Reaction of a sterically encumbered iron(I) aryl/arene with organoazides: formation of an iron(V) bis(imide)†

Chengbao Ni,[a] James C. Fettinger,[a] Gary J. Long,[b] Marcin Brynda[a] and Philip P. Power*[a]

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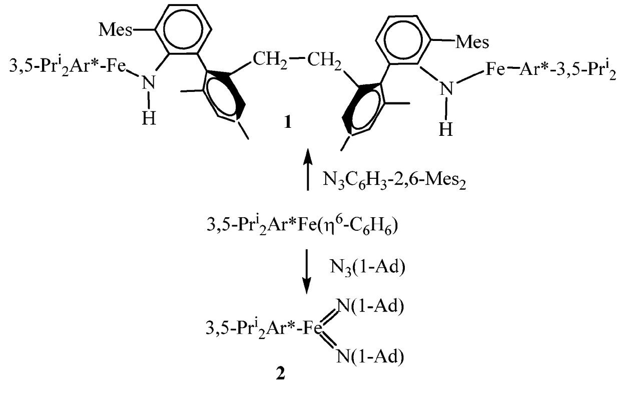
Reaction of 3,5-Pr$^i_2$Ar*Fe(η^6-C$_6$H$_6$)(3,5-Pr$^i_2$Ar* = C$_6$H$_1$-2,6-(C$_6$H$_2$-2,4,6-Pr$^i_3$)$_2$-3,5-Pr$^i_2$) with N$_3$C$_6$H$_3$-2,6-Mes$_2$ (Mes = C$_6$H$_2$-2,4,6-Me$_3$) afforded the dimeric iron(II) amido/aryl complex {CH$_2$C$_6$H$_2$-2(C$_6$H$_3$-2-N(H)FeAr*-3,5-Pr$^i_2$)-3,5-Me$_2$}$_2$ (1) which arises *via* methyl hydrogen abstraction by nitrogen and dimerization of the radical *via* C–C bond formation; in contrast, reaction of 3,5-Pr$^i_2$Ar*Fe(η^6-C$_6$H$_6$) with N$_3$(1-Ad) (1-Ad = 1-adamantanyl) gave the iron(V) bis(imido) complex 3,5-Pr$^i_2$Ar*Fe{N(1-Ad)}$_2$ (2).

The chemistry of late transition metal imido (NR^{2-}) derivatives and their amido (NR$_2$$^-$) counterparts is considerably less developed than that of their earlier metal analogues.[1,2] This is thought to be due to the lack of stabilizing π-interactions by the nitrogen lone pair(s) with metal d-orbitals that are either energetically disparate or already occupied.[3–5] Until recently this lack of development was particularly marked for the later first row elements where stable complexes having terminal imido ligands were unknown. In 2000, Lee and co-workers showed that the cubane cluster Fe$_4$(μ$_3$-NBu^t)$_4$(NBu^t)Cl$_3$, which carries a terminal imido group at one of the four irons, could be isolated from FeCl$_3$/LiNHBu^t reaction mixtures.[6] The terminal NBu^t group featured a short Fe(IV)–N bond length of 1.635(4) Å and an almost linear (Fe–N–C = 178.6(3)°) imido ligand geometry. Hillhouse and Mindiola reported the stable, mononuclear nickel(II) complex (Bu$^t_2$PCH$_2$CH$_2$PBu$^t_2$)NiNC$_6$H$_3$-2,6-Pr$^i_2$ featuring a short (1.702(2) Å) Ni–N bond and a wide (162.8(8)°) Ni–N–C angle indicating a nitrogen lone-pair π-interaction with a nickel d-orbital.[7] These two reports heralded several important stable terminal imido metal complexes, particularly those of Fe(III) and Co(III), which are stabilized by multidentate ligands.[8–12] We now report that the reaction (Scheme 1) of the recently synthesized Fe(I) species 3,5-Pr$^i_2$Ar*Fe(η^6-C$_6$H$_6$) (Ar*-3,5-Pr$^i_2$ = C$_6$H-2,6(C$_6$H$_2$-2,4,6-Pr$^i_3$)$_2$-3,5-Pr$^i_2$)[13] with the organo azides N$_3$C$_6$H$_3$-2,6-Mes$_2$ (Mes = C$_6$H$_2$-2,4,6-Me$_3$)[14] or N$_3$(1-Ad) afforded, the Fe(II) amido derivative 1 and Fe(V) bis(imido) complex 2 with N$_2$ elimination.‡

The products 1 and 2 were initially characterized by X-ray crystallography and elemental analysis. For the reaction with N$_3$C$_6$H$_3$-2,6-Mes$_2$ the intention was to synthesize the stable two-coordinate Fe(III) imido complex 3,5-Pr$^i_2$Ar*-Fe=NC$_6$H$_3$-2,6-Mes$_2$. However 1, which is dimerized through an intermolecular C–C bond involving *ortho* methyl groups from the flanking mesityl rings (Fig. 1) was the only product isolated (46% yield) from the reaction mixture. Such behavior is precedented by that of the unstable species [HC{C(Me)N(C$_6$H$_3$-2,6-Pr$^i_2$)}$_2$FeN(1-Ad)][15] which undergoes intramolecular H abstraction from an *ortho* Pr^i group to afford an iron amide. The formation of 1 also has similarities to the behavior of the unstable Co(III) terminal imido complexes {HB(pyrazolyl-3-R-5-Me)$_3$}CoN(SiMe$_3$) (R = Pr^i or Bu^t) which rearrange by H atom abstraction from a Pr^i or Bu^t group to form, in the case of Pr^i, a product dimerized *via* C–C bonding.[16] Similarly, the first step in the formation of 1 may be H abstraction from an *ortho*-Me group of a flanking mesityl ring by the nitrogen center. The radical thus generated may dimerize intermolecularly rather than interact with the metal which may be sterically less favorable. The iron(II) centers in 1 have a rare two-coordinate, bent geometry (N(1)–Fe(1)–C(1) = 138.91(8) °). There is a relatively long interaction (Fe–C(49) = 2.866(2) Å) with the *ipso*-carbon of one of the flanking mesityl rings. Bending of the metal geometry in two coordinate transition metal species is often observed because of the tendency of the metals, which have low numbers of valence electrons (10 or 14 in the case of 1), to interact with electron rich moieties.[17] The Fe–N and Fe–C bond lengths are similar to those reported for two-coordinate iron amides[18] or aryls.[19] The magnetic properties of 1 were measured from 6 to 320 K in a 0.001 T applied



Scheme 1 Synthesis of compounds **1** and **2**.

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[a] *Department of Chemistry, University of California, One Shields Avenue, Davis, CA 95616, USA. E-mail: pppower@ucdavis.edu*
[b] *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409, USA. E-mail: glong@umr.edu*

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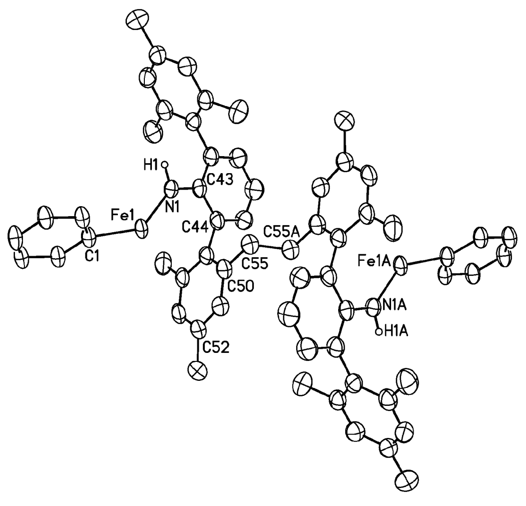

Fig. 1 Thermal ellipsoid (30%) plot of **1**. The C1 ring substituents and H atoms (except N–H) are not shown. Selected bond lengths (Å) and angles (°): Fe1–C1 2.0447(18), Fe–N1 1.9086(17), N1–C43 1.380(2), C50–C55 1.510(3), C55–C55A 1.537(4); C1–Fe1–N1 138.91(8), Fe1–N1–C43 132.26(14), Fe1–N1–H1 120.0(13), C43–N1–H1 107.4(14), C50–C55–C55A 112.2(2)

field. A plot of the inverse molar susceptibility *vs.* temperature revealed an almost linear relationship consistent with the presence of two paramagnetic iron(II) centers with very weak coupling ($J = -1.11\ \text{cm}^{-1}$). The $\mu_{\text{eff}} = 5.29\ \mu_B$/Fe is consistent with a high-spin d^6 electron configuration.

The compound **2** (Fig. 2) is notable not only because it is a stable Fe(V) imide, but it is also a rare example of a well characterized Fe(V) molecule.§[20,21] The iron has a planar three-coordinate geometry with interligand angles that have a maximum deviation of *ca.* 1.4° from the idealized 120° value.

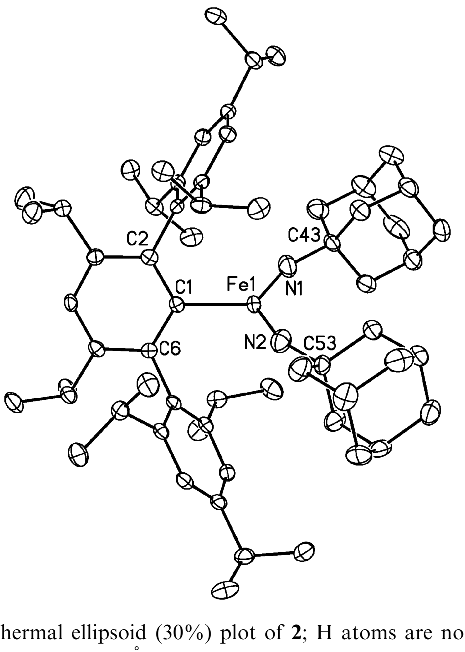

Fig. 2 Thermal ellipsoid (30%) plot of **2**; H atoms are not shown. Selected bond lengths (Å) and angles (°): Fe1–C1 2.013(2), Fe1–N1 1.642(2), Fe1–N2 1.619(2), N1–C43 1.448(3), N2–C53 1.455(3); C1–Fe1–N1 118.61(9), C1–Fe1–N2 119.46(9), N1–Fe1–N2 121.86(10), Fe1–N1–C43 156.6(2), Fe1–N2–C53 160.7(2).

The coordination planes at the imido nitrogens are almost coincident (maximum deviation 7.2°) with the central C(1)Fe(1)N(1)N(2) plane. However, the plane of the central aryl ring of the terphenyl ligand subtends an angle of *ca.* 55° with respect to the metal plane. The Fe–C distance is marginally shorter than that in **1**, whereas the iron nitrogen bond lengths, Fe(1)–N(1) = 1.642(2) and Fe(1)–N(2) = 1.619(2) Å are considerably shorter than the single Fe–N bond (1.909(2) Å) in **1**. The shorter Fe–N bond length is associated with the wider Fe–N–C bending angle. The Fe–N distances may be compared to those in the above mentioned $Fe_4(\mu_3\text{-}NBu^t)_4(NBu^t)Cl_3$ (Fe(IV)–N = 1.635(4) Å),[6] $[\{PhB(CH_2PBu^t_2)_2(3,5\text{-}Me_2\text{-pyrazolyl})\}FeN(1\text{-}Ad)][B\{C_6H_3\text{-}3,5\text{-}CF_3\}_2]_4]$ (Fe(IV)–N = 1.634(4) Å)[9b] $\{PhB(CH_2PPh_2)_3\}FeNC_6H_4\text{-}4\text{-}Me$ (Fe–N = 1.6578(2) Å),[9b] the Fe(III) complexes $\{PhB(CH_2PPr^i_2)_3\}FeN(1\text{-}Ad)$ (Fe–N = 1.638(2) Å),[9c] $\{PhB(CH_2PPh_2)_3\}FeN(1\text{-}Ad)$ (Fe–N = 1.641(2) Å),[9d] and the Fe(II) species $[NBu^n_4][\{PhB(CH_2PPh_2)_3\}FeN(1\text{-}Ad)]$ (Fe(II)–N = 1.651(3) Å).[9e] It is noteworthy that only 0.02 Å separate the longest Fe(II)–N = 1.651(3) Å and shortest Fe(IV)–N (1.634(4) Å) distances. The shortest Fe–N bond length in **2** is 1.618(2) Å and this distance approaches the *ca.* 1.61 Å observed in the Fe(V) nitride $[\textit{trans}\text{-(cyclam-OAc)FeN}]^+$,[22] although it is *ca.* 0.05 Å longer than the 1.57 Å measured by EXAFS in the Fe(VI) nitride species $[(Me_3\text{-cyclam-OAc})FeN]^{2+}$,[23,24] and considerably longer than the *ca.* 1.51–1.55 Å in Fe(IV) nitrides.[25,26] Magnetic studies of **2** afford a μ_{eff} which decreases linearly from 2.74 μ_B at 8 K to 2.43 μ_B at 320 K. A plot of $1/\chi_M$ *vs.* temperature is not strictly linear but the data indicate a low-spin d^3 configuration. The $S = 1/2$ ground state is consistent with that of $[\textit{trans}\text{-(cyclam-OAcFeN}]^+$ which is also low spin.[23]

The electronic structure of **2** was probed using DFT methods (the detailed description of the computational procedures, optimized geometrical parameters and molecular orbitals are presented in the ESI†). Geometry optimizations of the model species $Ar^{\#}Fe(NBu^t)_2$ ($Ar^{\#} = C_6H_3\text{-}2,6\text{-}Ph_2$) yielded bond lengths (Fe–C = 1.974 Å, Fe–N = 1.614 Å) and bond angles in reasonable agreement with the experimental values, except for the N(1)FeN(2) angle, which is wider than it is in the model species (by 12.2 to 18.5°, depending on the level of theory used). Such a discrepancy is not surprising, since no constraints were applied in the gas-phase optimized structures allowing a free rotation around the C_{ipso}–Fe bond, and indicate that the narrower experimental N(1)FeN(2) angle (121.86(10)°) is most probably a consequence of the very large size of the $3,5\text{-}Pr^i_2Ar^*$ substituent. The close-to-planar structure of the $C_{ipso}FeN(1)N(2)$ core is also well reproduced with the unpaired electron almost completely localized in the iron d_{xz} orbital of approximate B_1 symmetry and only very slight spin polarization on the nitrogen atoms.

The isolation of **1** and **2** emphasize the importance of steric effects in determining the type of product obtained. In **1**, the coordination of only one $NC_6H_3\text{-}2,6\text{-}Mes_2$ imide to the iron is allowed because of the large size of the nitrogen substituent. However, use of the less bulky imide group N(1-Ad) allows association of a second imido ligand to afford **2** which has 17 valence electrons (including the N lone pairs). The stability of **2** is probably a consequence of the sterically crowding, monodentate nature of the stabilizing $3,5\text{-}Pr^i_2Ar^*$ ligand which permits coordination of two N(1-Ad) groups without exceeding 18 valence electrons. Investigations of the chemistry of **2** and other high valent late transition metal imides are in hand.

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Notes and references

‡ All manipulations were carried out under strictly anhydrous and anaerobic conditions. (η^6-C_6H_6)FeAr*-3,5-Pr^i_2 and $N_3C_6H_3$-2,6-Mes_2 were prepared by published procedures.[13,14]

1: To a mixture of $N_3C_6H_3$-2,6-Mes_2 (Mes = mesityl, 2,4,6-$Me_3C_6H_2$) (0.153 g, 0.43 mmol) and (η^6-C_6H_6)FeAr*-3,5-Pr^i_2 (0.300 g, 0.43 mmol), *ca.* 30 mL of hexanes was added. The mixture was stirred at *ca.* 25 °C. overnight by which time the solution had become red. The solution was filtered and concentrated to *ca.* 3 mL, which afforded X-ray quality red crystals of **1** after storage for 1 day at 7 °C. Yield 0.188 g (46.1%). The compound melts at 128 °C. UV-Vis (hexane, nm [ε/M^{-1} cm^{-1}]): 450 (1500)

2: A solution of N_3(1-Ad) (0.152 g, 0.86 mmol) in *ca.* 15 mL of hexanes was added dropwise to an orange solution of (η^6-C_6H_6)FeAr*-3,5-Pr^i_2 (0.300 g, 0.43 mmol) in *ca.* 10 mL hexanes at room temperature. The mixture was stirred at room temperature for about 18 h by which time the solution had turned deep brown. The solution was filtered and concentrated to *ca.* 4 mL, which afforded X-ray quality dark brown crystals of **2** after storage for 3 days at 7 °C. Yield 0.107 g (27.0%). The compound melts at 155 °C. Calc. for $C_{62}H_{91}FeN_2$: C, 80.92; H, 9.97; N, 3.04. Found: C, 81.3; H, 9.63; N, 3.11. UV-Vis (hexane, nm [ε/M^{-1} cm^{-1}]): 416 (11 700)

Crystal data for **1** and **2** at 90 K with Mo-Kα (λ = 0.71073 Å) radiation. **1**: monoclinic, space group $I2/a$; a = 25.135(2), b = 28.011(3), c = 25.235(2) Å, β = 118.871(11)°, Z = 4, R_1 = 0.0612 for 12 369 ($I > 2\sigma(I)$) data. **2**: triclinic, space group, $P\bar{1}$, a = 13.9437(14), b = 14.9787(15), c = 15.5738(16) Å, α = 82.3806(15), β = 66.0829(14), γ = 65.8148(14)°, Z = 2, R_1 = 0.0387 for 8050 ($I > 2\sigma(I)$) data.

§ The complex may be viewed as an [3,5-^{i}Pr$_2$Ar*Fe]$^{4+}$ fragment bound to two [N(1-Ad)]$^{2-}$ ions or a neutral Fe (I) moiety 3,5-^{i}Pr$_2$Ar*Fe bound to two neutral N(1-Ad) nitrenes.

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