

Low Coordinate Germanium(II) and Tin(II) Hydride Complexes: Efficient Catalysts for the Hydroboration of Carbonyl Compounds

Terrance J. Hadlington,[†] Markus Hermann,[‡] Gernot Frenking,^{*,‡} and Cameron Jones^{*,†}

[†]School of Chemistry, Monash University, P.O. Box 23, Melbourne, VIC, 3800, Australia

[‡]Fachbereich Chemie, Philipps-Universität Marburg, 35032, Marburg, Germany

S Supporting Information

ABSTRACT: This study details the first use of well-defined low-valent p-block metal hydrides as catalysts in organic synthesis. That is, the bulky, two-coordinate germanium(II) and tin(II) hydride complexes, $L^{\dagger}(H)M$: ($M = \text{Ge}$ or Sn , $L^{\dagger} = -N(\text{Ar}^{\dagger})(\text{SiPr}^{\dagger}_3)$, $\text{Ar}^{\dagger} = \text{C}_6\text{H}_2\{\text{C}(\text{H})\text{Ph}_2\}_2\text{Pr}^{\dagger-2,6,4}$), are shown to act as efficient catalysts for the hydroboration (with HBpin, pin = pinacolato) of a variety of unactivated, and sometimes very bulky, carbonyl compounds. Catalyst loadings as low as 0.05 mol % are required to achieve quantitative conversions, with turnover frequencies in excess of 13 300 h^{-1} in some cases. This activity rivals that of currently available catalysts used for such reactions.

The advances that have been made in the chemistry of low oxidation state p-block compounds over the past several decades have been remarkable. More than being mere chemical curiosities, it has begun to be realized that the low coordination numbers and electronic structure of many of these compounds can lead to them displaying reactivity that closely mimics that of transition metal complexes. This is especially so for the facile activation of catalytically relevant small molecules (e.g., H_2 , NH_3 , CO_2 , alkenes, ketones, etc.), the regular demonstration of which has led to a recent drive to develop low-valent p-block compounds as replacements for transition metal based catalysts in a variety of synthetic processes.¹ Although efficient “transition metal-like” catalysis involving well-defined low-valent p-block metal systems is still essentially unknown,² any progress in this field would offer the enticing possibility of substituting often expensive, toxic, and increasingly scarce d-block metals with cheaper, less toxic, and earth abundant p-block metals in both the academic and industrial settings.

Recently we reported that the amido-digermene, $L^{\dagger}\text{GeGeL}^{\dagger}$ ($L^{\dagger} = -N(\text{Ar}^{\dagger})(\text{SiPr}^{\dagger}_3)$, $\text{Ar}^{\dagger} = \text{C}_6\text{H}_2\{\text{C}(\text{H})\text{Ph}_2\}_2\text{Pr}^{\dagger-2,6,4}$), activates dihydrogen at temperatures as low as -10 °C to quantitatively yield the hydrido-digermene, $L^{\dagger}(H)\text{Ge}=\text{Ge}(H)-L^{\dagger}$.³ Furthermore, because of the extreme steric bulk of its amide ligand, this compound, and its isomeric tin analogue, $L^{\dagger}\text{Sn}(\mu\text{-H})_2\text{SnL}^{\dagger}$, were shown to exist in equilibrium with significant amounts of the unprecedented monomeric, two-coordinate metal(II) hydrides, $L^{\dagger}(H)M$: ($M = \text{Ge}$ **1** or Sn **2**), in solution.³ Given the unsaturated nature of hydridic **1** and **2** (they possess an empty p-orbital at M), it seemed plausible that they could act as catalysts for the hydroelementation of unsaturated substrates. In order to test this hypothesis, the catalytic hydroboration of a

variety of aldehydes and ketones with the mild borane reagent, HBpin (pin = pinacolato), was chosen. This choice was made, first because the selective and efficient conversion of carbonyl compounds to alcohols is of great importance to organic synthesis.⁴ Moreover, it would allow for comparisons to be drawn with the many transition metal (e.g., Rh^{I} ,⁵ Ru^{II} ,⁶ Mo^{IV} ,⁷ $\text{Ti}^{\text{II/IV}}$) complexes, and the small number of “normal oxidation state” main group systems (e.g., $\{(\text{Dip}^{\text{Nacnac}})\text{MgH}\}_2$, $\text{Dip}^{\text{Nacnac}} = [(\text{Dip}^{\text{Nacnac}})_2\text{CH}]^-$, $\text{Dip} = \text{C}_6\text{H}_3\text{Pr}^{\dagger-2,6}$),⁹ that are known to effect hydroborations of carbonyl compounds under mild conditions. Another reason for the selection of carbonyl substrates in the present study was that a recent computational investigation predicted that related hydroelementations of the activated ketone, $\text{O}=\text{C}(\text{Ph})(\text{CF}_3)$, catalyzed by the three-coordinate germanium(II) hydride, $(\text{Dip}^{\text{Nacnac}})\text{GeH}$, should be both thermodynamically and kinetically viable.¹⁰ Here, we show that the markedly more reactive two-coordinate group 14 metal(II) hydrides, **1** and **2**, can efficiently and selectively catalyze the hydroboration of even unactivated and bulky ketones/aldehydes (Chart 1). Although the intermediacy of tin(II) hydrides in carbonyl hydroelementations has been previously proposed, this work represents the first use of well-defined low-valent p-block metal hydride species as catalysts in organic synthesis.¹¹

At the outset of this study, the stoichiometric reactions of **1** and **2** with either HBpin or the bulky carbonyl substrates, $\text{O}=\text{C}(\text{Pr}^{\dagger})_2$ and $\text{O}=\text{C}(\text{H})(\text{PhOMe-4})$, were carried out in order to assess the viability of the proposed catalytic protocols.¹² No noticeable reactions were observed between the metal(II) hydrides and HBpin, as evidenced by the fact that the characteristic low field hydride resonances (¹H NMR) of **1** and **2** shifted negligibly upon addition of HBpin to their solutions. In contrast, the reactions with 1 equiv of the carbonyl substrates were rapid at ambient temperature and afforded the hydro-metalation products, $L^{\dagger}\text{MOC}(\text{H})(\text{Pr}^{\dagger})_2$ ($M = \text{Ge}$ **3**, Sn **4**) and $L^{\dagger}\text{MOC}(\text{H})_2(\text{PhOMe-4})$ ($M = \text{Ge}$ **5**, Sn **6**), in a matter of seconds, and in essentially quantitative yields (as determined by ¹H NMR spectroscopic analyses of the reaction mixtures). All of **3–6** were crystallographically characterized (see Figure 1 for molecular structures of **3** and **5**) and were found to be monomeric in the solid state.

The reactivity of **1** and **2** can be compared to that of the only other group 14 metal(II) hydrides, $(\text{Dip}^{\text{Nacnac}})\text{MH}$ ($M = \text{Ge}$ or Sn), that are known to hydrometallate ketones.^{13,14} While **1** and

Received: January 21, 2014

Published: February 13, 2014

Chart 1. Catalysts Used in This Study

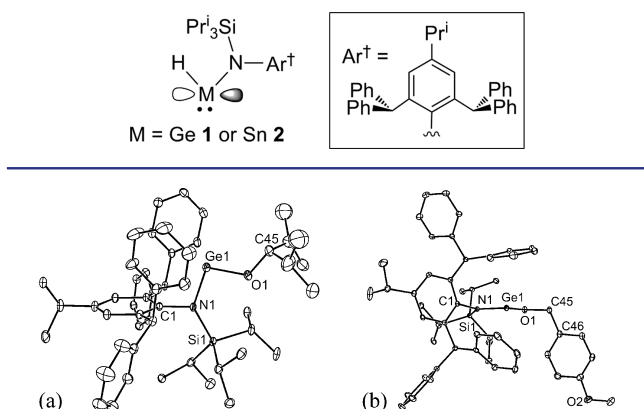


Figure 1. Thermal ellipsoid plot (20% probability surface) of (a) $L^+GeOC(H)(Pr^i)_2$ **3** and (b) $L^+GeOC(H)_2(PhOMe-4)$ **5** (hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg) for **3/5**: Ge(1)–N(1) 1.883(3)/1.877(2), Ge(1)–O(1) 1.797(3)/1.8120(19), N(1)–Ge(1)–O(1) 99.44(14)/97.49(9).

Table 1. Hydroborations of Aldehydes, $RC(H)O$, Catalyzed by **1** or **2** (see Scheme 1)

cat. ^a	loading (mol %)	R	time (h) ^b	yield (%) ^c	TOF (h ⁻¹) ^d
2	0.05	Ph	2.5	>99	800
2	0.05	PhBr-4	4.5	>99	450
2	0.05	PhOMe	5	>99	400
2	0.05	Et	<0.15	>99	>13 300 ^e
2	0.05	Pr ⁱ	<0.15	>99	>13 300 ^e
2	0.05	Cy	<0.15	>99	>13 300 ^e
1	1	Ph	1.5	>99	67
1	1	PhBr-4	4	>99	25
1	1	PhOMe	6	>99	17
1	0.05	Et	1	>99	2000
1	0.05	Pr ⁱ	0.4	>99	5000
1	0.05	Cy	0.33	>99	6000

^aCatalyst **2** generated *in situ* using the precatalyst, L^+SnOBu^t . ^bAll reactions carried out in d_6 -benzene at 20 °C using 1 equiv of HBpin. ^cObtained by integration of RCH_2OBpin signal against tetramethylsilane internal standard. ^dTurnover frequency - average value for complete reaction. ^eTOF lower limit.

2 rapidly hydrometallate the bulky, unactivated ketone, $O=C(Pr^i)_2$, at ambient temperature, $(D^{ip}Nacnac)GeH$ reacts only slowly (over 12 h) with activated ketones (e.g., $O=C(Ph)(CF_3)$),¹³ and forcing conditions (110 °C, 12 h) are required for $(D^{ip}Nacnac)SnH$ to hydrostannylate the bulky aliphatic ketone, $O=C(cyclopropyl)_2$.¹⁴ Undoubtedly, the empty p-orbital available at the metal centers of **1** and **2** give rise to their markedly enhanced reactivity, relative to intramolecularly base stabilized $(D^{ip}Nacnac)MH$. The two-coordinate nature of **3–6** is also the most likely reason why they subsequently react cleanly with 1 equiv of HBpin at ambient temperature (though at slower rates than the hydrometalation reactions) to give the borate esters, $pinBOC(H)(Pr^i)_2$ and $pinBOC(H)_2(PhOMe-4)_2$, and to regenerate the metal hydrides, **1** and **2**. Furthermore, the generated borate esters are unreactive toward regenerated **1** or **2**. These results gave a strong indication that **1** and **2** could act as efficient catalysts for the hydroboration of carbonyl compounds.

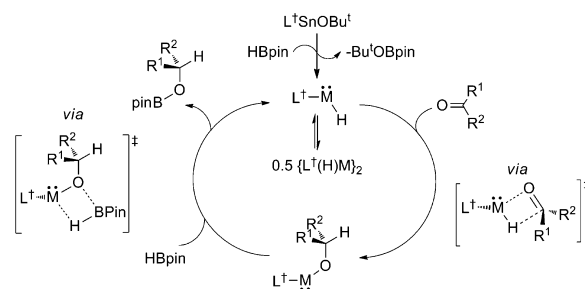
This was systematically explored, though given the fact that **2** slowly decomposes in solution at ambient temperature (over 2 days),^{3a} the thermally stable, monomeric precatalyst, L^+SnOBu^t

Table 2. Hydroborations of Ketones, $(R^1)(R^2)CO$, Catalyzed by **1** or **2** (see Scheme 1)

cat. ^a	loading (mol %)	R ¹	R ²	time (h) ^b	yield (%) ^c	TOF (h ⁻¹) ^d
2	0.5	Ph	CF ₃	<0.15	>99	1330
2	0.5	Ph	Ph	2.5	95	80
2	0.5	PhOMe	Me	0.25	98	800
2	0.5	PhEt-4	Me	0.25	>99	800
2	0.5	Ph	C(O)Ph ^e	0.33	96	600
2	0.5		Cy ^f	1.75	96	115
2	1		CyMe-2 ^g	0.5	99	200
2	0.5		2-cyclohexene ^{e,h}	0.5	>99	400
2	0.5		Ad ⁱ	2.5	95	80
2	2	Pr ⁱ	Pr ⁱ	24	95	1.7
1	2.5	Ph	CF ₃	0.25	>99	160
1	1.25	Ph	Ph	48	>99	1.7
1	2.5	PhOMe	Me	1.33	>99	30
1	2.5	PhEt-4	Me	1	>99	40
1	5	Ph	C(O)Ph ^e	0.4	94	50
1	5		Cy ^f	<0.15	>99	130
1	5		CyMe-2 ^g	0.5	>99	40
1	2.5		2-cyclohexene ^{e,h}	1	>99	40
1	1.25		Ad ⁱ	4	>99	20
1	1.25	Pr ⁱ	Pr ⁱ	168	80	0.47

^aCatalyst **2** generated *in situ* using the precatalyst, L^+SnOBu^t . ^bAll reactions carried out in d_6 -benzene at 20 °C using 1 equiv of HBpin (unless stated otherwise). ^cObtained by integration of $R_2CHOBpin$ signal against tetramethylsilane internal standard. ^dTurnover frequency - average value for complete reaction. ^e2 equiv of HBpin. ^fCyclohexanone. ^g2-Methylcyclohexanone. ^h2-Cyclohexen-1-one. ⁱAdamantanone.

Scheme 1. Proposed Cycle for the Hydroboration of Carbonyl Compounds, $(R^1)(R^2)CO$ ($R^1/R^2 =$ Alkyl, Aryl or H), Catalyzed by L^+MH ($M = Ge$ or Sn)



(see Supporting Information (SI)) was used for the tin based studies. Prior to the catalytic runs, it was confirmed that this does not itself react with the carbonyl substrates, but does react rapidly and cleanly with excess HBpin to generate **2** *in situ*. One other advantage of the use of L^+SnOBu^t is that it is considerably more moisture and oxygen tolerant than **2**. With regard to the hydroboration of aldehydes (see Table 1), (pre)catalyst loadings of only 0.05 mol % were typically required to generate the borate ester product, essentially quantitatively, and often in under 1 h. As the experiments were carried out in NMR tubes and monitored by ¹H NMR spectroscopy, a number of the tin catalyzed reactions (i.e., those marked time <0.15 h) were complete before the reaction mixture could be analyzed. Indeed, a qualitative visual assessment of all such reactions suggested that they were complete in <1 min and, therefore, that their turnover frequencies are likely to be considerably higher than the already impressive quoted lower limit of 13 300 h⁻¹.

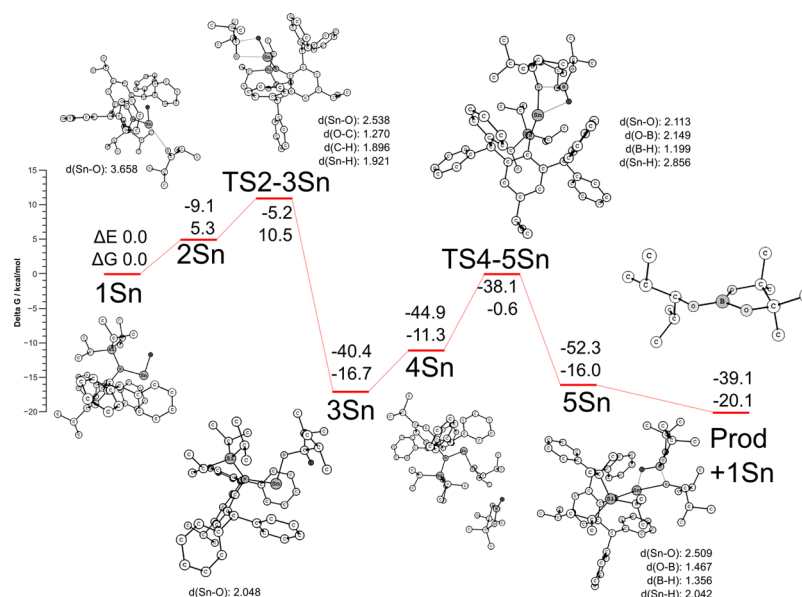


Figure 2. Calculated (BP86+D(BJ)/def2-TZVPP) free energy profile for the reaction of $\text{O}=\text{C}(\text{Pr})_2$ with HBpin, catalyzed by $\text{L}^\dagger\text{SnH 2}$. Selected bond lengths (Å), and free and electronic energies (kcal/mol), are shown.

It is clear from the results presented in Table 1 that the hydroboration of aliphatic aldehydes is significantly more efficient than that of the aromatic aldehydes. This is likely due to a combination of steric and electronic factors. That is, the bulkier the substrate, the more difficult it is for the O-center of its hydrometalated product, $\text{L}^\dagger\text{MOC}(\text{H})_2\text{R}$, to approach the boron center of HBpin in the rate-determining, σ -bond metathesis step of the catalytic cycle (*vide infra*). Similarly, aryl substituents (R) likely reduce the Lewis basicity of the O-center of $\text{L}^\dagger\text{MOC}(\text{H})_2\text{R}$, relative to aliphatic substituents (R) on the intermediate. Furthermore, it is apparent that reactions employing the tin precatalyst, $\text{L}^\dagger\text{SnO}^\dagger\text{Bu}^\dagger$ (and therefore the catalyst, **2**), are more rapid than those carried out with the Ge catalyst, **1**. This can be explained by the larger, more Lewis acidic metal center, and more polar $\delta^+\text{M}-\text{O}^\delta-$ bonds, in the hydrostannylated intermediates, thus making these intermediates more reactive toward HBpin than their Ge counterparts.¹⁵

Not surprisingly, to achieve near-quantitative hydroborations of ketones (Table 2), higher catalyst loadings were required than for the less bulky aldehyde substrates. In addition, the ketone hydroboration reactions were slower, though, as was the case for aldehydes, the reactions catalyzed by tin were more rapid than those employing the germanium hydride catalyst. With that said, the hydroborations of the aldehydes and ketones reported here are typically more efficient than all similar, previously reported transition metal catalyzed hydroborations utilizing HBpin.^{6,8a} It should be noted, however, that the group 14 catalysts show similar efficiencies to the highly active magnesium hydride hydroboration catalyst, $\{(\text{D}^\text{ip}\text{Nacnac})\text{MgH}\}_2$, recently reported by Hill et al.^{9a}

Although all hydroborations are completely regioselective for the formation of borate esters, preliminary investigations were carried out to determine the chemo- and diastereoselectivity of the ketone reductions. First, it was found that dihydroborations of the α -diketone, benzil, were rapid with both catalysts (using 200 mol % of HBpin) and that there was no evidence for the formation of the singly hydroborated product in either reaction. In contrast, the catalyzed reactions of 2-cyclohexen-1-one with 2 equiv of HBpin were complete in under 1 h, but led only to the

chemoselective and quantitative reduction of the ketone functionality, leaving the alkene fragment intact. With respect to diastereoselectivity, the hydroboration of 2-methylcyclohexanone was carried out with both catalysts. While little selectivity was observed for the tin catalyst, significant *cis*-/*trans*-selectivity (*ca.* 72:28) was reproducibly achieved for the Ge catalyst under several catalyst loadings. Although the origin of this selectivity is not yet clear, it is intriguing that this is the opposite of the (less pronounced) *trans*-/*cis*-diastereoselectivity typically observed for the hydroboration of this substrate.¹⁶

In order to shed some light on the mechanism of the observed reactions, a kinetic analysis of the hydroboration of 4-ethylacetophenone catalyzed by the germanium hydride compound, **1**, was undertaken using the initial rates method (see SI for full details).¹⁷ The results of that analysis clearly indicate first-order dependence of the reaction in both HBpin and catalyst and zero-order dependence in ketone. This implies that the rate-determining step of the catalytic cycle is the reaction of the alkoxide intermediate, $\text{L}^\dagger\text{GeOC}(\text{H})(\text{Me})(\text{PhEt-4})$, with HBpin, and therefore that the intermediate is the resting state in the cycle. This conclusion is consistent with the preliminary stoichiometric reaction studies mentioned above and also implies that the equilibrium between $\text{L}^\dagger(\text{H})\text{Ge}=\text{Ge}(\text{H})\text{L}^\dagger$ and $\text{L}^\dagger(\text{H})\text{Ge}$, **1**, should have little effect on the overall reaction rate. While it cannot be certain, it seems very likely that the active species in that equilibrium is two-coordinate **1**, which is rapidly consumed by reaction with the ketone,¹² and is thus only present in the reaction mixture in negligible amounts throughout the cycle.

We propose that the mechanism of the Ge- and Sn-catalyzed reactions initially involves attack of the O-center of the substrate at the two-coordinate metal center, with hydrometalation subsequently proceeding *via* a four-membered transition state (Scheme 1). The monomeric, two-coordinate metal alkoxide intermediate then undergoes a σ -bond metathesis reaction with HBpin to generate the borate ester and return the catalyst. It is noteworthy that this mechanism is reminiscent of that proposed by Hill et al. for $\{(\text{D}^\text{ip}\text{Nacnac})\text{MgH}\}_2$ catalyzed ketone hydroborations.^{9a} So as to assess the feasibility of our proposal,

the free energy profile of the tin hydride catalyzed reaction of HBpin with the very bulky substrate, $\text{O}=\text{C}(\text{Pr}^i)_2$, was calculated using DFT, with the inclusion of dispersion interactions (BP86+D(BJ)/def2-TZVPP). The calculated profile (Figure 2)¹⁸ closely matches the proposed general mechanism and shows that both the hydrostannylation and σ -bond metathesis reactions are exergonic, by -16.7 and -3.4 kcal/mol, respectively. Furthermore, the fact that these reactions exhibit kinetic barriers of 10.5 and 16.1 kcal/mol, respectively, is fully consistent with the experimental observation that the σ -bond metathesis reaction is the rate-determining step in the catalytic cycle. Considering that these calculations were carried out on the experimentally most difficult substrate to hydroborate, it would be expected that the kinetic barriers to the hydroboration of less bulky substrates would be significantly lower. Accordingly, the computational study clearly highlights the thermodynamic and kinetic viability of the proposed general mechanism.

In conclusion, the use of well-defined low-valent p-block metal hydrides as catalysts in organic synthesis has been demonstrated for the first time. In this respect, the highly reactive, two-coordinate germanium(II) and tin(II) hydride compounds, **1** and **2**, have effected the catalytic addition of HBpin to a range of carbonyl compounds, with efficiencies that rival the most active catalysts presently available for such reactions. It seems reasonable that low-valent group 14 metal compounds, such as **1** and **2**, will find a range of other catalytic applications in organic synthetic methodologies (e.g., alkene hydrosilylations, CO_2 reductions, etc.). We are currently investigating this possibility and will report on our findings in due course.

■ ASSOCIATED CONTENT

■ Supporting Information

Details of the synthesis and characterizing data for all new compounds. Full details and references for the catalysis, kinetic, crystallographic, and computational studies. Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

■ Corresponding Authors

frenking@chemie.uni-marburg.de
cameron.jones@monash.edu

■ Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the Australian Research Council (C.J., DP120101300), the USAF Asian Office of Aerospace Research and Development (C.J.), and the Deutsche Forschungsgemeinschaft (G.F.) are acknowledged. The EPSRC National Mass Spectrometry Facility is also thanked. We are also grateful to Prof. Andrew S. Weller, Oxford University, for many helpful discussions.

■ REFERENCES

(1) Selected recent reviews: (a) Power, P. P. *Chem. Rec.* **2012**, *12*, 238. (b) Mandal, K. S.; Roesky, H. W. *Acc. Chem. Res.* **2012**, *45*, 298. (c) Power, P. P. *Acc. Chem. Res.* **2011**, *44*, 627. (d) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354. (e) Yao, S.; Xiong, Y.; Driess, M. *Organometallics* **2011**, *30*, 1748. (f) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389. (g) Power, P. P. *Nature* **2010**, *463*, 171.

(2) N.B. Excellent progress has been made in the development of catalysis involving "normal oxidation state" p-block frustrated Lewis pairs. See, for example: Erker, G.; Stephan, D. W. *Frustrated Lewis Pairs II: Expanding the Scope*; Springer: Heidelberg, 2013.

(3) (a) Hadlington, T. J.; Hermann, M.; Li, J.; Frenking, G.; Jones, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 10199. (b) Hadlington, T. J.; Jones, C. *Chem. Commun.* **2014**, *50*, 2321. For the first activations of H_2 by group 14 centers, see: (c) Spikes, G. H.; Fetting, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232. (d) Frey, G. D.; Lavallo, V.; Donnadiu, B.; Schöller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439.

(4) Relevant reviews: (a) Cho, B. T. *Chem. Soc. Rev.* **2009**, *38*, 443. (b) Togni, A.; Grützmacher, H. *Catalytic Heterofunctionalization*; Wiley-VCH: Weinheim, 2001.

(5) Fu, G. C.; Evans, D. A. *J. Org. Chem.* **1990**, *55*, 5678.

(6) Koren-Selfridge, L.; Query, I. P.; Hanson, J. A.; Isley, N. A.; Guzei, I. A.; Clark, T. B. *Organometallics* **2010**, *29*, 3896.

(7) Khalimon, A. Y.; Farha, P.; Kuzmina, L. G.; Nikonov, G. I. *Chem. Commun.* **2012**, *48*, 455.

(8) (a) Oluyadi, A. A.; Ma, S.; Muhoro, C. N. *Organometallics* **2013**, *32*, 70. (b) Almqvist, F.; Torstensson, L.; Gudmundsson, A.; Frejd, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 376. (c) Giffels, G.; Dreisbach, C.; Kragl, U.; Weigerding, M.; Waldmann, H.; Wandrey, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2005.

(9) (a) Arrowsmith, M.; Hadlington, T. J.; Hill, M. S.; Kociok-Kohn, G. *Chem. Commun.* **2012**, *48*, 4567. (b) Blake, A. J.; Cunningham, A.; Ford, A.; Teat, S. J.; Woodward, S. *Chem.—Eur. J.* **2000**, *6*, 3586.

(10) Takagi, N.; Sakaki, S. *J. Am. Chem. Soc.* **2013**, *135*, 8955.

(11) N.B. (a) One report on the reduction of ketones using high loadings (10 mol%) of tin(II) triflate as a catalyst in the presence of a silane invoked the intermediacy of a tin(II) hydride in the reaction. No evidence for this proposal was presented. Lawrence, N. J.; Bushell, S. M. *Tetrahedron Lett.* **2000**, *41*, 4507. (b) Tilley et al. have described several cationic transition metal hydridosilylene complexes ($[\text{L}_n\text{TM}=\text{Si}(\text{H})\text{R}]^+$) that catalyze hydrosilylations of unsaturates. For a recent example, see: Fasulo, M. E.; Lipke, M. C.; Tilley, T. D. *Chem. Sci.* **2013**, *4*, 3882.

(12) We assume that the monomeric species, **1** and **2**, which are in equilibrium with dimeric $\text{L}^\dagger(\text{H})\text{Ge}=\text{Ge}(\text{H})\text{L}^\dagger$ and $\text{L}^\dagger\text{Sn}(\mu\text{-H})_2\text{SnL}^\dagger$ in solution, are the active species in the stoichiometric and catalytic reactions reported here (see ref 3 and Supporting Information).

(13) Jana, A.; Roesky, H. W.; Schulzke, C. *Dalton Trans.* **2010**, *39*, 132.

(14) (a) Jana, A.; Roesky, H. W.; Schulzke, C.; Döring, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 1106. (b) Jana, A.; Roesky, H. W.; Schulzke, C. *Inorg. Chem.* **2009**, *48*, 9543.

(15) All aldehyde and ketone substrates were found to be either unreactive or poorly reactive (max. 5% conversion) towards HBpin in catalyst-free control experiments. No enolization byproducts were observed for the catalyzed hydroborations of any substrate.

(16) Query, I. P.; Squier, P. A.; Larson, E. M.; Isley, N. A.; Clark, T. B. *J. Org. Chem.* **2011**, *76*, 6452.

(17) Sewell, L. J.; Huertos, M. A.; Dickinson, M. E.; Weller, A. S. *Inorg. Chem.* **2013**, *52*, 4509.

(18) The weakly bonded adducts **2Sn** and **4Sn**, which are minima on the potential energy surface, are energetically lower-lying than **1Sn** and **3Sn**, respectively. The former species are less stable than the latter molecules when temperature and entropic effects are considered.