Structure and Bonding of [E−Cp−E′]$^+$ Complexes (E and E′ = B−Tl; Cp = Cyclopentadienyl)

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The geometries and metal–ligand bond dissociation energies of [E−Cp−E′]$^+$ complexes (E, E′ = group 13 element; Cp = cyclopentadienyl) have been calculated within the density functional theory framework. The geometries of the title complexes were optimized at the BP86 level with the TZ2P valence basis set. The nature of the metal–ligand bonding has been studied using the energy decomposition analysis (EDA). The calculated bond strengths for the homoleptic complexes [E−Cp−E]$^+$ with respect to loss of a neutral or charged group 13 atom are Ga > Al > In > Tl ≫ B. While the energetically most favorable pathway for the boron complex [B−Cp−B]$^+$ is the loss of a neutral boron atom, heavier homologues [E−Cp−E]$^+$ (E = Al−Tl) dissociate via loss of the charged atom E$^+$. The heteroleptic species [E−Cp−E′]$^+$ are less stable than the homoleptic complexes [E−Cp−E]$^+$. The lowest energy pathway for dissociation is the loss of the positively charged heavier atom E′$^+$. The B−Cp interactions in the boron complexes have a larger (covalent) orbital character than the E−Cp bonding in the heavier homologues. The energy decomposition analysis of [E−Cp−E′]$^+$, using Cp$^-$ and (E···E′)$^{2+}$ as ligands, suggests that the a$_1$(σ) bonding has nearly the same strength as the e$_1$(π) bonding.

I. Introduction

The coordination chemistry of low-valent group 13 ligand systems constitutes an interesting area of modern main group chemistry with considerable progress in recent years.[1–7] Over the years, half-sandwich complexes containing low-valent group 13 elements have become one of the most important sets of cyclopentadienyl (Cp) compounds.[8] A remarkable electronic feature of these organometallic compounds is that the group 13 elements have an electron lone-pair (see Figure 1), and therefore they can act as excellent σ-donor ligands. Using these amazing features, several unusual complexes have been synthesized or theoretically proposed. For example, the novel homoleptic metal-rich clusters of the type [M$_a$(E−Cp*)$_b$] (M = Pd, Pt; E = Al, Ga, In; Cp* = permethylcyclopentadienyl) have been reported.[9] In the latter systems, the metal cores (M$_a$E$_b$) are surrounded only by Cp* ligands.

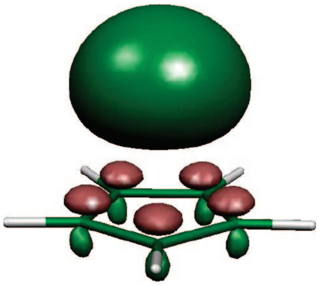

Figure 1. Lone-pair orbital of E in E−Cp.

The inverted sandwich complex [Ga−Cp*−Ga]$^+$ was recently isolated by Fischer and co-workers through treatment of Ga−Cp* with one-half molar equivalent of [H(OEt$_2$)$_2$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$].[10] The atypical complex has a symmetric bipyramidal double-cone structure in which both gallium atoms are collinear with the C_5 symmetry axis of the organic ring. A theoretical study on the analogous cation [Ga−Cp−Ga]$^+$ showed that (1) the Cp ring adopts the role of a bridging ligand in an electron-deficient compound with multicenter bonds and (2) the π−π* splitting in [Ga−Cp−Ga]$^+$ is slightly larger than the corresponding half-sandwich Ga−Cp, which leads to a significant weakening of the π bond to each individual Ga atom. The authors proposed that [Ga−Cp*−Ga]$^+$ can be used as a selective source for highly reactive Ga$^+$. In fact, when it reacts with the electron-rich d^{10} platinum(0) complex [Pt(Ga−Cp*)$_4$], a novel species [GaPt(Ga−Cp*)$_4$]$^+$[B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] is obtained.[11]The structure of the latter compound possesses an approximately trigonal-bipyramidal geometry at the platinum center with Ga$^+$ placed in the apical position.

What about analogous complexes [E−Cp*−E]$^+$ where E is a group 13 element B−Tl? Is there a particular reason that explains why until now only the homoleptic gallium complex [Ga−Cp*−Ga]$^+$ could be synthesized? Here we report an extensive computational study, using density functional theory (DFT),

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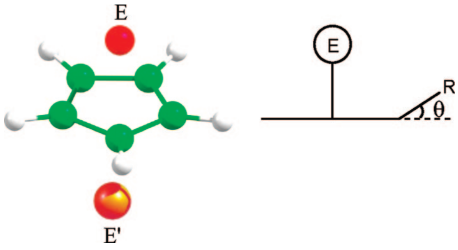
Table 1. Bond Lengths (in Å), θ Angles (in deg), and Hirshfeld Charges for Cationic Complexes $[E{-}Cp{-}E']^+$



E	E′	$r(E{-}Cp)^a$	$r(E'{-}Cp)^a$	θ	$q(E)$	$q(E')$
B	B	1.796	1.796	0.0	0.206	0.206
B	Al	1.665	2.459	4.7	0.101	0.538
B	Ga	1.633	2.541	5.4	0.080	0.578
B	In	1.608	2.784	6.0	0.057	0.643
B	Tl	1.602	2.878	6.2	0.046	0.684
Al	Al	2.288	2.288	0.0	0.445	0.445
Al	Ga	2.257	2.375	0.6	0.425	0.500
Al	In	2.226	2.612	1.1	0.397	0.580
Al	Tl	2.207	2.715	1.3	0.378	0.635
Ga	Ga	2.345 $(2.228)^b$	2.345 $(2.237)^b$	0.0	0.481	0.481
Ga	In	2.317	2.583	0.5	0.453	0.562
Ga	Tl	2.303	2.687	0.7	0.437	0.620
In	In	2.551	2.551	0.0	0.535	0.535
In	Tl	2.533	2.656	0.2	0.517	0.595
Tl	Tl	2.638	2.638	0.0	0.578	0.578

[a] Distance to the center of the Cp ring. All values have been calculated at the BP86/TZ2P level. [b] Bond lengths in Å obtained in the solid state structure.

of the symmetrical and unsymmetrical $[E{-}Cp{-}E']^+$ complexes (E and E′ = group 13 element). We think that the model compounds, where Cp* is replaced by Cp, should give valuable information about the relative stabilities and the bonding situation in the complexes. To this purpose, we calculated the equilibrium geometries and the bond dissociation energies of the inverted group-13 sandwich complexes. The nature of the metal–ligand bonding has been studied using the energy decomposition analysis (EDA). The results give quantitative information about the relative strength of the covalent and electrostatic interactions between E and Cp.

II. Computational Details

All calculations were carried out with the program package ADF 2006.01.[12] The geometries of the molecules have been optimized at the nonlocal DFT level, using the exchange functional of Becke[13] with the correlation functional of Perdew[14] (BP86). Uncontracted Slater-type orbitals (STOs) were employed as basis functions for the SCF calculations.[15] The basis sets have triple-ζ quality augmented by two sets of polarization functions, that is, p and d functions for the hydrogen atoms and d and f functions for the other atoms. This level is denoted as BP86/TZ2P. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle. Scalar relativistic effects have been considered using the zero-order regular approximation (ZORA).[16–20] The vibrational frequencies of the optimized structures have been calculated in order to investigate the nature of the stationary points. In all cases, the Hessian matrices of the optimized geometries have only positive eigenvalues, which means that the fully optimized structures reported here are minima on the corresponding potential energy surface. The atomic partial charges were calculated by using the Hirshfeld partitioning scheme.[21]

The nature of the metal–ligand interactions was studied by an energy decomposition analysis, which was developed by Ziegler and Rauk[22] following a similar procedure suggested by Morokuma.[23] The EDA has proven to give important information about the nature of the bonding in main-group compounds and transition-metal complexes.[24–28] The focus of the bonding analysis is the instantaneous interaction energy, ΔE_{int}, of the bond, which is the energy difference between the molecule and the fragments in the electronic reference state and frozen geometry of the compound. The interaction energy can be divided into three main components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \tag{1}$$

ΔE_{elstat} gives the electrostatic interaction energy between the fragments, which are calculated using the frozen electron density distribution of the fragments in the geometry of the molecules. The second term in eq 1, ΔE_{Pauli}, refers to the repulsive interactions between the fragments, which are caused by the fact that two electrons with the same spin cannot occupy the same region in space. ΔE_{Pauli} is calculated by enforcing the Kohn–Sham determinant on the superimposed fragments to obey the Pauli principle by antisymmetrization and renormalization. The stabilizing orbital interaction term, ΔE_{orb}, is calculated in the final step of the energy partitioning analysis when the Kohn–Sham orbitals relax to their optimal form. This term can be further partitioned into contributions by the orbitals belonging to different irreducible representations of the point group of the interacting system. The interaction energy, ΔE_{int}, can be used to calculate the bond dissociation energy, D_e, by adding ΔE_{prep}, which is the necessary energy to promote the fragments from their equilibrium geometry to the geometry in the compounds (eq 2). The advantage of using ΔE_{int} instead of D_e is that the instantaneous electronic interaction of the fragments becomes analyzed, which yields a direct estimate of the energy components.

$$-D_e = \Delta E_{prep} + \Delta E_{int} \tag{2}$$

III. Geometries and Energies

Geometry optimizations were carried out using D_{5h} symmetry for homoleptic complexes $[E{-}Cp{-}E]^+$ and C_{5v} symmetry for the heteroleptic $[E{-}Cp{-}E']^+$ species. The harmonic frequency analysis revealed that the title compounds with the imposed symmetries are minima on the corresponding potential energy surface. The main geometrical features of the $[E{-}Cp{-}E']^+$

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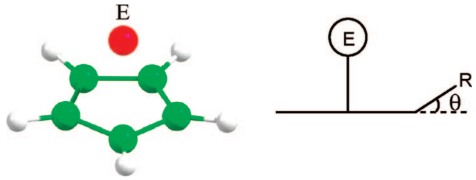
Table 2. E−Cp Distances (in Å)[a] and θ Angle (in deg) for Half-Sandwich Complexes E−Cp



E	E−Cp	θ
B	1.586	5.8
Al	2.073	0.4
Ga	2.169	−0.7
In	2.373	−1.5
Tl	2.474	−2.0

[a] Distance to the center of the Cp ring. All values have been calculated at the BP86/TZ2P level.

cations are summarized in Table 1. In the case of the heteroleptic systems, E refers to the lighter group 13 atom, while E′ is the heavier element. All complexes show a bipyramidal double-cone structure similar to the experimental complex [Ga−Cp*−Ga]$^+$. From the data in Table 1, it is evident that the heavier elements E′ induce a shortening of the E−Cp distance of the lighter atom E with a concomitant opening of the θ angle. We exemplify this for the case of the boron series. While the B−Cp distance decreases from 1.796 Å when E′ = B to 1.602 Å when E′ = Tl, the θ angle increases from 0.0° in [B−Cp−B]$^+$ to 6.2° in [B−Cp−Tl]$^+$. At the same time, while the calculated atomic charge on the E atom decreases, the charge on the E′ atom increases (see Table 1). Note that the atomic partial charge at the E atom is rather small, which points to a very large formal electron donation from E to Cp. In fact, the above geometrical features and the Hirshfeld charge values are strongly correlated. When one plots the E−Cp distances versus the θ angle, a linear correlation (R = 0.99) is observed (Figure 2). A linear correlation is also observed in the plots of the E−Cp distances versus the values of the Hirshfeld charges.

The bending of the hydrogen atoms with respect to the planarity of the cyclopentadienyl ring (θ angle) is a geometrical feature that is also shared by the corresponding η^5-E−Cp complexes (see Table 2). There is an earlier discussion in the literature about the θ angle variation in Cp complexes. The "electrostatic interpretation" was first proposed by Alexandratos et al.[29] and reinvestigated by Jemmis et al.[30] This effect may be ascribed to the diffuseness of the p orbitals of the E atom, which modifies the overlap with the π orbital of the Cp ring in the bonding 3e$_1$ orbital (Figure 3). The overlap is smaller for heavier group 13 elements. Consequently, the bending of the hydrogen atoms is much stronger in the boron complex. The same explanation can be applied to the [E−Cp−E′]$^+$ analogues.

We calculated the bond dissociation energies of the homoleptic and heteroleptic complexes [E−Cp−E′]$^+$ for loss of neutral and charged atoms E and E$^+$. The results are summarized in Table 3. The energetically most favorable pathway for breaking one metal–ligand bond of the boron complex is the loss of a neutral boron atom, [B−Cp−B]$^+$ → [Cp−B]$^+$ + B (reaction D3, Table 3). The calculated BDE is D_e = 29.8 kcal·mol^{-1}. In contrast to the homoleptic boron complex, the calculations indicate that the energetically most favorable bond-breaking reaction of the heavier homologues E = Al−Tl is the dissociation of the charged atomic species [E−Cp−E]$^+$ → [Cp−E] + E$^+$ (reactions D1 and D2, Table 3). The calculated bond reaction energies are clearly higher than those for the reactions D3 and D4. Moreover, the least energy pathway for dissociation of the heavier atomic species, which is in the range D_e = 40.3–45.1 kcal·mol^{-1}, is clearly higher than for the boron complex. This result is at first sight surprising, and it turns common wisdom upside down. Chemical bonds of elements of the first octal row are usually stronger than analogous bonds of the higher rows. We should point out that the ionization energy of B giving B$^+$ is much higher (8.298 eV) than for the heavier homologues, which are between 5.99 (Al) and 6.11 eV (Tl). It explains why B would relatively easily dissociate as the neutral atom, but not as a cation.

The results for the homoleptic complexes [E−Cp−E]$^+$ suggest that the heavier species with E = Al−Tl have stronger Cp−E bonds than for E = B. This surprising finding can be explained with the change in the least energy pathway for the bond dissociation, which yields a neutral boron atom for [B−Cp−B]$^+$, while a charged atom E$^+$ dissociates from the heavier homologues [E−Cp−E]$^+$. The results imply that the interactions between charged B$^+$ and the Cp ligand are much stronger compared to the heavier congeners. For a further discussion we refer to the bonding analysis below. We want to point out that the homoleptic complex [E−Cp−E]$^+$ with the highest BDE is the gallium species [Ga−Cp-Ga]$^+$, which according to the calculations is thus the thermodynamically most stable [E−Cp−E]$^+$ species. The least stable complex is the boron homologue [B−Cp−B]$^+$ (Table 3). The calculations indicate that the stability of the [E−Cp−E]$^+$ complexes with respect to loss of a neutral or charged group-13 atom is Ga > Al > In > Tl ≫ B. It is interesting to note that it was indeed a gallium complex [Ga−Cp*−Ga]$^+$ that could be isolated as the first stable inverted sandwich complex [E−Cp−E]$^+$. The reader should consider that the calculated energies reported here refer to isolated species in the gas phase. In a condensed phase, the stabilization of the fragments needs to be considered.

The calculated bond dissociation energies for the heteroleptic complexes [E−Cp−E′]$^+$ suggest that the most favorable dissociation pathway is always the loss of the positively charged heavier element, [E−Cp−E′]$^+$ → [Cp−E] + E′$^+$ (reaction D1, Table 3). The theoretical values also show that the heteroleptic species should be less stable than the homoleptic complexes of the heavier elements E = Al−Ga. According to the calculated bond energies, the most stable species are [In−Cp−Tl]$^+$ (D_e = 35.4 kcal·mol^{-1}), [Ga−Cp−In]$^+$ (D_e = 34.9 kcal·mol^{-1}), and [Al−Cp−Ga]$^+$ (D_e = 33.7 kcal·mol^{-1}). The least stable heteroleptic complexes [E−Cp−E′]$^+$ are those where E = boron.

IV. Bonding Analysis

Figure 4 shows the orbital correlation diagram between the valence orbitals of the (E···E′)$^{2+}$ fragment and the π orbitals of the Cp$^-$ fragment in the [E−Cp−E′]$^+$ cations. Four bonding valence electrons of the double-cone cations occupy the lowest lying degenerate e$_1$ orbitals, which is the combination of the corresponding e$_1$ orbital of the Cp$^-$ moiety with the p$_x$ and p$_y$ atomic orbitals of the (E···E′)$^{2+}$ fragment. The a$_1$ orbital of the complex is formed by combination of the a$_1$ orbital of Cp$^-$ and the antisymmetric combination of the s atomic orbitals of the (E···E′)$^{2+}$ fragment. A related correlation diagram was previously proposed for the half-sandwich E−Cp analogues,[7] which suggests a similar bonding situation in [E−Cp−E′]$^+$

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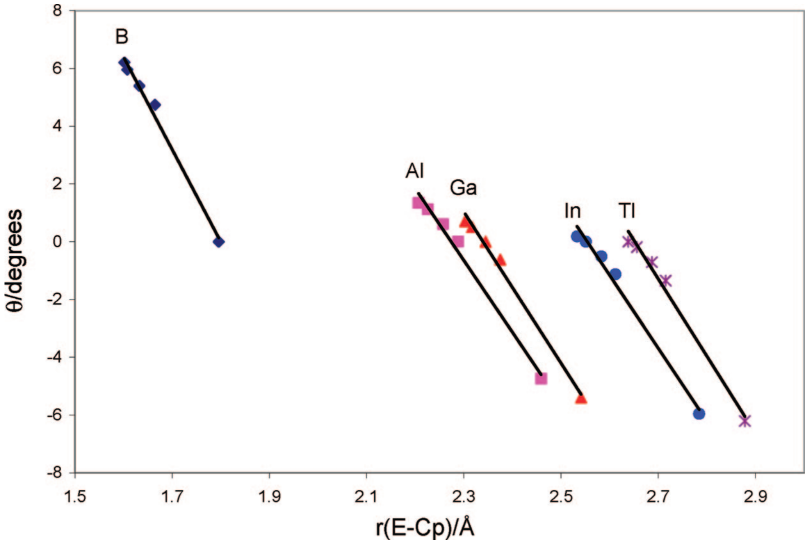


Figure 2. Plot of the E−Cp bond lengths versus the θ angle for complexes.

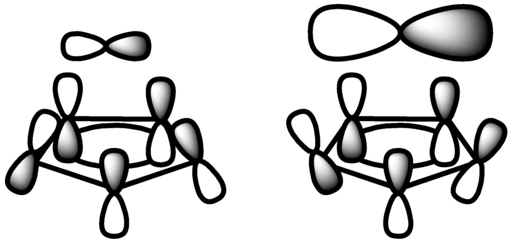


Figure 3. Schematic representation of the inward and outward bending of the p(π) orbitals of Cp following the size of the valence p functions of E in E−Cp.

cations. Using an energy partitioning analysis, it was found that the covalent and electrostatic attractions in the B−Cp complex have nearly equal strength, while the covalent bonding in the heavier analogues contributes between 28% (in Tl−Cp) to 35% (in Al−Cp) to the total attraction. Interestingly, the a_1 (σ) orbital interactions contribute from 37 to 44% to the ΔE_{orb} term, while 51–58% comes from the e_1 (π) orbitals.[7]

The EDA of the homoletic complexes with D_{5h} symmetry was done in the C_{5v} point group in order to compare the data for homoleptic complexes with those of the heteroleptic species. In both cases we used closed-shell Cp^- and $(\mathrm{E\cdots E'})^{2+}$ moieties as fragments. First, we analyzed the bonding in the homoleptic double-cone cations $[\mathrm{E{-}Cp{-}E}]^+$. From the data in Table 4, it becomes obvious that the boron complex has the highest value of the interaction energy ($\Delta E_{\mathrm{int}} = -416.4$ kcal·mol^{-1}) between the $(\mathrm{E\cdots E})^{2+}$ and Cp^- fragments, and this value monotonically decreases when one goes from aluminum to thallium. Note that the strength of the interactions clearly does not correlate with the thermodynamical stability of the complexes. As shown above, the homoleptic boron complex is the least stable, while the gallium complex is the most stable species. Interestingly, the covalent and electrostatic attractions in the $[\mathrm{B{-}Cp{-}B}]^+$ complex have similar strengths, while the electrostatic bonding, which contributes from 76% in $[\mathrm{Al{-}Cp{-}Al}]^+$ to 81% in $[\mathrm{Tl{-}Cp{-}Tl}]^+$, is the main contribution to the total attraction in the heavier analogues. This result is in very good agreement with the suggestion that the bonding situation in $[\mathrm{E{-}Cp{-}E'}]^+$ cations is similar to E−Cp complexes. However, we want to remark that the presence of a second E atom in $[\mathrm{E{-}Cp{-}E'}]^+$cations leads to a higher electrostatic contribution (ca. 10% higher) compared to the one of half-sandwich E−Cp.[7] The partition of the orbital term into contributions by the orbitals belonging to different irreducible representations of the point group shows that the $a_1(\sigma)$ bonding has nearly the same strength as the $e_1(\pi)$ bonding. Our EDA data support the suggestion by Fischer et al. that the slightly larger $\pi{-}\pi^*$ splitting in the ionic $[\mathrm{E{-}Cp{-}E}]^+$ complexes compared to E−Cp leads to a significant weakening of the π bond to each individual E atom. In fact, the $e_1(\pi)$ bonding is computed to be ca. 6–10% lower in $[\mathrm{E{-}Cp{-}E}]^+$ cations than in E−Cp species.[7]

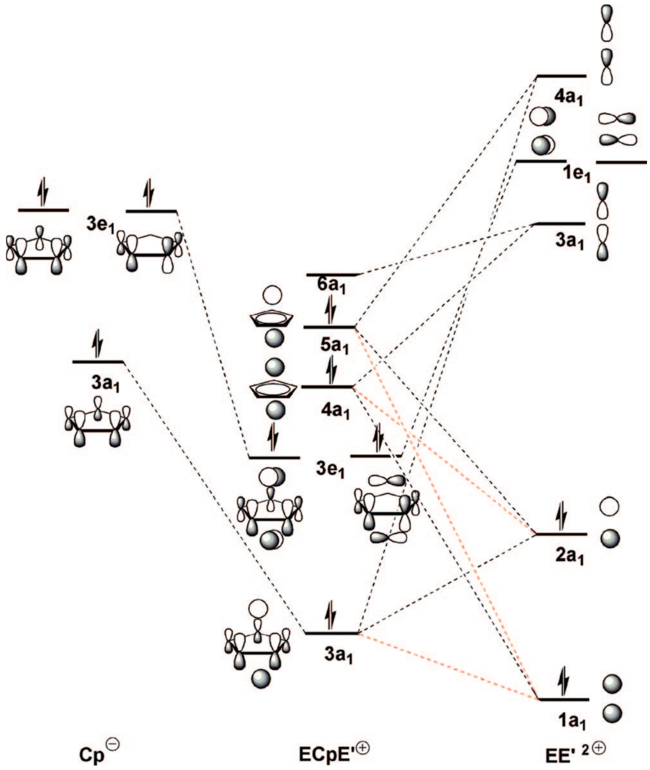
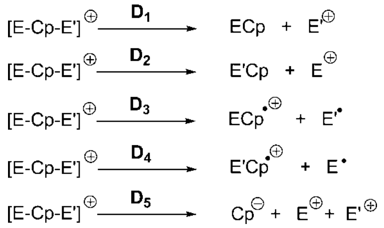


Figure 4. Qualitative correlation diagram for $[\mathrm{E{-}Cp{-}E'}]^+$ cationic complexes. The dashed lines in red indicate orbital interactions that appear only in the heteroleptic complexes where E ≠ E′.

Table 5 shows the EDA data for the heteroleptic complexes $[\mathrm{E{-}Cp{-}E'}]^+$. Similar to the symmetrical species, the boron complexes have the highest values of the interaction energy

Table 3. Dissociation Energies for Complexes at the BP86/TZ2P Level[a]



E	E′	D_1	D_2	D_3	D_4	D_5
B	B	71.3	71.3	29.8	29.8	326.6
B	Al	27.1	95.9	45.0	81.9	282.3
B	Ga	27.2	101.6	44.4	107.5	282.5
B	In	20.5	111.3	45.5	117.5	275.7
B	Tl	17.5	117.8	48.3	146.6	272.7
Al	Al	42.4	42.4	82.0	82.0	228.9
Al	Ga	33.7	46.7	79.9	112.0	227.5
Al	In	31.4	53.5	78.2	119.2	217.9
Al	Tl	27.3	58.9	79.9	147.2	213.8
Ga	Ga	45.1	45.1	109.6	109.6	225.9
Ga	In	34.9	51.3	107.3	116.3	215.7
Ga	Tl	30.5	56.4	108.7	143.9	211.3
In	In	40.3	40.3	113.2	113.2	204.8
In	Tl	35.4	44.9	114.0	140.3	199.9
Tl	Tl	39.8	39.8	141.0	141.0	194.7

[a] Energy values in kcal·mol^{-1}. The electronic states for the neutral (E or E′) and cationic (E^+ or E'^+) metal fragments are ns^2np^1 and ns^2, respectively.

between the $(E\cdots E')^{2+}$ and Cp^- fragments. Furthermore, the strength of interactions is always higher in boron-containing complexes $[B{-}Cp{-}E']^+$ than in the corresponding $[E{-}Cp{-}E']^+$ ($E \neq B$) cations. This is again evidence of the better orbital overlap for boron complexes, which is also reflected in the geometrical features of the complexes. We also found that the electrostatic bonding is the main term in the total attraction and becomes even more important in the heavier analogues (for instance, ΔE_{elstat} contributes 81% in $[In{-}Cp{-}Tl]^+$ compared to 61.1% in $[B{-}Cp{-}Tl]^+$). Finally, the partition of the orbital term into contributions by the orbitals belonging to different irreducible representations of the point group shows that the $a_1(\sigma)$ bonding and $e_1(\pi)$ bonding have nearly the same strength.

Table 4. Results of the EDA for Homoleptic Complexes $[E{-}Cp{-}E]^+$ (interacting fragments are $(E\cdots E)^{2+}$ and Cp^-; energy values in kcal·mol^{-1})

	$[E{-}Cp{-}E]^+$				
	B	Al	Ga	In	Tl
ΔE_{int}	−416.4	−299.1	−295.2	−268.4	−256.7
ΔE_{Pauli}	267.7	149.3	118.0	105.3	89.0
ΔE_{elstat}[a]	−397.5	−339.0	−315.3	−298.9	−280.8
	(58.1%)	(75.6%)	(76.3%)	(80.0%)	(81.2%)
ΔE_{orb}[a]	−286.6	−109.5	−97.9	−74.8	−64.9
	(41.9%)	(24.4%)	(23.7%)	(20.0%)	(18.8%)
a_1[b]	−129.3	−55.9	−45.9	−36.4	−29.3
	(45.1%)	(51.0%)	(46.9%)	(48.6%)	(45.1%)
a_2[b]	0.0	0.0	0.0	0.0	0.0
	(0.0%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)
e_1[b]	−142.8	−46.1	−45.2	−33.1	−31.0
	(49.8%)	(42.1%)	(46.2%)	(44.2%)	(47.8%)
e_2[b]	−14.5	−7.5	−6.8	−5.3	−4.6
	(5.1%)	(6.9%)	(6.9%)	(7.1%)	(7.1%)

[a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. [b] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}.

IV. Conclusions

From the computational study reported in this paper the following conclusions can be drawn: (i) The presence of a E′ atom different from E in the bipyramidal double-cone structure of $[E{-}Cp{-}E']^+$ complexes induces a shortening of the E−Cp distance with the concomitant bending of the hydrogen atoms with respect to the cyclopentadienyl ring. The latter effect may be ascribed to the diffuseness of the p orbitals of the E atom, which modifies the overlap with the π orbital of the Cp ring. (ii) The calculated bond strengths for the homoletic complexes $[E{-}Cp{-}E]^+$ with respect to loss of a neutral or charged group-13 atom is Ga > Al > In > Tl ≫ B. The energetically most favorable pathway for the boron complex $[B{-}Cp{-}B]^+$ is the loss of a neutral boron atom, while the heavier homologues $[E{-}Cp{-}E]^+$ (E = Al−Tl) dissociate via loss of the charged atom E^+. (iii) The heteroleptic species $[E{-}Cp{-}E']^+$ are less stable than the homoleptic complexes $[E{-}Cp{-}E]^+$. The lowest energy pathway for dissociation is the loss of the positively charged heavier atom E'^+. (iv) The B−Cp interactions in the boron complexes have a larger orbital (covalent) character than the E−Cp bonding in the heavier homologues. The energy decomposition analysis of $[E{-}Cp{-}E']^+$ using Cp^- and

Table 5. Results of the EDA for heteroleptic complexes $[E{-}Cp{-}E']^+$. The interacting fragments are $(E\cdots E')^{2+}$ and Cp^-. Energy values in kcal·mol^{-1}

	$(E{-}Cp{-}E')^+$									
E	B	B	B	B	Al	Al	Al	Ga	Ga	In
E′	Al	Ga	In	Tl	Ga	In	Tl	In	Tl	Tl
ΔE_{int}	−360.2	−360.7	−350.0	−346.4	−297.4	−284.8	−279.9	−282.1	−276.8	−262.7
ΔE_{Pauli}	232.8	231.6	235.6	232.2	135.6	131.2	125.5	112.1	104.7	97.2
ΔE_{elstat}[a]	−374.0	−366.2	−360.7	−353.7	−328.5	−321.0	−313.3	−307.1	−298.5	−289.9
	(63.1%)	(61.8%)	(61.6%)	(61.1%)	(75.9%)	(77.1%)	(77.3%)	(77.9%)	(78.2%)	(80.6%)
ΔE_{orb}[a]	−219.0	−226.2	−224.9	−224.9	−104.5	−95.1	−92.1	−87.1	−83.0	−70.0
	(36.9%)	(38.2%)	(38.4%)	(38.9%)	(24.1%)	(22.9%)	(22.7%)	(22.1%)	(21.8%)	(19.4%)
a_1[b]	−99.3	−100.7	−99.4	−97.9	−51.6	−47.6	−45.1	−41.4	−38.2	−32.9
	(45.3%)	(44.5%)	(44.2%)	(43.5%)	(49.3%)	(50.1%)	(49.0%)	(47.6%)	(46.0%)	(47.0%)
a_2[b]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	(0.0%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)	(0.0%)
e_1[b]	−108.7	−114.3	−114.8	−116.5	−45.7	−40.9	−40.7	−39.6	−39.1	−32.1
	(49.6%)	(50.5%)	(51.0%)	(51.8%)	(43.8%)	(43.0%)	(44.2%)	(45.5%)	(47.1%)	(45.9%)
e_2[b]	−11.1	−11.3	−10.7	−10.5	−7.2	−6.6	−6.3	−6.0	−5.7	−5.0
	(5.0%)	(5.0%)	(4.8%)	(4.7%)	(6.9%)	(6.9%)	(6.8%)	(6.9%)	(6.9%)	(7.1%)
r(E−C)/Å	2.060	2.034	2.013	2.008	2.562	2.535	2.518	2.616	2.603	2.808
r(E′−C)/Å	2.741	2.815	3.036	3.123	2.667	2.880	2.974	2.854	2.948	2.920

[a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. [b] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}.

$(E\cdots E')^{2+}$ as ligands suggests that the $a_1(\sigma)$ bonding has nearly the same strength as the $e_1(\pi)$ bonding.

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Supporting Information Available: Cartesian coordinates (in Å) and total energies (in au) of all the stationary points discussed in the text are available free of charge via the Internet at http://pubs.acs.org.

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