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COMPLEXES OF SiH_2^{2+} WITH CARBODIPHOSPHORANE AND ANALOGUES $\{E(PPh_3)_2\}$ IN UNUSUAL BONDING MODE (E = C, Si, Ge, Sn, Pb)

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Abstract

Quantum chemical calculations at the BP86 level with various basis sets (SVP, TZVPP) were carried out for complexes of carbodiphosphorane analogues $E(PPh_3)_2$ with E = C, Si, Ge, Sn, Pb. The equilibrium geometries of the complexes $[SiH_2^{2+}–\{E(PPh_3)_2\}]$ (Si^{2+}-1E) possess the carbodiphosphorane ligand 1C is slightly bonded in a tilted way to SiH_2^{2+} in the complex Si^{2+}-1C, whereas the heavier group-14 ligands $E(PPh_3)_2$ (E = Si, Ge, Sn, Pb) in the complexes Si^{2+}-1Si – Si^{2+}-1Pb are strongly bonded in side-on fashions. The surprising structures SiH_2^{2+}-tetrylone complexes possess a strong Si-C1 bond between the Si atom of the SiH_2^{2+} fragment and atom C1 of the phenyl group. The trend of the bond dissociation energies (BDEs) for the Si-E bond in the Si^{2+}-1E complexes is Si^{2+}-1C ~ Si^{2+}-1Si ~ Si^{2+}-1Ge < Si^{2+}-1Sn < Si^{2+}-1Pb. Bonding analysis of the complexes shows that the Si-E bonds have a significant contribution from $H_2Si^{2+}\leftarrow E(PPh_3)_2$ π-donation.

Keywords: Donor-acceptor interactions; bonding analysis; density functional theory, bond dissociation energy.

1. INTRODUCTION

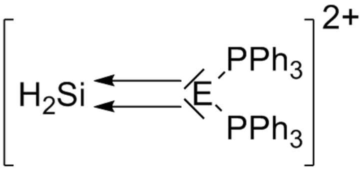
A detailed bonding analysis of the molecules $C(PMe_3)_2$, $C(NHC_H)_2$, $C(PPh_3)_2$, and analogues in transition metal complexes have been presented with charge- and energy-partitioning methods in the recent past [1]. The experimental observations and the theoretical investigations of divalent carbon(0) compounds [1, 2] indicated that the donor-acceptor chemistry of those complexes may lead to surprising new discoveries which should be studied with experimental and theoretical methods.

Recent theoretical studies suggested that the donor-acceptor bonding model of carbodiphosphorane is not limited to carbon as central atom but could be extended to the heavy homologues $E(PPh_3)_2$ with E = Si, Ge, Sn, Pb [3]. The finding indicated that the ligands $E(PPh_3)_2$ possess two lone-pairs orbitals at atom E which makes them potential four-electron donors motivated us to investigate the structures and bonding situation of $[SiH_2^{2+}–\{E(PPh_3)_2\}]$ with E = C, Si, Ge, Sn, Pb. To see whether the unusual bonding situation in $[SiH_2^{2+}–\{E(PPh_3)_2\}]$ complexes, which is revealed by the bonding analysis has any relevance to their chemical behavior, we calculated complexes in which the divalent carbon(0) compounds serve as Lewis bases.

In this study, the comprehensive density functional studies on the bonding situation in donor-acceptor complexes using quantum chemical methods have been performed. The calculated systems were composed of ligands of the types $E(PPh_3)_2$ as the donor fragments bonded to the acceptor fragments SiH_2^{2+}. Scheme 1 shows an overview of the compounds investigated in this work. Equilibrium geometries of the complexes and the bond dissociation energies are predicted with gradient corrected density functional theory (DFT). The electronic structures were analyzed with charge partitioning method.

2. COMPUTATIONAL METHODS

The geometries of molecules were optimized without symmetry constraints using the Gaussian03 [4] optimizer together with Turbomole 6.0.1 [5] energies and gradients at the BP86 [6, 7] /def2-SVP [8] level of theory (denoted BP86/SVP). The nature of the stationary points on the potential energy surface has been confirmed as energy minima by frequency calculations. Single point calculations with the same functional but the larger def2-TZVPP [9] basis set and the small-core quasi-relativistic effective core potentials [10] (ECPs) for heavier atoms Sn and Pb is carried out with Gaussian03 on the structures derived on BP86/SVP level (denoted as BP86/def2-TZVPP//BP86/def2-SVP) and used for the calculation of the bond dissociation energies (BDEs), Wiberg bond orders [11], and natural charges using the NBO 3.1 program [12].



E	Complex	Fragment
C	Si^{2+}-1C	1C
Si	Si^{2+}-1Si	1Si
Ge	Si^{2+}-1Ge	1Ge
Sn	Si^{2+}-1Sn	1Sn
Pb	Si^{2+}-1Pb	1Pb

Scheme 1: Compounds investigated in this study: [SiH_2^{2+}–{$E(PPh_3)_2$}] (Si^{2+}-1E) and the fragments $E(PPh_3)_2$ (1E) with E = C, Si, Ge, Sn, Pb

3. RESULTS AND DISCUSSION

3.1. Geometries and Energies

Figs. 1 and 2 show the optimized geometries of the complexes Si^{2+}-1C – Si^{2+}-1Pb and the geometries of the free ligands 1C – 1Pb. There are no experimental values available for the complexes Si^{2+}-1E. Examination of the equilibrium geometries of Si^{2+}-1E shows that only the carbodiphosphorane ligand 1C is slightly bonded in a tilted way to SiH_2^{2+} in the complex Si^{2+}-1C, whereas the heavier group-14 ligands $E(PPh_3)_2$ (E = Si, Ge, Sn, Pb) in the complexes Si^{2+}-1Si – Si^{2+}-1Pb are strongly bonded in side-on fashions. The bending angle, α, which is 164.7° in Si^{2+}-1C, and becomes much more acute in the heavier systems where the values decrease from $\alpha = 89.7°$ in Si^{2+}-1Si to $\alpha = 79.2°$ in Si^{2+}-1Pb. The theoretically predicted Si-C bond length of Si^{2+}-1C (1.885 Å) has the shortest bond length and increases for the heavier homologues. Fig. 1 shows the theoretically predicted structures for the SiH_2^{2+} fragment of Si^{2+}-1E which exhibit a surprising trend.

The distance between the Si atom of the SiH_2^{2+} fragment and the C1 atom of the phenyl ring in all members of Si^{2+}-1E complexes indicates that they are bonded. The Si-C1(phenyl) bond length is 1.915 Å in Si^{2+}-1C, and the Si-C1(phenyl) bond lengths become shorter (2.013-2.041 Å) than the Si-E bond lengths when E becomes heavier (2.390-2.743 Å). The small discrepancies between bond lengths E-P are in the cause of different-atomic radius of elements C, Si, Ge, Sn and Pb. Note that the Si-C1 (phenyl) bonds make the hydrogen atom connected to C1 bend out to a different side from the other H atoms of phenyl ring. The bond angle P-E-P in Si^{2+}-1C is 129.7° and become more acute in the heavier homologues. Note that the geometries of the free ligands shown in Fig. 2 demonstrate that the bond angle P-C-P becomes more acute in Si^{2+}-1C by approximately 6°. The bond angle P-E-P for E = Si, Ge, and Sn is almost the same in the complexes as that in the free ligands, whereas the angle for E = Pb in Si^{2+}-1Pb is approximately 4° more acute than that in the free ligands. The E-P bonds of all ligands $E(PPh_3)_2$ are clearly longer in Si^{2+}-1C – Si^{2+}-1Pb by 0.1–0.2 Å than those in the free tetrylones.

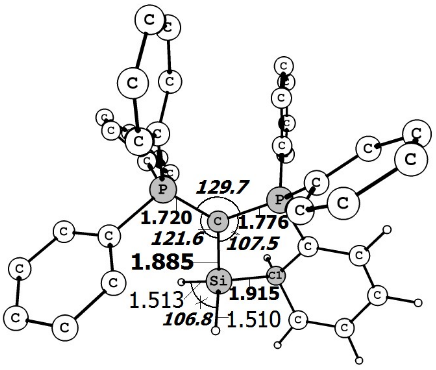
Fig. 1 also gives the theoretically predicted BDEs for the Si-E bonds of Si^{2+}-1Si – Si^{2+}-1Pb, which exhibit an interesting trend. The calculated bond energies suggest that the SiH_2^{2+}-tetrylone bond strength slightly increases from Si^{2+}-1C (D_e = 381.8 kcal/mol) to Si^{2+}-1Pb (D_e = 389.2 kcal/mol). There is continuous strengthening of the BDE for the heavier group-14 ligands, except for a small decrease from Si^{2+}-1C to Si^{2+}-1Si (D_e = 380.3 kcal/mol). The data suggest that the heavier tetrylone complexes have slightly stronger bonds than the lighter homologues. The above structures and the theoretically predicted BDEs show that the trend of the BDEs for the Si-E bond in the Si^{2+}-1E complexes is Si^{2+}-1C ~ Si^{2+}-1Si ~ Si^{2+}-1Ge < Si^{2+}-1Sn < Si^{2+}-1Pb.

The structures of complexes Si^{2+}-1C – Si^{2+}-1Pb were considered for dispersion interaction to affirm that these interactions might have an influence on the theoretically predicted BDEs. Table 1 shows the calculated BDEs, D_e [kcal/mol], with and without corrections for dispersion interactions for the complexes Si^{2+}-1E, which have been calculated at the BP86/TZVPP and BP86/TZVPP-D3 levels using BP86/SVP-optimized geometries. The calculated D_e values for Si^{2+}-1E show that the dispersion interactions are significantly large. This can be explained by the fact that the accepting fragment SiH_2^{2+} has much more bulky substituents in the complexes.

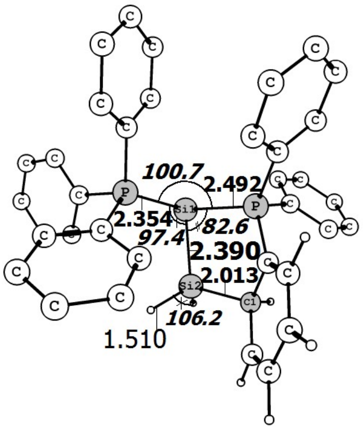
The calculated BDEs for the complexes Si^{2+}-1E at the BP86/TZVPP-D3 level have almost constant values between 391.9–401.4 kcal/mol. The contributions from dispersion interaction in Si^{2+}-1E possess uniform values between 9.8–15.8 kcal/mol. Note that the Si^{2+}-1E systems have weak attractive forces between the PPh3 substituents and the fragments SiH_2^{2+}. The calculated data suggest that it is useful to consider dispersion interactions separately from energies that come from covalent bonding in the bonding interactions which have open shell fragment in complexes.

Table 1: Calculated bond dissociation energies, D_e [kcal/mol], with and without corrections for dispersion interactions for complexes Si^{2+}-1E

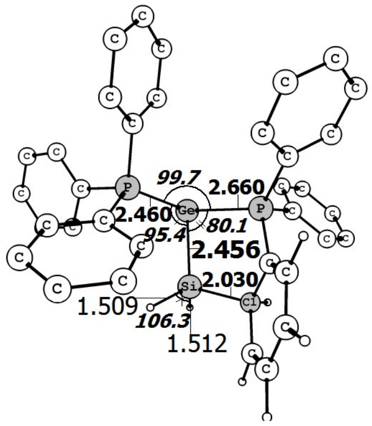
Compound	BP86/TZVPP	BP86/TZVPP-D3	ΔE
Si^{2+}-1C	381.8	397.6	15.8
Si^{2+}-1Si	380.3	392.1	11.8
Si^{2+}-1Ge	382.1	391.9	9.8
Si^{2+}-1Sn	386.9	397.7	10.8
Si^{2+}-1Pb	389.2	401.4	12.2



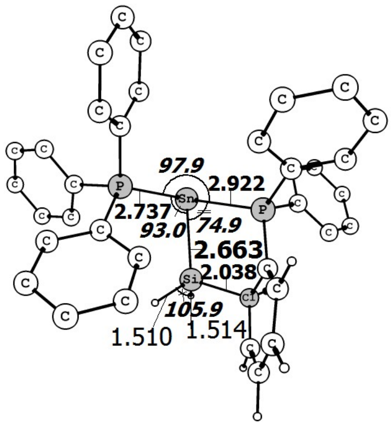
Si_2^{2+}-1C
α = 164.7°; D_e = 381.8 kcal/mol



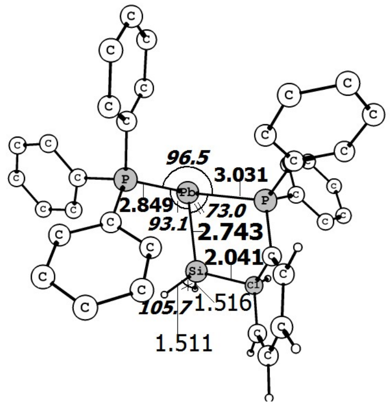
Si_2^{2+}-1Si
α = 89.7°; D_e = 380.3 kcal/mol



Si_2^{2+}-1Ge
α = 86.1°; D_e = 382.1 kcal/mol

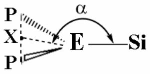


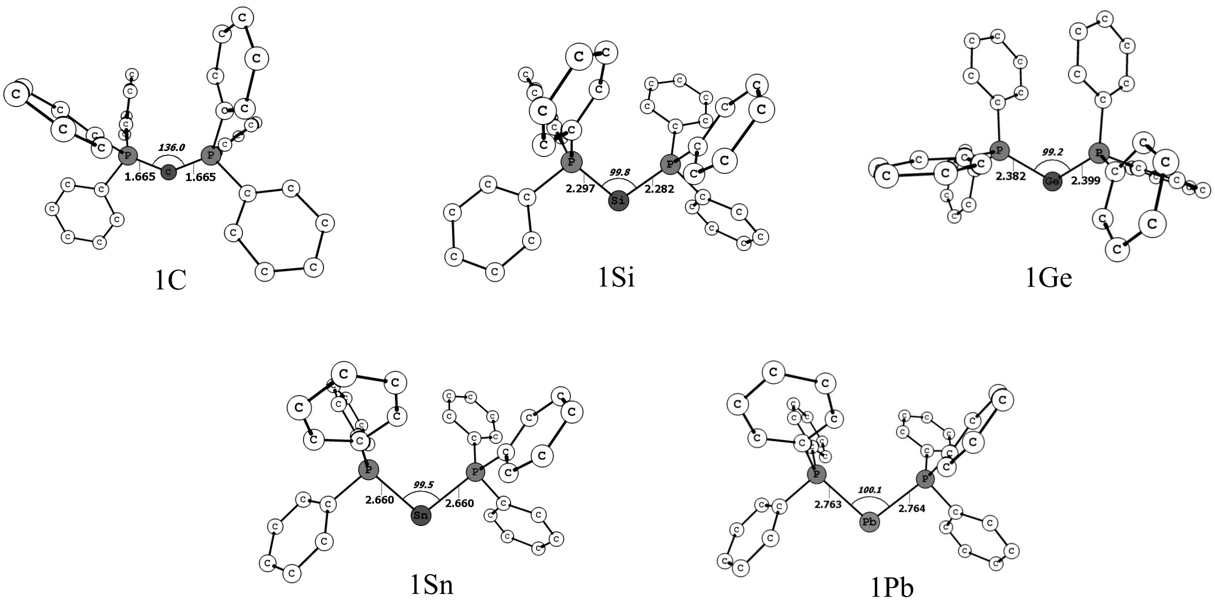
Si_2^{2+}-1Sn
α = 84.0°; D_e = 386.9 kcal/mol



Si_2^{2+}-1Pb
α = 79.2°; D_e = 389.2 kcal/mol

Fig. 1: Optimized geometries (bond lengths [Å], angles [°]) of the complexes Si^{2+}-1E at the BP86/def2-SVP level. Calculated metal-ligand bond dissociation energies, D_e, at the BP86/def2 TZVPP//BP86/def2-SVP level for the SiH_2^{2+}-1E bonds in kcal/mol. The bending angle α is the angle Si^{2+}-E-X where X is the midpoint between the P-P distance:





1C 1Si 1Ge

1Sn 1Pb

Fig. 2: Optimized geometries (bond lengths [Å], angles [°]) fragments $E(PPh_3)_2$ (1C–1Pb) at the BP86/def2-SVP level

3.2. Bonding analysis

Wiberg bond orders and partial charges in compounds Si^{2+}-1E and the free ligands 1E were calculated at the BP86/def2-TZVPP//BP86/def2-SVP level. Table 2 gives the numerical results of the NBO analysis with the calculated partial charges and bond orders of the SiH_2^{2+}-tetrylone complexes. The partial charges of the SiH_2^{2+} fragment are always positive and decrease from Si^{2+}-1C to Si^{2+}-1Pb. The calculated value for $q[SiH_2^{2+}]$ is largest in Si^{2+}-1C (0.92) and then it remains less constant for Si^{2+}-1E (0.40) when E = Si and Ge. The same trend is observed for Si^{2+}-1Sn (0.27) and Si^{2+}-1Pb (0.25). The Wiberg bond order for the Si-C bond in Si^{2+}-1C is smaller (0.81) than those in the heavier complexes where the values are between 0.90 for Si^{2+}-1Si and 0.89 for Si^{2+}-1Ge. In contrast, the Si-Sn bond (0.81) in Si^{2+}-1Sn is similar to the Si-C bond in Si^{2+}-1C, and then the Wiberg bond order is only 0.77 when E = Pb. Note that the bond order for the E-P bond becomes smaller in the complexes Si^{2+}-1C – Si^{2+}-1Pb compared with the free ligands 1C–1Pb. Thus, it follows that neither the charge distribution nor the bond order correlate with the BDEs of the tetrylone ligands 1E in the SiH_2^{2+}-tetrylone complexes. It is important to realize the surprising SiH_2^{2+}-tetrylone structures, with a strong Si-C1 bond between the Si atom of the SiH_2^{2+} fragment and the C1 atom of the phenyl ring are totally different. This shows that neither the charge distribution nor the bond order correlate with the BDEs of the tetrylone ligands $E(PPh_3)_2$. The Si^{2+}-1E complexes have an Mg-E bond that always carries positive charges for the Si atom in SiH_2^{2+} fragment and a negative charge for the E atom; this means there may still be a small electrostatic attraction.

A central question of the bonding analysis of the compounds Si^{2+}-1E concerns the strength of the π donation $SiH_2^{2+} \leftarrow E(PPh_3)_2$ which may be expected from the π lone-pair orbital of the tetrylone ligand $E(PPh_3)_2$ into the second vacant coordination side of SiH_2^{2+}. The molecules have C1 symmetry and therefore, there are no genuine σ and π orbitals since there is no mirror plane in the molecular structure. However, visual inspection of the shape of the orbitals makes it easy to identify σ-type and π-type MOs.

Fig. 3 graphically shows the energy levels of the two highest lying occupied MOs, which have σ or π symmetry, of the ligands $E(PPh_3)_2$ (1E). It becomes obvious that the energy level of the π orbital increases in 1E, whereas the π orbital becomes lower in energy when atom E becomes heavier. The trend of the energy levels of the energetically highest lying σ and π orbitals of 1E rationalize the preference of the heavier ligands for side-on coordination to the Si atom where σ-donation takes places through the π orbital of the ligand. The slightly end-on coordination of the lighter adduct 1C can be explained by various factors that also influence the bending angle, α, of the ligands.

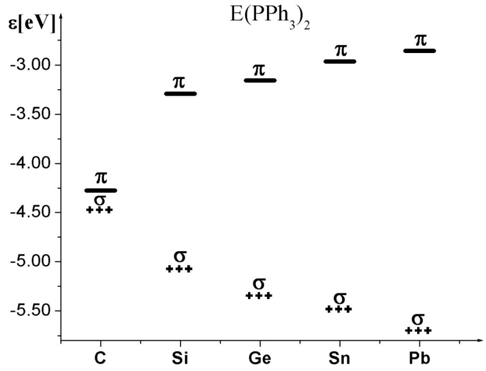


Fig. 3: Plot of the energy levels of the energetically highest lying σ and π orbitals of $E(PPh_3)_2$ (1C – 1Pb)

Table 2: NBO results with Wiberg bond indices (WBI) and partial charges *q* (in e) at the BP86/def2-TZVPP // BP86/def2-SVP level for complexes Si^{2+}-1C – Si^{2+}-1Pb and fragments 1C – 1Pb in C_1 symmetry

Molecule	Bond	WBI	$q[SiH_2^{2+}]$	Atom	q
				Si	1.13
Si^{2+}-1C	Si-C	0.81	0.92	C	-1.41
	$C-P_1$	1.03		P	1.59
	$C-P_2$	1.04		H	-0.11
1C	C-P	1.34		C	-1.43
				P	1.53
				Si_2	0.59
Si^{2+}-1Si	Si_2-Si_1	0.90	0.40	Si_1	0.22
	Si_1-P_1	0.70		P	1.03
	Si_1-P_2	0.81		H	-0.10
1Si	$Si-P_1$	0.96		Si	-0.26
	$Si-P_2$	0.97		P	0.93
	Si-Ge	0.89	0.40	Si	0.59
Si^{2+}-1Ge	$Ge-P_1$	0.77		Ge	0.24
	$Ge-P_2$	0.60		P	1.04
				H	-0.10
1Ge	$Ge-P_1$	0.91		Ge	-0.28
	$Ge-P_2$	0.90		P	0.95
	Si-Sn	0.81	0.27	Si	0.47
Si^{2+}-1Sn	$Sn-P_1$	0.62		Sn	0.59
	$Sn-P_2$	0.50		P	0.96
				H	-0.10
1Sn	Sn-P	0.71		Sn	-0.10
				P	0.88
	Si-Pb	0.77	0.25	Si	0.45
Si^{2+}-1Pb	$Pb-P_1$	0.57		Pb	0.68
	$Pb-P_2$	0.41		P	0.95
				H	-0.10
1Pb	Pb-P	0.65		Pb	-0.08
				P	0.87

The shorter Si^{2+}-C distance in the lighter homologues naturally invoke stronger steric (Pauli) repulsion, which favors slight end-on coordination. Another factor is the hybridization of the valence s/p donor orbitals of E. Fig. 3 also show that the energy levels of the π-type donor orbitals of Si^{2+}-1C – Si^{2+}-1Pb are higher lying than the σ-type donor orbitals. The energy levels of the two highest lying occupied

MOs indicate that $SiH_2^{2+} \leftarrow E(PPh_3)_2$ π donation might be important in complexes. We continue considering the polarization of the Si-E σ-bonds which is given by the natural bond orbitals in Si^{2+}-1E and hybridization of the Si-E bonds at atom E. Polarization of the Si^{2+}-E σ-bonds hybridization of the Si^{2+}-E bonds at atom E, is shown in table 3. The polarization of Mg-E bonds is slightly localized toward the E atom, which has %p character > 70 %. The Si-C bond in the slightly end-on-bonded carbone complex Si^{2+}-1C is localized toward the carbon atom (73.4 %) which has almost exact sp^2 hybridization. The Si-E bonds of the side-on bonded heavier homologues Si^{2+}-1Si – Si^{2+}-1Pb are strongly less polarized, decreasing from 73.4 to 34.2 %. The trend of the polarization of the Si-E bonds, which can be explained by the trend of the electronegativities of E and with the energy levels of the π HOMO of the ligands 1E (figure 3), agrees with the trend partial charges $q[SiH_2^{2+}]$ (table 2). Table 3 also shows the hybridization at atom E. The Si-E bonds in Si^{2+}-1C – Si^{2+}-1Pb at atom E have a %p character that increases from 70.9 % in Si^{2+}-1C to 96.1 % in Si^{2+}-1Pb. Thus, it follows that the tetrylones $E(PPh_3)_2$ have two lone-pair orbitals and they can use their π lone-pair electrons for donor-acceptor interactions in the side-on-bonded complexes.

Table 3: Polarization of the Si-E σ-bonds and hybridization of σ-donor orbital at atom E from NBO analysis of Si^{2+}-1E. The calculations were carried out at the BP86/TZVPP//BP86/SVP level

Complex	Polarization		Hybridization	
	%(Si)	%(E)	% s (E)	% p (E)
Si^{2+}-1C	26.6	73.4	28.9	70.9
Si^{2+}-1Si	56.5	43.6	10.3	88.7
Si^{2+}-1Ge	57.2	42.8	7.6	92.0
Si^{2+}-1Sn	64.4	35.7	5.2	94.5
Si^{2+}-1Pb	65.8	34.2	3.7	96.1

4. CONCLUSION

The structures of SiH_2^{2+}-tetrylone complexes are completely surprised with a strong Si-C1 bond between the Si atom of the SiH_2^{2+} fragment and the C1 atom of phenyl. The trend of the BDEs for the Si-E bond in Si^{2+}-1E complexes is Si^{2+}-1C ~ Si^{2+}-1Si ~ Si^{2+}-1Ge < Si^{2+}-1Sn < Si^{2+}-1Pb. Calculation of the BDEs for the Si-E bonds in Si^{2+}-1E, when considering dispersion interactions, shows that the effect of bulky ligands may have obscured the intrinsic Si-E bond strengths. The results give an interesting view of the structures and bonding interactions between the open shell and close shell fragments of equilibrium form in complexes.

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