

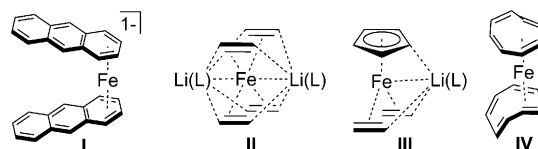
(Aminocarbene)(Divinyltetramethyldisiloxane)Iron(0) Compounds: A Class of Low-Coordinate Iron(0) Reagents**

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Dedicated to Professors Lixin Dai and Chengye Yuan on the occasion of their 90th birthdays, and to Professor Changtao Qian on the occasion of his 80th birthday

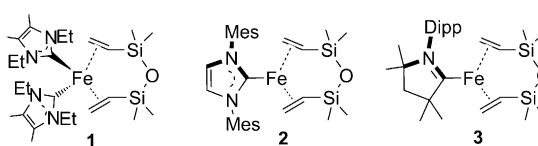
Abstract: The combined use of aminocarbene and divinyltetramethyldisiloxane (dvtms) as supporting ligands enables the access of unprecedented low-coordinate iron(0) alkene compounds $[L_nFe(\eta^2:\eta^2\text{-dvtms})]$ ($L = N$ -heterocyclic carbene (NHC) or cyclic (alkyl)(amino)carbene (CAAC), $n = 1$ or 2) from the reactions of $FeCl_2$ with alkali-metal reducing agents, free aminocarbene ligands, and dvtms. The iron(0) species deliver their $[L_nFe^0]$ fragments to perform redox reactions with Ph_2SiH_2 , S_8 , Se, and $DippN_3$, furnishing novel aminocarbene-supported iron(IV) silylene, all-ferrous iron–sulfur/selenium cubanes, and bis(imido)iron(IV) compounds. These conversions demonstrate the potential synthetic utility of the carbene-supported iron(0) complexes as a valuable class of low-coordinate iron(0) reagents.

Low-valent transition-metal alkene complexes are valuable organometallic species owing to their wide applications as catalysts in organic synthesis and as precursors for preparing new complexes.^[1] Along with growing interests in base metal chemistry in the recent years,^[2] low-valent iron alkene compounds have been subjected to extensive investigation.^[3] Notable recent examples include the preparation of the 17-electron anionic ferrate complex $[Fe(1,2,3,4-\eta^4-C_{14}H_{10})_2]^-$ (**I** in Scheme 1) by Brennessel, Jilek, and Ellis,^[3c] and its catalytic application in alkene hydrogenation demonstrated by Wolf, Jacobi von Wangelin, and co-workers;^[3d] the employment of Jonas' 18-electron iron ethylene complexes, $[Li(tmeda)]_2[Fe(CH_2CH_2)_4]$ (**II**) and $[Li(tmeda)][CpFe(CH_2CH_2)_2]$ (**III**) ($tmeda$ = tetramethylethylenediamine)^[4] as catalysts for cross-coupling reactions pioneered by Fürstner et al.,^[3e] as well as the novel carbene-catalyzed organometallic transformation from $[Fe(cot)_2]$ (**IV**) to $[Fe_3(cot)_3]$ revealed by Grubbs and Lavallo.^[3f]



Scheme 1. Examples of low-spin low-valent iron alkene compounds. L = tetramethylethylenediamine or dimethoxyethane.

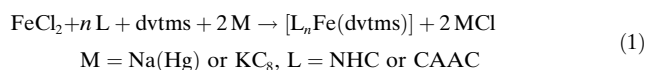
While these studies focused on low-spin 17- and 18-electron poly(alkene) species, we report herein a class of unprecedented high-spin 16- and 14-electron iron(0) alkene complexes supported by aminocarbene ligands,^[5] $[L_nFe(\text{dvtms})]$ (**1–3** in Scheme 2, $L = N$ -heterocyclic carbene



Scheme 2. Preparation of the carbene-supported iron(0) alkene compounds.

(NHC) or cyclic (alkyl)(amino)carbene (CAAC), $n = 1$ or 2, dvtms = divinyltetramethyldisiloxane). These iron(0) alkene complexes are readily accessible. Their propensity to undergo oxidation, as demonstrated by the reactions with Ph_2SiH_2 , S_8 , Se, and $DippN_3$ to form novel aminocarbene-supported (silylene)iron(IV), iron(II)–sulfur/selenium cubanes, as well as bis(imido)iron(IV) compounds, shows their potential synthetic application.

The synthesis of these aminocarbene iron(0) alkene compounds can be readily achieved in a one-pot reaction [Eq. (1)].



The addition of KC_8 or Na/Hg (two equiv) to the mixtures of $FeCl_2$, dvtms, and the corresponding free aminocarbene ligands (one or two equiv) produced dark blue suspensions, from which air- and moisture-sensitive green or greenish blue crystals of $[(IET_2Me_2)_2Fe(dvtms)]$ (**1**), $[(IMes)Fe(dvtms)]$ (**2**), and $[(Me_2\text{-CAAC})Fe(dvtms)]$ (**3**) (IET_2Me_2 = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene, $IMes$ = 1,3-di(2',4',6'-trimethylphenyl)imidazol-2-ylidene, $Me_2\text{-CAAC}$ = 1-(2',6'-diisopropyl-

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phenyl)-3,3,5,5-tetramethyl- pyrrolidine-2-ylidene) were isolated in 44–87 % yields.^[6] Complexes **1–3** have been characterized by ¹H NMR spectroscopy, solution magnetic susceptibility measurement, UV/Vis-NIR spectroscopy, infrared resonance, single-crystal X-ray diffraction, ⁵⁷Fe Mössbauer spectroscopy, and elemental analysis.^[6] Their ¹H NMR spectra measured in C₆D₆ showed paramagnetically shifted broad peaks, and solution magnetic susceptibility measurement (3.5(1), 3.5(1), and 4.0(2) μ B for **1–3**, respectively)^[7] indicated their common high-spin electronic configuration ($S = 1$).

Single-crystal X-ray diffraction studies revealed that **1** is a pseudo-tetrahedral iron(0) complex with the iron center coordinated by one dvtms in an $\eta^2:\eta^2$ -fashion and two IET₂Me₂ ligands, whereas, **2** and **3** are trigonal planar iron(0) species bearing one bulky aminocarbene (IMes or Me₂-CAAC) and one $\eta^2:\eta^2$ -dvtms (Figure 1). The C–C bond lengths of the vinyl moieties in **1–3** are in the range 1.41 to 1.43 Å, which are significantly longer than the typical C=C bond of 1.32 Å observed in vinylsilanes,^[8] and suggest the contribution of $d \rightarrow \pi^*$ back donation in these iron(0) compounds. The Fe–C(carbene) separations in **1–3** are 2.078(9) (in average), 2.030(2), and 1.977(1) Å, respectively. These distances are shorter than those of the reported four- and three-coordinate high-spin iron(II) carbene compounds,^[9] because of the

presence of enhanced π interactions between the iron(0) centers and carbene ligands.^[10] The zero-field ⁵⁷Fe Mössbauer spectra of **1–3** measured on polycrystalline samples feature single doublets with the corresponding isomer shifts (δ) of 0.47, 0.40, and 0.33 mm s^{−1} and quadruple splitting values (ΔE_Q) of 2.06, 3.02, and 3.04 mm s^{−1}, respectively. These data, especially the ΔE_Q values, are distinct from those observed in the corresponding four- and three-coordinate high-spin iron(I) alkyne compounds [PhB(CH₂SiBu)₃Fe(PhCCPh)] ($\delta = 0.62$ mm s^{−1}, $\Delta E_Q = 1.62$ mm s^{−1}),^[11a] and [(DippN–C(Me))₂CH]Fe(PhCCPh)] ($\delta = 0.44$ mm s^{−1}, $\Delta E_Q = 2.05$ mm s^{−1}),^[11b] and also those of the low-spin iron(0) compound [Fe{(DippC)₂CH₂}(η -(C₆H₆))] ($\delta = 0.43$ mm s^{−1}, $\Delta E_Q = 1.37$ mm s^{−1}).^[11c] The smaller δ value observed in **3** compared to **2** is suggestive of the increased covalency of the C(CAAC)–iron bond.

The majority of iron(0) species feature strong π -accepting ligands and/or higher coordination numbers as exemplified by the classical tricarbonyliron(0) alkene compounds,^[3a] the cot complexes [(BAC)Fe(η^4 -cot)₂] and [(BAC)₂Fe(η^4 -cot)] (BAC: bis(diisopropylamino)cyclopropenylidene),^[3g] and the π -arene complexes [Fe{(DippC)₂CH₂}(η^6 -(C₆H₅R))] and [(μ - η^1 (C): η^6 (arene)-NHC)Fe]₂ (NHC = IMes, IPr).^[12] On the other hand, iron(0) species with relatively weaker ligand

fields or low-coordination number, such as [Fe(PMe₃)₄],^[13] [Fe{(DippC)₂CH₂}(PMe₃)₂],^[11c] [Fe(IMes)₂],^[14] and [(PEt₃)₂Fe- $\{\eta^2$ -(CH₂=CH₂)₂}]^[15] are prone to intramolecular cyclometallation or decomposition. Complexes **1–3** are coordinatively unsaturated. However, they show remarkable thermal stability in both the solution phase and solid state.^[6] The stability might come from the joint effect of the strongly electron-donating aminocarbenes' capability to bind strongly with iron centers^[16] and the good π -accepting nature of the chelating vinyl-siloxane ligand. To our surprise, while such a combined ligand set has proved useful for creating stable three-coordinate Pt⁰, Pd⁰, and Ni⁰ species, the iron analogues have remained elusive until now.^[17]

The synthesis of these low-coordinate iron(0) compounds^[18] has prompted further study on their synthetic application. Our preliminary investigation revealed that **1–3** can perform oxidative addition with hydrosilanes, chalcogen elements, and organic azides to form novel aminocarbene-supported iron complexes [(IET₂Me₂)₂Fe(H)(SiHPh₂)-(IET₂Me₂)] (**4**), [(IET₂Me₂)₄FeX₄]

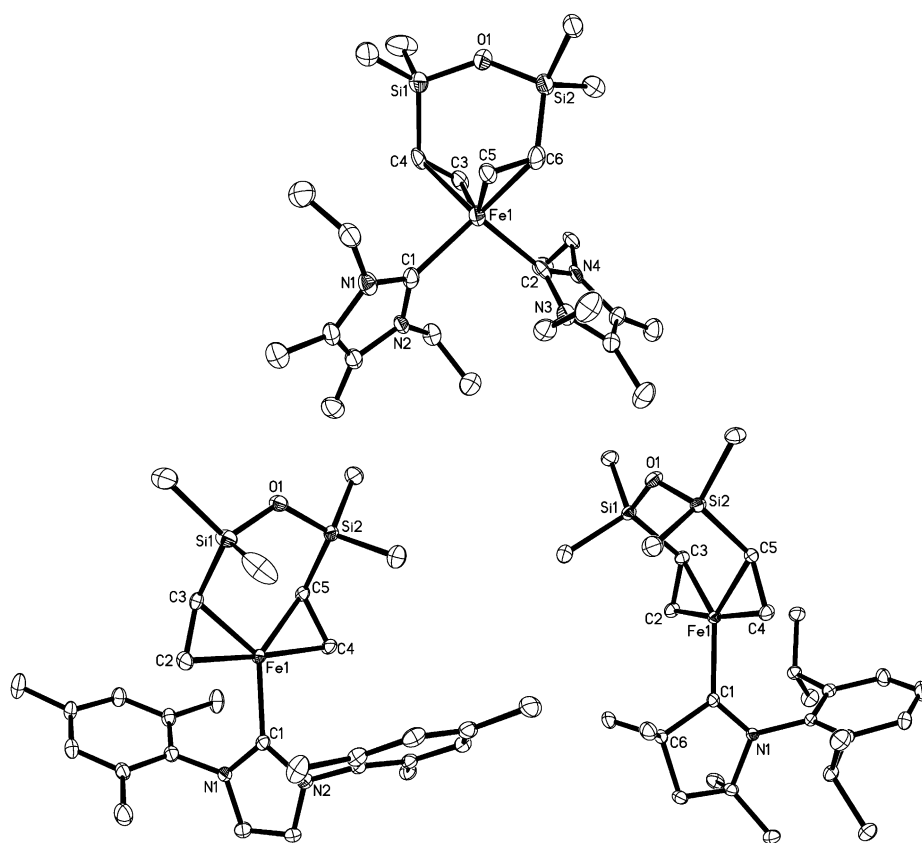
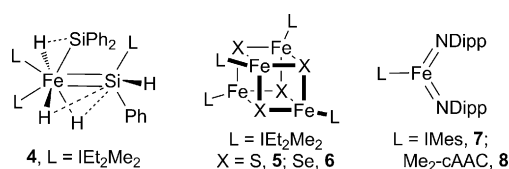


Figure 1. Molecular structures of **1** (top), **2** (bottom, left), and **3** (bottom, right).^[30] Thermal ellipsoids set at 30% probability. Selected bond lengths [Å] for **1**: Fe1–C1 2.109(8), Fe1–C2 2.046(9), Fe1–C3 2.070(8), Fe1–C4 2.155(9), Fe1–C5 2.056(9), Fe1–C6 2.115(9), C3–C4 1.41(1), C5–C6 1.42(1); for **2**: Fe1–C1 2.030(2), Fe1–C2 2.052(3), Fe1–C3 2.049(2), Fe1–C4 2.059(2), Fe1–C5 2.052(2), C2–C3 1.425(4), C4–C5 1.432(3); and for **3**: Fe1–C1 1.977(1), Fe1–C2 2.066(1), Fe1–C3 2.056(1), Fe1–C4 2.037(1), Fe1–C5 2.056(1), C1–N1 1.327(2), C2–C3 1.425(2), C4–C5 1.420(2).



Scheme 3. Schematic structural formula of complexes 4–8.

(X = S, **5**; Se, **6**), and [LFe(NDipp)₂] (L = IMes, **7**, Me₂-CAAC, **8**; Scheme 3).^[6] In these reactions, the iron(0) alkene compounds have effectively functioned as precursors of (aminocarbene)iron(0) fragments.

Complex **4**, which was isolated from the reaction of **1** with four equivalents of Ph₂SiH₂, is formally a seven-coordinate iron(IV) compound being analogous to Caulton's seven-coordinate (trihydrido)(silyl)(silylene)cobalt(V) complexes.^[19] The molecular structure of **4** established by single-crystal X-ray diffraction indicated the presence of a NHC-coordinated silylene ligand, SiHPh(IET₂Me₂), with a short Fe–Si separation of 2.170(1) Å (Figure 2).^[20] Three iron-bound

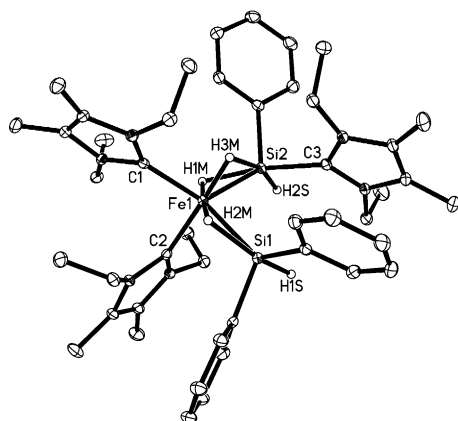
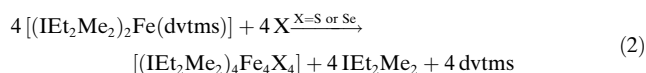


Figure 2. Molecular structure of **4**.^[30] Thermal ellipsoids set at 30% probability. Selected bond lengths [Å]: Fe1–C1 1.989(2), Fe1–C2 1.939(2), Fe1–Si1 2.239(1), Fe1–Si2 2.170(1), Fe1–H1M 1.53(2), Fe1–H2M 1.48(2), Fe1–H3M 1.49(2), Si1–H1S 1.53(2), Si2–H2S 1.46(2), Si1–H2M 1.92(2), Si2–H1M 1.77(2), Si(2)–H3M 1.81(2), Si(1)–Si(2) 2.95.

hydrides and two silicon-bound hydrides were located on the electron density map and refined freely. ¹H and ²⁹Si NMR spectra corroborated these structure features, and agreed closely with the spectra of Caulton's cobalt(V) complexes.^[6,19] The occurrence of the SiHPh(IET₂Me₂) ligand in **4** implies the involvement of hydrosilane redistribution in the reaction of **1** with Ph₂SiH₂,^[21] probably facilitated by (IET₂Me₂)₂Fe. The conversion of **1** into **4** has demonstrated the capability of the aminocarbene-stabilized iron(0) alkene compound to deliver its (aminocarbene)iron(0) fragment during the reaction course. Moreover, it revealed the intriguing activity of (IET₂Me₂)₂Fe in tailoring the Si–C bond. This activity is unknown for 2,6-di(imine)pyridine and 2,6-di(carbene)pyridine ligand-supported iron(0) species.^[22]

The iron–sulfur and -selenium cubanes [(IET₂Me₂)₄Fe₄S₄] (**5**) and [(IET₂Me₂)₄Fe₄Se₄] (**6**), whose formation can be rationalized by Equation (2), represent the rare synthetic



analogues of the super-reduced iron–sulfur clusters in metalloproteins.^[23] Holm and Deng accessed a carbene-stabilized cluster, [(IPr₂Me₂)₄Fe₄S₄], by the reaction of [(PⁱPr₃)₂FeCl₂] with (TMS)₂S, followed by ligand substitution of PⁱPr₃ with IPr₂Me₂.^[23a] The current synthetic route that exploits the redox reaction of the low-coordinate iron(0) species **1** with chalcogen elements and surpasses the traditional route for its simplicity. Furthermore, it enables the first synthesis of the all-ferrous iron–selenium cubane **6**. X-ray diffraction studies revealed that the metric data of the [Fe₄S₄]⁰ core in **5** are similar to that of [(IPr₂Me₂)₄Fe₄S₄], and that the [Fe₄Se₄]⁰ core in **6** have resemble its sulfur analogues, but with longer interatomic separations. Figure 3 depicts the structure of **6**. Complexes **5** and **6** have similar paramagnetically shifted ¹H NMR spectra. A solution magnetic moment of 7.7(2) μB suggests an S = 3 spin state for **5** that is consistent with its analogue with IPr₂Me₂ ligation.^[24]

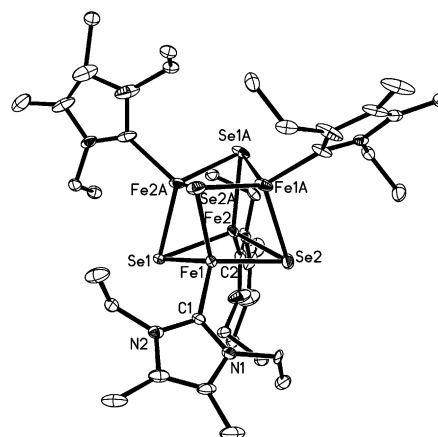
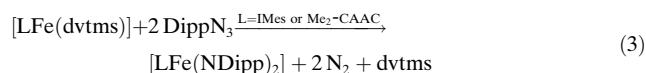


Figure 3. Molecular structure of **6**.^[30] Thermal ellipsoid set at 30% probability. Selected interatomic separations [Å] and angles [°]: Fe1–C1 2.111(6), Fe2–C1 2.100(6), Fe1–Se1 2.443(1), Fe1–Se2 2.441(1), Fe1–Se2A 2.449(1), Fe2–Se1 2.481(1), Fe2–Se2 2.426(1), Fe2–Se1A 2.448(1), Fe1–Fe2 2.715(2), Fe1–Fe1A 2.716(2), Fe1–Fe2A 2.766(1), Fe2–Fe1A 2.766(1), Fe2–Fe2A 2.596(2); C1–Fe1–Se1 112.9(2), C1–Fe1–Se2 112.4(2), C1–Fe1–Se2A 107.5(2), Se1–Fe1–Se2 108.9(1), Se1–Fe1–Se2A 104.5(1), Se2–Fe1–Se2A 110.4(1).

The reactions yielding the bis(imido)iron complexes **7** and **8** proceeded according to Equation (3). These reactions



vigorously released N₂ bubbles, and dvtms was detected as the byproduct by ¹H NMR spectroscopy.^[6] X-ray diffraction studies revealed that **7** and **8** are bis(imido)iron(IV) com-

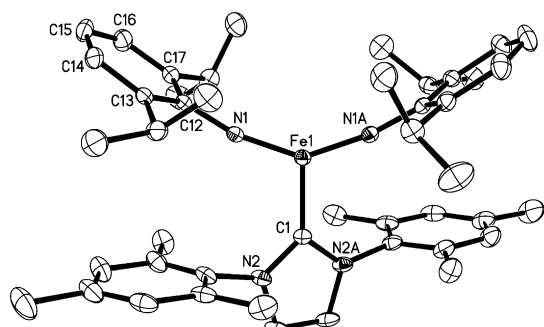


Figure 4. Molecular structure of **7**.^[30] Thermal ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°]: Fe1–C1 1.899(3), Fe1–N1 1.633(2), N1–C12 1.377(3); C1–Fe1–N1 109.5(1), N1–Fe1–N1A 141.0(1), C12–N1–Fe1 166.5(2).

pounds supported by aminocarbene ligands. Figure 4 shows the structure of **7**. Both **7** and **8** feature distorted trigonal-planar FeCN_2 cores with large N–Fe–N angles (around 140°), short Fe–C(carbene) (1.899(3) and 1.878(2) Å for **7** and **8**, respectively) and Fe–N (ca. 1.64 Å) distances. These bond lengths are shorter than the corresponding ones in the ferrous amido complex $[(\text{IPr})\text{Fe}(\text{NHDipp})_2]$ by 0.25 and 0.30 Å, respectively.^[25] Meanwhile, the Fe–N–C alignments in **7** and **8** ($164.9(1)$ to $170.0(1)^\circ$) are less bent than those in $[(\text{IPr})\text{Fe}(\text{NHDipp})_2]$ (139° in average). When compared to the iron imido species, the Fe–N distances in **7** and **8** are comparable to those in Power's $[(\text{Ar}^*)\text{Fe}(\text{NAd})_2]$ (1.63 Å in average)^[26] ($\text{Ar}^* = 3,5\text{-diisopropyl-2,6-di}(2',4',6'\text{-triisopropylphenyl})\text{-phenyl}$) and many of the four-coordinate compounds with tetrahedral or square planar coordination geometry,^[27] but shorter than those in Holland's three-coordinate β -diketidinato iron(III) imido compounds (1.67 and 1.70 Å).^[28] The ^{57}Fe Mössbauer spectra revealed $\delta = -0.32 \text{ mm s}^{-1}$ and $\Delta E_{\text{O}} = 1.89 \text{ mm s}^{-1}$ for **7**, and $\delta = -0.39 \text{ mm s}^{-1}$ and $\Delta E_{\text{O}} = 1.60 \text{ mm s}^{-1}$ for **8**.^[6] The negative δ values form sharp contrast to the δ values of **2**, **3**, $[(\text{IPr})\text{Fe}(\text{NHDipp})_2]$ ($\delta = 0.58 \text{ mm s}^{-1}$, $\Delta E_{\text{O}} = 1.39 \text{ mm s}^{-1}$),^[6] and $[(\text{DippNC}(\text{Me})_2\text{CH})\text{Fe}(\text{NAd})]$ ($\delta = 0.47 \text{ mm s}^{-1}$),^[29a] and more close to those observed in the low-spin complexes, for example, Que's six-coordinate iron(IV) imido species ($\delta = +0.02 \text{ mm s}^{-1}$),^[29b] Meyer's four-coordinate iron(IV) nitride ($\delta = -0.27 \text{ mm s}^{-1}$),^[29c] and Peter's four-coordinate iron(IV) nitride ($\delta = -0.34 \text{ mm s}^{-1}$).^[29d] These characterization data, in addition with their diamagnetic nature as referred from their well-resolved ^1H and ^{13}C NMR spectra, suggest that **7** and **8** are low-spin iron(IV) species.

In conclusion, we have prepared and characterized novel 16- and 14-electron high-spin iron(0) alkene compounds by using aminocarbene and dtms as ancillary ligands. These coordinatively unsaturated iron(0) compounds can serve as useful synthons for $[\text{L}_2\text{Fe}^0]$ and $[\text{LFe}^0]$ (L = aminocarbene) complexes, which has been demonstrated by their reactions with hydrosilanes, elemental sulfur/selenium, and organic azides to produce aminocarbene-supported (silylene)iron(IV), all-ferrous iron–sulfur/selenium cubanes, as well as mononuclear bis(imido)iron(IV) compounds. Further exploration of the reactivity and catalytic application of these

aminocarbene-supported iron(0) alkene complexes are underway.

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