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Theoretical Studies of the [2 + 4] Diels–Alder Cycloaddition Reactions of Alkene Analogues of the Group 13 Elements with Toluene

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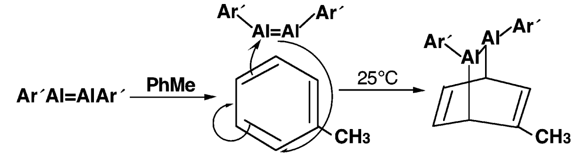
The potential energy surfaces for the cycloaddition reactions of formally double-bonded molecules containing group 13 elements have been studied using density functional theory (B3LYP/LANL2DZ). Five group 13 alkene analogues, ArX═XAr, where X = B, Al, Ga, In, and Tl, have been chosen as model reactants in this work. Our present theoretical work predicts that the smaller the singlet–triplet splitting in ArX═XAr, the lower the activation barrier and, in turn, the more rapid are its [4 + 2] cycloaddition reactions. Moreover, the theoretical investigations suggest that the relative dimeric reactivity decreases in the order B > Al > Ga > In > Tl. That is, the heavier the group 13 atom (X), the more stable is its dimetallene toward chemical reactions. In consequence, our results predict that the dimetallenes containing heavier group 13 elements (in particular, X = Ga, In, and Tl) should be stable and should be readily synthesized and isolated at room temperature. This is in good agreement with available experimental observations. Besides this, the singlet–triplet energy splitting of a dimetallene, as described in the configuration mixing model attributed to the work of Pross and Shaik, can be used as a diagnostic tool to predict its reactivity. The results obtained allow a number of predictions to be made.

I. Introduction

During the past decade, the synthesis of monomeric group 13 compounds of the type $RX{=}XR$ (X = group 13 elements) has received wide interest because of their unusual structure and properties when compared with compounds containing group 14 elements, such as olefins ($R_2C{=}CR_2$) and ketones ($R_2C{=}O$).[1] In fact, the development of techniques for the synthesis of multiply bonded group 13 molecules has increased the possibility of experimental investigations of group 13 species. Very recently, through the elegant research performed by Power and co-workers,[2] it was found that the reaction of $Ar'AlI_2$ ($Ar' = C_6H_3$-2,6-Dipp$_2$, Dipp = C_6H_3-2,6-Pr$^i_2$) with KC_8 afforded the 1,2-diiodoalane and, probably the dialuminene ($Ar'Al{=}AlAr'$). Although so far the dialuminene has not yet been isolated and characterized, it was reported to crystallize with toluene to afford the cycloaddition product as shown in Scheme 1.

Scheme 1



Besides this, three examples of homonuclear formally double bonded systems between group 13 elements have been reported.[3−5] The first is neutral digallene, $Ar'Ga{=}GaAr'$,[3] a novel doubly bonded system involving gallium. The second is the first stable diindene ($Ar'In{=}InAr'$),[4] which was also synthesized by taking advantage of the bulky Ar′ group. Dimeric $Ar'Tl{=}TlAr'$ (dithallene)[5] was the first compound synthesized containing a thallium−thallium double

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(1) For the most recent reviews, see: (a) Driess, M.; Grutzmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 829. (b) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939. (c) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (d) Robinson, G. H. *Acc. Chem. Res.* **1999**, *32*, 773. (e) Leigh, W. J. *Pure Appl. Chem.* **1999**, *71*, 453. (f) Tokitoh, N. *Pure Appl. Chem.* **1999**, *71*, 495. (g) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1665. (h) Okazaki, R.; Tokitoh, N. *Acc. Chem. Res.* **2000**, *33*, 625. (i) Downs, A. J.; Himmel, H.-J.; Manceron, L. *Polyhedron* **2002**, *21*, 473.

(2) Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 10784.

(3) For the $Ar'Ga{=}GaAr'$, compound, see the following: Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2842.

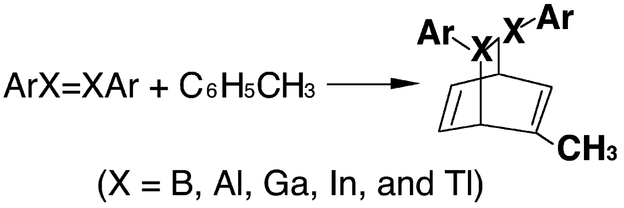
(4) For the $Ar'In{=}InAr'$, compound, see the following: Wright, R. J.; Phillips, A. D.; Hardman, N. J.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 8538.

(5) For the $Ar'Tl{=}TlAr'$, compound, see the following: Wright, R. J.; Phillips, A. D.; Hino, S.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 4794.

10.1021/ic061100u CCC: $37.00

bond, the heaviest double bond containing a group 13 element. As a result, formally doubly bonded systems between heavier group 13 elements are no longer hypothetical species even in the case of thallium. Nevertheless, attempts to isolate other analogues, diboronene ($RB{=}BR$)[6] and dialuminene ($RAl{=}AlR$),[2] have all been unsuccessful up to now.

It is these fascinating experimental results[2] that aroused our interest to investigate the potential energy surfaces of such cycloaddition reactions using theoretical methods. Moreover, if the dialuminene species can be crystallized with toluene to form the cycloaddition product, would it be possible to extend this to other potentially double-bonded compounds $ArX{=}XAr$ (such as X = B, Ga, In, and Tl) to form the cycloaddition product?[2−5] To the best of our knowledge, no quantum chemical calculations on such cycloaddition reactions have yet been carried out,[7] let alone a systematic theoretical study of group 13 element effects on the reactivities of the double-bonded $ArX{=}XAr$ (X = B, Al, Ga, In, and Tl) species. To elucidate the mechanism of the cycloaddition reactions in these systems, we have undertaken an investigation of the potential energy surfaces of the model reactions by means of density functional theory (DFT).



(1)

The purpose of this work is 4-fold: (i) to determine both the energies and structures of the transition states of the reactions; (ii) to obtain a detailed understanding of the energetics and kinetics of the chemical interactions between double-bonded $ArX{=}XAr$ and toulene molecules; (iii) to probe element effects on reactivities in a variety of group 13 alkene analogues; (iv) to obtain a better understanding of the origin of barrier heights for such cycloaddition reactions. Despite the numerous theoretical studies carried out on physical properties of the group 13 “dimetallenes” $HX{=}XH$ area,[7] we believe that a somewhat different approach and some new aspects emphasized here may increase our understanding of this system.

II. Theoretical Methods

All geometries were fully optimized without imposing any symmetry constraints, although in some instances the resulting structure showed various elements of symmetry. For our DFT calculations, we used the hybrid gradient-corrected exchange functional proposed by Becke,[8] combined with the gradient-corrected correlation functional of Lee, Yang, and Parr.[9] This functional is commonly known as B3LYP and has been shown to be quite reliable both for geometries and energies.[10] These B3LYP calculations were carried out with relativistic effective core potentials on the group 13 elements modeled using the double-ζ (DZ) basis sets[11] augmented by a set of d-type polarization functions.[11e] The DZ basis set for the hydrogen element was augmented by a set of p-type polarization functions (p exponents 0.356). Accordingly, we denote our B3LYP calculations by B3LYP/LANL2DZ. The spin-unrestricted (UB3LYP) formalism was used for the open-shell (triplet) species. The S^2 expectation values of the triplet state for the unpaired reactants all showed an ideal value (2.00) after spin annihilation, so that their geometries and energetics are reliable for this study. Vibrational frequency calculations at the B3LYP/LANL2DZ level were used to characterize all stationary points as either minima (the number of imaginary frequencies (NIMAG = 0) or transition states (NIMAG = 1). The relative energies were thus corrected for vibrational zero-point energies (ZPE, not scaled). Thermodynamic corrections to 298 K, ZPE corrections, heat capacity corrections, and entropy corrections (ΔS) obtained were applied at the B3LYP/LANL2DZ level. Thus, the relative free energy (ΔG) at 298 K was also calculated at the same level of theory. All of the DFT calculations were performed using the GAUSSIAN 03 package of programs.[12]

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(6) For related experimental papers, see the following: (a) Meller, A.; Seebold, U.; Maringgele, W.; Noltemeyer, M.; Sheldrick, G. M. *J. Am. Chem. Soc***.** **1989**, *111*, 8299. (b) Meller, A.; Bromm, D.; Maringgele, W.; Heine, A.; Stalke, D.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1990**. (c) Mennekes, T.; Paetzold, P.; Boese, R. *Angew. Chem., Int. Ed. Engl*. **1990**, *29*, 889. (d) Grigsby, W. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 7981.

(7) For related theoretical studies on double-bonded hydrides $HX{=}XH$ with group 13 elements, see the following: (a) Schwerdtfeger, P.; Heath, G. A.; Dolg. M.; Bennett, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 7518. (b) Palagyi, Z.; Grev, R. S.; Schaefer, H. F, *J. Am. Chem. Soc.* **1993**, *115*, 1936. (c) Treboux, G.; Barthelat, J.-.C. *J. Am. Chem. Soc.* **1993**, *115*, 4870. (d) Palagyi, Z.; Schaefer, H. F., III. *Chem. Phys. Lett*. **1993**, *203*, 195. (e) Knight, L. B., Jr.; Kerr, K.; Miller, P. K.; Arrington, C. A. *J. Phys. Chem.* **1995**, *99*, 16842. (f) Allen, T. L.; Fink, W. H.; Power, P. P. J. *Chem. Soc., Dalton Trans.* **2000**, 407. (g) Takagi, N. Schmidt, M. W.; Nagase, S. *Organometallics* **2001**, *20*, 1646. (h) Himmel, H. J.; Manceron, L.; Downs, A. J.; Pullumbi, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 976. (i) Himmel, H.-J.; Manceron, L.; Downs, A. J.; Pullumbi, P. *J. Am. Chem. Soc.* **2002**, *124*, 4448. (j) Himmel, H.-J.; Manceron, L.; Downs, A. J.; Manceron, L. *Polyedron* **2002**, *21*, 473.

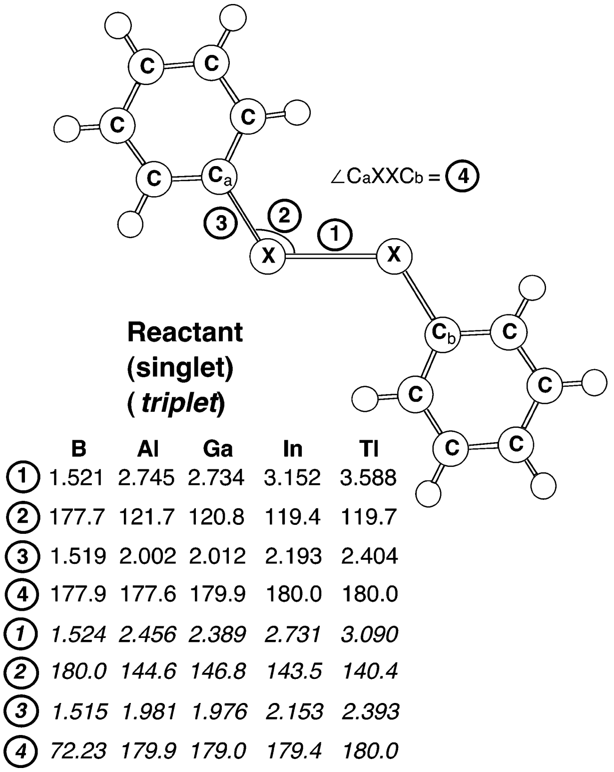
(8) (a) Becke, A. D. Phys. Rev. A. 1988, 38, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(9) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(10) (a) Su, M.-D. J. *Phys. Chem. A* **2004**, *108*, 823. (b) Su, M.-D. *Inorg. Chem*., 2004, *43*, 4846. (c) Su, M.-D. *Eur. J. Chem.* **2005**, *10*, 5877 and related references therein.

(11) (a) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*, Schaefer, H. F., III, Ed.; Plenum: New York, 1976; pp 1−28. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 270. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 284. (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 299. (e) Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. J. *Phys. Chem. A* **2001**, *105*, 8111.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 03*; Gaussian, Inc.: Wallingford CT, 2003.



	B	Al	Ga	In	Tl
①	1.521	2.745	2.734	3.152	3.588
②	177.7	121.7	120.8	119.4	119.7
③	1.519	2.002	2.012	2.193	2.404
④	177.9	177.6	179.9	180.0	180.0
①	*1.524*	*2.456*	*2.389*	*2.731*	*3.090*
②	*180.0*	*144.6*	*146.8*	*143.5*	*140.4*
③	*1.515*	*1.981*	*1.976*	*2.153*	*2.393*
④	*72.23*	*179.9*	*179.0*	*179.4*	*180.0*

Figure 1. B3LYP/LANL2DZ optimized geometries (in Å and deg) of the reactants (singlet and triplet) ArX=XAr (X = B, Al, Ga, In, and Tl). For the relative energies of each species, see Table 1. Hydrogens are omitted for clarity.

III. Results and Discussion

1. Geometries and Electronic Structures of ArX=XAr. Before discussing the geometrical optimizations and the potential energy surfaces for the chemical reactions studied in this work, we shall first discuss the geometries and energies of the group 13 element alkene analogues, i.e., ArX=XAr. The electronic structures and geometries of hydride HX=XH species have been extensively studied by many groups as mentioned in the Introduction.[7] At present, the specific alkene analogues we have investigated are ArB=BAr, ArAl=AlAr, ArGa=GaAr, ArIn=InAr, and ArTl=TlAr. The optimized geometries for these compounds were calculated at the B3LYP/LANL2DZ level of theory. Their selected geometrical parameters are collected in Figure 1 and Table 1, where they are compared with available experimental observations.[3−5] In addition, the open-shell triplet states of these species have been investigated. As a result, the triplet energies relative to the singlet reactants on the basis of the B3LYP level are given in Table 1. Their Cartesian coordinates are included in the Supporting Information.

Although only a handful of crystallographic investigations on substituted double-bonded compounds (Ar′X=XAr′, X = Ga, In, and Tl)[3−5] have been carried out during the last 5 years, no experimental geometries are so far available in the literature for the ArX=XAr systems.[13] Due to this fact, the reliability of the predicted geometries can only be estimated by comparison between some available experimental structures. For comparison, the optimized geometries of the ArX=XAr (X = B, Al, Ga, In, and Tl) species calculated at the B3LYP/LANL2DZ level of theory are listed in Table 1 along with available experimental values.[3−5] Calculated vibrational frequencies for these reactants (ArX=XAr) reveal that their structures are true minima on the potential energy surface (also see Supporting Information). Indeed, all the experimentally substituted Ar′X=XAr′ species reported so far adopt a trans-bent structure.[3−5] The main difference between experimental and theoretical geometries concerns the X=X and the X−C bond distances as well as the −XXAr angle, respectively. For instance, as can be seen in Table 1, the Ga=Ga, In=In, and Tl=Tl bond lengths in the experimental conformations are significantly shorter than those in the corresponding computed geometries by 0.107, 0.173, and 0.494 Å, respectively.[14] Similarly, the experimental X−C bond distances are longer than those in the corresponding theoretical reactant structures by 0.013 and 0.063 Å for the gallium and indium cases but shorter by 0.091 Å for the thallium case. On the other hand, the −XXAr angle is apparently larger in the experimental structure (123.2, 121.2, and 119.7°, respectively) than in the calculated geometry (120.8, 119.4, and 119.7°, respectively). The wider angles at the group 13 element are somewhat surprising and are presumably due to the larger size of the experimental aryl-like substituent at the group 13 element. It should be emphasized here that our computational results presented in Table 1 predict that the X=X bond length in the singlet ArX=XAr molecule increases in the order B=B (1.521 Å) < Al=Al (2.734 Å) < Ga=Ga (2.745 Å) < In=In (3.152 Å) < Tl=Tl (3.588 Å). This finding can be explained in terms of the expected size of the group 13 atom X, which increases as X changes from B down to Tl. In addition, as demonstrated in Table 1, the −XXAr angle in the singlet ArX=XAr species decreases in the order B (177.7°) > Al (121.7°) > Ga (120.8°) > Tl (119.7°) > In (119.4°). The reason for this can be understood simply by considering reactant electronic structures (vide infra).

Figure 2 is a molecular orbital correlation diagram for the valence orbitals of the dimetallenes (ArX=XAr; X = B, Al, Ga, In, and Tl). The substitution of two group 13 atoms at the carbon centers by boron, aluminum, gallium, indium, and thallium pushes the antibonding π^* orbitals up in energy. However, the bonding π orbitals (HOMO) are pulled down in energy, albeit by a smaller amount than the antibonding orbitals are pushed up. Note that the nature of the LUMO in the dimetallenes is quite different from that encountered in most group 14 alkene compounds.[15] Here, the HOMO is essentially the bonding p-π orbitals, whereas the LUMO+1 are essentially antibonding π^* orbitals. The reason for this is due to the size difference and energy gap between the

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(13) The reason for choosing the ArX=XAr model rather than the Ar′X=XAr′ system in this work is simply because of clarity. Nevertheless, despite the simplifications used to assemble the model, the calculations successfully mimic the geometric parameters in experimentally determined structures as shown in the text.

(14) The reason for this could be due to an indication of basis set or pseudopotential problems. Such studies, however, are beyond the scope of this work. We thank reviewer B for pointing out this to our attention.

(15) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985; pp 164.

Table 1. Selected Geometric Values and Relative Energies for Singlet and Triplet Group 13 Alkene Analogues, ArX═XAr, Where X = B, Al, Ga, In, and Tl[a,b]

param	X = B	X = Al	X = Ga[c]	X = In[d]	X = Tl[e]
			Singlet		
X═X (Å)	1.521	2.734	2.745 (2.627)	3.152 (2.979)	3.588 (3.094)
X−C (Å)	1.519	2.002	2.012 (2.025)	2.193 (2.256)	2.404 (2.313)
−XXAr (deg)	177.7	121.7	120.8 (123.2)	119.4 (121.2)	119.7 (119.7)
			Triplet		
X═X (Å)	1.524	2.389	2.456	2.731	3.090
X−C (Å)	1.515	1.981	1.976	2.153	2.393
−XXAr (deg)	180.0	144.6	146.8	143.5	140.4
ΔE_{st}[f] (kcal mol^{-1})	−13.87	11.07	15.34	19.95	36.21

[a] All were calculated at the B3LYP/LANL2DZ (singlet) and UB3LYP/LANL2DZ (triplet) levels of theory. [b] The parameters from experiments are given in parentheses. [c] See ref 3. [d] See ref 4. [e] See ref 5. [f] Energy relative to the corresponding singlet state. A positive value means the singlet is the ground state.

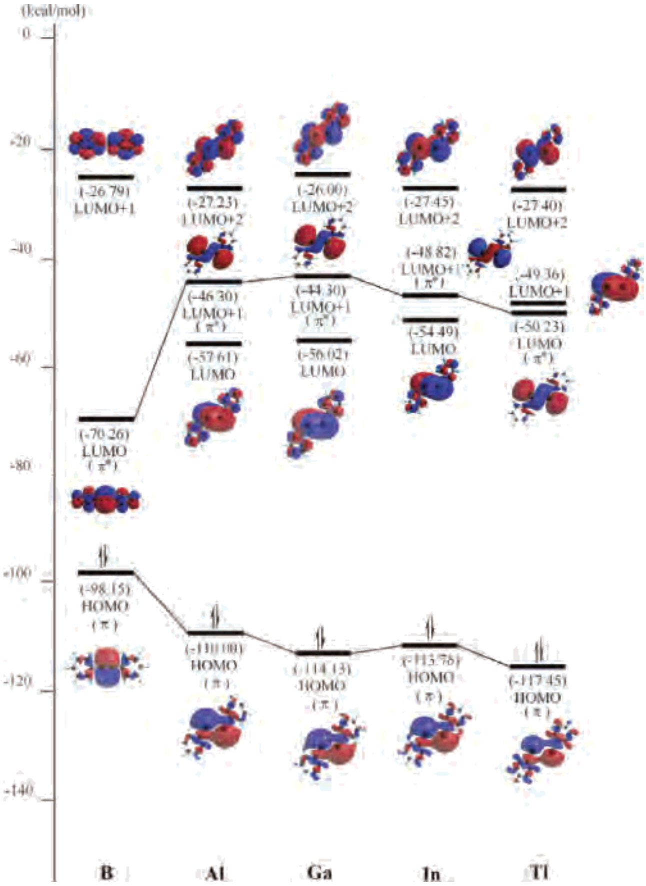

Figure 2. Calculated frontier molecular orbital for the ArX═XAr (X = B, Al, Ga, In, and Tl) species. For more information, see the text.

valence s and p orbitals both of which increase upon going from B to Tl atoms due to the relativistic effect.[16] As a result, the heavier group 13 atoms maintain the $(ns)^2(np)^1$ valence electron configuration. Consequently, the use of almost pure np orbitals instead of more hybridized orbitals leads to a smaller bond angle at each heavier group 13 atom center. In other words, the reason for ArX═XAr (such as X = Al, Ga, In, and Tl) adopting the trans-bent form can be attributed to the phenomenon of orbital nonhybridization (or the so-called "inert s-pair effect").[16] Basically, bearing in mind that the synthesized molecules contain bulkier groups,[3−5] our predicted B3LYP structures for double-bonded group 13 elements are in reasonable agreement with these experimental values.[3−5] In any event, the good agreement between our computational results and available experimental data is quite encouraging.[17] This gives us confidence that the B3LYP/LANL2DZ level employed in this work can provide accurate molecular geometries for those chemical reactions, for which experimental data are not available.

Let us now consider the first excited-state of ArX═XAr (X = B, Al, Ga, In, and Tl), a triplet, which, to our knowledge, has not been studied theoretically. Likewise, no experimental study of triplet ArX═XAr isomers has appeared to date. As expected, all of the triplet structures are nonplanar, except for triplet ArB═BAr which adopts a linear (planar) structure as shown in Table 1. Moreover, an interesting trend that can be observed in Table 1 (or Figure 1) is the decrease in the bond distances (i.e., X═X and X−C) on going from the singlet to the triplet state, except in the ArB═BAr case. On the other hand, the triplet state has significantly larger bond angles (−XXAr) than the corresponding closed shell singlet state. Again, the reason for these trends can be traced directly to electronic factors. From Figure 2, it is apparent that one electron occupies the LUMO, which can greatly shorten the X═X bond length as well as enlarge the −XXAr bond angle in the triplet state. Accordingly, our theoretical findings indicate that the relativistic effect,[16] where the symmetry of frontier orbitals changes, should play a significant role in determining the geometric parameters of the dimetallene species.

Furthermore, as demonstrated in Table 1, the DFT results show that the ΔE_{st} ($\Delta E_{st} = E_{triplet} - E_{singlet}$) for boron, aluminum, gallium, indium, and thallium increases in the order ArB═BAr (−13.87 kcal/mol) < ArAl═AlAr (+11.07 kcal/mol) < ArGa═GaAr (+15.34 kcal/mol) < ArIn═InAr (+19.95 kcal/mol) < ArTl═TlAr (+36.21 kcal/mol). Namely, the heavier the group 13 atoms in the dimetallene, the larger is its singlet−triplet splitting. Again, this can be satisfactorily explained by the relativistic effect[16] as mentioned previously. Beside this, it should be emphasized that the stabilities of the dimetallenes are determined by the singlet−triplet splitting. That is to say, compounds with a small ΔE_{st} will

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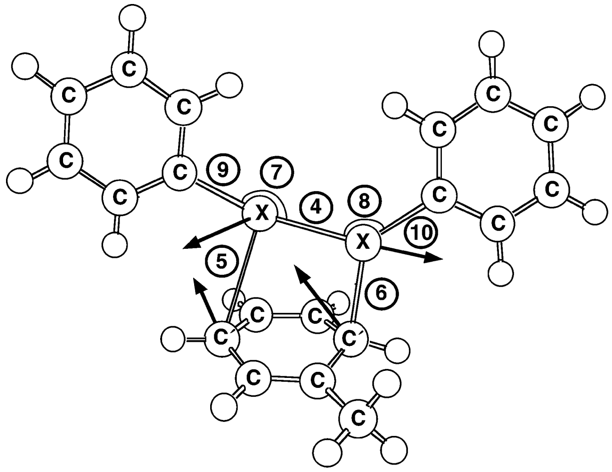
(16) (a) Pykkö, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276. (b) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. (c) Pykö, P. *Chem. Rev.* **1988**, *88*, 563. (d) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(17) As pointed out by one reviewer, although relativistic effects are important in the "inert-pair effect" observed for thallium, relativistic effects are generally considered to be much weaker (and less significant) for the lighter group 13 elements.



Transition State

	B	Al	Ga	In	Tl
④	1.587	2.519	2.454	2.751	2.931
⑤	2.877	3.207	2.887	2.635	2.473
⑥	1.661	2.315	2.240	2.377	2.382
⑦	166.5	147.9	152.7	157.9	153.5
⑧	128.8	122.5	125.8	126.5	133.0
⑨	1.529	1.990	1.982	2.132	2.257
⑩	1.588	2.000	1.987	2.137	2.259

Figure 3. B3LYP/LANL2DZ optimized geometries (in Å and deg) of the transition states of ArX═XAr (X = B, Al, Ga, In, and Tl) and toluene nolecules. For the relative energies for each species, see Table 2. Hydrogens are omitted for clarity.

be unstable and will be capable of facile chemical reactions (such as with solvents, etc.). It will be shown below that the singlet−triplet splitting of the group 13 alkene analogues (ArX═XAr) can be a guide to predict its reactivity for chemical reactions.[18]

2. Transition States. The results for the transition states (TSs) of the dimetallene (ArX═XAr) cycloaddition with toluene are the most interesting results of this study since very little is known about their barrier heights. These transition states will be referred to as **B**-**TS**, **Al**-**TS**, **Ga**-**TS**, **In**-**TS**, and **Tl**-**TS** for eq 1, respectively. The main geometrical parameters of the transition states corresponding to the cycloaddition reactions as well as their appearance are shown in Figure 3, together with the meaningful components of their transition vector. The activation barriers are given in Table 2. Their Cartesian coordinates are included in the Supporting Information. The major conclusions that can be drawn from Figure 3 and Table 2 are as follows.

Regarding the [4 + 2] cycloadditions, one can observe that the main components of the transition vector correspond to the motion of the ring cycloaddition between the group 13 and the carbon atoms of toluene, whose eigenvalue gives an imaginary frequency of 83.4i (**B**-**TS**), 125i (**Al**-**TS**), 126i (**Ga**-**TS**), 138i (**In**-**TS**), and 136i (**Tl**-**TS**) cm^{-1}. Indeed, inspection of the transition vector shows clearly that the reaction proceeds toward formation of the cycloaddition product. Besides this, the group 13 atoms of the ArX═XAr molecule make angles, with respect to the X═X bond, of (167, 129°), (148, 123°), (153, 126°), (158, 127°), (154, 133°) for **B**-**TS**, **Al**-**TS**, **Ga**-**TS**, **In**-**TS**, and **Tl**-**TS**, respectively. One of the interesting points to emerge from calculations of TS geometries is the extent to which the X−C′ bonds are formed in the transition state. Relative to its value in the product (vide infra), one of the X−C′ bonds in **B**-**TS**, **Al**-**TS**, **Ga**-**TS**, **In**-**TS**, and **Tl**-**TS** is 78, 58, 42, 18, and 3.8% longer than that in the corresponding products, respectively. The other X−C′ bond is 25, 14, 9.8, 5.1, and 0.775% longer than that of the corresponding cycloaddition product, respectively. This suggests that the ArB═BAr [4 + 2] cycloaddition reaction arrives at the TS relatively early, whereas the ArIn═InAr and ArTl═TlAr [4 + 2] cycloaddition reactions reach the TS relatively late. Consequently, the barriers are encountered earlier in the cycloaddition of the former than of the latter. As will be shown below, this is consistent with the Hammond postulate,[19] which associates an earlier transition state with a smaller barrier and a more exothermic reaction.

In the [4 + 2] cycloaddition reactions, examination of the energy values collected in Table 2 shows that at the B3LYP/LANL2DZ level, only the ArB═BAr [4 + 2] cycloaddition reaction is favored. The present calculations predict that the energies of **Al**-**TS**, **Ga**-**TS**, **In**-**TS**, and **Tl**−**TS** are above those of the reactants by 8.63, 14.5. 23.3, and 76.8 kcal/mol, respectively. In contrast, the DFT energy of **B**-**TS** (−11.0 kcal/mol) is below that of the reactants, so that no net barrier to reaction exists.[18] Also, we have calculated the activation free energy differences ($\Delta G^{\ddagger}$ for eq 1 at 298 K, which are also given in Table 2. As shown in this table, the values of $\Delta G^{\ddagger}$ (kcal/mol) are 3.14, 23.3, 30.3, 37.1, and 80.7 for boron, aluminum, gallium, indium, and thallium, respectively. Again, the B3LYP results show that the overall barrier heights are determined to be in the order **B**-**TS** < **Al**-**TS** < **Ga**-**TS** < **In**-**TS** < **Tl**-**TS**. In any event, the above reflects the greater ease of cycloaddition with toluene by boron over that by indium and thallium. Namely, our theoretical findings suggest that the more electronegative the element attached to the dimetallene, the more facile the [4 + 2] cycloaddition reaction with toluene.

3. [4 + 2] Cycloaddition Products. The B3LYP/LANL2DZ geometries of the [4 + 2] cycloaddition products (**B-Pro**, **Al-Pro**, **Ga-Pro**, **In-Pro**, and **Tl-Pro**) for eq 1 are displayed in Figure 4. To simplify comparisons and to emphasize the trends, the calculated reaction enthalpies for cycloaddition are also collected in Table 2. Unfortunately, experimental structures for most of these [4 + 2] cycloaddition products are not yet known.

As mentioned in the Introduction, only one substituted [4 + 2] cycloaddition product has been synthesized and characterized unequivocally.[2] Although only a few details

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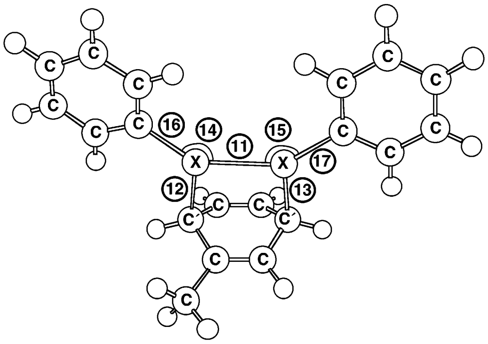
(18) Hammond, G. S. *J. Am. Chem. Soc.* **1954**, *77*, 334.

(19) In fact, it should be pointed out that the diboronene (ArB═BAr) species may attack toluene to form a precursor complex, which then rearranges to the eventual cycloaddition product via a transition state. The reason for this is because diboronene has a triplet ground state as shown in Table 1. Nevertheless, for consistency, all computed mechanisms in this work would proceed on the singlet surface.

Table 2. Relative Energies for Singlet and Triplet Group 13 Alkene Analogues, ArX═XAr, and for the Toluene Cycloaddition Process: Reactants (ArX═XAr + $C_6H_5CH_3$) → Transition State → Cycloaddition Product[a,b]

system	$\Delta E_{st}{}^{c}$ (kcal mol^{-1})	ΔE^{d} (kcal mol^{-1})	ΔG^{d} (kcal mol^{-1})	ΔH^{e} (kcal mol^{-1})	ΔG^{e} (kcal mol^{-1})
X = B	−13.87	−10.95	3.138	−36.88	−22.37
X = Al	11.07	8.630	23.27	−12.52	1.613
X = Ga	15.34	14.52	30.30	−1.940	12.44
X = In	19.95	23.34	37.10	16.69	32.10
X = Tl	36.21	76.76	80.68	24.35	36.90

[a] All were calculated at the B3LYP/LANL2DZ level of theory. For the B3LYP-optimized structures of the stationary points, see Figure 3. [b] Energies differences have been zero-point corrected. See the text. [c] Energy relative to the corresponding singlet state. A positive value means the singlet is the ground state. [d] The activation energy of the transition state, relative to the corresponding reactants. [e] The reaction enthalpy of the product, relative to the corresponding reactants.



Cycloaddition Product

	B	Al	Ga	In	Tl
⑪	1.721	2.566	2.511	2.803	3.627
⑫	1.620	2.032	2.041	2.224	3.806
⑬	1.617	2.033	2.037	2.227	3.398
⑭	131.2	143.5	143.0	145.1	149.8
⑮	130.7	143.2	142.6	145.7	101.6
⑯	1.556	1.975	1.971	2.139	2.418
⑰	1.558	1.975	1.970	2.138	2.432

Figure 4. B3LYP/LANL2DZ optimized geometries (in Å and deg) of the cycloaddition products of ArX═XAr (X = B, Al, Ga, In, and Tl). For the relative energies for each species, see Table 2. Hydrogens are omitted for clarity.

concerning the geometrical parameters are as yet available, we may compare some of our results with those obtained for a substituted [4 + 2] cycloaddition product. Our calculated Al═Al bond length in **Al-Pro** (2.566 Å at B3LYP) compares favorably with Al═Al bond length determined from X-ray data (2.583 Å).[2] Moreover, our predicted B3LYP Al−C′ bond lengths for ArAl═AlAr (2.033 Å in Figure 4) are also in reasonable agreement with the experimental values (2.003 Å), bearing in mind that the synthesized molecules contain bulkier substituents. It is therefore believed that the present models with the current method (B3LYP/LANL2DZ) employed in this study should provide reliable information for the discussion of the reaction mechanism.

As discussed earlier, a dimetallene with more electronegative group 13 elements reaches the transition state relatively early, whereas a dimetallene with more electropositive group 13 atoms arrives relatively late. The former is therefore predicted to undergo a more exothermic cycloaddition, which is borne out by our theoretical calculations. For instance, the order of reaction enthalpy follows a trend similar to that for the activation energy: **B-Pro** (−36.9 kcal/mol) < **Al-Pro** (−12.5 kcal/mol) < **Ga-Pro** (−1.94 kcal/mol) < **In-Pro** (+16.7 kcal/mol) < **Tl-Pro** (+24.4 kcal/mol). We also calculated the free energy differences (Δ*G*) for eq 1 at 298 K, which shows the same trend as that in the 0 K case, i.e., **B-Pro** (−22.4 kcal/mol) < **Al-Pro** (+1.61 kcal/mol) < **Ga-Pro** (+12.4 kcal/mol) < **In-Pro** (+32.1 kcal/mol) < **Tl-Pro** (+36.9 kcal/mol). It is worth noting that our model calculations suggest that ArAl═AlAr and **Al-Pro** molecules are nearly thermoneutral, with an endothermicity of less than 2 kcal/mol. This could be the reason that we can observe the cycloaddition product in the aluminum case. Moreover, this small energy difference between the double-bonded dialuminene species and its cycloaddition product could be a general feature of aluminum−aluminum multiply bonded compounds. The supporting evidence can be found in the recent paper by Power and co-workers.[2] Furthermore, it is also noted that the energies of the gallium, indium, and thallium cycloaddition products are all above those of their corresponding reactants. This strongly indicates that the [4 + 2] cycloaddition reactions by digallene, diindene, and dithallene are energetically unfavorable and would be endothermic. Namely, our computational results suggest that the [4 + 2] cycloaddition products (**Ga-Pro**, **In-Pro**, and **Tl-Pro**) are not produced from a ring cyclization reaction as in eq 1 but possibly exist if these they are produced through other reaction paths.

In brief, considering both the activation barrier and enthalpy, on the basis of the model calculations presented here, we conclude that the dimetallene reactivity order should be as follows: ArB═BAr > ArAl═AlAr > ArGa═GaAr > ArIn═InAr > ArTl═TlAr. In other words, electronegative group 13 elements on the dimetallene accelerate the [4 + 2] cycloaddition reaction, whereas elentropositive group 13 elements on the dimetallene will retard it. Our theoretical predictions are in accordance with the available experimental observations.[2−5]

IV. Origin of the Barrier Height and the Reaction Enthalpy for Cycloaddition of Dimetallene

To understand the key factors that determine the general features of these [4 + 2] cycloaddition reactions, a configuration mixing (CM) model, which was developed by Pross and Shaik,[20,21] has been used to gain a better understanding of the reactivity of the various species. According to this model,[20−22] the stabilization of a cycloaddition transition state depends on the singlet−triplet splitting ΔE_{st} ($=E_{triplet} - E_{singlet}$) in the reactant (dimetallene); i.e., a smaller ΔE_{st} results in a more stable transition state, a lower activation energy, and a faster [4 + 2] cycloaddition reaction. Interested readers can find excellent reviews in refs 20 and 21.

Our model calculations confirm the above prediction and suggest a decreasing trend in ΔE_{st} for ArB═BAr (−13.87 kcal/mol) > ArAl═AlAr (11.07 kcal/mol) > ArGa═GaAr (15.34 kcal/mol) > ArIn═InAr (19.95 kcal/mol) > ArTl═TlAr (36.21 kcal/mol). From Table 2, it can be seen that this result agrees well with the trend in activation free energies ($\Delta G^{\ddagger}$ at 298 K): **B-TS** (3.138 kcal/mol) > **Al-TS** (23.27 kcal/mol) > **Ga-TS** (30.30 kcal/mol) > **In-TS** (37.10 kcal/mol) > **Tl-TS** (80.68 kcal/mol). Also, our theoretical calculations demonstrate that ΔE_{st} of the dimetallene is in accordance with the cycloaddition enthalpy at room temperature (ΔG at 298 K): **B-Pro** (−22.37 kcal/mol) > **Al-Pro** (1.613 kcal/mol) > **Ga-Pro** (12.44 kcal/mol) > **In-Pro** (32.10 kcal/mol) > **Tl-Pro** (36.90 kcal/mol). All these investigations provide strong evidence that the singlet−triplet gap (ΔE_{st}) plays a crucial role in determining the reactivity of dimetallene species.

One may thus wonder why the singlet−triplet splitting (ΔE_{st}) of a dimetallene increases monotonically from boron to thallium. The reason for this can be easily understood by the relativistic effect[16] as discussed previously. That is, as X changes from boron to thallium, the valence s orbital is more strongly contracted than the corresponding p orbitals.[16] Namely, the size difference between the valence s and p orbitals increases from B to Tl (the so-called “inert s-pair effect” or “nonhybridization effect”).[16] Consequently, the valence s and p orbitals differ in spatial extension and overlap less to form strong hybrid orbitals. Also, the valence orbital energy between s and p will increase from boron to thallium. This, in turn, will enlarge the singlet−triplet splitting (ΔE_{st}) as X changes from B down to Tl.[16]

V. Conclusion

This study has provided the first theoretical demonstration concerning the reaction trajectory and theoretical estimation of the activation energy and reaction enthalpy for the [4 + 2] cycloaddition processes. Taking all aforementioned five reactions (ArX═XAr + $C_6H_5CH_3$) studied in this paper together, one can draw the conclusions as follows. Our theoretical findings suggest that the [4 + 2] cycloadditions of dimetallene species with electronegative group 13 elements should be preferable to those of the electropositive group 13 atoms since it is demonstrated not only that the former are thermodynamically favorable but also that the kinetic barriers associated with them are typically small.

We encourage experimentalists to carry out further experiments to confirm our predictions.

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Supporting Information Available: Additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) For details, see the following: (a) Shaik, S.; Schlegel, H. B.; Wolfe, S. In *Theoretical Aspects of Physical Organic Chemistry*; John Wiley & Sons, Inc.: New York, 1992. (b) Pross, A. In *Theoretical and Physical Principles of Organic Reactivity*; John Wiley & Sons, Inc.: New York, 1995. (c) Shaik, S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197. (d) Shaik, S. In *Theory and Applications of Computational Chemistry*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: New York, 2003.

(21) (a) For the first paper that originated the CM model, see the following: Shaik, S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. (b) For about the most updated review of the CM model, one should see the following: Shaik, S.; Shurki, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 586.

(22) (a) Su, M.-D. *Inorg. Chem.* **1995**, *34*, 3829. (b) Su, M.-D.; Liao, H.-Y.; Chung, W.-S.; Chu, S.-Y. *J. Org. Chem.* **1999**, *64*, 6710. (c) Su, M.-D. *J. Phys. Chem. A* **2004**, *108*, 823. (d) Su, M.-D. *Inorg. Chem.*, **2004**, *43*, 4846. (e) Su, M.-D. *Eur. J. Chem.* **2005**, *10*, 5877 and related references therein.