

## Hydrogenolysis of $[\text{PhBP}_3]\text{Fe}\equiv\text{N}-p\text{-tolyl}$ : Probing the Reactivity of an Iron Imide with $\text{H}_2$

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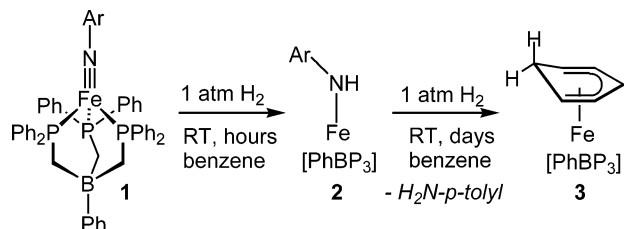
It is generally accepted that low-coordinate iron nitride species are formed and hydrogenated on the surface of solid-state iron catalysts in the Haber–Bosch process.<sup>1</sup> Moreover, it has been postulated that Fe–N (and/or Mo–N) multiple bonds may be formed from  $\text{N}_2$  and further reduced by hydrogen equivalents (i.e.,  $\text{H}^+/\text{e}^-$ ) during turnover in nitrogenase enzymes.<sup>2</sup> Studying the reactivity patterns of hydrogen with molecular iron complexes featuring Fe–N multiple bond linkages is therefore of considerable interest but has been difficult to undertake due to the historical absence of well-defined Fe=NR and/or Fe $\equiv$ N species.<sup>3</sup>

Our group has recently reported the synthesis of a number of mononuclear imides of iron and cobalt (e.g.,  $[\text{PhBP}^R_3]\text{M}(\text{NR})$  where  $[\text{PhBP}^R_3] = [\text{PhB}(\text{CH}_2\text{PPh}_2)_3]^-$  and  $[\text{PhB}(\text{CH}_2\text{P}^i\text{Pr}_2)_3]^-$ ).<sup>4</sup> These trivalent imides are characterized by relatively robust M $\equiv$ NR triple bonds ( $1\sigma + 2\pi$ ) but are nonetheless able to release their imide functionalities, an example being transfer to CO producing isocyanate.<sup>4a,b</sup> This group transfer reactivity prompted us to survey their respective reactivities toward hydrogen.

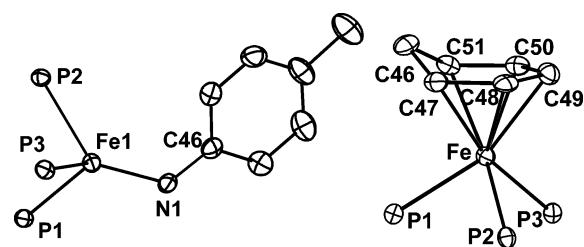
The low-spin cobalt complex  $[\text{PhBP}_3]\text{Co}\equiv\text{N}-p\text{-tolyl}$ <sup>4b</sup> is stable to hydrogen pressure (1–3 atm) at modest temperatures ( $\leq 70^\circ\text{C}$ ). By contrast, low-spin  $[\text{PhBP}_3]\text{Fe}\equiv\text{N}-p\text{-tolyl}$  (**1**)<sup>4a</sup> gives rise to a fascinating reaction profile upon exposure to 1 atm of  $\text{H}_2$  at room temperature. Both partial and complete hydrogenolysis of the Fe $\equiv$ NR linkage is observed. Whereas  $\text{H}_2$ -promoted reduction of an imide to its corresponding amide was first described by Wolczanski,<sup>5</sup> reductive scission of a metal imide by hydrogen to release amine has not to our knowledge been previously reported.<sup>6</sup>

Fingerprint resonances for imide **1** are conveniently monitored by  $^1\text{H}$  NMR spectroscopy despite its paramagnetic  $S = 1/2$  ground state.<sup>4a</sup> When a sealable NMR tube is charged with forest green **1** in  $\text{C}_6\text{D}_6$  under an atmosphere of  $\text{H}_2$ , its resonances fully decay within a period of 3 h at room temperature. During this time, the reaction solution remains homogeneous and the color changes to an intense red/purple. The major reaction product at this stage is the paramagnetic anilido complex  $[\text{PhBP}_3]\text{Fe}(\text{N}(\text{H})-p\text{-tolyl})$  (**2**) (Scheme 1).<sup>7</sup> Assignment of **2** from its paramagnetically shifted

### Scheme 1



$^1\text{H}$  NMR resonances is aided by comparison to a spectrum of an independently generated sample of **2** prepared by the reaction between  $[\text{Li}][\text{N}(\text{H})-p\text{-tolyl}]$  and  $[\text{PhBP}_3]\text{FeCl}$ .<sup>4a</sup>



**Figure 1.** 50% displacement ellipsoid representations of  $[\text{PhBP}_3]\text{Fe}(\text{N}(\text{H})-p\text{-tolyl})$  (**2**), left, and  $[\text{PhBP}_3]\text{Fe}(\eta^5\text{-cyclohexadienyl})$  (**3**), right. For clarity, only the  $\text{P}_3\text{FeX}$  core is shown. Selected bond lengths (Å) and angles (deg) for **2**: Fe1–N1, 1.913(2); Fe1–P1, 2.392(1); Fe1–P2, 2.452(1); Fe1–P3, 2.427(1); Fe1–N1–C46, 127.4(2). For **3**: Fe–P1, 2.273(1); Fe–P2, 2.270(1); Fe–P3, 2.265(1); C46–C47, 1.477(4); C47–C48, 1.394(4); C48–C49, 1.415(4); C49–C50, 1.410(4); C50–C51, 1.385(4); C51–C46, 1.493(4).

Anilide **2** features a weak N–H vibration at  $3326\text{ cm}^{-1}$  (Nujol), a temperature-independent magnetic moment of  $4.92\ \mu_{\text{B}}$  (SQUID,  $S = 2$ ), and relatively intense charge-transfer bands ( $450\text{ nm}$ ,  $3400\text{ M}^{-1}\text{ cm}^{-1}$ ;  $547\text{ nm}$ ,  $3000\text{ M}^{-1}\text{ cm}^{-1}$ ). The solid-state structure of **2** (Figure 1) is related to that of **1** by the addition of a single H-atom at nitrogen. Although both **1** and **2** are four-coordinate and pseudotetrahedral, **2** features an Fe–N bond distance (1.913(2) Å) and an Fe–N–C bond angle ( $127.4(2)^\circ$ ) very different from **1** (Fe–N = 1.6578(2) Å; Fe–N–C =  $169.96(2)^\circ$ ).<sup>4a</sup> Of additional note are the Fe–P bond distances, which are appreciably expanded in the structure of **2** (Fe– $\text{P}_{\text{avg}}$  for **1** = 2.24 Å; Fe– $\text{P}_{\text{avg}}$  for **2** = 2.42 Å). These structural differences reflect the low- versus high-spin configurations of **1** and **2**, respectively, in addition to the diminished Fe–N  $\pi$ -bond character of **2** by comparison to **1**.

Prolonged monitoring of the hydrogenation of **1** in  $\text{C}_6\text{D}_6$  over a period of days establishes a new diamagnetic product ( $^31\text{P}$  NMR: 52 ppm (s)) and the release of  $\text{H}_2\text{N}-p\text{-tolyl}$  (40% after 3 days). In a preparative-scale reaction, imide **1** was exposed to an atmosphere of  $\text{H}_2$  in benzene for 3 days in a sealed reaction flask. Extraction of the crude solids into diethyl ether left behind the diamagnetic species as a bright orange powder in 25% yield. XRD analysis of a single crystal confirmed it to be the cyclohexadienyl complex  $[\text{PhBP}_3]\text{Fe}(\eta^5\text{-cyclohexadienyl})$  (**3**) (Figure 1). Complex **2** was then isolated in 60% yield from the ethereal extract by crystallization. The combined isolated yield of **2** and **3** accounted for 85% of the total iron content of the reaction. Similar yields were provided by in situ monitoring and integration of  $^1\text{H}$  NMR spectra of sealed NMR tube experiments after 3 days. Ill-defined paramagnetic resonances indicative of at least one side product account for the remaining iron material ( $\sim 15\%$ ) in these sealed-tube experiments. We suspect that the side-product(s) arise from the kinetically competitive degradation of **2** during the course of the reaction. As a control experiment, it is noted that the storage of **2** in benzene under  $\text{N}_2$  leads to some degradation after 3 days but does not produce **3**.<sup>8</sup>

To ensure that the H-atoms being delivered to both benzene and the imide functionality arise from H<sub>2</sub>, the hydrogenation of **1** by D<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> was examined. The consumption of **1** proceeds in this case much more slowly ( $k_{\text{rel}} = k(\text{H}_2)/k(\text{D}_2) = 5.6$ ), and the product yields after 3 days are consequently much lower. The overall reaction is moreover less clean than for the case of H<sub>2</sub> due to the increased role of kinetically competitive side reactions given the longer reaction time. Nonetheless, the expected products [PhBP<sub>3</sub>]-Fe(N(D)-*p*-tolyl) (**2b**), [PhBP<sub>3</sub>]Fe( $\eta^5$ -cyclohexadienyl-*d*<sub>7</sub>) (**3b**), and D<sub>2</sub>N-*p*-tolyl can be identified. Compound **2b** is identified on the basis of its <sup>1</sup>H NMR resonances and the isotopically shifted N–D stretch in its IR spectrum (Nujol:  $\nu_{\text{ND}} = 2462 \text{ cm}^{-1}$  (w)). Diamagnetic **3b** is assigned from its <sup>31</sup>P and <sup>1</sup>H NMR spectra. In particular, no cyclohexadienyl ring resonances are present in its <sup>1</sup>H NMR spectrum due to complete deuteration. Compound **3b** also exhibits the expected ES-MS molecular ion peak at 828 *m/z*. The organic byproduct D<sub>2</sub>N-*p*-tolyl is identified by GC-MS as the only amine-containing product of the reaction.

The reduction of **1** to anilide **2** and then to **3** appears to proceed in a stepwise fashion (Scheme 1). The detailed mechanism by which these steps occur is clearly of interest but somewhat difficult to unravel due to the paramagnetic nature of **1** and **2**, in addition to the presence of at least one paramagnetic side-product(s) that is formed during the course of the reaction. A reasonable mechanistic outline to suggest is as follows: The first step ( $\mathbf{1} + 1/2 \text{ H}_2 \rightarrow \mathbf{2}$ ) involves the addition of H<sub>2</sub> to **1** to generate an unobservable species “[PhBP<sub>3</sub>]Fe<sup>III</sup>(H)(NHAr)”, which, if formed, must bimolecularly release H<sub>2</sub> to provide observable **2**. A second addition of H<sub>2</sub> would occur at **2** to generate an unobservable “Fe<sup>II</sup>-H” source (with loss of H<sub>2</sub>N-*p*-tolyl) that adds to benzene via insertion.<sup>9</sup> Evidence consistent with a reactive “Fe<sup>II</sup>-H” intermediate comes from the following set of observations: First, the incubation of **2** under an atmosphere of H<sub>2</sub> at 25 °C in C<sub>6</sub>D<sub>6</sub> slowly generates **3** (30% after 3 days) with concomitant evolution of H<sub>2</sub>N-*p*-tolyl (50% after 3 days). Second, the addition of KBHET<sub>3</sub> to a benzene solution of [PhBP<sub>3</sub>]Fe<sup>II</sup>Cl generates **3** in high yield (77% isolated). Moreover, when this latter reaction is carried out in THF rather than benzene a new and diamagnetic species is generated that can be assigned as the complex [PhBP<sub>3</sub>]Fe<sup>II</sup>(HBET<sub>3</sub>) (**4**) on the basis of its solution IR and NMR data in THF ( $\nu_{\text{BH}} = 2448 \text{ cm}^{-1}$ ; <sup>31</sup>P NMR 55 ppm (br s); <sup>11</sup>B NMR  $\delta$  25.5 ppm (br s, HBET<sub>3</sub>), –12.8 ppm (s, PhB(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub><sup>–</sup>). Most importantly, complex **4** serves as a “[PhBP<sub>3</sub>]Fe<sup>II</sup>-H” equivalent and is instantly converted to **3** with loss of BET<sub>3</sub> upon addition of benzene to a THF solution. We also note that the hydrogenation of **1** in CD<sub>2</sub>Cl<sub>2</sub> generates H<sub>2</sub>N-*p*-tolyl and the chloride complex [PhBP<sub>3</sub>]Fe<sup>II</sup>Cl. Reactive metal hydrides are known to exchange with halocarbons,<sup>10</sup> and it is reasonable to expect that a “[PhBP<sub>3</sub>]Fe<sup>II</sup>-H” intermediate might behave similarly.

Whereas iron cyclohexadienyl complexes structurally related to **3** are known,<sup>11–13</sup> their formation from the insertion of benzene into a reactive Fe–H bond is, to our knowledge, unprecedented. A curious reactivity comparison to note in this context concerns Holland's four-coordinate iron hydride dimer {LFe<sup>II</sup>H}<sub>2</sub>, in which L represents a bulky  $\beta$ -diketiminate ligand.<sup>7</sup> This low-coordinate hydride system is isolable and, while reactive toward certain

unsaturated substrates (e.g., azobenzene), appears to be stable in aromatic solvents such as benzene.

In summary, the low-spin iron(III) imide **1** undergoes partial and then complete hydrogenation under ambient conditions to release aniline in what appears to be a well-defined, stepwise process. We can directly observe the intermediate Fe(II) anilido species, **2**, and have provided evidence for the subsequent intermediacy of a reactive Fe<sup>II</sup>-H species that is trapped by benzene solvent to provide **3**. Interesting mechanistic issues remain to be resolved and are currently under investigation.

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**Supporting Information Available:** Detailed experimental procedures, characterization data, and crystallographic information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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