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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*FeCI]_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 monomeric² and bridged³ 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 $[Cp*Ru(\mu_2-NHPh)]_2$, 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

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Scheme 1



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

The interaction of $[Cp*FeCl]_x^7$ with LiNHPh (1 equiv to Fe) did not give the expected Fe(II) μ_2 -amido complex $[Cp*Fe(\mu_2-NHPh)]_2$ 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), ¹H 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 1⁺ at m/z 565. The ¹H 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 $S = \frac{1}{2}$ ground state, which is also supported by the low-temperature SQUID magnetometry ($\mu_{\rm eff} = 1.73 \ \mu_{\rm B}$ at 2 K). The moment increased as the temperature was raised (2.85 $\mu_{\rm B}$ at 300 K), indicating an

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- (8) Preparation of $[(Cp*Fe)_2(\mu_2-NHPh)(\mu_2-NPh)]$ (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 FeCl₂ (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, darkgreen-brown crystals of 1 were collected by filtration and dried in vacuo. Yield: 565 mg, 44%. Anal. Calcd for C₃₂H₄₁N₂Fe₂: 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]⁺. ¹H 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, ~ 2 H), -43.43 (br, ~ 2 H). 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.



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), 7.7.12(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).

antiferromagnetic coupling between the two high-spin Fe centers. Similar behavior has been observed for other Fe-(II)-Fe(III) complexes.^{4c}

The single-crystal X-ray structure of **1** is shown in Figure 1.⁹ The molecule contains a nonplanar Fe₂N₂ core in which the two FeN₂ 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 $[Cp*Ru(\mu_2-NHPh)]_2$ 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.

- (10) The deviation from planarity is smaller than that for the Ru₂N₂ core of [Cp*Ru(μ_2 -NHPh)]₂ (121.6° between RuN₂ planes). See ref 4e.
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⁽⁹⁾ Crystal data for 1: C₃₂H₄₁N₂Fe₂, fw = 565.37, orthorhombic, space group *Pnn2*, a = 12.0653(17) Å, b = 15.218(2) Å, c = 15.969(3) Å, V = 2939.0(8) Å³, 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 *Pnn2* as a racemic twin (Flack parameter 0.33), while no workable solution was obtained with centrosymmetric *Pnnm*. Crystal data for 2: C₃₂H₄₀N₂Fe₂, fw = 1075.03, monoclinic, space group C2/c, a = 17.918(6) Å, b = 11.820(3) Å, c = 13.751(3) Å, β = 93.07(2)°, V = 2908.1(14) Å³, 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.



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(2,4dimethylvaleronitrile) 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 ¹H 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 Fe₂N₂ 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-

- (15) Hydrogen atom abstraction from Fe and Mn hydroxo complexes is known: Gupta, R.; Borovik, A. S. J. Am. Chem. Soc. 2003, 125, 13234–13242.
- (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.
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(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(μ_2 -NHPh)(μ_2 -NPh)]OTf (1⁺OTf⁻), which is cleanly produced upon oxidation of **1** with ferrocenium triflate (Scheme 1).¹⁸ The salt 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 (¹H and ¹³C) spectroscopy. Deprotonation of **1**⁺OTf⁻ with NaN(SiMe₃)₂ affords the bis(μ_2 -imido) complex **2** in 51% isolated yield,¹⁹ while no reaction took place with a weaker base, NEt₃.

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 **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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- (18) Preparation of $[(Cp*Fe)_2(\mu_2-NHPh)(\mu_2-NPh)]OTf (1+OTf^-)$. To a cooled (-80 °C) solution of 1 (359 mg, 0.635 mmol) in 20 mL of THF was added [Cp₂Fe]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 C₃₃H₄₁N₂O₃F₃SFe₂: C, 55.48; H, 5.78; N, 3.92. Found: C, 55.06; H, 5.37; N, 4.02. ¹H 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*). ¹³C{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, CF₃), 120.23 (s, Ph), 119.14 (s, Ph), 118.63 (s, Ph), 97.48 (s, C5Me5), 9.38 (s, C₅Me₅). The ¹H NMR data contain an unusually high-field-shifted phenyl resonance (δ 3.82). The ¹H-¹H and ¹³C-¹H COSY experiments suggest that the high-field aryl proton would be one of the *o*-phenyl protons (possibly of the amido phenyl). Because the ${}^{1}J_{CH}$ 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.
- (19) The synthetic strategy is similar to that employed for the conversion of a Ni(I) amide to a Ni(II) imide: Midiola, D. J.; Hillhouse, G. L. J. Am. Chem. Soc. 2001, 123, 4623–4624.

⁽¹³⁾ Preparation of $[Cp*Fe(\mu_2-NPh)]_2$ (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 1⁺OTf⁻ (97 mg, 0.136 mmol) in 10 mL of THF was added NaN(SiMe₃)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%. ¹H NMR (C₆D₆): δ 7.98 (m, 4H, Ph), 7.28 (m, 2H, Ph), 6.62 (m, 4H, Ph), 2.48 (s, 30H, Cp*). Anal. Calcd for C₃₂H₄₀N₂Fe₂: 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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