Synthesis and Catalytic Activity of Iron Hydride Ligated with Bidentate N-Heterocyclic Silylenes for Hydroboration of Carbonyl Compounds

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ABSTRACT: We report the synthesis of a novel bidentate N heterocyclic silylene (NHSi) ligand, N(LSi:N)methyl 2 pyridinamine (1) (L = PhC(NtBu)2), and the first bischelate disilylene iron hydride, [(Si,N)(Si,C)Fe(H)(PMe3)] (2), and monosilylene iron hydride, [(Si,C)Fe(H)(PMe3)] (2′), through Csp2-H activation of the NHSi ligand. Compounds 1 and 2 were fully characterized by spectroscopic methods and single crystal X-ray diffraction analysis. Density functional theory calculations indicated the multiple bond character of the Fe-Si bonds and the π back donation from Fe(II) to the Si(II) center. Moreover, the strong donor character of ligand 1 enables 2 to act as an efficient catalyst for the hydroboration reaction of carbonyl compounds at room temperature. Chemoselective hydroboration is attained under these conditions. This might be the first example of hydroboration of ketones and aldehydes catalyzed by a silylene hydrido iron complex. A catalytic mechanism was suggested and partially experimentally verified.

INTRODUCTION

In recent years, the design of novel N heterocyclic silylenes (NHSis) and the construction of NHSi ligated metal complexes have received increasing interest.1 Compared with N heterocyclic carbenes (NHCs), the divalent Si center in a singlet state has unique σ donating/π accepting and steric hindrance properties. Therefore, transition metal complexes with NHSi ligands have been proved to be highly active precatalysts in the Suzuki2 and Heck3 coupling reactions, reduction of amides,4 borylation5 and amination of arenes,6 the [2 + 2 + 2] cyclotrimerization reaction of phenylacetylene,7 hydroamination of alkenes or ketones,8 and Sonogashira10 and Kumada11 cross coupling reactions. However, there are few reports on multidentate NHSi ligands, and NHSi ligated hydrido metal complexes remain virtually unknown.

Hydroboration of carbonyl compounds has found widespread application in conversion into the corresponding alcohols.12 However, most of the studies on these reactions have focused on transition metals (Ru13, Co14, Th15, Mo16, Mn17, and Zn18), main group elements (Li19, Mg20, Ca21, Al22, Ge23, Sn24, and P25), and lanthanides26 as catalysts. Only a few cases have been reported to be catalyzed by base metals.27 Tamang and Findlater28 utilized Fe(acac)3 to achieve efficient conversion for the hydroboration of aldehydes and ketones. More recently, Baker and co-workers reported the remarkable catalytic activity of an imine coupled [Fe–N,S2]2 complex in the selective hydroboration of various aliphatic and aromatic aldehydes. Although hydrido iron complexes are postulated as key intermediates in these catalytic mechanisms,29 there is no report on efficiently catalyzed hydroboration of carbonyl compounds by hydrido iron complexes.

A variety of hydrido metal complexes are now employed in catalytic synthetic chemistry, coordination chemistry, and homogeneous catalysis. Recently, our group obtained the first example of cobalt(III) hydride supported by chlorosilylene.30 This complex displayed a more efficient catalytic ability for the Kumada cross coupling reaction than the hydridic Co(III) chloride stabilized by the trimethylphosphine ligand. Inspired by these results, in this work we synthesized N(LSi:)N methyl 2 pyridinamine (1) (L = PhC(NtBu)2) as a new example of a bidentate silylene ligand and the hydridic iron(II) complex [(Si,N)(Si,C)Fe(H)(PMe3)] (2) in an unexpected coordination mode. Complex 2 can act as an efficient precatalyst for...
RESULTS AND DISCUSSION

Synthesis of the Bidentate N-Heterocyclic Silylene Ligand. Given the interest in approaches for the synthesis of base stabilized NHSi, we intended to synthesize the pyridine based bidentate ligand via a salt metathesis reaction of N methyl 2 pyridinamine as the backbone (Scheme 1). After lithiation of the precursor with 1 equiv of nBuLi in diethyl ether, a toluene solution of 1 equiv of the chlorosilylene LSiCl was added dropwise to the reaction mixture at −78 °C to afford the desired bidentate NHSi compound 1 in 88% yield. In the 1H NMR spectrum of 1, two singlets for the tBu and Me groups appear at 1.05 and 3.26 ppm, respectively, with an integral ratio of 18:3. One signal of Si(II) exists at 12.0 ppm in the 29Si NMR spectrum of 1. This chemical shift is comparable to the value of 14.6 ppm for chlorosilylene reported by Roesky and co-workers.

The molecular structure of compound 1 is shown in Figure 1. In the solid state, the silicon atom is three coordinate (3 × N) and features a trigonal pyramidal geometry. The angle of 112.0° between the Si1–C15–N3–N4 plane and the Si1–N2 bond illustrates the predominant character of the silicon center with a lone pair. Si1–N3 (1.885(2) Å) and Si1–N4 (1.875(2) Å) are longer than Si1–N2 (1.782(2) Å). It is obvious that the lone pair of electrons on the Si atom occupies the vertex of the trigonal pyramid, emphasizing the predominant silylene character. The sum of the four inner angles of the Si1–N3–C15–N4 ring is 356.7°, deviating from 360°. This shows that the four atoms are not completely coplanar. The phenyl ring is almost parallel to the pyridine ring and perpendicular to the four membered cycle.

Reaction of Fe(PMe3)4 with Bidentate N-Heterocyclic Silylene Ligand 1. Compound 1 is a potential chelating ligand because of the good coordination abilities of the nitrogen atom on the pyridine ring and the silylene Si atom. Surprisingly, the reaction of bidentate preligand 1 with Fe(PMe3)4 in diethyl ether resulted in the formation of air sensitive bis(NHSi) hydrido Fe(II) complex 2 with an unexpected coordination mode (Scheme 2). On the one hand, one molecule of 1 is (Si,N) chelate coordinated to the Fe center; on the other hand, the other molecule of 1 is (Si,C) chelate coordinated to the Fe atom via Csp2-H bond activation of the pyridine ring. Complex 2 was isolated as dark red crystals from n pentane at 0 °C in 85% yield. To the best of our knowledge, 2 is the first example of a silylene hydrido iron(II) complex produced through activation of the Csp2-H bond of the pyridine ring in the NHSi ligand.

In the infrared spectrum of complex 2, the typical stretching band for the Fe–H bond was found at 1900 cm⁻¹. The 1H NMR spectrum of 2 in C6D6 provides evidence for the hydrido ligand at −10.68 ppm as a doublet due to coupling of the hydrido H atom with the coordinated P atom \( (J_{PH} = 9 \text{ Hz}) \). The signal of the PMe3 ligand appears at 15.7 ppm as a singlet in the 31P NMR spectrum of 2. In the 29Si NMR spectrum of 2, the signals of two kinds of Si(II) atoms were detected at 48.7 and 59.6 ppm as two doublets with \( J_{SP} = 29.8 \text{ and } 23.8 \text{ Hz} \). The signal of the PMe3 ligand appears at 15.7 ppm as a singlet in the 31P NMR spectrum of 2. In the 29Si NMR spectrum of 2, the signals of two kinds of Si(II) atoms were detected at 48.7 and 59.6 ppm as two doublets with \( J_{SP} = 29.8 \text{ and } 23.8 \text{ Hz} \), respectively, showing the inequivalence of the two silylene moieties.

Single crystal X ray diffraction data for complex 2 confirmed a distorted hexacoordinate octahedral geometry around the Fe(II) center (Figure 2). The axial H126–Fe1–P4 moiety (175.1°) is almost perpendicular to the equatorial plane formed by Fe1, Si2, N6, S3, and C15. The sum of the coordination bond angles in the equatorial plane is 351.8°, which deviates significantly from 360°. This result illustrates that the five atoms are not within one plane. The Fe1–H126 bond length of 1.48(3) Å is within the normal scope of Fe–H bond lengths. A summary of the Fe–Si bond distances for silylene→Fe complexes is presented in Table 1. The Fe–Si bond distances in complex 2 are shorter than those in the silylene→Fe(CO)4 and silylene→Fe(dmpe)2 complexes. Moreover, they are comparable to the silylene→Fe bond distances with formal...
double bonds between Fe and Si, indicating the multiple bond character. The Fe1−Si3 bond distance (2.159(1) Å) is shorter than the Fe1−Si2 bond distance (2.177(1) Å), potentially indicating stronger π acceptor character of Si3 versus Si2. This is reasonable because the coordination of the nitrogen atom on the pyridine ring causes electron de
cency at Si3. This is consistent with the comparison of the natural bond orbital (NBO) charges of C31 and C34 (Table 2).

To our surprise, from the mother solution for the reaction of PMe3 byproduct was obtained as a red powder. In the infrared spectrum of 2′, the typical stretching band for the Fe−H bond was found at 1920 cm⁻¹. Compared with that of complex 2 (1900 cm⁻¹), this is a hypsochromic shift due to the fact that there is only one π back donation from Fe to Si. The hydrido H signal in the ¹H NMR spectrum of 2′ is located at -15.66 ppm as a doublet of doublets of doublets caused by the multiple P−H couplings (²J_{P,H} = 9 Hz, ³J_{P,H} = 21 Hz, ⁴J_{P,H} = 51 Hz). In the ¹³C NMR spectrum of 2′, the signals of three PMe3 ligands appear at 37.9 (t, ²J_{P,P} = 36 Hz), 30.9 (dd, ²J_{P,P} = 48 Hz, 24 Hz), and 28.5 (m) respectively, indicating that the three PMe3 ligands in 2′ have different chemical environments, as shown in Scheme 2. In the ²⁹Si NMR spectrum of 2′, a signal at 57.8 ppm caused by the P−Si couplings (dd, ²J_{P,Si} = 89.1 Hz, 49.5 Hz, 19.8 Hz) is comparable with the values of 48.7 and 59.6 ppm for complex 2. It must be noted that an efficient synthesis of 2′ has not been realized by adjusting the reactant ratio and reaction temperature. It is probable that 2′ is an intermediate in the formation of 2.

We deduce that the reaction in Scheme 2 begins with the ligand replacement of PMe3 by NHSi to afford intermediate A1 (Scheme 3). This precoordination brings the iron close to the C−H bond of 1 and results in the cleavage of the C−H bond to form intermediate 2′ as an iron(II) hydride. Complex 2′ is not stable and can be further transformed to 2 by the second ligand replacement of two PMe3 ligands by 1 with the chelate effect. Complex 2 is thermodynamically stabilized by one neutral (Si,N) chelate ligand and one anionic (Si,C) chelate ligand.

To further clarify the electronic structure of the iron center in 2, we particularly performed detailed density functional theory (DFT) calculations at the B3LYP/6 31G(d,p)/LANL2DZ[Fe] level of theory.⁵⁷ Reasonable agreement exists between the bond distances of the Fe center found in the geometry optimized structures and those observed by X ray structure determinations. The lengths of the two Fe−Si bonds are 2.240 and 2.187 Å, respectively, which are slightly longer than the experimentally determined values in 2. The pertinent calculated structural parameters of 2 are presented in Table 2.

The calculated NBO charges on the donor atoms indicate the heavy polarization of the bonds with the Fe center. The NBO charges on the Si atoms are slightly less positive and point to enhanced π back donation from the Fe(II) center to Si(II). Furthermore, the calculated Wiberg bond indices (WBIs) for complex 2 differ for each donor atom with the Fe center. The values for the Fe−Si bonds (WBI > 1) clearly indicate some multiple bond character.⁵⁸

Figure 3 shows the energies and shapes of the frontier molecular orbitals of complex 2. The HOMO and HOMO−1 also show the multiple bond character of the Fe−Si bond through π back donation from the distorted d\(\sigma\)\(_p\) and d\(\pi\) orbitals of the Fe center to the 3p orbitals of the Si(II) atom. It is important to note that the polarization of the frontier molecular orbitals shows the inequivalence of the two NHSi ligands. Moreover, the LUMO in complex 2 is centered on the phenyl ring of one NHSi ligand.

**Catalytic Activity of Complex 2 for Hydroboration of Carbonyl Compounds.** Currently, iron catalysts are being applied more and more in various organic synthetic reactions. Hydrobired iron complexes often play an important role in the catalytic cycle. Some hydrido iron complexes have been used to establish efficient catalytic systems for hydrogenation⁵⁹ and hydrosilylation processes.⁶⁰ Encouraged by these results, we were interested in exploring the catalytic ability of complex 2 for the hydroboration of carbonyl compounds.

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**Table 1. Comparison of the Fe−Si Distances in Silylene−Fe Complexes**

<table>
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<tr>
<th>Compound</th>
<th>Fe−Si (Å)</th>
<th>ref</th>
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<tr>
<td>[Si(NBuCH(_2))(_2)]Fe(CO)(_4)</td>
<td>2.196</td>
<td>33</td>
</tr>
<tr>
<td><a href="N(Bu)(_2)">Si(OBu)</a>[CPh]Fe(CO)(_4)</td>
<td>2.237(7)</td>
<td>34</td>
</tr>
<tr>
<td>[Si(NHC)(H)Si(Bu)(_2)]Fe(CO)(_4)</td>
<td>2.371(16)</td>
<td>35</td>
</tr>
<tr>
<td>[Si(X)(N(Bu)(_2))[CPh]Fe(dmepe)(_2)]</td>
<td>2.1634(9) (X = Cl)</td>
<td>9a</td>
</tr>
<tr>
<td></td>
<td>2.200(2) (X = Me)</td>
<td>9a</td>
</tr>
<tr>
<td></td>
<td>2.184(2) (X = H)</td>
<td>9a</td>
</tr>
<tr>
<td>Cp*Fe(CO)(SiMe(_2))SiMe(_2)</td>
<td>2.154(1)</td>
<td>36</td>
</tr>
<tr>
<td>[SiNSi]Fe(PMe(_3))(_2)</td>
<td>2.1579(15), 2.1664(15)</td>
<td>9b</td>
</tr>
<tr>
<td>complex 2</td>
<td>2.159(1), 2.177(1)</td>
<td>this work</td>
</tr>
</tbody>
</table>

**Table 2. NBO Charges, Wiberg Bond Indices (WBIs), and Selected Calculated Bond Lengths for Complex 2**

<table>
<thead>
<tr>
<th>Atom</th>
<th>NBO Charge</th>
<th>Bond</th>
<th>WBI</th>
<th>Bond Length (Å)</th>
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<tr>
<td>Fe1</td>
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<td>Fe1  Si2</td>
<td>1.0978</td>
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<td>Si2</td>
<td>+1.423</td>
<td>Fe1  Si3</td>
<td>1.1705</td>
<td>2.187</td>
</tr>
<tr>
<td>Si3</td>
<td>+1.394</td>
<td>Fe1  P4</td>
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<tr>
<td>P4</td>
<td>+1.065</td>
<td>Fe1  N6</td>
<td>0.5521</td>
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<tr>
<td>N6</td>
<td>0.470</td>
<td>Fe1  C15</td>
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<td>C15</td>
<td>0.251</td>
<td>Fe1  H126</td>
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<td>H126</td>
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<td>C31</td>
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<tr>
<td>C34</td>
<td>0.38221</td>
<td>C31</td>
<td>0.44082</td>
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</table>

*Level of theory: B3LYP functional with the 6 31G(dp) basis set for C, H, N, P, and Si and the LANL2DZ basis set for Fe.*

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**Figure 2.** Molecular structure of complex 2. The ORTEP representation of complex 2 is shown at the 50% probability level (most of the H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1−Si2 2.177(1), Fe1−Si3 2.159(1), Fe1−P4 2.190(1), Fe1−N6 2.045(3), Fe1−C15 2.010(3), Fe1−H126 1.48(3), C15−Fe1−Si2 81.5(1), C15−Fe1−Si3 94.2(1), N6−Fe1−Si2 93.76(8), N6−Fe1−Si3 82.38(8), H126−Fe1−P4 175(1).
The studies of the influence of the reaction conditions were carried out with acetophenone as a model substrate using pinacolborane in THF at room temperature (Table 3). The control experiment without catalyst confirmed that hydroboration of acetophenone is a catalytic process. When the reaction mixture was stirred at room temperature for 6 h, no reaction was observed (Table 3, entry 1). However, when iron(II) hydride was added as a catalyst, conversion of acetophenone was realized. To our delight, 99% conversion was observed in the presence of 1 mol % (Table 3, entry 5). When the reaction temperature was raised to 50 °C, the substrate was completely transformed after 2 h. However, we decided to focus on exploring convenient catalytic conditions for operation and chose to explore further conditions at room temperature. The conversion decreased significantly with a decrease in the catalyst loading (Table 3, entry 2) or with shortening of the reaction time (Table 3, entries 3–5). It was found that THF was the best reaction medium in comparison with the other tested solvents (Table 3, entries 6–10).

Under the optimized experimental conditions, we examined the scope of the hydroboration with a variety of ketones (Table 4). The purification of hydroborated products by SiO2 column chromatography led uniquely to the isolation of 2° alcohols 4 via silica promoted hydrolysis of alkoxyboronate pinacol esters. A high isolated yield of 1 phenylethanol (4a) was achieved. Acetophenones with electron withdrawing substituents at the para position were hydroborated effectively, according the corresponding alcohols in good to excellent yields (4a–d).

This iron catalyzed hydroboration reaction of ketones tolerates various functionalities, including nitro (4e), ether (4f, 4l), cyano (4h), trifluoromethyl (4i), and alkenyl (4p) moieties. Moderate yields were obtained for acetophenones with strong electron donating Me groups at the ortho or para position (4g, 4m). 1 (2 pyridyl)ethanol (4n) was isolated in a yield of 81%. As expected, steric hindrance factors also led to a reduction in the isolated yield (4j, 4k, 4o). An αβ unsaturated ketone was selectively reduced to the αβ unsaturated alcohol (4p).

Furthermore, the catalytic reactions of derivatives of benzaldehyde took place for a shorter time in excellent yields because they are more active than ketones (Table 5). Benzyl alcohol (6a) was isolated in quantitative yield. Notably, high yields of the corresponding alcohols (6b–f, 6i) were achieved in

<table>
<thead>
<tr>
<th>entry</th>
<th>loading (mol %)</th>
<th>solvent</th>
<th>time (h)</th>
<th>conv. (%)</th>
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<tr>
<td>1</td>
<td>0</td>
<td>THF</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>THF</td>
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<td>3</td>
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<td>4</td>
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<tr>
<td>5</td>
<td>1</td>
<td>THF</td>
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<td>99</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>Et2O</td>
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<td>7</td>
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<td>DMSO</td>
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<td>dioxane</td>
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<td>9</td>
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<td>toluene</td>
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<td>51</td>
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<tr>
<td>10</td>
<td>1</td>
<td>DMF</td>
<td>6</td>
<td>17</td>
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*aCatalytic conditions: PhCOCH3 (1.0 mmol) and HBpin (1.1 mmol) in 2 mL of solvent. bDetermined by GC with n dodecane as an internal standard.*
the presence of halide substituents irrespective of their positions on the phenyl ring. The benzaldehydes with CN and MeO groups at the para position provided quantitative conversion (6g, 6h). When phenylacetaldehyde was subjected to the catalysis, 1 phenylethyl alcohol (6k) was isolated in 92% yield. For other aromatic aldehydes, such as furan 2 carbaldehyde and 1 naphthaldehyde, excellent yields were obtained for this catalytic system (6j, 6l). Interestingly, 2 exhibited excellent selectivity for the hydroboration of the C=O bond of \(\alpha,\beta\)-unsaturated aldehydes in excellent yields (6m–p).

The chemoselective hydroboration of different carbonyl substrates was studied (Scheme 4). These results are consistent with previous reports.\(^{19b,21,26c,d,28}\) It is obvious that the chemoselectivity is determined by the two molecular moieties linked with carbonyls. The competitive intermolecular catalytic hydroboration of benzaldehyde and acetophenone resulted in almost exclusive conversion of the aldehyde (Scheme 4a). The competitive hydroboration between \(p\) fluorobenzaldehyde and \(p\) methoxybenzaldehyde gave rise to \(p\) fluorobenzyl borate as the main product (Scheme 4b), and the similar reaction with \(p\) fluoroacetophenone and \(p\) methylacetophenone delivered the related \(p\) fluorobenzyl borate as the main product (Scheme 4c). Similar chemoselectivities for benzaldehyde and cinnamaldehyde were observed in the competitive reactions of benzaldehyde, cinnamaldehyde, and acetophenone (Scheme 4d). Until the addition of 2.2 equiv of HBpin, only the equivalent conversions of the aldehyes were achieved. This also shows that the conjugated \(\alpha,\beta\) double bond of the \(\alpha,\beta\)-unsaturated aldehydes has no effect on the selectivity. These results indicate that this catalytic system allows the chemoselective conversion of aldehydes to the related borates even in the presence of ketones. From Scheme 4 we know that the substrates (aldehydes or ketones) with electron withdrawing groups are preferentially reduced.

Study of the Catalytic Reaction Mechanism. To understand the intermediates involved in this efficient hydroboration, the following two experiments were designed (Scheme 5). It was verified that no reaction between complex 2 and HBpin occurred at room temperature in the first experiment. In contrast, the brown solution of 2 changed quickly to dark red upon addition of \(p\) fluorobenzaldehyde, showing that reaction had taken place. Our attempts to isolate 2c proved to be

Table 4. Scope of Hydroboration of Ketones\(^{a,b}\)

<table>
<thead>
<tr>
<th>R1, R2</th>
<th>Product</th>
<th>Yield</th>
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<tr>
<td>4a</td>
<td>94%</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>97%</td>
<td></td>
</tr>
<tr>
<td>4c</td>
<td>95%</td>
<td></td>
</tr>
<tr>
<td>4d</td>
<td>91%</td>
<td></td>
</tr>
<tr>
<td>4e</td>
<td>88%</td>
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<td>4f</td>
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<td>4g</td>
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<td>4o</td>
<td>85%</td>
<td></td>
</tr>
<tr>
<td>4p</td>
<td>80%</td>
<td></td>
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</table>

\(^a\)Catalytic conditions: substrate (1.0 mmol) and HBpin (1.1 mmol) in 2 mL of THF at rt. \(^b\)Isolated yields are shown.
unsuccessful. It is likely that 2c is very unstable. However, the disappearance of signals for $\nu$(H–Fe) and $\rho$(PCH$_3$) was obviously observed in the infrared spectrum, indicating breaking of the H–Fe bond and dissociation of PMe$_3$. Concomitantly, the signal of H–Fe ($-10.68$ ppm) disappeared in the in situ $^1$H NMR spectrum. These results imply that the catalytic cycle for iron hydride catalyzed hydroboration of aldehydes and ketones involves the insertion of the carbonyl group into an Fe–H bond, giving the possible reactive intermediate 2c, which was further detected by MS.

On the basis of the above results and the precedent of metal catalyzed hydroboration reactions of carbonyl compounds,$^{14,24,28}$ we propose a possible catalytic cycle for this hydrido iron complex catalyzed hydroboration reaction (Scheme 6). At first, the dissociation of PMe$_3$ group takes place to form highly active iron hydride intermediate 2a as the real catalyst with a vacant coordination site. Subsequently, coordination of the oxygen atom of the carbonyl group to the metal center enhances the polarity of the C═O bond, making it easier to insert the Fe–H bond and generate intermediate 2c. In the presence of HBpin, 2c delivers the alkoxyboronate pinacol ester via B–H bond activation with recovery of the real catalyst 2a.

### CONCLUSION

The novel N heterocyclic silylene 1 was synthesized by the salt metathesis reaction of N methyl 2 pyridinamine with a chlorosilylene. We also successfully obtained the first bis(NHSi) chelated hydrido Fe(II) complex 2 and mono(NHSi) chelated hydrido Fe(II) complex 2' via chelate assisted C$_{sp^2}$–H bond activation of 1. Similarly, the hydroboration reactions of carbonyl compounds were proved for the first time to be efficiently catalyzed by the iron hydride at room temperature. A novel iron hydride catalyzed mechanism was suggested and was partially experimentally verified.

### EXPERIMENTAL SECTION

**General Procedures and Materials.** All air sensitive and volatile materials were processed under a nitrogen atmosphere using standard vacuum techniques. Diethyl ether, n pentane, THF, and toluene were dried and distilled under nitrogen according to known methods before use. Fe(PMe$_3$)$_4$ and the chlorosilylene were prepared according to the known literature methods. All of the other chemicals were purchased and used as received without further purification. Infrared
spectra (4000–400 cm$^{-1}$) were obtained from Nujol mulls between KBr disks and recorded on a Bruker ALPHA FT IR instrument. $^1$H, $^{13}$C($^1$H), $^{31}$P($^1$H), and $^{29}$Si($^1$H) NMR spectra were recorded on Bruker Avance 300 and 600 MHz spectrometers. Gas chromatography was performed with n dodecane as an internal standard. Elemental analyses were carried out on an Elementar Vario ELIII instrument.

**Synthesis of N-Methyl-2-pyridinamine.** Under a N$_2$ atmosphere, copper powder (0.1 g, 1.6 mmol), 2 bromopyridine (5.4 g, 34.2 mmol), and 30 mL of methylamine solution in water (25%) were added...
to a 100 mL Schlenk tube containing a magnetic stirrer. The reaction mixture was stirred at 95 °C for 48 h. After cooling, the product was extracted with 150 mL of ethyl acetate three times and dried over Na2SO4. After filtration, volatile materials were evaporated in vacuo and then refluxed for 3 h. The resulting solution was cooled to ~78 °C, and a solution of the chlorosilylene (2.67 g, 9.1 mmol) in THF (1 mL) was added to a 20 mL Schlenk tube containing a magnetic stirrer. The ketone or aldehyde (1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then weighed and added.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00700.

Crystallographic data for 1 and 2; IR and 1H, 31P, 13C, and 29Si NMR spectra of 1 and 2; 1H NMR spectra of the hydroboration reduction products; and IR, 1H and 19F NMR, and MS spectra for the study of the catalytic mechanism; and computational details (PDF)
Analogues with Low Valent Group 13 and Group 14 Elements: as Powerful Steering Ligands in Catalysis. − and (d) Silylenes.

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REFERENCES


