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Hydrosilylation of an Iron(IV) Nitride Complex

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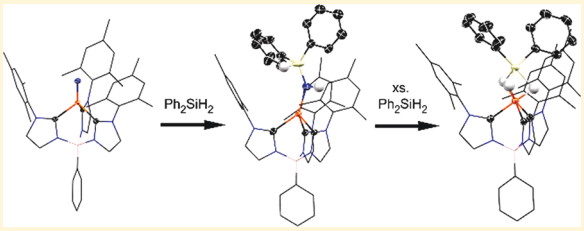
Supporting Information

ABSTRACT: The nitride ligand in iron(IV) complex PhB(MesIm)$_3$Fe≡N reacts with excess H_3SiPh to afford PhB(MesIm)$_3$Fe(μ-H)$_3$(SiHPh) as the major product, which has been structurally and spectroscopically characterized. Bulkier silane H_aSiPh_2 provides iron(II) amido complex PhB(MesIm)$_3$FeN(H)(SiHPh$_2$) as the initial product of the reaction, with excess H_2SiPh_2 affording diamagnetic PhB(MesIm)$_3$Fe(μ-H)$_3$(SiPh$_2$) as the major product. Unobserved iron(II) hydride PhB(MesIm)$_3$Fe−H is implicated as an intermediate in this reaction, as suggested by the results of the reaction between iron(II) amido PhB(MesIm)$_3$FeN(H)^{t}Bu and H_3SiPh, which provides PhB(MesIm)$_3$Fe(H)(μ-H)$_2$(Si(NH^{t}Bu)Ph) as the sole product.



INTRODUCTION

Because transition-metal nitride complexes (M≡N) are accessible via reductive N_2 cleavage,[1] investigations into their reactivity are of interest for developing new methods of N_2 functionalization. Although there are currently no examples of reductive N_2 cleavage by iron complexes, iron nitrides are of particular interest because of their proposed involvement as intermediates in both biological and industrial N_2 fixation.[2] Iron nitrides have been established as intermediates in the homogeneously catalyzed formation of NH_3 from N_2.[3]

While multielectron nitrogen atom transfer reactions from metal nitride complexes are relatively well established (e.g., the oxidation of phosphines), reactions involving the insertion of the nitride ligand into σ-bonds are less common.[4] For example, despite the relevance to Haber−Bosch ammonia synthesis, there are few examples of the hydrogenation of terminal nitride ligands. Interestingly, different reaction mechanisms have been invoked for these scattered reports. Specifically, while the hydrogenation of an iridium(III) nitride to the corresponding iridium(I) amido complex involves the direct attack of hydrogen at the nitride ligand, albeit acid-catalyzed,[5] the hydrogenation of a ruthenium(IV) nitride (and possibly its osmium(IV) analogue[6]) to produce ammonia requires the pincer ligand to assist in the cooperative heterolytic cleavage of H_2.[7]

Although the nonpolar Si−H bond can be considered to be a surrogate for H_2, there are also few reports on the reaction of nitride complexes with organosilanes. Despite the paucity of examples, a number of reaction pathways have also been observed for these reactions. For example, an iridium(III) nitride inserts into the Si−H bond of Ph_3SiH and Et_3SiH, yielding the corresponding iridium(I) silylamido products,[8] whereas a ruthenium(VI) nitride is reduced by Et_3SiH to provide an ammine ligand.[9]

Over the last several years, we have shown that four-coordinate iron(IV) nitride complexes supported by bulky tris(carbene)borate ligands are reactive toward many hydrocarbon substrates.[10] In addition to two-electron nitrogen atom transfer reactions,[11] these complexes also participate in one-electron reactions that lead to new N−H and N−C bonds.[12] The diverse reactivity of these complexes can be partially attributed to nature of their frontier orbitals, namely, the σ-symmetry LUMO and π-symmetry HOMO, both of which are partially localized on the nitride ligand.[13] This symmetry of these frontier orbitals is also appropriate for concerted reactions that insert the nitride ligand into Si−H bonds.

In this article, we investigate the reactivity of one such iron nitride complex, PhB(MesIm)$_3$Fe≡N,[12a] toward primary and secondary phenylsilanes. A series of synthesis investigations suggest that the reactions involve initial Si−H insertion to provide the corresponding iron(II) silylamido complexes, akin to a recent report in which H_3SiPh intercepts a transient and electrophilic iron(IV) nitride.[14] Excess organosilane yields new iron(II) silane complexes as the final products.

RESULTS AND DISCUSSION

The previously reported iron(IV) nitride, PhB(MesIm)$_3$Fe≡N,[12a] reacts with excess $PhSiH_3$ to provide the orange diamagnetic complex PhB(MesIm)$_3$Fe(H$_3$)SiHPh (**1**) (Scheme 1) in 75% isolated yield.[15] The solid-state molecular structure of this complex has been determined by single-crystal X-ray diffraction (Figure 1). The most notable aspect of the structure is the η^2-H_3SiPh silane adduct resulting from "arrested" oxidative addition of the Si−H bond. Similar arrested η^2-silane complexes have been reported for iron

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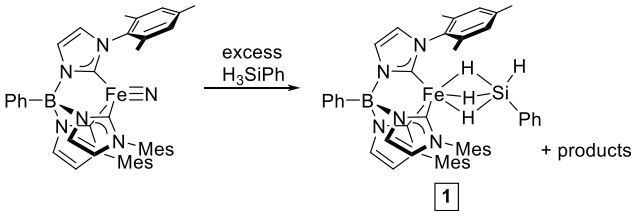
Scheme 1



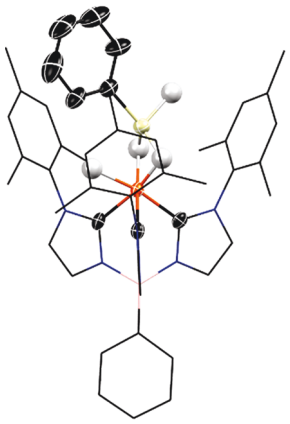


Figure 1. Single-crystal X-ray structure of **1**, with thermal ellipsoids shown at 50%, most of the tris(carbene)borate ligand shown as a wire frame, and most hydrogen atoms omitted for clarity. Carbon, hydrogen, nitrogen, boron, iron, and silicon atoms are shown in black, white, blue, pink, orange, and yellow, respectively.

tris(phosphino)borate complexes.[16] At 2.101(1) Å, the Fe–Si distance in **1** is even shorter than that observed for iron silylene complex Cp*Fe(CO)($SiMes_2$)$SiMe_3$ (2.154(1) Å)[17] The three hydride ligands could be located in the Fourier difference map, two of which are within bonding distance of the silicon atom (Si–H 1.34 and 1.54 Å). The Fe–C distances (1.808–1.953 Å) are typical for a low-spin iron(II) tris(carbene)borate complex.[18]

In contrast to the solid-state structure, the silane ligand of **1** is tridentate in solution, as revealed by multinuclear NMR spectroscopy. Most notably, the room-temperature ^{1}H NMR spectrum reveals a single resonance the integrates for three hydrogen atoms at δ −13.0 ppm, consistent with three chemically equivalent hydride ligands. The hydride ligands are also bound to silicon, as revealed by ^{29}Si satellites ($^1J_{SiH}$ = 76 Hz).[19] Consistent with this observation, a quartet ($^1J_{SiH}$ = 76 Hz) at δ 89.9 ppm in the ^{29}Si NMR spectrum collapses to a singlet in the ^{29}Si{^{1}H} NMR spectrum (Figure 2). Furthermore, a correlation between the ^{29}Si resonance and the ^{1}H hydride resonance is observed in a ^{29}Si/^{1}H HMQC experiment, confirming the Si–H connectivity.

Although it is evident that the formation of **1** requires more than 1 equiv of H_3SiPh, efforts to obtain insight into the nature of the reaction intermediates have been unsuccessful. We reasoned that a bulkier silane may allow for the observation or isolation of intermediates along the reaction pathway. In support of this hypothesis, the reaction of PhB(MesIm)$_3$Fe≡N with 1 equiv of H_2SiPh_2 cleanly provides the paramagnetic iron(II) amido complex PhB(MesIm)$_3$Fe–N(H)Si(H)Ph_2 (**2**) (Scheme 2) in 70% isolated yield. A similar transformation has been reported for the reaction of transient iron(IV) nitride complex {(Ar*N)$_2$CNC^{t}Bu$_2$}Fe≡N(py)

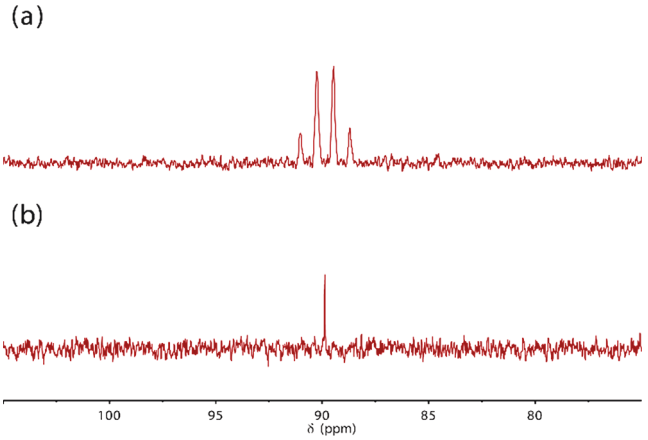
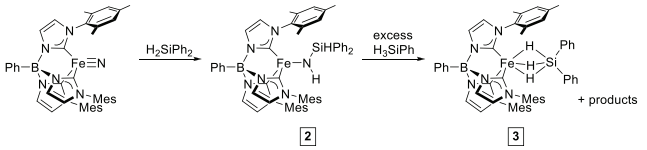


Figure 2. (a) ^{29}Si NMR and (b) ^{29}Si{^{1}H} NMR spectra of PhB(MesIm)$_3$Fe(H$_3$)SiHPh.

Scheme 2



(Ar* = 2,6-bis(diphenylmethyl)-4-*tert*-butylphenyl) with H_3SiPh.[14] A related Si–H insertion reaction involving an iron(IV) bis(imido) complex has also been observed and is proposed to occur via the [2σ + 2π] cycloaddition mechanism.[20]

The solid-state structure of **2** reveals a new silylamido ligand that is formed by nitride ligand insertion into one Si–H bond of H_2SiPh_2 (Figure 3a). The structural metrics of the

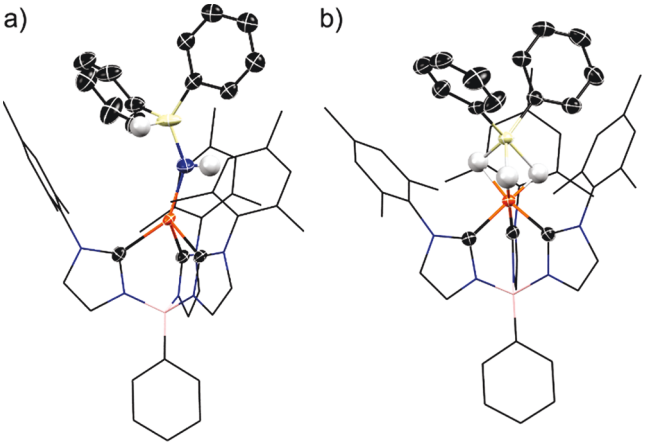


Figure 3. Single-crystal X-ray structures of **2** and **3**, thermal ellipsoids shown at 50%, most of the tris(carbene)borate ligands shown as wire frame, and most hydrogen atoms omitted for clarity. Carbon, hydrogen, nitrogen, boron, iron, and silicon atoms are shown in black, white, blue, pink, orange, and yellow, respectively.

silylamido ligand in complex **2** (Fe–N 1.930(4) Å and Si–N 1.662(4) Å) are similar to those of the previously reported iron silylamido complex, while all other metrics are typical for a high-spin iron(II) tris(carbene)borate complex.[14] The solution structure of **2** is consistent with that observed in the solid state. Eleven paramagnetically shifted resonances are observed for

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the complex, as expected for a structure that is 3-fold symmetric on the NMR time scale. The magnetic moment (μ_{eff} = 4.7(3)μ_B) is consistent with high spin (S = 2) iron(II).

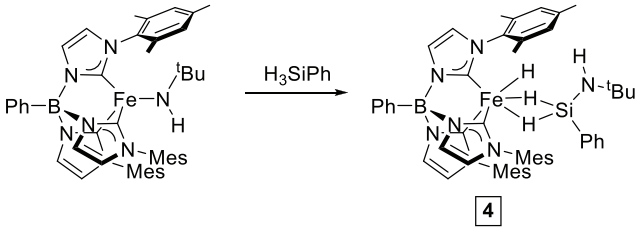
Complex **2** complex slowly reacts with a large excess of H_2SiPh_2 to provide diamagnetic iron(II) product PhB(MesIm)$_3$Fe(H$_3$)SiPh$_2$ (**3**), the diphenylsilane analogue of complex **1** (Figure 3b). Because of the similar solubilities of the reactants and reaction products, this complex can be isolated only in low yield (31%). Interestingly, and in contrast to the solid-state structure of **1**, the X-ray crystal structure of **3** reveals an η^3-H$_3$SiPh$_2$ ligand with all three Si−H distances (1.47, 1.70, and 1.79 Å) within bonding range. Interestingly, the Fe−Si distance (2.1204(7) Å) is slightly longer than the corresponding distance in **1**. This solid-state structure of **3** is maintained in solution, as characterized by ^{1}H NMR spectroscopy, where a single resonance for the three chemically equivalent hydride ligands is observed at δ −11.70 ppm ($^1J_{SiH}$ = 76 Hz).

Complex **3** is a rare example of a structurally characterized η^3-H$_3$SiR$_2$ complex. In contrast to related complexes,[21] the silicon atom in **3** is five-coordinate and is not base-stabilized. It is likely that the unusual coordination mode of the silane ligand in **3** is stabilized in part by the bulky tris(carbene)borate.

Taken together, the synthesis results suggest that the formation of **1** occurs by the initial insertion of PhB(MesIm)$_3$Fe≡N into the Si−H bond of PhSiH$_3$ to provide the corresponding iron(II) silylamido complex, which reacts in turn with additional PhSiH$_3$ to provide **1**, presumably with the concomitant formation of the aminosilane, PhSi(N(H)SiH$_2$Ph)H$_2$. However, we have been unable to determine the ultimate fate of the nitride ligand in either of the silylation reactions discussed above.[22] For example, the reaction of PhB(MesIm)$_3$Fe≡N with 2 equiv of PhSiH$_3$ results in the formation of multiple iron hydride products, suggesting that the putative aminosilane byproducts are reactive toward the iron(IV) nitride or iron(II) amido complexes. Unfortunately, we were unable to separate these other products in sufficient quantities to allow for structural and/or spectroscopic characterization. Similarly, attempts to ascertain the fate of the nitride ligand in the reaction with H_2SiPh_2 have also been unsuccessful.

We hypothesized that the silylation of an iron amido complex that is bereft of Si−H bonds would provide insight into the second silylation reaction by avoiding complications associated with multiple reactive SiH bonds. Gratifyingly, iron(II) alkylamido complex PhB(MesIm)$_3$Fe−N(H)^{t}Bu reacts cleanly with 1 equiv of H$_3$SiPh to yield PhB(MesIm)$_3$Fe(H)(μ-H)$_2$(Si(NH^{t}Bu)Ph) (**4**) as the sole reaction product (Scheme 3). The molecular structure of this complex reveals the formation of a new η^2-H$_2$SiPh(NH^{t}Bu) ligand (Figure 4). The Fe−Si distance (2.100(1) Å) is the same as that in **1**,

Scheme 3



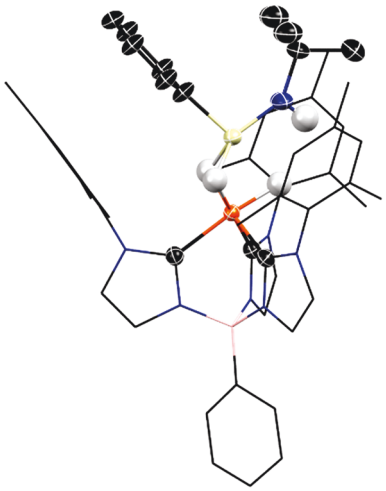
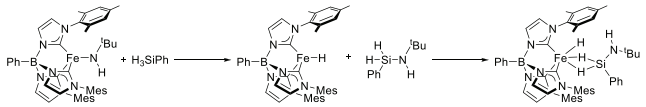


Figure 4. Single-crystal X-ray structure of **4**, with thermal ellipsoids shown at 50%, most of the tris(carbene)borate ligand shown as wire frame, and most hydrogen atoms omitted for clarity. Carbon, hydrogen, nitrogen, boron, iron, and silicon atoms are shown in black, white, blue, pink, orange, and yellow, respectively.

while the Si−N distance (1.694(4) Å) is similar to that of **3**. In contrast to the solid-state structure and similar to **1**, the solution ^{1}H and ^{29}Si spectroscopic data for **4** is consistent with a tridentate silane ligand.

A reaction mechanism can be proposed to account for the formation of **4** (Scheme 4). The reaction of PhB(MesIm)$_3$Fe−N(H)^{t}Bu with H$_3$SiPh initially results in the formation of silylamine H$_2$SiN(H)^{t}BuPh along with transient iron(II) hydride PhB(MesIm)$_3$FeH. A similar four-coordinate hydride, PhB(CH$_2$PPh$_2$)$_3$FeH, which adds to benzene, has been implicated in the hydrogenation of the corresponding tris(phosphino)borate iron(II) anilido complex.[23] We propose that PhB(MesIm)$_3$FeH reacts with the silylamine byproduct to the form observed product **4**.

Scheme 4



SUMMARY AND CONCLUSIONS

The combined synthesis experiments suggest that the hydrosilylation of an iron(IV) nitride proceeds by the insertion of the nitride ligand into an Si−H bond, yielding an iron(II) amido product. This product can be further hydrosilylated to yield transient iron(II) hydride PhB(MesIm)$_3$FeH. When stoichiometric H$_3$SiPh or H$_2$SiPh$_2$ is used, the silylamine byproducts react with the iron hydride to provide iron silane products. Because these silylamines possess multiple Si−H bonds, multiple iron(II) silane products are obtained. With excess H$_3$SiPh and H$_2$SiPh$_2$, these reagents intercept PhB(MesIm)$_3$FeH to provide **1** and **3** as the sole iron-containing products. These observations are inconsistent with a mechanism involving σ-bond metathesis, as was proposed for the reaction of PhB(CH$_2$PPh$_2$)$_3$FeH with H$_3$SiPh.[16]

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b02831.

Experimental details, including crystallographic data (PDF)

Accession Codes

CCDC 1955366−1955369 contain 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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