Dalton Transactions

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Cite this: Dalton Trans., 2013, 42, 5607 Received 22nd February 2013,

Accepted 26th February 2013 DOI: 10.1039/c3dt50518a

www.rsc.org/dalton

The bis(anilido)iminophosphorane complex, abbreviated as $[(^{Mes}N_2N^{Ad})Fe(THF)]$, can react with alkyl azides to yield ligand-based C–H bond amination products suggesting the high reactivity of iron(IV)-imido species supported by the tripodal bis(anilido)-iminophosphorane ligand platform $[^{Mes}N_2N^{Ad}]^{2-}$.

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The potency of protein-bound non-heme iron(w)-oxo species in mediating C-H bond activation¹⁻³ has stimulated interest in the synthesis, structure, and reactivity of their small-molecule analogs of iron(iv)-oxo and -imido complexes bearing versatile multidentate nitrogen-, phosphorus-, and carbon-based ligands.^{4–17} Possibly due to the relatively strong-field nature of these multidentate ligands, the majority of the isolated iron(IV)oxo and -imido complexes display low- or intermediatespin states, and only a handful of them are high-spin.^{12,13,16,18} As theoretical studies have pointed out that the reactivity of iron(IV)-oxo and -imido species could be affected by their spin states,19-21 isolable high-spin iron(IV)-oxo and -imido complexes are highly sought after in the synthetic community. Recently Holland,^{22,23} Chang,^{24,25} and Betley^{26,27} have independently shown that the amido-based ligands, β-diketimi-(nacnac), tris(pyrrolido)amines nates (tpa), and dipyrromethene (dpm) (Fig. 1), can endow the iron centres in $[(nacnac)Fe(NBu^{t})(py-p-Bu^{t})], [(dpm)Fe(NC_{6}H_{4}-p-Bu^{t})Cl], and$ [(tpa)Fe(O)]⁻ with high-spin electronic configurations.

Inspired by their pioneering work, we envisioned that amido anions could serve as weak-field ligands to support high-valent iron species in high-spin states. Subsequently, we initiated a project to study the coordination chemistry of bis-(anilido) ligands with iron. Our previous work has shown that



Iron-mediated C–H bond amination by organic azides

on a tripodal bis(anilido)iminophosphorane platformt



Fig. 1 Amido-based ligands.

the sulfur-bridged bis(anilido) ligands, bis(*N*-mesityl-2-amidophenyl)thioether, can coordinate to an iron(π) center in a facial fashion, but the resultant iron(π) complex is susceptible to degradation as Fe–N and C–S cleavage reactions could occur when it was treated with strong field ligands.²⁸ Consequently, we altered the bridge with a phosphine. Herein, we report the construction of a tripodal bis(anilido)iminophosphorane platform from a bis(anilido)phosphine–iron(π) complex, on which iron-mediated benzylic C–H bond amination by organic azides could occur to produce new bis(anilido)iminophosphorane–iron(π) complexes bearing appended amine side arms (Scheme 1). The achievement of these iron-mediated C–H bond amination reactions emphasizes the high reactivity of iron–imido species supported by the novel dianionic tripodal ligand.

The bis(anilido)phosphine ligand bis(*N*-mesityl-2-amidophenyl)phenylphosphine (H₂(^{Mes}N₂P)) was prepared using modified procedures reported by Fryzuk.²⁹ Treatment of H₂(^{Mes}N₂P) with 0.5 equiv. of [Fe(N(SiMe₃)₂)₂]₂ in THF, after recrystallization in diethyl ether, gave the four-coordinate ferrous complex [(^{Mes}N₂P)Fe(OEt₂)] (1) in 58% yield as red crystals (Scheme 1). Complex 1 has a high-spin electronic configuration ($\mu_{eff} = 4.9(1)\mu_B$ in C₆D₆),^{30,31} and its ¹H NMR spectrum in d₈-THF exhibits 12 sets of paramagnetically shifted signals in the range +51 to -58 ppm, suggesting restricted rotation of the mesityl groups. Similar to the bis(anilido)thioether–iron(π) complex,²⁸ the structure of **1** in the solid state also displays

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[†]Electronic supplementary information (ESI) available: Text giving synthesis details, characterization data, and NMR spectra for the bis(anilido)phosphine ligand, **1–3b**, and CIF files giving X-ray crystallographic data for **1–3b**. CCDC 920392–920395. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50518a



Scheme 1 Preparation of the bis(anilido)iminophosphorane–iron(II) complex 2 and its reactions with organic azides.

distorted trigonal monopyramidal geometry with Fe–N distances of 1.966(2) and 1.945(2) Å, an Fe–O distance of 2.063(2) Å, and an Fe–P distance of 2.367(1) Å (Fig. 2).

In order to construct a more oxidation-tolerant ligand platform, the bis(anilido)phosphine iron(II) complex was treated with 1 equiv. of adamantyl azide in THF, by which the phosphine bridge was oxidized to iminophosphorane to furnish a new four-coordinate iron(II) complex [($^{Mes}N_2N^{Ad}$)Fe(THF)] (2) in 77% yield (Scheme 1). Complex 2 is air- and moisture-sensitive, soluble in THF, and slightly soluble in diethyl ether, benzene and *n*-hexane. In C₆D₆, its ¹H NMR spectrum shows broad peaks in the range 82 to -54 ppm, revealing its paramagnetic nature. The solution magnetic susceptibility of 2 (5.0(2) μ_B in d₈-THF) agrees with an *S* = 2 spin state.

The formation of the tripodal bis(anilido)iminophosphorane ligand platform has been unequivocally established by an X-ray crystallographic study. As shown in Fig. 2, complex 2 displays a distorted tetrahedral geometry in which the tripodal ligand coordinates to the iron center with Fe–N(anilido)



Fig. 2 Molecular structures of **1** (left) and **2** (right), showing 30% probability ellipsoids and the partial atom numbering scheme. Selected distances (Å) and angles (°) for **1**: Fe(1)-N(1) 1.945(2), Fe(1)-N(2) 1.966(2), Fe(1)-P(1) 2.367(1), Fe(1)-O(1) 2.063(2), N(1)-Fe(1)-N(2) 124.4(1), N(1)-Fe(1)-O(1) 117.1(8), N(2)-Fe(1)-O(1) 117.6(1), O(1)-Fe(1)-P(1) 112.6(1); for **2**: Fe(1)-N(1) 2.014(2), Fe(1)-N(2) 1.989(2), Fe(1)-N(3) 2.015(2), Fe(1)-O(1) 2.165(2), P(1)-N(3) 1.609(2), N(1)-Fe(1)-N(2) 124.2(1), N(1)-Fe(1)-N(3) 98.61(8), N(2)-Fe(1)-N(3) 96.33(8), O(1)-Fe(1)-N(3) 143.7(1).

distances of 2.014(2) and 1.989(2) Å, an Fe-N(imide) distance of 2.015(2) Å, and N-Fe-N angles of 124.2(1), 98.61(8), and 96.33(8)°. These Fe-N distances are comparable to those of 1. The P-N separation of 1.609(2) Å is close to those of its congeners in the known complexes with iminophosphorane ligation, such as [(2,6-(Me₃SiNPPh₂)₂C₅H₃N)FeBr₂] (1.55-1.58 Å),³² [(6-Ph-2-(DippNPPh₂)-C₅H₃N)FeCl₂] (1.60 Å),³³ [(Si(C₆H₄PPh₂)₂ Å),³⁴ $(C_6H_4PNHPh_2))Fe(NH_3)]^+$ (1.59 and [Co-(Bu^t₂PCH₂CH₂NCH₂CH₂PBu^t₂NPh)] (1.60 Å).³⁵ The remaining coordination site on the iron center is surrounded by the steric demanding mesityl and adamantyl groups, but can accommodate a THF molecule with long Fe-O separation (2.165(2) Å). The weak Fe-THF interaction apparently comes from steric repulsion between the THF molecule and the adamantyl group that is also reflected by the large O-Fe-N(imide) angle of 143.7(1)°.

Oxidation of phosphines with organic azides to form iminophosphoranes is well-known in the literature.^{33,34} In contrast, our control experiments indicated that the neutral ligand $H_2(^{Mes}N_2P)$ is inert toward adamantyl azide in THF or dichloromethane at ambient temperature. The inertness is probably due to steric shielding of the phosphorus center exerted by the mesitylamine side arms. It also hints that the formation of 2 might involve an iron(iv)-imido intermediate, [($^{Mes}N_2P$)Fe-(NAd)], reminiscent of the cobalt(i)-mediated imidation of phosphine and *N*-heterocyclic carbene ligands with organic azides.^{35–37} In light of this, we further investigated the reactions of 2 with organic azides with the aim to trap iron(iv)imido species with the more oxidation-tolerant tripodal bis-(anilido)iminophosphorane platform.

The reaction of **2** with 1 equiv. of n-C₈H₁₇N₃ in THF formed a brown solution with rapid N₂ gas evolution, from which a paramagnetic compound **3a** was obtained in 58% yield (Scheme 1). Complex **3a** has been characterized by ¹H NMR, IR, magnetic moment measurement ($\mu_{eff} = 5.1(2)\mu_B$ in d₈-THF), as well as a single-crystal X-ray diffraction study (*vide infra*). In contrast, the reaction of **2** with the steric bulky adamantyl azide proceeded incompletely even at 70 °C as followed by ¹H NMR. Recrystallization on the brown solution gave **3b** in 25% yield (Scheme 1). Complex **2** is also reactive with aryl azides, PhN₃ and 2,6-Cl₂-C₆H₃N₃ to produce green solutions, but the attempts to isolate the products by recrystallization were unsuccessful.

Single-crystal X-ray diffraction studies revealed that **3a** and **3b** are bis(anilido)iminophosphorane–iron(π) complexes with anchored amine side arms (Fig. 3). Both molecules feature distorted FeN₄ tetrahedra with the corresponding Fe–N distances close to each other and comparable to those in **2**. The newly formed side arms in these two complexes have Fe–N distances of 2.144(3) and 2.109(3) Å, N–C distances in the range 1.479(5) to 1.499(4) Å, and non-planar geometry for the nitrogen atoms. These structural features are characteristic of ligating amino groups rather than amido anions. In accord with this, characteristic N–H stretching resonances were observed (3255 and 3234 cm⁻¹, respectively) in their infrared resonance spectra.



Fig. 3 Molecular structures of **3a** (left) and **3b** (right), showing 30% probability ellipsoids and the partial atom numbering scheme. For clarity a mesityl group on each structure has been omitted. Selected distances (Å) and angles (°) for **3a**: Fe(1)-N(3) 2.144(3), Fe(1)-N(1) 2.022(3), Fe(1)-N(2) 2.009(3), Fe(1)-N(5) 1.982(2), P(1)-N(1) 1.591(3), N(5)-Fe(1)-N(2) 111.1(1), N(1)-Fe(1)-N(3) 122.5(1); for **3b**: Fe(1)-N(3) 2.109(3), Fe(1)-N(4) 2.044(2), Fe(1)-N(1) 2.062(2), Fe(1)-N(2) 1.962(2), P(1)-N(4) 1.617(2), N(1)-Fe(1)-N(2) 105.6(1), N(3)-Fe(1)-N(4) 145.7(1).

The isolation of 3a and 3b suggests that iron-mediated C(sp³)-H bond amination reactions have occurred on the tripodal ligand platform, which represents a rare example of $C(sp^3)$ -H bond amination facilitated by non-heme iron after Betley's benzylic C-H bond amination reactions from (dipyrromethene)iron-imido complexes,^{26,27} and Che's intramolecular amidation of sulfamate esters catalyzed by iron-pyridyl complexes.³⁸ Besides these, Que,³⁹ Latour,⁴⁰ and Jensen⁴¹ have reported non-heme iron complex-mediated and -catalyzed aromatic substitution reactions with tosyliminoiodane as the nitrene precursor, and Borovik,42 Peters,43 and Holland22,23 have demonstrated the hydrogen-atom-abstraction reactivity by iron-imido species toward C-H bonds but without C-N bond formation. Accordingly, we propose that the formation of 3a and **3b** might involve iron(w)-imido intermediates ($^{Mes}N_2N^{Ad}$) Fe(NR) generated by the interaction of 2 with the alkyl azides. Once formed, the iron(iv)-imido moiety could then perform hydrogen-atom-abstraction followed by a radical-rebound step to produce iron(II) complexes with appended amine side arms. The whole process should be similar to the mechanism of iron(IV)oxo mediated C-H bond hydroxylation reactions.44,45 The success of C-N bond formation in our system implies greater reactivity of iron(IV)-imido species versus that of the iron(III) imides.9,22 However, the proximity of benzylic C-H bonds to the iron center should also play a role as we found that in the presence of an excess of indene, 9,10-dihydroanthracene, or 1,4-cyclohexadiene the reactions of 2 with n-C₈H₁₇N₃ in C₆D₆ still afforded 3a with the retention of all external hydrogendonors although the α -C-H bonds of these substrates are much weaker than benzyl C–Hs.⁴⁶

In conclusion, high-spin iron(π) complexes supported by dianionic tridentate ligands, bis(anilido)phosphine and bis-(anilido)iminophosphorane, have been synthesized and structurally characterized. The reactions of the bis(anilido)iminophosphorane–iron(π) complex with alkyl azides afforded ligand-based C–H bond amination products, demonstrating the high reactivity of iron–imido intermediates supported by the dianionic tripodal platform. Further exploration to approach iron(n)-imido species with modified bis(anilido)iminophosphorane ligands is under way in our laboratory.

This work was supported by the National Natural Science Foundation of China (nos. 20923005, 21121062, and 21222208) and the Science and Technology Commission of Shanghai Municipality (no. 11PJ1412100).

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