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

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Supporting Information

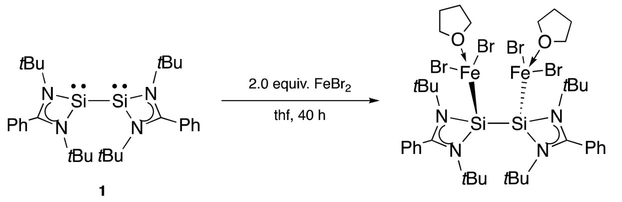
ABSTRACT: The reaction of the amidinatosilicon(I) dimer $[LSi:]_2$ (**1**; L = PhC(N*t*Bu)$_2$) with $FeBr_2$ in tetrahydrofuran (THF) at ambient temperature afforded the silicon(I)−iron(II) dimer $[LSi(FeBr_2{\cdot}THF)]_2$ (**2**) after 40 h. Compound **2** can catalyze hydroboration of aliphatic and 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 amidinatosilylene ligands can support iron(0) centers to catalyze the hydrosilylation or hydrogenation of carbonyl compounds.[3] In addition, low-coordinate and low-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, $NaHBEt_3$, activated magnesium, and KO*t*Bu.[4] For example,Tamang and Findlater reported that the iron(III) complex $Fe(acac)_3$ is inactive toward catalytic hydroboration, unless it reacts with $NaHBEt_3$ 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 commencement of 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 selectively catalyze the hydroboration of aliphatic and aromatic aldehydes without using any strong reducing agents because of participation of the noninnocent ligand in catalysis.[6]

In the past few years, we showed that an amidinatosilicon(I) dimer $[PhC(NtBu)_2Si:]_2$ 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, because the silicon(I) dimer comprises two silicon donors, it could be a noninnocent ligand and participate in catalysis. Herein, we report the synthesis of an amidinatosilicon(I)−iron(II) complex and its application toward the catalytic hydroboration of carbonyl compounds in the absence of any strong reducing reagents.

The treatment of **1** with $FeBr_2$ in tetrahydrofuran (THF) at ambient temperature afforded the silicon(I)−iron(II) dimer $[LSi(FeBr_2{\cdot}THF)]_2$ [**2**; L = PhC(N*t*Bu)$_2$; Scheme 1] after 40 h.

Scheme 1. Synthesis of the Iron Complex 2



1

2 (50%)

In the reaction, **1** acted as a Lewis base to coordinate to Lewis acidic $FeBr_2$, together with concomitant coordination by a THF molecule, to generate the product. It should be noted that reducing the reaction time (ca. 16 h) or employing equimolar $FeBr_2$ only compromised the yield of **2** with the 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) μ_B, 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 $S = 2$ iron(II) centers: 6.9 μ_B),[10] suggesting the existence of antiferromagnetic coupling between the two iron(II) centers. A similar

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phenomenon was observed in the halide-bridged diiron complex with N-heterocyclic carbene ligands [μ_{eff}: 6.5(1) μ_B].[8b]

The X-ray crystal structure of **2** (Figure 1) shows that it is in a gauche-bent fashion. The silicon and iron 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) Å and Si2−Fe2 = 2.490(3) Å] coincide well with the Si−Fe bonds in other silylene−iron(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 bond measures 2.407(4) Å, which is only marginally shortened compared to that of **1** [2.413(2) Å]. A similar observation was noted when the amidinatogermanium(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)−2.55(5) Å].[11]

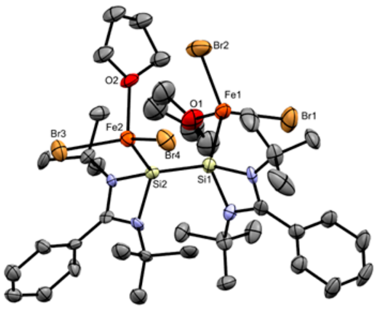


Figure 1. ORTEP drawing of **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules are elided for clarity. Selected bond lengths (Å) and bond angles (deg): Si1−Si2 2.407(4), Si1−Fe1 2.508(3), Si2−Fe2 2.490(3); Br2−Fe1−Si1 114.93(11), Si1−Fe1−Br1 106.18(10), Si2−Si1−Fe1 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 based on the foundation of its practicality and versatility. First, insignificant conversion occurred in the absence of **2** (entry 1, Table S1). Second, only low conversion was achieved when only $FeBr_2$ (entries 3 and 4, Table S3) or $FeBr_2\cdot 2THF$ (entries 5 and 6, Table S3) was employed, highlighting that the presence of the amidinatosilicon(I) dimer in **2** plays a crucial role in activating possible catalytic intermediates. Third, solvent screening (entries 1−4, Table 1) with 3 mol % **2** as the catalyst and equimolar HBpin suggested acetonitrile (MeCN) and toluene to be relatively superior (entries 2 and 3) at room temperature over 16 h. When the amount of **2** and HBpin increased, toluene was outperformed by MeCN (entry 8 vs 7). This could be ascribed to the relatively poor solubility of **2** in toluene. Through evaluation of the catalyst and hydroborating agent loadings, we surmised that the reaction with 1.5 equiv of HBpin and 10 mol % **2** in MeCN afforded the best results (entry 7).

Table 1. Condition Optimization for 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 were carried out at room temperature for 16 h in 0.2 mL of solvent. [b] Conversion determined by gas chromatography (GC) with *n*-dodecane as the internal standard; based on **3a**.

With optimized conditions in hand, the scope of the reaction was then evaluated (Scheme 2 and Chart 1). Both electron-donating and -withdrawing groups on the aryl rings of the ketone were tolerated (**4a**−**4e**). 3-Acetylthiophene (**3f**) could also react well and led to the desired product **4f** in 95% yield. An 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 the proposed product because of steric effects. Interestingly, no reducing agent was required to evoke catalysis. Hence, the mechanism of catalysis mediated by **2** was investigated.

Scheme 2. Catalytic Hydroboration of 3

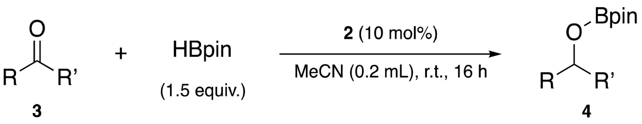
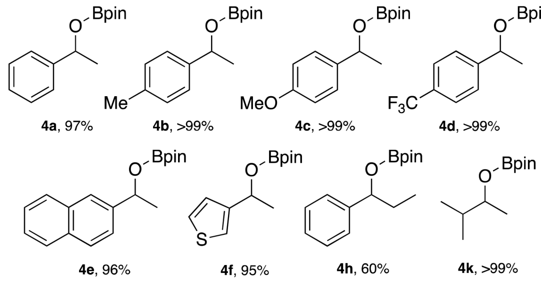


Chart 1. Scope of Hydroboration by Complex 2 with Ketone Substrates[a]



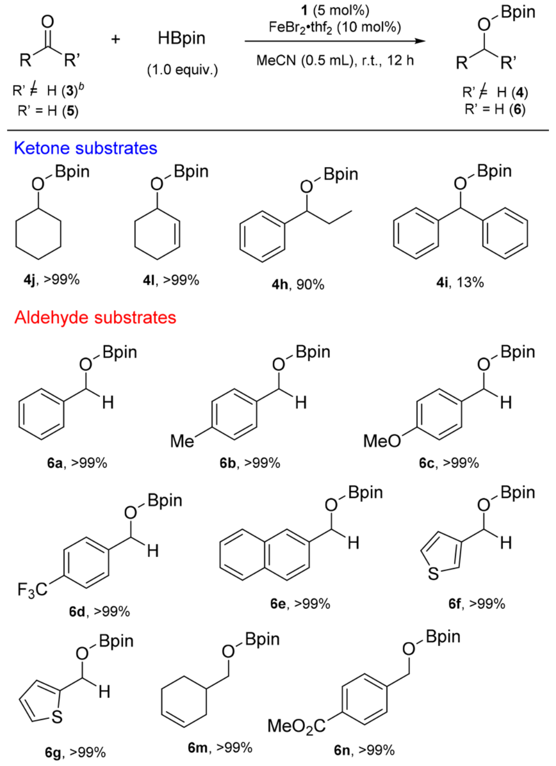
[a] All reactions were carried out under the conditions outlined in Table 1, entry 7; GC conversion based on the ketone starting material is reported.

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

Second, a combination of **1** (10 mol %) and $FeBr_2\cdot 2THF$ (20 mol %) is capable of catalyzing aromatic and nonaromatic 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 indicate that carbonyl compounds could insert into the Si−Fe bond in **2**-catalyzed hydroboration. Selectivity for the carbonyl functionality over olefins (**3l** and **5m**) and esters (**5n**) was also observed.

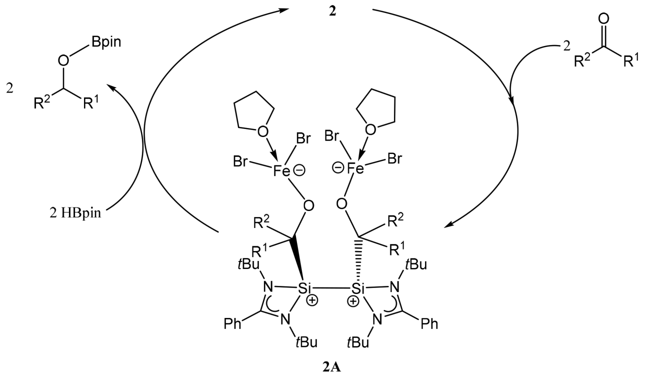
In this context, it is proposed that carbonyl compounds could insert into the Si−Fe bonds in **2** to form zwitterionic intermediate **2A** in the first step of catalysis (Scheme 3). There is another possibility that compound **2** could dissociate

Chart 2. Scope of Carbonyl Substrates Hydroborated by a Mixture of Compound 1 and $FeBr_2·2THF$[a]



[a] GC conversion based on a carbonyl starting material is reported. [b] Catalytic loading for ketone substrates: **1** (10 mol %); $FeBr_2·2THF$ (20 mol %).

Scheme 3. Proposed Mechanism for the Hydroboration of Carbonyl Compounds Mediated by 2



into **1** and $FeBr_2(solvent)_x$ during the catalysis, which function as 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 a mechanism is not known in both silicon and iron chemistry as yet. The isolation of intermediates in the catalysis is currently under investigation.

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

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01760.

Condition optimization, experimental section, and NMR spectra (PDF)

Accession Codes

CCDC 1846543 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Chong, C. C.; Kinjo, R. Catalytic Hydroboration of Carbonyl Derivatives, Imines, and Carbon Dioxide. *ACS Catal.* **2015**, *5*, 3238−3259. (b) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. Nickel and Iron Pincer Complexes as Catalysts for the Reduction of Carbonyl Compounds. *Acc. Chem. Res.* **2015**, *48*, 1995−2003.

(2) (a) Chirik, P. J. Iron- and Cobalt-Catalyzed Alkene Hydrogenation: Catalysis with Both Redox-Active and Strong Field Ligands. *Acc. Chem. Res.* **2015**, *48*, 1687−1695. (b) Obligacion, J. V.; Chirik, P. J. Highly Selective Bis(imino)pyridine Iron-Catalyzed Alkene Hydroboration. *Org. Lett.* **2013**, *15*, 2680−2683. (c) Tondreau, A. M.; Atienza, C. C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. Iron Catalysts for Selective Anti-Markovnikov Alkene Hydrosilylation Using Tertiary Silanes. *Science* **2012**, *335*, 567−570. (d) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. Preparation and Molecular and Electronic Structures of Iron(0) Dinitrogen and Silane Complexes and Their Application to Catalytic Hydrogenation and Hydrosilation. *J. Am. Chem. Soc.* **2004**, *126*, 13794−13807.

(3) (a) Luecke, M.-P.; Porwal, D.; Kostenko, A.; Zhou, Y.-P.; Yao, S.; Keck, M.; Limberg, C.; Oestreich, M.; Driess, M. Bis(silylenyl)-substituted Ferrocene-stabilized η6-Arene Iron(0) Complexes: Synthesis, Structure and Catalytic Application. *Dalton Trans* **2017**, *46*, 16412−16418. (b) Blom, B.; Enthaler, S.; Inoue, S.; Irran, E.; Driess, M. Electron-Rich N-Heterocyclic Silylene (NHSi)-Iron Complexes: Synthesis, Structures, and Catalytic Ability of an Isolable Hydridosilylene-Iron Complex. *J. Am. Chem. Soc.* **2013**, *135*, 6703−6713. (c) Gallego, D.; Inoue, S.; Blom, B.; Driess, M. Highly Electron-rich Pincer-type Iron Complexes Bearing Innocent Bis(metallylene)-pyridine Ligands: Syntheses, Structures, and Catalytic Activity. *Organometallics* **2014**, *33*, 6885−6897.

(4) (a) Cabrera-Lobera, N.; Rodriguez-Salamanca, P.; Nieto-Carmona, J. C.; Bunuel, E.; Cardenas, D. J. Iron-Catalyzed Hydroborylative Cyclization of 1,6-Enynes. *Chem. - Eur. J.* **2018**, *24*, 784−788. (b) Chen, C.; Shen, X.; Chen, J.; Hong, X.; Lu, Z. Iron-Catalyzed Hydroboration of Vinylcyclopropanes. *Org. Lett.* **2017**, *19*, 5422−5425.

(c) Gorgas, N.; Alves, L. G.; Stoeger, B.; Martins, A. M.; Veiros, L. F.; Kirchner, K. Stable, Yet Highly Reactive Nonclassical Iron(II) Polyhydride Pincer Complexes: Z-selective Dimerization and Hydroboration of Terminal Alkynes. *J. Am. Chem. Soc.* **2017**, *139*, 8130−8133. (d) Chen, X.; Cheng, Z.; Lu, Z. Iron-Catalyzed, Markovnikov-Selective Hydroboration of Styrenes. *Org. Lett.* **2017**, *19*, 969−971. (e) McNeill, E.; Ritter, T. 1,4-Functionalization of 1,3-Dienes With Low-Valent Iron Catalysts. *Acc. Chem. Res.* **2015**, *48*, 2330−2343. (f) Gilbert-Wilson, R.; Chu, W.-Y.; Rauchfuss, T. B. Phosphine-iminopyridines as Platforms for Catalytic Hydrofunctionalization of Alkenes. *Inorg. Chem.* **2015**, *54*, 5596−5603. (g) Chen, J.; Xi, T.; Lu, Z. Iminopyridine Oxazoline Iron Catalyst for Asymmetric Hydroboration of 1,1-Disubstituted Aryl Alkenes. *Org. Lett.* **2014**, *16*, 6452−6455. (h) Jones, A. S.; Paliga, J. F.; Greenhalgh, M. D.; Quibell, J. M.; Steven, A.; Thomas, S. P. Broad Scope Hydrofunctionalization of Styrene Derivatives Using Iron-Catalyzed Hydromagnesiation. *Org. Lett.* **2014**, *16*, 5964−5967. Greenhalgh, M. D.; Thomas, S. P. Chemo-, Regio-, and Stereoselective Iron-Catalyzed Hydroboration of Alkenes and Alkynes. *Chem. Commun.* **2013**, *49*, 11230−11232. (j) Zhang, L.; Peng, D.; Leng, X.; Huang, Z. Iron-Catalyzed, Atom-Economical, Chemo- and Regioselective Alkene Hydroboration with Pinacolborane. *Angew. Chem., Int. Ed.* **2013**, *52*, 3676−3680. (k) Li, L.; Liu, E.; Cheng, J.; Zhang, G. Iron(II) Coordination Polymer Catalysed Hydroboration of Ketones. *Dalton Trans* **2018**, *47*, 9579−9584.

(5) Tamang, S. R.; Findlater, M. Iron Catalyzed Hydroboration of Aldehydes and Ketones. *J. Org. Chem.* **2017**, *82*, 12857−12862.

(6) (a) Das, U. K.; Higman, C. S.; Gabidullin, B.; Hein, J. E.; Baker, R. T. Efficient and Selective Iron-Complex-Catalyzed Hydroboration of Aldehydes. *ACS Catal.* **2018**, *8*, 1076−1081.

(7) Khoo, S.; Yeong, H.-X.; Li, Y.; Ganguly, R.; So, C.-W. Amidinate-Stabilized Group 9 Metal-Silicon(I) Dimer and -Silylene Complexes. *Inorg. Chem.* **2015**, *54*, 9968−9975.

(8) (a) Xiang, L.; Xiao, J.; Deng, L. Synthesis, Structure, and Reactivity of Organo-Iron(II) Complexes with N-Heterocyclic Carbene Ligation. *Organometallics* **2011**, *30*, 2018−2025. (b) Przyojski, J. A.; Arman, H. D.; Tonzetich, Z. J. Complexes of Iron(II) and Iron(III) Containing Aryl-Substituted N-Heterocyclic Carbene Ligands. *Organometallics* **2012**, *31*, 3264−3271.

(9) Hawrelak, E. J.; Bernskoetter, W. H.; Lobkovsky, E.; Yee, G. T.; Bill, E.; Chirik, P. J. Square Planar vs Tetrahedral Geometry in Four Coordinate Iron(II) Complexes. *Inorg. Chem.* **2005**, *44*, 3103−3111.

(10) (a) Zhang, Y.; Mei, T.; Yang, D.; Zhang, Y.; Wang, B.; Qu, J. Synthesis and Reactivity of Thiolate-bridged Multi-iron Complexes Supported by Cyclic (Alkyl)(amino)carbene. *Dalton Trans* **2017**, *46*, 15888−15896. (b) Kahn, O. *Molecular Magnetism*; Wiley, 1993.

(11) Sen, S. S.; Kratzert, D.; Stern, D.; Roesky, H. W.; Stalke, D. Reactivity studies of a GeI-GeI compound with and without cleavage of the Ge-Ge bond. *Inorg. Chem.* **2010**, *49*, 5786−5788.

(12) The catalytic hydroboration of benzaldehyde **5a** with HBpin can be activated by compound **1** and FeBr$_2$·2THF alone, albeit without full conversion (entries 2 and 5, Table S4).