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Diiron Amido–Imido Complex [(Cp*Fe)$_2$(μ_2-NHPh)(μ_2-NPh)]: Synthesis and a Net Hydrogen Atom Abstraction Reaction To Form a Bis(imido) Complex

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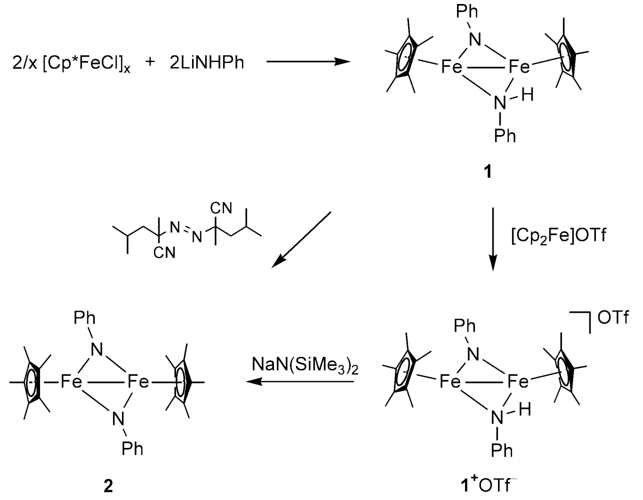
A reaction between [Cp*FeCl]$_x$ and LiNHPh (1 equiv to Fe) produces a new paramagnetic Fe(II)–Fe(III) μ_2-amido–μ_2-imido complex [(Cp*Fe)$_2$(μ_2-NHPh)(μ_2-NPh)] (**1**), which, upon interaction with 2,2′-azobis(2,4-dimethylvaleronitrile), undergoes a net N–H hydrogen atom abstraction reaction to give a diamagnetic Fe(III)–Fe(III) μ_2-imido dimer [Cp*Fe(μ_2-NPh)]$_2$ (**2**). The molecular structures of **1** and **2** have been determined by single-crystal X-ray diffraction.

Amido and imido complexes of late transition metals have attracted intense interest because of their importance in understanding and developing catalytic transformations of nitrogenous compounds.[1] Pentamethylcyclopentadienyl (Cp*) metal fragments have extensively been utilized in the study on the nature of late metal−amido and −imido bonds in both monomeric[2] and bridged[3] compounds. However, the chemistry of the corresponding Fe derivatives is far less developed,[2d] although a growing number of Fe amido and imido complexes have recently been reported for non-Cp Fe systems.[4,5] We have recently shown the unique reactivity of the diruthenium bridging amido complex [Cp*Ru(μ_2-NHPh)]$_2$, including its conversion into imido complexes and C−N bond formation with an alkyne.[3h] These findings prompted us to develop a synthetic route to analogous Cp*Fe amido and imido derivatives. Herein we report the synthesis of a paramagnetic Fe(II)−Fe(III) μ_2-amido−μ_2-imido complex [(Cp*Fe)$_2$(μ_2-NHPh)(μ_2-NPh)] (**1**) and its transformation into a diamagnetic bis(μ_2-imido) complex [Cp*Fe(μ_2-NPh)]$_2$ (**2**).[6]

Scheme 1



The interaction of [Cp*FeCl]$_x$[7] with LiNHPh (1 equiv to Fe) did not give the expected Fe(II) μ_2-amido complex [Cp*Fe(μ_2-NHPh)]$_2$ but instead resulted in the formation of the Fe(II)−Fe(III) μ_2-amido−μ_2-imido complex **1**.[8] After recrystallization from hexanes, the product was isolated as dark-green-brown crystals (44% yield based on Fe) and has been characterized by spectroscopic [infrared, mass spec-

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trometry (MS), ^{1}H NMR, and electron paramagnetic resonance (EPR)], magnetometric (SQUID), and X-ray crystallographic studies. The IR spectrum of **1** (THF) shows a ν(N−H) band at 3296 cm^{-1}, and the fast atom bombardment (FAB)-MS spectrum gives an isotope cluster of the molecular ion $\mathbf{1}^+$ at *m*/*z* 565. The ^{1}H NMR spectrum of **1** shows paramagnetically shifted broad resonances. Although an intense signal assignable to the Cp* group is observed at δ 3.76 ppm, other signals are not safely assigned because of the unreliable integration of some extremely broad resonances. The rhombic EPR spectrum of **1** (toluene, 77 K) is consistent with the expected $S = {}^1/_2$ ground state, which is also supported by the low-temperature SQUID magnetometry ($\mu_{\mathrm{eff}} = 1.73\ \mu_{\mathrm{B}}$ at 2 K). The moment increased as the temperature was raised (2.85 μ_{B} at 300 K), indicating an antiferromagnetic coupling between the two high-spin Fe centers. Similar behavior has been observed for other Fe(II)−Fe(III) complexes.[4c]

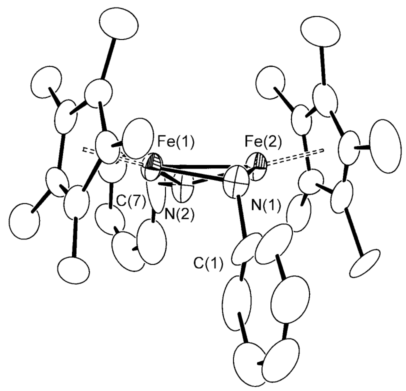

Figure 1. Molecular structure of **1**. Ellipsoids are drawn at a 35% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2), 2.4916(6); Fe(1)−N(1), 1.990(4); Fe(2)−N(1), 2.007(4); Fe(1)−N(2), 1.751(3); Fe(2)−N(2), 1.747(4); N(1)−C(1), 1.480(8); N(2)−C(7), 1.463(8); Fe(1)−N(1)−Fe(2), 77.12(15); Fe(1)−N(1)−C(1), 114.4(6); Fe(2)−N(1)−C(1), 115.6(6); Fe(1)−N(2)−Fe(2), 90.86(17); Fe(1)−N(2)−C(7), 130.1(5); Fe(2)−N(2)−C(7), 131.5(4).

The single-crystal X-ray structure of **1** is shown in Figure 1.[9] The molecule contains a nonplanar Fe_2N_2 core in which the two FeN_2 planes make a dihedral angle of 146.5°.[10] The two bridging N moieties are significantly dissimilar in their geometries; the N(1) atom constitutes a distorted pyramid with Fe(1), Fe(2), and C(1) atoms [sum of the bond angles around N(1) = 307°][11] and exhibits relatively long Fe−N bond lengths [1.990(4) and 2.007(4) Å], while the N(2) atom is nearly trigonal planar [sum of the bond angles around N(2) = 353°] and shows very short Fe−N(2) bond distances [1.747(4) and 1.751(3) Å]. These features are consistent with the assignment of N(1) as an amido N and N(2) as an imido N. The short Fe−Fe distance [2.4916(6) Å] may suggest an Fe−Fe multiple bond.[12]

The formation of the mixed-valence complex **1** is rather unexpected and markedly contrasts to the near-quantitative formation of the Ru(II) dimer [Cp*Ru(μ_2-NHPh)]$_2$ from [Cp*RuCl]$_4$ and LiNHPh.[3h] The mechanism of the partial oxidation of the Fe center in the synthesis of **1** is currently unknown, but some redox reaction between the intermediate Fe(II) amido species and the residual [Cp*FeCl]$_x$ may be a possibility.

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(8) Preparation of [(Cp*Fe)$_2$(μ_2-NHPh)(μ_2-NPh)] (**1**). To a stirred solution of 1,2,3,4,5-pentamethylcyclopentadiene (0.72 mL, 4.6 mmol) in 12 mL of THF was added *n*-BuLi (1.85 mL, 2.5 M solution in *n*-hexane) at 0 °C. The resulting white suspension was cooled to −80 °C and then transferred via a cannula to a cooled (−80 °C) suspension of anhydrous $FeCl_2$ (583 mg, 4.6 mmol) in THF (15 mL). After the transfer was complete, the mixture was stirred for 30 min, while the temperature was maintained at −80 °C. Separately, a THF solution of LiNHPh was prepared by adding *n*-BuLi (1.85 mL, 2.5 M solution in *n*-hexane) to a solution of aniline (0.43 mL, 4.6 mmol) in THF (10 mL) at −80 °C followed by warming to room temperature. The solution of LiNHPh was cooled again to −80 °C and then transferred via a cannula to the cooled suspension of [Cp*FeCl]$_x$. After the addition was complete, the mixture was allowed to warm slowly to room temperature and stirred for 16 h. The dark-greenish-brown solution obtained was evaporated to dryness, and the residue was extracted with hexanes (70 mL). The extract was concentrated to ca. 35 mL and then stored in a freezer (−25 °C). After 2 days, dark-green-brown crystals of **1** were collected by filtration and dried in vacuo. Yield: 565 mg, 44%. Anal. Calcd for $C_{32}H_{41}N_2Fe_2$: C, 67.98; H, 7.31; N, 4.95. Found: C, 67.26; H, 7.66; N, 4.32. The low C percentage could be due to the extreme O sensitivity of the compound. Repeated analyses failed to give the expected results. IR (THF): 3296 cm^{-1} [ν(N−H)]. MS (FAB): *m*/*z* 565 [M]$^+$. ^{1}H NMR (toluene-d_8): δ 16.1 (br, 2H), 7.53 (br, 2H), 4.39 (br, 1H), 3.76 (br, 30H), 0.20 (br, 2H), −34.48 (br, ∼2H), −43.43 (br, ∼2H). The spectral pattern retains over the temperature range of +80 to −20 °C. The signals became extremely broad at lower temperature. The EPR and SQUID data are provided in the Supporting Information.

(9) Crystal data for **1**: $C_{32}H_{41}N_2Fe_2$, fw = 565.37, orthorhombic, space group *Pnn*2, a = 12.0653(17) Å, b = 15.218(2) Å, c = 15.969(3) Å, V = 2939.0(8) Å^3, T = 296 K, Z = 4, μ(Mo Kα) = 1.011 mm^{-1}, 27 158 reflections measured, 6715 unique (R_{int} = 0.0654), R1 = 0.0485, wR2 = 0.1309, GOF = 1.008. The refinement was successful with the acentric *Pnn*2 as a racemic twin (Flack parameter 0.33), while no workable solution was obtained with centrosymmetric *Pnnm*. Crystal data for **2**: $C_{32}H_{40}N_2Fe_2$, fw = 1075.03, monoclinic, space group *C*2/*c*, a = 17.918(6) Å, b = 11.820(3) Å, c = 13.751(3) Å, β = 93.07(2)°, V = 2908.1(14) Å^3, T = 296 K, Z = 4, μ(Mo Kα) = 1.020 mm^{-1}, 13 725 reflections measured, 3308 unique (R_{int} = 0.0478), R1 = 0.0373, wR2 = 0.0943, GOF = 0.993.

(10) The deviation from planarity is smaller than that for the Ru_2N_2 core of [Cp*Ru(μ_2-NHPh)]$_2$ (121.6° between RuN_2 planes). See ref 4e.

(11) The N−H hydrogen atom was not found in the Fourier synthesis and, hence, was located at the calculated position.

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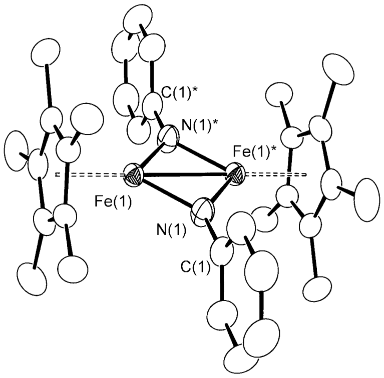

Figure 2. Molecular structure of **2**. Ellipsoids are drawn at a 35% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(1)*, 2.44492(9); Fe(1)−N(1), 1.8022(19); Fe(1)*−N(1), 1.8100(18); N(1)−C(1), 1.402(3); Fe(1)−N(1)−Fe(1)*, 85.38(8); Fe(1)−N(1)−C(1), 135.63(15); Fe(1)*−N(1)−C(1), 138.79(15).

Treatment of **1** with a radical precursor 2,2′-azobis(2,4-dimethylvaleronitrile) produces a diamagnetic bis(μ_2-imido) complex **2** (Scheme 1).[13] Homolytic N−H hydrogen atom abstraction by the 2-cyano-4-methylpentyl radical is a likely mechanism,[14−17] though we cannot rule out the possibility of a stepwise oxidation−deprotonation pathway. Complex **2** crystallizes as dark-brown plates (45% yield) from hexanes and has been characterized by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction (Figure 2). The molecule is composed of the two inversion-related “Cp*FeNPh” units, which constitute a planar Fe_2N_2 ring with an Fe−Fe separation of 2.44492(9) Å. The bridging imido moieties are planar at N (sum of the bond angles around N = 360°) and exhibit short Fe−N bond distances [1.8022(19) and 1.8100(18) Å]. These features indicate strong π donation from imido N atoms to the coordinatively unsaturated Fe centers.

The imido dimer **2** can also be prepared via a cationic Fe(III)−Fe(III) complex $[(Cp^*Fe)_2(\mu_2\text{-}NHPh)(\mu_2\text{-}NPh)]OTf$ ($\mathbf{1}^+OTf^-$), which is cleanly produced upon oxidation of **1** with ferrocenium triflate (Scheme 1).[18] The salt $\mathbf{1}^+OTf^-$, which is soluble in acetone and acetonitrile, moderately soluble in THF, but insoluble in toluene and hexanes, was isolated in 70% yield as an olive-green microcrystalline solid and has been characterized by elemental analysis and NMR (^{1}H and ^{13}C) spectroscopy. Deprotonation of $\mathbf{1}^+OTf^-$ with $NaN(SiMe_3)_2$ affords the bis(μ_2-imido) complex **2** in 51% isolated yield,[19] while no reaction took place with a weaker base, NEt_3.

In summary, this work has provided access to new dinuclear Cp*Fe bridging amido and imido complexes. The reaction between $[Cp^*FeCl]_x$ and LiNHPh proceeded via partial oxidation of the Fe(II) centers to yield the paramagnetic Fe(II)−Fe(III) μ_2-amido−μ_2-imido complex **1**. The mixed-valence complex **1** can be transformed into the Fe(III) μ_2-imido dimer **2** either directly by interaction with an azobis(isobutyronitrile)-like azo compound or in a stepwise manner via $\mathbf{1}^+OTf^-$. The former reaction indicated the ability of the Fe-bound amido NH moiety to undergo homolytic N−H bond cleavage. Works are now in progress to find out the further reactivity of these complexes as well as their applications to catalysis.

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Supporting Information Available: Experimental details and characterization data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Preparation of $[Cp^*Fe(\mu_2\text{-}NPh)]_2$ (**2**). Method A: To a stirred solution of **1** (162 mg, 0.287 mmol) in 10 mL of hexanes was added 2,2′-azobis(2,4-dimethylvaleronitrile) (71 mg, 0.287 mmol). The mixture was stirred at 50 °C for 24 h, at which time the dark-brown mixture was filtered hot. Allowing the filtrate to stand at −25 °C afforded dark-brown plates, which were collected by filtration, washed twice with cold hexanes (3 mL, −25 °C), and then dried in vacuo. Yield: 73 mg, 45%. Method B: To a stirred suspension of $\mathbf{1}^+OTf^-$ (97 mg, 0.136 mmol) in 10 mL of THF was added $NaN(SiMe_3)_2$ (0.15 mL, 1.1 M solution in THF, 0.165 mmol) at room temperature. After stirring for 2 h, the mixture was evaporated to dryness and the residue extracted with hexanes (15 mL). Concentration to ca. 5 mL and cooling to −25 °C afforded dark-brown plates, which were collected by filtration and dried in vacuo. Yield: 39 mg, 51%. ^{1}H NMR (C_6D_6): δ 7.98 (m, 4H, Ph), 7.28 (m, 2H, Ph), 6.62 (m, 4H, Ph), 2.48 (s, 30H, Cp*). Anal. Calcd for $C_{32}H_{40}N_2Fe_2$: C, 68.10; H, 7.14; N, 4.96. Found: C, 67.01; H, 7.31; N, 5.05. Repeated analyses failed to give the expected results.

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(16) Hydrogen atom transfer involving N−H bond cleavage: Mader, E. A.; Larsen, A. S.; Mayer, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 8066−8067.

(17) Hydrogen atom addition to an imido N atom: (a) Thyagarajan, S.; Shay, D. T.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **2003**, *125*, 4440−4441. (b) Kogut, E.; Wiencko, H. L.; Zhang, L.; Cordeau, D. E.; Warren, T. H. *J. Am. Chem. Soc.* **2005**, *127*, 11248−11249. (c) Lucas, R. L.; Powell, D. R.; Borovik, A. S. *J. Am. Chem. Soc.* **2005**, *127*, 11596−11597.

(18) Preparation of $[(Cp^*Fe)_2(\mu_2\text{-}NHPh)(\mu_2\text{-}NPh)]OTf$ ($\mathbf{1}^+OTf^-$). To a cooled (−80 °C) solution of **1** (359 mg, 0.635 mmol) in 20 mL of THF was added $[Cp_2Fe]OTf$ (212 mg, 0.631 mmol), and the mixture was allowed to warm to room temperature with stirring over 17 h to form a green suspension. The mixture was evaporated to dryness, and the residue was extracted with acetone (20 mL). Evaporation of the solvent gave an olive-green solid, which was washed twice with diethyl ether (15 mL) and dried in vacuo. Yield: 317 mg, 70%. Anal. Calcd for $C_{33}H_{41}N_2O_3F_3SFe_2$: C, 55.48; H, 5.78; N, 3.92. Found: C, 55.06; H, 5.37; N, 4.02. ^{1}H NMR (acetone-d_6): δ 8.82 (d, 1H, Ph), 7.62 (m, 2H, Ph), 7.55 (t, 2H, Ph), 7.34 (m, 1H, Ph), 7.27 (t, 1H, Ph), 7.12 (d, 1H, Ph), 6.71 (t, 1H, Ph), 3.82 (d, 1H, Ph), 3.76 (s, 1H, NH), 1.16 (s, 30H, Cp*). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 171.39 (s, Ph), 164.09 (s, Ph), 130.24 (s, Ph), 130.18 (s, Ph), 129.79 (s, Ph), 129.69 (s, Ph), 128.76 (s, Ph), 126.16 (s, Ph), 124.48 (s, Ph), 121.54 (q, CF_3), 120.23 (s, Ph), 119.14 (s, Ph), 118.63 (s, Ph), 97.48 (s, C_5Me_5), 9.38 (s, $C_5\mathit{Me}_5$). The ^{1}H NMR data contain an unusually high-field-shifted phenyl resonance (δ 3.82). The ^{1}H−^{1}H and ^{13}C−^{1}H COSY experiments suggest that the high-field aryl proton would be one of the *o*-phenyl protons (possibly of the amido phenyl). Because the $^1J_{CH}$ of 160 Hz disagrees with an agostic interaction, we tentatively assume the effect of the Cp* ring current as a reason for such a high-field shift.

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