

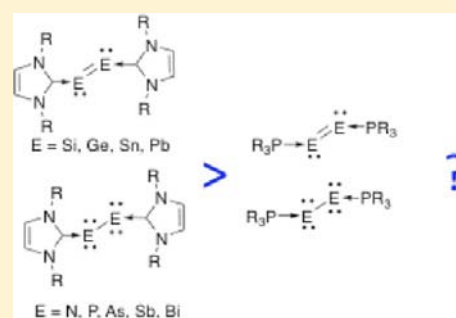
Are N-Heterocyclic Carbenes “Better” Ligands than Phosphines in Main Group Chemistry? A Theoretical Case Study of Ligand-Stabilized E₂ Molecules, L-E-E-L (L = NHC, phosphine; E = C, Si, Ge, Sn, Pb, N, P, As, Sb, Bi)

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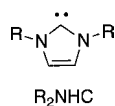
Supporting Information

ABSTRACT: A theoretical examination of the L-E-E-L class of molecules has been carried out (E = group 14, group 15 element; L = N-heterocyclic carbene, phosphine), for which Si, Ge, P, and As-NHC complexes have recently been synthesized. The focus of this study is to predict whether it is possible to stabilize the elusive E₂ molecule via formation of L-E-E-L beyond the few known examples, and if the ligand set for this class of compounds can be extended from the NHC to the phosphine class of ligands. It is predicted that thermodynamically stable L-E-E-L complexes are possible for all group 14 and 15 elements, with the exception of nitrogen. The unknown ligand-stabilized Sn₂ and Pb₂ complexes may be considered attractive synthetic targets. In all cases the NHC complexes are more stable than the phosphines, however several of the phosphine derivatives may be isolable. The root of the extra stability conferred by the NHC ligands over the phosphines is determined to be a combination of the NHCs greater donating ability, and for the group 15 complexes, superior π acceptor capability from the E-E core. This latter factor is the opposite as to what is normally observed in transition metal chemistry when comparing NHC and phosphine ligands, and may be an important consideration in the ongoing “renaissance” of low-valent main group compounds supported by ligands.



INTRODUCTION

The discovery of an isolable N-heterocyclic carbene (NHC) by Arduengo and co-workers in 1991 is considered a landmark report in synthetic chemistry.¹



Since that time, NHCs have found a myriad of uses, most conspicuously in transition metal (TM) catalysis and organocatalysis. In the area of NHC–TM coordination chemistry, the field did not grow to any great extent immediately after Arduengo’s discovery. As pointed out in a review by Nolan,² at that stage NHCs were simply considered phosphine alternatives as neutral two-electron ligands, and significantly less convenient than the commercially available phosphines. However, following the report by Herrmann et al.³ of a catalytically relevant NHC complex, the field of NHC–TM-based chemistry expanded rapidly. It has become clear that NHCs are not simply an alternative to phosphines, but they are often a superior choice. This preference for NHCs arises from differences in the electronic structures of NHC–TM complexes versus phosphine–TM complexes. The NHCs exhibit a highly directional sp²-type lone pair in comparison with the nondirectional s-type lone pair in phosphines, from which

NHCs form stronger σ -bonds to a wide variety of TMs. This stronger donating ability of NHCs versus phosphines can be reflected by larger proton affinities found for NHCs.^{4–6} N-heterocyclic carbenes also do not participate in π backbonding interactions with TMs as readily as phosphines (although it is now clear this interaction cannot be ignored).^{7–13} As a result, a given metal will be more electron rich as a NHC-metal complex compared to the corresponding phosphine complex, which has major implications in the rates of a variety of catalytic processes. For example, the use of NHCs as a ligand for Pd in Suzuki coupling allows for unactivated aryl chlorides to be used as a substrate.² Additionally, NHC–TM bonds are less prone to dissociation, which has implications for catalyst decomposition and can lead to an increase in turnover numbers. A good example of this effect is the evolution of the Grubbs olefin metathesis catalyst from generation I to II, with a substantial increase in stability of the active species in moving from a bis-phosphine catalyst to a mixed phosphine–carbene catalyst.¹⁴ Thus, in the realm of transition metal catalysis, it could be said that there is an “NHC” effect. Several excellent reviews and books are now devoted to the area of NHC–TM complexes in catalysis, with a much greater depth

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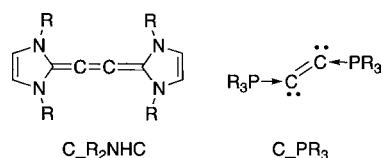
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and breadth on the subject than can be done justice here.^{2,10,15,16}

N-heterocyclic carbene and phosphine coordination chemistry is less developed for the main group (MG), and specifically the p-block elements. Despite the existence of examples of NHC and phosphine complexes for virtually every element,^{17,18} the relatively reduced activity in MG coordination chemistry compared to TM chemistry may be rationalized by the reduced opportunities in catalysis and organic bond activations. Additionally, the tools available to introduce NHCs to MG centers are more limited than in TM chemistry. Transition metal chemists can use air/moisture stable NHC precursors such as imidazolium salts or silver complexes to form NHC–metal bonds through in situ deprotonation, oxidative addition or transmetalation, without the need for inert conditions and the required specialized equipment. These reactions are not typically compatible with common MG starting materials (i.e., p-block halides), so the highly moisture-sensitive free NHCs must be employed.

Despite the challenges, a renaissance in NHC-p-block coordination chemistry is ongoing. There are many reports of fascinating, unusual or long sought after molecular frameworks being isolated as NHC complexes, particularly as low-valent, low-oxidation state species or highly charged species.^{19–25} There are also recent examples of remarkable p-block compounds being isolated as phosphine adducts,²⁶ but currently these are somewhat more rare than NHC complexes. The most well established examples are the family of phosphine-stabilized phosphorus cations from the work of Burford et al.²⁷ However, the implications of switching an NHC ligand for a phosphine and vice versa on a single system have not often been explicitly considered in p-block chemistry. An exception is theoretical studies of the carbodiphosphorane and carbodicarbene class of molecules, related to the feature molecules in this study as base stabilized C₁ molecules,^{28–30} which will be discussed in the context of our observations.

Recently, we performed a theoretical evaluation of the L-C-C-L system, where L = R₃P or R₂NHC.³¹ Major differences were found in the electronic and geometrical structures of these two derivatives. Despite phosphines being superior π acids in TM chemistry, in the case of dicarbon, distinct double bonds were predicted to form between the NHC carbene carbons and the C₂ core, while for phosphines only single bonds were found. This resulted in the NHC complex being calculated to be far more stable than the phosphine adduct as it could exist in a cumulene “resting state”, even though the reactivities of the two molecules in forming complexes with the model Lewis acids H⁺ and BH₃ were calculated as being very similar.

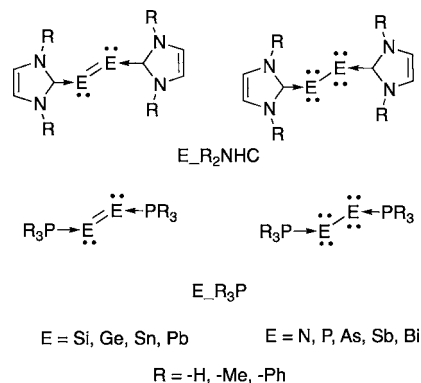


This class of L-E-E-L compounds is experimentally known for L = R₂NHC and E = Si,³² Ge,³³ P,³⁴ and As.³⁵ Very recently E = B was proposed, and experimentally verified soon after.^{36,37} Bertrand and co-workers have also employed cyclic alkyl amino carbenes (CAACs) or NHCs to isolate several P_n fragments with the phosphorus atoms in the formal oxidation state of 0.^{24,38,39} The synthesis of these molecules has been of major interest in forming the new field of p-block molecular

allotropy.^{40,41} The accepted bonding environment for these compounds is a donor–acceptor coordination complex of E₂ (L → EE ← L). In each of these cases where a successful synthesis has been achieved, NHCs were used as the stabilizing ligand.

In light of the reported synthesis of several L-E-E-L compounds and our previous theoretical study, we became interested as to whether other elusive and highly reactive E₂ molecules from group 14 and 15 might also be stabilized in this manner, which would provide impetus for further synthetic advances in this newly developing field. Moreover, our previous theoretical study considered both NHC and phosphine ligands, from which arose a more fundamental question: Why use NHC ligands rather than phosphines for such p-block complexes, and is there a distinct “NHC effect” for main group systems, analogous to that seen in TM chemistry? A wide variety of phosphines are commercially available, easily handled and many can be stored for years in a cap-sealed bottle on the benchtop without any appreciable decomposition (e.g., the ubiquitous PPh₃), which might make them an attractive alternative to NHCs in MG chemistry.

These twin aims have been investigated through a systematic theoretical analysis of L-E-E-L compounds from groups 14 and 15 to compare the stability of the NHC complexes with the analogous, unknown phosphine complexes. To evaluate which unknown L-E-E-L complexes may be the most feasible targets for synthetic efforts, we have additionally evaluated the stability of the donor–acceptor L-EX_n (X = Cl, Br) complexes, which may be considered precursors to the L-E-E-L species.



EXPERIMENTAL SECTION

Geometry optimizations without symmetry constraints were carried out using B3LYP-DFT.^{42,43} Functional dependence was investigated with M06-2X⁴⁴ calculations for geometries and energetics of a subset of L-E-E-L systems, which yielded very similar results to that of B3LYP. The TZVP⁴⁵ basis set was employed for all atoms except the heavier elements Sn, Pb, Sb and Bi, for which the def2-TZVP⁴⁶ basis set and effective core potential were used (simply labeled as TZVP in the following). While relativistic effects are not treated explicitly, the def2-TZVP effective core potentials for heavier elements implicitly account for relativistic effects. Stationary points were characterized as minima by calculating the Hessian matrix analytically at the same level of theory. Thermodynamic corrections were taken from these calculations (standard state of $T = 298.15$ K and $p = 1$ atm). Test calculations with the def2-TZVPP⁴⁶ basis set also produced very similar geometries and energies. The full set of B3LYP/TZVP calculated geometries is given in the Supporting Information (all structures are minima with no imaginary frequencies). Single-point MP2/TZVP energies were calculated using the B3LYP/TZVP optimized geometries. SCS-MP2⁴⁷ and SOS-MP2⁴⁸ single-point energies were also calculated, with results included as Supporting

Information. All tabulated MP2 energies are presented as ΔG values, which combine the MP2/TZVP electronic energy and B3LYP/TZVP thermochemical correction.

Calculations of dissociation of L-E-E-L to $E_2 + 2 L$ employed B3LYP/TZVP optimized E_2 and L geometries and thermal corrections along with MP2/TZVP electronic energies. All L-E-E-L complexes were considered as singlet states. A singlet ground state was used for dicarbon, while all other group 14 homonuclear diatomics were considered as triplet ground states.^{49–51} All group 15 homonuclear diatomics were considered as singlet ground states.^{52–55}

All calculations were carried out within Gaussian 09.⁵⁶ Natural bond orbital (NBO) analysis was carried out with NBO 5.9⁵⁷ at the B3LYP/TZVP level of theory with the exception of natural resonance theory (NRT) calculations, which were carried out at the Hartree–Fock/TZVP level of theory.

RESULTS AND DISCUSSION

Optimized Geometries. Optimized geometries of L-E-E-L for L = R_2 NHC and R_3 P (R = Me) and E = C, Si, Ge, Sn, Pb, N, P, As, Sb, and Bi are represented in Figure 1, with selected geometry parameters collected in Tables 1 and 2. Computational studies have been previously carried out for L = R_2 NHC and E = C,³¹ Si,³² Ge,³³ P,³⁴ and As.³⁵ Our optimized geometries are in good agreement with those previously reported, and in all cases there are no significant changes in the L-E-E-L geometry for R = H, Me, or Ph.

In the C_2 system, major differences were observed in the optimized geometries between L = R_2 NHC and R_3 P.³¹ For L = R_2 NHC, a linear L-E-E-L framework was observed, consistent with a cumulene type structure. For L = R_3 P, a trans-bent geometry was calculated, with P–C and C=C single and double bonds, respectively.

In the heavier group 14 systems (E = Si, Ge, Sn, Sb, Pb), a trans-bent geometry is calculated for E- R_2 NHC rather than the linear geometry calculated for C. This is mirrored in the experimentally verified structures for E = Si and Ge. Substitution of the NHC ligand for R_3 P has virtually no effect on the E–E bond distances or overall molecular geometries for the elements below carbon.

For the noncarbon group 14 systems, the E–E calculated bond distances may be compared to the single-bond covalent radii of Pyykko and Atsumi:⁵⁸ Si–Si 2.32 Å, Ge–Ge 2.42 Å, Sn–Sn 2.80 Å, and Pb–Pb 2.88 Å. Fischer and Power⁵⁹ have reviewed MG complexes with E–E multiple bonds, with E=E double bonds exhibiting ranges of Si 2.138–2.360 Å, Ge 2.212–2.509 Å, Sn 2.601–2.961 Å, and Pb 2.990–4.129 Å. The calculated E–E bonds reported in Table 1 for group 14 complexes are all shorter than the covalent radii single bonds.

For Si- R_2 NHC and Si- R_3 P the Si–Si bond distances (2.250–2.272 Å) are shorter than found in solid silicon (2.35 Å)⁵⁸ and marginally longer than 2.2294(11) Å in the L–E–E–L complex reported by Robinson and co-workers.³² Similarly, the Ge–Ge bond distances in Ge- R_2 NHC and Ge- R_3 P (2.390–2.402 Å) are marginally longer than that reported experimentally for L–Ge–Ge–L (2.3490(8) Å),³³ although slightly shorter than in solid germanium (2.45 Å).⁵⁸

Calculated Sn–Sn bonds (2.762–2.776 Å) are comparable to 2.80 Å in elemental (gray) tin,⁶⁰ 2.77 Å in the first distannene (Sn=Sn) complex of Lappert,⁶¹ 2.6683(10) Å in (tBuMeSi)₂Sn=Sn(tBuMeSi)₂,⁶² and 2.782–2.824 Å in a series of Ar–Sn=Sn–Ar complexes.⁶³ Calculated Pb–Pb bond distances (2.903–2.915 Å) are comparable to 2.9033(9) Å in trans-[(Me3Si)3Si]MesPb₂, 2.8697 Å in (Bp)₃Pb–Pb–(Bp)₃,⁶⁴ 3.1881(3) Å in a trans-bent Ar*–Pb–Pb–Ar*.⁵⁹

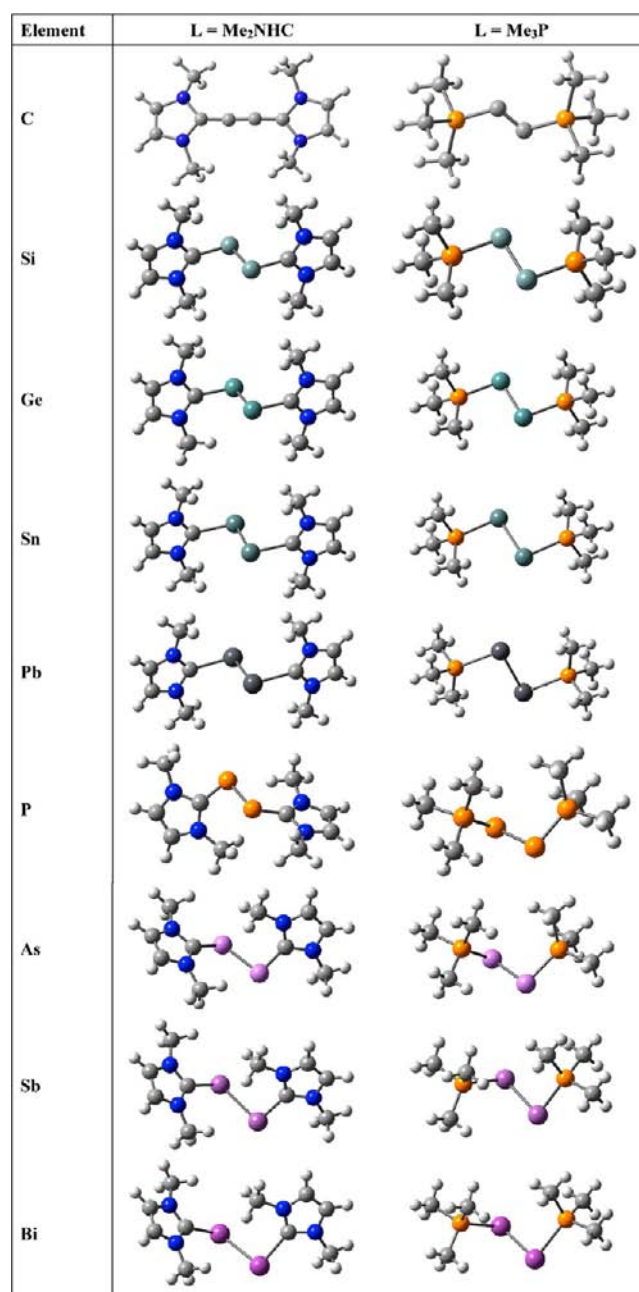


Figure 1. B3LYP/TZVP optimized geometries of L-E-E-L compounds for L = Me_2 NHC and Me_3 P.

All calculated group 14 E–E bonds fall within the range of E=E bonds reviewed by Fischer and Power,⁵⁹ suggesting that the group 14 L-E-E-L complexes are best described as L–E=E–L. In the heavier analogues for both ligand types, the Wiberg Bond Index (WBI) for the E–E bond all lie within the range of 1.63 (Si- H_2 NHC) to 1.84 (Pb- Me_3 P), which is consistent with double bond character. The E–E double bond character is unusual for heavy (e.g., Ge, Sn, Pb), multiply bound group 14 compounds, which typically prefer to adopt singly bound structures with the electrons formally incorporated into the double bond taking on nonbonding character. A rapidly increasing effect is typically observed down the period, particularly for Sn and Pb.⁵⁹

The E–L bond distances for both ligands (R_2 NHC and R_3 P) are consistent with single bond character, corresponding with

Table 1. Optimized Geometries for L-E-E-L Compounds (E = Group 14) with Selected Bond Distances (Å), L-E-E Angles (deg), and L-E-E-L Dihedral Angles (deg)

compound	E	bond distance ^b			angle ^b L-E-E	dihedral L-E-E-L	WBI ^a	
		E-E	E-L	C-N			E-E	E-L
C_H ₂ NHC	C	1.260	1.328	1.418	178.8	180.0	2.11	1.57
C_Me ₂ NHC	C	1.263	1.336	1.412	172.4	180.0	2.12	1.53
C_Ph ₂ NHC	C	1.252	1.343	1.415	173.7	179.8	2.17	1.49
C_H ₃ P	C	c						
C_Me ₃ P	C	1.349	1.780		116.2	180.0	2.00	1.14
C_Ph ₃ P	C	1.316	1.772		125.0	179.1	2.08	1.10
Si_H ₂ NHC	Si	2.272	1.942	1.362	92.4	180.0	1.63	0.86
Si_Me ₂ NHC	Si	2.257	1.957	1.366	93.6	180.0	1.75	0.84
Si_Ph ₂ NHC	Si ^d	2.250	1.960	1.378	97.0	178.4	1.72	0.86
Si_H ₃ P	Si	2.268	2.367		86.5	180.0	1.76	0.77
Si_Me ₃ P	Si	2.260	2.343		91.7	180.0	1.81	0.83
Si_Ph ₃ P	Si	2.259	2.379		92.0	180.0	1.77	0.77
Ge_H ₂ NHC	Ge	2.402	2.052	1.360	89.7	180.0	1.65	0.81
Ge_Me ₂ NHC	Ge	2.393	2.076	1.364	91.1	179.1	1.74	0.78
Ge_Ph ₂ NHC	Ge ^e	2.392	2.087	1.374	91.2	175.7	1.67	0.78
Ge_H ₃ P	Ge	2.400	2.472		84.9	180.0	1.76	0.72
Ge_Me ₃ P	Ge	2.390	2.442		90.3	180.0	1.81	0.78
Ge_Ph ₃ P	Ge	2.392	2.483		90.9	180.0	1.77	0.73
Sn_H ₂ NHC	Sn	2.776	2.296	1.357	86.6	180.0	1.73	0.67
Sn_Me ₂ NHC	Sn	2.766	2.317	1.362	88.0	180.0	1.78	0.66
Sn_Ph ₂ NHC	Sn	2.763	2.345	1.370	88.1	174.6	1.71	0.62
Sn_H ₃ P	Sn	2.767	2.721		82.8	180.0	1.77	0.57
Sn_Me ₃ P	Sn	2.762	2.683		88.5	180.0	1.83	0.64
Sn_Ph ₃ P	Sn	2.767	2.738		88.5	176.9	1.77	0.56
Pb_H ₂ NHC	Pb	2.915	2.433	1.358	84.9	180.0	1.77	0.60
Pb_Me ₂ NHC	Pb	2.910	2.450	1.361	86.8	180.0	1.79	0.60
Pb_Ph ₂ NHC	Pb	2.904	2.493	1.369	90.4	178.0	1.75	0.55
Pb_H ₃ P	Pb	2.904	2.838		82.1	180.0	1.78	0.50
Pb_Me ₃ P	Pb	2.903	2.798		87.9	179.9	1.84	0.58
Pb_Ph ₃ P	Pb	2.905	2.855		87.7	175.7	1.77	0.50

^aWBI = Wiberg Bond Index. ^bAverage values for E-L and C-N bond distances and L-E-E angles. ^cNo minima located. ^dReported experimental values (where the flanking NHC -R groups are dip) have an E-E distance of 2.229 Å, E-L distance 1.927 Å, E-E-L angle 93.4°, L-E-E-L torsion 180°. ^eReported experimental values (where the flanking NHC -R groups are dip) have an E-E distance of 2.349 Å, E-L distance 2.030 Å, and E-E-L angle 89.9°.

single-bond covalent radii for E-C bonds: Si-C 1.91 Å, Ge-C 1.96 Å, Sn-C 2.15 Å, and Pb-C 2.19 Å, and E-P bonds: Si-P 2.27 Å, Ge-P 2.32 Å, Sn-P 2.51 Å and Pb-P 2.55 Å, respectively.⁵⁸ For example, the Si-C bond distances in Si_R₂NHC (1.942–1.960 Å) may be compared to 1.927 Å in the known L-Si=Si-L complex (L = 2,6-ⁱPrPh-NHC)³² and 1.875 Å in Si(CH₃)₄,⁵⁸ while the Ge-C bond distance in Ge_R₂NHC (2.052–2.087 Å) is comparable to 2.030(3) Å in the known L-Ge=Ge-L complex.³³ With the exception of E = C, the E-L WBI values for all cases are well below 1, ranging from 0.50 (L = PPh₃, E = Pb) to 0.86 (L = R₂NHC, E = Si). The general trend is for the E-L bond order to progressively decrease for the heavier elements, and to be slightly larger for L = R₂NHC than for the corresponding R₃P complex.

For group 15 with E = N, P, As, Sb and Bi, the geometries are also very similar for L = R₂NHC and R₃P in the cases whereby reasonable minimum geometries were obtained. The minimum energy structures of Sb_H₃P, Sb_Ph₃P, Bi_H₃P, and Bi_Ph₃P complexes are best described as van der Waals clusters rather than a covalent molecule and so are not discussed in any detail here. For all the group 15 complexes the E-E bond distances are consistent with a single bond description: N-N (L-E-E-L is 1.389–1.499 Å, cf. 1.42 Å for typical single

bonds),⁵⁸ P-P (2.226–2.237 Å, cf. 2.21–2.22 Å),^{34,58} As-As (2.419–2.460 Å, cf. 2.42–2.56 Å),^{35,58} Sb-Sb (2.777–2.818 Å, cf. 2.83–2.85 Å),^{58,65} and Bi-Bi (2.900–2.959 Å, cf. 2.98–3.05 Å).^{58,66} Analogous E=E double bond distances are: P=P 1.985–2.141 Å, As=As 2.219–2.333 Å, Sb=Sb 2.642–2.751 Å, and Bi=Bi 2.821–2.870 Å.⁵⁹

The calculated P-P bond distance of 2.226 Å in P_Ph₂NHC is very similar to that of 2.205 Å reported for the experimentally known NHC(dipp)₂-P-P-NHC(dipp)₂ complex.³⁴ Similarly, the calculated As-As bond distance of 2.445 Å in As_Ph₂NHC is almost identical to the 2.442 Å reported for the known NHC(dipp)₂-As-As-NHC(dipp)₂ complex.³⁵

Calculated Sb-Sb bond distances of 2.777–2.818 Å may be compared to 2.642(2) Å in the first reported Sb=Sb complex (TbtSb=SbTbt)⁵⁹ and 2.678(1) Å in the Sb=Sb complex {[η⁵-C₅H₅Mo(CO)₂]₂(μ,η²-Sb₂)},⁶⁷ and single-bond Sb-Sb distance of 2.818 Å in Me₂Sb-SbMe₂.⁵⁶ Ashe and co-workers have reported 2.87 Å as a typical Sb-Sb single bond distance.⁶⁸ The calculated Bi-Bi bond distance (2.900–2.959 Å) is consistent with reported Bi-Bi single bond distances of 3.04 Å in (SiMe₃)₂Bi-Bi(SiMe₃)₂⁵⁸ and 2.990(2) Å in Ph₂BiBiPh₂,⁶⁸ and are longer than reported Bi=Bi bond distances: 2.821 Å in

Table 2. Optimized Geometries for L–E–E–L Compounds (E = Group 15) with Selected Bond Distances (Å), L–E–E Angles (deg) and L–E–E Dihedral Angles (deg)^a

compound	E	bond distance ^b			angle ^b	dihedral	WBI	
		E–E	E–L	C–N	L–E–E	L–E–E–L	E–E	E–L
N_H ₂ NHC	N	1.420	1.289	1.383	110.6	180.0	1.05	1.58
N_Me ₂ NHC	N	1.401	1.295	1.395	115.9	179.8	1.07	1.56
N_Ph ₂ NHC	N	1.389	1.288	1.405	115.4	166.1	1.08	1.59
N_H ₃ P	N	1.478	1.599		107.9	180.0	1.02	1.27
N_Me ₃ P	N	1.499	1.602		107.5	180.0	1.00	1.24
N_Ph ₃ P	N	1.457	1.611		111.2	180.0	1.03	1.20
P_H ₂ NHC	P	2.237	1.790	1.368	98.2	99.1	1.03	1.25
P_Me ₂ NHC	P	2.231	1.796	1.381	106.3	113.3	1.04	1.28
P_Ph ₂ NHC	P ^c	2.226	1.781	1.398	103.3	126.4	1.01	1.32
P_H ₃ P	P	2.229	2.150		93.2	96.8	1.06	1.10
P_Me ₃ P	P	2.235	2.147		97.9	109.0	1.05	1.14
P_Ph ₃ P	P	2.227	2.159		100.0	127.2	1.05	1.12
As_H ₂ NHC	As	2.460	1.933	1.362	95.7	94.4	1.03	1.15
As_Me ₂ NHC	As	2.459	1.942	1.377	104.8	106.1	1.04	1.17
As_Ph ₂ NHC	As ^d	2.455	1.927	1.384	102.4	118.4	1.01	1.24
As_H ₃ P	As	2.419	2.307		92.4	92.9	1.10	0.98
As_Me ₃ P	As	2.443	2.287		96.5	106.3	1.07	1.05
As_Ph ₃ P	As	2.419	2.322		99.7	115.8	1.12	0.99
Sb_H ₂ NHC	Sb	2.818	2.185	1.356	93.0	91.3	1.10	0.94
Sb_Me ₂ NHC	Sb	2.818	2.199	1.369	103.5	99.5	1.10	0.95
Sb_Ph ₂ NHC	Sb	2.807	2.202	1.380	102.2	107.6	1.08	0.97
Sb_H ₃ P	Sb	<i>e</i>						
Sb_Me ₃ P	Sb	2.777	2.559		95.8	101.1	1.18	0.85
Sb_Ph ₃ P	Sb	<i>e</i>						
Bi_H ₂ NHC	Bi	2.958	2.324	1.353	91.8	90.3	1.15	0.83
Bi_Me ₂ NHC	Bi	2.959	2.345	1.365	102.5	96.8	1.15	0.82
Bi_Ph ₂ NHC	Bi	2.933	2.363	1.374	102.9	104.7	1.17	0.82
Bi_H ₃ P	Bi	<i>e</i>						
Bi_Me ₃ P	Bi	2.900	2.702		96.1	99.8	1.28	0.73
Bi_Ph ₃ P	Bi	<i>e</i>						

^aWBI = Wiberg Bond Index. ^bAverage values for E–L and C–N bond distances and L–E–E angles. ^cReported experimental values (where the flanking NHC –R groups are dipp) have an E–E distance of 2.205 Å, E–L distance 1.750 Å, E–E–L angle 103.2°, L–E–E–L torsion 180°. For R = 2,4,6-trimethylphenyl, the E–E distance is 2.190 Å, E–L distance is 1.754 Å, E–E–L angle is 102.6°, and L–E–E–L dihedral is 134.1°. ^dReported experimental values (where the flanking NHC –R groups are dipp) have an E–E distance of 2.442 Å, E–L distance 1.881 Å, E–E–L angle 101.1°, L–E–E–L dihedral 180°. ^eNo covalent minimum located.

the first reported Bi=Bi containing complex⁶⁹ and 2.833 Å in *trans*-(2,6-Mes₂C₆H₃Bi)₂.^{66,70}

The general trend is for the E–E bond index (WBI) to increase gradually down the group (ranging from 1.00 in N_Me₃P to 1.28 in Bi_Me₃P) and indeed the E–E bond distances are slightly shortened from standard single bonds for the heaviest species Sb and Bi.

The E–L bond distances may also be compared to the single-bond covalent radii for R₂NHC ligands, N–C 1.46 Å, P–C 1.86 Å, As–C 1.96 Å, Sb–C 2.15 Å, Bi–C 2.26 Å, and R₃P ligands, N–P 1.82 Å, P–P 2.22 Å, As–P 2.32 Å, Sb–P 2.51 Å, Bi–P 2.62 Å.⁵⁸ In the lighter homologues, particular for the esoteric E = N complexes, the E–L bond distances are shorter than typical single bonds, which is indicative of some double bond character, and is supported by the WBI values. The effect is more important for L = R₂NHC than for R₃P, and becomes progressively less important for the heavier species down the group. For E = Sb and Bi, no E–L multiple bond character is evident in the metrical parameters. The importance of the E=L double bond character in the group 15 analogues will be discussed in detail in the bonding section. Except for E = N, which is trans-bent, a gauche arrangement about the E–E core

is the calculated geometrical minimum, which is consistent with previous calculations for the known systems where E = P and As.^{34,35} Experimentally, a trans-bent geometry was observed for P and As. For P, the trans-bent geometry was only obtained if extremely bulky R₂NHC ligands were used (R = 2,6-diisopropylphenyl (dipp)), with the slightly smaller R = 2,4,6-trimethylphenyl a gauche arrangement was observed.³⁴ With the marginally smaller R = 2,4,6-trimethylphenyl, a gauche arrangement of P_R₂NHC was produced. It is hypothesized that calculations with bulkier NHC-Ph ligands may produce a trans-bent minimum energy structure. Indeed, preliminary B3LYP/SVP (Lanl2DZ for Sb) calculations predict a trans-bent geometry for As_R₂NHC and Sb_R₂NHC (R = 2,6-dimethylphenyl or dipp).

Thermodynamic Stability Calculations. In the following discussion, similar trends arise from conventional MP2, SCS-MP2 and SOS-MP2 results, however in all cases the stability of the L-E-E-L, L-ECl_n, and L-EBr_n systems decreased monotonically from MP2 to SCS-MP2 to SOS-MP2. Only MP2 results are discussed, with SCS-MP2 and SOS-MP2 results included as Supporting Information.

To evaluate the relative thermodynamic stabilities of the L-E-E-L complexes, ΔG for the reaction $E_2 + 2 L \rightarrow L-E-E-L$ was calculated (Table 3). For $L = R_2NHC$ in group 14, ΔG is most

Table 3. MP2/TZVP//B3LYP/TZVP Calculated Free Energies (ΔG_{298K}) of Reaction for $E_2 + 2 L \rightarrow L-E-E-L$ (Units of kJ/mol)

E	R_2NHC			R_3P		
	H	Me	Ph	H	Me	Ph
C	-566.2	-584.8	-662.0	<i>a</i>	-341.5	-349.6
Si	-328.0	-332.6	-352.4	-93.6	-215.0	-230.1
Ge	-275.3	-289.3	-300.8	-74.6	-186.9	-206.7
Sn	-245.0	-264.6	-279.5	-70.3	-170.7	-200.8
Pb	-196.3	-214.7	-240.1	-54.9	-149.6	-185.6
N	91.8	140.0	93.3	543.7	367.7	367.3
P	-117.8	-78.3	-114.7	204.1	33.4	-67.7
As	-92.1	-56.7	-89.1	187.9	42.8	26.7
Sb	-111.7	-38.5	-108.4	<i>a</i>	49.1	<i>a</i>
Bi	-69.3	-41.7	-66.9	<i>a</i>	28.7	<i>a</i>

^aNo covalent minima located (dissociates).

strongly negative for C_2 (-566.2 to -662.0 kJ/mol), and steadily becomes more positive down the group with **Pb** R_2NHC having values between -196.3 and -240.1 kJ/mol. There is a substantial change between **C** R_2NHC and **Si** R_2NHC (-328.0 to -352.4 kJ/mol), as compared to the smaller successive differences further down the group. It is likely that this jump is due to the ability of the C_2 species to enter into a cumulene-like "resting" state, conferring much greater stability onto the C_2 derivative with respect to dissociation. The Ph_2NHC complexes have a greater thermodynamic stability than the alkyl substituted Me_2NHC and purely model H_2NHC complexes in all cases.

For group 15 with $L = R_2NHC$, ΔG for the reaction $E_2 + 2 L \rightarrow L-E-E-L$ is strongly positive for $E = N$ (92 – 140 kJ/mol), which is expected given the high thermodynamic stability of N_2 . For the other members of the group ΔG is negative, although less so than for the group 14 elements; **P** H_2NHC is the most stable calculated complex at -117.8 kJ/mol. The ΔG for this reaction generally becomes more positive down the group, with the formation of **Bi** R_2NHC between -41.7 and -69.3 kJ/mol. At -89 kJ/mol, the reaction forming **As** Ph_2NHC represents the least stable species (with respect to L and E_2) that has actually been isolated ($R = \text{dipp}$ in the isolated complex).³⁵ This upper boundary suggests that L-E-E-L species ($L = R_2NHC$) with a ΔG for the reaction $E_2 + 2 L \rightarrow L-E-E-L$ that is more negative than -89 kJ/mol may be considered a thermodynamically viable compound. Moreover, the slightly less stable **Bi** analogues (-67 kJ/mol) should be at least stable with respect to direct dissociation.

For group 14, the $L = R_3P$ complexes are generally less thermodynamically stable than for $L = R_2NHC$, but in all cases ΔG is strongly negative. Values of ΔG range from -349.6 (**C** Ph_3P) to -149.6 kJ/mol (**Pb** Me_3P) for the synthetically relevant Me_3P and Ph_3P ligands. The same trends are observed moving down the group as found for $L = R_2NHC$, with the complexes gradually becoming less stable with respect to dissociation. Again, the C_2 analogues, excepting $L = H_3P$, are most stable, although not nearly to the degree observed for $L = R_2NHC$ as the cumulene-like resting state is not the minimum for the **C** R_3P derivatives. The PPh_3 complexes are slightly more stable than the PMe_3 complexes, with the model PH_3

analogues being the least stable. The only species which has been reported experimentally is the C_2 complex of Ph_3P , which was found to decompose at temperatures above -30 °C, although the decomposition products were not analyzed.⁷¹ The situation for $L = R_3P$ is significantly different for a group 15 E_2 core. As expected, the N_2 complexes are highly unstable with strongly positive ΔG values >350 kJ/mol. However, unlike group 14, the heavier group 15 $R_3P-E-E-PR_3$ complexes are not favored in the reaction $E_2 + 2 L \rightarrow L-E-E-L$. The data indicates that these complexes are likely not viable targets for synthesis as dissociation into highly reactive E_2 species is favored. A possible exception is the formation of **P** Ph_3P , which is product favored ($\Delta G = -68$ kJ/mol), and only 21 kJ/mol less stable than the least stable experimentally known species ($\Delta G = -89$ kJ/mol for the formation of **As** Ph_2NHC).

Main Group Halide Precursor Stabilities. Since several of the unknown compounds appear to be viable molecules, particularly the heavier group 14 analogues with both $L = R_2NHC$ and R_3P , we turned our attention to the key $L-ECln$ and $L-EBr_n$ precursors and an evaluation of their relative stabilities. As aptly outlined by Frenking and Jones in a theoretical paper concerning related group 13 compounds, it is important to consider the viability of potential precursors when using theory to predict new molecules.³⁶ In Table 4 we report

Table 4. MP2/TZVP//B3LYP/TZVP Calculated Free Energy of Reaction (ΔG) of $ECln + L \rightarrow L-ECln$ ($L = R_2NHC$ and R_3P , $R = H, Me, Ph$) for $E = Si-Pb, P-Bi$ (Units of kJ/mol)

E	<i>n</i>	R_2NHC			R_3P		
		H	Me	Ph	H	Me	Ph
Si	4	-43.6	-35.3	-56.2	<i>a</i>	41.4	87.5
Si	2	-134.1	-130.3	-137.9	11.5	-56.1	-52.7
Ge	2	-126.2	-123.1	-133.8	2.9	-59.9	-58.5
Sn	2	-122.8	-120.5	-133.9	-9.1	-64.5	-62.8
Pb	2	-116.8	-111.9	-130.2	-12.3	-63.7	-63.3
P	3	-92.1	-72.3	-97.3	141.3	23.5	-14.7
As	3	-104.9	-75.2	-102.0	117.2	9.0	15.6
Sb	3	-109.8	-78.7	-108.9	87.1	-11.1	<i>a</i>
Bi	3	-123.2	-89.5	-117.8	50.9	-46.4	<i>a</i>

^aNo minima located.

only results for Cl as similar trends were noted for both Cl and Br precursors, although Br generally gave slightly more favorable ΔG values (Br results provided as Supporting Information).

In group 14, $SiCl_4$ and $GeCl_2$ have been used as the precursors for molecules related to **Si** Ph_2NHC and **Ge** Ph_2NHC , respectively, where the NHC R-group is the bulkier *dipp*.^{32,33} The first step is formation of coordination complexes between the main group halides and the NHC; this adduct is then reduced giving the L-E-E-L complexes. The robustness of this adduct is likely critical for successful synthesis of the L-E-E-L compounds, particularly for $E = Si$, where molecules containing Si in oxidation states lower than +4 are unstable but may be isolated as NHC adducts (e.g., $R_2NHC-SiX_2$; $R = \text{dipp}$, $X = Cl, Br$).^{19,72} The ΔG for the reaction of $R_2NHC + SiCl_4 \rightarrow R_2NHC-SiCl_4$ was calculated to be -35.3 and -56.2 kJ/mol for $R = Me$ and Ph , respectively. For $GeCl_2$, the same reaction in the formation of $R_2NHC-GeCl_2$ gives a ΔG of -123.1 and -133.8 kJ/mol for $R = Me$ and Ph , respectively. In both cases the reactions are product favored,

consistent with the experimental isolation of these adducts with aryl R-substituents. The SnCl_2 and PbCl_2 adducts are also calculated to be stable molecules, with $\Delta G = -133.9$ and -130.2 kJ/mol for $\text{Ph}_2\text{NHC-SnCl}_2$ and $\text{Ph}_2\text{NHC-PbCl}_2$, respectively. An $\text{R}_2\text{NHC-SnCl}_2$ complex is known experimentally with aryl R-groups,²¹ the corresponding lead complex has not been reported. In general very little NHC-Pb chemistry is present in the literature, with only a single known example of an adduct of the form NHC-PbR_2 .⁷³ Coupled with the apparent thermodynamic stability of the L-E-E-L complexes for $\text{L} = \text{R}_2\text{NHC}$ and $\text{E} = \text{Sn, Pb}$, the isolation of the E_2 complexes of tin and lead appears to be very possible and could be expected to open up new avenues for tin and lead chemistry.

As was the case for the E_2 complexes, L- ECl_n species where $\text{L} = \text{R}_3\text{P}$ are calculated to be far less stable than with the R_2NHC analogues. The calculated ΔG for $\text{R}_3\text{P} + \text{SiCl}_4 \rightarrow \text{R}_3\text{P-SiCl}_4$ is $+41$ and $+88$ kJ/mol for $\text{L} = \text{Me}_3\text{P}$ and Ph_3P , respectively. This is consistent with there being no reported isolation of these compounds. There are a few reports of octahedral bis-phosphine coordination complexes for SiCl_4 , which are noted to be quite unstable and exceptionally moisture sensitive. However, they can be isolated in the solid state and have been crystallographically characterized for $\text{L} = \text{Me}_3\text{P}$.⁷⁴ The ΔG for formation of the bis-phosphine complex ($\text{Me}_3\text{P-SiCl}_4\text{-PMe}_3$) was calculated to be $+15$ kJ/mol in the gas phase. These results indicate that use of a mono- or bis-phosphine- SiCl_4 complex as a precursor for reduction to $\text{Si-R}_3\text{P}$ is likely to be unfeasible as a stable adduct is probably an important feature of the reduction reaction. However, if we replace SiCl_4 with SiCl_2 , the phosphine complexes are predicted to be stable entities, with ΔG for $\text{R}_3\text{P} + \text{SiCl}_2 \rightarrow \text{R}_3\text{P-SiCl}_2$ calculated to be -56.1 and -52.7 kJ/mol for $\text{R} = \text{Me}$ and Ph , respectively. This is comparable to the reported dissociation enthalpy for NHC-SiBr_2 (-57.3 kJ/mol), which is a stable, isolable, crystallographically characterized compound.⁷² MP2/TZVP calculations for $\text{R}_2\text{NHC-SiBr}_2$ give dissociation energies (ΔG) of -142.9 to -151.8 kJ/mol for $\text{R} = \text{H, Me, Ph}$. The $\text{R}_3\text{P-SiCl}_2$ compounds could be viable targets for synthesis if a suitable route can be found. Such compounds would be valuable not only as precursors for L-Si-Si-L type compounds, but also offer additional ligand options in the expanding field of Si(II) chemistry.

For GeCl_2 the phosphine adducts are also favored, with ΔG for $\text{R}_3\text{P} + \text{GeCl}_2 \rightarrow \text{R}_3\text{P-GeCl}_2$ calculated to be -60 and -59 kJ/mol for $\text{R} = \text{Me}$ and Ph , respectively. Monophosphine adducts of GeCl_2 are known, in line with their relative calculated stability.⁷⁵ This trend continues down the group, with the SnCl_2 and PbCl_2 phosphine adducts having similar stabilities, and all are potentially viable precursors for reduction to $\text{R}_3\text{P} \rightarrow \text{E-E} \leftarrow \text{PR}_3$ complexes. Tertiary phosphines in complexes can be resilient to powerful reducing agents such as KC_8 .⁷⁶

The precursor for $\text{P_Dipp}_2\text{NHC}$ was reported to be $\text{Dipp}_2\text{NHC-PCl}_3$, from the direct combination of the Lewis base and Lewis acid, but the authors did not give further characterization details.³⁴ There is an incongruity in the literature regarding this reaction, as Macdonald isolated a bis-NHC stabilized P(I) cation using identical NHCs, with formation of $[\text{NHC-Cl}][\text{Cl}]$ as a byproduct from the reductive elimination of Cl_2 from PCl_3 .⁷⁷ Our calculations show that ΔG for the reaction of $\text{R}_2\text{NHC} + \text{PCl}_3 \rightarrow \text{R}_2\text{NHC-PCl}_3$ to be -72.3 and -97.3 kJ/mol for $\text{R} = \text{Me}$ and Ph , respectively. For As, ΔG for the same reactions were calculated to be -75.2 and -102.0

kJ/mol. For AsCl_3 , the R_2NHC adduct has been structurally characterized.³⁵ The R_2NHC adducts of SbCl_3 and BiCl_3 are also calculated to be stable entities, and are thus potential precursors for the formation of the as yet unknown E_2 complexes of those elements.

The phosphine complexes of PCl_3 and AsCl_3 are much less favored than the NHC complexes, with slightly positive ΔG values. The exception is $\text{Ph}_3\text{P-PCl}_3$, which is calculated to be stable by -14.7 kJ/mol with respect to dissociation. Despite the slightly negative calculated ΔG values, Ph_3P and PCl_3 have been reported not to react in the absence of another reagent, although it is possible the adduct forms, but in equilibrium with the free species. It is not observed in solution using techniques such as ^{31}P NMR.⁷⁸

For AsCl_3 , one phosphine adduct has been crystallographically characterized from the reaction of PMe_3 with AsCl_3 , which immediately precipitates from solution as a dimer with bridging As-Cl interactions.⁷⁹ The heavier SbCl_3 and BiCl_3 phosphine adducts are calculated to be more stable, and appear to be viable targets for isolation. However, given that the $\text{R}_3\text{P-E-E-PR}_3$ complexes for these elements are predicted to be unstable, the use of the $\text{R}_3\text{P-ECl}_3$ adducts in this context is moot.

Bonding. We have carried out an analysis of bonding in these systems in an effort to shed light on the differences in the stabilities of the NHC vs phosphine adducts for this L-E-E-L class of compounds. It may be expected that results from such an analysis will be generally applicable to low-valent main group chemistry.

The preference for a trans-bent geometry for group 14 and a gauche geometry for group 15 (in the absence of steric considerations important for bulky NHC -R groups) can be explained with an examination of the molecular orbitals (MOs) in the E_2 molecule, or even more clearly from the fleeting L-E-E species (Figure 2). Here, the second ligand (donor), interacts

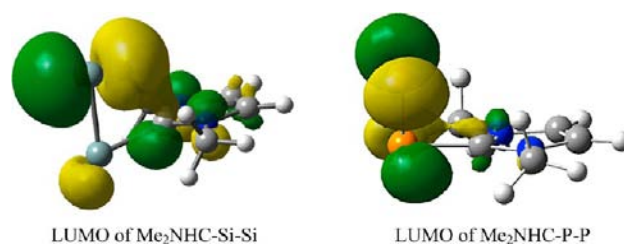


Figure 2. LUMO of $\text{Me}_2\text{NHC-Si-Si}$ and $\text{Me}_2\text{NHC-P-P}$.

with the LUMO of the L-E-E species (acceptor) to form the final donor-acceptor complex. For group 14, the accepting LUMO, which has σ symmetry with respect to the bond axis for the new interaction, is orientated trans-bent, while for group 15 the corresponding acceptor orbital is orientated gauche.

Plots of frontier MOs for the -Me derivatives the L-E-E-L compounds are found in Figures 3–6. Plots of MOs for -Ph and -H substituted derivatives are in the Supporting Information.

For the L-E-E-L complexes, the bonding picture of the dicarbon-NHC complexes $\text{C-R}_2\text{NHC}$ is unique with respect to the rest of the family of molecules and was discussed in detail in our initial communication.³¹ In this system, π bonds are formed between the central C atoms and the C_{NHC} atoms, which are found in the HOMO-1 and HOMO, respectively, while no lone-pair type orbitals are present on the central carbon atoms.

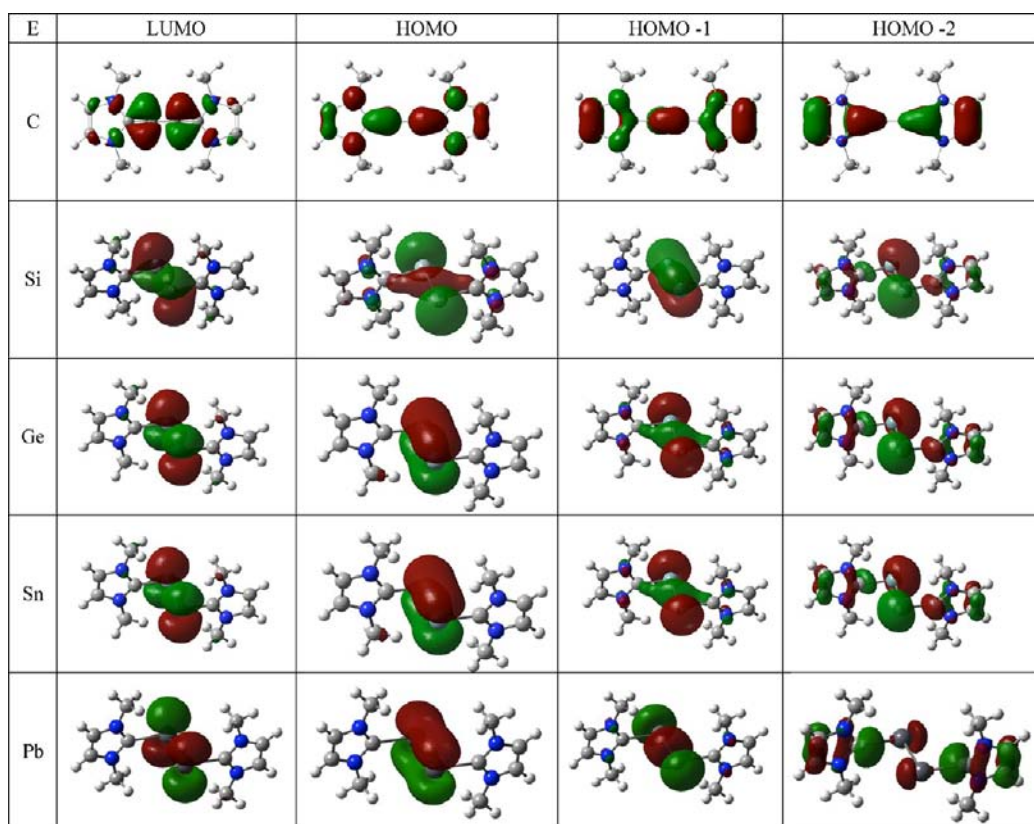


Figure 3. Frontier molecular orbitals for E_Me_2NHC ($E = C, Si, Ge, Sn, Pb$).

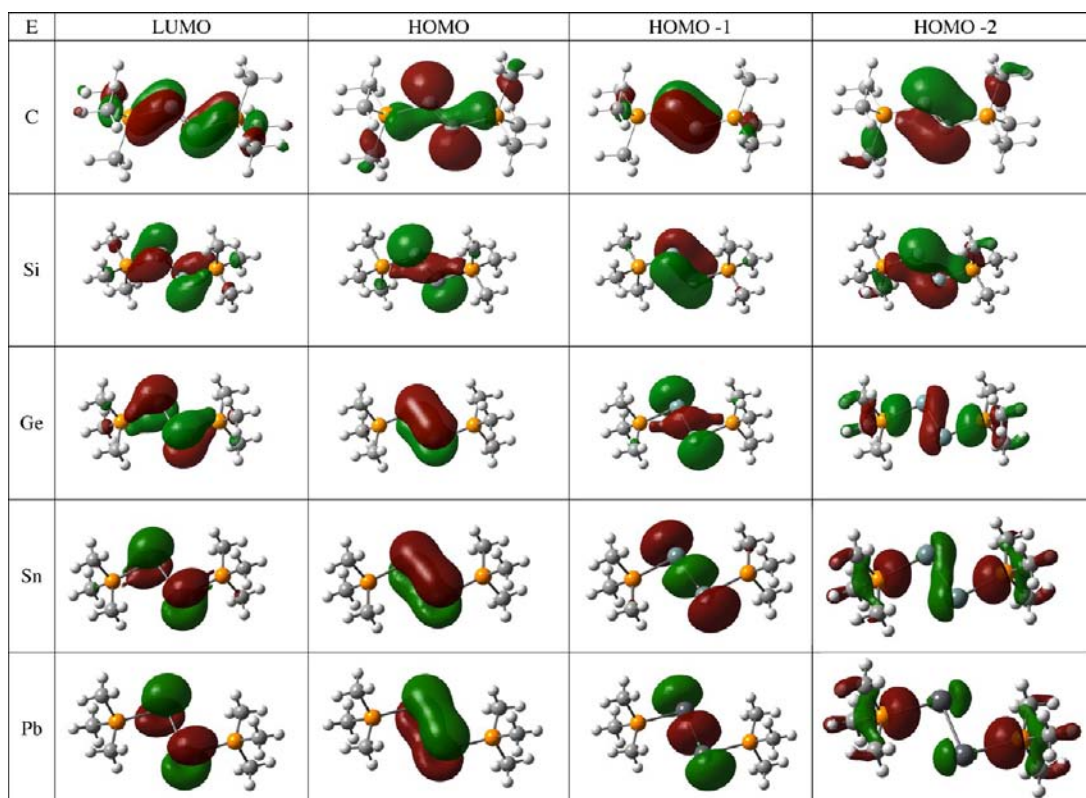


Figure 4. Frontier molecular orbitals for E_R_3P ($E = C, Si, Ge, Sn, Pb$).

For Si_Ph_2NHC , our calculations are consistent with those reported by Robinson et al. in finding the HOMO to be

dominated by the Si–Si π bond, the HOMO–1 by the Si–Si σ bond, and the Si lone pairs residing in the HOMO–2.³²

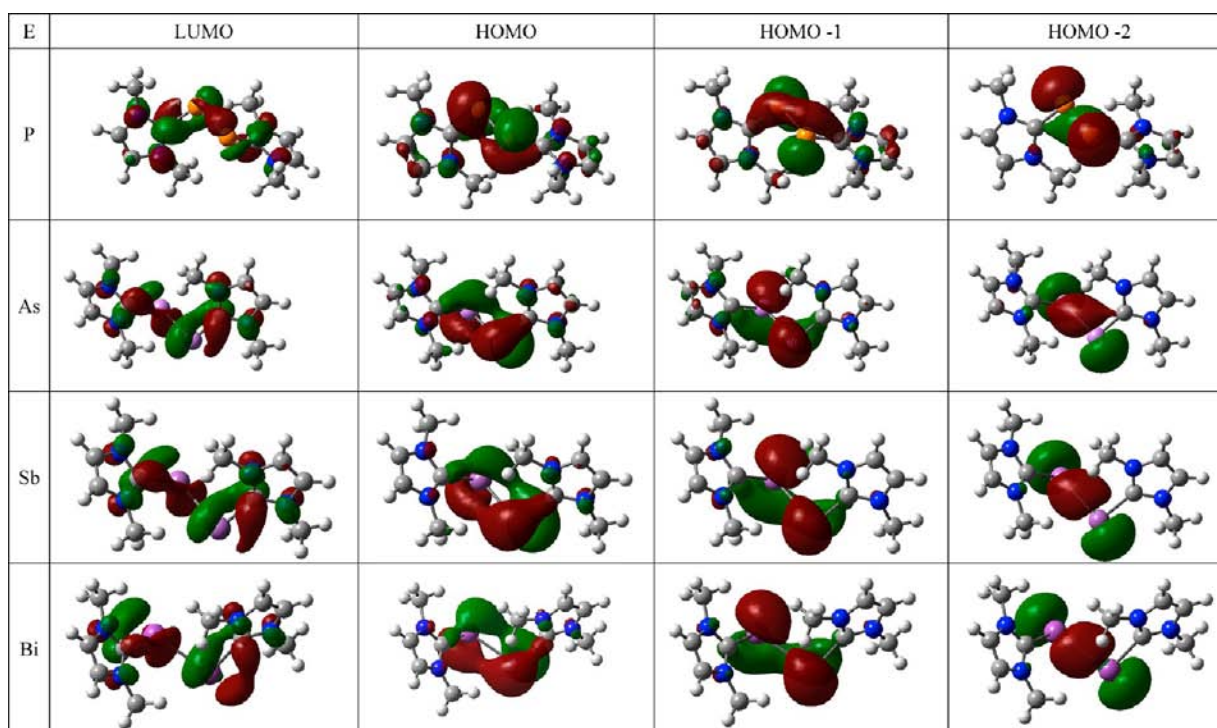


Figure 5. Frontier molecular orbitals for E_Me₂NHC (E = P, As, Sb, Bi).

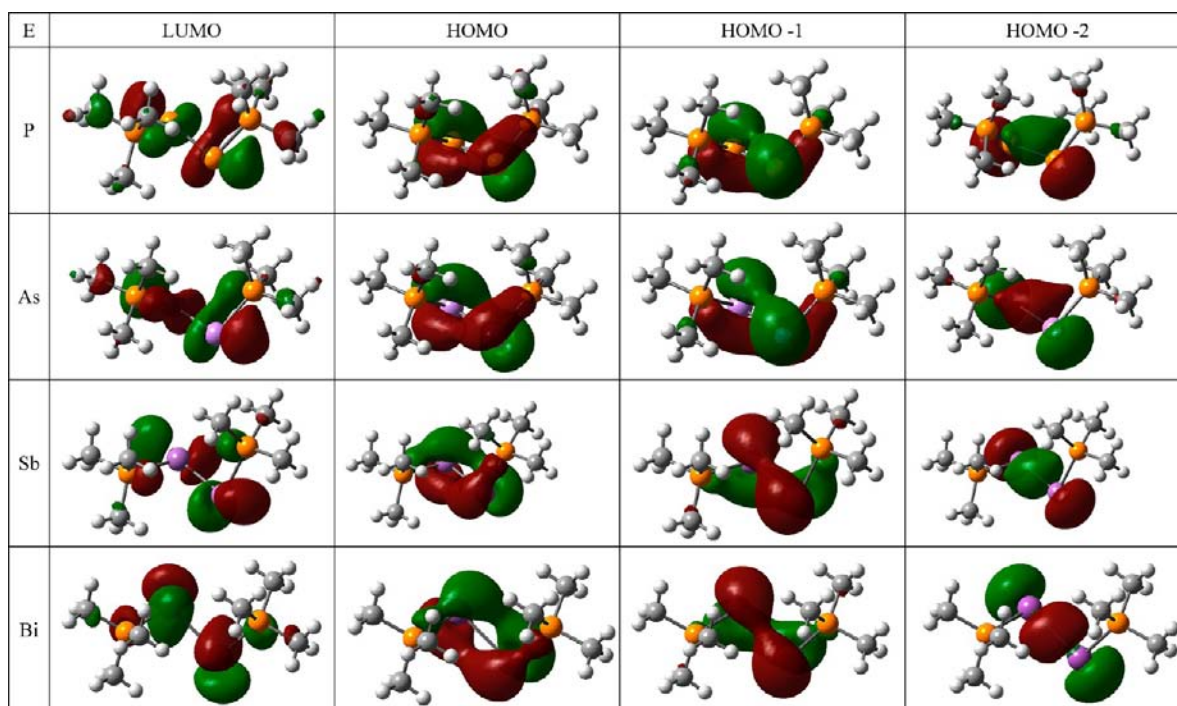


Figure 6. Frontier molecular orbitals for E_Me₂NHC (E = P, As, Sb, Bi).

Replacement of the Ph group with H, or the more synthetically relevant Me group, causes a swap in the relative order of the Si–Si bonding MOs: the Si–Si σ bond becomes the HOMO and the Si–Si π bond becomes the HOMO–1. The gap between the HOMO and HOMO–1 for Si_Ph₂NHC is 9.3 kJ/mol (B3LYP/TZVP), while for Si_Me₂NHC and Si_H₂NHC it is 7.4 and 5.0 kJ/mol, respectively. The small differences indicate that only a minor electronic rearrangement occurs, although perhaps enough to impact the reactivity of the

compounds. For Si_Me₂NHC the LUMO is centered on the Si–Si fragment as a π^* orbital, but for Si_Ph₂NHC the LUMO is delocalized onto the Ph groups of the NHC ligand, which may be another way in which changing the aryl substituted NHC for alkyl analogues would impact the reactivity of these compounds.

The frontier orbitals of Ge_R₂NHC have the same order for R = H, Me and Ph, with the HOMO containing the Ge–Ge π bond, the HOMO–1 the Ge–Ge σ bond and HOMO–2

containing contributions from the lone-pair electrons on the Ge atoms. The same MO framework is calculated for the unknown Sn analogues Sn_RNHC . For Pb_RNHC , again the HOMO is representative of the Pb–Pb π bond, but the contribution from the lone pairs on the lead atoms are now buried in the HOMO–5. For these very heavy analogues the resilience of the distinct E–E π interaction is unusual. In related “doubly” bound heavy group 14 compounds R_2EER_2 , where the formal oxidation state of the central E atoms is +2, the electrons which formally make up the double bond have mostly nonbonding character.⁵⁹

The bonding picture in the group 14-phosphine complexes is very similar to the NHC complexes. For $\text{Si}_R\text{R}_3\text{P}$, the HOMO is representative of the Si–Si σ bond, the HOMO–1 the Si–Si π bond and the HOMO–2 the Si lone pairs. For $\text{Ge}_R\text{R}_3\text{P}$ and $\text{Sn}_R\text{R}_3\text{P}$, the HOMO and HOMO–1 are inverted with respect to silicon, with the π bond being highest in energy for all R_3P species. For $\text{Pb}_R\text{R}_3\text{P}$, the HOMO and HOMO–1 are again representative of Pb–Pb π and σ bonds, respectively, but the lone pairs on the central atoms drop out of the frontier MOs as was the case for Pb_RNHC . For all noncarbon group 14 complexes, the E–L bonds have little π character. Therefore the extra stability of the NHC adducts compared to the as yet unknown phosphine adducts can be rationalized purely by the superior σ -donating ability of NHCs, although the phosphine adducts are still predicted to be viable species. In Robinson, Schaefer, and Schleyer’s reports^{32,34,35,80} of P_RNHC and As_RNHC , only localized MOs (LMOs) and NBOs were discussed and the MOs were not described. The localized bonding picture gives clear E–E single bonds for P and As, with significant double bond character in the E–C_{NHC} bonds, arising from π backbonding from the second lone pair on the central atoms. Analysis of the molecular orbitals is consistent with this description as well. For all elements P–Bi the E_RNHC frontier orbitals are similar. The E–C_{NHC} π bond/E–p lone pair dominates the HOMO, with the HOMO–1 containing significant contributions from the other lone pairs on the central E atom. An orbital with σ character in the HOMO–2 is attributed to the E–E single bond.

For the unknown and significantly less stable phosphine analogues, the key difference is that the E–P π backbonding interaction is significantly less important; being only a small factor for E = P and As, and negligible for the heavier analogues. This is evident by use of perturbation theory analysis of donor–acceptor interactions in the NBO basis (evidenced by lower occupations of E–P π^* NBOs). For L = R_2NHC the population of this N–C–N π^* orbital can be interpreted as an E \rightarrow NHC π -backbonding contribution of 0.60 for $\text{P}_R\text{Me}_2\text{NHC}$, 0.64 for $\text{As}_R\text{Me}_2\text{NHC}$, 0.59 for $\text{Sb}_R\text{Me}_2\text{NHC}$, and 0.54 for $\text{Bi}_R\text{Me}_2\text{NHC}$. The corresponding backbonding interactions for L = Me_3P (in this case $\pi \rightarrow \sigma^*$) have populations of 0.27, 0.28, 0.10, and 0.14 for $\text{P}_R\text{Me}_3\text{P}$ to $\text{Bi}_R\text{Me}_3\text{P}$ down the group, smaller than the populations in the NHC complexes. Natural resonance theory (NRT) gives similar results (see Supporting Information); in the group 15 E_2 complexes, resonance structures containing a backbonding component have relatively greater contributions for L = R_2NHC than L = R_3P .⁸¹

The NBOs for these complexes are consistent with the analysis of MOs. NBO populations of important σ , π , and lone pair orbitals for ligands with R = Me are presented in Table 5. All group 14 NHC complexes demonstrate both E–E σ and π bonds consistent with an E=E description of bonding,

Table 5. B3LYP/TZVP Calculated NBO Populations of Selected Orbitals for L–E–E–L (L = Me_2NHC and Me_3P)

		NBO					
		E–E σ	E–E π	E–L σ	E–L π	E LP ₁	E LP ₂
		group 14					
C	NHC	1.975	1.908	1.975	1.870		
Si	NHC	1.882	1.792	1.949		1.870	
Ge	NHC	1.887	1.790	1.947		1.918	
Sn	NHC	1.922	1.812	1.945		1.950	
Pb	NHC	1.936	1.826	1.941		1.973	
C	Me_3P	1.988	1.881	1.945		1.791	
Si	Me_3P	1.917	1.839	1.943		1.927	
Ge	Me_3P	1.915	1.848	1.938		1.948	
Sn	Me_3P	1.918	1.881	1.933		1.965	
Pb	Me_3P	1.921	1.895	1.979		1.928	
		group 15					
N	NHC	1.972		1.987	1.946	1.902	
P	NHC	1.940		1.952	1.840	1.960	
As	NHC	1.938		1.968	1.927	1.965	
Sb	NHC	1.944		1.946		1.981	1.767
Bi	NHC	1.952		1.939		1.988	1.766
N	Me_3P	1.964		1.979	1.882	1.923	
P	Me_3P	1.940		1.952	1.840	1.960	
As	Me_3P	1.940		1.951	1.846	1.971	
Sb	Me_3P	1.944		1.946		1.981	1.629
Bi	Me_3P	1.952		1.939		1.988	1.722

although for C the occupation is significantly greater than for heavier group 14 elements. The NBOs of C_RNHC also indicate an E–L double bond (σ and π C–C bonds), while for the heavier analogues only σ E–L bonds are identified, consistent with E–L single bonds. Occupation of the E–L σ bond decreases going down the group, while occupation of the E lone pair increases in going down the group.

The character of the NBOs offers further insight (percentage s, p, d character of NBOs and bond polarization is given as Supporting Information). For group 14 (Si–Pb), the E–E σ and π bonds are predominantly p character, which progressively increases down the group (L = Me_2NHC ; Si σ 82.3% p character, π 99.6% p character; Ge σ 87.2%, π 99.5%; Sn σ 89.6%, π 99.7%; Pb σ 92.9%, π 99.9%). The E lone pair is mainly s-character (Si 73.2%, Ge 80.6, Sn 85.4, Pb 90.9). Moreover, the proportion of E character in the E–L bond (bond polarization) systematically decreases. These trends are all consistent with reduced hybridization going down the group.

Similar trends are noted for group 15 (P–Bi), where the E–E σ bonds have progressively more p character and the E lone-pair has increasingly s character. The proportion of E character in the E–L bond systematically decreases from P to Bi. Again these trends are consistent with reduced hybridization going down the group. For Sb and Bi there is a second LP NBO, which is almost exclusively of p character. For Me_2NHC the E composition of the E–L bond is almost identical to the composition in the E–E bond.

NBO analysis additionally illustrates the weak s-p hybridization in these complexes (L–C–C–L is an exception), which is consistent with the almost 90° L–E–E angles (either trans-bent or gauche).

■ SUMMARY AND CONCLUSIONS

The results presented in this paper shed light on several issues, which are summarized as follows: (1) For L = R_2NHC , the as-

yet-unreported heavy group 14 analogues (E = Sn, Pb) are calculated to be accessible, stable species. These molecules are interesting in that they appear to contain distinct E-E π bonds, which is unusual for these very heavy group 14 elements. Diantimony and dibismuth stabilized by NHCs are also calculated to be stable entities. (2) For E = group 14 elements, L-E-E-L complexes where L = R₃P are also calculated to be stable compounds if a suitable synthetic route can be found. The R₃P-ECl₂ molecules that are the most straightforward precursors are calculated to be thermodynamically stable. The corresponding group 15 L-E-E-L complexes for L = R₃P are predicted to be unstable, with the possible exception of E = P. (3) While the main difference in the stability of the complexes can be explained by the greater σ donating ability of the NHCs, π backbonding interactions are also an important consideration in the bonding of these compounds. This is especially the case for the group 15 E-E complexes. While NHCs are considered weaker π -acids than phosphines in transition metal chemistry, our results show that the opposite is true in this system. We surmise that this is due to the better overlap between the p-orbitals of the E₂ fragments and the NHC π^* orbital, as compared to the phosphine σ^* orbital. The ability of NHCs to enter into such extra bonding interactions may be key to stabilizing these compounds, and allowing for their isolation, as compared with the phosphine complexes, which are predicted not to be stable when E is a group 15 atom. In low-oxidation state main group coordination chemistry these backbonding interactions may be a critical factor in stabilizing targeted complexes. The situation has also been observed in the C₁ carbodiphosphorane (R₃P-C-PR₃) and carbodicarbene (R₂NHC-C-R₂NHC) complexes considered by Frenking et al.^{28–30} The central C atom in these compounds carries two lone pairs of electrons, one σ -symmetric, and one π -symmetric. In both cases, some π backdonation was found, being more significant for L = R₂NHC than for L = R₃P, but it was not noted that this implied that NHCs were superior π acids to phosphines in this system. In the C₁ compounds, the NHC complexes are also much more thermodynamically stable than the corresponding phosphine complexes. Taken together with our results, it is apparent that when the backbonding contribution from the central fragment is based on p-orbitals, NHCs are indeed better π acids than phosphines, the opposite of what is found for transition metals.

■ ASSOCIATED CONTENT

■ Supporting Information

Cartesian coordinates for all compounds calculated, frontier molecular orbitals of all L-E-E-L complexes, NBO statistics, NRT contributing resonance structures, SCS-MP2 and SOS-MP2 reaction energies, and reaction energies for the formation of L-EBr_n are found in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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