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Theoretical Study on Inverse Sandwich Complexes $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ and $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ ($n=1, 2, 3$; $\text{E}=\text{Al, Ga, In, Tl}$)Nan-nan Liu^{a*}, Yi-hong Ding^{b*}*a. Chemistry Center, College of Food Engineering, Harbin University of Commerce, Haerbin 150028, China**b. State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130012, China*

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The inverse sandwiches $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ and $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ ($n=1, 2, 3$; $\text{E}=\text{Al, Ga, In, Tl}$) with low-valent boron group elements are studied. The (η^5, η^5) coordinated inverse sandwich $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ is unstable in energy or nonexistent. However, the (η^5, η^5) coordinated $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ is not only stable in energy, but also stable against dissociation. The dissociation stability $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ with the same E element decreases as the number n increases, while for the certain n number, the dissociation energies with different E elements are close to each other. $[\text{E-C}_4\text{H}_4\text{P-E}]^+$ has similar dissociation stability to the well-known $[\text{E-C}_5\text{H}_5\text{-E}]^+$. The interaction between $\text{C}_{5-n}\text{H}_{5-n}\text{P}_n$ and low-valent E element is mainly ionic. Since lone pairs of electrons locate on both E and P atoms, the (η^5, η^5) coordinated inverse sandwich $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ would act as multi electron-donors.

Key words: Low-valent, Boron group elements, Electron-donor, Organometallic, Heterocyclic

I. INTRODUCTION

Low-valent boron group elements complexes have drawn a wide range of interest in the fields of coordination chemistry and organometallic chemistry in the past decade [1–3]. The accessibility of low-valent boron group elements in ER , ECp^* *etc.* ($\text{E}=\text{boron group elements}$, $\text{Cp}^*=\text{C}_5\text{Me}_5$, $\text{R}=\text{C}(\text{SiMe}_3)_3$) makes them potential electron-rich σ -donor ligands in materials chemistry [4–6]. The assembly between poly ECp^* and transition metals can produce the multi-core sandwiches $[\text{M}_a(\text{ECp}^*)_b]$ ($\text{M}=\text{Pb, Pt}$) [7, 8]. Aiming at the type $[\text{M}(\text{ECp}^*)_n]^{m+}$ ($\text{M}=\text{transition metals}$), the $[\text{Ga-Cp}^*\text{-Ga}]^+$ cation with a special inverse sandwich structure was surprisingly synthesized [9]. As a nearly “naked” Ga^+ ion, $[\text{Ga-Cp}^*\text{-Ga}]^+$ was proposed to be a potential selective source for highly reactive Ga^+ .

The important discovery inspired theoretical studies on the inverse sandwiches $[\text{E-Cp-E}]^+$ and $\text{E-C}_4\text{H}_4\text{-E}$ ($\text{E}=\text{B, Al, Ga, In, Tl}$, $\text{Cp}=\text{C}_5\text{H}_5$) [10, 11]. For $[\text{E-Cp-E}]^+$, $[\text{B-Cp-B}]^+$ dissociates via the loss of the neutral B atom, while heavier $[\text{E-Cp-E}]^+$ ($\text{E}=\text{B, Al, Ga, In, Tl}$) dissociates via the loss of the charged E^+ . For $\text{E-C}_4\text{H}_4\text{-E}$, inverse sandwich $\text{B-C}_4\text{H}_4\text{-B}$ is not available, the $\text{E-C}_4\text{H}_4\text{-E}$ ($\text{E}=\text{Al, Ga, In, Tl}$) dissociates via the

loss of the neutral E atom. Obviously, different ligands bring different properties for inverse sandwiches. However, the cases of low-boron group inverse sandwiches with other aromatic ligand are still seldom known so far.

Cp^- anion is a widely used aromatic ligand in organometallic and coordination chemistry [12–16]. Heterocyclic polyphospholyl $(\text{CH})_{5-n}\text{P}_n^-$ have similar aromaticity to that of Cp^- , various researches focused on the coordination mode of $(\text{CH})_{5-n}\text{P}_n^-$ with metals. Generally the η^5 -coordination is common for these heterocyclic rings, such as the ferrocene-like $[\text{Fe}(\eta^5\text{-Cp})(\eta^5\text{-(CH)}_{5-n}\text{P}_n)]$ and $[\text{Fe}(\eta^5\text{-C}_2(\text{Me})_2\text{P}_3)_2]$ [17, 18]. Since the coordination mode of $(\text{CH})_{5-n}\text{P}_n^-$ is similar to Cp^- , the inverse sandwich $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ might exist like $[\text{E-Cp-E}]^+$. Although the low-valent boron group elements generally act as electron-donors, the vacant p-orbitals also make them potential acceptors to form donor-acceptor bond with P atom. Therefore, it is of interest whether the inverse sandwiches $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ are available or not. Herein, a series of inverse sandwiches $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ and $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ ($\text{E}=\text{Al, Ga, In, Tl}$; $n=1, 2, 3$) are theoretically considered.

The geometries of all structures were fully optimized using the density functional theory methods PBEPBE, B3LYP and MPW91PW91 with the def2-TZVP basis set by mean of Gaussian 09 program packages [19–27]. Bonding analyses are performed using NBO 3.0, Multi-

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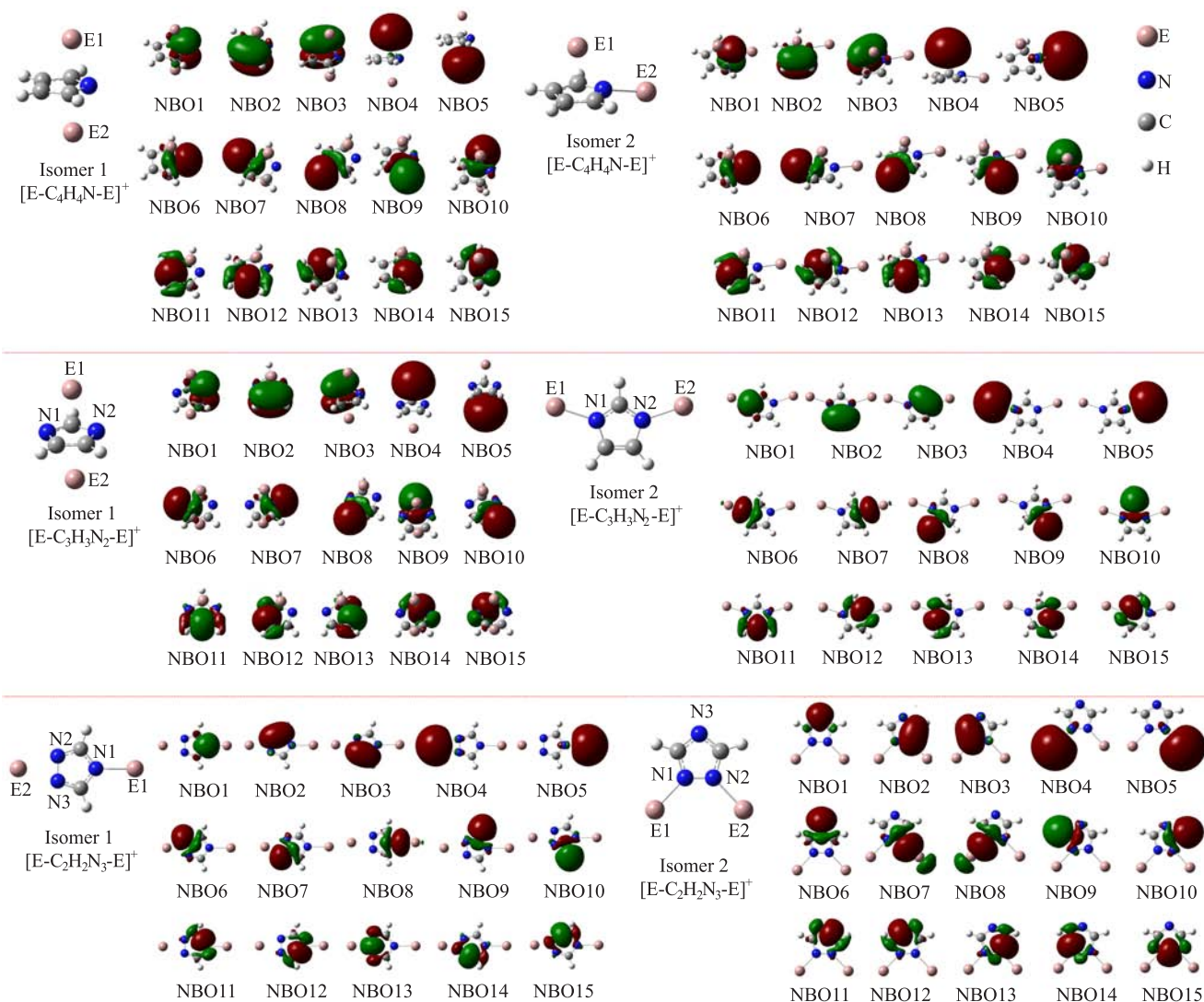


FIG. 1 The structures and NBOs of $[E-C_{5-n}H_{5-n}N_n-E]^+$.

wfn and Visual Molecular Dynamics (VMD) programs [28, 29].

II. RESULTS AND DISCUSSION

A. Geometries and bonding of $[E-C_{5-n}H_{5-n}N_n-E]^+$ ($E=Al, Ga, In, Tl; n=1, 2, 3$)

The structures and the natural bond orbitals (NBOs) of $[E-C_{5-n}H_{5-n}N_n-E]^+$ isomers are shown in Fig.1. Table I shows the relative energies of $[E-C_{5-n}H_{5-n}N_n-E]^+$ or $[E-C_{5-n}H_{5-n}P_n-E]^+$ ($E=Al, Ga, In, Tl$) isomers.

$[E-C_4H_4N-E]^+$ has two isomers, isomer 1 is a typical inverse sandwich structure with the (η^5, η^5) coordination, isomer 2 is with the (η^5, η^1) coordination. Isomer 1 of $[E-C_4H_4N-E]^+$ is about 2.7–10.8 kcal/mol higher in energy than the isomer 2. Noted

that the inverse sandwich isomer 1 of $[Al-C_4H_4N-Al]^+$, which has an imaginary frequency of -93.6 cm^{-1} at PBE/PBE/TZVP, is not a local minimum. Thus, (η^5, η^5) coordinated isomer 1 of $[Al-C_4H_4N-Al]^+$ would not exist. As the element grows heavier from Ga to Tl, the stability of isomer 1 is increased. The bonding is studied by NBO analysis at PBE/PBE/def2-TZVP level. Since the NBO orbitals for $[E-C_{5-n}H_{5-n}N_n-E]^+$ or $[E-C_{5-n}H_{5-n}P_n-E]^+$ with different E are similar, we only take $[Ga-C_{5-n}H_{5-n}N_n-Ga]^+$ or $[Ga-C_{5-n}H_{5-n}P_n-Ga]^+$ as an example for illustration. For isomer 1, the vertical distances $Ga-C_4H_4N$, $In-C_4H_4N$, $Tl-C_4H_4N$ are 2.320, 2.548 and 2.629 Å, respectively. As shown in Fig.1, NBOs 1–3 correspond to the delocalized π_5^6 bond of C_4H_4N , NBOs 4 and 5 correspond to the $n_{Ga}(s)$ LPs, NBO 6 for the $n_N(sp^2)$ lone-pair (LP), NBOs 7–10 for the four σ_{C-H} bonds, NBOs 11–15 for the five σ_{C-C} and σ_{C-N} bonds. The NBO numbers are arranged in an

TABLE I The relative energies, coordination mode and dissociation energies of $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ and $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$, the isomer 1 of $[\text{Al-C}_4\text{H}_4\text{N-Al}]^+$ marked by (*i*) is not a local minimum.

		Relative energies/(kcal/mol)			Coordination mode	Dissociation energies ^a /(kcal/mol)			
		PBEPBE	B3LYP	MPW91PW91		ΔD_1	ΔD_2	ΔD_3	ΔD_4
$[\text{E-C}_4\text{H}_4\text{N-E}]^+$	Al-isomer 1	(<i>i</i>)	(<i>i</i>)	(<i>i</i>)	(η^5, η^5)				
	Ga-isomer 1	0	0	0	(η^5, η^5)	41.1	41.1	110.5	110.5
	In-isomer 1	0	0	0	(η^5, η^5)	37.8	37.8	77.5	77.5
	Tl-isomer 1	0	0	0	(η^5, η^5)	38.1	38.1	77.7	77.7
	Al-isomer 2	0	0	0	(η^5, η^1)	51.9	50.8	89.7	94.2
	Ga-isomer 2	-7.6	-9.4	-7.9	(η^5, η^1)	52.8	48.8	86.9	118.1
	In-isomer 2	-4.8	-6.2	-4.7	(η^5, η^1)	48.2	42.6	82.3	82.3
	Tl-isomer 2	-3.1	-4.1	-2.7	(η^5, η^1)	48.3	41.2	80.8	80.8*
$[\text{E-C}_3\text{H}_3\text{N}_2\text{-E}]^+$	Al-isomer 1	0	0	0	(η^5, η^5)	32.1	32.1	87.7	87.7
	Ga-isomer 1	0	0	0	(η^5, η^5)	34.1	34.1	79.6	79.6
	In-isomer 1	0	0	0	(η^5, η^5)	32.2	32.2	79.4	79.4
	Tl-isomer 1	0	0	0	(η^5, η^5)	33.0	33.0	80.1	80.1
	Al-isomer 2	-31.5	-39.8	-33.5	(η^1, η^1)	60.6	60.6	110.0	110.0
	Ga-isomer 2	-23.4	-28.9	-24.4	(η^1, η^1)	57.8	57.8	102.9	102.9
	In-isomer 2	-17.9	-21.8	-18.2	(η^1, η^1)	52.5	52.5	97.3	97.3
	Tl-isomer 2	-14.0	-16.5	-13.4	(η^1, η^1)	51.0	51.0	94.1	94.1
$[\text{E-C}_2\text{H}_2\text{N}_3\text{-E}]^+$	Al-isomer 1	0	0	0	(η^2, η^1)	47.7	63.0	93.2	122.5
	Ga-isomer 1	0	0	0	(η^2, η^1)	48.3	61.2	109.6	119.6
	In-isomer 1	0	0	0	(η^2, η^1)	43.7	57.2	109.8	116.1
	Tl-isomer 1	0	0	0	(η^2, η^1)	43.2	56.5	113.2	113.7
	Al-isomer 2	11.1	11.2	11.8	(η^1, η^1)	36.6	36.6	82.1	82.1
	Ga-isomer 2	12.7	12.0	12.6	(η^1, η^1)	35.6	35.6	96.9	96.9
	In-isomer 2	14.1	13.8	14.1	(η^1, η^1)	29.7	29.7	95.7	9.7
	Tl-isomer 2	13.8	13.8	14.0	(η^1, η^1)	29.4	29.4	99.3	99.3
$[\text{E-C}_4\text{H}_4\text{P-E}]^+$	Al-isomer 1	0	0	0	(η^5, η^5)	43.3	43.3	76.7	76.7
	Ga-isomer 1	0	0	0	(η^5, η^5)	43.8	43.8	93.7	93.7
	In-isomer 1	0	0	0	(η^5, η^5)	39.2	39.2	91.2	91.2
	Tl-isomer 1	0	0	0	(η^5, η^5)	39.0	39.0	90.6	90.6
$[\text{E-C}_3\text{H}_3\text{P}_2\text{-E}]^+$	Al-isomer 1	0	0	0	(η^5, η^5)	41.0	41.0	75.7	75.7
	Ga-isomer 1	0	0	0	(η^5, η^5)	41.1	41.1	94.6	94.6
	In-isomer 1	0	0	0	(η^5, η^5)	36.4	36.4	92.1	92.1
	Tl-isomer 1	0	0	0	(η^5, η^5)	36.1	36.1	91.3	91.3
	Al-isomer 2	25.9	18	26.8	(η^1, η^1)	45.2	45.2	75.7	75.7
	Ga-isomer 2	23.4	18	24.6	(η^1, η^1)	45.3	45.3	74.9	74.9
	In-isomer 2	19.7	15.8	20.9	(η^1, η^1)	41.0	41.0	73.2	73.2
	Tl-isomer 2	18.1	15.3	19.3	(η^1, η^1)	40.7	40.7	73.2	73.2
$[\text{E-C}_2\text{H}_2\text{P}_3\text{-E}]^+$	Al-isomer 1	0	0	0	(η^5, η^5)	38.3	38.3	51.4	51.4
	Ga-isomer 1	0	0	0	(η^5, η^5)	38.1	38.1	91.5	91.5
	In-isomer 1	0	0	0	(η^5, η^5)	33.7	33.7	90.8	90.8
	Tl-isomer 1	0	0	0	(η^5, η^5)	33.4	33.4	91.5	91.5
	Al-isomer 2	10.2	6.6	10.7	(η^5, η^1)	57.6	28.1	91.9	63.1
	Ga-isomer 2	9.5	6.8	9.8	(η^5, η^1)	56.3	28.6	92.2	82.0
	In-isomer 2	8.3	6.4	8.7	(η^5, η^1)	50.1	25.4	86.7	82.6
	Tl-isomer 2	7.8	6.4	8.3	(η^5, η^1)	48.8	25.5	83.7	86.1
	Al-isomer 3	7.8	4.2	8.3	(η^5, η^1)	57.5	30.4	92.1	65.5
	Ga-isomer 3	7.2	4.5	7.4	(η^5, η^1)	56.2	30.9	90.5	84.3

To be continued.

TABLE I continued.

		Relative energies/(kcal/mol)			Coordination mode	Dissociation energies ^a /(kcal/mol)			
		PBEPBE	B3LYP	MPW91PW91		ΔD_1	ΔD_2	ΔD_3	ΔD_4
[E-C ₂ H ₂ P ₃ -E] ⁺	In-isomer 3	6.2	4.2	6.5	(η^5, η^1)	27.5	27.5	87.3	84.6
	Tl-isomer 3	5.7	4.3	6.0	(η^5, η^1)	27*	27.6	85.8	86.7
	Al-isomer 4	21.9	16.7	23.7	(η^2, η^1)	38.9	45.9	75.4	80.2
	Ga-isomer 4	20.7	17.2	22.3	(η^2, η^1)	39.3	45.1	80.7	78.8
	In-isomer 4	17.2	14.6	18.7	(η^2, η^1)	35.6	41.2	80.1	77.8
	Tl-isomer 4	16.1	14.1	17.3	(η^2, η^1)	35.3	40.6	80.2	77.8

^a The dissociation energies are at PBEPBE/TZVP level.

ascending order according to the orbital energies. The NBO charge distributed on each Ga atom is high to 0.857, the Ga-(η^5 -C₄H₄N) interactions are mainly ionic. The sum of the Mayer bond orders for Ga-(η^5 -C₄H₄N) interaction is 0.68, where the N-Ga contribution is 0.22 (32.4%).

For isomer 2 of [E-C₄H₄N-E]⁺, the vertical distances Al1-C₄H₄N, Ga1-C₄H₄N, In1-C₄H₄N, Tl1-C₄H₄N are 2.252, 2.383, 2.524, and 2.615 Å; the distances N-Al2, N-Ga2, N-In2 and N-Tl2 are 2.021, 2.146, 2.369, 2.466 Å, respectively. NBOs 4 and 5 correspond to the n_{Ga(s)} LPs, NBO 6 for the n_{N(sp²)} LP. The NBO charges on Ga1 and Ga2 atoms are 0.754 and 0.912. The sum of the Mayer bond orders for Ga1-(η^5 -C₄H₄N) is 0.81, where the Ga1-N contribution is 0.11 (13.6%). By second order perturbation theory analysis, the n_{N(sp²)}→n_{Ga2}^{*}(sp^{26.9}d^{0.5}) interaction represents the donor-acceptor N-Ga2 bond, of which the Mayer bond order is 0.53 (see Fig.2).

[E-C₃H₃N₂-E]⁺ has two isomers, isomer 1 is a (η^5, η^5) coordinated inverse sandwich structure, isomer 2 is (η^1, η^1) coordinated. Isomer 2 of [E-C₃H₃N₂-E]⁺ is much lower in energy (13.4–39.8 kcal/mol) than isomer 1. For isomer 1, the vertical distances Al-C₃H₃N₂, Ga-C₃H₃N₂, In-C₃H₃N₂, and Tl-C₃H₃N₂ are 2.324, 2.371, 2.599, and 2.666 Å, respectively. NBOs 6 and 7 correspond to the n_{N(sp^{1.60}, sp^{1.58})} LPs, NBOs 4 and 5 for the n_{Ga(s)} LPs. The NBO charge on each Ga atom is 0.874. The sum of the Mayer bond orders for Ga-(η^5 -C₃H₃N₂) is 0.51, where each N-Ga contribution is 0.15 (29.4%).

For isomer 2 of [E-C₃H₃N₂-E]⁺, the distances N1-Al1 (N2-E2), N1-Ga1, N1-In1, and N1-Tl1 are 2.012, 2.118, 2.348, and 2.443 Å, respectively. NBOs 4 and 5 correspond to the n_{Ga(s)} LPs, NBOs 6 and 7 for the n_{N(sp^{1.95})} LPs. The NBO charge on Ga1 atom is 0.892. The two n_{N1(sp^{1.95})}→n_{Ga1}^{*}(sp^{27.5}d^{0.6}) interactions represent the two donor-acceptor N-Ga bonds in isomer 2 with the Mayer bond order of 0.57 (Fig.2).

[E-C₂H₂N₃-E]⁺ has two isomers, isomer 1 is a (η^2, η^1) coordinated structure, isomer 2 is a (η^1, η^1) coordinated structure. Isomer 1 is 11.1–14.1 kcal/mol lower in energy than isomer 2. For isomer 1, the distances N2-Al2 (N3-E2), N2-Ga2,

N2-In2, and N2-Tl2 are 2.178, 2.284, 2.482, and 2.575 Å; the distances N1-Al1, N1-Ga1, N1-In1, and N1-Tl1 are 2.066, 2.167, 2.387, and 2.480 Å, respectively. NBOs 6 and 7 correspond to the n_{N(sp^{1.6})} LPs, NBO 8 for the n_{N(sp^{1.9})} LP, NBOs 4 and 5 for the n_{Ga(s)} LPs. The NBO charges on Ga1 and Ga2 atom are 0.902 and 0.873. The two donor-acceptor interactions of n_{N2(sp^{1.6})}→n_{Ga2}^{*}(sp^{49.6}d^{0.7}), n_{N3(sp^{1.6})}→n_{Ga2}^{*}(sp^{49.6}d^{0.7}) form one three-center/two-electron bond 3c/2e (1), the interactions of n_{N2(sp^{1.6})}→n_{Ga2}^{*}(p), and n_{N3(sp^{1.6})}→n_{Ga2}^{*}(p) form another three-center/two-electron bond 3c/2e (2). The total Mayer order for N2-Ga2 and N3-Ga2 is 0.60 (each is 0.30). The n_{N1(sp^{1.9})}→n_{Ga1}^{*}(sp^{30.2}d^{0.7}) interaction indicates the donor-acceptor N1-Ga1 bond with the Mayer bond order of 0.52 (Fig.2).

For isomer 2 of [E-C₂H₂N₃-E]⁺, the distances N1-Al1 (N2-E2), N1-Ga1, N1-In1, and N1-Tl1 are 1.997, 2.146, 2.355, and 2.478 Å, respectively. NBOs 4 and 5 correspond to the n_{Ga(s)} LPs, NBO 6 for the n_{N(sp^{1.6})} LP, NBOs 7 and 8 for the non-Lewis N-Ga bonds of $\sigma_{N-Ga}=0.976(sp^{3.38})_N+0.217(sp^{34.3}d^{0.8})_Ga$. The natural ionicity parameter i_{N-Ga} could be defined as:

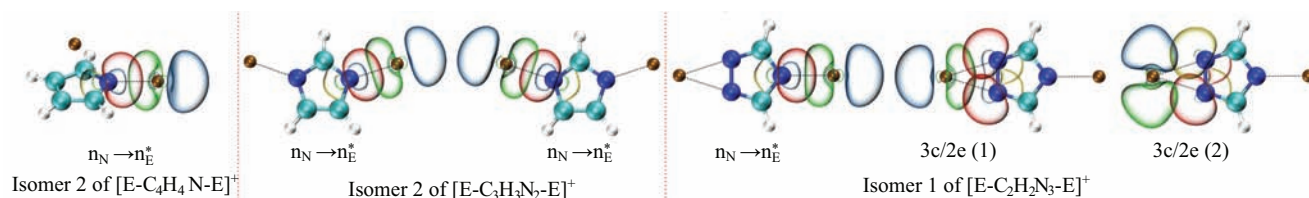
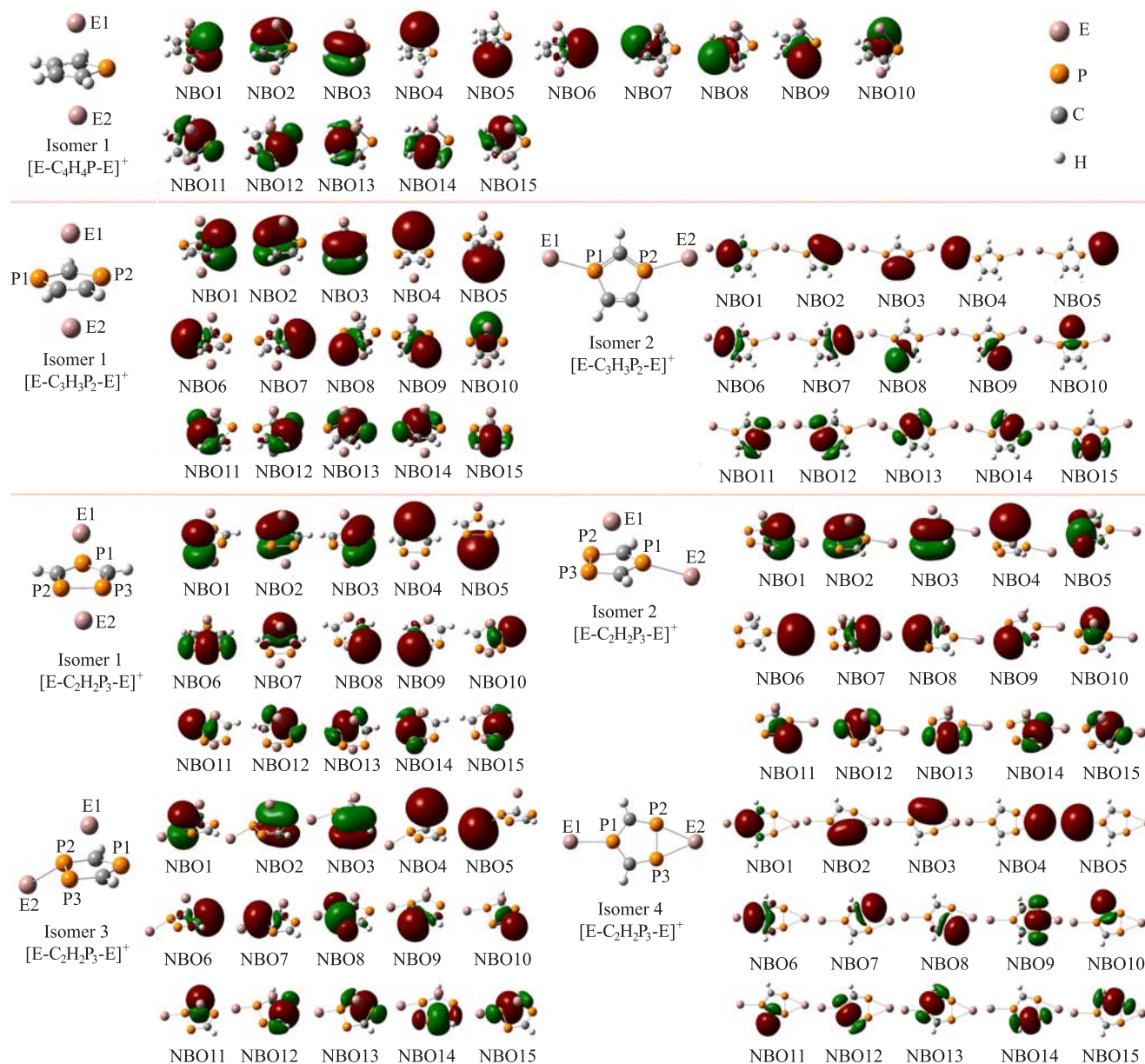
$$i_{N-Ga} = \frac{C_N^2 - C_{Ga}^2}{C_N^2 + C_{Ga}^2}$$

The value of i_{N-Ga} is 0 for a pure covalent bond, -1 and 1 are for a pure ionic bond. As the value for N1-Ga1 is 0.905, the bond is mainly ionic and strongly polarized toward N atom.

In addition, the (η^5, η^5) coordinated inverse sandwich [E-C_{5-n}H_{5-n}N_n-E]⁺ is unstable in energy compared with other isomers. C_{5-n}H_{5-n}N_n rings prefer to form direct N-E bonds with E elements. The high NBO charges on E atoms (Ga as an example) state the E-C_{5-n}H_{5-n}N_n interactions are mainly ionic.

B. Geometries and bonding of [E-C_{5-n}H_{5-n}P_n-E]⁺

[E-C₄H₄P-E]⁺ has only one inverse sandwich structure with the (η^5, η^5) coordination (Fig.3). The vertical distances Al-C₄H₄P, Ga-C₄H₄P, In-C₄H₄P, and

FIG. 2 Donor-acceptor bonds in $[E-C_{5-n}H_{5-n}N_n-E]^+$.FIG. 3 The structures and natural bond orbitals (NBOs) of $[E-C_{5-n}H_{5-n}P_n-E]^+$.

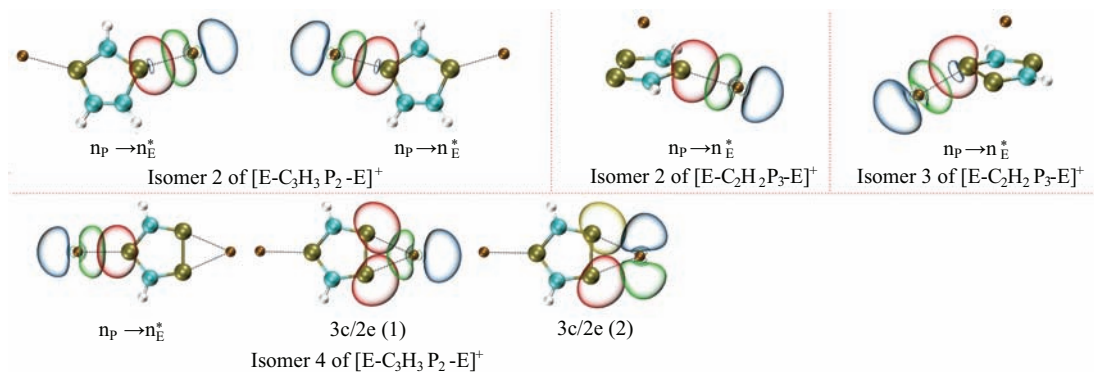


FIG. 4 Donor-acceptor bonds in $[E-C_{5-n}H_{5-n}P_n-E]^+$.

Tl–C₄H₄P are 2.301, 2.351, 2.596, and 2.672 Å, respectively. NBOs 1–3 correspond to the delocalized π_5^6 bond of C₄H₄P, NBOs 4 and 5 for the $n_{Ga}(s)$ LPs, NBO 6 for the $n_P(sp^{0.5})$ LP, NBOs 7–10 for the σ_{C-H} bonds and NBOs 11–15 for the σ_{C-C} and σ_{C-P} bonds. The NBO charge on Ga atom is 0.792, which is lower than 0.857 in $[Ga-C_4H_4N-Ga]^+$. The sum of the Mayer bond orders for Ga-(η^5 -C₄H₄P) interaction is 0.79, where the P-Ga contribution is 0.28 (35.4%). The NBO charges indicate the Ga-(η^5 -C₄H₄P) interaction is mainly ionic, but more covalent compared with the Ga-(η^5 -C₄H₄N) interaction.

$[E-C_3H_3P_2-E]^+$ has two isomers, isomer 1 is (η^5 , η^5) coordinated, isomer 2 is (η^1 , η^1) coordinated. Isomer 1 is more stable (15.8–26.8 kcal/mol) than isomer 2. For isomer 1, the vertical distances Al–C₃H₃P₂, Ga–C₃H₃P₂, In–C₃H₃P₂, and Tl–C₃H₃P₂ are 2.330, 2.380, 2.625, and 2.696 Å, respectively. NBOs 4 and 5 correspond to the $n_{Ga}(s)$ LPs, NBOs 6 and 7 for the $n_P(sp^{0.5})$ LP. The NBO charge on each Ga atom is 0.764. The sum of the Mayer bond orders for Ga-(η^5 -C₃H₃P₂) is 0.87, where the each Ga-P contribution is 0.25 (28.7%).

For isomer 2 of $[E-C_3H_3P_2-E]^+$, the distances P1–Al1 (P2–E2), P1–Ga1, P1–In1, and P1–Tl1 are 2.601, 2.626, 2.827, 2.884 Å, respectively. NBOs 4 and 5 correspond to the $n_{Ga}(s)$ LPs, NBOs 6 and 7 correspond to the $n_P(sp^{0.8})$ LPs. The NBO charge on Ga1 atom is 0.762. The two $n_P(sp^{0.8}) \rightarrow n_{Ga}^*(sp^{53.5}d^{0.7})$ interactions make known the two donor-acceptor P–Ga bonds with the Mayer bond order of 0.5 (Fig.4).

$[E-C_2H_2P_3-E]^+$ has four isomers, isomer 1 is (η^5 , η^5) coordinated, isomer 2 and isomer 3 are (η^5 , η^1) coordinated, isomer 4 is (η^2 , η^1) coordinated. Isomer 1 is the lowest energy structure, while isomer 4 is the highest. For isomer 1, the vertical distances Al–C₄H₄P, Ga–C₄H₄P, In–C₄H₄P, and Tl–C₄H₄P are 2.359, 2.400, 2.646, and 2.719 Å, respectively. NBOs 4 and 5 correspond to the $n_{Ga}(s)$ LPs, NBO 6 for the P–P bond ($0.707(sp^{7.2})_P + 0.707(sp^{7.2})_P$), NBO 7, 8 and 9 for the $n_P(sp^{0.5})$ for P1, $sp^{0.4}$ for P2 and P3) LPs.

The NBO charge on each Ga atom is 0.742. The sum of the Mayer bond orders for Ga-(η^5 -C₂H₂P₃) is 0.91, where P1–Ga contribution is 0.21 (23.1%), P2–Ga and P3–Ga contributions are both 0.22 (24.2%).

For isomer 2 of $[E-C_2H_2P_3-E]^+$, the vertical distances Al1–C₂H₂P₃, Ga1–C₂H₂P₃, In1–C₂H₂P₃, and Tl1–C₂H₂P₃ are 2.283, 2.336, 2.589, and 2.666 Å; the distances P1–Al2, P1–Ga2, P1–In2 and P1–Tl2 are 2.653, 2.741, 2.900, 2.953 Å, respectively. NBOs 4 and 6 correspond to the $n_{Ga}(s)$ LPs, NBO 5 for the P–P bond ($0.707(sp^{7.3})_P + 0.707(sp^{7.3})_P$), NBO 6, 7 and 8 for the $n_P(sp^{0.8})$ for P1, $sp^{0.4}$ for P2 and P3) LPs. The NBO charges on Ga1 and Ga2 atom are 0.618 and 0.830. The sum of the Mayer bond orders for Ga1-(η^5 -C₄H₄N) is 1.06, where the P1–Ga1, P2–Ga1, and P3–Ga1 contribution are 0.26 (24.5%), 0.27 (25.5%), and 0.27 (25.5%), respectively. The $n_{P1}(sp^{0.8}) \rightarrow n_{Ga2}^*(sp^{84.0}d^{1.2})$ interaction represents the donor-acceptor P1–Ga2 bond, of which the Mayer bond order is 0.40 (Fig.4).

For isomer 3 of $[E-C_2H_2P_3-E]^+$, the vertical distances Al1–C₂H₂P₃, Ga1–C₂H₂P₃, In1–C₂H₂P₃, Tl1–C₂H₂P₃ are 2.300, 2.337, 2.597 and 2.673 Å; the distances P2–Al2, P2–Ga2, P2–In2, and P2–Tl2 are 2.623, 2.695, 2.876, and 2.929 Å, respectively. NBOs 4 and 5 correspond to the $n_{Ga}(s)$ LPs, NBO 6, 7 and 9 for the $n_P(sp^{0.5})$ for P1, $sp^{0.4}$ for P2 and $sp^{0.6}$ for P3) LPs, NBO 8 for the P–P bond ($0.707(sp^{7.5}d^{0.1})_P + 0.707(sp^{7.5}d^{0.1})_P$). The NBO charges on Ga1 and Ga2 atom are 0.641 and 0.852. The sum of the Mayer bond orders for Ga1-(η^5 -C₄H₄N) is 1.09, where the P1–Ga1, P2–Ga1, and P3–Ga1 contribution are 0.13 (11.9%), 0.24 (22.0%), and 0.26 (23.9%), respectively. The $n_{P3}(sp^{0.6}) \rightarrow n_{Ga2}^*(sp^{37.3}d^{0.2})$ interaction represent the donor-acceptor P3–Ga2 bond with the Mayer bond order of 0.48 (Fig.4).

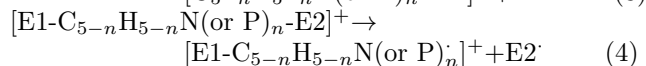
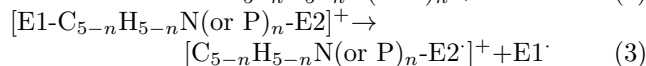
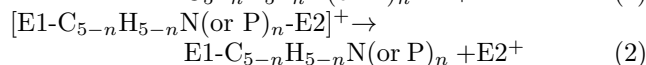
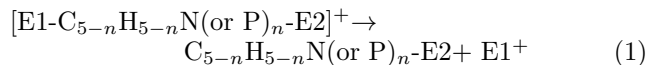
For isomer 4 of $[E-C_2H_2P_3-E]^+$, the distances P1–Al1, P1–Ga1, P1–In1, and P1–Tl1 are 2.662, 2.689, 2.883, and 2.980 Å, the distances P2–Al2 (P3–Al2), P2–Ga2 (P3–Ga2), P2–In2 (P3–In2), and P2–Tl2 (P3–Tl2) are 2.655, 2.686, 2.922, and 2.959 Å, respectively. NBOs 4 and 5 correspond

to the $n_{\text{Ga}}(\text{s})$ LPs, NBOs 6–8 for the $n_{\text{P}}(\text{sp}^{0.9})$ for P1, $\text{sp}^{0.6}$ for P2 and P3) LPs. The NBO charges on Ga1 and Ga2 atom are 0.782 and 0.758. The interactions of $n_{\text{P}2}(\text{sp}^{0.6}) \rightarrow n_{\text{Ga}2}^*(\text{sp}^{80.1}\text{d}^{0.3})$ and $n_{\text{P}3}(\text{sp}^{0.6}) \rightarrow n_{\text{Ga}2}^*(\text{sp}^{80.1}\text{d}^{0.3})$ form one $3\text{c}/2\text{e}(1)$ bond, $n_{\text{P}2}(\text{sp}^{0.6}) \rightarrow n_{\text{Ga}2}^*(\text{p})$, and $n_{\text{P}3}(\text{sp}^{0.6}) \rightarrow n_{\text{Ga}2}^*(\text{p})$ form another $3\text{c}/2\text{e}(2)$ bond (Fig.4). The total Mayer order for N1–Ga1 and N2–Ga1 is 0.84 (each 0.44). The $n_{\text{P}1}(\text{sp}^{0.8}) \rightarrow n_{\text{Ga}1}^*(\text{sp}^{84.0}\text{d}^{1.2})$ interaction represents the donor-acceptor N1–Ga1 bond with the bond order of 0.50.

The (η^5, η^5) coordinated inverse sandwich $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ is stable in energy than other isomers. Unlike direct N–E bonds in $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ which is favorable, $\text{C}_{5-n}\text{H}_{5-n}\text{P}_n$ binds with E elements by E– $(\eta^5\text{-C}_{5-n}\text{H}_{5-n}\text{P}_n)$ interactions. The NBO charges distributed on E atoms in $\text{C}_{5-n}\text{H}_{5-n}\text{P}_n$ are generally lower than those in $\text{C}_{5-n}\text{H}_{5-n}\text{N}_n$. Therefore, the $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ interactions are mainly ionic, but more covalent compared with $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ interactions. Since there are LPs of electrons on both E and P atoms, the inverse sandwich $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ would be multielectron-donors (Fig.5).

C. The dissociation stability of $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ and $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$

The first-step dissociation reactions of $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ or $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ respect to the loss of a neutral or charged E are represented as follows:



The dissociation energies for reactions (1)–(4) represent as ΔD_1 , ΔD_2 , ΔD_3 , and ΔD_4 are listed in Table II. Similar to $[\text{E-Cp-E}]^+$, $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}(\text{or P})_n\text{-E}]^+$ dissociates via loss of the charged E^+ .

For the (η^5, η^5) coordinated $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}(\text{or P})_n\text{-E}]^+$, the structures dissociate via dividing into the charged E^+ cation and the half-sandwich E– $(\eta^5\text{-C}_{5-n}\text{H}_{5-n}\text{N}(\text{or P})_n)$. The ΔD_1 (or ΔD_2) values for isomer 1 of $[\text{E-C}_4\text{H}_4\text{N-E}]^+$, $[\text{E-C}_3\text{H}_3\text{N}_2\text{-E}]^+$, $[\text{E-C}_4\text{H}_4\text{P-E}]^+$, $[\text{E-C}_3\text{H}_3\text{P}_2\text{-E}]^+$, and $[\text{E-C}_2\text{H}_2\text{P}_3\text{-E}]^+$ are 37.8–41.1, 32.1–34.1, 39.0–43.3, 36.1–41.1, and 33.4–38.3 kcal/mol. The dissociation energies of the inverse sandwich $[\text{E-C}_4\text{H}_4\text{P-E}]^+$ are very close to those of $[\text{E-C}_5\text{H}_5\text{-E}]^+$ [10, 11]. As the number of N or P increases, the dissociation stability of the (η^5, η^5) coordinated $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}(\text{or P})_n\text{-E}]^+$ decreases. The dissociation energies of $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}(\text{or P})_n\text{-E}]^+$ with different E are close to each other, while $[\text{Ga-}$

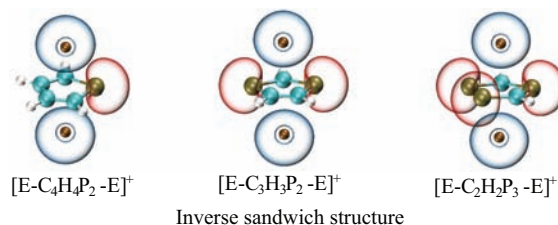


FIG. 5 The orbitals of Ga LPs (in blue) and E LPs (in red) in $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$.

$\text{C}_{5-n}\text{H}_{5-n}\text{N}(\text{or P})_n\text{-Ga}]^+$ is the most stable one among them. The (η^5, η^5) coordinated $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ is relatively stable both in energy and dissociation reaction, meanwhile, the (η^5, η^5) coordinated $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ is just the other way round.

For the (η^5, η^1) coordinated structures, the dissociation energies ΔD_2 are lower than ΔD_1 . The isomer 2 of $[\text{E-C}_4\text{H}_4\text{N-E}]^+$, isomer 2 of $[\text{E-C}_2\text{H}_2\text{P}_3\text{-E}]^+$ and isomer 3 of $[\text{E-C}_2\text{H}_2\text{P}_3\text{-E}]^+$ dissociate via dividing into the charged E^+ cation and the half-sandwich E– $(\eta^5\text{-C}_{5-n}\text{H}_{5-n}\text{N}(\text{or P})_n)$.

The (η^2, η^1) and (η^1, η^1) coordinated structures include at least two N–E (or P–E) bonds. The former dissociates into the E– $(\eta^2\text{-C}_{5-n}\text{H}_{5-n}\text{N}(\text{or P})_n)$ and E^+ cation, the latter dissociates into the E– $(\eta^1\text{-C}_{5-n}\text{H}_{5-n}\text{N}(\text{or P})_n)$ and E^+ cation. The dissociation energies indicate stronger N–E interaction than P–E.

III. CONCLUSION

In this work, inverse sandwiches $[\text{E-C}_{5-n}\text{H}_{5-n}\text{N}_n\text{-E}]^+$ and $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ ($n=1, 2, 3$; $\text{E}=\text{Al}, \text{Ga}, \text{In}, \text{Tl}$) with low-valent boron group elements are theoretically studied. The (η^5, η^5) coordinated inverse sandwiches $[\text{E-C}_4\text{H}_4\text{N-E}]^+$ and $[\text{E-C}_3\text{H}_3\text{N}_2\text{-E}]^+$ are unstable in energy, the (η^5, η^5) coordinated $[\text{E-C}_2\text{H}_2\text{N}_3\text{-E}]^+$ could not be obtained during the optimization. However, the (η^5, η^5) coordinated inverse sandwiches $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ are not only stable in energy, but also stable against dissociation. Similar to the well-known $[\text{E-Cp-E}]^+$, the (η^5, η^5) coordinated $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ dissociates via the division of the half-sandwich E– $(\eta^5\text{-C}_{5-n}\text{H}_{5-n}\text{P}_n)$ and the charged E^+ cation. For the (η^5, η^5) coordinated structures with the same E element, the dissociation stability of $[\text{E-C}_{5-n}\text{H}_{5-n}\text{P}_n\text{-E}]^+$ decreases as the number n increases; for the structures with the certain n number, the dissociation energies with different E are close to each other, while $[\text{Ga-C}_{5-n}\text{H}_{5-n}\text{P-Ga}]^+$ is generally the most stable one among them. The dissociation energies of the (η^5, η^5) coordinated $[\text{E-C}_4\text{H}_4\text{P-E}]^+$ are very close to those of $[\text{E-C}_5\text{H}_5\text{-E}]^+$, thus, the former might exist like the latter. The high NBO charges on E atoms indicate the E– $\text{C}_{5-n}\text{H}_{5-n}\text{N}_n$ and E– $\text{C}_{5-n}\text{H}_{5-n}\text{P}_n$ interactions are

mainly ionic, but the former is more covalent than the latter. For the relatively stable (η^5 , η^5) coordinated $[E-C_{5-n}H_{5-n}P_n-E]^+$, since both E and P atoms possess lone pairs of electrons, the inverse sandwiches would be potential multielectron-donors for further application.

IV. ACKNOWLEDGMENTS

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