ORGANOMETALLICS

High-Spin Iron(II) Alkynyl Complexes with N-Heterocyclic Carbene Ligation: Synthesis, Characterization, and Reactivity Study

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S Supporting Information

ABSTRACT: High-spin iron(II) alkynyl complexes $[(IPr_2Me_2)_2$ -Fe $(C \equiv CBu^t)_2]$ (1) and $[(IPr_2Me_2)_2$ Fe $(C \equiv CR)(NHMes)]$ (R = Bu^t 2, SiMe₃ 3) bearing a monodentate N-heterocyclic carbene ligand IPr_2Me_2 (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) have been prepared by salt metathesis and/or amine elimination methods and characterized by various spectroscopic methods. Complex 1 reacts with PMe₃ (4 equiv) and Bu^tNC (4 equiv) to form *trans*- $[(PMe_3)_4$ Fe $(C \equiv CBu^t)_2]$ (4) and $[\eta^3$ - $\{(Bu^tC \equiv C)-(Bu^t)CC(IPr_2Me_2)C(NBu^t)\}$ Fe $(NCBu^t)_3]$ (5), respectively. In contrast, the reactions of 1 with 4-Prⁱ-C₆H₄NCO and PrⁱNCNPrⁱ



lead to the formation of the zwitterionic salts 4-Pr^{*i*}-C₆H₄NC(O)(IPr₂Me₂) and (Pr^{*i*}N)₂C(IPr₂Me₂), respectively. The interaction of 1 with I₂ gives Bu^{*t*}C≡CC≡CBu^{*t*} and (IPr₂Me₂)₂FeI₂. The C(sp)−C(sp³) cross-coupling products n-C₈H₁₇C≡CBu^{*t*} and c-C₆H₁₁C≡CBu^{*t*} are formed in high yields when 1 is treated with the corresponding alkyl halides n-C₈H₁₇X and c-C₆H₁₁X (X = Br, Cl). The formation of the ring-opening product 7,7-dimethyloct-1-en-5-yne in the reaction of 1 with cyclopropylmethyl bromide supports the radical character of the cross-coupling reaction.

INTRODUCTION

The study of transition-metal alkynyl complexes represents a research area of great interest due to the roles of these species as key intermediates in metal-catalyzed organic transformations and their use as molecular wires and optoelectronic materials.¹ Iron alkynyl compounds are representative examples, but mostly involve ancillary ligands such as phosphine, cyclo-pentadienyl, and CO.^{1b,2} With the strong field provided by these ligands, iron alkynyl compounds are usually coordinatively saturated and in the low-spin states. As for coordinatively unsaturated iron alkynyl complexes, there are only a handful of examples, which include the cube-type compounds $[(\mu_3$ - $Et_3PN)_4Fe_4(C \equiv CSiMe_3)_4]^3$ and $[(\mu_3-Bu_3^tSiS)_4Fe_4(C \equiv CSi Bu_{3}^{t}_{4}$],⁴ three-coordinate complexes [(nacnac)Fe(C \equiv CR)] (nacnac = $(2,6-Pr_{2}^{i}C_{6}H_{3})NC(Bu^{t})CHC(Bu^{t})N(2,6-Pr_{2}^{i}C_{6}H_{3});$ R = Ph, SiMe₃)⁵ and [$(2,6-(2',6'-Pr_{2}^{i}C_{6}H_{3})_{2}C_{6}H_{3})Fe(C \equiv CBu^{t})_{2}Li(THF)_{2}$],⁶ trisphosphine-supported complexes [(HB- $(C_6H_4-o-PPr_2^i)_3)$ Fe $(C \equiv CAr)$] (Ar = Ph, p-tolyl),⁷ and a bulky alkynyl complex, $[Fe(C \equiv CC_6H_3 - 2, 6 - (SiMe_3)_2)_4Li_2(THF)_2]$. Given the scarcity of this type of complex, the chemistry of coordinatively unsaturated iron alkynyl compounds remains poorly understood. Recently, we and others have found that Nheterocyclic carbenes (NHCs) can serve as excellent ancillary ligands to support three- and four-coordinate iron(II) alkyl, aryl, and amido complexes.^{9,10} The success then prompted us to study iron(II) alkynyl complexes with NHC ligation. Herein, we report the synthesis and characterization of the fourcoordinate iron(II) alkynyl complexes [(IPr₂Me₂)₂Fe(C≡ $(\operatorname{CBu}^{t})_{2}$ (1) and $[(\operatorname{IPr}_{2}\operatorname{Me}_{2})_{2}\operatorname{Fe}(\operatorname{C} \equiv \operatorname{CR})(\operatorname{NHMes})]$ (R =

Bu^t, 2; SiMe₃, 3), as well as the reactivity of 1 toward unsaturated organic substrates, oxidants, and alkyl halides.

RESULTS AND DISCUSSION

Preparation and Characterization of Iron(II) Alkynyl **Complexes.** Iron(II) dialkynyl complex $[(IPr_2Me_2)_2Fe(C \equiv$ $(\operatorname{Bu}^t)_2$ (1) can be prepared by a salt metathesis method. Treatment of $[(\operatorname{IPr}_2\operatorname{Me}_2)_2\operatorname{FeCl}_2]^{10a}$ with 2 equiv of $\operatorname{LiC} \cong \operatorname{CBu}^t$ in THF gave a pale green solution. After workup, 1 was isolated as green crystals in 82% yield (Scheme 1). Alternatively, 1 was prepared in 41% isolated yield by elimination of MesNH₂ from $[(IPr_2Me_2)_2Fe(NHMes)_2]^{10h}$ in C_6H_6 using 8 equiv of HC= CBu^t. For the amine elimination method, the use of a large excess of the alkyne is necessary, as the reaction with 2 equiv of $HC \equiv CBu^{t}$ resulted in a mixture of 1, the monoalkynyl complex $[(IPr_2Me_2)_2Fe(C \equiv CBu^t)(NHMes)]$ (2), and the unreacted $[(IPr_2Me_2)_2Fe(NHMes)_2]$. Attempts to prepare $(IPr_2Me_2)_2Fe(C \equiv CSiMe_3)_2$ via either salt metathesis or amine elimination reaction were unsuccessful. However, the amine elimination method produced the monoalkynyl complex $[(IPr_2Me_2)_2Fe(C \equiv CSiMe_3)(NHMes)]$ (3) as pale yellow crystals in 18% yield (Scheme 1). Both methods were also applied to the synthesis of $(IPr_2Me_2)_2Fe(C \equiv CPh)_2$. Unfortunately, these attempts generally yielded intractable brown mixtures.

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Scheme 1. Preparation of the Iron(II) Alkynyl Complexes



Complex 1 was characterized by ¹H NMR spectroscopy, solution magnetic susceptibility, IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction study. The ¹H NMR spectrum of 1 in THF- d_8 shows three paramagnetically shifted broad signals in the range +24 to +16 ppm. After standing at room temperature for 24 h, the ¹H NMR signals corresponding to the free NHC ligand appear, indicating the dissociation of IPr₂Me₂.¹¹ The solution magnetic moment of 1 measured by Evans' method is 5.1(1) μ B, which corroborates a high-spin *S* = 2 electronic configuration.¹² The ⁵⁷Fe Mössbauer spectrum of 1 measured at 80 K features a quadrupole doublet (Figure 1) with the fitting isomer shift (δ = 0.52 mm/s) and the



Figure 1. Zero-field ⁵⁷Fe Mössbauer spectra of $[(IPr_2Me_2)_2Fe(C \equiv CBu')_2]$ (1, a), $[(IPr_2Me_2)_2Fe(C \equiv CBu')(NHMes)]$ (2, b), $[(IPr_2Me_2)_2Fe(NHMes)_2]$ (c), and $[(IEt_2Me_2)_2Fe(CH_2SiMe_3)_2]$ (d),^{10m} recorded at 80 K.

quadrupole splitting ($\Delta E_Q = 2.44 \text{ mm/s}$), which are close to those of the iron(II) dialkyl complex [(IPr_2Me_2)₂FePh₂]¹⁰¹ ($\delta = 0.47 \text{ mm/s}$, $\Delta E_Q = 2.38 \text{ mm/s}$) and [(IEt_2Me_2)₂Fe-(CH₂SiMe₃)₂]^{10m} ($\delta = 0.49 \text{ mm/s}$, $\Delta E_Q = 2.53 \text{ mm/s}$). Table 1 compiles these data for comparison.

The molecular structure of 1 established by a single-crystal X-ray diffraction study is shown in Figure 2. Its FeC_4 core displays distorted tetrahedral geometry, with the C-Fe-C angles varying from $103.12(10)^\circ$ to $118.39(11)^\circ$. The Fe-C(alkynyl) distances (2.049(3) and 2.052(3) Å) are longer

Table 1. Zero-Field ⁵⁷Fe Mössbauer Data of Selected Iron(II) Complexes Measured at 80 K

complex	$\delta~({ m mm/s})$	$\Delta E_{\rm Q} ({\rm mm/s})$
$[(IPr_2Me_2)_2Fe(C \equiv CBu^t)_2]$	0.52	2.44
$[(IPr_2Me_2)_2Fe(C \equiv CBu^t)(NHMes)]$	0.61	2.55
[(IPr ₂ Me ₂) ₂ Fe (NHMes) ₂]	0.72	2.54
$[(IPr_2Me_2)_2FeI_2]$	0.71	2.98
$[(\mathrm{IPr}_2\mathrm{Me}_2)_2\mathrm{FePh}_2]^a$	0.47	2.38
$[(\mathrm{IEt}_2\mathrm{Me}_2)_2\mathrm{Fe}(\mathrm{CH}_2\mathrm{SiMe}_3)_2]^b$	0.49	2.53
^a Data from ref 10l. ^b Data from ref 10m		



Figure 2. Molecular structure of 1 showing 30% probability ellipsoids and the partial atom-numbering scheme. Selected bond distances (Å) and angles (deg): Fe(1)-C(1) 2.128(2), Fe(1)-C(2) 2.144(3), Fe(1)-C(3) 2.049(3), Fe(1)-C(4) 2.052(3), C(3)-C(10) 1.223(4), C(4)-C(5) 1.194(4); C(1)-Fe(1)-C(2) 108.22(10), C(3)-Fe(1)-C(4) 118.39(11), Fe(1)-C(3)-C(10) 179.1(3), Fe(1)-C(4)-C(5) 175.6(2).

than those in the reported high-spin four-coordinate complexes $[(\mu_3\text{-}\text{Et}_3\text{PN})_4\text{Fe}_4(\text{C}\equiv\text{CSiMe}_3)_4]$ (1.99 Å),³ $[(\mu_3\text{-}\text{Bu}_3^*\text{SiS})_4\text{-}\text{Fe}_4(\text{C}\equiv\text{CSiBu}_3^*)_4]$ (2.00 Å),⁴ and $[(\text{HB}(\text{C}_6\text{H}_4\text{-}o\text{-}\text{PPr}_2^i)_3)\text{Fe}(\text{C}\equiv\text{Ctolyl-}p)]$ (1.92 Å).⁶ The long Fe–C(alkynyl) bonds could be attributed to the strong σ -donating property of NHCs.¹³ Compared to the Fe–C(Ph) bonds in [bis(NHC)-FePh_2] (2.08 Å on average)^{10k} and the Fe–C(alkyl) bonds in $[(\text{IEt}_2\text{Me}_2)_2\text{Fe}(\text{CH}_2\text{SiMe}_3)_2]$ (2.11 Å on average),^{10a} the Fe–C(alkynyl) bonds in 1 are shorter. The C(alkynyl)–C(alkynyl) distances (1.194(4) and 1.223(4) Å) in 1 are typical of C–C triple bonds observed in the reported high-spin iron(II) alkynyl complexes.^{3–7} The Fe–C(carbene) distances (2.128(2) and 2.144(3) Å) are comparable to those reported for iron(II) alkyl complexes, e.g., 2.132(3) and 2.140(3) Å in [(\text{IEt}_2\text{Me}_2)_2\text{Fe}(\text{CH}_3)_2] and 2.160(4) and 2.140(4) Å in [(\text{IEt}_2\text{Me}_2)_2\text{Fe}(\text{CH}_2\text{SiMe}_3)_2].^{10a}

To probe the electronic structure of the alkynyl complex, density functional theory¹⁴ calculation at the B3LYP level¹⁵ (TZVP/SVP,¹⁶ S = 2) based on the molecular structure of **1** established by X-ray diffraction (XRD) has been performed.¹⁷ The calculation revealed that its highest five occupied frontier UHF natural orbitals (UNOs 160–156) are mainly composed of the iron atom's 3d orbitals, with four of them being singly occupied (Figure S1). The dominant metal–ligand interaction is the σ -type interaction between the lone pairs of alkynyl ligands and the iron center's 4s orbital (Figure S2). In addition, a weak π -interaction that occurs between the filled π orbital of the C–C triple bond and the iron atom's 4p orbital is noticed

(Figure S3). The sum of these interactions leads to Mayer bond orders of 0.60 and 0.83 for the Fe–C(carbene) and Fe– C(alkynyl) bonds, respectively. The bond order of the Fe– C(carbene) bonds (0.60) is smaller than that of their congeners (0.85 and 0.88) in the cyclometalated square planar iron(II)-NHC complex [(IMes')Fe(IMes-Si)] with an S = 1 spin state (IMes' and IMes-Si denoting a cyclometalated IMes ligand and a bidentate NHC-silyl ligand, respectively).¹⁰ⁱ Meanwhile, the bond order of the Fe–C(alkynyl) bonds (0.83) is larger than that of the Fe–C(benzyl) bond in [(IMes')Fe(IMes-Si)] (0.73). The difference in these bond orders suggests that the NHC ligands can readily dissociate in the four-coordinate alkynyl complex.

Complexes 2 and 3 were characterized by ¹H NMR spectroscopy, solution magnetic susceptibility, IR spectroscopy, and elemental analysis. The molecular structure of 3 was further established by a single-crystal X-ray diffraction study. The ¹H NMR spectra of 2 and 3 in C₆D₆ show 12 paramagnetically shifted broad signals, suggesting the restricted rotation of the NHC ligands. Their solution magnetic moments (5.0(1) and4.9(1) μ B, respectively) are indicative of a high-spin nature.¹² For comparison, the ⁵⁷Fe Mössbauer spectrum of 2 was recorded (Figure 1). The isomer shift ($\delta = 0.61 \text{ mm/s}$) of its quadrupole doublet is located between that of 1 ($\delta = 0.52 \text{ mm}/$ s) and the dianilido complex $[(IPr_2Me_2)_2Fe(NHMes)_2]$ ($\delta =$ 0.72 mm/s) (Table 1). The gradual decreasing isomer shift going from $[(IPr_2Me_2)_2Fe(NHMes)_2]$ to 2 and to 1 reflects the higher covalency of the Fe-C(alkynyl) bond versus the Fe-N(anilido) bond.

The molecular structure of 3 established by an X-ray diffraction study is shown in Figure 3. The molecule has a



Figure 3. Molecular structure of 3, showing 30% probability ellipsoids and the partial atom-numbering scheme. Selected bond distances (Å) and angles (deg): Fe(1)-N(1) 1.979(2), Fe(1)-C(1) 2.153(2), Fe(1)-C(2) 2.096(2), Fe(1)-C(3) 2.130(2), C(2)-C(33) 1.199(3); N(1)-Fe(1)-C(2) 124.91(8), N(1)-Fe(1)-C(3) 113.72(8), C(2)-Fe(1)-C(3) 104.01(8), N(1)-Fe(1)-C(1) 98.46(8), C(2)-Fe(1)-C(1) 112.68(9), C(3)-Fe(1)-C(1) 100.65(8).

severely distorted tetrahedral FeC₃N core with the angles around the iron center ranging from 98.46(8)° to 124.91(8)° (Figure 3). The Fe–C(carbene) (2.153(2) and 2.130(2) Å), Fe–N(anilido) (1.979(2) Å), and C(alkynyl)–C(alkynyl) (1.199(3) Å) distances are typical of four-coordinate high-spin iron(II) species, and its Fe–C(alkynyl) bond (2.096(2) Å) is apparently longer than those of the aforementioned high-spin iron(II) alkynyl complexes.^{3–7}

Reactions of 1 with PMe₃ and Bu^tNC. With the dialkynyliron(II) complex $[(IPr_2Me_2)_2Fe(C \equiv CBu^t)_2]$ in hand, we subsequently examined its reactions with phosphines, unsaturated organic substrates, and organic halides. Treatment of **1** with 4 equiv of PMe₃ in benzene yielded a pale yellow solution immediately, from which the diamagnetic complex $[trans-(PMe_3)_4Fe(C \equiv CBu^t)_2]$ (4) was isolated as a yellow crystalline solid in 55% yield (Scheme 2). The ³¹P NMR

Scheme 2. Reactions of 1 with PMe₃ and Bu^tNC



spectrum of the reaction mixture shows only one signal at 22.11 ppm. The molecular structure established by XRD revealed a *trans*-configuration for the two alkynyl groups (Figure S4), which is similar to those of the reported six-coordinate iron(II) alkynyl complexes with phosphine ligation, e.g., [*trans*-(PMe₃)₄Fe(C≡CSiMe₃)₂]¹⁸ and [*trans*-(depe)₂Fe(C≡CPh)₂] (depe = 1,2-bis(diethylphosphino)ethane).^{2a} In contrast to the reaction with PMe₃, complex 1 is inert toward PPh₃.

Complex 1 can readily react with Bu^tNC (4 equiv) to produce yellow diamagnetic compound 5 (Scheme 2). Crystal structure determination revealed its structure as an iron(0)complex bearing three Bu^tNC ligands and one zwitterionic vinyliminacyl ligand η^3 -{(Bu^tC=C)(Bu^t)CC(IPr₂Me₂)CNBu^t} with Fe-C(1), Fe-C(2), and Fe-C(3) distances of 2.1192(14), 2.0025(13), and 1.9364(14) Å, respectively (Figure 4). The two C–C bonds in the allylic backbone have similar bond distances (1.4648(19) and 1.4594(19) Å). The terminal alkynyl moiety connected to C(1) has C(26)-C(27)and C(26)-C(1) distances of 1.204(2) and 1.451(2) Å, respectively, implying their localized triple- and single-bond feature. The imidazolium moiety is bonded to the central carbon atom C(2) of the allylic moiety, and its five-membered plane forms a dihedral angle of 75.3° with the C(1)-C(2)-C(3) plane. Both bent and linear geometries are observed for the Bu^tNC ligands, with the C-N bond distances in the two bent Bu^tNC ligands (1.1982(19) and 1.1934(19) Å) being longer than that of the linear one (1.1682(19) Å). In accord with these structure features, its infrared resonance spectrum shows four resonances at 2161, 2112, 2040, and 1860 cm⁻¹. Complex 5 was characterized by ¹H and ¹³C NMR spectroscopy. Three ¹³C NMR signals appearing at +205.6, +206.5, and +211.1 ppm further prove the presence of three Bu^tNC ligands in the complex. One possible route explaining the formation of 5 is shown in Scheme 3. Complex 1 might initially react with four *tert*-butyl isocyanide molecules to afford *cis*-(Bu^tNC)₄Fe- $(C \equiv CBu^{t})_{2}$ (A). While the attempts to isolate intermediate A were unsuccessful, the analogous complex cis-[(Bu^tNC)₄Fe-(CN)₂] is known.¹⁹ Intermediate A undergoes migratory insertion to produce iron vinylidene species B.20 This



Figure 4. Molecular structure of **5**, showing 30% probability ellipsoids and the partial atom-numbering scheme. For simplicity, all the methyl groups on the Bu^t moieties have been removed. Selected bond distances (Å) and angles (deg): Fe(1)–C(1) 2.1192(14), Fe(1)–C(2) 2.0025(13), Fe(1)–C(3) 1.9364(14), Fe(1)–C(4) 1.7926(15), Fe(1)–C(5) 1.8338(15), Fe(1)–C(6) 1.8245 (15), N(1)–C(3) 1.2726(18), N(2)–C(4) 1.1982(19), N(3)–C(5) 1.1682(19), N(4)–C(6) 1.1934(19), C(26)–C(27) 1.204(2), C(1)–C(2) 1.4648(19), C(2)–C(3) 1.4594(19); C(1)–Fe(1)–C(6) 93.07(6), C(1)–Fe(1)–C(2) 41.52(5), C(3)–Fe(1)–C(2) 43.45(6), C(3)– Fe(1)–C(4) 94.60(6), C(6)–Fe(1)–C(5) 94.78(6), C(4)–Fe(1)– C(5) 95.82(6), C(3)–N(1)–C(22) 122.15(12), C(4)–N(2)–C(32) 141.40(15), C(5)–N(3)–C(40) 178.21(16), C(6)–N(4)–C(36) 137.99(15).

Scheme 3. Possible Pathway for the Formation of 5



intermediate can undergo further migratory insertion reaction of the Fe=C bond toward the isocyanide to yield C.²¹ The migration of the $(Bu^tC\equiv N)_3$ Fe fragment along the cummulene chain on C then gives D. One released NHC attacks the C=C bond of D to give E, which can isomerize to 5.

Reactions of 1 with 4-Prⁱ-C₆H₄NCO and PrⁱNCNPrⁱ. To further examine the reactivity of the Fe(II)–C(alkynyl) bonds of 1, the reactions of 1 with other unsaturated organic substrates were investigated. Complex 1 is inert toward benzonitrile and 3-hexyne, whereas its reactions with 4-Prⁱ-C₆H₄NCO and PrⁱNCNPrⁱ lead to the isolation of 4-Prⁱ-C₆H₄NC(O)(IPr₂Me₂) (6) and (PrⁱN)₂C(IPr₂Me₂) (7),

respectively, as colorless crystals in 47% and 54% yields, respectively (Scheme 4).²² Compounds 6 and 7 were

Scheme 4. Reactions of 1 with 4-Prⁱ-C₆H₄NCO and PrⁱNCNPrⁱ



characterized by ¹H and ¹³C NMR spectroscopy and HRMS. The formation of the NHC adducts is in stark contrast to that of $[(IPr_2Me_2)Fe(Mes)_2]$ with Pr^iNCNPr^i , wherein the insertion of the carbodiimide into an Fe-C(aryl) bond took place to afford $[(IPr_2Me_2)Fe(Pr^iNCMesNPr^i)(Mes)]$.^{10a} The reactivity difference described here, together with NHC-dissociation behavior and the lower Fe-C(carbene) bond order, highlights the lability of the Fe-C(carbene) bonds in **1**. The reactions of **1** with a large excess of isocyanate and the carbodiimide afforded ill-defined oily materials.

Thermal- and Oxidation-Induced Decomposition of 1. Carbon–carbon bond-forming reductive elimination is a wellestablished reactivity for closed-shell diorganyl transition-metal species,²³ but has remained poorly understood for open-shell complexes.¹⁰¹ To probe the potential of 1 to undergo C(alkynyl)-C(alkynyl) reductive elimination, its thermal- and oxidation-induced decomposition reactions were studied.

The C_6D_6 solution of 1 is stable at room temperature, but decomposes slowly at 50 °C. Heating the solution at 80 °C for 5 h leads to the full decomposition. However, gas chromatography-mass spectroscopy (GC-MS) analysis of the hydrolyzed solution did not reveal the formation of the coupling product $Bu^tC \equiv CC \equiv CBu^t$, suggesting the difficulty of 1 to undergo thermal-induced C(sp)-C(sp) reductive elimination. Although no $Bu^tC \equiv CC \equiv CBu^t$ was detected in the reaction of 1 with [Cp₂Fe][BAr^F₄] (1 equiv), GC-MS analysis indicated the formation of ferrocene. Attempts to identify the resulting iron-containing products were unsuccessful. The outcome of the oxidation reaction differs from that of the one-electron oxidation reaction of [(bpy)₂FeR₂] (bpy = 2,2'-bipyridine; R = Et, Pr^n , Bu^n), where a small amount of alkyl-alkyl coupling products was detected.^{23b} However, it should be mentioned that the observed difference does not necessarily reflect the unique reactivity of high-spin iron alkynyl species, as the system might be complicated by the redox reaction of a ferrocenium cation with an NHC.²

In contrast to the above reactions, the interaction of 1 with 1 equiv of iodine in THF affords $Bu^tC \equiv CC \equiv CBu^t$ and $(IPr_2Me_2)_2FeI_2$ in high yields (Scheme 5). The composition of $(IPr_2Me_2)_2FeI_2$ has been confirmed by elemental analysis, and its fitting ⁵⁷Fe Mössbauer parameters ($\delta = 0.71 \text{ mm/s}, \Delta E_Q$ = 2.98 mm/s) (Figure S5) are found close to those of the tetrahedral iron(II) diiodide supported by a methylene-bridged bis(NHC) ligand ($\delta = 0.70 \text{ mm/s}, \Delta E_Q = 3.74 \text{ mm/s}$).^{10c} Closely following the reaction by GC-MS indicates the involvement of the alkynyl iodide $Bu^tC \equiv CI$ as an intermediate in the early stage of the reaction. As the reaction proceeds, the amount of $Bu^tC \equiv CI$ decreases, while that of $Bu^tC \equiv CC \equiv$ Scheme 5. Reaction of 1 with Iodine and Its Possible Route



CBu^t increases. Figure S6 depicts the change in the amounts of Bu^tC \equiv CI and Bu^tC \equiv CC \equiv CBu^t versus time. These observations point out a stepwise reaction mechanism for the formation of Bu^tC \equiv CC \equiv CBu^t (Scheme 5), in which the reaction between the plausible intermediate (IPr₂Me₂)₂Fe(C \equiv CR)I and Bu^tC \equiv CC \equiv CBu^t. Whether an oxidative addition-reductive elimination mechanism, a radical-type mechanism, or a σ -bond metathesis one is involved in the conversion remains unknown to us at the moment.

Reactions of 1 with Alkyl Halides. Iron alkynyl complexes have been proposed as key intermediates in iron-catalyzed cross-couplings of alkynyl Grignard reagents with alkyl halides.²⁵ However, the exact nature of iron-alkynyl intermediates, e.g., the metal center's oxidation state and the reactivity of iron alkynyl species toward alkyl halides, has not yet been fully established. To probe whether iron(II) alkynyl species can promote the cross-coupling reaction, the stoichiometric reactivity of **1** toward alkyl halides was been examined.

Complex 1 can react with both alkyl bromides and chlorides to afford cross-coupling products.²⁶ The interaction of 1 with 1 equiv of n-C₈H₁₇Br or c-C₆H₁₁Br in benzene at room temperature produced a brown solution. After 12 h, GC-MS analysis of the quenched solution indicated the full consumption of the organic halides and the formation of the cross-coupling products n-C₈H₁₇C \equiv CBu^t and c-C₆H₁₁C \equiv CBu^t in 95% and 96% yields, respectively (entries 1 and 2 in Table 2). Analyzing the ¹H NMR spectrum of the resulting

Table 2. Reactions of 1 with Alkyl Halides^a

<u>т</u> 1

R-X		→ R-	Bu ^t +	alkane +	- alkene
	С ₆ н ₆ , temp., t	ime	Е	F	G
		GC yield of			
entry	R-X	temp	$time^{b}$ (h)	E	F and G
1	n-C ₈ H ₁₇ Br	rt	12	95%	5%
2	c-C ₆ H ₁₁ Br	rt	12	96%	4%
3	n-C ₈ H ₁₇ Cl	60 °C	12	83%	17%
4	c-C ₆ H ₁₁ Cl	60 °C	12	74%	22%

^{*a*}[(IPr_2Me_2)₂Fe(CCBu^{*i*})₂] (1, 0.10 mmol) and halides (0.10 mmol) in C₆H₆ (1 mL) at 30 °C with *n*-dodecane (0.10 mmol) as the internal standard,. ^{*b*}Time required for the full conversions of the halides.

mixture (the reaction 1 with n- $C_8H_{17}Br$) indicates the formation of a new paramagnetic species along with small amounts of $(IPr_2Me_2)_2FeBr_2$ and 1. The ¹H NMR peak pattern of this unknown paramagnetic species is similar to that of $(IPr_2Me_2)_2Fe(C \equiv CBu^t)I$, suggesting it might be $(IPr_2Me_2)_2$ -Fe $(C \equiv CBu^t)Br$ (Figure S7). The reaction of 1 with the radical

clock reagent cyclopropylmethylene bromide revealed the radical character of the C–Br bond-cleavage step²⁷ supported by the formation of the ring-opening product 7,7-dimethyloct-1-en-5-yne (Scheme 6).

Scheme 6. Reaction of 1 with Cyclopropylmethyl Bromide



Compared to the reactions with organic bromides, the reactions of 1 with the alkyl chlorides $n-C_8H_{17}Cl$ and $c-C_6H_{11}Cl$ proceeded more slowly at room temperature.²⁸ The full consumption of the organic chlorides was achieved after heating the mixtures at 60 °C for 12 h, and the cross-coupling products $n-C_8H_{17}C\equiv CBu^t$ and $c-C_6H_{11}C\equiv CBu^t$ were detected in 83% and 74% GC yields, respectively (entries 3 and 4). These transformations thus established the capability of high-spin iron(II) alkynyl species to promote cross-coupling reactions with alkyl halides.

CONCLUSION

In this study, we have accomplished the synthesis, characterization, and reactivity study of high-spin iron(II) alkynyl complexes with NHC ligation. The salt metathesis reaction of $[(IPr_2Me_2)_2FeCl_2]$ with 2 equiv of LiC=CBu^t leads to the formation of the dialkynyl complex $[(IPr_2Me_2)_2Fe(C=CBu^t)_2]$ in high yield. On the other hand, the amine elimination reactions of $[(IPr_2Me_2)_2Fe(NHMes)_2]$ with a large excess of HC=CBu^t or HC=CSiMe_3 produce the iron(II) monoalkynyl complexes $[(IPr_2Me_2)_2Fe(C=CR)(NHMes)]$ (R = Bu^t or SiMe_3). Characterization data obtained from solution magnetic susceptibility measurement, ⁵⁷Fe Mössbauer spectroscopy, and single-crystal X-ray diffraction studies confirm the high-spin nature (S = 2) of the four-coordinate iron(II) complexes. DFT calculation reveals both σ - and π -donating nature of the alkynyl groups in the dialkynyl iron(II) species.

Reactivity studies of $[(IPr_2Me_2)_2Fe(C \equiv CBu^t)_2]$ have disclosed its ligand-substitution reaction with PMe₃ to form *trans*- $[(PMe_3)_4Fe(C \equiv CBu^t)_2]$, its reaction with Bu^tNC (4 equiv) to produce the iron(0) complex $[\eta^3-\{(Bu^tCC)(Bu^t)-CC(IPr_2Me_2)C(NBu^t)\}Fe(NCBu^t)_3]$, the reactions with isocyanate and carbodiimide to form the adducts of IPr_2Me_2 with the polar unsaturated substrates as zwitterionic salts, and its reactions with 1 equiv of iodine, $n-C_8H_{17}X$, and $c-C_6H_{11}X$ (X = Br, Cl) to furnish Bu^tC = C-C = CBu^t, $n-C_8H_{17}C = CBu^t$, and $c-C_6H_{11}C \equiv CBu^t$, respectively, along with iron(II) species. These conversions indicate (i) the tendency of the NHC ligand to dissociate from the high-spin iron(II) center and (ii) the capability of high-spin iron(II) alkynyl species to promote cross-coupling with alkyl halides.

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. Organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $[(IPr_2Me_2)_2FeCl_2]^{10a}$ and $[(IPr_2Me_2)_2FeCl_2]^{10b}$ were prepared according to our reported methods. All

chemicals were purchased from either Strem or J&K Chemical Co. and used as received unless otherwise noted. NMR spectra were recorded on a Varian Mercury 300 or 400 MHz spectrometer. Chemical shifts were reported in δ units with references to the residual protons of the deuterated solvents for proton chemical shifts, the ¹³C of deuterated solvents for carbon chemical shifts, and the ³¹P of phosphoric acid (85%) for phosphorus chemical shifts. GC-FID was performed on a Shimadzu GC-2014 spectrometer. GC-MS was performed on a Shimadzu GCMS-QP2010 Plus spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Magnetic moments were measured at 29 °C by the method originally described by Evans with stock and experimental solutions containing a known amount of a (CH₃)₃SiOSi-(CH₃)₃ standard.¹² IR spectra were recorded with a Nicolet Avatar 330 FT-IR spectrophotometer. The ⁵⁷Fe Mössbauer for samples were measured with a constant acceleration spectrometer at 80 K. Low temperature was maintained by a CCS-850 Mössbauer Cryostat system (Janis Research Company). Data were analyzed with MossWinn 4.0Pre (Provider: Beijing Shengtianjiayuan Keji Company). Isomer shifts are relative to iron metal at room temperature.

X-ray Structure Determinations. Crystallizations were performed at room temperature. Crystals were coated with Paratone-N oil and mounted on a Bruker APEX CCD-based diffractometer equipped with an Oxford low-temperature apparatus. Cell parameters were retrieved with SMART software and refined using SAINT software on all reflections. Data integration was performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS.²⁹ Space groups were assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP. All structures were solved and refined using SHELXTL.³⁰ Metal and first coordination sphere atoms were located from direct-methods Emaps; other non-hydrogen atoms were found in alternating difference Fourier synthesis and least-squares refinement cycles and during final cycles were refined anisotropically. Hydrogen atoms were placed in calculated positions employing a riding model. Final crystal parameters and agreement factors are reported in Table S1.

Computational Details. Density functional theory (DFT)¹⁴ studies have been performed with the ORCA 2.8 program¹⁷ using the B3LYP¹⁵ method. The SVP basis set^{16a} was used for the C, N, and H atoms, and the TZVP basis set^{16b} was used for the Fe atom. The RIJCOSX approximation³¹ with matching auxiliary basis sets^{16a,32} was employed to accelerate the calculation. TIGHTSCF was used for SCF calculation.³³ The single-point calculation on $[(IPr_2Me_2)_2Fe(C \equiv CBu^t)_2]$ (S = 2) was based on the coordinates obtained from an X-ray diffraction study without optimization.

Preparation of [(IPr₂Me₂)₂Fe(C=CBu^t)₂] (1). Method A: To a white suspension of [(IPr₂Me₂)FeCl₂] (1.44 g, 2.96 mmol) in THF (10 mL) was added a THF solution of LiC≡CBu^t, which was prepared in situ by the reaction of $HC \equiv CBu^t$ (694 mg, 8.44 mmol) and n-BuLi (5.92 mmol) at -78 °C in THF and stirred for 12 h. The color of the solution turned green during stirring. After removal of the solvent, the residue was extracted with diethyl ether $(20 \text{ mL} \times 3)$ and filtered. The filtrate was concentrated to about 40 mL, and *n*-hexane (5 mL) was added. Slow evaporation of diethyl ether afforded the product as green crystals. Yield: 1.40 g, 82%. ¹H NMR (600 MHz, THF- d_8): δ (ppm) 23.49 (9H, $\equiv CC(CH_3)_3$), 18.84 (12H, NCH(CH₃)₂), 16.53 (6H, =CCH₃). Anal. Calcd for $C_{34}H_{58}FeN_4$: C, 70.57; H, 10.10; N, 9.68. Found: C, 70.40; H, 10.19; N, 9.10. Magnetic susceptibility: μ_{eff} = 5.1(1) $\mu B.$ IR (KBr, $cm^{-1}):$ $\nu_{C\equiv C}$ 2060(w). Method B: To a pale yellow solution of [(IPr₂Me₂)₂Fe(NHMes)₂] (0.44 g, 0.64 mmol) in C_6H_6 (8 mL) was slowly added a solution of HC=CBu^t (0.42 g, 5.12) mmol) in C_6H_6 (5 mL) at room temperature. The mixture was stirred for 12 h. The color of the solution turned yellow-brown during stirring. After removal of the solvent under vacuum, the residue was extracted with *n*-hexane (10 mL \times 3). After filtration, some light green solid was left, which was then extracted with diethyl ether $(10 \text{ mL} \times 3)$ and filtered. The filtrate was concentrated to about 20 mL, and nhexane (5 mL) was added to the filtrate. Slow evaporation of diethyl ether afforded the product as green crystals. Yield: 0.15 g, 41%. The

product shows an identical ¹H NMR spectrum as that prepared via method A.

Preparation of [(IPr₂Me₂)₂Fe(C=CBu^t)(NHMes)] (2). To a pale yellow solution of [(IPr₂Me₂)₂Fe(NHMes)₂] (0.52 g, 0.76 mmol) in C_6H_6 (5 mL) was slowly added a solution of HC \equiv CBu^t (0.13 g, 1.52 mmol) in C_6H_6 (5 mL) at room temperature in 10 min. The color of the solution quickly turned yellow-brown. After stirring for 14 h and the removal of the solvent, the residue was extracted with *n*-hexane (10 $mL \times 3$) and filtered. The filtrate was concentrated to about 20 mL, and hexamethyldisiloxane (3 mL) was added. Slow evaporation of nhexane afforded the product as yellow crystals. Yield: 0.11 g, 36%. The ¹H NMR spectrum shows 12 peaks in the range +127 to +7 ppm, and satisfactory integration for these peaks has not been obtained. ¹H NMR (400 MHz, C₆D₆): δ (ppm) 126.75, 91.21, 81.16, 53.04, 45.51, 17.30, 13.45, 13.02, 11.76, 11.18, 9.08, 7.84. Anal. Calcd for C37H61FeN5: C, 70.34; H, 9.73; N, 11.09. Found: C, 70.26; H, 9.76; N, 11.45. Magnetic susceptibility: $\mu_{\text{eff}} = 5.0(1) \ \mu\text{B}$. IR (KBr, cm⁻¹): $\nu_{C\equiv C}$ 2058(w).

Preparation of [(IPr₂Me₂)₂Fe(C=CTMS)(NHMes)] (3). To a pale yellow solution of [(IPr₂Me₂)₂Fe(NHMes)₂] (0.14 g, 0.20 mmol) in C_6H_6 (5 mL) was slowly added a solution of HC \equiv CSiMe₃ (0.039 g, 0.40 mmol) in C_6H_6 (5 mL) at room temperature in 10 min. The color of the solution quickly turned yellow-brown. After stirring for 14 h and the removal of the solvent, the residue was extracted with nhexane $(5 \text{ mL} \times 3)$ and filtered. Some yellow solid was left and was extracted with diethyl ether $(5 \text{ mL} \times 3)$ and filtered. *n*-Hexane (3 mL)was added to the filtrate. Slow evaporation of diethyl ether afforded the product as yellow crystals. Yield: 0.017 g, 18%. ¹H NMR (400 MHz, C_6D_6 : δ (ppm) 131.67, 95.98, 81.26, 57.13, 45.59, 16.89, 12.82, 12.22, 10.22, 9.78, 9.14, 4.87. In addition to the peaks with their chemical shifts paralleling with those of 2, three minor peaks at 92.34, 55.64, and 17.47 ppm were also observed in the ¹H NMR spectrum of 3. The origin of these peaks is unknown yet. Even the sample that passed elemenal analysis still exhibits these peaks. Anal. Calcd for C36H61FeN5Si: C, 66.74; H, 9.49; N, 10.81. Found: C, 66.38; H, 9.35; N, 10.49. Magnetic susceptibility: $\mu_{\text{eff}} = 4.9(1) \ \mu\text{B}$. IR (KBr, cm⁻¹): $\nu_{C \equiv C}$ 2005(m).

Preparation of [(**PMe**₃)₄**Fe**(**C**≡**CBu**⁴)₂] (4). To a solution of [(IPr₂Me₂)₂Fe(C≡CBu⁴)₂] (0.23 g, 0.40 mmol) in C₆H₆ (5 mL) was added PMe₃ (0.12 g, 1.60 mmol) at room temperature. The color of the solution quickly turned pale yellow. After stirring for 14 h and removal of the solvent, the residue was extracted with *n*-hexane (3 mL) and filtered. Hexamethyldisiloxane (2 mL) was added to the filtrate. Slow evaporation of *n*-hexane afforded the product as yellow crystals. Yield: 0.11 g, 55%. Steric congestion renders the free rotation of the Fe−P bonds and the chemical nonequivalence of the methyl groups on the phosphine ligands. ¹H NMR (400 MHz, C₆D₆): δ (ppm) 1.52 (24H, P(CH₃)₃), 1.38 (12H, P(CH₃)₃), 1.36 (18H, ≡CC(CH₃)₃). ¹³C NMR (100 MHz, C₆D₆): δ (ppm) 119.31, 109.91, 33.05, 29.89, 21.57, 16.51. ³¹P NMR (121.4 MHz, C₆D₆): δ (ppm) 22.11. Anal. Calcd for C₂₄H₅₄FeP₄: C, 55.18; H, 10.42. Found: C, 55.06; H, 10.16. IR (KBr, cm⁻¹): ν_{C=C} 2056(m).

IR (KBr, cm⁻¹): $\nu_{C \equiv C}$ 2056(m). Preparation of $[\eta^3-{(Bu^tCC)(Bu^t)CC(IPr_2Me_2)C(NBu^t)}Fe$ -(NCBu^t)₃] (5). To a solution of $[(IPr_2Me_2)_2Fe(C \equiv CBu^t)_2]$ (0.23 g, 0.40 mmol) in C_6H_6 (5 mL) was added a solution of Bu^tNC (0.14 g, 1.60 mmol) in C_6H_6 (5 mL) at room temperature. The color of the solution quickly turned orange. After stirring for 16 h and the removal of the solvent, the residue was extracted with *n*-hexane (3 mL) and filtered. Hexamethyldisiloxane (2 mL) was added to the filtrate. Slow evaporation of *n*-hexane afforded the product as orange crystals. Yield: 0.15 g, 57%. ¹H NMR (400 MHz, C_6D_6): δ (ppm) 7.72 (sept, J = 6.8Hz, 1H, NCH), 5.94 (sept, J = 6.8 Hz, 1H, NCH), 1.86 (d, J = 6.8 Hz, 3H, NCH(CH₃)₂), 1.76 (s, 9H, C(CH₃)₃), 1.69 (s, 9H, C(CH₃)₃), 1.66 (s, 3H, =CCH₃), 1.64 (d, J = 7.6 Hz, 3H, NCH(CH₃)₂), 1.63 (s, $3H_{1} = CCH_{3}$, 1.62 (s, 9H, $CC(CH_{3})_{3}$), 1.54 (s, 9H, $C(CH_{3})_{3}$), 1.49 (d, J = 7.2 Hz, 3H, NCH(CH₃)₂), 1.43 (s, 9H, C(CH₃)₃), 1.41 (d, J = 7.2 Hz, 3H, NCH(CH₃)₂), 1.36 (s, 9H, C(CH₃)₃). ¹³C NMR (100 MHz, C₆D₆): δ (ppm) 211.12, 206.49, 205.58, 186.89, 150.97, 122.99, 122.34, 110.0, 93.49, 89.07, 55.51, 55.05, 54.93, 53.68, 50.15, 46.59, 41.90, 41.50, 32.47, 32.34, 32.32, 32.27, 31.56, 31.27, 28.22, 24.00,

23.02, 22.56, 21.92, 9.68, 9.48. Anal. Calcd for $C_{43}H_{74}FeN_6$: C, 70.66; H, 10.20; N, 11.50. Found: C, 70.42; H, 10.39; N, 11.79. IR (KBr, cm⁻¹): $\nu_{C \equiv C,C \equiv N}$ 1886, 2040, 2113, 2161.

Reaction of 1 with $4-Pr^{i}-C_{6}H_{4}NCO$. To a solution of $\lceil(IPr_2Me_2)_2Fe(C{\equiv}CBu^{f})_2\rceil$ (0.18 g, 0.30 mmol) in C_6H_6 (5 mL) was added 4-Prⁱ-C₆H₄NCO (0.10 g, 0.60 mmol) at room temperature. The color of the solution immediately turned red-brown and eventually turned yellow-brown after stirring for 12 h. After the removal of the solvent, the residue was extracted with diethyl ether (5 $mL \times 3$). After filtration, some white solid was left, and then the white solid was extracted with THF (5 mL \times 3) and filtered. The filtrate was concentrated to about 8 mL. Slow evaporation of THF afforded 4-Pri-C₆H₄NC(O)(IPr₂Me₂) (6) as colorless crystals. Yield: 0.096 g, 47%. ¹H NMR (400 MHz, C_6D_6): δ (ppm) 7.52 (d, J = 8.0 Hz, 2H, C_6H_4), 7.10 (d, J = 8.4 Hz, 2H, C_6H_4), 4.96 (sept, J = 6.8 Hz, 2H, NCH(CH₃)₂), 2.82 (sept, J = 6.8 Hz, 1H, C₆H₄CH(CH₃)₂), 2.22 (s, $6H_1 = CCH_3$, 1.58 (d, J = 7.2 Hz, 12H, NCH $(CH_3)_2$), 1.19 (d, J =7.2 Hz, 6H, $C_6H_4CH(CH_3)_2$). ¹³C NMR (100 MHz, THF- d_8): δ (ppm) 158.72, 153.24, 150.93, 142.99, 128.40, 128.04, 126.11, 54.47, 37.38, 27.56 (overlapping with THF signal), 23.94, 12.08. HRMS: calcd for $[C_{21}H_{31}N_3OH]^+$ 342.2545; found 342.2538. Attempts to

isolate the iron-containing species were unsuccessful. **Reaction of 1 with Pr^{i}NCNPr^{i}.** To a solution of $[(IPr_{2}Me_{2})_{2}Fe$ - $(C \equiv CBu^{t})_{2}$] (0.12 g, 0.20 mmol) in C₆H₆ (5 mL) was added a solution of Pr^iNCNPr^i (0.10 g, 0.80 mmol) in C_6H_6 (5 mL) at room temperature. The color of the solution quickly turned brown. After stirring for 12 h and removal of the solvent, the residue was extracted with *n*-hexane (3 mL \times 3). After filtration, some white solid was left, which was extracted with diethyl ether (5 mL \times 3) and filtered. The filtrate was concentrated to about 6 mL, and n-hexane (2 mL) was added. Slow evaporation of diethyl ether afforded $(Pr'N)_2C(IPr_2Me_2)$ (7) as colorless crystals. Yield: 0.033 g, 54%. ¹H NMR (400 MHz, C_6D_6 : δ (ppm) 5.08 (sept, J = 6.0 Hz, 1H, $CH(CH_3)_2$), 4.99 (sept, J= 7.2 Hz, 2H, $CH(CH_3)_2$), 2.93 (sept, J = 6.0 Hz, 1H, $CH(CH_3)_2$), 1.80 (d, J = 6.0 Hz, 6H, CH(CH₃)₂), 1.52 (s, 6H, =CCH₃), 1.50 (d, J= 7.2 Hz, 6H, CH(CH₃)₂), 1.25 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.07 (d, J = 7.2 Hz, 6H, CH(CH₃)₂). ¹³C NMR (100 MHz, C₆D₆): δ (ppm) 149.69, 148.33, 122.27, 51.79, 50.63, 46.75, 28.33, 25.05, 24.45, 20.86, 20.58, 9.20. HRMS: calcd for [C₁₈H₃₄N₄H]⁺ 307.2862; found 307.2861. The attempts to isolate the iron-containing species were unsuccessful.

Reaction of 1 with lodine. To a solution of $[(IPr_2Me_2)Fe(C \equiv$ $(CBu^{t})_{2}$ (0.174 g, 0.30 mmol) and *n*-dodecane (0.053 g, 0.31 mmol) in THF (2 mL) was added iodine (0.082 g, 0.32 mmol) at -78 °C. The mixture was allowed to warm to room temperature and stirred. A drop of the solution was withdrawn once every hour in the first 7 h and then every 2 h until 15 h. The aliquot was guenched by a saturated ammonium chloride aqueous solution. The quenched mixture was extracted with diethyl ether and separated. The organic phase was then dried over MgSO₄, analyzed by gas GC-MS to confirm the identity of the organic products, and further analyzed by GC with a flame ionization detector (GC-FID) to quantify the yields with n-dodecane as the internal standard. Figure S6 shows the yield change of $Bu^tC \equiv$ $CC \equiv CBu^t$ and $Bu^tC \equiv C-I$ versus time. The identity of the two organic products isolated from similar reaction without the addition of *n*-dodecane was further confirmed by NMR spectroscopy. For $Bu^{t}C \equiv$ CC=CBu^t:³⁴ ¹H NMR (400 MHz, CDCl₃): δ (ppm) 1.21 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 86.21 (C=CC(CH₃)₃), 63.62 (C \equiv CC(CH₃)₃), 30.56 (C(CH₃)₃), 27.92 (C(CH₃)₃). For Bu^tC \equiv C-I:³⁵¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.23 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 102.85, 30.77, 29.75, -8.05. The identity of the iron-containing product (IPr₂Me₂)₂FeI₂ was supported by ⁵⁷Fe Mössbauer spectroscopy characterization (Figure S5) and elemental analysis. For (IPr₂Me₂)₂FeI₂: Anal. Calcd for C22H40FeI2N4: C, 39.42; H, 6.02; N, 8.36. Found: C, 39.49; H, 6.12; N, 8.32.

General Procedure for Reactions of 1 with $n-C_8H_{17}X$ and $c-C_6H_{11}X$ (X = Br, Cl) and Cyclopropylmethyl Bromide. A dried Schlenk tube was charged with the alkyl halides (0.10 mmol), C_6H_6 (1.0 mL), *n*-dodecane (0.10 mmol), and 1 (0.10 mmol) in a glovebox

at room temperature. The reaction mixture was stirred and monitored by GC. For the alkyl bromides, the reactions proceeded smoothly at room temperature, and the color of the solution turned vellow-brown. For the alkyl chlorides, the reactions were heated to 60 °C. When the alkyl halides were consumed completely (determined by GC), part of the solution was withdrawn and guenched with a saturated ammonium chloride aqueous solution. The quenched mixture was extracted with dichloromethane and separated. The organic phase was then dried over MgSO₄, analyzed by GC-MS to confirm the identity of the products, and further analyzed by GC-FID to quantify the yields with *n*-dodecane as the internal standard. For the unquenched solution, the solvent was removed and the residue was redissolved in C₆D₆. ¹H NMR analysis revealed the characteristic ¹H NMR resonances for a new paramagnetic product, but attempts to isolate this complex failed. Table 1 tabulates the GC yields of the organic products. The identities of the cross-coupling products $n-C_8H_{17}C \equiv CBu^t$, $c-C_6H_{11}C \equiv CBu^t$, and $CH_2 = CHCH_2CH_2C \equiv CBu^t$ have been authenticated by comparing their NMR spectra to the reported ones. For n- $C_8H_{17}C \equiv CBu^{t;36}$ ¹H NMR (300 MHz, CDCl₃): δ (ppm) 2.11 (t, J = 6.9 Hz, 2H, ≡CCH₂), 1.50−1.22 (m, 12H, ≡CCH₂ (CH₂)₆), 1.18 (s, 9H, (CH₃)₃C≡), 0.87 (t, J = 6.9 Hz, 3H, CH₃CH₂). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 88.79, 78.43, 31.77, 31.33, 29.14, 29.03, 28.70, 27.22, 22.60, 18.59, 14.04. For c-C₆H₁₁C≡CBu^{t:³⁷ ¹H NMR (400} MHz, CDCl₃): δ (ppm) 2.33–2.28 (m, 1H, CH), 1.75–1.64 (m, 4H, CH₂), 1.51–1.25 (m, 6H, CH₂), 1.19 (s, 9H, C(CH₃)₃). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 88.94, 82.73, 33.19, 31.51, 30.58, 28.91, 27.23, 26.01, 24.80. For CH₂=CHCH₂CH₂C=CBu^t:³⁸ ¹H NMR (400 MHz, CDCl₃): δ (ppm) 5.89–5.78 (m, 1H, H₂C=CH), 5.06– 5.97 (m, 2H, H₂C=CH), 2.20 (m, 4H, =CHCH₂CH₂), 1.17 (s, 9H, C(CH₃)₃). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 137.25, 115.19, 89.43, 77.67, 33.52, 31.32, 27.27, 18.56. HRMS-EI: calcd for [C₁₀H₁₅]⁺ 135.1174; found 135.1178.

ASSOCIATED CONTENT

S Supporting Information

X-ray crystallographic files in CIF format, molecular structure of 4, the reaction profile of 1 with I₂, ⁵⁷Fe Mössbauer spectrum of $(IPr_2Me_2)_2FeI_2$, selected orbital graphs of $(IPr_2Me_2)Fe(C \equiv CBu')_2$, NMR spectra, and GC graphs of selected reactions. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00028.

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Notes

The authors declare no competing financial interest.

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