lithium, with **7** analyzing specifically for the $(THF)_3$ species $[[(C_5H_5)_2Lu(\mu\text{-}H)]_3(\mu_3\text{-}H)][Li(THF)_3]$. Complex **5** shows a $Li(THF)_3^+$ cation can be fully coordinated in a cyclopentadienyl system.

Conclusion

The complex $[[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)]^-$ and its derivatives are ideally suited both chemically and spectroscopically to evaluate the integrity of the trimetallic unit during reactions. The reactions of these complexes with varying amounts of CH_3OH clearly demonstrate that yttrium can participate in polymetallic reaction chemistry. This is quite remarkable considering that (a) organolanthanide complexes are traditionally thought to be highly ionic and prone to ligand redistribution reactions and (b) formal metal-metal bonds are not present. In these systems, bridging hydride and alkoxide ligands hold the trinuclear array of metals intact. It is likely that the central μ_3-H ligand is most important in this regard. This result adds a new dimension to the chemistry of yttrium and related metals. By developing polymetallic derivatives of these metals, we will have new ways to precisely control reactivity.[23] Attempts to increase the number of classes of Y_3-(μ_3-H) complexes are in progress.

Structurally, the unusual arrangement of the lithium ions in **5** emphasizes the variability possible in placing cations in these cyclopentadienyl systems. The existence of weak lithium interactions with coordinated cyclopentadienyl rings may be more prevalent than previously expected. The isolation of **5** is a rare example of a case in which this phenomenon has been directly observable.

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Registry No. 1, 90762-81-5; **2**, 111435-08-6; **3**, 111435-10-0; **4**, 111409-63-3; **5**, 111409-64-4.

Supplementary Material Available: Complete tables of interatomic distances and selected angles for $[[(C_5H_5)_2Y(\mu\text{-}OCH_3)]_3(\mu_3\text{-}H)]_2[Li(THF)_3]_2$ (4 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

Synthesis and Spectroscopic and Structural Characterization of the Novel Lithium Borylamide Salts *trans*-$[Li(Et_2O)NHBMes_2]_2$, a Dimer, and the Ion Pair $[Li(Et_2O)_3][Mes_2BNBMes_2]$ with a Linear Allene-like, $[R_2B{=}N{=}BR_2]^-$, Moiety

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Abstract: Treatment of the primary aminoborane H_2NBMes_2 (**1**) with *n*-BuLi in Et_2O/hexane gives an almost quantitative yield of the novel dimeric lithium amide $[Li(Et_2O)NHBMes_2]_2$ (**2**). The addition of 1 equiv of Mes_2BF to $LiNHBMes_2$, generated in situ, gives the recently published diborylamine $HN(BMes_2)_2$ (**3**). The compound **3** reacts with 1 equiv of *n*-BuLi to give the salt $[Li(Et_2O)_3]^+[Mes_2BNBMes_2]^-$ (**4**) in quantitative yield. Details of the ^{11}B NMR spectra and X-ray crystal structures of **1**, **2**, and **4** are reported. Crystal data [Mo Kα (λ = 0.71069 Å)] at 130 K (293 K for **2**) are as follows: **1**, a = 8.602 (3) Å, b = 9.637 (2) Å, c = 10.248 (2) Å, β = 109.38 (2)°, Z = 2, monoclinic, space group $P2_1$, 1505 unique data, $R(F)$ = 0.069; **2**, a = 9.010 (4) Å, b = 9.440 (5) Å, c = 25.958 (12) Å, β = 97.56 (4)°, Z = 2, monoclinic, space group $P2_1/n$, 3859 unique data, $R(F)$ = 0.063; **4**, a = 12.699 (3) Å, b = 12.889 (6) Å, c = 14.371 (5) Å, β = 91.87 (2)°, Z = 2, monoclinic, space group $P2_1$, 5645 unique data, $R(F)$ = 0.058. The structures of the compounds are notable for a number of reasons. For example, **1** is the first primary aminoborane, i.e. R_2BNH_2 (where R = alkyl or aryl group), to be structurally characterized. It possesses a short B-N distance of 1.375 (8) Å. The X-ray crystal structure of **2** is the first for a lithium salt of a primary aminodiarylborane. The structure of the unique diborylamide anion $[Mes_2B{=}N{=}BMes_2]^-$ (**4**) reveals the first example of an essentially linear 176.2 (3)° BNB system. The BN distances are 1.343 (5) and 1.348 (5) Å, and the CBC planes have a dihedral angle of 88°. Thus, it is isoelectronic to and isostructural with the corresponding allene system and the borinium cations $[R_2B{=}N{=}BR_2]^+$.

Lithium amides[2,3] have found considerable use as amide transfer agents in both inorganic and organometallic chemistry. Their structures[3,4] are also of considerable interest from the point of view of interest in lithium compounds in general and the comparison with their carbon analogues, the structures of which seldom follow classical bonding considerations. In this laboratory, attention on lithium compounds has been focused on their interaction with crown ethers to give separate, nonbridging, ionic species rather than the associated structures typical of many lithium salts.[5] In general, association of lithium amides and indeed many other metal amides stems from ionic forces and the availability of a nonbonded pair of electrons on nitrogen, which may be used for bridging. The degree of association may, in principle, be reduced by increasing the size of the nitrogen substituents or by changing the electronic properties of the amide so as to reduce the availability of the

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nitrogen lone pair(s). The former, steric approach has received considerable attention.[6] The latter, electronic approach is relatively unexplored. We have initiated a program to investigate the electronic effects of the dimesitylboryl group on various groups such as phosphides,[7] alkoxides,[8] or carbanions.[9,10] In the context of the amide ligand, we have found that the $BMes_2$ moiety is able to induce (even without a crown ether) a monomeric structure in $Li(Et_2O)_2NPhBMes_2$.[11] By the same token, the two-coordinated manganese compound $Mn(NMesBMes_2)_2$ is monomeric,[11] whereas the sterically crowded $[Mn(N(SiMe_3)_2)_2]_2$ species is dimeric in the solid state.[12,13]

In order to explore the scope of borylamide ligands further, we have investigated the structure of a simpler primary aminoborane precursor H_2NBMes_2 (**1**) and its lithium salt $[Li(Et_2O)NHBMes_2]_2$ (**2**) and extended this to the unique lithium ion-pair salt $[Li(Et_2O)_3][N(BMes_2)_2]$ (**4**). Primary aminodialkyl- or diarylboranes are of considerable interest in their own right but have received little attention due to their instability. For example, with the exception of the triaminoborane $B(NH_2)_2NH(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$,[14] no other stable, structurally characterized derivatives of primary aminoboranes have been reported.[15] Also, the X-ray structure of **2** is the first for a lithium salt of a primary aminoborane, although similar species, e.g. $LiNMeBMe_2$, have been known in solution for a number of years.[16,17] The compound **4** is the first structurally characterized example of a new class of B–N compound. It is related structurally and electronically to the allenes and also to the borinium cations $[R_2NBNR_2]^+$.[18] In addition, since it bears a negative charge, it may display interesting ligand properties.

Experimental Section

General Procedures. All work was performed by Schlenk techniques under N_2 or a Vacuum Atomospheres HE43-2 drybox under Ar. Solvents were freshly distilled under N_2 from Na/K alloy–benzophenone ketyl and degassed twice immediately before use.

Physical Measurements. ^{11}B NMR spectra were obtained with a Nicolet NT200 spectrometer operating at 64.17 MHz. All ^{11}B NMR data were referenced to external $BF_3{\cdot}Et_2O$.

Starting Materials. Mes_2BF was synthesized by the method of Pelter.[19] Ammonia was dried by distillation from sodium. *n*-BuLi (1.6 M in hexane) was purchased from Aldrich and used as received.

Synthesis of Compounds 1–4. H_2NBMes_2 (1). The synthesis of this compound was via a slight modification of the procedure of Coates and Livingstone.[20] After 1 h the mixture of liquid NH_3 (~5 mL), Et_2O (75 mL), and Mes_2BF (6 g) cooled in a dry ice/alcohol bath was allowed to warm to ambient temperature and then refluxed for 30 h. All the volatiles were removed under reduced pressure, and the residue was extracted with warm (50 °C) hexane (50 mL). Filtration and reduction in volume of the filtrate under reduced pressure followed by slow (24-h) cooling in a −20 °C freezer gave ~5 g of **1** as colorless crystals: mp 119–122 °C (lit.[20] mp 118–120 °C); ^{11}B NMR (PhMe) δ 43.8 (br s) (lit.[21] δ 44.5).

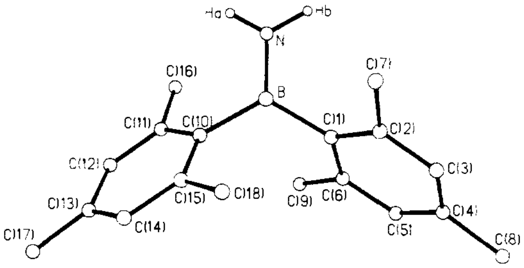
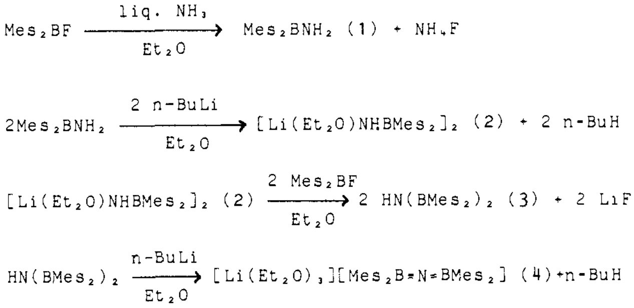


Figure 1. Computer-generated plot of **1** (all isotropic atoms given arbitrary fixed radius circles). Important bond distances (Å) and angles (deg) are the following: B–N = 1.375 (8), B–C(1) = 1.606 (6), B–C(2) = 1.597 (8), N–H(a) = 0.89 (9), N–H(b) = 0.98 (7); B–N–H(a) = 118 (7), B–N–H(b) = 119 (4), H(a)–N–H(b) = 122 (8), N–B–C(1) = 119.9 (5), N–B–C(10) = 119.8 (4), C(1)–B–C(10) = 120.3 (5). Angle of NBC(1)C(10) plane with NBH(a)H(b) plane, 3.1°; angle of aromatic ring C(1) to NBC(1)C(10) plane, 60.3°; angle of aromatic ring C(10) to NBC(1)C(10) plane, 60.7°.

Scheme I



$$Mes_2BF \xrightarrow[Et_2O]{liq.\ NH_3} Mes_2BNH_2\ (1) + NH_4F$$

$$2Mes_2BNH_2 \xrightarrow[Et_2O]{2\ n\text{-}BuLi} [Li(Et_2O)NHBMes_2]_2\ (2) + 2\ n\text{-}BuH$$

$$[Li(Et_2O)NHBMes_2]_2\ (2) \xrightarrow[Et_2O]{2\ Mes_2BF} 2\ HN(BMes_2)_2\ (3) + 2\ LiF$$

$$HN(BMes_2)_2 \xrightarrow[Et_2O]{n\text{-}BuLi} [Li(Et_2O)_3][Mes_2B{=}N{=}BMes_2]\ (4) + n\text{-}BuH$$

***trans*-$[Li(Et_2O)NHBMes_2]_2$ (2).** H_2NBMes_2 (1.82 g, 6.87 mmol) in Et_2O (25 mL) cooled in an ice bath was treated dropwise with *n*-BuLi (4.3 mL of 1.6 M hexane solution) with stirring. The addition produced a white precipitate of the product **2**. Further stirring for 1 h followed by cooling for 3 h in a −20 °C freezer and filtering afforded the product in near quantitative yield: mp 158–164° C; ^{11}B NMR (Et_2O) δ 44.0 (br s).

$HN(BMes_2)_2$ (3). The synthesis of this compound was the same as that described in the literature,[22] and its properties and structure were identical with those described.

$[Li(Et_2O)_3][Mes_2BNBMes_2]$ (4). $HN(BMes_2)_2$ (1 g, 2 mmol) in Et_2O (25 mL) was treated dropwise via syringe via syringe with 1.25 mL of a hexane solution of *n*-BuLi (1.6 M). The solution was stirred for 1 h and its volume halved under reduced pressure. Addition of ca. 5 mL of hexane and cooling in a −20 °C freezer afforded 1.04 g (1.4 mmol) of product: yield 70%; mp 187–193 °C; ^{11}B NMR (Et_2O) δ 27.7 (br s).

X-ray Data Collection, Solutions, and Refinement of Structures. All X-ray data were collected with a Syntex $P2_1$ diffractometer equipped with a graphite monochromator and a modified LT-1 low-temperature device. Crystallographic programs used were those of SHELXTL, Version 5, installed on a Data General Eclipse computer. Scattering factors were from Vol. IV of ref 23. An absorption correction was applied with the method described in ref 24. All compounds were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fiber by silicone grease, and immediately placed in the low-temperature N_2 stream. Table I (supplementary material) summarizes the crystal data and refinement for each compound. Notes on the solution of each structure are also provided therein.

Results

The compounds were synthesized as summarized in Scheme I. The synthetic routes are straightforward, and the yields are high. All the compounds readily formed colorless crystals suitable

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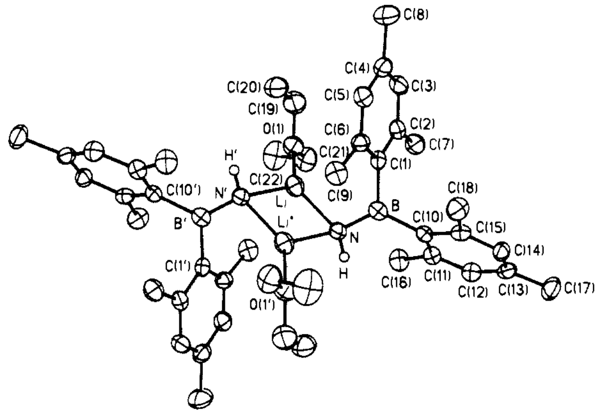

Figure 2. Computer-generated thermal ellipsoid plot of **2** (thermal ellipsoids at 30% probability level, arbitrary fixed radius circle used for H). Important bond distances (Å) and angles (deg) are the following: N–B = 1.386 (7), N–Li = 2.005 (11), N–Li′ = 2.018 (10), N–H = 0.85 (4), B–C(1) = 1.606 (8), B–C(10) = 1.609 (8), Li–O(1) = 1.956 (11); B–N–Li = 107.9 (4), B–N–Li′ = 135.4 (4), B–N–H = 105 (2), Li–N–Li′ = 74.9 (5), N–Li–N′ = 105.1 (5), Li–N–H = 139 (2), Li′–N–H = 98 (3), N–B–C(1) = 117.8 (5), N–B–C(10) = 124.8 (5), C(1)–B–C(10) = 117.4 (4), N–Li–O(1) = 133.7 (5), N′–Li–O(1) = 120.6 (5). Angle between LiLi′NN′ plane and LiO(1)C(19)C(21), 59.1°; angle between LiLi′NN′ plane and aromatic ring C(1), 57.1°; angle between LiLi′NN′ plane and aromatic ring C(10), 111.4°; angle between NBC(1)C(10) plane and aromatic ring C(1), 61.0; angle between NBC(1)C(10) plane and aromatic ring C(10), 51.8.

for X-ray crystal structural studies. The complete crystallographic results are provided in the supplementary material. Brief structural descriptions of compounds **1–4** are as follows:

H_2NBMes_2 (1). The compound crystallizes, as experimentally described, as well-separated monomers. Hydrogen atoms were included at calculated positions by use of a riding model with the exception of the NH_2 hydrogens, which were allowed to freely refine. The numbering scheme is given in Figure 1. Important bond distances and angles are provided in the figure caption. Both the boron and nitrogen centers are planar with a small 3.1° twist angle between them. All the bond distances and angles are in the normal range. The more important B–N distance is 1.375 (8) Å, which is at the shorter end of the envelope for R_2BNR_2 compounds.

$[Li(Et_2O)NHBMes_2]_2$ (2). The compound crystallizes as noninteracting, well-separated centrosymmetric dimers, with two ether-solvated Li^+ ions bridging the $[NHBMes_2]^-$ groups, as illustrated in Figure 2. Non-hydrogen atoms were refined anisotropically, and hydrogens were refined by a riding model after they were located on a difference map. Bond distances and angles within the $BMes_2$ group are similar to those previously reported. The B–N distance is marginally longer than in **1**, being 1.386 (7) Å. The planar Li_2N_2 core forms an almost perfect rhombus with internal angles of 74.9 (5)° at N and 105.1 (5)° at Li. The three-coordinate lithium is also planar, with considerable angular distortions from regularity due to the asymmetry of the $[NHBMes_2]$ moiety. The difference in size between the $BMes_2$ and H substituents on nitrogen is also reflected in the tilt angle (59.1°) between the O(1), C(19), C(21), and Li_2N_2 planes.

$HN(BMes_2)_2$ (3). The structure of this compound has already been described by Nöth, Wilson, and co-workers.[22] The major structural features of note are the planar HNB_2 array, the wide BNB angle of 139.3 (2)°, and the comparatively long BN distance of 1.435 (2) Å.

$[Li(Et_2O)_3][N(BMes_2)_2]$ (4). The compound **4** crystallizes as discrete, noninteracting anions and cations as illustrated in Figure 3. The refinement was the same as for **2** and **3**. The major structural features involve the separation of the cation and anion in the lattice, the essentially linear 176.2 (3)° nature of the B(1)NB(2) array, and the near 90° angle between the two BC_2 planes. The B–N distances are also remarkably short. Distances and angles within the $BMes_2$ groups are normal. The $[Li(Et_2O)_3]^+$ cation involves planar three-coordinate Li^+, with Li–O distances of 1.879 (8), 1.900 (7), and 1.906 (7) Å and OLiO angles that deviate slightly from regularity.

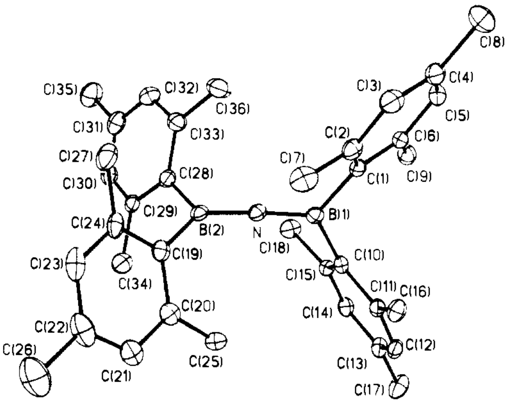

Figure 3. Computer-generated thermal ellipsoid (30% probability level) plot of the anion of **4**. Important bond distances (Å) and angles (deg) are the following: N–B(1) = 1.343 (5), N–B(2) = 1.348 (5), B(1)–C(1) = 1.615 (5), B(1)–C(10) = 1.621 (5), B(2)–C(19) = 1.604 (5), B(2)–C(28) = 1.623 (5); B(1)–N–B(2) = 176.2 (3), N–B(1)–C(1) = 121.9 (3), N–B(1)–C(10) = 117.7(3), C(1)–B–C(10) = 120.5 (3), N–B(2)–C(19) = 120.3, N–B(2)–C(28) = 120.5 (3), C(19)–B(2)–C(28) = 119.2 (3). Angle between NB(1)C(1)C(10) plane and NB(2)C(19)C(28) plane, 88.1; angle between NB(1)B(2) plane and aromatic ring C(1), 54.2; angle between NB(1)B(2) plane and aromatic ring C(10), 60.7.

Discussion

Boron–nitrogen compounds have been the subject of much investigation due mainly to the isoelectronic relationship of the BN and CC moieties. The BN compounds of some recent interest involve, among others, the borinium cations $[BR_2]^+$,[18] which are most stable when the substituents are bulky amido groups, e.g. $[B(TMP)_2]^+$ (TMP = 2,2,6,6-tetramethylpiperidine). However, even simpler classes of BN compounds are characterized by significant absences involving potentially useful and structurally interesting compounds. For example, primary aminoboranes H_2NBR_2 can be unstable due to condensation and amine elimination, which can lead to a variety of products.[2] Until the recent crystallization of the compound $B(NH_2)_2NH(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)$ by Lappert and co-workers,[14] there were no structurally characterized three-coordinate boron compounds with $>B\text{–}NH_2$ moieties. In a more narrow vein there have been no structurally characterized compounds of formula H_2NBR_2 (R = alkyl, aryl) of which **1** is the first example. Primary aminoboranes are potentially more useful than secondary or tertiary derivatives since the N–H group is more synthetically versatile than alkyl or aryl substituents.

Conversion of **1** to its lithium derivative **2** gives a useful primary borylamide transfer agent. Lithium salts of substituted borylamides such as $LiNMeBMes_2$ were originally reported by Nöth[16,17] and co-workers and spectroscopically characterized in solution. Some other metal derivatives, for example of Hg[25] and Sn,[26] have also been reported, and the Sn compounds have interesting cage structures.[20] The primary amide ligand $[NHBMes_2]^-$, however, differs from conventional primary amides due to the significantly reduced basicity of the nitrogen lone pair and the existence of the synthetically versatile NH group. The low basicity is caused by π-bonding between the B and N atoms and is reflected in the short BN distance of 1.386 (7) Å in **2**. Despite the implied low availability of the lone pairs of the nitrogens, dimerization is not prevented, at least, in the solid state. This association is essentially ionic in nature.[3] However, the ^{11}B chemical shift of **2**, 44 ppm, suggests a monomeric formation in ether solution. The X-ray structure of **2**, in fact, bears a close resemblance to that of the extremely bulky lithium primary amide derivative $[Li(Et_2O)NH(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)]_2$.[27] It is notable, however, that association in the crystal does not occur in the case of the substituted

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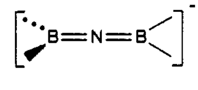
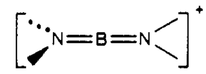
compound $Li(Et_2O)_2NPhBMes_2$[11] (**5**), which is monomeric and has a three-coordinate planar environment at the nitrogen. The higher degree of association seen in **2** compared to **5** is presumably due to reduced steric crowding or, perhaps, a preference of the Li^+ ion for solvation by N donors over O donors. This also results in longer BN distances compared with the precursor **1**, whereas a decrease was noted in the case of **5**. The increase seen in **2** is presumably due to the higher (4) coordination number at the nitrogen.

The reaction between **2** and a further 1 equiv of Mes_2BF gives the diborylamine $HN(BMes_2)_2$ as recently described in the literature.[22] Although both di- and triborylamines have been known for some time, it was only recently that the structures of some diborylamines were reported. The main feature of interest in the structure of **3** is the wide BNB angle of 139.3 (2)°. This is much wider than the corresponding angle in secondary amines. It is perhaps comparable with the SiNSi angle (~136°) in K(1,4-dioxane)$_2$N(SiMe$_3$)$_2$.[28] The **BN** distance in **3**, 1.435 (2) Å, is considerably longer than that in **1** since the two borons compete for the nitrogen lone pair.

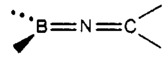
The wide BNB angle in **3** suggested that the removal of the proton would effect an increase in this parameter and perhaps afford a linear BNB system. This hypothesis proved to be correct. compound **3** reacts smoothly with *n*-BuLi in Et_2O to give **4** in quantitative yield. The X-ray crystal structure reveals that the BNB moiety is essentially linear with rather short[29] BN distances and CBC planes, which are almost perpendicular (88°) to each other. The moiety is thus electronically and structurally very similar to allenes,



the borinium cations[18]



and the neutral hybrid system



in $Mes_2B{=}N{=}CPh_2$.[30] The similarity is underlined by the almost identical BN distances in **4** and in $[B(NCH_2Ph(t\text{-}Bu))_2]^+$ [18,31] (1.331 (5) and 1.334 (5) Å) or $[Me_2NBTMP]^+$ (1.30 (4) Å and 1.42 (4)°; av 1.36 (4) Å).

In summary, the use of the $BMes_2$ group allows ready stabilization of monomeric primary borylamines, which can be lithiated to the synthetically useful **2**. Two $BMes_2$ groups on nitrogen produce the secondary diborylamine **3**, which can be readily and quantitatively converted to the interesting "inorganic allene" species **4**.

Note Added in Proof. After this paper had been submitted, the synthesis and spectroscopic characterization of the diborylamide species $[(t\text{-}Bu)_2BNB(t\text{-}Bu)_2]^-$ was published (see ref 32).

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Supplementary Material Available: Notes on structural solutions, thermal ellipsoid plot of **3**, summary of data collection and refinement, and tables of atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates (26 pages). Ordering information is given on any current masthead page.

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Transition-Metal-Promoted Reactions of Boron Hydrides. 9.[1] Cp*Ir-Catalyzed Reactions of Polyhedral Boranes and Acetylenes

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Abstract: The complex $[Cp^*IrCl_2]_2$, in the presence of Proton Sponge, has been found to catalyze reactions of pentaborane(9) with terminal and internal acetylenes, resulting in the formation, in good yields, of the corresponding alkenylpentaboranes. Reaction rates in excess of 30 catalyst turnovers/h were found and represent the fastest turnover rates reported for this type of transformation. The $[Cp^*IrCl_2]_2$/Proton Sponge catalyst system was also found to catalyze the reactions of alkynes with several polyhedral boranes that were previously found to be unreactive for borane/alkyne addition. Thus, hexaborane(10), 1,2-$C_2B_{10}H_{12}$, and 1,7-$C_2B_{10}H_{12}$ reacted with propyne and catalyst to form, respectively, 2-(1-propenyl)hexaborane(10), 3-(*trans*-1-propenyl)-*o*-carborane, and 2-(*trans*-1-propenyl)-*m*-carborane.

We have previously reported[2-5] the discovery of transition-metal-catalyzed synthetic routes to a variety of alkenylboranes and carboranes (eq 1 and 2).

$$B_5H_9 + RC{\equiv}CH \xrightarrow{IrCl(CO)(PPh_3)_2} 2\text{-}(RHC{=}CH)B_5H_8 \quad (1)$$

$$B_5H_9 + RHC{=}CH_2 \xrightarrow{PdBr_2} 1\text{- and }2\text{-}(RHC{=}CH)B_5H_8 + RC_2H_5 \quad (2)$$

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