Organometallics **2007,** *26,* 223−229

Activation of the Vinylic C−Cl Bond by Complexation of $Fe(CO)_3$: Palladium-Catalyzed Coupling Reactions of (η^4-Chlorodiene)tricarbonyliron Complexes[†]

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Received July 30, 2006

The reactions of 1-chloro- or 2-chloro-substituted (η^4-1,3-cyclohexadiene)$Fe(CO)_3$ complexes with terminal alkynes under the catalysis of $PdCl_2(PPh_3)_2$/CuI at 45−60 °C led to the formation of the corresponding Sonogashira coupling products in 64−97% yields. The complexes also underwent smoothly the intermolecular Heck reactions with activated alkenes under the catalysis of $Pd(OAc)_2/PPh_3$ at 60 °C to afford the expected coupling products in 39−83% yields. On the other hand, the corresponding uncomplexed molecule 2-chloro-1,3-cyclohexadiene remained inert under the same reaction conditions. These results clearly demonstrated the strong activation effect of $Fe(CO)_3$ on the oxidative cleavage of the vinylic C−Cl bond.

Introduction

Aryl and vinyl halides are important materials in synthetic organic chemistry. Among them, aryl and vinyl chlorides are especially attractive for synthetic purposes because of their ready availability and low cost. However, the high stability of the $C(sp^2)-Cl$ bond makes them inert in many cases.[1]

It is well documented that the coordination of a $Cr(CO)_3$ or $Mn(CO)_3^+$ moiety on an arene ring significantly reduces the electron density of the arene ring and facilitates nucleophilic[2] and radical[3,4] additions. The complexation of $Cr(CO)_3$ or $Mn(CO)_3^+$ also activates aryl C−Cl bonds toward oxidative addition to Pd^0 complexes, thus allowing a number of subsequent reactions such as the Heck reaction or carbonylation to proceed smoothly.[5,6] More recently, we demonstrated that the coordination of $Cr(CO)_3$ to chloroarenes also significantly reduces the C−Cl bond dissociation energies (BDEs).[7]

While the activation of aryl C−Cl bonds by the complexation of a $M(CO)_3$ moiety has been extensively investigated, the possibility of activating vinylic C−Cl bonds remains virtually unknown,[8] although it is also well documented that the coordination of a $M(CO)_3$ such as $Fe(CO)_3$ on a diene strongly reduces the electron density of the C═C double bonds and facilitates nucleophilic additions.[9] Owing to the similarity between aryl chlorides and vinyl chlorides and the even more versatile chemistry of the latter, we extended our interests[4,7] to the activation of vinylic C−Cl bonds in alkene−metal complexes. We here report that the complexation of $Fe(CO)_3$ on chlorodienes significantly activates the $C(sp^2)-Cl$ bond toward oxidative Pd^0 insertion. The effect of $Fe(CO)_3$ on the C−Cl BDEs is also briefly discussed.

Results and Discussion

The Sonogashira coupling of terminal alkynes with aryl/vinyl halides and triflates serves as a straightforward and powerful method for the formation of carbon−carbon bonds.[10] However, aryl/vinyl iodides or bromides are typically employed for the coupling, while ordinary vinyl chlorides are usually unreactive

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[†] Dedicated to Professor Jiabi Chen on the occasion of his 65th birthday.

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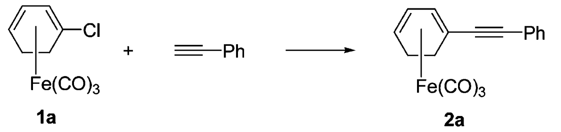
10.1021/om0606800 CCC: $37.00

Table 1. The Sonogashira Coupling of Complex 1a with Phenylacetylene



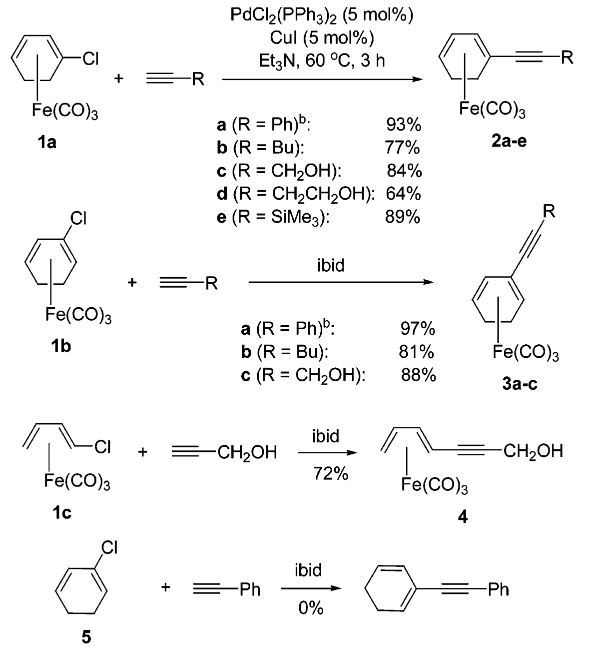
entry	conditions[a]	time (h)	yield (%)[b]
1	Pd(OAc)$_2$ (2.5 mol %), PPh$_3$ (10 mol %), Cs$_2$CO$_3$ (2 equiv), CH$_3$CN, 65 °C	4	20
2	Pd(OAc)$_2$ (10 mol %), PPh$_3$ (20 mol %), in Et$_3$N, 45 °C	4	64
3	PdCl$_2$(PPh$_3$)$_2$ (5 mol %), CuI (5 mol %), in Et$_3$N, 45 °C	3	93

[a] Phenylacetylene (1.0 equiv) was used. [b] Isolated yield based on **1a**.

under mild reaction conditions. In order to test the possible activation of the vinylic C−Cl bond by coordination of Fe(CO)$_3$, (η^4-1-chloro-1,3-cyclohexadiene)Fe(CO)$_3$ (**1a**),[11] (η^4-2-chloro-1,3-cyclohexadiene)Fe(CO)$_3$ (**1b**), and (η^4-1-chloro-1,3-butadiene)Fe(CO)$_3$ (**1c**) were first prepared. The reaction of 2-chloro-1,3-cyclohexadiene with triiron dodecacarbonyl in refluxing benzene afforded the mixture of **1a** (62%) and **1b** (15%).[12] Apparently the chlorodiene underwent partial isomerization during the complexation process. Complex **1c** was synthesized similarly by reaction of triiron dodecacarbonyl with 1-chloro-1,3-butadiene (E/Z = 6:1 determined by ^{1}H NMR), which in turn was prepared in situ by the Wittig reaction of acrolein with (chloromethyl)triphenylphosphonium bromide. We then chose complex **1a** as the model substrate to explore its coupling reaction with phenylacetylene. Three conventional literature procedures[13] for the Sonogashira coupling of aryl iodides were directly applied to the reaction of complex **1a**, and the results are listed in Table 1. To our delight, the expected coupling product **2a** was achieved in all three cases. With 5 mol % of PdCl$_2$(PPh)$_3$ as the catalyst and 5 mol % of CuI as the cocatalyst,[13c] the reaction of **1a** with phenylacetylene in triethylamine at 45 °C for 3 h afforded complex **2a** in 93% yield (entry 3, Table 1).

We then prepared Fe(CO)$_3$ complexes **1a**−**c** and carried out their Sonogashira reactions with terminal alkynes under the catalysis of PdCl$_2$(PPh)$_3$/CuI without further optimization. The results are summarized in Table 2. The coupling of **1a** with 1-hexyne did not occur at 45 °C. However, when the reaction temperature was raised to 60 °C, the reaction proceeded smoothly and the coupling product **2b** was achieved in 77% yield. Other terminal alkynes such as 2-propyn-1-ol and 3-butyn-1-ol also gave the expected coupling products **2c**,**d** in high yields. Similarly, the 2-chloro-substituted diene−Fe(CO)$_3$ complex **1b** underwent smooth coupling with terminal alkynes in high efficiency. The yields of products **3a**−**c** in the reactions of **1b** were even slightly higher than those of **2a**−**c** in the corresponding reactions of **1a**. As the simpler analogue of **1a**, complex **1c** also gave the corresponding coupling product **4** in high yield. In all the cases tested for complexes **1a**−**c**, the expected coupling products were obtained in satisfactory yields under mild experimental conditions. On the other hand, the corresponding uncomplexed vinyl chlorides such as 2-chloro-1,3-cyclohexadiene (**5**) did not give the expected coupling products in reaction with phenylacetylene under the same conditions (Table 2). Only the self-coupling of phenylacetylene leading to the formation of 1,4-diphenyl-1,3-butadiyne was observed, while the chloride **5** remained unchanged under the above experimental conditions.

Table 2. Sonogashira Reactions of Vinyl Chlorides 1a−c and 5 at 60 °C[a]



[a] The yields were isolated yields based on the starting vinyl chlorides. [b] The reaction temperature was 45 °C.

The above different reactivities of **1a**−**c** and **5** in Sonogashira coupling are noteworthy, which strongly indicates the activation of the vinylic C−Cl bond toward Pd(0) insertion by complexation with Fe(CO)$_3$. The activation should be attributed to the powerful electron-withdrawing effect of the Fe(CO)$_3$ moiety. The above mild reaction conditions also imply that the reactivity of the complexed vinyl chlorides **1** toward Pd(0) insertion is similar to that of an ordinary aryl iodide or bromide.[13c] Moreover, the activation effect of Fe(CO)$_3$ on vinylic C−Cl bonds is comparable to that of Cr(CO)$_3$ on aryl C−Cl bonds,[14] as the Sonogashira coupling of (η^6-chlorobenzene)Cr(CO)$_3$ with phenylacetylene was conducted under similar experimental conditions but at refluxing temperature of THF.[14c]

Having succeeded in the Sonogashira reactions of vinyl chloride−Fe(CO)$_3$ complexes **1**, we were encouraged to explore

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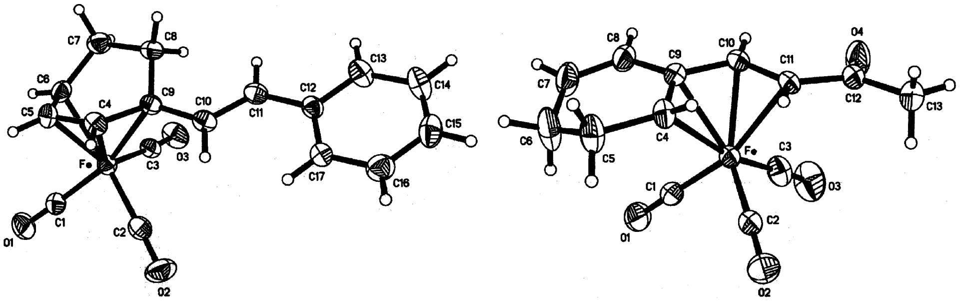


6a **8b**

Figure 1. ORTEP drawings of complexes **6a** and **8b**.

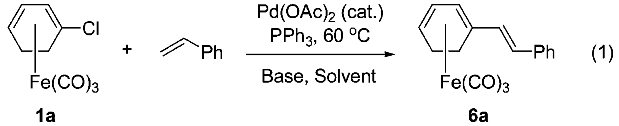
Table 3. Synthesis of 6a via the Reaction of 1a at 60 °C

entry[a]	[Pd]/[PPh$_3$]	base	solvent	yield (%)[b]
1	1/4	Et$_3$N	THF	26
2	1/4	Cs$_2$CO$_3$	THF	30
3	1/4	Cs$_2$CO$_3$	CH$_3$CN	43
4	1/10	Cs$_2$CO$_3$	CH$_3$CN	19
5	1/2	Cs$_2$CO$_3$	CH$_3$CN	63
6	1/1	Cs$_2$CO$_3$	CH$_3$CN	65
7	2/1	Cs$_2$CO$_3$	CH$_3$CN	72
8	10/1	Cs$_2$CO$_3$	CH$_3$CN	60
9	2/1	K$_2$CO$_3$	CH$_3$CN	65
10[c]	2/1	Cs$_2$CO$_3$	CH$_3$CN	47

[a] Reaction conditions: **1a** (0.22 mmol), styrene (0.88 mmol), Pd(OAc)$_2$ (0.022 mmol), base (0.33 mmol), solvent (3 mL), PPh$_3$, 60 °C, 1 h. [b]Isolated yield based on **1a**. [c]Pd(dba)$_2$ was used.

their Heck reactions with alkenes. Palladium-catalyzed Heck reactions have been intensively studied and firmly established as a powerful tool in synthetic organic chemistry.[15] However, aryl (or vinyl) iodides or bromides are generally employed as the substrates, while aryl or vinyl chlorides are usually unreactive under similar conditions. To facilitate the Heck coupling of aryl chlorides, harsh reaction conditions (higher temperature, longer reaction time, etc.) or the use of exquisite electron-rich phosphane ligands is usually required.[10c,16]

We first examined the reaction of complex **1a** with styrene under typical conditions for the Heck reaction of aryl iodides: 10 mol % of Pd(OAc)$_2$ as the catalyst, 40 mol % of PPh$_3$ as the ligand, Et$_3$N as the base, and THF as the solvent.[17] When the mixture was heated at 60 °C for 1 h, the expected product **6a** was obtained in 26% yield (eq 1), whose structure was unambiguously determined by an X-ray diffraction experiment shown in Figure 1.



1a **6a** (1)

We then carried out a brief optimization of experimental conditions for **1a**, and the results are summarized in Table 3. With the use of Cs$_2$CO$_3$ as the base, the yield of **6a** was slightly increased (entry 2, Table 3). Switching the solvent from THF to CH$_3$CN increased the yield further to 43% (entry 3, Table 3). The amount of PPh$_3$ employed proved to be critical to the outcome (entries 3−8, Table 3). When the ratio of Pd(OAc)$_2$ to PPh$_3$ was 2:1, **6a** was achieved in 72% yield (entry 7, Table 3). Changing the base from Cs$_2$CO$_3$ to K$_2$CO$_3$ or the palladium source from Pd(OAc)$_2$ to Pd(dba)$_2$ resulted in a decrease of the product yield (entries 9 and 10, Table 3). Thus, we concluded that the optimized combination for the Heck reaction of **1a** was to use 10 mol % of Pd(OAc)$_2$ as the catalyst, 5 mol % of PPh$_3$ as the ligand, 1.5 equiv of Cs$_2$CO$_3$ as the base, and CH$_3$CN as the solvent, and the reaction was set at 60 °C for 1 h.

We then conducted the Heck reactions of complexes **1a**−**c** under the optimized conditions. The results are illustrated in Table 4. The reactions of **1a** with activated alkenes afforded the corresponding coupling products **6a**−**e** in 34−72% yields with an excellent stereoselectivity. Electron-rich alkenes such as 1-octene were unreactive. Interestingly, the side-chain in complexes **6** exists predominantly in an s-trans conformation, as evidenced by the X-ray crystal structure of **6a** and the 2D NOESY spectra of **6b**. This might be attributed to the steric effect of the Fe(CO)$_3$ moiety, which increases the rotational barrier between s-trans and s-cis conformations.

Complex **1b** also underwent smoothly the Heck reactions with activated alkenes to give the coupling products as a mixture of **7a**−**d** and **8b**−**d** in moderate to good yields. Complexes **7b**−**d** and their isomers **8b**−**d** could not be separated by column chromatography on silica gel. Fortunately, we were able to isolate compound **8b** in a pure form by repeated recrystallization, whose structure was firmly established by an X-ray diffraction experiment (Figure 1). Apparently the initially formed complexes **7b**−**d** underwent partial isomerization to complexes **8b**−**d** under the experimental conditions, which might be caused by the electron-withdrawing carbonyl group in **7b**−**d**.[18] The open-chain analogue of **1a**, complex **1c**, also reacted with styrene to give the coupling product **9**, albeit in 39% yield. As a comparison, the parent vinyl chloride **5** was unreactive under the above reaction conditions.

The results in Table 4 have again demonstrated the powerful activation effect of Fe(CO)$_3$ on vinylic C−Cl bonds. The vinyl chlorides in **1** are even more reactive than an ordinary aryl bromide toward Heck coupling. For example, the Heck reaction of an aryl bromide with acrolein under the catalysis of Pd(OAc)$_2$/PPh$_3$ had to be conducted at a much higher temperature (130 °C).[19] Again, the effect of Fe(CO)$_3$ on a vinylic C−Cl bond closely resembles that of Cr(CO)$_3$ on a aryl C−Cl bond[20] as the Heck reaction of the *p*-chlorotoluene−Cr(CO)$_3$ complex with methyl vinyl ketone proceeded under similar experimental conditions (PdCl$_2$(PPh$_3$)$_2$, Et$_3$N, 70 °C, 58% yield).[20a]

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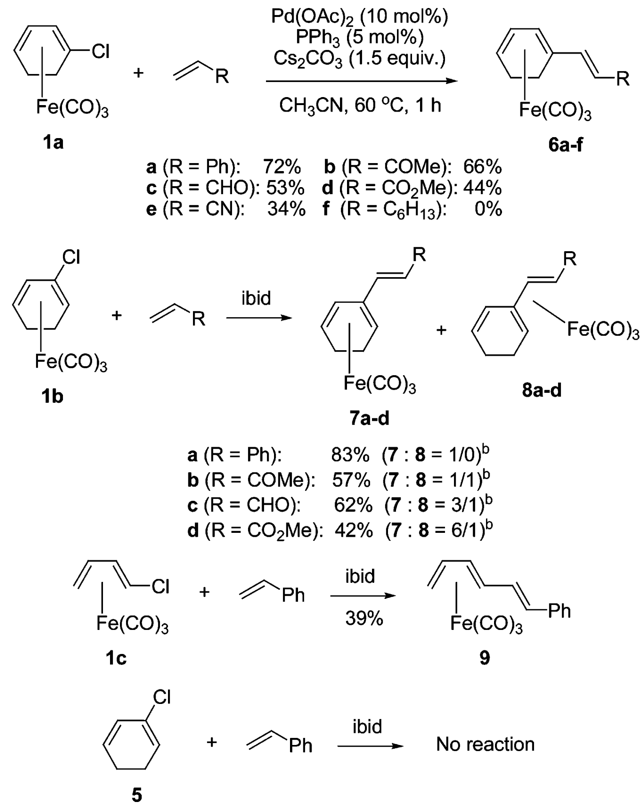
[16] For a review, see: (a) Whitcombe, N. J.; Hii, K. K.; Gibson, S. E. *Tetrahedron* **2001**, *57*, 7449.

[17] For an example, see: Herrmann, W. A.; Brossmer, C.; Oefele, K.; Beller, M.; Fischer, H. *J. Mol. Catal. A: Chem.* **1995**, *103*, 133.

[18] For similar examples, see: (a) Martina, D.; Brion, F. *Tetrahedron Lett.* **1982**, *23*, 865. (b) Goldschmidt, Z.; Bakal, Y. *J. Organomet. Chem.* **1984**, *269*.191. (c) Hafner, A.; von Philipsborn, W.; Salzer, A. *Angew. Chem.* **1985**, *97*, 136; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 126.

[19] For an example, see: Spencer, A. *J. Organomet. Chem.* **1984**, *270*, 115.

Table 4. Heck Reactions of Vinyl Chlorides 1a−c and 5[a]

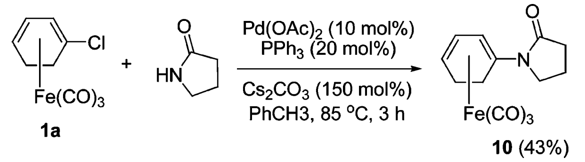


a (R = Ph): 72% **b** (R = COMe): 66%
c (R = CHO): 53% **d** (R = CO_2Me): 44%
e (R = CN): 34% **f** (R = C_6H_{13}): 0%

a (R = Ph): 83% (**7** : **8** = 1/0)[b]
b (R = COMe): 57% (**7** : **8** = 1/1)[b]
c (R = CHO): 62% (**7** : **8** = 3/1)[b]
d (R = CO_2Me): 42% (**7** : **8** = 6/1)[b]

[a] The yields were isolated yields based on the corresponding complexes **1**. [b]Determined by ^1H NMR.

The above successful Sonogashira reactions and Heck reactions of complexes **1** clearly indicate the efficient activation of the vinylic C−Cl bond toward Pd(0) insertion by complexation of $Fe(CO)_3$, which should be of important application in the synthesis of other functionalized (η^4-diene)$Fe(CO)_3$ complexes. For example, as a preliminary result, the palladium-catalyzed reaction of complex **1a** with 2-pyrrolidinone afforded the corresponding substitution product **10** in 43% isolated yield without further optimization (eq 2).



(2)

With the easy complexation of dienes with the $Fe(CO)_3$ moiety[21] and the ready decomplexation of diene−$Fe(CO)_3$ complexes under mild conditions,[22] the above methodology should be of application in organic synthesis. As an example, complex **2c** underwent decomplexation to afford the corresponding ynediene in 68% yield by treatment with H_2O_2 according to the literature procedure[22f] (see Supporting Information). It should also be noted that the complexation offers not only a reactivity enhancement but also an opportunity for asymmetric synthesis because all complexes are chiral.[6i]

The vinylic C−Cl bond activation toward oxidative addition also implies that the C−Cl BDEs of complexes **1** might be lowered relative to the noncomplexed chlorodiene. Therefore, as an extension, the C−Cl BDEs of complexes **1a** and **1b** as well as their parent uncomplexed chlorodienes were estimated by density functional calculations (B3LYP), which have been demonstrated to be an accurate tool in the theoretical study of iron complex systems.[23] The geometries were optimized with basis set I (BSI)—6-31G* for C, H, O, and Cl and LANL2DZ for Fe—and the energies were estimated with basis set II (BSII)—6-311+G* for C, H, O, Cl and SDDALL for Fe.[7] Vibrational frequency calculation was done for each structure, and the calculated BDEs were enthalpy corrected (see the Supporting Information for details). The calculations reveal that the C−Cl BDE of complex **1a** is 4.1 kcal/mol lower in energy than that of 1-chloro-1,3-cyclohexadiene, while the C−Cl BDE of **1b** is 6.4 kcal/mol lower in energy than that of 2-chloro-1,3-cyclohexadiene (**5**). The results indicate that the coordination of $Fe(CO)_3$ significantly reduces the C−Cl BDEs of chlorodienes by more than 4 kcal/mol, which is comparable to the effect of $Cr(CO)_3$ complexation on chlorobenzene (a reduction of 4.5 kcal/mol).[7] This implies that the radical chemistry of (η^6-chloroarene)$Cr(CO)_3$ complexes might be extended to chlorodiene−$Fe(CO)_3$ complexes, which is now being actively pursued in our laboratory.

Conclusion

In summary, the chemistry detailed above provides a facile entry to the synthesis of various triene− and ynediene−$Fe(CO)_3$ complexes with the simple (η^4-chlorodiene)$Fe(CO)_3$ complexes as the starting materials. More importantly, these results clearly demonstrate for the first time that the vinylic C−Cl bond is significantly activated upon complexation with $Fe(CO)_3$, thus allowing a number of reactions such as Heck coupling and Sonogashira coupling to proceed smoothly under mild reaction conditions typical for aryl iodides. This finding should be of important application in organic synthesis.

Experimental Section

NMR spectra were recorded in $CDCl_3$ (^1H at 300 MHz and ^{13}C at 75.4 MHz) using TMS as an internal standard. Most products were purified by flash chromatography on silica gel with hexane−ethyl acetate in an appropriate ratio as the eluent. Melting points are uncorrected. 2-Chloro-1,3-cyclohexadiene (**5**) was prepared according to the literature method.[24]

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(η^4-1-Chloro-1,3-cyclohexadiene)tricarbonyliron (1a) and (η^4-2-chloro-1,3-cyclohexadiene)tricarbonyliron (1b). To a solution of 2-chloro-1,3-cyclohexadiene (**5**) (5.3 g, 46 mmol) in anhydrous benzene (350 mL) was added triiron dodecacarbonyl (11.6 g, 23 mmol) under nitrogen atmosphere. The mixture was refluxed for 24 h and then cooled to room temperature. The resulting mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using hexane as the eluent to give complex **1a** (3.6 g, 62% yield based on triiron dodecacarbonyl) and complex **1b** (0.85 g, 15% yield based on triiron dodecacarbonyl). Complex **1a**: yellowish oil. IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2051, 1974. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.68−1.72 (1H, m), 1.85−2.14 (3H, m), 3.08−3.13 (1H, m), 5.12 (1H, dd, J = 6.3, 5.4 Hz), 5.55 (1H, d, J = 4.5 Hz). ^{13}C NMR (CDCl$_3$): δ 25.3, 34.0, 60.3, 81.8, 84.6, 85.5, 210.6. EIMS: m/z (rel intensity) 254 (M$^+$, 6), 226 (37), 198 (13), 170 (40), 134 (88), 84 (30), 77 (51), 56 (100). HRMS calcd for C$_9$H$_8$ClFeO$_3$ (M$^+$ + 1): 254.9511. Found: 254.9506. Complex **1b**: yellowish oil. IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2051, 1979. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.49−1.60 (2H, m), 1.72−1.79 (2H, m), 2.96−3.00 (1H, m), 3.47−3.50 (1H, m), 5.64 (1H, d, J = 6.3 Hz). ^{13}C NMR (CDCl$_3$): δ 23.3, 25.3, 55.6, 63.6, 87.5, 109.0, 210.2. EIMS: m/z (rel intensity) 254 (M$^+$, 6), 226 (43), 198 (17), 170 (43), 134 (100), 91 (43), 77 (26), 56 (31). Anal. Calcd for C$_9$H$_7$ClFeO$_3$: C, 42.48; H, 2.77. Found: C, 42.55; H, 3.03.

(η^4-1-Chloro-1,3-butadiene)tricarbonyliron (1c). Butyllithium (23 mL, 57.5 mmol, 2.5 M solution in hexanes) was added slowly to (chloromethyl)triphenylphosphonium bromide (23 g, 59 mmol) in anhydrous THF (150 mL) at −78 °C under nitrogen atmosphere. After stirring for 15 min, acrolein (3.5 mL, 55 mmol) was introduced slowly. The mixture was stirred at room temperature for 4 h. Water (25 mL) was added. The reaction mixture was directly distilled to give 1-chloro-1,3-butadiene solution in THF (65−70 °C/760 mmHg). The solution was dried over anhydrous Na$_2$SO$_4$ and then directly added to anhydrous hexane (200 mL) under nitrogen atmosphere. Triiron dodecacarbonyl (5.8 g, 11.5 mmol) was then introduced. The mixture was refluxed for 24 h and then cooled down to room temperature. The resulting mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using hexane as the eluent to give complex **1c** (1.2 g, 47% yield based on triiron dodecacarbonyl) as a yellowish oil. IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2048, 1975. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.19 (1H, dd, J = 12.3, 3.0 Hz), 1.71−1.74 (1H, m), 2.48 (1H, d, J = 6.3 Hz), 5.17−5.25 (1H, m), 5.51 (1H, dd, J = 11.1, 6.0 Hz). ^{13}C NMR (CDCl$_3$): δ 38.8, 63.7, 82.2, 86.1. EIMS: m/z (rel intensity) 228 (M$^+$, 4), 200 (17), 172 (13), 144 (21), 108 (100), 91 (16), 84 (20), 56 (49). HRMS calcd for C$_7$H$_5$ClFeO$_3$ (M$^+$): 227.9277. Found: 227.9275.

Typical Procedure for the Sonogashira Reaction of Complexes 1. PdCl$_2$(PPh$_3$)$_2$ (7 mg, 0.01 mmol) and CuI (2 mg, 0.01 mmol) were added successively to complex **1a** (51 mg, 0.2 mmol) in anhydrous Et$_3$N (2 mL) under nitrogen atmosphere. After stirring for 5 min at room temperature, phenylacetylene (0.024 mL, 0.2 mmol) was introduced. The mixture was stirred at 45 °C for 3 h. Cold ice water (10 mL) was then added, and the reaction mixture was extracted twice with diethyl ether (20 mL) and then dried over anhydrous Na$_2$SO$_4$. After removal of the solvent, the residue was then purified by flash chromatography on silica gel using hexane as the eluent to give complex **2a** as a yellowish oil. Yield: 58 mg (93%). IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2044, 1971. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.71−1.80 (2H, m), 1.92−1.98 (2H, m), 3.25−3.28 (1H, m), 5.25 (1H, dd, J = 6.3, 4.5 Hz), 5.63 (1H, d, J = 4.5 Hz), 7.25−7.28 (3H, m), 7.36−7.41 (2H, m). ^{13}C NMR (CDCl$_3$): δ 25.2, 28.1, 59.0, 61.7, 83.8, 85.5, 88.0, 93.9, 123.6, 127.8, 128.2, 131.4, 211.3. EIMS: m/z (rel intensity) 320 (M$^+$, 1), 292 (15), 264 (25), 236 (35), 234 (100), 202 (19), 178 (58), 56 (48). Anal. Calcd for C$_{15}$H$_{16}$FeO$_3$: C, 63.78; H, 3.78. Found: C, 63.91; H, 3.76.

Complex 2b: yellowish oil. IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2044,1969. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.91 (3H, t, J = 6.9 Hz), 1.36−1.47 (4H, m), 1.63−1.68 (2H, m), 1.84−1.88 (2H, m), 2.20 (2H, t, J = 6.9 Hz), 3.16−3.18 (1H, m), 5.17 (1H, dd, J = 6.3, 4.2 Hz), 5.47 (1H, d, J = 4.8 Hz). ^{13}C NMR (CDCl$_3$): δ 13.6, 19.0, 21.9, 25.0, 28.7, 30.9, 60.7, 61.2, 83.1, 84.4, 86.4, 88.2, 211.6. EIMS: m/z (rel intensity) 272 (M$^+$ − CO, 17), 244 (40), 216 (46), 214 (46), 172 (97), 115 (54), 91 (54), 56 (100). Anal. Calcd for C$_{15}$H$_{16}$FeO$_3$: C, 60.03; H, 5.37. Found: C, 60.16; H, 5.19.

Complex 2c: yellowish oil. IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2044, 1969. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.53 (1H, t, J = 6.0 Hz), 1.64−1.68 (2H, m), 1.84−1.90 (2H, m), 3.24−3.26 (1H, m), 4.31 (2H, d, J = 6.3 Hz), 5.23 (1H, dd, J = 6.3, 4.2 Hz), 5.52 (1H, d, J = 4.2 Hz). ^{13}C NMR (CDCl$_3$): δ 24.0, 27.1, 50.6, 56.7, 60.8, 82.1, 82.9, 87.1, 89.0, 210.1. EIMS: m/z (rel intensity): 273 (M$^+$ − 1, 2), 246 (16), 218 (38), 190 (18), 172 (60), 150 (14), 115 (53), 56 (100). Anal. Calcd for C$_{12}$H$_{10}$FeO$_4$: C, 52.59; H, 3.68. Found: C, 52.51; H, 3.88.

Complex 2d: yellowish oil; IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2043, 1969. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.62−1.77 (3H, m), 1.85−1.89 (2H, m), 2.50 (2H, t, J = 6.0 Hz), 3.21−3.24 (1H, m) 3.69 (2H, dt, J = 6.6, 6.0 Hz), 5.21 (1H, dd, J = 6.3, 4.2 Hz), 5.49 (1H, d, J = 4.2 Hz). ^{13}C NMR (CDCl$_3$) δ 23.8, 25.0, 28.5, 59.3, 61.2, 61.6, 82.1, 83.5, 86.4, 88.2, 211.5. EIMS: m/z (rel intensity) 287 (M$^+$ − 1, 0.4), 260 (2), 232 (11), 148 (21), 128 (45), 117 (43), 115 (100), 91 (45). Anal. Calcd for C$_{13}$H$_{12}$FeO$_4$: C, 54.20; H, 4.20. Found: C, 54.31; H, 4.16.

Complex 2e: yellowish oil. IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2047, 1975. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.00 (9H, s), 1.48−1.54 (2H, m), 1.69−1.74 (2H, m), 3.07−3.09 (1H, m), 5.05 (1H, dd, J = 5.4, 5.1 Hz), 5.38 (1H, d, J = 4.2 Hz). ^{13}C NMR (CDCl$_3$): δ 0.0, 25.1, 27.8, 58.7, 61.6, 83.8, 88.4, 89.6, 109.8, 211.2. ESIMS: m/z 317 (M$^+$ + 1). Anal. Calcd for C$_{14}$H$_{16}$FeO$_3$Si: C, 53.18; H, 5.10. Found: C, 53.08; H, 4.90.

Complex 3a: yellowish oil. IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2045, 1972. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.54−1.84 (4H, m), 3.16−3.21 (1H, m), 3.43−3.45 (1H, m), 5.67 (1H, d, J = 6.3 Hz), 7.30−7.33 (3H, m), 7.45−7.48 (2H, m). ^{13}C NMR (CDCl$_3$): δ 23.7, 24.3, 60.9, 65.0, 84.9, 86.4, 87.6, 89.6, 122.7, 128.4, 128.5, 131.7, 211.0. EIMS: m/z (rel intensity) 320 (M$^+$, 1), 292 (16), 264 (35), 236 (20), 234 (100), 202 (19), 178 (61), 56 (40). Anal. Calcd for C$_{15}$H$_{16}$FeO$_3$: C, 63.78; H, 3.78. Found: C, 64.13; H, 3.74.

Complex 3b: yellowish oil. IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2044, 1971. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.91 (3H, t, J = 6.9 Hz), 1.38−1.78 (8H, m), 2.30 (2H, t, J = 6.9 Hz), 3.07−3.11 (1H, m), 3.32−3.34 (1H, m), 5.52 (1H, d, J = 6.3 Hz). ^{13}C NMR (CDCl$_3$): δ 13.6, 18.9, 21.9, 23.6, 24.2, 30.6, 60.1, 65.3, 78.4, 86.4, 87.8, 89.2, 211.2. EIMS: m/z (rel intensity) 272 (M$^+$ − CO, 12), 244 (29), 216 (33), 214 (31), 186 (29), 172 (65), 115 (49), 56 (100). Anal. Calcd for C$_{15}$H$_{16}$FeO$_3$: C, 60.03; H, 5.37. Found: C, 60.24; H, 5.56.

Complex 3c: yellowish oil. IR (CH$_2$Cl$_2$): ν (cm^{-1}) 2046, 1971. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.52−1.79 (5H, m), 3.13−3.18 (1H, m), 3.32−3.34 (1H, m) 4.39 (2H, d, J = 6.0 Hz), 5.58 (1H, d, J = 6.6 Hz). ^{13}C NMR (CDCl$_3$): δ 23.6, 24.1, 51.4, 60.9, 64.9, 83.8, 84.0, 84.4, 89.7, 210.9. EIMS: m/z (rel intensity) 273 (M$^+$ − 1, 1), 246 (17), 218 (34), 190 (8), 172 (63), 150 (87), 115 (55), 56 (100). Anal. Calcd for C$_{12}$H$_{10}$FeO$_4$: C, 52.59; H, 3.68. Found: C, 52.40; H, 3.83.

Complex 4: yellowish oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.41 (1H, dd, J = 9.0, 1.8 Hz), 0.96 (1H, d, J = 8.1 Hz), 1.49 (1H, t, J = 5.4 Hz), 1.85 (1H, dd, J = 7.2, 2.7 Hz), 4.25 (2H, d, J = 3.6 Hz), 5.26−5.33 (1H, m), 5.50 (1H, dd, J = 8.4, 4.8 Hz). ^{13}C NMR (CDCl$_3$): δ 38.1, 39.7, 51.6, 82.6, 83.5, 87.4, 88.1, 210.4. EIMS: m/z (rel intensity) 230 (M$^+$ − H$_2$O, 18), 202 (5), 201 (49), 186

(30), 139 (29), 122 (47), 76 (49), 59 (100). HRMS calcd for $C_{10}H_6FeO_3$ ($M^+ - H_2O$): 229.9666. Found: 229.9675.

Typical Procedure for the Heck Reaction of Complexes 1. $Pd(OAc)_2$ (5 mg, 0.022 mmol), PPh_3 (3 mg, 0.011 mmol), and cesium carbonate (108 mg, 0.33 mmol) were added successively to the solution of complex **1a** (56 mg, 0.22 mmol) in anhydrous CH_3CN (3 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 30 min. Styrene (0.11 mL, 0.88 mmol) was then introduced, and the resulting mixture was stirred at 60 °C for 1 h. The reaction solution was cooled to room temperature, and CH_2Cl_2 (20 mL) was added. The mixture was then filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using hexane as the eluent to give complex **6a** as a yellowish solid. Yield: 51 mg (72%). Mp: 109−110 °C. IR (KBr): ν (cm^{-1}) 2028, 1974. ^1H NMR (300 MHz, $CDCl_3$): δ 1.52−1.68 (1H, m), 1.76−1.87 (1H, m), 1.93−2.04 (1H, m), 2.23−2.33 (1H, m), 3.27−3.32 (1H, m), 5.27 (1H, dd, J = 6.3, 4.5 Hz), 5.45 (1H, d, J = 4.2 Hz), 6.47 (2H, AB, J = 16.8 Hz), 7.18−7.40 (5H, m). ^{13}C NMR ($CDCl_3$): δ 24.3, 24.4, 61.3, 78.2, 82.3, 87.2, 125.6, 126.0, 127.2, 128.7, 134.8, 137.3, 212.1. EIMS: m/z (rel intensity) 322 (M^+, 3), 294 (25), 266 (19), 238 (21), 237 (18), 236 (100), 234 (15), 178 (17). Anal. Calcd for $C_{17}H_{14}FeO_3$: C, 63.38; H, 4.38. Found: C, 63.22; H, 4.47.

Complex 6b: yellowish solid. Mp: 78−79 °C. IR (CH_2Cl_2): ν (cm^{-1}) 2043, 1969, 1665. ^1H NMR (300 MHz, $CDCl_3$): δ 1.49−1.53 (1H, m), 1.82−1.84 (1H, m), 1.98−2.06 (2H, m), 2.26 (3H, s), 3.42−3.46 (1H, m), 5.36 (1H, dd, J = 6.3, 4.5 Hz), 5.55 (1H, d, J = 4.2 Hz), 6.09 (1H, d, J = 16.2 Hz), 6.81 (1H, d, J = 15.9 Hz). ^{13}C NMR ($CDCl_3$): δ 23.9, 24.7, 27.2, 62.9, 73.2, 84.4, 89.1, 124.3, 150.7, 197.9, 210.8. EIMS: m/z (rel intensity) 288 (M^+, 1), 260 (5), 232 (27), 204 (36), 202 (96), 148 (100), 105 (38), 56 (75). Anal. Calcd for $C_{13}H_{12}FeO_4$: C, 54.20; H, 4.20. Found: C, 54.22; H, 4.15.

Complex 6c: yellowish solid. Mp: 110−111 °C. IR (CH_2Cl_2): ν (cm^{-1}) 2044, 1972, 1673. ^1H NMR (300 MHz, $CDCl_3$): δ 1.50−1.56 (1H, m), 1.80−1.87 (1H, m), 1.97−2.09 (2H, m), 3.48−3.50 (1H, m), 5.38 (1H, dd, J = 6.3, 4.2 Hz), 5.60 (1H, d, J = 4.2 Hz), 6.13 (1H, dd, J = 15.6, 7.8 Hz), 6.79 (1H, d, J = 15.6 Hz), 9.50 (1H, d, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ 23.9, 24.8, 63.5, 72.5, 84.9, 89.1, 126.1, 160.3, 193.4, 210.5. EIMS: m/z (rel intensity) 274 (M^+, 1), 246 (8), 218 (27), 190 (27), 188 (62), 160 (30), 56 (100), 40 (61). Anal. Calcd for $C_{12}H_{10}FeO_4$: C, 52.59; H, 3.68. Found: C, 52.50; H, 3.66.

Complex 6d: yellowish oil. ^1H NMR (300 MHz, $CDCl_3$): δ 1.43−1.53 (1H, m), 1.74−1.86 (1H, m), 1.92−2.09 (2H, m), 3.37−3.42 (1H, m), 3.74 (3H, s), 5.33 (1H, dd, J = 6.3, 4.2 Hz), 5.53 (1H, d, J = 4.2 Hz), 5.82 (1H, d, J = 15.6 Hz), 7.03 (1H, d, J = 15.6 Hz). ^{13}C NMR ($CDCl_3$): δ 23.9, 24.6, 51.5, 62.7, 73.0, 84.1, 89.0, 114.6, 151.7, 167.5, 210.8. EIMS: m/z (rel intensity) 304 (M^+, 3), 276 (25), 248 (23), 220 (30), 218 (66), 190 (17), 160 (100), 56 (23). HRMS calcd for $C_{13}H_{12}FeO_5$: 304.0034. Found: 304.0034.

Complex 6e: yellowish solid. Mp: 112−113 °C. IR (KBr): ν (cm^{-1}) 2214, 2045, 1970. ^1H NMR (300 MHz, $CDCl_3$): δ 1.44−1.48 (1H, m), 1.80−2.06 (3H, m), 3.43−3.48 (1H, m), 5.22 (1H, d, J = 15.9 Hz), 5.36 (1H, dd, J = 6.0, 5.1 Hz), 5.60 (1H, d, J = 3.9 Hz), 6.70 (1H, d, J = 15.9 Hz). ^{13}C NMR ($CDCl_3$): δ 23.2, 24.4, 63.1, 71.7, 84.5, 88.4, 92.4, 118.7, 157.3, 210.3. EIMS: m/z (rel intensity) 271 (M^+, 3), 243 (15), 215 (26), 187 (60), 185 (100), 91 (14), 84 (18), 56 (49). Anal. Calcd for $C_{12}H_9FeNO_3$: C, 53.17; H, 3.35; N, 5.17. Found: C, 53.07; H, 3.28; N, 5.01.

Complex 7a: yellowish oil. ^1H NMR (300 MHz, $CDCl_3$): δ 1.52−1.72 (2H, m), 1.74−1.94 (2H, m), 3.20−3.24 (1H, m), 3.66−3.68 (1H, m), 5.50 (1H, d, J = 6.3 Hz), 6.79 (2H, AB, J = 15.9 Hz), 7.23−7.46 (5H, m). ^{13}C NMR ($CDCl_3$): δ 24.2, 24.5, 59.1, 61.2, 85.8, 101.1, 126.6, 127.9, 128.0, 128.1, 128.6, 136.5, 211.6. EIMS: m/z (rel intensity) 322 (M^+, 4), 294 (29), 266 (20), 238 (12), 236 (100), 179 (16), 178 (19), 56 (16). Anal. Calcd for $C_{17}H_{14}FeO_3$: C, 63.38; H, 4.38. Found: C, 63.44; H, 4.31.

Complexes 7b and 8b: yellowish oil. Two isomers in ∼1:1 ratio. ^1H NMR (300 MHz, $CDCl_3$) **7b**: δ 1.63−1.67 (2H, m), 1.74−1.89 (2H, m), 2.33 (3H, s), 3.37−3.39 (1H, m), 3.51−3.53 (1H, m), 5.57 (1H, d, J = 7.5 Hz), 6.43 (1H, d, J = 16.2 Hz), 7.20 (1H, d, J = 15.3 Hz); **8b**: δ 1.15 (1H, d, J = 8.1 Hz), 1.77−1.79 (1H, m), 1.93−2.13 (2H, m), 2.13 (3H, s), 2.23−2.32 (2H, m), 5.72 (1H, d, J = 8.1 Hz), 6.04−6.08 (1H, m), 6.40 (1H, d, J = 9.6 Hz). ^{13}C NMR ($CDCl_3$) **7b**: δ 23.9, 24.4, 27.7, 59.6, 64.0, 89.1, 97.8, 125.5, 143.9, 203.6, 210.7; **8b**: δ 22.8, 23.8, 29.7, 51.5, 57.9, 78.3, 95.4, 125.4, 132.4, 197.7, 209.6. EIMS: m/z (rel intensity) 288 (M^+, 1), 260 (2), 232 (21), 204 (28), 202 (88), 148 (68), 56 (100), 40 (84). Anal. Calcd for $C_{13}H_{12}FeO_4$: C, 54.20; H, 4.20. Found: C, 54.19; H, 4.21.

Complexes 7c and 8c: yellowish oil. Two isomers in ∼3:1 ratio. IR (CH_2Cl_2): ν (cm^{-1}) 2046, 1972, 1674. ^1H NMR (300 MHz, $CDCl_3$) **7c**: δ 1.61−1.69 (2H, m), 1.84−1.94 (2H, m), 3.40−3.43 (1H, m), 3.50−3.52 (1H, m), 5.60 (1H, d, J = 7.5 Hz), 6.38 (1H, dd, J = 15.9, 7.5 Hz), 7.20 (1H, d, J = 15.6 Hz), 9.63 (1H, d, J = 7.2 Hz); **8c**: δ 1.17 (1H, dd, J = 8.1, 4.2 Hz), 1.77−1.79 (1H, m), 1.93−2.13 (2H, m), 2.23−2.32 (2H, m), 5.70 (1H, d, J = 8.1 Hz), 6.08−6.12 (1H, m), 6.40 (1H, d, J = 9.6 Hz), 9.32 (1H, d, J = 4.2 Hz). ^{13}C NMR ($CDCl_3$) **7c**: δ 23.8, 24.4, 59.9, 64.8, 78.0, 89.5, 125.0, 153.2, 192.9, 210.4; **8c**: δ 22.8, 23.7, 52.3, 58.8, 94.2, 98.8, 126.9, 133.0, 196.8, 209.1. EIMS: m/z (rel intensity) 274 (M^+, 1), 246 (2), 218 (14), 190 (17), 188 (32), 160 (14), 56 (65), 40 (100). Anal. Calcd for $C_{12}H_{10}FeO_4$: C, 52.59; H, 3.68. Found: C, 52.36; H 3.65.

Complexes 7d and 8d: yellowish oil. Two isomers in ∼6:1 ratio. IR (KBr): ν (cm^{-1}) 2043, 1968, 1717. ^1H NMR (300 MHz, $CDCl_3$) **7d**: δ 1.60−1.65 (2H, m), 1.81−1.87 (2H, m), 3.32−3.34 (1H, m), 3.46−3.49 (1H, m), 3.77 (3H, s), 5.54 (1H, d, J = 6.6 Hz), 6.12 (1H, d, J = 15.6 Hz), 7.37 (1H, d, J = 15.6 Hz); **8d**: δ 1.19 (1H, d, J = 8.1 Hz), 1.77−1.79 (1H, m), 1.93−2.13 (2H, m), 2.23−2.32 (2H, m), 3.66 (3H, s), 5.72 (1H, d, J = 8.1 Hz), 6.01−6.08 (1H, m), 6.41 (1H, d, J = 9.6 Hz). ^{13}C NMR ($CDCl_3$) **7d**: δ 23.8, 24.4, 51.7, 59.4, 63.7, 80.0, 89.0, 116.5, 145.3, 166.5, 210.8. EIMS: m/z (rel intensity) 304 (M^+, 2), 276 (13), 248 (21), 220 (15), 218 (52), 160 (100), 131 (27), 56 (49). Anal. Calcd for $C_{13}H_{12}FeO_5$: C, 51.35; H, 3.98. Found: C, 51.64; H, 4.01.

Complex 9: yellowish solid. Mp: 109−110 °C. IR (CH_2Cl_2): ν (cm^{-1}) 2042, 1971. ^1H NMR (300 MHz, $CDCl_3$): δ 0.61 (1H, dd, J = 9.3, 2.7 Hz), 1.86 (1H, dd, J = 6.6, 2.1 Hz), 2.00 (1H, dd, J = 9.6, 9.3 Hz), 5.23−5.31 (1H, m), 5.48 (1H, dd, J = 9.0, 4.5 Hz), 6.22 (1H, dd, J = 15.3, 9.9 Hz), 6.57 (1H, d, J = 15.3 Hz), 7.18−7.36 (5H, m). ^{13}C NMR ($CDCl_3$): δ 39.6, 63.1, 81.5, 85.8, 126.0, 127.4, 128.7, 130.2, 131.0, 137.2, 211.5. EIMS: m/z (rel intensity) 296 (M^+, 1), 268 (21), 240 (20), 212 (76), 134 (94), 115 (28), 91 (49), 56 (100). Anal. Calcd for $C_{15}H_{12}FeO_3$: C, 60.84; H, 4.08. Found: C, 60.72; H, 4.40.

Complex 10. $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), and cesium carbonate (98 mg, 0.3 mmol) were added successively to the solution of complex **1a** (51 mg, 0.2 mmol) in anhydrous toluene (5 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 30 min. 2-Pyrrolidinone (20 mg, 0.24 mmol) was then introduced, and the resulting mixture was stirred at 85 °C for 1 h. The resulting solution was cooled to room temperature, and CH_2Cl_2 (20 mL) was added. The mixture was then filtered, and the filtrate was concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to give complex **10** as a yellowish oil. Yield: 26 mg (43%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.52−1.58 (1H, m), 1.65−1.74 (1H, m), 1.79−1.90 (1H, m), 1.96−2.08 (3H, m), 2.39−2.45 (2H, m), 3.17−3.20 (1H, m), 3.28−3.35 (1H, m), 3.70−3.77 (1H, m), 5.22 (1H, dd, J = 6.0, 5.4

Hz), 6.32 (1H, d, $J = 4.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 18.3, 24.1, 25.7, 32.3, 49.9, 61.3, 80.9, 84.6, 85.2, 173.7, 211.7. EIMS: *m*/*z* (rel intensity) 303 (M^+, 1), 217 (78), 163 (43), 162 (100), 106 (86), 77 (50), 56 (39), 41 (41). HRMS calcd for $C_{13}H_{13}FeNaNO_4$ ($M^+ + Na$): 326.0092. Found: 326.0099.

Acknowledgment. This project was supported by the National Natural Science Foundation of China (Nos. 20325207 and 20672136). We thank Prof. Yun-Dong Wu of HKUST for valuable discussions on this project.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of the compounds without elemental analysis, 2D NOESY spectrum of **6b**, and DFT calculation results (PDF) as well as X-ray crystal data of complexes **6a** and **8b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM0606800