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Theoretical Study of Stabilizing Molecular Fragments of Group 15 Diatomic by Phosphine and N-Heterocyclic Carbene

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As a way to investigate the stabilization mechanisms of carbene ligands with main-group species, computational methods have become indispensable. It is commonly known that these ligands have an extraordinary ability to arrange highly reactive elements from the main group in their zero states of oxidation is well known. Recent research has shown that by forming exceptionally strong complexes, main-group compounds must be stabilized by NHC and cAAC ligands. Based on this understanding, our research further enhances their stabilizing capacity by theoretically examining phosphorus carbenes, which have higher electron-donating properties. The interaction of two group 15 elements and two donor ligands intricately determines the bonding design of E_2L_2 molecules, providing important information for the creation of novel molecular bonding frameworks. The ligands' ability to donate electrons stabilizes the two group 15 atoms in this configuration. Unlike the E=E bond configurations that are common in nitrogen carbene complexes, phosphorus carbene complexes usually display an E=L double-bond pattern, which can be expressed as L=E–E=L. In this case, the complex's ligand (L) serves as a strong electron donor. Furthermore, orbital investigations and thermodynamic analyses verify that in every compound examined, L=E–E=L complexes are sufficiently stable to be isolated as condensed-phase molecules.

Keywords: Phosphorus carbenes, stabilizing Group 15 Diatomic, molecular fragments, theoretical calculations

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Since the commercial cyclic diaminocarbenes (NHCs) were produced by Arduengo and associates in 1991 [1]. Heterocyclic carbene chemistry has become a thriving field of study, both theoretically and experimentally. Considerable attention has been paid to their uses in transition-metal chemistry, main-group element chemistry, and catalysis [2], in addition to these molecules' structural changes. The nitrogen atoms' planar arrangement in α-position centers, which improves their π-donor properties toward the carbene center, is what gives NHCs their distinct qualities. Furthermore, it has been shown that the ability to donate σ is impacted by the steric effects of substituents that are connected to these nitrogen atoms [3]. To optimize electron-donating properties, researchers have mostly concentrated on changing substituents attached to atoms of nitrogen or the carbon core. But other research has shown that changing the NHC structure might also result in better qualities. In order to improve carbene performance, recent developments have looked into replacing one or both nitrogen atoms with elements of lower electronegativity.

The substitution of phosphorus for nitrogen is particularly intriguing because of its strong π-donor ability and lower electronegativity [4].

When Bertrand created the first phosphorus-based carbenes in 2005, they demonstrated that, with a correct structural design, cyclic diphosphinocarbenes (PHCs) might function as strong σ-donors [5].

They noticed that interactions between the carbene's vacant orbital and its lone electron pair were restricted by the heavily pyramidal zed phosphorus centers. They proposed using large substituents at phosphorus atoms to minimize the pyramidal structure in order to overcome this restriction. Figure 1(A). In 2008, Frey et al. used a similar approach to create acyclic (amino) (phosphino) carbenes by replacing a single nitrogen atom with phosphorus. According to their research, unsaturated five-membered N-PHCs might provide several coordination modes in which phosphorus remained a spectator substituent with an active lone pair and nitrogen acted as a π-donor. Because phosphorus has a higher electro positivity than nitrogen carbenes, these PHCs showed better σ-donation and higher stability than NHCs [6]. Figure 1(B). By adding alkyl amino carbenes (cAACs), which substitute an alkyl group for one nitrogen atom to improve electron donation, Bertrand further extended this domain. [7] Later, a theoretical study looked into using oxy, silyl, phosphino, or thio groups in place of the nitrogen atom in cAACs. Results showed that phosphino and amino alkyl carbenes were less electrophilic and more nucleophilic. [8] Compared to their oxy- and thio-substituted counterparts Figure 1(C). Practical uses of these compounds are still limited, even though these developments have offered light on the synthesis and characteristics of NHC analogues.

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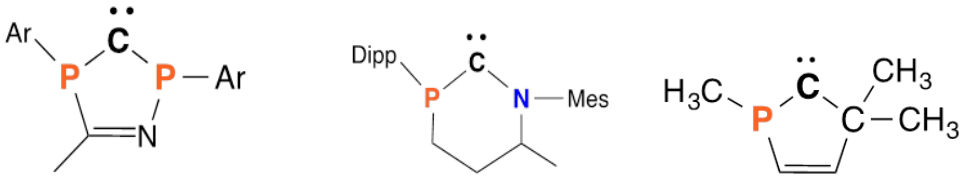


Bertrand et al. (2005) Frey et al. (2008) Kassaee et al.(2010)

A B C

Figure 1. Phosphorus carbenes experimentally and theoretically.

PHCs have been used as ligands to create transition-metal complexes with zirconium and rhodium, producing stable products with minor disintegration and great efficiency. NHCs and cAACs have distinguished themselves as potent ligands in main-group chemistry for stabilizing extremely reactive low-oxidation-states through interactions with vacant orbitals and fostering novel bonding frameworks this has been further confirmed by computational research and experimental synthesis. Growing data highlights the significance of potent σ-donating carbenes in preserving p-block fragment-based diatomic allotropes at lower oxidation states and creating distinctive bonding structures for these substances. New studies keep emphasizing how useful it is to use NHCs as strong ligands in unusual systems [9-12].

Dutton and colleagues have also shown that diatomic compounds like C2 are very well-stabilized by carbene ligands like NHC and cAAC [13]. Additionally, theoretical research by Wilson et al. has demonstrated that E2L2 systems use carbene ligands (L), where E stands for elements from group 15 (As, P, Bi, and Sb). Their results provide important new information on these systems' bonding geometries, bond properties, and thermodynamic stability [14, 15]. Two NHC ligands with E=E double bonds typically interact with group 14 elements in a trans-bent shape, according to the study. [16] However, carbon is an exception, taking a linear form. In the lowest potential energy structures, the elements in group 15 are arranged gauchely and have a single EE bond. The diatomic moiety E2 is involved in donor-acceptor coordination during the bonding contacts in these compounds (L → EE ← L). Numerous systematic investigations have shown that the formation of extremely stable L-E-E-L complexes is made possible by the remarkable coordination ability of NHC ligands. The influence of employing carbene analogues connected to cAAC and NHC ligands for low oxidation state stabilization of diatomic p-block elements is being investigated theoretically for the first time. Furthermore, this study provides fresh insights into the properties of L-E-E-L complexes to evaluate whether they have special qualities that would make them attractive options for expanding synthetic applications in chemistry.

Recent achievements in stabilizing molecular fragments with main-group elements using a donor-acceptor approach expand the concept of coordination beyond its conventional use in transition-metal chemistry and allow for the investigation of coordination chemistry of elements that typically form covalent bonds, like carbon [17-18].

Ramirez et al.'s initial report of the synthesis of hexaphenylcarbodiphosphorane, $(C_6H_5)_3PCP(C_6H_5)_3$, in the 1960s may be considered the beginning of the field [19]. The significance of the bonding description is demonstrated by the isolation of this molecule. Two resonance structures were proposed to explain the bonding in agreement with an expected linear geometry with C-P covalent bonds (Figure 2) [20].

When hexaphenylcarbodiphosphorane's X-ray crystallographic structure with a bent P-C-P geometry was revealed in 1972, it challenged this covalent bonding concept with C=P [21]. Frenking reanalyzed the carbodiphosphorane molecule using new coordinate bonding models. He rationalized using natural bond orbital calculations and molecular orbital analysis. Kaska's bonding model of the molecule. The presence of two lone pairs on the carbon atom is evident from the shape of the MO analysis-derived HOMO and HOMO-1 orbitals (Figure 3). The substantial negative charge indicated in the calculations could be caused by the two lone pairs on the carbon atom. It was deduced that the divalent carbon accepts lone pairs from the ligand's phosphorus atom to create two two-coordinate bonds. The carbon was found to be in the zero oxidation state C (0) because the central carbon atom had two lone pairs while the neighboring phosphorus atoms had none [22].

Figure 2. Resonance structures of hexaphenylcarbodiphosphorane.

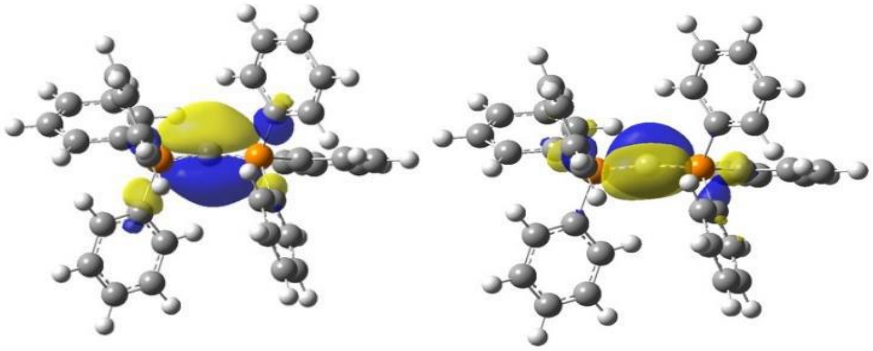
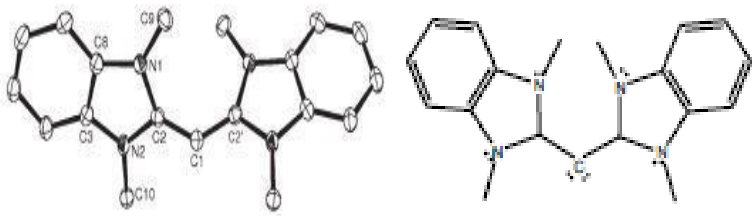


Figure 3. The two lone pairs on the core carbon atom of carbohydratephosphorane are indicated by the HOMO (left) and HOMO-1 (right) molecular orbitals.



(a) (b)

Figure 4. $C(NHCBz)_2$ molecule.(a) Crystal structure (b) proposed Lewis structure.

Bertrand reported synthesizing the C(NHCBz)2 compound (Figure 4). This molecule's shape, which is curved around the core Carbon atom, is in line with Franking's theoretical expectations [23].

The purpose of the current project is to investigate the characteristics, stability, structure, and reactivity of group 15 (E= P, As, Sb, and Bi) stabilized by donor ligands. Comparing several DFT methods and donor ligands to stabilize the 2E molecular system is one aspect of this research. The initiative also intends to examine the ligands' capacity to stabilize group 15 diatomics (2E), since different ligands have varying binding affinities. To stabilize E2 molecules (L-E-E-L complexes) with group 15, PHCMe, PNHCMe, and cPACMe ligands were used as two-electron phosphorus ligands that are neutral. We looked at their cAACMe and NHCMe counterparts. Two considerations can be highlighted to explain the benefit of NHCs as donor ligands for the main group chemistry. First, the strong directionality of the sp^2 hybridized lone pairs in NHCs suggests that NHCs are stronger σ donors [24, 25] and, Second, the effective overlap between the π* orbitals of NHCs and the p-orbitals of molecular fragments suggests that NHCs are superior π acceptors.

The electronic structure of cAAC and NHC is similar, but cAAC has a stronger σ-donor and a better π-acceptor than NHC because it has a tetravalent carbon atom in place of one of the nitrogen atoms in NHC. For the carbene carbon, the nitrogen atoms serve as π-donating and σ-withdrawing groups. Therefore, compared to cAAC, NHCs Weaker σ-donors and π-acceptors are found in compounds with two nitrogen atoms (Figure 5). The planar shape of NHC contrasts with the envelope conformation of cAAC. is another effect of the tetrahedral carbon in the molecule [26].

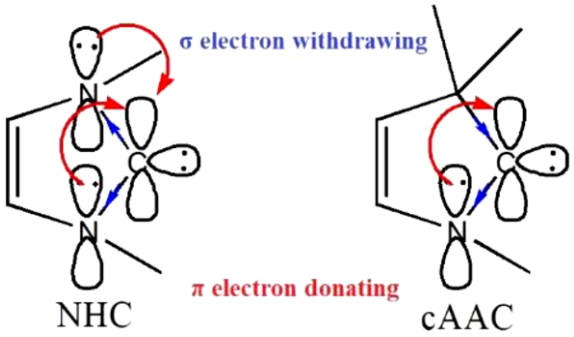


Figure 5. Nitrogen impact on the carbene carbon of donor ligands for cAAC and NHC.

NHC or cAAC have been utilized in most documented synthetic successes as donor ligands for separating ligand-stabilized molecular fragments. The C=C bond, that is unsaturated in NHC and cAAC, is a C-C single bond in its saturated versions [27]. Saturated forms are therefore expected to be more reactive than their corresponding unsaturated forms because the delocalized π-ring system is upset and the energy of the HOMO orbital containing the lone pair rises.

In order to better understand the nature of these compounds, molecular materials created by stabilizing these diatomic systems with a donor ligand would then allow for an investigation of the reactivity of these ligand-stabilized molecular fragments. In addition to the project's objectives, a comparison of various donor ligands and computation methods has been done to guarantee the accuracy of the findings. The analysis and methods provided by computational chemistry are ideal for the project's objectives.

In this work, their stabilizing capacity by theoretically examining phosphorus carbenes, which have higher electron-donating properties.

The electronic structure was examined through the band structure and density of states. The interaction of two group 15 elements and two donor ligands intricately determines the bonding design of E2L2 molecules, and to investigate the characteristics, stability, structure, and reactivity of group 15 (E= P, As, Sb, and Bi) stabilized by donor ligands. Comparing several DFT methods and donor ligands to stabilize the 2E molecular system is one aspect of this research.

MATERIALS AND METHODOLOGIES

Electronic structure theory was used to simulate molecule formations for optimum geometries through computational chemistry calculations [28]. These computations, which are based on the ideas of quantum mechanics, yield extremely precise molecular properties, stable configurations, and thermochemical information.

These methods are particularly helpful for examining gas-phase molecular systems, which are often difficult to investigate by experimentation. Geometries were optimized for this study utilizing the B3LYP/def2-TZVP and M06-2X/def2-TZVP methods. Starting geometries for ligands, all group 15 diatomic, and L-E-E-L compounds were the main focus of the investigation. In order to evaluate thermodynamic stability, Single-point MP2/def2 TZVP simulations were used to calculate each structure's Gibbs free energies by combining electronic energy and thermal adjustments for the optimized geometries. The equation was used to determine the reaction Gibbs free energies at 25°C.

$$\mathbf{2L + E2 \rightarrow L{=}E{-}E{=}L.}$$

With acetonitrile-specific constants and Truhlar's SMD solvation model, the polarizable continuous model within the self-consistent reaction field (SCRF) framework was used to account for solvent effects. Furthermore, investigations of molecular orbitals (MO) and natural bonding orbitals (NBO) were carried out at the theoretical level of B3LYP/def2-TZVP. The software programs Gaussian 09 and Gaussian 16 were used for all computational investigations.

COMPUTATIONAL METHODS

The accuracy of theoretical and experimental chemistry is now comparable, but they also benefit from complementary methodologies. Because to technological advancements in computational software packages and hardware. Numerous computations can be performed to investigate molecular systems, and highly accurate findings can be obtained [29]. In addition to guiding experimental synthesis, computational techniques

can be used to forecast a reaction's energetics, which can help experimental chemists achieve efficiencies.

One effective technique for analyzing the characteristics of molecules is computational chemistry. To make sure that the global minima were found in this project, several conformers were usually tuned. The frequency computation on the ideal structure of the chemical system can be categorized using stationary points. In order to fully understand a molecular system's electrical composition and bonding, MO and NBO calculations are performed at the optimal geometry.

RESULTS AND DISCUSSION

Optimized Geometries

Complexes in group 15 where E= P, As, Sb, and Bi. The ideal molecular arrangements for each L-E-E-L complex are displayed in Figure 6, while table 1 presents the basic geometry parameters. With every ligand, no appreciable variations in the general molecular geometries are found. Comparisons with consistent E-E bonds of manufactured compounds reveal that there is a single bond character for all E-E bonds. The statement is likely referring to that many compounds with E-E bonds exhibit a single covalent bond character for those bonds, meaning they share one pair of electrons.

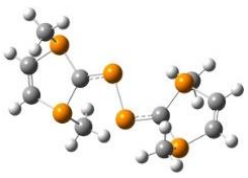
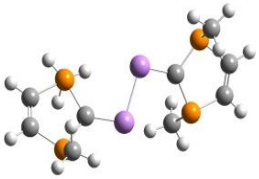
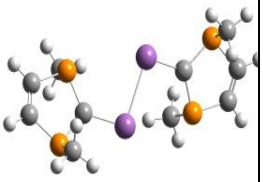
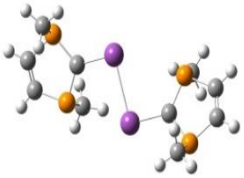
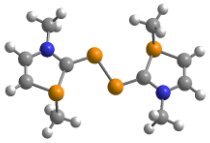
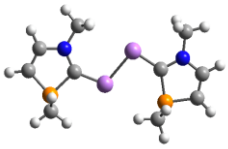
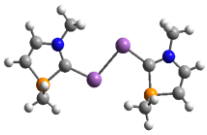
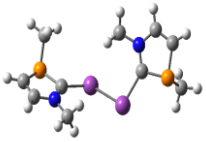
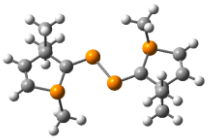
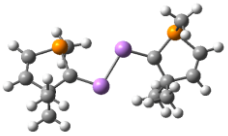
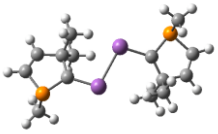
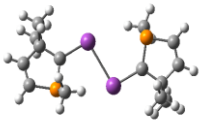
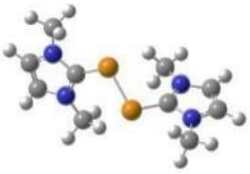
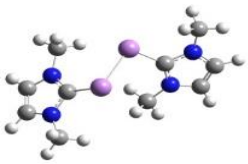
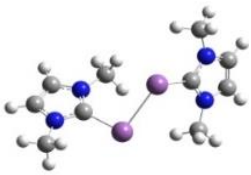
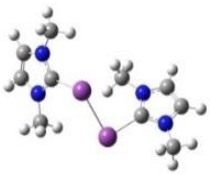
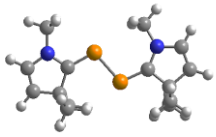
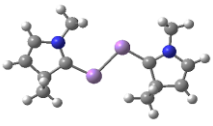
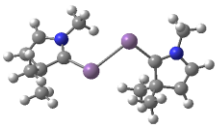
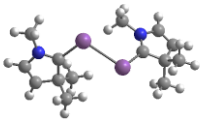
Carbenes	P	As	Sb	Bi
PHC^{Me}				
$PNHC^{Me}$				
$cPAC^{Me}$				
NHC^{Me}				
$cAAC^{Me}$				

Figure 6. B3LYP/def2-TZVP developed group 15 L-E-E-L compounds with specific ligands (E = P, As, Sb, and Bi).

Table 1. Group (15) L-E-E-L compounds' optimized properties include chosen bond lengths (Å), L-E-E angles (°), and L-E-E-L dihedral angles (°).

		Bond distance			Angle [a]	Dihedral [a]	WBI [b]
Compound	E	E-E	E-L	L-EE	L-EE-L	E-E	E-L
P_PHC^{Me}	P	2.196	1.698	102.90	167	1.08	1.61
P-PNHC^{Me}	P	2.183	1.725	100.41	180	1.07	1.49
P_cPAC^{Me}	P	2.203	1.691	102.60	180	1.04	1.71
P_cAAC^{Me}	P	2.203	1.728	103.84	176	1.07	1.53
P_NHC^{Me}	P	2.207	1.780	106.10	126	1.04	1.27
As_PHC^{Me}	As	2.443	1.829	100.70	163	1.05	1.56
As _PNHC^{Me}	As	2.452	1.851	107.49	176	1.03	1.44
As_cPAC^{Me}	As	2.459	1.817	106.46	162	1.01	1.70
As_cAAC^{Me}	As	2.461	1.862	102.14	180	1.03	1.49
As_NHC^{Me}	As	2.454	1.933	104.70	107	1.03	1.17
Sb_PHC^{Me}	Sb	2.833	2.043	97.80	165	1.07	1.41
Sb_PNHC^{Me}	Sb	2.860	2.079	95.03	177	1.03	1.33
Sb_cPAC^{Me}	Sb	2.869	2.030	103.95	176	1.00	1.55
Sb_cAAC^{Me}	Sb	2.869	2.093	103.27	123	1.02	1.34
Sb_NHC^{Me}	Sb	2.820	2.195	103.70	100	1.10	0.96
Bi_PHC^{Me}	Bi	2.997	2.146	96.20	171	1.07	1.38
Bi-PNHC^{Me}	Bi	3.043	2.198	105.35	113	1.01	1.26
Bi_cPAC^{Me}	Bi	3.035	2.129	103.11	177	1.01	1.54
Bi_cAAC^{Me}	Bi	3.028	2.211	104.56	105	1.03	1.27
Bi_NHC^{Me}	Bi	2.962	2.339	102.70	97	1.15	0.83

[a] Average values for corresponding bond distances and angles. [b]WBI = Wiberg Bond Index.

The P-P (2.21-2.22 Å, and As-As (2.4-2.56 Å) single bond distances are consistent with the P-P and As-As bond calculations with all ligands. 4, 12. However, Sb−Sb (2.83−2.85 Å)[30] single bonds are consistent with the estimated Sb−Sb bonds with PHC^{Me} and NHC^{Me} ligands.[31]. With ligands for PNHC^{Me}, cPAC^{Me}, and cAAC^{Me}, these bonds are marginally longer. With every ligand, the Bi-Bi bonds are in agreement with the Bi−Bi bond distances (2.98−3.05 Å)[32]. The E-E bond values for group 15 L-E-E-L complexes within Fischer and Power's major group complexes do not lie within the range of E=E double bonds: P 1.985−2.141 Å, As 2.219−2.333 Å, Sb 2.642−2.751 Å, and Bi 2.821−2.870 Å. L = NHC (dipp)2.16 and the P-P bond distance of NHC stabilized L−P−P−L is 2.205 Å, is slightly similar to the P-P bonds in cPAC^{Me}, cAAC^{Me}, and NHC^{Me} (2.2031, 2.033, and 2.07 Å), respectively. Likewise, the As-As bond distance of 2.443Å in As_PHC^{Me} can be the same as the As-As bond distance of 2.442Å in the NHC (dipp)2 stable complex[33].

Me2Sb−SbMe2 (2.818 Å) single bond character is similar to that of Sb−Sb bonds computed in Sb_PHC^{Me} and Sb_NHC^{Me} (2.817, 2.840 Å). However, found 2.87 Å as the typical single bond distance in another investigation of single bound characters, which is consistent with Sb_PNHC^{Me}, Sb_cPAC^{Me}, and Sb_cAAC^{Me}. Sb=Sb double bond (2.642Å) for the synthesized complex TbtSb=SbTbt is significantly shorter than that of complexes [34]. All of the complexes' Bi-Bi bond values can be compared to the Bi-Bi single bond of (SiMe3)2Bi−Bi (SiMe3)2 (3.04 Å)[4] and (2.99 Å) in Ph2 BiBiPh2, However, they are significantly longer than the experimentally confirmed Bi=Bi double bond (2.821 Å). (2,6-Mes2 C6 H3 Bi)2 complex .The E-L bonds have also somewhat decreased along the group in the same pattern for all ligands, according to the table.

The Wiberg bond index (WBI), which indicates that the multiple bond character is expected to be reduced from P to Bi with various ligands, supports this conclusion. For instance, ligands having a strong P=P double bond character that range from 1.54 (Bi_cPAC^{Me}) to 1.71 (P_cPAC^{Me}). The E−L WBI values for NHC^{Me} ligands show some double bond character for P and As, but no such character can be deduced from the optimized parameters of Sb and Bi analogues. The significance of the double bond feature in the group 15 analogues will be carefully investigated in the section on the electronic structure and orbital analysis. On the basis of the WBI values, the bond orders for the B≡P bond are 2.39, 1.96, 2.15, and 1.97 for SiMe(SitBu3)2, Tbt, SiiPrDis2, and Ar, respectively.

This data is similar to the values that are calculated using NRT, of 2.55, 2.47, and 2.27, respectively [35].

Table 2. SCS-MP2/def2-TZVP//B3LYP/def2-TZVP calculated (ΔG_{298K}) (kJ/mol.) for $E_2 + 2L \rightarrow$ L-E-E-L reaction.

E	NHC^{Me}	$PNHC^{Me}$	PHC^{Me}	$CAAC^{Me}$	$CPAC^{Me}$
P	-117	-301	-358	-265	-489
As	-106	-249	-327	-233	-441
Sb	-85	-205	-294	-176	-379
Bi	-59	-141	-269	-135	-346

THE CALCULATION OF THERMODYNAMIC STABILITY

Thermodynamic Parameter Calculations for the Complexes Free Energies Stability

The stability of L-E-E-L complexes was predicted using thermodynamic analysis by computing ΔG for the production process E2 + 2L → L-E-E-L. The data in table (2) shows that all L-E-E-L complexes have negative ΔG values, indicating that these entities are stable with regard to dissociation.[36] The findings is intriguing because all phosphorus carbenes have significantly lower ΔG values than NHC^{Me} and $cAAC^{Me}$ carbenes. This table shows that for all complexes, ΔG values decrease from P to Bi. Despite the fact that all ligands exhibit the same downward trends, the situation with $PNHC^{Me}$ and PHC^{Me} is more negative to their NHC^{Me} counterparts. It is evident that the ΔG values with L=$PNHC^{Me}$ and PHC^{Me} decrease from P (-301.3, -357.9 kJ/mol) to Bi (-141.3, -268.5 kJ/mol), respectively, while the values with L=NHC^{Me} decrease from P (-117.1 kJ/mol) to Bi (-58.6 kJ/mol). $CPAC^{Me}$ complexes are more stable than $CAAC^{Me}$ complexes, and the ΔG values for both carbenes follow the same trend at the group level (less negative from P to Bi; -489.4 to -346.4 kJ/mol for $CPAC^{Me}$ and -265.2 to -135.3 kJ/mol for $CAAC^{Me}$.

The negative ΔG values indicates that both dissociation of the ligand and the complexation process are spontaneous. According to negative ΔG effects was predicted towards an increase in the number of particles after the reaction to give more negative ΔG [36,37]. In respect to dissociation, a comparison of the data for all phosphorus carbenes shows that L = $CPAC^{Me}$ has remarkable thermodynamic stability when compared to L=$PNHC^{Me}$ and PHC^{Me}. All of these phosphorus carbene studies show that these ligands are good targets for stabilizing group 15 extremely reactive E2 molecules and offer valuable information on their application in synthetic chemistry.

Electronic Structure and Orbital Analysis

The most popular techniques for evaluating the consistency of L-E-E-L systems are molecular orbital and natural bond analysis. They are employed here to understand the differences in reactivity and molecular geometries for each complex under question. The L-E-E precursor1's acceptor orbital orientation has been determined, as the primary cause of the geometry difference in group 15 systems for NHC^{Me}.

According to this analysis, all group 15 fragments exhibited a gauche structure in the L-E-E-L complexes. The NHC^{Me} and $CAAC^{Me}$ complexes exhibit a significantly distinct picture in comparison to the PHC^{Me}, $PNHC^{Me}$, and $cPAC^{Me}$ complexes figures (7-9), according to the results of the MOs study, the PHC^{Me}, $PNHC^{Me}$, and $cPAC^{Me}$ complexes have different configurations, the NHC^{Me} and $CAAC^{Me}$ complexes showed the same pattern. Figures show plots comparing $CAAC^{Me}$ and $CPAC^{Me}$. In contrast to the other compounds, the bonding image for the L-CC-L system is distinct. No lone pair is found on the central carbon atoms of any ligand type in this system. A full linear cumulate-like structure is formed by π bonds between the central carbon atoms (E−E) and between the carbons of the ligand rings (E−L/E−C) and the central carbons. HOMO contains the E-L π bonds, whereas HOMO-1 contains the E-E π bonds [38].

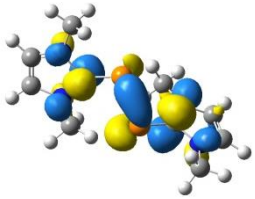
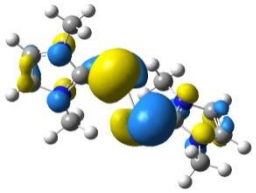
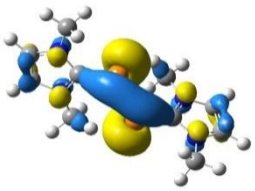
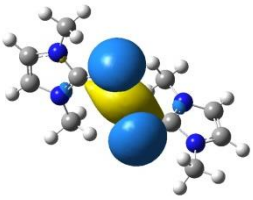
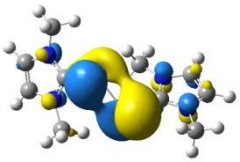
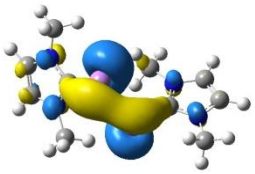
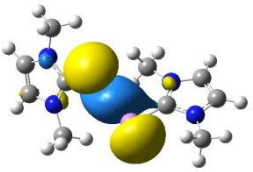
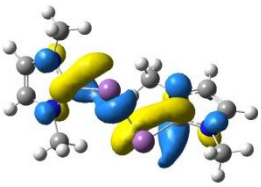
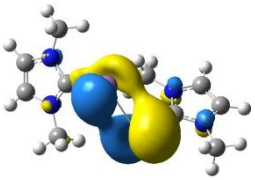
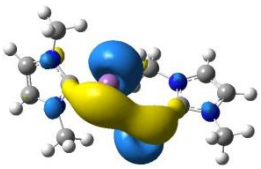
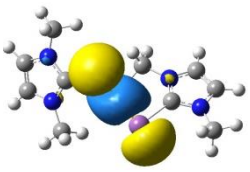
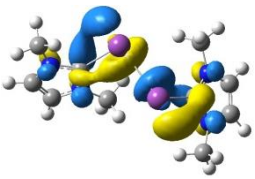
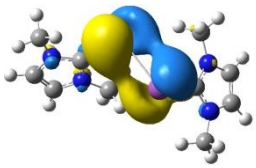
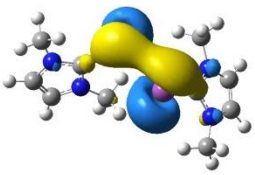
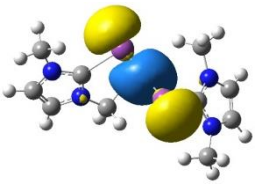
E	LUMO	HOMO	HOMO-1	HOMO-2
P				
As				
Sb				
Bi				

Figure 7. Frontier MOs for E_ NHC^{Me} (E = P, As, Sb, Bi).

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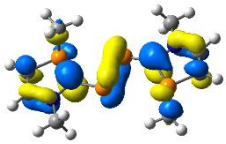
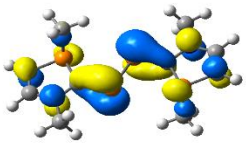
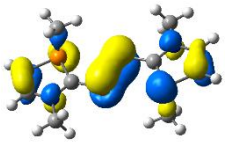
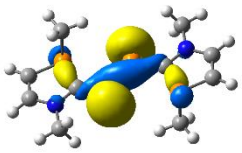
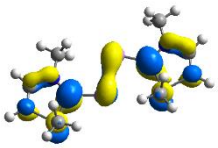
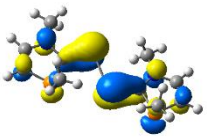
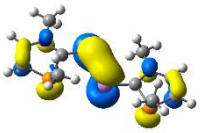
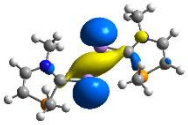
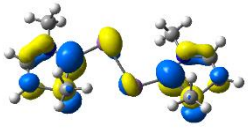
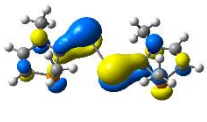
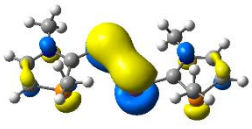
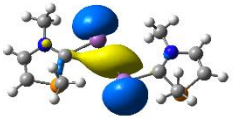
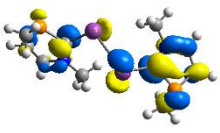
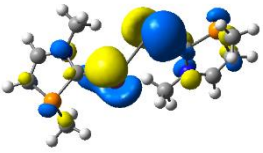
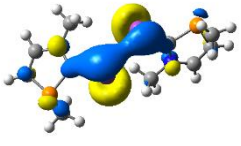
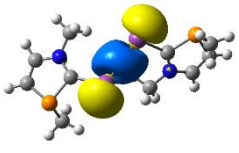
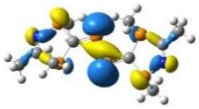
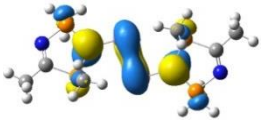
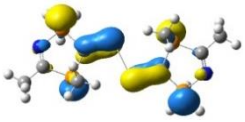
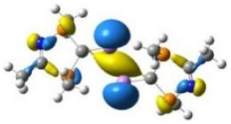
P				
As				
Sb				
Bi				

Figure 8. Frontier MOs for E_ $PNHC^{Me}$ (E = P, As, Sb, Bi).

E	LUMO	HOMO	HOMO-1	HOMO-2
P				
As				
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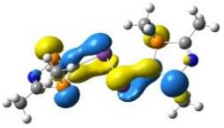
Bi				

Figure 9. Frontier MOs for E_ PHC^{Me} (E = P, As, Sb, Bi).

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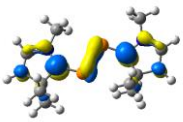
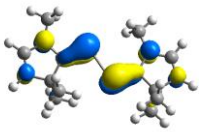
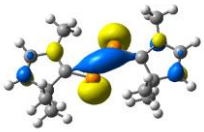
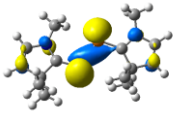
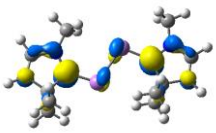
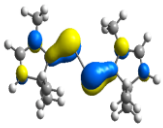
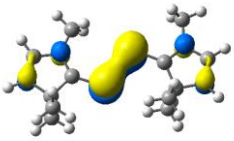
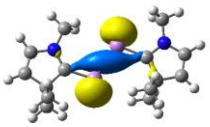
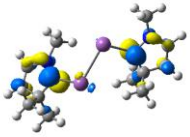
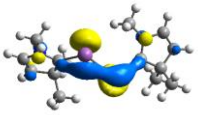
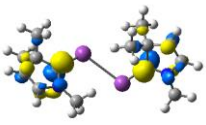
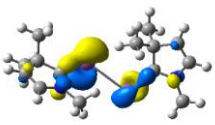
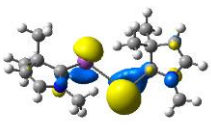
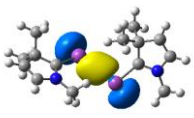
P				
As				
Sb				
Bi				

Figure 10. Frontier MOs for E_cAAC^{Me} (E = P, As, Sb, Bi).

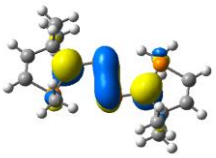
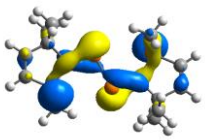
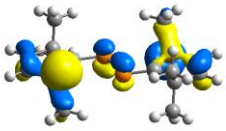
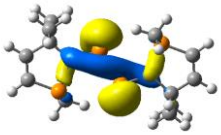
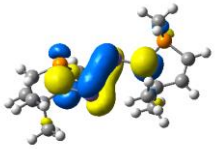
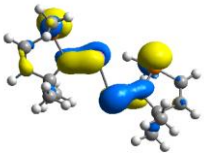
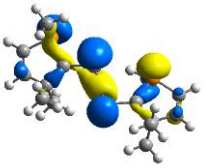
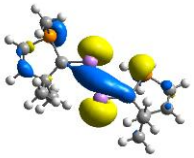
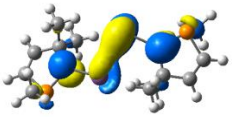
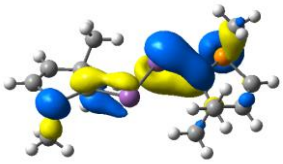
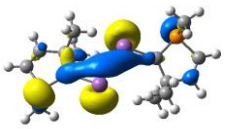
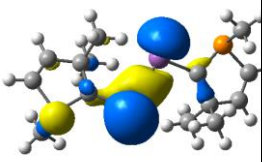
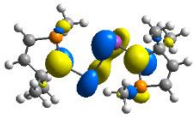
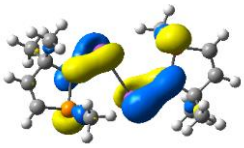
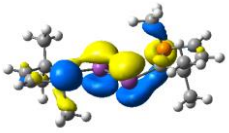
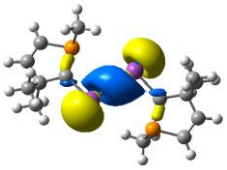
E	LUMO	HOMO	HOMO_1	HOMO_2
P				
As				
Sb				
Bi				

Figure 11. Frontier MOs for E_CPAC^{Me} (E = P, As, Sb, Bi).

The border molecular orbital figures support the findings of earlier NHC^{Me} studies, which show that the lone pairs of the central atom and the E_L π bond occupy the HOMO and HOMO_1, respectively. The E_E π bond occupies the LUMO, while the E_E σ bond engages the HOMO_2.

These figures show that, for all elements with some variation down the group, the MO frameworks of the CAAC^{Me} and CPAC^{Me} complexes are similar. The contributions of the E-L π interactions and the p-type lone pair of central atoms occupy the HOMO. HOMO-1 contains the contributions of additional lone pairs to central atoms. The π back bonding from the core atoms onto the ligand ring results in a substantial E−L double bond character. The unique single bond character for P and As supplied by the E−E σ bond occupying the HOMO-2 is consistent with the localized bonding appearance of Robinson's P_R2NHC and As_R2NHC complexes.

The NBOs study for cAACMe and CPACMe shows similar trends in both instances. This bond's P_L σ character is 65.18% from C and 34.82% from P for P_CAACMe, and 64.40% from C carbene and 35.60% from P for P_CPACMe. For P_ CAACMe, the P_L π bond has 44.04% from C and 55.96% from P, while for P_ CPACMe, it has 53.51% from C and 46.49% from P. Characteristics of the P_ CAACMe P_P σ bond are 13.48% s, 85.65% p, and 0.851% d. The P_P σ for P_ CPACMe contains 11.69% s, 87.32% p, and 0.97% d character, and neither complex showed an E_E π bond.

The MO framework for each element in group 15, which includes the NHCMe and cAACMe complexes, is similar. The contributions of the E-L NHC, π interactions, and the p-type lone pair of central atoms occupy the HOMO. HOMO-1 contains the contributions of additional lone pairs to central atoms.

There is significant E−L double bond character due to π back bonding from the central atoms onto the ligand ring. E−E σ bond occupying the HOMO-2 gives clear single bond character for P and As, which is consistent with the localized bonding picture of Robinson's P_R2NHC and As_R2NHC complexes.

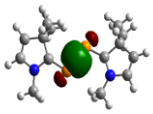
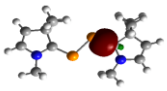
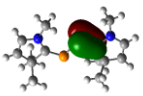
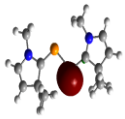
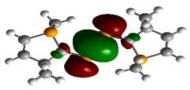
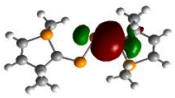
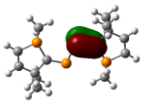
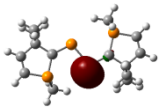
Complexes	E−E σ bond	E−E π bond	E−L σ bond	E−L π bond	P_lone pair
P_ CAAC^{Me}		No double bond			
P_ CPAC^{Me}		No double bond			

Figure 12. NBO orbitals for P_ CAAC^{Me} and P_ CPAC^{Me}.

CONCLUSIONS

Five different carbenes containing E2 elements from group 15 have been studied computationally at various theoretical and analytical levels in this work in order to gather preliminary data regarding their interactions and make inferences. The final L-E-E-L structural conformation does not exist for every ligand with the molecules of E2. However, the evidence indicates that it has gotten more stable in regard to the bond arrangements and lengths.

The L-E-E-L molecules appear to be promising candidates for synthesis if an appropriate chemical pathway can be found. For the other heavier group 15 species with the majority of ligands, a Trans bending geometry is taken into consideration with all ligands for C_2 in lieu of the L-C-C-L structure. For these complexes, transbent geometers display the dihedral and L-E-E angle values.

These ligands are excellent targets for stabilizing group 15 very reactive E2 molecules, as demonstrated by all of these phosphorus carbene investigations, which also provide important insights into their use in synthetic chemistry. In most documented synthetic successes, NHC or cAAC have been used as donor ligands to isolate ligand-stabilized molecular fragments; all L-E-E-L complexes exhibit negative ΔG values, suggesting that these entities are stable with respect to dissociation. The results are interesting since the ΔG values of all phosphorus carbenes are much lower than those of NHCMe and cAACMe carbenes.

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SUPPORTING INFORMATION

Provide an extra information about Cartesian coordinates of reactant optimized geometries relating to the current task as needed. If the submission is accepted, the editors will offer a complete link to the article and the SI.

CONFLICT OF INTEREST

State that the authors have no conflict of interest.

AUTHOR CONTRIBUTIONS

ABC conducted the experiment, XY conducted the DFT calculations, ABC and XY wrote and revised the manuscript. All authors agreed to the final version of this manuscript

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