

Group 14 Hydrides with Low Valent Elements for Activation of Small Molecules

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CONSPECTUS

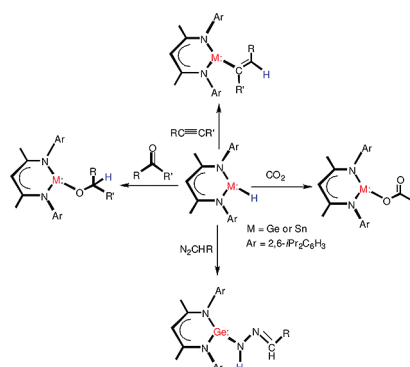
Transition metal compounds are well known as activators of small molecules, and they serve as efficient catalysts for a variety of homogeneous and heterogeneous transformations. In contrast, there is a general feeling that main group compounds cannot act as efficient catalysts because of their inability to activate small molecules. Traditionally, the activation of small molecules is considered one of the key steps during a catalytic cycle with transition metals. As a consequence, researchers have long neglected the full range of possibilities in harnessing main group elements for the design of efficient catalysts.

Recent developments, however, have made it possible to synthesize main group compounds with low-valent elements capable of activating small molecules. In particular, the judicious use of sterically appropriate ligands has been successful in preparing and stabilizing a variety of Group 14 hydrides with low-valent elements. In this Account, we discuss recent advances in the synthesis of Group 14 hydrides with low-valent elements and assess their potential as small-molecule activators.

Group 14, which comprises the nonmetal C, the semimetals Si and Ge, and the metals Sn and Pb, was for years a source of hydrides with the Group 14 element almost exclusively in tetravalent form. Synthetic difficulties and the low stability of Group 14 hydrides in lower oxidation states were difficult to overcome. But in 2000, a divalent Sn(II) hydride was prepared as a stable compound through the incorporation of sterically encumbered aromatic ligands. More recently, the stabilization of GeH₂ and SnH₂ complexes using an N-heterocyclic carbene (NHC) as a donor and BH₃ or a metal carbonyl complex as an acceptor was reported. A similar strategy was also employed to synthesize the Si(II) hydride. This class of hydrides may be considered coordinatively saturated, with the lone pair of electrons on the Group 14 elements taking part in coordination.

We discuss the large-scale synthesis of hydrides of the form LMH (where M is Ge or Sn, L is CH(N(Ar)(CMe)₂), and Ar is 2,6-*i*-Pr₂C₆H₃), which has made it possible to test their reactivity in the activation of small molecules. Unlike the tetravalent Group 14 hydrides, the Ge(II) and Sn(II) hydrides were found to be able to activate a number of small molecules in the absence of any externally added catalyst. For example, the Ge(II) hydride and Sn(II) hydride can activate CO₂, and the reaction results in the formation of Ge(II) and Sn(II) esters of formic acid. This product represents a prototype of a new class of compounds of Group 14 elements. Moreover, we examined the activation of carbonyl compounds, alkynes, diazo and azo compounds, azides, and compounds containing the C=N bond. These Group 14 hydrides with low-valent elements are shown to be able to activate a number of important small molecules with C≡C, C=O, N=N, and C=N bonds.

The activation of small molecules is an important step forward in the realization of main group catalyst development. Although it is not yet customary to assay the potential of newly synthesized main group compounds for small-molecule activation, our results offer good reason to do so.



1. Introduction

Metal hydrides and their complexes are considered valuable synthons in chemistry. It has been demonstrated that

main group and transition metal hydrides are important intermediates in industrial processes and also function as catalysts.¹ In comparison to the main group hydrides, the

chemistry of transition metal hydrides is well-documented.² Main group metal hydrides are of practical interest as a result of their widespread application in synthetic organic chemistry and their employment as precursors for high-purity element and alloy devices for the electronics industry.³ Organometallic hydrides of Group 14 elements play an important role in various metathesis reactions, and therefore, the reactivity of hydrides such as R_3SiH , R_3GeH , and R_3SnH is well-studied.⁴ In the case of Group 14 hydrides, examples of stable hydrides had been restricted to derivatives of the tetravalent state. The main reason for this imbalance is the synthetic difficulty and the stability of Group 14 hydrides with low valent elements. The situation changed in 2000 when it was shown by Power and co-workers that the divalent tin(II) hydride (Ar^*SnH_2) could be prepared by using the sterically encumbered Ar^* ligand ($Ar^* = C_6H_3-2,6-(C_6H_2-2,4,6-iPr_3)_2$).⁵ Despite considerable research in this area, the parent free heavy methylenes EH_2 ($E = C, Si, Ge, Sn, Pb$) have remained unattainable, because the hydrogen atoms can fulfill neither the steric nor the electronic requirements. The lightest member, methylene, can be stabilized via $M=CH_2$ coordination ($M =$ transition metal).⁶ Rivard and co-workers recently reported the stabilization of parent GeH_2 and SnH_2 complexes using a N-heterocyclic carbene (NHC) as a donor and BH_3 or metal carbonyl complex as an acceptor.^{7,8} A similar strategy was also recently employed to synthesize the Si(II) hydride by Robinson and co-workers.⁹ This class of hydrides with low valent elements may be considered as coordinatively saturated where the lone pair of electrons takes part in coordination. These Group 14 hydrides with low valent elements have not been tested for their ability toward activation of small molecules.

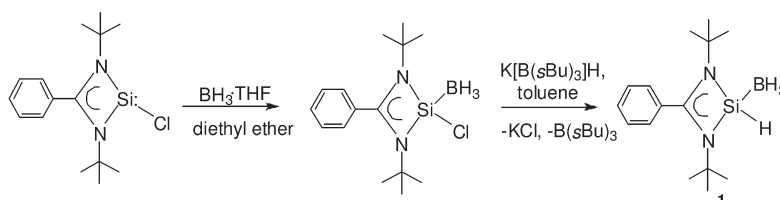
The activation of small molecules is an important step in realizing the main group based catalyst development. However, it was only discovered recently that a number of Group 14 compounds with low valent elements can activate small molecules under ambient conditions that led to comparisons of their reactivity with that of open shell transition metal species.¹⁰ For example, in 2005, it was shown that the Ge alkyne analogue $Ar'GeGeAr'$ [$Ar' = C_6H_3-2,6-(C_6H_3-2,6-iPr_2)_2$] reacted directly with H_2 under ambient conditions to give the hydrogenated products $Ar'(H)GeGe(H)Ar'$, $Ar'(H)_2GeGe(H)_2Ar'$, and $Ge(H)_3Ar'$.¹¹ The initial interaction involves donation of electron density from the σ -orbital of H_2 into the LUMO of $Ar'GeGeAr'$. There is a synergetic electron donation from the π -HOMO orbital of the germanium species into the σ^* -orbital of H_2 . This weakens the H–H bond sufficiently to enable oxidative addition to occur and clearly

shows the mechanism of H_2 activation by main group compounds in analogy to transition metal compounds from the point of symmetry of the frontier orbitals. Later on, Bertrand and his group showed in 2007 that the reaction of the related stable carbenes such as $:C(tBu)NiPr_2$ with H_2 affords the addition product $H_2C(tBu)NiPr_2$.¹² In addition to the activation of H_2 , Bertrand and co-workers also demonstrated that carbenes can activate NH_3 molecules.¹² In another investigation, it was displayed that the deep green distannyne $Ar'SnSnAr'$ can activate ethylene at room temperature under 1 atm pressure of ethylene.¹³ In this account, we discuss the recent advances of the synthesis of Group 14 hydrides with low valent elements and their potential toward small molecule activation. We show that monomeric terminal hydrides LMH [$M = Ge$ or Sn , $L = CH\{N(Ar)(CMe)_2\}_2$, $Ar = 2,6-iPr_2C_6H_3$] can be isolated in large scale and these hydrides are used to activate a number of small molecules containing C=O, $C\equiv C$, $N=N$, and $C=N$ bonds.

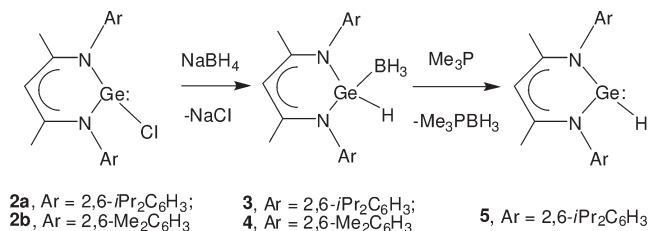
2. Synthesis of Terminal Silicon(II), Germanium(II), and Tin(II) Hydrides

At present, the chemistry of divalent Group 14 elements is quite rich with numerous well-defined examples of stable monomeric carbenes, silylenes, germlyenes, stannylenes, and plumbylenes of general formula R_2E .¹⁴ However, the realization of free silicon(II) dihydride, SiH_2 , has been so far elusive at room temperature. SiH_2 plays a central role in the field of silicon chemistry, and it is considered as a transient species. SiH_2 is unstable at room temperature and polymerizes or disproportionates to give insoluble products. We aimed at synthesizing a silicon(II) monohydride species stable at room temperature. The synthesis of Lewis acid base stabilized monohydrosilylene $L'SiH(BH_3)$ (**1**) by employing the chelating benzamidinate ligand L' [where L' indicates $PhC(NtBu)_2$] was accomplished in 2011.¹⁵ The chlorosilylene, $L'SiCl$,¹⁶ with a stereoactive lone pair of electrons present at the silicon atom was used as starting material for the synthesis of $L'SiH(BH_3)$. The lone pair of electrons was arrested by treating $L'SiCl$ with a Lewis acceptor BH_3 to yield the Lewis acid base stabilized chlorosilylene, $L'SiCl(BH_3)$. $L'SiCl(BH_3)$ was reacted with the hydrogenating agent $K[B(sBu)_3]H$ in toluene at $-30^\circ C$ to afford the stable monohydrosilylene, $LSiH(BH_3)$ (**1**), in good yield (Scheme 1). A solution of **1** in benzene- d_6 did not show any evidence of oligomerization or decomposition after 48 h of heating in an oil bath at $80^\circ C$. The central structural element of $L'SiH(BH_3)$ (**1**) is a planar SiN_2C

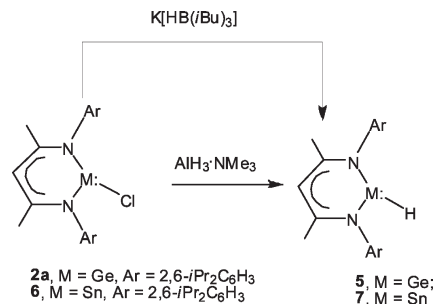
SCHEME 1. Synthesis of Lewis Acid Base Stabilized Si(II) Hydride



SCHEME 2. Synthesis of Germanium(II) Hydride



SCHEME 3. Synthesis of Germanium(II) and Tin(II) Hydrides



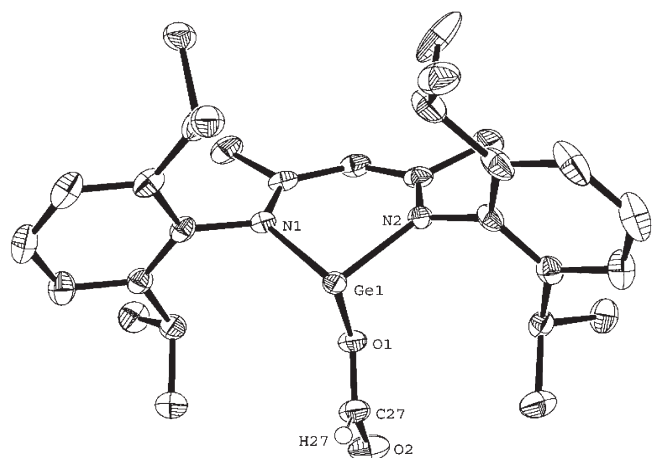
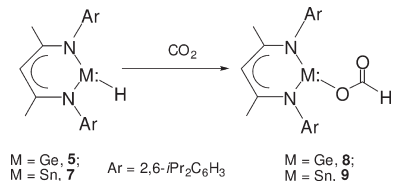
four-membered ring, with the silicon atom in the plane of the chelating benzamidinate monoanionic ligand. A detailed experimental charge density investigation reveals a central positively charged silicon atom bound to a negatively charged hydrogen atom.

To realize heavier Group 14 hydrides with low valent elements, Power and co-workers reported dimeric germanium(II) and tin(II) hydrides, Ar'(H)GeGe(H)Ar' [Ar' = C₆H₃-2,6-Dipp₂; Dipp = C₆H₃-2,6-*i*Pr₂] and (Ar*SnH)₂ [Ar* = C₆H₃-2,6-(C₆H₂-2,4,6-*i*Pr₃)] using the sterically encumbered ligand.^{5,17} Recently, Rivard and co-workers reported on the parent GeH₂ complex utilizing NHC as donor and BH₃ or metal fragment as acceptor by the Cl/H metathesis reaction of carbene-stabilized dichlorogermylene with lithium tetrahydroborate in diethyl ether.⁷ However, there was no report on monomeric terminal monohydrides of Ge(II) and Sn(II) with the free lone pair of electrons on the Ge(II) or on Sn(II). In 2001, we reported the formation of an adduct of germanium(II) hydride with BH₃, [(CH(CMeNAr)₂)Ge(H)(BH₃); Ar = 2,6-*i*Pr₂C₆H₃ (**3**) or 2,6-Me₂C₆H₃ (**4**)] by refluxing the suspension of chlorogermylene **2a** or **2b** with NaBH₄ in THF for 12 h (Scheme 2).¹⁸ The desired germanium(II) hydride was obtained by using a Lewis acid scavenger such as PMe₃ under elimination of Me₃PBH₃ with a smooth color change from pale yellow to orange (Scheme 2).¹⁸ **5** is the first three coordinate germanium(II) hydride compound stable at room temperature. Amazed by the stability of this compound, we explored a number of alternative synthetic pathways to obtain **5** as well as similar low valent tin(II) hydride.

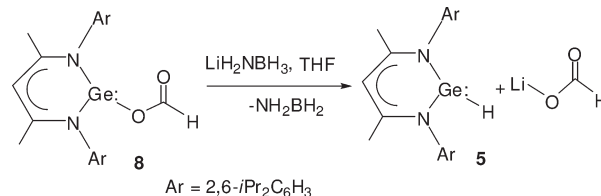
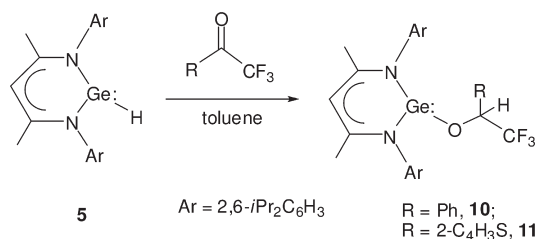
In 2006, we found that AlH₃·NMe₃ is a suitable candidate for transformation of germanium(II) chloride into the orange-red germanium(II) hydride (Scheme 3).¹⁹ Similarly, the reaction of LSnCl **6** with AlH₃·NMe₃ in toluene at -4 °C yields the first monomeric and terminal tin(II) hydride **7** (Scheme 3).¹⁹ Preparation of **5** or **7** using AlH₃·NMe₃ resulted in the formation of the expected hydride contaminated with small amounts of the starting material **2a** or **6**. Therefore, the method of preparation needed some improvement, and in 2009 we reported on the modified synthetic procedure of **5** and **7** starting from **2a** and **6**, respectively. Treatment of **2a** or **6** with potassium triisobutylborohydride (K[HB(*i*Bu)₃]) in toluene at -10 °C afforded **5** or **7** in high yield (Scheme 3).^{20,21} Compounds **5** and **7** are thermally stable over a long period of time when stored in a glovebox. The structure of orange-red single crystals of **5** reveals that the germanium atom is tetrahedrally coordinated by the β-diketiminato ligand, a hydrogen atom, and, we assume, a lone pair of electrons at the fourth coordination site. The solid state structure of **7** revealed the weak intermolecular contacts between the lone pair of electrons on the tin atom and the Sn-H hydrogen atom from another molecule generating a hydrogen bridged dimer [(Sn···H), 4.01(3) Å; (Sn···Sn), 3.71 Å].

3. Activation of Carbon Dioxide

There is increased recognition by the world's scientific, industrial, and political communities that the concentrations of greenhouse gases in the earth's atmosphere, particularly

SCHEME 4. Activation of Carbon Dioxide by Germanium(II) and Tin(II) Hydrides**FIGURE 1.** Molecular structure of **8** revealing insertion of CO₂ into the Ge(II)–H bond.

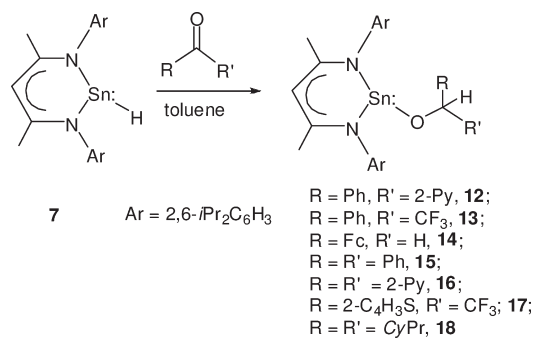
CO₂, are increasing. As a result, there is more and more effort to reduce concentrations of atmospheric CO₂. Carbon dioxide is a readily accessible atmospheric gas that could be a useful feedstock for organic compounds.²² Catalytic hydrogenation is one of the most promising approaches to CO₂ fixation. Mostly CO₂ insertion into the M–H bond has been limited to transition metal and alkali metal hydrides. For Group 14 metal hydrides, there are only a few reports on the hydrogenation of carbon dioxide using silicon(IV) hydride and tin(IV) hydride.²³ The reaction of carbon dioxide and silicon(IV) hydride requires a transition metal catalyst. To the best of our knowledge, there were no reports on the hydrogenation of carbon dioxide using Group 14 metal hydrides with low valent elements before 2009. Later on, in 2011, the activation of carbon dioxide by divalent tin alkoxide complexes was reported by Fulton and co-workers.²⁴ In 2009, the synthesis of a germylene formate, LGe–O–C(O)H (**8**), and stannylene formate, LSn–O–C(O)H (**9**), was reported in quantitative yield by the reaction of **5** and **7**, respectively, with carbon dioxide at room temperature without using any additional catalyst (Scheme 4).^{20,21} The solid state structures of **8** (Figure 1) and **9** confirm that the normal insertion of CO₂ takes places in the present cases.

SCHEME 5. Regeneration of Germanium(II) Hydride (**5**) from Germanium(II) Formate (**8**)**SCHEME 6.** Activation of Ketones by Germanium(II) Hydride, **5**

One step ahead to realize the catalytic hydrogenation process mediated by low valent hydrides, one must consider the regeneration of starting hydride releasing formic acid, and this process will in turn lead to another CO₂ insertion. The 1:1 reaction of LGe–O–C(O)H (**8**) with LiH₂NBH₃ in THF at –78 °C leads to the reformation of LGeH (**5**) and lithium formate (Li–O–C(O)H) (Scheme 5).²⁵ The ¹H NMR spectrum of the crude reaction mixture in C₆D₆ indicates the conversion of LGe–O–C(O)H (**8**) to LGeH (**5**) in almost quantitative yield. Lithium formate can easily be converted to formic acid by reaction with hydrochloric acid. The conversion of LGe–O–C(O)H (**8**) to LGeH (**5**) regenerates the primary CO₂-capturing agent. Here it is worth mentioning that LGeH is stable toward water and can therefore be easily separated from the other reaction products by extraction with benzene.

4. Activation of Carbonyl Compounds

The carbonyl group and its transformation into other functional groups are very important in organic chemistry. There are numerous reports on hydrostannylation of compounds with carbonyl groups using tin(IV) hydride.²⁶ However, there were no protocols of hydrogermylation or hydrostannylation using hydrides with the low valent germanium or tin. The germanium(II) hydride **5** displayed no reactivity toward unactivated ketones such as acetone or benzophenone at room temperature; however, it reacted cleanly with activated ketones, namely, 2,2,2-trifluoroacetophenone and 2,2,2-trifluoroacetothiophene. Treatment of **5** with

SCHEME 7. Activation of Ketones by Tin(II) Hydride, **7**

2,2,2-trifluoroacetophenone and 2,2,2-trifluoroacetothiophene leads quantitatively to the germylene alkoxides **10** and **11**, respectively, with a Ge(II)–O–C framework that is formed by nucleophilic hydride addition to the respective carbon of the carbonyl group (Scheme 6).²⁷ The molecular structures of **10** and **11** reveal that the three coordinate germanium atom is surrounded by two N atoms of the β -diketiminato ligand and an exocyclic O atom establishing a Ge(II)–O–CH core.

Further we studied the activation of tin(II) hydrides with a variety of activated and unactivated ketones. Ketone insertion into the tin(IV)–hydrogen bond of various complexes is well established.^{28,29} The first report on the hydrostannylation of a variety of carbonyl compounds by tin(II) hydride was documented only in 2009.^{21,30} The tin(II) hydride does not display any reactivity toward activation of acetone at ambient temperature; however, it reacts cleanly with a variety of other ketones including aromatic ketones. Treatment of **7** with 2-benzoylpyridine, 2,2,2-trifluoroacetophenone, ferrocene carbaldehyde, benzophenone, di(2-pyridyl)ketone, 2,2,2-trifluoroacetothiophene, and dicyclopropylketone led to the stannylene alkoxides **12**–**18** (Scheme 7). Molecular structures of **12**, **14** (Figure 2), **17**, and **18** were determined by single crystal X-ray crystallography revealing the three coordinate tin atom surrounded by two N atoms of the β -diketiminato ligand, and an exocyclic O atom. Additionally, the reaction of fluorinated aromatic ketones with tin(II) hydride **7** was studied.³¹ The reactions of **7** with fluorinated aromatic ketones such as pentafluorobenzophenone (PhCOC₆F₅) and perfluorobenzophenone (C₆F₅COC₆F₅), respectively, in toluene at room temperature, lead to the nucleophilic addition products LSnOCHPh(C₆F₅) (**19**) and LSnOCH(C₆F₅)₂ (**20**) as well as to metathesis products PhCO(4-C₆F₄H) (**21**) and C₆F₅CO(4-C₆F₄H) (**22**) with the formation of LSnF (**23**) (Scheme 8). The tin(II) fluoride LSnF (**23**) is obtained by cleavage of one of the C–F bonds of the C₆F₅ group. The para fluorine atom of the pentafluorophenyl

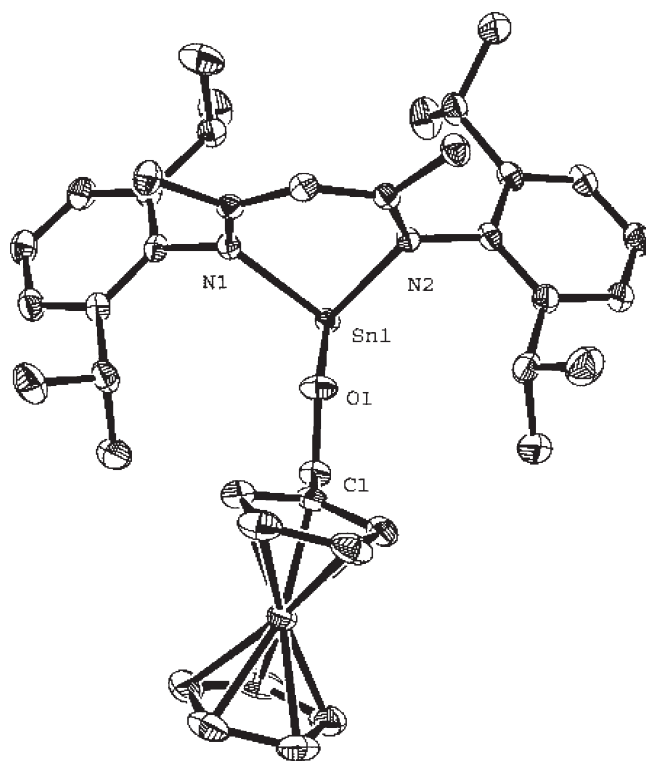
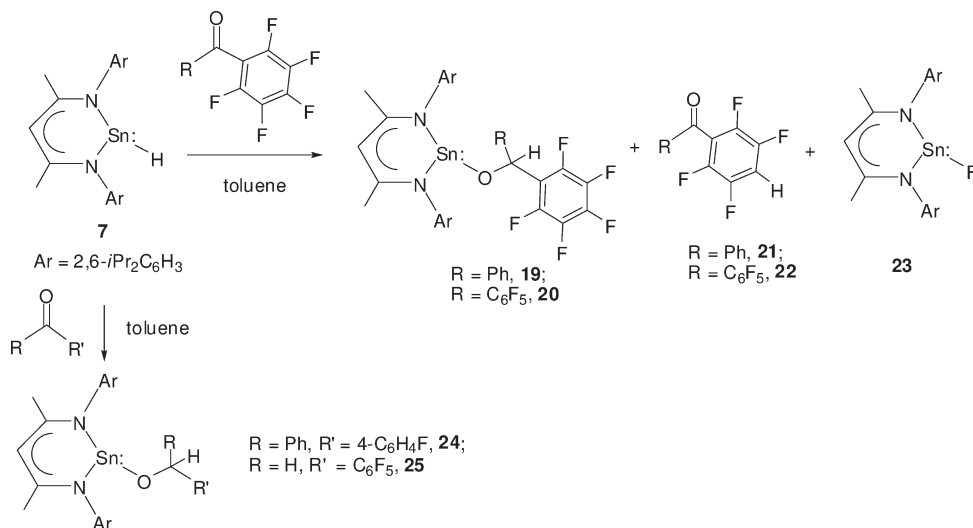
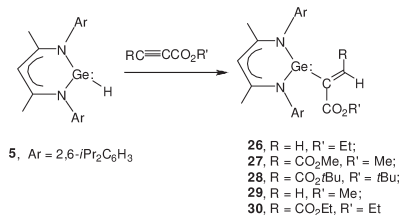


FIGURE 2. Molecular structure of **14** revealing activation of a carbonyl compound by a tin(II) hydride compound.

group is replaced by the hydrogen atom of the starting tin(II) hydride **7**. In contrast, the reactions of 4-fluorobenzophenone (PhCO-4-C₆H₄F) and pentafluorobenzaldehyde (C₆F₅CHO) with **7** provide the normal tin(II) alkoxide products LSnOCHPh (4-C₆H₄F) (**24**) and LSnOCH₂C₆F₅ (**25**) as a result of nucleophilic addition of hydride to the carbonyl group. From the above reactions, it may be argued that there is a competition between the metathesis reaction and the nucleophilic addition reaction. The para C–F bond is activated during the metathesis reaction most probably due to steric reasons.

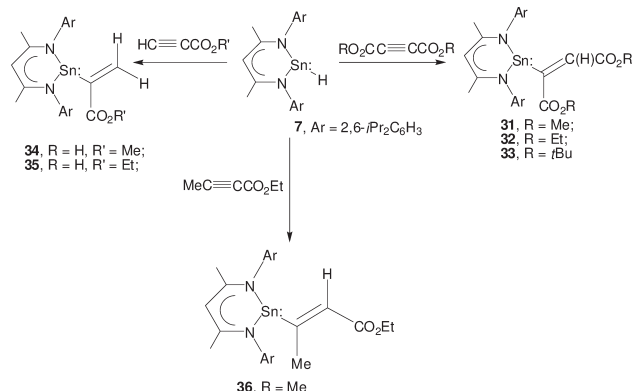
5. Alkyne Activation through Hydrogermylation and Hydrostannylation

The hydrogermylation and hydrostannylation of olefins and alkynes have been established for nearly 50 years and follow either a polar or a free-radical pathway, depending on substituents and conditions.^{32,33} The hydrogermylation and hydrostannylation of unsaturated hydrocarbon compounds with Ge(IV)–H and Sn(IV)–H reagents give a variety of acyclic and cyclic carbon functional germanium compounds in the presence of externally added catalyst.^{32,33} Because of the variable polarity of the M–H bond, various catalysts have been used in hydrogermylation reactions to initiate different pathways. In contrast to this, we recently

SCHEME 8. Competition of Metathesis and Nucleophilic Addition of Fluorinated Aromatic Ketones with Tin(II) Hydride, **7****SCHEME 9.** Hydrogermylation of Alkynes

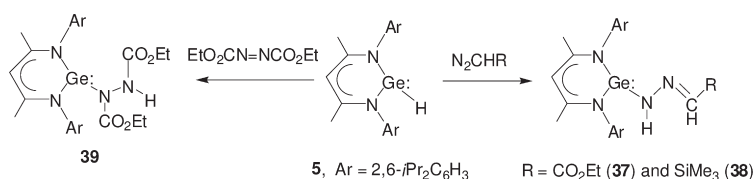
reported hydrogermylation reactions of alkynes using germanium(II) hydride without any catalyst.^{20,27} Compounds **5** and **7** were used for hydrogermylation and hydrostannylation of a number of alkyne compounds in the absence of any added catalyst as a result of transfer of the hydrogen atom and germylene or stannylene across the carbon–carbon triple bond rather than the elimination of H₂ owing to the differently polarized Ge–H and C–H bonds.

The germanium(II) hydride **5** reacts with a variety of alkynes HC≡CCO₂Et, MeO₂CC≡CCO₂Me, *t*BuO₂CC≡CCO₂-*t*Bu, HC≡CCO₂Me, and EtO₂CC≡CCO₂Et at room temperature to form the germanium(II) substituted alkenes **26–30** (Scheme 9). The disubstituted alkynes dimethyl acetylenedicarboxylate and di-*tert*-butyl acetylenedicarboxylate were chosen to check the selectivity of the addition across the carbon–carbon triple bond. It was observed that **5** reacts with these dialkyl acetylenedicarboxylates (RO₂CC≡CCO₂R; R = Me, *t*Bu) in toluene at room temperature to form only the corresponding isomers **27** and **28** with the (*E*)-germylene-substituted alkene. The solid state structures of **27** and **28** also confirmed the presence of only the (*E*)-isomer. The

SCHEME 10. Hydrostannylation of Alkynes Using Tin(II) Hydride, **7**

formal oxidation state (II) at the germanium atom persisted during the transfer of the hydrogen to the corresponding carbon–carbon triple bond (alkyne).

In 2009, we reported the hydrostannylation reaction of alkynes with **7** without any catalyst.^{21,30} Compound **7** reacts with a number of alkynes resulting in the insertion of alkyne into the Sn(II)–H bond producing compounds **31–36** (Scheme 10). **31–36** were characterized completely by spectroscopic methods, and a few representative compounds were characterized by single crystal X-ray studies. Compound **7** reacts with symmetrically substituted alkynes RO₂CC≡CCO₂R (R = Me, Et, *t*Bu) in toluene at room temperature to form both the *E*- and *Z*-stannylene-substituted alkenes **31–33** in a ratio of 1:0.7 (**31**), 1.00:0.69 (**32**), and 1.00:1.52 (**33**). The molecular structure of **32** was determined by X-ray crystallography revealing the presence of only one isomer (*Z*-isomer) in the solid state. **7** reacts with

SCHEME 11. Activation of Diazo and Azo Compounds by Germanium(II) Hydride, **5**

HC≡CCO₂Me and HC≡CCO₂Et, respectively, at room temperature to form the vinyl stannylenes **34** and **35** (Scheme 10). The unsymmetrically substituted alkyne MeC≡CCO₂Et reacts with **7** at room temperature to form the hydrostannylated product **36** (Scheme 10). The crystal structure of **36** reveals a *cis* orientation of the tin and hydrogen atom across the double bond. In solution, also, only one isomer is detected, indicating that **36** is obtained by 1,2-*syn*-addition of **7** to the alkyne resulting from the transfer of the hydrogen atom and stannylenes across the carbon–carbon triple bond.

6. Activation of Diazo and Azo Compounds

The reaction of diazoalkanes with transition metals has a long history in the cyclopropanation of olefins.³⁴ Coordinative unsaturation at the metal center allows transition-metal complexes to react as electrophiles (Lewis acids) with diazo groups. Numerous diazoalkane complexes of transition metals have been prepared in which the metal center is coordinated to the terminal nitrogen group (end-on) or to the N=N bond (side-on).³⁵ In contrast, the reaction of diazoalkane with compounds of main group elements is scarcely known in literature.^{36,37} In 1996, Meller and co-workers reported the reaction of dimethyl 2-diazomalonate and 2-diazo-1,3-indanedione with germylenes and stannylenes resulting in oxadiazametallane core with six-membered heterocyclic ring formation around the germanium or tin center.³⁷ In 2009, we reported an end-on nitrogen insertion of a diazo compound into a germanium(II) hydrogen bond and a comparable reaction with diethyl azodicarboxylate.³⁸

The reaction of diazoalkane N₂CHR (R = CO₂Et or SiMe₃) with germanium(II) hydride **5** leads to the first stable germanium(II) substituted hydrazone derivative, [LGeN(H)NCHR], where R = CO₂Et (**37**) or SiMe₃ (**38**), in high yields (Scheme 11). Also the reaction of **5** with diethyl azodicarboxylate (DEAD) proceeds rapidly at room temperature to give compound **39** in high yield (Scheme 11). The reaction takes action by the unprecedented end-on insertion of diazoalkane into the Ge–H bond. Dinitrogen elimination with subsequent insertion or an oxidative addition reaction is generally expected. The end-on N₂CHR insertion into the

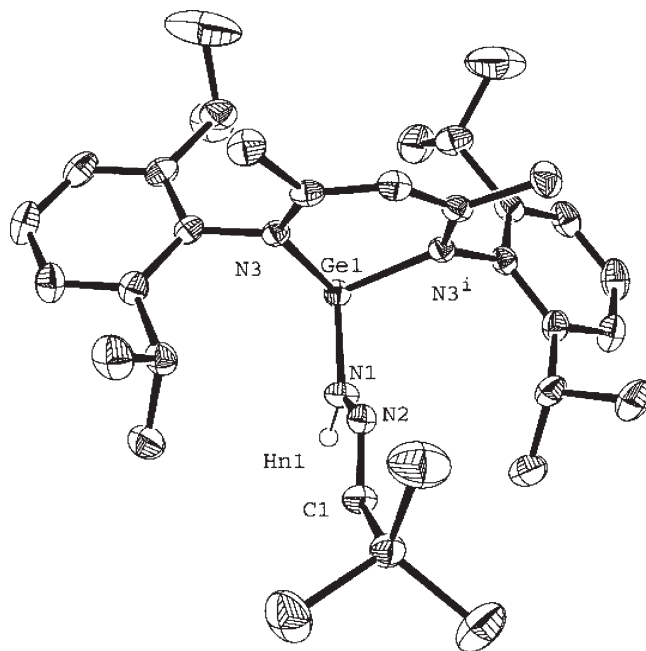
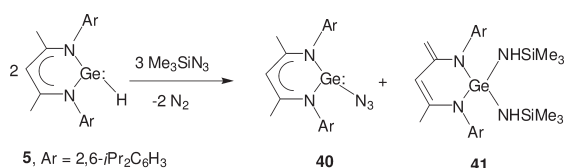
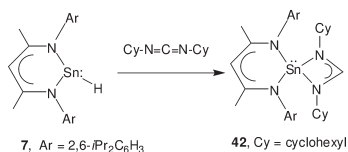


FIGURE 3. Molecular structure of **38** revealing end-on nitrogen insertion of a diazo compound into the Ge(II)–H bond.

Ge–H bond unambiguously in the present case reveals the initial interaction between the germanium center and the terminal nitrogen atom of the diazo group followed by hydrogen transfer from the germanium center to nitrogen. Compounds **37**, **38** (Figure 3), and **39** were characterized by spectroscopic, analytical, and X-ray crystallographic measurements. The X-ray structures reveal that the coordination polyhedron around the germanium atom features a distorted tetrahedral geometry with a stereochemically active lone pair of electrons with zigzag orientation of the N–N moiety. To investigate the electronic structure and bonding properties of **37** and **38**, *ab initio* DFT calculations were performed. The calculations reveal that the stabilities of compounds **37** and **38** arise from the electron density shift from the N–N bond of the diazoalkane to the Ge–N bond between germanium and ligating nitrogen. As a consequence, the N–N bond deviates from a triple bond and the initial linear geometry of the ligating end in N₂CHR transforms into a planar zigzag structure in **37** and **38**.

SCHEME 12. Germanium(II) Hydride Activating Trimethylsilyl Azide**SCHEME 13.** Reaction of Tin(II) Hydride, **7**, with C–N Multiple Bond Present in Dicyclohexyl Carbodiimide (DCC)

7. Activation of Azide

After activation of azo and diazo compounds, we became interested in studying the reactivity of **5** with substituted azide. Trimethylsilyl diazomethane and trimethylsilyl azide are isoelectronic, and both exhibit 1,3-dipolar properties. Therefore, it was expected that the azide might also insert end-on into the germanium–hydrogen bond of **5**. However, the reaction of **5** with trimethylsilyl azide at room temperature affords two products germanium(II) azide **40** and germanium(IV) diamide **41** in a ratio of 1:1 (Scheme 12).²⁵ Compound **40** was formed by metathesis reaction of **5** with Me₃SiN₃ under elimination of Me₃SiH, whereas compound **41** was generated by elimination of dinitrogen from azide, with the resulting nitrene (:NSiMe₃), inserting into the germanium–hydrogen bond. The final oxidative addition of another nitrene is followed by simultaneous hydrogen transfer from one methyl group, which is attached to the heterocyclic ring backbone. The formation of **41** requires the oxidation of germanium(II) to germanium(IV). Therefore, the synthesis of **41** involves a unprecedented oxidative addition–insertion with nitrene which is formed in situ from trimethylsilyl azide by elimination of dinitrogen, and insertion into the Ge(II)–H bond. The molecular structures of **40** and **41** were established by single crystal X-ray studies. In the solid state, **41** exists as a monomer without any intermolecular hydrogen bonds.

8. Activation of C=N Bond

Activation of C=C, C=O, and C=N bonds by transition metal complexes has substantial precedent. Examples of direct observation of activating C–N multiple bonds by main group compounds are not common, since the C–N multiple

bond is very stable and requires high activation energy. In 2009, the activation of the C–N multiple bond by tin(II) hydride **7** was reported.²¹ The reaction of **7** with compounds containing C–N multiple bonds was studied by its reaction with dicyclohexyl carbodiimide (DCC) (Scheme 13). This reaction proceeded rapidly and quantitatively at room temperature to give the spirocyclic compound **42**, which contained the four- and six-membered heterocycles of composition C₃N₂Sn and CN₂Sn.

9. Summary and Conclusions

In summary, we document in this account the synthesis of terminal low valent hydrides of Si(II), Ge(II), and Sn(II). The Ge(II) and Sn(II) hydrides were studied for their ability to activate small molecules. It was observed that, unlike the tetravalent Group 14 hydrides, the Ge(II) and Sn(II) hydrides can activate a plethora of small molecules in the absence of any externally added catalyst. The germanium(II) hydride and tin(II) hydride can activate CO₂, and the reaction resulted in the formation of a germanium(II) and tin(II) ester of formic acid, which represents a prototype of a new class of compounds of Group 14 elements. For example, a low valent stable carbon analogue of composition RC–O–C(O)H has not been reported to date. A RC–O–C(O)H species should be extremely unstable and will rearrange to the corresponding 1,2-dicarbonyl compound, RC(O)–C(O)H. The reaction of Ge(II) and Sn(II) hydrides with alkynes resulted in the formation of germanium(II)- or tin(II)-substituted alkenes. The germanium(II)- and tin(II)-substituted alkenes have a lone pair of electrons on the germanium center and a carbon–carbon double bond, both of which are prone to react further. The activation of small molecules is an important step in the realization of main group based catalyst development. So far it is not yet customary to check the potential of newly synthesized main group compounds with low valent elements toward small molecule activation. One step ahead to realize the catalytic process mediated by Group 14 hydrides with low valent elements, one must consider the regeneration of the hydride precursor. It has been successfully shown that the conversion of LGe–O–C(O)H to the starting hydride LGeH can be regenerated, indicating its potential to be utilized as a main group based catalyst.

BIOGRAPHICAL INFORMATION

Swadhin K. Mandal was born in Nadia in 1973. He is currently an Assistant Professor at the Indian Institute of Science Education and Research-Kolkata in the area of Chemical Sciences. He studied chemistry at the University of Kalyani and obtained his doctoral

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FOOTNOTES

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REFERENCES

- (a) Kaesz, H. D.; Saillant, R. B. Hydride Complexes of the Transition Metals. *Chem. Rev.* **1972**, *72*, 231–281. (b) McGrady, G. S.; Guilera, G. The Multifarious World of Transition Metal Hydrides. *Chem. Soc. Rev.* **2003**, *32*, 383–392. (c) Lefebvre, F.; Basset, J.-M. Surface Organometallic Chemistry of Tin, Germanium and Arsenic. *Main Group Met. Chem.* **2002**, *25*, 15–32. (d) Zhao, J.; Goldman, A. S.; Hartwig, J. F. Oxidative Addition of Ammonia to Form a Stable Monomeric Amido Hydride Complex. *Science* **2005**, *307*, 1080–1082. (e) West, N. M.; Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. Homogeneous Syngas Conversion. *Coord. Chem. Rev.* **2011**, *255*, 881–898.
- (a) Sabo-Etienne, S.; Chaudret, B. Quantum Mechanical Exchange Coupling in Polyhydride and Dihydrogen Complexes. *Chem. Rev.* **1998**, *98*, 2077–2091. (b) Hoskin, A. J.; Stephan, D. W. Early Transition Metal Hydride Complexes: Synthesis and Reactivity. *Coord. Chem. Rev.* **2002**, *233–234*, 107–129. (c) Murahashi, S.-I.; Takaya, H. Low-Valent Ruthenium and Iridium Hydride Complexes as Alternatives to Lewis Acid and Base Catalysts. *Acc. Chem. Res.* **2000**, *33*, 225–233.
- Ekerdt, J. G.; Sun, Y.-M.; Szabo, A.; Szulcowski, G. J.; White, J. M. Role of Surface Chemistry in Semiconductor Thin Film Processing. *Chem. Rev.* **1996**, *96*, 1499–1517 and references therein.
- (a) Shirobokov, O. G.; Gorelsky, S. I.; Simionescu, R.; Kuzmina, L. G.; Nikonov, G. I. The Unexpected Mechanism of Carbonyl Hydrosilylation Catalyzed by (Cp)(ArN)Mo(H)(PMe₃). *Chem. Commun.* **2010**, *46*, 7831–7833. (b) Beard, C. D.; Craig, J. C. Insertion of Vinylidene Carbenes into Carbon-Hydrogen and Silicon-Hydrogen Bonds. *J. Am. Chem. Soc.* **1974**, *96*, 7950–7954. (c) Saegusa, T.; Ito, Y.; Kobayashi, S.; Hirota, K. Synthetic Reactions by a Complex Catalyst. VI. by Copper Catalyst. *J. Am. Chem. Soc.* **1967**, *89*, 2240–2241. (d) Bradley, G. F.; Stobart, S. R. Reaction of Octacarbonyldicobalt with Organosilanes, -germanes, and -stannanes: Formation, Properties, and Vibrational Spectra of Trimethylgermyltetracarbonylcobalt and Related Complexes. *J. Chem. Soc., Dalton Trans.* **1974**, 264–269. (e) Adams, R. D.; Cotton, F. A.; Cullen, W. R.; Hunter, D. L.; Mihichuk, L. Fluxional Behavior of Some Dinuclear Iron and Cobalt Hexacarbonyl Compounds with Alkylsulfur and Dialkylphosphorus-, arsenic-, germanium-, and -tin Bridges. *Inorg. Chem.* **1975**, *14*, 1395–1399.
- Eichler, B. E.; Power, P. P. [2,6-Trip₂H₃C₆Sn(μ -H)]₂ (Trip = C₆H₂-2,4,6-*i*-Pr₃): Synthesis and Structure of a Divalent Group 14 Element Hydride. *J. Am. Chem. Soc.* **2000**, *122*, 8785–8786.
- (a) Schrock, R. R. Alkylidene Complexes of Niobium and Tantalum. *Acc. Chem. Res.* **1979**, *12*, 98–104. (b) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. Titanium-Catalyzed Olefin Metathesis. *J. Am. Chem. Soc.* **1979**, *101*, 5074–5075. (c) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. A Series of Well-Defined Metathesis Catalysts—Synthesis of [RuCl₂(=CHR')(PR₃)₂] and Its Reactions. *Angew. Chem.* **1995**, *107*, 2179–2181; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039–2041. (d) Scott, J.; Minciola, D. J. A Tribute to Frederick Nye Tebbe. Lewis Acid Stabilized Alkylidene, Alkylidene, and Imides of 3d Early Transition Metals. *Dalton Trans.* **2009**, 8463–8472.
- (a) Al-Rafia, S. M. I.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; Rivard, E. Stabilization of the Heavy Methylene Analogues, GeH₂ and SnH₂, within the Coordination Sphere of a Transition Metal. *J. Am. Chem. Soc.* **2011**, *133*, 777–779. (b) Thimer, K. C.; Al-Rafia, S. M. I.; Ferguson, M. J.; McDonald, R.; Rivard, E. Donor/Acceptor Stabilization of Ge(II) Dihydride. *Chem. Commun.* **2009**, 7119–7121.
- Inoue, S.; Driess, M. Parent Heavy Methylenes: Chemical Tricks to Access Isolable Complexes of Elusive H₂E Species (E = Ge and Sn). *Angew. Chem.* **2011**, *123*, 5728–5730; *Angew. Chem., Int. Ed.* **2011**, *50*, 2–4.
- Abraham, M. Y.; Wang, Y.; Xie, Y.; Wei, P.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. Cleavage of Carbene-Stabilized Disilicon. *J. Am. Chem. Soc.* **2011**, *133*, 8874–8876.
- (a) Power, P. P. Interaction of Multiple Bonded and Unsaturated Heavier Main Group Compounds with Hydrogen, Ammonia, Olefins, and Related Molecules. *Acc. Chem. Res.* **2011**, *44*, 627–637. (b) Power, P. P. Main-group Elements as Transition Metals. *Nature* **2010**, *463*, 171–177.
- Spikes, G. H.; Fettinger, J. C.; Power, P. P. Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound. *J. Am. Chem. Soc.* **2005**, *127*, 12232–12233.
- Frey, G. D.; Lavallo, B.; Donnadiu, B.; Schoeller, W. W.; Bertrand, G. Facile Splitting of Hydrogen and Ammonia by Nucleophilic Activation at a Single Carbon Center. *Science* **2007**, *316*, 439–441.
- Peng, Y.; Ellis, B. D.; Wang, X.; Fettinger, J. C.; Power, P. P. Reversible Reactions of Ethylene with Distannynes under Ambient Conditions. *Science* **2009**, *325*, 1668–1670.
- (a) Mandal, S. K.; Roesky, H. W. Interstellar Molecules: Guides for New Chemistry. *Chem. Commun.* **2010**, *46*, 6016–6041. (b) Mizuhata, T. S.; Tokitoh, N. Stable Heavier Carbene Analogues. *Chem. Rev.* **2009**, *109*, 3479–3511. (c) Nagendran, S.; Roesky, H. W. The Chemistry of Aluminum(II), Silicon(II), and Germanium(II). *Organometallics* **2008**, *27*, 457–492. (d) Waterman, R.; Hayes, P. G.; Tilley, T. D. Synthetic Development and Chemical Reactivity of Transition-Metal Silylene Complexes. *Acc. Chem. Res.* **2007**, *40*, 712–719.
- Jana, A.; Leusser, D.; Objartel, I.; Roesky, H. W.; Stalke, D. A Stable Silicon(II) Monohydride. *Dalton Trans.* **2011**, *40*, 5458–5463.
- So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. Synthesis and Characterization of [PhC(NtBu)₂]SiCl: A Stable Monomeric Chlorosilylene. *Angew. Chem.* **2006**, *118*, 4052–4054; *Angew. Chem., Int. Ed.* **2006**, *45*, 3948–3950.
- Richards, A. F.; Phillips, A. D.; Olmstead, M. M.; Power, P. P. Isomeric Forms of Divalent Heavier Group 14 Element Hydrides: Characterization of Ar'(H)GeGe(H)Ar' and Ar'(H)₂GeGeAr'PMe₃ (Ar' = C₆H₃-2,6-Dipp₂; Dipp = C₆H₃-2,6-Pr₂). *J. Am. Chem. Soc.* **2003**, *125*, 3204–3205.
- Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. Synthesis and Structures of Germanium(II) Fluorides and Hydrides. *Organometallics* **2001**, *20*, 4806–4811.
- Pineda, L. W.; Jancik, V.; Starke, K.; Oswald, R. B.; Roesky, H. W. Stable Monomeric Germanium(II) and Tin(II) Compounds with Terminal Hydrides. *Angew. Chem.* **2006**, *118*, 2664–2667; *Angew. Chem., Int. Ed.* **2006**, *45*, 2602–2605.
- Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. A Germanium(II) Hydride as an Effective Reagent for Hydrogermylation Reactions. *J. Am. Chem. Soc.* **2009**, *131*, 1288–1293.
- Jana, A.; Roesky, H. W.; Schulzke, C.; Döring, A. Reactions of Tin(II) Hydride Species with Unsaturated Molecules. *Angew. Chem.* **2009**, *121*, 1126–1129; *Angew. Chem., Int. Ed.* **2009**, *48*, 1106–1109.
- For recent examples, see (a) Mizuno, H.; Takaya, J.; Iwasawa, N. Rhodium(I)-Catalyzed Direct Carboxylation of Arenes with CO₂ via Chelation-Assisted C-H Bond Activation. *J. Am. Chem. Soc.* **2011**, *133*, 1251–1253. (b) Boogaerts, I. I. F.; Nolan, S. P. Carboxylation of C-H Bonds Using N-Heterocyclic Carbene Gold(I) Complexes. *J. Am. Chem. Soc.* **2010**, *132*, 8858–8859. (c) Boogaerts, I. I. F.; Fortman, G. C.; Furst, M. R. L.; Cazin, C. S. J.; Nolan, S. P. Carboxylation of N-H/C-H Bonds Using N-Heterocyclic Carbene Copper(I) Complexes. *Angew. Chem.* **2010**, *122*, 8856–8859; *Angew. Chem., Int. Ed.* **2010**, *49*, 8674–8677. (d) Zhang, L.; Cheng, J.; Ohishi, T.; Hou, Z. Copper-Catalyzed Direct Carboxylation of C-H Bonds with Carbon Dioxide. *Angew. Chem.* **2010**, *122*, 8852–8855; *Angew. Chem., Int. Ed.* **2010**, *49*, 8670–8673.

- 23 (a) Jansen, A.; Görls, H.; Pitter, S. trans-[RuCl(MeCN)₅][RuClCl₄(MeCN)₂]: A Reactive Intermediate in the Homogeneous Catalyzed Hydrosilylation of Carbon Dioxide. *Organometallics* **2000**, *19*, 135–138. (b) Deglmann, P.; Ember, E.; Hofmann, P.; Pitter, S.; Walter, O. Experimental and Theoretical Investigations on the Catalytic Hydrosilylation of Carbon Dioxide with Ruthenium Nitrile Complexes. *Chem.—Eur. J.* **2007**, *13*, 2864–2879. (c) Albertin, G.; Antoniutti, S.; Castro, J.; García-Fontán, S.; Zanardo, G. Preparation and Reactivity of Stannyl Complexes of Manganese and Rhenium. *Organometallics* **2007**, *26*, 2918–2930.
- 24 Ferro, L.; Hitchcock, P. B.; Coles, M. P.; Cox, H.; Fulton, J. R. Activation of Carbon Dioxide by Divalent Tin Alkoxides Complexes. *Inorg. Chem.* **2011**, *50*, 1879–1888.
- 25 Jana, A.; Tavčar, G.; Roesky, H. W.; John, M. Germanium(II) Hydride Mediated Reduction of Carbon Dioxide to Formic Acid and Methanol with Ammonia Borane as the Hydrogen Source. *Dalton Trans.* **2010**, *39*, 9487–9489.
- 26 For example: He, A.; Falck, J. R. Synthesis of Enantioenriched α -(Hydroxyalkyl)-tri-*n*-butylstannanes. *Angew. Chem.* **2008**, *120*, 6688–6691; *Angew. Chem., Int. Ed.* **2008**, *47*, 6586–6589.
- 27 Jana, A.; Roesky, H. W.; Schulzke, C. Reactivity of Germanium(II) Hydride with Nitrous Oxide, Trimethylsilyl Azide, Ketones, and Alkynes and the Reaction of a Methyl Analogue with Trimethylsilyl Diazomethane. *Dalton Trans.* **2010**, *39*, 132–138.
- 28 Shibata, I.; Suzuki, T.; Baba, A.; Matsuda, H. Reduction of α -Chlorocarbonyl Compounds by the Tributyltin Hydride–Phosphine Oxide Combined System. Chemoselective Reduction of the Carbonyl Group. *J. Chem. Soc., Chem. Commun.* **1988**, 882–883.
- 29 (a) Fisch, M. H.; Dannenberg, J. J.; Pereyre, M.; Anderson, W. G.; Rens, J.; Grossman, W. E. L. Photoreduction of Carbonyl Compounds by Tributyl Tin Hydrides. *Tetrahedron* **1984**, *40*, 293–298. (b) Clive, D. L. J.; Chittattu, G.; Wong, C. K. New Method for Reduction of Ketones and Primary Alcohols to Hydrocarbons: Reaction of the Derived Selenides with Tin Hydrides. *J. Chem. Soc., Chem. Commun.* **1978**, 41–42.
- 30 Jana, A.; Roesky, H. W.; Schulzke, C. Hydrostannylation of Ketones and Alkynes with LSnH [L = HC(CMeNAr)₂, Ar = 2,6-*i*Pr₂C₆H₃]. *Inorg. Chem.* **2009**, *48*, 9543–9548.
- 31 Jana, A.; Roesky, H. W.; Schulzke, C.; Samuel, P. P. Reaction of Tin(II) Hydride with Compounds Containing Aromatic C–F Bonds. *Organometallics* **2010**, *29*, 4837–4841.
- 32 (a) Davies, A. G.; Smith, P. J. Tin. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, pp 519–627. (b) Rivière, P.; Rivière-Baudet, M.; Satgé, J. Germanium. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 2, pp 399–518.
- 33 Smith, N. D.; Mancuso, J.; Lautens, M. Metal-Catalyzed Hydrostannations. *Chem. Rev.* **2000**, *100*, 3257–3282.
- 34 (a) Doyle, M. P.; Forbes, D. C. Recent Advances in Asymmetric Catalytic Metal Carbene Transformations. *Chem. Rev.* **1998**, *98*, 911–935. (b) Du, G.; Andrioletti, B.; Rose, E.; Woo, L. K. Asymmetric Cyclopropanation of Styrene Catalyzed by Chiral Macrocyclic Iron(II) Complexes. *Organometallics* **2002**, *21*, 4490–4495. (c) Kirmse, W. Copper Carbene Complexes: Advanced Catalysts, New Insights. *Angew. Chem.* **2003**, *115*, 1120–1125; *Angew. Chem., Int. Ed.* **2003**, *42*, 1088–1093. (d) Marcoux, D.; Charette, A. B. trans-Directing Ability of Amide Groups in Cyclopropanation: Application to the Asymmetric Cyclopropanation of Alkenes with Diazo Reagents Bearing Two Carboxy Groups. *Angew. Chem.* **2008**, *120*, 10309–10312; *Angew. Chem., Int. Ed.* **2008**, *47*, 10155–10158.
- 35 Review: (a) Dartiguenave, M.; Menu, M. J.; Deydier, E.; Dartiguenave, Y.; Siebald, H. Crystal and Molecular Structures of Transition Metal Complexes with N- and C-bonded Diazoalkane Ligands. *Coord. Chem. Rev.* **1998**, *180*, 623–663. (b) Mizobe, Y.; Ishii, Y.; Hidai, M. Synthesis and Reactivities of Diazoalkane Complexes. *Coord. Chem. Rev.* **1995**, *139*, 281–311. (c) Herrmann, W. A. Organometallic Syntheses with Diazoalkanes. *Angew. Chem.* **1978**, *90*, 855–868; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800–812.
- 36 Bamier, J.-P.; Blanco, L. Reaction of Dihydrosilanes with Ethyl Diazoacetate: Synthesis of 3,3-Disubstituted 3-Silaglutarates. *J. Organomet. Chem.* **1996**, *514*, 67–71.
- 37 Ossig, G.; Meller, A.; Freitag, S.; Müller, O.; Gomitka, H.; Herbst-Imer, R. Products of the Reactions of 2-Diazomalonnate and of 2-Diazoindanedione with Germynes and Stannylenes. *Organometallics* **1996**, *15*, 408–414.
- 38 Jana, A.; Sen, S. S.; Roesky, H. W.; Schulzke, C.; Dutta, S.; Pati, S. K. End-On Nitrogen Insertion of a Diazo Compound into a Germanium(II) Hydrogen Bond and a Comparable Reaction with Diethyl Azodicarboxylate. *Angew. Chem.* **2009**, *121*, 4310–4312; *Angew. Chem., Int. Ed.* **2009**, *28*, 4246–4248.