Table III

Rate Constants for Silver(II) and Cobalt(III) Oxidations in 4 M Perchloric Acid at 25.0°

Reductant	$k_{Ag(II)}$, M^{-1} sec^{-1}	$k_{Co(III)}$, M^{-1} sec^{-1}	$\frac{k_{Ag(II)}}{k_{Co(III)}}$	$\frac{k_{Ag(I)}}{k_{Co(II)}}$
V(IV)	5×10^3	1.37[a]	3.6×10^3	8×10^1
Cr(III)	1.5×10^3 [b]	≤ 4[c]	$\geq 4 \times 10^2$	≥ 9
Mn(II)	3×10^4	1.0×10^2 [d]	3×10^2	7
Fe(II)	4×10^5 [e]	3.3×10^2	1.2×10^3	3×10^1
Co(II)	1.75×10^3	20[f]	0.9×10^2	2
Ce(III)	5×10^3 [g]	10[h]	5×10^2	1×10^1

[a] The vanadium(IV)–cobalt(III) reaction has also been studied by D. R. Rosseinsky and W. C. E. Higginson, *J. Chem. Soc.*, 31 (1960). Their value for the rate constant is in good agreement with the value determined in the present work after allowance is made for the effect of temperature and perchloric acid concentration on the reaction rate. [b] 3 M $HClO_4$: ref 6. [c] Calculated from the data reported in ref 6. [d] 3 M $HClO_4$: H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964). [e] At high iron(II) concentrations (*e.g.*, [Fe(II)] $\sim 1 \times 10^{-1}$ M and [Ag(II)] $\sim 2 \times 10^{-3}$ M) some slower secondary reactions were observed. These reactions, which may be associated with dimeric reactants or products, were not investigated in detail. [f] H. S. Habib and J. P. Hunt, *J. Am. Chem. Soc.*, **88**, 1668 (1966). [g] Calculated from the data reported by W. C. E. Higginson, *et al.*[4] [h] 1 M $HClO_4$: L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **52**, 1225 (1956).

lated from the formal oxidation potentials of the silver(I)–silver(II) and cobalt(II)–cobalt(III) couples. The formal potentials of these couples are 2.00 v in 4 M perchloric acid[11,12] and 1.84 v in 4 M nitric acid,[13] respectively, at 25°. We have determined[14] the formal potential of the cobalt(II)–cobalt(III) couple to be 1.92 ± 0.02 v in 4 M perchloric acid at 25°.[15,16] From these potentials we calculate that $K_1 = (4 \pm 2) \times 10^{-2}$, in satisfactory agreement with the equilibrium constant obtained from the kinetic measurements.

The rates of oxidation of vanadium(IV), chromium(III), manganese(II), iron(II), cobalt(II), and cerium(III) by silver(II) and cobalt(III) are compared in Table III. It will be seen that the silver(II) oxidations proceed about 10^2 to 10^4 times more rapidly than do the corresponding cobalt(III) oxidations. Moreover, since the equilibrium constant for the oxidation of cobalt(II) by silver(II) is known, we can calculate the relative rates of oxidation of silver(I) and cobalt(II) in the reverse of the above reactions. The results of these calculations are presented in the last column of Table III. It is apparent from this column that the reductions by silver(I), despite their more unfavorable free energy changes, proceed at least as rapidly as the reductions by cobalt(II). The relatively rapid rates of reduction by silver(I) and oxidation by silver(II) suggest that silver(I) is likely to be more efficient than cobalt(II) as a catalyst of oxidation–reduction reactions, a conclusion consistent with the widespread use of silver(I) as an electron mediator.

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[11] E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, New York, N. Y., 1939, p 543.

[12] A. A. Noyes, D. DeVault, C. D. Coryell, and T. J. Deahl, *J. Am. Chem. Soc.*, **59**, 1326 (1937).

[13] A. A. Noyes and T. J. Deahl, *ibid.*, **59**, 1337 (1937).

[14] In order to avoid the precipitation of potassium perchlorate during the potential measurements, the saturated potassium chloride solution in the calomel electrode was replaced by a saturated sodium chloride solution. The cobalt(III) solution was separated from the calomel electrode by a perchloric acid bridge in order to suppress the reaction of cobalt(III) with chloride ions. Silver(I) was added as a potential mediator[13] in some measurements.

[15] D. A. Johnson and A. G. Sharpe, *J. Chem. Soc.*, 3490 (1964), report a value of 1.95 ± 0.1 v for the formal potential of the cobalt(II)–cobalt(III) couple in 4 M perchloric acid at 25°. This value was calculated from the heat and entropy changes of the iron(II)–cobalt(III) reaction.

[16] The lower value of the potential in 4 M nitric acid suggests that extensive complex formation occurs between cobalt(III) and nitrate ions.

Contribution from the Olin Mathieson
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The Synthesis of Perfluorovinylborazines[1]

By A. J. Klanica, J. P. Faust, and C. S. King

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Prior to this investigation, a limited number of halogen derivatives of borazine were known. The B-trihaloborazines $(HNBX)_3$ where the boron hydrogen atom was replaced by either fluorine, chlorine, bromine, or iodine had been prepared.[2–6] Only two partially halogenated alkyl derivatives had been reported. Leffler had prepared N-(β,β,β-trifluoroethyl)borazine, $(CF_3CH_2NBH)_3$,[7] and a partially chlorinated alkyl derivative B-(β-chloroethoxy)borazine, $(HNBOCH_2CH_2Cl)_3$ was prepared by Niedenzu, Dawson, and George.[8]

No definitive studies had been reported on the synthesis and properties of borazine derivatives where a perfluoroalkyl group was bonded to either boron or nitrogen at the time this work was started. Since then Gutmann and his co-workers have prepared a series of N-fluoroalkylborazines and B-fluoroarylborazines.[9] Stafford and Stone,[10] however, had described the preparation and certain properties of perfluorovinylborane compounds.

These investigators had observed that organoboron compounds, having halogen atoms in the organo groups bonded to boron, readily decompose to form the more stable boron trihalides. The perfluorovinyl boron compounds, notably trisperfluorovinylborane, decomposed to perfluorovinyldifluoroborane and boron trifluoride on heating to 100° for 5 hr.

It was expected that a perfluorovinyl group bonded to a boron of a six-membered boron–nitrogen ring system would comprise a more stable system with

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[1] Presented at the 3rd International Symposium on Fluorine Chemistry, Aug 30–Sept 2, 1965, Munich, Germany.

[2] C. A. Brown and A. W. Laubengayer, *J. Am. Chem. Soc.*, **77**, 3699 (1955).

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[6] H. Noeth, *Z. Naturforsch*, **16b**, 619 (1961).

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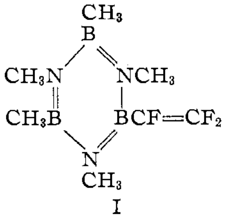
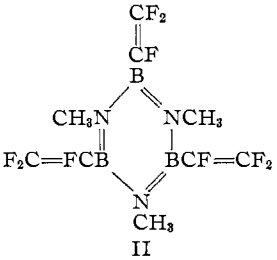
[10] S. L. Stafford and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6238 (1960).

respect to hydrolysis and thermal decomposition than the perfluorovinylborane described by Stafford and Stone. In addition, polyfunctional perfluorovinyl borazines appeared to be attractive monomers for synthesis of thermally stable polymers. We therefore selected for synthesis two borazine derivatives, B,B′-dimethyl-B″-perfluorovinyl-N,N′,N″-trimethylborazine, I, and B,B′,B″-tris(perfluorovinyl)-N,N′-N″-trimethylborazine, II, for thermal stability and hydrolytic stability studies. These structures are


I


II

We were successful in the preparation of these two perfluorovinylborazines. These derivatives are hydrolytically unstable at 25° in moist air but they are stable to temperatures exceeding 300° in the absence of water.

Also, since the completion of our work, Massey and Park[11] prepared B-tris(pentafluorophenyl)borazine, $(C_6H_5)_3B_3N_3H_3$, by treating B-trichloroborazine with either pentafluorophenyllithium or pentafluorophenylmagnesium bromide in ether.

In agreement with our findings that a perfluorocarbon group bonded to boron of a six-membered B–N ring is more stable than such a group bonded to boron in a borane, these investigations observed that B-tris(perfluorophenyl)borazine is stable above 200°.

Experimental Section

(1) **Preparation of B,B′-Dimethyl-B″-perfluorovinyl-N,N′,-N″-trimethylborazine.**—The reaction sequence shown below was utilized to prepare the selected borazine derivative I.

$3CH_3NH_2\cdot HCl + 3NaBH_4 \longrightarrow (CH_3NBH)_3 + 9H_2 + 3NaCl$[12]

$(CH_3NBH)_3 + 2CH_3MgI \longrightarrow (CH_3N)_3(BCH_3)_2BH + 2MgHI$[13]

$(CH_3N)_3(BCH_3)_2BH + HCl \longrightarrow (CH_3N)_3(BCH_3)_2BCl + H_2$[14]

$BrCF{=}CF_2 + Li(CH_2)_3CH_3 \longrightarrow LiCF{=}CF_2 + Br(CH_2)_3CH_3$[15]

$(CH_3N)_3(BCH_3)_2BCl + LiCF{=}CF_2 \longrightarrow (CH_3N)_3(BCH_3)_2BCF{=}CF_2 + LiCl$

The last two steps represent an adaptation of the use of the reagent fluorovinyllithium described by Tarrant.[15]

In a typical preparation, a four-neck, 500-ml, round-bottom Pyrex flask, two 125-ml addition funnels, and one 300-ml cold finger condenser were dried in a vacuum oven. The apparatus was assembled so that the condenser vented to a line equipped for vacuum or the addition of dry nitrogen to the reactor system. The reactor and attached apparatus were then evacuated and filled to atmospheric pressure with dry nitrogen gas. Fifteen milliliters of dry diethyl ether was placed in the reactor with a Teflon-coated magnetic stirring bar. A Dry Ice–acetone bath (−78°) was placed around the reactor and the cold finger condenser was cooled to −78° with a Dry Ice–acetone mixture. The reactor was then evacuated to about 200 mm and 1.43 g (89 mmoles) of perfluorovinyl bromide was condensed into the reactor. The reactor pressure was then increased to 760 mm with dry nitrogen and the reactor contents were stirred vigorously at −78°.

Methyllithium (1.3 g, 5.9 mmoles) dissolved in 15 ml of dry diethyl ether was placed in one addition funnel attached to the reactor. B-Chloro-B′,B″-dimethyl-N,N′,N″-trimethylborazine (11 g, 5.9 mmoles) dissolved in 15 ml of dry diethyl ether was placed in the second addition funnel.

While the reactor was cooled to −78°, 5 ml of the methyllithium solution was added to the reactor followed 30 sec later by the addition of 5 ml of the B-chloro-B′,B″-dimethyl-N,N′,-N″-trimethylborazine–ether solution. The reactor contents were stirred vigorously for 5 min. This addition sequence was repeated until all of the reactants were added.

The reaction mixture was then stirred at −78° for an additional 1.5 hr and then warmed slowly over a period of 3.5 hr to 25°. The reactor contents were filtered in a nitrogen drybox and the solid was identified as lithium chloride by X-ray powder pattern. The filtrate was placed in a 200-ml round-bottom Pyrex flask and the ether was removed at reduced pressure leaving a dark brown solid wetted with a high-boiling liquid. This high-boiling liquid was vaporized at 0.03 mm and 150° and the vapors condensed in a second 100-ml round-bottom flask cooled to about −78°. About 2 ml of a clear, colorless liquid was obtained.

This liquid was then fractionated on an F & M Model 500 vapor fractometer with a 2-m $^3/_{16}$-in. diameter aluminum column packed with Carbowax 20M on Chromosorb W, 80–100 mesh. The temperature was programmed from 60 to 125° at 8° min. The purified product was identified as B,B′-dimethyl-B″-perfluorovinyl-N,N′,N″-trimethylborazine by infrared spectrophotometry, mass spectrometry, and element analysis.

The infrared spectrum was obtained as a thin film between sodium chloride plates using a Perkin-Elmer Model 137 spectrophotometer. The vibrational frequencies (cm^{-1}) of compound I, B,B′-dimethyl-B″-perfluorovinyl-N,N′,N″-trimethylborazine, are tabulated as: 2941 (m), C–H str; 1740 (ms), C=C str, 1479 (vs), asym CH_3 def; 1450 (vs), B–N str; 1400 (vs), sym CH_3 def; 1316 (w), 1282 (s), CF-str; 1220 (m), 1190 (w), 1136 (m), 1099 (ms), 1042 (s), 1020 (w), 980 (s), N–CH_3 def; 885 (m), B–CH_3 def; 835 (w), 675 (m), B–N def.

Mass spectrometric analysis of the compound showed major fragments postulated for the structure B,B′-dimethyl,B″-perfluorovinyl-N,N′,N″-trimethylborazine as well as a parent species *m/e* 231 (mol wt 231).

The element analysis was consistent with the theoretical values. *Anal.* Calcd: B, 14.06; N, 18.22; C, 36.44; F, 24.71; H, 6.57. Found: B, 13.96; N, 18.22; C, 36.42; F, 25.25; H, 6.67.

The product is a colorless liquid at 25° with an extrapolated boiling point of 685°. The temperatures and vapor pressures are: 1.5°, 3.7 mm; 28.5°, 6.7 mm; 42.6°, 9.3 mm; and 50.7°, 11.8 mm.

The vapor pressure in the range 1.5–50.7° can be expressed by

$$\log P_{\text{mm}} = 3.8135 - \frac{894.1}{T(°\text{K})}$$

The compound melts at 7° and has a specific gravity of 1.03 at 34.5°. It hydrolyzes readily in moist air, but it is stable indefinitely in the absence of water at 25°.

This compound is thermally stable to approximately 370°. Above this temperature, slow decomposition occurs with the evolution of methane and hydrogen.

(2) **B,B′,B″-Tris(perfluorovinyl)-N,N′,N″-trimethylborazine.**—The polyfunctional B,B′,B″-tris(perfluorovinyl)-N,N′,N″-trimethylborazine derivative II was prepared by a sequence of re-

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[11] A. G. Massey and A. J. Park, *J. Organometal. Chem.* (Amsterdam), **2**, 461 (1964).

[12] D. T. Haworth and T. F. Hohnstedt, *Chem. Ind.* (London), 559 (1960).

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[14] R. I. Wagner and J. F. Bradford, *Inorg. Chem.*, **1**, 93 (1962).

[15] P. Tarrant, P. Johncock, and J. Savory, Preprints of Papers, 2nd International Symposium on Fluorine Chemistry, Estes Park, Colo., July 17-20, 1962.

actions similar to that employed for the preparation of the mono derivative

$$3CH_3NH_2\cdot HCl + 3BCl_3 \longrightarrow (CH_3NBCl)_3 + 9HCl^{16}$$

$$BrCF{=}CF_2 + Li(CH_2)_3CH_3 \longrightarrow LiCF{=}CF_2 + Br(CH_2)_3CH_3{}^{15}$$

$$(CH_3NBCl)_3 + 3LiCF{=}CF_2 \longrightarrow (CH_3NBCF{=}CF_2)_3 + 3LiCl$$

The apparatus and procedure for the preparation of this compound were identical with the procedure used for the preparation of B,B′-dimethyl-B″-perfluorovinyl-N,N′,N″ trimethylborazine. Three grams of B-trichloro-N-trimethylborazine, 0.87 g of methyllithium, and 7.0 g of perfluorovinyl bromide yielded 2 ml of pale yellow liquid. This liquid was then purified by vpc.

The purified product was identified by infrared spectrophotometry, mass spectrometric analysis, nuclear magnetic resonance, and element analysis as B,B′,B″ tris(perfluorovinyl)-N,N′,N″-trimethylborazine.

The observed vibrational frequencies of B,B′,B″-tris(perfluorovinyl)-N,N′,N″-trimethylborazine are: 2941 (m), C–H str; 1740 (s), C=C str; 1479 (vs), asym CH_3 def; 1450 (vs), B–N str; 1400 (vs), sym CH_3 def; 1316 (sh), 1282 (vs), 1176 (m), 1099 (ms), 1042 (s), 950 (s), N–CH_3 def; 735 (ms), B–N def; 725 (ms), B–N def.

The mass spectrometric analysis showed a molecular ion at m/e 363. The isotope ratios indicated that the compound contains three boron atoms and no chlorine. The mass fragmentation pattern was consistent with the postulated structure.

The element analysis is also consistent with the calculated values. *Anal.* Calcd: B, 8.94; N, 11.59; C, 29.81; F, 47.15; H, 2.51. Found: B, 8.2; N, 11.15; C, 29.32; F, 47.30; H, 2.89.

The ^1H nmr spectrum contained only one broad peak at 3.28 ppm. This is compatible with methyl bonded to a nitrogen atom. Methyl bonded to a boron atom should give resonance at higher field.

The ^{19}F spectrum contained three peaks of equal intensity: A, +95.7 ppm; B, +117.2 ppm; C, +195.3 ppm. The coupling constants for J_{ab}, J_{ac}, and J_{bc} were found to be 72.7, 23.7, and 115.8 Hz, respectively. These data support the presence of the perfluorovinyl group[17] and further indicate that all such groups are equivalent.

The ^{11}B spectrum contained one very broad peak (about 1000 Hz wide) around −18 ppm. This broadness could arise either from a large quadrupole coupling constant or from boron–nitrogen coupling.

All spectra were determined with a Varian HR-60 spectrometer. The ^1H spectrum was recorded at 60 MHz and referenced to tetramethylsilane, the ^{19}F at 56.4 MHz and referenced to $CFCl_3$, and the ^{11}B at 19.3 MHz and referenced to external boron trifluoride etherate.

B,B′,B″-Tris(perfluorovinyl)-N,N′,N″-trimethylborazine hydrolyzes readily in moist air but is thermally stable to temperatures exceeding 300°. The product melts at −50° and the extrapolated boiling point is 526°. The temperatures and vapor pressures are: 28.2°, 5.00 mm; 40.2°, 6.90 mm; 51.5°, 10.10 mm; 61.2°, 14.85 mm; and 71.1°, 22.00 mm.

The vapor pressure between 71.1 and 28.2° can be expressed by

$$\log P_{\mathrm{mm}} = 5.865 - \frac{1571}{T(^\circ\mathrm{K})}$$

This work demonstrates that perfluoro groups can be bonded to the boron atoms of a borazine ring and the resulting configurations are thermally stable to temperatures exceeding 300°.

In contrast to the mono-, bis-, and trisperfluorovinylboranes described by Stafford and Stone[10] which decompose readily to liberate boron trifluoride, the perfluorovinylborazines are considerably more stable thermally, undoubtedly owing to the contributions of the B–N ring. When a sample of B,B′-dimethyl-B″-perfluorovinyl-N,N′,N″-trimethylborazine purified by vapor phase chromatography was heated to 482° for 2 hr, the gaseous decomposition products consisted of methane and hydrogen; there was no evidence of boron trifluoride.

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CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC AND
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Dimorphism of Rare Earth Disilicides

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The preparation and crystal structures of the rare earth disilicides has been the subject of a number of works.[1–4] The preparation of these compounds was carried out by direct reaction of the two metals in the proper atomic ratio, or by silicon reduction of the metal oxides.

In relation to their crystal structures, rare earth disilicides can be classified into three structure types: $ThSi_2$-type tetragonal form (La–Pr, Eu), a slightly distorted orthorhombic version of the $ThSi_2$ structure (Nd–Ho, α-Y), and AlB_2-type hexagonal form (Er–Lu, β-Y).

Studies of the stoichiometric composition of the rare earth disilicides have shown deficiency of silicon in the La–Ho series ($GeSi_{1.4}$). In the case of the hexagonal disilicides, the metal : silicon ratio for the ytterbium compound has been found to be 1:2.

The polymorphism of the La–Dy disilicide was studied by Perri, *et al.*[5] High-temperature X-ray study of these compounds has shown transformation of the orthorhombic disilicides to tetragonal form in the temperature range 400–600°. In those cases when the tetragonal form is the stable one at room temperature, the orthorhombic version was obtained below room temperature (−120 to 150°).

Dimorphism was observed in the case of YSi_2.[3] This compound, when prepared at 1100°, crystallizes in the AlB_2-type structure and by heating to 1500° changes to the orthorhombic form. Similar dimorphism has been observed for $ThSi_2$[6] and USi_2.[7]

A new method of preparation of the rare earth disilicides was devised by the present authors.[8] In this

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