ORGANOMETALLICS

Three-Coordinate Iron(II) Dialkenyl Compound with NHC Ligation: Synthesis, Structure, and Reactivity

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Supporting Information

ABSTRACT: The reaction of $[(IPr_2Me_2)_2FePh_2]$ with PhC≡CPh furnished a three-coordinate iron(II) dialkenyl complex, $[(IPr_2Me_2)Fe(\sigma$ -CPh=CPh_2)_2] (**1**, $IPr_2Me_2 = 1,3$ -diisopropyl-4,5-dimethylimidazol-2-ylidene), that represents a rare example of isolable low-coordinate iron alkenyl complexes with a high-spin ground state. Complex **1** was characterized by ¹H NMR spectroscopy, solution magnetic susceptibility measurement, Mössbauer spectroscopy, single-crystal X-ray diffraction study, and elemental analyses. A reactivity study revealed the reactions of **1** with PhCH₂Cl to produce cross-coupling product Ph₂C=CPhCH₂Ph (**2**), with [Cp₂Fe]-[BAr^F₄] to yield Ph₂C=CPh−CPh=CPh₂ (**3**), and with



CO, 2,6-dimethylphenyl isocyanide, and phenyl azide to produce novel iron(0) and iron(II) complexes 4–6 bearing triphenylvinyl-derived ligands. These transformations demonstrated the high reactivity of the low-coordinate iron alkenyl complex.

INTRODUCTION

The renaissance of iron catalysis¹ in recent years urges deeper knowledge of the chemistry of organoiron species beyond that of the classical closed-shell complexes.² Iron alkenyl species are reactive intermediates proposed in iron-catalyzed crosscouplings³ and the carbometalation⁴ and hydrosilylation⁵ of alkynes. Peoples' knowledge on them, however, has been limited to the coordinatively saturated low-spin 18e⁻ complexes with cyclopentadienyl anion, carbonyl, and phosphines as ancillary ligands.⁶ As for coordinatively unsaturated iron alkenyl complexes, very limited examples were reported and their reactivity is unknown. Holland et al. found that the iron(II) hydride complexes (nacnac)Fe(H) (nacnac = β -diketiminate ligand) can react with the alkynes PhC=CPh and EtC=CEt to form the *cis*-addition products [(nacnac)Fe(σ -CR=C(H)-R)] (R = Ph, Et, A and B in Chart 1).⁷ The three-coordinate

Chart 1. Known Examples of Open-Shell Iron Alkenyl Complexes



iron(II) alkenyl complexes are high-spin and were characterized by X-ray crystallographic studies. Power isolated a dinuclear iron(I) alkenyl complex, [Fe₂(ArC=C(Ph)C(Ph)=CAr] (Ar = C₆H₃-2,6-(C₆H₃-2',6'-Prⁱ₂)₂, C in Chart 1), from the reaction of [ArFe(μ -Br)]₂ with PhC=CLi (2 equiv).⁸ Magnetic property studies indicated that the dinuclear complex contained two antiferromaganetically coupled high-spin iron(I) centers. In addition to these, Chirik found that [(PrⁱPDI)Fe(N₂)₂] (PrⁱPDI) = 2,6-(2,6-Prⁱ₂-C₆H₃N=CMe)₂C₅H₃N) can react with CH₂= CHBr to produce (PrⁱPDI)FeBr and (PrⁱPDI)Fe(σ -CH= CH₂).⁹ Unfortunately, the instability of the formal iron(I) alkenyl species prevented detailed spectroscopic characterization.

In view of the wide use of N-heterocyclic carbene (NHC) in iron-catalzyed organometallic transformations in recent years,¹⁰ we launched a project to study reactive organoiron species with NHCs as supporting ligands. Our previous studies showed that, with the selection of NHCs with appropriate steric property, four-coordinate iron(II) alkyl, aryl, and alkynyl complexes in the form of (NHC)₂FeR₂ were accessible (Chart 2).^{11,12} Reactivity studies enabled the establishment of versatile C–C bond formation reactions of these open-shell iron(II) dihydrocarbyl compounds with polar unsaturated organic substrates, organic halides, and oxidants.¹¹ In addition to these, we wish to report herein the synthesis, characterization, and reactivity study of a high-spin iron(II) alkenyl complex,

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Chart 2. Examples of Four-Coordinate Organoiron(II) Complexes with NHC Ligation



 $[(IPr_2Me_2)Fe(\sigma-CPh=CPh_2)_2]$. The iron(II) dialkenyl complex, in addition to the alkyl, aryl, and alkynyl complexes, completes the series of high-spin organoiron(II) species with NHCs as ancillary ligands.

RESULTS AND DISCUSSION

Preparation and Characterization of the Iron(II) Alkenyl Complex. Treatment of $[(IPr_2Me_2)_2FePh_2]^{11d}$ with 2 equiv of PhC=CPh in THF produced a dark brown solution. After workup, the iron(II) complex $[(IPr_2Me_2)Fe(\sigma\text{-CPh}=CPh_2)_2]$ (1) was isolated as an orange crystalline solid in 41% yield (Scheme 1). The synthetic method is reminiscent of

Scheme 1. Preparation of the Iron(II) Alkenyl Complex

 $(IPr_2Me_2)_2Fe^{II}Ph_2 + 2 PhC \equiv CPh$

[(IPr₂Me₂)Fe^{ll}(CPh=CPh₂)₂] (**1**) + IPr₂Me₂

Holland's preparation of $[(nacnac)Fe(\sigma-CR=C(H)R)]$, wherein alkynes were inserted into Fe–H bonds.⁷ The reaction using 1 equiv of the alkyne, however, did not result in the formation of the probable intermediate $(IPr_2Me_2)FePh(\sigma-CPh=CPh_2)$, but afforded a mixture of 1 and $[(IPr_2Me_2)_2FePh_2]$. The establishment of the conversion of $[(IPr_2Me_2)_2FePh_2]$ to 1 implies that the reaction of open-shell organo-iron(II) species with alkynes could be responsible for the C–C bond-forming step in iron-catalyzed carbometalation of alkynes.⁴

Complex 1 is air and moisture sensitive. It is insoluble in nhexane, slightly soluble in Et₂O, and highly soluble in THF. Its solution magnetic moment (5.3(1) $\mu_{\rm B}$) measured in C₆D₆ indicates its high-spin nature. Consistent with this, the ¹H NMR spectrum of 1 in C_6D_6 shows broad paramagnetically shifted resonances in the range +65 to -55 ppm. The molecular structure of 1 was established by X-ray crystallographic study. As shown in Figure 1, the iron center in 1 displays a trigonal planar coordination geometry via coordination with one IPr₂Me₂ ligand and two triphenylvinyl groups with the sum of the three C-Fe-C angles around the iron center being 360°. Likely due to steric repulsion between the bulky triphenylvinyl ligands, the two vinyl groups are pointing above and below the coordination plane, respectively, and the C(alkenyl)-Fe-C(alkenyl) angle $(137.95(5)^{\circ})$ is larger than the C(carbene)-Fe-C(alkenyl) angles. The Fe-C(alkenyl)distances of 2.061(2) and 2.066(2) Å are comparable to those of the Fe-C(mesityl) bonds in $[(IPr_2Me_2)Fe(Mes)_2]$ (2.073 Å).^{11a} As compared to the reported iron alkenyl complexes, the Fe-C(alkenyl) distances in 1 are longer than those of its congeners in the high-spin complex $[(nacnac)Fe(\sigma-CPh=$ C(H)Ph)] (2.017 Å)^{7b} and the low-spin complexes [*cis*-Fe(PMe₃)₂(CO)₂(CH=CH₂)₂] (ca. 2.014 Å)^{6g} and [CpFe- $(CO)_2(CPh=CPh(C_6H_2-3,5-Bu_2^t-4-OH))]$ (ca. 2.043 Å).¹³ The C(alkenyl)-C(alkenyl) lengths in 1 (1.363 Å on average) are comparable to those of $[Sn(Bu^n)(\sigma-CPh=CPh_2)_3]$ (1.34 Å



Figure 1. Molecular structure of 1 showing 30% probability ellipsoids and partial atom schemes. Selected distances (Å) and angles (deg) for 1: Fe1-C1 2.096(2), Fe1-C2 2.061(2), Fe1-C3 2.066(2), C2-C4 1.362(2), C3-C5 1.363(2), C1-Fe1-C2 110.59(5), C1-Fe1-C3 111.45(5), C2-Fe1-C3 137.95(5).

on average),¹⁴ Ph₂C=CPh₂ (1.34 Å),¹⁵ [CpFe(CO)₂(CPh= CPh(C₆H₂-3,5-Bu^t₂-4-OH))] (ca. 1.338 Å),¹³ and [(nacnac)-Fe(σ -CPh=C(H)Ph)] (1.347 Å),^{7b} suggesting its double-bond nature. The Fe–C(carbene) bond distance (2.096(2) Å) is typical of three-coordinate high-spin iron(II)-NHC complexes.^{11,12,16}

The zero-field ⁵⁷Fe Mössbauer spectrum of 1 measured on the polycrystalline sample at 200 K is shown in Figure 2. The



Figure 2. Zero-field ⁵⁷Fe Mössbauer spectra measured on a polycrystalline solid of 1 at 200 K.

single quadrupole doublet has the fitting isomer shift $\delta = 0.33$ mm/s and the quadruple splitting $\Delta E_{\rm Q} = 2.20$ mm/s. These data are comparable to those of the three-coordinate high-spin iron(II) diaryl complex [(IPr₂Me₂)Fe(Mes)₂] ($\delta = 0.30$ mm/s, $\Delta E_{\rm Q} = 1.38$ mm/s)¹⁷ and [Fe(Mes)₃]⁻ ($\delta = 0.20$ mm/s, $\Delta E_{\rm Q} = 1.44$ mm/s),¹⁸ supporting its high-spin S = 2 ground state.

Reactivity of the Iron(II) Alkenyl Complex. The attainment of 1 completed the series of high-spin organoiron-(II)-NHC complexes with the hydrocarbyl groups ranging from alkyl to phenyl to alkenyl and to alkynyl. With this iron(II) dialkenyl complex in hand, we then studied its reactions with various organic substrates and oxidants.

Testing the reactions of 1 with organic halides indicated that it can react slowly with benzyl chloride (2 equiv) to afford the cross-coupling product $Ph_2C=CPhCH_2Ph$ (2) in 48% yield (Scheme 2). The iron(II) chloride species $[(IPr_2Me_2)FeCl_2]_4^{19}$ was identified as the major iron-containing product based on

Scheme 2. C–C Bond Formation Reactions of 1



the ¹H NMR spectrum of the resulting mixture. The reaction of 1 with 1-bromooctane required harsher conditions. At 50 °C, the interaction of 1 with 2 equiv of 1-bromooctane in 36 h produced Ph₂C=CPhC₈H₁₇-*n* in 69% GC yield (Figures S17 and S18). The coexistence of a large amount of Ph₂C=CPhH in the quenched reaction mixture rendered the isolation of the cross-coupling product via chromatographic separation on silica gel difficult. The lower reactivity of the iron(II) alkenyl complex toward the organic halides as reflected by the slow rates versus those of the reactions with $[(IPr_2Me_2)_2Fe(C=CBu^{t})_2]^{11d,f}$ is likely due to steric factors, as the bulky alkenyl groups in 1 might prevent the organic halide from interacting with the iron center.

Similar to the iron(II) diphenyl and dialkynyl complexes, ^{11a,d,f} no C–C bond-forming reductive elimination reaction occurred when the solution of **1** was kept at room temperature or 60 °C. The interaction of **1** with 1 equiv of the one-electron oxidant $[Cp_2Fe][BAr^F_4]$ ($Ar^F = 3,5$ -ditrifluoromethylphenyl), however, led to the formation of the reductive elimination product hexaphenyl-1,3-butadiene (**3**) in 70% isolated yield (Scheme 2). The high yield of **3** suggests the occurrence of the iron(III)/iron(I) reductive elimination process from $[(IPr_2Me_2)Fe^{III}(\sigma$ -CPh=CPh₂)₂]⁺. Probably due to their instability, the efforts to isolate the iron(III) intermediate and the iron(I) product were unfruitful. Indeed, only an irreversible oxidation wave with an $E_p = 0.48$ V (vs SCE) was observed in the cyclic voltammogram of **1** in THF (Figure S2).

Examining the reactions of 1 with unsaturated organic substrates revealed the fascinating conversions of the triphenylvinyl groups in 1 to versatile metal-bound unsaturated organic molecules. As shown in Scheme 3, 1 can react with CO, CNC₆H₃-2,6-Me₂, and PhN₃ at -78 °C or room temperature to furnish the iron(0) complexes 4 and 5 and the iron(II)complex 6, respectively, in moderate yields. The mild reaction conditions form a sharp contrast to the harsh reaction conditions required for the insertion reactions of coordinatively saturated iron alkenyl complexes. For example, the intramolecular migratory insertion reaction of the 18e⁻ species $[CpFe(CO)_2(\sigma-CPh=CPh_2)]$ takes place at 190 °C.²⁰ Accordingly, we propose that the readiness of 1 to react with unsaturated substrates should be related to the low-coordinate nature of 1, which enables the coordination of the substrates to form transient coordinatively unsaturated species, presumably the 14e⁻ species (IPr₂Me₂)Fe(L)(σ -CPh=CPh₂)₂, that could undergo a facial migratory insertion reaction.

Both 4 and 5 are diamagnetic. Their ¹H NMR spectra display two characteristic heptetes (5.58 and 4.90 ppm for 4 and 6.14 and 5.16 ppm for 5) corresponding to the methine protons of the IPr_2Me_2 ligand, indicating the restricted rotation of the NHC ligands in 4 and 5. The ¹³C NMR signals of their

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C(carbene) atoms appear at ca. 186 ppm. X-ray diffraction studies have revealed 4 and 5 are five-coordinate iron(0)complexes, and their iron centers are coordinating with one IPr₂Me₂, two CO or isocyanide ligands, and one newly formed η^4 -bound ligand (Figure 3). In the structure of 4, the η^4 -bound hexaphenylpentadien-3-one ligand has the C4-C5-C6-O1 atoms coplanar to each other and the noncoordinated alkenyl fragment positioning away from the plane with the torsion angle C8-C7-C6-C5 being 56.2°. The C-C and C-O distances of the C4-C5-C6-O1 fragment display enhanced delocalization versus the free α_{β} -unsaturated ketone. This pattern is consistent with that observed in other η^4 -($\alpha_{,\beta}$ unsaturated ketone)-iron(0) complexes, e.g., [(η^4 -PhCH= CHCH=O)Fe(CO)₃]²¹ and $[(\eta^4-PhCH=CHCH=O)Fe (CO)_2(PPh_3)$].²² In the structure of 5, the indenimine ligand is bonded with the iron center via the C5-C6-C7-C8 fragment. The C-N(imine) bond distance (1.297(2) Å) is double-bond in character. The alternating short-long-short C-C distances within the benzo fragment are suggestive of the enhanced electron localization versus the free indenimines.²³ In both complexes 4 and 5, the Fe-C(carbene) distances (2.012(2) and 2.032(2) Å, respectively) are close to that in the low-spin complex [(IMes)Fe(CO)₄] (2.00 Å).²

Complex 6 is a rare example of an iron complex bearing a triazenido ligand.²⁵ Its measured solution magnetic moment $(4.7(1) \mu_B \text{ in } C_6 D_6)$ suggests its high-spin nature. As depicted in Figure 4, the iron complex features an IPr₂Me₂ and two chelating triphenylvinyltriazenido ligands. Its Fe–C(carbene) bond distance (2.105(4) Å) is typical of high-spin iron(II)-NHC compounds.^{11,12,16} The triphenylvinyltriazenido ligands chelate to the iron center with the Fe–N(phenyl) separations (2.062(4) and 2.088(3) Å) being much shorter than the Fe–N(vinyl) ones (2.279(4) and 2.208(4) Å). Moreover, the two N–N distances within each triazenido are close to each other. The vinyl moieties are noncoplanar with the triazenido plane, and the bond distances of C18–C25 and C44–C51 are suggestive of their C=C double-bond nature.

The formations of 4-6 demonstrate the unique reactivity of the low-coordinate iron(II) alkenyl complex toward polar unsaturated organic molecules beyond simple insertion reactions. While the formation of **6** apparently resulted from

Scheme 3. Reactions of 1 with Unsaturated Organic Substrates



Figure 3. Molecular structures of 4 (top) and 5 (bottom) showing 30% probability ellipsoids and partial atom-numbering schemes. Selected distances (Å) for 4: Fe1-C1 2.012(2), Fe1-C2 1.806(2), Fe1-C3 1.741(2), Fe1-C4 2.158(2), Fe1-C5 2.082(2), Fe1-C6 2.085(2), Fe1-O1 2.008(2), O2-C2 1.143(2), O3-C3 1.158(2), O1-C6 1.304(2), C4-C5 1.470(2), C5-C6 1.434(2), C6-C7 1.505(2), C7-C8 1.345(2); for 5: Fe1-C1 2.032(2), Fe1-C2 1.803(2), Fe1-C3 1.772(2), Fe1-C4 2.490(2), Fe1-C5 2.195(2), Fe1-C6 2.052(2), Fe1-C7 2.098(2), Fe1-C8 2.184(2), C4-C5 1.468(3), C5-C6 1.445(3), C6-C7 1.427(3), C7-C8 1.434(3), C4-C8 1.485(3), N3-C2 1.178(2), N5-C3 1.177(2), N4-C4 1.297(2).



Figure 4. Molecular structure of **6** showing 30% probability ellipsoids and the partial atom-numbering scheme. Selected distances (Å): Fe1– C1 2.105(4), Fe1–N3 2.062(4), Fe1–N5 2.279(4), Fe1–N6 2.088(3), Fe1–N8 2.208(4), N3–N4 1.297(6), N4–N5 1.304(5), N6–N7 1.323(5), N7–N8 1.325(5), N5–C18 1.428(6), N8–C44 1.396(5), C18–C25 1.326(6), C44–C51 1.377(6).

the direct insertion of the azide molecules into the Fe–C(alkenyl) bonds in 1, the formation of the hexaphenylpentadien-3-one ligand in 4 should involve a CO-coordinationtriggered reductive elimination step after the initial CO insertion reaction. Similar mechanisms for the formation of ketones were proposed in the reactions of other organoiron species with CO.^{11a,26} On the other hand, the evidence of the indenimine ligand in 5 suggests the occurrence of a C–H bond activation step in the reaction of 1 with the isocyanide. A probable mechanism could be the insertion of one ArNC molecule into one of the Fe–C(alkenyl) bonds to produce the iminacyl intermediate A (Scheme 4).²⁷ Intermediate A might



eliminate Ph_2C =CPhH via an intramolecular C–H activation step to furnish the iron(II) metallacycle **B**. The coordination of ArNC to the iron center in **B** could induce C–C bond-forming reductive elimination to produce the product **5**. In this proposed pathway, the formation of Ph_2C =CPhH was verified by its isolation and characterizations from the reaction mixture, and the C–H bond activation step might be reminiscent to the C(arene)–H activation reaction of Tatsumi's cyclometalated high-spin iron(II)-NHC complexes.^{12a}

CONCLUSION

In this study, we achieved the synthesis, characterization, and reactivity study of a three-coordinate iron(II) dialkenyl complex, $[(IPr_2Me_2)Fe(\sigma-CPh=CPh_2)_2]$ (1). The preparation route to 1, upon the interaction of $[(IPr_2Me_2)_2FePh_2]$ with 2 equiv of diphenyl acetylene, proves the ability of the Fe–C bond in open-shell organo-iron(II) species to undergo an insertion reaction with alkyne, being relevant to the C–C bond-forming step of iron-catalyzed carbometalation reactions. Characterization data indicated a ground spin state of S = 2 for 1. Further study revealed the diversified reactivity of 1 toward benzyl chloride, ferrocenium salt, and unsaturated polar organic substrates, which enabled the buildup of versatile C–C and C–N bond-forming transformations involving the triphenylvinyl groups in the iron complex.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk techniques, or in a glovebox. Phenyl azide was synthesized according to literature procedures.²⁸ All other chemicals were purchased from chemical vendors and used as received unless otherwise noted. Organic solvents were dried with a solvent purification system (Innovative Technology) and degassed prior to use. ¹H and ¹³C NMR spectra were recorded on Varian Mercury 300 and 400 MHz or Agilent 400 and 600 MHz spectrometers. Chemical shifts were reported in units with references to the residual protons of the deuterated solvents for proton chemical shifts and the ¹³C of deuterated solvents for carbon chemical shifts. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Magnetic moments were measured by the method originally described by Evans with stock and experimental solutions containing a known amount of a (CH₃)₃SiOSi(CH₃)₃ standard.²⁹ Absorption spectra were recorded with a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. IR spectra were recorded with a Nicolet Avatar 330 FT-IR spectrophotometer. Cyclic voltammetry

measurements were made with a CHI 600D potentiostation in THF solutions using a sweep rate of 100 mV/s, a glassy carbon working electrode, 0.1 M (Bu₄N)(PF₆) supporting electrolyte, and a SCE reference electrode. Under these conditions, $E_{1/2} = 0.55$ V for the $[Cp_2Fe]^{0/+}$ couple. The ⁵⁷Fe Mössbauer spectra were measured with a constant-acceleration spectrometer under zero-applied magnetic field. Low temperature was maintained by a CCS-850 Mössbauer Cryostat system (Janis Research Company). Data were analyzed with MossWinn 4.0 Pre (provider: Beijing Shengtianjiayuan Keji Company). Isomer shifts are relative to iron metal at room temperature.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N₂ in thin-walled glass capillaries. Data were collected at 153 or 140 K on a Bruker AXSD8 X-ray diffractometer using Mo K radiation. An empirical absorption correction was applied using the SADABS program.³⁰ All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.³¹ All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements for **1** and **4–6** are given in Table S1.

Preparation of [(IPr₂Me₂)Fe(σ-CPh=CPh₂)₂] (1). To a stirring THF solution (15 mL) of [(IPr₂Me₂)₂FePh₂] (1.00 g, 1.75 mmol) was added PhC=CPh (640 mg, 3.59 mmol) at room temperature. The color of the solution changed to dark brown immediately. After stirring for 15 min, the solvent was removed under vacuum. The brown residue was quickly washed with *n*-hexane (5 mL × 3) and diethyl ether (2 mL × 3) to leave an orange solid. After drying under vacuum, I was obtained as an orange powder (530 mg, 41%). Single crystals of I suitable for X-ray crystallography were obtained by slow evaporation of its Et₂O solution at room temperature. ¹H NMR (300 MHz, C₆D₆, 302 K): δ (ppm) 62.30 (br, 4H), 52.23 (br, 4H), 10.84 (br, 4H), 8.90 (br, 2H), 6.46 (br, 6H), −1.36 (br), −18.65 (br, 4H), −22.70 (br, 2H), −53.30 (br, 2H). Anal. Calcd for C₅₁H₅₀FeN₂: C 82.02, H 6.75, N 3.75. Found: C 81.46, H 7.03, N 3.47. Magnetic susceptibility (C₆D₆, 302 K): μ_{eff} = 5.3(1) μB. Absorption spectrum (C₆H₆): λ_{max} nm (ε, M⁻¹ cm⁻¹) = 280 (61 500).

Reaction of 1 with PhCH₂Cl. To a stirring THF solution (5 mL) of 1 (150 mg, 0.20 mmol) was added PhCH₂Cl (53 mg, 0.42 mmol) at room temperature. After 36 h, GC analysis on the reaction mixture indicated that the amount of PhCH₂Cl was no longer decreasing. During this time, the color of the solution gradually turned from orange to light yellow. After removal of the solvent, the residue was extracted with *n*-hexane $(2 \text{ mL} \times 3)$ and filtered through Celite. The filtrate was subjected to vacuum to remove the volatiles. Chromatographic separation in silica gel with n-hexane as eluent led to the isolation of 1,1,2,3-tetraphenyl-1-propene (Ph₂C=CPhCH₂Ph, 2) as a white solid in 48% yield. ¹H NMR (400 MHz, CDCl₃, 295 K): δ (ppm) 7.35-7.27 (m, 5H), 7.22-7.16 (m, 2H), 7.14-7.11 (m, 3H), 7.08-7.01 (m, 8H), 6.98-6.94 (m, 2H), 3.92 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, 295 K): δ (ppm) 143.09, 142.81, 142.04, 141.59, 140.05, 137.90, 130.71, 129.91, 129.43, 128.70, 128.21, 128.11, 127.66, 127.43, 126.84, 126.19, 125.98, 125.69, 41.39. HRMS (EI): calcd for [C₂₇H₂₂]⁺ 346.1722; found 346.1730. Further ¹H NMR analysis on the solid redidue indicated its identity as a mixture of [(IPr₂Me₂)- $\operatorname{FeCl}_2_4^{19}$ and $[(\operatorname{IPr}_2\operatorname{Me}_2)_2\operatorname{FeCl}_2]^{11a}$ (Figure S7).

Reaction of 1 with [Cp₂Fe][BAr^F₄]. To a stirring toluene solution (5 mL) of 1 (75 mg, 0.10 mmol) was added [Cp₂Fe][BAr^F₄] (105 mg, 0.10 mmol) at -78 °C. The color of the solution quickly changed from orange to brown. The reaction mixture was then warmed to room temprature and further stirred for 2 h. After quenching by H₂O, extracting with Et₂O, and drying over anhydrous MgSO₄, the organic phase was subjected to vacumm to remove the solvents. Chromotographic separation on silica gel with *n*-hexane as eluent afforded hexaphenyl-1,3-butadiene (Ph₂C=CPhCPh=CPh₂, 3) as a white solid (36 mg, 70%). ¹H NMR (400 MHz, CDCl₃, 292 K): δ (ppm) 7.22–7.17 (m, 4H), 7.02–6.93 (m, 12H), 6.90–6.81 (m, 12H), 6.90–6.85 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, 292 K): δ (ppm) 143.95, 143.73, 142.93, 141.45, 140.48, 131.33, 131.27, 129.83, 127.44, 127.24,

127.18, 126.57, 126.38, 125.89. The NMR spectra were identical to those reported in the literature. 32

Reaction of 1 with CO. A solution of 1 (150 mg, 0.20 mmol) in THF (3 mL) was cooled with liquid N₂, and then 1 atm of CO was added via a CO balloon. The color of the mixture changed from orange to light brown. After stirring for 30 min at room temperature, the color of the solution turned to red. The reaction mixture was further stirred for 1 h and was then subjected to vacuum to remove the volatiles. The residue was washed with *n*-hexane $(2 \text{ mL} \times 3)$ and then dried under vacuum to afford 4 as an orange solid (117 mg, 71%). Single crystals of 4 suitable for X-ray crystallography were obtained by slow evaporation of its Et₂O solution at room temperature. ¹H NMR (400 MHz, $C_{4}D_{4}$, 294 K): δ (ppm) 8.55 (d, I = 7.6 Hz, 1H), 7.85 (br, 1H), 7.65 (br, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.28–7.18 (m, 4H), 7.13-7.07 (m, 1H), 7.05-6.86 (m, 10H), 6.86-6.79 (m, 5H), 6.77-6.65 (m, 5H), 6.56 (d, J = 7.6 Hz, 1H), 5.58 (hept, J = 7.0 Hz, 1H, $CH(CH_3)_2$, 4.90 (hept, J = 7.0 Hz, 1H, $CH(CH_3)_2$), 1.87 (s, 3H), 1.67 (s, 3H), 1.38 (d, J = 6.8 Hz, 3H), 1.30 (d, J = 7.2 Hz, 3H), 0.93 (d, J = 7.0 Hz, 3H), 0.78 (d, J = 6.9 Hz, 3H). ¹³C NMR (100 MHz, C₆D₆, 294 K): δ (ppm) 214.10, 203.07, 184.96, 148.92, 147.99, 145.37, 143.39, 142.55, 142.09, 139.78, 138.32, 134.13, 134.05, 133.40, 133.23, 133.01, 129.82, 129.61, 127.67, 127.07, 126.88, 126.70, 126.64, 126.61, 126.57, 126.31, 126.16, 126.06, 125.96, 125.70, 125.68, 125.48, 125.05, 122.36, 100.17, 70.66, 52.48, 51.35, 21.55, 21.16, 20.59, 9.61, 9.39. Absorption spectrum (C₆H₆): $\lambda_{max, nm}$ (ϵ , M⁻¹ cm⁻¹) = 370 (6810). Anal. Calcd for C₅₄H₅₀FeN₂O₃: C 78.05, H 6.07, N 3.37. Found: C 78.05, H 6.22, N 3.11. IR (KBr, cm⁻¹): ν = 3047 (w), 2973 (w), 1980 (s), 1909 (s), 1593 (w), 1574 (w), 1557 (w), 1489 (w), 1463 (w), 1455 (w), 1352 (w), 1288 (w), 770 (w), 748 (w), 738 (w), 697 (m), 602 (w), 556 (w).

Reaction of 1 with 2,6-Dimethyphenyl Isocyanide. To a stirring THF solution (5 mL) of 1 (100 mg, 0.13 mmol) was added 2,6-dimethyphenyl isocyanide (53 mg, 0.40 mmol) at -78 °C. The color of the solution changed immediately to dark red. The mixture was allowed to warm to room temperature and stirred for 4 h, during which time the color of the solution turned from red to dark brown. After removal of the solvent, the residue was washed with n-hexane (2) mL) and then extracted with diethyl ether (3.0 mL) and filtered. Slow evaporation of diethyl ether afforded 5 as dark brown crystals (43 mg, 37%). ¹H NMR (400 MHz, C₆D₆, 294 K): δ (ppm) 7.72 (br, 2H), 7.74 (br, 2H), 7.29–7.22 (m, 3H), 7.20–7.07 (m, 5H), 7.00 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 8.7 Hz, 1H), 6.75–6.65 (m, 7H), 6.29 (dd, J =8.8, 6.0 Hz, 1H), 6.14 (hept, J = 7.0 Hz, 1H, $CH(CH_3)_2$), 5.16 (hept, J= 7.0 Hz, 1H, CH(CH₃)₂), 2.12 (s, 3H), 2.05 (s, 6H), 1.99 (s, 6H), 1.87 (s, 3H), 1.82 (s, 3H), 1.65 (s, 3H), 1.29 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$, 1.12 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.07 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.06 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$). ¹³C NMR (100 MHz, C₆D₆, 294 K): 194.54, 190.72, 186.02, 156.15, 154.52, 139.95, 137.98, 133.28, 132.69, 132.47, 131.98, 131.58, 131.19, 130.89, 129.64, 128.55, 128.28, 128.19, 127.89, 127.85, 127.61, 127.39, 127.27, 127.15, 126.59, 125.89, 125.70, 124.85, 124.73, 124.15, 123.65, 119.72, 119.15, 103.83, 87.42, 84.73, 68.89, 54.87, 52.01, 22.62, 22.47, 22.24, 21.34, 19.11, 18.44, 18.38, 18.05, 10.18, 10.00. Anal. Calcd for C58H61FeN5: C 78.80, H 6.96, N 7.92. Found: C 78.57, H 6.91, N 7.78. Absorption spectrum (THF): λ_{max} nm (ϵ , M⁻¹ cm⁻¹) = 327 (26730), 414 (20 620), 515 (2730). IR (KBr, cm⁻¹): $\nu = 3057$ (w), 2968 (w), 2940 (w), 2047 (s), 1978 (s), 1560 (w), 1546 (s), 1495 (w), 1463 (w), 1356 (w), 1271 (w),1207 (w), 770 (w), 756 (w), 746 (w), 701 (w), 593 (w), 521 (w). On the other hand, the *n*-hexane solution and the mother liquor of the ethereal solution were combined, guenched with D_2O (0.5 mL), and extracted with diethyl ether. After chromatographic separation on silica gel with n-hexane as eluant, Ph₂C= C(H)Ph was isolated as a white solid (11 mg, 33%). ¹H NMR (400 MHz, CDCl₃, 294 K): δ (ppm) 7.37–7.28 (m, 8H), 7.24–7.20 (m, 2H), 7.15-7.10 (m, 3H), 7.07-7.02 (m, 2H), 6.98 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, 294 K): δ (ppm) 143.41, 142.55, 140.33, 137.35, 130.37, 129.53, 128.62, 128.19, 128.15, 127.95, 127.60, 127.50, 127.40, 126.73. The NMR spectra were identical to those reported in the literature.³³ The isolation of Ph₂C=CHPh, rather than Ph₂C=CDPh,

indicates that Ph_2C =CHPh was formed before the quenching experiment.

Reaction of 1 with Phenyl Azide. To a stirring THF solution (5 mL) of 1 (150 mg, 0.2 mmol) was added PhN_3 (50 mg, 0.42 mmol) at room temperature. The color of the solution immediately changed to brown. After further stirring for 8 h, all the volatiles were removed under vacuum. The residue was then extracted with diethyl ether (5.0 mL) and filtered. Slow evaporation of diethyl ether afforded 6 as a brown, crystalline solid (121 mg, 65%). ¹H NMR (300 MHz, C₆D₆, 302 K): δ (ppm) 22.77 (br), 14.74 (br), 11.46 (br), 10.50 (br), 8.99 (br), 8.75 (br), 8.56 (br), 8.09 (br), 6.84 (br), 6.52 (br), 5.64 (br), 4.09 (br), 3.56 (br), 2.68 (br), -4.06 (br), -5.50 (br), -10.51 (br), -34.55 (br). The attempts to integrate the peaks did not result in a reasonable integration set. Anal. Calcd for C₆₃H₆₀FeN₈: C 76.82, H 6.14, N 11.38. Found: C 75.70, H 6.71, N 10.58. Magnetic susceptibility (C₆D₆, 302 K): $\mu_{\text{eff}} = 4.7(1) \ \mu$ B. Absorption spectrum $(C_6H_6): \lambda_{max}$ nm (ε , M⁻¹ cm⁻¹) = 374 (59 500), 449 (19 900). IR (KBr, cm⁻¹): ν = 3055 (w), 3023 (w), 2969 (w), 2938 (w), 2869 (w), 1593 (m), 1484 (w), 1440 (w), 1400 (w), 1350 (w), 1296 (w), 1260 (s), 1106 (w), 1072 (w), 1027 (w), 906 (w), 804 (w), 781 (w), 759 (w), 696 (s), 661 (w), 554 (w).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b00632.

Absorption, ⁵⁷Fe Mössbauer, and NMR spectra (PDF) X-ray crystallographic files in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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