

The room-temperature solution magnetic moment measured in C_6D_6 using NMR line shift analysis for complex **2** ($4.3 \mu_B$) is consistent with an $S = 3/2$ species. While unusual,

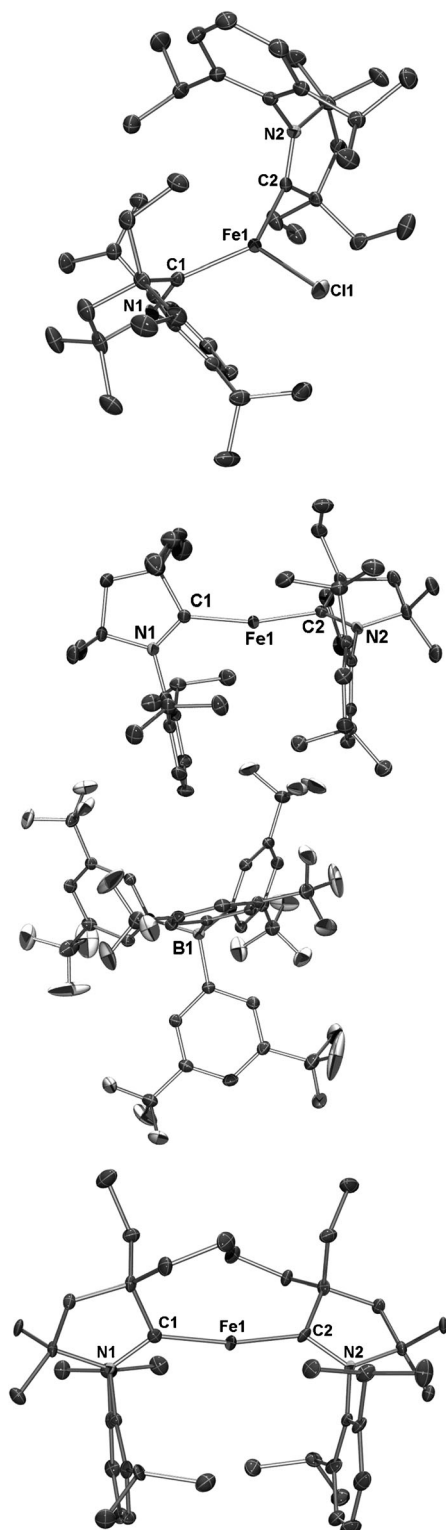


Figure 2. Structure of **2** (top), **3** (middle), and **4** (bottom) in the solid state. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond length [Å] and angles [°] are given in Table 1.^[16]

several related three-coordinate, $S = 3/2$ iron complexes have been reported by Holland and co-workers.^[17] Abstraction of the chloride ligand of **2** by sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate yielded the Fe^I complex **3**, isolated as dark purple crystals in good yield (73%). The two-coordinate nature of **3** was confirmed by an X-ray diffraction study (Figure 2, middle). The complex is modestly bent [$C-Fe-C = 165.36(6)^\circ$], with a torsion angle between the two carbenes of 108.6° , and populates an $S = 3/2$ spin state in solution at room temperature ($4.3 \mu_B$ in $[D_8]THF$). Additionally, **3** is EPR silent at 77 K but low field features down to $g = 6-6.5$ appear when the sample is cooled to 10 K (Figure 3, top). These data are consistent with previously observed quartet ground state $Fe^{[18]}$ or $Co^{[6b]}$ species. The bent nature of two-coordinate **3** differs from the two-coordinate Fe^I complex $[[[(Me_3Si)_3C]_2Fe]\{K(2,2,2-crypt)\}]$ (**A**) which is almost perfectly linear (179.2°) while also $S = 3/2$.^[7] This difference in structure is not simply a reflection of a change of ligand [CAAC versus $(Me_3Si)_3C^-$]: the isoelectronic complex $[(CAAC)_2Mn]$ is perfectly linear, and likewise $S = 3/2$.^[4]

The reduction of complex **3** with various reducing agents in THF was canvassed and yielded intractable mixtures and iron particles. However, flash-reduction (see Supporting Information) of **3** in diethyl ether with one equivalent of potassium graphite allowed for the isolation of dark green

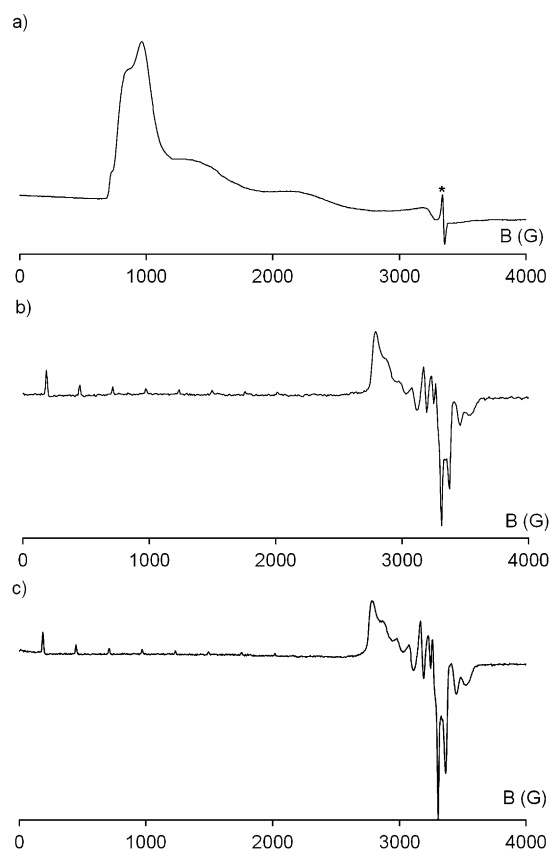


Figure 3. Top: X-Band EPR spectrum for complex $[(CAAC)_2Fe]BAR_{24}^F$ (**3**) in a 2-methyltetrahydrofuran glass at 10 K; * denotes a trace impurity. Middle: X-Band EPR spectrum for complex $[(CAAC)_2Co]$ (**7**) in a toluene glass at 10 K. Bottom: X-Band EPR spectrum for complex **7** in a toluene glass at 77 K.

crystals in high yield (89 %, Scheme 1). A single-crystal X-ray diffraction study of this product unambiguously demonstrated that **4** is the neutral, two-coordinate $[(\text{CAAC})_2\text{Fe}]$ complex (Figure 2, bottom). Similar to **3**, the C–Fe–C angle in complex **4** is modestly bent $[169.3(3)^\circ]$. Furthermore, the solution moment of **4** in C_6D_6 at room temperature is $3.0 \mu_{\text{B}}$, suggesting an $S = 1$ spin state as is to be expected for a high-spin $\text{Fe}^0 \text{d}^8$ species. A toluene glass X-band EPR spectrum of **4** was collected at 77 K (See Supporting Information) and features an extremely ill-resolved signal. This feature suggests substantial iron-centered spin density.^[19]

The ^{57}Fe Mössbauer spectra for $[(\text{CAAC})_2\text{FeCl}]$ (**2**), $[(\text{CAAC})_2\text{Fe}]\text{BARF}_{24}$ (**3**), and $[(\text{CAAC})_2\text{Fe}]$ (**4**) were recorded in the solid state at 80 K (Figure 4). Fits to the data for **2** and **3** provide isomer shifts at $\delta = 0.495$ and $\delta = 0.812 \text{ mm s}^{-1}$, respectively, and large corresponding quadrupole splittings of $\Delta E_{\text{Q}} = 2.164$ and $\Delta E_{\text{Q}} = 3.476 \text{ mm s}^{-1}$.^[20] The isomer shift of $\delta = 0.812 \text{ mm s}^{-1}$ for the Fe^{I} species **3** is markedly higher than those of other two-coordinate complexes.^[5a,7] For example, the isomer shift for $[\{(\text{Me}_3\text{Si})_3\text{C}\}_2\text{Fe}\{\text{K}(2,2,2\text{-crypt})\}]$ (**A**) is reported at $\delta = 0.28 \text{ mm s}^{-1}$.^[7] The doublet of **3** does not resolve into a sextet at $T < 50 \text{ K}$ in contrast to what is observed for **A**,^[7] perhaps a result of its bent structure which could effectively quench the magnetic anisotropy of the complex.^[21] Additional studies on the magnetic properties of this compound are currently underway. The ^{57}Fe Mössbauer

spectrum of complex **4** (Figure 4, bottom) was fit^[22] to a doublet at $\delta = 0.165 \text{ mm s}^{-1}$ with a very large quadrupole splitting (4.786 mm s^{-1}). A DFT calculation (see below) for complex **4** gave a consistent quadrupole splitting of 4.97 mm s^{-1} .^[23] The markedly different isomer shifts of **3** and **4** reflect a change in oxidation/spin state, and are consistent with increased covalency in the C–Fe bonds upon reduction.

Utilizing the same synthetic strategy, we sought to isolate the analogous two-coordinate $[(\text{CAAC})_2\text{Co}]$ complex. Dark amber colored, three-coordinate $[(\text{CAAC})_2\text{CoCl}]$ (**5**) was obtained in high yield (88 %; Scheme 1) by allowing two equivalents of the ligand **1** to react with CoCl_2 , followed by reduction with one equivalent of sodium amalgam. Like **2**, complex **5** features a distorted trigonal planar geometry (XRD; see Supporting Information), reminiscent of the analogous NHC complex.^[8] The solution magnetic moment of **5** at room temperature is $2.9 \mu_{\text{B}}$ as expected for an $S = 1$ spin state. Abstraction of chloride with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate yielded the two-coordinate Co^{I} complex $[(\text{CAAC})_2\text{Co}]\text{BARF}_{24}$ (**6**), isolated as dark orange crystals in moderate yield (44 %). Single crystals of **6** are isomorphous with those of **3**, and the two-coordinate geometry was confirmed by an XRD study (See Supporting Information). Complex **6** is moderately bent $[168.35(9)^\circ]$, contrasting the almost linear nature of the analogous NHC complex (178.58°).^[8] The $S = 1$ spin state is preserved on going from three-coordinate **5** to two-coordinate **6** ($3.2 \mu_{\text{B}}$ in $[\text{D}_8]\text{THF}$). In contrast with **3**, the cyclic voltammogram of a solution of **6** in THF (0.5 mM) containing $0.1 \text{ M } n\text{Bu}_4\text{NPF}_6$ as electrolyte exhibits a reversible reduction event at $E_{1/2} = -1.79 \text{ V}$ (Fc^+/Fc ($\text{Fc} = [(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]$); see Supporting Information). Chemical reduction using one equivalent of sodium amalgam in diethyl ether or THF resulted in a rapid color change from dark orange to dark green. After work-up, neutral $[(\text{CAAC})_2\text{Co}]$ (**7**) was isolated as dark green crystals in moderate yield (47 %). Single crystals of **7**, isomorphous to those of **4**, were grown by slow evaporation of a saturated solution in diethyl ether, and were subjected to a single-crystal X-ray diffraction study. An analogous two-coordinate structure for **7** was readily confirmed (see Supporting Information).

The EPR spectrum of **7** at room temperature features a broad signal that resolves at 77 K to an unusual rhombic signal with a remarkably sharp eight-line feature centered at $g = 6.07$ that exhibits large hyperfine coupling (ca. 260 G) to the $^{59}\text{Co}(\text{I}=7/2)$ center (Figure 3, bottom). While EPR features are expected at high g for $S = 3/2$ systems (g values as high as 9.5 have been observed),^[24] the appearance of a sharp signal at a field as low as $g = 6$ is uncommon for an $S = 1/2$ system. Shifts to high g can arise from an orbitally degenerate 2E state, as expected for the d^9 complex **7**. For instance, the EPR spectra of $S = 1/2$ $[\{\text{NN}_3\}\text{Mo}^{\text{III}}\text{-L}]$ complexes were studied by Hoffman and co-workers and showed features for $g_{\parallel}$ greater than 3.0.^[25] Simulation of the spectrum of **7** was attempted but was hampered by the generation of large artifacts when sufficiently large hyperfine constants were introduced at low field.^[24a] Nonetheless, the EPR signal for **7** is highly intense and sharp at 77 K, and additionally, the spectrum is unchanged at 10 K (Figure 3). These reasons push

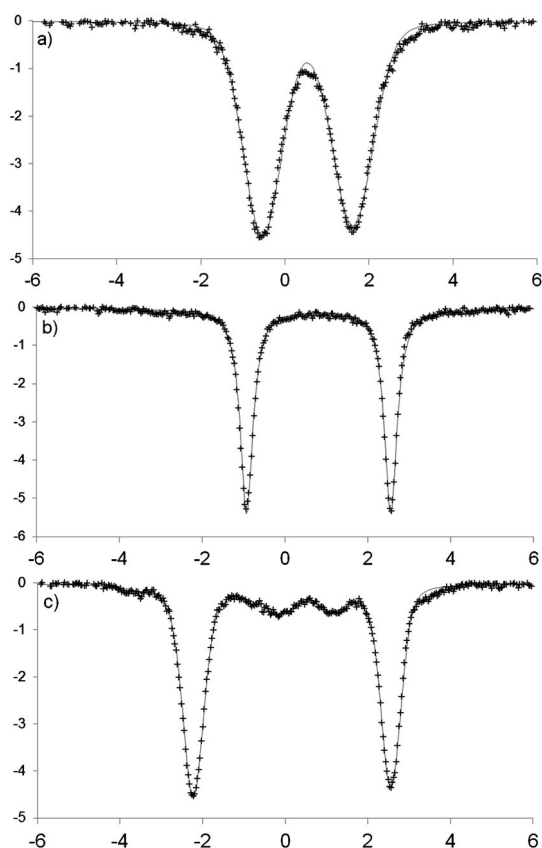


Figure 4. ^{57}Fe Mössbauer spectra for microcrystalline samples of **2** (top), **3** (middle), and **4** (bottom), obtained at 80 K in boron nitride pellets. Solid gray lines correspond to the simulated data.

us to rule-out population of an admixed $S = 3/2$ state. Furthermore, the room-temperature solution moment in C_6D_6 for **7** is $2.0 \mu_B$, also consistent with the presence of an $S = 1/2$ species without substantial higher spin contaminants.

While the EPR spectra for all of the aforementioned formal $[(CAAC)_2M^I]BAR^F_{24}$ and $[(CAAC)_2M^0]$ complexes reflect substantial metal-centered spin character, CAAC ligands are known to be redox-active and substantial spin leakage onto the ligands is hence anticipated as the systems are reduced. Indeed, the C–N bond lengths of the CAAC ligands are elongated on transitioning from the cationic M^I complexes **3** and **6** to the neutral M^0 complexes **4** and **7** (Table 1), indicative of some spin delocalization onto the

Table 1: Selected bond lengths [Å] and angles [°] for **3**, **4**, **6** and **7**.

Compound	C1–N1	C2–N2	C1–M	C2–M	C1–M–C2
3	1.317(2)	1.312(2)	1.985(2)	1.985(2)	165.36(6)
4	1.371(2)	1.374(2)	1.923(1)	1.922(1)	169.52(5)
6	1.308(3)	1.313(3)	1.957(2)	1.957(2)	168.35(9)
7	1.355(5)	1.358(5)	1.882(4)	1.875(4)	170.48(18)

carbene carbon centers.^[13,15] The C–M bond lengths of the neutral species are correspondingly significantly shortened compared to those of their cationic precursors. Still, in the complexes reported here, a majority of the spin is metal-centered. This situation differs from the cases of rigorously linear $[(CAAC)_2M]$ complexes ($M = Mn, Zn$), where perfect overlap exists between π -symmetric orbitals owing to the planar alignment of the CAAC ligands, thus allowing for the spin density to largely delocalize onto the carbon centers to afford biradical species.^[4,13c] The torsion angle between the carbenes in **4** and **7** described herein is large (**4**: 104.89° ; **7**: 105.56°) and thereby does not favor as high a degree of spin delocalization.^[4,13] In our $[(CAAC)_2Fe]$ and $[(CAAC)_2Co]$ systems, density functional theory (DFT) calculations performed at the (U)B3LYP/TZVP level using NBO methods suggest that the majority of spin density resides on the metal atoms ($Fe = 72\%$; $Co = 60\%$) with moderate but still substantial delocalization onto the carbon and nitrogen atoms ($Fe = 20$ and 6% , respectively; $Co = 24$ and 5% , respectively) (Figure 5). These results are in line with the reported $[(CAAC)_2Ni]$ complex,^[4,13a] but contrast greatly with the $[(CAAC)_2Au]$ species, which only features a small degree of spin density (17%) on the metal center.^[13b] These data underscore CAACs as polarizable ligands, a highly desirable

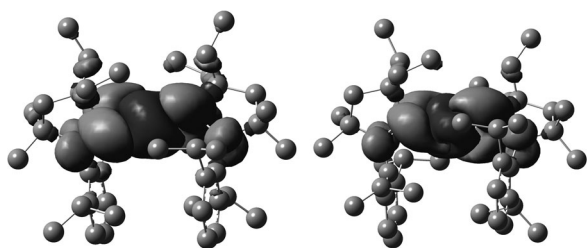


Figure 5. Graphical representation of the spin density of complex **4** (left) and complex **7** (right). See Supporting Information for details.

property for the isolation of zero-valent mononuclear Fe and Co complexes.

Experimental Section

4: A cold solution ($-20^\circ C$) of **3** (55 mg, 0.036 mmol, 1 equiv) in diethyl ether (3 mL) was passed through a glass pipette containing a glass microfiber filter and KC_8 (5.4 mg, 0.036 mmol, 1.1 equiv). The rate of filtration was about one drop per second. The dark green filtrate was then concentrated under vacuum to a dark powder. The residue was extracted with pentane and the filtrate was concentrated to a dark green powder. The powder was dissolved in a minimum of benzene and lyophilized to a dark green cotton-like powder (22 mg, 0.032 mmol, 89%). Single crystals were obtained by slow diffusion of a saturated solution of **4** in diethyl ether into hexamethyldisiloxane at $-35^\circ C$; the crystals were handled with cold Paratone oil ($-78^\circ C$) and mounted as quickly as possible on a nylon loop. μ_{eff} (C_6D_6 , Evans method, $20^\circ C$): $3.0 \mu_B$. UV/Vis (pentane, nm [$cm^{-1}M^{-1}$]): 355 {16200}, 379 {18800}, 412 {14600}, 447 {13000}, 569 {11400}, 684 {11300}, 803 {10300}. Elemental analysis (%) calculated for $C_{44}H_{70}N_2Fe$: C 77.39, H 10.33, N 4.10; found: C 77.53, H 10.43, N 4.38.

7: Freshly prepared sodium amalgam (2 mg, 0.087 mmol Na, 2.4 equiv; 0.5 g Hg) was slowly added to a stirred solution of **6** (58 mg, 0.037 mmol, 1 equiv) in diethyl ether (7 mL). The reaction mixture gradually turned from dark orange to dark green. After 30 min, the supernatant solution was separated from mercury and spiked with benzene (2 mL). The solution was dried under vacuum. The oily residue was extracted with pentane and filtered over Celite. The filtrate was lyophilized to a dark green cotton-like powder (12 mg, 0.017 mmol, 47%). The residue from the extraction was found to be residual **6** that could be recrystallized (22 mg, 0.014 mmol, 38%) and subjected to reduction again (yield based on recovered starting material: 84%). Single crystals were obtained by slow diffusion of a saturated solution of **7** in diethyl ether into hexamethyldisiloxane at $-35^\circ C$. μ_{eff} (C_6D_6 , Evans method, $20^\circ C$): $2.0 \mu_B$. UV/Vis (pentane, nm [$cm^{-1}M^{-1}$]): 329 {12600}, 377 {15300}, 475 {10600}, 602 {18500}, 652 {17300}, 741 {11600}, 886 {8300}. Elemental analysis (%) calculated for $C_{44}H_{70}N_2Co$: C 77.04, H 10.29, N 4.08; found: C 77.32, H 10.50, N 4.12.

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- [1] P. P. Power, *Chem. Rev.* **2012**, *112*, 3482.
- [2] a) C. A. Laskowski, D. J. Bungum, S. M. Baldwin, S. A. Del Ciello, V. M. Iluc, G. L. Hillhouse, *J. Am. Chem. Soc.* **2013**, *135*, 18272; b) C. A. Laskowski, G. L. Hillhouse, *J. Am. Chem. Soc.* **2008**, *130*, 13846.
- [3] a) K. Matsubara, S. Miyazaki, Y. Koga, Y. Nibu, T. Hashimura, T. Matsumoto, *Organometallics* **2008**, *27*, 6020; b) A. A. Danopoulos, D. Pugh, *Dalton Trans.* **2008**, 30; c) S. Caddick, F. G. N. Cloke, P. B. Hitchcock, A. K. de K. Lewis, *Angew. Chem.* **2004**, *116*, 5948; *Angew. Chem. Int. Ed.* **2004**, *43*, 5824; d) A. J. Arduengo III, S. F. Gamper, J. C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* **1994**, *116*, 4391.
- [4] 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; *Angew. Chem. Int. Ed.* **2013**, *52*, 11817.
- [5] For examples with iron, see: a) W. A. Merrill, T. A. Stich, M. Brynda, G. J. Yeagle, J. C. Fetting, R. D. Hont, P. P. Power, J.

- Am. Chem. Soc.* **2009**, *131*, 12693; b) C. Ni, P. P. Power, *Chem. Commun.* **2009**, 5543; c) D. L. Kays (née Coombs), A. R. Cowley, *Chem. Commun.* **2007**, 1053; d) T. Nguyen, A. Panda, M. M. Olmstead, A. F. Richards, M. Stender, M. Brynda, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 8545.
- [6] For examples with cobalt, see: a) A. M. Bryan, G. J. Long, F. Grandjean, P. P. Power, *Inorg. Chem.* **2014**, *53*, 2692; b) A. M. Bryan, W. A. Merrill, W. M. Reiff, J. C. Fetting, P. P. Power, *Inorg. Chem.* **2012**, *51*, 3366, and references [5c,d].
- [7] J. M. Zadrozny, D. J. Xiao, M. Atanasov, G. J. Long, F. Grandjean, F. Neese, J. R. Long, *Nat. Chem.* **2013**, *5*, 577.
- [8] Z. Mo, D. Chen, X. Leng, L. Deng, *Organometallics* **2012**, *31*, 7040.
- [9] Z. Ouyang, L. Deng, *Organometallics* **2013**, *32*, 7268.
- [10] T. Hashimoto, R. Hoshino, T. Hatanaka, Y. Ohki, K. Tatsumi, *Organometallics* **2014**, *33*, 921.
- [11] For the synthesis of CAACs, see: a) V. Lavallo, Y. Canac, C. Prasang, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705; b) R. Jazzar, R. D. Dewhurst, J.-B. Bour, B. Donnadieu, Y. Canac, G. Bertrand, *Angew. Chem.* **2007**, *119*, 2957; *Angew. Chem. Int. Ed.* **2007**, *46*, 2899.
- [12] For Reviews on CAACs, see: a) D. Martin, M. Melaimi, M. Soleilhavoup, G. Bertrand, *Organometallics* **2011**, *30*, 5304; b) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2010**, *122*, 8992; *Angew. Chem. Int. Ed.* **2010**, *49*, 8810.
- [13] a) K. C. Mondal, P. P. Samuel, Y. Li, H. W. Roesky, S. Roy, L. Ackermann, N. S. Sidhu, G. M. Sheldrick, E. Carl, S. Demeshko, S. De, P. Parameswaran, L. Ungur, L. F. Chibotaru, D. M. Andradá, *Eur. J. Inorg. Chem.* **2014**, 818; b) D. S. Weinberger, M. Melaimi, C. E. Moore, A. L. Rheingold, G. Frenking, P. Jerabek, G. Bertrand, *Angew. Chem.* **2013**, *125*, 9134; *Angew. Chem. Int. Ed.* **2013**, *52*, 8964; c) A. P. Singh, P. P. Samuel, H. W. Roesky, M. C. Schwarzer, G. Frenking, N. S. Sidhu, B. Ditttrich, *J. Am. Chem. Soc.* **2013**, *135*, 7324.
- [14] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem.* **2013**, *125*, 3011; *Angew. Chem. Int. Ed.* **2013**, *52*, 2939.
- [15] CAACs have also been shown to stabilize organic and main-group radicals: a) J. K. Mahoney, D. Martin, C. E. Moore, A. L. Rheingold, G. Bertrand, *J. Am. Chem. Soc.* **2013**, *135*, 18766; b) K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, B. Niepötter, H. Wolf, R. Herbst-Irmer, D. Stalke, *Angew. Chem.* **2013**, *125*, 3036; *Angew. Chem. Int. Ed.* **2013**, *52*, 2963; c) K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, I. Tkach, H. Wolf, D. Kratzert, R. Herbst-Irmer, B. Niepötter, D. Stalke, *Angew. Chem.* **2013**, *125*, 1845; *Angew. Chem. Int. Ed.* **2013**, *52*, 1801.
- [16] CCDC 995147 (2), 995148 (3), 995149 (4), 995150 (5), 995151 (6) and 995152 (7) 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.
- [17] Y. Yu, J. M. Smith, C. J. Flaschenriem, P. L. Holland, *Inorg. Chem.* **2006**, *45*, 5742.
- [18] a) J. S. Anderson, M.-E. Moret, J. C. Peters, *J. Am. Chem. Soc.* **2013**, *135*, 534; b) S. A. Stoian, Y. Yu, J. M. Smith, P. L. Holland, E. L. Bominaar, E. Münck, *Inorg. Chem.* **2005**, *44*, 4915; c) K. L. Kostka, B. G. Fox, M. P. Hendrich, T. J. Collins, C. E. F. Rickard, L. J. Wright, E. Münck, *J. Am. Chem. Soc.* **1993**, *115*, 6746.
- [19] A. Takaoka, M.-E. Moret, J. C. Peters, *J. Am. Chem. Soc.* **2012**, *134*, 6695.
- [20] The broader quadrupole doublet (line width = 0.5 mm s⁻¹) for **2** was fit with a Voigt function instead of a typical Lorentzian. The broadness could arise from small conformational changes of the compound in the crystalline powder. For usage of Voigt-based method on molecular complexes, see: Y. Dong, H. Fujii, M. P. Hendrich, R. A. Leising, G. Pan, C. R. Randall, E. C. Wilkinson, Y. Zang, L. Que, Jr., B. G. Fox, K. Kauffmann, E. Münck, *J. Am. Chem. Soc.* **1995**, *117*, 2778; For the Voigt-based method, see: D. G. Rancourt, J. Y. Ping, *Nucl. Instrum. Methods Phys. Res. Sect. B* **1991**, *58*, 85. See Supporting Information for details.
- [21] a) J. M. Zadrozny, M. Atanasov, A. M. Bryan, C.-Y. Lin, B. D. Rekkien, P. P. Power, J. R. Long, *Chem. Sci.* **2013**, *4*, 125; b) M. Atanasov, J. M. Zadrozny, J. R. Long, F. Neese, *Chem. Sci.* **2013**, *4*, 139; c) J. M. Zadrozny, D. J. Xiao, J. R. Long, M. Atanasov, F. Neese, F. Grandjean, G. J. Long, *Inorg. Chem.* **2013**, *52*, 13123; d) W. M. Reiff, C. E. Schulz, M. H. Whangbo, J. I. Seo, Y. S. Lee, G. R. Potratz, C. W. Spicer, G. S. Girolami, *J. Am. Chem. Soc.* **2009**, *131*, 404; e) W. A. Merrill, T. A. Stich, M. Brynda, G. J. Yeagle, R. De Hont, J. C. Fetting, W. M. Reiff, P. P. Power, *J. Am. Chem. Soc.* **2009**, *131*, 12693; f) W. M. Reiff, A. M. LaPointe, E. H. Witten, *J. Am. Chem. Soc.* **2004**, *126*, 10206.
- [22] The fit includes an impurity integrating to 13.9% of the total Fe content, with an isomer shift of 0.511 mm s⁻¹, and a quadrupole splitting of 1.436 mm s⁻¹.
- [23] a) T. Liu, T. Lovell, W.-G. Han, L. Noodleman, *Inorg. Chem.* **2003**, *42*, 5244; b) F. Neese, *Inorg. Chim. Acta* **2002**, *337*, 181; c) Y. Zhang, J. Mao, E. Oldfield, *J. Am. Chem. Soc.* **2002**, *124*, 7829.
- [24] a) M. Plois, W. Hujo, S. Grimme, C. Schwickert, E. Bill, B. de Bruin, R. Pöttgen, R. Wolf, *Angew. Chem.* **2013**, *125*, 1352; *Angew. Chem. Int. Ed.* **2013**, *52*, 1314; b) I. Krivokapic, M. Zerara, M. Lawson Daku, A. Vargas, C. Enachescu, C. Ambrus, P. Tregenna-Piggott, N. Amstutz, E. Krausz, A. Hauser, *Coord. Chem. Rev.* **2007**, *251*, 364.
- [25] a) R. L. McNaughton, M. Roemelt, J. M. Chin, R. R. Schrock, F. Neese, B. M. Hoffman, *J. Am. Chem. Soc.* **2010**, *132*, 8645; b) R. L. McNaughton, J. M. Chin, W. W. Weare, R. R. Schrock, B. M. Hoffman, *J. Am. Chem. Soc.* **2007**, *129*, 3480.