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Theoretical Investigations of Mechanisms for the Reactions of Seven-Member Ring N-Heterocyclic Carbene and Its Heavier Analogues

Zheng-Feng Zhang, Ling-Hsuan Liu and Ming-Der Su

Additional information is available at the end of the chapter

Abstract

The potential energy surfaces for the chemical reactions of group 14 carbenes were studied using density functional theory (B3LYP/LANL2DZ + dp). Five group 14 carbene species containing a seven-member ring, **7-Rea-E**, where E = C, Si, Ge, Sn and Pb, were chosen as model reactants for this work. Three types of chemical reactions (water addition, imine cycloaddition and dimerization) were used to study the reactivity of these **7-Rea-E** molecules. Present theoretical investigations suggest that the relative reactivity of carbenes decreases in the order: **7-Rea-C** > **7-Rea-Si** > **7-Rea-Ge** > **7-Rea-Sn** > **7-Rea-Pb**. That is, the heavier the group 14 atom (E), the more stable its corresponding **7-Rea-E** compound to chemical reaction. This study's theoretical findings suggest that all of the seven-member **7-Rea-E** should be readily synthesized and isolated at room temperature, since they are quite inert to chemical reaction, except for reaction with moisture. Furthermore, the group 14 **7-Rea-E** singlet-triplet energy splitting, as described in the configuration-mixing model of Pross and Shaik, can be used as a diagnostic tool to predict their reactivity. The results obtained allow a number of predictions to be made.

Keywords: N-heterocyclic carbenes, seven-member carbene, group 14 elements, density functional theory, imine cycloaddition, dimerization, water addition

1. Introduction

Since the first synthesis and isolation of thermally stable carbenes, imidazol-2-ylidenes, by Arduengo and co-workers [1, 2], the chemistry of N-heterocyclic carbenes (NHCs) has been the subject of intense research and has been studied both experimentally and theoretically during the last two decades [3–23]. Indeed, the isolation of stable NHCs has led to a renaissance for the nucleophilic

carbenes. In particular, NHCs were found to be strong, two-electron σ-donors and to be highly air- and moisture-stable substituents, which allowed the preparation of organometallic catalysts of enormous utility in organic synthesis [24–34]. Nevertheless, although a broad range of geometrical structures of NHCs have been synthesized and structurally characterized, their architectures are still limited to the three- [25], four- [36, 37], five- [35–40], and six-membered rings [41–47].

(E = C, Si, Ge, Sn, and Pb)
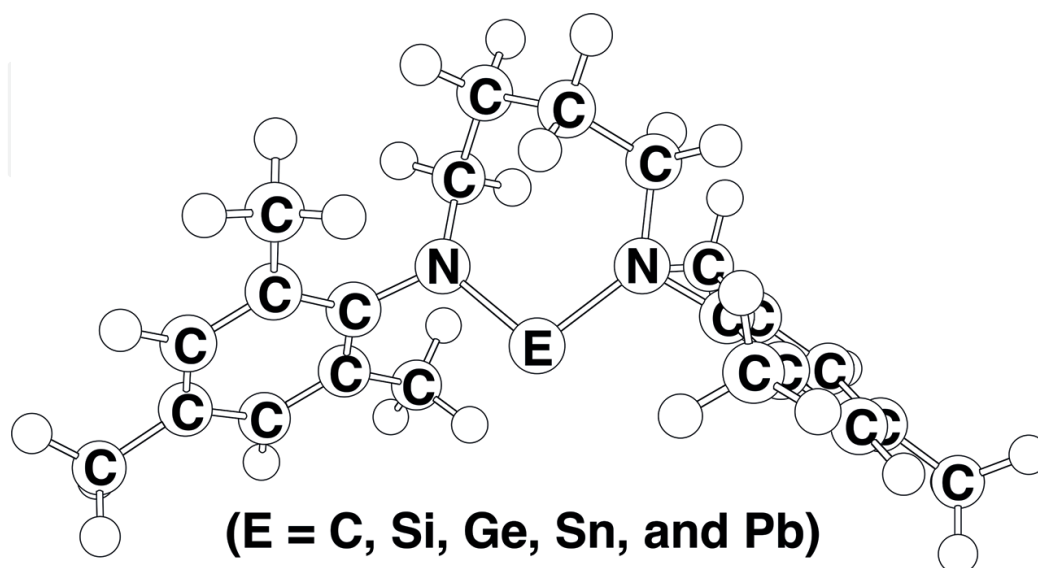
Recently, because of the elegant studies performed by Cavell, Dervisi, Fallis and many coworkers, thermally stabilized molecules that possess the seven-member ring unit, in which the carbene center is flanked by two nitrogen atoms, have been synthesized and structurally characterized [48–50]; one is 1,3-bis(2,4,6-trimethylphenyl)-4,5,6,7-tetrahydro-3H-[1,3]diazepine (**7-Mes**), a novel seven-member carbene system and the other is the first stable 1,3-bis(2,6-dimethylphenyl)-4,5,6,7-tetrahydro-3H-[1,3]diazepine (**7-Xyl**) to have been isolated, again by taking advantage of bulky substituent groups. As a result, carbene systems that feature a seven-member ring are no longer imaginary species. However, attempts to isolate other heavy carbene analogues containing the heavy group 14 elements (such as Si, Ge, Sn, and Pb) have all been unsuccessful, until now.

The objective of this work is, therefore, to enlarge upon previous experimental approaches by studying the mechanism and reactivity of seven-member heavy carbene systems, wherein the carbene center (E) is represented by group 14 atoms from carbon to lead. To the best of the authors' knowledge, neither experimental nor theoretical studies have yet been performed on seven-member-rings that possess main group elements, let alone a systematic theoretical study of the elemental effects on the reactivity of such species. In consequence, a study of three kinds of typical reactions for seven-member carbene analogues (E$^{..}$ = C, Si, Ge, Sn and Pb), Eqs. (1)–(3), using the density functional theory (DFT), is represented as follows:

(1)

(2)

(3)
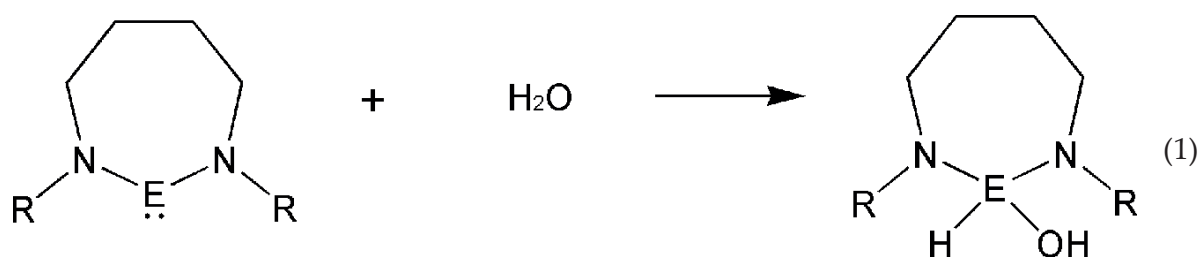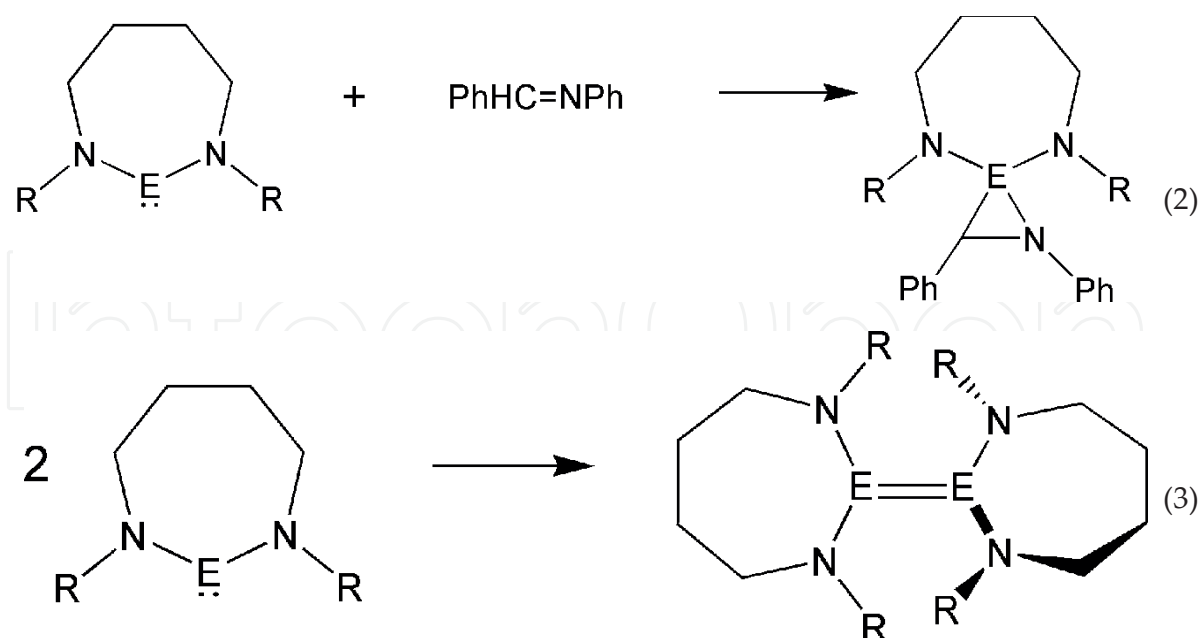
(R = 2,4,6-trimethylbenzene)

It is hoped that this theoretical study will (i) clarify the reaction mechanism and determine the possible transition-state structures and the relative energetics for Eqs. (1)–(3), (ii) examine the thermodynamics of the seven-member carbene analogues' reactions with various substrate molecules and (iii) establish general trends and predictions for the chemical reactions of seven-member-ring heavy NHCs.

2. Computational details

Geometries were fully optimized using the B3LYP level of theory, which is implemented by the Gaussian 03 program package [51]. Moreover, the LANLADZ basis sets were utilized in this study. The LANL2DZ basis sets contain the pseudo-relativistic effective core potentials on the group 14 elements modeled, using the double-zeta (DZ) basis sets augmented by a set of d-type polarization functions [52], in which the d exponents used for C, Si, Ge, Sn and Pb were 0.587, 0.296, 0.246, 0.186 and 0.179, respectively. As a result, B3LYP/LANL2DZ + dp represents the B3LYP computations. It is noteworthy that the model reactant (**7-Ring-E**; E = group 14 element) has a total of 604 (180 electrons) basis functions for LANL2DZ + dp sets. Frequency computations were executed on all of the stationary points in order to make sure whether they are the minimum points (no imaginary frequencies) or the transition states (only one imaginary frequency). Therefore, the relative energies were corrected by using the zero-point energies (ZPE, not scaled). Also, the relative free energies (ΔG) at 298 K were computed at the same level of theory.

3. Results and discussion

3.1. Geometric structures of 7-Mes

In order to verify that the computational method used in this work is suitable for discussion of the potential energy surfaces for the related chemical reactions (Eqs. (1)–(3)), the geometry

of free seven-member N-heterocyclic carbene, **7-Mes** is firstly considered. Since the structure of **7-Mes** has been determined by X-ray crystal analysis, its geometry optimization was first performed, in order to calibrate the B3LYP/LANL2DZ + dp calculations. As shown in **Figure 1**, the calculated average C-N and N-C (ring) distances are 1.356 and 1.493 Å, respectively. These values are very close to those of 1.348 and 1.493 Å, observed for the X-ray crystal structure [48–50]. In addition, the calculated ∠N-C-N and average ∠C-N-C (ring) angles are estimated to be 118.2° and 128.6°, which values are in good agreement with the experimental values (116.6° and 128.8° [48–50], respectively). These results strongly suggest that the B3LYP/LANL2DZ + dp calculations are reliable enough for the present purpose.

3.2. Geometric and electronic structures of 7-Rea-E

Other reactants for seven-member heavy carbene analogues (**7-Rea-E**) were also examined at both singlet and triplet states, which were calculated at the B3LYP/LANL2DZ + dp level.
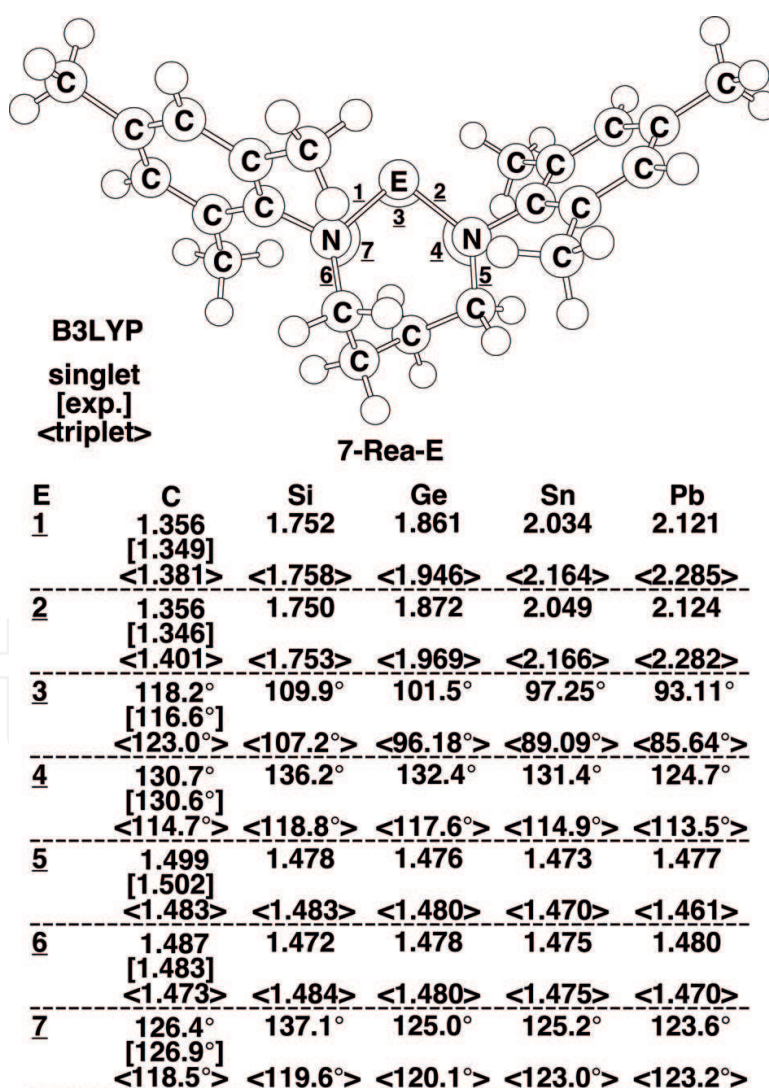

B3LYP singlet [exp.] <triplet>					
7-Rea-E					
E	C	Si	Ge	Sn	Pb
1	1.356 [1.349] <1.381>	1.752 <1.758>	1.861 <1.946>	2.034 <2.164>	2.121 <2.285>
2	1.356 [1.346] <1.401>	1.750 <1.753>	1.872 <1.969>	2.049 <2.166>	2.124 <2.282>
3	118.2° [116.6°] <123.0°>	109.9° <107.2°>	101.5° <96.18°>	97.25° <89.09°>	93.11° <85.64°>
4	130.7° [130.6°] <114.7°>	136.2° <118.8°>	132.4° <117.6°>	131.4° <114.9°>	124.7° <113.5°>
5	1.499 [1.502] <1.483>	1.478 <1.483>	1.476 <1.480>	1.473 <1.470>	1.477 <1.461>
6	1.487 [1.483] <1.473>	1.472 <1.484>	1.478 <1.480>	1.475 <1.475>	1.480 <1.470>
7	126.4° [126.9°] <118.5°>	137.1° <119.6°>	125.0° <120.1°>	125.2° <123.0°>	123.6° <123.2°>

Figure 1. B3LYP/LANL2DZ + dp optimized geometries (in Å and deg) of the reactants **7-Rea-E** (E = C, Si, Ge, Sn, and Pb) at the singlet and triplet states. The experimental values (see ref. [51]) are in parenthesis. Hydrogens are omitted for clarity.

The selected geometrical parameters of **7-Rea-E** for the singlet and triplet states are detailed in **Figure 1** and compared with some available experimental data [48–50]. The calculated molecular orbitals (MOs) for the **7-Rea-E** molecules are given in **Figure 2**. Several important conclusions can be drawn from these figures.

Firstly, as seen in **Figure 1**, regardless of whether it is a singlet or triplet of neutral **7-Rea-E** compounds, the E—N bond length shows a monotonic increase in the period, from C toward Pb. For instance, for the singlet neutral group 14 **7-Rea-E**, the E—N distances increase in the order: **7-Rea-C** (1.356 Å) <**7-Rea-Si** (1.751 Å) <**7-Rea-Ge** (1.867 Å) <**7-Rea-Sn** (2.042 Å) <**7-Rea-Pb** (2.123 Å). The same phenomenon is observed for the triplet neutral group 14 **7-Rea-E**, as given in **Figure 1**.

However, irrespective of its multiplicity, the bond angle, ∠NEN, decreases uniformly as the central atom, E, progresses from C to Pb. For example, the bond angle, ∠NEN, decreases in the order: 118.2° (**7-Rea-C**) > 109.9° (**7-Rea-Si**) > 101.5° (**7-Rea-Ge**) > 97.25° (**7-Rea-Sn**) > 93.11° (**7-Rea-Pb**)
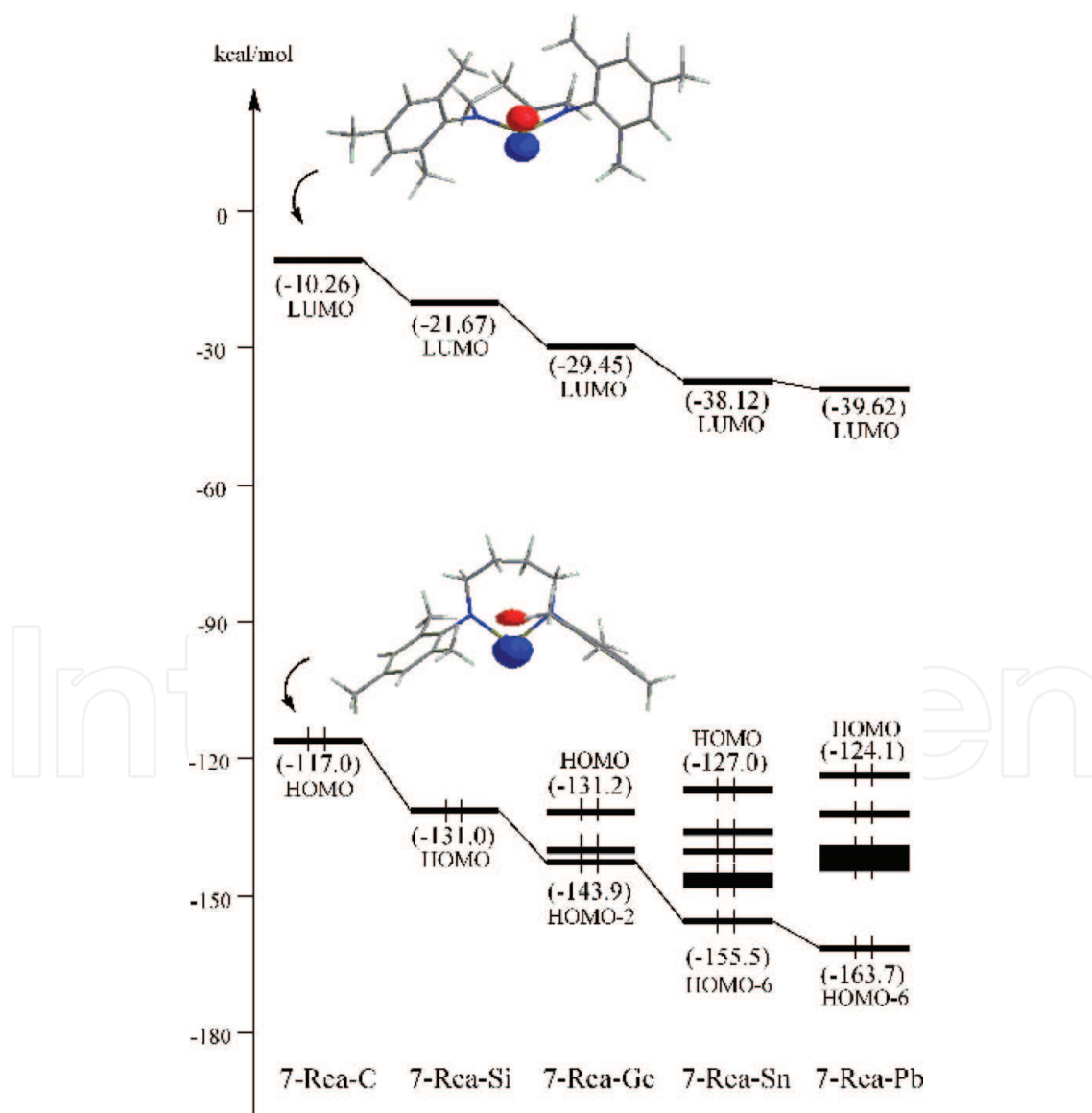

Figure 2. Calculated frontier molecular orbitals for the **7-Rea-E** (E = C, Si, Ge, Sn, and Pb) species. For more information see the text.

and 123.0° (**7-Rea-C**) > 107.2° (**7-Rea-Si**) > 96.18° (**7-Rea-Ge**) > 89.09° (**7-Rea-Sn**) > 85.64° (**7-Rea-Pb**), at the singlet and triplet states, respectively. Accordingly, it is apparent that the angles at the group 14 elements generally decrease as atomic number increases (from C to Pb). This can be attributed to the relativistic effect [54–57]. As a result, the heavier group 14 elements have a stronger tendency to maintain the $(ns)^2(np)^3$ valence electron configuration. Subsequently, the ∠NEN angle monotonously decreases from **7-Rea-C** to **7-Rea-Pb**, for both singlet and triplet states.

Secondly, in order to gain a greater understanding of the nature of the chemical bonding in the series of **7-Rea-E** reactants, the valence molecular orbitals based on the B3LYP/LANL2DZ + dp calculations are represented in **Figure 2**. Basically, there are two important key orbitals, which determine both the chemical and physical properties off the traditional carbene systems, i.e., the nonbonding σ (sp^2) orbital and the unoccupied p-π orbital, both of which are strongly located on the carbonic center [53].

Note that the nature of the σ and the p-π orbitals in **7-Rea-E** are quite similar to those encountered in traditional group 14 divalent compounds [53]. Nevertheless, their energy levels no longer exist on the HOMO and LUMO, respectively, as is already known for the CH2 system [53]. As seen in **Figure 2**, the substitution of a single E atom at the **7-Rea-E** center decreases the energy of the σ orbital, on going from **7-Rea-C** to **7-Rea-Pb**. Likewise, this substitution also decreases the energy of the unoccupied p-π orbital. The reason for such molecular orbital locations may be attributed to the "orbital non-hybridization effect", also known as the "inert s-pair effect", as discussed earlier [54–57].

Thirdly, the other interesting feature is the singlet-triplet splitting ΔEst (= Etriplet-Esinglet). From **Figure 2**, it is apparent that the magnitude of the difference in energy between the occupied σ (sp^2) and unoccupied p-π for the seven-member-ring heavy NHCs becomes larger along the series from **7-Rea-C** to **7-Rea-Pb**. The DFT calculations indicate that the ΔEst for the **7-Rea-E** species increases in the order: 107 (**7-Rea-C**) < 109 (**7-Rea-Si**) < 114 < (**7-Rea-Ge**) < 123 (**7-Rea-Sn**) 124 (**7-Rea-Pb**) kcal/mol, respectively. In other words, the heavier the central group 14 atom (E), the larger is the ΔEst of the seven-member **7-Rea-E** molecule. Again, as discussed earlier, the reason for this difference can be traced directly to electronic factors. In consequence, the theoretical findings reveal that the electronic perturbation effect, wherein the symmetry of frontier orbitals changes, should play a decisive role in determining the energy ordering of the frontier orbitals. This, in turn, affects the magnitude of ΔEst for the seven-member carbene analogues. It should be noted that the stability of the seven-member-ring heavy NHCs is determined by the singlet-triplet energy separations in **7-Rea-E** . If ΔEst is small, the carbene-type structures are unstable and subsequently easily undergo chemical reaction (such as reaction with solvents, etc.). As already mentioned, the B3LYP calculations demonstrate that the group 14 **7-Rea-E** species have comparatively large ΔEst (> 107 kcal/mol). Accordingly, these molecules should be stable enough to be detected experimentally. The supporting evidence comes from the fact that, so far, one NHC compound with a seven-member ring (i.e., **7-Rea-C**) has been synthesized and characterized [48–50]. Also, the synthesis and structure of a dialkylplumbylene with a similar substitution pattern was reported recently in which the lead atom is part of a seven-member ring [58].

Finally, since the DFT calculations indicate that the **7-Rea-E** (E = C, Si, Ge, Sn and Pb) molecules all possess a singlet ground state, then all related chemical reactions (Eqs. (1)–(3)) should proceed on the singlet surface. This study shall, therefore, herewith focus on the singlet surface.

3.3. Geometries and energetics of 7-Rea-E+ H_2O

The mechanisms, which proceed via Eq. (1), are now considered, focusing on the transition states, as well as on the addition products themselves. That is, the addition mechanisms may be thought to proceed as follows: reactants (**7-Rea-E+ H2O**) → transition state (**7-TS-E-1**) → product (**7-Pro-E-1**). The optimized geometries, calculated at the B3LYP/LANL2DZ + dp level of theory, involving **7-TS-E-1** and **7-Pro-E-1** are detailed in **Figure 3**. The corresponding relative energies at the B3LYP level of theory are given in **Table 1**. There are several important conclusions that can be drawn from these results.

Firstly, in relation to the O-H bond addition reaction path, the transition state for each **7-Rea-E** case (**7-TS-C-1**, **7-Rea-Si-1**, **7-TS-Ge-1**, **7-TS-Sn-1**, and **7-TS-Pb-1**) has been located at the DFT level of theory. As can be seen in **Figure 3**, all five transition state structures show the same three-center pattern, involving E, oxygen and hydrogen atoms. The transition state vectors indicate an addition process, primarily with O━H bond stretching, accompanied by migration of a hydrogen atom to the E center.

However, in the transition state, there is a trend for the stretching O━H′ bond to become longer and for the forming E━H′ bond length to increase, as E increases in atomic weight. For instance, the breaking O━H′ bond lengths (Å) are 1.241 (**7-TS-C-1**), 1.303 (**7-TS-Si-1**), 1.419 (**7-TS-Ge-1**), 1.496 (**7-TS-Sn-1**) and 1.656 (**7-TS-Pb-1**), respectively, whereas the forming E━O bond lengths (Å) are 0.682 (**7-TS-C-1**), 0.459 (**7-TS-Si-1**), 0.413 (**7-TS-Ge-1**), 0.284 (**7-TS-Sn-1**) and 0.357 (**7-TS-Pb-1**) longer than that in the (7-Rea-E)(H)(OH) addition product. That is to say, the O-H bond addition happens earlier along the reaction coordinate for **7-Rea-E** with lighter carbene centers. In other words, the E━H′ and E━O bond lengths in the transition structure are more product-like for E = Sn and Pb, and more reactant-like for E = C and Si. On the basis of the Hammond postulate [59], **7-TS-Sn-1** and **7-TS-Pb-1** should have the highest activation barriers and **7-TS-C-1** and **7-TS-Si-1** the smallest. Additionally, the barrier height (Gibbs free energy) for the O━H addition reaction decreases in the order (kcal/mol): **7-TS-Pb-1** (+66) >**7-TS-Sn-1** (+48) >**7-TS-Ge-1** (+44) >**7-TS-Si-1** (+30) >**7-TS-C-1** (+21). These values strongly suggest that the heavier the atomic number of the E center, the greater is the barrier to O━H addition.

System	$\Delta E^{\ddagger 2}$ (kcal mol^{-1})	ΔH^3 (kcal mol^{-1})
7-Rea-C	8.51 [21.1]	−51.3 [−41.4]
7-Rea-Si	21.1 [30.2]	−19.4 [−8.96]
7-Rea-Ge	33.7 [44.2]	−12.2 [−0.105]
7-Rea-Sn	37.0 [48.2]	−7.50 [+3.89]
7-Rea-Pb	56.5 [66.4]	+29.0 [+39.0]

[1]All were calculated at the B3LYP/LANL2DZ + dp level of theory. The B3LYP optimized structures of the stationary points see **Figure 3**. The Gibbs free energies are given in the square bracket.

[2]The activation energy of the transition state, relative to the corresponding reactants.

[3]The reaction enthalpy of the product, relative to the corresponding reactants.

Table 1. Relative energies for the addition reaction of the singlet group 14 **7-Rea-E** species with water: Reactants (**7-Rea-E** + H_2O) → Transition state (**7-TS-E-1**) → Addition product (**7-pro-E-1**)[1].

7-Rea-E + H₂O

E	C	Si	Ge	Sn	Pb
E-O	2.089	2.131	2.193	2.230	2.375
E-H'	1.094	1.621	1.639	1.780	1.791
O-H'	1.241	1.303	1.419	1.496	1.656
∠O-E-H'	37.49°	38.58°	41.71°	42.64°	47.15°
E-N₁	1.342	1.731	1.832	2.009	2.085
E-N₂	1.340	1.728	1.836	2.013	2.084

7-TS-E-1

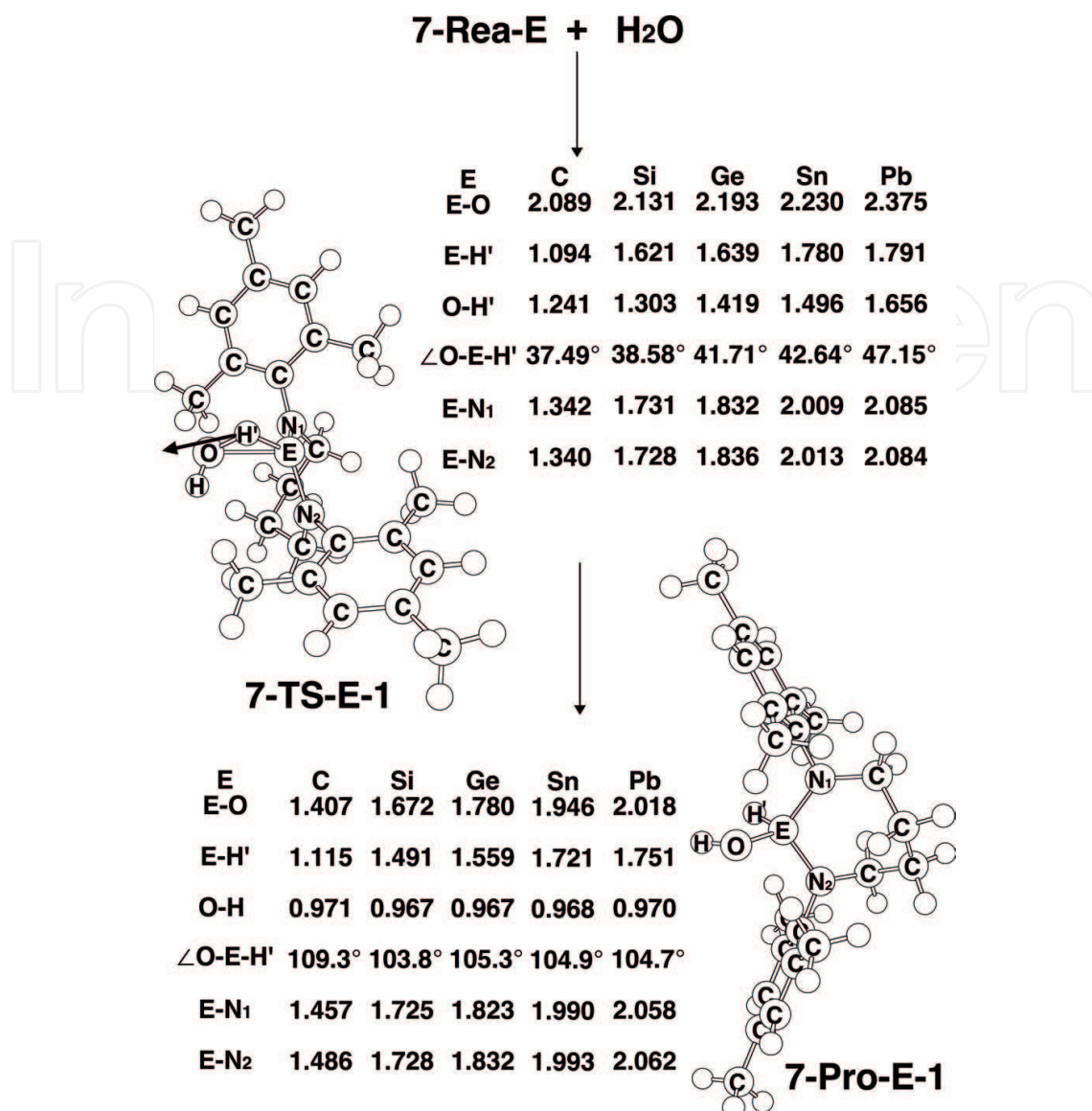| E	C	Si	Ge	Sn	Pb
E-O	1.407	1.672	1.780	1.946	2.018
E-H'	1.115	1.491	1.559	1.721	1.751
O-H	0.971	0.967	0.967	0.968	0.970
∠O-E-H'	109.3°	103.8°	105.3°	104.9°	104.7°
E-N₁	1.457	1.725	1.823	1.990	2.058
E-N₂	1.486	1.728	1.832	1.993	2.062

7-Pro-E-1

Figure 3. B3LYP/LANL2DZ + dp optimized geometries (in Å and deg) of transition states (**7-TS-E-1**), and water addition products (**7-pro-E-1**) of **7-Rea-E** (E = C, Si, Ge, Sn, and Pb). The relative energies for each species see **Table 1**. Hydrogens are omitted for clarity.

Secondly, as **Figure 3** shows, the order of the E-O bond length for the water addition product increases as the atomic weight of the carbene atom, E: **7-Pro-C-1** (1.407 Å) <**7-Pro-Si-1** (1.672 Å) <**7-Pro-Ge-1** (1.780 Å) <**7-Pro-Sn-1** (1.946 Å) <**7-Pro-Pb-1** (2.018 Å). To the authors' best knowledge, experimental structures for such compounds have not yet been identified [48–50]. As already mentioned, a group 14 **7-Rea-E** with a lighter atomic weight carbene E atom reaches the transition state relatively early, whereas one with a carbene atom, E, of a heavier atomic weight arrives relatively late. For example, the order of Gibbs free enthalpy follows the same trend as the activation energy (kcal/mol): **7-Pro-C-1** (−41) <**7-Pro-Si-1** (−9.0) <**7-Pro-Ge-1** (−0.11) <**7-Pro-Sn-1** (+3.9) <**7-Pro-Pb-1** (+39). Note that the free energies of **7-Pro-C-1** and **7-Pro-Si-1** are lower than those of their corresponding starting materials, whereas the free energies of **7-Pro-Sn-1** and **7-Pro-Pb-1** are higher than those of their corresponding starting materials. Consequently, the theoretical findings strongly indicate that the seven-member carbene (**7-Rea-C**) and silylene (**7-Rea-Si**) should be greatly damaged in moist environments, while the

seven-member heavy carbene analogues (such as **7-Rea-Sn** and **7-Rea-Pb**) are moisture-stable compounds. Unfortunately, to the best of the authors' knowledge, no experiments relating to the effect of moisture on **7-Rea-E** molecules have been reported. Therefore, this is a prediction.

Thirdly, all of the above DFT results can be rationalized on the basis of the configuration-mixing (CM) model of Pross and Shaik [60–63]. According to this model, the stabilization of an addition transition state depends on the singlet-triplet splitting, ΔEst (= $E_{triplet}$-$E_{singlet}$), of the reactant group 14 **7-Rea-E**; i.e., a smaller ΔEst results in a more stable transition state, a lower activation energy, a faster addition reaction and a more exothermic reaction. It is necessary to emphasize the importance of the status of the triplet states of the group 14 **7-Rea-E** reactants. Since two new covalent bonds must be formed in the addition product, 7-Rea-E(OH)(H) (**7-Pro-E-1**), i.e., the E-OH and E-H bonds (**Figure 3**), the bond-prepared **7-Rea-E** state thus must have at least two open shells and the lowest state of this type is the triplet state. Therefore, from the standpoint of valence-bonding [60–63], the bonding in the product can be considered to be between the triplet **7-Rea-E** state and the two doublet radicals (overall singlet), the OH radical and the hydrogen atom. This is much the same as bonding in the water molecule. Namely, H_2O is considered to be between two doublet hydrogen atoms and a triplet oxygen atom [60–63]. As indicated earlier, the DFT results suggest an increasing trend in ΔEst for the **7-Rea-E** reactant, along the group 14 family. This result is in accordance with the trends in activation energy and reaction enthalpy ($\Delta E^{\ddagger}$, ΔH) for group 14 seven-member **7-Rea-E** species, as already discussed. These results strongly support the previous predictions that the smaller the ΔEst of the group 14 seven-member **7-Rea-E**, the lower is the barrier height and, in turn, the faster is the water addition reaction and the more exothermic is the reaction.

3.4. Geometries and energetics of 7-Rea-E+ PhHC = NPh

The cycloaddition reactions, which proceed via Eq. (2), are now considered. To ensure consistency with previous work, the following reaction mechanism is used to examine the cycloaddition reaction of group 14 **7-Rea-E** molecules with imine: reactants (**7-Rea-E** + PhHC = NPh) → transition state (**7-TS-E-2**) → cycloaddition product (**7-Pro-E-2**). The geometries and energetics of the systems (E = C, Si, Ge, Sn and Pb) were calculated using the B3LYP/LANL2DZ + dp level of theory. Selected geometrical parameters and the relative energies of stationary points for the above mechanism are detailed in **Figure 4** and **Table 2**, respectively. The major conclusions to be drawn from the current study can be summarized as follows.

Firstly, a seven-member **7-Rea-E** species and imine (PhHC = NPh) are predicted to undergo a [1 + 2] cycloaddition to produce a cycloaddition product. From **Figure 4**, all of these transition states (i.e., **7-TS-C-2**, **7-TS-Si-2**, **7-TS-Ge-2**, **7-TS-Sn-2** and **7-TS-Pb-2**) proceed in a three-center pattern that involves the carbon, nitrogen and the group 14, E, atoms. The B3LYP computational normal modes associated with the single imaginary frequency are consistent with the C = N activation process, primarily the C = N bond stretching with the migration of an E atom to the double bond. It should be noted that these characteristic three-centered cyclic transition states are quite analogous to the mechanisms observed for the cycloaddition reactions of singlet carbenes [64].

Secondly, the DFT results demonstrate that the larger the ∠N1EN2 bond angle, the more reactant-like is the transition state structure, as shown in **Figure 4** [54–57]. Comparison of the C1━N′ bond length in the TS structures with the corresponding distance in imine (1.283 Å)
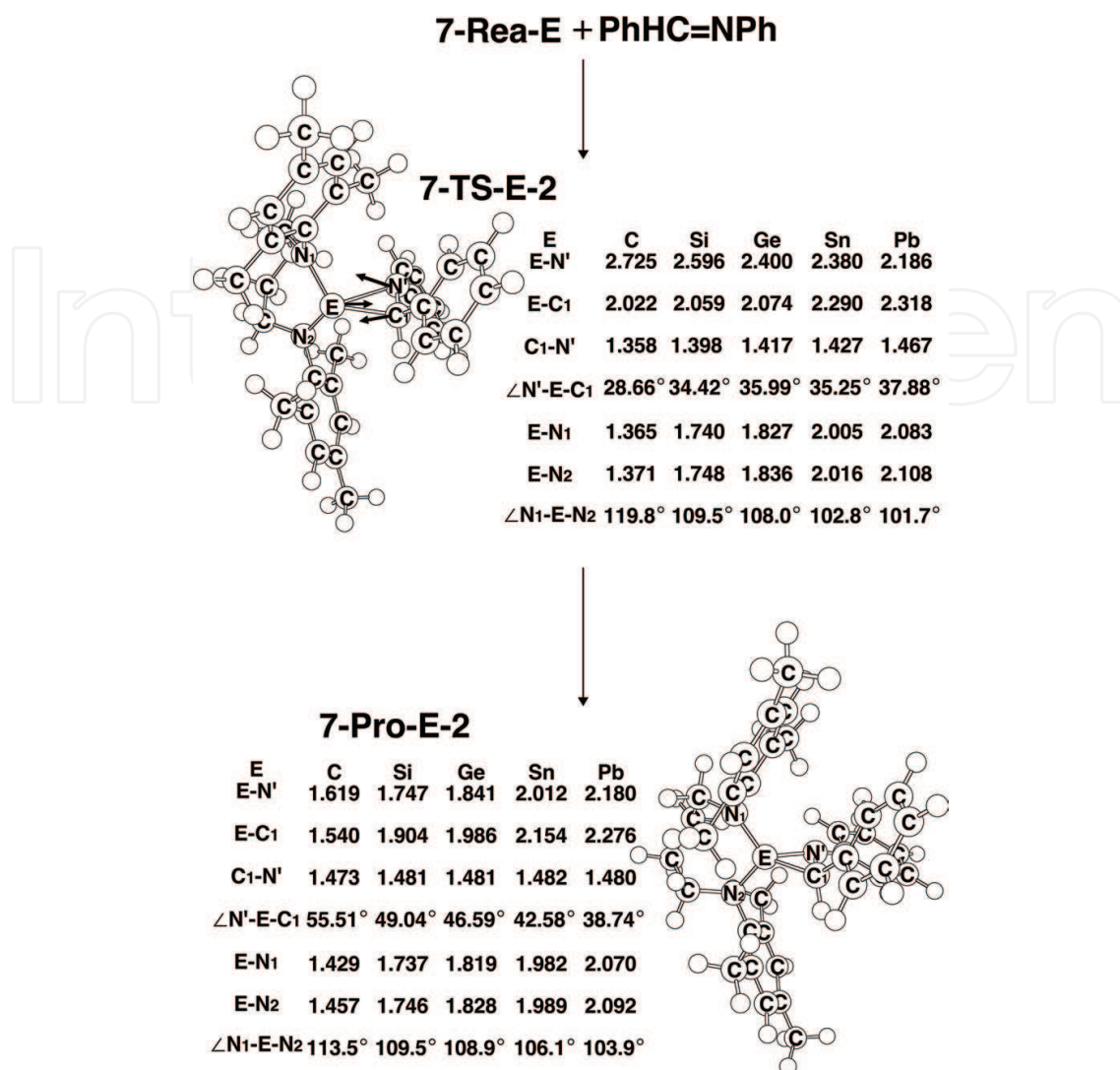
7-Rea-E + PhHC=NPh

7-TS-E-2

E	C	Si	Ge	Sn	Pb
E-N'	2.725	2.596	2.400	2.380	2.186
E-C$_1$	2.022	2.059	2.074	2.290	2.318
C$_1$-N'	1.358	1.398	1.417	1.427	1.467
∠N'-E-C$_1$	28.66°	34.42°	35.99°	35.25°	37.88°
E-N$_1$	1.365	1.740	1.827	2.005	2.083
E-N$_2$	1.371	1.748	1.836	2.016	2.108
∠N$_1$-E-N$_2$	119.8°	109.5°	108.0°	102.8°	101.7°

7-Pro-E-2

E	C	Si	Ge	Sn	Pb
E-N'	1.619	1.747	1.841	2.012	2.180
E-C$_1$	1.540	1.904	1.986	2.154	2.276
C$_1$-N'	1.473	1.481	1.481	1.482	1.480
∠N'-E-C$_1$	55.51°	49.04°	46.59°	42.58°	38.74°
E-N$_1$	1.429	1.737	1.819	1.982	2.070
E-N$_2$	1.457	1.746	1.828	1.989	2.092
∠N$_1$-E-N$_2$	113.5°	109.5°	108.9°	106.1°	103.9°

Figure 4. B3LYP/LANL2DZ + dp optimized geometries (in Å and deg) of transition states (**7-TS-E-2**), and cycloaddition products (**7-pro-E-2**) of **7-Rea-E** (E = C, Si, Ge, Sn, and Pb) and imine. The relative energies for each species see **Table 2**. Hydrogens are omitted for clarity.

System	$\Delta E^{\ddagger 2}$ (kcal mol^{-1})	ΔH^3 (kcal mol^{-1})
7-Rea-C	9.62 [14.9]	−27.0 [−20.5]
7-Rea-Si	12.4 [18.9]	+4.85 [+11.2]
7-Rea-Ge	20.9 [26.7]	+5.10 [+12.1]
7-Rea-Sn	25.5 [30.1]	+19.6 [+25.2]
7-Rea-Pb	47.5 [51.7]	+48.3 [+52.8]

[1]All were calculated at the B3LYP/LANL2DZ + dp level of theory. The B3LYP optimized structures of the stationary points see **Figure 4**. The Gibbs free energies are given in the square bracket.

[2]The activation energy of the transition state, relative to the corresponding reactants.

[3]The reaction enthalpy of the product, relative to the corresponding reactants.

Table 2. Relative energies for the cycloaddition reaction of the singlet group 14 **7-Rea-E** species with imine: Reactants (**7-Rea-E** + PhHC=NPh) → transition state (**7-TS-E-2**) → addition product (**7-pro-E-2**)[1].

shows that the C1━N′ bond distance in the transition structures is stretched by 5.9, 9.0, 10, 11 and 14% for **7-TS-C-2**, **7-TS-Si-2**, **7-TS-Ge-2**, **7-TS-Sn-2** and **7-TS-Pb-2**, respectively. All of the theoretical data indicate that the structures of the TSs (**7-TS-E-2**) are as expected from Hammond's postulate [59]. Namely, the [1 + 2] cycloaddition for the seven-member **7-Rea-E** that possesses lighter group 14 elements, E, has lower activation energy, since its TS resembles the corresponding reactants more closely than the final products. From **Table 2**, it is easily seen that the Gibbs free activation energy (kcal/mol) of the **7-TS-E-2** follows the same trend as the ΔEst in the seven-member **7-Rea-E** system, i.e., **7-TS-C-2** (+15) <**7-TS-Si-2** (+19) <**7-TS-Ge-2** (+27) <**7-TS-Sn-2** (+30) <**7-TS-Pb-2** (+52). That is to say, according to the CM model [60–63], it is predicted that seven-member **7-Rea-E** molecules with a lighter atomic weight E atom have a larger ∠N1EN2 bond angle, a smaller ΔEst and experience easier cycloaddition to imine.

Thirdly, as can be seen in **Table 3**, the Gibbs free energy of the final cycloproducts, relative to their corresponding reactants, increases in the order: **7-Pro-C-2** (−21) <**7-Pro-Si-2** (+11) <**7-Pro-Ge-2** (+12) <**7-Pro-Sn-2** (+25) <**7-Pro-Pb-2** (+53), indicating that the reactions of seven-member **7-Rea-E** molecules with heavier group 14 atoms (E) are endothermic. It should also be noted that the order of the reaction enthalpy follows the same trend as the ∠N1EN2 bond angle and the ΔEst. In other words, the model calculations demonstrate that the values of ΔEst can be used as a criterion to predict the reactivity of seven-member **7-Rea-E** compounds.

3.5. Geometries and electronic structures of dimerization reactions

The dimerization reaction of the seven-member **7-Rea-E** molecule was examined in this work in order to understand more about their kinetic stability. Selected geometrical parameters along the pathway, shown in Eq. (3) and computed at the B3LYP/LANL2DZ + dp level, are collected in **Figure 5**. The relative energies at the same level of theory are listed in **Table 3**. **Figure 5** and **Table 3** have several noteworthy features.

Firstly, as predicted, a double bond between the two group 14 E atoms should be formed during the dimerization reaction of two **7-Rea-E** molecules. However, repeated attempts to determine the transition state for the concerted dimerization of two **7-Rea-E** compounds, using the B3LYP/LANL2DZ + dp level of theory, are always unsuccessful. That is to say, no transition states exist on the B3LYP surface for such dimerization reactions. Further, the B3LYP calculations demonstrate that all five dimers (i.e., **7-Pro-C-3**, **7-Pro-Si-3**, **7-Pro-Ge-3**, **7-Pro-Sn-3** and **7-Pro-Pb-3**) do not have the imaginary frequency. Therefore, they can be considered as true minima on the potential energy surfaces. As stated earlier, unfortunately, because of a lack of experimental and data on such species, geometrical information studied in this work should be considered as predictions for future investigations.

Secondly, as demonstrated in **Figure 4**, the E━E bond length in the dimer molecule was calculated to decrease in the order: 1.436 Å (**7-Pro-C-3**) < 2.491 Å (**7-Pro-Si-3**) < 2.602 Å (**7-Pro-Ge-3**) < 2.941 Å (**7-Pro-Sn-3**) < 3.493 Å (**7-Pro-Pb-3**), which correlates with the atomic size of the main group 14 element, E, as it changes from carbon to lead. It must be stressed that the computed E = E double bond lengths are somewhat larger than the experimental values (1.356 [65, 66], 2.139–2.360 [67, 68], 2.212–2.509 [69, 70], 2.601–2.961 [71, 72] and 2.990–3.537 [73, 74] Å, for C=C, Si = Si, Ge = Ge, Sn = Sn and Pb = Pb, respectively). The former
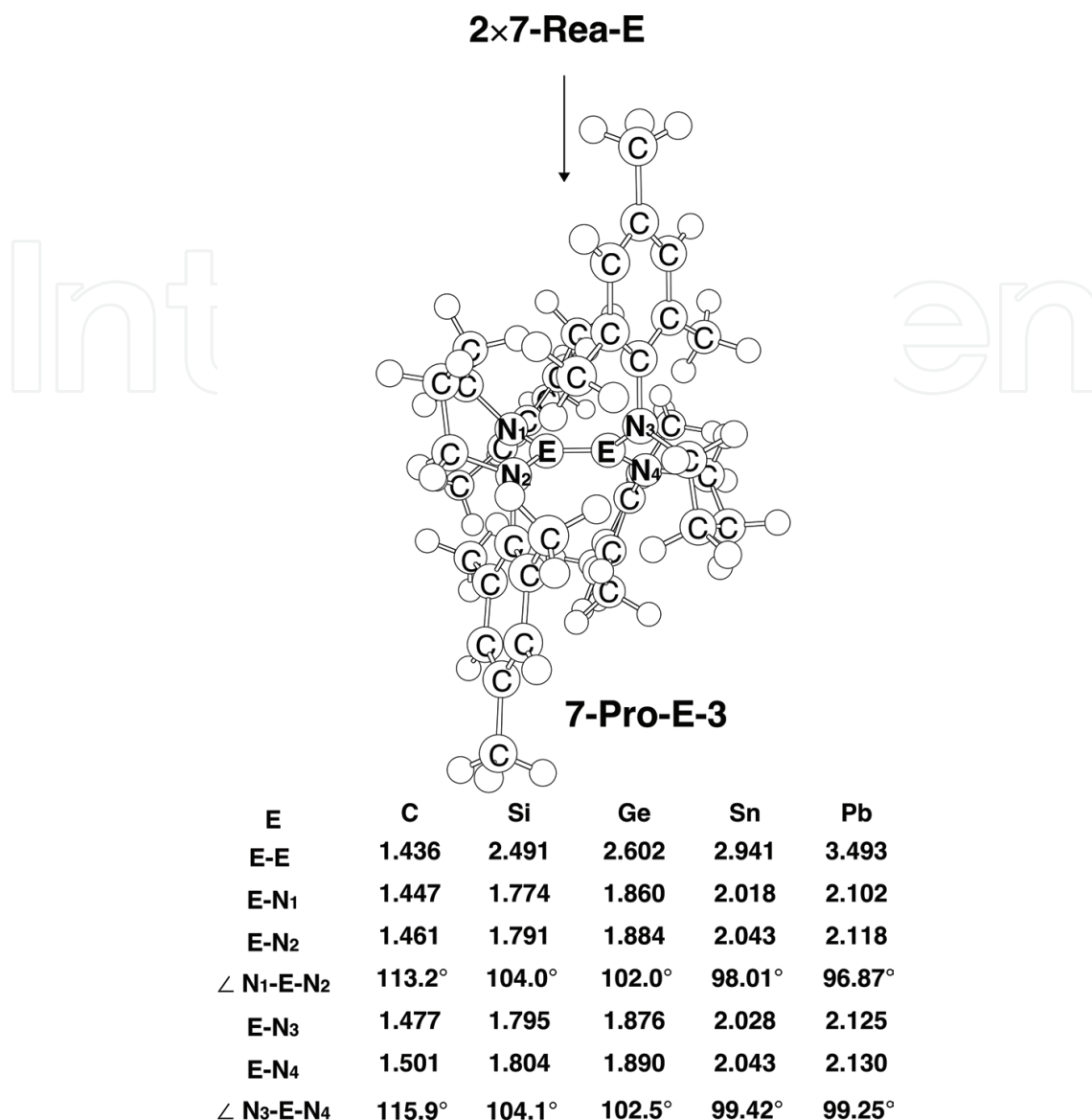
2×7-Rea-E

7-Pro-E-3

E	C	Si	Ge	Sn	Pb
E-E	1.436	2.491	2.602	2.941	3.493
E-N$_1$	1.447	1.774	1.860	2.018	2.102
E-N$_2$	1.461	1.791	1.884	2.043	2.118
∠ N$_1$-E-N$_2$	113.2°	104.0°	102.0°	98.01°	96.87°
E-N$_3$	1.477	1.795	1.876	2.028	2.125
E-N$_4$	1.501	1.804	1.890	2.043	2.130
∠ N$_3$-E-N$_4$	115.9°	104.1°	102.5°	99.42°	99.25°

Figure 5. B3LYP/LANL2DZ + dp optimized geometries (in Å and deg) of the dimer products of **7-Rea-E**(E = C, Si, Ge, Sn, and Pb). The relative energies for each species see **Table 3**. Hydrogens are omitted for clarity.

System	ΔH^2 (kcal mol^{-1})	ΔG^3 (kcal mol^{-1})
7-Rea-C	+9.31	+16.3
7-Rea-Si	+13.1	+21.0
7-Rea-Ge	+20.7	+28.7
7-Rea-Sn	+23.0	+31.2
7-Rea-Pb	+44.1	+56.0

[1]All were calculated at the B3LYP/LANL2DZ + dp level of theory. The B3LYP optimized structures of the stationary points see **Figure 5**.

[2]The reaction enthalpy of the product, relative to the corresponding reactants.

[3]The Gibbs free enthalpy of the product, relative to the corresponding reactants.

Table 3. Relative energies for the dimerization reaction of the singlet group 14 **7-Rea-E** species: Reactants (2 **7-Rea-E**) → dimerization product (**7-pro-E-3**)[1].

computed values might be attributable to steric effects, which cause the dimer formed by seven-member N-heterocyclic carbene analogues to have a longer double bond distance than the less substituted dimetallene itself. However, the DFT calculations show that the energy of the final product (dimers), relative to its corresponding reactants, is 33 (**7-Pro-C-3**), 38 (**7-Pro-Si-3**), 43 (**7-Pro-Ge-3**), 49 (**7-Pro-Sn-3**) and 54 (**7-Pro-Pb-3**) kcal/mol. Also, as seen in **Table 3**, the difference in the values of ΔG between the reactants and the dimer are 46, 58.4, 55, 57 and 68.2 kcal/mol, for carbon, silicon, germanium, tin and lead species, respectively. Consequently, the computational results predict that the dimerization reaction should not occur during the formation of the seven-member **7-Rea-E** (E = C, Si, Ge, Sn and Pb) species at room temperature.

4. Conclusion

This study uses the B3LYP level of theory to study the mechanisms and reactivity for three types of chemical reactions of carbene analogues, **7-Rea-E** (E = C, Si, Ge, Sn and Pb), which possess a seven-member-ring. It should be noted that this study provides the first theoretical demonstration of the reaction trajectory and the first theoretical estimation of the activation energy and the reaction enthalpy for these chemical processes. In relation to the aforementioned five seven-member heavy carbine systems and their related chemical reactions, as studied in this paper, the following conclusions can be drawn:

1. With regard to both the activation barrier and the reaction enthalpy, based on the model calculations presented here, it is concluded that the seven-member **7-Rea-E** reactivity order is as follows: **7-Rea-C** > **7-Rea-Si** > **7-Rea-Ge** > **7-Rea-Sn** > **7-Rea-Pb**. In other words, a **7-Rea-E** molecule possessing a group 14 atom, E, of lower atomic number accelerates chemical reactions, whereas a **7-Rea-E** compound bearing a group 14 atom, E, of higher atomic number hinders reactions. From this conclusion, it is predicted that the heavy carbene analogues with a seven-membered ring can be synthesized and isolated. Indeed, it was recently reported that the stable carbon(II) and lead(II) compounds bearing a seven-membered ring, the so-called dialkylcarbene (**7-Rea-C**) and dialkylplumbylene, have been synthesized and structurally characterized [48–50, 58].

2. This theoretical work suggests that seven-member cyclic **7-Rea-E** compounds that feature a lighter group 14 element, E (such as **7-Rea-C** and **7-Rea-Si**), should be moisture-sensitive, whereas the seven-member heavy carbene analogues (such as **7-Rea-Sn** and **7-Rea-Pb**) are moisture-stable compounds.

3. This theoretical work reveals that the [1 + 2] imine cycloadditions of seven-member **7-Rea-E** molecules produces the final cycloadduct in a concerted manner. That is, these cycloadditions proceed stereospecifically and result in cycloproducts that retain their stereochemistry.

4. These theoretical investigations strongly suggest that the dimerization reaction should not occur during the formation of the seven-member **7-Rea-E** (E = C, Si, Ge, Sn and Pb) species. Indeed, this theoretical conclusion is in good agreement with the available experimental observations [48–50].

5. This study shows that knowledge of the singlet-triplet splitting (ΔE_{st}) of the seven-member carbene analogues **7-Rea-E** is of great importance in achieving a deeper understanding of their reactivity, since it is the driving force for the related reactions.

6. This study demonstrates that the heavier the atomic weight of group 14 elements, E, involved in the seven-member **7-Rea-E**, the larger is the ΔE_{st}, the higher is the activation barrier and the smaller is the enthalpy of its final product. Consequently, based on these theoretical conclusions, it is easily predicted that the heavier seven-member **7-Rea-E** (such as E = Si, Ge, Sn and Pb) should be readily synthesized and isolated at room temperature.

Acknowledgements

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