A Stable Terminal Imide on Iron

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The terminal organoimido−metal unit, [M═NR]^z, is a fundamental functional group in d- and f-element chemistry.[1] Across the transition series, well-characterized examples are numerous but occur exclusively within a zone of stability bounded by the group 4 elements and by the descending diagonal of manganese, ruthenium, and iridium.[1,2] Terminal imido−metal complexes at the margins of this interval are the least stable and attract special interest for their reactivity.[3] On iron, terminal imido ligation has never been directly observed,[4] although its intermediacy has been invoked in reaction mechanisms by analogy to isoelectronic oxo chemistry.[5] As noted in a comprehensive review by Wigley,[1a] "...species thought to contain Fe═NR groups appear to be fleeting transients that are inherently unstable and, in the absence of organic substrate to accept the [NR] ligand, will quickly rearrange or decompose."[6] We report here the first characterized, stable terminal organoimide on iron.

The anaerobic reaction of $FeCl_3$ with 2 equiv of $LiNH^tBu$[7] in THF immediately gives a deep brown-black solution. Heating at 70 °C for 6 h, followed by solvent removal, *n*-pentane extraction, and filtration affords a dark solution containing almost exclusively $[Fe_4(\mu_3\text{-}N^tBu)_4Cl_4]$ (**1**) and $[Fe_4(\mu_3\text{-}N^tBu)_4(N^tBu)Cl_3]$ (**2**). Clusters **1** and **2** usually form in approximately equimolar ratios, with a combined yield of ∼15% based on iron. Separation of the two products is problematic due to comparable solubilities and instability toward standard chromatographic adsorbents; nonetheless, successive fractional crystallizations at −30 °C allow isolation of pure **1** (from benzene, as the solvate) or pure **2** (from toluene) as black crystals (∼1−2% yield for each).[8a,b,9] The majority of the solid reaction mass remains undissolved after both *n*-pentane and benzene washes. The presence of LiCl has hindered our efforts to fully define the composition of this fraction, but dissolution of the material in DME, followed by cooling to −30 °C, gives black crystals of $[Li(DME)_3][Fe_4(\mu_3\text{-}N^tBu)_4Cl_4]$ (**[Li(DME)$_3$]$^+$[1]$^-$**).[8c] The reaction stoichiometry appears optimum for the formation of species **1** and **2**; at higher (1:2.5) or lower (1:1.5) iron/amide ratios, yields of clusters **1** and **2** diminish, while other paramagnetic species, currently under investigation, become prominent.

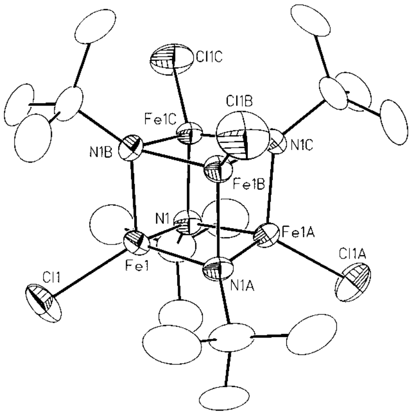

Figure 1. Structure of $[Fe_4(\mu_3\text{-}N^tBu)_4Cl_4]$ (benzene monosolvate, **1·C$_6$D$_6$**) with thermal ellipsoids (35% probability level) and selected atom labels; hydrogens are omitted for clarity. Selected distance (Å) and angle (deg) ranges [mean]: Fe−N, 1.932(3)−1.938(3) [1.934(3)]; Fe1−Cl1, 2.166(2); Fe···Fe, 2.592(1)−2.616(1) [2.60(1)]; N−Fe−N, 94.3(2)−95.8(1) [95.3(8)]; Fe−N−Fe, 84.1(1)−85.2(2) [84.5(6)]; Cl−Fe−N, 118.3(1)−122.99(8) [121(3)]. The anionic reduced cubane in $[Li(DME)_3][Fe_4(\mu_3\text{-}N^tBu)_4Cl_4]$ (**[Li(DME)$_3$]$^+$[1]$^-$**, structure not shown) is nearly indistinguishable from **1**, and has the following selected distance (Å) and angle (deg) ranges [mean]: Fe−N, 1.936(5)−1.961(6) [1.952(8)]; Fe−Cl, 2.207(2)−2.215(2) [2.211(3)]; Fe···Fe, 2.593(1)−2.635(1) [2.61(2)]; N−Fe−N, 94.6(2)−96.9(2) [95.7(7)]; Fe−N−Fe, 83.0(2)−84.7(2) [84.0(6)]; Cl−Fe−N, 118.5(2)−123.7(2) [121(2)].

Compounds **1**, **[Li(DME)$_3$]$^+$[1]$^-$**, and **2** are close structural relatives of our previously reported $[Fe_4(\mu_3\text{-}NPh)_4(SR)_4]$ imidocubanes (**3**).[8,10,11] Cluster **1** crystallizes from benzene with imposed D_{2d} ($\bar{4}m2$) symmetry; the equivalent tetrahedral Fe(III) sites are each ligated by a terminal chloride and three bridging *tert*-butylimides (Figure 1). The anion (**[1]$^-$**) present in **[Li(DME)$_3$]$^+$[1]$^-$** is related to **1** by a one-electron reduction; the structural metrics (see Figure 1 legend) of the 1Fe(II)/3Fe(III) cluster, however, are virtually identical to those of the all-ferric species, with only very minor increases in iron-ligand bond lengths for the reduced cluster. Cluster **2**, which crystallizes from toluene with mirror symmetry, is a site-differentiated derivative of cubane **1**, with one terminal chloride ligand replaced by a terminal *tert*-butylimide

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(1) (a) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(2) In the f-elements, the terminal imidometal fragment is known only for thorium and uranium in the actinide series.[1a]

(3) For some recent examples, see: (a) Polse, J. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 13405 and references therein. (b) Au, S.-M.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120. (c) DuBois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *Acc. Chem. Res.* **1997**, *30*, 364.

(4) We exclude terminal [MNNR]^z and [MNNR$_2$]^z units from classification as metal imides due to bond delocalization in the [MNN] fragment.[4a] For example, the terminal [FeNNR$_2$]$^{2+}$ group, observed in stable heme complexes,[4b,c] allows other resonance forms, with different oxidation states and bond orders, in addition to Fe(IV)−hydrazide(2−):

$$[\overset{2+}{Fe}{=}N{-}NR_2] \leftrightarrow [\overset{+}{Fe}{-}N{=}\overset{+}{N}R_2] \leftrightarrow [Fe{=}\overset{+}{N}{=}\overset{+}{N}R_2]$$

Structural analysis reveals long Fe−N (1.81 Å) and short N−N (1.23 Å) contacts that favor an Fe(II)−azamine description; a high-spin Fe(II) formulation is also supported by magnetic susceptibility, NMR, and Mössbauer data. (a) Kahlal, S.; Saillard, J.-Y.; Hamon, J.-R.; Manzur, C.; Carrillo, D. *J. Chem. Soc., Dalton Trans.* **1998**, 1229. (b) Mahy, J.-P.; Battioni, P.; Mansuy, D.; Fisher, J.; Weiss, R.; Mispelter, J.; Morgenstern-Badarau, I.; Gans, P. *J. Am. Chem. Soc.* **1984**, *106*, 1699. (c) Mansuy, D.; Battioni, P.; Mahy, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 4487.

(5) (a) Mansuy, D. *Pure Appl. Chem.* **1990**, *62*, 741 and references therein. (b) Simonato, J.-P.; Pécaut, J.; Scheidt, W. R.; Marchon, J.-C. *Chem. Commun.* **1999**, 989. (c) Bach, T.; Körber, C. *Eur. J. Org. Chem.* **1999**, 1033. (d) Nichols, P. J.; Fallon, G. D.; Murray, K. S.; West, B. O. *Inorg. Chem.* **1988**, *27*, 2795. (e) Mahy, J.-P.; Battioni, P.; Bedi, G.; Mansuy, D.; Fischer, J.; Weiss, R.; Morgenstern-Badarau, I. *Inorg. Chem.* **1988**, *27*, 353. (f) Mahy, J.-P.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1986**, *108*, 1079. (g) Svastis, E. W.; Dawson, J. H.; Breslow, R.; Gellman, S. H. *J. Am. Chem. Soc.* **1985**, *107*, 6427. (h) Barton, D. H. R.; Hay-Motherwell, R. S.; Motherwell, W. B. *J. Chem. Soc., Perkin Trans. 1* **1983**, 445.

(6) See Reference 1a, p 430.

(7) Barnett, N. D. R.; Clegg, W.; Horsburgh, L.; Lindsay, D. M.; Liu, Q.; Mackenzie, F. M.; Mulvey, R. E.; Williard, P. G. *Chem. Commun.* **1996**, 2321.

(8) Crystal data (Mo Kα, 200(2) K) are given as *a*, *b*, *c* (Å); α, *β*, *γ* (deg); space group, *Z*; $2\theta_{min/max}$ (deg), unique/observed [$I > 2\sigma(I)$] data, R1/wR2 for observed data (%), GooF. (a) **1·C$_6$D$_6$**: 10.8890(7), 10.8890(7), 13.7824(9); 90, 90, 90; *P*4$_2$/*nmc*, 2; 4.8/55.0, 1037/664, 3.89/8.83, 1.017. (b) **2**: 19.553(2), 13.904(1), 11.449(1); 90, 90, 90; *Pnma*, 4; 4.1/54.9, 3692/2528, 3.86/7.72, 1.028. (c) **[Li(DME)$_3$]$^+$[1]$^-$**: 14.2324(7), 20.204(1), 15.8431(5); 90, 90.315(3), 90; *P*2$_1$/*n*, 4; 3.2/52.8, 9305/4298, 7.27/14.18, 1.035.

(9) ^1H NMR (500 MHz, C_6D_6, 293 K). (a) **1**: δ 7.71. (b) **2**: δ 2.69 (9H), 5.56 (27H), 9.62 (9H).

(10) While this manuscript was in review, alternate syntheses and structures for **1** and **[Li(DME)$_3$]$^+$[1]$^-$** were reported (Link, H.; Decker, A.; Fenske, D. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1567); synthetic procedures, while based on $FeCl_3$ and $LiNH^tBu$, differ significantly from conditions described here.

(11) Verma, A. K.; Lee, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 10838.

10.1021/ja001147t CCC: $19.00

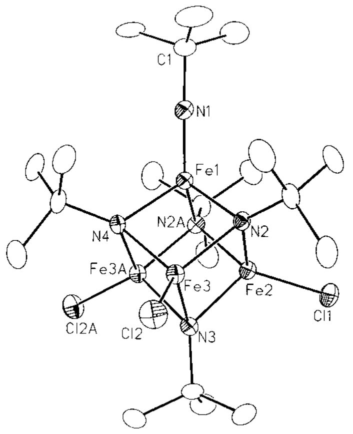

Figure 2. Structure of $[Fe_4(\mu_3\text{-N}^t\text{Bu})_4(\text{N}^t\text{Bu})Cl_3]$ (**2**) with thermal ellipsoids (35% probability level) and selected atom labels; hydrogens are omitted for clarity. The cluster is bisected by a crystallographic mirror plane, generating two orientations for the *tert*-butyl substituent of the terminal imido ligand; only one orientation is shown. Selected distance (Å) and angle (deg) ranges [mean]: Fe1−N1, 1.635(4); Fe1−N(2,4), 1.913(2)−1.917(3) [1.914(2)]; Fe(2,3)−N(2−4), 1.938(3)−1.953(3) [1.945(5)]; Fe−Cl, 2.1794(9)−2.194(1) [2.184(9)]; Fe$\cdots$Fe, 2.5774(9)−2.6157(7) [2.60(1)]; C1−N1−Fe1, 178.6(3); N−Fe−N, 93.7(1)−96.7(1) [95(1)]; Fe−N−Fe, 83.1(1)−85.1(1) [84.5(7)]; N1−Fe−N(2,4) 120.6(1)−122.1(2) [121.1(9)]; Cl−Fe−N, 119.47(9)−125.02(8) [121(2)].

(Figure 2). The complex is charge neutral and, therefore, formally possesses an oxidized 3Fe(III)/1Fe(IV) core. The near-linear terminal imide moiety is firmly established by the short Fe−N distance (1.64 Å), indicative of a metal−ligand multiple bond; this distance is comparable to the shortest equivalent length found in nitrido-bridged iron dimers (Fe═N−Fe, 1.62−1.74 Å, mean 1.68(4) Å)[12] and is much shorter than that of terminal iron-amide ($Fe-NR_2$, 1.88−1.93 Å, mean 1.91(1) Å)[13] or iron-alkoxide (Fe−OR, 1.78−1.90 Å, mean 1.85(4) Å)[13] bonds. Aside from the short terminal $Fe{=}N^t$Bu bond length, the general molecular dimensions of **2** differ little from those of **1**, $[\mathbf{1}]^-$, or **3**. The self-assembly of clusters **1**, $[\mathbf{1}]^-$, and **2** from $FeCl_3$ represents a new synthetic avenue[10] to the chemistry of imidoiron cubanes that complements the oxidative route developed for thiolatocubane **3**.[11]

Clusters **1** and **2** are readily identified in solution by their distinctive paramagnetically shifted ^{1}H NMR spectra.[9] Molecular composition and solution integrity are supported by the mass spectrometric detection of prominent parent ion signals from evaporated solutions of pure **1** or pure **2**.[14] The IR spectra of **1** and **2** are almost identical and dominated by prominent bands associated with the bridging *tert*-butylimide ligands.[15] Terminal imide **2** also shows two additional weak, but sharp bands at 1262 and 955 cm^{-1} that might be the coupled ν(Fe═N) and ν(N−C) modes.[16]

The electronic properties of **1** and **2** were probed by EPR and Mössbauer spectroscopies. The even-spin, all-ferric cubane **1** is EPR silent at 5 K in perpendicular and parallel modes. At the same temperature, terminal imidocubane **2** exhibits in perpendicular mode an axial EPR signal.[17] Pulsed EPR nutation experiments assign this signal to an apparent $S = {}^1/_2$ state; the temperature dependence of the signal indicates that this state is either the ground spin state or a very low-lying excited state (<4 K). The zero-field Mössbauer spectrum of polycrystalline **1** at 4.2 K displays a quadrupole doublet with an isomer shift and a quadrupole splitting ($\delta = 0.35(1)$ mm/s, $|\Delta E_Q| = 0.55(1)$ mm/s) characteristic of high-spin Fe(III).[18,19] The zero-field 150 K spectrum of a mixture of **1** and **2** (29(2) and 71(2)%, respectively, as quantitated by ^{1}H NMR) shows two quadrupole doublets. The predominant doublet represents 79(2)% of the iron in the sample and has average Mössbauer parameters ($\delta = 0.36$ mm/s, $|\Delta E_Q| = 0.43$ mm/s) that again indicate high-spin Fe(III). The minority doublet ($\delta = -0.17(2)$ mm/s, $|\Delta E_Q| = 0.38(3)$ mm/s) has an isomer shift and quadrupole splitting that identifies the remaining 21(2)% of the iron in the sample as Fe(IV). If a valence-localized 3Fe(III)/1Fe(IV) formulation is assumed for cluster **2**, we would expect an iron distribution of 82(2)% Fe(III) and 18(2)% Fe(IV) in the 29:71 mixture of clusters. The Mössbauer data confirm this calculated distribution and therefore the presence of valence localization in the 3Fe(III)/1Fe(IV) core of **2**.[20]

Although the $[Fe{=}NR]^{2+}$ functionality is expected to parallel the well-studied $[Fe{=}O]^{2+}$ moiety in aggressive reactivity,[1a,5] terminal imidocubane **2** is surprisingly inert. Preliminary reactivity studies show that both chlorocubane **1** and terminal imidocubane **2** are chemically robust and unreactive at room temperature toward a number of reagents including aniline, styrene, and triphenylphosphine; in contrast, thiolatocubane **3** rapidly exchanges arylimido core ligands with free anilines under the same conditions.[11] We believe the *tert*-butyl substituents, as arrayed around the cubane geometry, enforce steric barriers that hinder access to both the cluster core and the terminal iron-ligand bonds, while the N-anion donors establish an environment that supports high-valent iron.[12,21] These steric and electronic characteristics would explain the stability of the unprecedented terminal imidoiron group on **2**, and furthermore suggest the $[Fe_4(\mu_3\text{-N}^t\text{Bu})_4]^z$ cubane motif as a platform to access other "reactive"iron-ligand multiple bonds for close study.

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Supporting Information Available: Preparative procedure; crystallographic and other characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] (a) Jüstel, T.; Müller, M.; Weyhermüller, T.; Kressl, C.; Bill, E.; Hildebrandt, P.; Lengen, M.; Grodzicki, M.; Trautwein, A. X.; Nuber, B.; Wieghardt, K. *Chem. Eur J.* **1999**, *5*, 793. (b) Kienast, A.; Homborg, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 233. (c) Ercolani, C.; Jubb, J.; Pennesi, G.; Russo, U.; Trigiante, G. *Inorg. Chem.* **1995**, *34*, 2535. (d) Jüstel, T.; Weyhermüller, T.; Wieghardt, K.; Bill, E.; Lengen, M. Trautwein, A. X.; Hildebrandt, P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 669. (e) Moubaraki, B.; Benlian, D.; Baldy, A.; Pierrot, M. *Acta Crystallogr., Sect. C.* **1989**, *45*, 393. (f) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 6623.

[13] (a) *Cambridge Structural Database*, Version 5.18; Cambridge University: Cambridge University: Cambridge, England, October, 1999. (b) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.

[14] Anion-mode LDI-TOF MS. (a) **1**: *m/z* 649.5 [M$^-$ (calcd 649.8)]. (b) **2**: *m/z* 685.2 [M$^-$ (calcd 685.3), 56], 669.9 [(M − Me)$^-$ (calcd 670.3), 27], 649.1 [(M − Cl)$^-$ (calcd 649.8), 100], 629.8 [(M − C_4H_8)$^-$ (calcd 629.2) 19].

[15] FTIR (KBr, cm^{-1}). (a) **1**: 2967 (s), 2924 (m), 2858 (m), 1460 (m), 1386 (m), 1363 (s), 1216 (m), 1169 (s), 1118 (m), 1025 (m), 784 (m), 598 (m), 412 (m). (b) **2**: 2970 (s), 2927 (m), 2861 (m), 1461 (m), 1384 (m), 1361 (s), 1262 (w), 1214 (m), 1167 (s), 1111 (m), 1021 (m), 955 (w), 785 (m), 597 (m), 410 (m).

[16] The identification of the terminal imidometal group by vibrational spectroscopy is problematic[1] − the M═NR fragment cannot be approximated as a simple diatomic oscillator and coupling between M═N and N−C modes is significant. Thus, there is uncertainty whether "ν(M═N)" occurs between 1100 and 1350 cm^{-1} or between 900 and 1000 cm^{-1}.

[17] EPR (X-band, perpendicular mode) spectrum for **2**: $g_\perp = 1.98$, $g_\| = 1.77$. Experimental conditions: 5 K, microwave frequency 9.578 GHz, microwave power 8.009 mW, modulation amplitude 10 G.

[18] (a) Münck, E. Aspects of ^{57}Fe Mössbauer Spectroscopy. In *Physical Methods in Bioinorganic Chemistry*; Que, L., Ed.; University Science Books: Sausalito, CA, 2000; pp 287−319. (b) Gütlich, P.; Link, R.; Trautwein, A. *Mössbauer Spectroscopy and Transition Metal Chemistry*; Springer-Verlag: Berlin, 1978.

[19] Isomer shifts for (5,6)-coordinate high-spin Fe(III) sites with N/O/X-donors typically range from 0.4 to 0.6 mm/s. The lower values for Fe(III) in **1** and **2** are due to decreased coordination number and the unprecedented imide environment.

[20] If the minority doublet represented a valence-delocalized ensemble of iron sites, the intrinsic isomer shift of the Fe(IV) site would lie well outside the known range of values for Fe(IV).

[21] (a) Cummins, C. C.; Schrock, R. R. *Inorg. Chem.* **1994**, *33*, 395. (b) Kostka, K. L.; Fox, B. G.; Hendrich, M. P.; Collins, T. J.; Rickard, C. E. F.; Wright, L. J.; Münck, E. *J. Am. Chem. Soc.* **1993**, *115*, 6746.