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An Isolable Iron(II) Bis(supersilyl) Complex as an Effective Catalyst for Reduction Reactions

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An isolable 14-electron iron bis(supersilyl) complex, Fe[Si(SiMe_3)_3]_2(THF)_2, was successfully synthesized from the reaction of FeBr₂ with K[Si(SiMe_3)_3] and its structure was unambiguously determined by single-crystal X-ray diffraction analysis. The complex is coordinatively unsaturated and exhibits high catalytic activity toward the hydrosilylation of carbonyl compounds and the reductive silylation of dinitrogen.

Catalytic transformations mediated by transition-metal complexes are some of the most important tools in modern organometallic chemistry. Owing to the increasing demand for environmentally benign organic syntheses, the development of highly active base-metal catalysts has received much attention in the last decade.1 The design and development of coordinatively unsaturated base-metal complexes is the most straightforward approach to such green chemistry. It is well known that the introduction of organosilyl ligands to a metal center effectively contributes to the formation of coordinatively unsaturated complexes due to the strong σ -donating properties and high trans influence of the organosilyl ligands.² As representative examples, in-situ-generated coordinatively unsaturated 14-electron iron species of the type "Fe(R₃Si)₂(L)(L')" show desirable catalytic performance in reductive transformation reactions, i.e., hydrogenations or hydrosilylations $\{(R_3Si)_2 = o-(SiMe_2)_2C_6H_4; L = L' = CO \text{ or } CNR\}^3 \text{ or }$ reductive silvlations of dinitrogen (R = Me; L = THF, L' = N_2)⁴. If the analogous 14-electron iron species can be isolated and used in catalysis, more effective catalytic systems could be potentially developed. However, to the best of our knowledge, crystallographically characterized 14-electron iron(II) bis(organosilyl) complexes have not been reported so far.

organosilyl complexes is based on the oxidative addition of the "H-Si" group in hydrosilanes to low-valent transition-metal centers.^{2b,c} Low-valent iron carbonyls have been effectively employed as precursors to afford a variety of iron complexes with organosilyl ligands.^{2b,c,5} However, this approach generally allows only the preparation of coordinatively saturated complexes, and the liberation of CO requires harsh reaction conditions such as high temperatures or UV irradiation. The lack of suitable isolable low-valent 3d metal precursors that do not contain CO ligands has hitherto prevented the direct synthesis of coordinatively unsaturated iron organosilyl complexes. A clue to overcome this drawback was provided by Tilley and coworkers, who described the synthesis of the anionic iron bis(supersilyl) complex, Li(THF)₃{FeCl[Si(SiMe₃)₃]₂}, by reaction of FeCl₂ with the lithium salt of the supersilyl anion.⁶ Subsequent treatment with Me₃SiOSO₂CF₃ afforded the neutral coordinatively unsaturated bis(supersilyl) complex Fe[Si(SiMe₃)₃](THF), which was examined by IR spectroscopy and hydrolytic degradation studies. This prompted us to explore a potentially facile synthetic route to bis(organosilyl) iron complexes based on a salt metathesis with appropriate modifications. In the present study, we describe a one-step synthesis of the first crystallographically characterized 14electron bis(organosilyl) iron(II) complex Fe[Si(SiMe₃)₃]₂(THF)₂ (1) using the potassium salt of the supersilyl anion (Scheme 1). The obtained iron complex displays good catalytic activity in reduction reactions, including the hydrosilylation of carbonyl compounds and the reductive silvlation of dinitrogen. The facile in situ generation of catalytically active iron species was demonstrated by simply mixing the widely available and easyto-handle precursors of 1, which will undoubtedly facilitate the development of further practical catalytic transformations.

The most widely used synthetic method to generate

The potassium salt of the supersilyl anion, KSi(SiMe₃)₃, was obtained from the reaction of Si(SiMe₃)₄ and KO^tBu according to the report of Marschner.⁷ We found that the 14-electron bis(supersilyl)iron(II) complex Fe[Si(SiMe₃)₃]₂(THF)₂ (**1**) was readily obtained within 1 h from the reaction of FeBr₂ with 2

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equiv. of KSi(SiMe₃)₃ in THF at room temperature (Scheme 1). Complex **1** was isolated in 89% yield as red purple crystals after recrystallization from THF/pentane at -30 °C. An advantage of this procedure is that **1** is easily prepared in one step without the use of reagents that are difficult to handle such as Me₃SiOSO₂CF₃.



Scheme 1. Synthesis of 1.

The solid-state structure of 1, which represents the first example of a crystallographically characterized 14-electron iron(II) bis(organosilyl) complex, is shown in Figure 1. The iron center in 1 is coordinated to two supersilyl and two THF ligands and exhibits a distorted tetrahedral coordination geometry. The Si(1)-Fe-Si(2) angle of 135.23(3)° is considerably wider than that for a tetrahedral geometry, which should be attributed to the steric repulsion between the two supersilyl ligands. The Fe-Si bond distances (Fe–Si(1) = 2.5445(8) Å; Fe–Si(5) = 2.5445(8) Å) are longer than those in the anionic bis(supersilyl) complex reported by Tilley, (NEt₄){FeCl[Si(SiMe₃)₃]₂} (Fe-Si = 2.488(6)/2.491(6) Å). These Fe-Si bonds are also significantly longer than those found in previously reported neutral 18electron Fe(II) bis(organosilyl) complexes (2.25-2.5 Å)⁸, presumably due to steric hindrance as well as the open-shell spin state of 1.9 It should be noted that Tilley et al. have also reported the synthesis of Fe[Si(SiMe₃)₃]₂(THF) and Fe[Si(SiMe₃)₃]₂(DME), albeit that a crystallographic analysis was not undertaken. Related manganese analogues such as $Mn[Si(SiMe_3)_3]_2(L)_2$ [(L)₂ = dmpe or (O=CPh₂)₂] have been reported by Tilley and exhibit a tetrahedral coordination geometry with Si-Mn-Si angles of ca. 133° and Mn-Si bond distances of ca. 2.64 Å.6a



Figure 1. Molecular structure of 1 with 50% probability ellipsoids.

Complex **1** is paramagnetic and its ¹H NMR spectrum (C_6D_6 ; room temperature) exhibits a broad signal at 7.27 ppm for SiMe₃ as well as resonances at 20.60 and 27.33 ppm for the coordinated molecules of THF. The solution magnetic moment, measured by the Evans' method ($\mu_{eff} = 5.36$), is consistent with an open-shell *S* = 2 ground state. Complex **1** is highly sensitive toward air and moisture, but the results of the elemental analysis are consistent with the theoretically expected values.



Scheme 2. Facile ligand exchange to afford 2.

One interesting feature is that the two THF ligands in 1 can be easily replaced by other auxiliary ligands. For instance, the reaction of 1 with 2 equiv. of pyridine at room temperature instantly furnishes Fe[Si(SiMe₃)₃]₂(pyridine)₂ (2) quantitatively within 1 h (Figure S3 in the Supporting Information), and 2 was isolated in 40% yield (Scheme 2). The formation of 2 was confirmed by NMR spectroscopy, elemental analysis, and X-ray diffraction measurements. In the ¹H NMR spectrum of **2**, three broad resonances are observed at -13.02, 8.36, and 46.69 ppm, which were assigned to the pyridine ligands coordinated to the iron center, while the signal of the SiMe₃ groups was observed as a broad singlet at 6.56 ppm. The molecular structure of **2** was unequivocally determined by X-ray diffraction analysis (Figure S14 in the Supporting Information). These results clearly indicate that the iron center in 1 can generate two vacant sites via facile dissociation of the THF ligands.

The coordinatively unsaturated nature of 1 is reflected in its good catalytic activity in reduction reactions, including the hydrosilylation of carbonyl compounds, which is important for the production of alcohols in the absence of hazardous reagents such as LiAlH₄. The development of iron-catalyzed hydrosilylation reactions is currently a hot topic in synthetic chemistry.¹⁰ For instance, Tilley et al. have reported a coordinatively unsaturated iron bis(amide) complex. Fe[N(SiMe₃)₂]₂, with high catalytic activity toward the hydrosilylation of aldehydes and ketones with Ph₂SiH₂ at room temperature and a catalyst loading of 0.03-2.7 mol%.11 Turculet's iron amide complex, which bears an Nphosphinoamidinate ligand, also exhibits high catalytic activity toward the reduction of carbonyl compounds with Ph₂SiH₂ under mild reaction conditions in the presence of 0.01-1 mol% of the catalyst.¹² Despite the large number of iron-catalyzed hydrosilylation reactions developed, only a limited number of reactions can be conducted using relatively low catalyst loadings (<1 mol%) under mild reaction conditions, which include short reaction times (within a few hours) and low reaction temperatures such as room temperature. In other words, the development of iron-catalyzed reactions that fulfill these requirements remains challenging.

Complex 1 exhibits good catalytic activity for the reduction of aldehydes and ketones with Ph_2SiH_2 ; all reactions were completed within a few hours at room temperature in the presence of 0.1–0.5 mmol% of the catalyst. For instance, benzaldehyde underwent the hydrosilylation by Ph_2SiH_2 at room temperature within 1 h in the presence of 0.5 mol% of 1. The product was isolated as benzyl acetate in 71% yield after a workup with aqueous [nBu_4N]F and acetylation by acetyl chloride (Table 1, entry 1). An aliphatic aldehyde was also reduced under the same reaction conditions, affording 3Published on 06 February 2019. Downloaded on 2/7/2019 1:43:55 AM

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phenyl-1-propanol in 86% yield after workup with aqueous [$^{n}Bu_{4}N$]F (entry 2).

Table 1. Reduction of aldehydes or ketones catalyzed by 1. ^a					
	O ∐ + Ph₂SiH₂	cat: 1 [ⁿ Bu ₄	N]F aq. ►	он 	
	R' R (2 equiv.)	r.t., time	I	R' R	
ontry	Substrata	Cat. Loading	time	Conv.	Yield
entry	Substrate	(mol%)	(h)	(%) ^b	(%) ^c
1	ОН	0.5	1	> 99	71 ^g
2	O H	0.5	1	> 99	86
3	e e e e e e e e e e e e e e e e e e e	0.5	1	> 99	87
4 ^d	Ph	0.1	4	> 99	92
5	Br	0.5	2	> 99	90
6 ^e		0.5	2	> 99	77
7		0.5	1	> 99	82
8 ^f	°	0.1	4	> 99	98 ^h

^oAll reactions were carried out with carbonyl compounds (1 mmol), catalytic amount of **1**, and Ph₂SiH₂ (2.2 mmol) at room temperature. ^bConversion of the starting materials was determined by ¹H NMR in the presence of an internal standard. ^cisolated yield. ^dreaction was performed with 3 mmol of 4-acetylbiphenyl in dioxane (1.5 mL). ^ereaction was performed in dioxane (0.5 mL). ^freaction was performed with 3 mmol of cyclohexanone. ^gisolated as acetylated product. ^hyield was determined by ¹H NMR by using hexamethylbenzene as an internal standard.

The hydrosilylation of ketones with Ph₂SiH₂ catalyzed by 1 also proceeded effectively at room temperature within 1-4 h. For instance, complete consumption of acetophenone was confirmed in the reaction with Ph₂SiH₂ in the presence of 0.5 mol% of 1 after 1 h; the subsequent workup with aqueous [ⁿBu₄N]F afforded 2-phenylethyl alcohol in 87% isolated yield (entry 3). In contrast, no reaction occurred when monohydrosilanes such as PhMe₂SiH or bifunctional hydrosilane Me₂(H)SiOSi(H)Me₂ were used as the reducing reagent. The high catalytic activity of 1 was demonstrated by the reaction with 4-acetylbiphenyl with a lower catalyst loading; the reaction with 0.1 mol% of 1 afforded the product in quantitative yield with a catalyst turn over number (TON) of 1000 (entry 4). Reductive dehalogenation did not occur in the reaction with *p*-bromoacetophenone (entry 5), furnishing the corresponding alcohol in 90% yield. Methyl-4-acetylbenzoate underwent a smooth and selective hydrosilylation of the ketone moiety to furnish the alcohol with an intact ester 3 group (entry 6). Both aliphatic and alicyclic ketones were converted into the corresponding alcohols in good yield within a few hours using 0.1–0.5 mol% of **1** at room temperature (entries 7 and 8).



Scheme 3. Deoxygenation of 4'-methoxyacetophenone catalyzed by 1 or in-situgenerated Fe catalyst.

To our surprise, the reaction of 4'-methoxyacetophenone with Ph₂SiH₂ proceeded in a deoxygenative manner to quantitatively afford 4-ethylanisole as the sole product (Scheme 3). This reaction was completed within 1 h at room temperature in the presence of 0.5 mol% of 1. The deoxygenation of ketones is an important tool in organic synthesis, exemplified by the Clemmensen and Wolff-Kishner reactions. However, they are generally associated with the use of stoichiometric amounts of toxic reagents and harsh reaction conditions. Iron-catalyzed reactions with hydrosilanes as the deoxygenating reagent could represent a convenient alternative to these conventional methods, albeit that they have scarcely been investigated thus far. A system composed of FeCl₃ as the catalyst and polymethylhydrosiloxane (PMHS) as the reducing reagent has recently been investigated by Campagne and co-workers.13 However, this reaction requires harsh reaction conditions including high catalyst loadings (10 mol%) and microwave irradiation. To the best of our knowledge, the deoxygenation reaction shown in Scheme 3 is the first iron-catalyzed reaction that proceeds under very mild reaction conditions and low catalyst loading.

Complex **1** is highly active, but sensitive to air and moisture. Therefore, it is of particular importance that the catalytically active species can be generated by simply mixing the iron salt and precursors of the supersilyl ligand. Namely, catalytic amounts of FeBr₂ (1 mol%), Si(SiMe₃)₄, and KO^tBu in a 1:2:2 ratio were mixed in tetrahydropyran, before this solution was added to a mixture of 4'-methoxyacetophenone and Ph₂SiH₂ at room temperature. Although the yield of the product was lower than that obtained by the reaction catalyzed by isolated 1 (53% after 1 h; 76% after 24 h), a ¹H NMR analysis of the crude product confirmed the formation of the corresponding deoxygenated product (Scheme 3). Product formation was not observed when the reaction was conducted in the absence of FeBr₂.[‡] It should be emphasized that all reagents used in the present catalyst system can be handled under aerobic conditions and are commercially available. These advantages render the present catalyst system very attractive for iron-catalyzed reactions.§

Another reduction reaction catalyzed by **1** is the reductive silylation of atmospheric dinitrogen. Recently, Nishibayashi and Yoshizawa have reported that iron species such as $Fe(CO)_5$ and

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 $Cp'_{2}Fe$ ($Cp' = C_{5}H_{2}(SiMe_{3})_{3}$) mediate this reaction to afford 25 and 35 equiv. of N(SiMe₃)₃, respectively.⁴ An interesting feature of this reaction is that theoretical calculations suggest that the bis(organosilyl) iron(II) complex "Fe(SiMe₃)₂(THF)" acts as the key intermediate, although experimental evidence to support that hypothesis has not been provided. In the present work, we discovered that 1 catalyzes the reductive silylation of dinitrogen using excess SiMe_3Cl and KC_8 at room temperature under atmospheric pressure of N_2 . Complex **1** (0.2 mol%) generated 22.9 equiv. of N(SiMe₃)₃ per Fe atom in THF, under concomitant formation of byproducts including Me₃Si-SiMe₃ and mono- and bis-silylated ring-opened THF, i.e., Me₃SiO(CH₂)₃CH₂R (R = H or SiMe₃). In contrast, the TON slightly increased to 25.9 when the reaction was conducted in 1,2-dimethoxyethane (DME), and the formation of the aforementioned byproducts was suppressed (Scheme 4). A reaction was not observed in toluene, despite the high solubility of **1** in toluene. Although the detailed mechanism for this reaction is still unclear, our results seem to support the notion that a coordinatively unsaturated bis(organosilyl)iron "Fe(SiMe3)2(THF)" complex can effectively mediate the reductive silylation of dinitrogen.



Scheme 4. Reductive silylation of atmospheric dinitrogen catalyzed by 1.

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have synthesized first conclusion. we the In crystallographically characterized 14-electron iron bis(organosilyl) complex, Fe[Si(SiMe₃)₃]₂(THF)₂, by a salt metathesis reaction between FeBr₂ and K[Si(SiMe₃)₃] in THF. The high catalytic activity of 1, resulting from its coordinative unsaturation, was demonstrated for the hydrosilylation of aldehydes and ketones with Ph₂SiH₂, as well as by the reductive silvlation of dinitrogen. It should be emphasized that the hydrosilylation reactions proceeded effectively with relatively low catalyst loadings (0.1-0.5 mol%) and were all completed within 1-4 h at room temperature. Of particular interest is that the reaction of 4'-methoxyacetophenone with Ph₂SiH₂ catalyzed by 1 proceeds in a deoxygenative manner. The catalytically active species for this reaction can be easily generated in situ by simply mixing commercially available and easy-to-handle precursors. The present study thus presents a simple and promising strategy to generate coordinatively unsaturated base-metal organosilyl catalysts that may open new ways to construct well-designed and highly reactive basemetal catalysts. Research in this direction is currently in progress in our laboratories.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

[‡] We found that *in-situ*-generated active species based on this method can also catalyze the hydrosilylation of acetophenone or cyclohexanone with Ph₂SiH₂. However, this reaction also proceeds with the same rate in the absence of FeBr₂; in other words, KO'Bu may be the true catalyst for the hydrosilylation of aldehydes and ketones with Ph₂SiH₂. Details on this reaction will be reported in the near future. § In Tilley's catalytic system, the reduction of ketones with Ph₂SiH₂ also occurs when a 1:2 mixture of FeBr₂ and NaN(SiMe₃)₂ is used as the catalyst, albeit that the addition of air- and moisture sensitive NaN(SiMe₃)₂ is required as an activator.

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