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Synthesis of Fe−H/Si−H and Fe−H/Ge−H Bifunctional Complexes and Their Catalytic Hydrogenation Reactions toward Nonpolar Unsaturated Organic Molecules

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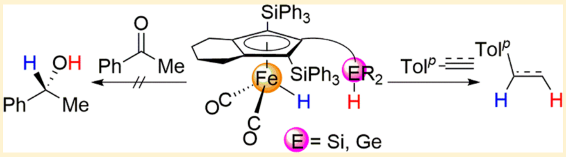
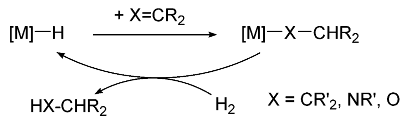
Supporting Information

ABSTRACT: The iron hydride complexes bearing a Si−H or a Ge−H functional group in a ligand [2,5-SiPh$_3$-3,4-butylene-(η^5-C$_4$COEEt$_2$H)]Fe(CO)$_2$H (E = Si (**4**), Ge (**5**)) and [2,5-SiPh$_3$-3,4-butylene-(η^5-C$_4$COSiMe$_2$OSiMe$_2$H)]Fe(CO)$_2$H (**6**), were synthesized in the reaction of the iron acetonitrile complex [2,5-SiPh$_3$-3,4-butylene-(η^4-C$_4$CO)]Fe(CO)$_2$(NCCH$_3$) (**3**) with Et$_2$EH$_2$ or HSiMe$_2$OSiMe$_2$H. These complexes did not hydrogenate a polar unsaturated bond in either ketones or aldehydes but did hydrogenate a nonpolar unsaturated bond in alkynes and alkenes to give alkenes and alkanes selectively. These complexes also catalyzed a transfer hydrogenation reaction from isopropyl alcohol (IPA) to alkynes and alkenes.



The hydrogenation reaction of unsaturated bonds promoted by a transition-metal catalyst is one of the most fundamental transformations in organic synthesis. Most hydrogenation reactions promoted by a transition-metal catalyst proceed via insertion of an unsaturated bond (R$_2$C=X, where X stands for CR′$_2$, NR′, O) into a metal−hydrogen bond to give M−X−CHR$_2$ followed by a coupling of the X−CHR$_2$ moiety and a hydride on M which is produced in the reaction of M with H$_2$ (Figure 1a). A metal−ligand bifunctional catalyst is another type of hydrogenation catalyst and is effective for catalytic hydrogenation of unsaturated organic compounds in the presence of H$_2$ and for a transfer hydrogenation reaction from HCOOH or isopropyl alcohol (IPA) as alternative hydrogen sources. The Shvo complex was the first example of a metal−ligand bifunctional catalyst that has Ru−H and O−H functional groups.[1] Since its discovery in 1986, various types of metal−ligand bifunctional complexes have been developed.[2−5] These complexes are characterized by two kinds of active hydrogen atoms: one bonded to a metal as a hydride and the other bonded to an oxygen or a nitrogen atom in its ligand as an acidic proton. Both of the hydrogen atoms cooperatively interact with a polar unsaturated bond in an organic molecule such as a ketone or an aldehyde via an outer-sphere mechanism (Figure 1b).[6] These properties make effective hydrogenation of organic molecules with a polar unsaturated bond possible. Several examples involving the Shvo complex catalyze hydrogenation of even a nonpolar unsaturated bond in organic molecules such as alkenes and alkynes.[7] In these cases, alkene/alkyne insertion into an M−H bond has been proposed, whereas an acidic proton on a ligand does not serve as a hydrogen source and remains intact during the course of the hydrogenation reaction. Milstein and co-workers reported new type ligand−metal bifunctional Ru catalysts with an active C−H bond on the pincer PNP or PNN ligands which transfer two hydrogen atoms from alcohols to imines.[8,9]

(a) Transition Metal Catalyzed Hydrogenation



(b) Hydrogenation via Outer Sphere Mechanism

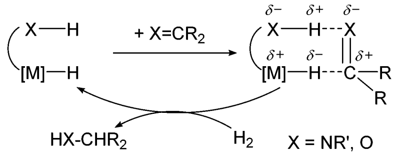


Figure 1. Hydrogenation mechanism of unsaturated organic compounds.

In iron cases, several bifunctional complexes with Fe−H and O−H functional groups similar to the Shvo complex (Ru complex) have been reported and preferential activity has been exhibited toward a polar unsaturated bond but not toward a nonpolar bond.[10,11] For example, the Knölker complex, being the first bifunctional iron complex, showed catalytic activity for a hydrogenation or transfer hydrogenation reaction (hydrogenation reaction using IPA as a hydrogen source) toward ketones or aldehydes.[12] However, the complex showed no hydrogenation activity toward alkynes and alkenes. This preferential reactivity toward polar double bonds is considered to stem from the nature of the polar transition state in an outer-sphere mechanism. If a new type of bifunctional complex with nonpolar (nonacidic) active hydrogen atoms such as a Si−H functional group on its ligand is used, preferential hydrogenation

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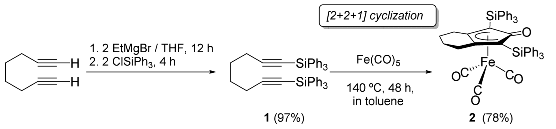
toward nonpolar unsaturated bonds is expected. However, a bifunctional catalyst with such a functional group has not been reported to date.

In this communication, we report the preparation and isolation of new iron hydride complexes bearing a Si−H or a Ge−H bond tethered to the Cp derivative ligand and their hydrogen transfer activity toward unsaturated organic compounds.

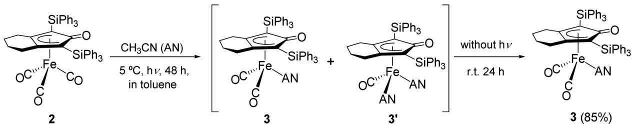
The iron tricarbonyl complex [2,5-bis(triphenylsilyl)-3,4-butylene-(η^4-C_4CO)]Fe$(CO)_3$ (**2**) was synthesized by the reaction of 1,8-bis(triphenylsilyl)-1,7-octadiyne (**1**) with Fe$(CO)_5$ through [2 + 2 + 1] cycloaddition (Scheme 1).[13] To introduce a hydride ligand onto Fe and a silyl group onto the cyclopentadienone ligand in **2**, reactions of **2** with hydrosilanes were carried out, as Casey and co-workers reported the synthesis of a ruthenium hydride complex with a silyl group on the cyclopentadienyl ligand in the reaction of the Shvo complex (Ru complex) with triethylsilane.[14] However, in our case, no reaction took place under thermal conditions, and several hydride complexes were formed under the photoirradiation conditions. These results indicate that not even one CO ligand in **2** dissociates from the iron center under thermal conditions but that more than one CO dissociation followed by Si−H oxidative addition toward the Fe center takes place under photoirradiation to give several hydride complexes. We sought another method to produce a 16e species without photoirradiation and found that [2,5-bis(triphenylsilyl)-3,4-butylene-(η^4-C_4CO)]Fe$(CO)_2(NCCH_3)$ (**3**), having one acetonitrile in place of one CO, was a good starting complex.

Scheme 1



The photoreaction of **2** in the presence of an excess amount of acetonitrile at 5 °C showed the formation of monoacetonitrile complex **3**, but diacetonitrile complex **3′** was also produced in the first stage of the reaction (Scheme 2). Stirring the reaction mixture at ambient temperature for 24 h without photolysis caused the conversion of **3′** to **3**, and **3** could be isolated in 85% yield. A similar AN/CO exchange reaction has been reported by Knölker and co-workers.[15]

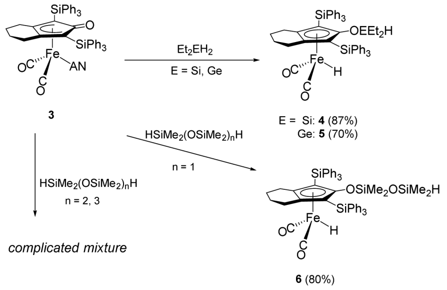
Scheme 2



The reaction of Et_2EH_2 (E = Si, Ge) with **3** gave the corresponding iron hydride complexes bearing an Si−H or Ge−H functional group on the ligand, [2,5-bis(triphenylsilyl)-3,4-butylene-(η^5-C_4COEEt_2H)]Fe$(CO)_2$H (E = Si (**4**; 87% yield), Ge (**5**; 70% yield)) (Scheme 3). Characteristic Fe−H signals of C_6D_6 solutions of **4** and **5** in the ^{1}H NMR spectra were recorded at −10.89 and −11.04 ppm, respectively. The Si−H and Ge−H signals were also observed at 4.06 and 5.04 ppm, respectively.

Reactions of **3** with $HSiMe_2(OSiMe_2)_nH$ (n = 1−3) were also carried out to obtain a series of iron complexes bearing an Si−H moiety connected to the Cp carbon through a $(SiMe_2O)_n$ chain, [2,5-bis(triphenylsilyl)-3,4-butylene-(η^5-$C_4COSiMe_2(OSiMe_2)_nH$)]Fe$(CO)_2$H. Complex **6** (n = 1) was obtained in 80% yield in the same way as for of **4** and **5**. However, the reactions with a longer tether (n = 2, 3) caused formation of a mixture of the desired products (60−70% yield) and byproducts which could not be identified, although their ^{1}H NMR spectra indicated the formation of iron hydride complexes. These byproducts could not be removed because their solubility was similar to that of the desired complex.

Scheme 3



The identification of **1**−**6** was carried out on the basis of their spectroscopic data and elemental analyses. Molecular structures of **2**−**4** and **6** were confirmed by X-ray diffraction studies, and their ORTEP drawings are depicted in Figure 2. Complexes **2** and **3** have typical three-legged piano-stool geometries with one η^4-2,5-bis(triphenylsilyl)-3,4-butylenecyclopentadienone ligand and three carbonyl ligands for **2** and two carbonyl ligands and one η^1-acetonitrile ligand for **3**. These molecular structures are similar to those of the trimethylsilyl analogues reported by Knölker and co-workers [2,5-bis(trimethylsilyl)-3,4-butylene-(η^4-C_4CO)]Fe$(CO)_3$[16] and [2,5-bis(trimethylsilyl)-3,4-butylene-(η^4-C_4CO)]Fe(CO)$(NCCH_3)_2$.[15] Complexes **4** and **6** have one hydride ligand, one η^5-2,5-bis(triphenylsilyl)-3,4-butylene-1-diethylsiloxycyclopentadienyl (or η^5-2,5-bis(triphenylsilyl)-3,4-butylene-1-tetramethyldisiloxyl) ligand, and two carbonyl ligands.

Although the main frameworks of **4** and **6** are the same as those of **2** and **3**, the phenyl rings in the triphenylsilyl moieties are twisted to avoid steric hindrance with the diethylsilyl and tetramethyldisiloxyl moieties. The C3−O3 bond distance is 1.355(3) Å for both **4** and **6**. This is clearly longer than those for **2** and **3**, indicating that the C3−O3 has single-bond character. The Fe−H bond distances are 1.43(3) Å for **4** and 1.44(3) Å for **6**, and the Si−H distances are 1.38(5) Å for **4** and 1.50(3) Å for **6**. These are similar to the bond distances of the relevant iron hydride complexes[17] and hydrosilanes.[18] The bond distances (6.27(5) Å for **4** and 7.66(5) Å for **6**) between the two hydrogen atoms on the Fe and Si show no interaction between them.

As bifunctional iron complexes **4**−**6** were obtained, reactions of these complexes with various unsaturated organic compounds were conducted. Conventional bifunctional complexes which possess O−H on the ligand and M−H bonds have been reported to react predominantly with ketone or aldehyde rather than with alkyne or alkene.[6,11] In stark contrast, **4** did not react with methyl phenyl ketone even under thermal reaction conditions (up to 80 °C), but **4** reacted with a stoichiometric amount of p-tolylacetylene to give the corresponding alkene and alkane in 18 and 9% yields, respectively (Scheme 4). The reactivity of **4** is considered to be attributable to the polarity of the Si−H bond being opposite to that of an O−H or N−H bond.

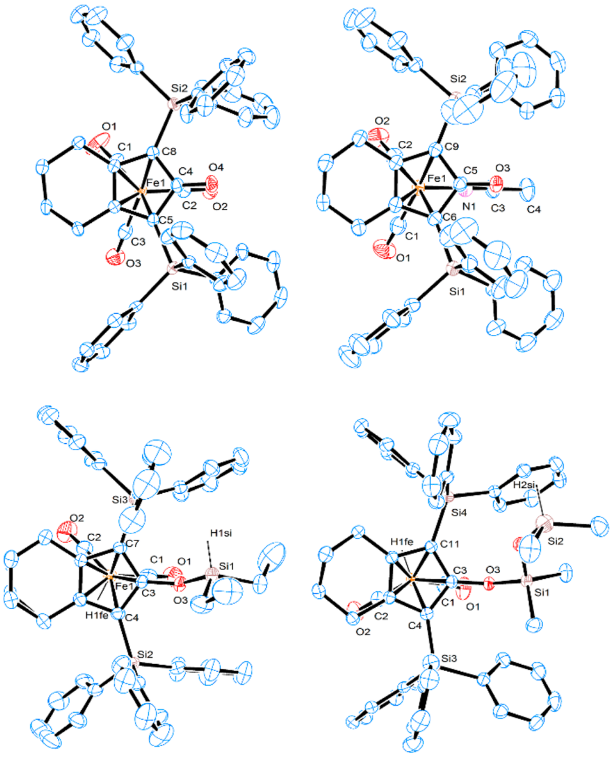


Figure 2. ORTEP drawings of **2** (upper left), **3** (upper right), **4** (lower left), and **6** (lower right) with 50% thermal ellipsoid plots. One of the independent molecules in each crystal structure of **2** and **3** is shown. The crystallization solvent and hydrogen atoms except for Fe−H and Si−H are omitted for clarify. Selected bond lengths (Å) are as follows. For **2**: Fe1−C1, 1.828(4); Fe1−C2, 1.787(4); Fe1−C3, 1.788(4); C1−O1, 1.132(5); C2−O2, 1.143(5); C3−O3, 1.139(5); C5−Si1, 1.877(3); C8−Si2, 1.888(3); C4−O4, 1.238(4). For **3**: Fe1−N1, 1.942(3); Fe1−C1, 1.779(4); Fe1−C2, 1.774(4); C1−O1, 1.143(5); C2−O2, 1.140(6); C6−Si1, 1.878(4); C9−Si2, 1.878(4); C5−O3, 1.244(4); N1−C3, 1.133(5); C3−C4, 1.458(5). For **4**: Fe1−C1, 1.765(3); Fe1−C2, 1.745(3); Fe1−H1Fe, 1.43(3); C1−O1, 1.150(4); C2−O2, 1.143(4); C4−Si2, 1.878(3); C7−Si3, 1.881(2); C3−O3, 1.355(3); O3−Si3, 1.703(3); Si1−H1Si, 1.38(5); H1Fe−H1Si, 6.27(5). For **6**: Fe1−C1, 1.749(3); Fe1−C2, 1.747(3); Fe1−H1Fe, 1.44(3); C1−O1, 1.145(3); C2−O2, 1.150(3); C3−O3, 1.355(3); C4−Si3, 1.876(2); C11−Si4, 1.879(2); Si2−H2Si, 1.50(3), H1Fe−H2Si, 7.66(5).

Scheme 4

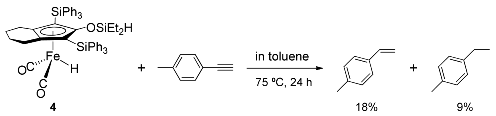
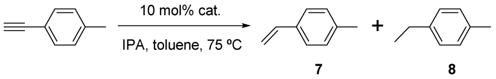


Table 1. Transfer Hydrogenation Reaction from IPA to *p*-Tolylacetylene by 4−6[a]



entry	complex	time (h)	yield (%)[b] product 7	yield (%)[b] product 8
1	**4**	24	8	trace
2	**5**	24	7	trace
3	**6**	24	27	8
4	**6**	48	30	14
5	**2**	24	0	0
6	**3**	24	0	0

[a] The reaction was carried out with 2-propanol (320 μmol), alkyne (63 μmol), and catalyst (6.3 μmol (10 mol % based on alkyne)) in toluene (20 mL) at 75 °C for 24 h, except for entry 4. [b] Determined by GC-MS measurements.

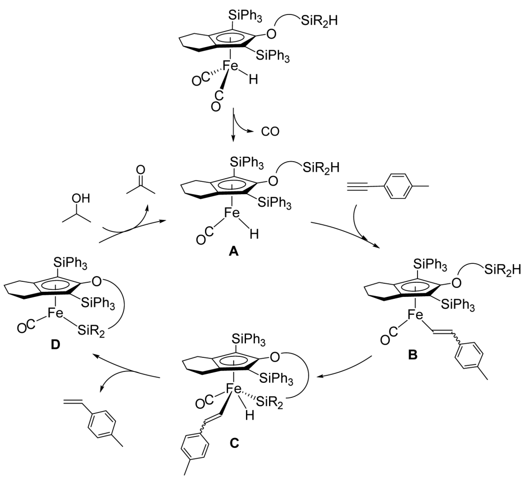
Next, this stoichiometric reaction was extended to a catalytic reaction. Treatment of **4** with 10 equiv of *p*-tolylacetylene and 5 equiv of IPA as a hydrogen source at 75 °C resulted in the formation of only 8% of 4-methylstyrene (**7**) and a trace amount of 4-ethylmethylbenzene (**8**) (Table 1, entry 1). Complex **5** also showed poor reactivity similar to that of **4** under the same reaction conditions (entry 2). However, **6** exhibited catalytic activity and gave the corresponding **7** and **8** in 27% and 8% yields, respectively (entry 3).

Slightly better conversion was obtained by using prolonged reaction time (entry 4). The low catalytic activities of **4** and **5** in comparison with that of **6** indicate that a sufficient length of the chain between the Cp ring and the Si−H functional group is necessary to have a contact of the Si−H group with the Fe center. The nonfunctionalized complexes **2** and **3** did not show activity toward hydrogen transfer reaction (entries 5 and 6).[19] This is the first example of iron promoting a transfer hydrogenation reaction from an alcohol to an alkyne or an alkene in one pot. Such catalytic transfer hydrogenation reactions have been reported for Ru, Rh, Ir, and Pd,[20] and most of them require addition of a base such as K_2CO_3, Na_2CO_3, or KOH.

To obtain insight into the reaction mechanism of the hydrogenation reaction of alkyne or alkene catalyzed by **6**, the stoichiometric reaction of **6** with *p*-tolylacetylene in C_6D_6 was monitored using ^{1}H NMR spectrometry. After the reaction mixture of **6** was heated with *p*-tolylacetylene at 75 °C for 1 h, new signals assignable to a vinyl group were observed at 5.82 and 6.45 ppm. In addition, the appearance of a new signal at 3.69 ppm (assignable to a Si−H bond) appeared and the Si−H and Fe−H signals of the starting materials disappeared. These results suggest the formation of a vinyl iron complex, [2,5-SiPh$_3$-3,4-butylene-(η^5-C$_4$COSiMe$_2$OSiMe$_2$H)]Fe(CO)$_2${CH=CH(*p*-tolyl)}. In addition, two hydrogen atoms on Fe−H and Si−H are not cooperatively introduced into alkyne/alkene but are introduced stepwise into the substrates.

A plausible catalytic cycle is shown in Scheme 5. CO dissociation of the starting complex (**4**−**6**) forms the 16e species **A**. The alkyne coordinates to **A** and inserts into the Fe−H bond

Scheme 5



to give **B**. Intramolecular oxidative addition of the Si−H bond in the Cp tether takes place to give **C**. The low activity of **4** and **5** may be ascribed to the ring strain in **C**. Reductive elimination of the H and vinyl group on Fe yields alkene and **D**. Finally, the starting hydride complex **A** is reproduced by the abstraction of two hydrogen atoms from IPA to form Si−H and Fe−H bonds. IPA is simultaneously oxidized to acetone. A similar catalytic cycle for alkene in place of alkyne is conceivable to form the alkane. [2,5-SiPh$_3$-3,4-butylene-(η^5-C$_4$COSiMe$_2$OSiMe$_2$H)]Fe(CO)$_2${CH═CH(p-tolyl)} produced in the stoichiometric reaction mentioned above corresponds to the iron complex which is formed by CO coordination to **B**. An alternative pathway involving ring slippage of η^5-Cp to η^3-Cp in place of the CO dissociation cannot be ruled out because the slippage pathway was reported in a reaction of a ruthenium complex with an alkyne by Shvo and co-workers.[7] Further mechanistic studies on the dehydrogenation step (**D** to **A**) will be reported elsewhere.

In summary, a new series of bifunctional piano-stool iron complexes with an Fe−H and a Si−H/Ge−H bond tethered to the Cp ligand were prepared. The investigation of the activity of these complexes with organic compounds with an unsaturated bond revealed that they did not transfer the two hydrogens to a polar unsaturated bond in ketones and aldehydes but could transfer them to a nonpolar unsaturated bond in alkynes and alkenes when the length of the Si−H tether is appropriate. In addition, these iron complexes served as a catalyst in the reaction of alkynes with IPA. This is the first example of an iron-catalyzed transfer hydrogenation reaction from alcohols to alkyne/alkene.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF files giving detailed experimental procedures and the characterization data for the products and crystallographic data for **2**−**4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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