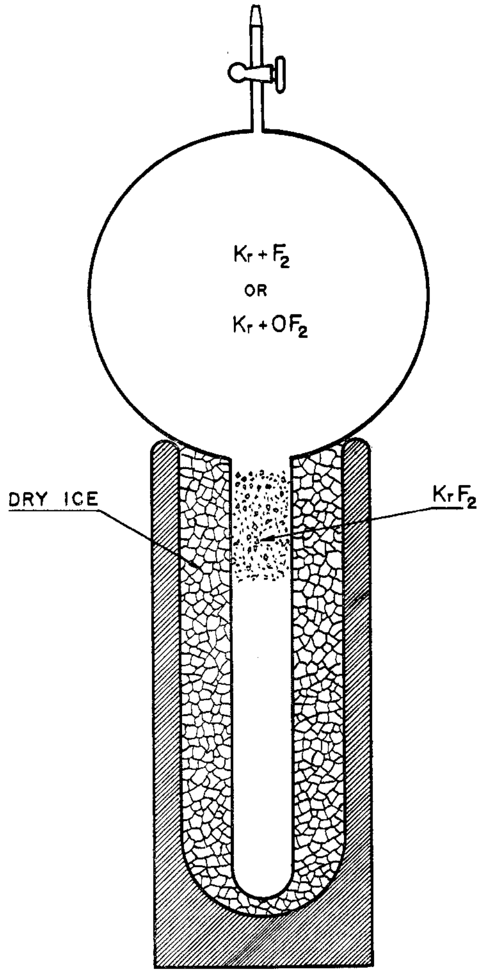

Figure 1.—Reaction flask.

experiment evolved 10.06 cm.^{3} of gas which consisted of equal volumes of krypton and fluorine. Thus, the product was also KrF_2.

Both krypton tetrafluoride and krypton difluoride are known to be unstable at room temperature. Therefore, under the conditions of our experiments only those portions of krypton difluoride formed which got into the cooled extension tube of the flask were entrapped (quenched) and remained undecomposed. The amount of the KrF_2 produced depends, therefore, not only upon the amount of radiation energy absorbed but, to a very large extent, upon the effectiveness of cooling.

In the experiments with $Kr–F_2$ mixtures the total amount of KrF_2 formed in a 2-l. flask during 5 weeks of standing varied from 70 to 100 mg.; *i.e.*, the average rate of production was 2–3 mg. of KrF_2 per day. In the experiments with $Kr–OF_2$ mixtures the rate of formation was about 1 mg. of KrF_2 per day.

The yield of KrF_2 may probably be increased by use of a wider tubular extension of the flask and by lowering the cooling temperature (to the boiling point of krypton, 120°K.).

Acknowledgment is due to Dr. A. V. Grosse for valuable suggestions.

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Preparation and Properties of The Monoborane Adduct of N,N,N′,N′-Tetramethylethylenediamine

BY A. R. GATTI AND THOMAS WARTIK

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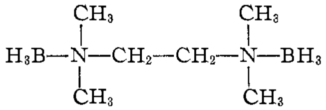
Generally, when a simple monofunctional Lewis acid is treated with a simple difunctional Lewis base, only one of the two possible adducts is observed and, in most cases, regardless of the proportions of reactants, this is the one involving two moles of the acid per mole of difunctional base. Presumably this rather unexpected preference for the diadduct is due to lattice stabilization effects resulting from considerations of symmetry.

In the case of simple boron acids, only a few monoadducts of simple difunctional bases have been reported,$^{1-4}$ and, of these, only one appears to have been isolated in reasonably pure condition. We now wish to report the preparation, isolation, and identification of the monoborane adduct of N,N,N′,N′-tetramethylethylenediamine (hereafter referred to as TMED).

Miller and Muetterties, in 1964, reported the preparation of the bis-borane adduct of TMED,^{5} a white solid which our B^{11} n.m.r. studies indicate to be a symmetrical molecule with the structure



$$H_3B\text{—}\overset{CH_3}{\underset{CH_3}{N}}\text{—}CH_2\text{—}CH_2\text{—}\overset{CH_3}{\underset{CH_3}{N}}\text{—}BH_3$$

We found that $TMED{\cdot}2BH_3$, although virtually insoluble in TMED at room temperature, was quite soluble in this liquid at 60°. (The resulting solution showed a strong tendency to supersaturate on cooling, and 3 days at room temperature passed before precipitation of $TMED{\cdot}2BH_3$ commenced.) When a portion of the supersaturated solution was cooled to $-23°$ and subjected to pumping, a white crystalline solid remained which, on being warmed slowly, melted to a clear, colorless liquid at $-3°$ to $-1°$. The clear melt almost immediately became turbid and, after 1 hr., the sample had decomposed to a new white solid (shown by its infrared spectrum^6 to be $TMED{\cdot}2BH_3$) and a colorless liquid (shown by its infrared spectrum and vapor pres-

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(1) S. V. Urs and E. S. Gould, *J. Am. Chem. Soc.*, **74**, 2948 (1952).

(2) C. A. Brown, E. L. Muetterties, and E. G. Rochow, *ibid.*, **76**, 2537 (1954).

(3) E. L. Muetterties, *Z. Naturforsch.*, **12b**, 265 (1957).

(4) A. K. Holliday and W. Jeffers, 16th International Congress of Pure and Applied Chemistry, Paris, 1957, Section on Inorganic Chemistry, p. 541.

(5) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

(6) The infrared spectrum of $TMED{\cdot}2BH_3$, which does not appear to have been previously reported, showed the following absorption (cm.$^{-1}$): 2955 (m), 2905 (m), 2390 (vs), 2280 (sh), 2250 (s), 2170 (w), 2055 (w), 1470 (vs), 1435 (s), 1405 (m), 1350 (m), 1310 (m), 1250 (w), 1205 (s), 1168 (vs), 1148 (s), 1010 (s), 875 (s), 800 (m), 725 (w), 685 (w).

sure[7] to be TMED). The clear melt produced TMED and $TMED\cdot 2BH_3$ in the ratio 1.06:1, in good agreement with the values required by the equation

$$2TMED\cdot BH_3 \longrightarrow TMED + TMED\cdot 2BH_3$$

Proton magnetic resonance measurements support the view that the solution prepared by dissolving solid $TMED\cdot 2BH_3$ in liquid TMED at elevated temperatures contains only the monoadduct. The proton n.m.r. spectrum of such a solution showed four peaks at +2.24, +2.61, +2.73, and +2.78 p.p.m. relative to tetramethylsilane as the external reference. While the proximity of the solvent peak at +2.22 p.p.m. rendered impractical measurement of the relative area of the first resonance, the remaining three had relative areas of 3:1:1, respectively.

Protons attached to boron atoms were not observable with the techniques employed; in consequence, these do not appear in the assignment of the resonances reported above. Both TMED and $TMED\cdot 2BH_3$, being symmetrical molecules, exhibit only two resonances, of relative areas 3:1. The monoadduct $TMED\cdot BH_3$ is quite unsymmetrical and, therefore, should show four proton resonances in the ratio 3:3:1:1. On the assumption that the methyl groups most distant from the boron atom in $TMED\cdot BH_3$ do not differ greatly from those in TMED itself, and that the methyl groups closest to the boron atom do not differ greatly from those in $TMED\cdot 2BH_3$, the assignments in Table I appear reasonable. (All protons on carbons adjacent to B–N bonds are referred to as α protons, all protons on other carbons as β protons.) The expected quartet was observed in the B^{11} spectrum of $TMED\cdot BH_3$. This was located at +26.3 p.p.m. relative to trimethoxyborane as an external reference. Relative areas were approximately 1:3:3:1 with $J = 96$ c.p.s. For $TMED\cdot 2BH_3$ the shift was +28.4 p.p.m. with $J = 96$ c.p.s.

Table I

Assignment of Proton Shifts[a] in TMED, $TMED\cdot 2BH_3$, and $TMED\cdot BH_3$[b]

	α-Methyl	β-Methyl	α-Methylene	β-Methylene
TMED		+2.22 (2.8)		+2.37 (1)
$TMED\cdot 2BH_3$	+2.59 (3.0)		+3.12 (1)	
$TMED\cdot BH_3$	+2.61 (3.2)	+2.24 (*c*)	+2.78 (1)	+2.73 (1)

[a] Relative to tetramethylsilane as an external reference. [b] Observed relative areas indicated in parentheses. [c] Masked by solvent.

The monoadduct $TMED\cdot BH_3$ can be stored below its melting point at least 24 hr. without decomposition. Above its melting point, however, it quickly decomposes in the absence of excess TMED.

Extension of the above studies to boron halide adducts is currently in progress.

Experimental Section

Preparations and purifications were carried out in conventional Stock-type vacuum apparatus. $TMED\cdot 2BH_3$ was made by the direct reaction of TMED with excess B_2H_6 at −45° and was purified by sublimation at 110°.

Proton n.m.r. spectra were determined with a Varian A60 spectrometer and B^{11} n.m.r. spectra with a Varian 4300-2 12-Mc. spectrometer. Chloroform was employed as a solvent for both TMED and $TMED\cdot 2BH_3$.

Infrared spectra were run on mineral oil and perchlorobutadiene mulls using a Beckman IR 5A spectrophotometer.

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(7) The vapor pressure of the liquid recovered (18 mm. at 21.7°) was identical with that of the TMED originally employed.

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Pseudohalo Silicon and Germanium Phthalocyanines[1]

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For the pseudohalo compounds of silicon and germanium there is always at least a possibility that the groups are nitrogen-bonded to the metal. This possibility has led, in the course of a search for silicon and germanium phthalocyanines having the central metal octahedrally coordinated by nitrogen, to the study of the pseudohalo phthalocyanino derivatives of these two metals.

Experimental Section

Bisisocyanato(phthalocyanino)silicon, $PcSi(NCO)_2$.—A mixture of 0.61 g. of $PcSiCl_2$,[2] 1.50 g. of silver cyanate (*caution*),[3] and 25 ml. of 1,2-dichlorobenzene was refluxed for 30 min. The product was cooled, filtered off, washed with ethanol, 7.4 *M* aqueous ammonium thiocyanate, and water, and dried; yield 566 mg. (91%). Recrystallization gave purple reflecting crystals.

Anal. Calcd. for $C_{34}H_{16}N_{10}O_2Si$: C, 65.37; H, 2.58; Si, 4.50. Found: C, 65.18; H, 2.74; Si, 4.72.

Bisisothiocyanato(phthalocyanino)silicon, $PcSi(NCS)_2$.—A slurry of 1.22 g. of $PcSiCl_2$ and 3.32 g. of silver thiocyanate in 50 ml. of 1,2-dichlorobenzene was refluxed for 30 min. The product was cooled, filtered off, washed with ethanol, aqueous ammonium thiocyanate, and water, and dried; yield 1.19 g. (91%). Recrystallization gave purple reflecting crystals.

Anal. Calcd. for $C_{34}H_{16}N_{10}S_2Si$: C, 62.10; H, 2.56; S, 9.77; Si, 4.28. Found: C, 62.23; H, 2.50; S, 9.77; Si, 4.08.

Bisisoselenocyanato(phthalocyanino)silicon, $PcSi(NCSe)_2$.—A mixture of 215 mg. of recrystallized $PcSiCl_2$, 795 mg. of silver selenocyanate, and 49 ml. of chlorobenzene was refluxed under nitrogen for 30 min. and cooled. The product, after being washed with ethanol, aqueous ammonium thiocyanate, water, and acetone and dried, weighed 331 mg. (87%). Attempted purifications of this green product failed because of its thermal and chemical instability. The similarity of its infrared spectrum to that of its sulfur analog was taken as evidence of its nature.

Bisisocyanato(phthalocyanino)germanium, $PcGe(NCO)_2$.—A mixture of 1.30 g. of $PcGeCl_2$ and 2.91 g. of silver cyanate in 50 ml. of 1,2-dichlorobenzene was refluxed for 30 min. and cooled. The product, after being washed with acetone, aqueous ammonium thiocyanate, and water and dried, weighed 1.22 g.

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(1) This work was supported first by the Air Force Office of Scientific Research under Contract AF 49(638)-773 and later by the Office of Naval Research under Contract Nonr-1141(18).

(2) M. K. Lowery, A. J. Starshak, J. N. Esposito, P. C. Krueger, and M. E. Kenney, *Inorg. Chem.*, **4**, 128 (1965).

(3) The reactivity of the silver pseudohalides should be kept in mind. See B. L. Evans and A. D. Yoffe, *Proc. Roy. Soc.* (London), **A238**, 568 (1957).