Synthesis of a Base-Stabilized Silicon(I)–Iron(II) Complex for Hydroboration of Carbonyl Compounds

Sabrina Khoo, ‡ Jiajia Cao, ‡ Fiona Ng, ‡ Cheuk-Wai So*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371

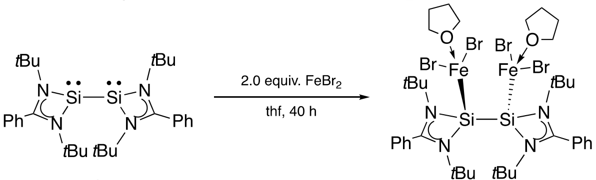
Supporting Information Placeholder

ABSTRACT: The reaction of the amidinato silicon(I) dimer $[\mathrm{LSi:}]_2$ (**1**, L = $\mathrm{PhC(N}t\mathrm{Bu)_2}$) with $\mathrm{FeBr_2}$ in THF at ambient temperature afforded the silicon(I)-iron(II) dimer $[\mathrm{LSi(FeBr_2{\bullet}thf)}]_2$ (**2**) after 40 hours. Compound **2** can catalyse hydroboration of aliphatic and aromatic ketone compounds with HBpin in the absence of any strong reducing agent. Mechanistic studies show that complex **2** reacts with ketone compounds to form a zwitterionic intermediate in the first step of catalysis. Subsequent reaction with HBpin affords the corresponding boron esters and then regenerates complex **2**.

Catalytic hydroboration of carbonyl compounds to alcohols is an important process for the synthesis of chemicals that are essential to our daily life.[1a] Such processes usually rely on catalysts containing ruthenium, osmium, or other precious metals. The high cost and limited availability of these metals necessitate the development of catalysts based on more abundant and less expensive first-row transition metals, such as iron.[1b] In addition, it is essential to identify ligand systems that can increase the thermal stability and reactivity of iron catalysts, along with avoiding one-electron pathways in catalysis. This synthetic challenge has been tackled by numerous research groups, who have demonstrated that a series of formally iron(0) complexes are capable of catalyzing hydroboration of unsaturated compounds with exceptional selectivity, turnover frequencies and turnover numbers.[2] For example, Driess and co-workers illustrated that amidinato silylene ligands can support iron(0) centers to catalyze hydrosilylation or hydrogenation of carbonyl compounds.[3] In addition, low-coordinate and -oxidation state iron species can be in situ generated by reacting more robust iron(II/III) precursors with strongly reducing organometallic reagents such as Grignard reagents, $\mathrm{NaHBEt_3}$, activated magnesium and KO*t*Bu.[4] For example, Findlater and co-workers reported that the iron(III) complex $\mathrm{Fe(acac)_3}$ is inactive toward catalytic hydroboration, unless it reacts with $\mathrm{NaHBEt_3}$ to form an [Fe-H] species, in order to catalytically convert carbonyl compounds into their corresponding boron esters.[5] Reduction to such metal hydride intermediates are typically key to commence the catalytic cycle for saturated or higher oxidation state iron species. Very recently, Baker and co-workers showed a new catalysis strategy, where the imine-coupled iron(II) complex can catalyze selectively the hydroboration of aliphatic and aromatic aldehydes without using any strong reducing agents due to the participation of the non-innocent ligand in catalysis.[6]

In the past few years, we showed that an amidinato silicon(I) dimer $[\mathrm{PhC(N}t\mathrm{Bu)_2Si:}]_2$ can serve as a ligand to coordinate with iridium and rhodium complexes.[7] These results aroused our interest in investigating whether the silicon(I) dimer can coordinate with first-row transition metals. In addition, since the silicon(I) dimer comprises two silicon donors, it could be a non-innocent ligand and participate in catalysis. Herein, we report the synthesis of an amidinato silicon(I)-iron(II) complex and its application toward catalytic hydroboration of carbonyl compounds in the absence of any strong reducing reagents.

Scheme 1. Synthesis of the iron complex 2.



1

2 (50%)

Treatment of **1** with $\mathrm{FeBr_2}$ in THF at ambient temperature afforded the silicon(I)-iron(II) dimer $[\mathrm{LSi(FeBr_2{\bullet}thf)}]_2$ (**2**, L = $\mathrm{PhC(N}t\mathrm{Bu)_2}$, Scheme 1) after 40 hours. In the reaction, **1** acted as a Lewis base to coordinate to Lewis acidic $\mathrm{FeBr_2}$, together with the concomitant coordination by a THF molecule, to generate the product. It should be noted that reducing the reaction time (ca. 16 hours) or employing equimolar $\mathrm{FeBr_2}$ only compromised the yield of **2** with recovery of precursor **1**. This indicates that any mononuclear iron complex could not be formed in the reaction. The solution state magnetic susceptibility measurement (Evans method) of **2** in THF-d_8 at room temperature shows that its effective magnetic moment (μ_{eff}) is 6.47(1) μB, which is remarkably higher than those of other mononuclear iron carbene complexes[8] and four-coordinated iron phosphine complexes[9] with a high-spin ferrous center. However, the effective magnetic moment of **2** is lower than expected for a system with two uncoupled high-spin ferrous centers (spin only value for two uncoupled S = 2 Fe^{II} centers: 6.9 μB),[10] suggesting the existence of antiferromagnetic coupling between the two Fe(II) centers. A similar phenomenon was observed in the halide-bridged diiron complex with N-heterocyclic carbene ligands (μ_{eff}: 6.5(1)μB).[8b]

The X-ray crystal structure of **2** (Figure 1) shows that it is in a gauche-bent fashion. The Si and Fe centers in **2** are all four-coordinate and adopt tetrahedral geometries, albeit with that around silicon experiencing a greater degree of distortion. The Si-Fe interactions (Si1–Fe1: 2.508(3), Si2–Fe2: 2.490(3) Å) coincide well with the silicon-iron bonds in other silylene-Fe(II) complexes (ca. 2.5 Å) while being considerably elongated with respect to related compounds bearing iron in a formal oxidation state of zero (ca. 2.2 Å).[3] The Si1–Si2 measures 2.407(4) Å, which is only marginally shortened compared to **1** (2.413(2) Å). A similar observation was noted when the amidinato germanium(I) dimer $[LGe:]_2$, reacted with $Fe_2(CO)_9$ to generate $[L\{Fe(CO)_4\}Ge]_2$, whereby the retained Ge–Ge bond is only reduced slightly from its original length (2.57(5) to 2.55(5) Å).[11]

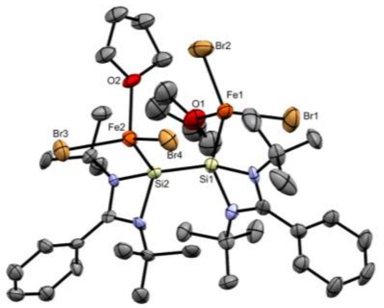


Figure 1. ORTEP drawing of **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (º): Si1-Si2 2.407(4), Si1-Fe1 2.508(3), Si2-Fe2 2.490(3); Br2-Fe1-Si1 114.93(11), Si1-Fe1-Br1 106.18(10), Si2-Si1-Fe1 127.14(15).

Our efforts were then focused on the catalytic hydroboration of ketone compounds. Condition optimization was conducted with acetophenone (**3a**) and pinacolborane (HBpin), which was selected on the foundation of its practicality and versatility. Firstly, insignificant conversion occurred in the absence of **2** (entry 1, Table S1, see Supporting Information). Secondly, only low conversion was achieved when only $FeBr_2$ (entries 3 and 4, Table S3) or $FeBr_2$•thf_2 (entries 5 and 6) was employed, highlighting that presence of the amidinato silicon(I) dimer in **2** plays a crucial role in activating possible catalytic intermediates. Thirdly, solvent screening (entries 1 to 4, Table 1) with 3 mol% of **2** as catalyst and equimolar HBpin suggested MeCN and toluene to be relatively superior (entries 2 and 3) at room temperature over 16 hours. When the amount of **2** and HBpin increased, toluene was outperformed by acetonitrile (entry 8 *vs.* 7). This could be ascribed to relatively poor solubility of **2** in toluene. Through the evaluation of catalyst and hydroborating agent loadings, we surmised that the reaction with 1.5 equivalents of HBpin and 10 mol% of **2** in MeCN afforded the best results (entry 7).

Scheme 2. Catalytic hydroboration of 3.

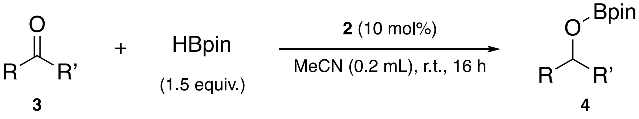
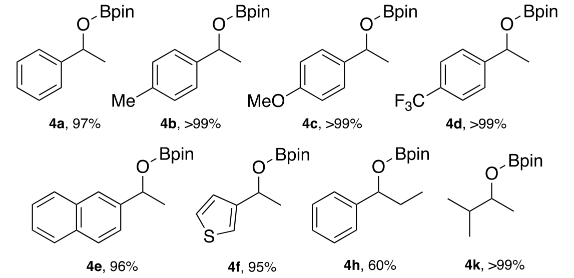


Table 1. Condition optimization for the hydroboration of acetophenone mediated by complex 2.[a]

entry	HBpin (equiv.)	2 (mol%)	solvent	conv. (%)[b]
1	1	3	THF	42
2	1	3	MeCN	61
3	1	3	toluene	63
4	1	3	dioxane	35
5	1	5	MeCN	71
6	1	10	MeCN	90
7	**1.5**	**10**	**MeCN**	**97**
8	1.5	10	toluene	90

[a]All reactions carried out at room temperature for 16 hours in 0.2 mL of solvent. [b]Conversion determined by GC with *n*-dodecane as internal standard; based on **3a**.

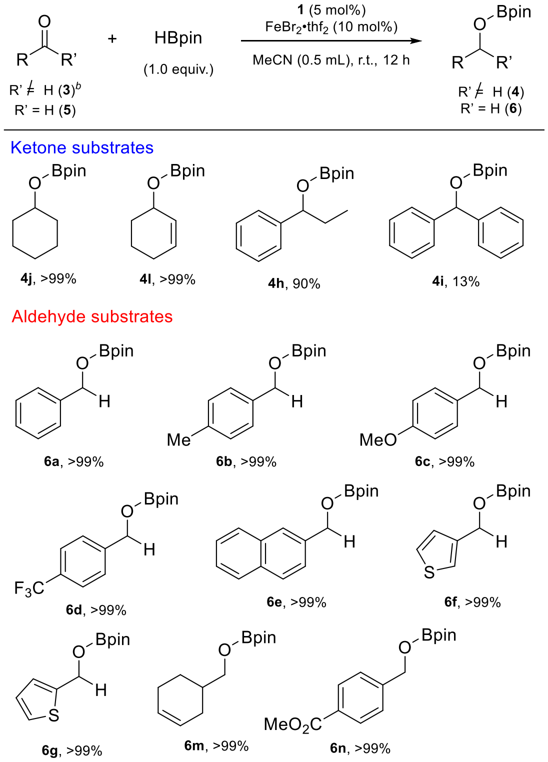
Chart 1. Scope of hydroboration by complex 2 with ketone substrates.[a]



[a]All reactions carried out under conditions outlined in Table 1, entry 7; GC-conversion based on ketone starting material is reported.

With optimized conditions in hand, the scope of the reaction was then evaluated (Scheme 2, Chart 1). Both electron-donating and electron-withdrawing groups on the aryl rings of the ketone were tolerated (**4a-e**). 3-Acetylthiophene **3f** could also react well and led to the desired product **4f** in 95% yield. Aliphatic ketone, 3-methyl-2-butanone **3k**, was also converted smoothly by this methodology. It should be noted that the reaction of propiophenone **3h** with HBpin led to **4h** in only 60% yield, and the use of benzophenone **3i** did not lead to proposed product due to steric effect. Interestingly, no reducing agent was required to evoke catalysis. Hence, the mechanism of the catalysis mediated by **2** was investigated.

Chart 2. Scope of carbonyl substrates hydroborated by a mixture of compound 1 and FeBr$_2$•thf$_2$.[a]



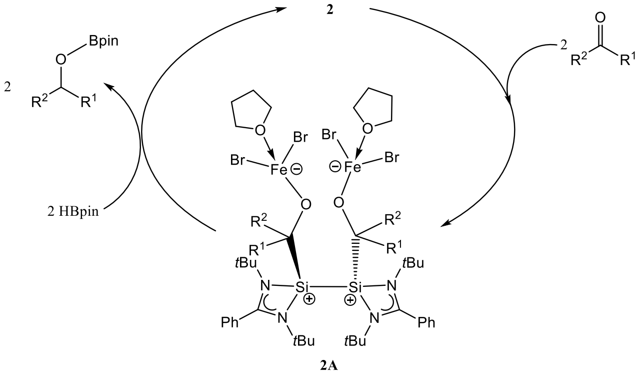
[a]GC-conversion based on carbonyl starting material is reported. [b]Catalytic loading for ketone substrates: **1** (10 mol%), FeBr$_2$•thf$_2$ (20 mol%).

Firstly, there is no reaction between compound **2** and HBpin in stoichiometric amount over 16 hours, which was confirmed by ^{11}B NMR spectroscopy. This indicates that the initial step of the catalysis should involve compound **2** and carbonyl substrates only.

Secondly, a combination of **1** (10 mol%) and FeBr$_2$•thf$_2$ (20 mol%) is capable of catalyzing aromatic and non-aromatic ketones, as well as a series of aldehydes **5** (Chart 2).[12] This modified protocol is found to be capable of overcoming steric constraints, affording 90% conversion of **3h** to **4h** (60%, Chart 1) and 13% conversion of **3i** to **4i** (previously not detected, Scheme 2). These indicates that carbonyl compounds could insert into the Si-Fe bond in the **2**-catalyzed hydroboration. Selectivity for the carbonyl functionality over olefins (**3l** and **5m**) and esters (**5n**) was also observed.

In this context, it is proposed that carbonyl compounds could insert into the Si-Fe bonds in **2** to form zwitterionic intermediate **2A** in the first step of catalysis (Scheme 3). There is another possibility that compound **2** could dissociate into **1** and FeBr$_2$(solvent)$_x$ during the catalyses, which function as a Lewis base and acid, respectively, to react with carbonyl compounds to form **2A**. Subsequent reaction with HBpin affords the corresponding boron esters and regenerates complex **2**. Such mechanism is not known in both silicon and iron chemistry as yet. The isolation of intermediates in the catalyses is currently under investigation.

Scheme 3. Proposed mechanism for the hydroboration of carbonyl compounds mediated by 2.



In conclusion, the amidinato silicon(I)-iron(II) dimer **2** was capable of catalysing various carbonyl compounds by HBpin without using any reducing reagents. Mechanistic studies showed that carbonyl compounds could inserted into the Si-Fe bond in **2**, followed by reacting with HBpin to form boron esters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website

Experimental section (pdf) X-ray data for compound **2** (cif)

AUTHOR INFORMATION

Corresponding Author

Email: CWSo@ntu.edu.sg

Author Contributions

‡S.K., J.C. and F.N. contributed equally

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12. The catalytic hydroboration of benzaldehyde **5a** with HBpin can be activated by compound **1** and $FeBr_2{\bullet}thf_2$ alone, albeit without full conversion (entries 2 and 5, Table S4)

Synopsis

The amidinato silicon(I)-iron(II) dimer complex was synthesized by coordinating the amidinato silicon(I) dimer with $FeBr_2$ in THF, which was capable of catalysing a variety of carbonyl compounds without using any strong reducing reagent.