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Theoretical Study for Stabilizing Group 14 Elements by Five Different Carbene Ligands as L-E-E-L Complexes

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ABSTRACT: *Background: The computational calculations have been employed as a great tool to understand the stabilization of main group species by carbene ligands, which have been recognized as excellent compounds for coordinating highly reactive main-group elements in their zero oxidation state.* ***Objective:*** *The most important results that have been published up to now shown that N-Heterocyclic carbene and Cyclic (Alkyl)(Amino)Carbene ligands can stabilize main group compounds as highly stable complexes.* ***Methods:*** *That led us to further theoretically investigate the possibility of expanding this feature with phosphorus carbenes which have more electron contributing ability.* ***Results:*** *The bonding condition of the E2L2 molecules (where E is group 14 main group elements and L is Carbene ligands) may be understood in depth due to the combination of two ligands with two groups of 14 elements. The combination provides a guideline for synthesizing molecules with novel bonding motifs. Two atoms of group 14 are stabilized by two donor ligands in this bonding picture. In contrast to the E=E bonds seen in nitrogen carbene complexes, all phosphorus carbene complexes exhibit the E=L double bond character notation L=EE=L. L acts as a strong donor ligand in this complex.* ***Conclusions:*** *the thermodynamic calculations and orbital analysis can predict that complexes of L=E−E=L are stable enough to become isolated in a condensed phase for all compounds.*

KEYWORDS: *Main group compounds; Phosphorus carbenes; Bonding motifs; Electron donation; Theoretical Study*

INTRODUCTION

Following the synthesis of commercial cyclic diaminocarbenes (NHCs) by Arduengo *et. al* [1] in 1991, the chemistry of heterocyclic carbene has extensive research in both experimental and theoretical studies. Most of these studies are concentered on application areas such as in main group element chemistry [2], and transition-metal chemistry [3] as well as catalysis [4] with several modification in the scaffold of this molecule. As we know, the key aspect of the unusual properties of NHCs is mainly due to that the nature of nitrogen atoms in α-position centers are perfectly planar which increases the π-donor ability to carbene center. Additionally, it has previously been observed that the steric impact of an attached group to these nitrogen atoms can strongly effect on σ-donating ability of this carbene [5]. Therefore, to induce electron donating capability, extensive researches are focused on changing the substitutes on the nitrogen atoms or the carbon backbone atoms. However, other studies have indicated that modification of the NHC skeleton itself can play a significant role to improve its properties. Accordingly, recently investigators have examined the effects of the replacement of one or two nitrogen atoms by other various low electronegativity elements [6]. There is evidence that the replacement of nitrogen atoms with their heavier analogues, namely, phosphorus has low electronegativity and a strong π-donor ability [6]. In 2005, the first example of phosphorus carbenes was prepared by Bertrand and co-workers who indicate that the suitable design of cyclic diphoapninocarbenes PHCs might act as a strong σ-donor [7]. It has been noticed that the environment around phosphorus canters is strongly pyramidalized, therefore the lone pair

of phosphorus does not seem to interact with the vacant orbital on the carbene. Consecutively, they recognized that the use of bulky substituents at phosphorus atoms might be a suitable technique to circumvent pyramidal configuration (Figure 1A). Frey *et. al.* (2008) performed a similar study but by changing one nitrogen atom with phosphorus to prepare acyclic (amino)(phosphino) carbenes (Figure 1B) [8]. It is shown that the preparation of unsaturated five-membered N-PHCs might be an excellent option to achieve a different coordination mode since the nitrogen atom can act as a π-donor and the phosphorus act as a spectator substituent and that means the lone pair of phosphorus probably remains active. As a further consequence, this study found that this carbene should be equally stable, and significantly behave as a strong σ-donor than NHC since phosphorus is more electropositive than nitrogen. In the same vein, Bertrand (2005) [9] also prepared alkyl amino carbenes (cAACs) by replacing one nitrogen atom with high σ-donor alkyl group, which revealed enhanced electron donating ability. Another major theoretical study has probed the impact of replacement nitrogen atom by oxy, silyl, phosphino and thio groups in CAAC carbene to examine the reactivity of these species in term of nucleophilicity and electrophilicity [10]. This study indicates that amino and phosphino alkyl carbenes (Figure 1C) appear more nucleophilic and less electrophilic than oxy- and thio alkyl carbenes, respectively.
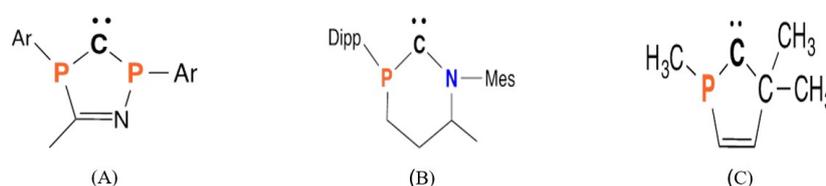

Figure 1. The known phosphorus carbenes experimentally and theoretically:(A) Bertrand *et. al.* (2005); (B) Frey *et. al.* (2008); (C) Kassaee *et. al.* (2010) .

Despite these studies are provided interesting information about NHC analogues in both preparation area and highlighting some information about their properties, the application scope of most of these carbenes is still limited. Up to now, only PHC are successfully used as a ligand with transition-metal (rhodium and zirconium) to prepare their stable complexes with a high percentage yield and no significant decomposition was observed [11], [12]. For the main group area, only NHCs and cAAC successfully demonstrated unique capabilities in the synthesis and theoretical assessment as attractive ligands in stabilizing high reactive, low-oxidation-state elements [11]–[13]. There is a growing body of literature that recognizes the importance of σ-donating carbenes into a vacant σ-accepting orbital in stabilizing diatomic "allotropes" of p-block fragments in low oxidation states which introduced a special bonding environment for these compounds [14]. Moreover, there are several types of research have investigated that the molecule preparations at a low-oxidation state not only exhibit structural novelty but also provide a unique platform from which novel main-group molecules may be further accessed [15]. Many recent studies (e.g. Robinson 2008; Jones 2009) have shown that the devoting of NHCs as ligand could be a powerful tool for stabilizing group14 elements E= (Si, Ge, and Sn) by creating L-E-E-L complexes (Figure 2) which indicate that all these complexes do not have planer arrangement and electronic structures can describe as dative bond more than electron-sharing double bonds [14]–[16].
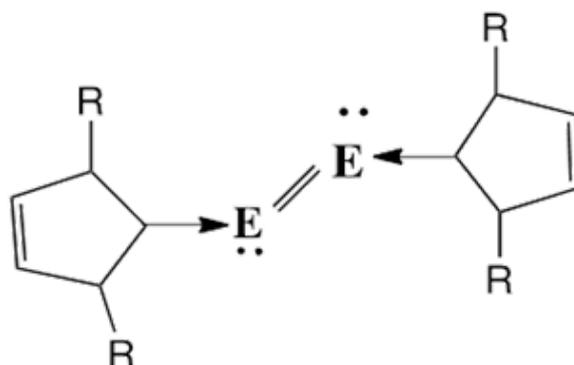

Figure 2. the structure of group 14 complexes $E_2(NHC)_2$.

Dutton and co-worked also reported that carbenes ligands such as NHC and cAAC are particularly suitable to stabilize diatomic molecules C2 [17]. In addition, Wilson *et. al* theoretical research has shown that carbene ligands are employed in E_2L_2 systems with L = ligand and E = group 14 (Si, C, Sn, Pb, and Ge) or group 15 (As, P, Bi, and Sb), which provides highly interesting information. This information includes the geometries of the bonds, the nature of the bonds, and the thermodynamic stability of the system [18]. According to their research findings, the geometry of two NHC ligands containing group 14 elements might observe a trans-bent arrangement alongside E=E double bonds, except for C, which has a linear shape. On the other hand, group 15 had a gauche arrangement with EE single bonds in the structures with the lowest potential energy. Additionally, the bonding environment for these compounds could be explained as a donor-acceptor coordination nature with diatomic moiety E2 (L →EE ← L). Collectively, several systematic reviews are shown that the strong coordination ability of NHC has allowed to synthesis of highly stable L-E-E-L complexes[19]. The present theoretical research explores, for the first time, the effects of using analogue carbenes to NHC and cAAC ligands for stabilizing diatomic of p-block elements in low oxidation states. This research also sheds new light on the properties of L-E-E-L complexes to investigate if there is a unique oddity that could possible to recommend these molecules as attractive extending in the synthesis area [20].

MATERIALS AND METHODS

Computational chemistry calculations allow us to model molecule formations by using electronic structure theory and optimizing geometries [21], [22]. The law of quantum mechanics is firmly embedded in electronic structure approach calculations. By supplying accurate molecular characteristics, stable configuration, and thermochemical data, electronic structure approaches may forecast molecular systems. These approaches also enable us to investigate gas-phase molecular systems, which are sometimes challenging to perform and assess experimentally. As a result, the geometries M06-2X/def2-TZVP and B3LYP/def2-TZVP were optimized [23]. The research was conducted in a single initial state for ligands, all group 14 diatomics, and L-E-E-L compounds. The Gibbs free energy of every structure was determined by combining the electronic energies at a single point with the thermal corrections of the best-fit geometries using the single-point MP2/def2 TZVP method. The reaction Gibbs free energies were computed at 25 °C using the equation below to investigate the thermodynamic stabilities of stabilized L-E-L compounds.

$$2L + E_2 \rightarrow L - E - E - L \tag{1}$$

Furthermore, solvent effects were included with polarizable scale classic (PCM) self-consistent reaction field (SCRF) collected with Truhlar's SMD solvation model [24] with parameters for acetonitrile. Natural bonding orbital (NBO) and molecular orbital (MO) studies were performed at the B3LYP/def2-TZVP theoretical level. All these theoretical revisions were performed by using Gaussian 09 [25], and Gaussian 16 [26].

RESULTS AND DISCUSSION

Optimized Geometries

Neutral two-electron phosphorus ligands (PHC^{Me}, PNHC^{Me}, and cPAC^{Me}) were employed to stabilize E2 molecules in L-E-L complexes with group 14. They were compared to and contrasted with NHC^{Me} and cAAC^{Me}. The optimized structures of ligands with HOMO-LUMO gaps at the B3LYP/def2-TZVP level of theory are illustrated in Figure 3. To enable ready comparisons, these carbene ligands have five membered rings, and an unsaturated backbone with methyl group as substituent on P and N atoms. All ligand structures are minimal with no extreme disparity. The NHC^{Me} and cAAC^{Me} achieve a fully planar configuration whereas PHC^{Me}, PNHC^{Me}, and cPAC^{Me} are recognized to be slightly non-planar with trans-methyl groups. The Wiberg bond index, on the other hand, is a total of bond orders between two orbitals. Each bond order in this equation indicates the difference between two times the electronic density and its square structure [27].
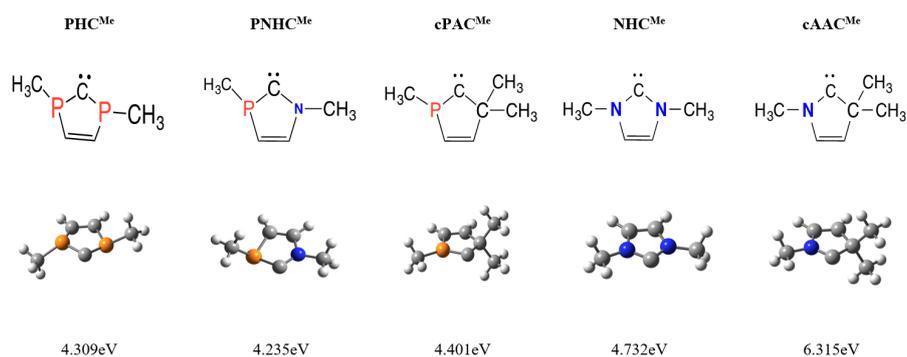
Figure 3. B3LYP/def2-TZVP optimized geometries of neutral two-electron ligands with HOMO-LUMO gap and chemical structures

As can be seen from Figure 3 the PHC^{Me}, PNHC^{Me}, cPAC^{Me} and cAAC^{Me} ligands are more active compared to NHC^{Me} because they have small HOMO-LUMO gaps. According to molecular orbital analysis, because of the existence of lone pairs on the carbon atom, all of these carbenes have similar donor capacities. For each element, each ligand produced a distinct shape of the L-E-E-L complex.

Figure 4 provides an overview of minimum optimized geometries at the B3LYP/def2-TZVP level of theory in the gas phase of L-E-E-L compounds for PHC^{Me}, PNHC^{Me}, cPAC^{Me}, NHC^{Me}, and cAAC^{Me} and E=C, Si, Ge, Sn, and Pb with selected geometry parameters presented in Table 1. Our optimized geometries provide findings that agree well with those of these earlier theoretical investigations of NHC^{Me} and cAAC^{Me} ligands [1], [3]. Following the optimization of the PHC^{Me}, PNHC^{Me}, and cPAC^{Me} ligands with E2 fragments, significant planer structure were observed in the ligands ring and also the bond distance for P-Carbon carbene at the phosphors carbenes increased around (0.2 Å). The linear C=C=C=C geometry was detected at the minimal energy structures of the L-C-C-L system, which makes the carbon complexes in this table extremely interesting. All of the ligands are compatible with a cumulene-type structure, another reason this geometry was found. Most ligands in the heavier group 14 systems are shown with a trans-bent geometry compared to the linear geometry in C. This is due to the linear nature of C's geometry.
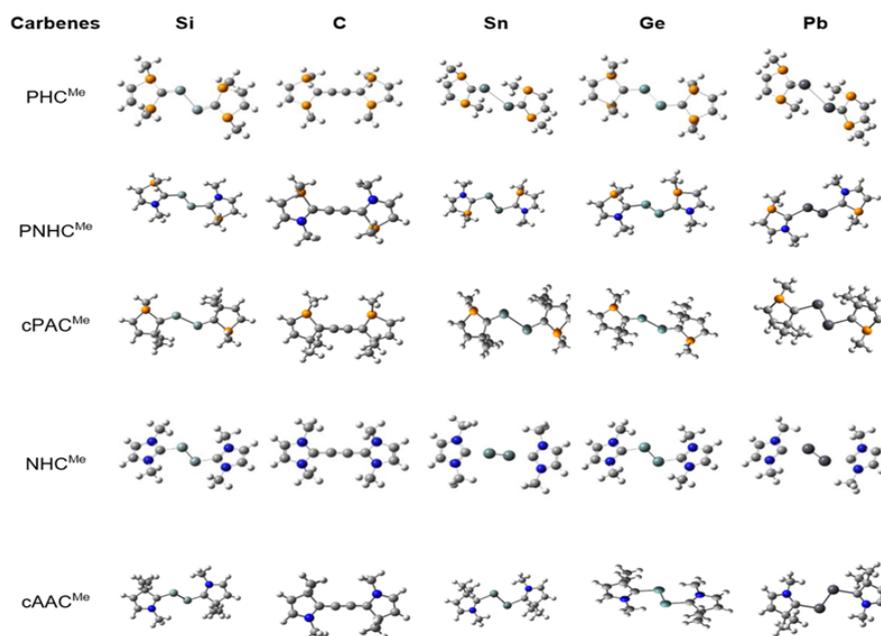

Figure 4. Group 14 L-E-E-L compounds optimized molecular geometries using B3LYP/def2-TZVP

Table 1. Group-14 L-E-E-L compounds optimized geometries with specified L-E-E angles (°), L-E-E-L dihedral angles (°), and bond distances (Å).

| Compound | E | bonding distance | | Angle | Dihedral | Wiberg Bond Index | |
		E-E	E-L	L-EE	L-EE-L	E-E	E-L
C_PHC^{Me}	C	1.262	1.321	179.8	0	2.01	1.72
C-PNHC^{Me}	C	1.255	1.333	176.6	160	2.12	1.59
C_cPAC^{Me}	C	1.264	1.318	178.5	29	2.02	1.74
C_cAAC^{Me}	C	1.259	1.329	177.3	180	2.11	1.61
C_NHC^{Me}	C	1.262	1.337	172.8	180	2.11	1.53
Si_PHC^{Me}	Si	2.348	1.761	109.3	179	1.12	1.29
Si_PNHC^{Me}	Si	2.279	1.847	104.1	178	1.41	1.10
Si_cPAC^{Me}	Si	2.314	1.728	128.9	180	1.45	1.49
Si_cAAC^{Me}	Si	2.263	1.871	101.4	180	1.49	1.07
Si_NHC^{Me}	Si	2.245	1.939	93.6	179	1.75	0.84
Ge_PHC^{Me}	Ge	2.473	1.840	119.3	180	1.15	1.37
Ge_PNHC^{Me}	Ge	2.448	1.971	102.0	169	1.21	1.03
Ge_cPAC^{Me}	Ge	2.461	1.831	122.8	180	1.19	1.46
Ge_cAAC^{Me}	Ge	2.409	1.989	96.9	180	1.41	1.01
Ge_NHC^{Me}	Ge	2.390	2.063	90.9	180	1.74	0.79
Sn_PHC^{Me}	Sn	2.962	2.087	113.1	55	0.82	1.12
Sn-PNHC^{Me}	Sn	2.818	2.211	87.4	180	1.34	0.96
Sn_cPAC^{Me}	Sn	2.904	2.090	107.3	180	0.87	1.18
Sn_cAAC^{Me}	Sn	2.787	2.241	91.9	180	1.45	0.15
Sn_NHC^{Me}	Sn	2.768	2.319	88.2	180	1.77	0.66
Pb_PHC^{Me}	Pb	3.099	2.203	112.6	45	0.74	1.03
Pb_PNHC^{Me}	Pb	2.961	2.348	88.3	180	1.33	0.77
Pb_cPAC^{Me}	Pb	3.077	2.202	102.3	180	0.73	1.12
Pb_cAAC^{Me}	Pb	2.927	2.374	89.5	180	1.47	0.75
Pb_NHC^{Me}	Pb	2.908	2.460	87.1	180	1.79	0.59

The E-E bond distance might be contrasted to the single-bond covalent Pyykko and Atsumi radii [4], Ge-Ge 2.42, Si-Si 2.32, Pb-Pb 2.88, and SnSn 2.80 angstroms. These values are found in Table 1 for the heavier group 14 systems. According to Wilson *et. al.* findings, the E-E bond distance in PNHC^{Me}, PHC^{Me}, and CPAC^{Me}, which are all stable L-E-E-L complexes of group 14, is longer than in NHC^{Me} and cAAC^{Me}. This was found by examining the cases of PHC^{Me}, PNHC^{Me}, and CPAC^{Me}. The values of L-E-E angles and dihedral are reflected in the trans-bent geometers for these complexes which increase steadily from Si to Pb with all complexes and these values is likely to increase according to these sequences (NHC^{Me}<cAAC^{Me}<PNHC^{Me}< PHC^{Me} < cPAC^{Me}). For all Si complexes, the bond distances of Si-Si are shorter than the single bond covalent radii excepting Si_PHC^{Me} which is reported 2.348 Å, and marginally to this in solid silicons (2.35 Å) [4] and slightly more than 2.2294 Å which reported by Robinson and co-worker [20]. Ge and Sn, complexes have longer bond distances E-E than the single bond covalent radii with L = PHC^{Me}, PNHC^{Me}, and cPAC^{Me}, however, it is shorter with NHC^{Me}, and cAAC^{Me} complexes. The values of Ge-Ge for PHC^{Me}, PNHC^{Me} and cPAC^{Me} complexes are marginally longer than that reported experimentally distances in all Sn complexes are longer than the 2.80 Å gray tin allotrope[7], Considering the spectrum of LSn=SnL complexes studied by Power and colleagues (2.782−2.824 Å)[8], excluding Sn_NHC^{Me} complex which slightly shorter than these values. Compared to the trans-bent-oriented L−Pb−Pb−L complex of Fischer and Power and the 2.8697 experimental results with the (Bp)3Pb−Pb(Bp)3 complex, the Pb-Pb bond distances for all complexes are longer [10]. The WBI values support the result of all NHC^{Me} complexes which is indicated that the bond orders of E−E bonds are significantly larger than the other carbene complexes. For NHC^{Me} and cAAC^{Me} complexes with non-Carbon group 14 systems (Si to Pb), the values of the E-E bond are changed from 1.75 (Si_NHC^{Me}) to 1.79(Pb_NHC^{Me}), and 1.49 (Si_ cAAC^{Me}) to 1.47(Pb_cAAC^{Me}) that can consistent with the double bond character. The values

of the E-E bond with other carbenes have revealed different results which is suggested a single bond character relatively double bond characters. The propensity of compounds in the heavier group 14 with multiple electrons to choose single-bonded structures when the electrons that usually contribute to double bonds take on a nonbonding character might explain this observation. The distance values of E-L bonds for all ligands are consistent with the general trend of heavier elements which decrease considerably from Si to Pb. For Si_PHC^{Me}, Si_ cPAC^{Me}, Ge_ PHC^{Me}, and Ge_ cPAC^{Me}, multiple E−L bonds bond characters and confirm WBI from (1.29, 1.49, 137, and 1.46) respectively, which is established in the optimized parameters. This analysis assumes that the (L-E-E-L) complexes have the double bond character for E-E bonds with all complexes and the E-L bond with PHC^{Me}, and cPAC^{Me} ligands has a double bond character, but with PNHC^{Me}, cAAC^{Me} and, NHC^{Me} ligands has single bond character[28].

Thermodynamic Parameter Calculations for the Complexes Stability

The thermodynamic analysis predicted the L-E-E-L stability complexes by estimating Gibbes free energy for the E2 + 2L → L-E-E-L formation reaction [28]. The data of our calculation decrease steadily from MP2 to SCS-MP2 and from the gas phase to solvent with all complexes of L-E-E-L. In the following discussion, we considered the result of ΔG with SCS-MP2 in both gas phase and acetonitrile solvent [29]. It can be seen from the data in Table 2 that the values of ΔG are negative for all L-E-EL complexes which suggests that these entities are stable concerning to dissociation. What is interesting about the data in this table is that the ΔG values for all phosphorus carbenes are significantly more negative than NHC^{Me} and cAAC^{Me} Carbenes. This table reveals also that ΔG values are strongly negative for C2 systems (PHC, -977.08, CPAC, -1119.44 and PNHC -,1416.16 kJ/mol) and gradually become less negative down the group with Pb (PHC, -281.8 kJ/mol), (CPAC, -409.6 kJ/mol) and (PNHC, -277.32 kJ/mol). A closer inspection of the table shows that there is the substantial jump between L-Si-Si-L and L-C-C-L with all carbenes. A possible explanation for these results may be due to the ability of dicarbon be present in cumulene-like structures which reflects numerous thermodynamic stability into C2 species with prospective to dissociation. For group 14, the complexes of L=PNHC^{Me} and PHC^{Me} were typically superior, more stable thermodynamically compared to L= NHC^{Me}, and the results are indicated that there is a systematic decline change from Si (-459.2, -507.8 kJ/mol) to Pb (-277.3, -281.8kJ/mol) with L=PNHC^{Me} and PHC^{Me} respectively while in case L= NHC^{Me} the values of ΔG range from Si (-368.9 kJ/mol) to Pb (-227.8 kJ/mol). Moreover, comparing the CPAC^{Me} with CAAC^{Me} to stabilize group 14, it can be seen that the CPAC^{Me} complexes have greater stability than CAAC^{Me} in all cases, and the ΔG values have a similar trend which decreases from Si to Pb with CPAC^{Me} (-659.2 to-409.6 kJ/mol) and also with CAAC^{Me} (-453.7 to -270.5 kJ/mol).

Table 2. Free Energies (25°C) for E2+2L→L-E-E-L reaction to calculate SCS-MP2/def2-TZVP//B3LYP/def2-TZVP at acetonitrile solvent

E	NHC^{Me}	PNHC^{Me}	PHC^{Me}	CAAC^{Me}	CPAC^{Me}
C	-1119	-612	-1416	-972	-874
Si	-369	-459	-508	-454	-659
Ge	-331	-429	-424	-397	-581
Sn	-257	-349	-320	-306	-455
Pb	-228	-277	-282	-271	-410

Electronic Structure and Orbital Analysis

The most well-known tools for assessing the L-E-E-L stabilities [30] are molecular orbital (MOs) and natural bond analysis (NBOs) which are employed here to explain the variations in the molecular geometries and reactivity for all complexes. For NHC^{Me} It has been shown that the fundamental variable in the geometry of the group 14 system is related to the acceptor orbitals orientation of the L-E-E precursor1. This study indicates that the L-E-E-L complexes with group 14 have trans bent. The results obtained from MOs analysis observed that the NHC^{Me} and CAAC^{Me} complexes have a quite different pictures compared to PHC^{Me}, PNHC^{Me}, and cPAC^{Me} complexes. The same pattern was observed for NHC^{Me} and CAAC^{Me} complexes, whereas, PHC^{Me}, PNHC^{Me} and cPAC^{Me} complexes have a different configuration. To compare complexes for group 14, Figures 5, 6 and 7 show plots of

frontier molecular orbitals for NHC^Me complexes with PNHC^Me and PHC^Me. The bonding image for all L-EE-L systems is distinct from the rest of the compounds. In this system, no ligand was found to include a lone pair on any of the core carbon atoms. The core carbon atoms (E-E) and the ligand ring carbons (E-L/E-C) may be identified as bonds, producing a whole linear cumulene-like arrangement. The E-L bonds may be found in the HOMO structure, whereas the E-E bonds can be found in the HOMO-1 structure.
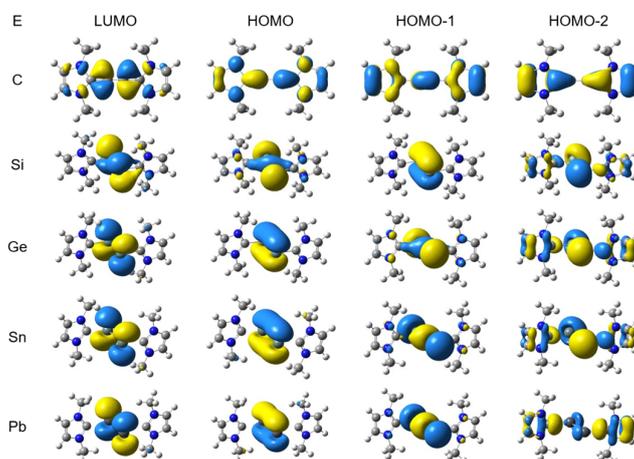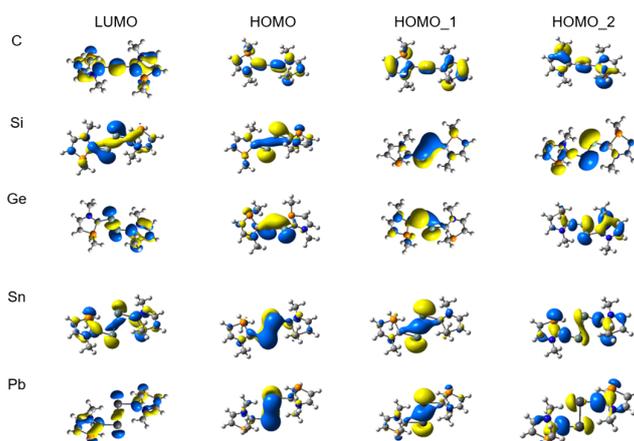

Figure 5. Limit MOs of E_NHC^Me
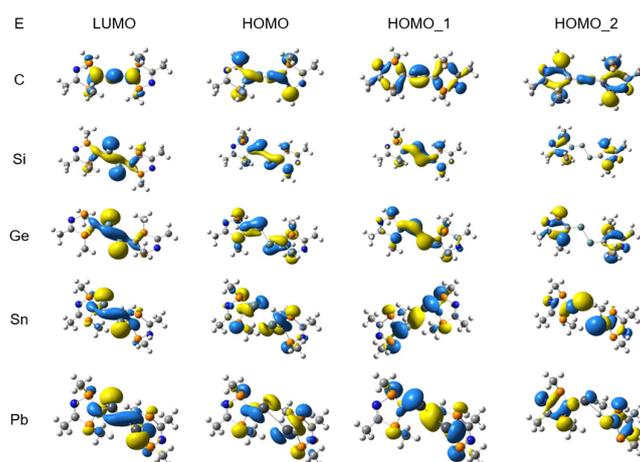

Figure 6. Limit MOs of E_PNHC^Me

Figure 7. Limit MOs of E_PHC^{Me}

The Si Me2NHC frontier orbitals feature HOMO-1 and HOMO-accepting bonds, as well as bonds between the central disilicon atoms (Si-Si). In contrast, the Ge, Sn, and Pb counterparts present HOMO and HOMO-1 accepting bonds, as well as bonds between the central disilicon atoms (Si-Si). The MO structure is inverted because the HOMO can accommodate the E-E bond, whereas HOMO-1 cannot. All non-carbon groups, 14 systems with L = NHC, have HOMO-2 additions of central atoms lone pairs excluding Pb NHC.

The bonding picture in the PNHC^{Me} complexe is similar to the NHC^{Me} complexes with several conversions. For Si-PNHC^{Me} the calculation shows that the HOMO and HOMO-1 are tolerating bonds and bonds between central disilicon atoms (Si-Si), and the lone HOMO-2 pairs residing. The LUMO for Si-PNHC^{Me} is centered on the Si—Si fragment as a π^* orbital. The Ge-PNHC^{Me} complex has quite a different division, the HOMO and HOMO-1 hold the p-type lone pair contributions of Ge-Ge π bond and the central atoms Ge-Ge , with expansion into the ligand rings. The HOMO-2 is taken by the p-type lone pair of central atoms and the same result for the LUMO orbital holds Si Ge-Ge π^*. The Sn and Pb complexes have the same picture as the NHC^{Me} Sn and Pb complexes, the π bond and σ bond are held in the HOMO and HOMO-1 respectively, lone pairs in HOMO-2 and π^* orbital assets LUMO.

The electronic density structures and orbital analysis for CAAC^{Me} and CPAC^{Me} complexes are given in Figures 8 and 9.
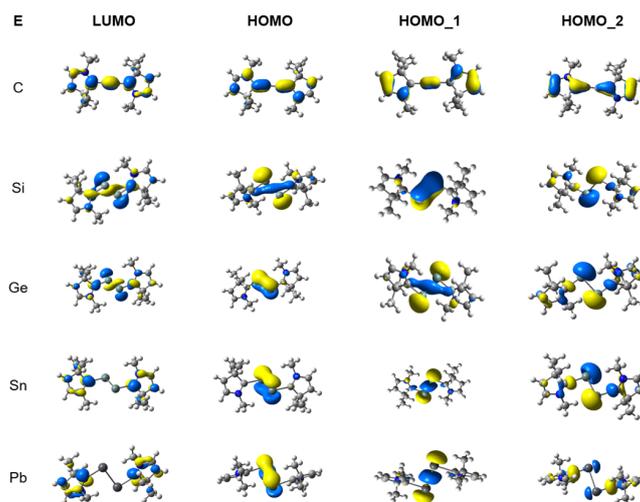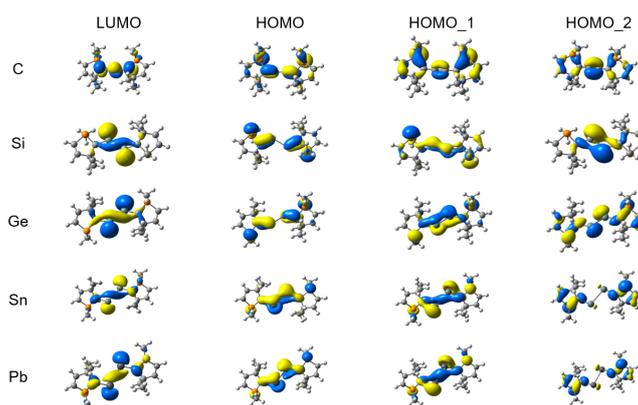

Figure 8. Limit MOs for E_cAAC^{Me}

Figure 9. Limit MOs for E_CPAC^{Me} (E = C, Si, Ge, Sn, Pb)

The bonding picture in the Si-CAAC^{Me} is quite different compared to the Si-CPAC^{Me} complex. For Si-CAAC^{Me} the calculation indicates that the HOMO and HOMO-1 are tolerating bonds and bonds between central disilicon atoms (Si-Si), and the lone pairs residing in the HOMO-2, which is consistent with Robinson and Wilson studies [1], [5]. For Si-CPAC^{Me}, the HOMO is occupied by the C-Si π bond, HOMO-1 is dominated.

by Si-Si π bond character with delocalization onto the ligand rings. As interactions, a p-type lone pair of core atoms (Si-Si) and carbon from the ligand ring occupy the HOMO-2. However, in Si-CAAC^{Me}, the LUMO is delocalized onto the ring of the CAAC^{Me} ligand. Still, in Si-CPAC^{Me}, it is concentrated on the Si Si fragment as a π* orbital.

The frontier orbitals and neural bond analysis of Ge complexes have the same result of Si analogue, For Ge-CPAC^{Me}, the HOMO holds the C-Ge π bond, HOMO-1 holds Ge-Ge π bond with expansion into the ligand rings. The p-type lone pair of central atoms, Ge-Ge, contributes to the HOMO-2. The LUMO of Si-CPAC^{Me} is localized on the Si Si fragment as a π* orbital, but in Ge-CPAC^{Me}, it is delocalized onto the ring of the CPAC^{Me} ligand. The bonding pictures for Sn and Pb complexes with CAAC^{Me} are very similar to Si and Ge complexes, but for the Sn and Pb complexes with CPAC^{Me} the analysis of the MOs suggests that the HOMO accommodates the E$-$Eπ bond and π interactions with the ligand ring. Single central atomic pairs and ligand ring carbon hold the HOMO-1 together, but no central atomic atoms have any electronic impact on the HOMO-2.
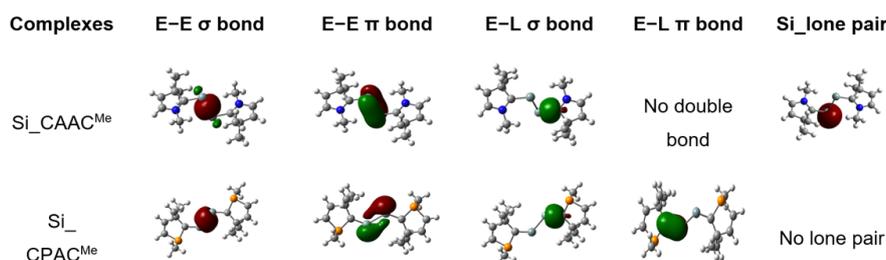

Figure 10. The NBO orbitals for Si_ CAAC^{Me} and Si_ CPAC^{Me}

To understand the bonding structure of our complexes, we employed Neural Bond Analysis (NBO) analysis [31] (percent s, p, d NBOs character and bond polarization, as a chief comparison is drawn for isolable Si-CAAC^{Me} and Si-CPAC^{Me}. From Figure 10 we can see that the electron distribution of Si-CAAC^{Me} has enormous differences compare with Si-CPAC^{Me}. For Si-CAAC^{Me} the Si-Si σ has 14.68% s, 84.37% p, and 0.92% d characters; the π bond has 0.2% s, 99.11% p, and 0.85 % d characters and the Si lone pair orbital has 71.76% s, 28.09% p, and 0.15% d characters. However, for Si-CPAC^{Me}, the Si-Si σ has 36.14% s, 63.34% p, and 0.46% d characters; the π bond has 21.68% s, 78.15% p, and 0.17% d characters and there is no lone pair character was perceived. The Si-L σ bond character for Si-CAAC^{Me} 77.22% from C carbene and 22.78% from and for Si-CPAC^{Me} this bond has 73.85% from C and 26.15% from Si and the π bond has 65.29% from C and 34.71% from Si. These simplified models with MOs and NBOs might be indicated that the Si-Si bond character in Si-CPAC^{Me}, determines the

nature of multiple bonds.

These findings imply that for all heavier group 14 L-E-E-L compounds, the bond distances and WBI are not ruled out, despite significant contributions to the EL bonds for PHC^{Me}, PNHC^{Me}, and CPAC^{Me} complexes. No π contributions to the EL bonds were seen for NHC^{Me} or CAAC^{Me} complexes. The E-L single bond character seen in the NHC^{Me} and CAAC^{Me} complexes is replaced by the E=L double bond character observed in the

PHC^{Me}, PNHC^{Me}, and CPAC^{Me} ligands in this bonding picture. The bonding structure of the PHC^{Me}, PNHC^{Me}, and CPAC^{Me} with group 14 complexes is L=EE=L.

Although there are considerable contributions to the EL bonds for PHC^{Me}, PNHC^{Me}, and CPAC^{Me} complexes, this conclusion does not rule out the bond distances and WBI for any heavier group 14 L-E-E-L elements. The EL bonds in NHC^{Me} and CAAC^{Me} complexes do not seem to be influenced by. In contrast to the E-L single bond character seen in the NHC^{Me} and CAAC^{Me} complexes, this bonding image depicts character of E=L double bond for the PHC^{Me}, PNHC^{Me}, and CPAC^{Me} ligands. The bonding structure of the group 14 complexes of PHC^{Me}, PNHC^{Me}, and CPAC^{Me} is L=EE=L.

CONCLUSION

The current computational study has examined five different carbenes with E2 elements from group 14 at a different level of theory and analysis to have early information about their interaction to draw conclusions. There is no ultimate conformation of L-E-E-L structure for all ligands with The E2 molecules, according to the bond lengths, and configurations, however, the data can predict that it has become more stable. If a suitable chemical route can be identified, L-E-E-L molecules seem as potential candidates for synthesis. Instead of the L-C-C-L structure with all ligands for C2, a trans bent geometry is reckoned for the other heavier group 14 species with most ligands. Trans-bent geometers for these complexes reflect the values of L-E-E angles and dihedral, which grow progressively from Si to Pb for all complexes. PHC stabilized L-E-E-L compounds appear to exhibit E=L double bond and EE single bond character (opposite of NHC complexes). PHC stabilized L-E-E-L compounds, dissimilar NHC analogues for heavier elements the border orbitals of Sn and Pb indicate that they are stable dimers rather than covalent compounds. Although thermodynamic calculations have similar stable results, the bonding picture for all elements indicate higher stability for the phosphorus carbenes compounds compared to the corresponding analogues of nitrogen carbene complexes. Phosphorus carbene complexes have a considerable double bond between the carbon for EL bonds in all situations, but nitrogen carbine complexes have no EL character in their frontier orbitals.

SUPPLEMENTARY MATERIAL

The following supporting information can be downloaded at: https://mjs.uomustansiriyah.edu.iq/index.php/MJS/article/view/1395/769.

AUTHOR CONTRIBUTIONS

Khalidah H. M. Al Furaiji suggested the research idea and performed the theoretical chemistry section. Sarah Badri Jasim organized all the results and data and wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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