Dalton Transactions

Hydroboration of Carbonyls and Imines by an Iminophosphonamido Tin(II) Precatalyst

Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-06-2021-001856.R3
Article Type:	Paper
Date Submitted by the Author:	10-Sep-2021
Complete List of Authors:	Nakaya, Kazuki; Saitama University Takahashi, Shintaro; Saitama University Ishii, Akihiko; Saitama University, Department of Chemistry Boonpalit, Kajjana; Mahidor University, Chemistry Surawatanawong, Panida; Mahidol University, Chemistry Nakata, Norio; Saitama Universtiy, Deaprtment of Chemistry

ARTICLE

Hydroboration of Carbonyls and Imines by an Iminophosphonamido Tin(II) Precatalyst

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Kazuki Nakaya,[a] Shintaro Takahashi,[a] Akihiko Ishii,[a] Kajjana Boonpalit,[b] Panida Surawatanawong,*[b] Norio Nakata*[a]

A novel three-coordinated tin(II) chloride [$Ph_2P(N^tBu)_2$]SnCl (**1**) supported by an *N,N′*-di-*tert*-butyliminophosphonamide having two phenyl groups on the phosphorus atom was synthesized by the reaction of the starting lithium iminophosphonamide [$Ph_2P(N^tBu)_2$]Li with $SnCl_2$·(dioxane) in toluene. The molecular structure of **1** was established by X-ray diffraction analysis. Tin(II) chloride **1** can act as an efficient precatalyst for the hydroboration of a wide variety of aldehydes, ketones, and imines at –10 °C. DFT calculations propose that the hydroboration involves the hydride transfer from the corresponding tin(II) hydride intermediate [$Ph_2P(N^tBu)_2$]SnH (**10**) to the carbonyl substrates via four-membered transition states (**TS-12**) affording three-coordinated tin(II) alkoxide intermediates [$Ph_2P(N^tBu)_2$]SnOR (**13**), followed by the stepwise reaction of **13** with HBpin (pin = pinacolate) to release the boronate esters and regenerate the tin(II) hydride **10**. The stoichiometric reaction of the in site-generated **10** with benzophenone **2a** at –10 °C led to the formation of **13**. Moreover, **13** also stoichiometrically reacted with HBpin at –10 °C, forming the corresponding boronate ester **3a** and **10** based on the ^1H NMR spectrum of the reaction mixture.

Introduction

In recent years, developments in the area of low-valent main-group compounds have grown significantly due to their ability to activate small molecules (e.g., H_2, NH_3, aldehydes, ketones, etc.).[1,2] It has begun to be realized that the low coordination numbers and electronic structure of these compounds can lead to reactivities resembling precious transition metal complexes. There are numerous demonstrations of the low-valent p-block compounds developed as replacements for precious transition metal-based catalysts in various synthetic processes. Much interest has been focused on transforming carbonyl compounds, which is one of the crucial processes in organic synthesis, using low-valent heavier Group 14 element precatalysts.[3,4] Roesky and coworkers reported that low valent three-coordinated germanium(II) and tin(II) hydrides (**A**) incorporated with a β-diketiminato ligand give rise to the nucleophilic hydride addition to the carbonyl carbon of 2,2,2-yrifluoroacetophenone resulting in the formation of germanium(II) and tin(II) alkoxide products (**B**) (Scheme 1).[1d,5] A recent computational investigation by Sakaki showed that the germanium(II) alkoxide **B** can further react with SiF_3H to regenerate germanium(II) hydride **A** giving the corresponding silyl ether.[6] The free energy profile for this predicted catalytic cycle is thermodynamically and kinetically viable, suggesting that the germanium(II) hydride **A** should catalyse the hydrosilylation of 2,2,2-trifluoroacetophenenone with SiF_3H. Later, Jones and Frenking reported well-defined low-valent two-coordinate germanium(II) and tin(II) hydrides (**C**) that catalyse the addition of HBpin (pin = pinacolate) to a range of carbonyl compounds efficiently.[7] Wesemann and coworkers also presented the three-membered intramolecular tetrylene Lewis pairs (**D**), which were found to catalyse hydroboration of hexanal.[8] Recently, Nagendran and coworkers disclosed the synthesis of triflatostannylene (**E**) and - germylene (**F**) stabilized by an aminotroponate and aminotroponiminate ligands, respectively.[9] These tetrylenes were also utilized as precatalysts in the reduction of carbonyl compounds with HBpin. In particular, stannylene **E** achieved lower catalyst loading of 0.025–0.25 mol% and extremely high turnover frequencies (TOF) up to 30,000 h^{-1}. Quite recently, Inoue and coworkers demonstrated the synthesis of stable heavier analogues of nitriles as monomeric tetrylene-phosphinidenes (**G**) by taking advantage of *N*-heterocyclic carbene coordination to the low-valent phosphorus centre;[10] the stannylene derivative showed high catalytic activity in the hydroboration of aromatic aldehydes and ketones. At the same time, Yang and coworkers described that three-coordinated tin(II) chalcogenides (**H**, **I**) supported by a β-diketiminato ligand act as precatalysts for the hydroboration of aldehydes and ketones.[11] Khan and Pati also reported the hydroboration and cyanosilylation of various aldehydes by employing the benzannulated *N*-heterocyclic germylene and stannylene (**J**) as precatalysts.[12]

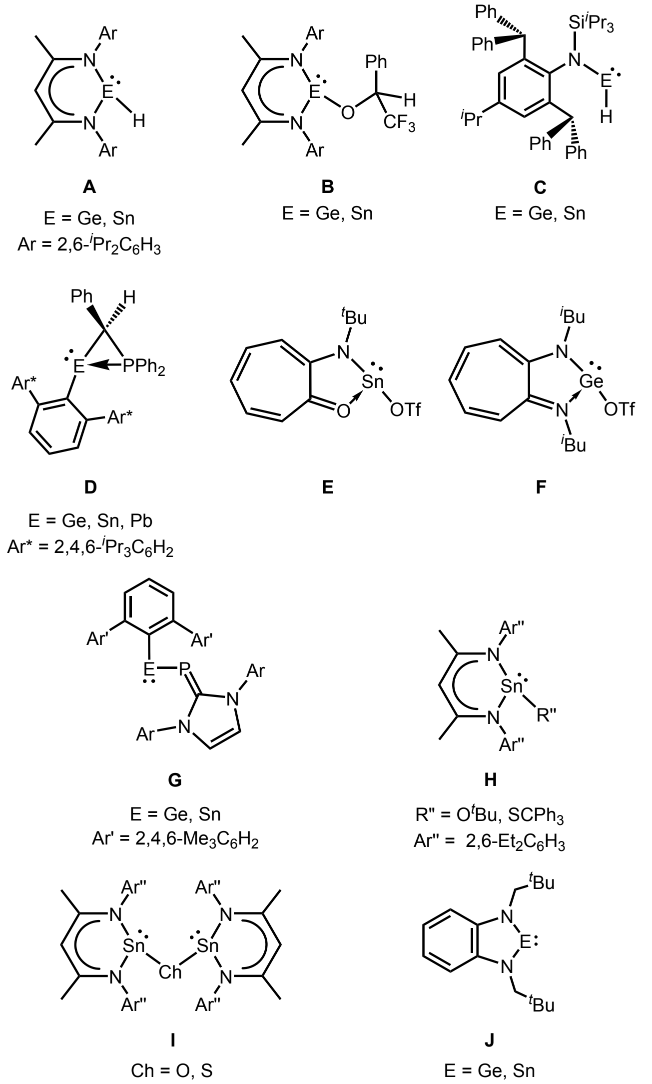
---

[a] *Department of Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-okubo, Sakura-ku, Saitama 338-8570, Japan*

[b] *Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand*

† Electronic Supplementary Information (ESI) available. CCDC: 2021242 (for **1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

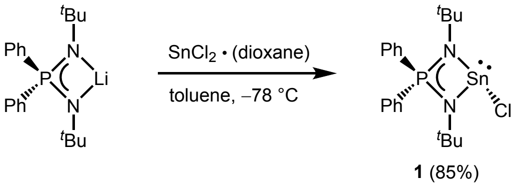
In this article, we wish to present the synthesis of novel three-coordinated tin(II) chloride (**1**) (Scheme 2), which is supported by an iminophosphonamide ligand[13] isoelectronic to the well-known monoanionic amidinate ligand, and the study of its ability to catalyse the hydroboration of a range of aldehydes, ketones, and imines with HBpin. We also discuss density functional theory (DFT) calculation to give an insight into the mechanism of the catalytic hydroboration of carbonyls using **1** and HBpin.



Scheme 1. Low-valent heavier Group 14 element precatalysts for the hydroboration of carbonyls with HBpin.

Results and discussion

The reaction of lithium iminophosphonamide with $SnCl_2$·(dioxane) proceeded in toluene at –78 °C to give the corresponding three-coordinated tin(II) chloride **1** as air- and moisture-sensitive colourless crystals in 85% yield (Scheme 2). The ^{1}H NMR spectrum of **1** in C_6D_6 exhibited a sharp signal due to *tert*-butyl protons at 0.97 ppm and one set of aromatic protons at 7.08–7.12 ppm and 8.09 ppm. In the ^{31}P{^{1}H} NMR spectrum of **1**, a singlet resonance was observed at 37.4 ppm, which is comparable to those of the related iminophosphonamido tin(II) compounds (38.2–44.3 ppm) having different substituents on the phosphorus atom.[14] The ^{119}Sn{^{1}H} NMR spectra of **1** displayed a signal at 48.8 ppm, which lies in the range for amidinato tin(II) chlorides reported (–124.0 to 78.9 ppm).[12] The crystal structure of **1** was confirmed unambiguously by X-ray diffraction (Fig. 1). Compound **1** crystallises in the triclinic space group *P*-1 with two independent molecules, and both molecules show very similar structures. The four-membered SnN_2P ring takes non-planar geometry with a puckered angle of 7.16° between each SnNP plane. The three-coordinated tin atom has a distorted trigonal-pyramidal environment; the sum of the bond angles around tin atom (259.25°) is larger by 12.3° than that of the corresponding amidinato tin(II) chloride (246.94°),[15b] and comparable to that of the corresponding diimidosulfinato tin(II) chloride (262.3°).[16] The Sn–N bond lengths [2.187(2) and 2.181(2) Å] are similar to those of the reported amidinato [2.177(3)–2.243(3) Å][15] and diimidosulfinato [2.1694(14) Å][16] analogues. The Sn–Cl bond length is 2.4929(8) Å, which is in the typical region for three-coordinated tin(II) chlorides [2.4059(19)–2.4928(16) Å].[14,15a-15c,16]



Scheme 2. Synthesis of three-coordinated tin(II) chloride **1** supported by an iminophosphonamido ligand.

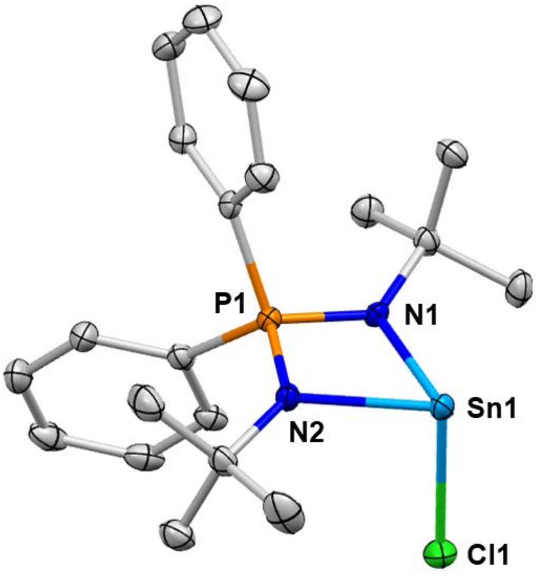
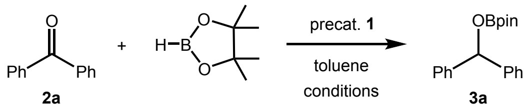


Fig. 1 ORTEP of **1** with 50% thermal ellipsoids. All hydrogen atoms and one of the two independent molecules of **1** in the unit cell are omitted for clarity. Selected bond lengths [Å] and angles [deg.]: Sn1–N1 = 2.187(2), Sn1–N2 = 2.181(2), Sn1–Cl1 = 2.4929(8), N1–Sn1–N2 = 67.60(8), N1–Sn1–Cl1 = 95.84(6), N2–Sn1–Cl1 = 95.82(7).

First, the hydroboration of benzophenone **2a** with HBpin was selected as the prototypical case to optimize the reaction conditions. The results are summarised in Table 1. The yields were calculated based on the integral ratio of the hydroboration product and the starting material in ^{1}H NMR spectra using ferrocene as an internal standard. When the reaction of benzophenone **2a** with 1.1 equiv. of HBpin was carried out using 5 mol % of **1** as a precatalyst in toluene at 20 °C or 0 °C for 2 h, the corresponding boronate ester **3a** was formed in only 13 or 9% yields, respectively (Runs 1 and 2). During the reaction at ambient temperature, grey precipitates, which appeared to be decomposed tin species, formed immediately. Thus, the hydroboration using precatalyst **1** was examined at lower temperatures, and then the reaction was quenched by raising the temperature at 90 °C. Upon using 5 mol % of **1** at –10 °C for 2 h, the yield of **3a** was slightly increased to 23% (Run 3). When the reaction conducted with 10 mol % of **1** at –10 °C for 1 h, the product yield increased drastically to 96% (Run 4). The reaction carried out at –20 °C employing 10 mol % of **1** promoted the reduction of **2a** in 63% conversion after 1 h (Run 5). As a control experiment, the reaction of HBpin with **2a** without **1** was conducted at –10 °C in toluene. However, the reaction did not proceed under the conditions, even at 90 °C.

Table 1. Optimization of reaction conditions for the hydroboration of benzophenone **2a** using **1** as a precatalyst.

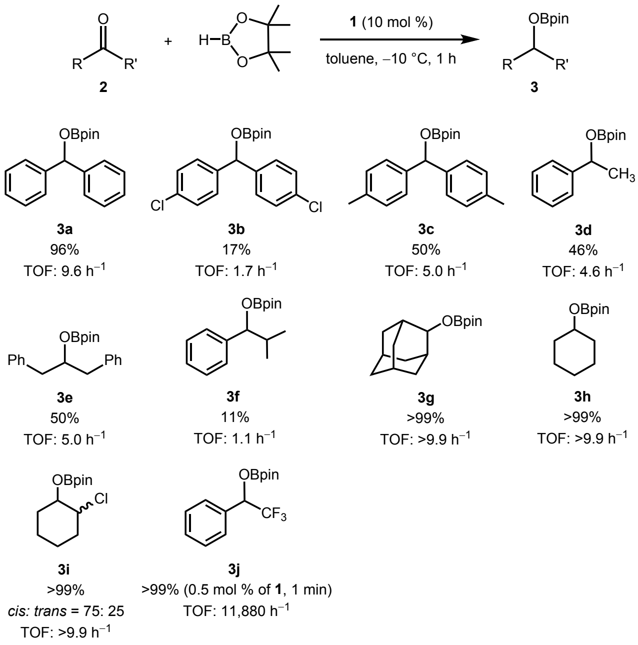


Run	Cat. loading [mol %]	Temp. [˚C]	Time [h]	Yield [%][a]	TOF [h^{-1}]
1	5	20	2	13	1.3
2	5	0	2	9	0.9
3	5	–10	2	23	2.3
4	10	–10	1	96	9.6
5	10	–20	1	63	6.3

[a] Obtained by integral ratios of **2a**/**3a** in the ^{1}H NMR spectra of reaction mixtures using ferrocene as an internal standard.

We next sought to evaluate the hydroboration of several aromatic and aliphatic ketones **2** using **1** (Scheme 3) with the optimised reaction conditions in hand. While this catalyst system is not tolerant of 4,4'-dichlorobenzophenone **2b**, 4,4'-dimethylbenzophenone **2c**, acetophenone **2d**, and dibenzyl ketone **2e** were converted to the corresponding boronate esters **3c**, **3d**, and **3e** in moderate yields. Isobutyrophenone **2f** resulted in poor conversion of 10%, probably due to steric influence. It should be noted that alicyclic ketones **2g**–**2i** were effectively reduced to afford alkyl boronate esters **3g**–**3i** in excellent yields; in the case of 2-chlorocyclohexanone **2i**, the boronate ester **3i** was formed as a mixture of *cis*/*trans* diastereomers (75/25) in over 99% yield. Electron-deficient 2,2,2-trifluoroacetophenone **2j** was utterly consumed with only 0.5 mol % loading of precatalyst **1** within 1 min to give the hydroboration product **3j** quantitatively. The corresponding TOF is over 11,880 h^{-1}, which is comparable to that of Jones's tin(II) hydride **C** (13,300 h^{-1}).[7]

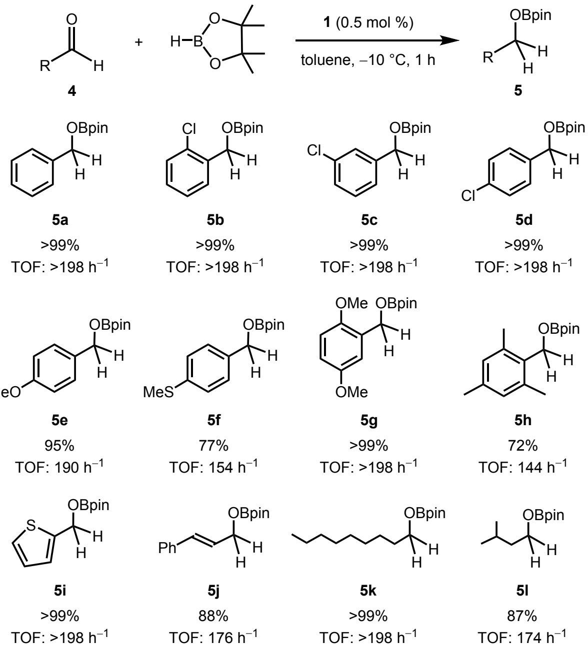
The hydroboration employing **1** was expanded to various aldehydes as shown in Scheme 4. In all experiments with aldehydes, the catalyst loading of **1** could be reduced to 0.5 mol %, and the reactions were performed at –10 °C. Benzaldehyde **4a** and functionalized aromatic aldehydes **4b**–**4g** having electron-withdrawing chloro and electron-donating methoxy and methylthio substituents were all tolerated. The TOF values for these substrates were recorded in the range of 154–198 h^{-1}. Bulky mesitaldehyde **4h** was also hydroborated under the same conditions to provide the corresponding product **5h** in 72% yield. Heteroaromatic aldehyde **4i** was also a suitable substrate and was converted to the corresponding boronate ester **5i** quantitatively. An α,β-unsaturated aldehyde, *trans*-cinnamaldehyde **4j** was reduced to the corresponding product **5j** in 88% yield without forming the 1,4-reduction product. Aliphatic aldehydes such as nonanal **4k** and 3-methylbutanal **4l** were efficiently converted to the corresponding boronate esters **5k** and **5l** in >99% and 87% yields with TOF values of >198 and 174 h^{-1}, respectively.



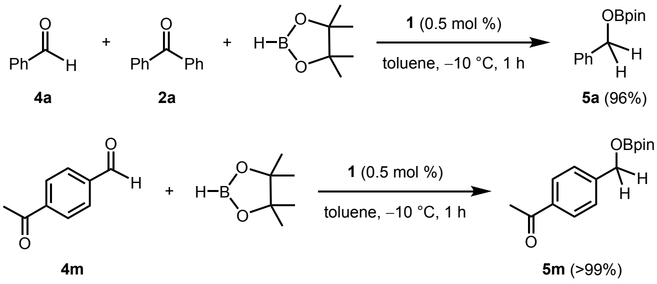
Scheme 3. Hydroborations of ketones using precatalyst **1**.

To investigate the chemoselectivity in the hydroboration using precatalyst **1**, we conducted competition experiments between aldehydes and ketones (Scheme 5). The hydroboration of equimolar amounts of benzaldehyde, benzophenone, and HBpin with 0.5 mol % of **1** led to the exclusive formation of the boronate ester **5a** from benzaldehyde **2a** with 96% conversion. An intramolecular chemoselective hydroboration was also studied with 4-acetylbenzaldehyde **4m**. The reduction occurred exclusively at the aldehyde moiety giving the corresponding product **5m** in quantitative yield after 1 h without affecting the acetyl group in **4m**.

Compared with the related *N*,*N'*-chelating three-coordinate tin(II) chlorides, we performed the hydroboration of carbonyls under the same conditions (Scheme 6). Similarly to precatalyst **1**, the hydroboration of benzaldehyde with 0.5 mol % of tin(II) chlorides **6**[15b] and **7**[16] supported by amidinate- and diimidosulfonate ligands, respectively, proceeded at –10 °C to produce the corresponding boronate ester **5a** in 95% and 69% yields, respectively. In the case of benzophenone as a substrate, tin(II) chlorides **6** and **7** showed much smaller yields and TOF values (**6**: 11%, 1.1 h^{-1}, **7**: 18%, 1.8 h^{-1}) than **1** (96%, 9.6 h^{-1}).



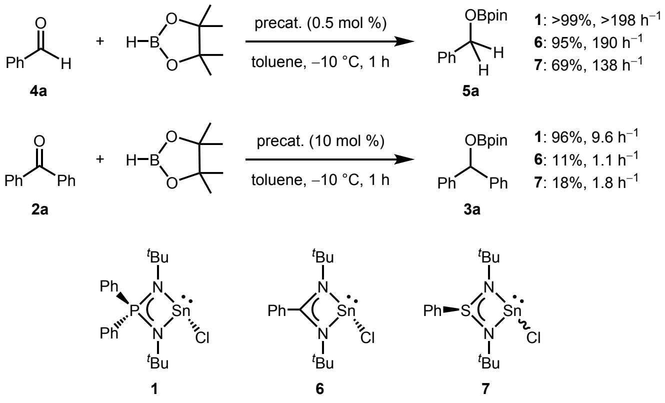
Scheme 4. Hydroborations of aldehydes using precatalyst **1**.



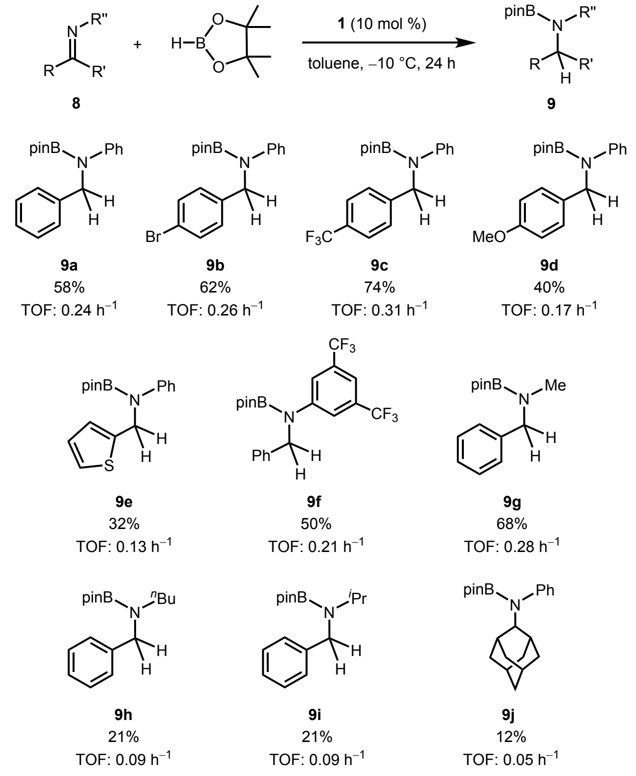
Scheme 5. Chemoselective hydroborations of carbonyls using 0.5 mol % of **1**.

To optimise the borane source, we also performed the reactions with 9-BBN and HBcat (cat = catechol). The reduction of benzaldehyde **4a** with 9-BBN or HBcat using 0.5 mol % of **1** efficiently proceeded under the same conditions to give the hydroboration products quantitatively. In sharp contrast, the hydroboration of benzophenone **2a** with 9-BBN or HBcat in the presence of **1** (10 mol %) afforded the corresponding hydroboration products in low yields (35% and 30%). Furthermore, our system using **1** did not show the hydrosilylation of carbonyls with $PhSiH_3$ or Ph_2SiH_2.

The successful results in the hydroboration of carbonyls using **1** prompted us to extend this catalytic system to the hydroboration of imines (Scheme 7). In the presence of 10 mol % of **1** as a precatalyst, *N*-benzylideneaniline **8a** and its derivatives **8b**-**d** containing electron-withdrawing and -donating substituents at the *para*-position were treated with HBpin at −10 °C for 24 h to produce the desired borylamines **9a**-**9c** in 40–74% yields with TOFs of 0.17–0.31 h^{-1}. *N*-arylimine derivative **8f** having two CF_3 groups at the *meta*-positions also underwent hydroboration in moderate yield (50%) under the same conditions. However, lower conversions were obtained for the *para*-methoxy derivative **8d** and heteroaromatic imine **8e**. *N*-Benzylidenemethylamine **8g** was a suitable substrate to provide a borylamine **9g** in 68% yield with TOF of 0.28 h^{-1}, while the hydroboration of *N*-alkylimine derivatives **8h** and **8i** derived from butylamine and isopropylamine gave low yields of both 21%, probably due to steric hindrance. Unfortunately, ketimines were not tolerated as imine substrates, and only adamantane derivative **8j** could be hydroborated in 12% yield. Our system using **1** is slightly more active than a reported p-block catalyst, benz-amidinato calcium iodide (0.14–0.27 h^{-1}).[17]



Scheme 6. Hydroborations of benzaldehyde **4a** and benzophenone **2a** using **1**, **6**, and **7**.

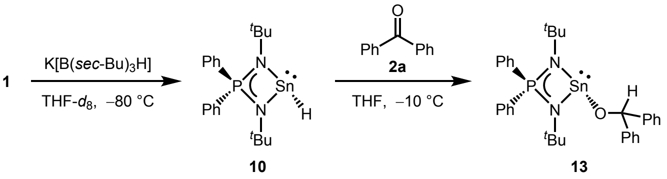


Scheme 7. Hydroborations of imines using precatalyst **1**.

We performed DFT calculations to explore the mechanism of the hydroboration of benzaldehyde **4a** and acetophenone **2d** with HBpin. We first studied the pathway involving the direct hydroboration between **4a** and HBpin, to which the tin compound **1** anchors, similarly to the previous study by Khan and coworkers.[12] However, the energy barrier for this pathway is prohibitively high (46.21 kcal/mol) (Figure S70); notably, the oxygen of HBpin only weakly coordinates to tin compound **1**. Therefore, this pathway is not considered further. Furthermore, the LUMO (–1.69 ev) of **1** is primarily the antibonding orbitals of the two phenyl groups on the phosphorus atom, while the vacant p-orbital on the tin atom appears in the higher energy LUMO+4 (–0.51 ev) (Figure S74). Therefore, it is unlikely that **1** is catalyzing the hydroboration as a Lewis acid.

Tin(II) hydride compounds were found to be generated from the corresponding tin(II) chloride compounds.[1d,5,18,19] Although it is comparatively unstable under ambient conditions, tin(II) hydride compounds were reported to be used as reactive species for hydrostannylation of ketones and aldehydes.[1d,5] The generation of the corresponding tin(II) hydride **10** was confirmed by the reaction of **1** with K[B(*sec*-Bu)$_3$H] in THF-d_8 at –80 °C to result in the formation of a dark orange reaction mixture. In the ^{1}H NMR spectrum measured at –20 °C, a characteristic broad singlet due to the hydride resonance was observed at 14.8 ppm ($\Delta\nu_{1/2}$ = 415 Hz), which is comparable to those of reported monomeric tin(II) hydride species in solution (10.6–16.4 ppm).[18] The ^{119}Sn{^{1}H} NMR spectrum at –20 °C exhibited a broad signal at 307.1 ppm ($\Delta\nu_{1/2}$ = 285 Hz), which is remarkably downfield shifted compared with that of the starting **1** (48.8 ppm). The tendency of the characteristic downfield shift in the ^{119}Sn NMR spectrum for **10** is consistent with the change between the tin(II) hydride (–18 ppm) and tin(II) chloride (–192 ppm) supported by an amino-functionalized β-diketiminato ligand.[18b] The ^{31}P{^{1}H} NMR spectrum at –20 °C displayed a broad signal at 27.2 ppm. Even for long acquisition times, however, ^{1}H-$^{117/119}$Sn coupling or correlation were not observed in the ^{1}H-coupled ^{119}Sn NMR or ^{1}H-^{119}Sn HMQC NMR experiments, respectively, probably due to an equilibrium between monomeric tin(II) hydride **10** and its hydride-bridged isomer.[19d]

To gain more insight into the reaction mechanism, various control experiments were performed. We found that the stoichiometric reaction of the generated **10** with benzophenone **2a** in THF at –10 °C resulted in the formation of a three-coordinated tin(II) alkoxide **13** (Scheme 8). In the ^{1}H NMR spectrum of the reaction mixture, the methine proton in the alkoxy moiety of **13** was resonated at 6.50 ppm. In the ^{119}Sn{^{1}H} NMR spectrum of **13**, a doublet signal with a $J_{\mathrm{Sn-P}}$ coupling of 34.9 Hz was observed at –12.3 ppm, which is comparable to that of the related amidinato tin(II) compound (–28.6 ppm).[20] It was confirmed that tin(II) alkoxide **13** also stoichiometrically reacted with HBpin at –10 °C in toluene-d_8, forming **3a** and **10** based on the ^{1}H NMR spectrum of the reaction mixture. We next examined the reaction of benzophenone **2a** or benzaldehyde **4a** with HBpin at –10 °C in the presence of the generated **10** (10 or 0.5 mol %) as a catalyst. As a result, the corresponding hydroborated products **3a** and **5a** were obtained in 90% or 97% yields, respectively. The hydroborations with less reactive substrates such as acetophenone **2d** and imine **8c** also proceeded effectively under the same conditions to give the corresponding products **3d** and **9c** in 72% and quantitative yields, respectively. However, the equimolar reaction of HBpin with **1** revealed no reaction between them and no observation of tin(II) hydride **10**.[21] Additionally, the stoichiometric reaction with benzophenone **2a**, HBpin, and **1** showed that ca. 90% of **1** remained, and neither **10** nor **13** was observed by the ^{31}P NMR spectrum of the reaction mixture. Note that the ^{1}H and ^{11}B NMR spectra of the reaction mixture indicated the complete consumption of HBpin and the formation of **3a** in 81% yield.



Scheme 8. Generation of tin(II) hydride **10** and the stoichiometric reaction of **10** with benzophenone **2a**.

Recently, Thomas has proposed that the nucleophilic decomposition of 1,3,2-dioxaborolanes such as HBpin and HBcat to borohydride species and that [H$_2$Bpin]$^-$ and [HBpin(OR)]$^-$ can efficiently catalyse the hydroboration of carbonyls above room temperature.[21] However, neither [H$_2$Bpin]$^-$ nor alkoxide [RO]$^-$ was observed in the NMR analysis. Thus, these results indicate that the hydroboration system using **1** is completely different from the nucleophile-promoted hydroboration.

As mentioned above, the direct observation of **10** by the stoichiometric reaction has not been achieved at this time, but if **10** is assumed to be an intermediate, the pathway shown in Fig. 2 can be considered. Thus, the catalytic cycle involves (i) the hydride transfer from the tin(II) hydride **10** to the carbonyl substrate via a four-membered transition state **TS-12** to afford a tin(II) alkoxide intermediate **13**, and (ii) the stepwise reaction of **13** with HBpin to yield the corresponding boronate ester and to regenerate the catalyst **10**. We, therefore, investigated the mechanism for **10**-catalysed hydroboration of **4a** and **2d** with HBpin theoretically.

In the transition state **TS-12a** for the hydride transfer from **10** to benzaldehyde **4a** to form tin(II) alkoxide **13a**, the tin centre weakly interacts with the carbonyl oxygen, while the hydride of **10** strongly interacts with the carbonyl carbon; the Sn···O distance is 2.747 Å and the C···H distance is 1.607 Å (Fig. 3). This interaction is similar to that in the case of the hydride transfer from germanium(II) hydride **A** (Scheme 1) to 2,2,2-trifluoroacetophenone previously reported by Sakaki and coworkers.[6]

Then, the alkoxide oxygen of hydrostannylated intermediate **13a** approaches the boron atom of HBpin to reach **TS-15a**, in which the O···B distance decreases to 2.105 Å. Note that in the case of the reaction of HBpin with tin(II) alkoxide derived from tin(II) hydride **C** reported by Jones and coworkers, four-membered σ-bond metathesis transition state was found.[7] Not only that the alkoxide oxygen comes close to the boron of HBpin (2.149 Å), the hydride of HBpin also interacts with the tin atom (2.856 Å).[7] In contrast, here the interaction between the hydride and the tin atom was not found in **TS-15a**; the Sn···H distance is considerably long (3.394 Å) (Fig. 3). Thus, the reaction of **13a** with HBpin did not occur through the σ-bond metathesis. In **TS-15a**, only the alkoxide oxygen plays a role as a nucleophile to attack at the boron of HBpin. Then, the complex **16a** is generated as a stable four-membered intermediate instead (Fig. 3). The O—B bond is formed (1.515 Å) and the Sn···H interaction is found (2.450 Å). This type of intermediate geometry has not been found in the σ-bond metathesis mechanism.[7]

The subsequent step involving the hydride transfer from HBpin to the tin atom was explored. Although several attempts have been made to locate the transition state from **16a** to produce **5a** and regenerate **10** by the hydride transfer from boron to tin atom, they were unsuccessful. Accordingly, we performed the relaxed potential energy surface scan along with the Sn···H distance and found that the Sn–H bond formation step is rather facile. The intermediate **17a** is located as the complex between **16a** and boronate ester **5a**/**10**, from which the boronate ester product **5a** is released and **10** is regenerated (Fig. 2a).

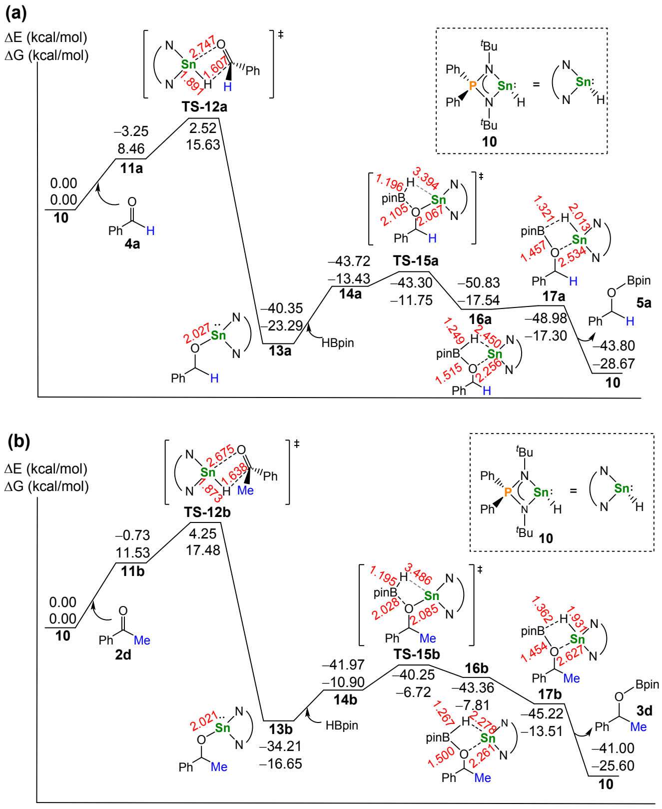


Fig. 2 Solvent corrected free energy profiles in toluene for the reaction of (a) benzaldehyde **4a** and (b) acetophenone **2d** with HBpin catalysed by tin(II) hydride **10**.

The free energy profile in Fig. 2a shows that both the hydrostannylation to form **13a** and the reaction of **13a** with HBpin are exergonic by −23.29 and −5.38 kcal/mol, respectively; the two reactions exhibit the energy barriers of 15.63 and 11.54 kcal/mol, respectively. Similar reaction steps were calculated for acetophenone **2d** with the corresponding energy barriers of 17.48 and 9.93 kcal/mol, respectively (Fig. 2b). These calculations suggest that hydrostannylation is the rate-determining step for the present catalytic hydroboration of carbonyls like benzaldehyde **4a** and acetophenone **2d**. This differs from the reaction of tin(II) hydride **C** with O=C(^{i}Pr)$_2$ substrate and HBpin,[7] in which the σ-bond metathesis was found as the rate-determining step. On the other hand, in the case of 2,2,2-trifluoroacetophenone **2j**, the energy barriers for hydrostannylation and the subsequent reaction with HBpin are 8.35 kcal/mol and 13.84 kcal/mol, respectively (see ESI, Figure S57). Thus, the second step becomes the rate-determining step for **2j**. The energy barrier for **2j** at the rate-determining step is lower than those for benzaldehyde **4a** and acetophenone **2d** by 1.79 and 3.64 kcal/mol, respectively, which is in good agreement with the experimental results in which **2j** is the most reactive substrate followed by benzaldehyde **4a** and then acetophenone **2d**.

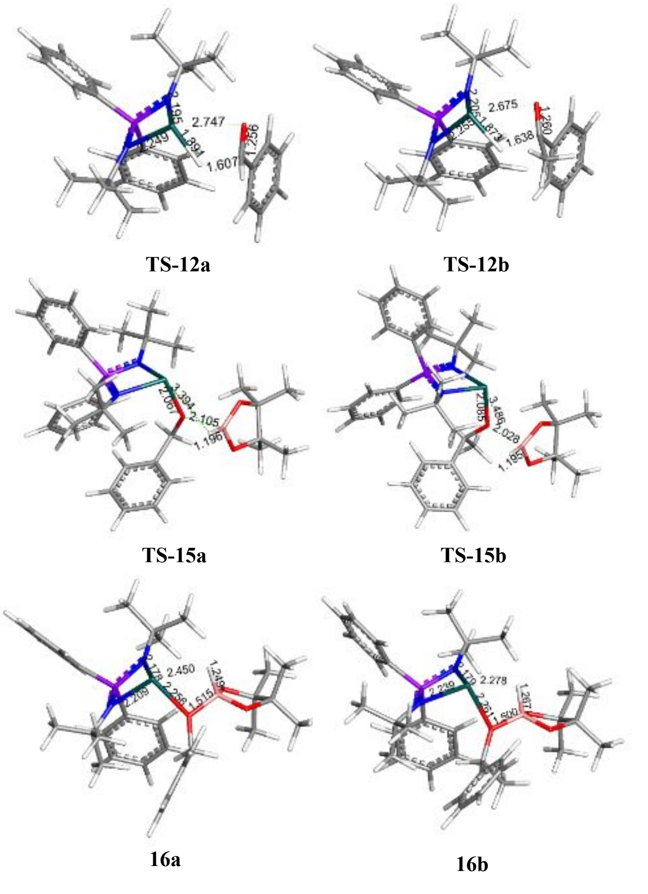


Fig. 3 Optimized geometries of key intermediates and transition states in the hydroboration of benzaldehyde **4a** and acetophenone **2d** with HBpin by tin(II) catalyst **10**.

In the hydrostannylation step, benzaldehyde **4a** undergoes a lower energy barrier than acetophenone **2d**, possibly due to steric and electronic factors. **TS-12b** in the hydrostannylation of acetophenone **2d** has the C···H distance of 1.638 Å, which is slightly longer than that of **TS-12a** for **4a** (1.607 Å) (Fig. 3). The bulky substituent (Me) in **2d** would make it difficult for the hydride transfer from catalyst **10** to approach the carbonyl oxygen of **2d**. From NBO analysis, the electron populations in

C=O π*-orbital of benzaldehyde **4a** (0.09*e*) and acetophenone **2d** (0.11*e*) are both increased to 0.44*e* in **TS-12a** and 0.44*e* in **TS-12b**, while the electron populations in Sn–H σ-bonding orbital are decreased from 1.99*e* in **10** to 1.59*e* in **TS-12a** and 1.62*e* in **TS-12b** (see ESI, Table S1). These calculations suggest that the charge transfer from the Sn–H σ-bonding orbital of **10** to the C=O π*-orbital of benzaldehyde **4a** is larger than that of acetophenone **2d**. The larger charge transfer corresponds to the higher reactivity of benzaldehyde **4a**.

Conclusions

We have disclosed that the three-coordinated tin(II) chloride (**1**) supported by an *N,N'*-di-*tert*-butyliminophosphonamide ligand can act as a precatalyst in the hydroboration of a wide variety of aldehydes, ketones, and imines at low reaction temperatures. In particular, the hydroboration of various aldehydes with functional groups showed good tolerance and chemoselectivity. DFT calculations support that the catalytic cycle involves the hydride transfer from the tin(II) hydride intermediate **10** to the carbonyl substrates via four-membered transition state **TS-12** to afford three-coordinated tin(II) alkoxide intermediate **13**, followed by the stepwise reaction of **13** with HBpin via transition state **TS-15** having a short O···B distance to release the boronate ester and to regenerate the tin(II) hydride **10**. Further development of p-block precatalysts for the hydroboration of carbonyl derivatives is currently underway.

Experimental

General

All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a UNICO 650-F Glovebox under an inert atmosphere of argon. Anhydrous solvents were further dried by passage through columns of activated alumina and supported copper catalyst supplied by Hansen & Co., Ltd. Deuterated benzene (C_6D_6), THF, and toluene were dried and degassed over a potassium mirror by the freeze-thaw cycle prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE-400 (400 and 101 MHz, respectively) or Bruker AVANCE-500 spectrometers (500 and 126 MHz, respectively), and ^{11}B, ^{19}F, ^{31}P, and ^{119}Sn NMR spectra were recorded on a Bruker AVANCE-500 (126, 470, 202, and 186 MHz, respectively) spectrometer. Elemental analysis was performed at Molecular Analysis and Life Science Centre of Saitama University. All materials were obtained from commercial suppliers and used without further purification except *N,N′*-di-*tert*-butyl-diphenyliminophosphonamide[22], $SnCl_2$·dioxane[23], *N*-benzylideneaniline **8a**[24], *N*-(4-bromobenzylidene)aniline **8b**[25], *N*-[4-(trifluoromethyl)benzylidene]aniline **8c**[24], *N*-(2-thienylmethylene)aniline **8e**[25], *N*-benzylidene-3,5-bis(trifluoromethyl)aniline **8f**[25], *N*-(1-phenylethylidene)butylamine **8h**[25], *N*-(1-phenylethylidene)-2-propanamine **8i**[25], 2-adamantylidene(phenyl)amine **8j**[26] and three-coordinated chlorostannylenes **6**[15b] and **7**[16] that were prepared by the respective literature procedures.

Synthesis of tin(II) chloride 1.

In a Schlenk tube, lithium iminophosphonamide (606 mg, 1.81 mmol), prepared by the lithiation of *N,N′*-di-*tert*-butyl-*P,P*-diphenylphosphinimidic amide with BuLi in hexane, and $SnCl_2$·dioxane (502 mg, 1.81 mmol) were dissolved into toluene (10 mL) at –78 °C. The mixture was gradually warmed up to room temperature and was kept stirring at this temperature for 2 h. The reaction mixture was filtered and all volatiles of the filtrate were removed under reduced pressure. Recrystallisation from THF at room temperature gave **1** (734 mg, 85%) as colourless crystals.

Mp: 110–112 °C (decomp.) ^{1}H NMR (500 MHz, 25 °C, C_6D_6) δ 0.96 (s, 18H, CH_3), 7.11 (br, 6H, Ar), 7.83–8.31 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR (126 MHz, 25 °C, C_6D_6) δ 33.4 (d, J_{C-P} = 6.9 Hz, CH_3), 52.4 (C_{tBu}), 128.7 (d, J_{C-P} = 11.7 Hz, Ar(CH)), 132.0 (d, J_{C-P} = 2.9 Hz, Ar(CH)), 133.4 (d, J_{C-P} = 11.0 Hz, Ar(CH)), 134.6 (d, J_{C-P} = 90.9 Hz, Ar(C)). $^{31}P\{^1H\}$ NMR (202 MHz, 25 °C, C_6D_6) δ 37.4. $^{119}Sn\{^1H\}$ NMR (186 MHz, 25 °C, C_6D_6) δ 48.8. Anal. Calcd for $C_{20}H_{28}N_2ClPSn$: C, 49.88; H, 5.86; N, 5.82. Found: C, 49.88; H, 5.90; N, 5.73.

Reaction of in situ-generated tin(II) hydride 10 with benzophenone 2a.

In a Schlenk tube, tin(II) chloride **1** (148.1 mg, 0.31 mmol) was dissolved into THF (2 mL). K[B(*sec*-Bu)$_3$H] (1.0 M in THF solution, 0.31 mL, 0.31 mmol) was added to the solution at –10 °C. The mixture was stirred for 10 minutes, benzophenone **2a** (56.0 mg, 0.31 mmol) of THF solution (1 mL) was added, and the reaction mixture was stirred for 1 h at –10 °C. After removing volatile materials under reduced pressure, the residue was extracted with hexane, and all volatiles were removed under reduced pressure to give a mixture containing tin(II) alkoxide **13** as the main product. The formation of **13** was confirmed by NMR spectroscopy.

^{1}H NMR (500 MHz, 25 °C, C_6D_6) δ 0.91 (s, 18H, CH_3), 6.50 (s, 1H, CH), 7.08–7.13 (br, 6H, Ar), 7.25–7.28 (m, 6H, Ar), 7.77 (d, J_{HH} = 7.3 Hz, 4H, Ar), 7.89–7.93 (m, 2H, Ar), 8.40–8.44 (m, 2H, Ar). $^{13}C\{^1H\}$ NMR (101 MHz, 25 °C, C_6D_6) δ 33.4 (d, J_{C-P} = 7.1 Hz, CH_3), 51.7 (C_{tBu}), 78.6 (CH), 126.4 (Ar(CH)), 127.5 (Ar(CH)), 128.2(Ar(CH)), 128.4 (d, J_{C-P} = 8.2 Hz, Ar(CH)), 128.5 (d, J_{C-P} = 7.9 Hz, Ar(CH)), 131.5 (d, J_{C-P} = 2.6 Hz, Ar(CH)), 131.7 (d, J_{C-P} = 2.7 Hz, Ar(CH)), 133.0 (d, J_{C-P} = 10.6 Hz, Ar(CH)), 134.1 (d, J_{C-P} = 11.1 Hz, Ar(CH)), 135.8 (d, J_{C-P} = 89.0 Hz, Ar(C)), 135.9 (d, J_{C-P} = 90.6 Hz, Ar(C)), 151.0 (Ar(C)). $^{31}P\{^1H\}$ NMR (202 MHz, 25 °C, C_6D_6) δ 34.3. $^{119}Sn\{^1H\}$ NMR (186 MHz, 25 °C, C_6D_6) δ –12.3 (d, J_{Sn-P} = 34.8 Hz).

General procedures for the hydroboration of carbonyls and imines.

A toluene solution of carbonyls or imines and HBpin were prepared (carbonyls or imines: 2.1×10^{-1} M and HBpin: 2.3×10^{-1} M). A toluene solution of tin(II) chloride **1** as a precatalyst was also prepared in the concentration of 1.0×10^{-3} M and 2.1×10^{-2} M. To a 50 mL Schlenk-flask, aliquots of the prepared solutions of a substrate and HBpin were added (1.0 mL each), and the mixture was cooled to –10 °C. The temperature was held for the course of the following reaction. Then an aliquot of the stock solution of **1** (1.0 mL) was added to the reaction mixture. The reaction was quenched by raising the temperature to 90 °C. After removing volatile materials under reduced pressure, the residue was added ferrocene (3.9 mg, 0.021 mmol) as the internal standard, and then ^{1}H NMR was measured. The yield of the product was confirmed by comparing the integral ratios of the product and ferrocene.

X-ray Crystallographic Analysis of 1.

Colourless single crystals of **1** were grown by slow evaporation of its saturated toluene solution at room temperature. The intensity data were collected at 100 K on a Bruker SMART APEX II diffractometer employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXT)[27] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL).[28] Hydrogen atoms were located by assuming ideal geometry and were included in the structure calculations without the further refinement of the parameters. Crystal data for **1** at 100 K: $C_{20}H_{28}ClN_2PSn$, MW = 481.55, triclinic, space group P-1, Z = 4, a = 10.4791(9) Å, b = 15.2552(13) Å, c = 15.7058(13) Å, α = 117.4000(10)°, β = 99.5250(10)°, γ = 90.4380(10)°, V = 2188.3(3) Å^3, D_{calcd} = 1.462 g cm^{-3} , R_1 ($I > 2\sigma(I)$) = 0.0302, wR_2 (all data) = 0.0753 for 8379 reflections, 463 parameters, GOF = 1.005.

Computational details.

All calculations were performed by Gaussian 09[29] program. All gas-phase geometry optimizations and frequency calculations were carried out by ωB97XD[30] functional and basis set 1 (BS1). In BS1, the def2-TZVP[31] basis set with the effective core potentials (ECPs) was used for Sn, 6-31++G(d,p)[32] basis set for B, N, O, P, the transferred hydrogen and C and H atoms of benzaldehyde **4a**, acetophenone **2d**, and HBpin, and 6-31G(d)[33] basis set for other atoms. Single point energy calculation for solvent correction was performed on all structures using a basis set 2 (BS2). In BS2, def2-TZVP[31] basis set was employed for Sn and 6-31++G(d,p)[31] basis set for all other atoms. SMD[31] continuum solvation model was chosen to calculate solvent corrected free energy with the solvation parameter of toluene. Natural population analysis (NPA) was performed using NBO 6.0.[34]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was partially supported by JSPS KAKENHI grant 17K05771 and Shorai Foundation for Science and Technology (to N.N.). Financial support from the Thailand Research Fund grant no. RSA6280041 and the Centre of Excellence for Innovation in Chemistry (PERCH-CIC) are gratefully acknowledged (to P.S.). We are also grateful to the JST Japan-Asia Youth Exchange Program in Science (Sakura Science Plan).

Notes and references

1 Selected recent reviews: (a) P. P. Power, *Nature,* 2010, **463**, 171–177; (b) S. Yao, Y. Xiong and M. Driess, *Organometallics,* 2011, **30**, 1748–1767; (c) P. P. Power, *Acc. Chem. Res.,* 2011, **44**, 627–637; (d) S. K. Mandal and H. W. Roesky, *Acc. Chem. Res.,* 2012, ***45***, 298–307; (e) P. P. Power, *Chem. Rec.,* 2012, **12**, 238–255; (f) S. Yadav, S. Saha and S. S. Sen, *ChemCatChem*, 2016, **8**, 486–501; (g) T. J. Hadlington, M. Driess and C. Jones, C. *Chem. Soc. Rev.*, 2018, **47**, 4176–4197.

2 *On the Catalytic Efficacy of Low-Oxidation State Group 14 Complexes*, Ed. T. J. Hadlington, Springer, Cham, 2017.

3 Selected recent reviews: (a) C. Chang and R. Kinjo, *ACS Catal.,* 2015, **5**, 3238–3259; (b) M. L. Shegavi and S. K. Bose, *Catal. Sci. Technol.*, 2019, **9**, 3307–3336. (c) N. Sen and S. Khan, *Chem. - Asian. J.,* 2021, **16**, 705–719.

4 Selected recent papers: (a) C. C. Chong, H. Hirao and R. Kinjo, *Angew. Chem. Int. Ed.,* 2015, **54**, 190–194; (b) Z. Yang, M. Zhong, X. Ma, S. De, C. Anusha, P. Parameswaran and H. W. Roesky, *Angew. Chem. Int. Ed.,* 2015, **54**, 10225–10229; (c) Y. Wu, C. Shan, Y. Sun, P. Chen, J. Ying, J. Zhu, L. Liu and Y. Zhao, *Chem. Commun.,* 2016, **52**, 13799–13802; (d) M. K. Bisai, S. Pahar, T. Das, K. Vanka and S. S. Sen, *Dalton Trans.,* 2017, **46**, 2420–2424; (e) Z. Zhu, X. Wu, X. Xu, Z. Wu, M. Xue, Y. Yao, Q. Shen and X. Bao, *J. Org. Chem.,* 2018, **83**, 10677–10683.

5 (a) A. Jana, H. W. Roesky and C. Schulzke, *Inorg. Chem.,* 2009, **48**, 9543–9548; (b) A. Jana, H. W. Roesky, C. Schulzke and A. Döring, *Angew. Chem. Int. Ed.,* 2009, **48**, 1106–1109; (c) A. Jana, H. W. Roesky, C. Schulzke, *Dalton Trans.,* 2010, **39**, 132–138.

6 N. Takagi and S. Sakaki, *J. Am. Chem. Soc.,* 2013, **135**, 8955–8965.

7 T. J. Hadlington, M. Hermann, G. Frenking and C. Jones, *J. Am. Chem. Soc.,* 2014, **136**, 3028–3031.

8 J. Schneider, C. P. Sindlinger, S. M. Freitag, H. Schubert and L. Wesemann, *Angew. Chem. Int. Ed.,* 2017, **56**, 333–337.

9 M. K. Sharma, M. Ansari, P. Mahawar, G. Rajaraman and S. Nagendran, *Dalton Trans.,* 2019, **48**, 664–672.

10 V. Nesterov, R. Baierl, F. Hanusch, A. E. Ferao and S. Inoue, *J. Am. Chem. Soc.,* 2019, **141**, 14576–14580.

11 (a) Y. Liu, X. Liu, Y. Liu, W. Li, Y. Ding, M. Zhong, X. Ma and Z. Yang, *Inorg. Chim. Acta*, 2018, **471**, 244–248; (b) M. Zhong, Y. Ding, D. Jin, X. Ma, Y. Liu, B. Yan, Y. Yang, J. Peng and Z. Yang, *Inorg. Chim. Acta*, 2019, **486**, 669–674.

12 R. Dasgupta, S. Das, S. Hiwase, S. K. Pati and S. Khan, *Organometallics,* 2019, **38**, 1429–1435.

13 (a) U. Kilimann, M. Noltemeyer and F. T. Edelmann, *J. Organomet. Chem*., 1993, **443**, 35–42; (b) B. Prashanth and S. Singh, *Dalton Trans*., 2016, **45**, 6079–6087; (c) S. Takahashi, J. Sekiguchi, A. Ishii and N. Nakata, *Angew. Chem. Int. Ed*., 2020, **60**, 4055–4059; (d) S. Takahashi, A. Ishii and N. Nakata, *Chem. Commun*., 2021, **57**, 3203–3206.

14 C.-Y. Qi and Z.-X. Wang, *Polym. Sci. Part A: Polym. Chem.,* 2006, **44**, 4621–4631.

15 (a) N. Nimitsiriwat, V. C. Gibson, E. L. Marshall, A. J. P. White, S. H. Dale and M. R. J. Elsegood, *Dalton Trans.,* 2007, 4464–4471; (b) S. S. Sen, M. P. Kritzler-Kosch, S. Nagendran, H. W. Roesky, T. Beck, A. Pal and R. Herbst-Irmer, *Eur. J. Inorg. Chem.,* 2010, 5304–5311; (c) C. Jones, S. J. Bonyhady, N. Holzmann, G. Frenking, and A. Stasch, *Inorg. Chem.,* 2011, **50**, 12315–12325; (d) T. Chlupatý, Z. Padělková, A. Lyčka, J. Brus and A. Růžička, *Dalton Trans.,* 2012, **41**, 5010–5019.

16 N. Nakata, N. Hosoda, S. Takahashi and A. Ishii, *Dalton Trans.,* 2018, **47**, 481–490.

17 S. Yadav, S. Pahar and S. S. Sen, *Chem. Commun.,* 2017, **53**, 4562–4564.

18 Monomeric tin(II) hydrides, see: (a) S. Khan, P. P. Samuel, R. Michel, J. M. Dieterich, R. A. Mata, J.-P. Demers, A. Lange, H. W. Roesky and D. Stalke, *Chem. Commun*., 2012, **48**, 4890–4892; (b) D. C. H. Do, A. Keyser, A. Protchenko, B. Maitland, I. Pernik, H. Niu, E. L. Kolychev, A. Rit, D. Vidovic, A. Stasch, C. Jones and S. Aldridge, *Chem. Eur. J.,* 2017, **23**, 5830–5841; (c) A. R. Leverett, V. Diachenko, M. L. Cole, A. I. Mckay, *Dalton Trans.,* 2019, **48**, 13197–13204.

19 Dimeric tin(II) hydrides, see: (a) L. W. Pineda, V. Jancik, K. Starke, R. B. Oswald and H. W. Roesky, *Angew. Chem. Int. Ed.,* 2006, **45**, 2602–2605; (b) E. Rivard, R. C. Fischer, R. Wolf, Y. Peng, W. A. Merrill, N. D. Schley, Z. Zhu, L. Pu, J. C. Fettinger, S. J. Teat, I. Nowik, R. H. Herber, N. Takagi, S. Nagase and P. P. Power, *J. Am. Chem. Soc.,* 2007, ***129***, 16197–16208; (c) Y. Peng, B. D. Ellis, X. Wang and P. P. Power, *J. Am. Chem. Soc.,* 2008, **130**, 12268–12269; (d) T. J. Hadlington, M. Hermann, J. Li, G. Frenking and C. Jones, *Angew. Chem. Int. Ed.,* 2013, **52**, 10199–10203; (e) T. J. Hadlington, M. Hermann, G. Frenking and C. Jones *Chem. Sci.,* 2015, **6**, 7249–7257.

20 N. Nimitsiriwat, V. C. Gibson, E. L. Marshall, A. J. P. White, S. H. Dale and M. R. J. Elsegood, *Dalton Trans.,* 2007, **36**, 4464–4471.

21 (a) I. P. Query, P. A. Squier, E. M. Larson, N. A. Isley and T. B. Clark, *J. Org. Chem*., 2011, **76**, 6452–6456; (b) A. D. Bage, T. A. Hunt and S. P. Thomas, *Org. Lett*, 2020, **22**, 4107–4112; (c) A. D. Bage, K. Nicholson, T. A. Hunt, T. Langer and S. P. Thomas, *ACS Catal*., 2020, **10**, 13479–13486.

22 K. A. Rufanov, N. K. Pruß and J. Sundermeyer, *Dalton Trans.,* 2016, **45**, 1525–1538.

23 J. S. Morrison and H. M. Haendler, *J. Inorg. Nucl. Chem.,* 1967, **29**, 393–400.

24 J. R. Lawson, L. C. Wilkins and R. L. Melen, *Chem. Eur. J.,* 2017, **23**, 10997–11000.

25 D. C. Elliott, A. Marti, P. Mauleón and A. Pfaltz, A. *Chem. Eur. J.,* 2019, **25**, 1918–1922.

26 Y. V. Popov, V. M. Mokhov, N. A. Tankabekyan and O. Y. Safronova, *Russ. J. Appl. Chem.,* 2012, **85**, 1387–1394.

27 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.,* 2015, **A71**, 3–8.

28 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.,* 2015, **C71**, 3–8.

29 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr. J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision C.01,* Gaussian Inc., Wallingford CT, 2010.

30 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.,* 2008, **10**, 6615–6620.

31 F. Weigend, and R. Ahlrichs, *Phys. Chem. Chem. Phys.,* 2005, **7**, 3297–3305.

32 (a) P. C. Hariharan, and J. A. Pople, *Theoret. Chim. Acta,* 1973, **28**, 213–222. (b) J. A. Montgomery Jr., J. W. Ochterski, and G. A. Petersson, *J. Chem. Phys.,* 1994, **101**, 5900–5909. (c) G. A. Petersson, M. A. Al-Laham, *J. Chem. Phys.,* 1991, 94, 6081–6090.

33 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B,* 2009, **113**, 6378–6396.

34 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A.Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, *NBO 6.0.,* Theoretical Chemistry Institute, University of Wisconsin: Madison., WI, 2013, http://nbo6.chem.wisc.edu/.