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Three-Coordinate Iron(0) Complexes with N-Heterocyclic Carbene and Vinyltrimethylsilane Ligation: Synthesis, Characterization, and **Ligand Substitution Reactions**

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Supporting Information

ABSTRACT: Low-coordinate iron(0) species are implicated as intermediates in a range of iron-catalyzed organic transformations. Isolable iron(0) complexes with coordination numbers of less than four, however, are rarely known. In continuing with our interests in three-coordinate iron(0) complexes with N-heterocyclic carbene (NHC) and alkene ligation, we report herein the synthesis and ligand substitution reactivity of three-coordinate iron(0) complexes featuring monodentate alkene ligands, $[(NHC)Fe(\eta^2-vtms)_2]$ (vtms = vinyltrimethylsilane, NHC = 1,3bis(2',6'-diisopropylphenyl)-imidazol-2-ylidene (IPr), 1; 1,3-bis(2',6'-diisopropylphenyl)-4,5-tetramethylene-imidazol-2-ylidene (cyIPr), 2; 1,3-bis(2',6'-diisopropylphenyl)-4,5,6,7-tetrahydro-1,3-diazepin-2-ylidene (7-IPr), 3). Complexes 1-3 were synthesized from the one-pot reactions of ferrous dihalides with the N-(2,6diisopropylphenyl)-substituted NHC ligands, vtms, and KC8. Reactivity study of 1 revealed its facile ligand substitution reactions with terminal aryl alkynes, ketones,



isocyanides, and CO, by which iron(0) complexes [(IPr)Fe(η^2 -HCCAr)] (Ar = Ph, 5; p-CH₃C₆H₄, 6; 3,5-(CF₃)₂C₆H₃, 7), $[(IPr)Fe(\eta^2 - OCPh_2)_2]$ (8), $[(IPr)Fe(CNR)_4]$ (R = 2,6-Me₂C₆H₃, 9; Bu^t, 10), and (IPr)Fe(CO)₄ (11) were prepared in good yields. These iron(0) complexes have been characterized by ¹H NMR, solution magnetic susceptibility measurement, singlecrystal X-ray diffraction study, ⁵⁷Fe Mössbauer spectroscopy, and elemental analysis. Characterization data and computational studies suggest S = 1 ground-spin states for three-coordinate iron(0) complexes 1–3 and 5–8 and S = 0 ground states for 9– 11. Theoretical studies on the three-coordinate complexes 1, 6, and 8 indicated pronounced metal-to-ligand backdonation from occupied Fe 3d orbitals to the π^* orbitals of the C=C, C=C, and C=O moieties of the π ligands. In addition, 1 proved an effective precatalyst for the cyclotrimerization reaction of alkynes.

INTRODUCTION

The renaissance of iron catalysis in the recent years has created great interest in iron(0) species with coordination unsaturation, which are considered as reactive intermediates in the iron-catalyzed reactions of alkyne cyclotrimerization, Diels-Alder reaction of dienes with alkynes, hydrogenation of alkenes and alkynes, and so on.¹⁻⁵ It is known from the literature that coordinatively unsaturated iron(0) complexes are amenable to C-H bond activation reactions. For example, the 16e⁻, fourcoordinate iron(0) complex $[Fe(PMe_3)_4]$ in solution phase is known to convert reversibly to the iron(II) complex [Fe- $(PMe_3)_3(CH_2PMe_2)H$] upon intramolecular $C(sp^3)$ -H bond oxidative addition reaction.⁶ Unsuccessful attempts to prepare the iron(0) species with N-heterocyclic carbene (NHC) ligation $Fe(IMes)_2^7$ [IMes = 1,3-bis(2',4',6'-trimethylphenyl)imidazol-2-ylidene] and $Fe(PMe_3)_2((^{Dipp}C:)_2CH_2)^8$ $[(^{\text{Dipp}}\text{C}:)_2\text{CH}_2 = \text{bis}(N-(2',6'-\text{diisopropylphenyl})-\text{imidazole-}2$ ylidene)methylene] via the reduction of their iron(II) precursors were also ascribed to the facile intramolecular C-H bond oxidative addition reactions of low-coordinate iron(0) species, wherein iron(II) complexes bearing cyclometalated IMes and phosphine ligands were obtained as the final products.

The aforementioned C-H bond activation reactions indicate the necessity of attenuating the strong reducing power of low-coordinate iron(0) species for the stabilization of low-coordinate iron(0) complex. In this regard, the combined ligand set of phosphine with alkene proved amenable to the task. Upon the reduction of ferrous salts in the presence of phosphine and alkene ligands, Hoberg,⁹ Jolly,¹⁰ Fürstner,^{11,12} and Breuil¹³ achieved syntheses of four-coordinate iron(0)complexes, e.g., $[(PEt_3)_2Fe(\eta^2-C_2H_4)_2]^9$, $[(dippp)Fe(\eta^2:\eta^2-C_2H_4)_2]^9$ $CH_2CHCH_2CH_2CH_2CHCH_2$],¹⁰ [(dippp)Fe(η^2 -C₂H₄)₂]¹¹ (dippp = 1,3-bis(diisopropylphosphino)propane), and $[(dppe)Fe(\eta^2:\eta^2-dvtms)]^{13}$ (dppe = 1,2-bis-(diphenylphosphino)ethane, dvtms = divinyltetramethyldisiloxane) (Chart 1). Reactivity studies showed that the alkene

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Chart 1. Examples of Low-Coordinate Iron(0)-Alkene Complexes



ligands in these four-coordinate iron(0) complexes can be replaced by CO, alkyne, and alkenes to form new iron(0) complexes.¹⁰⁻¹³ These iron(0) complexes are also known to perform reductive coupling reactions with substrates. For instance, $[(PEt_3)_2Fe(\eta^2-C_2H_4)_2]$ reacts with CO₂ and phosphine to give carboxylate compounds,⁹ and the interaction of $[(dippp)Fe(\eta^2-C_2H_4)_2]$ with cyclopropenone-1,3-propanediol ketal gives a ferracyclopentane derivative.¹² These fourcoordinate iron(0) complexes were also applied as catalysts for the cyclotrimerization of alkynes and heterocyclotrimerization of alkynes with nitriles.¹¹⁻¹³ Being analogous to bis-(phosphine)iron(0) diene complexes, four-coordinate iron complexes in the form of $(\alpha$ -diimine)Fe(diene) are also known.¹⁴ The redox noninnocent nature of α -diimine, however, might render these (α -diimine)-iron-alkene complexes electronically much different from the phosphineiron(0)-alkene complexes.

As a recent advance in the stabilization of low-coordinate iron(0) complexes, we found that the combined ligand set of NHC with alkene can effectively stabilize three-coordinate iron(0) complexes.¹⁵ Using the one-pot reaction of FeCl₂ with NHC, dvtms, and KC₈ or Na/Hg, the three-coordinate iron(0)complexes [(NHC)Fe($\eta^2:\eta^2$ -dvtms)] (NHC = IMes, 1,3bis(2',6'-diisopropylphenyl)imidazol-2-ylidene (IPr), 3,3,5,5tetramethyl-1-(2',6'-diisopropylphenyl)pyrrolidin-2-ylidene $(Me_2$ -cAAC)) (Chart 1) were synthesized in high yields.¹⁵ More recently, we found that the three-coordinate iron(0)complex bearing monodentate alkene ligands $[(IPr)Fe(\eta^2$ vtms)₂ (1, vtms = vinyltrimethylsilane, Chart 1) is also accessible by the one-pot reaction protocol.¹⁶ The monodentate nature of the alkene ligand in 1 hints at its lability over the bidentate dvtms ligand in [(NHC)Fe(η^2 : η^2 -dvtms)], which led to our further study. Herein, we report the synthetic efforts toward (NHC)Fe(η^2 -vtms)₂ using different NHC ligands, which led to the synthesis of two new three-coordinate iron(0)alkene complexes $[(NHC)Fe(\eta^2 - vtms)_2]$ (NHC = cyIPr, 2; 7-IPr, 3, Scheme 1) and more intriguingly the reactivity of the iron(0)-vtms complexes with that of $[(IPr)Fe(\eta^2-vtms)_2]$ (1) as the representative. The reactivity study disclosed facile ligand substitution reactions of 1 with terminal aryl alkynes, ketones, isocyanides, and CO to form new three- and fivecoordinate iron(0) complexes. In the case of reactions with alkynes, complex 1 has also proved effective in catalyzing alkyne cyclotrimerization.





RESULTS AND DISCUSSION

Synthesis and Characterization of [(NHC)Fe(η^2 **vtms**)₂]. The successful preparation of $[(IPr)Fe(\eta^2 - vtms)_2]$ (1) prompted us to investigate the accessibility of other NHC-iron(0)-vtms complexes. Examining the one-pot reaction of FeX_2 (X = Cl or Br) with different NHC ligands (1 equiv), vtms (5 equiv), and KC_8 (2 equiv) revealed that the reactions using the N-Dipp (Dipp = 2,6-diisopropylphenyl)substituted NHC ligands, cyIPr (1,3-bis(2',6'-diisopropylphenyl)-4,5-tetramethylene-imidazol-2-ylidene) and 7-IPr (1,3-bis-(2',6'-diisopropylphenyl)-4,5,6,7-tetrahydro-1,3-diazepin-2-ylidene) can furnish the desired iron(0) complexes [(cyIPr)Fe- $(\eta^2 \text{-vtms})_2$ (2) and $[(7 \text{-IPr})\text{Fe}(\eta^2 \text{-vtms})_2]$ (3) in 28 and 50% yields, respectively (Scheme 1). The isolated yields of these NHC-iron(0)-vtms complexes are lower than those (50-80%) of the NHC-iron(0)-dvtms complexes, which should be related to their decreased stability associated with the lability of the monodentate alkene ligand. In contrast to the accessibility of 1–3, the synthetic efforts toward (IMes)Fe(η^2 vtms)₂ using the one-pot reaction protocol was unsuccessful. The trial produced large amount of free IMes ligand (ca. 42% yield as quantified by ¹H NMR analysis using 1,3,5trimethoxybenzene as the internal standard), and attempts to isolate the desired iron(0) complex (IMes)Fe(η^2 -vtms)₂ upon recrystallization gave IMes as the only isolable crystalline solid. This outcome differs from the ready accessibility of [(IMes)- $Fe(\eta^2:\eta^2-dvtms)$].¹⁵ Similarly, the trial to prepare (IAd)Fe(η^2 $vtms)_2$ (IAd = 1,3-bisadamantylimidazol-2-ylidene) produced IAd as the major isolable compound, which again indicates the important role of the steric property of NHCs in the stabilization of (NHC)Fe(η^2 -vtms)₂. In addition to the use of KC₈ as reductant, we also attempted to prepare 1 using the one-pot reaction protocol with activated magnesium powder or sodium amalgam as reductant. The trial using activated magnesium can give the three-coordinate iron(0) complex in 35% isolated yield, whereas the reaction with sodium amalgam merely produced a trace amount of the iron(0) complex.

Complexes 2 and 3 have been characterized by ^IH NMR spectroscopy, elemental analysis, and ⁵⁷Fe Mössbauer spectroscopy. The molecular structure of 2 has been further confirmed by single-crystal X-ray diffraction study (Figure 1). The iron center in 2 displays a trigonal planar geometry, and its Fe-C(carbene), Fe-C(alkene), and C(alkene)-C(alkene) distances are comparable to the corresponding ones in 1. For comparison, Table 1 compiles the key interatomic distances and angles. As is characteristic for these three-coordinate NHC-iron(0)-alkene complexes, the Fe-C(carbene) distances in 1 and 2 are shorter than those of three-coordinate NHC-iron(II) complexes, e.g., [(IPr)Fe-(CH₂C₆H₅)₂] (2.122(2) Å)¹⁷ and [(IPr)Fe(NHDipp)₂]



Figure 1. Molecular structure of **2**, showing 30% probability ellipsoids and the partial atom numbering scheme. Hydrogen atoms are omitted for clarity.

(2.142(2) Å).¹⁸ As DFT calculation on (IPr)Fe(vtms)₂ indicated the backbonding from iron to IPr is weak (vide infra), the short Fe-C(carbene) distances might come from strong electrostatic interaction between NHC and Fe(vtms)₂ fragment in the three-coordinate iron complexes. Cavallo and co-workers showed that electrostatic contribution plays important role in the attractive interaction between NHC and metal center in some transition metal NHC complexes.¹ Further theoretic study is needed to disclose whether or not a similar situation exists in the low-coordinate iron complexes. Their C(alkene) – C(alkene) separations (1.414(4) - 1.431(2))Å) are remarkably longer than the C=C double bond in free vinylsilanes $(1.32 \text{ Å})^{20}$ Similar phenomena were also observed in low-valent iron(I)-alkene complexes [NaFe(trop2dae)- $(THF)_3$] (1.437(5) Å in average, trop = 5H-dibenzo[a,d]cyclohepten-5-yl, dae = N-CH₂CH₂N) and [LiFe(trop₂dae)-(Et₂O)₂] (1.416(9) Å in average).²¹ These structure features reflect the high covalency of the Fe-C interaction and pronounced Fe(0)-to-alkene π -backdonation in these NHCiron(0)-alkene complexes.¹

The zero-field ⁵⁷Fe Mössbauer spectra of **2** and **3** measured at 80 K feature single quadrupole doublets (Figure 2). Their fitting isomer shifts ($\delta = 0.39$ and 0.34 mm/s for **2** and **3**, respectively) and quadrupole splitting values ($|\Delta E_Q| = 2.92$ and



Figure 2. ⁵⁷Fe Mössbauer spectra (80 K zero-filed) of $[(cyIPr)Fe(\eta^2 vtms)_2]$ (2, top), $[(7-IPr)Fe(\eta^2 -vtms)_2]$ (3, middle), and (7-IPr)Fe($\eta^2 -vtms$) (4, bottom). The data (dots) and best fits (solid line) are shown. The fitting data are compiled in Table 2.

2.79 mm/s, respectively) are comparable to those of 1 (Table 2) and [(IMes)Fe($\eta^2:\eta^2$ -dvtms)] (δ = 0.40 mm/s, $|\Delta E_Q|$ = 3.02 mm/s),¹⁵ but they are distinct from those of the low-spin iron(0) complex Fe(CO)₅ (δ = -0.10 mm/s, $|\Delta E_Q|$ = 2.05 mm/s).²² As compared to those of the other three-coordinate iron complexes, the isomer shifts of 1–3 are found between those of the three-coordinate iron(II) complex [(IPr₂Me₂)Fe-

Гable 1.	Selected	Distances	(Å)	and	Angles	(deg)) of	the	Iron())	Complexes	Observed	from	XRD	Studies
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	F	ArN _C NAr	For (IMes)Fe(dvtms) For 1 and 2: X = C, r For 6 and 7: X = C, r For 8: X = O, n = 0;): X = C, n = 2; n = 2; n = 1;		
	[(IMes)Fe(dvtms)] ^a	1	2	6	7	8
Fe-C	2.030(2)	2.019(3)	2.033(2)	1.985(2)	1.990(2)	2.083(2)
	2.052(2)	2.033(3)	2.032(2)	1.936(2)	1.932(2)	1.859(1)
Fe-X	2.049(2)	2.035(3)	2.039(2)		1.937(2)	1.859(1)
T C	2.059(2)	2.049(3)	2.046(2)	1.956(2)	1.940(2)	2.078(2)
Fe-C _a	2.052(3)	2.044(3)	2.054(2)		1.943(2)	2.083(2)
X–C _a	1.425(4)	1.418(4)	1.431(2)	1.273(3)	1.274(3)	1.336(2)
	1.432(3)	1.414(4)	1.422(2)	1.273(3)	1.263(3)	1.336(2)
α^{b}	65.6	65.4	61.2	89.2	85.5	34.9

^{*a*}Data from ref 15. ^{*b*}Dihedral angle between the FeX2C_a2 plane and the carbene plane.

Table 2. Zero-Field ⁵⁷Fe Mössbauer Spectroscopic Data of 1–10 Measured at 80 K

	$\delta~({ m mm/s})$	$ \Delta E_{\rm Q} \ ({\rm mm/s})$		$\delta~({ m mm/s})$	$ \Delta E_{\rm Q} \ ({\rm mm/s})$
1	0.39	2.86	6	0.22	1.85
2	0.39	2.92	7	0.27	2.89
3	0.34	2.79	8	0.54	1.96
4	0.45	1.06	9	-0.11	1.21
5	0.29	3.15	10	-0.14	0.58

(Mes)₂] (δ = 0.30 mm/s, | ΔE_Q | = 1.38 mm/s, IPr₂Me₂ = 1,3isopropyl-4,5-dimethylimidazol-2-ylidene)²³ and the iron(I) complex [(DippNC(Me))₂CH)Fe(PhCCH)] (δ = 0.44 mm/s, | ΔE_Q | = 2.05 mm/s).²⁴

To probe the electronic structure of these NHC-iron(0)vtms complexes, spin-unrestricted DFT calculations at the B3LYP level^{25,26} has been performed on **1**. Calculations based on the molecular structure of **1** established by XRD study indicated that the S = 1 state is lower in energy than the S = 0state by 37.5 kcal/mol. Figure 3 shows the orbital composition



Figure 3. UNO orbitals of 1 (S = 1). The occupation number along with the dominant atomic contribution are indicated near each orbital.

and occupation of selected frontier molecular orbitals for the S = 1 state. At this spin state, the low occupation numbers in the unrestricted natural orbitals $(\text{UNOs})^{27}$ 176 and 177 implies that the electronic configuration of $(d_{xy} + \pi_{C=C}^*)^2 (d_{x^2-y^2} + \pi'_{C=C}^*)^2 (d_z^2)^2 (d_{xz})^1 (d_{yz})^1$ is dominant among the possible electronic structures of **1**. The π -backdonation interactions from the Fe d_{xy} and $d_{x^2-y^2}$ orbitals to the C==C π^* orbitals can be discerned from UNOs 172, 173, 176, and 177 in Figure 3. When gauged by the percentage of metal's d-orbital contributions in the bonding orbitals, the π -backdonation in **1** (61 and 72% for UNOs 172 and 173) is not as pronounced

as that in the three-coordinate manganese(0)–alkene complex [(Et₂-cAAC)Mn(dvtms)] (51 and 60%),²⁸ which is consistent with the Pauling electronegativity value of iron (1.83) being larger than that of manganese (1.55). Notably, in contrast to the pronounced Fe to vtms π -backdonation, the π -interaction between the iron center and carbene carbon atom is rather weak. These data indicated that the interaction between the Fe center and vtms remains rather covalent; therefore, 1 should be interpreted as an S = 1 species having a series of limiting valence electronic structures ranging from Fe^{IV}(vtms^{2–})₂ to Fe⁰(vtms⁰)₂, similar to [(Et₂-cAAC)Mn(dvtms)].²⁸ This notion also holds true for complexes 2, 3, and 5–8 (vide infra).

Under a dinitrogen atmosphere, the solids of 1-3 can be kept for months at room temperature without noticeable decomposition. When dissolved in C_6D_6 , the solutions of 1 and 2 also show good stability at ambient temperature. However, when 3 was dissolved in C_6D_6 or toluene, dissociation of vtms took place (Figure S14). Dissolution of 3 in toluene, followed by removing all the volatiles by vacuum evaporation left a red solid. Elemental analysis (C, H, and N) on the solid suggests a composition of (7-IPr)Fe(vtms) (4). The attempts to grow single-crystals of 4 suitable for XRD study were unsuccessful. However, the ⁵⁷Fe Mössbauer parameters of 4 (δ = 0.45 mm/s, $|\Delta E_0| = 1.06 \text{ mm/s})$ is comparable to those of Driess' bis(NHC)iron(0)-arene complex $[Fe((^{Dipp}C:)_2CH_2)(\eta^6 C_6H_6$] ($\delta = 0.43 \text{ mm/s}, |\Delta E_0| = 1.37 \text{ mm/s}$),⁸ hinting that 4 might adapt a "two-legged" piano-stool geometry (Scheme 2). Arene-metal interaction was observed in a (7-IPr)Pd(0)

Scheme 2. Possible Equilibrium between 3 and 4



complex $[(7-\text{IPr})\text{Pd}(\eta^2-\text{maleic anhydride})].^{29}$ Interestingly, treatment of 4 with vtms could lead to the formation 3, suggesting the reversibility of the conversion between 3 and 4. The vtms-dissociation behavior of 3 seems to originate from the steric nature of the seven-membered ring NHC ligand.³⁰

Reactions of 1 with Alkynes. Our previous study on NHC–iron(0)–alkene complexes showed that the iron(0)– vtms complex 1 can react with the azide bearing a bulky organic substituent N_3Ar ,¹⁶ which might associate with the lability of the monodentate alkene ligand in the three-coordinate iron(0) complex. Further study on the reactions of 1 with unsaturated organic molecules revealed that the vtms ligands in 1 indeed can be replaced readily by alkynes, ketone, and isocyanides.

The ligand substitution reactions of 1 with the terminal aryl alkynes (two equiv) PhC=CH, p-CH₃C₆H₄C=CH, and 3,5-(CF₃)₂C₆H₃C=CH completed in minutes at room temperature and gave the NHC-iron(0)-alkyne complexes [(IPr)-Fe(η^2 -HCCAr)₂] (Ar = Ph, **5**; p-CH₃C₆H₄, **6**; 3,5-(CF₃)₂C₆H₃, 7) as brown solids in 42–71% yields (Scheme 3). NMR-scale reactions indicated that these reactions have the complete conversion of **1** to the iron(0)-alkyne complexes with vtms as the byproduct. In contrast, the interaction of **1** with n-C₆H₁₃C=CH (2 equiv) merely led to the formation of trace amount of new paramagnetic species with a majority of **1** Scheme 3. Ligand Substitution Reactions of 1 with ArCCH, Ph₂CO, RNC, and CO



remaining. No reaction was observed when 1 was treated with the internal alkynes PhC \equiv CPh or PhC \equiv CMe in C_6D_6 at ambient temperature. The ineffective ligand substitution reaction of 1 with n- $C_6H_{13}C\equiv$ CH might be due to the relatively weak π -accepting ability of the alkyl chain-substituted alkyne over vinylsilane. The inertness of 1 toward the internal alkynes should be due to steric congestion.

Complexes 5-7 have been characterized by ¹H NMR, ⁵⁷Fe Mössbauer spectroscopy, and elemental analysis. The solidstate structures of 6 and 7 were confirmed by single-crystal Xray diffraction studies. As shown in Figure 4, the iron centers in 6 and 7 are coordinating with one IPr ligand and two η^2 -HCCAr ligands, forming a trigonal planar geometry. Probably due to the steric demanding nature of IPr, the two η^2 -HCCAr ligands in both complexes align in a tail-to-tail fashion, rather than a head-to-tail fashion. The distances of the C(alkyne)-C(alkyne) bonds in 6 and 7 span a narrow range of 1.263(3)-1.274(3) Å, longer than the C \equiv C distance in free acetylenes (1.17 Å),³¹ comparable to the C(alkyne)–C(alkyne) bond in the iron(I) complex [(DippNC(Me))₂CH)Fe(η^2 -HCCPh)] (1.268(3) Å),³² and slightly shorter than those of the fourcoordinate iron(0) complexes [Fe(dppe)(PMe₃)(η^2 -EtCCEt)] $(1.303(6) \text{ Å})^{13}$ and $[(dippp)Fe(\eta^2-PhCCPh)_2]$ (1.286(2) and $1.290(2) \text{ Å})^{.11}$ The coordination of the alkyne ligands to the iron centers also renders bent C(alkyne)-C(alkyne)-C(aryl) alignments that have the angles in the range of 144.8-146.5°. The Fe-C(alkyne) distances of 6 and 7 (in the range of 1.932(2)-1.956(2) Å) are comparable to the ones in $[(dippp)Fe(\eta^2-PhCCPh)_2]$ $(1.92-2.01 \text{ Å})^{11}$ and longer than the ones in [Fe(dppe)(PMe₃)(η^2 -EtCCEt)] (1.874(5) and 1.860(5) Å).¹³ The relatively shorter C(alkyne)-C(alkyne) and longer Fe-C(alkyne) distances observed on 6 and 7 as compared to those in $[(dippp)Fe(\eta^2-PhCCPh)_2]$ and [Fe- $(dppe)(PMe_3)(\eta^2$ -EtCCEt)] imply relatively weaker metal-toalkyne backdonation in the NHC-Fe(0)-alkyne complexes. This difference should associate with the different coordination

Article



Figure 4. Molecular structures of 6 (top) and 7 (bottom), showing 30% probability ellipsoids and the partial atom numbering scheme.

numbers and the different numbers of the alkynes ligands of these iron(0) alkyne complexes. As compared to the NHC– iron(0)–alkene complexes, the Fe–C distances in 6 and 7 are shorter than those in 1 and 2. Accordingly, the ⁵⁷Fe Mössbauer isomer shifts (0.29, 0.22, and 0.27 mm/s for 5–7, respectively, Table 2) of 5–7 (Figures S7–S9) are smaller than those of NHC–iron(0)–alkene complexes 1-3 (0.34–0.39 mm/s; Table 2).²²

Three-coordinate iron(0) alkyne complexes 5–7 are paramagnetic. Since accurate determination of their solution magnetic susceptibilities by Evans' method^{33,34} was hampered by the ease with which these complexes to undergo decomposition in solution phase, DFT calculations were used to get knowledge on their electronic structures. Calculation studies on **6** indicated that this iron–alkyne complex possesses an S = 1 ground spin-state with an electronic configuration of $(d_{xy} + \pi_{C \equiv C}^*)^2 (d_{x^2-y^2} + \pi'_{C \equiv C}^*)^2 (d_{xz})^1 (d_{yz})^1$, similar to that of **1**. The π backdonation orbitals (UNOs 178 and 179 in Figure 5) have Fe 3d percentages of 61 and 70%, respectively, close to the corresponding percentage values of the π -backdonation orbitals in **1** (vide supra).

Complexes 1–3 and 5–7, in addition with the aforementioned four-coordinate iron(0) bis(alkene) and bis(alkyne) complexes with phosphine ligation, 9^{-13} represent an unique class of open-shell iron(0) complexes bearing two π -ligands. The attainment of these iron(0) bis(alkene) and bis(alkyne) complexes rather than their further reductive coupling products, 35-38 five-membered metallacycles, indicates limited capability of iron(0) species in mediating reductive coupling reactions of nonactivated alkenes and alkynes. Indeed, only a



Figure 5. UNO orbitals of 6 (S = 1). The occupation number along with the dominant atomic contribution are indicated near each orbital.

few of stoichiometric reductive coupling reactions of iron complexes with alkenes and alkynes are known. As the rare examples, Chirik et al. showed the formal iron(0) complexes (PDI)Fe(N₂)₂ (PDI denotes pyridine-2,6-diimine ligands) can react with certain dienes, enynes, and diynes to give five-membered metallacycles.³⁹ Fürstner et al. isolated a ferracyclopentane complex from the reaction of [(dippp)Fe- $(\eta^2$ -C₂H₄)₂] with a cyclopropene compound.¹² The limited ability of those iron(0) species in mediating the reductive coupling reactions of nonactivated alkenes and alkynes might have its thermodynamics cause as a calculation study by Houk et al. showed that the conversions of the nickel(0) species (PMe₃)Ni(RCCR)₂ (R = Me and COOMe) to their reductive coupling products are energetically uphill.⁴⁰

It should be mentioned that while no effective ligand substitution reaction between 1 and terminal alkyl alkynes or internal alkynes at room temperature was observed, treatment of these alkynes with a catalytic amount of 1 at elevated temperature can result in alkyne cyclotrimerization. Using 5 mol % 1 as catalyst, the cyclotrimerization reactions of EtC \equiv CEt, PhC \equiv CPh, PhC \equiv CMe, *p*-CH₃C₆H₄C \equiv CH, and *n*-C₆H₁₃C \equiv CH at 50 °C in 20 h gave the substituted benzenes in 62–95% isolated yields (Scheme 4). For the reaction of PhC \equiv CMe, the two products 1,2,4-Me₃-3,5,6-Ph₃C₆ to 1,3,5-Me₃-2,4,6-Ph₃C₆ have the ratio of 8:1, whereas the reactions of *p*-CH₃C₆H₄C \equiv CH and *n*-C₆H₁₃C \equiv CH gave the 1,2,4- and





1,3,5-substitued benzenes in a ratio of 3:2. The regioselectivity of the cyclotrimerization reaction is moderate and differs from that observed in Tilley's system using [(IPr)Fe(N(SiMe₃)-(Dipp))] as precatalyst (7:3 ratio for cyclotrimerization of PhC=CMe).⁴¹ It is also distinct from von Wangelin's system employing Fe(N(SiMe₃)₂)₂ as the precatalyst (100% and 98:2 selectivity for cyclotrimerization of *p*-CH₃C₆H₄C=CH and *n*-C₆H₁₃C=CH, respectively).⁴² In the latter case, the iron particle was thought to be the genuine catalyst for the cyclotrimerization reaction.⁴²

The mechanism of the current iron-catalyzed alkyne cyclotrimerization reaction is not clear at this stage. Following the classical mechanism of low-valent transition-metalcatalyzed [2+2+2]-cycloaddition of alkynes,^{43,44} we propose that the reaction catalyzed by 1 might start from the ligand substitution of vtms in 1 by alkynes to afford alkyne complex A. The ligand substitution step might involve an intermediate (IPr)Fe(vtms) that could be formed from the dissociation of one vtms ligand from 1 and have a structure similar to that of 4. Intermediate A undergoes a reductive coupling reaction to form ferracyclopentadidene intermediate (B). Further alkyne insertion into one of the Fe-C(alkenyl) bond in B gives ferracycloheptatriene C that undergoes reductive elimination reaction to form NHC-iron(0)-arene intermediate D. The further steps of arene extrusion and alkyne coordination from D will then regenerate A (Scheme 5). In support of this proposed cycle, iron(0)-alkyne complexes 5-7 that are representatives of A have been isolated. While no intermediate A bearing terminal alkyl alkyne or internal alkyne ligands was synthesized yet, the relative higher temperature used for the catalytic reaction might enable their generation via ligand substitution reactions with terminal alkyl alkynes or internal alkynes (1 to A and D to A). When standing the solutions of 5-7 at room temperature for hours, the bis(alkyne) complexes undergo full decomposition to form alkyne cyclotrimerization products as indicated by ¹H and ¹⁹F NMR spectra and GC-MS analysis. However, neither 1,3-dienes nor cyclobutadienes that could be formed from the proposed ferracyclopentadidene intermediates B was detected. The failure to detect ferracyclopentadidene intermediates B might be related to the high activity of this species.⁴⁰

In addition to the mechanistic proposal having molecular iron complexes as intermediates, an alternative mechanism for Scheme 5. Proposed Catalytic Cycle for the Alkyne Cyclotrimeriztion Reaction Catalzyed by 1



the iron-catalyzed alkyne cyclotrimerization reaction could be a heterogeneous iron nanoparticles-catalyzed process. In accord with this mechanism, we noticed that the addition of mercury or PMe₂Ph to the catalytic alkyne cyclotrimerization reaction of EtCCEt using 1 as catalyst could halt the formation of C₆Et₆. However, this negative effect could be inconclusive for the heterogeneous nature of the catalytic system in as much as Hg is hard to form an amalgam with iron,⁴⁵ and its interaction with 1 at 50 °C was found to induce the decomposition of the iron(0) complex as indicated by the formation of black precipitate in the NMR-scale reaction of 1 with Hg in C_6D_6 . As for the effect of the addition of PMe₂Ph, the π -accepting ability of PMe₂Ph might make it potential competent ligand to bind to the open coordination site of the genuine iron catalyst, hence resulting in catalyst poisoning. Moreover, we noticed that reaction of 6 with 1 equiv of p-CH₃C₆H₄C \equiv CH gave the cyclotrimerization products 1,2,4-(p-CH₃C₆H₄)₃C₆H₃ and $1_{,3,5}$ -(p-CH₃C₆H₄)₃C₆H₃ in 54% yield with the ratio of the two products being ca. 5:4 (Scheme 6). This regioselectivity is close to that of the catalytic reaction using p-CH₃C₆H₄C \equiv CH, but is distinct from that of von Wangelin's system that was proposed to have iron nanoparticles as the genuine catalyst.⁴² With this limited information in hand, it is hard to determine whether this iron-catalyzed cyclotrimerization reaction oper-

Scheme 6. Reaction of $[(IPr)Fe(\eta^2-HCCC_6H_4-p-CH_3)_2$ (6) with $p-CH_3C_6H_4C\equiv CH$



ates in a way of heterogeneous or homogeneous catalysis and further study is needed.

Reaction of 1 with Ph₂CO. The ligand substitution reaction of 1 with the ketone Ph₂CO (2 equiv) also took place quickly at room temperature and the resultant NHC–iron–ketone complex $[(IPr)Fe(\eta^2-OCPh_2)_2]$ (8) was isolated in 82% yield (Scheme 3).

The molecular structure of **8** established by X-ray diffraction study shows that both ketone ligands are coordinating to the iron center in an η^2 -fashion with the averaged Fe–O distance of 1.859(1) Å and Fe–C(ketone) distance of 2.081(2) Å (Figure 6). The C–O distance (1.336(2) Å in avarage) in **8** is



Figure 6. Molecular structure of 8, showing 30% probability ellipsoids and the partial atom numbering scheme.

distinctly longer than that of the free ketone Ph₂CO (1.23 Å),⁴⁶ close to those of $[(dtbpe)Ni(\eta^2 - OCPh_2)]$ (1.331(6) Å, dtbpe = 1,2-bis(di-tert-butylphosphino)ethane)⁴⁷ and $[(PEt_3)_2Ni(\eta^2-OCPh_2)]$ (1.335(4) Å),⁴⁸ and shorter than the distances observed in the oxametallacyclopropane complexes $[(2,6-Ph_2C_6H_3O)_2Ti(PMe_3)(OCPh_2)] (1.397(8) Å)^{49}$ and [Cp₂Ti(PMe₃)(OCPh₂)] (1.360(2) Å).⁵⁰ The displacement between the two carbonyl carbon atoms (C(2)) and C(3) is 3.21 Å, precluding any bonding interaction between them. The outcome of the reaction of 1 with OCPh₂ thus differs from the C-C coupling reactions of some Hf(II), Zr(II), and Ti(II) complexes with ketones,^{51,52} The Fe-C(carbene) bond length in 8 (2.083(2) Å) is much longer than the Fe–C(carbene) distances in 1, 2, 6, and 7 (1.985(2) -2.033(2) Å). Coincidently, in parallel with its long Fe-C distance, the ⁵⁷Fe Mössbauer isomer shift of 8 ($\delta = 0.54$ mm/ s) is found the highest in the series of three-coordinate iron complexes 1-3 and 5-8.

We have also performed theoretic calculations to probe the electronic structure of the ketone complex. Single point energy calculations on **8** revealed its S = 1 ground spin-state. As depicted in Figure 7, the qualitative frontier molecular orbital diagram for the S = 1 state shows a $(d_z^2)^2(d_{xy} + \pi_{C=0}^{-})^2(d_{xz}^2)^1(d_{yz})^1$ electronic configuration. Compared with **1** and **6**, the Fe 3d percentage of the UNOs involving π -backdonation in **8** (43 and 71% in UNOs 212 and 213) are apparently lower, indicating more pronounced π -backdonation in the ketone complex. Complex **8** has a solution magnetic moment of 4.2(1) $\mu_{\rm B}$. This value locates between the spin-only values of 2.83 and 4.90 $\mu_{\rm B}$ for 3d metal ions with S = 1 and 2,



Figure 7. UNO orbitals of 8 (S = 1). The occupation number along with the dominant atomic contribution are indicated near each orbital.

respectively. The magnetic moment hints at the presence of unquenched orbital magnetic moment contribution in the low-coordinate d⁸ complex 8.⁵³

Reactions of 1 with Isocyanides and CO. Different from the reactions with the π -ligands, the interaction of 1 with isocyanides CNR (R = 2,6-Me₂C₆H₃, Bu^t, 4 equiv) gave fivecoordinate diamagnetic iron(0) complexes [(IPr)Fe(CNR)₄] (R = 2,6-Me₂C₆H₃, 9; Bu^t, 10) in high yields (Scheme 3). These 18e⁻-complexes are diamagnetic. Their ¹³C NMR spectra show signals at 203.77 and 209.27 ppm for 9 and 10, respectively, assignable to the signals of isocyanide carbon atoms. A single-crystal X-ray diffraction study on 9 revealed that its iron center adopts a distorted square-pyramidal geometry ($\tau_5 = 0.17$) with the four isocyanide ligands sitting on the basal positions (Figure 8). This geometry is different



Figure 8. Molecular structure of **9**, showing 30% probability ellipsoids and the partial atom numbering scheme. Hydrogen atoms are omitted for clarity.

from the trigonal bipyramidal geometry of $[(NHC)Fe(CO)_4]$ $(NHC = IPr, Me_2 - cAAC)^{54,55}$ and might originate from the unique steric nature of the ligand set in 9. Despite their different coordination geometries, the Fe-C(carbene) (1.979(6) Å) and Fe-C(isocyanide) distances (1.794(5) Å)in average) in 9 are comparable to their counterparts in $[(IPr)Fe(CO)_4]^{55}$ and $[Fe(CO)(CNAr^{Mes})_4]^{56}$ (Ar^{Mes} = 2,6bismesitylphenyl). The ⁵⁷Fe Mössbauer data ($\delta = -0.11 \text{ mm}/$ s, $|\Delta E_0| = 1.21$ for 9, and $\delta = -0.14$ mm/s, $|\Delta E_0| = 0.58$ mm/s for 10) are typical of low-spin iron(0) complexes. Similarly, the reaction of 1 with an excess amount of CO (1 atm.) gave the ligand substitution product $[(IPr)Fe(CO)_4]$ (11) in 77% yield (Scheme 3). The ¹H and ¹³C NMR spectra of the resultant iron carbonyl complex is consistent with those reported in literature.⁵⁷ In contrast, 1 proved unreactive with PPh₃ at room temperature.

CONCLUSION

In this study, we found that the combined ligand set of the monodentate alkene ligand vtms with sterically bulky NHC ligands, IPr, cyIPr, and 7-IPr, can stabilize three-coordinate iron(0) complexes in the form of $[(NHC)Fe(\eta^2-vtms)_2]$ (NHC = IPr, 1; cyIPr, 2; 7-IPr, 3). Reactivity study with 1 as the representative disclosed facile ligand substitution reactions of the NHC-iron(0)-vtms complex with terminal aryl alkynes, ketones, isocyanides, and CO, by which new iron(0)complexes with alkyne, ketone, and isocyanide ligation $[(IPr)Fe(\eta^2-HCCAr)]$ (Ar = Ph, 5; p- CH₃C₆H₄, 6; 3,5- $(CF_3)_2C_6H_3$, 7), $[(IPr)Fe(\eta^2-OCPh_2)_2]$ (8), [(IPr)Fe- $(CNR)_4$ (R = 2,6-Me₂C₆H₃, 9; Bu^t, 10), and [(IPr)Fe(CO)₄] (11) were synthesized in moderate to good yields. These iron(0) complexes have been characterized by ¹H NMR spectroscopy, single-crystal X-ray diffraction studies, elemental analysis, and ⁵⁷Fe Mössbauer spectroscopy. Characterization data and computational studies revealed that the threecoordinate complexes 1-3 and 5-8 have a common S = 1ground-spin state and that the five-coordinate complexes 9-11 are low-spin iron(0) species. Orbital composition analysis of 1, 6, and 8 revealed pronounced π -backdonation interaction between filled Fe 3d orbitals and the empty π^* orbitals of η^2 - $H_2CCHSiMe_3$, η^2 -HCCC₆ H_4 -p-CH₃, and η^2 -OCPh₂ in these iron(0) complexes. Hence, the effective stabilization of these three-coordinate iron(0) species benefits from the joint effect of the steric demanding nature of the bulky NHC ligands and the π -accepting nature of the π -ligands.

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 dried with a solvent purification system (Innovative Technology) and bubbled with dry N2 gas prior to use. 1,3-Bis(2,6diisopropylphenyl)-4,5-tetramethylene-imidazol-2-ylidene (cyIPr), 1,3-bis(2',6'-diisopropylphenyl)-4,5,6,7-tetrahydro-1,3-diazepin-2-ylidene (7-IPr),⁵⁹ and potassium graphite $(KC_8)^{60}$ were synthesized according to literature methods. All other chemicals were purchased from either Strem or J&K Chemical Co. and used as received. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on an Agilent 400, Agilent 600, or Bruker DRX400 MHz spectrometers. All chemical shifts were reported in units of ppm with references to the residue of the deuterated solvents for proton and carbon chemical shifts and to CF₃COOH for fluorine chemical shifts. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Solution magnetic

moments were measured by the method originally described by Evans with stock and experimental solutions containing a known amount of a $(CH_3)_3SiOSi(CH_3)_3$ standard.^{33,34} IR spectra of solid samples were recorded with a NICOLET AVATAR 330 FT-IR spectrophotometer on KBr pallets. Absorption spectra were recorded with a Shimadzu UV-3600 UV–vis-NIR spectrophotometer.

X-ray Structure Determination. Diffraction-quality crystals were obtained from recrystallizations in $Et_2O(2, 7, 8, 9)$ and toluene (6). Crystals were coated with Paratone-N oil and mounted on a Bruker APEX-II CCD-based diffractometer or a Bruker D8 Venture 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.⁶¹ Space groups were assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP. All structures were solved and refined using SHELXTL.⁶² Metal and first coordination sphere atoms were located from direct-methods E-maps. Non-hydrogen atoms were found in alternating difference Fourier synthesis and leastsquares refinement cycles and during final cycles were refined anisotropically. Tables S1 summarizes the crystal data and summary of data collection and refinement for the complexes. CCDC 1937521-1937525 contain the supplementary crystallographic data for complexes 2, 6-toluene, and 7-9. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

⁵⁷Fe Mössbauer Spectroscopy. All solid samples for ⁵⁷Fe Mössbauer spectroscopy were run on nonenriched samples of the asisolated complexes. Each sample was loaded into a Delrin Mössbauer sample cup for measurements and loaded under liquid nitrogen. Low-temperature ⁵⁷Fe Mössbauer measurements on 1–3 and 5–9 were performed using a See Co. MS4Mössbauer spectrometer integrated with a Janis SVT-400T He/N₂ cryostat for measurements at 80 K. The zero-field Mössbauer spectrum of 4 was recorded on a conventional spectrometer with alternating constant acceleration of the γ-source (⁵⁷Co/Rh, 1.8 GBq), which was kept at room temperature. The sample temperature was maintained constant (80 K) in an Oxford Instruments Variox cryostat. Isomer shifts were determined relative to α-Fe at 298 K. All Mössbauer spectra were fit using the program WMoss (SeeCo).

Preparation of [(IPr)Fe(η^2 -vtms)₂] (1). Method A: Complex 1 was synthesized according to the literature by using KC8 as the reducing reagent.¹⁶ Method B: To a THF (30 mL) solution of IPr (1.46 g, 3.70 mmol) was added FeCl₂ (480 mg, 3.80 mmol). The mixture was stirred overnight at room temperature, and then vinyltrimethylsilane (vtms, 2.2 mL, 15.1 mmol, 4 equiv) and Mg powder (110 mg, 4.6 mmol, 1.2 equiv) were added. The resultant mixture was further stirred for 48 h at room temperature. During the course of the stirring, the color of the mixture changed gradually to green. The reaction mixture was then filtered through diatomaceous earth, and the filtrate was concentrated under vacuum to leave a green residue. The residue was extracted with n-hexane (60 mL) and filtered. The filtrate was subjected to vacuum to remove all the volatiles. The resultant green solid was washed with *n*-hexane (3 mL) and dried under vacuum to afford $[(IPr)Fe(vtms)_2](1)$ as a green powder (854 mg, 35%). ¹H NMR (400 MHz, C_6D_6 , 298 K): δ (ppm) 25.01 ($\nu_{1/2}$ = 17 Hz), 22.95 ($\nu_{1/2}$ = 54 Hz), 10.29 ($\nu_{1/2}$ = 17 Hz), 4.65 $(\nu_{1/2} = 11 \text{ Hz}), 0.25 \text{ (very br)}, -0.90 (\nu_{1/2} = 13 \text{ Hz}), -8.44 (\nu_{1/2} = 21 \text{ Hz}), -12.08 (\nu_{1/2} = 41 \text{ Hz}), -15.52 (\nu_{1/2} = 57 \text{ Hz}).$ The NMR data of 1 is identical to those reported previously.¹⁶

Preparation of [(cylPr)Fe(η^2 -vtms)₂] (2). This complex was prepared as a green powder (0.6 g, 28%) by the reaction of FeCl₂ (0.40 g, 3.12 mmol) with cylPr (1.38 g, 3.12 mmol), vtms (2.4 mL, 16.4 mmol, 5 equiv), and KC₈ (0.93 g, 6.88 mmol, 2.2 equiv) using procedures similar to that of [(IPr)Fe(η^2 -vtms)₂] (Method A). Green crystals of 2 suitable for single-crystal X-ray diffraction study were obtained by standing its Et₂O solution at room temperature via slow evaporation of Et₂O. ¹H NMR (400 MHz, C₆D₆, 292 K): δ (ppm) 22.75 ($v_{1/2}$ = 81 Hz), 10.62 ($v_{1/2}$ = 50 Hz), 5.83 ($v_{1/2}$ = 44 Hz), 4.89 $(v_{1/2} = 54 \text{ Hz})$, 3.84 $(v_{1/2} = 47 \text{ Hz})$, 3.22 $(v_{1/2} = 57 \text{ Hz})$, 0.81 (very br), 0.29 (very br), -1.35 $(v_{1/2} = 48 \text{ Hz})$, -7.75 $(v_{1/2} = 53 \text{ Hz})$, -11.25 $(v_{1/2} = 82 \text{ Hz})$, -17.85 $(v_{1/2} = 117 \text{ Hz})$. Anal. Calcd for C₄₁H₆₆FeN₂Si₂: C, 70.45; H, 9.52; N, 4.01. Found: C, 70.41; H, 9.38; N, 4.24. Magnetic susceptibility $(C_6D_6, 294 \text{ K})$: $\mu_{\text{eff}} = 3.6(1) \mu_{\text{B}}$. Absorption spectrum (THF): λ_{max} nm $(\varepsilon, \text{M}^{-1} \text{ cm}^{-1}) = 410$ (1630), 580 (180), 720 (210). IR (KBr, cm⁻¹): $\nu = 2959$ (s), 2866 (m), 1701 (s), 1666 (m), 1589 (w), 1529 (w), 1470 (m), 1460 (w), 1400 (m), 1379 (w), 1362 (w), 1248 (w), 1179 (w), 1059 (w), 939 (w), 837 (w), 804 (w), 755 (s).

Preparation of [(7-IPr)Fe(η^2 -vtms)₂] (3). To a THF (50 mL) solution of 7-IPr (1.95 g, 4.64 mmol) was added FeBr₂ (1.00 g, 4.64 mmol) at room temperature. The mixture was stirred overnight at room temperature and then vtms (2.6 mL, 18.2 mmol, 4 equiv) was added. After stirring for 10 min, the mixture was cooled to -30 °C and then a THF (40 mL) suspension of KC₈ (1.25 g, 9.28 mmol, 2 equiv) was added. The mixture was further stirred for 18 h at -30 °C, during which the color of the mixture changed gradually to tan. The resultant mixture was then filtered through diatomaceous earth, and the filtrate was subjected to vacuum to remove all the volatiles. The resultant green solid was washed with *n*-hexane $(3 \times 3 \text{ mL})$ and Et₂O $(3 \times 2 \text{ mL})$ and then dried under vacuum to leave $[(7-\text{IPr})\text{Fe}(\eta^2 - \eta^2)]$ $vtms)_2$] (3) as a green powder (1.58 g, 50%). ¹H NMR (400 MHz, C_6D_6 , 298 K): δ (ppm) 22.88 ($\nu_{1/2}$ = 89 Hz), 14.31 ($\nu_{1/2}$ = 36 Hz), 10.88 ($\nu_{1/2}$ = 36 Hz), 9.32 ($\nu_{1/2}$ = 41 Hz), 8.23 ($\nu_{1/2}$ = 94 Hz), 4.68 (very br), 4.56 (very br), $-3.06 (\nu_{1/2} = 70 \text{ Hz}), -5.05 (\nu_{1/2} = 39 \text{ Hz}),$ -13.22 ($\nu_{1/2}$ = 62 Hz), -28.59 ($\nu_{1/2}$ = 460 Hz). Anal. Calcd for C₃₉H₆₆FeN₂Si₂: C, 69.40; H, 9.86; N, 4.15. Found: C, 67.73; H, 9.68; N, 4.22. The deviation of carbon content from the theoretic value could be caused by the ease with which 3 to release vtms. IR (KBr, cm^{-1}): $\nu = 3068$ (w), 2963 (s), 2930 (m), 2867 (m), 1629 (s), 1584 (w), 1470 (s), 1420 (m), 1382 (w), 1361 (m), 1323 (w), 1254 (m), 1182 (w), 1098 (w), 1062 (w), 997 (m), 937 (w), 838 (m), 804 (w), 756 (m), 523 (w), 456 (w).

Preparation of (7-IPr)Fe(η²-vtms) (4). A toluene solution (20 mL) of 3 (300 mg, 0.44 mmol) was stirred at room temperature for 4 h, during which the mixture was periodically concentrated under vacuum to remove the released alkene ligand vtms. The reaction mixture was then subjected to vacuum to remove the volatiles, which leaves (7-IPr)Fe(η²-vtms) (4) as a red powder (206 mg, 81%). ¹H NMR (400 MHz, C₆D₆, 298 K): δ (ppm) 6.86 (very br), 6.26 (very br), 5.61 (very br), 3.24 ($\nu_{1/2}$ = 39 Hz), 1.99 (very br), 1.74 (very br), 1.71 (very br), 1.57 (very br), 1.24 (very br), 0.08 ($\nu_{1/2}$ = 6 Hz), -0.33 (very br). Anal. Calcd for C₃₄H₅₄FeN₂Si: C, 71.05; H, 9.47; N, 4.87. Found: C, 70.48; H, 9.36; N, 4.80. Absorption spectrum (THF): λ_{max} , nm (ε, M⁻¹ cm⁻¹) = 390 (3010). IR (KBr, cm⁻¹): ν = 2962 (s), 2935 (m), 2867 (m), 1654 (s), 1628 (s), 1586 (w), 1487 (w), 1465 (s), 1419 (w), 1360 (w), 1323 (w), 1260 (s), 1184 (w), 1100 (s), 1055 (s), 1021 (s), 939 (w), 805 (s), 755 (m), 450 (w).

Reaction of 1 with PhC=CH. To a green solution of 1 (315 mg, 0.49 mmol) in n-hexane (10 mL) was added PhCCH (95 mg, 0.93 mmol) at room temperature. The color of the solution changed to brown immediately with precipitation of a brown solid. After stirring for 20 min, the solid was collected by filtration, washed with Et_2O (3) \times 2 mL), and dried under vacuum, which afforded (IPr)Fe(η^2 - $HCCPh)_2$ (5) as a brown solid (160 mg, 50%). ¹H NMR (400 MHz, C_6D_6 , 292 K): δ (ppm) 11.98 ($\nu_{1/2}$ = 78 Hz), 8.91 (very br), 1.42 (very br), 0.36 (very br), 0.31 (very br), $-0.79 (\nu_{1/2} = 34 \text{ Hz}), -1.91$ $(\nu_{1/2} = 33 \text{ Hz}), -2.38 (\nu_{1/2} = 33 \text{ Hz}), -10.63 (\nu_{1/2} = 113 \text{ Hz}).$ Anal. Calcd for $C_{43}H_{48}FeN_2$: C, 79.61; H, 7.46; N, 4.32. Found: C, 79.36; H, 7.20; N, 4.18. Magnetic susceptibility (C_6D_6 , 294 K): $\mu_{eff} = 3.6(1)$ $\mu_{\rm B}$. Absorption spectrum (THF): $\lambda_{\rm max}$ nm (ϵ , M⁻¹ cm⁻¹) = 317 (11 980), 331 (13 380), 348 (9490). IR (KBr, cm⁻¹): ν = 3085 (w), 2960 (s), 2927 (w), 2868 (w), 1679 (s), 1590 (w), 1532 (w), 1471 (s), 1422 (w), 1383 (w), 1330 (w), 1258 (w), 1231 (w), 1131 (w), 1061 (w), 923 (w), 810 (w), 751 (w), 691 (w).

Reaction of 1 with p-CH₃C₆H₄C \equiv CH. To a green solution of 1 (454 mg, 0.71 mmol) in *n*-hexane (10 mL) was added p-CH₃C₆H₄CCH (167 mg, 1.44 mmol) at room temperature. The color of the solution changed to brown immediately with precipitation

of a brown solid. After stirring for 20 min, the precipitate was collected by filtration, washed with Et_2O (3 × 2 mL), and dried under vacuum, which afforded [(IPr)Fe(η^2 -HCCC₆H₄CH₃-p)₂] (6) as a brown solid (340 mg, 71%). Single-crystals of 6 suitable for X-ray crystallography were obtained by cooling its saturated toluene solution at -30 °C. ¹H NMR (400 MHz, C₆D₆, 294 K): δ (ppm) 10.93 ($\nu_{1/2}$ = 86 Hz), 9.26 ($\nu_{1/2}$ = 29 Hz), 8.43 (very br), 4.10 ($\nu_{1/2}$ = 39 Hz), 0.88 (very br), 0.01 (very br), -0.59 ($\nu_{1/2}$ = 34 Hz), -1.48 $(\nu_{1/2} = 29 \text{ Hz})$, -11.19 $(\nu_{1/2} = 122 \text{ Hz})$. Anal. Calcd for C₄₅H₅₂FeN₂: C, 79.86; H, 7.74; N, 4.14. Found: C, 79.55; H, 7.92; N, 3.72. Magnetic susceptibility (C₆D₆, 294 K): $\mu_{eff} = 3.5(1) \mu_B$. Absorption spectrum (THF): λ_{max} nm (ϵ , M⁻¹ cm⁻¹) = 291 (17 960), 336 (11 680), 355 (8250). IR (KBr, cm⁻¹): ν = 3290 (w), 3085 (w), 2960 (s), 2926 (w), 2868 (w), 1679 (s), 1590 (w), 1533 (w), 1507 (w), 1471 (m), 1422 (w), 1383 (w), 1361 (w), 1331 (w), 1131 (w), 1060 (w), 923 (w), 817 (m), 811 (m), 750 (w), 689 (w).

Reaction of 1 with 3,5-(CF₃)₂C₆H₃C≡CH. To a green solution of 1 (193 mg, 0.30 mmol) in n-hexane (10 mL) was added 3,5-(CF₂)₂C₆H₂CCH (148 mg, 0.62 mmol) at room temperature. The color of the solution changed to brown immediately with precipitation of a brown solid. After stirring for 10 min, the precipitate was collected by filtration, washed with *n*-hexane $(3 \times 2 \text{ mL})$, and dried under vacuum, which furnished [(IPr)Fe(η^2 -HCCC₆H₃-(CF₃)₂-3,5)₂] (7) as a brown solid (117 mg, 42%). Single-crystals of 7 suitable for X-ray crystallography were obtained by cooling its saturated Et₂O solution at -30 °C. ¹H NMR (400 MHz, C₆D₆, 292 K): δ (ppm) 12.18 ($\nu_{1/2}$ = 52 Hz), 8.25 (very br), 3.40 ($\nu_{1/2}$ = 7 Hz), 0.43 ($\nu_{1/2}$ = 16 Hz), -1.05 ($\nu_{1/2}$ = 11 Hz), -1.32 ($\nu_{1/2}$ = 15 Hz), -2.68 ($\nu_{1/2}$ = 14 Hz), -11.03 ($\nu_{1/2}$ = 88 Hz). ¹⁹F NMR (376 MHz, C₆D₆, 292 K): δ (ppm) -67.88 ($\nu_{1/2}$ = 94 Hz). Anal. Calcd for C₄₇H₄₄F₁₂FeN₂: C, 61.31; H, 4.82; N, 3.04. Found: C, 61.18; H, 4.81; N, 2.81. Magnetic susceptibility (C₆D₆, 294 K): $\mu_{\text{eff}} = 3.2(1) \mu_{\text{B}}$. Absorption spectrum (THF): λ_{max} nm (ϵ , M⁻¹ cm⁻¹) = 319 (15 190), 332 (15 530), 349 (10 710). IR (KBr, cm⁻¹): ν = 3310 (w), 3085 (w), 2964 (s), 2929 (w), 2869 (w), 1679 (s), 1591 (w), 1534 (w), 1470 (m), 1422 (w), 1379 (s), 1331 (w), 1280 (s), 1179 (s), 1135 (s), 1107 (w), 922 (w), 898 (m), 848 (w), 750 (w), 700 (w), 684 (w), 663 (w).

General Procedure for the Alkynes Cyclotrimerization Reactions Catalyzed by 1. A toluene (1 mL) solution of an alkyne with the catalyst 1 (5 mol %) was heated at 50 °C for 20 h. The mixture was then subjected to vacuum to remove the volatiles. The residue was subjected to fast column chromatography (silica gel) that gave substituted benzene derivative(s) as colorless solids.

For the reaction of PhC=CPh (46 mg, 0.25 mmol), *n*-hexane/EA (20:1) was used as the eluent for separation, and the substituted benzene C_6Ph_6 was isolated in 84% yield. ¹H NMR (400 MHz, CDCl₃, 293 K): δ (ppm) 6.84 (m). ¹³C NMR (101 MHz, CDCl₃, 293 K): δ (ppm) 140.56, 140.25, 131.37, 126.53, 125.14. These NMR data are in accordance with the literature.⁶³

For the reaction of EtC=CEt (43 mg, 0.50 mmol), *n*-hexane/EA (20:1) was used as the eluent for separation, and the substituted benzene C₆Et₆ was isolated in 80% yield. ¹H NMR (400 MHz, CDCl₃, 292 K): δ (ppm) 2.64 (q, J = 7.5 Hz, 12H), 1.20 (t, J = 7.5 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃, 292 K): δ (ppm) 137.84, 22.16, 15.72. These NMR data are in accordance with the literature.⁶³

For the reaction of PhC=CMe (126 mg, 1.08 mmol), *n*-hexane/ EA (30:1) was used as the eluent for separation, and a mixture of 1,2,4-Me₃-3,5,6-Ph₃C₆ and 1,3,5-Me₃-2,4,6-Ph₃C₆ were obtained in 95% yield. ¹H NMR analysis indicated a ratio of 8:1 for 1,2,4-Me₃-3,5,6-Ph₃C₆/1,3,5-Me₃-2,4,6-Ph₃C₆. For 1,2,4-Me₃-3,5,6-Ph₃C₆: ¹H NMR (400 MHz, C₆D₆, 292 K): δ (ppm) 2.17 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H). The ¹H NMR signals of hydrogen atoms on aromatic rings overlap with those of its isomer. ¹³C NMR (101 MHz, CDCl₃, 292 K): δ (ppm) 142.40, 141.58, 141.56, 141.38, 140.59, 139.18, 133.91, 131.86, 131.23, 130.27, 129.35, 128.40, 127.30, 127.27, 126.45, 125.70, 125.64, 19.44, 18.29, 18.11. For 1,3,5-Me₃-2,4,6-Ph₃C₆: ¹H NMR (400 MHz, C₆D₆, 292 K): δ (ppm) 2.07 (s). The ¹H NMR signals of hydrogen atoms on aromatic rings overlap with those of its isomer. ¹³C NMR (101 MHz, CDCl₃, 292 K): δ (ppm) 142.09, 139.78, 133.20, 129.35, 128.45, 126.44, 19.44. These NMR data are in accordance with the literature. 63

For the reaction of p-CH₃C₆H₄C \equiv CH (58.7 mg, 0.50 mmol), nhexane/EA (50:1) was used as the eluent for separation, and a mixture of the substituted benzenes $1,2,4-(p-CH_3C_6H_4)_3C_6H_3$ and $1_{3}_{5}-(p-CH_{3}C_{6}H_{4})_{3}C_{6}H_{3}$ were isolated in 62% yield as a white solid. ¹H NMR analysis indicated a ratio of 3:2 for the 1,2,4- and 1,3,5isomers. 1,2,4-(p-CH₃C₆H₄)₃C₆H₃: ¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 7.47 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 6.2 Hz, 2H), 7.12-7.04 (m, 8H), 2.41 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H). The ¹H NMR signals of other hydrogen atoms on aromatic rings overlap with those of its isomer. ¹³C NMR (101 MHz, CDCl₃, 298 K): δ (ppm) 140.78, 140.03, 139.15, 138.75, 138.40, 137.80, 137.14, 136.12, 136.02, 131.11, 129.74, 129.70, 129.54, 129.28, 128.68, 128.66, 126.95, 125.72, 21.15. 1,3,5- $(p-CH_3C_6H_4)_3C_6H_3$: ¹H NMR (400 MHz, $CDCl_{3}$, 298 K): δ (ppm) 7.73 (s, 3H), 7.29 (d, J = 8.4 Hz, 6H), 2.43 (s, 9H). The ¹H NMR signals of other hydrogen atoms on aromatic rings overlap with those of its isomer. ¹³C NMR (101 MHz, CDCl₃, 298 K): δ (ppm) 142.17, 138.40, 137.27, 129.54, 127.19, 124.58, 21.17. These NMR data are in accordance with the literature. 64,6

For the reaction of n-C₆H₁₃C \equiv CH (60 mg, 0.55 mmol), n-hexane was used as the eluent for separation, and a mixture of the substituted benzenes $1,2,4-(n-C_6H_{13})_3C_6H_3$ and $1,3,5-(n-C_6H_{13})_3C_6H_3$ were isolated in 68% yield as a pale yellow oil. ¹H NMR analysis indicated a ratio of 3:2 for the 1,2,4- and 1,3,5-isomers. $1,2,4-(n-C_6H_{13})_3C_6H_3$: ¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 7.05 (d, J = 7.6 Hz, 1H), 6.96-6.93 (m, 2H). The ¹H NMR signals of other hydrogen atoms on alkyl chains overlap with those of its isomer. ¹³C NMR (101 MHz, CDCl₃, 298 K): δ (ppm) 140.30, 140.13, 137.66, 129.19, 128.91, 125.66, 35.98, 35.61, 32.78, 32.34, 31.76, 31.58, 31.39, 29.52, 29.14, 22.65, 22.62, 14.16. 1,3,5- $(n-C_6H_{13})_3C_6H_3$: ¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) 6.82 (s, 3H). The ¹H NMR signals of other hydrogen atoms on alkyl chains overlap with those of its isomer. ¹³C NMR (101 MHz, CDCl₃, 298 K): δ (ppm) 142.68, 125.79, 31.76, 31.56, 31.39, 29.14, 22.62, 14.10. These NMR data are in accordance with the literature $\frac{66,67}{6}$ with the literature.

Reaction of 1 with Ph₂CO. To a green solution of 1 (159 mg, 0.25 mmol) in toluene (10 mL) was added Ph₂CO (93 mg, 0.51 mmol) at room temperature. The color of the solution changed to brown immediately. The reaction mixture was stirred at room temperature for 2 h and then was subjeted to vacuum to remove all the volatiles. The residue was washed with *n*-hexane $(3 \times 2 \text{ mL})$ and dried under vacuum to afford [(IPr)Fe(η^2 -OCPh₂)₂] (8) as a brown solid (164 mg, 82%). Single-crystals of 8 suitable for X-ray crystallography were obtained by standing its Et₂O solution at room temperature via slow evaporation of Et₂O.¹H NMR (400 MHz, C₆D₆, 295 K): δ (ppm) 54.04 (very br), 13.85 ($\nu_{1/2}$ = 174 Hz), 8.99 ($\nu_{1/2}$ = 24 Hz), 8.68 ($\nu_{1/2}$ = 44 Hz), -5.51 ($\nu_{1/2}$ = 30 Hz), -17.91 (very br), -20.27 ($\nu_{1/2}$ = 41 Hz), -28.74 ($\nu_{1/2}$ = 47 Hz). Anal. Calcd for C₅₃H₅₆FeN₂O₂: C, 78.70; H, 6.98; N, 3.46. Found: C, 78.33; H, 7.22; N, 3.40. Magnetic susceptibility (C₆D₆, 294 K): $\mu_{eff} = 4.2(1) \mu_{B}$. Absorption spectrum (THF): λ_{max} , nm (ε , M⁻¹ cm⁻¹) = 348 (2310), 527 (280), 789 (140). IR (KBr, cm⁻¹): ν = 3085 (w), 2960 (s), 2927 (w), 2868 (w), 1680 (s), 1659 (s), 1598 (m), 1578 (w), 1534 (w), 1475 (m), 1450 (m), 1422 (w), 1383 (w), 1360 (w), 1318 (m), 1278 (s), 1177 (w), 1150 (w), 1060 (w), 941 (m), 922 (m), 810 (m), 764 (w), 703 (s), 639 (m).

Reaction of 1 with 2,6-Me₂C₆H₃NC. To a green solution of 1 (141 mg, 0.22 mmol) in Et₂O (10 mL) was added 2,6-Me₂C₆H₃NC (114 mg, 0.87 mmol) at room temperature. The color of the solution changed to red immediately. The mixture was stirred for 2 h and was then subjected to vacuum to remove all the volatiles. The residue was washed with *n*-hexane (2 × 2 mL) and dried under vacuum to afford [(IPr)Fe(CNC₆H₃-2,6-Me₂)₄] (9) as a red solid (170 mg, 80%). Single-crystals of 9 suitable for X-ray crystallography were obtained by standing its Et₂O solution at room temperature via slow evaporation of Et₂O. ¹H NMR (400 MHz, C₆D₆, 292 K): δ (ppm) 7.09–7.07 (m, 4H), 7.02–6.99 (m, 2H), 6.76–6.69 (m, 12H), 6.67 (s, 2H), 3.40–3.33 (m, 4H), 2.23 (s, 24H), 1.58 (d, *J* = 6.8 Hz, 12H), 1.17 (d, *J* =

6.8 Hz, 12H). ¹³C NMR (101 MHz, C_6D_{62} , 292 K): δ (ppm) 206.32 ($C_{carbene}$), 203.77, 145.87, 139.35, 133.13, 132.35, 128.64, 123.67, 123.53, 123.40, 28.52, 25.49, 23.25, 19.11. Anal. Calcd for $C_{63}H_{72}$ FeN₆: C, 78.08; H, 7.49; N, 8.67. Found: C, 78.07; H, 7.53; N, 8.76. Absorption spectrum (THF): λ_{max} nm (ε , M^{-1} cm⁻¹) = 422 (21 580). IR spectrum (KBr, cm⁻¹): ν = 2962 (s), 2926 (m), 2868 (w), 2094 (s), 1679 (s), 1624 (w), 1588 (w), 1386 (w), 1328 (w), 1286 (w), 1091 (w), 1061 (w), 800 (w), 766 (m), 755 (m), 670 (w), 481 (w).

Reaction of 1 with Bu^tNC. To a green solution of 1 (178 mg, 0.28 mmol) in Et₂O (10 mL) was added Bu^tNC (96 mg, 1.16 mmol) at room temperature. The color of the solution changed to yellow immediately. The mixture was stirred for 2 h and was then subjeted to vacuum to remove all the volatiles. The residue was washed with nhexane $(2 \times 2 \text{ mL})$ and dried under vacuum to afford (IPr)Fe- $(CNBu^{t})_{4}$ (10) as a yellow solid (152 mg, 72%). ¹H NMR (400 MHz, C_6D_{61} 294 K): δ (ppm) 7.31–7.27 (m, 2H), 7.24–7.22 (m, 4H), 6.48 (s, 2H), 3.25 (hept, J = 6.9 Hz, 4H), 1.59 (d, J = 6.7 Hz, 12H), 1.26 (s, 36H), 1.20 (d, J = 6.9 Hz, 12H). ¹³C NMR (101 MHz, C₆D₆, 294 K): δ (ppm) 209.27, 206.95 (C_{carbene}), 146.87, 140.06, 128.25, 123.20, 123.03, 53.91, 31.40, 28.19, 25.33, 24.17. Anal. Calcd for C₄₇H₇₂FeN₆: C, 72.66; H, 9.34; N, 10.82. Found: C, 72.82; H, 9.55; N, 10.83. Absorption spectrum (THF): λ_{max} nm (ϵ , M⁻¹ cm⁻¹) = 307 (13 380). IR spectrum (KBr, cm⁻¹): ν = 3068 (w), 2962 (s), 2924 (m), 2868 (m), 2107 (s), 1678 (s), 1614 (m), 1557 (w), 1474 (s), 1386 (w), 1362 (w), 1284 (w), 1065 (w), 939 (m), 810 (w), 754 (m), 688 (w), 447 (w).

Reaction of 1 with CO. A green solution of 1 (102 mg, 0.16 mmol) in THF (10 mL) was cooled with liquid N₂, and CO was introduced to the solution mixture via a CO balloon (1 atm.). The solution was then warmed to room temperature and stirred for 5 h, during which the color of the solution changed to yellow gradually. The mixture was then subjected to vacuum to remove solvent. The yellow residue was washed with *n*-hexane (2 mL) and then dried under vacuum to give [(IPr)Fe(CO)₄] (11) as a yellow solid (68 mg, 77%).¹H NMR (400 MHz, C₆D₆, 298 K): δ (ppm) 7.30–7.26 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 4H), 6.57 (s, 2H), 2.72 (hept, *J* = 6.8 Hz, 4H), 1.42 (d, *J* = 6.8 Hz, 12H), 1.00 (d, *J* = 6.9 Hz, 12H). ¹³C NMR (101 MHz, C₆D₆, 298 K): δ (ppm) 215.53 (CO), 191.05 (C_{carbene}), 146.34, 136.72, 130.62, 125.47, 124.32, 28.67, 25.60, 22.50. These NMR data are identical to those reported in the literature.⁵⁷

Computational Details. To have a better understanding of the electronic structures of 1, 6, and 8, DFT^{68,69} study was performed with the ORCA 4.1.0 program⁷⁰ using the B3LYP methods.^{25,26} The SVP^{71,72} basis set was used for the C, N, and H atoms, and the TZVP⁷³ basis set was used for the other atoms. The RIJCOSX⁷⁴ approximation with matching auxiliary basis sets^{71,72} was employed to accelerate the calculations. The calculation utilizes the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ).^{75,76} The atomic coordinates of 1, 6, and 8 used for calculation were obtained from X-ray diffraction studies, and only the positions of hydrogen atoms were optimized. Table S2 summarizes the corresponding single point energies relative to the S = 0 and 1 states. Mulliken spin populations of 1, 6, and 8 are listed in Figures S38-S40. The UNO orbitals of 1, 6, and 8 are listed in Figures 3, 5, and 7. The natural orbitals of 1, 6, and 8 are listed in Figures S41-S43.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02009.

Table for crystal data and summary of data collection and refinement, absorption spectra, ⁵⁷Fe Mössbauer spectra, NMR spectra, graphs for the Mulliken spin populations, and natural orbitals for **1**, **6**, and **8**, and Cartesian coordinates for the calculated structures of 1, 6, and 8 (PDF)

Accession Codes

CCDC 1937521–1937525 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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