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]

Acknowledgment.—The authors are grateful to the U. S. Army Research Office (Durham) for financial support of this research under Grant No. USDA-G-72.

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

CONTRIBUTION FROM THE REACTION MOTORS DIVISION,
THIOKOL CHEMICAL CORPORATION, DENVILLE, NEW JERSEY

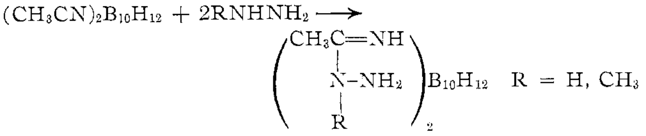
Reaction of Decaborane and Its Derivatives. II. Addition Reactions of 6,9-Bis(acetonitrile)decaborane with Hydrazine

BY MARVIN M. FEIN, JACK BOBINSKI, JOHN E. PAUSTIAN, DANIEL GRAFSTEIN, AND MURRAY S. COHEN

Received September 14, 1964

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.



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

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.

[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).

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.

Acknowledgments.—The authors wish to thank Mr. Stanley Mutnick for his assistance. This work was supported by the United States Air Force under Contract AF 33(616)5867.

[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,
SAINT LOUIS UNIVERSITY, SAINT LOUIS, MISSOURI

Preparation and Properties of Tetrakis(trifluorophosphine)palladium(0)

BY G. F. SVATOS AND E. E. FLAGG

Received September 25, 1964

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

---

[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).

amounts of carbonyl adduct used ranged from 0.2 to 1 g.; to this was added PF_3 to give a mole ratio of 1:2. Though attempts were made to increase the yield by altering concentrations and temperature, optimum results were obtained when the reaction was allowed to proceed at room temperature for 1 week under the conditions given. At lower temperatures the reaction proceeded slowly, while at higher temperatures excessive decomposition was observed. The bombs were then cooled and opened under anhydrous conditions. A white solid, black metal, and clear liquid were observed. None of the yellow carbonyl appeared to be present. The tubes were placed in a vacuum system, and the temperature was raised slowly from −196° to room temperature. A white solid intermediate (stable at −22°) was then collected. Subsequent fractionation gave a colorless, low-viscosity liquid collected in the range −100 to −78°. Though the product is reasonably stable at atmospheric pressure in a sealed system, it is somewhat unstable under reduced pressure, dissociating into free metal and PF_3. Yields were generally low (approximately 15% of theory). The product melted at approximately −100°.

Analysis.—The $[Pd(PF_3)_4]$ complex was first hydrolyzed in 0.25 *M* sodium hydroxide at ice temperature. Palladium was determined as the free metal[5] and fluorine as the insoluble calcium fluoride.[6]

Anal. Calcd.: Pd, 23.22; F, 49.75. Found: Pd, 24.65; F, 48.70.

Infrared Spectra.—Spectra were recorded with a Perkin-Elmer Model 21 infrared spectrophotometer using sodium chloride optics. Samples were contained in a 10-cm. gas cell at pressures up to 20 mm. With the exception of trace impurities such as SiF_4, which gave a band at 1027 cm.$^{-1}$, the rather complex spectrum consisted of stretching modes in the region of 890 cm.$^{-1}$ (see Table I). A band at 792 cm.$^{-1}$ appears to be characteristic of zerovalent complexes. Band intensities of coordinated PF_3 are substantially lower than those of free PF_3.

TABLE I

INFRARED SPECTRA[a]

PF_3	Obsd.	890 w	864 s	
	Lit.[2]	898	848	
$[Ni(PF_3)_4]$	Obsd.	903 w	864 s	793 m
	Lit.[2]	898	859	
$[Pd(PF_3)_4]$	Obsd.	888 w	861 s	792 m

[a] Frequency given in cm.$^{-1}$.

Nuclear Magnetic Resonance.—Magnetic resonance data were obtained on high resolution Varian equipment. P^{31} and F^{19} spectra were run at 24.288 and 56.445 Mc./sec., respectively. Phosphoric acid (85%) and trifluoroacetic acid were used as reference standards employing audio side-band techniques[7] for measurements. Samples were run as liquids in 5-mm. o.d. Pyrex sealed tubes. Bulk susceptibility corrections were assumed to be small and were not made. The P^{31} magnetic resonance spectra of $[Ni(PF_3)_4]$ and $[Pd(PF_3)_4]$ are very similar, both giving rise to a multiplet structure containing four lines with an intensity ratio of 1:3:3:1. F^{19} magnetic resonance spectra are made up of equal intensity doublets. Results are given in Table II.

Discussion

The relatively low stability of the palladium complex is expected when one considers its large d^{10}–d^9 ionization potential.[8] This is reflected in the P^{31} magnetic resonance spectra of palladium and nickel complexes: δ_P and J_{P-F} in $[Pd(PF_3)_4]$ more closely approach those in PF_3. Only small perturbation of the ground state of PF_3 is expected for a weakly complexed system. This gives rise to correspondingly small changes in paramagnetic terms and coupling constants.[9]

TABLE II

NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	δ_{CF_3COOH}, p.p.m.	$\delta_{H_3PO_4}$, p.p.m.	J_{P-F}, c.p.s.
PF_3	−42.3[a]	−97[b]	1441[c]
$[Ni(PF_3)_4]$	−60	−128	1300
$[Pd(PF_3)_4]$	−55	−116	1400

[a] H. S. Gutowsky and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953). [b] H. S. Gutowsky and D. W. McCall, *ibid.*, **22**, 162 (1954). [c] E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

It is probable that $[Pt(PF_3)_4]$ may be formed under conditions similar to those used to prepare the palladium complex and that its properties resemble those of the nickel and palladium compounds.

Acknowledgment.—The authors wish to acknowledge the use of nuclear magnetic resonance facilities of the Monsanto Chemical Company.

---

(5) N. H. Furman, "Standard Methods of Chemical Analysis," Vol. I, D. Van Nostrand Co., Inc., Princeton, N. J., p. 884.

(6) Reference 5, p. 460.

(7) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(8) R. S. Nyholm (Tilden Lecture), *Proc. Chem. Soc.*, 273 (1961).

(9) G. F. Svatos, being submitted for publication.

CONTRIBUTION FROM THE SPERRY RAND
RESEARCH CENTER, SUDBURY, MASSACHUSETTS

The Preparation and Crystallographic Properties of $KMnCl_3$

BY WILLIAM J. CROFT, MICHAEL KESTIGIAN,
AND FREDRIC D. LEIPZIGER

Received September 21, 1964

This note is concerned with the preparation and crystallographic properties of anhydrous $KMnCl_3$. The formation of this phase has been previously reported[1]; however, the compound has not been fully characterized. A viscosity study of the KCl–$MnCl_2$ system by Ermolenko and Vasil'eva[2] indicated the presence of a compound containing equimolar quantities of potassium chloride and manganous chloride.

Experimental

The compound $KMnCl_3$ was prepared by heating an intimate equimolar mixture of KCl and $MnCl_2 \cdot 4H_2O$ in an atmosphere of dry hydrogen chloride transported by dry argon carrier gas. The sample, contained in a platinum (or dense graphite) vessel, was slowly heated to above its melting point and the temperature maintained for 2 hr. Single-crystal growth experiments were carried out by use of the horizontal Bridgman technique. Nominally, a 100° temperature gradient between the hot and cool temperature zone and a furnace travel rate of 0.05 in./hr. were used. Single-crystal growth experiments were also carried out utilizing an evacuated sealed ampoule technique, by use of the vertical Bridgman and temperature gradient methods.

---

(1) C. Sandonnini and G. Scarpa, *Atti accad. nazl. Lincei*, **22**, II 163 (1913).

(2) N. F. Ermolenko and G. I. Vasil'eva, *Uch. Zap. Belorussk. Gos. Univ., Ser. Khim.*, 295 (1956).