was removed through a −196° U trap, by an automatic Sprengel pump,[5] and measured. The remaining mixture was subjected to high-vacuum fractional condensation (using U traps at −78, −17, and 0°), for isolation of the main products and remaining reactants. The following reaction balance (with quantities in millimoles) summarizes the results

$$\begin{array}{ccccccc} \mathrm{CoNO(CO)_3} & + & \mathrm{(CF_3)_3P} & \longrightarrow & \mathrm{CO} & + & \mathrm{(CF_3)_3PCoNO(CO)_2}\ + \\ 0.604 & & 2.30 & & 0.93 & & 0.24 \\ \underline{-0.024} & & \underline{-1.38} & & & & \\ 0.580 & & 0.92 & & & & \mathrm{[(CF_3)_3P]_2CoNOCO} \\ & & & & & & 0.34 \end{array}$$

The rate of the first-stage CO displacement was roughly indicated by the action of 0.410 mmol of $(CF_3)_3P$ upon 0.658 mmol of $CoNO(CO)_3$ in a sealed tube for 6 hr at 50°. The yield of $(CF_3)_3PCoNO(CO)_2$ was 0.218 mmol, and no $[(CF_3)_3P]_2CoNOCO$ could be detected. For a quantitative conversion of the 0.218-mmol product to the bis-phosphine complex, it was necessary to heat it for 12 hr at 102°, with 0.60 mmol of $(CF_3)_3P$.

Characterization.—The purity of each product was verified by its reasonable vapor tension curve (Tables I and II) and by its infrared and ^{19}F nmr spectra:

TABLE I

VOLATILITY OF $(CF_3)_3PCoNO(CO)_2$

$(\log P = 5.9542 + 1.75 \log T - 0.0045T - 2307/T)$

$(t_{760} = 122°$; Trouton Constant = 22.1 eu)

	Temp, °C						
	−17.4	−12.5	−3.1	11.8	16.0	18.2	20.6
P_{obsd}, mm	1.00	1.44	2.82	7.48	9.56	10.90	12.52
P_{calcd}, mm	1.00	1.44	2.82	7.44	9.58	10.90	12.52

TABLE II

VOLATILITY OF $[(CF_3)_3P]_2CoNOCO$

$(\log P = 6.6432 + 1.75 \log T - 0.0047T - 2772/T)$

$(t_{760} = 165°$; Trouton Constant = 23.0 eu)

	Temp, °C					
	7.4	10.3	15.4	17.0	21.0	27.0
P_{obsd}, mm	0.52	0.68	0.96	1.08	1.44	2.32[a]
P_{calcd}, mm	0.53	0.67	0.97	1.08	1.44	2.15

[a] High value due to incipient evolution of CO.

neither was appreciably contaminated by the other or by the reactants. With purity recognized, the quantitative synthesis and the vapor phase molecular weight results (381 and 590 *vs.* calcd 383 and 593, respectively) sufficed to prove the molecular formulas.

The Trinuclear Complex

The trimer $[(CF_3)_3PCoNOCO]_3$ was formed in yields representing about 3% of a sample of $(CF_3)_3PCoNO(CO)_3$, stored in a sealed tube for 3 weeks at 40°. The only liberated ligand was CO. Higher temperatures or longer times led to some removal of NO and $(CF_3)_3P$, with formation of gray insoluble material.

The dark brown product, soluble in various organic solvents, was analyzed in two ways: by direct thermal decomposition to liberate CO and NO (but not the phosphine ligand as such) and by the action of iodine at 150° to liberate the phosphine ligand. The evolution of CO and NO was completed by moderate heating, and then flame heating gave no more. Results: 7.6% CO, 8.1% NO, 68% $(CF_3)_3P$, and, by difference, 16% Co (calcd: 7.9, 8.5, 67, and 16.4%, respectively). The osmometric molecular weight result (in benzene) was 1057 (calcd, 1063).

The infrared spectrum of the trimer (in cyclohexane) showed very strong C–F stretching peaks at 1140 and 1166 cm^{-1}, with a strong satellite at 1093 cm^{-1}, as well as the previously mentioned C–O bridge and N–O terminal stretching bands. These 1860- and 1826-cm^{-1} peaks were fairly sharp despite possible solvent effects. The absence of a second C–O stretching mode is ascribed to the symmetric character of the $(CoCO)_3$ pattern, for which the in-phase (A_1) mode would be weak, or even infrared inactive if this pattern is planar. The N–O units are too far apart for splitting due to in-phase *vs.* out-of-phase modes to be observable.[6]

The ^{19}F nmr spectrum of the trimer showed the expected doublet (J_{FP} = 91.3 cps) at 59 ppm upfield of Cl_3CF. The peaks were not seriously broadened by the cobalt quadrupole. For such results, the substance must be diamagnetic (as expected for the proposed structure, with d^{10} cobalt), in contrast to the probably analogous $[(C_6H_5)_3PCoNO(CO)_2]_3$,[7] wherein the d^9 cobalt would have oxidation state +1.

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[5] B. Bartocha, W. A. G. Graham, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **6**, 119 (1958).

[6] Among numerous literature references relevant to this case, we mention the following: (a) F. A. Cotton, *Inorg. Chem.*, **3**, 300 (1964); (b) E. W. Abel and I. H. Sabherwal, *J. Organometal. Chem.* (Amsterdam), **10**, 491 (1967); (c) A. Jahr, *Z. Anorg. Allgem. Chem.*, **301**, 301 (1959).

[7] G. Pregaglia, A. Andreeta, G. Ferrari, and R. Ugo, *Chem. Commun.*, 590 (1969).

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Boron–Nitrogen Compounds. XXXI.[1,2] The Interaction of Boron Trihalides with Hexafluoroisopropylidenimine

BY KURT NIEDENZU, KENNETH E. BLICK,
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Received October 6, 1969

Boron–nitrogen compounds which are substituted with organofluorine derivatives are exceedingly rare. However, the recent discovery of hexafluoroisopropylidenimine[3] (hexafluoroacetone imine, $(CF_3)_2CNH$) and hexafluoro-2,2-propanediamine[3] ($(CF_3)_2C(NH_2)_2$) supplies two materials of potential value for the synthesis of fluorinated carbon–nitrogen–boron derivatives.

We have initiated an investigation of the borane chemistry of the two cited compounds and wish to report on the interaction of boron trihalides with hexafluoroisopropylidenimine.

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[1] Part XXX: K. Niedenzu, C. D. Miller, and S. L. Smith, *Z. Anorg. Allgem. Chem.*, in press.

[2] Supported by U. S. Department of Defense, Department of the Army, Project Themis Grant DAAB 07-69-C0366, administered by the U. S. Army Electronics Command, Fort Monmouth, N. J.

[3] W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

The reaction of boron trifluoride with $(CF_3)_2CNH$ has been described to yield a solid material, probably the 1:1 adduct.[3] In contrast, BCl_3 and BBr_3 interact readily with $(CF_3)_2CNH$ by addition of the boron trihalide across the CN double bond of the imine (eq 1). Since compounds of type I feature reactive sites at a

$$BX_3 + (CF_3)_2CNH \longrightarrow \underset{\textstyle I}{(CF_3)_2CXNHBX_2} \qquad (1)$$

carbon atom and at the boron atom they may be of particular interest for subsequent reactions leading to either heterocyclic or polymeric boron–nitrogen–carbon systems.

Experimental Section

Hexafluoroisopropylidenimine was prepared by the literature method.[3] Boron trichloride was purified commercial grade (Matheson Gas Co.) and boron tribromide was supplied by Columbia Organic Chemicals Co., Inc., Columbia, S. C.

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Mass spectral data were supplied by the University of Kentucky Mass Spectroscopy Center and were recorded with a Hitachi-Perkin-Elmer double focusing mass spectrometer, Model RMU-6E. Infrared spectra in the 4000–400-cm^{-1} range were recorded with a Perkin-Elmer Model 337 spectrophotometer utilizing a gas cell of 10-cm path length, equipped with KBr windows. The spectra were obtained through the courtesy of Dr. E. B. Bradley, Department of Electrical Engineering, University of Kentucky.

1,1,1,3,3,3-Hexafluoro-2-chloroisopropylaminodichloroborane, $(CF_3)_2CClNHBCl_2$.—A three-necked flask equipped with a Dry Ice condenser was cooled in an ice–salt bath and was charged with boron trichloride. An equimolar amount of hexafluoroisopropylidenimine was added slowly while a temperature of −15° was maintained in the reaction vessel. The liquid reaction product was warmed slowly to room temperature and was distilled in inert atmosphere to give a nearly quantitative yield of $(CF_3)_2CClNHBCl_2$, bp 105°. *Anal.* Calcd for $C_3HF_6Cl_3NB$: C, 12.8; H, 0.36; F, 40.4; Cl, 37.7; B, 3.8; N, 5.0; mol wt, 282.2. Found: C, 12.7; H, 0.4; F, 39.8; Cl, 37.6; B, 4.2; N, 4.95.

In a similar fashion equimolar amounts of boron tribromide and hexafluoroisopropylidenimine were allowed to react to give $(CF_3)_2CBrNHBBr_2$, bp 38–40° (0.1 mm). *Anal.* Calcd for $C_3HF_6Br_3NB$: C, 8.65; H, 0.24; F, 27.4; Br, 57.6; B, 2.6; N, 3.4; mol wt, 416.6. Found: B, 2.2; mol wt (by mass spectroscopy), 418.

Discussion

The addition of boron trichloride and boron tribromide across the CN double bond of hexafluoroisopropylidenimine is to be contrasted with the interaction of BF_3 and $(CF_3)_2CNH$. In the latter case, the (solid) adduct $(CF_3)_2CNH \cdot BF_3$ is obtained.[3] The difference in the nature of products obtained from the interaction of hexafluoroisopropylidenimine with boron trihalides may already be deduced from their physical constants. Moreover, mass spectra of the boron trichloride and boron tribromide derivatives exhibit a very similar fragmentation pattern with appropriate parent ions. In contrast, the mass spectrum of the $(CF_3)_2CNH \cdot BF_3$ exhibits parent ions for both, $(CF_3)_2CNH$ and BF_3, and the fragmentation pattern can be superimposed on those of the two pure materials. These observations suggest weak bonding between the imine and boron trifluoride and refute the supposition of the BF_3 adding across the CN double bond of the imine.

Table I

Gas Phase Infrared Spectra[a]

$(CF_3)_2C{=}NH$	$(CF_3)_2CClNHBCl_2$	$(CF_3)_2CBrNHBBr_2$
		3452 sh
3306 wm	3408 wm	3428 wm
	1900 w	1870 vw
	1825 vw	1800 vw
1701 w		
	1503 sh	1482 sh
	1495 ms	1475 ms
1391 ms		
	1373 w	1360 w
1339 vw	1320 vw	1340 wm
	1308 sh	1310 wm
	1290 s	1292 s
1260 vs	1254 m	1260 sh
1244 sh	1229 ms	1248 m
1209 s	1208 sh	1212 ms
1196 vs		
	1192 sh	1152 sh
	1161 m	1141 wm
1124 w		
	1114 m	1095 sh
		1089 mw
1076 vw		
	1035 vw	994 vw
	992 s	
973 vw		
	952 vs	952 m
929 s		
		909 mw
	863 vw	848 vw
	832 w	832 w
	796 vw	808 wm
774 vw	780 vw	769 vw
734 vw	748 vw	740 w
709 m	712 wm	708 m
	660 w	
		630 wm
	619 vw	
	582 vw	580 w
	540 w	
		518 wm
500 sh		
485 wm	482 w	
	472 vw	
	462 wm	

[a] w, weak; m, medium; s, strong; v, very; sh, shoulder; frequencies in cm^{-1}.

The proposed structure I for the products of the interactions of $(CF_3)_2CNH$ with BCl_3 and BBr_3 rests primarily on spectroscopic data as listed in Table I. The vibrational spectra of the borane derivatives can be evaluated by comparing them with the vibrational spectrum of hexafluoroisopropylidenimine. (A complete discussion of the latter will be reported elsewhere.[4]) The spectra of the two boranes reveal the absence of any CN double bond stretch in the 1700 cm^{-1} region. Moreover, strong absorptions near 1495 cm^{-1} and 1475 cm^{-1}, respectively, are readily assigned to B–N valence vibrations particularly since the imine does not exhibit any absorption whatsoever in this region. In the spectra of both boranes NH deformational modes are observed near 1290 cm^{-1}. Lack of sufficient data delays a more complete assignment of the spectra of the boranes.

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(4) K. Niedenzu and coworkers, to be published.

In order to substantiate structure I, a quantity of 1,1,1,3,3,3-hexafluoro-2-chloroisopropylaminodichloroborane was hydrolyzed (eq 2). The resultant amine II

$$(CF_3)_2CClNHBCl_2 + 3H_2O \longrightarrow \underset{\text{II}}{(CF_3)_2CClNH_2} + 2HCl + H_3BO_3 \quad (2)$$

is a solid at room temperature which is quite unstable and readily decomposes to hexafluoroisopropylidenimine and HCl. The structure of II was ascertained by the presence of two NH stretching modes in the infrared spectrum of the compound which were observed at 3140 and 3020 cm^{-1}, respectively. These frequencies are substantially lower than those observed in the spectrum of $(CF_3)_2C(NH_2)_2$.[4]

Compounds of type I fume strongly on contact with air, react violently with water, and are extremely corrosive. However, in inert atmosphere, they can be stored for prolonged periods of time, and they seem to be thermally stable since they can be distilled without decomposition.

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Boron-Nitrogen Compounds. XXXII.[1] 2-Amino-1,3,2-diazaboracycloalkanes

BY KURT NIEDENZU, PAUL J. BUSSE, AND CLIFFORD D. MILLER

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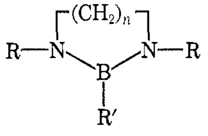
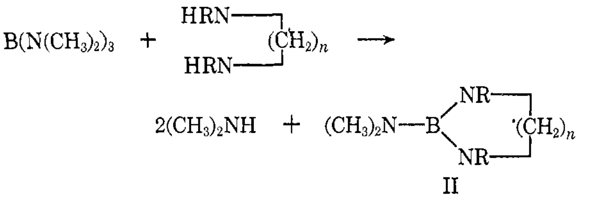
The first synthesis of a σ-bonded boron-nitrogen-carbon heterocycle was reported by Goubeau and Zappel in 1955.[2] Since that date several preparative routes have been explored to provide access to the 1,3,2-diazaboracycloalkane system, I.[3] However, with the exception of a few compounds, only those derivatives of I in which R′ = alkyl or aryl have been described



I

In particular, 1,3,2-diazaboracycloalkanes with an exocyclic boron-nitrogen bond are unknown. Since B-N groups are very reactive, 2-amino-1,3,2-diazaboracycloalkanes may be potential precursors for the synthesis of a variety of boron-substituted 1,3,2-diazaboracycloalkanes.

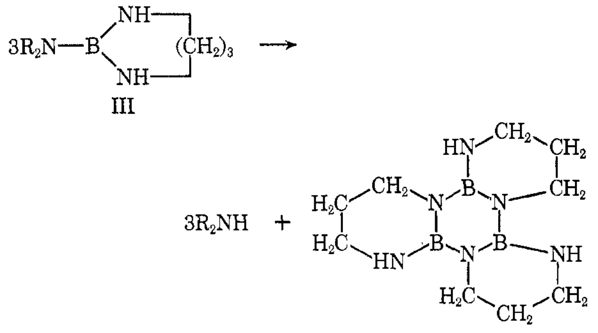
The present study reports on the synthesis of 2-amino-1,3,2-diazaboracycloalkanes. These compounds are readily produced through a transamination reaction between tris(dialkylamino)boranes such as $B[N(CH_3)_2]_3$ and aliphatic N,N′-disubstituted α,ω-diamines in inert organic solvents (eq 1). In order



II (1)

to obtain reasonable yields it is necessary to reflux the reaction mixture for several hours.

The utilization of ethylenediamine in an analogous reaction with tris(dimethylamino)borane did not yield the desired product II, R = H, n = 2. Rather, a polymeric material was obtained which could not be purified. Impure 2-dimethylamino-1,3,2-diazaboracyclohexane (III) was obtained on refluxing tris(dimethylamino)borane with 1,3-diaminopropane in ether.[4] On attempts to purify the product by distillation additional elimination of dimethylamine and trimerization occur yielding the borazine derivative IV (eq 2).



III

IV

(2)

Experimental Section[5]

Tris(dimethylamino)borane was prepared by a literature procedure.[6] All diamines were obtained from the Ames Laboratories, Milford, Conn.; they were dried over potassium hydroxide and were used without additional purification. Solvents were dried over metallic sodium.

1,3-Dimethyl-2-dimethylaminodiazaboracyclohexane (I, **R = CH$_3$, R′ = N(CH$_3$)$_2$, n = 3**) (Typical Experiment).—A solution of 51 g (0.5 mol) of N,N′-dimethyl-1,3-diaminopropane in 600 ml of pentane was added with stirring to a solution of 48.9 g (0.5 mol) of tris(dimethylamino)borane in 600 ml of pentane. The mixture was refluxed for about 5 hr. Pentane was stripped off at normal pressure and the residue was distilled under reduced pressure to yield 56.5 g (73%) of 1,3-dimethyl-2-dimethylaminodiazaboracyclohexane, bp 50° (2 mm). *Anal.* Calcd for $BN_3C_7H_{18}$: B, 7.0; N, 27.1; C, 54.2; H, 11.7; mol wt, 155.0. Found: B, 6.9; N, 27.3; C, 53.9; H, 11.6; mol wt (by mass spectroscopy and cryscopy in benzene), 155.

1,3-Dimethyl-2-dimethylaminodiazaboracyclopentane, bp 33–34° (2 mm), was obtained in an analogous procedure in 52% yield. Pentane was used as a solvent. *Anal.* Calcd for $BN_3C_6H_{16}$: B, 7.7; N, 29.8; C, 51.1; H, 11.4; mol wt, 141.0. Found: B, 7.5; N, 29.9; C, 50.8; H, 11.3; mol wt (by mass spectroscopy and cryoscopy in benzene), 141.

1,3-Diethyl-2-dimethylaminodiazaboracyclohexane, bp 68° (6 mm), was obtained in an analogous procedure using n-hexane as solvent in 37% yield. *Anal.* Calcd for $BN_3C_9H_{22}$: B, 5.9;

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[1] Part XXXI: K. Niedenzu, K. E. Blick, and C. D. Miller, *Inorg. Chem.*, **9**, 975 (1970).

[2] J. Goubeau and A. Zappel, *Z. Anorg. Allgem. Chem.*, **279**, 38 (1955).

[3] K. Niedenzu, *Allgem. Prakt. Chem.*, **17**, 596 (1966).

[4] K. Niedenzu and P. Fritz, *Z. Anorg. Allgem. Chem.*, **340**, 329 (1965).

[5] Infrared spectra of the materials were recorded on a Perkin-Elmer Model 621 spectrophotometer using cesium iodide windows. The instrument was purchased with funds made available by the University of Kentucky Major Research Equipment Committee. Analyses were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[6] K. Niedenzu and J. W. Dawson, *Inorg. Syn.*, **10**, 135 (1967).