2654 *Organometallics* **2001,** *20,* 2654−2656

$\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si^tBu_2)$, a Versatile Precursor for Bimetallic Active Species

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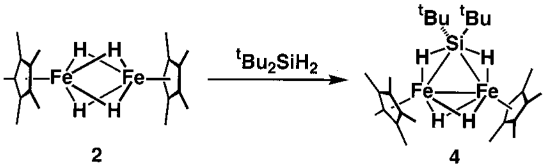
Summary: Reaction of $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_4$ *with* $^tBu_2SiH_2$ *provides the first dinuclear iron μ-silane complex,* $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si^tBu_2)$, *in which two Si−H σ-bonds are coordinated to two iron centers. The coordinated Si−H bond is readily cleaved and the μ-silane ligand is eliminated to give a dinuclear iron active species which reacts in situ with organic substrates.*

Coordinatively unsaturated transition-metal cluster complexes often undergo efficient and unique organic transformations by the synergy of the adjacent metal centers.[1] We have demonstrated examples of the cooperative activation of organic substrates on a bimetallic site in the dinuclear ruthenium tetrahydride complex $\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_4$ (**1**)[2] and have recently synthesized the dinuclear iron analogue $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_4$ (**2**).[3] The latter, like the ruthenium complex **1**, can generate a reactive species. As anticipated from the vertical trends of the transition elements, diiron tetrahydride **2** is much more reactive than the ruthenium complex **1** and, also, is less stable. Several years ago, we prepared a $\mu\text{-}H_2Si^tBu_2$ complex of ruthenium, $\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si^tBu_2)$ (**3**).[4] We have now prepared the analogous diiron complex $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si^tBu_2)$ (**4**) and find it to be more stable than **2**; hence, it is more useful as a synthetic reagent. Mononuclear late-transition-metal complexes having a Si−H−M 3c−2e bond often generate unsaturated metal intermediates by eliminating a Si−H σ-bond.[5] Our novel diiron $\mu\text{-}\eta^2{:}\eta^2$-silane complex **4** serves as a precursor for bimetallic active species, presumably $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_2$, by elimination of the bridging silane ligand.

Treatment of **2** with di-*tert*-butylsilane in toluene at room temperature gave **4**, in which two Si−H σ-bonds are coordinated to two iron centers (eq 1).[6] To our knowledge, this is the first dinuclear iron μ-silane complex. The μ-silane complex **4** is less reactive than **2** toward air and moisture, both in solution and in the solid state. Its ^{29}Si resonance occurs at δ_{Si} 71. This shift is comparable to that observed for **3** at δ_{Si} 75.[4] A broad band was observed at 1736 cm^{-1} in the infrared spectrum of **4**. This absorption was assigned as $\nu_{Si-H-Fe}$ by subtracting the spectrum of **4**-d_4 from that of **4**, as shown in Figure 1. Compared with a ν_{Si-H} value of 1790 cm^{-1} in **3** and 2116 (sharp) cm^{-1} in free $^tBu_2SiH_2$, this indicates reduction in the Si−H bond order due to the Fe−H−Si 3c−2e interaction. The ^1H NMR of **4** at room temperature showed three signals at δ 1.86 (30 H), 0.85 (18 H), and −16.25 (4 H) attributable to C_5Me_5, ^tBu, and hydride ligands, respectively. The signal of the hydride at room temperature (δ −16.25) split into two sharp singlets at δ −5.28 and −27.12 at −110 °C. This clearly shows that an exchange of the hydride ligands occurs between Fe−*H*−Si and Fe−*H*−Fe in **4** by way of Si−H bond cleavage. Line shape analysis of the variable-temperature spectra gave the free activation energy at the coalescence temperature $\Delta G^\ddagger(-50\ °C) = 8.6$ kcal/mol. This value is also similar to that of the ruthenium analogue **3** ($\Delta G^\ddagger(-60\ °C) = 8.5$ kcal/mol).[4]



2 **4** (1)

The structure of **4** was confirmed by an X-ray diffraction study.[7] The perspective view of **4** is shown in Figure

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[1] (a) Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41. (b) *Metal Clusters in Catalysis*; Gates, B. C., Guzci, L., Knozinger, V. H., Eds.; Elsevier: Amsterdam, 1986. (c) *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Ed.; Wiley-VCH: New York, 1998.

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[3] Ohki, Y.; Suzuki, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3120.

[4] Takao, T.; Yoshida, S.; Suzuki, H. *Organometallics* **1995**, *14*, 3855.

[5] For reviews, see: (a) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151. (b) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

[6] The reaction of **2** with $^iPr_2SiH_2$ affords the analogous μ-silane complex $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si^iPr_2)$. The preliminary result of the X-ray diffraction study showed the dinuclear structure bridged by the $\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si^iPr_2$ ligand. See the Supporting Information.

[7] X-ray structural determination of **4**: crystals of **4** were grown at −30 °C from a diethyl ether solution of the compound. Data were collected at −40 °C on an RAXIS-II imaging plate area detector equipped with graphite-monochromated Mo Kα radiation. The compound crystallizes in space group $R\bar{3}$, with $a = 18.6083(4)$ Å, $\alpha = 58.1220(7)°$, $V = 4360(2)$ Å^3, $Z = 6$, $d_{calcd} = 1.208$ g cm^{-3}. A total of 6640 unique reflections were recorded in the range $5° \leq 2\theta \leq 55°$, of which 4405 were used ($F > 2\sigma(F)$) for solution and refinement. In the reduction of the data, Lorentz/polarization corrections were applied to the data. The structure was solved by direct methods (SHELXS 97), and all non-hydrogen atoms were refined anisotropically by using SHELXL 97 on F^2. The final structure of **4** was refined to R1 = 0.076, wR2 = 0.149, and GOF = 1.07 for 313 parameters.

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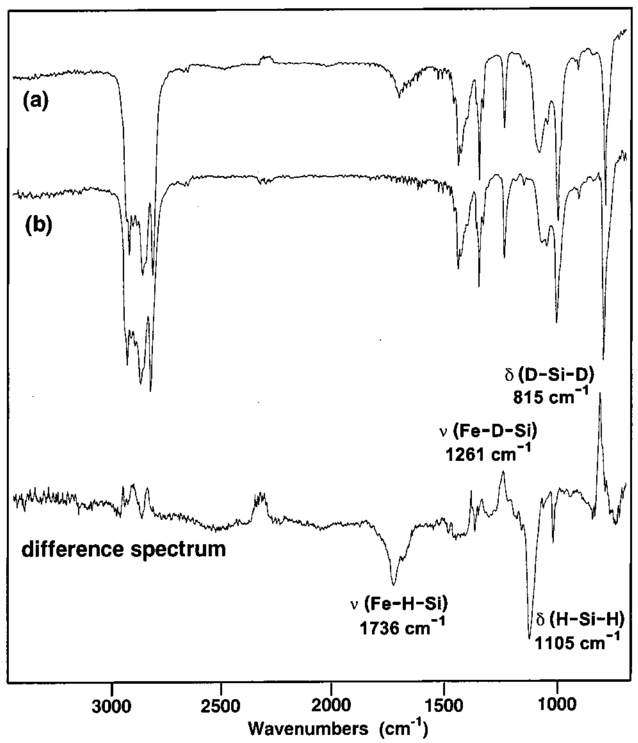


Figure 1. Infrared spectra of (a) **4**, (b) **4**-d_4, and the difference spectrum between (a) and (b).

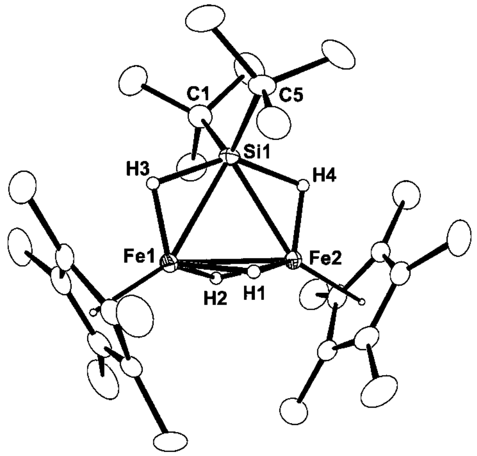
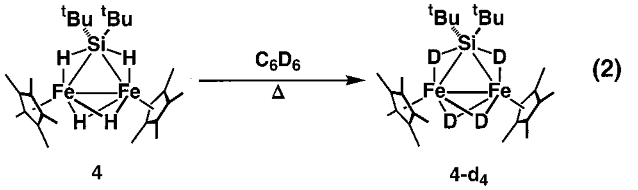


Figure 2. Molecular structure of $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}{}^tBu_2SiH_2)$ (**4**), with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.5055(8), Fe(1)−Si(1) = 2.3820(12), Fe(2)−Si(1) = 2.3692(13), Fe(1)−H(3) = 1.51(5), Fe(2)−H(4) = 1.51(5), Si(1)−H(3) = 1.60(5), Si(1)−H(4) = 1.64(5); Fe(1)−Si(1)−Fe(2) = 63.64(3), C(1)−Si(1)−C(5) = 112.5(2).

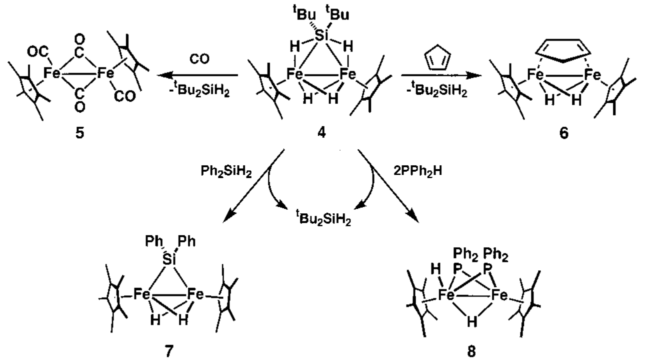
2, along with selected bond lengths and angles in the caption. The hydride ligands of Fe−*H*−Si are almost on the Fe_2Si plane, in agreement with the determined M−H−Si complexes. The Fe−Si lengths of 2.376(1) Å (average) are longer than the usual σ-bond and typical for the M−H−Si complexes.[5b] The Si−H lengths of 1.62(5) Å (average) are also in the range of the reported Si−H lengths for the M−H−Si interaction. The Fe−Fe distance of 2.5055(8) Å is indicative of an iron−iron double bond,[8] as expected from the EAN rule.

The μ-silane complex **4** undergoes C−H bond activation with benzene (eq 2). When a C_6D_6 solution of **4** was warmed to 60 °C, a gradual decrease in the intensity of the hydride NMR signal was observed. The intermolecular H/D exchange between the hydride ligands in **4** and C_6D_6 was completed within 24 h at 60 °C, leading to **4**-d_4. In contrast, the H/D exchange reaction between the ruthenium analogue **3** and C_6D_6 required more than 13 days at 80 °C.



The $\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si^tBu_2$ group in **4** was easily replaced by various organic substrates. Representative examples are summarized in Scheme 1. Treatment of **4** with CO at atmospheric pressure afforded exclusively $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(CO)_4$ (**5**)[9] and $^tBu_2SiH_2$. Complex **4** also reacted with cyclopentadiene to give the $\mu\text{-}\eta^2{:}\eta^2$-cyclopentadiene complex $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_5H_6)$ (**6**) together with free $^tBu_2SiH_2$. These results indicate the generation of a reactive bimetallic intermediate in the reactions formed by elimination of the silane ligand. In contrast, the diisopropylsilane analogue $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}H_2Si^iPr_2)$[6] does not undergo such μ-silane displacement reactions. This suggests that steric repulsion between the *tert*-butyl group on the bridging silane and the C_5Me_5 group most likely is responsible for the silane displacement reactions of **4**. The reactions of the parent iron tetrahydride complex **2** with CO and cyclopentadiene gave **5** or **6**, respectively, together with several unidentified byproducts, but the corresponding reactions of **4** yielded **5** or **6** cleanly, without any byproduct formation. The yields of **5** and **6** based on the diiron tetrahydride **2** were 70% and 61%, respectively, while the same reactions of **4** resulted in quantitative formation of **5** and **6**.

Scheme 1



The cyclopentadiene complex **6** was identified on the basis of its ^{1}H NMR spectral data (Chart 1). The signal for one of the methylene protons (*endo*-H) was observed

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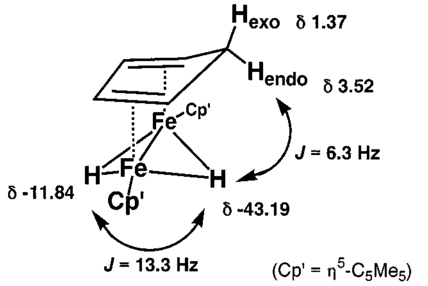
(8) For example, see: (a) Schmitt, H.-J.; Ziegler, M. L. *Z. Naturforsch., B* **1973**, *28*, 508. (b) Jonas, K.; Koepe, G.; Schieferstein, L.; Mynott, R.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 620. (c) Schaufele, H.; Pritzkow, H.; Zenneck, U. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1519. (d) Cotton, F. A.; Daniels, L. M.; Falvello, L. R.; Matonic, J. H.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 269. (e) Böttcher, H.-C.; Merzweiler, K.; Wagner, C. *Z. Anorg. Allg. Chem.* **1999**, *625*, 857.

(9) Teller, R. G.; Williams, J. M. *Inorg. Chem.* **1980**, *19*, 2770.

Chart 1



at δ 3.52 coupled with the hydride signal at δ −43.19 (J = 6.3 Hz). The structure of **6** was confirmed by an X-ray diffraction study (Figure 3).[10] The two Cp* ligands tilt to the same side with respect to the dinuclear framework. The cyclopentadiene ligand is coordinated to the two iron atoms in an μ-η^2:η^2 fashion. The iron−iron distance of 2.483(1) Å lies in the range of iron−iron double bonds.[8]

The reactions of **4** with diphenylsilane and diphenylphosphine proceeded at room temperature, resulting in quantitative formation of the known[3] μ-silylene complex **7** and bis(μ-diphenylphosphido) complex **8** via Si−H and P−H bond cleavage, respectively (Scheme 1). In contrast to $^tBu_2SiH_2$, the Si−H bond of Ph_2SiH_2 is cleaved easily to afford the μ-silylene complex **7**. The reactivity of the coordinated hydrosilane is dominated by the steric properties of the SiR_2 group. The Cp* ligands in the μ-silylene complex **7** are almost perpendicular to the Fe−Fe vector, while these ligands in the μ-silane complex **4** are mutually cis with respect to the Fe−Fe vector. In the case of the bulky R group, the transformation from μ-silane complex to μ-silylene complex generates steric repulsion between Cp* and R. Thus, the transformation of the $^iPr_2SiH_2$ complex needs to be heated,[6] and complex **4** cannot afford the corresponding μ-silylene complex.

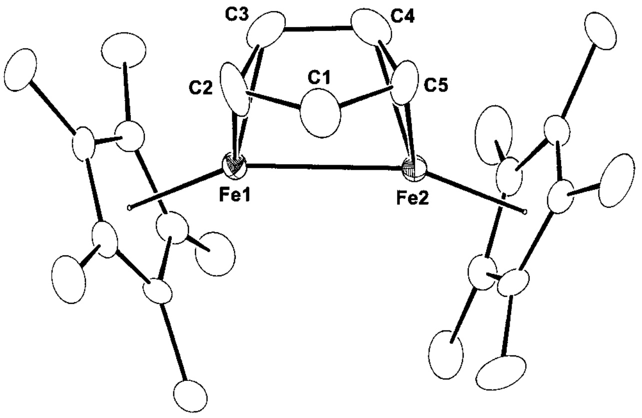


Figure 3. Molecular structure of $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_5H_6)$ (**6**), with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å): Fe(1)−Fe(2) = 2.483(1), Fe(1)−C(2) = 2.075, Fe(1)−C(3) = 2.095, Fe(2)−C(4) = 2.173(6), Fe(2)−C(5) = 2.067(4), C(1)−C(2) = 1.487(8), C(1)−C(5) = 1.468(8), C(2)−C(3) = 1.385(8), C(3)−C(4) = 1.434(8), C(4)−C(5) = 1.377(7).

The results illustrated in Scheme 1 show that the silane complex **4** can substitute well for the unstable diiron tetrahydride **2**. This is the first example of a dihydrosilane acting as a labile bridging ligand.

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Supporting Information Available: A table of ^1H, ^{13}C, and $^{29}Si\{^1H\}$ NMR spectral assignments for **4**, a table of ^1H and ^{13}C NMR spectral assignments for **6**, ORTEP diagrams, text describing X-ray procedures, and tables of X-ray data, positional and thermal parameters, and distances and angles for **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) X-ray structural determination of **6**: crystals of **6** were grown at −30 °C from a diethyl ether solution of the compound. Data were collected at −50 °C on an RAXIS-II imaging plate area detector equipped with graphite-monochromated Mo Kα radiation. The compound crystallizes in space group $P2_1/n$, with a = 16.0682(3) Å, b = 19.6255(8) Å, c = 16.2646(5) Å, β = 117.618(2)°, V = 4544.6(3) Å^3, Z = 8, d_{calcd} = 1.316 g cm^{-3}. A total of 9554 unique reflections were recorded in the range 5° ≤ 2θ ≤ 55°, of which 5662 were used ($F > 3\sigma(F)$) for solution and refinement. In the reduction of the data, Lorentz/polarization corrections were applied to the data. The structure was solved by the Patterson method (DIRDIF92 PATTY), and all non-hydrogen atoms were refined anisotropically by using full-matrix least-squares techniques on F. The final structure of **6** was refined to R = 0.049, R_w = 0.044, and GOF = 2.12 for 487 parameters. Crystallographic data for **6** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-153550. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)-1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).