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## Two- and three-coordinate formal iron(i) compounds featuring monodentate aminocarbene ligands†

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Bulky monodentate aminocarbene ligands, IMes and Me<sub>2</sub>-cAAC (IMes: 1,3-bis(2',4',6'-trimethylphenyl)-imidazol-2-ylidene; Me<sub>2</sub>-cAAC: 3,3,5,5-tetramethyl-1-(2',6'-diisopropylphenyl)pyrrolidine-2-ylidene), have been shown to be effective in supporting formal 13- and 11-electron iron(i) species. From the reactions of ferrous precursors and one equivalent of a reducing agent, three-coordinate complexes of the type [L<sub>2</sub>FeCl] (L = IMes or Me<sub>2</sub>-cAAC) have been synthesized in good yields. A mixed-ligand complex [(IMes)(Me<sub>2</sub>-cAAC)FeCl] was prepared from the ligand substitution reaction of [(IMes)<sub>2</sub>FeCl] with Me<sub>2</sub>-cAAC. All of the three-coordinate iron complexes can react with Na[Bar<sup>F</sup>]<sub>4</sub>, from which a two-coordinate species [(Me<sub>2</sub>-cAAC)<sub>2</sub>Fe][Bar<sup>F</sup>]<sub>4</sub> has been isolated. Single-crystal X-ray diffraction studies established their molecular structures to be the first examples of two- and three-coordinate formal iron(i) species supported by carbene ligands. The large solution magnetic moments, differentiated Fe–C(carbene) distances and <sup>57</sup>Fe Mössbauer isomer shifts are indicative of their rich electronic properties.

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The +1 oxidation state is an uncommon oxidation state for iron,<sup>1</sup> but the possible involvement of iron(i) species in important chemical transformations, such as H<sub>2</sub>-activation and production by [Fe,Fe]-hydrogenases,<sup>2</sup> N<sub>2</sub>-reduction in nitrogenases,<sup>3</sup> and iron-catalyzed cross-coupling reactions,<sup>4</sup> has spurred great synthetic interest. Iron(i) complexes have mostly been known for the six-, five- and four-coordinate compounds with CO, arene, alkene, and phosphine ligation.<sup>5</sup> On the other hand, low-coordinate iron(i) species, those with coordination numbers less than four, are much less common.<sup>6</sup> Up to now, three-coordinate iron(i) compounds have been limited to Holland's β-diketiminato complexes,<sup>3a,7</sup> Caulton's T-shaped compound [((<sup>t</sup>Bu<sub>2</sub>PCH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>N)Fe],<sup>8</sup> and Jones' dinuclear guanidionate complex [(DippN)<sub>2</sub>C(*cis*-2,6-Me<sub>2</sub>NC<sub>5</sub>H<sub>8</sub>)Fe]<sub>2</sub>.<sup>9</sup> Isolable two-coordinate iron(i) compounds had remained unknown until Long's recent report on [K(crypt-222)][Fe(C(SiMe<sub>3</sub>)<sub>3</sub>)<sub>2</sub>].<sup>10</sup>

The effective stabilization of low-coordinate iron(i) species necessitates suitable supporting ligands. Recently, Cárdenas *et al.* reported the detection of an iron(i) intermediate in Fe(OAc)<sub>2</sub>-IMes-catalyzed alkyl-alkyl cross-coupling reactions by low temperature EPR experiments.<sup>4c</sup> Importantly, an IMes-stabilized iron(i) species such as (IMes)<sub>n</sub>FeX could be the potential active catalyst species in this chemistry. Unfortunately, iron(i) species supported by monodentate NHCs are critically absent from the literature.<sup>11</sup> Prompted by this and recent success of NHCs in stabilizing two-coordinate first row late 3d transition metal species,<sup>12</sup> we envisioned that NHCs might be amenable to support low-coordinate iron(i) compounds. In this context, herein we report the synthesis and structural characterization of a three-coordinate formal iron(i) NHC compound [(IMes)<sub>2</sub>FeCl] (**1**), as well as its analogs with cyclic (alkyl)(amino)carbene (cAAC)<sup>13</sup> ligands, [(IMes)(Me<sub>2</sub>-cAAC)FeCl] (**2**) and [(Me<sub>2</sub>-cAAC)<sub>2</sub>FeCl] (**3**). Compounds **1–3** are the first examples of three-coordinate iron-aminocarbene species with formal iron(i) centers. Their stability at ambient temperature has enabled spectroscopic characterization by <sup>1</sup>H NMR, solution magnetic susceptibility measurement, single crystal X-ray diffraction, and zero-field <sup>57</sup>Fe Mössbauer spectroscopy. Moreover, we examined the reactions of **1–3** with Na[Bar<sup>F</sup>]<sub>4</sub>, from which the two-coordinate aminocarbene iron complex [(Me<sub>2</sub>-cAAC)<sub>2</sub>Fe][Bar<sup>F</sup>]<sub>4</sub> (Ar<sup>F</sup> = 3,5-bis(trifluoromethyl)phenyl) (**4**), as the close relative of two-coordinate NHC and cAAC complexes [L<sub>2</sub>M] (M = zinc,<sup>14</sup> copper,<sup>15</sup> nickel,<sup>16</sup> manganese<sup>17</sup>), has been obtained.

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**Scheme 1** Preparation routes for the low-coordinate formal iron(II) complexes.

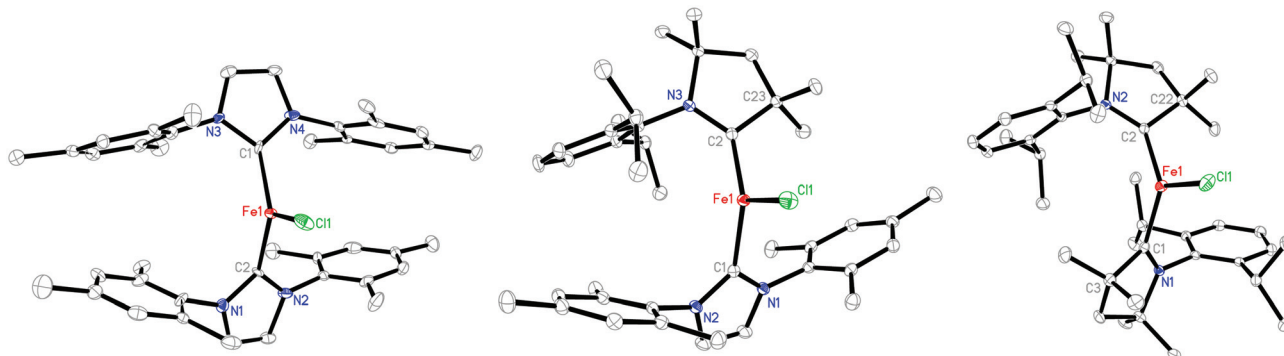
Previously, we found that the reaction of  $[(\text{IMes})_2\text{FeCl}_2]$ , prepared from the interaction of  $\text{FeCl}_2$  with IMes (2 equiv.), with an excess amount of sodium amalgam in THF produces the cyclometallated iron(II)-NHC compound  $[\text{Fe}(\text{IMes}')_2]$  (IMes' denoted for the cyclometallated IMes ligand) and  $\text{H}_2$ .<sup>18</sup> By carefully controlling reaction conditions, we found that a three-coordinate compound  $[(\text{IMes})_2\text{FeCl}]$  (**1**) can be prepared from the reaction of  $[(\text{IMes})_2\text{FeCl}_2]$  with one equiv. of potassium graphite or sodium amalgam in toluene (Scheme 1).<sup>19</sup> The solvent plays a crucial role in the preparation of **1**. When the reaction was conducted in THF, iron black and  $[\text{Fe}(\text{IMes}')_2]$  were observed as the dominant products, even if only one equiv. of the reducing reagent was used. In contrast to the reaction with IMes, the one-electron reduction reactions of  $\text{FeCl}_2$  in the presence of two equiv. of IPr, SIMes, or IAD (IPr = 1,3-bis(2',6'-diisopropylphenyl)imidazole-2-ylidene, SIMes = 1,3-bis(2',4',6'-trimethylphenyl)-4,5-dihydroimidazole-2-ylidene, IAD = 1,3-bis(adamantyl)imidazole-2-ylidene) generally produced iron black and free carbene ligands.

Single crystals of **1** were obtained by freezing its toluene solution at  $-30^\circ\text{C}$ . An X-ray diffraction study revealed that **1** is isostructural to  $[(\text{IMes})_2\text{CoCl}]$ ,<sup>12a</sup> in which the iron center adopts a distorted trigonal planar geometry with a C1–Fe1–C2 angle of  $125.6(3)^\circ$ , and Fe–Cl and Fe–C(IMes) distances of 2.258(3) and 2.014(9) Å, respectively (Fig. 1). Consistent with the larger atomic radius of iron *versus* that of cobalt, the Fe–C(IMes) distances are longer than the Co–C(IMes) bonds in  $[(\text{IMes})_2\text{CoCl}]$  (1.953(5) Å). Notably, the Fe–C(IMes) bonds in **1** are significantly shorter than previously found in three-coordinate iron(II)-NHC compounds,  $[(\text{IPr}_2\text{Me}_2)\text{Fe}(\text{Mes})_2]$  (2.125(3) Å),<sup>20a</sup>  $[(\text{SIPr})\text{Fe}(\text{CH}_2\text{TMS})\text{Cl}]$  (2.128(3) Å),<sup>20b</sup> and  $[(\text{t}^t\text{Bu})\text{Fe}-$

$(\text{N}(\text{SiMe}_3)_2)_2]$  (2.152(2) Å).<sup>20c</sup> The decrease of the Fe–C(IMes) distance from the iron(II) compounds to the formal iron(I) compound is unusual and is likely induced by  $\pi$ -bonding between the low-valent iron center and the NHC ligands.

As isolated, **1** is an air- and moisture-sensitive brown crystalline solid, but can be stored under a  $\text{N}_2$  atmosphere at room temperature for weeks without noticeable decomposition. When dissolved in  $\text{C}_6\text{D}_6$ , it decomposed into  $[(\text{IMes})_2\text{FeCl}_2]$ , IMes, iron black, and  $[\text{Fe}_2(\text{IMes})_2]$ <sup>21</sup> in 3 days at room temperature. The  $^1\text{H}$  NMR spectrum of **1** measured in  $\text{C}_6\text{D}_6$  shows four paramagnetically shifted peaks at +51.73, +7.86, –12.57, and –12.77 ppm with an integrated ratio of 1 : 6 : 3 : 2, suggesting the free rotation of the NHC ligand around the Fe–C(carbene) bond. Solution magnetic susceptibility measurement in  $\text{C}_6\text{D}_6$  indicated a solution magnetic moment of  $5.0(1)\mu_{\text{B}}$  for **1**. This value is much larger than the spin-only value of  $3.8\mu_{\text{B}}$  for high-spin,  $S = 3/2$   $d^7$  ions, likely due to the presence of unquenched orbital angular momentum as found in Holland's  $\beta$ -diketiminato-iron(I)-alkyne compound  $[(\text{DippNC}^t\text{Bu})_2\text{CH})\text{Fe}(\eta^2\text{-HCCPh})]$  ( $4.7\mu_{\text{B}}$ ).<sup>7b</sup>

The propensity of **1** to undergo decomposition in solution rendered attempts to access its three-coordinate derivatives by salt elimination reactions unsuccessful. However, **1** can readily undergo a ligand replacement reaction with  $\text{Me}_2\text{-cAAC}$  to furnish a new three-coordinate complex  $[(\text{IMes})(\text{Me}_2\text{-cAAC})\text{FeCl}]$  (**2**) and free IMes in high yield (Scheme 1).<sup>19</sup> The conversion of **1** to **2** provides direct evidence for the stronger affinity of  $\text{Me}_2\text{-cAAC}$  to transition metals *versus* IMes, consistent with Bertrand's determination that cAACs with small HOMO–LUMO energy-gaps are both stronger electrophiles and nucleophiles than NHCs.<sup>13</sup> The isolation of **1** and **2** prompted attempts to access their bis(cAAC) analogs. While the ligand substitution protocol starting from either **1** or **2** was unsuccessful, the desired complex  $[(\text{Me}_2\text{-cAAC})_2\text{FeCl}]$  (**3**) was eventually prepared by the reaction of  $\text{FeCl}_2$  with two equiv. of  $\text{Me}_2\text{-cAAC}$  and one equiv. of sodium amalgam or potassium graphite in THF in 60% isolated yield (Scheme 1).<sup>19</sup> Both **2** and **3** are stable in the solid state under an inert atmosphere. When dissolved in  $\text{C}_6\text{D}_6$ , **2** does not show decomposition after standing at room temperature for 3 days, whereas **3** displays partial decomposition (less than 10%). The improved thermal stability



**Fig. 1** Molecular structures of **1** (left), **2** (middle), and **3** (right), showing 30% probability ellipsoids and partial atom schemes.

**Table 1** Selected bond lengths (Å) and angles (°) of **1–4** from X-ray diffraction studies at 140(2) K

	1	2	3	4 <sup>c</sup>
Fe–Cl	2.258(3)	2.267(1)	2.264(1)	
Fe–C	1.998(9)	2.099(2) <sup>a</sup>	1.979(2)	1.997(3)
	2.030(8)	1.925(2) <sup>b</sup>	2.004(2)	
C–N	1.349(13)–1.404(11)	1.360(2) <sup>a</sup>	1.335(2)	1.310(3)
		1.369(2) <sup>a</sup>	1.339(2)	
		1.360(2) <sup>b</sup>		
C–Fe–C	125.6(3)	126.0(1)	121.0(1)	180.0(1)
C–Fe–Cl	116.4(3)	116.8(1)	119.3(1)	
	118.0(3)	116.4(1)	119.7(1)	

<sup>a</sup> Parameters of the Fe(IMes) fragment. <sup>b</sup> Parameters of the Fe(Me<sub>2</sub>-cAAC) fragment. <sup>c</sup> Data are the average of two crystallographically independent cations in the unit cell.

of **2** and **3** versus that of **1** could be attributed to the good  $\pi$ -accepting ability of cAACs.<sup>13</sup> Similar to **1**, large solution magnetic moments of 5.1(1) and 4.7(1) $\mu_B$  for **2** and **3**, respectively, have been determined by the Evans method.

The molecular structures of **2** and **3** in the solid state have been established by X-ray diffraction studies (Fig. 1). Their key structure data are compiled in Table 1 along with those of **1** for comparison. These three complexes hold similar trigonal planar FeC<sub>2</sub>Cl cores, but their Fe–C(carbene) distances differ significantly. The Fe–C(IMes) bond in **2** with the distance of 2.099(2) Å shows significant elongation over its counterparts in **1** by 0.08 Å, and is slightly shorter than those of the aforementioned three-coordinate iron(II)–NHC compounds.<sup>18</sup> On the other hand, the Fe–C(Me<sub>2</sub>-cAAC) bond in **2** with the distance of 1.925(2) Å is substantially shorter than those observed in **3** (1.991(2) Å on average) and the iron(II) complex [Cl(cAAC)Fe(μ-Cl)<sub>2</sub>Fe(cAAC)Cl] (2.094(3) Å).<sup>22</sup> Along with the short Fe–C(Me<sub>2</sub>-cAAC) distance, the C(carbene)–N distance of the cAAC ligand in **2** (1.360(2) Å) is found to be longer than its counterparts in **3** (1.335(2) and 1.339(2) Å), approaching the distances in [(Me<sub>2</sub>-cAAC)<sub>2</sub>Mn] (1.359(2) Å),<sup>17</sup> but still shorter than those in [(Me<sub>2</sub>-cAAC)<sub>2</sub>Zn] (1.376(2) Å).<sup>14</sup> The C(carbene)–N distances in **3** are close to those observed in [(Me<sub>2</sub>-cAAC)<sub>2</sub>Ni] (1.338(2) and 1.342(2) Å)<sup>16c</sup> and [(Me<sub>2</sub>-cAAC)<sub>2</sub>CoCl] (1.334 Å),<sup>23</sup> and are longer than the ones in [Cl(cAAC)Fe(μ-Cl)<sub>2</sub>Fe(cAAC)Cl] (1.31 Å)<sup>22</sup> and free cAAC ligands (1.32 Å).<sup>13a,b</sup>

We then examined the reactions of these three-coordinate species with Na[BarF<sub>4</sub>] with the aim to obtain two-coordinate iron species. The interactions of **1** or **2** with one equiv. of Na[BarF<sub>4</sub>] in THF at –30 °C could produce red and deep blue solutions, which turned into intractable deep brown suspensions upon standing at room temperature. In contrast, the reaction of **3** with one equiv. of Na[BarF<sub>4</sub>] in THF could produce a stable deep blue suspension, from which a two-coordinate complex [(Me<sub>2</sub>-cAAC)<sub>2</sub>Fe][BarF<sub>4</sub>] (**4**) was isolated as a green crystalline solid in 45% yield (Scheme 1).<sup>19</sup> The <sup>1</sup>H NMR spectrum of **4** shows heavily broadened resonances in the range +50 to –61 ppm. Its solution magnetic moment is 5.1(2) $\mu_B$ , similar to the values observed for complexes **1–3**.

**Fig. 2** Molecular structure of the cation [(Me<sub>2</sub>-cAAC)<sub>2</sub>Fe]<sup>+</sup> in **4** showing one of the two crystallographically independent cations in the unit cell with 30% probability ellipsoids.

Single-crystals of **4** were grown from its diethyl ether solution. An X-ray diffraction study revealed that the unit cell contains two sets of well-separated ion pairs [(Me<sub>2</sub>-cAAC)<sub>2</sub>Fe]<sup>+</sup> and [BarF<sub>4</sub>]<sup>–</sup> and one diethyl ether molecule. The closest distance between the cations is around 12.8 Å. Since the metric data of the two cations are very similar, only one is shown as a representative example (Fig. 2). In this cation, the iron atom sits on the inversion center with a C(carbene)–Fe–C(carbene) angle of 180.0(1)°. A similar conformation has been observed in Roesky's neutral complexes [(Me<sub>2</sub>-cAAC)<sub>2</sub>M] (M = Zn, Cu, Mn).<sup>14,15,17</sup> The Fe–C(Me<sub>2</sub>-cAAC) distance of 1.997(3) Å in **4** approximates the corresponding distances found in **3**, but is shorter than its congeners in the sterically encumbered aryl complexes Fe(Ar\*)<sub>2</sub> (2.04–2.06 Å),<sup>6c</sup> [Fe(C(SiMe<sub>3</sub>)<sub>3</sub>)<sub>2</sub>] (2.05 Å),<sup>24</sup> and [K(crypt-222)][Fe(C(SiMe<sub>3</sub>)<sub>3</sub>)<sub>2</sub>] (2.06 Å).<sup>10</sup> The C(carbene)–N distance (1.310(3) Å) in **4** is also close to those observed in **3**.

<sup>57</sup>Fe Mössbauer spectroscopy was utilized to further characterize complexes **1–4**. The isomer shifts ( $\delta$ ) and quadrupole splittings ( $\Delta E_Q$ ) determined for the 80 K spectra of **1–4** (see ESI† for spectra), as well as those of other previously reported two- and three-coordinate iron(I) compounds, are given in Table 2. The 80 K Mössbauer spectrum of **1** is well-fit to a quadrupole doublet with  $\delta$  = 0.65 mm s<sup>–1</sup> and  $\Delta E_Q$  = 2.63 mm s<sup>–1</sup>. These parameters compare closely to those of the *S* = 3/2 sulfide-bridged iron(I) complex [K(nacnac)Fe(μ-S)Fe(nacnac)K]

**Table 2** <sup>57</sup>Fe Mössbauer spectroscopic data of **1–4** and related low-coordinate iron(I) compounds

	$\delta$ /mm s <sup>–1</sup>	$\Delta E_Q$ /mm s <sup>–1</sup>		$\delta$ /mm s <sup>–1</sup>	$\Delta E_Q$ /mm s <sup>–1</sup>
<b>1</b>	0.65	2.63	<b>5<sup>a</sup></b>	0.67	2.17
<b>2</b>	0.52	2.04	<b>6<sup>b</sup></b>	0.44	2.05
<b>3</b>	0.49	2.03	<b>7<sup>c</sup></b>	0.40	1.93
<b>4</b>	0.49	4.58	<b>8<sup>d</sup></b>	0.40	2.55

<sup>a</sup> **5** = [K(nacnac)Fe(μ-S)Fe(nacnac)K], 80 K, ref. 7d. <sup>b</sup> **6** = [(nacnac)Fe(HCCPh)], 80 K, ref. 7b. <sup>c</sup> **7** = [K(crypt-222)][(nacnac)FeH], 80 K, ref. 7c. <sup>d</sup> **8** = [K(crypt-222)][Fe(C(SiMe<sub>3</sub>)<sub>3</sub>)<sub>2</sub>], 80 K, ref. 25. Mössbauer fitting errors are ±0.02 mm s<sup>–1</sup> for  $\delta$  and ±2% for  $\Delta E_Q$ .

(5),<sup>7d</sup> further indicative of its high-spin ( $S = 3/2$ ) iron(i) nature. The spectra of 2–4 have  $\delta$  values of 0.52, 0.49 and 0.49 mm s<sup>-1</sup>, respectively, lower than the isomer shift observed for 1, but comparable to those of 3-coordinate  $S = 3/2$  alkyne- and hydrido-coordinated  $\beta$ -diketiminate iron(i) species (6 and 7).<sup>7b,c</sup> The reduced isomer shifts for 2–4 are suggestive of increased covalency in these complexes compared to 1, consistent with the observation of reduced Fe–C(carbene) bond lengths and long C(carbene)–N distances of the cAAC moieties in 2–4. Interestingly, the spectrum of the two-coordinate complex 4 shows a very large  $\Delta E_Q$  of 4.57 mm s<sup>-1</sup>, distinct from that observed for [K(crypt-222)][Fe(C(SiMe<sub>3</sub>)<sub>3</sub>)<sub>2</sub>] (8).<sup>25</sup> While the isomer shifts for 4 and 8 are similar, the significantly increased  $\Delta E_Q$  value for 4 likely indicates a significant covalent contribution to the electric field gradient (EFG) in 4.<sup>26</sup> Intrigued by their unique structural and spectroscopic features, we are now pursuing further spectroscopic and theoretical studies in order to develop a more complete understanding of the electronic structure and bonding in these low-coordinate iron aminocarbene compounds.

## Conclusions

In summary, we have achieved the synthesis of the series of three-coordinate formal iron(i) complexes [(L)(L')FeCl] (L, L' = IMes, Me<sub>2</sub>-cAAC) with the bulky aminocarbenes as supporting ligands. Associated with the different electronic properties of NHCs versus cAACs, these three-coordinate complexes exhibit differentiated thermal stability, Fe–C(carbene) distances, and <sup>57</sup>Fe Mössbauer isomer shifts. The three-coordinate iron complexes can react with Na[Bar<sup>F</sup><sub>4</sub>], from which we have successfully isolated and structurally characterized a two-coordinate iron aminocarbene complex [(Me<sub>2</sub>-cAAC)<sub>2</sub>Fe][Bar<sup>F</sup><sub>4</sub>].<sup>27</sup> The attainment of 1–4 demonstrates that both monodentate NHCs and cAACs are capable of supporting low-coordinate formal iron(i) species.

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## Notes and references

- 1 M. V. Twigg and J. Burgess, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier, 2005, vol. 5, p. 460.
- 2 For example, see: (a) D. Seyferth, R. S. Henderson and L. C. Song, *Organometallics*, 1982, **1**, 125; (b) T. Liu and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 2007, **129**, 7008; (c) J. M. Camara and T. B. Rauchfuss, *Nat. Chem.*, 2011, **4**, 26.
- 3 For example, see: (a) J. M. Smith, R. J. Lachicotte, K. A. Pittard, T. R. Cundari, K. A. Lukat-Rodgers, K. R. Rodgers and P. L. Holland, *J. Am. Chem. Soc.*, 2001, **123**, 9222; (b) M. P. Hendrich, W. Gunderson, R. K. Behan, M. T. Green, M. P. Mehn, T. A. Betley, C. C. Lu and J. C. Peters, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 17107; (c) M. M. Rodriguez, E. Bill, W. W. Brennessel and P. L. Holland, *Science*, 2011, **334**, 780; (d) J. S. Anderson, J. Rittle and J. C. Peters, *Nature*, 2013, **501**, 84.
- 4 For example, see: (a) C. J. Adams, R. B. Bedford, E. Carter, N. J. Gower, M. F. Haddow, J. N. Harvey, M. Huwe, M. ÁngelesCartes, S. M. Mansell, C. Mendoza, D. M. Murphy, E. C. Neeve and J. Nunn, *J. Am. Chem. Soc.*, 2012, **134**, 10333; (b) M. Guisán-Ceinos, F. Tato, E. Bunuel, P. Calle and D. J. Cárdenas, *Chem. Sci.*, 2013, **4**, 1098; (c) J. Kleimark, A. Hedström, P.-F. Larsson, C. Johansson and P.-O. Norrby, *ChemCatChem*, 2009, **1**, 152.
- 5 For recent examples, see: (a) S. D. Brown, T. A. Betley and J. C. Peters, *J. Am. Chem. Soc.*, 2003, **125**, 322; (b) R. P. Rose, C. Jones, C. Schulten, S. Aldridge and A. Stasch, *Chem. – Eur. J.*, 2008, **14**, 8477; (c) C. Ni, B. D. Ellis, J. C. Fetting, G. J. Long and P. P. Power, *Chem. Commun.*, 2008, 1014; (d) T. Nguyen, W. A. Merrill, C. Ni, H. Lei, J. C. Fetting, B. D. Ellis, G. J. Long, M. Brynda and P. P. Power, *Angew. Chem., Int. Ed.*, 2008, **47**, 9115; (e) M. T. Mock, C. V. Popescu, G. P. A. Yap, W. G. Dougherty and C. G. Riordan, *Inorg. Chem.*, 2008, **47**, 1889; (f) I. Nieto, F. Ding, R. P. Bontchev, H. Wang and J. M. Smith, *J. Am. Chem. Soc.*, 2008, **130**, 2716; (g) C. Vogel, J. S. Heinemann, C. Anthon and K. Meyer, *Angew. Chem., Int. Ed.*, 2008, **47**, 2681; (h) Y. Nakajima, Y. Nakao, S. Sakaki, Y. Tamada, T. Ono and F. Ozawa, *J. Am. Chem. Soc.*, 2010, **132**, 9934; (i) J. M. Hoyt, K. T. Sylvester, S. P. Semproni and P. J. Chirik, *J. Am. Chem. Soc.*, 2013, **135**, 4862.
- 6 For reviews on low-coordinate 3d metal species, see: (a) C. C. Cummins, *Prog. Inorg. Chem.*, 1998, **47**, 685; (b) P. L. Holland, *Acc. Chem. Res.*, 2008, **41**, 905; (c) P. P. Power, *Chem. Rev.*, 2012, **112**, 3482; (d) D. L. Kays, *Dalton Trans.*, 2011, 769.
- 7 (a) J. M. Smith, A. R. Sadique, T. R. Cundari, K. R. Rodgers, G. Lukat-Rodgers, R. J. Lachicotte, C. J. Flaschenriem, J. Vela and P. L. Holland, *J. Am. Chem. Soc.*, 2006, **128**, 756; (b) S. A. Stoian, Y. Yu, J. M. Smith, P. L. Holland, E. L. Bominaar and E. Münck, *Inorg. Chem.*, 2005, **44**, 4915; (c) K. P. Chiang, C. C. Scarborough, M. Horitani, N. S. Lees, K. Ding, T. R. Dugan, W. W. Brennessel, E. Bill, B. M. Hoffman and P. L. Holland, *Angew. Chem., Int. Ed.*, 2012, **51**, 3658; (d) M. M. Rodriguez, B. D. Stubbett, C. C. Scarborough, W. W. Brennessel, E. Bill and P. L. Holland, *Angew. Chem., Int. Ed.*, 2012, **51**, 8247.
- 8 M. J. Ingleson, B. C. Fullmer, D. T. Buschhorn, H. Fan, M. Pink, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 2008, **47**, 407.
- 9 L. Fohlmeister, S. Liu, C. Schulten, B. Moubaraki, A. Stasch, J. D. Cashion, K. S. Murray, L. Gagliardi and C. Jones, *Angew. Chem., Int. Ed.*, 2012, **51**, 8294.



- 10 J. M. Zadrozny, D. J. Xiao, M. Atanasov, G. J. Long, F. Grandjean, F. Neese and J. R. Long, *Nat. Chem.*, 2013, **5**, 577.
- 11 For reviews and recent reports on iron-NHC complexes: see: (a) M. J. Ingleson and R. A. Layfield, *Chem. Commun.*, 2012, **48**, 3579; (b) D. Bézier, J.-B. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2013, **355**, 19; (c) K. Riener, S. Haslinger, A. Raba, M. P. Högerl, M. Cokoja, W. A. Herrmann and F. E. Kühn, *Chem. Rev.*, 2014, **114**, 5215; (d) S. Zlatogorsky, C. A. Muryn, F. Tuna, D. J. Evans and M. J. Ingleson, *Organometallics*, 2011, **30**, 4974; (e) S. Meyer, C. M. Orben, S. Demeshko, S. Dechert and F. Meyer, *Organometallics*, 2011, **30**, 6692; (f) J. A. Przyojski, H. D. Arman and Z. J. Tonzetich, *Organometallics*, 2012, **31**, 3264; (g) T. Hashimoto, S. Urban, R. Hoshino, Y. Ohki, K. Tatsumi and F. Glorius, *Organometallics*, 2012, **31**, 4474; (h) B. Blom, G. Tan, S. Enthaler, S. Inoue, J. D. Epping and M. Driess, *J. Am. Chem. Soc.*, 2013, **135**, 18108; (i) H. Li, L. C. Misal Castro, J. Zheng, T. Roisnel, V. Dorcet, J.-B. Sortais and C. Darcel, *Angew. Chem., Int. Ed.*, 2013, **52**, 8045.
- 12 For example, see: (a) Z. Mo, D. Chen, X. Leng and L. Deng, *Organometallics*, 2012, **31**, 7040; (b) C. A. Laskowski, D. J. Bungum, S. M. Baldwin, S. A. Del Ciello, V. M. Iluc and G. L. Hillhouse, *J. Am. Chem. Soc.*, 2013, **135**, 18272; (c) M. Ito, T. Matsumoto and K. Tatsumi, *Inorg. Chem.*, 2009, **48**, 2215.
- 13 (a) V. Lavallo, Y. Canac, C. Prasang, B. Donnadiou and G. Bertrand, *Angew. Chem., Int. Ed.*, 2005, **44**, 5705; (b) V. Lavallo, G. D. Frey, S. Kousar, B. Donnadiou and G. Bertrand, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 13569; (c) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122; (d) D. Martin, M. Melaimi, M. Soleilhavoup and G. Bertrand, *Organometallics*, 2011, **30**, 5304.
- 14 A. P. Singh, P. P. Samuel, H. W. Roesky, M. C. Schwarzer, G. Frenking, N. S. Sidhu and B. Dittich, *J. Am. Chem. Soc.*, 2013, **135**, 7324.
- 15 D. S. Weinberger, N. Amin SK, K. C. Mondal, M. Melaimi, G. Bertrand, A. Claudia Stückl, H. W. Roesky, B. Dittich, S. Demeshko, B. Schwederski, W. Kaim, P. Jerabek and G. Frenking, *J. Am. Chem. Soc.*, 2014, **136**, 6235.
- 16 (a) A. J. Arduengo III, S. F. Gamper, J. C. Calabrese and F. Davidson, *J. Am. Chem. Soc.*, 1994, **116**, 4391; (b) R. C. Poulten, M. J. Page, A. J. Algarra, J. J. Le Roy, I. López, E. Carter, A. Llobet, S. A. Macgregor, M. F. Mahon, D. M. Murphy, M. Murugesu and M. K. Whittlesey, *J. Am. Chem. Soc.*, 2013, **135**, 13640; (c) K. C. Mondal, P. P. Samuel, Y. Li, H. W. Roesky, S. Roy, L. Ackermann, N. S. Sidhu, G. M. Sheldrick, E. Carl, S. Demoshko, S. De, P. Parameswaran, L. Ungur, L. F. Chiboyaru and D. M. Andrada, *Eur. J. Inorg. Chem.*, 2014, 818.
- 17 P. P. Samuel, K. C. Mondal, H. W. Roesky, M. Hermann, G. Frenking, S. Demeshko, F. Meyer, C. Stückl, J. H. Christian, N. S. Dalal, L. Ungur, L. F. Chibotaru, K. Pröpper, A. Meenta and B. Dittich, *Angew. Chem., Int. Ed.*, 2013, **52**, 11817.
- 18 Z. Ouyang and L. Deng, *Organometallics*, 2013, **32**, 7268.
- 19 For detailed information, please see ESI.†
- 20 (a) L. Xiang, J. Xiao and L. Deng, *Organometallics*, 2011, **30**, 2018; (b) A. A. Danopoulos, P. Braunstein, N. Stylianides and M. Wesolek, *Organometallics*, 2011, **30**, 6514; (c) B. M. Day, T. Pugh, D. Hendriks, C. F. Guerra, D. J. Evans, F. M. Bickelhaupt and R. A. Layfield, *J. Am. Chem. Soc.*, 2013, **135**, 13338.
- 21 T. Hashimoto, R. Hoshino, T. Hatanaka, Y. Ohki and K. Tatsumi, *Organometallics*, 2014, **33**, 921.
- 22 S. Pelties and R. Wolf, *Z. Anorg. Allg. Chem.*, 2013, **639**, 2581.
- 23 K. C. Mondal, P. P. Samuel, H. W. Roesky, E. Carl, R. Herbst-Irmer, D. Stalk, B. Schwederki, W. Kaim, L. Ungur, L. F. Chibotaru, M. Hermann and G. Frenking, *J. Am. Chem. Soc.*, 2014, **136**, 1770.
- 24 A. M. Lapointe, *Inorg. Chim. Acta*, 2003, **345**, 359.
- 25 J. M. Zadrozny, D. J. Xiao and J. R. Long, *Inorg. Chem.*, 2013, **52**, 13123.
- 26 (a) E. J. Hawrelak, W. H. Bernskoetter, E. Lobkovsky, G. T. Yee, E. Bill and P. J. Chirik, *Inorg. Chem.*, 2005, **44**, 3103; (b) P. A. Rudd, S. Liu, N. Plana, E. Bill, L. Gagliardi and C. C. Lu, *Angew. Chem., Int. Ed.*, 2013, **52**, 4449.
- 27 During the submission of this manuscript, a study on three- and two-coordinate iron complexes with Et<sub>2</sub>-cAAC (3,3-diethyl-5,5-dimethyl-1-(2',6'-diisopropylphenyl)-pyrrolidine-2-ylidene) appeared: G. Ung, J. Rittle, M. Soleilhavoup, G. Bertrand and J. C. Peters, *Angew. Chem., Int. Ed.*, 2014, DOI: 10.1002/anie.201404078.