ORGANOMETALLICS

A New Approach to Directly Synthesize $(\eta^5-C_5H_4R)Fe(CO)_2SiR'_3$ by Reaction of Cyclopentadienes with Pentacarbonyliron and Hydrosilanes

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Supporting Information

ABSTRACT: A new approach to the direct synthesis of Fe–Si-bonded complexes $(\eta^{5}-C_{5}H_{4}R)Fe(CO)_{2}SiR'_{3}$ (1) by the reaction of cyclopentadienes $C_{5}H_{5}R$ (2) with pentacarbonyliron in the presence of hydrosilanes $R'_{3}SiH$ (5) has been developed. Thus, when the reaction of 2



INTRODUCTION

Transition-metal silyl complexes have attracted much interest, not only because they act as the key intermediates in catalytic hydrosilylation,¹ dehydrogenative coupling,² and bis-silylation³ reactions but also due to the fact that they exhibit interesting new chemistry and intriguing properties.⁴ Among the large number of complexes that have been reported,⁵ the family of Fe-Si-bonded complexes $(\eta^5-C_5H_4R)Fe(CO)_2SiR'_3$ (1) are perhaps the most developed, and the salt elimination reaction, first developed by Wilkinson and co-workers in 1956, has been frequently used for synthesis of such complexes.⁶⁻⁸ This synthesis starts from the reaction of cyclopentadienes (2) and pentacarbonyliron to produce the iron dimers $[(\eta^5-C_5H_4R)Fe$ - $(CO)_2]_2$ (3), which react in turn with Na/Hg to give the iron anions $(\eta^5-C_5H_4R)Fe(CO)_2Na$ (4); the latter then react with chlorosilanes R'₃SiCl to provide the final products accompanied by elimination of sodium chloride (Scheme 1). This three-step synthesis was later simplified by using hydrosilanes 5 as starting materials to react with iron dimers 3, which allows the desired complexes 1 to be obtained in only two steps.⁹ However, this two-step method has been successful in just a few cases due to the difficulty of the reaction, which requires rather severe reaction conditions. Here, we describe a new and the most straightforward synthetic approach to the Fe-Si-bonded complexes via the direct reaction of cyclopentadienes and pentacarbonyliron in the presence of hydrosilanes, which allows for the preparation of a wide variety of the target complexes in one step, as illustrated in Scheme 1.

Scheme 1



RESULTS AND DISCUSSION

Synthesis of Complexes. During the course of our study on the activation of Si–Si bonds in the system of the iron dimer $[(\eta^5-C_5H_4SiMe_2SiMe_3)Fe(CO)_2]_2$, which was normally prepared by the reaction of pentamethyldisilanyl-substituted cyclopentadiene **2a** with pentacarbonyliron, we attempted to add triphenylsilane to the reaction system, aiming to trap coordinatively unsaturated iron species possibly formed in a Si–Si bond activation process. The reaction of **2a** with pentacarbonyliron and triphenylsilane was performed in *p*xylene at refluxing temperature. To our surprise, the sole

Received: January 21, 2014 Published: April 2, 2014 product obtained was the unexpected Fe-Si-bonded complex $(\eta^{5}-C_{5}H_{4}SiMe_{2}SiMe_{3})Fe(CO)_{2}SiPh_{3}$ (1a) (eq 1). A series of



other disilarly-substituted cyclopentadiene ligands 2b-e were applied to the reaction under the above conditions, and the same kind of products 1b-e were also obtained.

These successes encouraged us to use a variety of other cyclopentadiene ligands in the reaction. When silyl-substituted cyclopentadiene (2f), unsubstituted cyclopentadiene (2g), alkyl-substituted cyclopentadienes (2h,i), disubstituted cyclopentadiene (2j), and even indene (2k) were utilized, to our delight, the desired respective products 1f-k were all obtained (eq 1).

To further evaluate the scope of the reaction, phenyldimethylsilane was employed to replace triphenylsilane. It is found that this hydrosilane reacted readily with substituted cyclopentadienes **2b**,**d**,**e**,**i** to provide the desired products **11**–**0**, respectively (eq 2).



All of the products were obtained in good yields in comparison to the classical pathways^{9,10} and were fully characterized by spectroscopic methods and elemental analyses. More direct evidence for the molecular structures was achieved by X-ray diffraction studies of **1e,h,l** (Figures 1–3, respectively). All of them demonstrate the Fe–Si-bonded structures. The Fe–Si bond lengths are 2.3395(9) Å for **1e**, 2.3311(12) Å for **1h**, and 2.3401(16) Å for **1l**, which are nearly identical with each other as well as with the length of the Fe–Si bond in (η^{5} -C₅H₅)Fe(CO)₂SiMePh₂ (2.3353(5) Å).¹¹ This indicates that there should be no obvious steric hindrance between iron and the silyl groups in all of the complexes, due probably to the relatively long distances of the Fe–Si bonds.

Proposed Mechanisms. The mechanism of the reaction could be rationalized as shown in Scheme 2. First, dissociation of a CO ligand from (η^4 -cyclopentadiene)tricarbonyliron (6), which is formed from the reaction of cyclopentadienes and pentacarbonyliron, produces the coordinatively unsaturated (η^4 -cyclopentadiene)dicarbonyliron (7). The Si-H bond then quickly adds to the coordinatively unsaturated iron center,



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Figure 1. Molecular structure of **1e**. Hydrogen atoms are omitted for clarity in the ORTEP plot (ellipsoids are given at the 30% probability level). Selected bond lengths (Å) and angles (deg): Fe(1)-Si(1), 2.3395(9); Fe(1)-C(21), 2.138(2); Fe(1)-C(22), 2.111(2); Fe(1)-C(23), 2.092(2); Fe(1)-C(24), 2.102(2); Fe(1)-C(25), 2.100(2); C(1)-Fe(1)-Si(1), 88.37(8); C(2)-Fe(1)-Si(1), 84.98(8); C(1)-Fe(1)-C(2), 96.14(11).



Figure 2. Molecular structure of **1h**. Hydrogen atoms are omitted for clarity in the ORTEP plot (ellipsoids are given at the 30% probability level). Selected bond lengths (Å) and angles (deg): Fe(1)-Si(1), 2.3311(12); Fe(1)-C(3), 2.0919(17); Fe(1)-C(4), 2.0951(17); Fe(1)-C(5), 2.0838(18); Fe(1)-C(6), 2.0987(18); Fe(1)-C(7), 2.1216(17); C(1)-Fe(1)-Si(1), 88.13(6); C(2)-Fe(1)-Si(1), 85.56(6); C(1)-Fe(1)-C(2), 96.98(7).

resulting in the adduct 8. There would be two possible pathways to continue the reaction, $\eta^4 - \eta^2$ slippage of the cyclopentadiene ligand or dissociation of a CO ligand, to afford 9 and 10, respectively, with vacant coordination sites. They would both be able to activate the C–H bond at the cyclopentadiene ring, followed by reductive elimination of H₂, to afford the final product.

The key step in the success of the reaction might be quick oxidative addition of the Si–H bond to 7, which should be much faster than activation of the C–H bond of cyclopentadiene. Facile oxidative addition of a Si–H bond to similar unsaturated iron centers has been mentioned for CpFe(CO)₂R systems,¹² which could easily occur in refluxing benzene. In contrast, activation of the C–H bond at cyclopentadiene rings



Figure 3. Molecular structure of 11. Hydrogen atoms are omitted for clarity in the ORTEP plot (ellipsoids are given at the 30% probability level). Selected bond lengths (Å) and angles (deg): Fe(1)-Si(1), 2.3401(16); Fe(1)-C(11), 2.103(5); Fe(1)-C(12), 2.104(4); Fe(1)-C(13), 2.092(5); Fe(1)-C(14), 2.106(5); Fe(1)-C(15), 2.134(4); C(1)-Fe(1)-Si(1), 86.48(17); C(2)-Fe(1)-Si(1), 83.77(16); C(1)-Fe(1)-C(2), 95.3(2).

has been reported to need much higher temperatures 13 or ultraviolet irradiation. 14 The iron hydride 13 thus formed has been well documented to quickly dimerize at room temperature, leading to the formation of the iron dimer $3.^{14a,15}$ Experimental results demonstrate that 3 does not react with hydrosilanes in refluxing *p*-xylene. Therefore, the formation of the final product from 3 could be ruled out under the present reaction conditions.

CONCLUSION

A new reaction of cyclopentadienes with pentacarbonyliron and hydrosilanes under thermal conditions has been described, which provides a one-step and general approach to synthesize the title Fe-Si-bonded complexes. Obviously, this method is advantageous over all traditional syntheses. Further work will focus on the application of this reaction to synthesize more complex molecules containing Fe-Si bonds.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an argon atmosphere using a vacuum line and Schlenk techniques. NMR spectra were recorded at 400 MHz (¹H) and 100 MHz (¹³C) using CDCl₃ as the solvent. Chemical shifts are given in terms of ppm. Elemental analyses were performed by using a Vario EL instrument. IR spectra were recorded with an FT-IR spectrometer. p-Xylene was distilled from sodium/benzophenone. $C_5H_5SiMe_2SiMe_3$ (2a),^{10c} $C_{s}H_{s}SiMe_{3}$ (2f),¹⁶ and $C_{s}H_{s}CH_{2}Ph$ (2i)¹⁷ were prepared according to the literature methods. $C_5H_6(2g)$ and $C_5H_5Me(2h)$ were used in

Scheme 2

the form of dimers as purchased. Other chemicals were purchased and

used without further purification. Synthesis of Cyclopentadiene Ligands 2b-e,j. C₅H₅SiMe₂SiMe₂Ph (2b), C₅H₅SiMe₂SiMePh₂ (2c), C₅H₅SiMe₂SiPh₃ (2d), and C₅H₅SiPh₂SiPh₃ (2e) were prepared following procedures similar to those used for the synthesis of 2a in the literature,^{10c} as mentioned above. MeC₅H₄SiMe₃ (2j) was prepared following procedures similar to those used for the synthesis of 2f in the literature.¹⁶ In addition, the crude products also were used directly in the subsequent reactions without further characterization.

Synthesis of $(\eta^5$ -C₅H₄SiMe₂SiMe₃)Fe(CO)₂SiPh₃ (1a). In a 100 mL flask were placed 2a (1.31 g, 6.7 mmol), pentacarbonyliron (2.62 g, 13.4 mmol), triphenylsilane (2.63 g, 10.1 mmol), and 20 mL of pxylene. The mixture was refluxed for 24 h with magnetic stirring. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure (unreacted $Fe(CO)_5$, which is poisonous, should be collected with a liquid nitrogen trap!). Then the residue was dissolved in dichloromethane, and the resulting solution was filtered through Celite to remove insoluble impurities. After removed of the dichloromethane under reduced pressure, the residue was dissolved in a small amount of dichloromethane once again and separated through a column of neutral alumina using hexane as eluent to give 1a as a yellow solid (0.94 g, 25% yield): mp 126–127 °C. IR (KBr): ν_{CO} 1942 (s), 1988 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 0.15 (s, 9H, SiCH₃), 0.40 (s, 6H, SiCH₃), 4.43 (s, 2H, C₃H₄), 4.73 (s, 2H, C₅H₄), 7.37 (m, 9H, C₆H₅), 7.60 (m, 6H, C₆H₅). ¹³C NMR (CDCl₃): δ -3.11, -2.19 (SiCH₃), 88.58, 89.65, 92.57 (C₅H₄), 127.59, 128.24, 135.60, 142.70 (C₆H₅), 215.95 (CO). Anal. Calcd for C₃₀H₃₄FeO₂Si₃: C, 63.58; H, 6.05. Found: C, 63.35; H, 5.93.

Synthesis of $(\eta^5-C_5H_4SiMe_2SiMe_2Ph)Fe(CO)_2SiPh_3$ (1b). Compound 1b was synthesized by using the same procedure as described for the preparation of 1a, starting from 2b (2.58 g, 10.0 mmol), pentacarbonyliron (3.92 g, 20.0 mmol), and triphenylsilane (3.91 g, 15.0 mmol). The product was obtained as a yellow solid (1.38 g, 22% yield): mp 117–119 °C. IR (KBr): $\nu_{\rm CO}$ 1930 (s), 1988 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 0.37 (s, 6H, SiCH₃), 0.41 (s, 6H, SiCH₃), 4.34 (s, 2H, C₅H₄), 4.56 (s, 2H, C₅H₄), 7.50 (m, 20H, C₆H₅). ¹³C NMR $(CDCl_3): \delta -3.98, -3.01$ (SiCH₃), 85.00, 88.58, 89.81 (C₅H₄), 127.59, 127.64, 128.02, 128.25, 128.30, 128.88, 133.94, 135.59, 142.68 (C₆H₅), 215.89 (CO). Anal. Calcd for C₃₅H₃₆FeO₂Si₃: C, 66.86; H, 5.77. Found: C, 66.59; H, 5.85.

Synthesis of $(\eta^5-C_5H_4SiMe_2SiMePh_2)Fe(CO)_2SiPh_3$ (1c). Compound 1c was synthesized by using the same procedure as described for the preparation of 1a, starting from 2c (2.56 g, 8.0 mmol), pentacarbonyliron (3.13 g, 16.0 mmol), and triphenylsilane (3.12 g, 12.0 mmol). The product was obtained as a yellow solid (1.21 g, 22% yield): mp 114–117 °C. IR (KBr): $\nu_{\rm CO}$ 1934 (s), 1988 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 0.44 (s, 6H, SiCH₃), 0.62 (s, 3H, SiCH₃), 4.27 (s, 2H, C₅H₄), 4.51 (s, 2H, C₅H₄), 7.30 (m, 25H, C₆H₅). ¹³C NMR (CDCl₃): δ -4.84, -2.43 (SiCH₃), 88.66, 90.15, 91.21 (C₅H₄), 127.59, 127.83, 128.13, 128.26, 129.26, 129.93, 134.97, 135.31, 135.57, 136.09, 142.59 (C₆H₅), 215.83 (CO). Anal. Calcd for C₄₀H₃₈FeO₂Si₃: C, 69.54; H 5.54. Found: C, 69.82; H, 5.78.



Synthesis of (η^5 -C₅H₄SiMe₂SiPh₃)Fe(CO)₂SiPh₃ (1d). Compound 1d was synthesized by using the same procedure as described for the preparation of 1a, starting from 2d (2.67 g, 7.0 mmol), pentacarbonyliron (2.74 g, 14.0 mmol), and triphenylsilane (2.73 g, 10.5 mmol). The product was obtained as a yellow solid (1.26 g, 24% yield): mp 153–154 °C. IR (KBr): ν_{CO} 1938 (s), 1988 (s) cm^{-1.} ¹H NMR (CDCl₃): δ 0.53 (s, 6H, SiCH₃), 4.23 (s, 2H, C₅H₄), 4.49 (s, 2H, C₅H₄), 7.41 (m, 30H, C₆H₅). ¹³C NMR (CDCl₃): δ –1.77 (SiCH₃), 88.51, 90.35, 90.84 (C₅H₄), 127.40, 128.04, 129.33, 134.17, 135.37, 135.87, 142.39 (C₆H₅), 215.63 (CO). Anal. Calcd for C₄₅H₄₀FeO₂Si₃: C, 71.79; H, 5.35. Found: C,72.00; H, 5.50.

Synthesis of (η^5 -C₅H₄SiPh₂SiPh₃)Fe(CO)₂SiPh₃ (1e). Compound 1e was synthesized by using the same procedure as described for the preparation of 1a, starting from 2e (2.02 g, 4.0 mmol), pentacarbonyliron (1.57 g, 8.0 mmol), and triphenylsilane (1.56 g, 6.0 mmol). The product was obtained as a yellow solid (0.88 g, 25% yield): mp 268–270 °C. IR (KBr): ν_{CO} 1943 (s), 1994 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 4.31 (s, 2H, C₅H₄), 4.38 (s, 2H, C₅H₄), 7.36 (m, 40H, C₆H₅). ¹³C NMR (CDCl₃): δ 86.74, 89.43, 91.64 (C₃H₄), 127.51, 128.11, 128.14, 128.20, 129.69, 129.93, 133.25, 133.84, 135.52, 136.60, 136.66, 142.31 (C₆H₅), 214.99 (CO). Anal. Calcd for C₅₅H₄₄FeO₂Si₃: C, 75.32; H, 5.06. Found: C, 75.39; H, 5.34.

Synthesis of (η⁵-C₅H₄SiMe₃)Fe(CO)₂SiPh₃ (1f). Compound 1f was synthesized by using the same procedure as described for the preparation of 1a, starting from 2f (0.93 g, 6.70 mmol), pentacarbonyliron (2.62 g, 13.4 mmol), and triphenylsilane (2.60 g, 10.0 mmol). The product was obtained as a yellow solid (0.98 g, 29% yield): mp 162–163 °C. IR (KBr): ν_{CO} 1930 (s), 1984 (s) cm^{-1.} ¹H NMR (CDCl₃): δ 0.33 (s, 9H, SiCH₃), 4.39 (s, 2H, C₅H₄), 4.78 (s, 2H, C₅H₄), 7.34 (m, 9H, C₆H₅), 7.58 (m, 6H, C₆H₅). ¹³C NMR (CDCl₃): δ –0.28 (SiCH₃), 86.62, 89.82, 92.43 (C₅H₄), 127.59, 128.26, 135.60, 142.27 (C₆H₅), 215.87 (CO). Anal. Calcd for C₂₈H₂₈FeO₂Si₂: C, 66.13; H, 5.55. Found: C, 65.95; H, 5.39.

Synthesis of $(\eta^5-C_5H_5)Fe(CO)_2SiPh_3$ (19).¹⁸ Compound 1g was synthesized by using the same procedure as described for the preparation of 1a, starting from dicyclopentadiene (4.06 g, 30.8 mmol), pentacarbonyliron (6.03 g, 30.8 mmol), and triphenylsilane (4.0 g, 15.4 mmol). The product was obtained as a yellow solid (0.67 g, 10% yield, based on Ph₃SiH): mp 162–163 °C. ¹H NMR (CDCl₃): δ 4.70 (s, 5H, C₅H₅), 7.35 (m, 9H, C₆H₅), 7.57 (m, 6H, C₆H₅). ¹³C NMR (CDCl₃): δ 85.00 (C₅H₅), 127.64, 128.30, 135.54, 142.54 (C₆H₅), 215.58 (CO). Anal. Calcd for C₂₅H₂₀FeO₂Si: C, 68.81; H, 4.62. Found: C, 68.99; H, 4.77.

Synthesis of (η⁵-C₅H₄Me)Fe(CO)₂SiPh₃ (1h). Compound 1h was synthesized by using the same procedure as described for the preparation of 1g, starting from methylcyclopentadiene dimer (2.46 g, 15.4 mmol), pentacarbonyliron (3.02 g, 15.4 mmol), and triphenylsilane (2.0 g, 7.7 mmol). The product was obtained as a yellow solid (0.45 g, 13% yield, based on Ph₃SiH): mp 156–157 °C. IR (KBr): ν_{CO} 1934 (s), 1980 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 1.92 (s, 3H, CH₃), 4.38 (s, 2H, C₅H₄), 4.56 (s, 2H, C₅H₄), 7.30 (m, 9H, C₆H₅), 7.54 (m, 6H, C₆H₅). ¹³C NMR (CDCl₃): δ 13.30 (CH₃), 84.14, 84.82, 103.14 (C₅H₄), 127.52, 128.13, 135.49, 142.74 (C₆H₅), 216.07 (CO). Anal. Calcd for C₂₆H₂₂FeO₂Si: C, 69.34; H, 4.92. Found: C, 69.28; H, 5.03.

Synthesis of (η^5 -C₅H₄CH₂Ph)Fe(CO)₂SiPh₃ (1i). Compound 1i was synthesized by using the same procedure as described for the preparation of 1a, starting from 2i (1.05 g, 6.7 mmol), pentacarbonyliron (2.62g, 13.4 mmol), and triphenylsilane (2.61 g, 10.0 mmol). The product was obtained as a yellow solid (0.98 g, 28% yield): mp 116–118 °C. IR (KBr): ν_{CO} 1926 (s), 1980 (s) cm^{-1. 1}H NMR (CDCl₃): δ 3.53 (s, 2H, CH₂), 4.38 (s, 2H, C₅H₄), 4.60 (s, 2H, C₅H₄), 7.18 (m, 2H, C₆H₅), 7.31 (m, 12H, C₆H₅), 7.56 (m, 6H, C₆H₅). ¹³C NMR (CDCl₃): δ 34.08 (CH₂), 84.56, 84.61, 106.76 (C₅H₄), 126.89, 127.63, 128.27, 128.63, 128.78, 135.56, 139.24, 142.63 (C₆H₅), 215.99 (CO). Anal. Calcd for C₃₂H₂₆FeO₂Si: C, 73.00; H, 4.98. Found: C, 73.06; H, 5.11.

Synthesis of (η^5 -MeC₅H₃SiMe₃)Fe(CO)₂SiPh₃ (1j). Compound 1j was synthesized by using the same procedure as described for the preparation of 1a, starting from 2j (1.22 g, 8.0 mmol), pentacarbonyliron (2.62 g, 16.0 mmol), and triphenylsilane (3.12 g,

12.0 mmol). The product was obtained as a yellow solid (0.92 g, 22% yield): mp 102–104 °C. IR (KBr): ν_{CO} 1922 (s), 1984 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 0.24 (s, 9H, SiCH₃), 1.39 (s, 3H, CH₃), 3.98 (s, 1H, C₅H₃), 4.54 (s, 1H, C₅H₃), 4.82 (s, 1H, C₅H₃), 7.31 (m, 9H, C₆H₅), 7.62 (m, 6H, C₆H₅). ¹³C NMR (CDCl₃): δ –0.61 (SiCH₃), 11.95 (CH₃), 86.42, 89.26, 91.88, 94.27, 102.88 (C₃H₃), 127.51, 128.15, 135.74, 142.76 (C₆H₅), 216.60 (CO). Anal. Calcd for C₂₉H₃₀FeO₂Si₂: C, 66.65; H, 5.79. Found: C, 66.61; H, 5.70.

Synthesis of (η⁵-**C**₉**H**₇)**Fe(CO)**₂**SiPh**₃ (1k). Compound 1k was synthesized by using the same procedure as described for the preparation of 1a, starting from 2k (0.58 g, 5.0 mmol), pentacarbonyliron (1.96 g, 10.0 mmol), and triphenylsilane (1.95 g, 7.5 mmol). The product was obtained as a yellow solid (0.32 g, 13% yield): mp 172–174 °C (lit.¹⁹ mp 166–167 °C). ¹H NMR (CDCl₃): δ 4.84 (s, 3H, C₉H₇), 7.32 (m, 11H, C₉H₇, C₆H₅), 7.54 (m, 8H, C₆H₅). ¹³C NMR (CDCl₃): δ 74.15, 92.32, 105.62, 124.53, 127.62, 127.67, 128.41, 135.47, 142.13 (C₉H₇), 215.17 (CO).

Synthesis of (η^5 -C₅H₄SiMe₂SiMe₂Ph)Fe(CO)₂SiMe₂Ph (11). Compound 11 was synthesized by using the same procedure as described for the preparation of 1a, starting from 2b (10.3 g, 40.0 mmol), pentacarbonyliron (15.6 g, 80.0 mmol), and phenyl-dimethylsilane (8.16 g, 60.0 mmol). The product was obtained as a yellow solid (4.44 g, 22% yield): mp 154–156 °C. IR (KBr): ν_{CO} 1922 (s), 1980 (s) cm^{-1.} ¹H NMR (CDCl₃): δ 0.23 (s, 6H, SiCH₃), 0.31 (s, 6H, SiCH₃), 0.56 (s, 6H, SiCH₃), 4.22 (s, 2H, C₅H₄), 4.33 (s, 2H, C₅H₄), 7.31 (m, 10H, C₆H₅). ¹³C NMR (CDCl₃): δ -3.95, -3.00, 5.46 (SiCH₃), 87.91, 88.47, 91.47 (C₅H₄), 127.70, 127.94, 128.79, 132.63, 133.92, 138.39, 147.48 (C₆H₅), 215.88 (CO). Anal. Calcd for C₂₅H₃₂FeO₂Si₃: C, 59.50; H, 6.39. Found: C, 59.52; H, 6.59.

Synthesis of (η⁵-C₅H₄SiMe₂SiPh₃)Fe(CO)₂SiMe₂Ph (1m). Compound 1m was synthesized by using the same procedure as described for the preparation of 1a, starting from 2d (1.91 g, 5.0 mmol), pentacarbonyliron (1.96 g, 10.0 mmol), and phenyldimethylsilane (1.02 g, 7.5 mmol). The product was obtained as a yellow solid (0.67 g, 21% yield): mp 150–152 °C. IR (KBr): ν_{CO} 1922 (s), 1988 (s) cm^{-1.} ¹H NMR (CDCl₃): δ 0.49 (s, 6H, SiCH₃), 0.64 (s, 6H, CH₃), 4.24 (s, 2H, C₅H₄), 4.35 (s, 2H, C₅H₄), 7.43 (m, 20H, C₆H₅). ¹³C NMR (CDCl₃): δ –1.60, 5.46 (SiCH₃), 88.00, 89.12, 90.99 (C₅H₄), 127.72, 127.96, 128.18, 129.44, 132.64, 134.58, 136.10, 147.47 (C₆H₅), 215.81 (CO). Anal. Calcd for C₃₅H₃₆FeO₂Si₃: C, 66.86; H, 5.77. Found: C, 66.69; H₂ 5.53.

Synthesis of (η^5 -C₅H₄SiPh₂SiPh₃)Fe(CO)₂SiMe₂Ph (1n). Compound 1n was synthesized by using the same procedure as described for the preparation of 1a, starting from 2e (2.53 g, 5.0 mmol), pentacarbonyliron (1.96 g, 10.0 mmol), and phenyldimethylsilane (1.03 g, 7.6 mmol). The product was obtained as a yellow solid (0.95 g, 25% yield): mp 154–156 °C. IR (KBr): ν_{CO} 1930 (s), 1984 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 0.53 (s, 6H, SiCH₃), 3.89 (s, 4H, C₅H₄),7.33 (m, 30H, C₆H₅). ¹³C NMR (CDCl₃): δ 5.18 (SiCH₃), 88.08, 88.33, 90.37 (C₅H₄), 127.49, 127.86, 127.95, 129.47, 129.65, 132.44, 133.51, 133.88, 136.48, 146.93 (C₆H₅), 214.89 (CO). Anal. Calcd for C₄₅H₄₀FeO₂Si₃: C, 71.79; H, 5.35. Found: C, 71.55; H, 5.48.

Synthesis of $(\eta^5-C_5H_4CH_2Ph)Fe(CO)_2SiMe_2Ph$ (10). Compound 10 was synthesized by using the same procedure as described for the preparation of 1a, starting from 2i (1.43 g, 9.2 mmol), pentacarbonyliron (3.62 g, 18.5 mmol), and phenyldimethylsilane (1.87 g, 13.8 mmol). The product was separated by a column of neutral alumina, loading samples by the dry method and using hexane as eluent, to give 1o as a yellow oil (0.55 g, 15% yield). IR (KBr): ν_{CO} 1922 (s), 1992 (s) cm^{-1.} ¹H NMR (CDCl₃): δ 0.65 (s, 6H, SiCH₃), 3.26 (s, 2H, CH₂), 4.29 (s, 2H, C₅H₄), 4.56 (s, 2H, C₅H₄), 7.07 (m, 2H, C₆H₅). ¹³C NMR (CDCl₃): δ 5.27 (SiCH₃), 33.87 (CH₂), 83.05, 85.14, 104.31 (C₅H₄), 126.68, 127.78, 128.02, 128.45, 128.64, 132.65, 139.73, 147.33 (C₆H₅), 215.86 (CO). Anal. Calcd for C₂₂H₂₂FeO₂Si: C, 65.67; H, 5.51. Found: C, 65.80; H, 5.35.

Crystallographic Analysis. Yellow single crystals of complexes **1e,h,l** suitable for an X-ray structural determination were obtained by recrystallization from CH_2Cl_2 /hexane solvents. All measurements were carried out on a Rigaku Saturn 70 diffractometer equipped with a

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rotating anode system at 113(2) K by using graphite-monochromated Mo K α radiation (ω -2 θ scans, λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares. All calculations were performed by using the SHELXL-97 program system. Hydrogen atoms were added theoretically and refined with isotropic thermal parameters. Crystal and structure refinement data and bond lengths and angles are shown in Tables S1–S7 in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Figures, tables and CIF files giving crystallographic data for **1e,h,l**. 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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