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Neutral Carbene Analogues of Group 13 Elements: The Dimerization Reaction to a Biradicaloid

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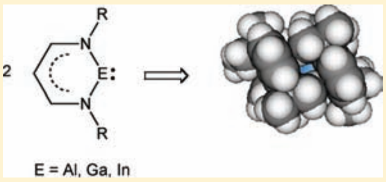
ABSTRACT: The dimerization reactions of the neutral carbene analogues with the group 13 elements boron, aluminum, gallium, and indium are studied. Besides boron, all monomeric species possess singlet ground states. For Al, bulky substituted cases were investigated; they reveal no essential changes in the singlet−triplet energy separations compared with the parent species. The dimerization energies increase with an increase in the bulk of the substituents; this is a consequence of an enhancement of van der Waals forces for association. The latter is opposed by entropic forces, which facilitate dissociation. An equilibrium between monomeric and dimeric structures is predicted because of enthalpy versus entropy control. The low-temperature domain association should prevail in the formation of a dimer with Al (Ga) within the formal oxidation state I+. The Al−Al bond refers to a chelated biradicaloid species with an energetically low-lying triplet state. It emerges from the metal−metal contacts in the dimer. The biradical character of the dimer decreases in the order E = Al ≫ Ga > In. The carbene analogue of In forms upon dimerization of only weak coordinative metal−metal interactions.



INTRODUCTION

The intense experimental work in the field of diazabutadiene ligands with group 13 elements has paved the way for the syntheses of carbene analogues, as is documented in the first reports on **1**, where E = Ga[1,2] and B,[3,4] and **2**, where E = Al,[5] Ga,[6] and In,[7] as reviewed lucidly (Scheme 1).[8] On the other hand, quantum chemical calculations predicted[9−11] the existence of **1** or analyzed bonding in more detail in **2**.[12−15]

It has been stated that these compounds are analogous to carbenes. One of the archetypal reactions of a carbene species is the self-dimerization reaction under the formation of a double-bonded system, as sketched in Scheme 2A.

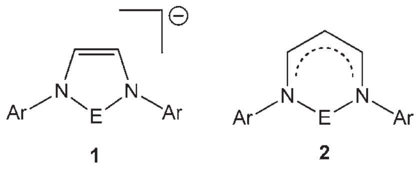
For reaction A, a large energy profit results; this is a consequence of the gain in strong C−C bond energy. In the formulation of such an equilibrium for reaction B, one would expect double bonds among group 13 elements, an attempt difficult to achieve.[16] This is, in general, viewed as a rationale for the fact that in all experimental investigations only monomeric carbene units are found as stable, isolable entities.

In the present quantum chemical investigation, a possible dimerization reaction for **2**, where E = Al, Ga, and In, is analyzed. It will be shown that dimers exist, held together by van der Waals forces, and their predicted stabilities depend strongly on the chosen reaction conditions. The complexes are predicted to be stable at low temperature; the resulting metal−metal contacts acquire E−E bonds with biradical character. Thus, these species should exert high reactivity.

RESULTS AND DISCUSSION

For **2** (E = Al, Ga, and In), all of the calculations[8] agree that the B derivative has a small adiabatic singlet−triplet (S−T), while the higher homologues (Ga, Al, and In) have large S−T energy separations. Our findings are in accordance with these previous reports and will not be repeated here. In addition, we find S−T energy separations, which are almost insensitive to the bulkiness of the substituents. For completeness, the investigations on the monomeric carbene analogues are summarized in Table 1. For E = Al, a variety of substituents were probed, mimicking the experimental situation in either the 2.6-diisopropylphenyl (Dipp) substitution[5] or the well-known terphenyl (Terph) ligand by Rivard and Power.[17]

Scheme 1



One important aspect is the bonding situation in **2**. What is the oxidation state of the metal? Insight is provided by population analysis, here recorded for E = Al and R = H. The partitioning of the electron density was conducted with the Reed−Weinhold scheme[18] [natural bond order (NBO) charges at the atoms and Wiberg bond indices between bonds; Figure 1].

The negative charge resides preferentially in the pentadienyl system, while the Al atom is strongly positive. The latter is only

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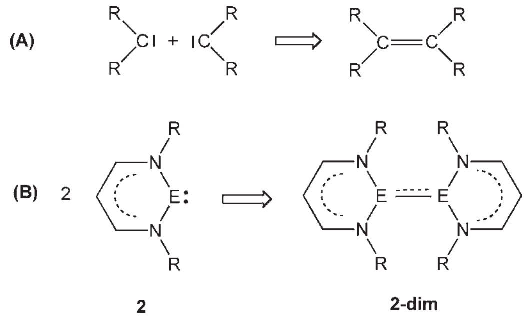
Table 1. S−T Energy Separations (in kcal/mol) at the BP86-D, MP2, and CC2 Levels and Kohn−Sham HOMO Energies (at the BP86-D Level)

		$-E_{S-T}$ (kcal/mol)			
E	R	BP86-D	MP2	CC2	$-E_\sigma$ (eV)
Al	H	34.8	40.8	38.7	4.1
	CH_3	28.4	42.8	42.7	4.1
	Ph[a]	28.5			4.3
	Mes[b]	31.8			4.2
	Dipp[c]	30.7			4.2
	Terph[d]	21.7			3.9
B	H	−0.5	7.7	6.8	3.5
Ga	H	52.6	55.6	52.5	4.9
In	H	54.5	64.5	61.5	4.8

[a] Phenyl. [b] 2,6-Dimethylphenyl. [c] 2,6-Diisopropylphenyl. [d] 2,6-Diphenylphenyl.

Scheme 2



weakly bound to the N atoms. This emphasizes an Al^+ atom chelated by a pentadienyl anion. The negative charge resides preferentially in this ligand, while the Al atom is strongly positive. This emphasizes a picture similar to that stressed for **1**.[12] In more simple terms, it can be grasped in the canonical structure **2a** in Scheme 3.

The expected bond lengths upon the dimerization reaction B can be estimated from the covalent radii of the group 13 elements.[19] Accordingly, Al and Ga have almost the same covalent radii (1.13 vs 1.17 Å), while In has a larger value (1.36 Å). In the case in which a single bond is observed, one expects bond lengths of 2.3−2.4 Å (Al and Ga) or 2.72 Å (In).

One further aspect must be considered here. In a carbene (E = C), the trigonal atom is comprised of three sp^2 hybrid orbitals; these are easily capable of forming the σ bond, while the residual p orbital constitutes the π bond. It is different, however, for the group 13 elements (E = Al, Ga, and In). The substituents R are here constituted by the 1,5-diazapentadienylid ligand, and the electronegative N atoms chelate the group 13 element E (Al, Ga, and In). According to the Bent rules,[20] the p character is now acquired in the acceptor orbitals, a, which leaves strong s character to the nonbonding orbitals, b (Scheme 4).

As a consequence, the σ-orbital b is very reluctant to form an E−E bond.

Overall, the bonding situation can be depicted as a donor (n, s^2 orbital) interacting with an acceptor (p orbital) between the two Al atoms (Scheme 5).

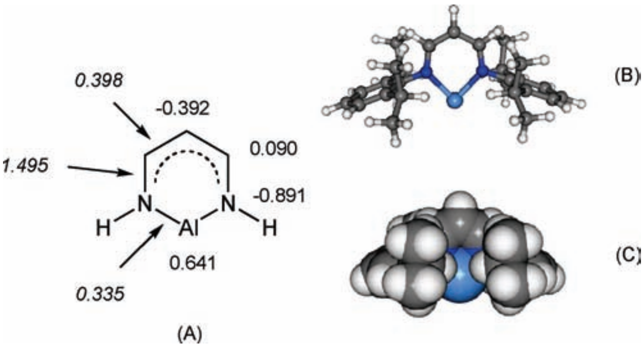
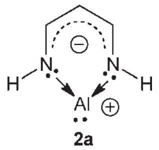
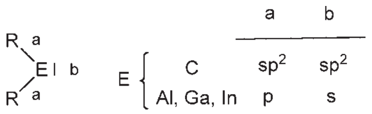


Figure 1. (A) NBO charge densities and Wiberg bond indices (in italics) for R = H and (B) ball-and-stick and (C) van der Waals representations for R = Dipp, at times given for singlet species **2**.

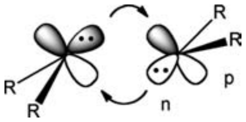
Scheme 3



Scheme 4



Scheme 5



The dimerization reaction according to B was probed for a variety of substituents, R = H, Me (methyl), Ph (phenyl), Mes (2,6-dimethylphenyl), Dipp, and Terph, at times with the group 13 elements E = Al, Ga, and In. These substituents meet the bonding situation in the "real" molecules of the experiment. They encompass bulky substituents mutually interacting by nonbonded interactions,[21] which can be sterically attractive (dispersion forces) or overall repulsive. The results of these investigations are summarized in Table 2.

The dimerization energies were calculated with (a) a density functional theory (DFT) method, which includes corrections for dispersion, and (b) an electron-correlated, wave-function-based method (MP2), which is known to properly account for van der Waals forces by nonbonded attractions.[21] If not noted otherwise, the calculations employed throughout a triple-ζ basis set (TZVP). For further computational details, see the Theoretical Section.

Table 2. (a) Dimerization Energies at the BP86-D [ΔE(DFT)] and MP2 [ΔE(MP2)] Levels at a TZVP or SVP Basis Set Level, (b) S−T Adiabatic Energy Separations [ΔE(S−T)] in the Dimer, and (c) ΔG Contributions from Thermodynamical Treatments (at the BP86-D Level, T = 298 K, p = 1 atm)[a]

E	R	r(EE), S(T)	$-\Delta E$(DFT)	$-\Delta G$	$-\Delta E$(S−T)	$-\Delta E$(MP2)
Al	H	2.731 (2.543)	12.9	2.7	7.0	8.6
	Me	2.659 (2.532)	18.8	5.9	11.1	15.4
	Ph	2.651 (2.507)	24.4	9.4	3.1	29.6
	Mes	2.653 (2.508)	33.8	11.3	10.7	36.9
	Dipp	2.723 (2.574)	27.9	1.2	6.5	20.7[b]
	Terph	2.702 (2.537)	23.1		2.9	
Ga	H	2.770 (2.478)	8.8	−1.6	44.3	6.9
	Me	2.652 (2.462)	8.4	2.4	29.5	
	Ph	2.670 (2.494)	17.5	4.7	27.6	
	Mes	2.672 (2.436)	27.9	7.5	31.5	
In	H	3.435 (2.867)	14.0	3.1	35.8	8.9
	Me	3.283 (2.845)	14.0	3.2	29.6	
	Mes	3.222 (2.954)	29.5	9.6	35.9	

[a] All energy values are in kcal/mol. r(EE) is the equilibrium distance (in Å) in the dimer. [b] Estimate from MP2 optimization at the SVP basis set level.

Both procedures, DFT as well as MP2, present a congruent picture. For the parent compounds (R = H), the dimerization energies [ΔE(DFT) and ΔE(MP2)] are essentially smaller compared with a C−C double bond. It is the reluctance to form an E−E bond. With an increase in the bulk of the substituents, the dimerization energy becomes more sizable. This effect is due to nonbonded dispersion interactions and is attractive in nature. For E = Al, they are most strongly pronounced for R = Mes. For R = Dipp, the steric bulk already exerts repulsion, which diminishes the van der Waals attraction. The last member in this series, E = In, forms stable dimers, but the In−In distances are, with 3.22−3.44 Å, already fairly large compared with twice the covalent radius of the element In. Hence, the metal−metal contacts are here fairly small. This view is in full accord with a study by Hill et al.[7b]

The dimerization reaction B (see Scheme 2) is second-order in rate. One expects that entropy will be favored in such reaction dissociations. For this purpose, we investigated the overall entropy contributions for this reaction, utilizing the standard formalism for an ideal behavior in the gas phase and solution, respectively. Of particular interest are the computed values for the free energy ΔG; they are most exothermic for the aluminum dimers with R = Mes and decrease with the bulkier Dipp substituent. For the higher homologues (E = Ga and In), the resulting free energies for reaction B are less than those for E = Al; the resulting E−E bonds become weaker.

Analysis reveals an important aspect in the dimer formation, the dependence of temperature control. The outcome of these findings is not totally unprecedented; e.g., it is known that weakly double-bonded systems, such as silylenes, can undergo dimerization at low temperatures but separate into monomeric species at room temperature, and the equilibrium is reversible.[22] Such a behavior is proposed here also. At low temperatures, dimers should be formed; they owe their stability to van der Waals binding forces. At elevated temperatures, dissociation into monomers takes place. Consequently, it would be of interest to record the reactivities of the carbene analogues **1** at modest encumbered structures under low-temperature conditions. In addition, the calculations indicate that separate monomers tighten together without any energy barrier. This gives further evidence for an equilibrium between monomeric and dimeric structures.

There is another aspect that has to be discussed here. The equilibrium geometries of dimeric **2** are strong antipyramidal. For one case (R = Dipp), a corresponding structural plot is shown in Figure 2.

The van der Waals model indicates that the molecule is sterically congested, and one expects a strong reluctance to further chemical reactions.

The first information on the electronic nature of the dimers is provided by population analysis. Accordingly, in the singlet, the NBO charge is 0.588+. This value for the charge in the dimer is very similar to that in the monomer (see Figure 1).

The triplet of the E−E bond differs in one essential aspect from the singlet. From each group 13 element, one electron is promoted from the s^2 orbital to the p orbital. This causes the formation of two equivalent sp-type orbitals. The two fragments have overall four orbitals (two nonbonding s orbitals and two empty p orbitals; see Scheme 5), of which two comprise the σ bond and the other occupy two orbitals with like spin (in the triplet). Overall, it strengthens the E−E interactions, and the bond distances become shorter (in reference to the singlet). This view is supported by the results of the calculations. As can be seen, in the triplet state, the equilibrium E−E distances shrink with reference to the corresponding singlet (see Table 2). Small S−T separations are only observed for the case E = Al, but even for E = Ga, the S−T separations are smaller than those in the monomer. For E = In, such an electronic coupling is least feasible and the bonding features of the monomers are preserved, even though the van der Waals complexes exert stability too.

The bonding features in the Al_2 fragment of the dimer are different from the expectations in aluminum chemistry. The two Al atoms are chelated together by four electronegative N atoms. Overall, this refers to a complex $Al_2R_4^{2-}$, where each Al atom formally has an oxidation state of I+. On the other hand, stable dialuminum complexes, such as Al_2Br_4, are structurally characterized as donor complexes[23] or Al_2Cl_4 characterized in solution,[24] including quantum chemical calculations.[25] The latter reveal Al−Al distances shorter than those found here, in the range of 2.5−2.6 Å, and a planar geometry with small rotational barriers results. Because these complexes are neutral, both Al atoms possess a formal oxidation state of II+; this yields an overall charge of 4+, which is neutralized by the four Cl^- anions.[26] Alternatively, one can assign to the Al atoms formal charges of I+ and III+ as a mixed-valence compound, but this classification is, in general, reserved for transition-metal compounds undergoing fast electron transfer.[27]

The S−T energy difference in the triplet states of **2-dim** is mainly determined by the gain in energy in shrinking of the Al−Al bond as opposed to decoupling of the electron pairs. Because the E−E bond energies decrease in the order Al > Ga > In, it is expected that the resulting S−T energy separation is smallest for **2-dim** with Al.

The analysis presented here is of general importance for group 13 carbene analogues, but it remains to be proven by calculations whether the presented concept holds equally well for the anionic group 13 carbenes of type **1**. Hitherto, the Al analogue of the

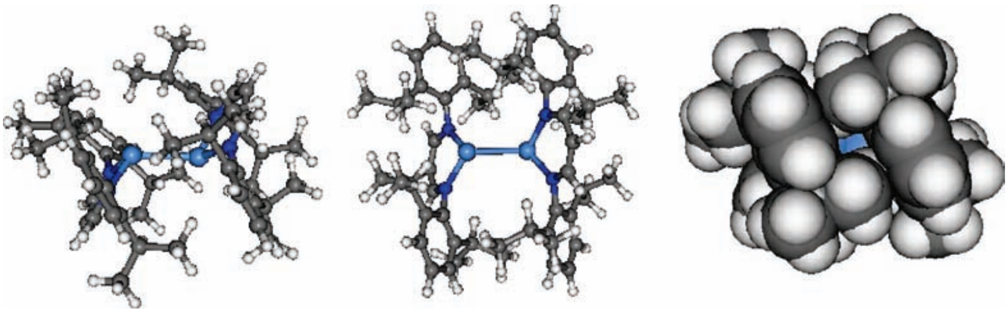


Figure 2. Plots of the equilibrium structures of dimeric **1** (R = Dipp). From left to right: side view, top view, and van der Waals model. Al−Al = 2.723 Å, ∠N−Al−N = 89.2°, and ∠Al−Al−N−N = 115.4°.

related anionic species **1** has escaped any experimental verification; instead, metal has been found.[2] If a similar reaction mechanism holds, upon dimer formation of the carbene, a highly unstable biradicaloid is formed, which can easily undergo an intramolecular redox reaction. The electron-rich ligands, in essence anions, reduce the Al_2 unit, $Al_2(0)$ is obtained,[28] which polymerizes, and finally the ligands are freed.

THEORETICAL SECTION

All calculations were performed with the *Gaussian 09*[29] and *Turbomole 6.0*[30] sets of programs. DFT was employed throughout. The structures were optimized at the BP86 level,[31] at times added by dispersion correction terms.[32] Alternatively, for the electron-correlated, wave-function-based procedures MP2[33] or CC2,[34] calculations were performed. In all cases, the RI ("resolution of the identity") approximation[35] was used. As a basis set, TZVP was used,[36] or for the very large structures, the SVP[36] basis set was utilized. Frequency calculations were performed numerically, and entropies and free energies were determined by standard equations from statistical thermodynamics.[37]

At the MP2 level, the phenyl-substituted (R = Ph, Mes, and Dipp) triplet states suffer from strong spin contamination, as is known for other cases, e.g., diphenyl-substituted disilenes. Hence, further analysis of the S−T energy separations at this level was not attempted.

CONCLUSIONS

The investigations can be summarized as follows:

(1) The neutral group 13 carbene analogues possess singlet ground states throughout. An exemption is the hitherto experimentally not described boron derivative, **1** (E = B). On the basis of population analysis, the oxidation number for the Al derivative is assigned to I+.

(2) Dimers are strongly stabilized by van der Waals forces but, at room temperature, strongly opposed by entropic forces, in general facilitating dissociation. At low temperature, dimerization is expected, a process with no activation energy between **2** and **2-dim**. A priori dissociation and dimerization are reversible processes.

(3) In contrast to known Al_2Cl_4 species, known as quite well-stable entities with a formal oxidation number of II+ at Al, in dimeric **2**, aluminum possesses one more electron; this gives rise to a low-lying triplet state. This indicates that these species should reveal a biradicaloid Al_2 entity, chelated by two pentadienylid anions. Steric protection, the basis for van der Waal complex stability also, helps to kinetically protect this species.

(4) The tendency for dimerization decreases in the order E = Al > Ga > In and makes the first member in this series a valuable target for experimental verification. In the same order, the S−T energy separation in the dimer increases.

The present study strongly dictates the importance of entropy in dimerization, but it also neglects the possible contributions of solvent stabilization of either of the reactant sites. Hence, proof of the presented concept must await experimental verification.

Just recently, a theoretical study on dimetallenes has been reported[38] and is in full conformity with the findings presented here. It predicts a strong biradical character for this class of compounds.

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