Inorganic Chemistry
Article
pubs.acs.org/IC

Doubly Bonded $E_{13}{=}P$ and $B{=}E_{15}$ Molecules and Their Reactions with H_2, Acetonitrile, Benzophenone, and 2,3-Dimethylbutadiene

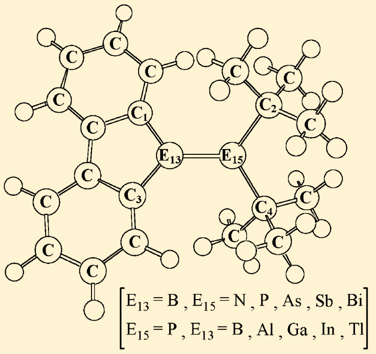
Tsung-Wei Shih,[†] Ming-Chung Li,[†] and Ming-Der Su*[,†,‡]

[†]Department of Applied Chemistry, National Chiayi University, Chiayi 60004, Taiwan

[‡]Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan

Supporting Information

ABSTRACT: The bonding properties and the potential energy surfaces for the chemical reactions of doubly bonded compounds that have the $>E_{13}{=}E_{15}<$ pattern are studied using density functional theory (M06-2X/Def2-SVPD). Nine molecules, $>E_{13}{=}P<$ (E_{13} = B, Al, Ga, In, and Tl) and $>B{=}E_{15}<$ (E_{15} = N, P, As, Sb, and Bi), are used as model reactants in this work. Four types of chemical reactions, H_2 addition, acetonitrile, benzophenone [2 + 2] cycloadditions, and dimethylbutadiene [4 + 2] cycloaddition, are used to study the chemical reactivity of these inorganic, ethylene-like molecules. The results of these theoretical analyses show that only the $>B{=}P<$ molecule has a weak B═P double bond, while the $>Al{=}P<$, $>Ga{=}P<$, $>In{=}P<$, $>Tl{=}P<$, $>B{=}N<$, $>B{=}As<$, $>B{=}Sb<$, and $>B{=}Bi<$ compounds are best described as having a strong single σ bond, instead of a traditional p−p π bond. The theoretical results also show that the singlet−triplet energy gap can be used to determine the relative reactivity of these doubly bonded molecules. According to these theoretical investigations, it is predicted that the order of reactivity is as follows: B═P > Al═P > Ga═P > In═P > Tl═P and B═N ≪ B═P < B═As < B═Sb < B═Bi. The conclusions drawn are consistent with the available experimental observations.



I. INTRODUCTION

Molecules that feature boron−nitrogen or boron−phosphorus double bonds have long been considered to be isoelectronic to alkenes, to which they are structurally analogous.[1] Although the similarities between these doubly bonded geometrical structures are strong, it is evident that both boron−nitrogen and boron−phosphorus double bonds are more electronically asymmetric than isoelectronic carbon−carbon double bonds, because of the differences in the electronegativity of the former.[2] As a result, the chemical relationships may not generally hold for these species. For instance, it is well accepted that benzene (with the C═C double bond) is isoelectronic and iso-structural with borazine (with the B═N double bond), but the effect on the related chemical reactions of benzene and borazine is a matter of debate.[3]

Recently, Lerner and co-workers reported an experimental investigation of the chemical behavior of 9-di-*tert*-butylphosphanyl-9-borafluorene, **1** (with the B═P double bond).[4] It is found that in the reaction of **1** with gaseous H_2 in the toluene solution at room temperature, a hydrogen addition product is formed, which demonstrates the ambiphilic character of its B═P bond.[4] The cycloaddition reactions of **1** with acetonitrile, benzophenone, and 2,3-dimethylbutadiene were also demonstrated, which shows that the boron−phosphorus bond in **1** has π-character.[4]

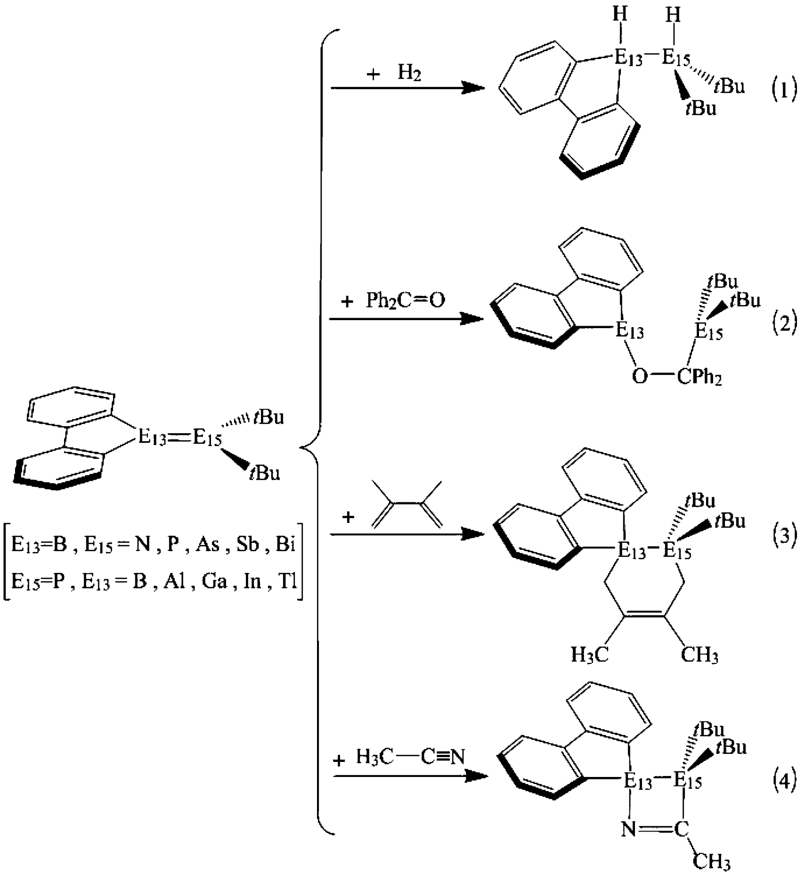
These interesting experimental results prompt this study. If boron and nitrogen and boron and phosphorus can be stabilized as inorganic analogues that have a double bond, it may be possible to extend this to other heteroanalogues that have a group that contains doubly bonded group 13 (E_{13}) and group 15 (E_{15}) elements. In fact, as far as the authors are aware, studies of the development of $E_{13}{=}E_{15}$ doubly bonded species are relatively few. In spite of current advances and given the powerful tools that are available for synthesis, it is surprising that the reactive activity and the molecular properties of compounds that have the $E_{13}{=}E_{15}$ double bonds remain elusive. Since reactivity with substrates is an extremely interesting aspect of the nature of the $E_{13}{=}E_{15}$ double bonds, **1** is used to systematically determine the chemical reactivity and the physical properties of compounds that have $E_{13}{=}E_{15}$ double bonds. Nine unique $E_{13}{=}E_{15}$ double-bonded molecules, $>B{=}P<$, $>Al{=}P<$, $>Ga{=}P<$, $>In{=}P<$, $>Tl{=}P<$, $>B{=}N<$, $>B{=}As<$, $>B{=}Sb<$, and $>B{=}Bi<$ (see Scheme 1), are used as model systems in this theoretical work. These compounds are used because they are all isoelectronic with ethylene, so they can be expected to show similar chemical behavior. Since most of such molecules have not been synthesized and well characterized,[5] it is logical to presume that they could potentially act as doubly bonded species which would allow further development of the chemistry of inorganic ethylene-like complexes.

In this work, four types of chemical reactions (eqs 1−4) are studied using the density functional theory (DFT), in order (i) to determine the potential inorganic molecules that stabilize an $E_{13}{=}E_{15}$ double bond, (ii) to understand the ground state

Received: November 12, 2014
Published: May 8, 2015

DOI: 10.1021/acs.inorgchem.5b00512

Scheme 1



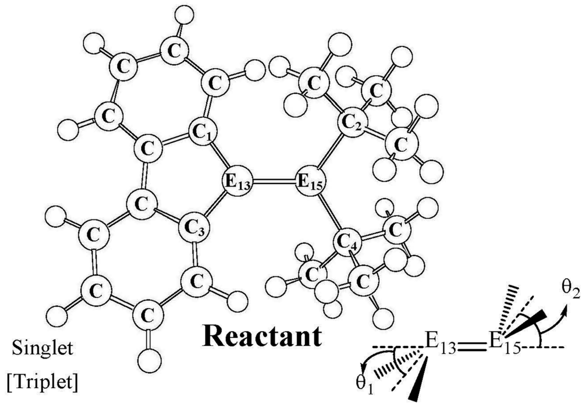
geometry in these compounds that feature double bonds, (iii) to determine the relative reactivity of these inorganic ethylene analogues, and (iv) to guide any future experimental investigations of unknown inorganic compounds that contain an $E_{13}{=}E_{15}$ double bond.

II. RESULTS AND DISCUSSION

1. The Geometries and Electronic Structures of $>E_{13}{=}E_{15}<$ Species. All calculations were performed using the Gaussian 09 package of programs[6] at the M06-2X/Def2-SVPD level of theory (Supporting Information).[7,8] Figure 1 shows the key geometrical parameters of the model reactants (i.e., >B=P< , >Al=P< , >Ga=P< , >In=P< , >Tl=P< , >B=N < , >B=As<, >B=Sb<, and >B=Bi<), which are calculated both as singlet and as triplet species. Cartesian coordinates, calculated for the stationary points at the M06-2X level, are available as Supporting Information.

All of the computations for the model reactants based on the M06-2X/Def2-SVPD method demonstrate that all of these molecules possess a singlet ground state. From Figure 1, the M06-2X calculations predict that the $B{=}E_{15}$ and $E_{13}{=}P$ double bond lengths (Å) for the model reactants in the singlet state are estimated to be 1.429 (B=N), 1.838 (B=P), 2.015 (B=As), 2.243 (B=Sb), 2.333 (B=Bi), 2.225 (Al=P), 2.290 (Ga=P), 2.468 (In=P), and 2.478 (Tl=P), the values of which agree well with available experimentally determined lengths for the double bonds: B=N (1.403−1.446 Å),[3] B=P (1.786−1.859 Å),[9] B=As (1.926−2.031 Å),[10] Al=P (2.342−2.377 Å,)[11] and Ga=P (2.295−2.423 Å).[12] Figure 1 shows that both $E_{13}{=}P$ and $B{=}E_{15}$ double bond distances for both the singlet and the triplet states exhibit a monotonic increase down the group 15 and 13 elements. This is mainly due to an increase in the atomic radius of either E_{13} or E_{15} in the $>E_{13}{=}P<$ and $>B{=}E_{15}<$ doubly bonded species. The M06-2X computations also show that both the $E_{13}{=}P$ and $B{=}E_{15}$ bond distances are longer for the triplet than for its corresponding singlet compound. The reason for this is easily understood by considering their electronic structures (vide infra).[13] Figure 1 also shows that in all cases, the heavier the atom (either E_{13} or E_{15}), the more likely it is that a distorted-trigonal-pyramidal conformation is formed. In particular, the out-of-plane angle (θ) is quite large for the heaviest >Tl=P< (59.5°) and >B=Bi< (73.3°) molecules. In fact, it is well-known that the heavier analogues of the olefins ($>E_{14}{=}E_{14}<$; E_{14} = Si, Ge, Sn, and Pb) do not have a classical planar structure but have a trans-bent conformation, with pyramidalization of both $>E_{14}$ fragments.[14,15] Similarly, the out-of-plane angles for both the $>E_{13}{=}P<$ and the $>B{=}E_{15}<$ systems are far from 0° (planar), which provides strong support for the core-like nature of the *ns* (n = 3−6) electrons, as stated earlier.[15]

Table 1 also shows natural population analyses (NPA) for both the $>E_{13}{=}P<$ and $>B{=}E_{15}<$ species, including the partial charges, the Wiberg bond indices (WBI),[16] the natural bond orbital (NBO) analysis,[17] the natural resonance theory (NRT),[18] and the bonding dissociation energy (BDE). It is found that for the $>E_{13}{=}P<$ systems, only the >B=P< molecule has a WBI that is larger than 1 (WBI = 1.45); the WBI of the other molecules (E_{13} = Al, Ga, In, and Tl) is less than 1 (WBI = 0.83−0.99). This implies that the former molecule has a weaker double bond and the latter species have



E_{13}	B	Al	Ga	In	Tl
E_{13}=P (Å)	1.838 [1.900]	2.225 [2.517]	2.290 [2.630]	2.468 [2.875]	2.478 [2.961]
$\angle C_1\text{-}E_{13}\text{-}E_{15}\text{-}C_2$ (°)	14.28 [40.39]	4.457 [29.92]	10.37 [47.56]	38.36 [57.19]	45.50 [67.84]
$\angle C_3\text{-}E_{13}\text{-}E_{15}\text{-}C_4$ (°)	52.64 [66.11]	71.29 [91.35]	10.02 [68.71]	49.27 [66.57]	51.85 [61.99]
θ_1 (°)	8.394 [4.576]	13.26 [50.48]	0.158 [53.00]	12.73 [54.99]	19.79 [56.74]
θ_2 (°)	22.33 [19.90]	53.88 [44.00]	51.19 [33.24]	51.51 [33.17]	59.52 [35.98]

E_{15}	N	P	As	Sb	Bi
B=E_{15} (Å)	1.429 [1.456]	1.838 [1.900]	2.015 [2.517]	2.243 [2.612]	2.333 [2.711]
$\angle C_1\text{-}E_{13}\text{-}E_{15}\text{-}C_2$ (°)	42.19 [47.00]	14.28 [40.39]	3.730 [40.47]	0.370 [35.98]	1.800 [41.54]
$\angle C_3\text{-}E_{13}\text{-}E_{15}\text{-}C_4$ (°)	43.31 [49.23]	52.64 [66.11]	72.50 63.50]	74.03 [62.34]	73.88 [60.31]
θ_1 (°)	0.650 [0.325]	8.390 [4.576]	10.08 [12.06]	10.22 [16.41]	10.14 [24.81]
θ_2 (°)	1.880 [2.266]	22.33 [19.90]	59.08 [32.94]	69.04 [41.02]	73.30 [43.26]

Figure 1. Selected geometrical parameters (in Å and deg) for the model reactants and >E_{13}═P< (E_{13} = B, Al, Ga, In, Tl) and >B═E_{15}< (E_{15} = N, P, As, Sb, Bi) at both singlet and triplet states calculated at the M06-2X/Def2-SVPD level of theory. Hydrogens are omitted for clarity.

a strong single bond. Supporting evidence is given by the M06-2X results for the NBO analyses of the B═P bonding interaction: BI(B═P) = $0.646(2s2p^{1.72})$B + $0.763(3s3p^{1.70})$P (Supporting Information), which strongly suggest that the predominant bonding interaction between the >B and the P< fragments originates from 2p(B) ←3p(P) donation. That is to say, the boron electron deficiency and the σ bond polarity are partially balanced by the donation of the phosphorus lone pair to the empty boron p orbital. This, in turn, forms a hybrid π bond. Indeed, the NBO model that uses the optimized wave functions shows the presence of a B═P π bonding orbital (Figure 2), which is composed of 20% natural boron orbitals and 80% natural phosphorus orbitals. This indicates that this π bond is polarized. In contrast, because the sizes of the p orbitals in both the E_{13} and the P atoms are quite different and there is a large difference between the atomic radius of the E_{13} and the P atoms, it is envisioned that when the E_{13} element becomes heavier, the p orbitals on Al, Ga, In, and Tl find it somewhat difficult to overlap with the p orbital in P. As a result, their p−p π bonding is quite weak, if they exist. Indeed, the NBO analyses in Table 1 anticipate that the bond order of the >E_{13}═P< species (E_{13} = Al, Ga, In, and Tl) is approximately 1. For the natural E_{13}═P (E_{13} = Al, Ga, In, and Tl) π bonding orbital patterns, see the Supporting Information. As a result, the theoretical evidence strongly suggests that these Al−P, Ga−P, In−P, and Tl−P bonds are best described as a single bond, rather than as a traditional double bond.

However, for the >B═E_{15}< molecules, the M06-2X data in Table 1 show that only the WBI of the >B═N < compound is somewhat less than 1 (WBI = 0.87), but the WBI of the other species (E_{15} = P, As, Sb, and Bi) is somewhat larger than 1 (WBI = 1.18−1.47). This shows that these compounds are better considered as having a strong single bond or a rather weak double bond. The NBO analyses using the M06-2X computations shown in Table 1 again provide evidence for the presence of these chemical bonds.

In Table 1, the NRT analyses of the electron density demonstrate that for the >E_{13}═P< species, only the B═P double bond in the >B═P< molecule has a greater covalent character, as evidenced by the greater covalent part of the NRT bond order (1.09), compared to its ionic part (0.80). However, the covalent and ionic characters of all of the other >E_{13}═P< molecules (i.e., >Al═P< , >Ga═P< , >In═P<, and >Tl═P<) are comparable, with values of 0.48−0.58 and 0.34−0.52, respectively. The NRT analyses show that the natural bond order for the >B═P< molecule is 1.89, but the natural bond order for the other >E_{13}═P< species is approximately 1. Again, these theoretical findings agree well with the WBI data for the NBO analyses. The nonpolar nature of the E_{13}═P double bond is also reflected in the natural population analysis (NPA) charges, shown in Table 1. However, for the >B═E_{15}< species, the NRT data indicate that only the B═N double bond in the >B═N < compound has a greater ionic character (0.69) and a smaller ionic character (0.39). The NRT values in Table 1 show that the double bond in the >B═As<, >B═Sb<, and >B═Bi< systems has a greater covalent character and a relatively smaller ionic character, with values of 0.93−0.89 and 0.11−0.10, respectively. This may be due to the fact that the differences between the electronegativity of these elements is small.[19] Consequently, the NRT predicts that these B−N, B−As, B−Sb, and B−Bi bonds are well characterized as a single bond, whereas the >B═P< molecule is recognized as possessing a π bond. In addition, the NBO analysis of >B═E_{15}< shows that the σ and π components of the B═E_{15} bond are apparently polarized toward the E_{15} atoms, as listed in Table 1.

The BDE values calculated using the M06-2X calculations collected in Table 1 are anticipated to decrease down the group 13 family, from >B═P< to >Tl═P< , and down the group 15 family, from >B═N < to >B═Bi<. These decreases apparently depend on the E_{13}═P and B═E_{15} double bond lengths, as shown in Figure 1. That is to say, the higher the atomic number of E_{13} or E_{15}, the longer is the E_{13}═P or B═E_{15} double bond distance, the smaller is its BDE value, and the easier is it for its two fragments to fall apart.

For a clearer insight into the nature of the bonding in the double bond in the series of >E_{13}═P< and >B═E_{15}< reactants, the main valence molecular orbitals (MOs) are schematically outlined in Figures 3 and 4, respectively, using the M06-2X/Def2-SVPD calculations. In terms of the frontier MOs of the >E_{13}═P< species, Figure 3 shows that the HOMO and LUMO of >B═P< correspond to the B−P π and π* orbitals, respectively. It should be noted that the out-of-plane angles (θ) for the >E_{13}═P< systems are similar (Figure 1). As a result, their np_π−$3p_\pi$ orbital overlap may be considered roughly the same. Therefore, based on the relativistic effect,[15] the substitution of a single E_{13} atom in the >E_{13}═P< species decreases the energy of the π bonding orbital, from boron to

Table 1. Selected Results for the Natural Bond Orbital (NBO) and Natural Resonance Theory (NRT) Analyses of the Compounds >E_{13}═P< (E_{13} = B, Al, Ga, In, and Tl) and >B═E_{15}< (E_{15} = N, P, As, Sb, and Bi)[a,b,c]

			NBO analysis		NRT analysis		
molecule	NPA partial charge	WBI	occupancy	polarization	total/covalent/ionic	resonance weight	BDE[d]
>B═P<	B = 0.54	1.45	σ = 1.97	41.77% (B)	1.89/1.09/0.80	B−P: 11.21%	76.81
	P = 0.52			58.23% (P)		B═P: 88.79%	
			π = 1.90	20.04% (B)			
				79.96% (P)			
>A1═P<	Al = 1.70	0.91	σ = 1.97	28.69% (Al)	1.00/0.48/0.52	Al−P: 95.18%	63.52
	P = 0.08			71.31% (P)		A1═P: 4.82%	
>Ga═P<	Ga = 0.96	0.99	σ = 1.91	27.82% (Ga)	1.02/0.54/0.48	Ga−P: 92.83%	60.04
	P = 0.96			72.18% (P)		Ga═P: 7.11%	
>In═P<	In= 1.52	0.83	σ = 1.86	27.69% (In)	0.97/0.52/0.45	In−P: 94.83%	49.73
	P = 0.15			72.31% (P)		In═P: 5.17%	
>T1═P<	Tl = 1.32	0.84	σ = 1.80	32.58% (Tl)	0.92/0.58/0.34	Tl−P: 95.53%	40.51
	P = 0.26			67.42% (P)		T1=P: 4.47%	
>B═N<	B = 1.18	0.87	σ =1.96	63.55% (N)	1.08/0.39/0.69	B−N: 89.55%	111.6
	N = −0.94			36.45% (B)		B═N: 10.45%	
>B═As<	B = 0.63	1.19	σ = 1.97	42.83% (B)	1.03/0.93/0.10	B−As: 10.01%	69.97
	As = 0.60			57.17% (As)		B═As: 89.99%	
			π = 1.93	18.62% (B)			
				81.38% (As)			
>B═Sb<	B = 0.53	1.18	σ = 1.95	48.46% (B)	1.00/0.89/0.11	B−Sb: 12.12%	59.46
	Sb = 0.91			51.54% (Sb)		B═Sb: 87.88%	
			π = 1.93	20.23% (B)			
				79.77% (Sb)			
>B═Bi<	B = 0.54	1.12	σ = 1.93	45.70% (B)	1.00/0.89/0.11	B−Bi: 14.90%	52.27
	Bi = 0.89			54.30% (Bi)		B═Bi: 85.10%	
			π = 1.93	19.76% (B)			
				80.24%(Bi)			

[a] Partial charges obtained by natural population analysis (NPA). [b] Wiberg bond index (WBI). [c] Occupancy of the corresponding σ and π bonding NBO. [d] Bonding dissociation energy (BDE), units: kcal/mol. That is, BDE = E(>E_{13}) + E(P<) − E(>E_{13}═P<) and BDE = E(>B) + E(E_{15}<) − E(>B═E_{15}<).

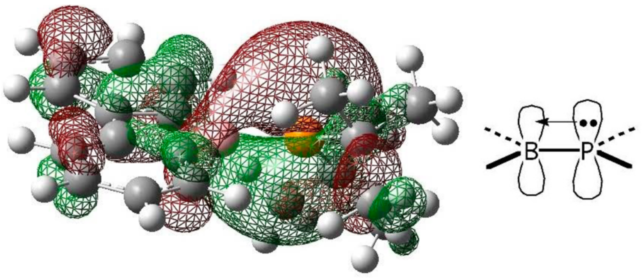


Figure 2. Natural B═P π bonding orbital of **1**.

thallium. However, after the E_{13} substitution, the energy of the LUMO of >E_{13}═P< increases along the series, from >B═P< to >Tl═P<. The two tendencies should cause the HOMO−LUMO energy gap for >E_{13}═P< increases, as the atomic number of E_{13} increases. This result is also reflected on the trend of the singlet−triplet energy separation, ΔE_{st} (= $E_{triplet}$ − $E_{singlet}$), of the >E_{13}═P< species. The M06-2X computations demonstrate that the ΔE_{st} (free energy; kcal/mol) of the doubly bonded >E_{13}═P< molecules increases in the order: 32.3 (>B═P<) < 36.9 (>Al═P<) < 42.0 (>Ga═P<) < 50.5 (>In═P<) < 51.9 (>Tl═P<). In other words, the heavier the group 13 element (E_{13}), the larger is the ΔE_{st} of the >E_{13}═P< molecule.

Likewise, as seen in Figure 4, the HOMO and LUMO of >B═E_{15}< are respectively in accord with the B−E_{15} π and π* orbitals, which are dominantly p-type orbitals with small contributions from the bonding orbitals of substituents. As already shown in Figure 1, the M06-2X/Def2-SVPD results reveal an increasing trend for the θ angle on the E_{15} atom with >B═N< (2.3°) < >B═P< (22°) < >B═As< (59°) < >B═Sb< (69°) < >B═Bi< (73°); that is, the introduction of the heavier E_{15} element in the >B═E_{15}< molecule results in greater pyramidality. A crucial consequence of the heavy E_{15} atom participating in the B═E_{15} bond is a significantly reduced $2p_{\pi}$−np_{π} orbital overlap and then partial bond breaking of B═E_{15} double bonds, which can destabilize the HOMO of the >B═E_{15}< compound but stabilize its LUMO from nitrogen to bismuth. Computational data (Figure 4) are in good agreement with the trends in the frontier MO levels: the HOMO energy levels of >B═E_{15}< increase from N to Bi, whereas the corresponding LUMO energy levels decrease in the opposite direction. As a result, the greater the atomic number of the group 15 atom (E_{15}), the smaller is the HOMO−LUMO energy gap of the >B═E_{15}< molecule. This trend is also consistent with that of the singlet−triplet energy splitting ΔE_{st} of the >B═E_{15}< systems. Indeed, the M06-2X calculations show that that the ΔE_{st} (free energy; kcal/mol) of the >B═E_{15}< compounds decreases in the order: 58.6 (>B═N<) > 32.3 (>B═P<) > 31.8 (>B═As<) > 30.9 (>B═Sb<) > 29.6 (>B═Bi<).

In fact, the stability of the inorganic doubly bonded molecules, >E_{13}═P< and >B═E_{15}<, can be verified by their singlet−triplet energy splitting (ΔE_{st}). If the ΔE_{st} is small, then >E_{13}═P< and >B═E_{15}< should be kinetically unstable, since

DOI: 10.1021/acs.inorgchem.5b00512

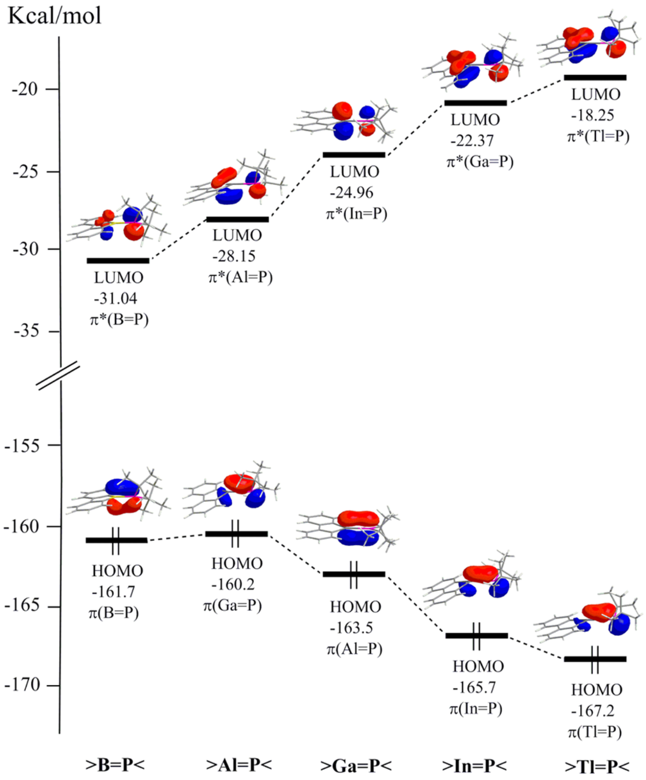


Figure 3. Calculated frontier molecular orbital for the singlet $>E_{13}{=}P<$ (E_{13} = B, Al, Ga, In, and Tl) species. For more information, see the text.

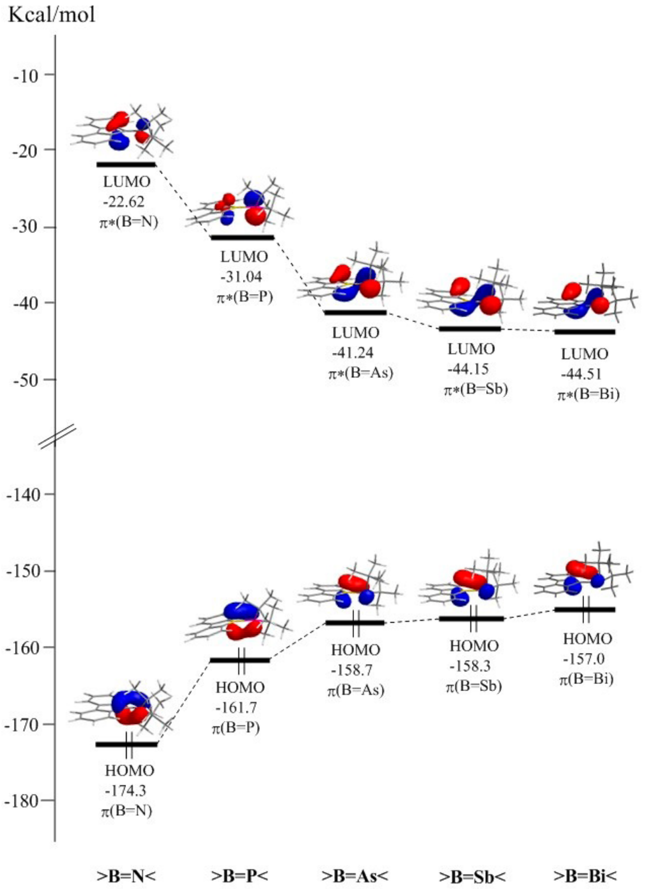


Figure 4. Calculated frontier molecular orbital for the singlet $>B{=}E_{15}<$ (E_{15} = N, P, As, Sb, and Bi) species. For more information, see the text.

their HOMO−LUMO energy gaps are also small, so they readily engage in reactions with other substrates. From the reactivity point of view, the ΔE_{st} of both the $>E_{13}{=}P<$ and the $>B{=}E_{15}<$ species can be used to determine whether they are stable enough to be perceived experimentally. The M06-2X computations predict that the order of the stability of the doubly bonded $>E_{13}{=}P<$ and $>B{=}E_{15}<$ inorganic compounds should be B=P < Al=P < Ga=P < In=P < Tl=P and B=N > B=P > B=As > B=Sb > B=Bi, respectively. These theoretical conclusions are in agreement with the available experimental observations. For instance, it has been experimentally reported that 9-di-*tert*-butylphosphanyl-9-borafluorene **1**, which features a B=P double bond, is a highly reactive compound and has the potential to react with many chemical substances.[4] The ethylene-like inorganic molecules that have the B=N double bond have also been extensively synthesized and well characterized.[20] These conclusions mean that it is predicted that >B=As<, >B=Sb<, and >B=Bi< doubly bonded molecules would not be easily characterized by experimental instruments, but >Al=P< , >Ga=P< , >In=P< , >Tl=P<, and >B=N< doubly bonded compounds should be easily distinguished, using an experimental apparatus. The next sections use the concept of ΔE_{st} to predict the chemical reactivity of both the $>E_{13}{=}P<$ and the $>B{=}E_{15}<$ species.

2. The Addition Reactions of the $>E_{13}{=}P<$ Molecules with Hydrogen, Acetonitrile, Benzophenone, and 2,3-Dimethylbutadiene.

In order to obtain a better understanding oft the mechanisms of the addition reactions for the $>E_{13}{=}P<$ (E_{13} = B, Al, Ga, In, and Tl) species with reactant-2 (i.e., H_2, benzophenone, acetonitrile, and 2,3-dimethylbutadiene), as schematically represented in eqs 1−4, DFT is used to determine their chemical behaviors. The addition mechanisms can be considered to proceed as follows: reactants ($>E_{13}{=}P<$ + reactant-2) → transition state → addition product. The relative free and zero-point energies (kcal/mol) for these stationary points, calculated at the M06-2X/Def2-SVPD level of theory, are summarized in Table 2. There are three noteworthy features of Table 2.

(1) All of the addition reactions for the $>E_{13}{=}P<$ species studied in this work can be considered as either [2 + 2] (e.g., with H_2, benzophenone and acetonitrile) or [4 + 2] (e.g., 2,3-dimethylbutadiene) cycloadditions. It is well established that on the basis of Woodward−Hoffmann rules for [2 + 2] cycloaddition reactions,[21] a concerted supra−supra process ($[{}_2\pi_s + {}_2\pi_s]$) is thermally forbidden. However, it is understood and widely accepted that the polarization of the double bond allows a relaxation of these rules.[22] That is, the different electronegativity values for the E_{13} and P elements signify the electronic polarity of the $E_{13}{=}P$ double bond. It is expected that the $E_{13}{=}P$ molecules that undergo [2 + 2] cycloaddition reactions advance through a concerted, $[{}_2\pi_s + {}_2\pi_s]$ path, which is made kinetically favorable by the relaxation of orbital symmetry restrictions.[23] Accordingly, the bimolecular addition reactions of the $>E_{13}{=}P<$ systems are no longer thermally forbidden. Indeed, these theoretical computations at the M06-2X level confirm this prediction. As seen in Table 2 and Supporting Information, the theoretical findings strongly indicate that the four types of addition reactions (eqs 1−4) produce a four-membered-ring cycloadduct or a quasi-four-

Table 2. Relative Gibbs Free Energies and Relative Zero-Point Energies (in Parentheses; kcal mol^{-1}) at the M06-2X/Def2-SVPD Level of Theory for the Process: >E$_{13}$═P< (E$_{13}$ = B, Al, Ga, In, Tl) + reactant 2 → transition state → product^a (see eqs 1−4)

system	>B═P<	>Al═P<	>Ga═P<	>In═P<	>Tl═P<
(1) >E$_{13}$═P< + H$_2$					
$\Delta E^{\ddagger b}$	24.0	31.2	39.5	46.0	56.8
	(17.0)	(23.7)	(32.8)	(38.4)	(49.2)
ΔH^c	−29.9	−16.4	−13.2	−8.0	−4.5
	(−35.9)	(−23.4)	(−19.6)	(−16.6)	(−12.3)
(2) >E$_{13}$═P< + Ph$_2$C═O					
$\Delta E^{\ddagger b}$	29.1	32.7	34.6	37.2	39.0
	(14.9)	(15.5)	(18.7)	(20.3)	(22.0)
ΔH^c	−19.6	−10.5	2.1	28.8	29.9
	(−34.5)	(−28.6)	(−13.1)	(9.1)	(11.6)
(3) >E$_{13}$═P< + 2,3-dimethylbutadiene					
$\Delta E^{\ddagger b}$	8.1	12.7	10.5	15.1	21.2
	(−8.1)	(−1.2)	(4.7)	(11.9)	(6.5)
ΔH^c	−45.0	−34.4	−28.4	−23.3	−16.6
	(−58.9)	(−51.0)	(−44.2)	(−38.7)	(−31.2)
(4) >E$_{13}$═P< + acetonitrile					
$\Delta E^{\ddagger b}$	8.2	18.4	23.8	24.7	34.5
	(−6.1)	(4.7)	(11.9)	(13.1)	(20.5)
ΔH^c	−14.3	−11.9	−3.1	4.0	14.7
	(−27.0)	(−22.6)	(−15.2)	(−8.8)	(2.0)

[a] The M06-2X optimized structures of the stationary points, see Supporting Information. [b] The activation energy of the transition state, relative to the corresponding reactants. [c] The reaction enthalpy of the product, relative to the corresponding reactants.

membered-ring compound, in a single step, in a concerted manner, and stereospecifically.

(2) As illustrated in Table 2, the M06-2X results show that the doubly bonded >E$_{13}$═P< molecules that contain a heavier E$_{13}$ atom have a higher activation barrier for the addition reactions with reactant-2. Similarly, from Table 2, it is apparent that the doubly bonded >E$_{13}$═P< compounds that have a heavier E$_{13}$ atom can lead to a more endothermic (or a less exothermic) reaction. Simply speaking, the model computations presented in Table 2 show that the chemical reactivity of the >E$_{13}$═P< species, which are isoelectronic with ethylene, decreases in the order B═P > Al═P > Ga═P > In═P > Tl═P. In reality, to the best of the authors' knowledge, only the chemical reactions of the >B═P< molecule (**1**) have been experimentally reported.[4]

(3) In this work, the valence bond state correlation diagram (VBSCD) model, which is based on the work of Shaik et al.,[24,25] is used to determine the key factors that define the general features of these addition reactions. This model[24,25] shows that the stabilization of an addition transition state relies on the $\Delta E_{\rm st}$ of the >E$_{13}$═P< reactant. Namely, a smaller $\Delta E_{\rm st}$ results in a more stable transition state, a lower activation energy and a faster addition reaction. As stated previously, these model calculations show an increasing trend in ΔE_{st}: B═P < Al═P < Ga═P < In═P < Tl═P. In fact, the trend for the $\Delta E_{\rm st}$ of the >E$_{13}$═P< species correlates well with the HOMO−LUMO energy gap, as already shown in Figure 3. From Table 2, it is readily seen that this tendency is in accord with the trend in barrier heights and with the reaction enthalpies. In brief, if the $\Delta E_{\rm st}$ of the >E$_{13}$═P< molecule is small (and its HOMO−LUMO energy difference is also small), the doubly bonded >E$_{13}$═P< molecules are kinetically unstable and allow chemical reactions (with other substances, e.g., solvents). All of this theoretical information shows that the $\Delta E_{\rm st}$ is crucial to verifying the chemical reactivity of the >E$_{13}$═P< molecules.

3. The Addition Reactions of the >B═E$_{15}$< Molecules with Hydrogen, Acetonitrile, Benzophenone, and 2,3-Dimethylbutadiene.

The mechanisms of the addition reactions of the >B═E$_{15}$< (E$_{15}$ = N, P, As, Sb, and Bi) species with reactant-2 (i.e., H$_2$, benzophenone, acetonitrile, and 2,3-dimethylbutadiene), as given in eqs 1−4, are considered, paying particular attention to the transition states and the addition products, themselves. To allow comparisons and to demonstrate the trends, the energies are expressed relative to the corresponding reactants, as illustrated in Table 3. There are three important conclusions to be drawn from these results.

Table 3. Relative Gibbs Free Energies and Relative Zero-Point Energies (in Parentheses; kcal mol^{-1}) at the M06-2X/Def2-SVPD Level of Theory for the Process: >B═E$_{15}$< (E$_{15}$ = N, P, As, Sb, Bi) + reactant 2 → transition state → product^a (see eqs 1−4)

system	>B═N<	>B═P<	>B═As<	>B═Sb<	>B═Bi<
(1) >B═E$_{15}$< + H$_2$					
$\Delta E^{\ddagger b}$	55.2	35.3	26.8	24.3	24.0
	(47.2)	(28.7)	(18.3)	(15.4)	(17.0)
ΔH^c	4.1	−8.7	−16.6	−20.7	−29.9
	(−3.6)	(−15.7)	(−23.5)	(−28.4)	(−35.9)
(2) >B═E$_{15}$< + Ph$_2$C═O					
$\Delta E^{\ddagger b}$	95.4	29.1	23.6	22.7	16.1
	(81.1)	(14.9)	(8.4)	(8.1)	(3.8)
ΔH^c	40.3	−16.4	−19.6	−22.2	−28.1
	(24.5)	(−32.4)	(−34.5)	(−39.1)	(−44.2)
(3) >B═E$_{15}$< + 2,3-dimethylbutadiene					
$\Delta E^{\ddagger b}$	51.6	12.7	12.5	14.4	7.3
	(35.0)	(−1.2)	(−0.6)	(−2.4)	(−7.1)
ΔH^c	13.4	−22.7	−29.5	−37.0	−45.0
	(−3.1)	(−36.0)	(−44.8)	(−44.8)	(−58.9)
(4) >B═E$_{15}$< + acetonitrile					
$\Delta E^{\ddagger b}$	46.8	28.4	24.7	15.7	14.3
	(32.3)	(13.9)	(13.1)	(4.4)	(3.6)
ΔH^c	2.4	3.3	−9.7	−11.8	−12.9
	(−10.4)	(−11.8)	(−23.5)	(−26.6)	(−27.6)

[a] The M06-2X optimized structures of the stationary points, see Supporting Information. [b] The activation energy of the transition state, relative to the corresponding reactants. [c] The reaction enthalpy of the product, relative to the corresponding reactants.

(1) Again, because of the difference in the electronegativity values of boron and the E$_{15}$ elements,[19] the B═E$_{15}$ double bond is electronically polar. As discussed previously, this polarization of the π bonds allows a relaxation of the Woodward−Hoffmann rules, which anticipate that the [2 + 2] reaction is thermally forbidden.[21] However, the M06-2X computations show that the [2 + 2] and [4 + 2] reactions of the >B═E$_{15}$< systems are concerted, since only one transition state is identified and verified for each addition reaction. This is a true transition state, based on the results of the frequency analysis. In particular, the calculated results show that all of the [2 + 2] addition products have a planar four-membered-ring (or a quasi four-membered-ring) structure (Supporting Information). This theoretical evidence confirms that the >B═E$_{15}$< compounds and reactant-2 undergo a one-step

process, so their [2 + 2] and [4 + 2] cycloaddition reactions lead concertedly to the final adducts. From a geometrical viewpoint, these [2 + 2] and [4 + 2] addition reactions progress stereospecifically and result in addition products with retained stereochemistry.

(2) The energetics presented in Table 3 show that a $>B{=}E_{15}<$ molecule with a heavier E_{15} element has a lower barrier height and produces a more exothermic reaction than a $>B{=}E_{15}<$ molecule with a lighter E_{15} atom.[26] This is strong evidence that both the [2 + 2] and the [4 + 2] cycloaddition reactions are more preferable for a $>B{=}E_{15}<$ reactant that contains a heaver group 15 element than for one with a lighter pnicogen atom from the same row.

(3) These theoretical results show that for both the calculated activation energies and the reaction enthalpies, for the [2 + 2] and [4 + 2] addition reactions of the $>B{=}E_{15}<$ compound, the order of chemical reactivity increases as $B{=}N \ll B{=}P < B{=}As < B{=}Sb < B{=}Bi$. Apparently, this is a reflection of $B{=}E_{15}$ bond strength. The heavier the group 15 atom (E_{15}), the larger is its atomic radius and the smaller is the $B{=}E_{15}$ bond breaking energy. This, in turn, results in a decrease in the barrier energies and a more exothermic bimolecular addition reaction (eqs 1−4). However, the reactivity of the $>B{=}E_{15}<$ species does not increase from nitrogen to bismuth. The theoretical data for the $>B{=}E_{15}<$ systems can be rationalized using the VBSCD model.[24,25] As shown in Figure 4, the HOMO−LUMO energy difference (and so the ΔE_{st}) for the $>B{=}E_{15}<$ molecules decreases from nitrogen to bismuth. Similarly to the $>E_{13}{=}P<$ systems, the theoretical findings strongly suggest that the ΔE_{st} is the crucial factor in the chemical reactivity of the doubly bonded $>B{=}E_{15}<$ molecules.

III. CONCLUSION

The mechanisms of four types of addition reactions for doubly bonded $>E_{13}{=}P<$ (E_{13} = B, Al, Ga, In, and Tl) and $>B{=}E_{15}<$ (E_{15} = N, P, As, Sb, and Bi) systems are studied using the M06-2X/Def2-SVPD level of theory. This study gives the first theoretical demonstration of the reaction trajectories and theoretical estimations of the barrier heights and reaction enthalpies for [2 + 2] and [4 + 2] cycloaddition reactions. The relationship between the experimental and the theoretical studies is very important for the further development of the chemistry of highly reactive species. For the nine doubly bonded reactants and the four kinds of addition reactions studied, the following conclusions can be drawn.

(1) On the basis of both NBO[17] and NRT[18] analyses, the theoretical evidence is that the $>B{=}P<$ molecules feature a weak double bond and the $>Al{=}P<$, $>Ga{=}P<$, $>In{=}P<$, $>Tl{=}P<$, $>B{=}N<$, $>B{=}As<$, $>B{=}Sb<$, and $>B{=}Bi<$ compounds are best characterized as having a strong single σ bond, instead of a conventional π bond.

(2) The theoretical findings show that the chemical reactivity of $>E_{13}{=}P<$ systems decreases in the order $B{=}P > Al{=}P > Ga{=}P > In{=}P > Tl{=}P$, whereas the chemical reactivity of $>B{=}E_{15}<$ species increases in the order $B{=}N \ll B{=}P < B{=}As < B{=}Sb < B{=}Bi$. The reasons for such trends are attributed to their HOMO−LUMO energy gap as well as their corresponding singlet−triplet energy splitting (ΔE_{st}). In other words, our theoretical study demonstrates that the overall reactivity of the double bond in both $>E_{13}{=}P<$ and $>B{=}E_{15}<$ molecules is totally governed by the central elements' effects as well as the substituents' steric effects. These, in turn, would cause the tendency of their HOMO−LUMO energy gaps.

Experimentalists are encouraged to perform further experiments, to prove these predictions.

■ ASSOCIATED CONTENT

Supporting Information

Theoretical methods, references, Table A, Figures A ($>Al{=}P<$) and B ($>Ga{=}P<$), Figures C ($>In{=}P<$) and D ($>Tl{=}P<$), Figures E ($>B{=}N<$) and F ($>B{=}As<$), Figures G ($>B{=}Sb<$) and H ($>B{=}Bi<$), Cartesian coordinates. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00512.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: midesu@mail.ncyu.edu.tw.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to the National Center for High-Performance Computing of Taiwan for generous amounts of computing time. They also thank the Ministry of Science and Technology of Taiwan for the financial support. Special thanks are also due to reviewers 1, 2, and 3 for very helpful suggestions and comments.

■ REFERENCES

(1) (a) Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 449. (b) Power, P. P.; Moezzi, A.; Pestana, D. C.; Petrie, M. A.; Shoner, S. C.; Waggoner, K. M. *Pure Appl. Chem.* **1991**, *63*, 859. (c) Paine, R. T.; Nöth, H. *Chem. Rev.* **1995**, *95*, 343. (d) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.

(2) Huheey, J. E. Keiter, E. A.; Keiter, R. L. In *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins, New York, 1993; p 246.

(3) For reviews, see: Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 6074 and references therein.

(4) Breunig, J. M.; Hübner, A.; Bolte, M.; Wagner, M.; Lerner, H.-W. *Organometallics* **2013**, *32*, 6792.

(5) However, relative aromaticity in heteropolar inorganic analogues of benzene has been theoretically studied. See: Fink, W. H.; Richards, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 3393. Also, pericyclic reactions between doubly bonded phosphinoboranes and alkenes/dienes were already theoretically studied. See: Gilbert, T. M.; Bachrach, S. M. *Organometallics* **2007**, *26*, 2672 and references therein.

(6) Frisch, M. J. et al. Gaussian, Inc.: Wallingford, CT, 2013.

(7) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

(8) The Def2-SVPD basis sets, see: (a) Andrae, D.; Haeussermann, U.; Stoll, M. H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123. (b) Metz, B.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2000**, *113*, 2563. (c) Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2003**, *119*, 11113.

(9) (a) Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817. (b) Paine, R. T.; Nöth, H. *Chem. Rev.* **1995**, *95*, 343. (c) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8426.

(10) Petrie, M. A.; Olmstead, M. M.; Hope, H.; Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 3221.

(11) (a) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 3205. (b) Knabel, K.; Krossing, I.; Nöth, H.; Schwenk-Kirchner, H.; Schmidt-Amelunxen, M.; Seifert, T. *Eur. J. Inorg. Chem.* **1998**, 1095.

(12) (a) Petrie, M. A.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1992**, *31*, 4038. (b) Petrie, M. A.; Power, P. P. *J. Chem. Soc., Dalton*

Trans. **1993**, 1737. (c) Linti, G.; Frey, R.; Köstler, W.; Schwenk, H. *Chem. Ber. Recl.* **1997**, *130*, 663.

(13) As can be seen in Figures 1 and 3, the triplet species has one electron occupying the LUMO. This phenomenon can increase either E_{13}−P or B−E_{15} bond length in the triplet state.

(14) For instance, see: (a) Su, M.-D *J. Phys. Chem.* **1996**, *100*, 4339 and related references therein. (b) Tokitoh, N.; Okazaki, R. *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: Chichester, 2002; Vol. 2, Chapter 13. (c) Klinkhammer, K. W. *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Rappoport, Z., Ed.; Wiley: Chichester, 2002; Vol. 2, Chapter 4.

(15) These phenomena are known to be attributed to the relativistic effect—the so-called "inert s-pair effect" and the "orbital nonhybridization effect". That is, the reason for this is due to the size difference and energy gap between the valence s and p orbitals, both of which increase upon going from B to Tl as well as from N to Bi atoms due to the relativistic effects. As a result, the heavier group 13 and group 15 atoms maintain the $(ns)^2(np)^1$ and $(ns)^2(np)^3$ valence electron configurations, respectively. Accordingly, the use of almost pure np orbitals instead of more hybridized orbitals leads to a smaller bond angle at each heavier group 13 and group 15 atom. See: (a) Pyykkö, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276. (b) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272. (c) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563. (d) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(16) Wiberg, K. B. *Tetrahedron* **1968**, 1083.

(17) Glendening, E. D.; Reed, A. E.; Carpenter, J.; Weinhold, F. *NBO*, version 3.1; Univeristy of Wisconsin: Madison, WI.

(18) (a) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593. (b) ibid., *J. Comput. Chem.* **1998**, *19*, 610. (c) Glendening, E. D.; Badenhoop, J. K.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628.

(19) (a) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. in *Inorganic Chemistry: Principles of Structure and reactivity*, 4th ed.; HarperCollins: New York, 1993; p 246. (b) According to the definition of the Mulliken-Jaffe method, the electronegativity of E_{13} and E_{15} is as follows: B (2.0), Al (1.5), Ga (1.8), In (1.5), Tl (1.4), N (3.1), P (2.1), As (2.2), Sb (1.8), and Bi (1.7).

(20) Indeed, the doubly bonded >B═N< molecules have been already synthesized and well characterized by several experimental groups. For instance, see ref 3.

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

(22) For instance, see: (a) Leigh, W. J. *Pure Appl. Chem.* **1999**, *71*, 453 and related references therein.. (f) Mosey, N. J.; Baines, K. M.; Woo, T. K. *J. Am. Chem. Soc.* **2002**, *124*, 13306. (g) Gusel'nikov, L. E. *Coord. Chem. Rev.* **2003**, *244*, 149.

(23) On the basis of the Woodward−Hoffmann rules, there is another possible thermally allowed [2 + 2] cycloaddition reaction mechanism, i.e., the $[_2\pi_s + {}_2\pi_a]$ mechanism. However, this mechanism would be too sterically congested, even in the case of the parent homonuclear doubly bonded compounds, needless to mention the steric overcrowding >E_{13}═P< and >B═E_{15}< systems studied in this work.

(24) For details, see: (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.; Hiberty, P. C. In *A Chemist's Guide to Valence Bond Theory*; Wiley, Interscience: New York, 2008.

(25) (a) The first paper that originated the VBSCD model, see: Shaik, S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. (b) About the most updated review of the VBSCD model, one can see: Shaik, S.; Shurki, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 586. (c) Hoffmann, R.; Shaik, S.; Hiberty, P. C. *Acc. Chem. Res.* **2003**, *36*, 750.

(26) An earlier computational study of [2 + 2] and [4 + 2] pericyclic reactions between phosphinoboranes and alkenes by Gilbert and Bachrach was reported. See: Gilbert, T. M.; Bachrach, S. M. *Orhanometallics* **2007**, *26*, 2672 In the above paper, they predicted that the $(F_3C)_2BP(CH_3)_2$ compound can undergo facile [2 + 2] cyclization with C_2H_2 and C_2H_4 and [4 + 2] cyclization with *cis*-C_4H_6 and *c*-C_5H_6, with barriers of <10 kcal/mol and exothermicities of >30 kcal/mol. In comparison to our work shown in Table 3, although the attached substitutes in the present model study are quite large, our computational results for the >B═P< case are similar to their work.