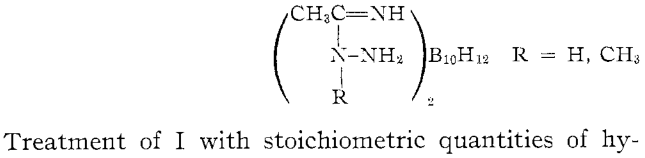
The structure of 6,9-bis(acetonitrile)decaborane (I) as reported by Reddy and Lipscomb[1] indicates that the $-B_{10}H_{12}-$ nucleus is electrophilic. Thus, the addition of an HX molecule (where H is labile and X has an unshared electron pair) to the CH_3CN moiety should be facile. That primary and secondary amines would add to I was shown by Hawthorne and Pitochelli[2] and by work in these laboratories.

We wish to report that hydrazine will react with I in a similar manner to form hydrazidine-like products.



$$(CH_3CN)_2B_{10}H_{12} + 2RNHNH_2 \longrightarrow \left(\begin{array}{l} CH_3C{=}NH \\ \quad | \\ \quad N\text{-}NH_2 \\ \quad | \\ \quad R \end{array} B_{10}H_{12}\right)_2 \quad R = H, CH_3$$

Treatment of I with stoichiometric quantities of hydrazine hydrate or methylhydrazine hydrate results in the formation of 6,9-bis(acethydrazidine)decaborane (II, R = H) and 6,9-bis(acet-N-methylhydrazidine)decaborane (III, R = CH_3), respectively.

It is of interest to note that the ease with which the amines and hydrazines add to the nitrile is parallel to the ease with which R_fCN compounds (R_f = fluoroalkyl) add HX materials.[3] In both situations, the nitrile functionality is bonded to a highly electrophilic group. In the fluoroalkyl nitriles the electrophilic group is covalently bonded to the nitrile carbon, whereas in I the bonding is coordinate covalent between $\equiv N:$ and $B_{10}H_{12}$. Nevertheless, both nitriles readily undergo HX addition.

Experimental

6,9-Bis(acethydrazidine)decaborane.—Hydrazine (9.1 g., 0.28 mole) was added slowly to a cooled, stirred suspension of bis(acetonitrile)decaborane (30.0 g., 0.15 mole) in 380 ml. of benzene. After addition, the mixture was heated for 16 hr. at reflux. After cooling, a white, crystalline solid (38.6 g.) was filtered, washed with benzene, and then dried under vacuum. The product does not melt up to 360°. Its infrared spectrum is consistent with that expected of a hydrazidine having N—H, NH_2, N—N, and C=N bands as well as the –BH absorption at 3.9 μ.

Anal. Calcd. for $C_4H_{26}N_6B_{10}$: C, 18.03; H, 9.83; N, 31.54; B, 40.60. Found: C, 17.6; H, 9.8; N, 31.3; B, 39.9.

6,9-Bis(acet-N-methylhydrazidine)decaborane.—Methyl hydrazine hydrate (25 ml.) was added slowly to a cooled, stirred suspension of bis(acetonitrile)decaborane (10 g.) in 100 ml. of benzene. The reaction was exothermic but there was no gas evolution. After addition, the mixture was heated for 3 hr. at reflux. On cooling, a white solid separated which was filtered, recrystallized from acetonitrile, then dried under vacuum. The solid decomposes explosively at 218–219°: its infrared spectrum is similar to that of II.

Anal. Calcd. for $C_6H_{30}N_6B_{10}$: B, 36.73. Found: B, 36.9.

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(1) J. V. Reddy and W. N. Lipscomb, *J. Am. Chem. Soc.*, **81**, 754 (1959).

(2) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **81**, 5519 (1959).

(3) D. R. Husted, U. S. Patent 2,676,985; W. L. Reilly and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6032 (1956); H. C. Brown and R. Pater, *J. Org. Chem.*, **27**, 2858 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Preparation and Properties of Tetrakis(trifluorophosphine)palladium(0)

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We wish to report the preparation of tetrakis(trifluorophosphine)palladium(0). This compound is of particular interest since no palladium compounds of this type have previously been prepared. Its properties are generally very similar to those of $[Ni(PF_3)_4]$.[1,2]

Experimental

Preparation of $[Pd(PF_3)_4]$.—The procedure employs $[Pd(CO)_2Cl_2]$[3] and PF_3[4] as reactants in a high-pressure Pyrex bomb. The

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(1) G. Wilkinson, *J. Am. Chem. Soc.*, **73**, 5501 (1951).

(2) F. Seel, K. Ballreich, and R. Schmutzler, *Chem. Ber.*, **94**, 1173 (1961).

(3) J. Chatt and A. Williams, *J. Chem. Soc.*, 3061 (1951).

(4) W. Manchot and J. Konig, *Chem. Ber.*, **59**, 883 (1926).