Iron(0) Reagents

DOI: 10.1002/anie.201404677

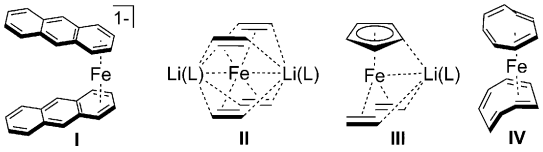
(Aminocarbene)(Divinyltetramethyldisiloxane)Iron(0) Compounds: A Class of Low-Coordinate Iron(0) Reagents**

*Hezhong Zhang, Zhenwu Ouyang, Yuesheng Liu, Qiang Zhang, Lei Wang, and Liang Deng**

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

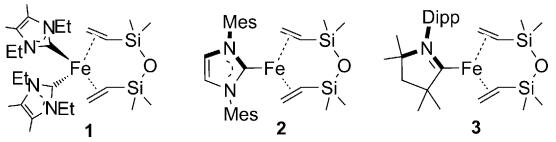
Abstract: *The combined use of aminocarbene and divinyltetramethyldisiloxane (dvtms) as supporting ligands enables the access of unprecedented low-coordinate iron(0) alkene compounds [$L_nFe(\eta^2{:}\eta^2$-dvtms)] (L = N-heterocyclic carbene (NHC) or cyclic (alkyl)(amino)carbene (CAAC), $n = 1$ or 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-η^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(dvtms)] (**1–3** in Scheme 2, L = N-heterocyclic carbene (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.



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

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

$$FeCl_2 + n\,L + dvtms + 2\,M \rightarrow [L_nFe(dvtms)] + 2\,MCl \quad (1)$$
$$M = Na(Hg) \text{ or } KC_8,\ L = NHC \text{ or } CAAC$$

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 [($IEt_2Me_2)_2$Fe(dvtms)] (**1**), [(IMes)Fe(dvtms)] (**2**), and [(Me_2-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-cAAC = 1-(2′,6′-diisopropyl-

[*] H. Zhang,[+] Z. Ouyang,[+] Y. Liu, Q. Zhang, L. Wang, Prof. Dr. L. Deng
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry, CAS
345 Lingling Road, Shanghai, 200032 (P. R. China)
E-mail: deng@sioc.ac.cn
Homepage: http://dengliang.sioc.ac.cn/
[+] These authors contributed equally to this work.

[**] This work was supported by the National Basic Research Program of China (No. 2011CB808705), the National Natural Science Foundation of China (Nos. 21121062 and 21222208), and the Chinese Academy of Sciences.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201404677.

phenyl)-3,3,5,5-tetramethyl- pyrrolidine-2-ylidene) were isolated in 44–87% yields.[6] Complexes **1**–**3** have been characterized by ^{1}H NMR spectroscopy, solution magnetic susceptibility measurement, UV/Vis-NIR spectroscopy, infrared resonance, single-crystal X-ray diffraction, ^{57}Fe Mössbauer spectroscopy, and elemental analysis.[6] Their ^{1}H NMR spectra measured in C_6D_6 showed paramagnetically shifted broad peaks, and solution magnetic susceptibility measurement (3.5(1), 3.5(1), and 4.0(2) μB 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 η^2:η^2-fashion and two IEt_2Me_2 ligands, whereas, **2** and **3** are trigonal planar iron(0) species bearing one bulky aminocarbene (IMes or Me_2-CAAC) and one η^2:η^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→π* 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 ^{57}Fe 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(CH_2S*t*Bu)$_3$Fe(PhCCPh)] ($\delta = 0.62$ mm s^{-1}, $\Delta E_Q = 1.62$ mm s^{-1}),[11a] and [({DippN-C(Me)}$_2$CH)Fe(PhCCH)] ($\delta = 0.44$ mm s^{-1}, $\Delta E_Q = 2.05$ mm s^{-1}),[11b] and also those of the low-spin iron(0) compound [Fe{(^{Dipp}C)$_2$CH$_2$}(η-(C_6H_6)] ($\delta = 0.43$ 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)$_2$Fe(η^4-cot)] (BAC: bis(diisopropylamino)cyclopropenylidene),[3g] and the π-arene complexes [Fe{(^{Dipp}C)$_2$CH$_2$}(η^6-(C_6H_5R)][11c] 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(PMe_3)$_4$],[13] [Fe{(^{Dipp}C)$_2$CH$_2$}(PMe_3)$_2$],[11c] [Fe(IMes)$_2$],[14] and [(PEt_3)$_2$Fe{η^2-(CH_2=CH_2)}$_2$][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 vinylsiloxane ligand. To our surprise, while such a combined ligand set has proved useful for creating stable three-coordinate Pt^0, Pd^0, and Ni^0 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 [(IEt_2Me_2)$_2$Fe(H)$_3$($SiHPh_2$)-(IEt_2Me_2)}] (**4**), [(IEt_2Me_2)$_4$Fe$_4$X$_4$]

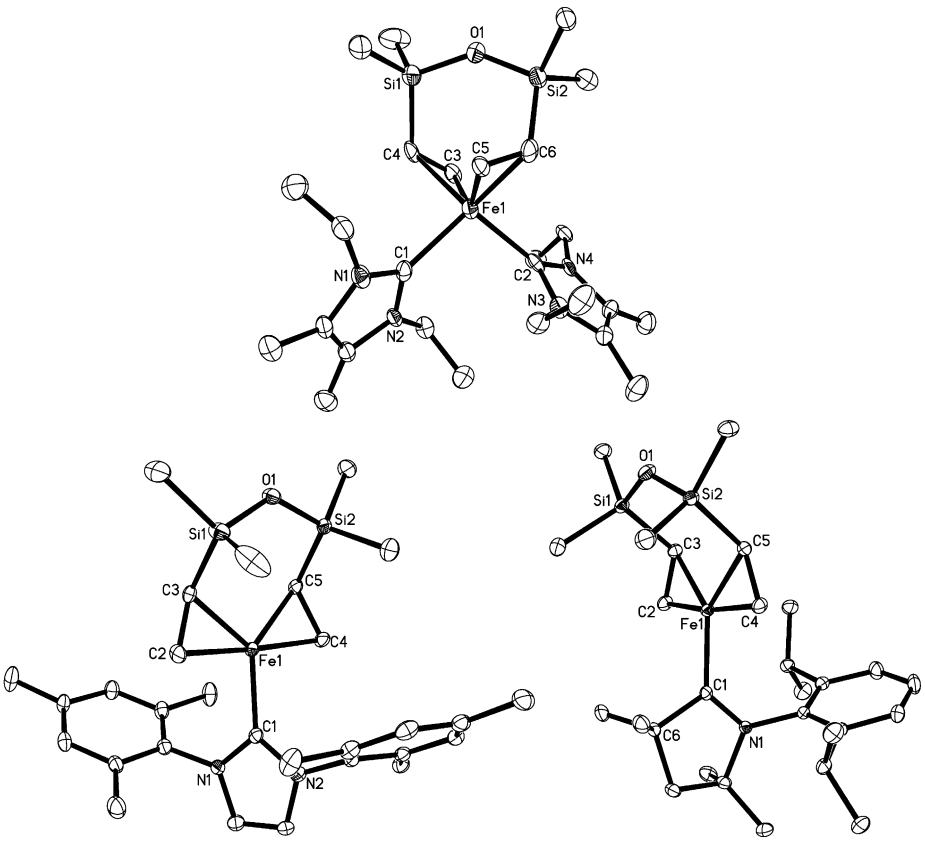
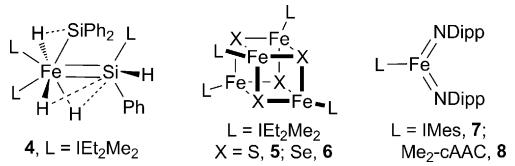


Figure 1. Molecular structures of **1** (top), **2** (bottom, left), and **3** (bottom, right).[30] Thermal ellipsoids set at 30% probability. Selected bond lengths [Å] for **1**: Fe1–C1 2.109(8), Fe1–C2 2.046(9), Fe1–C3 2.070(8), Fe1–C4 2.155(9), Fe1–C5 2.056(9), Fe1–C6 2.115(9), C3–C4 1.41(1), C5–C6 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**, Me$_2$-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 Ph_2SiH_2, 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(IEt$_2$Me$_2$), with a short Fe–Si separation of 2.170(1) Å (Figure 2).[20] Three iron-bound

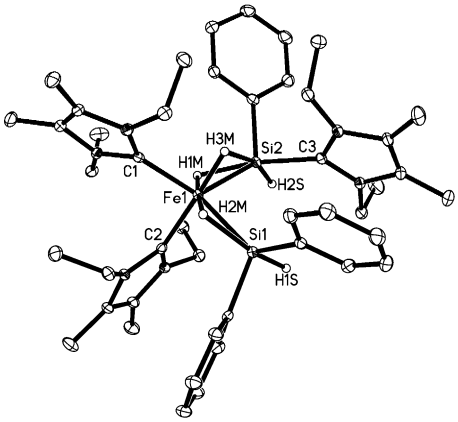


Figure 2. Molecular structure of **4**.[30] Thermal ellipsoids set at 30% probability. Selected bond lengths [Å]: Fe1–C1 1.989(2), Fe1–C2 1.939(2), Fe1–Si1 2.239(1), Fe1–Si2 2.170(1), Fe1–H1M 1.53(2), Fe1—H2M 1.48(2), Fe1–H3M 1.49(2), Si1–H1S 1.53(2), Si2–H2S 1.46(2), Si1–H2M 1.92(2), Si2–H1M 1.77(2), 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. ^{1}H and ^{29}Si 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(IEt$_2$Me$_2$) ligand in **4** implies the involvement of hydrosilane redistribution in the reaction of **1** with Ph_2SiH_2,[21] probably facilitated by (IEt$_2$Me$_2$)$_2$Fe. 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 (IEt$_2$Me$_2$)$_2$Fe 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 [(IEt$_2$Me$_2$)$_4$Fe$_4$S$_4$] (**5**) and [(IEt$_2$Me$_2$)$_4$Fe$_4$Se$_4$] (**6**), whose formation can be rationalized by Equation (2), represent the rare synthetic

$$4\,[(IEt_2Me_2)_2Fe(dvtms)] + 4\,X \xrightarrow{X=S\text{ or }Se} [(IEt_2Me_2)_4Fe_4X_4] + 4\,IEt_2Me_2 + 4\,dvtms \quad (2)$$

analogues of the super-reduced iron–sulfur clusters in metalloproteins.[23] Holm and Deng accessed a carbene-stabilized cluster, [(IPr$_2$Me$_2$)$_4$Fe$_4$S$_4$], by the reaction of [(P*i*Pr$_3$)$_2$FeCl$_2$] with (TMS)$_2$S, followed by ligand substitution of P*i*Pr$_3$ with IPr$_2$Me$_2$.[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 $[Fe_4S_4]^0$ core in **5** are similar to that of [(IPr$_2$Me$_2$)$_4$Fe$_4$S$_4$], and that the $[Fe_4Se_4]^0$ 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 ^{1}H 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 IPr$_2$Me$_2$ ligation.[24]

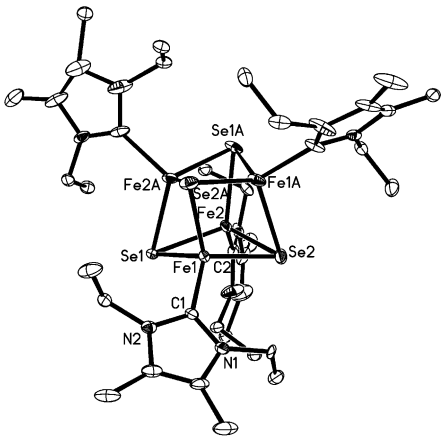


Figure 3. Molecular structure of **6**.[30] Thermal ellipsoid set at 30% probability. Selected interatomic separations [Å] and angles [°]: Fe1–C1 2.111(6), Fe2–C1 2.100(6), Fe1–Se1 2.443(1), Fe1–Se2 2.441(1), Fe1–Se2A 2.449(1), Fe2–Se1 2.481(1), Fe2–Se2 2.426(1), Fe2–Se1A 2.448(1), Fe1···Fe2 2.715(2), 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

$$[LFe(dvtms)] + 2\,DippN_3 \xrightarrow{L=IMes\text{ or }Me_2\text{-}CAAC} [LFe(NDipp)_2] + 2\,N_2 + dvtms \quad (3)$$

vigorously released N_2 bubbles, and dvtms was detected as the byproduct by ^{1}H NMR spectroscopy.[6] X-ray diffraction studies revealed that **7** and **8** are bis(imido)iron(IV) com-

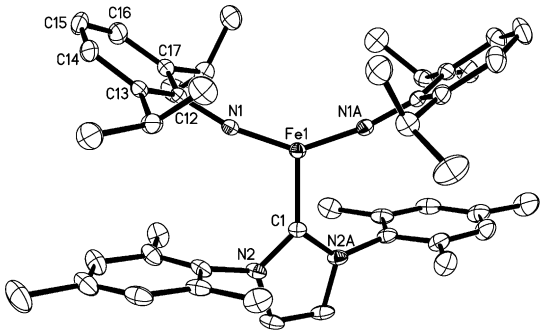


Figure 4. Molecular structure of **7**.[30] Thermal ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°]: Fe1–C1 1.899(3), Fe1–N1 1.633(2), N1–C12 1.377(3); C1-Fe1-N1 109.5(1), N1-Fe1-N1A 141.0(1), C12-N1-Fe1 166.5(2).

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 $[(IPr)Fe(NHDipp)_2]$ 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)°) are less bent than those in $[(IPr)Fe(NHDipp)_2]$ (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 $[(Ar^*)Fe(NAd)_2]$ (1.63 Å in average)[26] (Ar* = 3,5-diisopropyl-2,6-di(2′,4′,6′-triisopropylphenyl)-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-diketidiminato iron(III) imido compounds (1.67 and 1.70 Å).[28] The ^{57}Fe Mössbauer spectra revealed $\delta = -0.32\ mm\,s^{-1}$ and $\Delta E_Q = 1.89\ mm\,s^{-1}$ for **7**, and $\delta = -0.39\ mm\,s^{-1}$ and $\Delta E_Q = 1.60\ mm\,s^{-1}$ for **8**.[6] The negative δ values form sharp contrast to the δ values of **2**, **3**, $[(IPr)Fe(NHDipp)_2]$ ($\delta = 0.58\ mm\,s^{-1}$, $\Delta E_Q = 1.39\ mm\,s^{-1}$),[6] and $[(DippNC(Me))_2CH)Fe(NAd)]$ ($\delta = 0.47\ mm\,s^{-1}$),[29a] and more close to those observed in the low-spin complexes, for example, Que's six-coordinate iron(IV) imido species ($\delta = +0.02\ mm\,s^{-1}$),[29b] Meyer's four-coordinate iron(IV) nitride ($\delta = -0.27\ mm\,s^{-1}$),[29c] and Peter's four-coordinate iron(IV) nitride ($\delta = -0.34\ mm\,s^{-1}$).[29d] These characterization data, in addition with their diamagnetic nature as referred from their well-resolved ^{1}H 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 dvtms as ancillary ligands. These coordinatively unsaturated iron(0) compounds can serve as useful synthons for $[L_2Fe^0]$ and $[LFe^0]$ (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.

Received: April 24, 2014
Published online: June 24, 2014

Keywords: alkene complexes · carbene complexes · iron · low-coordinate complexes

[1] a) C. Elschenbroich, *Organometallics*, 3edrd edWiley-VCH, Weinheim, **2006**, chap. 15; b) H. Werner, *Landmarks in Organo-Transition Metal Chemistry*, Springer, New York, **2009**, chap. 7; c) O. García Mancheño, *Angew. Chem.* **2011**, *123*, 2264–2266; *Angew. Chem. Int. Ed.* **2011**, *50*, 2216–2218; d) N. Weding, M. Hapke, *Chem. Soc. Rev.* **2011**, *40*, 4525–4538.

[2] a) M. Bullock, *Catalysis Without Precious Metals*, Wiley-VCH, Weinheim, **2010**; b) B. Plietker, *Iron Catalysis in Organic Chemistry*, Wiley-VCH, Weinheim, **2008**.

[3] a) H.-J. Knölker, *Chem. Rev.* **2000**, *100*, 2941–2961; b) Y. Yu, J. M. Smith, C. J. Flaschenriem, P. L. Holland, *Inorg. Chem.* **2006**, *45*, 5742–5751; c) W. W. Brennessel, R. E. Jilek, J. E. Ellis, *Angew. Chem.* **2007**, *119*, 6244–6248; *Angew. Chem. Int. Ed.* **2007**, *46*, 6132–6136; d) D. Gärtner, A. Welther, B. R. Rad, R. Wolf, A. Jacobi von Wangelin, *Angew. Chem.* **2014**, *126*, 3796–3800; *Angew. Chem. Int. Ed.* **2014**, *53*, 3722–3726; e) A. Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard, C. W. Lehmann, *J. Am. Chem. Soc.* **2008**, *130*, 8773–8787; f) V. Lavallo, R. H. Grubbs, *Science* **2009**, *326*, 559–562; g) V. Lavallo, A. El-Batta, G. Bertrand, R. H. Grubbs, *Angew. Chem.* **2011**, *123*, 282–285; *Angew. Chem. Int. Ed.* **2011**, *50*, 268–271.

[4] a) K. Jonas, *Angew. Chem.* **1985**, *97*, 292–307; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 295–311; b) K. Jonas, L. Schieferstein, C. Krüger, Y.-H. Tsay, *Angew. Chem.* **1979**, *91*, 590–591; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 550–551.

[5] a) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676; b) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92; c) V. Lavallo, Y. Canac, A. DeHope, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 7402–7405; *Angew. Chem. Int. Ed.* **2005**, *44*, 7236–7239; d) W. A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256–2282; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187; e) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; f) T. Dröge, F. Glorius, *Angew. Chem.* **2010**, *122*, 7094–7107; *Angew. Chem. Int. Ed.* **2010**, *49*, 6940–6952.

[6] For detailed information, see the Supporting Information.

[7] These solution magnetic moments are larger than the spin-only value of 2.83 μ_B for an $S = 1$ d^8 systems, which may be caused by the presence of orbital moment contribution as observed in low-coordinate iron(I,II) compounds. For examples, see: a) H. Andres, E. L. Bominaar, J. M. Smith, N. A. Eckert, P. L. Holland, E. Münck, *J. Am. Chem. Soc.* **2002**, *124*, 3012–3025; b) W. M. Reiff, A. M. LaPointe, E. H. Witten, *J. Am. Chem. Soc.* **2004**, *126*, 10206–10207; c) W. A. Merrill, T. A. Stich, M. Brynda, G. J. Yeagle, J. C. Fettinger, R. De Hont, W. M. Reiff, C. E. Schulz, R. D. Britt, P. P. Power, *J. Am. Chem. Soc.* **2009**, *131*, 12693–12702.

[8] a) S. Bruña, A. M. González-Vadillo, D. Nieto, C. Pastor, I. Cuadrado, *Organometallics* **2010**, *29*, 2796–2807; b) U. H. Strasser, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1249–1254.

[9] For examples, see: a) L. Xiang, J. Xiao, L. Deng, *Organometallics* **2011**, *30*, 2018–2025; b) S. Zlatogorsky, C. A. Muryn, F. Tuna, D. J. Evans, M. J. Ingleson, *Organometallics* **2011**, *30*,

4974 – 4982; c) S. Meyer, C. M. Orben, S. Demeshko, S. Dechert, F. Meyer, *Organometallics* **2011**, *30*, 6692 – 6702; d) R. A. Layfield, J. J. W. McDouall, M. Scheer, C. Schwarzmaier, F. Tuna, *Chem. Commun.* **2011**, *47*, 10623 – 10625; e) J. A. Przyojski, H. D. Arman, Z. J. Tonzetich, *Organometallics* **2012**, *31*, 3264 – 3271; f) A. A. Danopoulos, P. Braunstein, M. Wesolek, K. Y. Monakhov, P. Rabu, V. Robert, *Organometallics* **2012**, *31*, 4102 – 4105; g) T. Hashimoto, S. Urban, R. Hoshino, Y. Ohki, K. Tatsumi, F. Glorius, *Organometallics* **2012**, *31*, 4474 – 4479; h) Q. Zhang, L. Xiang, L. Deng, *Organometallics* **2012**, *31*, 4537 – 4543; i) S. Pelties, R. Wolf, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2581 – 2585.

[10] For reference on the π acidity of NHC ligands, see: a) A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Gaunter, *Organometallics* **2012**, *32*, 5269 – 5272, and reference therein. The π acidity of CAACs is well established, see: b) D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2011**, *2*, 389 – 399; c) D. Martin, M. Melaimi, M. Soleilhavoup, G. Bertrand, *Organometallics* **2011**, *30*, 5304 – 5313; d) A. P. Signh, P. P. Samuel, H. W. Roesky, M. C. Schwarzer, G. Frenking, N. S. Sidhu, B. Dittrich, *J. Am. Chem. Soc.* **2013**, *135*, 7324 – 7329; e) P. P. Samuel, K. C. Mondal, H. W. Roesky, M. Hermann, G. Frenking, S. Demeshko, F. Meyer, A. C. Stückl, J. H. Christian, N. S. Dalal, L. Ungur, L. F. Chibotaru, K. Pröpper, A. Meents, B. Dittrich, *Angew. Chem.* **2013**, *125*, 12033 – 12037; *Angew. Chem. Int. Ed.* **2013**, *52*, 11817 – 11821, and references therein.

[11] a) M. T. Mock, C. V. Popescu, G. P. A. Yap, W. G. Dougherty, C. G. Riordan, *Inorg. Chem.* **2008**, *47*, 1889 – 1891; b) S. A. Stoian, Y. Yu, J. M. Smith, P. L. Holland, E. L. Bominaar, E. Münck, *Inorg. Chem.* **2005**, *44*, 4915 – 4922; c) B. Blom, G. Tan, S. Enthaler, S. Inoue, J. D. Epping, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 18108 – 18120.

[12] T. Hashimoto, R. Hoshino, T. Hatanaka, Y. Ohki, K. Tatsumi, *Organometallics* **2014**, *33*, 921 – 929.

[13] H. H. Karsch, *Chem. Ber.* **1977**, *110*, 2699 – 2711.

[14] Z. Ouyang, L. Deng, *Organometallics* **2013**, *32*, 7268 – 7271.

[15] H. Hoberg, K. Jenni, K. Angermund, C. Krüger, *Angew. Chem.* **1987**, *99*, 141 – 142; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 153 – 155.

[16] a) K. Riener, S. Haslinger, A. Raba, M. P. Högerl, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Chem. Rev.* **2014**, *114*, 5215 – 5272; b) M. J. Ingleson, R. A. Layfield, *Chem. Commun.* **2012**, *48*, 3579 – 3589.

[17] For examples of Group 10 transiton-metal dvtms complexes, see: a) I. E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J.-P. Declercq, *Science* **2002**, *298*, 204 – 206; b) R. Jackstell, M. G. Andreu, A. Frisch, K. Selvakumar, A. Zapf, H. Klein, A. Spannenberg, D. Röttger, O. Briel, R. Karch, M. Beller, *Angew. Chem.* **2002**, *114*, 1028 – 1031; *Angew. Chem. Int. Ed.* **2002**, *41*, 986 – 989; c) G. Berthon-Gelloz, B. de Bruin, B. Tinant, I. E. Markó, *Angew. Chem.* **2009**, *121*, 3207 – 3210; *Angew. Chem. Int. Ed.* **2009**, *48*, 3161 – 3164; d) J. Wu, J. W. Faller, N. Hazari, T. J. Schmeier, *Organometallics* **2012**, *31*, 806 – 809.

[18] The chemistry of low-coordinate iron(III), iron(II), and iron(I) compounds has witnessed a fast development since the early studies in the 1970s. For references, see: a) D. C. Bradley, M. H. Chisholm, *Acc. Chem. Res.* **1976**, *9*, 273 – 280; b) C. C. Cummins, *Prog. Inorg. Chem.* **1998**, *47*, 685 – 836; c) P. L. Holland, *Acc. Chem. Res.* **2008**, *41*, 905 – 914; d) P. P. Power, *Chem. Rev.* **2012**, *112*, 3482 – 3507.

[19] M. Ingleson, H. Fan, M. Pink, J. Tomaszewski, K. G. Caulton, *J. Am. Chem. Soc.* **2006**, *128*, 1804 – 1805.

[20] Donor-stabilized silylene iron complexes are known for formal iron(0) and iron(II) species, which generally have Fe–Si distances longer than 2.2 Å, for example, see: a) C. Zybill, G. Müller, *Angew. Chem.* **1987**, *99*, 683 – 684; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 669 – 670; b) U. Bodensieck, P. Braunstein, W. Deck, T. Faure, M. Knorr, C. Stern, *Angew. Chem.* **1994**, *106*, 2561 – 2564; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2440 – 2442; c) H. Kobayashi, K. Ueno, H. Ogino, *Organometallics* **1995**, *14*, 5490 – 5492; d) J. C. Corey, *Chem. Rev.* **2011**, *111*, 863 – 1071.

[21] a) H. Hashimoto, H. Tobita, H. Ogino, *J. Organomet. Chem.* **1995**, *499*, 205 – 211; b) N. S. Radu, F. J. Hollander, T. D. Tilley, A. L. Rheingold, *Chem. Commun.* **1996**, 2459 – 2460; c) H. Tobita, A. Matsuda, H. Hashimoto, K. Ueno, H. Ogino, *Angew. Chem.* **2004**, *116*, 223 – 226; *Angew. Chem. Int. Ed.* **2004**, *43*, 221 – 224.

[22] a) S. C. Bart, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2004**, *126*, 13794 – 13807; b) D. Pugh, N. J. Wells, D. J. Evans, A. A. Danopoulos, *Dalton Trans.* **2009**, 7189 – 7195.

[23] a) L. Deng, R. H. Holm, *J. Am. Chem. Soc.* **2008**, *130*, 9878 – 9886; b) A. Albers, S. Demeshko, K. Pröpper, S. Dechert, E. Bill, F. Meyer, *J. Am. Chem. Soc.* **2013**, *135*, 1704 – 1707.

[24] M. Chakrabarti, L. Deng, R. H. Holm, E. Münck, E. L. Bominaar, *Inorg. Chem.* **2009**, *48*, 2735 – 2747.

[25] X. Wang, Z. Mo, J. Xiao, L. Deng, *Inorg. Chem.* **2013**, *52*, 59 – 65.

[26] C. Ni, J. C. Fettinger, G. J. Long, M. Brynda, P. P. Power, *Chem. Commun.* **2008**, 6045 – 6047.

[27] For examples, see: a) A. K. Verma, T. N. Nazif, C. Achim, S. C. Lee, *J. Am. Chem. Soc.* **2000**, *122*, 11013 – 11014; b) S. D. Brown, T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2003**, *125*, 322 – 323; c) T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2003**, *125*, 10782 – 10783; d) S. C. Bart, E. Lobovsky, E. Bill, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 5302 – 5303; e) I. Nieto, F. Ding, R. P. Bontchev, H. Wang, J. M. Smith, *J. Am. Chem. Soc.* **2008**, *130*, 2716 – 2717; f) J. J. Scepaniak, J. A. Young, R. P. Bontchev, J. M. Smith, *Angew. Chem.* **2009**, *121*, 3204 – 3206; *Angew. Chem. Int. Ed.* **2009**, *48*, 3158 – 3160; g) E. R. King, E. T. Hennessy, T. A. Betley, *J. Am. Chem. Soc.* **2011**, *133*, 4917 – 4923; h) M.-E. Moret, J. C. Peters, *Angew. Chem.* **2011**, *123*, 2111 – 2115; *Angew. Chem. Int. Ed.* **2011**, *50*, 2063 – 2067.

[28] a) R. E. Cowley, N. J. DeYonker, N. A. Eckert, T. R. Cundari, S. DeBeer, E. Bill, X. Ottenwaelder, C. Flaschenriem, P. L. Holland, *Inorg. Chem.* **2010**, *49*, 6172 – 6187; b) R. E. Cowley, P. L. Holland, *Inorg. Chem.* **2012**, *51*, 8352 – 8361.

[29] a) N. A. Eckert, S. Vaddadi, S. Stoian, R. J. Lachicotte, T. R. Cundari, P. L. Holland, *Angew. Chem.* **2006**, *118*, 7022 – 7025; *Angew. Chem. Int. Ed.* **2006**, *45*, 6868 – 6871; b) E. J. Klinker, T. A. Jackson, M. P. Jensen, A. Stubna, G. Juhász, E. L. Bominaar, E. Münck, L. Que, Jr., *Angew. Chem.* **2006**, *118*, 7554 – 7557; *Angew. Chem. Int. Ed.* **2006**, *45*, 7394 – 7397; c) C. Vogel, F. W. Heinemann, J. Sutter, C. Anthon, K. Meyer, *Angew. Chem.* **2008**, *120*, 2721 – 2724; *Angew. Chem. Int. Ed.* **2008**, *47*, 2681 – 2684; d) M. P. Hendrich, W. Gunderson, R. K. Behan, M. T. Green, M. P. Mehn, T. A. Betley, C. C. Lu, J. C. Peters, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 17107 – 17112.

[30] CCDC 998443 – 998450, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

