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Supporting Information

Two- and Three-Coordinate Formal Iron(I) Compounds Featuring Monodentate Aminocarbene Ligands

Zhenbo Mo,^{*a*} Zhenwu Ouyang, ^{*a*} Lei Wang, ^{*a*} Kathlyn L. Fillman,^{*b*} Michael L. Neidig,^{*, *b*} and Liang Deng^{*, *a*}

^a State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, P. R. China 200032

^b Department of Chemistry, University of Rochester, Rochester, New York 14627, United States

neidig@chem.rochester.edu; deng@sioc.ac.cn

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1. Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk, or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. IMes,¹ Me₂-cAAC,² and (IMes)₂FeCl₂ ³ were prepared according to reported procedures. All other chemicals were purchased from either Strem or J&K Chemical Co. and used as received unless otherwise noted. ¹H spectra were recorded on a VARIAN 400 MHz or Agilent 400 MHz spectrometer. Chemical shifts were reported in units with references to the residual protons of the deuterated solvents for proton chemical shifts. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Magnetic moments were measured at 21 °C by the method originally described by Evans with stock and experimental solutions containing a known amount of a (CH₃)₃SiOSi(CH₃)₃ standard.⁴ Absorption spectra were recorded with a Shimadzu UV-3600 UV-vis-NIR spectrophotometer.

X-Ray Structure Determinations. The structures of **1-4** were determined. Crystallizations were performed at room temperature. Crystals were coated with Paratone-*N* oil and mounted on a Bruker APEX CCD-based diffractometer equipped with an Oxford low-temperature apparatus. Cell parameters were retrieved with SMART software and refined using SAINT software on all reflections. Data integration was performed with SAINT, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS.⁵ Space groups were assigned unambiguously by analysis of symmetry and systematic absences determined by XPREP. All structures were solved and refined using SHELXTL.⁶ Metal and first coordination sphere atoms were located from direct-methods *E*-maps; other non-hydrogen atoms were found in alternating difference Fourier synthesis and least-squares refinement cycles and during final cycles were refined anisotropically. Hydrogen atoms were placed in calculated positions employing a riding model. Final crystal parameters and agreement factors are reported in Table S1. CCDC 1010108-1010111 contain the supplementary crystallographic data for **1-4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

⁵⁷Fe Mössbauer Spectroscopy. All solid samples for ⁵⁷Fe Mössbauer spectroscopy were run on non-enriched samples of the as-isolated complexes. Each sample was loaded into a Delrin Mössbauer sample cup for measurements and loaded under liquid nitrogen. Low temperature ⁵⁷Fe Mössbauer measurements were performed using a See Co. MS4 Mössbauer spectrometer integrated with a Janis SVT-400T He/N₂ cryostat for measurements at 80 K with a 0.07 T applied magnetic field. Isomer shifts were determined relative to α -Fe at 298 K. All Mössbauer spectra were fit using the program WMoss (SeeCo).



Preparation of (IMes)₂FeCl (1). To a toluene (50 mL) suspension of (IMes)₂FeCl₂ (2.50 g, 3.40 mmol) was added KC₈ (690 mg, 5.10 mmol) at room temperature. The color of the suspension turned from white to dark brown within several minutes. The reaction mixture was stirred for 36 hours and then filtered through celite and concentrated. The residue was washed with *n*-hexane (10 mL x 3) to afford 1 as a reddish brown solid (1.60 g, 67%). Single-crystals of 1 suitable for X-ray diffraction studies were grown by freezing its brown toluene/hexane solution at -25 °C for two days. Complex 1 is unstable in solution, decomposing slowly in C₆D₆ at room temperature to [(IMes)₂FeCl₂], IMes, iron powder and [(IMes)₂Fe₂]⁷. ¹H NMR (400 MHz, in C₆D₆, at 21 °C): δ 51.73 (s, 4H, CH=C*H*), 7.86 (s, 24H, *o*-ArC*H*₃), -12.57 (s, 12H, *p*-ArC*H*₃), -12.77 (s, 8H, C₆*H*₂) ppm. Magnetic susceptibility (C₆D₆, 21 °C): μ_{eff} = 5.0(1) μB. Anal. Calcd for C₄₂H₄₈CIFeN₄: C, 72.05; H, 6.91; N, 8.00. Found: C, 72.03; H, 6.94; N, 8.21. Absorption spectrum (Toluene): λ_{max} (ε, M⁻¹cm⁻¹) = 324 (4380), 463 (5100), 581 (2730), 960 (450), 1547 (470) nm. Alternatively, 1 could also be prepared from the reaction of (IMes)₂FeCl₂ with Na(Hg) in *ca.* 30% yield using procedures similar to that of KC₈.



Preparation of (IMes)(Me₂₋cAAC)FeCl (2). To a toluene (20 mL) solution of (IMes)₂FeCl (246 mg, 0.35 mmol) was added Me₂-cAAC (100 mg, 0.35 mmol) at room temperature. The color changed from brown to red within several minutes. The reaction mixture was stirred for 2 hours and then concentrated under vacuum to afford a red solid. The red solid was extracted with a mix solvent of Et₂O (10 mL) with hexane (1.0 mL). The extraction was then filtered to afford a clear red liquid.

Compound **2** was obtained as a red crystalline solid (135 mg, 56%) by standing the solution at room temperature for two days. The ¹H NMR spectrum of this compound contains heavily broadened peaks preventing accurate integration. ¹H NMR (400 MHz, in C₆D₆, at 21 °C): δ 47.61, 10.38, 8.75, 8.19, 2.60, -3.10, -9.94, -10.69, -12.93, -102.48 ppm. Magnetic susceptibility (C₆D₆, 21 °C): $\mu_{eff} = 5.1(1) \mu$ B. Anal. Calcd for C₄₁H₅₅ClFeN₃: C, 72.29; H, 8.14; N, 6.17. Found: C, 71.67; H, 7.61; N, 6.15. Absorption spectrum (Toluene): λ_{max} (ϵ , M⁻¹cm⁻¹) = 325 (4200), 372 (2860), 508 (3460), 793 (330), 1124 (490) nm.



Preparation of (Me₂-cAAC)₂FeCl (3). To a THF (10 mL) solution of Me₂-cAAC (1.14 g, 4.0 mmol) was slowly added FeCl₂ (254 mg, 2.0 mmol) at room temperature, during which time the color of the solution turned from pale yellow to yellow brown. After stirring for 4 hours at room temperature, the yellow brown solution was transferred into a stirring sodium amalgam suspension (Na, 1.0%/w, 4.67 g, 2.0 mmol, in 5 mL THF). The color of the mixture turned from yellow brown to dark red within 30 minutes. The reaction mixture was further stirred for 24 hours and then filtered through celite and concentrated to leave a brown residue. The residue was washed with *n*-hexane (5 mL x 3) and then extracted with toluene (50 mL). The extraction was further filtrated. Removing all the volatiles under vacuum afforded **3** as a red solid (900 mg, 68%). Single-crystals of **3** suitable for X-ray diffraction studies were grown by freezing its saturated toluene solution at -25 °C for three days. The ¹H NMR spectrum of this paramagnetic complex displayed five heavily broadened peaks in the range -22.65 to 66.86 ppm. ¹H NMR (THF-*d*₈): δ 33.29, 4.63, 1.29, -1.22, -6.38. Magnetic susceptibility (THF- d_8 , 21 °C): $\mu_{eff} = 4.7(1) \mu_B$. Anal. Calcd for C₄₀H₆₄ClFeN₂: C, 72.33; H, 9.71; N, 4.22. Found: C, 71.91; H, 9.69; N, 4.30. Absorption spectrum (Toluene): λ_{max} ($\epsilon/M^{-1}cm^{-1}$) = 325 (4550), 366 (3470), 526 (5140), 839 (600), 1294 (1480) nm. Alternatively, complex 3 could also be prepared from the reaction of FeCl₂, Me₂-cAAC and KC₈ in ca. 60% yield using procedures similar to that of Na(Hg).



Preparation of [(Me₂-cAAC)₂Fe][BAr^F₄] (4). To a THF (10 mL) solution of (Me₂-cAAC)₂FeCl (3) (199)mg. 0.30 mmol) was slowly added $Na[BArF_4]$ (sodium tetra(3.5di(trifluoromethyl)phenyl)borate, 292 mg, 0.33 mmol) at room temperature. The color of the solution turned from dark red to violet slowly. After stirred 24 h at room temperature and removal of the solvent, the residue was extracted with ether (15 mL). The violet extraction was filtrated and added a small portion of hexane (2 mL). Slow evaporation of ether for 2 days afforded 4 Et₂O as a bluish green crystalline solid (200 mg, 45%). The ¹H NMR spectrum of this paramagnetic complex remained unchanged for three days in d_8 -THF at room temperature and displayed eight characteristic peaks in the range -60.44 to 49.71 ppm. ¹H NMR (THF- d_8): δ 49.71, 24.63, 7.85, 7.60, -6.29, -13.51, -33.40, -60.44 ppm. Magnetic susceptibility (THF- d_8 , 21 °C): $\mu_{eff} = 5.1(2) \mu_B$. Anal. Calcd for C₇₂H₇₆BF₂₄FeN₂: C, 58.04; H, 5.01; N, 1.88. Found: C, 57.78; H, 5.30; N, 2.01. Absorption spectrum (THF): λ_{max} (ϵ/M^{-1} cm⁻¹) = 310 (3540), 350 (1830), 400 (1800), 420 (1820), 485 (1780), 565 (2850), 675 (3230), 780 (830), 990 (180), 1200 (140), 1326 (130) nm.

2. References

- 1. L. Jafarpour, E. D. Stevens and S. P. Nolan, J. Organomet. Chem. 2000, 606, 49.
- V. Lavallo, Y. Canac, C. Prasang, B. Donnadieu and G. Bertrand, Angew. Chem. Int. Ed. 2005, 44, 5705.
- 3. J. A. Przyojski, H. D. Arman and Z. J. Tonzetich, Organometallics 2012, 31, 3264.
- 4. (a) D. F. Evans, J. Chem. Soc. 1959, 2003; (b) S. K. Sur, J. Magn. Reson. 1989, 82, 169.
- 5. G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen: Germany, 1996.
- 6. G. M. Sheldrick, SHELXTL 5.10 for Windows NT: Structure Determination Software Programs. Bruker Analytical X-ray systems, Inc.: Madison, Wisconsin, USA, 1997.
- T. Hashimoto, R. Hoshino, T. Hatanaka, Y. Ohki, K. Tatsumi, Organometallics 2014, 33, 921.

	1	2	3	$4 \cdot Et_2O$
formula	C42H48ClFeN4	C41H55ClFeN3	C40H62ClFeN2	C ₇₆ H ₈₄ BF ₂₄ FeN ₂ O
fw	700.14	681.18	662.22	1564.11
temperature (K)	140(2)	140(2)	140(2)	140(2)
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	P2(1)	P2(1)/n	P2(1)/c	<i>P</i> -1
<i>a</i> , Å	10.723(8)	9.3521(9)	11.2282(14)	12.8079(12)
<i>b,</i> Å	13.108(9)	23.226(2)	19.506(2)	13.0473(12)
<i>c,</i> Å	13.974(11)	17.0545(16)	16.892(2)	25.151(2)
α , deg	90	90	90	93.467(2)
β , deg	100.869(8)	97.944(2)	97.310(2)	102.677(2)
γ, deg	90	90	90	109.051(2)
<i>V</i> , Å ³	1929(2)	3668.9(6)	3669.6(8)	3836.0(6)
Ζ	2	4	4	2
D_{calcd} , Mg/m ³	1.205	1.233	1.199	1.354
radiation (λ), Å	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
2θ range, deg	2.97 to 55.60	2.98 to 61.21	3.20 to 61.56	4.38 to 55.68
μ , mm ⁻¹	0.493	0.516	0.513	0.299
<i>F</i> (000)	742	1460	1436	1618
no. of obsd reflns	4576	11260	11362	14276
no. of params refnd	446	429	413	1165
goodness of fit	1.115	1.039	1.009	1.007
R1	0.0614	0.0428	0.0510	0.0527
wR2	0.1540	0.0989	0.1519	0.1484

Table S1. Crystal Data and Summary of Data Collection and Refinement for 1-3, and 4·Et₂O.



Figure S1. UV-vis Spectra of 1, 2 and 3 Recorded at Room Temperature in Toluene.



Figure S2. NIR Spectra of 1, 2 and 3 Recorded at Room Temperature in Toluene.



Figure S3. UV-vis Spectrum of 4 Recorded at Room Temperature in Toluene.



Figure S4. NIR Spectrum of 4 Recorded at Room Temperature in Toluene.



Figure S5. 80 K ⁵⁷Fe Mössbauer spectrum of (IMes)₂FeCl (1). The data (dots) and best fit (solid line) are shown.



Figure S6. 80 K ⁵⁷Fe Mössbauer spectrum of (IMes)(Me₂-cAAC)FeCl (2). The data (dots) and best fit (solid line) are shown. The parameters of the major species (red line, ~ 96 % of iron) are given in the main text. A minor species (blue, ~ 4% of iron) is also present best fit to Mossbauer parameters of $\delta = 0.80$ mm/s and $\Delta E_Q = 1.49$ mm/s.



Figure S7. 80 K ⁵⁷Fe Mössbauer spectrum of $(Me_2-AAC)_2$ FeCl (**3**). The data (dots) and overall fit (black line) and individual components are shown. The parameters of the major species (red line, ~ 94 % of iron) are given in the main text. A minor species (blue, ~ 6% of iron) is also present with Mossbauer parameters of $\delta = 0.71$ mm/s and $\Delta E_0 = 3.22$ mm/s.



Figure S8. 80 K ⁵⁷Fe Mössbauer spectrum of $[(Me_2-AAC)_2Fe][BAr^F_4]$ (4). The data (dots) and best fit (solid line) are shown.





S11



Figure S10. ¹H NMR Spectrum of [(IMes)(Me₂-cAAC)FeCl] (2)

S12



Figure S11. ¹H NMR Spectrum of [(Me₂-cAAC)₂FeCl] (3)



