Reaction of Substituted Lithium Amides with Diborane

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Abstract: The stepwise addition of diborane to diethyl ether solutions of *N*-alkyl-substituted lithium amides (LiNHR, R = CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9, *sec*-C_4H_9, *tert*-C_4H_9, and *n*-C_5H_{11}; $LiNR_2'$, R′ = CH_3, C_2H_5, *n*-C_3H_7, and *i*-C_3H_7) at room temperature has been studied. The course of the reactions has been monitored by boron-11 nmr; in almost all cases species so detected have been isolated and identified. When the amide is still in excess, the first products to be distinguished are lithium borohydride and a tri(amino)borane. Addition of more diborane ultimately produces a μ-aminodiborane and an aminoborane; usually a di(amino)borane intermediate can be observed and isolated. When lithium methyl- or ethylamide reacts with diborane at room temperature, the major products are lithium borohydride and the appropriate *N*-trialkylborazine and monoalkylamine–borane. At 0° or below, these systems react normally to produce the μ-aminodiboranes in good yield. The physical and spectral properties of a number of new μ-aminodiboranes have been determined.

Our investigation of the reaction between lithium dimethylphosphide and diborane[1] (eq 1) has led

$$LiP(CH_3)_2 + B_2H_6 \longrightarrow Li(CH_3)_2P(BH_3)_2 \qquad (1)$$

us to study the behavior of *N*-alkyl-substituted lithium amides with diborane under similar conditions. The examination of this system has been discouraged by the report of Schaeffer and Basile[2] that lithium amide and diborane react in diethyl ether to form only lithium borohydride and polymeric aminoborane (eq 2). We

$$LiNH_2 + B_2H_6 \longrightarrow LiBH_4 + (^1/x)(H_2NBH_2)_x \qquad (2)$$

find reaction 2 to be unique; the presence of *N*-alkyl substituents alters the course of the process such that the major products are lithium borohydride and a μ-aminodiborane. The description of our investigation, the discussion of our results, and the characterization of a number of new μ-aminodiboranes are the subjects of this paper.

Experimental Section

General. Standard high-vacuum and inert-atmosphere techniques were used throughout this investigation. Diethyl ether and benzene were stored over lithium aluminum hydride in evacuated bulbs and, when needed, were condensed directly into the reaction vessel. Boron-11 nmr spectra were obtained using a Varian HA-100 spectrometer operating at 32.1 MHz; chemical shifts are in parts per million relative to diethyl ether–boron trifluoride. Reactions monitored by boron-11 nmr were performed in vessels described elsewhere.[3] Infrared spectra were obtained using Perkin-Elmer 137 and 337 spectrophotometers; gas samples were contained in 5- or 10-cm path-length cells with sodium chloride windows. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6M spectrometer

Diborane was prepared by treating sodium borohydride with warm polyphosphoric acid. Mono- and dimethylamine were purified on the vacuum line after preparation from the reaction of their hydrochlorides with concentrated aqueous sodium hydroxide. Reagent grade ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, *sec*-butyl-, *tert*-butyl-, *n*-pentyl-, diethyl-, di-*n*-propyl-, and diisopropylamine were obtained from commercial sources; before use, samples were dried with calcium hydride and purified on the vacuum line. Lithium wire containing 1% sodium (Alfa Inorganics, Inc.) was used with bromobenzene in diethyl ether to prepare phenyllithium.[4] Lithium *n*-propylamide, di-*n*-propylamide, and diisopropylamide were prepared by the reaction of phenyllithium with the appropriate amine in diethyl ether.[5,6] Lithium methylamide, ethylamide, isopropylamide, *n*-butylamide, *sec*-butylamide, *tert*-butylamide, *n*-pentylamide, dimethylamide, and diethylamide were prepared by the direct sealed-tube reaction between lithium wire and the respective amine in benzene.[5–7] Diethylamine–borane was prepared by the method of Nainan and Ryschkewitsch.[8] Diethylaminoborane dimer was prepared by the sealed-tube pyrolysis of diethylamine–borane.[9] Tri(*sec*-butylamino)borane was prepared from the reaction of boron trichloride and excess *sec*-butylamine at −78° in benzene.[10]

Reaction of Lithium Diethylamide with Diborane. With the exception of lithium methyl- and ethylamide, all systems behaved similarly; the detailed study of the lithium diethylamide–diborane system outlined here is typical. Two essentially parallel experiments are described. In the first, progress of the reaction was monitored by boron-11 nmr as diborane was added to the lithium diethylamide solution. In the second, the conditions of the nmr study were duplicated and the products were separated on the vacuum line and identified by their infrared and mass spectra.

A 1.12-mmol sample of diborane was added to a solution of 2.14 mmol of lithium diethylamide in 1 ml of diethyl ether in an nmr reaction vessel. The nmr spectrum of this solution is shown in Figure 1; isolation and identification of the products confirmed the assignment of the observed resonances to tris(diethylamino)borane (only the high-field side band of the broad singlet at −28.7 ppm is shown in Figure 1), μ-diethylaminodiborane (triplet, 19.0 ppm), and lithium borohydride (quintet, 38.0 ppm). Occasionally at this point a trace of diethylamine–borane was also isolated. Since this facet of the experiment was not reproducible, the origin of the compound is believed to stem from the interaction of diborane with a small amount of diethylamine either retained by the lithium diethylamide after its preparation or formed by slight hydrolysis of the lithium diethylamide during handling or storage. The latter is less likely, since inert atmosphere techniques were employed throughout this investigation. Addition of another 1.12 mmol of diborane to the nmr vessel produced the solution giving the nmr spectrum shown in Figure 2). Isolation and characterization of the products in the separate parallel experiment confirmed the assignment of the resonances to tris(diethylamino)borane and bis(diethylamino-borane (only overlapping high-field side bands of broad signals at −32 ppm are shown in Figure 2), diethylaminoborane dimer (triplet, −1.6 ppm), μ-diethylaminodiborane (triplet of doublets, 19.0 ppm), and lithium borohydride (quintet, 38.2 ppm). The spectrum shown in Figure 3 resulted after the addition of a final 1.12 mmol of diborane to the nmr vessel. Separation of the products from the

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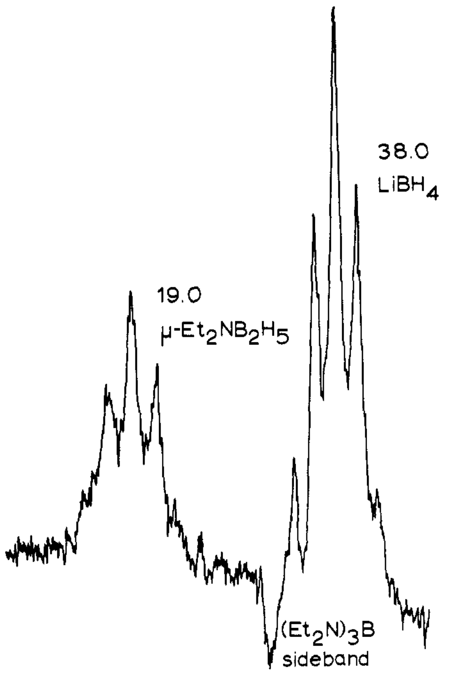

Figure 1. Boron-11 nmr spectrum of 2.14 mmol of $LiN(C_2H_5)_2$ and 1.12 mmol of B_2H_6 in $(C_2H_5)_2O$.

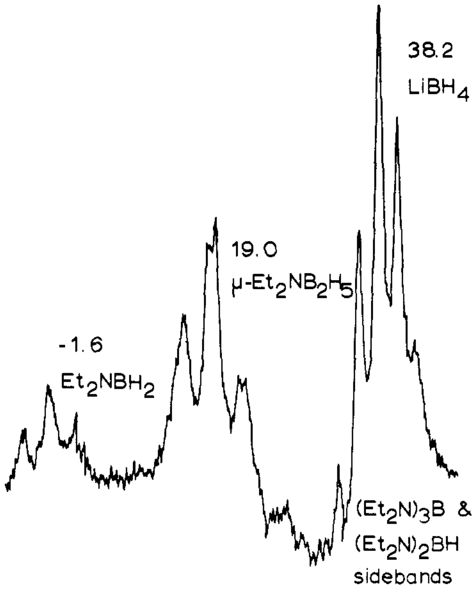

Figure 2. Boron-11 nmr spectrum of 2.14 mmol of $LiN(C_2H_5)_2$ and 2.24 mmol of B_2H_6 in $(C_2H_5)_2O$.

nmr reaction confirmed the assignment of the spectrum and produced the following: diethylaminoborane dimer, 0.025 g (0.15 mmol); μ-diethylaminodiborane, 1.81 mmol (85%); lithium borohydride, 2.10 mmol (by hydrolytic hydrogen); and diborane, 0.26 mmol, implying a net consumption of 3.10 mmol. The presence of the excess diborane caused the collapse of the borohydride quintet owing to rapid exchange.

Characterization of μ-Aminodiboranes. The yields (based on $LiNR_2$), boron-11 chemical shifts, infrared absorptions, and vapor pressure data are listed below. Nmr coupling constants are all J_{BH} = 130 Hz and J_{BHB} = 30 Hz within experimental error.

μ-*n*-$C_3H_7NHB_2H_5$: 50% yield; boron-11 nmr 23.2 ppm (neat liquid); ir 3400 (m), 2990 (vs), 2950 (sh s), 2880 (sh m), 2540 (vs), 1890 (m), 1625 (s), 1575 (w), 1450 (m), 1420 (m), 1380 (m), 1350 (m), 1290 (m), 1170 (vs), 1140 (m), 1050 (s), 950 (s), 830 (w), 700 (m); vapor pressure reported previously.[11]

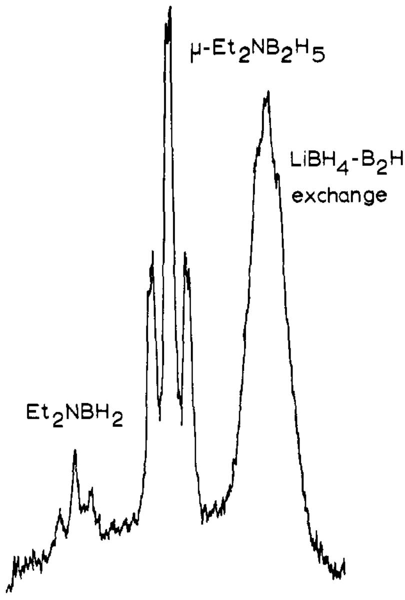

Figure 3. Boron-11 nmr spectrum of 2.14 mmol of $LiN(C_2H_5)_2$ and 3.36 mmol of B_2H_6 in $(C_2H_5)_2O$.

μ-*i*-$C_3H_7NHB_2H_5$: 80% yield; boron-11 nmr 24.5 ppm (neat liquid); ir 3390 (m), 2980 (vs), 2900 (sh s), 2870 (sh m), 2545 (vs), 2470 (vs), 2460 (w), 1890 (w), 1635 (s), 1580 (sh), 1470 (m), 1380 (m), 1320 (w), 1290 (w), 1170 (vs), 1080 (s), 1040 (m), 945 (s), 730 (w); vapor pressure $\log P_{mm} = 8.62 - 2065/T$, extrapolated bp 99°; T, °C, exptl (calcd) 0.0, 15.0 (13.8), 11.0, 25.0 (25.7), 15.0, 33.1 (33.2), 19.0, 37.2 (37.9), 24.0, 52.0 (52.5).

μ-*n*-$C_4H_9NHB_2H_5$: 60% yield; boron-11 nmr 22.5 ppm (diethyl ether); ir 3400 (w), 2960 (s), 2880 (m), 2800 (sh w), 2530 (vs), 2460 (s), 2280 (vw), 1970 (vw), 1890 (w), 1625 (s), 1575 (sh w), 1420 (m), 1340 (sh w), 1250 (m), 1180 (m), 1100 (m), 1050 (m), 950 (m), 920 (w), 870 (sh), 840 (m), 800 (m), 760 (w), 690 (w); vapor pressure $\log P_{mm} = 8.08 - 2058/T$, extrapolated bp 123°; T, °C, exptl (calcd) 20.5, 12.0 (11.8), 25.0, 14.6 (14.7), 30.0, 19.0 (19.0), 35.5, 26.6 (26.2), 42.7, 38.4 (38.1).

μ-*sec*-$C_4H_9NHB_2H_5$: 65% yield; boron-11 nmr 23.4 ppm (diethyl ether); ir 3390 (w), 2970 (vs), 2940 (sh m), 2890 (m), 2530 (vs), 2460 (s), 2330 (vw), 1910 (vw), 1880 (w), 1630 (s), 1580 (w), 1450 (m), 1380 (m), 1290 (vw), 1250 (vw), 1155 (vs), 1080 (vs), 1045 (s), 950 (s), 840 (vw), 725 (m); vapor pressure $\log P_{mm} = 8.07 - 2038/T$, extrapolated bp 119°; T, °C, exptl (calcd) 0.0, 4.7 (4.4), 18.0, 11.5 (11.9), 22.8, 15.0 (15.1), 29.0, 20.0 (20.1).

μ-*tert*-$C_4H_9NHB_2H_5$: 70% yield; boron-11 nmr 23.6 ppm (diethyl ether); ir 3380 (w), 2960 (s), 2900 (sh m), 2860 (sh w), 2530 (vs), 2470 (s), 2360 (sh w), 1870 (w), 1640 (sh w), 1625 (m), 1450 (w), 1370 (m), 1230 (m), 1185 (s), 1130 (w), 1068 (s), 950 (m), 800 (w), 725 (w); vapor pressure $\log P_{mm} = 7.69 - 1804/T$, extrapolated bp 102°; T, °C, exptl (calcd) 0.0, 12.3 (12.0), 23.0, 41.3 (40.8), 29.9, 55.0 (54.9), 35.0, 67.2 (67.5).

μ-*n*-$C_5H_{11}NHB_2H_5$: 50% yield; boron-11 nmr 22.2 ppm (diethyl ether); ir 3420 (vw), 2970 (sh m), 2940 (m), 2849 (m), 2870 (sh w), 2540 (s), 2470 (m), 1890 (vw), 1625 (m), 1465 (sh w), 1420 (w), 1380 (sh), 1170 (w), 1105 (w), 1045 (m), 935 (m), 800 (w); vapor pressure $\log P_{mm} = 7.71 - 2025/T$, extrapolated bp 145°; T, °C, exptl (calcd) 24.1, 8.2 (7.8), 30.3, 11.4 (11.5), 36.0, 15.0 (14.9), 41.0, 19.0 (18.6), 47.0, 24.0 (24.0).

μ-(*n*-$C_3H_7)_2NB_2H_5$: 50% yield; boron-11 nmr 18.6 ppm (neat liquid); ir 2977 (s), 2945 (sh m), 2880 (m), 2540 (vs), 2475 (s), 1880 (vw), 1640 (s), 1580 (w), 1470 (m), 1420 (m), 1380 (m), 1350 (m), 1190 (m), 1070 (s), 960 (s), 870 (vw); vapor pressure $\log P_{mm} = 7.71 - 2004/T$, extrapolated bp 143°; T, °C, exptl (calcd) 23.9, 8.2 (8.6), 30.7, 12.2 (12.3), 33.8, 14.3 (14.5), 42.0, 24.0 (24.0), 50.0, 31.0 (31.3).

μ-(*i*-$C_3H_7)_2NB_2H_5$: 70% yield; boron-11 nmr 21.0 ppm (neat liquid); ir 2985 (vs), 2945 (sh vs), 2885 (sh s), 2545 (vs), 2465 (s), 2400 (sh w), 1880 (vw), 1640 (m), 1470 (sh s), 1450 (s), 1325 (s), 1200 (vs), 1175 (sh), 1140 (m), 1105 (w), 1070 (m), 1040 (w), 985 (sh w), 945 (sh w), 910 (vw), 745 (w), 700 (w); vapor pressure $\log P_{mm} = 7.73 - 1972/T$, extrapolated bp 133°; T, °C, exptl (calcd) 24.0,

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[11] A. B. Burg and C. D. Good, *J. Inorg. Nucl. Chem.*, **2**, 237 (1956).

13.6 (13.2), 29.0, 16.8 (16.6), 31.0, 18.2 (18.2), 38.0, 25.6 (25.5), 49.0, 41.0 (40.8).

Reaction of Lithium Methylamide with Diborane. At ambient temperature the reaction of lithium ethyl- or methylamide with diborane differs from the above process; however, near 0° μ-aminodiboranes are produced in good yield. The lithium methylamide–diborane reaction is representative.

A stirred diethyl ether suspension of 0.0585 g (1.58 mmol) of the sparingly soluble lithium methylamide was treated with 1.80 mmol of diborane at room temperature for 3 hr. Vacuum-line separation of the products gave 0.20 mmol of diborane, 0.26 mmol of *N*-trimethylborazine, 0.80 mmol of methylamine–borane, 1.51 mmol of lithium borohydride (involatile residue by hydrolytic hydrogen), and a trace of μ-methylaminodiborane contaminated with diethyl ether (about 1% yield). Slightly more μ-ethylaminodiborane (10% yield) was recovered from the lithium ethylamide reaction.

In an experiment in which the temperature of the reaction vessel was maintained between 0 and 5°, a 0.044-g (1.20 mmol) sample of lithium methylamide reacting with 2.85 mmol of diborane in diethyl ether for 15 min gave the following products: 1.26 mmol of diborane (1.49 mmol consumed), 0.10 mmol of *N*-trimethylborazine, 0.30 mmol of methylamine–borane, 1.21 mmol of lithium borohydride (by hydrolytic hydrogen), and 0.47 mmol of μ-methylaminodiborane. In both experiments the *N*-trimethylborazine and methylamine–borane were isolated and weighed as a mixture; the proportions of the two were estimated from peak areas in the boron-11 nmr spectrum (benzene solution). Since the μ-methylaminodiborane was very difficult to separate from diethyl ether, the quantity produced was determined from the hydrogen evolved upon hydrolysis of the ether–μ-methylaminodiborane fraction.

Reaction of Diethylaminoborane with Diborane in Diethyl Ether. To determine whether diborane reacted with diethylaminoborane under the conditions of the above reactions, equal quantities of diborane and diethylaminoborane were allowed to interact in diethyl ether at room temperature for 30 min. Separation of the products resulted only in recovery of the starting materials, indicating no reaction had occurred.

Reaction of Tri(*sec*-butylamino)borane with Diborane. A solution of 1.0 mmol of tri(*sec*-butylamino)borane in 1 ml of diethyl ether in an nmr reaction vessel was treated with 1.0 mmol of diborane. The boron-11 nmr spectrum generally resembled that shown in Figure 2 with the exception of the absence of the borohydride quintet. Separation of the products confirmed the assignment of the spectrum by producing μ-*sec*-butylaminodiborane, tri(*sec*-butylamino)borane, di(*sec*-butylamino)borane, and trimeric *sec*-butylaminoborane.

Results and Discussion

The Course of the Reaction. Mono- and di-*N*-alkyl-substituted lithium amides react with excess diborane in diethyl ether according to eq 3, although the ratio of

$$3LiNR_2 + 4B_2H_6 \longrightarrow 2\mu\text{-}R_2NB_2H_5 + R_2NBH_2 + 3LiBH_4 \quad (3)$$

μ-aminodiborane to aminoborane is often significantly greater than 2:1. With the exception of lithium methyl- and ethylamide, discussed below, all reactions are complete within 30 min at room temperature, with μ-aminodiborane yields from 50 to 85%.

When diborane is added to the solution of lithium *N*-alkylamide, so that the latter is in excess, the first product that can be nmr detected and isolated is a tri(amino)borane (eq 4). The product distribution of

$$3LiNR_2 + 2B_2H_6 \longrightarrow B(NR_2)_3 + 3LiBH_4 \quad (4)$$

eq 4 is generally supported by relative nmr peak intensities. No aminoboranes are found at this point.

The next stages involve the reaction of diborane and the tri(amino)borane. The solvent-free behavior of tris(dimethylamino)borane and bis(dimethylamino)borane in the presence of diborane has been examined by Burg and Randolph,[12] who found that both compounds react readily below ambient temperature to produce a small quantity of μ-dimethylaminodiborane (compare with Figure 1) and a mixture of more complex intermediate species. Warming the latter with diborane resulted in quantitative conversion to μ-dimethylaminodiborane and some dimethylaminoborane.

Our work differs from the above in that only homogeneous solution reactions at room temperature in which the supply of diborane was controlled to observe intermediate species were studied. Under these conditions in many cases it was possible to detect, isolate, and identify a di(amino)borane formed through reaction 5. The action of more diborane upon the di(amino)borane is the final stage of the reaction, although often

$$(R_2N)_3B + B_2H_6 \longrightarrow \mu\text{-}R_2NB_2H_5 + (R_2N)_2BH \quad (5)$$

less aminoborane was found than predicted by eq 6.

$$(R_2N)_2BH + B_2H_6 \longrightarrow \mu\text{-}R_2NB_2H_5 + R_2NBH_2 \quad (6)$$

As expected, the aminoboranes are dimeric when formed from di-*N*-alkylamides and trimeric from mono-*N*-amides. As a check on our proposed sequence of reactions, we have demonstrated, using independently prepared tri(*sec*-butylamino)borane, that reactions 5 and 6 occur smoothly and quickly in diethyl ether at room temperature.

Burg and Randolph also found low aminoborane yields in their gas-phase studies,[12] but the results can be explained easily by their μ-dimethylaminodiborane synthesis (eq 7).[13] This process occurs too slowly in

$$2(CH_3)_2NBH_2 + B_2H_6 \longrightarrow 2\mu\text{-}(CH_3)_2NB_2H_5 \quad (7)$$

diethyl ether at room temperature to account for the aminoborane shortage in our experiments. The low rate at room temperature probably results from the dimeric or trimeric nature of the aminoboranes; in the gas phase at higher temperatures, a significant concentration of the more reactive monomer exists. If a monomeric aminoborane is produced by reaction 6, this species may have the opportunity to react with diborane before di- or trimerization occurs.

The Case of LiCH$_3$NH and LiC$_2$H$_5$NH. Near 0°, lithium methyl- and ethylamide react normally with diborane (eq 3); at room temperature, however, reaction 8 predominates. Assuming initial sequential for-

$$2LiRNH + 2B_2H_6 \longrightarrow (1/3)(RNBH)_3 + RNH_2\cdot BH_3 + 2LiBH_4 \quad (8)$$

mation of a tri- and di(amino)borane as outlined above, this deviation can be explained by the thermal instability of the di(amino)borane intermediate. Di(ethylamino)borane is known to decompose at room temperature in a manner approximating eq 9.[14] Di(methylamino)-

$$(C_2H_5NH)_2BH \longrightarrow C_2H_5NH_2 + (1/3)[C_2H_5NBH]_3 \quad (9)$$

borane might be expected to be less stable, and, indeed, information on the compound is not available. Since no intermediates were positively identified, it is impossible to say whether the tri(amino)borane is a precursor to the di(amino)borane. A process like reaction 10 could occur, followed by the decomposition of

$$2LiRNH + (3/2)B_2H_6 \longrightarrow (RNH)_2BH + 2LiBH_4 \quad (10)$$

the di(amino)borane (eq 9) and subsequently by the reaction of the amine with diborane to form the amine–borane. A related reaction involving several tri(alkyl-

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amino)boranes and boron trihalides has been reported by Greenwood, Hooton, and Walker (eq 11).[15] Intermediate formation of a di(alkylamino)boron halide was suggested.

$$2B(HNR)_3 + 4BX_3 \longrightarrow 3RNH_2BX_3 + [RNBX]_3 \quad (11)$$
$$R = CH_3C_2H_5, n\text{-}C_3H_7, sec\text{-}C_4H_9$$
$$X = Cl, F$$

Reactions of B_2H_6 with $LiNH_2$ and $LiP(CH_3)_2$. The reaction between diborane and lithium amide in diethyl ether (eq 2) is unique.[2] The precipitation of polymeric aminoborane probably eliminates the possibility of further reaction with diborane. In comparison, all intermediates in the *N*-alkylamide systems are ether soluble and labile, allowing ultimate formation of μ-aminodiboranes *via* reactions 4–6.

In complete contrast, the phosphorus analog of the amides, lithium dimethylphosphide, reacts quantitatively with diborane in diethyl ether without the formation of detectable intermediates to produce lithium bis(borane)dimethylphosphide(1−) (eq 1).[1] The crucial difference between the nitrogen and phosphorus systems is the π stabilization of all three-coordinate boron–nitrogen intermediates. Since boron–phosphorus π bonding is either very weak or nonexistent,[16] boron must remain four-coordinate in reaction 1 and give the bis(borane) adduct. The phosphorus analogs of the intermediates and products of reactions 4–6, monomeric phosphinoborane R_2PBH_2, di(phosphino)borane $(R_2P)_2BH$, and tri(phosphino)borane $(R_2P)_3B$ are unknown.[16]

In view of the low reactivity of polymeric dimethylphosphinoboranes,[17] it is at first surprising that no evidence for reaction 12 has been found. If this process requires the intermediate formation of monomeric dimethylphosphinoborane, it will be less favorable under mild conditions than simple adduct formation. The great resistance to ring opening and dissociation of dialkylphosphinoboranes may, in large part, result from the instability of the monomer.

$$LiP(CH_3)_2 + B_2H_6 \longrightarrow (1/n)[(CH_3)_2PBH_2]_n + LiBH_4 \quad (12)$$
$$n = 3, 4$$

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Reaction of Xenon with Dioxygenyl Tetrafluoroborate. Preparation of FXe–BF$_2$

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Abstract: A reaction between xenon and O_2BF_4 has been observed to liberate oxygen and fluorine at temperatures near 173°K. A white solid was produced which decomposed at 243°K into an equimolar mixture of Xe and BF_3. On the basis of analytical and vibrational spectroscopic data, it is believed that the structure of this solid is $FXe{-}BF_2$. This structure is novel in that a covalent xenon–boron bond is assumed.

The structure of dioxygenyl tetrafluoroborate was reported to be $O_2^+BF_4^-$ on the basis of isotopic tracer studies and kinetic data.[2] This structure recently has been confirmed[3] by a detailed infrared study.

Solomon, *et al.*,[4] reported that O_2BF_4 reacted with nitrogen dioxide to give NO_2BF_4 and oxygen. This reaction demonstrated that the dioxygenyl cation, in O_2BF_4, could react by a simple electron-transfer mechanism with compounds of lower ionization potential than oxygen. This suggested that a similar reaction might occur between xenon and O_2BF_4, since the ionization potential[5] of xenon (12.13 eV) is very close to that of oxygen (12.2 eV). In addition, it has been predicted[6] that the expected product, $Xe^+BF_4^-$, should be stable up to about 150°.

For these reasons, it seemed reasonable that a reaction between xenon and O_2BF_4 might occur if proper reaction conditions were met. The reaction of xenon with dioxygenyl cations has not been reported, and demonstration of this reaction would introduce into xenon chemistry a new method of preparing selected xenon salts. This paper describes the reaction between xenon and dioxygenyl tetrafluoroborate along with spectroscopic evidence for the structure of the product.

Experimental Section

O_2BF_4 was prepared by liquid phase radiolysis of a mixture of fluorine, oxygen, and boron trifluoride as described previously.[7]

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