Addition of Ammonia to AlH_3 and BH_3. Why Does Only Aluminum Form 2:1 Adducts?

Margaret Czerw, Alan S. Goldman,* and Karsten Krogh-Jespersen*

Department of Chemistry, Rutgers, The State University of New Jersey,
New Brunswick, New Jersey 08903

Received August 10, 1999

The electronic structures of the mono- and bisammonia adducts EH_3NH_3 and $EH_3(NH_3)_2$, E = B and Al, have been investigated using ab initio electronic structure methods. Geometries were optimized at the MP2/cc-pVTZ level. Higher-level correlated methods (MP4(SDTQ), QCISD(T), CCSD(T)), as well as the G2 and CBS-Q methods, were used to obtain accurate bond dissociation energies. The E−N bond dissociation energy (D_e) is computed near 33 kcal/mol (E = B) and 31 kcal/mol (E = Al), respectively. Whereas the Al−N bond energy pertaining to the second ammonia molecule in $AlH_3(NH_3)_2$ is 11−12 kcal/mol, only a transition-state structure may be located for the species $BH_3(NH_3)_2$. We analyze factors which may distinguish Al from B with respect to the formation of stable bisamine adducts. The most significant difference relates to electronegativity and hence the propensity of boron to engage in predominantly covalent bonding, as compared with the bonding of aluminum with ammonia, which shows substantial electrostatic character. Neither steric factors nor the participation of d-orbitals is found to play an important role in differentiating aluminum from boron. The lesser electronegativity of third-row elements appears to be the critical common feature allowing the formation of hypercoordinate complexes of these elements in contrast to their second-row analogues. Consideration of some group 14 analogues and hard/soft acid/base effects supports this view.

Introduction

The concept of periodicity is obviously one of the most fundamental in chemistry. The octet rule is equally pervasive. Yet, whereas second-row elements of the periodic table (Li−Ne) almost uniformly obey the octet rule and hence generally achieve a maximum coordination number of only four, their heavier congeners routinely form hypercoordinate species.[1] Highly stable molecules such as SF_6 and PF_5 lack even transient analogues in the second row; hypercoordination involving second-row elements appears possible only under special circumstances such as hypermetalation.[2] These phenomena have long been the subject of intensive considerations. An early, elegant, and seemingly satisfying explanation was based on the possible accessibility of d-orbitals for the third-row and lower elements.[3] However, recent computational studies have demonstrated the importance of ionic contributions in hypervalent molecules,[4,5] even in such prototypical species as SF_6 and PF_5, and have in effect obviated any need to invoke d-orbitals.[6]

The addition of simple two-electron ligands to neutral molecules via the formation of dative bonds is a conceptually simple route to the formation of hypercoordinate molecules (compare it, for example, to the reaction of PF_3 and F_2 to give PF_5). A prototypical example is provided by the reaction of alane (AlH_3) with amines, which offers a comparison with perhaps the most prototypical of Lewis acid−base reactions, those of amines with boranes.[7,8] Gay-Lussac reported the successful preparation of $H_3N{-}BF_3$ in 1809; the history of N−B donor−acceptor complexes is thus nearly 200 years old.[9] Trihydrides of the heavier group 13 elements also form ammonia adducts; unlike boranes, however, the heavier congeners readily complex with a second ammonia ligand to form hypercoordinate bisadducts (viz., $R_3N{-}EH_3{-}NR_3$).[7,8] In fact, the first compound in which aluminum was shown to adopt a pentacoordinate structure was $AlH_3(NMe_3)_2$.[10]

Here we present the results of ab initio electronic structure calculations on mono- and bisamine borane and alane adducts as well as some related species. Particular emphasis is placed on analysis of the factors which may differentiate aluminum from boron with respect to the formation of stable, hypercoordinate bisamine adducts.

Computational Details

A number of computational methods incorporated into the Gaussian 94 suite of electronic structure programs were used in this investigation.[11] Geometry optimizations, including full or partial relaxation of the structural parameters, were carried out at the level of second-order Møller−Plesset theory (MP2)[12] with standard basis sets developed by Pople, McLean, and co-workers (6-31G* and 6-311G**)[13] and with the correlation-consistent basis sets developed by Dunning et al. (cc-pV(D,T,Q)Z).[14] Most data mentioned in the text have been obtained

---

(1) *Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: New York, 1999.

(2) Schleyer, P. v. R.; Kapp, J. *Chem. Phys. Lett.* **1996**, *255*, 363. Kudo, H. *Nature* **1992**, *355*, 432.

(3) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367.

(4) (a) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434−1445. (b) Magnusson, E. *J. Am. Chem. Soc.* **1990**, *112*, 7940−7951 and references therein.

(5) (a) Cioslowski, J.; Mixon, S. T. *Inorg. Chem.* **1993**, *32*, 3209−3216. (b) Dobado, J. A.; Martinez-Garcia, H.; Molina, J. M.; Sundberg, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 8461−8471.

(6) Musher, J. I. *Angew. Chem.* **1969**, *81*, 68; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54. Pimentel, G. C. *J. Chem. Phys.* **1951**, *19*, 446. Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 4321.

(7) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999; pp 136−149, 191−192, and 382−383.

(8) Greenwood, N. N.; Earnshaw, A. In *Chemistry of the Elements*; Pergamon Press: 1984; pp 186−188 and 256−258.

(9) (a) Gay-Lussac, J. L.; Thenard, J. L. *Mem. Phys. Chim. Soc. d'Arcueil* **1809**, *2*, p 210; as cited in ref 9b. (b) Jonas, V.; Frenking, G. *Chem. Commun.* **1994**, *116*, 1989−1990.

(10) Fraser, G. W.; Greenwood, N. N.; Straughan, B. P. *J. Chem. Soc.* **1963**, 3742−3749.

10.1021/ic990961i CCC: $19.00

with the cc-pVTZ basis set, a large basis set of triple-ζ valence quality containing multiple sets of polarization functions (p- and d-type functions on H; d- and f-type functions on heavier elements). Reaction energies (ΔE) and equilibrium bond dissociation energies (D_e) were determined on the basis of fourth-order perturbation theory (MP4(SDTQ))[15] or configuration interaction (QCISD(T)[16] and CCSD(T)[16,17]) calculations with the cc-pVTZ basis set at the MP2/cc-pVTZ optimized geometries (MP4(SDTQ)/cc-pVTZ//MP2/cc-pVTZ, etc.). The CBS-Q[18] and G2[19] methods were also used. These methods also provided the vibrational zero-point energy corrections required to convert $\Delta E(\sim D_e)$ data into ΔE_{ZPE} ($\sim D_o$) values. A simple average of the values predicted by the G2 and CBS-Q methods was applied to the MP4(SDTQ), CCSD(T), or QCISD(T) data as appropriate. Molecular wave functions were analyzed using the natural orbital population scheme (NBO analysis) of Weinhold et al.[20] and the atoms in molecules (AIM) method developed by Bader.[21,22]

Results and Discussion

Computed reaction energies for the formation of the ammonia−borane and ammonia−alane adducts of interest (reactions 1−4) are presented in Table 1. The reaction energies

$$NH_3 + BH_3 \rightarrow H_3N{-}BH_3 \qquad (1)$$

$$H_3N{-}BH_3 + NH_3 \rightarrow H_3N{-}BH_3{-}NH_3 \qquad (2)$$

$$NH_3 + AlH_3 \rightarrow H_3N{-}AlH_3 \qquad (3)$$

$$H_3N{-}AlH_3 + NH_3 \rightarrow H_3N{-}AlH_3{-}NH_3 \qquad (4)$$

predicted by the G2 and CBS-Q methods differ little (at most 0.9 kcal/mol, reaction 3), and simple averaging leads to a predicted B−N bond dissociation energy in BH_3NH_3 of D_e = 31.7 kcal/mol (D_o = 26.2 kcal/mol); the Al−N bond dissociation energy in AlH_3NH_3 is only about 2 kcal/mol smaller at D_e = 29.7 kcal/mol (D_o = 26.0 kcal/mol). The computed MP4(SDTQ), QCISD(T), and CCSD(T) reaction energies for reactions 1 and 3 are nearly identical but uniformly 1−2 kcal/mol more negative than the G2/CBS-Q values. Thus, the computed D_e values from these methods cluster around an average value of 33.1 kcal/mol (D_o = 27.6 kcal/mol) for BH_3NH_3 and 31.0 kcal/mol (D_o = 27.3 kcal/mol) for AlH_3NH_3. These computed B−N and Al−N bond strengths are similar to those obtained in previous high-level calculations.[23−25] Experimental values are not available for the dissociation energies of these simple adducts. A value of 32.3 kcal/mol has been reported, however, for the bond dissociation energy of BH_3NMe_3,[26] and a value of 30.7 kcal/mol has been reported for the dissociation energy of the fully methylated species $AlMe_3NMe_3$;[27] it has been suggested that the dissociation energy of AlH_3NMe_3 should be similar in magnitude.[28] Thus, the computed results, which predict only a small difference (∼2 kcal/mol) in the B−N and Al−N bond dissociation energies in $H_3E{-}NH_3$ (with E = B providing the larger value), do appear to find support in the available, albeit somewhat indirect, experimental data.[29]

Table 1. Calculated Energies (ΔE, ΔE_{ZPE}; kcal/mol) for Reactions 1−4 (Products Shown)

method	eq 1, BH_3NH_3	eq 2, $BH_3(NH_3)_2$	eq 3, AlH_3NH_3	eq 4, $AlH_3(NH_3)_2$
		G2		
ΔE	−31.46	13.93	−29.20	−12.46
ΔE_{ZPE}	−26.09	12.77	−25.65	−10.06
		CBS-Q		
ΔE	−31.87	13.78	−30.08	−12.78
ΔE_{ZPE}	−26.27	12.54	−26.39	−10.25
		MP4(SDTQ)[a]		
ΔE	−33.21	12.91	−31.00	−12.33[b]
ΔE_{ZPE}	−27.63	11.71	−27.38	−9.79
		QCISD(T)[a]		
ΔE	−33.02	12.92	−30.93	−12.73[b]
ΔE_{ZPE}	−27.44	11.72	−27.31	−10.19
		CCSD(T)[a]		
ΔE	−33.01	12.33	−30.92	−11.28[b]
ΔE_{ZPE}	−27.43	11.13	−27.30	−8.74

[a] ΔE obtained using the cc-pVTZ basis set and the indicated method at MP2/cc-pVTZ-optimized geometries. ΔE_{ZPE} obtained from ΔE using an averaged G2 and CBS-Q vibrational zero-point energy as a correction. [b] Computed without d-type functions in the H basis set.[30]

The reaction energy for formation of $AlH_3(NH_3)_2$ from AlH_3NH_3 and NH_3 (reaction 4) is distinctly negative and in the vicinity of −12 kcal/mol: $D_e \sim 12.6$ kcal/mol ($D_o \approx 10.2$ kcal/mol) from the G2/CBS-Q methods; the average D_e is about 12.1 kcal/mol (D_o = 9.6 kcal/mol) from the MP4(SDTQ), QCISD(T), and CCSD(T) calculations.[30] Marsh and Schaefer obtained D_e = 11.8 kcal/mol (D_o = 9.4 kcal/mol) at the CCSD/DZP//

---

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision B.1; Gaussian, Inc.: Pittsburgh, 1995.

(12) (a) Frisch, M. J.; Head-Gordon, M.; Pople, J. *J. A. Chem. Phys. Lett.* **1990**, *166*, 275−281. (b) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(13) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(14) (a) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, J. R. *J. Chem. Phys.* **1992**, *96*, 6796. (c) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(15) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(16) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(17) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(18) Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1991**, *94*, 6091.

(19) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(20) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 3.1*; Theoretical Chemistry Institute, University of Wisconsin at Madison: Madison, WI, 1992.

(21) Bader, R. W. F. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, 1990.

(22) Cioslowski, J.; Surjan, P. R. *J. Mol. Struct.: THEOCHEM* **1992**, *255*, 9.

(23) Bauschlicher, C. W. J.; Ricca, A. *Chem. Phys. Lett.* **1995**, *237*, 14−19.

(24) Marsh, C. M. B.; Hamilton, T. P.; Xie, Y.; Schaefer, H. F., III. *J. Chem. Phys.* **1992**, *96*, 5310−5317.

(25) Marsh, C. M. B.; Schaefer, H. F., III. *J. Phys. Chem.* **1995**, *99*, 195−206.

(26) Gunn, S. R. *J. Phys. Chem.* **1956**, *69*, 1010.

(27) Henrickson, C. H.; Duffy, D.; Eyman, D. P. *Inorg. Chem.* **1968**, *7*, 1047.

(28) Marsh, C. M. B.; Schaefer, H. F., III. *J. Phys. Chem.* **1995**, *99*, 14309−14315.

(29) A low dissociation energy for AlH_3NMe_3 from the solid phase of only 26.3 kcal/mol has been reported: Nechiporenko, G. N.; Petukhova, L. B.; Rozenberg, A. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, *8*, 1697.

(30) For technical reasons, the d-type functions on all H atoms were excluded from the cc-pVTZ basis set in these $AlH_3(NH_3)_2$ calculations. The effect on the Al−N dissociation energy should be on the order of 0.1 kcal/mol, as established by a reference calculation on AlH_3NH_3 (D_e = 31.1 kcal/mol at the MP4(SDTQ)/cc-pVTZ level, 31.0 kcal/mol at the MP4(SDTQ) level with the cc-pVTZ basis set without d-type functions on H).

Table 2. Optimized Geometries for Ammonia−Borane and −Alane Adducts at the MP2/cc-pVTZ Level[a]

species	E−H	N−H	E−N	H−E−N	H−N−H	ΔE^b
BH_3	1.187					
NH_3	1.011				105.9	
AlH_3	1.579					
$H_3B{-}NH_3$	1.206	1.013	1.650	104.9	107.9	−33.9
planar-BH_3−NH_3	1.200	1.012	1.839	90.0	107.9	−20.8
$H_3N{-}BH_3{-}NH_3{}^c$	1.204	1.011	1.839[c]	90.0	110.5	−25.8
$H_3N{-}BH_3{-}NH_3{}^d$	1.197	1.013	2.211	90.0	107.3	+13.2
$H_3Al{-}NH_3$	1.598	1.014	2.072	99.2	107.3	−31.2
planar-AlH_3−NH_3	1.597	1.013	2.135	90.0	107.3	−26.5
$H_3N{-}AlH_3{-}NH_3{}^e$	1.621	1.013	2.135[e]	90.0	107.6	−13.9
$H_3N{-}AlH_3{-}NH_3$	1.618	1.013	2.173	90.0	107.7	−14.0

[a] Distances in angstroms, angles in degrees. The molecular point group for borane, alane, and the bisadducts is D_{3h}; the point group for ammonia and the monoadducts is C_{3v}. [b] Energy relative to that of the ground-state (unconstrained) precursor and NH_3. [c] B−N bond distance constrained to 1.839 Å. [d] Transition state, not a minimum (see the text). [e] Al−N bond distance constrained to 2.135 Å.

CCSD/DZP level for this reaction.[28] In contrast, the reaction energy for the formation of $BH_3(NH_3)_2$ from BH_3NH_3 and NH_3 appears to be quite positive (around 12.9 kcal/mol, averaged over all calculations). Indeed, normal-mode analysis shows that the bis(ammonia)borane structure obtained in maximum point-group symmetry (D_{3h}) is only a transition state with an imaginary frequency corresponding to the B−N asymmetric stretch (a_2'' symmetry).[31] When the two B−N distances are not constrained to be equal in the geometry optimization (C_{3v} symmetry), the $NH_3{-}BH_3{-}NH_3$ species dissociates spontaneously to $NH_3{-}BH_3$ plus NH_3. The highly symmetrical bis(ammonia)borane "adduct" may thus be viewed as an S_N2-type transition state for ammonia exchange.

Optimized geometries for the ammonia−borane and −alane adducts at the MP2/cc-pVTZ level are shown in Table 2. The microwave geometry[32] available for BH_3NH_3[33] is in good agreement with our calculated geometry. Computed and experimental (in parentheses) bond lengths and angles are B−N = 1.650 Å (1.672 Å), B−H = 1.206 Å (1.210 Å), N−H = 1.014 Å (1.013 Å), H−B−N = 104.9° (104.5°), and H−N−H = 107.9° (109.1°). In the bis(ammonia)borane transition-state structure, the B−N distance has increased significantly to 2.211 Å, a 34% increase relative to that of the monoadduct. The simple alane−ammonia complex has, to our knowledge, not been isolated (presumably because of facile elimination of H_2). However, our computed Al−N bond length of 2.072 Å in AlH_3-NH_3 compares favorably to the value of 2.063 Å (electron diffraction) reported for AlH_3NMe_3[34] and the results of previous high-level calculations.[24,25,28] Likewise, Muller et al. have very recently estimated the Al−N bond length in $Me_3Al{-}NH_3$ as 2.066 Å (by a combination of microwave spectroscopy and ab initio calculations).[35] Interestingly, the computed Al−N bond length in $AlH_3(NH_3)_2$ of 2.173 Å is only slightly larger than that of AlH_3NH_3 (2.072 Å; 5% increase). Marsh and Schaefer obtained Al−N = 2.20 Å in $AlH_3(NH_3)_2$,[28] and the experimentally determined Al−N bond length in $AlH_3(NMe_3)_2$ is 2.18 Å (X-ray)[36] or 2.19 Å (electron diffraction).[37]

Table 3. Optimized B−N and Al−N Bond Distances (Å) for Ammonia−Borane and −Alane Adducts at the MP2 Level with a Variety of Basis Sets

method/basis set	BH_3NH_3	$BH_3(NH_3)_2{}^a$	AlH_3NH_3	$AlH_3(NH_3)_2$
MP2/6-31G*	1.665	2.215	2.088	2.189
MP2/6-311G**	1.653	2.206	2.084	2.183
MP2/cc-pVDZ	1.656	2.211	2.116	2.223
MP2/cc-pVTZ	1.650	2.212	2.072	2.173
MP2/BasisA[b]	1.653	2.260	2.098	2.228
MP2/BasisB[c]	1.672	2.248	2.115	2.235

[a] Transition state; see the text. [b] BasisA: cc-pVTZ minus polarization functions on B or Al. [c] BasisB: 6-311G** minus polarization functions on B or Al.

In summary, aluminum accommodates the second ammonia ligand in bis(ammonia)alane without large structural changes occurring relative to mono(ammonia)alane, whereas bis(ammonia)borane exists only as a transition state. The binding energy for the second ammonia in bis(ammonia)alane is reduced considerably (by ca. 20 kcal/mol) relative to that computed for the first ammonia, but the corresponding change for borane is on the order of 45 kcal/mol. We now proceed to analyze the structure and bonding in these complexes with particular attention directed toward factors differentiating boron from aluminum with respect to formation of the bis(ammonia) adducts. Unless noted otherwise, all properties (geometries, energies, charges, etc.) are calculated at the MP2/cc-pVTZ level.

d-Orbital Participation. Is it possible that Al utilizes low-lying d-orbitals for pentacoordinate bonding, effectively using an sp^3d hybridization scheme?[38] Table 3 shows optimized E−N bond lengths in EH_3NH_3 and $EH_3(NH_3)_2$ obtained at the MP2 level of theory with a variety of basis sets. First, basis sets which are less extensive than cc-pVTZ yet still contain some polarization functions on B and Al (viz., cc-pVDZ, 6-311G**, or even 6-31G*) produce virtually no changes in the reoptimized B−N (less than 1%) or Al−N (1−2%) bond lengths, relative to the cc-pVTZ results. Second, we created two general basis sets by deleting all the B and Al polarization functions from the cc-pVTZ (d- and f-type functions deleted) and from the 6-311G** (d-type functions) basis sets to form BasisA and BasisB, respectively.[39] Absence of polarization functions in the Al basis sets tends to lengthen the Al−N bond by slightly more than 1% (∼0.03 Å) in AlH_3NH_3 and by about 2.5% (∼0.05 Å) in $AlH_3(NH_3)_2$ (Table 3); the computed changes in B−N distances under similar circumstances are even smaller.[40] Third, the limited sensitivity to the presence of polarization functions in the basis set observed in the computed bond lengths carries over to the computed bond dissociation energies. For example, at the MP4(SDTQ) level with the full cc-pVTZ basis set, the B−N and Al−N bond dissociation energies in the monoamine adducts are 33.2 and 31.0 kcal/mol, respectively (Table 1); omitting the

---

(31) Sana, M.; Leroy, G. *Int. J. Quantum Chem.* **1993**, *48*, 89−108.

(32) Thorne, L. R.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1983**, *78*, 167.

(33) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 6084−6085.

(34) Almenningen, A.; Gundersen, G.; Haugen, T.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 3928.

(35) Muller, J.; Ruschewitz, U.; Indris, O.; Hartwig, H.; Stahl, W. *J. Am. Chem. Soc.* **1999**, *121*, 4647−4652.

(36) Heitsch, C. W.; Nordman, C. E.; Perry, R. W. *Inorg. Chem.* **1963**, *2*, 508.

(37) Mastryukov, V. S.; Golubinskii, A. V. *Zh. Strukt. Khim.* **1979**, *20*, 921.

(38) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(39) Polarization functions in the N basis sets were kept, as they are important for the description of the (lone pair of the) ammonia ligand: Body, R. G.; McClure, D. S.; Clementi, E. *J. Chem. Phys.* **1968**, *49*, 4916.

(40) Further expansion of the basis sets to cc-pVQZ (quadruple-ζ quality in the valence plus p, d, and f functions on H; d, f, and g functions on B, N, and Al) has but a small effect on the geometries. Optimized values at B3LYP/cc-pVDZ, B3LYP/cc-pVTZ, and B3LYP/cc-pVQZ are as follows: B−N = 1.654, 1.658, and 1.657 Å in BH_3NH_3; B−N = 2.245, 2.288, and 2.295 Å in $BH_3(NH_3)_2$; Al−N = 2.112, 2.084, and 2.078 Å in AlH_3NH_3; Al−N = 2.227, 2.205, and 2.200 Å in AlH_3-$(NH_3)_2$. B3LYP: (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

polarization functions on B or Al (BasisA) leads to values of 30.9 and 28.1 kcal/mol, respectively. Finally, electron populations (natural population analysis, MP2/cc-pVTZ) in the d-type polarization functions on Al are 0.02_0 in AlH_3, 0.02_3 in AlH_3-NH_3, and 0.02_7 in $AlH_3(NH_3)_2$; on B, the corresponding populations are 0.01_6 in BH_3, 0.02_0 in BH_3NH_3, and 0.01_7 in $BH_3(NH_3)_2$. The populations in the d-type functions on B or Al in the complexes are thus essentially the same as in the isolated borane or alane, respectively. The populations in the f-type polarization functions are 1 order of magnitude less than those in the d-type functions.

Thus, the descriptions of the electronic structures and properties of the present ammonia−alane and −borane species do not depend significantly on the presence or absence of d (or higher angular momentum) type functions in the basis set on B or Al. The general effects of polarization functions are computed to be slightly larger in the Al than in the B complexes, but they are not particularly different from the roles played by d-functions in more conventional bonding situations and clearly not of such magnitudes that considerations of true extravalence d-orbital participation in the Al complexes are warranted.[4,5,41−44]

Steric Factors. Steric-based considerations constitute a commonly offered explanation as to why second-row elements do not generally display hypercoordination or hypervalency, and the idea has received support from theoretical studies. In some cases it has been concluded that ligand−ligand steric repulsion is a primary reason for the absence of hypervalent second-row complexes,[45] while in other studies sterics have been predicted to play a significant though perhaps not primary role.[4,5a,43] The covalent atomic radius of boron is considerably less than that of aluminum ($R_{cov} \approx 0.88$, 1.43, 0.74, and 0.37 Å for B, Al, N, and H, respectively).[38] Furthermore, B−H bond lengths (∼1.2 Å) are significantly shorter than Al−H bond lengths (∼1.6 Å), so the possibility should be considered that there is insufficient space available around the boron atom to comfortably accommodate two ammonia molecules.

The optimized B−N bond length in BH_3NH_3 (1.65 Å) is essentially equal to the sum of the covalent radii for B and N (1.62 Å). The H_B−H_N distance is 2.56 Å, more than twice the van der Waals radius for H (1.2 Å).[38] The computed adiabatic rotational barrier (hydrogens staggered going to eclipsed) is only 2.15 kcal/mol (without zero-point energy corrections), favorably close to the experimentally determined value of 2.07 kcal/mol.[32] Although the magnitude of a rotational barrier around a single bond is not necessarily determined by steric interactions,[46] it would appear that there are no strong repulsive H−H interactions in the mono(ammine)borane complex. However, to accept a second ammonia ligand, the BH_3 unit must assume a planar configuration. If we enforce a planar configuration upon BH_3 in the monoamine complex, with the B−N distance kept fixed at 1.650 Å, the H_B−H_N nonbonded distance decreases to 2.31 Å and the "rotational barrier" increases to 4.5 kcal/mol. Geometry relaxation, while a planar BH_3 unit is maintained, increases the B−N distance by 0.19 Å to a value of 1.84 Å (**planar-BN**; Figure 1) and increases the H_B−H_N distance by 0.14 Å to a value of 2.46 Å. The "binding energy" of **planar-BN** remains reasonably strong at 20.8 kcal/mol, and the rotational barrier returns to 2.2 kcal/mol, essentially its adiabatic value. The structural relaxation of the B−N bond (1.65 → 1.84 Å) is accompanied by a small energy release of 3.3 kcal/mol, a change which does not appear to reflect relief of repulsive H−H interactions but rather to be associated principally with changes in the orbitals forming the B−N chemical bond. Thus, even in the hypothetical case consisting of a planar BH_3 unit and a B−N distance constrained at the value from pyramidalized H_3B−NH_3 (1.65 Å), H_B−H_N repulsive interactions are apparently not large. We can discern no signs of severe nonbonded H_N−H_B repulsive interactions in any reasonably chosen BH_3−NH_3 adduct geometries, which would prevent a second ammonia molecule from approaching BH_3NH_3 to a B−N proximity where appreciable bonding might take place. Steric factors play no role in preventing formation of the bis(ammonia) adduct of BH_3.

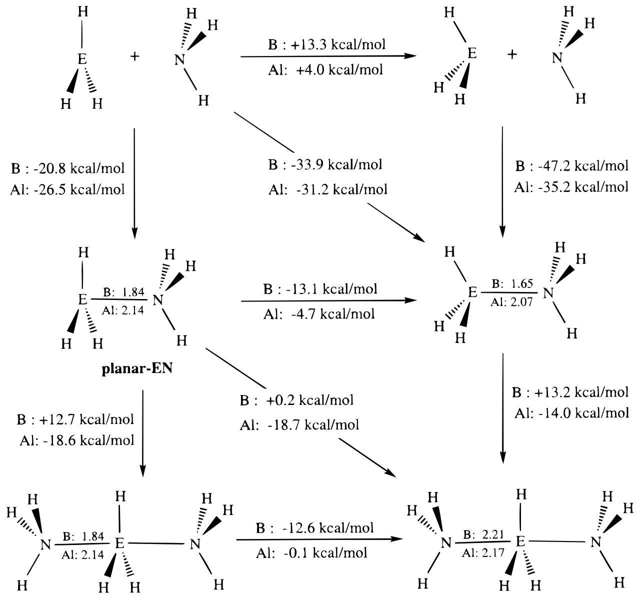

Figure 1. Decomposition of reaction energies associated with BH_3-NH_3 and AlH_3NH_3 formation (MP2/cc-pVTZ).

In the AlH_3NH_3 adduct, the H_E−H_N distances are considerably greater (∼3.0 Å) and steric interactions are presumably even less important than in the boron analogue. Nonetheless, the approach of holding the EH_3 unit in a planar geometry allows us to make very direct and useful comparisons between the two species. When AlH_3 is held planar, **planar-AlN** is formed with an Al−N distance of 2.14 Å (cf. 2.07 Å when the AlH_3 is allowed to pyramidalize) and a reaction energy of −26.5 kcal/mol (Figure 1). Formation of a second Al−N bond, fixed at the same distance of 2.14 Å, is exoergic by 18.6 kcal/mol. In contrast, formation of a second B−N bond is endoergic by 12.7 kcal/mol, relative to **planar-BN** and NH_3 (both B−N bond distances held at 1.84 Å). The difference of 7.9 kcal/mol between the first and second Al−N bond energies is strikingly different from the 33.5 kcal/mol obtained for the analogous experiment with BH_3. If the bis(ammonia)alane adduct is allowed to structurally relax, the Al−N distance hardly changes (2.14 → 2.17 Å) and the energy of addition for the second ammonia ligand becomes −18.7 kcal/mol (relative to **planar-AlN** and NH_3). However, in the boron case structural relaxation with the second ligand present leads to dissociation.

Even if steric factors were significant, steric repulsions should essentially cancel out when the first and second ammonia additions to planar EH_3 at a given E−N bond length are

---

(41) Cooper, D. L.; Cunningham, T. P.; Gerratt, J.; Karadakov, P. B.; Raimondi, M. *J. Am. Chem. Soc.* **1994**, *116*, 4414−4426.
(42) Gilheany, D. G. *Chem. Rev.* **1994**, *94*, 1339−1374.
(43) Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1998**, *120*, 11439−11448.
(44) See ref 43, refs 99−109 therein.
(45) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272−295.
(46) Goodman, L.; Pophristic, V. in *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; John Wiley & Sons: New York, 1998; Vol. 4, pp 2525−2541.

Table 4. Net Atomic Charges from Natural Population Analysis of MP2/cc-pVTZ Wavefunctions

species	E	H_E	N	H_N	Δq^a
BH_3	0.36	−0.12			
NH_3			−1.02	0.34	
AlH_3	1.26	−0.42			
H_3B-NH_3	−0.16	−0.07	−0.80	0.39	−0.38
planar-BH_3 $-NH_3$	−0.03	−0.09	−0.85	0.38	−0.29
$H_3N-BH_3-NH_3^b$	- 0.14	−0.12	−0.88	0.37	−0.46
$H_3N-BH_3-NH_3^c$	0.04	−0.10	−0.95	0.36	−0.27
H_3Al-NH_3	1.06	−0.41	−1.02	0.39	−0.16
planar-AlH_3 $-NH_3$	1.09	−0.41	−1.02	0.39	−0.16
$H_3N-AlH_3-NH_3^d$	1.01	−0.43	−1.01	0.38	−0.26
$H_3N-AlH_3-NH_3$	1.01	−0.42	−1.01	0.38	−0.26

[a] Δq = net charge transferred from ammonia unit(s) to borane or alane in the complex. [b] B−N bond distance constrained to 1.839 Å. [c] Transition state, not a minimum (see the text). [d] Al−N bond distance constrained to 2.135 Å.

compared. Thus, the difference in the difference between first and second additions for planar B vs planar Al (25.6 kcal/mol) must, at the very least, be attributed to nonsteric factors. If we accept that steric interactions are not significant in the planar boron (or alane) bisamine adducts, then the value that must be accounted for increases by 8.4 kcal/mol (the differential gain in binding energy upon Al(B) pyramidalization in the monoadducts, Figure 1). We believe that the resulting value, ca. 34 kcal/mol, most closely reflects the energy difference between the first and second additions to boron versus aluminum, no significant part of which is attributable to steric factors.

Bonding Analysis: Covalency versus Electrostatics. In the absence of significant steric factors it may be presumed that the pyramidalization at boron and aluminum in the mono(ammonia) adducts is driven by the favorability of developing B or Al s-orbital character into the B−N and Al−N bond orbitals. Figure 1 details the energetic consequences of pyramidalization around B or Al.

Addition of NH_3 to an isolated pyramidal BH_3, constrained as in the fully relaxed BH_3NH_3 species, is 26.4 kcal/mol more favorable than addition to a constrained planar BH_3. This contrasts with an analogous value of only 8.7 kcal/mol for addition to AlH_3. As with the energetic difference, the geometric changes pertaining to pyramidalization are much smaller for aluminum than for boron: the optimal Al−N distance in AlH_3NH_3 decreases by only 0.06 Å (2.13 → 2.07 Å) when the planarity of AlH_3 is relaxed, a much smaller change than that computed for BH_3NH_3 (0.19 Å). In accord with these "observables", the NBO analysis reveals that the orbital used by B to bond with the N lone pair in BH_3NH_3 effectively has $sp^{4.8}$ hybridization, whereas the orbital used by Al in AlH_3NH_3 contains less s-character with an effective $sp^{5.9}$ hybridization. Constraining the EH_3 units of the monoadducts to planarity requires 13.1 kcal/mol for BH_3NH_3 and 4.7 kcal/mol for AlH_3NH_3. Yet, even after the greater "preparation" energy for boron expended, the addition of a second NH_3 to **planar-BN** (at the same B−N distance as the first ligand) is endoergic by 12.7 kcal/mol, a full 31 kcal/mol less favorable than the analogous reaction of AlH_3NH_3.

The atomic net charges (Table 4; NPA, MP2/cc-pVTZ)[20] in the isolated fragments show a trend in magnitudes and sign in accordance with the relative electronegativities (H (2.20), B (2.04), N (3.04) and Al (1.61))[47] as follows: (BH_3) q(B) = 0.36, q(H) = −0.12; (AlH_3) q(Al) = 1.26, q(H) = −0.42; (NH_3) q(N) = −1.02, q(H) = 0.34. Despite the much greater positive charge present on Al than on B, monoadduct formation results in more than twice as much charge being transferred from the NH_3 unit to BH_3 (Δq = −0.38) as to AlH_3 (Δq = −0.16) with nearly equal contributions made by N and by the three H atoms. The B atom acquires a slightly negative charge in BH_3NH_3 (q(B) = −0.16), whereas the Al atom in AlH_3NH_3 maintains a very substantial positive charge (q(Al) = 1.06).

The extent of $NH_3 \rightarrow AlH_3$ charge transfer is almost unchanged when the AlH_3 unit in AlH_3NH_3 is made planar and the geometry is reoptimized: −0.14 (Al−N = 2.13 Å) vs −0.16 (Al−N = 2.07 Å). The total $NH_3 \rightarrow AlH_3$ charge transfer in $AlH_3(NH_3)_2$ is −0.26, i.e., −0.13 per NH_3 unit, and the second ammonia molecule is thus permitted to donate approximately the same amount of charge as is the first ammonia unit when bonded to a planar AlH_3. The amount of charge transfer is rather insensitive to the value of the Al−N distance, suggesting that the overlap between the donor lone pair on NH_3 and the acceptor orbital on Al (2p−3p overlap) is small.

Pyramidalization around B in free BH_3 intrinsically produces a transfer of charge to B from the H_B atoms of −0.03,[48] resulting in a charge on B of 0.33. In **planar-BN**, charge transfer has been reduced from −0.38 (B−N = 1.65 Å) to −0.29 (B−N = 1.84 Å). In the $BH_3(NH_3)_2$ transition-state structure (Δq = −0.27, B−N = 2.21 Å), the total amount of charge transferred to BH_3 is of this same magnitude, whereas the charge transfer to BH_3 in $BH_3(NH_3)_2$ at the fixed B−N distances of 1.84 and 1.65 Å would be much larger at −0.47 and −0.59, respectively. In BH_3NH_3, the charge donated by NH_3 must almost exclusively enter into the formally vacant B($2p_z$) orbital, and indeed, we find a net population in B($2p_z$) of $q(p_z)$ = 0.43. When the BH_3 unit is constrained to planarity with B−N = 1.65 Å, $q(p_z)$ is calculated to be 0.35; in **planar-BN**, with B−N = 1.84 Å, $q(p_z)$ = 0.32. In $BH_3(NH_3)_2$, the corresponding $q(p_z)$ values at B−N = 1.65, 1.84, and 2.21 Å are 0.53, 0.43, and 0.26, respectively. Thus, even when the second ammonia ligand is constrained to the same B−N distance as the first ligand, the amount of additional charge transfer to B($2p_z$) from the second ligand is much smaller (e.g., 0.11 vs 0.32 from the first ligand at a distance of 1.84 Å).

On the basis of the NBO analyses, we find much greater dative character and hence covalency in the H_3B-NH_3 bond than in the H_3Al-NH_3 bond. Reflecting the very strong electrostatic character of the Al−N bond, the Al−N bond length in AlH_3NH_3 is 5% shorter than the sum of the covalent radii and the bond dissociation energy is large. With the B($2p_z$) acceptor orbital significantly involved in bonding already in the BH_3NH_3 adduct, there is no remaining low-lying acceptor orbital on B to donate into for the lone pair of a second ammonia unit. However, favorable electrostatic interactions between the Al in AlH_3NH_3 and a second ammonia unit (viz., $H_3N^{\delta-}-Al^{\delta+}H_3-N^{\delta-}H_3$) are apparently strong, and bis(ammonia) adduct formation occurs.

The atoms in molecules (AIM) theory emphasizes the topology of the molecular charge density distribution, $\rho(\mathbf{r})$, in its analysis of chemical bonding.[21] In BH_3NH_3, the B−N bond critical point (CP_{BN}, local maximum in $\rho(\mathbf{r})$ along the bond axis) is located 0.51 Å away from B where $\rho(\mathbf{r})$ = 0.100, i.e., $F_{BN} = R(B-CP_{BN})/R(B-N)$ = 0.51 Å/1.65 Å = 0.31.[49] For AlH_3NH_3,

---

(47) Pauling electronegativities from Table 14.4, p 941, in Atkins, P. *Physical Chemistry*, Oxford University Press: Oxford, 1997.

(48) The pyramidalized BH_3 unit geometry was obtained by deleting the atoms in NH_3 from the optimized geometry of BH_3NH_3. The corresponding change on Al from pyramidalization of the AlH_3 unit is only −0.01.

(49) Glaser, R.; Horan, C. J. *J. Org. Chem.* **1995**, *60*, 7518−7528.

the Al−CP_{AlN} distance is 0.83 Å, $\rho(\mathbf{r}) = 0.046$, and $F_{AlN} = 0.83$ Å/2.07 Å $= 0.40$, and in $AlH_3(NH_3)_2$, the Al−CP_{AlN} distance is 0.86 Å, $\rho(\mathbf{r}) = 0.034$, and $F_{AlN} = 0.86$ Å/2.17 Å $=$ 0.40. These values indicate a greater charge accumulation along the E−N bond axis closer to E in BH_3NH_3 than in the AlH_3-NH_3 or $AlH_3(NH_3)_2$ species, as well as substantial similarities in the electron density features of the Al−N bonds in the two aluminum−ammonia adducts. The calculated covalent E−N bond orders are 0.30 in BH_3NH_3, 0.16 in AlH_3NH_3, and 0.12 in $AlH_3(NH_3)_2$, showing a considerably greater degree of covalency in the bonding of BH_3NH_3. On the basis of the electron counting scheme and definition of hypervalency proposed by Cioslowski and Mixon,[4a] there are no signs of hypervalency in any of the boron or aluminum species under consideration here.

Marsh and Schaefer used the generalized atomic polar tensor (GAPT) method[50] for charge density analysis at the SCF level and predicted a small charge transfer occurring *from* AlH_3 *to* NH_3 in AlH_3NH_3[24] but no charge transfer occurring in AlH_3-$(NH_3)_2$.[28] Our NPA analyses of AlH_3NH_3 and $AlH_3(NH_3)_2$ at the MP2/cc-pVTZ level (cf. above) support a more traditional description of the adducts with modest donor (ammonia)−acceptor (alane) character. However, our AIM analysis shows minimal charge transfer, similar to the results obtained by Marsh and Schaefer. Cioslowski has pointed out that the atomic charge values obtained from AIM and GAPT methods often are similar for bonding situations dominated by closed shell interactions, where limited distortion of atomic densities occurs.[50]

Our analyses (NBO, AIM), like those of Marsh and Schaefer,[24,25,28] and others,[51] indicate that the bonding in the ammonia−alane adducts is predominantly electrostatic. Direct evaluation of the electrostatic field shows a large, highly attractive (to a negative charge) region in the vicinity of Al, a region not present in the boron analogues. To obtain approximate estimates of the electrostatic interaction energy of an ammonia molecule in the respective electrostatic fields, we have calculated the interaction energy of a dipole composed of unit positive and negative charges located 0.306 Å apart (corresponding to the experimentally determined ammonia dipole moment of 1.47 D)[52] in the vicinity of the aluminum and boron species. When the negative end of the dipole is located 2.14 Å from the Al atom in AlH_3 (the Al−N distance in **planar-AlN**), the interaction energy is found to be 14.6 kcal/mol, compared to the calculated binding energy of 26.5 kcal/mol in **planar-AlN**. If the AlH_3 unit is pyramidalized as in the final product species, the interaction energy (with the negative end of the dipole at 2.07 Å) is 18.6 kcal/mol, to be compared to the calculated binding energy of 35.2 kcal/mol. When addition of a second ammonia is modeled by placing the dipole 2.14 Å from **planar-AlN**, the interaction energy is calculated as 11.7 kcal/mol; the corresponding binding energy of NH_3 to **planar-AlN** with NH_3 at this distance is 18.6 kcal/mol. Approximating the ammonia molecule as a static, extended dipole should underestimate the actual electrostatic interaction energy, since higher-order terms have been neglected. We consider the magnitudes and the relative values resulting from these calculations to be fully consistent with the picture of predominantly electrostatic Al−N bonding, particularly (and most importantly) in the case of the addition of a second ammonia ligand.

An ammonia dipole similarly located 1.65 Å from pyramidalized BH_3 has an interaction energy of 21.2 kcal/mol; this value is substantial though it represents a smaller fraction of the total calculated binding energy (47.2 kcal/mol) to the prepyramidalized EH_3 unit than is found for AlH_3 (45% vs 53%). The electrostatic interaction energy of the dipole placed 1.84 Å from constrained-planar BH_3 is 10.8 kcal/mol as compared with the calculated bond energy for this species of 20.8 kcal/mol (cf. analogous values of 14.6 and 26.5 kcal/mol for aluminum). Most importantly, the electrostatic interaction energy of the dipole located 1.84 Å from **planar-BN** is only 3.7 kcal/mol and insufficient to compensate for the 13.1 kcal/mol required to planarize the BH_3 unit. On the basis of these considerations alone, one could explain the failure of BH_3 to add a second ammonia ligand (as compared with aluminum). However, although small, the electrostatic interaction energy is attractive, and thus does not explain the calculated "negative" bond energy of 12.7 kcal/mol for the NH_3−**planar-BN** bond. Presumably Pauli repulsion, and not electrostatics, is the origin of the very high energy of the bis(ammonia) adduct of BH_3 (B−N distance of 1.84 Å). Thus, bonding of the first ammonia to BH_3 appears to be predominantly covalent though with a substantial electrostatic component. Addition of a second ammonia ligand is (a) electrostatically much less favorable (though still probably slightly exoergic in purely electrostatic terms) and (b) strongly repulsive according to the full calculations; effects (a) and (b) can both be attributed to the covalent nature of the first H_3B−NH_3 bond and the accompanying charge transfer.

Group 14 Analogues. We considered it of interest to further examine the covalent−electrostatic bonding issue using isoelectronic−isolobal analogies (i.e., BH_3/CH_3^+ and AlH_3/SiH_3^+) and have therefore also computed the energetics for the following reactions:

$$NH_3 + CH_3^+ \rightarrow H_3N{-}CH_3^+ \qquad \Delta E = -114.6\ \text{kcal/mol} \tag{5}$$

$$H_3N{-}CH_3^+ + NH_3 \rightarrow H_3N{-}CH_3{-}NH_3^+ \qquad \Delta E = +11.9\ \text{kcal/mol} \tag{6}$$

$$NH_3 + SiH_3^+ \rightarrow H_3N{-}SiH_3^+ \qquad \Delta E = -81.4\ \text{kcal/mol} \tag{7}$$

$$H_3N{-}SiH_3^+ + NH_3 \rightarrow H_3N{-}SiH_3{-}NH_3^+ \qquad \Delta E = -35.0\ \text{kcal/mol} \tag{8}$$

Naturally, the reaction energies (MP2/cc-pVTZ) for reactions 5 (−114.6 kcal/mol) and 7 (−81.4 kcal/mol) are far larger than those for reactions 1 and 3 (∼ −32 kcal/mol, Table 1). The additional positive charge greatly increases not only electrostatic attraction but also covalent bonding (by lowering the energy of the p_z acceptor orbital).

The reaction energy for addition of a second ammonia to SiH_3^+ is substantial (−35.0 kcal/mol, reaction 8) and much larger than the complexation energy for reaction 4 (AlH_3; ∼ −12 kcal/mol), reflecting the positive charge on the Si center. In contrast, not only is reaction 6 (CH_3^+) endoergic by 11.9 kcal/mol, it is essentially endoergic by the *same* amount as reaction 2 (BH_3; ∼13 kcal/mol), and indeed, the "product species" of reaction 6 is only a transition state for the symmetrical exchange of ammonia molecules (cf. reaction 2). Even though the affinity for complexing with the first ammonia molecule increases by over 80 kcal/mol when BH_3 is replaced by CH_3^+ (cf. 50 kcal/mol when AlH_3 is replaced by SiH_3^+), addition of a second

---

(50) Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333.

(51) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741−8753.

(52) *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990; pp 9−6.

ammonia molecule remains impossible for the covalently bonding C atom in $H_3NCH_3^+$ (yet, quite possible for the Si atom in $H_3NSiH_3^+$).

Is the sacrifice of a stable tetrahedral configuration at carbon, as required by reaction 6, the major factor preventing addition of the second ammonia? "Preparing" the carbon atom for bonding by constraining the CH_3 unit to planarity in $H_3CNH_3^+$ is endoergic by 23.8 kcal/mol, and addition of the second ammonia to this "prepared" species is exoergic but only by 11.9 kcal/mol. This compares with addition of the first ammonia to constrained-planar CH_3^+, which is exoergic by 90.8 kcal/mol (114.6−23.8 kcal/mol). The first and second additions to constrained-planar SiH_3^+ are far closer in energy: −71.6 and −44.8 kcal/mol. As with Al and B, the differences seem entirely consistent with a largely covalent mode of bonding for C^+ versus a much greater contribution from electrostatics in Si^+.

The relationship between CH_3^+ and BH_3 also sheds additional light on whether the presence of negative charge on boron is a primary factory preventing the addition of a second ammonia to BH_3NH_3. The positively charged $H_3NCH_3^+$ species cannot experience an unfavorable charge buildup on C, certainly not so far as to lead to a binding energy equally negative to that of BH_3NH_3 for a second ammonia molecule (vide supra). The long B−N distances in $BH_3(NH_3)_2$ ensure that a strong buildup of negative charge on B does not occur, but the presence of substantial charge on B is not in and of itself the major reason for the nonexistence of $BH_3(NH_3)_2$.

Hard/Soft Acid/Base Effects. If we associate electrostatic/covalent dominance in bonding with the "hard/soft" acid/base concepts,[53] our results suggest that a very "hard" base such as F^- would form a stronger complex with the "hard" acid AlH_3 than with the "soft" acid BH_3. Indeed, our calculations predict an Al−F heterolytic bond strength of 112.8 kcal/mol in AlH_3F^- as compared to a predicted B−F bond strength of 89.4 kcal/mol in BH_3F^-.[54] In contrast, replacement of NH_3 with the "softer" base PH_3 leads to a predicted B−P bond strength of 25.5 kcal/mol in BH_3PH_3, significantly greater than that predicted in AlH_3PH_3 (15.1 kcal/mol). However, in contrast to the greater affinity of BH_3 for the first phosphine, *only* AlH_3PH_3 is capable of adding a second phosphine ($\Delta E = -5.1$ kcal/mol); addition to BH_3PH_3 is highly unfavorable ($\Delta E = +13.3$ kcal/mol). Experimentally, $AlH_3(PR_3)_2$ and $AlH_3(PR_3)(NR'_3)$ are well-characterized compounds.[6,7,55]

Finally, substituting F for H on the trihydrides has very different effects for boron and aluminum. The B−N binding energy for BF_3NH_3 is computed to be less than that for BH_3NH_3 (23.1 kcal/mol vs 33.9 kcal/mol). Addition of a second NH_3 has a negative binding energy of −20.4 kcal/mol (B−N = 2.48 Å; transition state). In contrast, ammonia adds to AlF_3 considerably more exothermically than to AlH_3 (39.7 kcal/mol vs 31.2 kcal/mol), and the resulting Al−N bond is quite short at 2.003 Å (2.072 Å in AlH_3NH_3). Addition of a second ammonia to AlF_3NH_3 is also much more favorable relative to that of AlH_3NH_3 (22.9 kcal/mol vs 14.0 kcal/mol). Clearly, $p(\pi)-p(\pi)$ donation from F to B raises the energy of the B(2p) orbital, resulting in a weaker Lewis acid. With Al, this effect is more than compensated for by the increased partial atomic charge engendered by the electronegative fluorine substituents, which results in increased electrostatic interactions with either one or two ammonia ligands.

Concluding Remarks. The extent of d-orbital participation in the bis(ammonia) adduct of alane is clearly insufficient to explain the much greater stability of this complex vis-à-vis its boron analogue. This result is in accord with several previous studies of hypercoordinate or hypervalent molecules (although the participation of d-orbitals is still commonly invoked in discussions of hypervalency in textbooks[7,8,56]).

Geometric/steric factors are also shown to be far too insignificant to explain the much more favorable formation of bis(ammonia) adducts of alane. During the course of this work, Bettinger, Schleyer, and Schaefer reported a study of NF_5 in which they concluded that crowding "inhibits but does not preclude the existence of NF_5".[43] Our results demonstrate that this conclusion, i.e., that *steric effects do not play the key role* in explaining the instability of NF_5 versus PF_5, is applicable to other congener pairs. Indeed, in the present case, steric crowding does not even significantly inhibit, much less preclude, formation of the five-coordinate boron complex.

The results of all calculations conducted in this work on both mono- and bisamine adducts, including both quantum mechanical observables and nonobservables, appear consistent with a propensity of boron to engage in predominantly covalent (dative) bonding with ammonia. By comparison, ammonia−alane bonding has a much greater electrostatic component. Key results supporting this conclusion include (but are not limited to) the following: (a) the much greater difference in energy of binding to pyramidal versus planar EH_3 for boron (26 kcal/mol versus 9 kcal/mol for Al), (b) the much greater transfer of charge from NH_3 to BH_3 than to AlH_3, (c) only in the case of boron, a very large difference in $H_3N \rightarrow EH_3$ charge transfer when the first and the second ammonia ligands are compared, (d) a much greater effect of enforcing planarity on both the degree of charge transfer and the resulting bond lengths are computed when E = B, (e) the much greater calculated (AIM) covalent bond order in BH_3NH_3 than in AlH_3 or $AlH_3(NH_3)_2$, and (f) estimated electrostatic interaction energies that correlate fairly well with the E−N binding energies, including a substantial electrostatic attraction for the second ammonia in the case of aluminum, but not boron. Given the pronounced qualitative difference in the nature of the E−N bonds formed by the first ammonia ligand (despite the similarity of the E−N bond energies), the very large difference between the Al−N and B−N *second* bond energies is perhaps not surprising.

As Bettinger, Schleyer, and Schaefer concluded, the key to understanding the stability of PF_5 vs NF_5 lies, in simplest terms, with the much lower electronegativity of the heavier central element.[43] We draw the analogous conclusion here concerning aluminum vs boron. This may seem somewhat ironic when the standard routes (both synthetic and conceptual) for formation of these species are considered: PF_5 via oxidation of PF_3 by F_2; the aluminum complex via addition (coordination) of electron pairs of ammonia. Nevertheless, in both cases electrostatic attraction appears to be the key to the much greater stability of these and many other hypercoordinate complexes[4,5,44,57] in comparison with their second-row analogues.

Acknowledgment. We gratefully acknowledge the National Science Foundation for financial support (Grant CHE-9704304) and for a computer equipment grant (DBI-9601851-ARI).

IC990961I

---

(53) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(54) For electrostatic reasons neither BH_3F^- nor AlH_3F^- can accept a second F^- ion.

(55) Atwood, J. L.; Butz, K. W.; Gardiner, M. G.; Jones, C.; Koutsantonis, G. A.; Raston, C. L.; Robinson, K. D. *Inorg. Chem.* **1993**, *32*, 3482−3487.

(56) Shriver, D.; Atkins, P. *Inorganic Chemistry*, 3rd ed.; W. H. Freeman: New York, 1999; p 70.

(57) Wang, P.; Zhang, Y.; Glaser, R.; Reed, A. E.; Schleyer, P. v. R.; Streitwieser, A. *J. Am. Chem. Soc.* **1991**, *113*, 55−64.