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Low-Valent Group-13 Chemistry. Theoretical Investigation of the Structures and Relative Stabilities of Donor−Acceptor Complexes $R_3E-E'R'$ and Their Isomers $R_2E-E'RR'$ [†]

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Abstract: The results of quantum chemical calculations at the gradient-corrected density functional theory (DFT) level with the B3LYP functional of the donor−acceptor complexes $R_3E-E'R'$ and their isomers $R_2E-E'RR'$, where E, E′ = B−Tl and R, R′ = H, Cl, or CH_3, are reported. The theoretically predicted energy differences between the donor−acceptor form $R_3E-E'R'$ and the classical isomer $R_2E-E'RR'$ and the bond dissociation energies of the E−E′ bonds are given. The results are discussed in order to show which factors stabilize the isomers $R_3E-E'R'$. There is no simple correlation of the nature of the group-13 elements E, E′ and the substituents R, R′ with the stability of the complexes. The isomers $R_3E-E'R'$ come stabilized by π donor groups R′, while the substituents R may either be σ- or π-bonded groups. Calculations of Cl_3B-BR' [R′ = Cl, cyclopentadienyl (Cp), or Cp*] indicate that the Cp* group has a particularly strong effect on the complex form. The calculations show that the experimentally known complex Cl_3B-BCp^* is the strongest bonded donor−acceptor complex of main-group elements that has been synthesized until now. The theoretically predicted B−B bond energy is $D_o = 50.6$ kcal/mol. However, the calculations indicate that it should also be possible to isolate donor−acceptor complexes $R_3E-E'R'$ where R′ is a σ-bonded bulky substituent. Possible candidates that are suggested for synthetic work are the borane complexes $(C_6F_5)_3B-E'R'$ and $^tBu_3B-E'R'$ (E′ = Al−Tl) and the alane complexes $Cl_3Al-E'R'$ (E′ = Ga−Tl).

1. Introduction

The chemistry of group-13 elements in the oxidation state +1 has been extensively studied with experimental[1] and theoretical[2] methods in the past few years. Great progress has been made in the synthesis of compounds with the formula ER (E = B−Tl) with different substituents R that could be isolated either as monomers or as oligomers $(ER)_n$.[1,3] The diyl compounds ER behave like Lewis bases because they have an electron lone pair at atom E in the electronic ground state. Thus, ER compounds may interact with Lewis acids, yielding stable donor−acceptor complexes. Several mononuclear transition metal complexes with ER ligands where one or two diyl ligands are bonded to the metal have been made in recent years.[3e,4,5] Even homoleptical complexes $TM(ER)_4$ with TM = Ni, Pd, or Pt could be isolated.[6] The TM−ER bonding situation is schematically shown in terms of the Dewar−Chatt−Duncanson (DCD)[6] model in Figure 1.

The orbital interaction diagram given in Figure 1 indicates that the ER ligand donates electronic charge through its σ donor orbital and that the electron-deficient p(π) orbitals of atom E receive electronic charge from the metal TM and the substituent R. Early experimental work suggested that the E ← R π-donation is more important than the TM → ER π-back-donation because the first stable base-free diyl complexes L_nTM-ER that could be isolated have strong π-donor groups such as Cp* or

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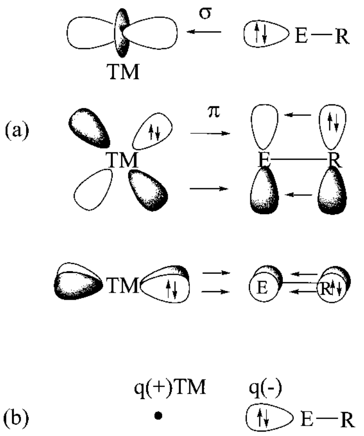

Figure 1. Schematic representation of the interactions between a transition metal TM and a group-13 diyl ligand ER. (a) Orbital interactions; (b) electrostatic interactions.

NR_2 as substituent.[4] Later work showed, however, that diyl complexes with bulky substituents R that are poor π-donors such as aryl[5] or silyl[6a,b] groups can also be synthesized and characterized by X-ray structure analysis. Results of charge and energy analyses of the bonding situation in TM diyl complexes showed that the TM → ER π-back-donation in $(CO)_4Fe(ER)$ and $(CO)_5W(ER)$ is not very large even when R is a poor π-donor.[7,8] The main component of the covalent TM−ER bonding comes from TM ← ER σ-donation, but the bonds also have a large electrostatic character that comes from the attraction between the local negative charge concentration at the donor atom E (which carries an overall positive partial charge) and the positively charged nucleus of the atom TM (which may carry an overall negative partial charge).[8] TM → ER π-back-donation becomes significantly larger, however, in homoleptical diyl complexes $TM(ER)_4$ (TM = Ni, Pd, or Pt).[7,8]

The finding that TM diyl complexes are stable when TM → ER π-back-donation is not very important suggests that main-group Lewis acids might also form stable adducts with group-13 Lewis bases ER. It could even be possible that group-13 Lewis acids ER_3 bind group-13 diyls E′R′, yielding stable complexes $X_3E{-}E'R'$, where E and E′ are the same or different elements B−Tl. In fact, some examples of the latter type of complexes have already been synthesized. Complexes of gallium and indium with the formula $I_3Ga{-}GaR$ and $I_3In{-}InR$, where R is a substituted tris(pyrazolyl)hydroborato (Tp) ligand, have been made and were characterized by X-ray structure analysis.[9] The bonding situation in the former compound was analyzed by density functional theory (DFT) methods.[10] Recently, Cowley and co-workers reported about the synthesis and X-ray structure analysis of $(C_6F_5)_3B{-}AlCp^*$ and $(C_6F_5)_3Al{-}AlCp^*$.[11] Jutzi and co-workers synthesized the analogous gallium complex $(C_6F_5)_3B{-}GaCp^*$ and the related species with gallium−gallium bonds $^tBu_3Ga{-}GaCp^*$ and $X_2Cp^*Ga{-}GaCp^*$ (X = Cl, I).[12] Siebert, Jutzi, and co-workers succeeded recently in the synthesis of the boranediyl complexes $Cl_3B{-}BCp^*$ and $Cl_2(SiCl_3)B{-}BCp^*$.[13] The experimental findings may be the starting point for a new class of molecules, i.e., donor−acceptor complexes where the donor and the acceptor atom belong to the same group of the periodic system. At the same time the results give rise to fundamental questions that need to be addressed.

One question concerns the importance of the substituent R′ in the complexes $R_3E{-}E'R'$. All examples of stable molecules that are known so far have R = Cp* or R = Tp. Is it possible to synthesize complexes where R′ is not a strong π-donor such as Cp* or Tp? The question can be addressed in the context of a more general topic. Compounds with the general formula $R_3E{-}E'R'$ are isomers of the classical forms $R_2E{-}E'RR'$. What are the relative stabilities of $R_3E{-}E'R'$ and $R_2E{-}E'RR'$ for different elements E, E′ and different substituents R, R′? Which combination of E, E′ and what substituents R, R′ favor the donor−acceptor form $R_3E{-}E'R'$ over $R_2E{-}E'RR'$? To what extend are the relative energies influenced by electronic factors? The answers to these questions are not only interesting from a theoretical point of view. They are also important to serve as a guideline for experimental studies in search of further examples of the still sparsely populated class of $R_3E{-}E'R'$ donor−acceptor complexes.

In this paper we address the above questions with theoretical methods. We report about the first systematic theoretical work where the relative energies of the parent systems of homo- and heteronuclear group-13 elements $R_3E{-}E'R'$ and $R_2E{-}E'RR'$ (E, E′ = B−Tl) with R, R′ = H are predicted and analyzed by quantum chemical DFT and ab initio methods. We investigated also the influence of chlorine and methyl substituents on the structures and relative stabilities of the isomers. To this end we calculated the isomers $R_3E{-}E'R'$ and $R_2E{-}E'RR'$ with R = H, R′ = Cl and with R = Cl, R′ = H. We also investigated the compounds $R_2E{-}E'RR'$ and the donor−acceptor complexes $R_3E{-}E'R'$ with R = Me, R′ = H and with R, R′ = Me.

Some of the above systems have been calculated before, but most studies focused on the potential energy surface (PES) of a particular species. The energy minima of B_2H_4 were studied by several authors.[14] The energy profile for rotation about the B−B axis of R_2BBR_2 (R = H, CH_3, NH_2, OH, F, Cl) was calculated by Demachy and Volatron.[15] Lammertsma and co-workers reported high-level ab initio calculations of Al_2H_4 and Ga_2H_4 isomers.[16,17] The only previous theoretical work in which the relative energies of isomeric forms of different E_2R_4 species was investigated is an older study for E = B, Al and R = H, F that was carried out at the Hartree−Fock level by Zakzhevskii and Charkin.[18]

2. Methods

The geometries of the molecules have been optimized with gradient-corrected density functional theory (DFT) by Becke's three-parameter

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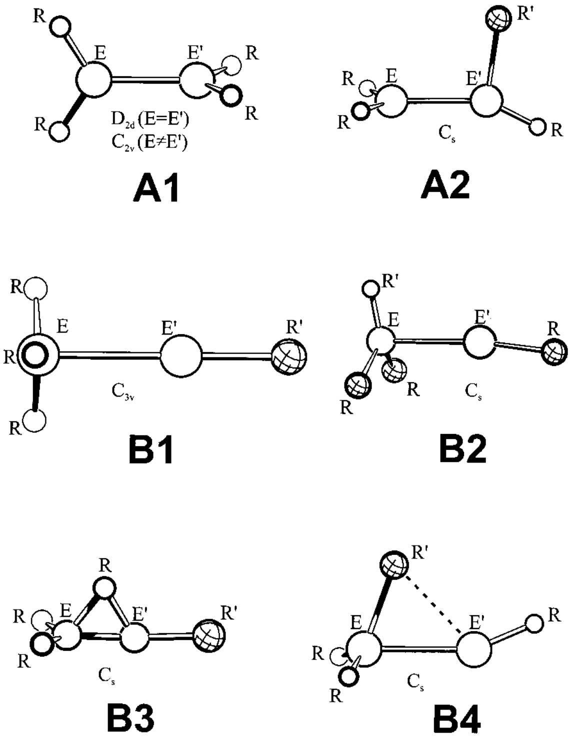

Figure 2. Structure types **A** and **B**, which have been found as energy minima of the classical isomers $R_2E{-}E'RR'$ (**A1** and **A2**) and $R_3E{-}E'R'$ (**B1**−**B4**).

hybrid method B3LYP.[19] The parent systems with R, R′ = hydrogen and some selected structures have also been calculated at the MP2 level.[20] The B3LYP and MP2 calculations were performed with all-electron basis sets that have TZ2P quality. The basis sets are (311/11) for H, (51111/311/11) for C and B, (631111/42111/11) for Al, and (631111/52111/11) for Cl.[21] For the heavier elements Ga, In, and Tl, quasi-relativistic effective core potentials (ECPs) with valence basis sets (211/211/11) were employed.[22] The nature of the stationary points on the PES was investigated by calculation of the Hessian matrixes. All structures are energy minima unless otherwise noted. The calculations have been carried out with Gaussian 98.[23]

3. Structures and Geometries

Table 1. Overview of the Structure Types That Have Been Obtained as Energy Minima of the Compounds $R_2E{-}E'RR'$ at B3LYP/TZ2P (MP2/TZ2P)[a]

	E′RR′				
R_2E	BH_2	AlH_2	GaH_2	InH_2	TlH_2
H_2B	**A1 (A1)**				
H_2Al	**A1 (A1)**	**A1 (A1)**			
H_2Ga	**A1 (A1)**	**A1 (A1)**	**A1 (A1)**		
H_2In	**A1 (A1)**	**A1 (A1)**	**A1 (A1)**	**A1 (A1)**	
H_2Tl	**A1 (A1)**	**A1 (A1)**	**A1 (A1)**	**A1 (A1)**	**A1 (A1)**

	E′RR′				
R_2E	BHCl	AlHCl	GaHCl	InHCl	TlHCl
H_2B	**A2**	**A2**	**A2**	**A2**	**A2 (A2)**
H_2Al	**A2**	**A2**	**A2**	**A2**	**B4 (B4)**
H_2Ga	**A2**	**A2**	**A2**	**A2**	**B4 (B4)**
H_2In	**A2**	**A2**	**A2**	**A2**	**B4 (B4)**
H_2Tl	**A2**	**A2**	**A2**	**A2**	**B4 (A2)**

	E′R′R				
R_2E	BHCl	AlHCl	GaHCl	InHCl	TlHCl
Cl_2B	**A2**	**A2**	**A2**	**A2**	**A2**
Cl_2Al	**A2**	**A2**	**A2**	**A2**	**A2**
Cl_2Ga	**A2**	**A2**	**A2**	**A2**	**A2**
Cl_2In	**A2**	**A2**	**A2**	**A2**	**A2**
Cl_2Tl	**A2**	**A2**	**A2**	**A2**	**A2**

	E′R′R				
ER_2	$BH(CH_3)$	$AlH(CH_3)$	$GaH(CH_3)$	$InH(CH_3)$	$TlH(CH_3)$
$B(CH_3)_2$	**A2**	**A2**	**A2**	**A2**	**A2**
$Al(CH_3)_2$	**A2**	**A2**	**A2**	**A2**	**A2**
$Ga(CH_3)_2$	**A2**	**A2**	**A2**	**A2**	**A2**
$In(CH_3)_2$	**A2**	**A2**	**A2**	**A2**	**A2**
$Tl(CH_3)_2$	**A2**	**A2**	**A2**	**A2**	**A2**

	E′RR′				
ER_2	$B(CH_3)_2$	$Al(CH_3)_2$	$Ga(CH_3)_2$	$In(CH_3)_2$	$Tl(CH_3)_2$
$B(CH_3)_2$	**A1**				
$Al(CH_3)_2$	**A1**	**A1**			
$Ga(CH_3)_2$	**A1**	**A1**	**A1**		
$In(CH_3)_2$	**A1**	**A1**	**A1**	**A1**	
$Tl(CH_3)_2$	**A1**	**A1**	**A1**	**A1**	**A1**

[a] For structures see Figure 2.

The geometry optimization of the molecules gave different types of structures for the $R_2E{-}E'RR'$ form and the donor−acceptor isomers $R_3E{-}E'R'$, which are designated as **A**- and **B**-type structures, respectively. The different structure types are schematically shown in Figure 2. Table 1 gives qualitatively the type of structures that have been obtained when the isomers with the general formula $R_2E{-}E'RR'$ became subject to geometry optimization. Table 2 shows qualitatively the results of the geometry optimization of the donor−acceptor complexes $R_3E{-}E'R'$. The bond lengths and angles of the optimized species are given as Supporting Information.

Geometry optimization of molecules $R_2E{-}E'R_2$ where the substituents R are identical (H or Me) yielded always the structure type **A1**. The optimized structures have either D_{2d} symmetry (E = E′) or C_{2v} symmetry (E ≠ E′). Some systems with R = Me have C_1 symmetry because the rotation of the methyl groups about the local C_{3v} axis yielded a lower symmetry. Geometry optimization of molecules $R_2E{-}E'RR'$ where R ≠ R′ gave species that belong to structure type **A2** except for some thallium compounds with the general formula $H_2E{-}TlHCl$ (Table 1). Geometry optimization of the latter species with E = Al−Tl yielded the donor−acceptor-type structure **B4** where the chlorine atom has migrated from Tl to E. This means that the thallium compounds have a tendency to favor the donor−acceptor form $H_2ClE{-}E'H$, where E′ has the formal oxidation state I rather than III. This is in agreement with the known chemistry of thallium, which, unlike the lighter group-13 elements, often prefers a low oxidation state over oxidation state III.

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Table 2. Overview of the Structure Types That Have Been Obtained as Energy Minima of the Donor−Acceptor Complexes $R_3E-E'R'$ and $R_2R'E-E'R$ at B3LYP/TZ2P (MP2/TZ2P)[a,b]

	E′R′				
R_3E	BH	AlH	GaH	InH	TlH
H_3B	→**A1** (→**A1**)	**B3 (B3)**	**B1 (B1)**	**B1 (B1)**	**B1 (B1)**
H_3Al	→**A1** (→**A1**)	**B1 (B1)**	**B1 (B1)**	**B1 (B1)**	**B1 (B1)**
H_3Ga	→**A1** (→**A1**)	**B1 (B1)**	**B1 (B1)**	**B1 (B1)**	**B1 (B1)**
H_3In	→**B1**[c] (**B1**)	**B1 (B1)**	**B1 (B1)**	**B1 (B1)**	**B1 (B1)**
H_3Tl	→**A1** (**B1**)	**B1 (B1)**	**B1 (B1)**	**B1 (B1)**	**B1 (B1)**

	E′R′				
R_3E	BCl	AlCl	GaCl	InCl	TlCl
H_3B	→**A2 (B3)**	**B1**	**B1**	**B1**	**B1**
H_3Al	**B1**	**B1**	**B1**	**B1**	**B1**
H_3Ga	**B1**	**B1**	**B1**	**B1**	**B1**
H_3In	**B1**	**B1**	**B1**	**B1**	**B1**
H_3Tl	**B1**	**B1**	**B1**	**B1**	**B1**

	E′R′				
R_3E	BH	AlH	GaH	InH	TlH
Cl_3B	→**A2**	→**A2**	**B3**	**B3**	**B1**
Cl_3Al	→**A2**	→**A2**	**B1**	**B1**	**B1**
Cl_3Ga	→**A2**	→**A2**	**B1**	**B1**	**B1**
Cl_3In	→**A2**	→**A2**	**B1**	**B1**	**B1**
Cl_3Tl	→**A2**	→**B2**	→**A2**	→**A2**	**B1**

	E′R				
$R'R_2E$	BCl	AlCl	GaCl	InCl	TlCl
HCl_2B	→**A2**[e]	diss	diss	diss	diss
HCl_2Al	→**A2**[e]	**B2**	**B2**	**B2**	**B2**
HCl_2Ga	→**A2**[e]	**B2**	**B2**	**B2**	**B2**
HCl_2In	→**A2**[e]	→**A2**[e]	**B2**	**B2**	**B2**
HCl_2Tl	→**B1**[d]	→**A2**[e]	**B2**	$HTl(\mu\text{-}Cl)_{2-}InCl$	$HTl(\mu\text{-}Cl)_{3-}Tl$

	E′R′				
ER_3	BH	AlH	GaH	InH	TlH
$B(CH_3)_3$	→**A2**	diss	diss	diss	diss
$Al(CH_3)_3$	→**A2**	**B1**	**B1**	**B1**	**B1**
$Ga(CH_3)_3$	→**A2**	**B1**	**B1**	**B1**	**B1**
$In(CH_3)_3$	→**A2**	**B1**	**B1**	**B1**	**B1**
$Tl(CH_3)_3$	→**A2**	**B1**	**B1**	**B1**	**B1**

	E′R′				
ER_3	$B(CH_3)$	$Al(CH_3)$	$Ga(CH_3)$	$In(CH_3)$	$Tl(CH_3)$
$B(CH_3)_3$	→**A1**	diss	diss	diss	diss
$Al(CH_3)_3$	→**A1**	**B1**	**B1**	**B1**	**B1**
$Ga(CH_3)_3$	→**A1**	**B1**	**B1**	**B1**	**B1**
$In(CH_3)_3$	**B1**	**B1**	**B1**	**B1**	**B1**
$Tl(CH_3)_3$	→**A1**	**B1**	**B1**	**B1**	**B1**

[a] For structures see Figure 2. [b] →**AN** indicates that the complex rearranges during the geometry optimization to the classical form **AN**. [c] Rearranges to H_3B-InH (**B1**). [d] Rearranges to Cl_3B-TlH (**B1**). [e] Chlorine migration to $HClE-E'Cl_2$ (**A2**).

Now we discuss the donor−acceptor-type isomers $R_3E-E'R'$. The results of the geometry optimizations are qualitatively given in Table 2. The all-hydrogen species of the heavier group-13 elements $H_3E-E'H$ (E, E′ = Al−Tl) have the C_{3v} symmetric structure **B1**. The boron analogues H_3B-BH, H_3Al-BH, and H_3In-BH are no minima on the PES. The structures rearrange during the geometry optimization to the **A1**-type isomers. The complex H_3B-AlH is predicted with a bridging hydrogen atom (structure type **B3**). The donor−acceptor complexes H_3In-BH and H_3Tl-BH are **B1**-type energy minima on the PES at the MP2/TZP level. The former species rearranges at B3LYP/TZP to the more stable **B1**-type structure H_3B-InH, while the latter rearranges to the **A1** form H_2Tl-BH_2. The calculations indicate that the complexes H_3E-BH do not exist or are at most very shallow energy minima.

All donor−acceptor complexes $H_3E-E'Cl$ are theoretically predicted to have a **B1**-type structure as energy minima except H_3B-BCl (Table 2). The latter species rearranges during geometry optimization to the classical isomer **A2**. The complexes with the general formula $Cl_3E-E'H$ are less stable with respect to substituent migration than the compounds $H_3E-E'Cl$. The boron and aluminum diyl species Cl_3E-BH and Cl_3E-AlH rearrange during geometry optimization to the classical **A2**-type isomers except $Cl_3Tl-AlH$. Geometry optimization of the latter species led to the **B2**-type complex $HCl_2Al-TlCl$. The complexes Cl_3B-GaH and Cl_3B-InH are not **B1** structures but belong to structure type **B3**, which has one bridging chlorine atom. The thallium complexes $Cl_3Tl-GaH$ and $Cl_3Tl-InH$ rearrange during geometry optimization to the classical **A2**-type isomers (Table 2).

Because the geometry optimization of $Cl_3Tl-AlH$ yielded the asymmetrically substituted **B2**-type donor−acceptor complex $HCl_2Al-TlCl$, we systematically studied the structures and energies of the compounds $HCl_2E-E'Cl$. Table 2 shows that several **B2**-type complexes $HCl_2E-E'Cl$ were found as minima on the PES while other species rearranged to more stable structures. The borylene complexes HCl_2E-BCl rearrange to the classical isomers $HClE-BCl_2$ (**A2**) except for the thallium species $HCl_2Tl-BCl$, which undergoes double chlorine migration, yielding the complex Cl_3B-TlH (**B1**). The boron complexes $HCl_2B-E'Cl$ with E′ = Al−Tl dissociate into the donor and acceptor fragments during the geometry optimization. The aluminum diyl complexes $HCl_2In-AlCl$ and $HCl_2Tl-AlCl$ rearrange to the classical isomers $HClE-AlCl_2$ (**A2**). The **B1** → **A2** migration of some $HCl_2E-E'Cl$ complexes suggests that chlorine migration is easier than hydrogen migration. The thallium complexes $HCl_2Tl-InCl$ and $HCl_2Tl-TlCl$ rearrange to the doubly and triply bridged species $HTl-(\mu Cl)_{2-}InCl$ and $HTl-(\mu Cl)_{3-}Tl$, respectively. It is obvious that particularly the boron and thallium compounds behave differently than the other group-13 species.

Table 2 shows that the geometry optimizations of $Me_3E-E'H$ and $Me_3E-E'Me$ gave similar results concerning the type of structures that were found as energy minima on the PES. All complexes with E, E′ = Al−Tl have **B1** structures as the energy minimum form. The boron species are different from the heavier group-13 analogues. The complexes $Me_3B-E'H$ and $Me_3B-E'Me$ (E′ = Al−Tl) dissociate during the geometry optimization into the donor and acceptor fragments. We did not search for weakly bonded van der Waals complexes $Me_3B-E'H$ and $Me_3B-E'Me$ (E′ = Al−Tl) because they are not important for the topic of this work. The geometry optimization of the complexes Me_3E-BH and Me_3E-BMe (E = B−Tl) yielded the classical forms **A2** and **A1**, respectively (Table 2). The only exception is $Me_3In-BMe$, which has a **B1**-type energy minimum structure. It is possible that the latter species is only a very shallow energy minimum. The relative energies of the **A**- and **B**-type structures shall now be discussed.

4. Energies

The focus of this work is the relative energies of the donor−acceptor complexes $R_3E-E'R'$ and their isomers $R_2E-E'RR'$.

Table 3. Calculated Dissociation Energies[a] of **A**-type $R_2E-E'RR'$ Compounds at B3LYP/TZ2P (MP2/TZ2P)

	E′RR′				
ER_2	BH_2	AlH_2	GaH_2	InH_2	TlH_2
BH_2	108.0 (104.6)				
AlH_2	75.8 (74.6)	58.8 (57.8)			
GaH_2	72.5 (71.8)	57.1 (56.5)	55.1 (55.1)		
InH_2	68.4 (66.9)	55.3 (53.7)	53.4 (52.4)	52.1 (50.1)	
TlH_2	62.7 (61.9)	52.6 (52.1)	50.4 (50.5)	49.7 (48.9)	46.6 (46.9)

	E′RR′				
ER_2	BHCl	AlHCl	GaHCl	InHCl	TlHCl
BH_2	102.6	74.8	70.3	66.6	60.5 (58.9)
AlH_2	72.9	58.4	56.3	54.4	*b* (*b*)
GaH_2	69.2	56.5	53.9	52.2	*b* (*b*)
InH_2	65.4	54.8	52.5	51.2	*b* (*b*)
TlH_2	59.2	51.8	49.1	48.5	*b* (47.4)

	E′R′R				
ER_2	BHCl	AlHCl	GaHCl	InHCl	TlHCl
BCl_2	97.4	72.3	66.5	63.4	55.4
$AlCl_2$	72.2	58.7	55.0	53.8	49.1
$GaCl_2$	65.9	55.3	50.5	49.9	44.1
$InCl_2$	62.7	53.5	49.2	48.7	43.8
$TlCl_2$	52.8	47.6	42.4	43.0	36.7

	E′RR′				
ER_2	$B(CH_3)H$	$Al(CH_3)H$	$Ga(CH_3)H$	$In(CH_3)H$	$Tl(CH_3)H$
$B(CH_3)_2$	95.6	67.8	64.7	60.6	54.4
$Al(CH_3)_2$	70.4	56.9	55.2	53.5	50.2
$Ga(CH_3)_2$	66.7	54.7	52.6	51.1	47.4
$In(CH_3)_2$	62.8	53.3	51.3	50.2	47.0
$Tl(CH_3)_2$	55.3	48.7	46.3	45.9	42.0

	E′RR′				
ER_2	$B(CH_3)_2$	$Al(CH_3)_2$	$Ga(CH_3)_2$	$In(CH_3)_2$	$Tl(CH_3)_2$
$B(CH_3)_2$	92.0				
$Al(CH_3)_2$	67.1	56.3			
$Ga(CH_3)_2$	63.6	54.2	51.7		
$In(CH_3)_2$	59.7	52.7	50.4	49.5	
$Tl(CH_3)_2$	52.4	48.4	45.6	45.4	40.3

[a] Values are given in kilocalories per mole without ZPE correction. [b] No **A**-type structure was found as energy minimum

Before we present and discuss the calculated results, we give the theoretically predicted E−E′ bond dissociation energies (BDEs) of the molecules. The calculated values of the $R_2E-E'RR'$ compounds are shown in Table 3. The data for the $R_3E-E'R'$ complexes are listed in Table 4. The data refer to the dissociation reactions 1 and 2:

$$R_2E-E'RR' \rightarrow R_2E + E'RR' \qquad (1)$$

$$R_3E-E'R' \rightarrow R_3E + E'R' \qquad (2)$$

The compounds R_3E and $E'R'$ have been calculated in the electronic singlet state while R_2E and $E'RR'$ were calculated in the doublet ground state.

The BDEs of the tetrahydrogen compounds $H_2E-E'H_2$ are rather high. The highest BDE is predicted for H_2B-BH_2. The theoretically predicted values at B3LYP/TZP ($D_e = 108.0$ kcal/mol) and MP2/TZP ($D_e = 104.6$ kcal/mol) are in good agreement with previous high-level calculations at the G1 level of theory, which gave $D_o = 105.8$ kcal/mol.[12d] Our values after (unscaled) zero-point energy (ZPE) corrections are $D_o = 101.9$ kcal/mol at B3LYP/TZP and $D_o = 99.7$ kcal/mol at MP2/TZP.

Table 4. Calculated Dissociation Energies[a] of **B**-type $R_3E-E'R'$ and $R_2R'E-E'R$ Compounds at B3LYP/TZ2P (MP2/TZ2P)

	E′R′				
ER_3	BH	AlH	GaH	InH	TlH
BH_3	*b* (*b*)	25.2 (26.1)	22.1 (22.7)	19.7 (20.3)	14.9 (15.0)
AlH_3	*b* (*b*)	13.9 (13.5)	13.7 (13.4)	12.9 (12.6)	11.5 (11.5)
GaH_3	*b* (*b*)	11.2 (11.2)	10.9 (10.9)	10.4 (10.4)	9.0 (9.2)
InH_3	*b* (22.3)	11.3 (11.3)	11.1 (11.0)	10.7 (10.6)	9.5 (9.6)
TlH_3	*b* (14.4)	7.6 (7.9)	7.3 (7.5)	7.3 (7.5)	6.3 (6.6)

	E′R′				
ER_3	BCl	AlCl	GaCl	InCl	TlCl
BH_3	*b*	14.8	10.0	9.8	3.8
AlH_3	23.2	6.9	4.8	4.9	2.2
GaH_3	17.9	5.1	3.2	3.5	1.2
InH_3	17.4	4.9	3.1	3.4	1.1
TlH_3	10.0	2.8	1.4	1.8	0.2

	E′R′				
ER_3	BH	AlH	GaH	InH	TlH
BCl_3	*b*	*b*	5.5	4.1	−3.1
$AlCl_3$	*b*	*b*	16.6	16.3	14.5
$GaCl_3$	*b*	*b*	16.1	16.4	14.3
$InCl_3$	*b*	*b*	17.6	17.9	16.2
$TlCl_3$	*b*	*b*	*b*	*b*	14.6

	E′R				
$ER'R_2$	BCl	AlCl	GaCl	InCl	TlCl
$BHCl_2$	*b*	*b*	*b*	*b*	*b*
$AlHCl_2$	*b*	5.1	2.2	−2.0	−0.1
$GaHCl_2$	*b*	3.9	1.6	2.0	0.0
$InHCl_2$	*b*	*b*	2.9	3.4	0.6
$TlHCl_2$	*b*	*b*	1.6	*b*	*b*

	E′R′				
ER_3	BH	AlH	GaH	InH	TlH
$B(CH_3)_3$	*b*	*b*	*b*	*b*	*b*
$Al(CH_3)_3$	*b*	6.0	6.1	5.4	4.6
$Ga(CH_3)_3$	*b*	3.9	4.0	3.4	2.8
$In(CH_3)_3$	*b*	6.0	6.0	5.5	4.7
$Tl(CH_3)_3$	*b*	3.3	3.3	3.1	2.6

	E′R′				
ER_3	$B(CH_3)$	$Al(CH_3)$	$Ga(CH_3)$	$In(CH_3)$	$Tl(CH_3)$
$B(CH_3)_3$	*b*	*b*	*b*	*b*	*b*
$Al(CH_3)_3$	*b*	6.9	7.2	6.3	5.3
$Ga(CH_3)_3$	*b*	4.7	4.8	4.2	3.4
$In(CH_3)_3$	20.7	6.9	7.0	6.5	5.4
$Tl(CH_3)_3$	*b*	4.0	4.0	3.8	3.1

[a] Values are given in kilocalories per mole without ZPE correction. [b] No **B**-type structure was found as energy minimum.

The calculated data (Table 3) of the homoatomic (E = E′) and heteroatomic (E ≠ E′) systems show the same trend for the bond energies B > Al > Ga > In > Tl. It is gratifying that B3LYP and MP2 give very similar bond energies. Substitution of *one* hydrogen by chlorine yields BDEs of $H_2E-E'HCl$ that are always slightly less than those of the respective $H_2E-E'H_2$ compound except for $H_2Tl-TlHCl$. The BDE at MP2 of the latter is 0.5 kcal/mol higher than that of $H_2Tl-TlH_2$ (Table 3). Substitution of *three* hydrogens of $H_2E-E'H_2$ by chlorine gives $Cl_2E-E'HCl$, which has BDEs that are still slightly lower than in $H_2E-E'HCl$. The mono- and trichlorine-substituted systems exhibit the same trend of the BDEs as the all-hydrogen compounds B > Al > Ga > In > Tl. The same trend is predicted for the trimethyl- and tetramethyl-substituted species $Me_2E-E'MeH$ and $Me_2E-E'Me_2$ (Table 3). The BDEs of the methyl-substituted compounds are similar to those of the chlorine-substituted species.

The trends of the calculated BDEs of the donor−acceptor complexes $R_3E-E'R'$ are very interesting. The all-hydrogen systems $H_3E-E'H$ have the order for the Lewis acids $H_3E = B > Al > Ga \sim In > Tl$. The trend of the Lewis bases EH is $E = B > Al > Ga > In > Tl$, but the decrease from AlH to TlH is very small with the heavier group-13 Lewis acids AlH_3 to TlH_3. The same trend is found for the complexes that have a chlorine-substituted Lewis base $H_3E-E'Cl$, but the absolute values of the BDEs are significantly smaller than those of $H_3E-E'H$. It is therefore interesting to note that the compounds H_3E-BCl ($E = Al-Tl$) are energy minima at B3LYP on the PES at B3LYP/TZP while the molecules H_3E-BH are not.

The calculated results of the complexes with ECl_3 as Lewis acids $Cl_3E-E'H$ are surprising at first sight because the trend of the donor−acceptor bond strength for the elements E is opposite to what has been found for the EH_3 species. The BDEs *increase* when E becomes a heavier element, i.e., the Lewis acidity increases with $Cl_3B < Cl_3Al \sim Cl_3Ga < Cl_3In$. The boron complexes $Cl_3B-E'H$ with $E' = Ga$ or In are weakly bonded species although the electron-deficient gallium and indium atoms become stabilized by a bridging chlorine atom. Cl_3B-TlH is only kinetically stable. The weaker Lewis acidity of BCl_3 compared with the heavier ECl_3 analogues can be explained by the $Cl \rightarrow E$ π-donation in ECl_3, which is much stronger in the boron compound than in the other trichlorides.

All complexes $HCl_2E-E'Cl$ have low BDEs; $D_e = 5.1$ kcal/mol (Table 4). It will be very difficult to observe the molecules experimentally. Slightly larger bond energies are calculated for the complexes with the Lewis acid EMe_3, i.e., $Me_3E-E'H$ and $Me_3E-E'Me$. Note that the BDEs of both sets of compounds have a zigzag trend for the Lewis acids Me_3E with $E = Al > Ga < In > Tl$. The nonmonotonic trend from Al to Ga and In, which is calculated for the Lewis acids EMe_3, ECl_3, and EH_3 (see above), can be explained by the filled 3d shell of Ga, which gives also a nonmonotonic trend of the electronegativities of Al (1.5), Ga (1.8), and In (1.5). Because the absolute values of the BDEs are not very large, we do not discuss the trend since it is not important for this work.

Now we will discuss the relative energies of the isomers $R_2E-E'RR'$ and $R_3E-E'R'$ on the PES. Table 5 gives the calculated energy differences between $R_3E-E'R'$ and $R_2E-E'RR'$. Table 6 shows the energy differences between $HCl_2E-E'Cl$ and the most stable classical isomer $Cl_2E-E'HCl$ or $HClE-E'Cl_2$. Negative values mean that the donor−acceptor form is more stable than the classical isomer.

The calculated energy differences between the donor−acceptor form and the classical isomer of the tetrahydrogen species $EE'H_4$ suggest that the relative stability of the $H_3E-E'H$ complexes increase when (i) the element E′ becomes heavier and (ii) the elements E becomes lighter. Thus, the trend of the relative stability of $H_3E-E'H$ over $H_2E-E'H_2$ for the Lewis acids H_3E is $H_3B > H_3Al > H_3Ga > H_3In > H_3Tl$, while the stability trend of the Lewis bases is $BH < AlH < GaH < InH < TlH$. All boron species $H_3B-E'H$ with $E' = Al-Tl$ and all thallium complexes H_3E-TlH are energetically lower lying than the classical isomers $H_2E-E'H_2$. The complex $H_3Al-GaH$ is energetically nearly degenerate with its isomer $H_2Al-GaH_2$, while $H_3Al-InH$ is slightly more stable than $H_2Al-InH_2$.

Table 5. Calculated Energy Differences between **B**- and **A**-type Structures at B3LYP/TZ2P (MP2/TZ2P)[a]

	E′R′				
R_3E	BH	AlH	GaH	InH	TlH
H_3B		−7.3 (−7.1)	−16.5 (−17.7)	−19.9 (−22.0)	−33.7 (−35.7)
H_3Al		10.5 (11.8)	0.0 (−0.5)	−2.8 (−4.2)	−16.9 (−18.9)
H_3Ga		16.8 (18.2)	6.0 (5.9)	3.2 (2.1)	−11.3 (−12.8)
H_3In	(58.7)	18.2 (20.0)	7.6 (7.8)	5.0 (4.2)	−9.0 (−10.2)
H_3Tl	(67.7)	26.1 (27.7)	15.2 (15.3)	12.9 (12.0)	−2.0 (−3.1)

	E′R′				
R_3E	BCl	AlCl	GaCl	InCl	TlCl
H_3B		−11.7	−23.2	−26.7	−41.8
H_3Al	33.7	3.3	−8.6	−10.5	
H_3Ga	40.6	8.5	−4.2	−6.0	
H_3In	40.7	10.4	−2.0	−3.5	
H_3Tl	48.8	16.5	3.2	2.3	

	E′R′				
R_3E	BH	AlH	GaH	InH	TlH
Cl_3B			17.0	17.5	−3.2
Cl_3Al			−2.7	−1.6	−22.8
Cl_3Ga			13.9	15.0	−7.1
Cl_3In			9.2	10.4	−11.0
Cl_3Tl					8.7

	E′R′				
ER_3	BH	AlH	GaH	InH	TlH
$B(CH_3)_3$					
$Al(CH_3)_3$		16.6	2.8	−0.1	−19.3
$Ga(CH_3)_3$		25.8	11.6	8.6	−11.1
$In(CH_3)_3$		26.0	12.0	9.4	−9.6
$Tl(CH_3)_3$		38.5	24.1	21.8	1.9

	E′R′				
ER_3	$B(CH_3)$	$Al(CH_3)$	$Ga(CH_3)$	$In(CH_3)$	$Tl(CH_3)$
$B(CH_3)_3$					
$Al(CH_3)_3$		13.0	−0.9	−2.8	−22.1
$Ga(CH_3)_3$		22.4	8.2	6.2	−13.7
$In(CH_3)_3$	50.3	22.5	8.5	6.8	−12.3
$Tl(CH_3)_3$		35.4	21.0	19.7	−0.7

[a] Energy differences are given in kilocalories per mole. Negative values indicate that the donor−acceptor form **B** is lower in energy than **A**.

Table 6. Calculated Energy Differences between $HCl_2E-E'Cl$ Isomers and the Most Stable Structure of **A**-type $R_2E-E'RR'$ at B3LYP/TZ2P[a]

	BCl	AlCl	GaCl	InCl	TlCl
$BHCl_2$	32.7	20.1^b	−6.2^b	−5.6^b	−38.0^b
$AlHCl_2$	17.6^c	7.1	−5.6^c	−2.5^c	−24.0^c
$GaHCl_2$	41.2^c	21.7^b	−0.6	−16.5^b	−13.1^c
$InHCl_2$	39.9^c	18.2^b	−18.5^c	−1.4	−18.4^c
$TlHCl_2$	0.1^c	34.6^b	18.8^b	14.7^b	−31.5

[a] Energy differences are given in kilocalories per mole. [b] Relative to $HClE-E'Cl_2$. [c] Relative to $Cl_2E-E'HCl$.

Table 5 shows that the trend of the energy differences $H_3E-E'Cl - H_2E-E'HCl$ is the same as above for the system $H_3E-E'H - H_2E-E'H_2$. The relative stability of the donor−acceptor complexes $H_3E-E'Cl$ is larger than for $H_3E-E'H$. However, the BDEs of the former species are significantly lower than for the latter compounds (Table 4). It is important to realize that not only the relative energy of the $R_3E-E'R'$ isomers with regard to $R_2E-E'RR'$ but also the E−E′ BDE values of the complexes are important in order to make them a possible target for synthesis.

The results that have been discussed so far could lead to the conclusion that the relative stability of the donor−acceptor form $R_3E-E'R'$ correlates only with the atomic weight of the atoms E, E′. The calculated data for the energy differences between $Cl_3E-E'H$ and $Cl_2E-E'HCl$ (Table 5) show that the nature of the substituents also plays an important role, which may lead to a stability trend of the complexes that is not straightforward. It becomes clear that the boron complexes Cl_3B-GaH and Cl_3B-InH not only have weak B−E′ bonds (Table 4) but also are much higher in energy than $Cl_2B-GaHCl$ and $Cl_2B-InHCl$. Cl_3B-TlH is only kinetically stable and therefore shall not be discussed. The aluminum complexes $Cl_3Al-E'H$ (E′ = Ga, In, Tl) not only have rather strong Al−E′ bonds (Table 4) but also are lower in energy than the classical isomers $Cl_2Al-E'HCl$. A comparison of the calculated energies of $H_3Al-E'H$ with the values of $Cl_3Al-E'H$ (E′ = Ga, In, Tl) shows that stable donor−acceptor complexes $R_3E-E'R'$ may have σ- or π-bonded substituents at the acceptor atom E. The gallium and indium analogues $Cl_3Ga-E'H$ and $Cl_3In-E'H$ (E′ = Ga, In) also have rather large BDEs but they are clearly *less* stable than the classical isomers $Cl_2Ga-E'HCl$ and $Cl_2In-E'HCl$. Only the complexes with the thallium Lewis base $Cl_3Ga-TlH$ and $Cl_3In-TlH$ are more stable than the classical isomers.

It is important to understand the reason for the peculiar trend of the energy differences between $Cl_3E-E'H$ and $Cl_2E-E'HCl$ because it shows that the smooth trend which was found for the systems $H_3E-E'H$ and $H_3E-E'Cl$ may be deceptive. The relative energies between the isomers $R_3E-E'R'$ and $R_2E-E'RR'$ are determined by two factors, which are (i) the differences between the metal−metal E−E′ bond energies and (ii) the differences between the metal−ligand E−R, E′−R, and E′−R′ bond energies. To separate the effect of the substituent exchange from the differences of the E−E′ bond energies, we calculated the energies of the disproportionation reactions 3, 4, and 5:

$$H_2E + E'H_2 \rightarrow H_3E + E'H \tag{3}$$

$$H_2E + E'HCl \rightarrow H_3E + E'Cl \tag{4}$$

$$Cl_2E + E'HCl \rightarrow Cl_3E + E'H \tag{5}$$

Table 7 gives the calculated reaction energies of reactions 3, 4, and 5. Note that the calculated values always show smooth trends from boron to thallium. The three reactions become more exothermic (less endothermic) when the atoms E′ become heavier and the atoms E become lighter. The trend is easy to understand. The bond strength between a group-13 element and hydrogen or chlorine has the trend B > Al > Ga > In > Tl; i.e., the bond becomes weaker when the group-13 element becomes heavier. Because one substituent migrates in reactions 3, 4, and 5 from E′ to E, the reaction becomes more favorable when E is a lighter atom and E′ is a heavier atom.

Next we consider the effect of the chlorine substituent on the energy of the disproportionation reaction *relative* to the reaction where R, R′ = hydrogen. To this end we calculated the *differences* between the disproportionation reactions 4 − 3 and 5 − 3. The calculated data are also shown in Table 7.

Table 7. Calculated Energies of Disproportionation Reactions 3, 4, and 5 and Differences between the Reaction Energies 4 − 3 and 5 − 3 at B3LYP/TZ2P[a]

Reaction 3: $H_2E + E'H_2 \rightarrow H_3E + E'H$

	E′H				
EH_3	BH	AlH	GaH	InH	TlH
BH_3	−19.2	−57.9	−66.9	−68.6	−81.4
AlH_3	4.3	−34.4	−43.5	−45.1	−58.0
GaH_3	9.5	−29.2	−38.2	−39.9	−52.7
InH_3	13.0	−25.7	−34.8	−36.4	−49.3
TlH_3	19.9	−18.8	−27.9	−29.5	−42.4

Reaction 4: $H_2E + E'HCl \rightarrow H_3E + E'Cl$

	E′Cl				
EH_3	BCl	AlCl	GaCl	InCl	TlCl
BH_3	−39.4	−71.6	−83.5	−83.4	−98.4
AlH_3	−16.0	−48.2	−60.1	−60.0	−75.0
GaH_3	−10.7	−42.9	−54.8	−54.7	−69.7
InH_3	−7.3	−39.4	−51.4	−51.3	−66.3
TlH_3	−0.4	−32.6	−44.5	−44.4	−59.4

Reaction 5: $Cl_2E + E'HCl \rightarrow Cl_3E + E'H$

	E′H				
ECl_3	BH	AlH	GaH	InH	TlH
BCl_3	−7.5	−30.1	−45.4	−43.4	−61.7
$AlCl_3$	−3.1	−25.8	−41.1	−39.1	−57.4
$GaCl_3$	17.4	−5.3	−20.6	−18.6	−36.8
$InCl_3$	15.5	−7.1	−22.4	−20.4	−38.7
$TlCl_3$	40.8	18.2	2.8	4.9	−13.4

Energy Differences Reaction 4 − 3

	E′Cl				
EH_3	BCl	AlCl	GaCl	InCl	TlCl
BH_3	−20.3	−13.7	−16.6	−14.8	−17.0
AlH_3	−20.3	−13.7	−16.6	−14.8	−17.0
GaH_3	−20.3	−13.7	−16.6	−14.8	−17.0
InH_3	−20.3	−13.7	−16.6	−14.8	−17.0
TlH_3	−20.3	−13.7	−16.6	−14.8	−17.0

Energy Differences Reaction 5 − 3

	E′H				
ECl_3	BH	AlH	GaH	InH	TlH
BCl_3	11.7	27.8	21.5	25.2	19.7
$AlCl_3$	−7.4	8.7	2.4	6.0	0.6
$GaCl_3$	7.9	23.9	17.6	21.3	15.9
$InCl_3$	2.6	18.6	12.3	16.0	10.6
$TlCl_3$	20.9	37.0	30.7	34.4	29.0

[a] Energies are given in kilocalories per mole.

It becomes obvious that the calculated energy differences between the disproportionation reactions 4 − 3 for the different Lewis acids H_3E are the same. This is because the energy values for H_3E *and* H_2E cancel when the two equations are subtracted from each other. Thus, the energy difference $H_3E-E'Cl - H_2E-E'HCl$ for a given Lewis base E′Cl depends only on the difference between the bond strengths E−E′ in the two isomers, which yields a smooth trend from $H_3B-E'Cl$ to $H_3Tl-E'Tl$ (Table 5). The differences between the disproportionation reactions 5 − 3 do *not* exhibit the same values for different Cl_3E complexes (Table 7) because only one term (E′H) cancels when the equations are subtracted. Note that the calculated energy differences between reaction 5 − 3 of the Cl_3Al species are very small or even negative. This is the reason the complexes $Cl_3Al-E'H$ are more favored over the classical isomer $Cl_2Al-E'HCl$ than the other $Cl_3E-E'H$ species (Table 5). The calculations predict that the molecules $Cl_3Al-E'H$ (E′ = Ga, In, Tl) are always more stable than the isomers $Cl_2Al-E'HCl$ (Table 5) and that the Al−E′ BDEs of the former species are rather high (Table 4). This is an important result that should be tested experimentally.

The energy differences between the donor−acceptor forms and the classical isomers of the $Me_3E-E'H$ and $Me_3E-E'Me$ species show the same smooth trend as the $H_3E-E'H$ and $H_3E-E'Cl$ compounds (Table 5). The relative stability of the donor−acceptor form of $Me_3E-E'H$ and $Me_3E-E'Me$ decreases with the trend $Me_3Al > Me_3Ga > Me_3In > Me_3Tl$, but the complexes become more stable with the trend $AlR' < GaR' < InR' < TlR'$ ($R' = H$, Me).

Table 6 shows the energy differences between $HCl_2E-E'Cl$ and the most stable classical isomer, $Cl_2E-E'HCl$ or $HClE-E'Cl_2$. There is a general tendency that the donor−acceptor form becomes more stable when the group-13 atom of the Lewis base E′Cl becomes heavier, i.e., $BCl < AlCl < GaCl < InCl < TlCl$, but the trend is not smooth for the same reason that was discussed above. Note that the BDEs of $HCl_2E-E'Cl$ are always very low (Table 4). The latter compounds may not be synthesized although some species are lower in energy than the classical isomers.

5. Discussion

The calculated energies of the donor−acceptor forms and their classical isomers of molecules that are taken as model compounds for larger systems shall now be used as a guide for the search of stable species with the general formula $R_3E-E'R'$. We will first compare the theoretical results with the experimental papers that report about the synthesis of the boranediyl complexes Cl_3B-BCp^* and $Cl_2(SiCl_3)B-BCp^*$, the alanediyl complexes $(C_6F_5)_3E-AlCp^*$ (E = B, Al), and the galanediyl complexes $(C_6F_5)_3B-GaCp^*$, ${}^tBu_3Ga-GaCp^*$, and $X_2Cp^*Ga-GaCp^*$ (X = Cl, I).[11−13] It is noteworthy that the diyl ligands in these complexes always carry a Cp* substituent. The only other stable complexes of this type are $I_3Ga-GaR$ and $I_3In-InR$, which have a diyl ligand with a Tp substituent R.[9] Both substituents Cp* and Tp are very bulky and are strong π-donors.[10]

An important result of our calculations is that none of the complexes with a boron−boron bond $R_3E-E'R'$, where $R' = H$, Cl, or Me, is a minimum on the PES. But the borane−borylene complexes Cl_3B-BCp^* and $Cl_2(SiCl_3)B-BCp^*$ are stable compounds that have been characterized by X-ray structure analysis![13] To investigate the effect of the Cp* ligand on the stability of the borane−borylene complexes, we calculated the structures and energies of the isomers $Cl_2B-BClX$ and Cl_3B-BX where X = Cl, Cp, or Cp*. The optimized geometries, the relative energies of the two forms, and the B−B BDEs of the complexes Cl_3B-BX are shown in Figure 3. The agreement between the calculated and experimental geometry of Cl_3B-BCp^* is very good.[13] The theoretical value for the B−B bond lengths (1.689 Å) is nearly the same as the experimental data [1.681(3) Å], and the interatomic distances between the B(borylene) atom and the carbon atoms of the ring (1.759−1.780 Å) are only slightly longer than the values obtained from X-ray structure analysis [1.747−1.756 (3) Å].[13]

The all-chlorine compound Cl_3B-BCl is not an energy minimum structure. The geometry optimization with C_{3v} symmetry constrained yielded a second-order saddle point on the PES that is 40.9 kcal/mol higher in energy than the classical (D_{2d}) form Cl_2B-BCl_2. It is interesting to compare this value with the energy differences between the classical and donor−acceptor forms of B_2HCl_3 (Cl_3B-BH is 49.9 kcal/mol higher in energy than $Cl_2B-BHCl$), B_2H_4 (H_3B-BH is 21.9 kcal/mol higher in energy than H_2B-BH_2), and B_2H_3Cl (H_3B-BCl is 13.5 kcal/mol higher in energy than H_2B-BH_2). The donor−acceptor form was in all cases calculated with enforced C_{3v} symmetry and had two imaginary frequencies. The calculated energies indicate that the σ-acceptor/π-donor substituent chlorine stabilizes the R_3B-BCl form ∼8−10 kcal/mol relative to hydrogen in R_3B-BH. The calculated bond dissociation energy (BDE) of the hypothetical species H_3B-BCl yielding BH_3 is $D_e = 22.8$ kcal/mol (Figure 3).

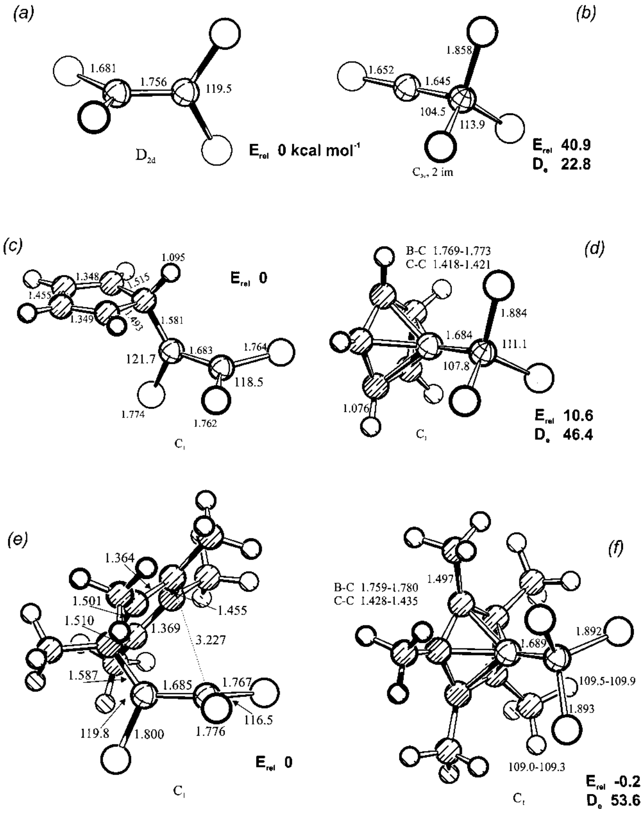

Figure 3. Optimized geometries and relative energies of the classical isomers and donor−acceptor forms of three molecules: (a) Cl_2B-BCl_2 and (b) Cl_3B-BCl; (c) $Cl_2B-BClCp$ and (d) Cl_3B-BCp; (e) $Cl_2B-BClCp^*$ and (f) Cl_3B-BCp^*. The bond dissociation energies D_e of the donor−acceptor forms are also given. Bond lengths are given in angstroms; angles, in degrees; energies, in kilocalories per mole.

Figure 3 shows that the Cp ligand has a much stronger effect than chlorine on the relative energy of the donor−acceptor form Cl_3B-BCp and the classical isomer $Cl_2B-BClCp$. However, the latter species remains 10.6 kcal/mol lower in energy than the former isomer, which is, unlike Cl_3B-BCl, an energy minimum on the PES. Thus, the relative stabilization of the donor−acceptor isomer by the Cp substituent at the diyl ligand compared with chlorine is ∼30 kcal/mol. Note that the BDE of Cl_3B-BCp ($D_e = 46.4$ kcal/mol) is much higher than the bond energy of Cl_3B-BCl ($D_e = 22.8$ kcal/mol) although the B−B bond in the latter complex is significantly *shorter* (1.645 Å) than in the former species (1.684 Å). Shorter and yet weaker bonds have been calculated for other complexes before.[2] The finding was explained with the hybridization of the lone-pair donor orbital. A higher percentage of s character yields a more compact orbital, which leads to shorter interatomic distances but also to weaker bonds because the donor orbital becomes lower in energy.[4b]

We also optimized the geometries of Cl_3B-BCp^* and $Cl_2B-BClCp^*$. The calculations predict now that the donor−acceptor form is slightly lower in energy than the classical isomer. It becomes obvious that the combined electronic and steric effect of the Cp* ligand is just enough to favor the donor−acceptor form Cl_3B-BCp^* over the classical isomer $Cl_2B-BClCp^*$. The calculations suggest that the stabilization of the donor−acceptor complex Cl_3B-BCp^* by the Cp* ligand is ∼40 kcal/mol higher compared with chlorine (Figure 3). The B−B bond in Cl_3B-BCp^* (1.689 Å) is slightly longer than in Cl_3B-BCp (1.684 Å), but the BDE of the former complex is again higher (D_e = 53.6 kcal/mol) than in the latter molecule (D_e = 46.4 kcal/mol). The very large calculated BDE of Cl_3B-BCp^* indicates that this complex is as strongly bonded as $Cl_3Al-NMe_3$ which is considered to be the strongest bonded donor−acceptor complex of main-group elements that has until now been synthesized.[24] The experimental BDE of $Cl_3Al-NMe_3$ is $D_o = 47.5 \pm 2.0$ kcal/mol.[25] The calculated values at MP2/TZ2P are $D_o = 46.9$ kcal/mol and $D_e = 49.5$ kcal/mol.[26]

The experimentally known stable complexes $(C_6F_5)_3B-AlCp^*$, $(C_6F_5)_3Al-AlCp^*$, $(C_6F_5)_3B-GaCp^*$, and $^tBu_3Ga-GaCp^*$ may be compared with the calculated structures of $H_3E-E'Cl$, because C_6F_5 and ^tBu are mainly σ-bonded substituents. The most promising $H_3E-E'Cl$ model compounds that might be stable should (i) have large $E-E'$ BDEs (Table 4) and (ii) be lower in energy than the classical isomer $H_2E-E'HCl$ (Table 5). The data in Tables 4 and 5 show that $H_3B-AlCl$ and $H_3B-GaCl$, which are models for $(C_6F_5)_3B-AlCp^*$ and $(C_6F_5)_3B-GaCp^*$, are clearly lower in energy than the classical forms *and* they have rather large BDEs. Using this result and the above finding that substituting Cl by Cp* enhances the BDE and stabilizes the donor−acceptor form over the classical structure, we can now understand why $(C_6F_5)_3B-AlCp^*$ and $(C_6F_5)_3B-GaCp^*$ are stable compounds. However, the complexes $^tBu_3Ga-GaCp^*$ and $(C_6F_5)_3Al-AlCp^*$ have also been synthesized, although the BDE of the model compound $H_3Ga-GaCl$ is rather small (Table 4) and the donor−acceptor isomer $H_3Al-AlCl$ is higher in energy than its classical form (Table 5). The large effect of the Cp* substituent, which is known to be a strong electron donor, stabilizes the real compounds, which makes it possible to isolate them. The calculated data for the other model compounds $H_3E-E'Cl$ (Tables 4 and 5) suggest that other complexes with the formula $(C_6F_5)_3E-E'Cp^*$ and $^tBu_3E-E'Cp^*$ might also be synthesized.

The calculated data shall now be used to make predictions about stable complexes with the formula $R_3E-E'R'$, where R′ is *not* a strong π-donor substituent such as Cp* and Tp. Will it be possible to synthesize a complex where R′ is a bulky σ-bonded ligand? What are the best candidates for this? Inspection of the results for the model compounds $H_3E-E'H'$, which are given in Tables 4 and 5, gives an answer. The relative energy of the donor−acceptor form $H_3E-E'H'$ increases when (i) E becomes a lighter element and (ii) E′ becomes a heavier element. The best candidates are the borane complexes $H_3B-E'H'$, where E′ = Al−Tl. We encourage experimentalists to try the synthesis of compounds $(C_6F_5)_3B-E'R'$ and $^tBu_3B-E'R'$ (E′ = Al−Tl) where R′ is a bulky σ-bonded substituent. Other possible candidates with bulky σ-bonded substituents R′ are the alane complexes $Cl_3Al-E'R'$ (E′ = Ga−Tl). Tables 4 and 5 show that the complex forms of the model compounds $Cl_3Al-E'H'$ are lower in energy than the respective classical isomer and that the Al−E′ BDE is rather large.

6. Summary and Conclusion

We present the first systematic theoretical investigation of the relative energies of the classical group-13 compounds $R_2E-E'RR'$ and the donor−acceptor isomers $R_3E-E'R'$. The results should be useful in the search for new stable complexes with the general formula $R_3E-E'R'$. The calculations show that there are several factors which determine the stability of the complex relative to the classical isomer $R_2E-E'RR'$. The donor−acceptor form is electronically stabilized by π-donor groups R′. The ligand Cp* is a particularly strongly stabilizing group. The calculations show that the experimentally known complex Cl_3B-BCp^* is the strongest bonded donor−acceptor complex of main-group elements that has been synthesized until now. However, the calculations suggest that complexes with the formula $R_3E-E'R'$ where R′ is a bulky σ ligand could also be isolated. Possible candidates that are suggested for synthetic work are the borane complexes $(C_6F_5)_3B-E'R'$ and $^tBu_3B-E'R'$ (E′ = Al−Tl) and the alane complexes $Cl_3Al-E'R'$ (E′ = Ga−Tl). The substituents R at the acceptor side of $R_3E-E'R'$ may be either σ- or π-bonded ligands.

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Supporting Information Available: Two tables with the calculated geometries and total energies of the investigated molecules (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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