Theoretical Study of Methyl-Pd^{II} N-Heterocyclic Silylene and Germylene Complexes: Comparisons to N-Heterocyclic Carbene Reactivity

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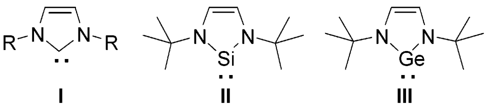
A theoretical study of methyl-Pd heterocyclic silylene and germylene complexes has been carried out and reveals a very low activation barrier for methyl migration to the silylene or germylene ligand, but indicates that, in the absence of solvent or counterion effects, reductive elimination of silicenium or germacenium cations is less likely. The results have been compared with those for the more common N-heterocyclic carbenes, and the activation barrier for coupling of the methyl group with C/Si/Ge was found to follow the order Si < Ge < C. The effect of solvent on the reaction has been modeled by incorporation of THF into the calculations on the silylene, which lowers the energy of all stationary points on the potential energy surface. Furthermore, with THF present reductive elimination of the silicenium cation becomes feasible. The results are discussed in terms of the implications they have on the potential application of these ligands in homogeneous catalysis.

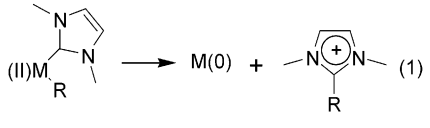
Introduction

The past 10 years has seen the development of N-heterocyclic carbene (**I**, Scheme 1) complexes of transition metals as effective catalysts for a number of organic transformations.[1] These ligands are formally neutral, two-electron donors with properties similar in some respects to the familiar tertiary phosphines. Unlike Fischer and Schrock carbenes, the heterocyclic carbenes are best described as pure σ-donor ligands, which in most cases undergo negligible M→L π-backbonding. This is due to a rather high occupancy of the formally empty p(π) orbital on the carbon, which results from p(π) electron donation from the adjacent nitrogen atoms.[2a−d] In the case of backbone unsaturated heterocyclic carbenes, the ligand is also stabilized by a degree of aromatic delocalization extending from the C═C to the N−C−N π system.[2a,b]

Scheme 1



The pure donor nature of N-heterocyclic carbenes leads to aspects of structure and chemical reactivity similar to other M−C single bonds, such as observed with anionic sp^3 and sp^2 alkyl/aryl ligands. In several recent reports we have shown that N-heterocyclic carbene complexes of Pd^{II} and Ni^{II} which contain alkyl, aryl, or acyl groups may decompose via concerted reductive elimination of 2-substituted imidazolium salts (reaction 1).[1l,m,o,3,4] Furthermore, it has also been shown



that the reverse reaction, oxidative addition of an imidazolium cation to yield a carbene complex, is

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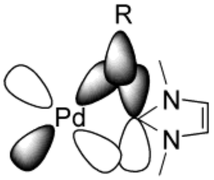

Figure 1. Orbital overlap in transition structure.

possible.[5,6] A theoretical (DFT) study of the reductive elimination reaction showed the carbene p(π) orbital to be intimately involved in the reaction, as the reductive elimination is facilitated by orbital overlap between the alkyl ligand σ orbital, the carbene p(π) orbital, and a Pd d-orbital (Figure 1).[4] As hydrocarbyl-metal species are considered to be intermediates in many catalytic transformations, this reaction represents a possible route to catalyst deactivation. For example, it has recently been shown to be the cause of decomposition of Ni-carbene olefin dimerization catalysts.[7] We have therefore investigated various methods by which it may be impeded.[1o,4−7] In this report the higher carbene analogues silylene and germylene have been studied within the framework of this reaction.

Following Arduengo's[8] 1991 report of the first synthesis and isolation of stable N-heterocyclic carbenes, analogous heterocyclic germylenes (**III**) were prepared for the first time in 1992 by Herrmann et al.,[9] although noncyclic Ge^{II} diamides had been prepared by Lappert many years previously.[10] In 1994 Denk et al. completed the series by isolating a stable N-heterocyclic silylene for the first time (**II**).[11] The electronic structure of silylenes and germylenes has been studied by both experimental and theoretical means and is generally thought to be qualitatively similar to that of the carbenes.[2a,b,12] These studies point toward the presence of at least some cyclic π delocalization in unsaturated heterocyclic silylenes and germylenes, albeit lower than in carbene analogues, but indicate that N−E−N delocalization is the most significant mode of delocalization. If the N−E−N system of the molecule is considered (E = C, Si, Ge), the p(π) occupancy of E is found to follow the order C > Ge > Si. This order is due to less p(π) electron donation from the adjacent N atoms in the Si and Ge analogues, reflecting a poorer orbital overlap between N and Si/Ge.

The complexation of silylenes and germylenes to transition metals has been studied both experimentally and theoretically.[2c,9,13] A theoretical study of N-heterocyclic carbene, silylene, and germylene complexes of Cu, Ag, and Au showed that metal−ligand bond dissociation energies follow the order C > Si > Ge.[2c] Similarly to the free ligand species, N(p$_\pi$)→E(p$_\pi$) donation is less in Si and Ge species than in carbenes. Additionally, while L→M σ-donation is still the dominant term, M→L back-donation is somewhat stronger in the silylene and germylene species than in carbene complexes, for which it is negligible. Given these differences in bonding and p(π) occupancy of silylene and germylene complexes, and that the p(π) orbital in carbene complexes plays a crucial role in the alkyl-carbene reductive elimination, the possibility of coupling of alkyl and silylene/germylene ligands is expected to be affected by the differences in electronic structure between carbenes, silylenes, and germylenes.

Among the group 15 elements, amines, phosphines, and arsines all find application as ancillary ligands in homogeneous catalysis, particularly the phosphines. On going down the group, changes in the nature of the M−L bonding have been used to influence the properties of resultant catalysts. In contrast, for the group 14 elements, only carbenes have been used as ligands for homogeneous catalysis, while the use of silylenes and germylenes for this purpose remains unexplored. Accordingly, it seems likely that complexes of these ligands may receive attention as potential catalysts. Therefore, it is important to study the potential susceptibility of silylenes and germylenes toward catalyst deactivation via the reductive elimination reaction. In this report the tendency of silylene and germylene alkyl complexes of Pd toward Si/Ge-alkyl coupling is studied from a theoretical perspective.

Theoretical Methods

Initial geometry optimizations were carried out with the B3LYP[14] density functional level of theory combined with the LANL2DZ basis set.[15] Sets of five d-functions were used in the basis sets throughout these calculations. For the optimized geometries, harmonic vibrational frequencies were calculated at the B3LYP level, and zero-point vibrational energy corrections were obtained using unscaled frequencies. All transition structures possessed one and only one imaginary frequency, and they were further characterized by following the corresponding normal mode toward each product and reactant. All structures were treated as singlets, and electronic wave function stability optimizations reveal no singlet−triplet instability. For comparison to previous results,[4] single-point energies on B3LYP/LANL2DZ optimized geometries were calculated at the B3LYP level with a LANL2DZaugmented 6-311+G(2d,p) basis set, which incorporates the LANL2 effective core potential and a large f-polarized valence basis set of Bauschlicher and co-workers[16] on Pd together with the 6-311+G(2d,p) basis set[17] on all other atoms. To obtain final high-level geometries and energies, full geometry optimizations were carried out at the B3LYP/LANL2DZaugmented 6-311+G-(2d,p) level, and the geometries and energies given in the text

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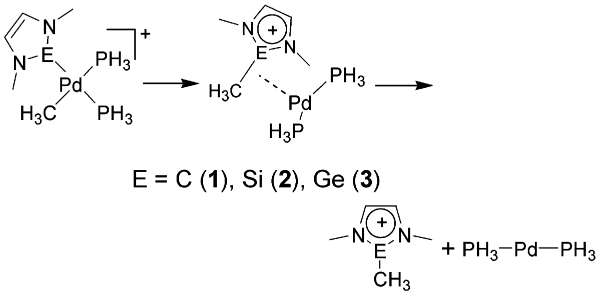
and figures refer to this final level of theory. In calculations where THF was incorporated however, the optimizations and energies reported are restricted to the B3LYP/LANL2DZ level.

Results and Discussion

Previous theoretical studies show that reductive elimination of 1,2,3-trimethylimidazolium from $[PdMe(dmiy)(PH_3)_2]^+$ (complex **1**, dmiy = 1,3-dimethlyimidazolin-2-ylidene) is slightly exothermic ($\Delta H = -3.7$ kcal mol^{-1}) with an activation barrier of 22.3 kcal mol^{-1} (reaction 2, E = C).[4] Herein, the tendency of silylene or germylene ligands to couple with an alkyl group has been studied for Pd^{II} using the cationic model complexes **2** and **3** (reaction 2). The optimized geometries of the stationary points on this PES are shown in Figure 2. The starting complexes (**2** and **3**), the transition structures, and the postreaction complexes are shown, as are the separated fragments, $Pd(PH_3)_2$, and the silicenium/germacenium cation. A potential energy plot for the reactions, including that for the carbene complex, is shown in Figure 3. It must be pointed out that, in the case of silylenes and germylenes, the representation of the final products as isolated silicenium or germacenium cations is somewhat unrealistic. Past studies show that silyl cations interact strongly with either the counterion or solvent.[18] For instance, the silyl cation $[SiH_3]^+$ has an association energy with benzene of ca. 25−50 kcal mol^{-1}. Further interaction of the silicenium cation with the counterion or solvent is addressed below. Of greatest interest however are the activation barrier to coupling of the methyl group and silylene and the relative energy of the immediate product of this reaction. The geometries and energies of the separated fragments are however included for completeness.



(2)

To our knowledge, there are no experimental structures of Pd^{II} silylene or germylene complexes with which to compare the theoretical structures. The theoretical structures of carbene complex **1** and 1,2,3-trimethylimidazolium have been compared to related crystal structures,[4] and agreement between experiment and theory was found to be very good. The geometry optimizations of the present work have been carried out at the same level of theory (B3LYP/LANL2DZ) as well as at a higher level of theory (B3LYP/LANL2DZaugmented 6-311+G(2d,p), see Theoretical Methods section); thus the geometries are assumed to be reliable. An apparent discrepancy exists in the structure of **3**, in which the Ge center is not trigonal planar as expected and experimentally found in a Ni-heterocyclic germylene complex.[9] The Ge−Pd bond axis lies ca. 47° out of the plane of the germylene ligand. The germacenium cation is likewise nonplanar, with the Ge-methyl group lying ca. 78° from the C_4N_2Ge plane (Figure 2). While carbocations and carbon radicals are usually planar as a result of π conjugation and hyperconjugation, in the higher congeners these effects are weaker, and Si and Ge are less compelled to be planar.[19] This effect is probably responsible for the nontrigonal planar geometry of Ge in complex **3** and the germacenium cation. However, when complex **3** is optimized (B3LYP/LANL2DZ) with a fixed trigonal planar geometry about Ge, the energy is only 0.8 kcal mol^{-1} higher than fully optimized **3**, so this effect makes an almost insignificant difference to the reaction energetics.

The starting complexes **2** and **3** both display the expected square planar coordination, somewhat distorted in both. In the transition structures the P−Pd−P angle increases as the methyl group and silylene/germylene approach. Generally, apart from different bond distances to Si and Ge, the geometries of **2** and **3**, and the respective transition structures, are very similar and much like those found for the reaction with carbene complex **1**. These similarities in geometry are not, however, reflected in the relative energies of the stationary points (Figure 3). The activation barriers to coupling of the methyl group with the silylene (+0.5 kcal mol^{-1}, or slightly negative at the lower level of theory) or germylene (+9.1 kcal mol^{-1}) are much lower than that predicted for the carbene ligand (+22.3 kcal mol^{-1}). There is also a large difference in the reaction with carbene as opposed to silylene/germylene in terms of the geometries of the products. In the case of the carbene complex, the product 1,2,3-trimethylimidazolium cation was planar and interacted only weakly with $Pd(PH_3)_2$; thus the reaction was described as reductive elimination.[4] In the present case, with Si and Ge, the products have short Pd−E bond lengths and the geometry about Si and Ge is approaching tetrahedral. The Pd−E bond lengths for the products are within the range of anionic sp^3 silyl and germyl bonds to Pd^{II} and Pt^{II}.[20] This fact, together with the geometries about E which are consistent with sp^3 hybridization, suggests the reaction may be better described as a migration of the methyl group onto the silylene/germylene to give a formally anionic silyl/germyl ligand. The division between a reductive elimination and alkyl migration is not clear in this type of reaction. Reductive elimination yields a weak coordination complex of the metal fragment and the imidazolium cation, but as this interaction becomes stronger, there will come a point where the reaction is better described as an alkyl migration, in which the metal center is not formally reduced. The effect is the same; however, the alkyl group couples with the ligand, which can no longer act as a neutral two-electron donor ligand. The migration reaction is exothermic for both complexes **2** and **3**. The reaction is most exothermic for the silylene,

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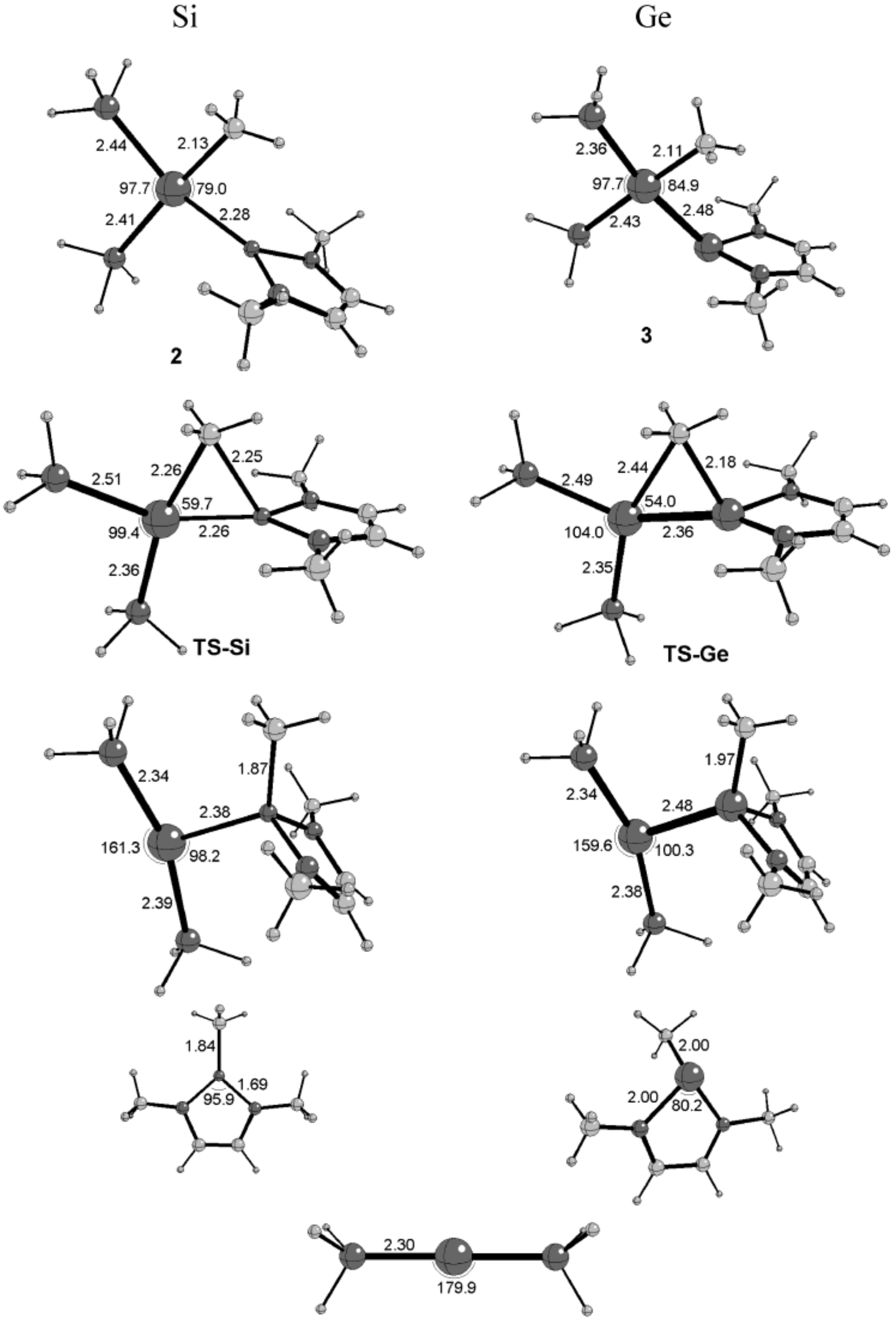

Figure 2. Optimized geometries of the reactants, transition structures, and products for the silylene complex (left) and germylene complex (right).

with the product lying 16.2 kcal mol^{-1} below the reactant. The product of the reaction of **3** lies 7.7 kcal mol^{-1} below the starting complex.

The separated fragments, the silicenium/germacenium cation and Pd(PH$_3$)$_2$, have a much higher energy than both the reaction products and the starting complexes. In the case of Si, these are 18.1 kcal mol^{-1} above the reactant, and for Ge 19.0 kcal mol^{-1} above the reactant. The high relative energies of these stationary points illustrate the strong bonding between Pd and the Si/Ge ligands postmigration. This also suggests the reaction is best described as a methyl migration to give a strongly bonded sp^3 anionic ligand.

As discussed above, the inclusion of solvent or anion is expected to affect the relative energy of the final products due to the possibility of interaction with the silicenium or germacenium cation. To guage the magnitude of this effect, we have studied the potential energy profile, at the B3LYP/LANL2DZ level, of the silylene reaction with a molecule of the moderately coordinating solvent THF present. Two pathways were found, as shown in Figure 4, in which the THF molecule sits either between the silylene and a phosphine ligand (left) or between the methyl group and a phosphine ligand (right). In both reactants (**4** and **5**) the THF molecule is at a distance to the Pd center that indicates

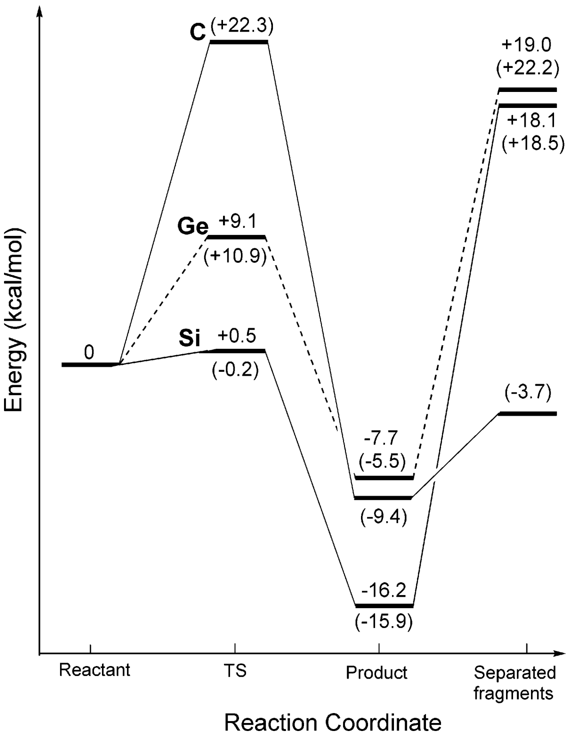

Figure 3. Potential energy surface for the reaction with C, Si, and Ge. Energy values shown result from B3LYP/LANL2DZaugmented 6-311+G(2d,p) calculations, while those in parentheses result from B3LYP/LANL2DZaugmented 6-311+G(2d,p)//B3LYP/LANL2DZ calculations (see text).

Table 1. Occupancy and Polarization of the E−N p(π) Bond

	reactant			TS		
E	occup	%N	%E	occup	%N	%E
C	1.89	75	25	1.79	83	17
Si	1.87	84	16	1.84	87	13
Ge	1.84	80	20	1.83	83	17

a weak interaction (3.79, 4.21 Å), but in **4** the O−Si distance is 2.48 Å, indicating a stronger interaction. The core geometry of the complexes is, however, very similar to that in the reactant complex without THF present (**2**), showing that the THF molecule does not greatly perturb the structure of the complex. This is also the case in the transition structure and product of migration, where the geometry about Pd and Si is not greatly affected by THF. In **TS4** the Si−O distance (3.15 Å) is elongated compared to that in the reactant, while in **TS5** there is little change in the position of the THF molecule. After migration the Si−O and Pd−O distances are increased in both cases.

Figure 5 shows the potential energy profile for both pathways (B3LYP/LANL2DZ energies), along with a comparison without THF present at the same level of theory. (Note that the unsolvated barrier is 4.2 kcal/mol at this level of theory compared with +0.5 in Figure 3.) The interaction with THF lowers the energy over the whole potential energy surface, but the activation energy relative to the THF bound reactant remains almost the same at 3−5 kcal mol^{-1}. (The barriers are 4.5, 5.0, and 3.0 kcal/mol for **2**, **4**, and **5**, respectively). The product of methyl migration is still the most stable stationary point on the potential energy surface; however as expected, the energy of the separated silicenium cation and $Pd(PH_3)_2$ is greatly reduced with THF present. This is due to a strong (28.6 kcal mol^{-1}) interaction between THF and the silicenium cation. These results therefore show that the effect of a counteranion or solvent will be to favor the migration of an alkyl group to the silylene ligand through lowering of the energy of the product and to lower the energy of the silicenium cation to an extent that reductive elimination becomes feasible. Therefore, the inclusion of solvent does not greatly alter the conclusions of the study.

We briefly note a number of observations about the levels of theory used in this work. First, Figure 3 allows us to compare the single-point versus optimized geometry values for Si and Ge (all with the large basis set); there is very little difference between the numbers in parentheses and those outside, which suggests that the effect of geometry reoptimization is small. This validates our previous approach of doing large basis set single-point calculations on geometries optimized with a smaller basis set. On the other hand, Figures 3 and 5 allow us to compare the effect of moving to the larger basis set for Si. This shows that the large basis set raises the energy of the reactant relative to the rest of the potential energy surface by about 5 kcal/mol (the numbers are 0, 0.5, −16.2, and 18.1 with the large basis set and 0, 4.2, −11.7, and 26.0 with the small basis set). The explanation of this is not clear, but reinforces the importance of obtaining results with the better quality basis sets.

The results of this study show that coupling of a hydrocarbyl ligand with a heterocyclic silylene or germylene ligand occurs with a very much lower barrier than that for hydrocarbyl-carbene coupling, which has been shown experimentally to be a facile process in many cases.[1l,m,3,4] In the case of the silylene ligand, the barrier is predicted to be around zero. To understand the trend in activation energies for the reaction (Si < Ge < C), we have carried out a natural bond orbital (NBO)[21] analysis on the reactant and transition structures for the Si and Ge systems. This has been compared with a previous analysis of the carbene system,[4] which showed that during the transition state there is interaction of a methyl group orbital with the partially occupied p(π) orbital on C and that this interaction facilitates coupling of the carbene and methyl moieties. As a result of this, in the transition structure the N−C p(π) donation is reduced compared to that in the reactant, and this bond becomes more polarized toward N. The same occurs in the Si and Ge systems and is shown in Table 1, which contains the N−E p(π) occupation and polarization of the reactants and transition structures. It can be seen for all systems that the N−E p(π) bond becomes more localized on N in the transition structure compared to in the reactant. As noted in the Introduction, N−E p(π) bonding is reduced in the Si and Ge analogues as compared to the carbenes, but it has also been found in a number of studies[2a,c] that the p(π) occupancy of Si is lower than in Ge. This is attributed to the higher electronegativity of Ge than Si. In agreement with this, as shown in Table 1, the p(π) bond that is least polarized toward E is the N−Si p(π) bond. The predicted activation energies of the reaction can be correlated with the amount of p(π) donation from N to E, and hence with

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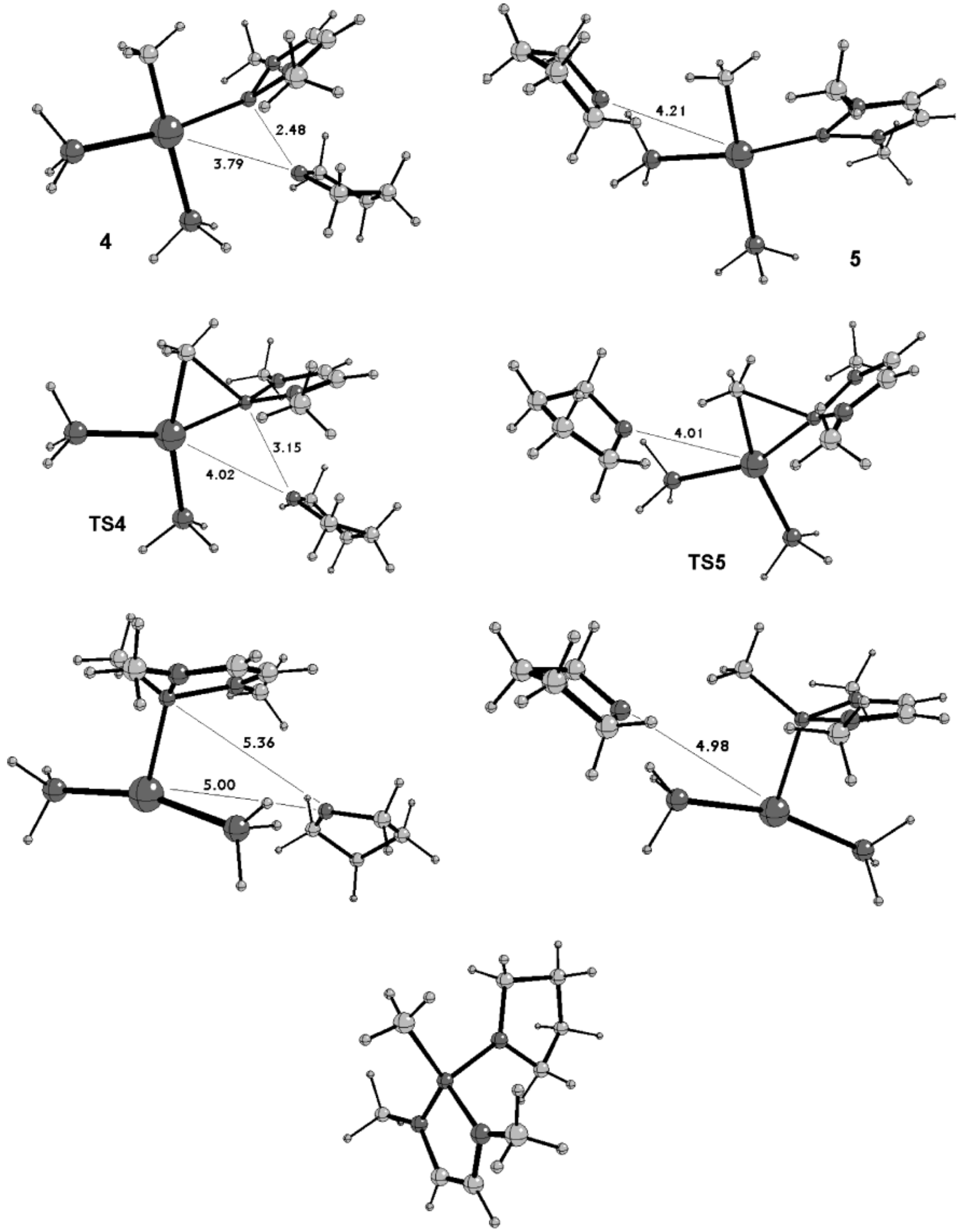

Figure 4. Optimized geometries (B3LYP/LANL2DZ) of the reaction (E = Si) with THF present.

the occupancy of the p(π) orbital on E. As the amount of N−E p(π) donation becomes reduced in the transition structure, we suggest that a lower p(π) occupancy in the reactant facilitates easier coupling of the methyl and C/Si/Ge groups. Because the N−E π bonding is reduced in silylene and germylene complexes, the bonding situation in these complexes is somewhat toward that in Fischer-type carbene complexes. Migration reactions in Fischer and Schrock carbene complexes are well known.[22] Migration reactions with dialkyl germylenes are also known.[23]

Finally, there is some experimental evidence for migration reactions involving heterocyclic silylene ligands in the literature. When Lappert reacted $PtCl_2(PPh_3)_2$ with 4 equiv of a heterocyclic silylene, insertion into the two Pt−Cl bonds took place to yield a Pt complex containing both neutral silylene and anionic chlorosilyl

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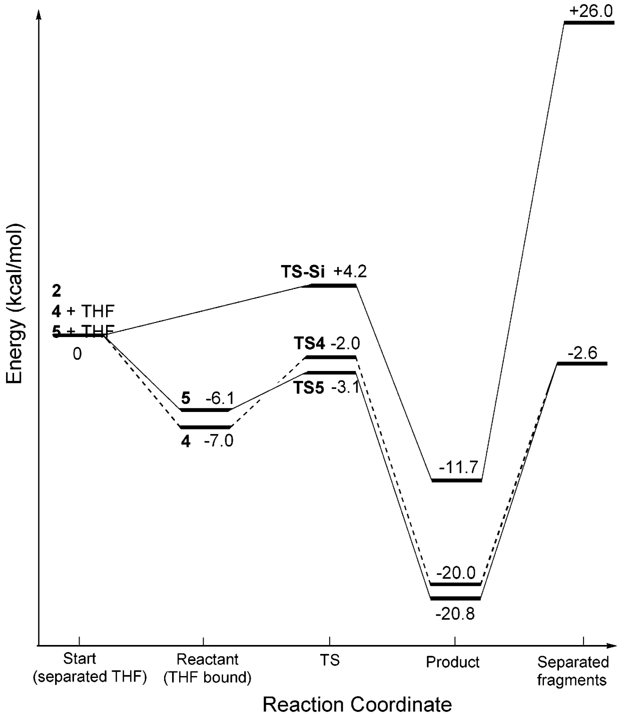
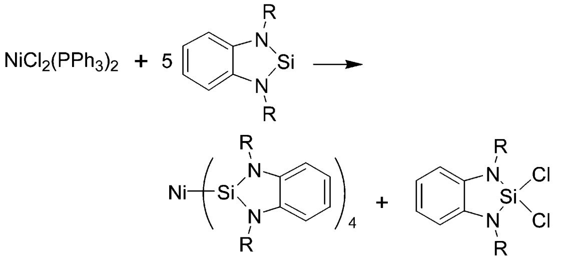


Figure 5. Potential energy surface for the reaction (E = Si) with and without THF present. Energy values shown result from B3LYP/LANL2DZ calculations.

ligands. When the same ligand (5 equiv) was reacted with $NiCl_2(PPh_3)_2$, a tetrasilylene Ni^0 complex was obtained (reaction 3).[13b] A possible route to this complex that fits the present results is initial Cl migration onto coordinated silylene to give a Ni-silyl complex, followed by reductive elimination of the silyl ligand and the second chloro ligand to give the dichlorosilane that was identified as the coproduct. If this is the case, it demonstrates that after migration the silyl ligand formed can react further via reductive elimination. Thus the reaction can also ultimately lead to reduction of the metal and loss of the silylene moiety from the metal center. In another study, Jutzi et al.[13c] reacted a heterocyclic silylene ligand with Mo and W hydrides and isolated M-silyl complexes. These complexes possibly result from coordination of the silylene followed by migration of hydride to give the silyl ligand.



(3)[13b]

Summary and Conclusion

A density functional analysis of Pd silylene and germylene complexes reveals a very low barrier to coupling of an alkyl ligand with the silylene or germylene ligand. Unlike the reaction with a carbene ligand, which theoretically and experimentally occurs via concerted reductive elimination, the reaction with silylene and germylene is better described as an alkyl migration to the neutral ligand. In any application of silylene or germylene ligands as ancillary ligands for homogeneous catalysts, if the catalytic cycle involves metal-hydrocarbyl species, then migration will likely be a significant factor in the chemistry of these complexes. This reaction would reduce the ligand's ability to act as a neutral two-electron donor ancillary ligand.

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Supporting Information Available: Table of optimized geometries and absolute energies of stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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