

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/280033414>

Aminotroponiminatosilathio- and Siloxygermylenes: Reactivity Comparison

ARTICLE *in* ORGANOMETALLICS · JUNE 2015

Impact Factor: 4.13

READS

6

4 AUTHORS, INCLUDING:



[Surendar Karwasara](#)

Indian Institute of Technology Delhi

10 PUBLICATIONS 8 CITATIONS

SEE PROFILE



[Rahul Kumar Siwatch](#)

Nanyang Technological University

10 PUBLICATIONS 58 CITATIONS

SEE PROFILE

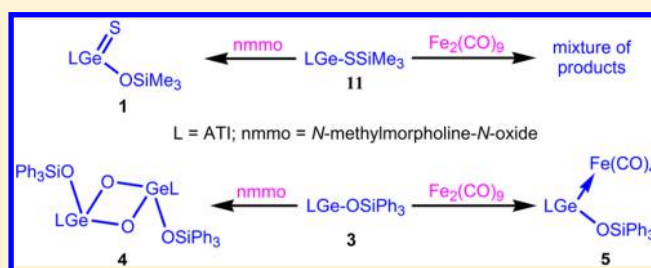
Aminotroponiminatosilathio- and Siloxygermylenes: Reactivity Comparison

Surendar Karwasara, Rahul Kumar Siwatch, Chandan Kumar Jha, and Selvarajan Nagendran*

Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110 016, India

Supporting Information

ABSTRACT: Aminotroponimate (ATI) ligand stabilized silathioethermylene $[(\text{Bu}_2\text{ATI})\text{GeSSiMe}_3]$ (**11**) and siloxygermylenes $[(\text{Bu}_2\text{ATI})\text{GeOSiR}_3]$ ($\text{R} = \text{Me}$ **2**, Ph **3**) react differently with the same reagents, i.e., *N*-methylmorpholine-*N*-oxide (nmmo), diironnonacarbonyl, and elemental sulfur/selenium. Whereas silathioethermylene **11** afforded the first *O*-silylthionogermaster $[(\text{Bu}_2\text{ATI})\text{Ge}(\text{S})\text{OSiMe}_3]$ (**1**) in its reaction with nmmo involving 1,3-silyl migration, siloxygermylenes **2** and **3** reacted with the same to give 1,3-dioxadigermetanes $\{[(\text{Bu}_2\text{ATI})\text{Ge}(\text{O})\text{OSiR}_3]_2\}$ ($\text{R} = \text{Me}$ **14** and Ph **4**, respectively) as dimerized products. Similarly, in the reaction with diironnonacarbonyl, compound **3** behaved in the anticipated way and led to its complex with iron tetracarbonyl $[(\text{Bu}_2\text{ATI})\text{Ge}(\text{Fe}(\text{CO})_4)\text{OSiPh}_3]$ (**5**), but compound **11** did not offer the desired complex. Further, unlike compound **11**, compounds **2** and **3** afford the anticipated *O*-silylthiono- and selenogermasters $[(\text{Bu}_2\text{ATI})\text{Ge}(\text{E})\text{OSiR}_3]$ ($\text{E} = \text{S}$; $\text{R} = \text{Me}$ **1**, Ph **7**; $\text{E} = \text{Se}$; $\text{R} = \text{Me}$ **6**, Ph **8**) when treated with elemental sulfur and selenium. As there is no report on the reactivity of germasters, the reactions of *O*-silylthiono- and selenogermasters **1** and **6–8** are also carried out with methanol and nmmo.



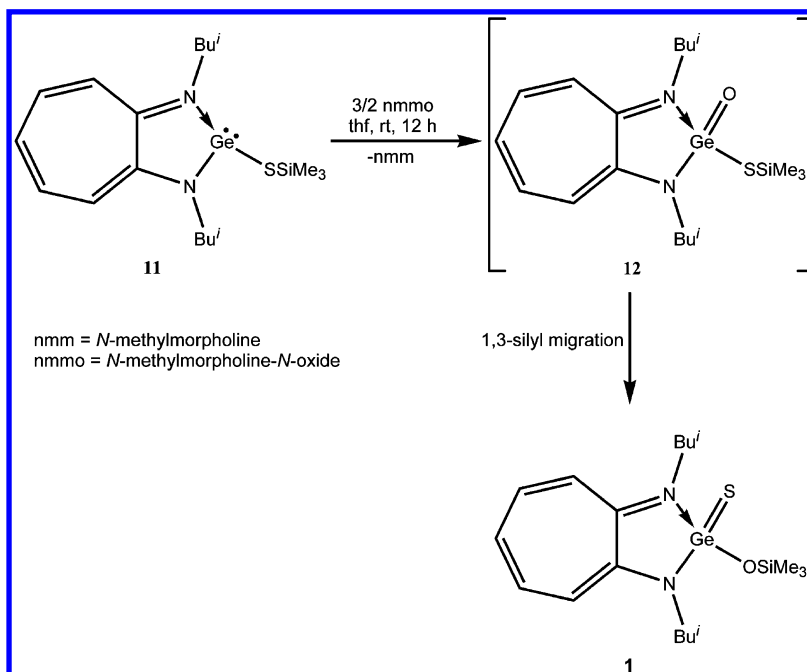
INTRODUCTION

In the last couple of decades, divalent germanium compounds (germylenes) have attracted huge interest in the synthetic main group chemistry.^{1–4} The reactivity of germynes of the type $\text{L}_2\text{Ge}/\text{L}'\text{Ge}$ ($\text{L} = \text{monoanionic monodentate ligand}$, $\text{L}' = \text{dianionic bidentate ligand}$) is attributed mainly to the lone pair of electrons and vacant p orbital on the germanium atom. In the germynes of the type $\text{L}''\text{GeX}$ ($\text{L}'' = \text{monoanionic chelating ligand}$; $\text{X} = \text{halogen, H, OH, NR}_2, \text{OR, and so forth}$), the reactivity is basically due to the lone pair of electrons on germanium and the Ge–X bond. Some of these germynes ($\text{L}''\text{GeX}$) are found to react unusually when a particular X group is present on the germanium atom. For instance, the reaction of $\text{L}''\text{GeH}$ ($\text{L}'' = \text{CH}\{(\text{CMe})(2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{N})_2\}$) with elemental sulfur carried out by Roesky and co-workers afforded germanium dithiocarboxylic acid analogue $\text{L}''\text{Ge}(\text{S})\text{SH}$ instead of the anticipated oxidative addition product $\text{L}''\text{Ge}(\text{S})\text{H}$.⁵ Here, the insertion of a sulfur atom into the Ge–H bond also occurred along with oxidative addition at the germanium center. Similarly, Fulton's group demonstrated that β -diketiminatogermanium(II) dicyclohexylphosphanide $[\text{L}''\text{GePCy}_2]$ behaved differently in its reactions with gray selenium.⁶ Its reaction with 1 equiv of selenium afforded an insertion product, $[\text{L}''\text{GeSePCy}_2]$, where the selenium is inserted into the Ge–P bond. Further, its reaction with around 5 equiv of selenium resulted in the anticipated oxidative addition product $[\text{L}''\text{Ge}(\text{Se})\text{PCy}_2]$ along with the unexpected product $[\text{L}''\text{GeSeP}(\text{Se})\text{Cy}_2]$ where both oxidative addition and insertion reactions occurred. Recently, we also found out that,

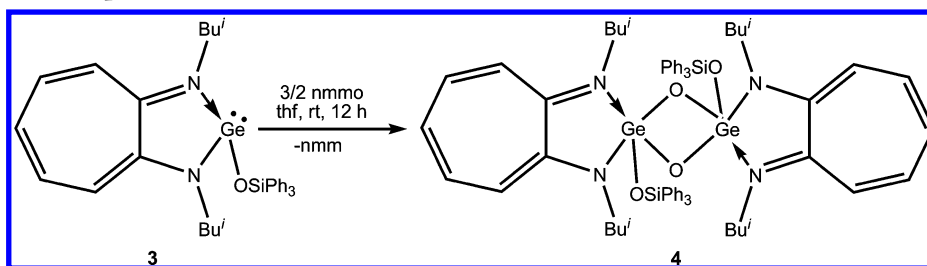
when a germylene $[(\text{Bu}_2\text{ATI})\text{GeSSiMe}_3]$ (**11**) with a labile SSiMe_3 group is treated with elemental chalcogens (sulfur, selenium, and tellurium), it unusually gives germaacid anhydrides $\{[(\text{Bu}_2\text{ATI})\text{Ge}(\text{E})]_2\text{E}\}$ ($\text{E} = \text{S, Se, and Te, respectively}$) instead of the usual oxidative addition products $[(\text{Bu}_2\text{ATI})\text{Ge}(\text{E})\text{SSiMe}_3]$.⁷ Interestingly, in these reactions, for the first time, condensation reaction was observed along with oxidative addition and insertion reactions. Nevertheless, when the oxygen analogue of compound **11**, i.e., $[(\text{Bu}_2\text{ATI})\text{GeOSiMe}_3]$ (**2**), is treated with elemental sulfur and selenium, only the anticipated oxidative addition products $[(\text{Bu}_2\text{ATI})\text{Ge}(\text{E})\text{OSiMe}_3]$ ($\text{E} = \text{S and Se, respectively}$) are obtained. As the germynes **11** and **2** with SSiMe_3 and OSiMe_3 groups, respectively, differed a lot in their reactivity with elemental sulfur and selenium, we became interested in studying the reactivity traits of these germynes containing SSiMe_3 and OSiR_3 groups with other reagents also. Accordingly, we report here the differences in the reactivity of compounds **11** and $[(\text{Bu}_2\text{ATI})\text{GeOSiR}_3]$ ($\text{R} = \text{Me}$ **2**, Ph **3**) with *N*-methylmorpholine-*N*-oxide (nmmo) and diironnonacarbonyl. In their reaction with nmmo, compound **11** afforded uniquely the first *O*-silylthionogermaster $[(\text{Bu}_2\text{ATI})\text{Ge}(\text{S})\text{OSiMe}_3]$ (**1**) and compounds **2–3** gave the expected 1,3-dioxadigermetanes $\{[(\text{Bu}_2\text{ATI})\text{Ge}(\text{O})\text{OSiR}_3]_2\}$ ($\text{R} = \text{Me}$ **14**, Ph **4**). In the reaction with diironnonacarbonyl, compound **3** afforded the anticipated iron tetracarbonyl–germylene complex $[(\text{Bu}_2\text{ATI})\text{Ge}(\text{Fe}(\text{CO})_4)\text{OSiPh}_3]$ (**5**), but compound **11** did not offer the desired complex.

Received: April 5, 2015

Scheme 1. Reaction of Compound 11 with nmmo



Scheme 2. Reaction of Compound 3 with nmmo



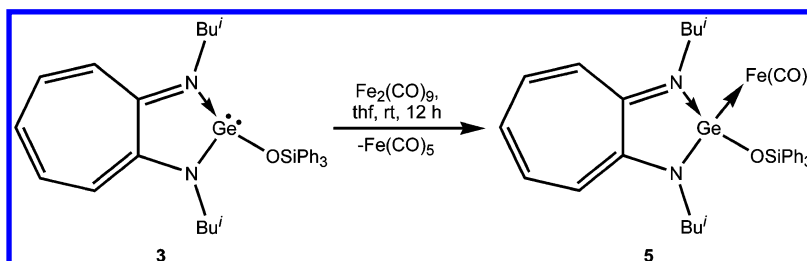
Ge(Fe(CO)₄)OSiPh₃] (5), whereas compound 11 did not. Further, as there is no reactivity studies reported on germaesters,⁸ the reactivity of the obtained *O*-silylthionogermaester 1 has been looked at along with its analogues [(Bu^{*i*}₂ATI)Ge(E)OSiR₃] (R = Me; E = Se 6 and R = Ph; E = S 7, Se 8).

RESULTS AND DISCUSSION

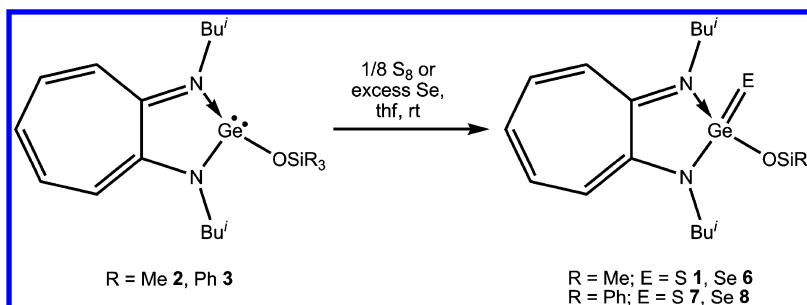
Synthesis and Spectra. As mentioned in the Introduction, to study further the reactivity differences between silathiogermylene 11 and siloxygermylenes 2–3, their reactivity with nmmo was carried out. Reaction of compound 11 with a little excess of nmmo resulted in the first *O*-silylthionogermaester 1 (Scheme 1). The formation of compound 1 from compound 11 suggested the formation of *S*-silylgermathioester 12 as an intermediate, which undergoes 1,3-silyl migration to afford compound 1 (Scheme 1). In order to compare this reactivity of silathiogermylene 11 with siloxygermylenes, compounds 2 and 3 with methyl and phenyl groups at the silicon atom were synthesized, respectively (Scheme S1, Supporting Information). The reaction of (Bu^{*i*}₂ATI)GeCl (13) with lithiated trimethylsilanol and triphenylsilanol in toluene at low temperature gave compounds 2 and 3, respectively (Scheme S1). As compound 2 was obtained as a red viscous liquid with some amount of impurity (Figures S4 and S5; see the Supporting Information), it was used for reactivity studies without further purification.

Compound 3 was isolated as a spectroscopically pure orange solid in 94% yield. Compounds 2 and 3 are the first examples of free monosiloxygermylene.^{9,10}

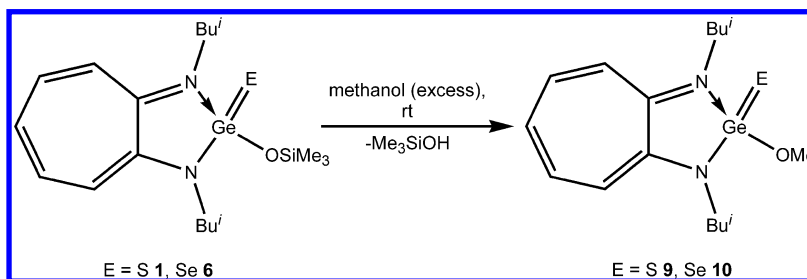
The reaction of siloxygermylene 2 with nmmo in a 1:1.5 molar ratio afforded a yellow solid. On the basis of NMR spectroscopic studies, it was found that the solid contained a mixture of products, and we attempted their separation. During the slow evaporation of solvent from the hexane solution of the yellow solid, yellow-colored single crystals were obtained and characterized as 1,3-dioxadigermetane [(Bu^{*i*}₂ATI)Ge(O)-OSiMe₃]₂ (14) through X-ray diffraction studies (Figure S1, Supporting Information). For recording the ¹H and ¹³C NMR spectra of these crystals, the following operations were performed: they were cooled to −40 °C, washed twice with cold hexane at −40 °C, and dried finally. In contrast to the anticipation to obtain clean NMR spectra, we obtained spectra that indicate still the presence of a mixture of products (Figures S6–S7; see the Supporting Information). This may be comprehended by stating that, in solution, 1,3-dioxadigermetane 14 gets converted to its monomeric form (germaester [(Bu^{*i*}₂ATI)Ge(O)OSiMe₃]) to some extent that may also decompose to other products. The similar reaction of analytically pure compound 3 (containing bulky SiPh₃ group) was carried out with nmmo in a 1:1.5 molar ratio. This reaction afforded the pure 1,3-dioxadigermetane [(Bu^{*i*}₂ATI)Ge(O)-OSiPh₃]₂ (4) via transient formation of the oxidized product

Scheme 3. Reaction of Compound 3 with $\text{Fe}_2(\text{CO})_9$ 

Scheme 4. Reaction of Compounds 2 and 3 with Elemental Sulfur and Selenium



Scheme 5. Reaction of Compounds 1 and 6 with Methanol



$[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{O})\text{OSiPh}_3]$ (**15**), which underwent dimerization (Scheme 2). As we obtained the hint that compound **14** can exist as a monomer in solution, we extended the same NMR spectroscopic study to compound **4** also. In the ^1H NMR spectra of compound **4** recorded at high and low concentrations, we did not observe any difference. Nevertheless, in the ^{13}C NMR spectra of compound **4** recorded at high and low concentrations, we did notice the following difference: at low concentration, for each signal, a very close extra signal can be seen (Figures S8 and S9; see the Supporting Information). This again can be explained by saying that, in solution, compound **4** gets converted to its monomeric form (*O*-silylgermaester (**15**)) to some extent. Interestingly, in contrast to the situation in compound **14**, we did not observe any decomposed product while the monomer is formed in dilute solution, and this may be due to the bulkiness of the SiPh_3 group compared with that of the SiMe_3 group. This observation gives the hope of isolating a monomeric germaester if the bulkiness is increased beyond the SiPh_3 group. As compound **2** had some amount of impurity, later studies were continued with compound **3**.

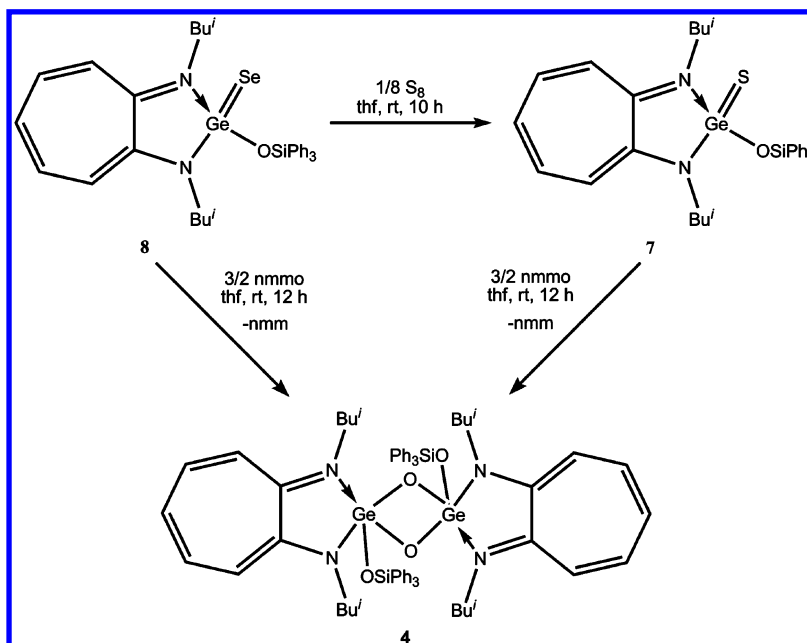
To further showcase the differences in the reactivity of siloxy- and silathio-germylenes, their reaction with diironnonacarbonyl ($\text{Fe}_2(\text{CO})_9$) was carried out. The equimolar reaction of siloxygermylene **3** with $\text{Fe}_2(\text{CO})_9$ in tetrahydrofuran at room temperature afforded the expected compound **5** as a dark brown solid in an excellent yield (97%) (Scheme 3). Interestingly, compound **5** is the first iron complex stabilized

through an aminotroponiminatogermylene. Contrary to this reactivity, the equimolar reaction of silathiogermylene **11** with $\text{Fe}_2(\text{CO})_9$ under similar reaction conditions gave an unidentified mixture of products. As the Ge-S and S-Si bonds (in compound **11**) are more labile than the Ge-O and O-Si bonds (in compound **3**), the former (compound **11**) might be undergoing other reactions giving a mixture of products.⁷

In the communication (*vide supra*) where we talked about the unusual reactivity of silathiogermylene $[(\text{Bu}^i_2\text{ATI})\text{GeSSiMe}_3]$ (**11**) with elemental sulfur and selenium, we hinted about the usual reactivity of siloxygermylene **2** with these reagents. Here, the complete details regarding this reactivity along with other information are also provided. Thus, the reaction of compound **2** with elemental sulfur and selenium afforded the expected *O*-silylthiono- and selenogermesters **1** and **6**. Though they are the anticipated products, they are the first examples of *O*-silylgermaesters. In order to generalize this route to *O*-silylgermaesters, further examples $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{E})\text{OSiPh}_3]$ ($\text{E} = \text{S}$ **7**, Se **8**) were obtained through the reaction of siloxygermylene **3** with elemental sulfur and selenium, respectively (Scheme 4).

Since there is no report on the reactivity of germaesters, it would be interesting to see how these compounds react toward nucleophiles. Accordingly, compounds **1** and **6** were treated with neat methanol at room temperature, and germaesters **9** and **10** were obtained in good yields (92% and 90%, respectively) (Scheme 5). This reaction of compounds **1** and

Scheme 6. Conversion of Compound 8 to Compound 7 and Compounds 7 and 8 to Compound 4



6 with methanol can also be called as metathesis. It is to be noted here that the Ge=S/Se bonds in these compounds are not affected during the reaction. Further, methanol used in these reactions was not anhydrous, and this suggests that these reactions can tolerate moisture. We also tried the hydrolysis reactions of compounds 1 and 6 at 60 °C in tetrahydrofuran with an excess of water. However, no reaction took place and the pure starting materials (compounds 1 and 6) were recovered after the evaporation of all the volatiles.

As the next reactivity study, the chalcogen replacement reactions (i.e., the replacement of a heavier chalcogen atom by the lighter one) were tried with these germaesters. Accordingly, compound 8 was treated with elemental sulfur in tetrahydrofuran in a 1:1 molar ratio, and we found that selenium in compound 8 is replaced by sulfur, resulting in compound 7 (Scheme 6).¹⁰ Expecting a similar reactivity with compounds 7 and 8 in the presence of an oxygen source (i.e., nmno), compounds 7 and 8 were treated with a little excess of nmno, and the expected 1,3-dioxadigermetane 4 was obtained. In these reactions, the replacement of S/Se atom by an oxygen atom might have resulted in an intermediate $[(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{O})\text{OSiPh}_3]$ (15), which underwent dimerization for the formation of compound 4 (Scheme 6). As suggested by Barrau and co-workers, these chalcogen substitution reactions are possible due to the following order of the bond energies of Ge=E bonds: Ge=Se < Ge=S < Ge=O.⁴¹

All the compounds 1–10 are thermally stable under a dry N₂ atmosphere and freely soluble in toluene, tetrahydrofuran, and chloroform. Compounds 2 and 3 are soluble in hexane also. Compounds 1 and 3–10 were characterized in solution by NMR spectroscopic studies. In the ¹H NMR spectrum of compound 1, a singlet (0.17 ppm) for methyl protons of the trimethylsilyl group was seen. For its isobutyl groups, a doublet (1.02 ppm) for methyl protons, a multiplet (2.24–2.37 ppm) for methine protons, and two double doublets (3.48 and 3.66 ppm) for methylene protons were observed. The five protons of its seven-membered ring were seen between 6.86 and 7.46 ppm. A similar resonance pattern was observed for all the protons of compound 6. For the isobutyl groups of compound

3, two doublets (0.89 and 0.91 ppm) for methyl protons, a multiplet (2.06–2.17 ppm) for methine protons, and a doublet (3.16 ppm) for methylene protons were observed. Its seven- and six-membered ring protons were observed in the range of 6.45–7.49 ppm. In compound 5, the resonance for the methyl protons (of its isobutyl groups) were slightly upfield shifted (broad signal, 0.86 ppm) in comparison to those of compound 3. Further, there is no significant chemical shift difference with respect to the rest. In line with compound 5, a similar upfield shift was seen for the methyl protons of compound 7 (two doublets, 0.85 and 0.88 ppm) and 8 (two doublets, 0.84 and 0.88 ppm), whereas the rest of their protons were slightly downfield shifted in comparison to the corresponding protons of compound 3. In compound 4, all the resonances appeared upfield shifted in comparison to the corresponding protons of compounds 7 and 8, but the splitting pattern is asymmetric probably due to steric congestion. The absence of any signal for the nine protons of the trimethylsilyl group at around 0.17 ppm and the appearance of a singlet for the methyl protons of the methoxy group at 3.68 ppm in compound 9 and 3.63 ppm in compound 10 suggest the formation of these compounds.

In the ¹³C NMR spectra, four signals (in the range of 20–54 ppm) for the isobutyl groups and eight signals (in the range of 113–161 ppm) for ring carbons were observed in compounds 3, 4, 5, 7, and 8. In the case of compound 5, an additional signal was observed at 214.45 ppm for the carbonyl carbons. In compounds 1 and 6, one signal (2.73 (1) and 2.88 ppm (6)) for the methyl carbons of trimethylsilyl group, three signals for isobutyl groups, and four signals for ring carbons were observed. In compounds 9 and 10, four signals for isobutyl carbons, five signals for ring carbons, and one signal for methyl carbon of the methoxy group (OCH₃, 52.39 (9) and 52.75 ppm (10)) were observed. In the ²⁹Si NMR spectra, a signal for the SiPh₃ group appeared at –24.72 ppm in compound 3 and –19.39 ppm in compounds 7 and 8. The SiMe₃ group in compounds 1 and 6 appeared at a downfield region (13.25 (1) and 13.29 ppm (6)) in comparison to the SiPh₃ group of compounds 7 and 8. However, no signal was detected for compounds 4 and 5 even after a very large number of scans.

The selenium resonances in the ^{77}Se NMR spectra of compounds **6**, **8**, and **10** were observed at -353.6 , -357.1 , and -338.0 ppm, respectively, and these are comparable to the corresponding resonances reported for similar compounds.^{7,8,11,12}

X-ray Crystal Structures of Compounds 1, 4, 5, 7, 8, and 14. The molecular structures of compounds **1**, **4**, **5**, **7**, **8**, and **14** were further confirmed by single-crystal X-ray crystallographic studies. The crystallographic data for these compounds are given in Table S1 (see the Supporting Information). Compounds **1** and **7–8** crystallized in the orthorhombic and monoclinic space groups $Pbca$ and $P2_1/c$, respectively. Compounds **4**, **5**, and **14** crystallized in the triclinic space group $P\bar{1}$. In all of these compounds, except **4** and **14**, the germanium atoms have a distorted tetrahedral geometry around them.

In compound **1** (Figure 1), the S–Ge–O bond angle ($117.9(1)^\circ$) is smaller than that in $(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{S})\text{O}(\text{Bu}^t)$ (**16**)

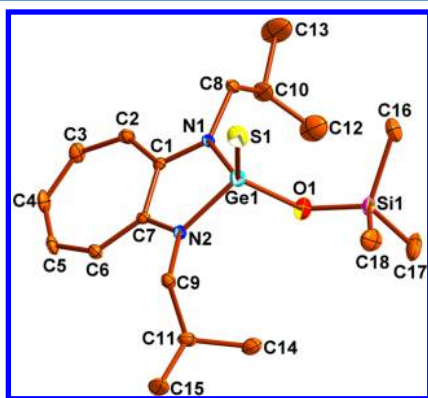


Figure 1. Molecular structure of compound **1**. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–S(1) 2.081(1), Ge(1)–O(1) 1.757(3), Ge(1)–N(1) 1.872(3), Ge(1)–N(2) 1.879(3), Si(1)–O(1) 1.648(3); N(1)–Ge(1)–N(1) 84.8(1), O(1)–Ge(1)–S(1) 117.9(1), Si(1)–O(1)–Ge(1) 132.3(2).

($123.1(2)^\circ$)⁸ and almost similar to the same in $\{(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{S})\}_2\text{O}$ (**17**) ($118.3(1)^\circ$).¹³ The Ge=S bond length in compound **1** (2.081(1) Å) is comparable to that in compound **16** (2.080(2) Å). The length of the Ge–O bond (1.757(3) Å) matches with the same bond in compound **16** (1.765(4) Å).

In compound **5** (Figure 2), the Fe–Ge–O bond angle is $111.5(1)^\circ$, which is slightly smaller than that in $\text{HC}\{\text{CMe}(\text{2,6-Pr}^i_2\text{C}_6\text{H}_3\text{N})\}_2\text{Ge}(\text{OH})\text{Fe}(\text{CO})_4$ (**18**) ($113.5(1)^\circ$).¹⁴ The Ge–O–Si bond angle ($143.9(1)^\circ$) is larger than the same in compound **1** ($132.3(2)^\circ$). The Ge–O bond length (1.785(2) Å) is similar to that found in $\{(\text{Bu}^i_2\text{ATI})\text{Ge}\}_2\text{O}$ (**19**) (1.791(6) Å)¹³ but shorter than that in compound **18** (1.840(2) Å).¹⁴ The Ge–Fe bond length (2.294(1) Å) is shorter than the length of the same bond present in compound **18** (2.330(1) Å). All the Fe–C bond lengths are almost similar, and the average is 1.781(3) Å. Apart from these, the O–Si bond length is found to be 1.627(2) Å.

In compound **7** (Figure S2; see the Supporting Information), the Ge=S (2.064(1) Å) and Ge–O (1.757(3) Å) bond lengths are shorter than and similar to the corresponding bonds in compound **1** (*vide supra*), respectively. The O–Si bond in compound **7** (1.621(2) Å) is slightly shorter than the same bond in compound **1** (1.648(3) Å). The Ge–O–Si bond angle

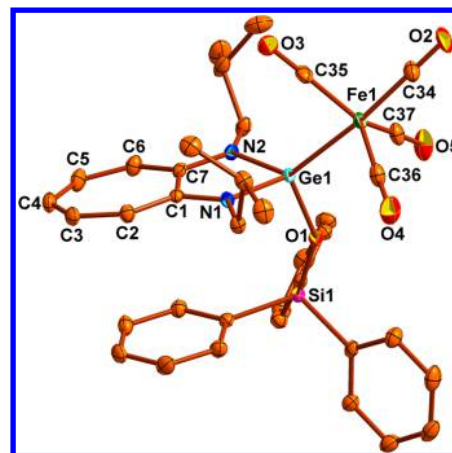


Figure 2. Molecular structure of compound **5**. One of the two molecules present in the asymmetric unit is shown here. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Molecule 1: Ge(1)–Fe(1) 2.294(1), Ge(1)–O(1) 1.785(2), Ge(1)–N(2) 1.892(2), Ge(1)–N(1) 1.896(2), Si(1)–O(1) 1.627(2); N(1)–Ge(1)–N(2) 83.3(1), O(1)–Ge(1)–Fe(1) 111.5(1), Si(1)–O(1)–Ge(1) 143.9(1). Molecule 2: Ge(2)–Fe(2) 2.295(1), Ge(2)–O(6) 1.785(2), Ge(2)–N(3) 1.895(2), Ge(2)–N(4) 1.896(2), Si(2)–O(6) 1.625(2); N(3)–Ge(2)–N(4) 83.6(1), O(6)–Ge(2)–Fe(2) 111.7(1), Si(2)–O(6)–Ge(2) 144.0(1).

($142.4(1)^\circ$) is greater than that in compound **1** ($132.3(2)^\circ$). In compound **8** (Figure 3), the Se–Ge–O bond angle

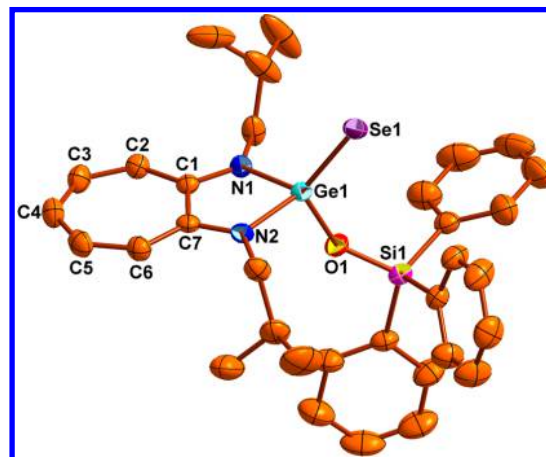


Figure 3. Molecular structure of compound **8**. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–Se(1) 2.200(1), Ge(1)–O(1) 1.764(2), Ge(1)–N(1) 1.879(2), Ge(1)–N(2) 1.886(2), Si(1)–O(1) 1.628(2); N(1)–Ge(1)–N(2) 84.5(1), O(1)–Ge(1)–Se(1) 118.5(1), Si(1)–O(1)–Ge(1) 141.8(1).

($118.5(1)^\circ$) is smaller than that in $\{(\text{Bu}^i_2\text{ATI})\text{Ge}(\text{Se})\text{O}(\text{Bu}^t)\}_2$ (**20**) ($123.4(1)^\circ$).⁸ The Ge–O–Si bond angle ($141.8(1)^\circ$) is almost similar to that in compound **7** ($142.4(1)^\circ$). The Ge=Se bond length (2.200(1) Å) is almost equal to the same in compound **20** (2.218(1) Å). The Ge–O bond length in compound **8** (1.764(2) Å) matches with that found in compound **7** (1.757(3) Å) and compound **20** (1.774(3) Å). The O–Si bond (1.628(2) Å) is also nearly equal to that in compound **7** (1.621(2) Å).

In compound **4** (Figure 4), the presence of two different Ge–O_(Ge) bond lengths (1.787(3) and 1.844(3) Å) reveals the

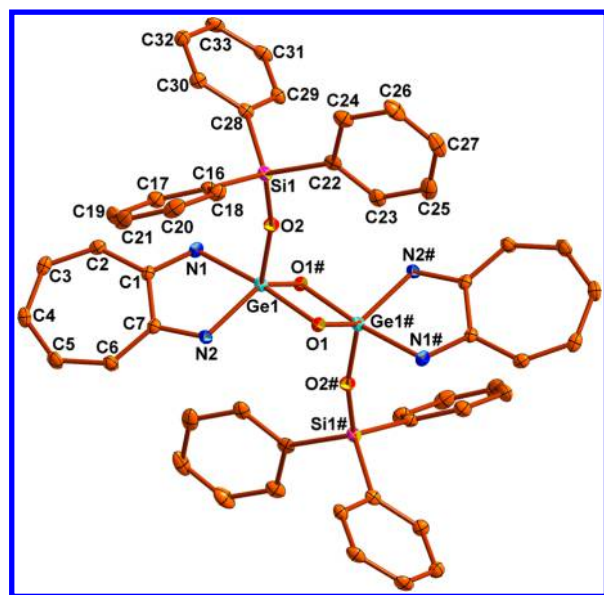


Figure 4. Molecular structure of compound 4. Thermal ellipsoids are drawn at 30% probability level. Isobutyl groups and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–O(1) 1.787(3), Ge(1)–O(1#) 1.844(3), Ge(1)–O(2) 1.767(3), Si(1)–O(2) 1.595(3), Ge(1)–N(1) 1.975(4), Ge(1)–N(2) 1.917(3); N(1)–Ge(1)–N(2) 80.4(2), O(1)–Ge(1)–O(1#) 85.6(1), Ge(1)–O(1)–Ge(1#) 94.4(1), O(2)–Ge(1)–O(1) 112.8(1), O(2)–Ge(1)–O(1#) 95.9(1), Si(1)–O(2)–Ge(1) 165.4(2). Equivalent atoms (#) are symmetry (inversion center) generated.

nonuniformity of the Ge–O bonds in the four-membered Ge_2O_2 ring. Also, these bond lengths are longer than the Ge–O_(Si) bond length (1.767(3) Å) in the same compound. The Ge–O_(Si) bond length in compound 4 is almost similar to the same in compounds 7 and 8 (*vide supra*). The O–Ge–O and Ge–O–Ge bond angles in the four-membered Ge_2O_2 ring are 85.6(1)° and 94.4(1)°, respectively. The Ge–O–Si bond angle in compound 4 (165.4(2)°) is greater than the same bond angle in compounds 1, 5, 7, and 8.

CONCLUSION

In the germynes of the type L^rGeX , we have demonstrated the role of a labile substituent in altering the usual reactivity of the germynes. Thus, the silathiogermylene 11 showed unusual reactivity with nmmo and afforded the first *O*-silylgermaester 1 through oxidative addition, followed by 1,3-silyl migration. In contrast, the ATI stabilized siloxygermylenes 2 and 3, the oxygen analogues of compound 11, yielded 1,3-dioxadigermetanes 14 and 4 through oxidative addition, followed by dimerization, respectively. Further in the reaction with $\text{Fe}_2(\text{CO})_9$, compound 11 did not result in the expected iron tetracarbonyl complex. However, the anticipated complexation reaction occurred with compound 3 and the first ATI ligand stabilized germylene–iron tetracarbonyl complex 5 was obtained. Apart from that, the reactivity of the first *O*-silylgermaesters 1 and 6 has also been studied with methanol as there was no previous report on the reactivity of germaesters. A neat reaction of compounds 1 and 6 with nondried methanol resulted in germaesters 9 and 10 with a OMe group without affecting the Ge=E bond (E = S/Se). The chalcogen replacement reactions on *O*-silylgermaesters 7–8 using nmmo as an oxygen source resulted in compound 4 through

the dimerization of the intermediate $[(\text{Bu}_2\text{ATI})\text{Ge}(\text{O})\text{OSiPh}_3]$ (15).

EXPERIMENTAL SECTION

All the air- and moisture-sensitive compounds were manipulated under a dry N_2 atmosphere using either standard Schlenk techniques or a glovebox [Jacomex (GP Concept)-T2 workstation]. Hexane, toluene, and tetrahydrofuran were dried over sodium and benzophenone. CDCl_3 was dried over 4 Å molecular sieves. $\text{Fe}_2(\text{CO})_9$, elemental sulfur, and selenium were purchased from Aldrich and used as received. *N*-Methylmorpholine-*N*-oxide (nmmo) was purchased from Aldrich and purified through sublimation prior to use. Compound 13 was prepared according to a literature procedure.^{3w,12,15} LiOSiMe_3 and LiOSiPh_3 were prepared through lithiation of Me_3SiOH and Ph_3SiOH using equimolar amounts of *n*-butyllithium (1.6 M in hexane) in hexane and tetrahydrofuran, respectively. Melting points were recorded on a Unitech Sales digital melting point apparatus by sealing the compounds in glass capillaries. CHN analyses were performed using a PerkinElmer CHN analyzer. ^1H , ^{13}C , ^{29}Si , and ^{77}Se NMR spectra were recorded in CDCl_3 on a 300 MHz Bruker DPX-300 NMR spectrometer. The chemical shifts δ are reported in ppm and internally referenced with respect to residual solvent (^1H NMR) and solvent (^{13}C NMR) resonances.¹⁶ $(\text{CH}_3)_4\text{Si}$ and $(\text{CH}_3)_2\text{Se}$ were used as external references for ^{29}Si and ^{77}Se NMR spectroscopic studies, respectively.

Synthesis of $(\text{Bu}_2\text{ATI})\text{Ge}(\text{S})\text{OSiMe}_3$ (1). To a solution of compound 11 (200 mg, 0.49 mmol) in tetrahydrofuran (20 mL) was added nmmo (86 mg, 0.73 mmol) at room temperature, and the reaction mixture was stirred for 12 h. The excess nmmo was removed by filtration, and the volatiles were removed from the filtrate under reduced pressure to result in a yellow residue. It was then washed twice with cold hexane to afford an analytically pure sample of compound 1 as a yellow solid. Slow diffusion of hexane into the saturated solution of compound 1 in toluene afforded its single-crystals suitable for structural analysis. Yield: 202 mg (0.47 mmol, 97%). mp: 158 °C. Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{GeN}_2\text{OSSi}$ ($M = 425.25$): C, 50.84; H, 7.58; N, 6.59. Found: C, 51.16; H, 7.67; N, 6.65. ^1H NMR (300 MHz, CDCl_3): δ 0.17 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.02 (d, $^3J_{\text{HH}} = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 2.24–2.37 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.48 (dd, $J_{\text{HH}} = 13.8$, 6.9 Hz, 2H, CH_2), 3.66 (dd, $J_{\text{HH}} = 13.8$, 7.8 Hz, 2H, CH_2), 6.86–6.92 (m, 1H, CH), 6.98 (d, $^3J_{\text{HH}} = 11.4$ Hz, 2H, CH), 7.39–7.46 (m, 2H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 2.73 ($\text{Si}(\text{CH}_3)_3$), 21.04 ($\text{CH}(\text{CH}_3)_2$), 27.81 ($\text{CH}(\text{CH}_3)_2$), 53.50 (CH_2), 116.44, 125.38, 138.44, 156.78 (CH_{ring}). $^{29}\text{Si}\{^1\text{H}\}$ NMR (60 MHz, CDCl_3): δ 13.25 (O– $\text{Si}(\text{CH}_3)_3$).

Synthesis of $(\text{Bu}_2\text{ATI})\text{GeOSiMe}_3$ (2). To a stirred solution of compound 13 (1.0 g, 2.95 mmol) in toluene (40 mL) was added freshly prepared lithium trimethylsiloxide (283 mg, 2.95 mmol) at 0 °C, and the reaction mixture was further stirred for 8 h at room temperature. The resulting red mixture was filtered through a sintered funnel with Celite. Then, all the volatiles were removed under reduced pressure to yield compound 2 as a red viscous liquid with some amount of impurity. It was used as such for reactivity studies without further purification.

^1H NMR (300 MHz, CDCl_3): δ –0.07 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.02 (d, $^3J_{\text{HH}} = 5.1$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 2.18–2.29 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.40 (d, $^3J_{\text{HH}} = 7.2$ Hz, 4H, CH_2), 6.47 (t, $^3J_{\text{HH}} = 9.3$ Hz, 1H, CH), 6.57 (d, $^3J_{\text{HH}} = 11.4$ Hz, 2H, CH), 7.08–7.15 (m, 2H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 2.92 ($\text{Si}(\text{CH}_3)_3$), 21.33 ($\text{CH}(\text{CH}_3)_2$), 21.42 ($\text{CH}(\text{CH}_3)_2$), 27.62 ($\text{CH}(\text{CH}_3)_2$), 53.89 (CH_2), 113.82, 120.23, 136.17, 160.79 (CH_{ring}) (Figures S4 and S5; see the Supporting Information).

Synthesis of $(\text{Bu}_2\text{ATI})\text{GeOSiPh}_3$ (3). To a stirred solution of compound 13 (1.0 g, 2.95 mmol) in toluene (50 mL) was added lithium triphenylsiloxide (0.8 g, 2.95 mmol) at 0 °C, and the reaction mixture was further stirred for 12 h at room temperature. The resulting orange mixture was filtered through a sintered funnel with Celite. Then, all the volatiles were removed under reduced pressure to give a solid residue. This residue was washed with cold hexane and dried to

afford compound **3** as a spectroscopically pure orange solid. Keeping its saturated solution in toluene at $-40\text{ }^{\circ}\text{C}$ afforded single crystals. Yield: 1.6 g (2.77 mmol, 94%). mp: $79\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{33}\text{H}_{38}\text{GeN}_2\text{OSi}$ ($M = 579.39$): C, 68.41; H, 6.61; N, 4.83. Found: C, 68.62; H, 6.68; N, 4.86. ^1H NMR (300 MHz, CDCl_3): δ 0.89 (d, $^3J_{\text{HH}} = 4.8\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 0.91 (d, $^3J_{\text{HH}} = 5.1\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 2.06–2.17 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.16 (d, $^3J_{\text{HH}} = 7.2\text{ Hz}$, 4H, CH_2), 6.45–6.54 (m, 3H, CH), 7.08 (t, $^3J_{\text{HH}} = 10.2\text{ Hz}$, 2H, CH), 7.21–7.31 (m, 9H, CH), 7.49 (d, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 6H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 21.02 ($\text{CH}(\text{CH}_3)_2$), 21.18 ($\text{CH}(\text{CH}_3)_2$), 27.56 ($\text{CH}(\text{CH}_3)_2$), 53.69 (CH_2), 113.83, 120.38, 127.25, 128.69, 135.06, 135.84, 139.13, 160.70 (CH_{ring}). $^{29}\text{Si}\{^1\text{H}\}$ NMR (60 MHz, CDCl_3): δ -24.72 (O-SiPh₃).

Synthesis of $\{(\text{Bu}_2\text{ATI})\text{Ge}(\text{O})\text{OSiPh}_3\}_2$ (4**).** To a solution of compound **3** (300 mg, 0.52 mmol) in tetrahydrofuran (20 mL) was added nmno (91 mg, 0.78 mmol) at room temperature, and the reaction mixture was stirred for 18 h. The excess nmno was removed by filtration, and the volatiles were removed under reduced pressure to give a yellow residue. This residue was washed with hexane to afford compound **4** as a yellow solid. The slow evaporation of its saturated solution in toluene afforded single crystals. Yield: 293 mg (0.25 mmol, 95%). mp: $103\text{ }^{\circ}\text{C}$ (decomp). Anal. Calcd for $\text{C}_{66}\text{H}_{76}\text{Ge}_2\text{N}_4\text{O}_4\text{Si}_2$ ($M = 1190.78$): C, 66.57; H, 6.43; N, 4.71. Found: C, 66.34; H, 6.47; N, 4.70. ^1H NMR (300 MHz, CDCl_3): δ 0.79 (d, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 0.84 (d, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 2.31 (broad, 4H, $\text{CH}(\text{CH}_3)_2$), 3.25–3.40 (m, 4H, CH_2), 3.52–3.59 (m, 4H, CH_2), 6.45–6.66 (m, 6H, CH), 6.98–7.22 (m, 22H, CH), 7.48 (d, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 8H, CH), 7.61 (d, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 4H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 21.07 ($\text{CH}(\text{CH}_3)_2$), 21.16 ($\text{CH}(\text{CH}_3)_2$), 27.89 ($\text{CH}(\text{CH}_3)_2$), 52.76 (CH_2), 114.71, 120.88, 126.97, 128.60, 135.40, 135.79, 138.14, 154.08 (CH_{ring}).

Synthesis of $\{(\text{Bu}_2\text{ATI})\text{Ge}(\text{O})\text{OSiMe}_3\}_2$ (14**).** The same procedure was followed as in the synthesis of compound **4**.

Synthesis of $(\text{Bu}_2\text{ATI})\text{Ge}(\text{Fe}(\text{CO})_4)\text{OSiPh}_3$ (5**).** To a stirred solution of compound **3** (300 mg, 0.52 mmol) in tetrahydrofuran (25 mL) was added $\text{Fe}_2(\text{CO})_9$ (188 mg, 0.52 mmol) at room temperature, and the reaction mixture was stirred for 12 h. It was then filtered, and all the volatiles from the filtrate were removed under reduced pressure. The resultant residue was washed with hexane and dried to afford a spectroscopically pure sample of compound **5** as a dark brown solid. Single crystals of compound **5** were obtained from its saturated solution in toluene by slow evaporation method. Yield: 375 mg (0.50 mmol, 97%). mp: $149\text{ }^{\circ}\text{C}$ (decomp). Anal. Calcd for $\text{C}_{37}\text{H}_{38}\text{FeGeN}_2\text{O}_5\text{Si}$ ($M = 727.28$): C, 59.47; H, 5.13; N, 3.75. Found: C, 59.11; H, 4.89; N, 3.73. ^1H NMR (300 MHz, CDCl_3): δ 0.86 (broad, 12H, $\text{CH}(\text{CH}_3)_2$), 2.21 (broad, 2H, $\text{CH}(\text{CH}_3)_2$), 3.24 (broad, 2H, CH_2), 3.39 (broad, 2H, CH_2), 6.70–6.74 (broad, 2H, CH), 6.86 (broad, 1H, CH), 7.21–7.29 (broad, 9H, CH), 7.48 (broad, 6H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 20.56 ($\text{CH}(\text{CH}_3)_2$), 20.94 ($\text{CH}(\text{CH}_3)_2$), 28.50 ($\text{CH}(\text{CH}_3)_2$), 52.76 (CH_2), 116.22, 125.09, 127.59, 129.46, 135.14, 136.87, 137.70, 158.01 (CH_{ring}), 214.45 ($\text{Fe}(\text{CO})_4$).

Alternative Synthesis of $(\text{Bu}_2\text{ATI})\text{Ge}(\text{S})\text{OSiMe}_3$ (1**).** To a stirred solution of compound **2** (100 mg, 0.25 mmol) in tetrahydrofuran (5 mL) was added elemental sulfur (8 mg, 0.25 mmol) at room temperature, and the reaction mixture was stirred for 1 h. Then, the reaction mixture was filtered, and the volatiles were removed from the filtrate under reduced pressure to give a yellow residue. This residue was washed with cold hexane twice and dried to result in compound **1** as a spectroscopically pure yellow solid in quantitative yield.

Synthesis of $(\text{Bu}_2\text{ATI})\text{Ge}(\text{Se})\text{OSiMe}_3$ (6**).** To a solution of compound **2** (100 mg, 0.25 mmol) in tetrahydrofuran (5 mL) was added elemental selenium (25 mg, 32 mmol) at room temperature, and the reaction mixture was stirred for 3 h. The reaction mixture was then filtered, and the volatiles were removed from the filtrate under reduced pressure to afford a yellow residue. This residue was washed with cold hexane twice and dried to result in compound **6** as a spectroscopically pure yellow solid. Single crystals of compound **6** were obtained by the slow diffusion of hexane into its saturated

toluene solution. Yield: 116 mg (0.24 mmol, 97%). mp: $136\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{GeN}_2\text{OSeSi}$ ($M = 472.14$): C, 45.79; H, 6.83; N, 5.93. Found: C, 45.64; H, 6.78; N, 5.99. ^1H NMR (300 MHz, CDCl_3): δ 0.17 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.02 (d, $^3J_{\text{HH}} = 6.6\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 2.25–2.38 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.48 (dd, $J_{\text{HH}} = 14.1$, 6.9 Hz, 2H, CH_2), 3.68 (dd, $J_{\text{HH}} = 13.8$, 7.8 Hz, 2H, CH_2), 6.85–6.91 (m, 1H, CH), 6.97 (d, $^3J_{\text{HH}} = 11.1\text{ Hz}$, 2H, CH), 7.39–7.46 (m, 2H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 2.88 ($\text{Si}(\text{CH}_3)_3$), 21.05 ($\text{CH}(\text{CH}_3)_2$), 27.79 ($\text{CH}(\text{CH}_3)_2$), 53.39 (CH_2), 116.50, 125.43, 138.26, 156.71 (CH_{ring}). $^{29}\text{Si}\{^1\text{H}\}$ NMR (60 MHz, CDCl_3): δ 13.19 (O-Si(CH_3)₃). $^{77}\text{Se}\{^1\text{H}\}$ (57 MHz, CDCl_3): δ -353.6 .

Synthesis of $(\text{Bu}_2\text{ATI})\text{Ge}(\text{S})\text{OSiPh}_3$ (7**).** To a stirred solution of compound **3** (200 mg, 0.35 mmol) in tetrahydrofuran (10 mL) was added elemental sulfur (11 mg, 0.35 mmol) at room temperature, and the reaction mixture was further stirred for 2 h. Then, all the volatiles were removed under reduced pressure to yield a yellow residue. This residue was washed with cold hexane twice and dried to give a spectroscopically pure sample of compound **7** as a yellow solid. Single crystals were obtained from its saturated solution in tetrahydrofuran by slow evaporation method. Yield: 209 mg (quantitative). mp: $196\text{ }^{\circ}\text{C}$ (decomp). Anal. Calcd for $\text{C}_{33}\text{H}_{38}\text{GeN}_2\text{OSSi}$ ($M = 611.46$): C, 64.82; H, 6.26; N, 4.58. Found: C, 64.54; H, 6.32; N, 4.60. ^1H NMR (300 MHz, CDCl_3): δ 0.85 (d, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 0.88 (d, $^3J_{\text{HH}} = 6.9\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 2.18–2.27 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.24–3.41 (m, 4H, CH_2), 6.83–6.93 (m, 3H, CH), 7.24–7.41 (m, 11H, CH), 7.61 (d, $^3J_{\text{HH}} = 6.6\text{ Hz}$, 6H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 20.81 ($\text{CH}(\text{CH}_3)_2$), 20.87 ($\text{CH}(\text{CH}_3)_2$), 27.77 ($\text{CH}(\text{CH}_3)_2$), 53.09 (CH_2), 116.55, 125.41, 127.52, 129.48, 135.30, 136.42, 138.14, 156.53 (CH_{ring}). $^{29}\text{Si}\{^1\text{H}\}$ NMR (60 MHz, CDCl_3): δ -19.39 (O-SiPh₃).

Synthesis of $(\text{Bu}_2\text{ATI})\text{Ge}(\text{Se})\text{OSiPh}_3$ (8**).** To a solution of compound **3** (200 mg, 0.35 mmol) in tetrahydrofuran (10 mL) was added elemental selenium (41 mg, 0.52 mmol) at room temperature, and the reaction mixture was stirred for 5 h. Then, all the volatiles were removed under reduced pressure to get a yellow residue. This residue was washed with cold hexane twice and dried to obtain a spectroscopically pure sample of compound **8** as a yellow solid. Single crystals of compound **8** were obtained from its saturated solution in tetrahydrofuran by a slow evaporation method. Yield: 220 mg (0.33 mmol, 97%). mp: $128\text{ }^{\circ}\text{C}$ (decomp). Anal. Calcd for $\text{C}_{33}\text{H}_{38}\text{GeN}_2\text{OSeSi}$ ($M = 658.35$): C, 60.20; H, 5.82; N, 4.26. Found: C, 60.01; H, 5.91; N, 4.23. ^1H NMR (300 MHz, CDCl_3): δ 0.84 (d, $^3J_{\text{HH}} = 6.6\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 0.88 (d, $^3J_{\text{HH}} = 6.6\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 2.19–2.30 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.25–3.43 (m, 4H, CH_2), 6.82–6.93 (m, 3H, CH), 7.24–7.41 (m, 11H, CH), 7.61 (d, $^3J_{\text{HH}} = 6.6\text{ Hz}$, 6H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 20.77 ($\text{CH}(\text{CH}_3)_2$), 20.91 ($\text{CH}(\text{CH}_3)_2$), 27.75 ($\text{CH}(\text{CH}_3)_2$), 52.89 (CH_2), 116.57, 125.48, 127.48, 129.47, 135.32, 136.38, 137.98, 156.52 (CH_{ring}). $^{29}\text{Si}\{^1\text{H}\}$ NMR (60 MHz, CDCl_3): δ -19.39 (O-SiPh₃). $^{77}\text{Se}\{^1\text{H}\}$ (57 MHz, CDCl_3): δ -357.1 .

Synthesis of $(\text{Bu}_2\text{ATI})\text{Ge}(\text{S})\text{OMe}$ (9**).** To compound **1** (150 mg, 0.35 mmol) was added methanol (5 mL, excess) at room temperature, and the reaction mixture was stirred for 5 h. Then, all the volatile were removed under reduced pressure to get a yellow residue. This residue was washed with hexane twice and dried to obtain a spectroscopically pure sample of compound **9** as a yellow solid. Yield: 119 mg (0.32 mmol, 92%). mp: $98\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{GeN}_2\text{OS}$ ($M = 367.10$): C, 52.35; H, 7.14; N, 7.63. Found: C, 51.98; H, 7.10; N, 7.55. ^1H NMR (300 MHz, CDCl_3): δ 1.04 (d, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 2.19–2.33 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 3.50 (dd, $J_{\text{HH}} = 14.1$, 6.9 Hz, 2H, CH_2), 3.67 (dd, $J_{\text{HH}} = 14.4$, 7.8 Hz, 2H, CH_2), 3.68 (s, 3H, OCH_3), 6.91–6.97 (m, 1H, CH), 7.04 (d, $^3J_{\text{HH}} = 11.4\text{ Hz}$, 2H, CH), 7.46 (m, 2H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 20.87 ($\text{CH}(\text{CH}_3)_2$), 21.06 ($\text{CH}(\text{CH}_3)_2$), 27.96 ($\text{CH}(\text{CH}_3)_2$), 52.39 (OCH_3), 53.83 (CH_2), 116.79, 125.77, 127.48, 138.56, 156.91 (CH_{ring}).

Synthesis of $(\text{Bu}_2\text{ATI})\text{Ge}(\text{Se})\text{OMe}$ (10**).** To compound **6** (150 mg, 0.32 mmol) was added methanol (5 mL, excess) at room temperature, and the reaction mixture was stirred for 7 h. Then, all the volatile were removed under reduced pressure to obtain a yellow

residue. This residue was washed with hexane twice and dried to afford a spectroscopically pure sample of compound **10** as a yellow solid. Yield: 118 mg (0.29 mmol, 90%). mp: 135 °C. Anal. Calcd for $C_{16}H_{26}GeN_2OSe$ ($M = 413.99$): C, 46.42; H, 6.33; N, 6.77. Found: C, 46.62; H, 6.40; N, 6.71. 1H NMR (300 MHz, $CDCl_3$): δ 1.05 (d, $^3J_{HH} = 6.6$ Hz, 12H, $CH(CH_3)_2$), 2.22–2.31 (m, 2H, $CH(CH_3)_2$), 3.50 (dd, $J_{HH} = 13.8, 6.6$ Hz, 2H, CH_2), 3.63 (s, 3H, OCH_3), 3.69 (dd, $J_{HH} = 18.9, 4.8$ Hz, 2H, CH_2), 6.91–6.97 (m, 1H, CH), 7.03 (d, $^3J_{HH} = 11.1$ Hz, 2H, CH), 7.43–7.50 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 20.84 ($CH(CH_3)_2$), 21.07 ($CH(CH_3)_2$), 27.94 ($CH(CH_3)_2$), 52.75 (OCH_3), 53.71 (CH_2), 116.81, 125.48, 125.81, 138.40, 156.91 (CH_{ring}). $^{77}Se\{^1H\}$ (57 MHz, $CDCl_3$): δ –338.0.

Conversion of Compound 8 to Compound 7. To a solution of compound **8** (200 mg, 0.35 mmol) in tetrahydrofuran (20 mL) was added elemental sulfur (12 mg, 0.37 mmol) at room temperature. The reaction mixture was stirred for 10 h and then filtered. All the volatiles from the filtrate were removed under reduced pressure to get a yellow residue. This residue was washed with hexane and dried to obtain a pure sample of compound **7** as a yellow solid. Yield: quantitative.

Conversion of Compound 8 to Compound 4. To a solution of compound **8** (200 mg, 0.35 mmol) in tetrahydrofuran (20 mL) was added nmmo (62 mg, 0.53 mmol) at room temperature. The reaction mixture was stirred for 12 h and then filtered. All the volatiles from the filtrate were then removed under reduced pressure to obtain a yellow residue. This residue was washed with hexane and dried to get a pure sample of compound **4** as a yellow solid. Yield: 188 mg (0.16 mmol, 90%).

Conversion of Compound 7 to Compound 4. To a solution of compound **7** (200 mg, 0.33 mmol) in tetrahydrofuran (20 mL) was added nmmo (57 mg, 0.49 mmol) at room temperature. The reaction mixture was stirred for 12 h. All the volatiles were then removed under reduced pressure to get a yellow residue. From this residue, the product was extracted in toluene. Removal of toluene from the extract under reduced pressure afforded a yellow residue. This residue was washed with hexane and dried to give a pure sample of compound **4** as a yellow solid. Yield: 181 mg (0.15 mmol, 93%).

X-ray Data Collection for Compounds 1, 4, 5, 7, 8, and 14. Single crystals of these compounds were coated with a cryoprotectant and then mounted on a glass fiber. The data were collected on a Bruker SMART APEX CCD diffractometer having a three-axis goniometer.¹⁷ SAINT and SADABS software were used for data integration and empirical absorption correction, respectively.¹⁸ The structure of these compounds were refined by full-matrix least-squares on F^2 using SHELXTL.¹⁹ All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated using a riding model and refined isotropically. Detailed crystal data and refinement parameters for these compounds are given in Table S1 (see the Supporting Information).

■ ASSOCIATED CONTENT

■ Supporting Information

Synthesis of compounds **2** and **3** (Scheme S1), molecular structure of compound **14** (Figure S1), molecular structure of compound **7** (Figure S2), crystallographic data and refinement parameters for compounds **1**, **4**, **5**, **7**, **8**, and **14** (Table S1), ^{77}Se NMR spectrum of compound **10** (Figure S3), 1H NMR spectrum of compound **2** (Figure S4), ^{13}C NMR spectrum of compound **2** (Figure S5), 1H NMR spectrum of crystals of compound **14** (Figure S6), ^{13}C NMR spectrum of crystals of compound **14** (Figure S7), ^{13}C NMR spectrum of compound **4** (in concentrated condition) (Figure S8), ^{13}C NMR spectrum of compound **4** (in dilute condition) (Figure S9), and crystallographic information files (CIFs) for compounds **1**, **4**, **5**, **7**, **8**, and **14**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00286.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +91-11-2659 1523. Fax: +91-11-2658 1102. E-mail: sisn@chemistry.iitd.ac.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.K. and R.K.S. thank the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for the Senior Research Fellowship (SRF). C.K.J. thanks the University Grants Commission (UGC), New Delhi, India, for the Senior Research Fellowship (SRF). S.N. thanks the Department of Science and Technology (DST), New Delhi, India, for financial support (SB/S1/IC-46/2013). He also thanks DST-FIST for the financial support to the Department of Chemistry, IIT Delhi, New Delhi, India, for establishing the single-crystal X-ray diffractometer and ESI-MS facilities.

■ REFERENCES

- (1) (a) Jones, C.; Asay, M.; Driess, M. *Chem. Rev.* **2011**, *111*, 354. (b) Mandal, S. K.; Roesky, H. W. *Chem. Commun.* **2010**, *46*, 6016. (c) Mandal, S. K.; Roesky, H. W. *Acc. Chem. Res.* **2012**, *45*, 298. (d) Fischer, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877. (e) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479. (f) Leung, W.-P.; Chan, Y.-C.; So, C.-W. *Organometallics* **2015**, *34*, 2067. (g) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457. (h) Zabula, A. V.; Hahn, F. E. *Eur. J. Inorg. Chem.* **2008**, *5165*. (i) Leung, W.-P.; Kan, K.-W.; Chong, K.-H. *Coord. Chem. Rev.* **2007**, *251*, 2253. (j) Saur, I.; Alonso, S. G.; Barrau, J. *Appl. Organomet. Chem.* **2005**, *19*, 414. (k) Köhl, O. *Coord. Chem. Rev.* **2004**, *248*, 411. (l) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251. (m) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (n) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311.
- (2) Lee, V. Y.; Sekiguchi, A. *Organometallic Compounds of Low-Coordinate Si, Ge, Sn, and Pb: From Phantom Species to Stable Compounds*; Wiley: Chichester, U.K., 2010.
- (3) (a) Krupski, S.; Schulte to Brinke, C.; Koppetz, H.; Hepp, A.; Hahn, F. E. *Organometallics* **2015**, *34*, 2624. (b) Hadlington, T. J.; Schwarze, B.; Izgorodina, E. I.; Jones, C. *Chem. Commun.* **2015**, *51*, 6854. (c) Walewska, M.; Baumgartner, J.; Marschner, C. *Chem. Commun.* **2015**, *51*, 276. (d) Xiong, Y.; Szilvási, T.; Yao, S.; Tan, G.; Driess, M. *J. Am. Chem. Soc.* **2014**, *136*, 11300. (e) Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2014**, *16*, 3028. (f) Li, Y.; Mondal, K. C.; Lübben, J.; Zhu, H.; Dittrich, B.; Purushothaman, I.; Parameswaran, P.; Roesky, H. W. *Chem. Commun.* **2014**, *50*, 2986. (g) Jana, A.; Huch, V.; Rzepa, H. S.; Scheschekwitz, D. *Angew. Chem., Int. Ed.* **2014**, *54*, 289. (h) Shan, Y.-L.; Yim, W.-L.; So, C.-W. *Angew. Chem., Int. Ed.* **2014**, *53*, 13155. (i) Su, B.; Ganguly, R.; Li, Y.; Kinjo, R. *Angew. Chem., Int. Ed.* **2014**, *53*, 13106. (j) Chia, S.-P.; Carter, E.; Xi, H.-W.; Li, Y.; So, C.-W. *Angew. Chem., Int. Ed.* **2014**, *53*, 8455. (k) Dube, J. W.; Brown, Z. D.; Caputo, C. A.; Power, P. P.; Ragnogna, P. J. *Chem. Commun.* **2014**, *50*, 1944. (l) Zabula, A. V.; Rogachev, A. Yu.; West, R. *Chem.—Eur. J.* **2014**, *20*, 16652. (m) Siwatch, R. K.; Nagendran, S. *Chem.—Eur. J.* **2014**, *20*, 13551. (n) Jha, C. K.; Karwasara, S.; Nagendran, S. *Chem.—Eur. J.* **2014**, *20*, 10240. (o) Gallego, D.; Brück, A.; Irran, E.; Meier, F.; Kaupp, M.; Driess, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 15617. (p) Ibrahim, S. M.; Rafia-A; Momeni, M. R.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Angew. Chem., Int. Ed.* **2013**, *52*, 6390. (q) Singh, A. P.; Roesky, H. W.; Carl, E.; Stalke, D.; Demers, J.-P.; Lange, A. *J. Am. Chem. Soc.* **2012**, *134*, 4998. (r) Brown, J. D.; Vasko, P.; Fetting, J. C.; Tuononen, H. M.; Power, P. P. *J. Am. Chem. Soc.* **2012**, *134*, 4045. (s) Katir, N.; Matioszek, D.; Ladeira, S.; Escudé, J.; Castel, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 5352. (t) Ayers, A. E.; Dias, H. V. R. *Inorg. Chem.* **2002**, *41*, 3259. (u) Ayers, A. E.; Marynick, D. S.; Dias, H. V. R.

- Inorg. Chem.* **2000**, 39, 4147. (v) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, 39, 3890. (w) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, 119, 4650.
- (4) (a) Li, L.; Fukawa, T.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. *Nat. Chem.* **2012**, 4, 361. (b) Okazaki, R.; Tokitoh, N. *Acc. Chem. Res.* **2000**, 33, 625. (c) Leung, W.-P.; Chiu, W.-K.; Chong, K.-H.; Mak, T. C. W. *Chem. Commun.* **2009**, 6822. (d) Yadav, D.; Siwatch, R. K.; Mukherjee, G.; Rajaraman, G.; Nagendran, S. *Inorg. Chem.* **2014**, 53, 10054. (e) Yao, S.; Xiong, Y.; Driess, M. *Chem. Commun.* **2009**, 6466. (f) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Angew. Chem., Int. Ed.* **2004**, 43, 5534. (g) Ding, Y.; Ma, Q.; Usón, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2002**, 124, 8542. (h) Hitchcock, P. B.; Hu, J.; Lappert, M. F.; Severn, J. R. *Dalton Trans.* **2004**, 4193. (i) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, 121, 8811. (j) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, 119, 2337. (k) Ossig, G.; Mellor, A.; Brönneke, C.; Müller, O.; Schäfer, M.; Herbst-Irmer, R. *Organometallics* **1997**, 16, 2116. (l) Barrau, J.; Rima, G.; Amraoui, T. E. *J. Organomet. Chem.* **1998**, 570, 163.
- (5) Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. *J. Am. Chem. Soc.* **2009**, 131, 1288.
- (6) Tam, E. C. Y.; Hariss, L. M.; Borren, E. S.; Smith, J. D.; Lein, M.; Coles, M. P.; Fulton, J. R. *Chem. Commun.* **2013**, 49, 10278.
- (7) Karwasara, S.; Yadav, D.; Jha, C. K.; Rajaraman, G.; Nagendran, S. *Chem. Commun.* **2015**, 51, 4310.
- (8) Siwatch, R. K.; Nagendran, S. *Organometallics* **2012**, 31, 3389.
- (9) Bibal, C.; Mazières, S.; Gornitzka, H.; Couret, C. *Organometallics* **2002**, 21, 2940.
- (10) Leung, W.-P.; Kan, K.-W.; So, C.-W.; Mak, T. C. W. *Appl. Organomet. Chem.* **2007**, 21, 814.
- (11) Karwasara, S.; Sharma, M. K.; Tripathi, R.; Nagendran, S. *Organometallics* **2013**, 32, 3830.
- (12) Sinhababu, S.; Siwatch, R. K.; Mukherjee, G.; Rajaraman, G.; Nagendran, S. *Inorg. Chem.* **2012**, 51, 9240.
- (13) Siwatch, R. K.; Yadav, D.; Mukherjee, G.; Rajaraman, G.; Nagendran, S. *Inorg. Chem.* **2013**, 52, 13384.
- (14) Pineda, L. W.; Jancik, V.; Colunga-Valladares, J. F.; Roesky, H. W.; Hofmeister, A.; Magull, J. *Organometallics* **2006**, 25, 2381.
- (15) Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, 34, 6100.
- (16) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, 29, 2176.
- (17) SMART: Bruker Molecular Analysis Research Tool, Version 5.618; Bruker AXS: Madison, WI, 2000.
- (18) SAINT-NT, Version 6.04; Bruker AXS: Madison, WI, 2001.
- (19) SHELXTL-NT, Version 6.10; Bruker AXS: Madison, WI, 2000.