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A Cationic Three-Coordinate Iron(II) Complex and the Reaction of *β*-Diketiminate with Ethyl Diazoacetate

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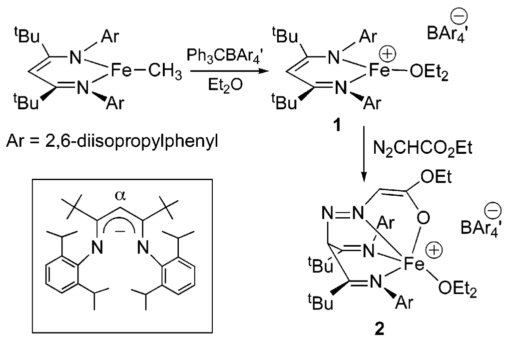
Summary: We report the synthesis of a cationic iron(II) complex in which the iron atom is 3-coordinate in solution and in the solid state. The complex undergoes an unusual addition of ethyl diazoacetate, in which the diketiminate forms a bond to the terminal nitrogen of the diazo group. Coordination of the ester group to iron is proposed to activate the diazo group so that it is attacked by the nucleophilic diketiminate ligand.

Bulky aryl-substituted β-diketiminate ligands (inset, Scheme 1) have become popular in the coordination chemistry of transition metals because they are easily synthesized and modified and because ortho substituents on the aryl ring provide great steric hindrance very close to the coordinated metal.[1] The use of β-diketiminates in ethylene polymerization[2] attests to their stability. However, recent examples show that certain modes of reactivity are available in which the backbone of the β-diketiminate ligand is compromised. In some very interesting early-metal complexes, the imine group of the diketiminate undergoes a metathesis-type reaction with multiply bonded ligands.[3] Aluminum diketiminate complexes react with ethylene to functionalize the central (α) carbon of the β-diketiminate through an apparent cycloaddition reaction,[4] and a platinum methyl complex transfers a methyl group to the same position.[5] More often, this site on the ligand acts as a nucleophile. For example, diketiminate complexes of copper(II) and zinc(II) are oxidized by O_2 to give a ketone at this position,[6] although some diketiminate−copper−O_2 complexes can be isolated.[7] Chlorophosphines,[8] alkyl halides,[9] triflyl chloride,[10] sulfur,[11] ketones,[9] and ketenes[12] are also attacked by the nucleophilic α-carbon of this ligand. In this communication, we report a different transformation of the β-diketiminate ligand, which arises from the reaction of a diazoalkane with the central carbon atom of the diketiminate and generates a new C−N bond. The precursor of this reaction is a rare cationic 12-electron iron(II) complex, and the product has an interesting new tridentate ligand that may be useful for organometallic chemistry.

Scheme 1



We have shown that the 3-coordinate, 12-electron iron(II) methyl complex $LFeCH_3$[13] (L = 2,2,6,6-tetramethyl-3,5-bis(2,6-diisopropylphenylimino)hept-4-yl, Scheme 1 inset) is thermally stable despite its flagrant violation of the “18-electron rule.” The reaction of $LFeCH_3$ with $Ph_3CBAr'_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) in diethyl ether results in abstraction of the methyl group and formation of the cationic high-spin iron(II) species $[LFe(OEt_2)]BAr'_4$ (**1**), which was isolated in 88% yield.[14]

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(1) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3066.

(2) (a) Vollmerhaus, R.; Rahim, M.; Tomaszewski, R.; Xin, S.; Taylor, N. J.; Collins, S. *Organometallics* **2000**, *19*, 2161−2169. (b) Hayes, P. G.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 2132−2133. (c) Gibson, V. C.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2001**, 1895−1903. (d) MacAdams, L. A.; Kim, W.-K.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **2002**, *21*, 952−960. (e) Theopold, K. H.; MacAdams, L. A.; Puttnual, C.; Buffone, G. P.; Rheingold, A. L. *Polym. Mater. Sci. Eng.* **2002**, *86*, 310. (f) Zhou, M.-S.; Huang, S.-P.; Weng, L.-H.; Sun, W.-H.; Liu, D.-S. *J. Organomet. Chem.* **2003**, *665*, 237−245. (g) Kogut, E.; Zeller, A.; Warren, T. H.; Strassner, T. *J. Am. Chem. Soc.* **2004**, *126*, 11984−11994.

(3) (a) Basuli, F.; Bailey, B. C.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6052−6053. (b) Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 10170−10171. (c) Basuli, F.; Kilgore, U. J.; Brown, D.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2004**, *23*, 6166−6175. (d) Basuli, F.; Bailey, B. C.; Brown, D.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 10506−10507.

(4) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384−9385.

(5) Fekl, U.; Kaminsky, W.; Goldberg, K. I., *J. Am. Chem. Soc.* **2001**, *123*, 6423−6424.

(6) Yokota, S.; Tachi, Y.; Itoh, S. *Inorg. Chem.* **2002**, *41*, 1342−1344.

(7) (a) Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108−2109. (b) Aboelella, N. W.; Lewis, E. A.; Reynolds, A. M.; Brennessel, W. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 10660−10661. (c) Cramer, C. J.; Tolman, W. B.; Theopold, K. H.; Rheingold, A. L., *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3635−3640. (d) Aboelella, N. W.; Kryatov, S. V.; Gherman, B. F.; Brennessel, W. W.; Young, V. G., Jr.; Sarangi, R.; Rybak-Akimova, E. V.; Hodgson, K. O.; Hedman, B.; Solomon, E. I.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2004**, *126*, 16896−16911.

(8) Ragogna, P. J.; Burford, N.; D'eon, M.; McDonald, R. *Chem. Commun.* **2003**, 1052−1053.

(9) Carey, D. T.; Cope-Eatough, E. K.; Vilaplana-Mafe, E.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Dalton* **2003**, 1083−1093.

(10) Jazdzewski, B. A.; Holland, P. L.; Pink, M.; Young, V. G., Jr.; Spencer, D. J. E.; Tolman, W. B. *Inorg. Chem.* **2001**, *40*, 6097−6107.

(11) Brown, E. C.; Aboelella, N. W.; Reynolds, A. M.; Aullón, G.; Alvarez, S.; Tolman, W. B. *Inorg. Chem.* **2004**, *43*, 3335−3337.

(12) Basuli, F.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chem.* **2003**, *42*, 8003−8010.

(13) Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J., *J. Am. Chem. Soc.* **2002**, *124*, 14416−14424.

10.1021/om0489913 CCC: $30.25

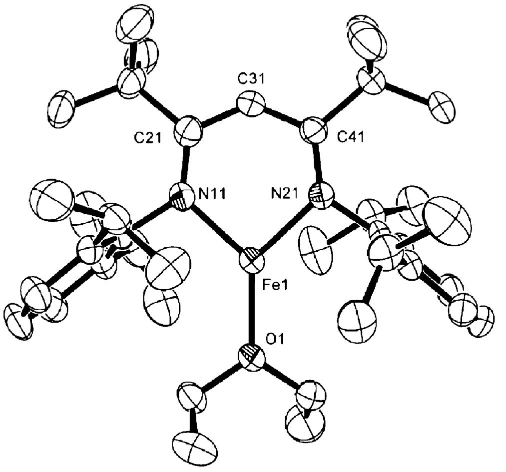

Figure 1. One of the cations in the crystal structure of **1**, with thermal ellipsoids at the 50% probability level. Selected bond lengths, averaged between the two independent cations (Å): Fe−N = 1.941(7), Fe−O = 1.978(4), N−C_{imine} = 1.33(2), C_{imine}−C_α = 1.40(2).

The crystal structure of **1** (Figure 1) shows two independent cations and anions, which have similar metrical parameters. The diketiminate π electrons are delocalized, as shown by the planarity of the FeN_2C_3 backbone and diketiminate bond lengths similar to those in other 3-coordinate iron(II) complexes.[15] The Fe, N, and O atoms lie in a plane (sum of angles at iron 360.0(1)°).

Because **1** has a high-spin electronic configuration (μ_{eff}(Evans) = 4.9 μ_B; $S = 2$), the ^{1}H NMR resonances are paramagnetically shifted. We have previously reported that planar three-coordinate (diketiminate)$Fe^{II}X$ complexes have anisotropic magnetic properties, with a large internal field along the iron−X bond, and that this phenomenon is a result of the specific orbital structure at iron.[16] As a result of the internal field, the paramagnetic shift of ligand proton resonances is dominated by the pseudocontact (dipolar) contribution,[17] and exceptionally large chemical shift dispersions are observed, with the aryl resonances shifted upfield by roughly 100 ppm and the alkyl and proton substituents of the diketiminate shifted downfield.[13,15] In Et_2O-d_{10} solution,[14] the ^{1}H NMR shifts of **1** are very similar to those in the other 3-coordinate iron(II) complexes,[15] providing strong evidence that the trigonal-planar geometry of the X-ray crystal structure is maintained in diethyl ether solution.

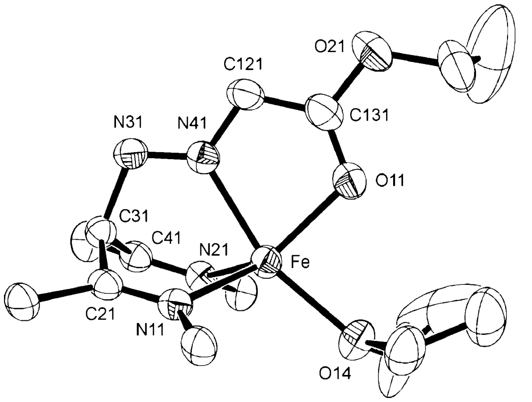

Figure 2. The cationic portion of **2**, with thermal ellipsoids at 50% probability. Aryl and methyl groups are omitted for clarity. Selected bond lengths (Å): Fe−N11 = 2.105(2), Fe−N21 = 2.118(2), Fe−N41 = 2.137(2), Fe−O11 = 2.051(2), N11−C21 = 1.279(3), C21−C31 = 1.538(4), C31−C41 = 1.541(4), C41−N21 = 1.281(3), C31−N31 = 1.514(3), N31−N41 = 1.279(3).

When a solution of **1** was treated with ethyl diazoacetate, a rapid, nearly quantitative reaction took place. The cationic, high-spin iron(II) product **2** (Scheme 1 and Figure 2) was isolated in 84% yield as its BAr′$_4$ salt, and its connectivity was established by crystallography.[18] There are substantial changes in the diketiminate ligand, with an apparent 10π cycloaddition between the diazo group in **2** and the diketiminate−iron unit. The ester is reduced to an alkoxide (C131−O11 = 1.269 Å), and the diketiminate is oxidized to a diketimine. In the crystal structure of **2** (Figure 2), C31 has sp^3 hybridization, as evidenced by the tetrahedral geometry and the bond lengths to C21 and C41. The N−C distances and N−N distances clearly indicate double bonds, as shown in Scheme 1. There is one example of a diazo ester reduction to an enolate at a transition metal,[19] but it does not create an N−C bond like the novel reaction shown here.

Several mechanisms can account for the unusual ligand transformation. First, the nucleophilic terminal nitrogen atom of the diazo group could coordinate to the metal, which is common in the literature.[20] To give the observed product, the diazo group would then migrate to the α-carbon followed by coordination. In another potential mechanism, the diazo reaction could occur in a concerted fashion, in a [5 + 4] cycloaddition that would be an extension of the well-known [3 + 2] cycloadditions of diazoalkanes.[21] Cycloaddition and methyl transfer reactions of other metal−diketiminate complexes may

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(14) For **1**: crystal data $C_{71}H_{75}BF_{24}FeN_2O$, M_r = 1494.99, monoclinic, $P2_1/c$, a = 23.6273(12) Å, b = 26.2410(13) Å, c = 24.4746(12) Å, β = 105.529(1)°, V = 14620.4(13) Å^3, T = 193 K, Z = 8, μ(Mo Kα) = 0.310 mm^{-1}, 52 023 reflections measured, 20 972 unique (R_{int} = 0.0442), R1 = 0.0835, wR2 = 0.1303 ($I > 2\sigma(I)$); μ_{eff}(Et_2O-d_{10}) 4.9 μ_B; ^{1}H NMR (δ/ppm, 400 MHz, Et_2O-d_{10}, 23 °C) 40.5 (s, 1H, C_αH), 36.8 (s, 18H, $C(CH_3)_3$), 20.4 (s, 4H, *m*-Ar), 8.7−7.1 (m, 15H, BAr$_4$′), −21.2 (s, 12H, $CH(CH_3)_2$), −66.6 (s, 4H, $CH(CH_3)_2$), −105.7 (s, 12H, $CH(CH_3)_2$), −128.6 (s, 2H, *p*-Ar); ^{19}F{^{1}H} NMR (δ/ppm, 400 MHz, diethyl ether-d_{10}, 23 °C) −63.29.

(15) (a) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Chem. Commun.* **2001**, 1542−1543. (b) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Organometallics* **2002**, *21*, 4808−4814. (c) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 15752−15753. (d) Eckert, N. A.; Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Inorg. Chem.* **2004**, *43*, 3306−3321. (e) Vela, J.; Vaddadi, S.; Cundari, T. R.; Smith, J. M.; Gregory, E. A.; Lachicotte, R. J.; Flaschenriem, C. J.; Holland, P. L. *Organometallics* **2004**, *23*, 5226−5239.

(16) Andres, H.; Bominaar, E.; Smith, J. M.; Eckert, N. A.; Holland, P. L.; Münck, E. *J. Am. Chem. Soc.* **2002**, *124*, 3012−3025.

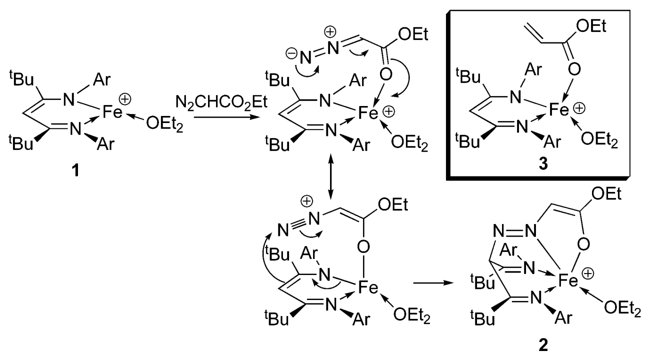
(17) La Mar, G. N., Horrocks, W. D., Holm, R. H., Eds. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(18) For **2**: crystal data $C_{75}H_{81}BF_{24}FeN_4O_3$, M_r = 1609.10, triclinic, $P\bar{1}$, a = 12.7104(9) Å, b = 17.6036(12) Å, c = 19.4980(14) Å, α = 111.046(1)°, β = 98.370(1)°, γ = 92.192(1)°, V = 4008.9(5) Å^3, T = 193 K, Z = 2, μ(Mo Kα) = 0.290 mm^{-1}, 24 639 reflections measured, 17 219 unique (R_{int} = 0.0172), R1 = 0.0790, wR2 = 0.1041 ($I > 2\sigma(I)$); μ_{eff}(THF-d_8) 4.9 μ_B; ^{1}H NMR (δ/ppm, 400 MHz, THF-d_8, 23 °C) 131.4 (s, 1H, C_αH), 52.9 (s, 2H, Ar H), 21.8 (s, 2H, Ar H), 16.5 (s, 18H, $C(CH_3)_3$, 15.0 (s, 4H, *m*-H), 7.9 (s, 8H, BAr′$_4$ *o*-H), 7.7 (s, 4H, BAr′$_4$ *p*-H), 4.5 (s, 2H, OCH_2CH_3), 3.4 (s, 4H, $(CH_3CH_2)_2O$), 1.2−0.9 (m, 9H, OCH_2CH_3, $(CH_3CH_2)_2O$), 0.1 (s, 0.3H), −8.2 (s, 3H), −11.4 (s, 6H, $CH(CH_3)_2$), −17.1 (s, 6H, $CH(CH_3)_2$) (some protons are not observed, presumably because of broadening from the paramagnetic iron center); ^{19}F NMR (δ/ppm, 400 MHz, diethyl ether-d_{10}, 23 °C) −64.09. The ligand was released with HCl and extracted. CIMS, positive ion: *m/z* 617.

(19) Cowie, M.; McKeer, I. R.; Loeb, S. J.; Gauthier, M. D. *Organometallics* **1986**, *5*, 860−868.

(20) (a) Mizobe, Y.; Ishii, Y.; Hidai, M., *Coord. Chem. Rev.* **1995**, *139*, 281−311. (b) Dartiguenave, M.; Menu, M. J.; Deydier, E.; Dartiguenave, Y.; Siebald, H. *Coord. Chem. Rev.* **1998**, *180*, 623−663.

Scheme 2



go through pericyclic routes to functionalize the C$_\alpha$ carbon atom of the diketiminate.[4,5]

We favor the mechanism shown in Scheme 2, in which the conversion of **1** to **2** is initiated by coordination of the ester group. The resonance structures show that coordination of the carbonyl oxygen to iron could withdraw electron density from the organic fragment, making the diazo group electrophilic. Coordination would also steer the terminal nitrogen atom of the diazo group into an ideal position for attack by C$_\alpha$ of the β-diketiminate, which is nucleophilic.[6–12] The cycloaddition reaction described here was extremely rapid at −80 °C, and we observed no spectroscopic evidence for any intermediate in the reaction.

In an effort to support the idea that ester coordination is important in the formation of **2**, **1** was treated with ethyl acrylate, an ester with steric demands similar to those of ethyl diazoacetate. This led to the adduct **3** (inset, Scheme 2), which was isolated in 78% yield.[22] The crystal structure of **3** (Figure 3) shows that the carbonyl oxygen of the ester is bound to the iron atom. Importantly, the vinyl group is in the same orientation that would place the diazo group close to the nucleophilic C$_\alpha$ atom of the diketiminate ligand in the formation of **2**. Therefore, we propose that **3** models the transient intermediate in Scheme 2. Activation of ethyl diazoacetate through coordination of the ester group could also explain a recently reported iron-catalyzed phosphine attack on ethyl diazoacetate.[23]

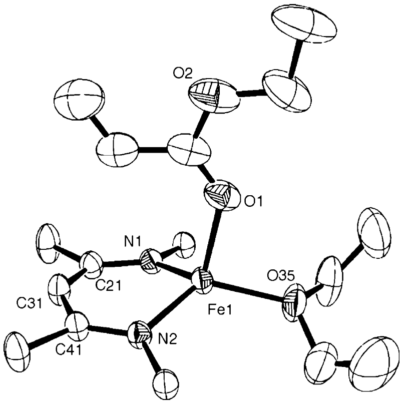


Figure 3. The cationic portion of **3**, with thermal ellipsoids at 50% probability. Aryl and methyl groups are omitted for clarity. The major conformation of the diethyl ligand is shown. Selected bond lengths (Å): Fe−N1 = 1.997(2), Fe−N2 = 1.988(2), Fe−O1 = 2.076(2), Fe−O35 = 2.024(2), C−O1 = 1.234(4).

The reaction of ethyl diazoacetate with the β-diketiminate is interesting, because it results in a new β-diketimine ligand. Upon treatment of **2** with an ethereal solution of HCl, the coordinated diazene is protonated and displaced from iron. Mass spectral evidence supports the formation of the free functionalized diketimine.[18] Further studies are necessary to understand the scope of this new C−N bond forming reaction and the utility of the tridentate ligand formed in the reaction.

In conclusion, we have characterized a cationic three-coordinate iron complex that is quite reactive. Its electrophilic character at iron is expected to be useful in various catalytic reactions. In a demonstration of its strong Lewis acidity, it coordinates the C=O bond of esters, activating a nearby functional group toward nucleophilic attack by the ligand.

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Supporting Information Available: Text, tables, and figures giving synthetic and crystallographic details; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Gothelf, K. V.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 863−910.

(22) For **3**: crystal data $C_{80}H_{93}BF_{24}FeN_2O_4$, M_r = 1669.22, monoclinic, $P2_1/n$, a = 18.1049(9) Å, b = 24.4665(13) Å, c = 18.9489(10) Å, β = 96.345(1)°, V = 8342.3(7) Å^3, T = 193 K, Z = 4, μ(Mo Kα) = 0.282 mm^{-1}, 52 334 reflections measured, 19 987 unique (R_{int} = 0.0267), R1 = 0.0558, wR2 = 0.0960 ($I > 2\sigma(I)$); ^{1}H NMR (δ/ppm, 400 MHz, diethyl ether-d_{10}, 23 °C) 25.6 (s, 4H), 11.3 (s, 18H), 8.0−7.7 (m, ~12H, BAr$'_4$ *o*-H and *p*-H), 7.0 (s, ~3H), 6.2 (s, ~24H), 4.5 (s, ~3H), −7.0 (br s, 3H), −57.3 (s, 1H), −59.8 (s, 1H), −81.5 (s, 1H) (some protons are not observed, presumably because of broadening from the paramagnetic iron center).

(23) Louie, J.; Grubbs, R. H. *Organometallics* **2001**, *20*, 481−484.