Design of Neutral Lewis Superacids of Group 13 Elements

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ⓢ *Supporting Information*

ABSTRACT: A general approach toward superstrong neutral Lewis acids, featuring both the pyramidalization of acceptor molecules and the introduction of electron-withdrawing substituents, is proposed and examined theoretically. Complexes of group 13 element derivatives with ammonia at the B3LYP and MP2 levels of theory with def2-TZVPP basis set are considered as examples. Pyramidalization of the acceptor molecule significantly increases its Lewis acidity (by 50–60 kJ mol^{-1} for aluminum and gallium compounds and by 120–130 kJ mol^{-1} for boron compounds). An additional increase of the complex stability of 55–75 kJ mol^{-1} may be achieved by fluorination. The combined increase of the bond dissociation energy amounts to 110–190 kJ mol^{-1}, which is equivalent to 19–33 orders of magnitude in Lewis acidity.

E^{diss}=233.4 kJ/mol

1. INTRODUCTION

Acid–base interactions form a core of modern chemistry. Brønsted and Lewis acids have found numerous applications in homogeneous and heterogeneous catalysis. In the recent past, it has been shown that the so-called "frustrated" neutral Lewis acid–base pairs exhibit remarkable activities in heterolytic hydrogen splitting.[1] Very strong group 13 Brønsted acids (for example, superacid AlBr$_3$–HBr) are capable of gas-phase activation of inert molecules such as methane.[2] In this respect, it is of interest to establish basic principles for the construction of even stronger neutral Lewis acids (superacids).

The term "superacids" is usually applied to Brønsted acids and was originally introduced to describe acids that are stronger than sulfuric acid (H$_2$SO$_4$).[3] Substantial progress has been made in the design of superstrong Brønsted acids, pioneered through works on superacids by Olah et al.[4] Important developments in this direction have also been conducted by Koppel et al.[5,6]

However, the formation of *Lewis* superacids is much less addressed from both the experimental and theoretical points of view. An early definition of Lewis superacids was given by Olah et al.,[4] who stated that "those stronger than anhydrous AlCl$_3$ should be categorized as Lewis superacids". However, Olah et al. also mentioned that, in a generalized sense, no a priori differentiation between Brønsted (protic) and Lewis acids seems to be justified. According to Krossing and coauthors,[7] the term "Lewis superacid" is used occasionally,[8] but no precise definition of this term has been given. They proposed the following definition of the term "Lewis superacid": "Molecular Lewis acids, which are stronger than monomeric SbF$_5$ in the gas phase, are Lewis superacids."[7] They also suggested to use fluoride ion affinities (FIA) as a quantitative measure for the

Lewis acidity and stated that several "Lewis acids stronger than SbF$_5$ are now available as compounds in the bottle".[7]

Analysis of the charge distribution in complexes of group 13 metal halides with ammonia X$_3$MNH$_3$ revealed that the electronegative terminal halogen atoms X accept most of the transferred charge from the hydrogen atoms of the ammonia molecule, while the central group 13 and 15 atoms predominantly serve as media for the charge transfer.[9] This observation is in line with the wide use of electron-withdrawing substituents to increase the Lewis acidity. Such an approach has been successfully employed to generate strong group 13 perfluorinated acceptors, such as B(C$_6$F$_5$)$_3$ and Al(C$_6$F$_5$)$_3$,[8a] as well as their more sophisticated analogues.[10] Both computational and experimental studies indicate that B(C$_6$F$_5$)$_3$ and Al(C$_6$F$_5$)$_3$ serve as strong Lewis acids, although their order of acceptor strength remains controversial.[11] Very recent computational studies of the Lewis acidity of partially fluorinated triphenylboranes B(C$_6$H$_x$F$_{5-x}$)$_3$ revealed that it is not only the number but also the placement of the fluorine substituents that determines the Lewis acidity.[12] According to the computational results of Gille and Gilbert,[13] B(CF$_3$)$_3$ is one of the strongest group 13 Lewis acids known to date. The bond dissociation energy of the B(CF$_3$)$_3$·NH$_3$ complex, predicted with 11 different density functional theory methods, ranges from 207 kJ mol^{-1} at B97-D/6-311++G-(3df,2p) to 283 kJ mol^{-1} at LSDA/6-311++G(3df,2p),[15] with a reference MP2/6-311++G(d,p) value of 262 kJ mol^{-1}.[16a] Bulky perfluorinated alkoxy ligands OR^F [R^F = TeF$_5$, C(CF$_3$)$_3$] have been successfully utilized to obtain Lewis superacids, such as As(OTeF$_5$)$_5$,[17] B(OTeF$_5$)$_3$,[18] and Al(OR^F)$_3$.[7] In 2002,

Koppel et al. generalized the design principle to obtain neutral Brønsted superacids and showed that the replacement of a terminal oxygen atom by highly electrophilic groups can lead to an enormous increase of the Brønsted acidity (by ca. 88 pK_a units).[6]

Besides the electron-withdrawing ability, other factors may significantly affect the Lewis acidity. One factor is dimerization of the Lewis acid, discussed by us previously.[11] It is well-known that group 13 metal derivatives exist as dimers in the solid state and in inert solvents. The dimers Al_2Cl_6 and Ga_2Cl_6 undergo reversible thermal dissociation into monomers in the gas phase. This fact significantly lowers their Lewis acidity because additional energy is required for dissociation of the dimer to the monomeric Lewis acid. As an example, the gas-phase dissociation enthalpies of Al_2Cl_6 and Ga_2Cl_6 into monomers are 122 and 88 kJ mol^{-1}, respectively.[19]

Another important factor, which is much less addressed, is the reorganization energy of the acceptor molecule. It is well-known that, upon complex formation, monomeric group 13 trihalides change their geometry from trigonal planar to tetrahedral. The energetic demands for such a transformation range from 36 kJ mol^{-1} for $AlCl_3$ to 119 kJ mol^{-1} for BCl_3 in $ECl_3 \cdot B_3N_3H_6$ complexes.[20a] Such an unfavorable reorganization energy of BCl_3 is one of the major factors limiting its acceptor ability. Thus, Lewis acids featuring large reorganization energies (like BCl_3), will form less stable complexes than those with small reorganization energies (like $AlCl_3$). In other words, the larger intrinsic Lewis acidity of BCl_3 compared to $AlCl_3$ (as indicated by a larger donor−acceptor B−N bond energy[20a]) may be partly or completely compensated for by the reorganization energy of the acceptor molecule. It has been shown in previous theoretical studies that amine and phosphane complexes of BCl_3, $R_3E−BCl_3$, have stronger interaction energies than $R_3E−AlCl_3$ (E = N, P), but the bond dissociation energies of the latter complexes are larger than those for the former species.[21] This is due to the much higher reorganization energy of BCl_3 compared to $AlCl_3$. This factor is also very important for group 14 metal tetrahalides MX_4, which undergo much larger structural reorganization: from tetrahedral to planar geometry in trans complexes MX_4-2D.[20b]

If the acceptor center were preorganized (i.e., if it possessed a pyramidal environment with coordination number 3), such group-13 element compounds would be much stronger Lewis acids. To force the acceptor fragment to remain pyramidal, a rigid (cage) structure is required. Several tripodal amino-aluminum and -boron compounds have been designed by Zhu and Chen.[22] In our recent report, we demonstrated that the rigidity of the pyramidalized Lewis acid moiety significantly enhances its reactivity, which allows one to design Lewis acid−base cryptands that are predicted to be capable of forming stable complexes with such weak donors as argon and other noble gases.[23]

In this report, we theoretically examine an approach for the design of superstrong neutral Lewis acids, based on the use of rigid molecules with pyramidal acceptor pockets. In order to reveal the influence of the induced pyramidality, we systematically explore Lewis acidities of several types of acceptors based on aryl, strained aryl, and adamantine-type cages and their respective fluorinated derivatives (Figure 1).

The first structural pattern, considered in the present work, is based on adamantane-type structures. Several heteroatom derivatives of adamantane featuring nitrogen, boron, and silicon
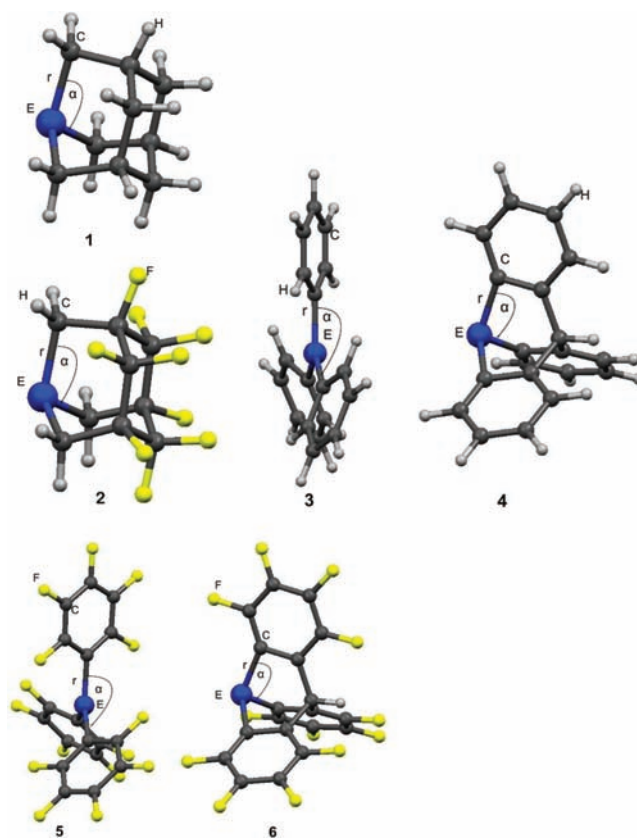
Figure 1. Optimized structures of adamantane-based acceptors EC_9H_{15} (**1**) and $EC_9H_6F_9$ (**2**), triphenyl-based acceptors $E(C_6H_5)_3$ (**3**) and $E(C_6F_5)_3$ (**5**), and caged acceptors $EC_{19}H_{13}$ (**4**) and EC_{19}-HF_{12} (**6**).

atoms have been prepared in the laboratory.[24−26] The compound 1-boraadamantane, reported by Mikhailov,[27] shows exceptionally high reactivity toward donor molecules. A broad chemistry involving boraadamantanes has been developed.[28] The complex of 1-boraadamantane with 1-azaadamantane, which is stable in air and insensitive to moisture, has been reported by Bubnov et al.[29] Another structural pattern considered in the present work features trisaryl ligands tied together by a CH unit.

Fluorination of the resulting molecules will allow a further increase of their acceptor ability.[12] The synthesis of perfluorinated compounds could be achieved by direct low-temperature fluorination by Lagow and Margrave.[30] However, one may expect a violent reaction between the aluminum atom of the acceptor pocket and nearby fluorine atoms. For example, $Al(C_6F_5)_3$ "tends to explode under circumstances not exactly determined"[8a] and is relatively stable only as an adduct with tetrahydrofuran.[8a] Taking this into account, we decided to study partially fluorinated compound **2** (Figure 1), which is analogous to perfluorinated **1** but lacks fluorine atoms near the acceptor pocket and therefore is expected to be more stable.

When the Lewis acidities are compared, the fluoride ion is widely accepted as the benchmark donor; the methodology for FIA computation was given by Christe et al.[31] In 2004, Krossing and Raabe performed extensive computational studies of the relative stabilities and coordinating abilities of large weakly coordinated anions and their parent Lewis acids.[32] In the present work, we choose a neutral Lewis base (ammonia) as the reference donor molecule. As a criterion of the Lewis

acidity, we will use the dissociation energy of the ammonia complexes. Since the reported experimental gas-phase dissociation enthalpy of the $AlCl_3 \cdot NH_3$ complex is 137.2 ± 3.8 kJ mol^{-1},[33] a direct comparison of the Lewis acidity of the considered compounds with that of $AlCl_3$ is straightforward. Structural parameters as well as bonding analysis, which play an equally important role in understanding the basic principles of the design of strong Lewis acids, will also be considered in the present work.

2. COMPUTATIONAL DETAILS

For geometry optimizations at the RHF/6-31G* and B3LYP/def2-TZVPP[34−36] levels of theory, the *Gaussian03*[37] program package was used. As confirmed by the analytical evaluation of the second derivatives, all structures reported here are minima on the potential energy surface. The basis set superposition error (BSSE) was estimated by the counterpoise method.[38,39] Geometry optimizations and an estimation of the BSSE at the RI-MP2/def2-TZVPP[40,41] level of theory were conducted using the *Turbomole 6.0* program package.[42]

Previous theoretical studies of complexes of group 13 metal halides with ammonia at the B3LYP/LANL2DZ(d,p) and B3LYP/TZVP levels of theory showed a satisfactory agreement with high-temperature experimental data.[9,20] Because the accuracy of B3LYP for B−N dative bonds is not sufficient and is system-dependent,[16] we performed reference computations at the RI-MP2/def2-TZVPP level of theory. As was shown before,[16] the MP2 results are in good agreement with both the experiment and CCSD(T) results. Natural bond orbital analyses[44] were carried out with the internal module of *Gaussian 03* on the B3LYP/def2-TZVPP level of theory.

3. RESULTS AND DISCUSSION

Structural Features. Structures of the acceptor molecules and their ammonia complexes are presented in Figures 1 and 2,
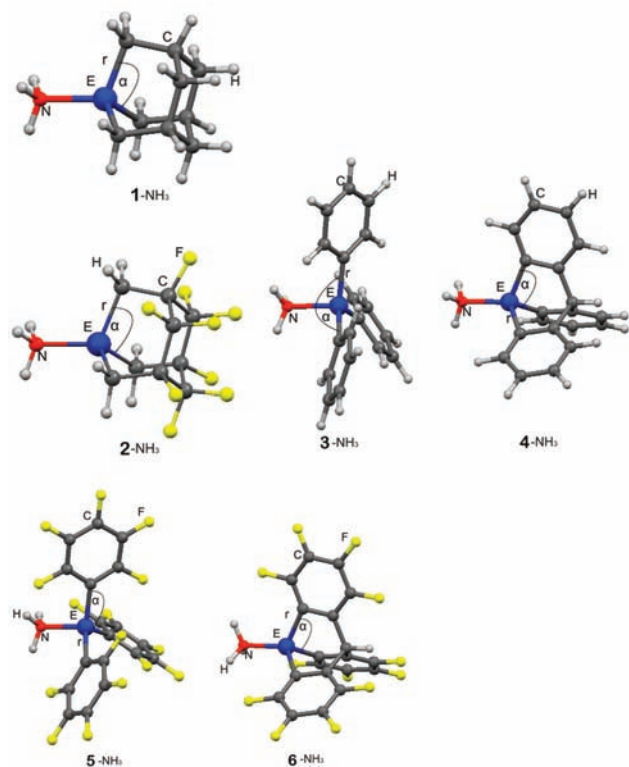
Figure 2. Optimized structures of the studied donor−acceptor complexes with ammonia.

respectively. The most important structural parameters are summarized in Table 1. By analogy with previously reported

Table 1. Selected Structural Parameters of Acceptor Molecules and Their Donor−Acceptor Complexes with Ammonia

compound	point group	r(E−C) (Å)		α(C−E−C) (deg)	
		B3LYP/ def2-TZVPP	RI-MP2/ def2-TZVPP	B3LYP/ def2-TZVPP	RI-MP2/ def2-TZVPP
B-1	C_{3v}	1.566	1.560	116.5	116.7
B-1-NH$_3$	C_{3v}	1.621	1.610	110.2	110.3
Al-1	C_{3v}	1.952	1.940	110.3	110.7
Al-1-NH$_3$	C_{3v}	1.975	1.963	106.5	106.7
Ga-1	C_{3v}	1.985	1.953	109.1	110.3
Ga-1-NH$_3$	C_{3v}	2.004	1.973	105.7	106.5
B-2	C_{3v}	1.573	1.567	116.1	116.3
B-2-NH$_3$	C_{3v}	1.629	1.617	110.0	110.1
Al-2	C_{3v}	1.957	1.945	108.3	108.4
Al-2-NH$_3$	C_{3v}	1.980	1.967	104.8	104.8
Ga-2	C_{3v}	1.989	1.958	108.4	108.9
Ga-2-NH$_3$	C_{3v}	2.008	1.978	104.6	105.2
B-3	D_3	1.567	1.554	120.0	120.0
B-3-NH$_3$	C_3	1.627	1.605	114.3	113.8
Al-3	C_1	1.960	1.947	120.0	120.0
Al-3-NH$_3$	C_3	1.988	1.970	117.1	117.3
Ga-3	D_3	1.978	1.948	120.0	120.0
Ga-3-NH$_3$	C_3	2.003	1.969	117.8	117.9
B-4	C_{3v}	1.564	1.554	113.2	113.3
B-4-NH$_3$	C_{3v}	1.613	1.595	105.9	105.8
Al-4	C_{3v}	1.939	1.931	107.0	107.2
Al-4-NH$_3$	C_{3v}	1.963	1.952	102.6	102.6
Ga-4	C_{3v}	1.972	1.945	105.0	105.8
Ga-4-NH$_3$	C_{3v}	1.988	1.960	101.1	101.5
B-5	C_3	1.581	1.554	120.0	120.0
B-5-NH$_3$	C_3	1.643	1.617	113.7	113.4
Al-5	D_3	1.959	1.944	120.0	120.0
Al-5-NH$_3$	C_3	2.000	1.978	115.5	114.9
Ga-5	C_1	1.976	1.943, 1.944	119.9, 120.2	120.0
Ga-5-NH$_3$	C_3	2.014	1.971	116.2	116.7
B-6	C_{3v}	1.566	1.556	112.8	112.9
B-6-NH$_3$	C_{3v}	1.622	1.604	104.8	104.7
Al-6	C_{3v}	1.934	1.925	105.6	105.8
Al-6-NH$_3$	C_1	1.960	1.948	100.4	100.4
Ga-6	C_{3v}	1.966	1.938	103.9	104.6
Ga-6-NH$_3$	C_1	1.985, 1.986	1.955	99.2, 99.0	99.5

bond angle−bond distance−bond energy relationships,[9,48] changes in the C−E−C angle upon complex formation can be used as an indicator for the strength of the corresponding Lewis acid. A larger decrease of the C−E−C angle corresponds to larger Lewis acidity. Generally, C−E−C angles become smaller when going to heavier group 13 elements.

Let us consider the structural changes in the free triphenyl-based acceptor molecules upon cage formation (transition from structure **3** to **4** and from **5** to **6**). The E−C bond distances slightly shorten (by 0.003−0.025 Å), while changes in the C−E−C angle are more pronounced. The C−E−C angle decreases from perfect 120° in **3** and **5** by about 7° for boron-containing compounds and by 13−15° for aluminum- and gallium-containing compounds. Smaller structural changes found for boron compounds may be attributed to the effect of stronger ligand−ligand repulsion (vide infra).

Upon complexation with ammonia, the E−C bond length expectedly[11] increases by about 0.06 Å for E = B and by 0.02−0.04 Å for E = Al, Ga. The C−E−C angle also expectedly

decreases by 2−6° for unstrained **3** and **5**, but it is somewhat surprising that a similar decrease (4−8°) is observed for strained (caged) acceptors **1**, **2**, **4**, and **6**, which already possess quite small C−E−C angles. This observation points out that the structures of the caged molecules **1**, **2**, **4**, and **6** are not completely rigid but are capable of structural relaxation upon complex formation. The structural changes upon complex formation with ammonia are more pronounced for boron compounds than for compounds containing aluminum or gallium.

In the cases of complexes of the prepyramidalized acceptors with ammonia E-**1**-NH$_3$, E-**2**-NH$_3$, E-**4**-NH$_3$, and E-**6**-NH$_3$, the C−E−C angles are close to or even smaller than a tetrahedral angle, indicating a strongly pyramidal environment of the group 13 element. In E-**6**-NH$_3$, this angle is exceptionally small (99−104°), which indicates high Lewis acidity of E-**6**.

Energetics of the Donor−Acceptor Bond. Dissociation energies of all studied ammonia complexes are presented in Table 2. Let us first consider trends upon enforcement of the

Table 2. Donor−Acceptor Bond Dissociation Energies E^{diss} (BSSE Energies Are in Parentheses), kJ mol^{-1}, of Studied Ammonia Complexes

compound	point group	RHF/6-31G*	B3LYP/def2-TZVPP	RI-MP2/def2-TZVPP
B-**1**-NH$_3$	C_{3v}	81.8 (14.9)	80.5 (4.8)	116.8 (14.1)
Al-**1**-NH$_3$	C_{3v}	135.3 (15.2)	113.6 (4.4)	135.8 (10.1)
Ga-**1**-NH$_3$	C_{3v}	125.0 (37.9)	83.9 (4.7)	113.3 (15.7)
B-**2**-NH$_3$	C_{3v}	158.4 (15.7)	152.3 (4.9)	190.9 (14.5)
Al-**2**-NH$_3$	C_{3v}	196.3 (16.2)	171.1 (4.3)	194.7 (11.0)
Ga-**2**-NH$_3$	C_{3v}	185.9 (39.7)	141.0 (4.9)	166.5 (16.9)
B-**3**-NH$_3$	C_3	23.9 (18.8)	33.9 (5.4)	91.9 (16.5)
Al-**3**-NH$_3$	C_3	107.6 (17.8)	93.7 (4.3)	126.4 (10.9)
Ga-**3**-NH$_3$	C_3	89.2 (33.2)	64.4 (4.5)	103.7 (16.4)
B-**4**-NH$_3$	C_{3v}	163.1 (16.0)	162.8 (5.0)	212.2 (15.8)
Al-**4**-NH$_3$	C_{3v}	173.5 (17.8)	148.0 (4.6)	173.2 (10.7)
Ga-**4**-NH$_3$	C_{3v}	156.0 (34.9)	121.2 (4.8)	154.9 (16.2)
B-**5**-NH$_3$	C_3	99.8 (25.0)	110.1 (6.1)	155.4 (21.4)
Al-**5**-NH$_3$	C_3	172.2 (24.8)	151.9 (5.8)	184.0 (15.1)
Ga-**5**-NH$_3$	C_3	151.1 (41.9)	118.7 (5.9)	157.6 (20.9)
B-**6**-NH$_3$	C_{3v}	246.3 (22.5)	233.4 (5.7)	284.0 (18.2)
Al-**6**-NH$_3$	C_1	244.5 (19.7)	214.0 (5.1)	232.2 (11.8)
Ga-**6**-NH$_3$	C_1	229.7 (38.7)	188.4 (5.3)	216.4 (17.6)

pyramidal environment of the acceptor atom. The pyramidalization pays off extremely well for boron, stabilizing complexes B-**4**-NH$_3$ and B-**6**-NH$_3$ by 120−130 kJ mol^{-1} (compared to B-**3**-NH$_3$ and B-**5**-NH$_3$, respectively; Table 3). The pyramidalization effect for aluminum and gallium analogues is smaller but still significant: 50−60 kJ mol^{-1}. Note that the agreement of the trends predicted at the B3LYP and MP2 levels of theory is satisfactory. The maximal energy difference between B3LYP and MP2 is only 14 kJ mol^{-1} (Table 3), while the absolute dissociation energies of the complexes differ by as much as 50 kJ mol^{-1} (Table 2).

Fluorination expectedly[12] increases the stability of the complex by 53−74 kJ mol^{-1} (Table 4). For boron complexes, the fluorination effect is about 10 kJ mol^{-1} larger than those for aluminum and gallium complexes. Note that absolute stabilization upon fluorination is very similar for both strained pyramidal (compounds **1** and **4**) and trigonal-planar (compound **3**) acceptors. Trends obtained at B3LYP and RI-MP2

Table 3. Difference between Complex Dissociation Energies upon Pyramidalization of the Acceptor, kJ mol^{-1}, at the B3LYP/def2-TZVPP Level of Theory (RI-MP2/def2-TZVPP Values in Parentheses)

E	E^{diss}(**4**-NH$_3$) − E^{diss}(**3**-NH$_3$)	E^{diss}(**6**-NH$_3$) − E^{diss}(**5**-NH$_3$)
B	129 (120)	123 (129)
Al	54 (47)	62 (48)
Ga	57 (51)	70 (59)

Table 4. Difference in Complex Dissociation Energies, in kJ mol^{-1}, upon Fluorination of the Acceptor Molecule at the B3LYP/def2-TZVPP Level of Theory (RI-MP2/def2-TZVPP Values in Parentheses)

E	E^{diss}(**2**-NH$_3$) − E^{diss}(**1**-NH$_3$)	E^{diss}(**5**-NH$_3$) − E^{diss}(**3**-NH$_3$)	E^{diss}(**6**-NH$_3$) − E^{diss}(**4**-NH$_3$)
B	72 (74)	76 (63)	70 (72)
Al	57 (59)	58 (58)	66 (59)
Ga	57 (53)	55 (54)	67 (61)

are again in close agreement with each other. It is interesting that predicted dissociation energies at the RHF/6-31G* level of theory show a surprisingly good agreement with the B3LYP/def2-TZVPP results for boron compounds, while for the heavier systems, the RHF/6-31G* and RI-MP2/def2-TZVPP values are similar (Table 2).

The BSSE values at B3LYP and MP2 in Table 2 reveal that the BSSE is much higher at MP2 compared to the B3LYP level of theory. This is in agreement with earlier studies.[13,14] BSSE values at the B3LYP/def2-TZVPP level of theory are in the range 4.3−6.1 kJ mol^{-1}, but at MP2/def2-TZVPP, they range from 10.1 to 21.4 kJ mol^{-1}. A similar situation was reported by Gille and Gilbert, who found that BSSE values at the MP2 level of theory are much larger compared to RHF and B3LYP values with the same basis set.[13] Because BSSE values at the B3LYP/def2-TZVPP level of theory are small and given the fact that the counterpoise method generally overestimates the BSSE,[43] in the following discussion, we will use uncorrected dissociation energies for BSSE.

Which Group 13 Element Is the Better Choice for a Lewis Superacid: Boron or Aluminum? This question is important with respect to the design of stronger Lewis acids. Therefore, it is of interest to compare the difference in the Lewis acidity of boron and aluminum derivatives of the studied compounds (Table 5). For adamantine-type acceptors **1** and **2**,

Table 5. Differences in Complex Dissociation Energies for Boron- and Aluminum-Containing Complexes with Ammonia,^{a} kJ mol^{-1}

level of theory/complex	**1**-NH$_3$	**2**-NH$_3$	**3**-NH$_3$	**4**-NH$_3$	**5**-NH$_3$	**6**-NH$_3$
RHF/6-31G*	−53	−38	−84	10	−72	2
B3LYP/def2-TZVP	−33	−19	−60	15	−42	19
RI-MP2/def2-TZVP	−19	−4	−35	39	−29	52

^{a}E^{diss}(B−N) − E^{diss}(Al−N). Negative values mean that the aluminum complex is more stable.

aluminum derivatives are predicted to be stronger Lewis acids at all levels of theory. Nonpyramidalized trisaryl acceptors **3** and **5** follow the same trend. However, after pyramidalization, boron-containing strained trisaryl-based acceptors **4** and **6** are

Table 6. Natural Charges $q(E)$ of the Group 13 Atom E (B, Al, Ga) in Free Acceptor Molecules, Wiberg Bond Indices (WBI), Charge-Transfer Values q_{CT}, Donor−Acceptor Bond Distances $R(E−N)$ in Angstroms, Reorganization Energies $E^{reorg}(A)$, and Element−Nitrogen Bond Energies $E(E−N)$ in kJ mol^{-1} at the B3LYP/def2-TZVPP Level of Theory (RI-MP2/def2-TZVPP Values in Parentheses)

acceptor	$q(E)$	WBI(E−C)	q_{CT}	WBI(E−N)	$R(E−N)$	$E^{reorg}(A)$	$E(E−N)$
B-**1**	0.85	0.92	0.37	0.65	1.662 (1.636)	49.6 (51.3)	128 ± 2 (162 ± 7)
Al-**1**	1.73	0.60	0.27	0.28	2.067 (2.042)	8.4 (9.7)	120 ± 2 (141 ± 5)
B-**2**	0.90	0.97	0.43	0.69	1.636 (1.615)	48.1 (47.9)	198 ± 2 (232 ± 7)
Al-**2**	1.77	0.57	0.33	0.32	2.027 (2.005)	8.1 (8.9)	177 ± 2 (198 ± 6)
B-**3**	0.82	0.92	0.37	0.63	1.693 (1.653)	81.2 (77.5)	113 ± 3 (162 ± 8)
Al-**3**	1.77	0.57	0.30	0.26	2.088 (2.054)	23.5 (20.9)	115 ± 2 (142 ± 5)
B-**4**	0.85	0.90	0.41	0.71	1.617 (1.595)	48.0 (48.7)	209 ± 3 (254 ± 8)
Al-**4**	1.70	0.60	0.25	0.32	2.035 (2.011)	10.2 (10.4)	156 ± 2 (179 ± 5)
B-**5**	0.81	0.92	0.43	0.70	1.654 (1.630)	101.4 (95.0)	209 ± 3 (241 ± 11)
Al-**5**	1.77	0.55	0.36	0.32	2.018 (1.993)	37.1 (42.2)	186 ± 3 (219 ± 8)
B-**6**	0.90	0.88	0.50	0.74	1.605 (1.588)	53.9 (52.7)	285 ± 3 (328 ± 9)
Al-**6**	1.74	0.58	0.34	0.35	1.994 (1.979)	12.7 (12.7)	225 ± 3 (240 ± 6)

predicted to be 2−50 kJ mol^{-1} stronger Lewis acids at all levels of theory (Table 5).

It is interesting that pyramidalization of the acceptor molecules affects boron-containing Lewis acids much more than aluminum-containing compounds (by up to 75−80 kJ mol^{-1}; Table 3). We attribute this difference to the following two factors: (1) larger reorganization energy of boron-containing Lewis acids EPh$_3$ and E(C$_6$F$_5$)$_3$ compared to aluminum analogues and (2) smaller size of the boron atom, which provides better overlap with the lone pair of the nitrogen atom.

Both factors play a role, with the major contribution coming from the reorganization energy. All studied Lewis acids undergo significant structural reorganization upon complex formation with ammonia (Table 1). Changes in the structural parameters are accompanied by the reorganization energy $E^{reorg}(A)$, which is required to transform the geometry of the free Lewis acid into the geometry of the Lewis acid in the donor−acceptor complex. Both structural (Table 1) and energetic (Table 6) data indicate much larger changes in boron-containing Lewis acids.

Larger reorganization energies of boron-containing Lewis acids may be understood on the basis of the ligand close-packing model.[49] If planar BR$_3$ (R = arbitrary substituent) is pyramidalized, the substituents come very close to each other and there is strong repulsion between them. If AlR$_3$ is pyramidalized, the same effect is observed, but because the Al−R bond distance is larger, the repulsion between the substituents is not as strong. Quantitatively, an estimate of this repulsive energy for some ligands can be indirectly obtained via the acceptor reorganization energy $E^{reorg}(A)$ (Table 6).

For boron-containing acceptors, which are not pyramidalized (compounds B-**3** and B-**5**), reorganization energies $E^{reorg}(A)$ are quite large (81−101 kJ mol^{-1}) and they are up to 65 kJ mol^{-1} higher than those for the respective aluminum compounds Al-**3** and Al-**5**. For pyramidalized Lewis acids **4** and **6**, reorganization energies are much smaller, and for Al-**4** and Al-**6**, they are less than 13 kJ mol^{-1}, but the difference in reorganization energy between boron and aluminum compounds still amounts to 38−41 kJ mol^{-1} (Table 6). By the design of even more rigid structures (with less reorganization energy upon complex formation), the boron-containing acceptors could be made about 40 kJ mol^{-1} stronger Lewis acids than B-**4** and B-**6**.

A comparison of the natural charges in acceptor molecules (Table 6) reveals that charges on the boron and aluminum

atoms are only to a small extent affected by the nature of the acceptors (0.81−0.90 for B; 1.70−1.77 for Al). Larger values for aluminum are expected because of its lower electronegativity (2.04 for B; 1.61 for Al).[45] Note that the Wiberg bond indices (WBI) for the B−C bond, which are between 0.88 and 0.97, are much larger than those for Al−C (0.55−0.60).

One could expect that the WBI in planar boron compounds would be larger than those in pyramidal species. The planar geometry allows π-back-bonding, which is ubiquitous in boron chemistry. However, the WBI show that the E−C bond index in the acceptor molecule does not depend on whether the acceptor is planar or pyramidal. This can be taken as another indicator for the validity of the ligand close-packing model for explaining the large pyramidalization energies of boron Lewis acids.

The energy of the donor−acceptor bond $E(E−N)$ was evaluated at the B3LYP/def-2TZVPP level of theory, taking into account the reorganization energies of the fragments and half of the BSSE value:[20b]

$$E(E - N) = E^{diss} + E^{reorg}(A) + E^{reorg}(D) - \frac{1}{2}E^{BSSE}$$

It is not surprising that the WBI values for the E−N bond, the charge transfer q_{CT}, and the energy of the donor−acceptor bond $E(E−N)$ increase with increasing dissociation energy of the complex E^{diss} (Table 6). When the B−N bond is compared to the Al−N donor−acceptor bond, the WBI(E−N), q_{CT}, and $E(E−N)$ values are larger for the corresponding boron-containing compounds. There is only a small difference between the B3LYP and RI-MP2 results for $E^{reorg}(A)$, while bond energies are significantly underestimated at the B3LYP level.

The bond distance $R(B−N)$ is, of course, much shorter than $R(Al−N)$ because of the much smaller size of the boron atom; however, the trends in the $R(E−N)$ shortening upon an increase of the dissociation energy E^{diss} are similar for the boron and aluminum compounds.

It is interesting to follow the trends in the bond energy $E(E−N)$. Upon pyramidalization of the acceptor moiety (transition from **3** to **4** or from **5** to **6**), the value for $E(B−N)$ increases by 75−96 kJ mol^{-1}, while the increase in the case of $E(Al−N)$ only amounts to 38−59 kJ mol^{-1}. We conclude that pyramidalization restores the stronger "intrinsic" Lewis acidity of the boron Lewis acid. Rigidly pyramidalized boron-containing

644

dx.doi.org/10.1021/ic202152h | *Inorg. Chem.* 2012, 51, 640−646

compounds are potentially much stronger Lewis acids toward ammonia than their heavier group 13 analogues.

Comparison of Lewis Acidities with Common Lewis Acids. We also compared the predicted complex dissociation energies of the compounds with ammonia complexes of common Lewis acids (Table 7). The fluorinated cage acceptors

Table 7. Comparison of the Dissociation Energies, kJ mol^{-1}, for Ammonia Complexes of 6 and Several Common Lewis Acids

compound	E^{diss}	method	reference
SbF$_5$·NH$_3$	152.9, 142.7^a	B3LYP/def2-TZVPP	present work
	181.3, 171.4^a	MP2/def2-TZVPP	present work
AlCl$_3$·NH$_3$	137.2 ± 3.8^{a,b}	tensimetry	33
	146.2, 135.9^a	B3LYP/def2-TZVPP	present work
	168.1, 158.2^a	MP2/def2-TZVPP	present work
Al(C$_6$F$_4$)$_3$CH·NH$_3$ (Al-**6**-NH$_3$)	214	B3LYP/def2-TZVPP	present work
	232	RI-MP2/def2-TZVPP	present work
B(CF$_3$)$_3$·NH$_3$	229	B3LYP/6-311++G(d)	46, 47
	216	B3LYP/6-311++G(d,p)	16a
	262	MP2/6-311++G(d,p)	16a
B(C$_6$F$_4$)$_3$CH·NH$_3$ (B-**6**-NH$_3$)	233	B3LYP/def2-TZVPP	present work
	284	RI-MP2/def2-TZVPP	present work
GaCl$_3$·NH$_3$	134.3 ± 0.8^{a,c}	tensimetry	33
	120.4, 110.8^a	B3LYP/def2-TZVPP	present work
	148.8, 139.3^a	MP2/def2-TZVPP	present work
Ga(C$_6$F$_4$)$_3$CH·NH$_3$ (Ga-**6**-NH$_3$)	188	B3LYP/def2-TZVPP	present work
	216	RI-MP2/def2-TZVPP	present work

^{a}Gas-phase dissociation enthalpy $\Delta H°$. ^{b}739 K. ^{c}728 K.

6 have acidities that by far exceed well-known Lewis acids such as SbF$_5$ and AlCl$_3$. The dissociation energy of B-**6**-NH$_3$ is only slightly higher than that of B(CF$_3$)$_3$·NH$_3$.

The very large dissociation energies of the compounds B-**6**-NH$_3$ and Al-**6**-NH$_3$ impressively demonstrate that both pyramidalization and fluorination result in strong acceptors that by far outperform common Lewis acids. Following the definition of Lewis superacids by Krossing et al.,[7] not only the cage acceptors **6** but also compounds Al-**2**, B-**4**, and Al-**4** exceed the Lewis acidity of SbF$_5$ with respect to ammonia and can be considered as Lewis superacids.

4. CONCLUSIONS

Pyramidalization enhances the Lewis acidity for boron-containing acceptor molecules by about 120−130 kJ mol^{-1} and for aluminum- and gallium-containing acceptors by 50−60 kJ mol^{-1}. Fluorination further enhances the complex stability by 55−75 kJ mol^{-1}. The combined increase of the bond dissociation energy amounts to 110−190 kJ mol^{-1}, which is equivalent to 19−33 orders of magnitude in Lewis acidity. If the pyramidalization energy of the acceptor moiety is considered, the bond energy in ammonia complexes is always larger for B−N bonds than for Al−N bonds. Thus, the B−N donor−acceptor interaction is potentially stronger than Al−N interactions, but in commonly used (not pyramidalized) boron-containing Lewis acids, it is usually masked by much larger unfavorable pyramidalization energy. Compared to common Lewis acids AlCl$_3$ and SbF$_5$, pyramidal group 13 element compounds designed in the present work are much stronger neutral Lewis acids toward ammonia. Our computa-

tions show that pyramidal rigid group 13 element compounds, if made, will serve as Lewis superacids and may have a significant impact on many areas of chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Optimized geometries (*xyz* coordinates) and total energies for studied compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

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646

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