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## High-Activity Iron Catalysts for the Hydrogenation of Hindered, Unfunctionalized Alkenes

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### Abstract

The activity of aryl-substituted bis(imino)pyridine and bis(arylimidazol-2-ylidene)pyridine iron dinitrogen complexes has been evaluated in a series of catalytic olefin hydrogenation reactions. In general, more electron donating chelates with smaller 2,6-aryl substituents produce more active iron hydrogenation catalysts. Establishment of this structure-activity relationship has produced base metal catalysts that exhibit high turnover frequencies for the hydrogenation of unfunctionalized, tri- and tetrasubstituted alkenes, one of the most challenging substrate classes for homogenous hydrogenation catalysts.

### Keywords

Iron; hydrogenation; catalysis; N-heterocyclic carbene

The hydrogenation of alkenes with soluble transition metal complexes, particularly in asymmetric form, has emerged as one of the most powerful and widely applied methods in homogeneous catalysis.<sup>1,2,3,4</sup> Precious metal compounds, principally those based on rhodium, iridium and ruthenium, have dominated the catalyst landscape.<sup>5,6,7,8,9</sup> The high cost, low terrestrial abundance, and environmental impact associated with these rare elements inspires the search for more catalysts with less toxic, more cost effective, earth abundant metals.<sup>10,11,12,13</sup>

While olefin hydrogenation in the presence of catalytic quantities of Fe(CO)<sub>5</sub> and related derivatives has been known for some time,<sup>14,15</sup> examples of iron catalysts that operate under mild conditions with high activity and a broad substrate scope are rare.<sup>16,17</sup> The aryl-substituted bis(imino)pyridine iron dinitrogen compound, (iPrPDI)Fe(N<sub>2</sub>)<sub>2</sub> (iPrPDI = 2,6-(2,6-<sup>i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-N=CMe)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N),<sup>18,19,20</sup> was reported in 2004 and exhibited high turnover frequencies for the hydrogenation of unfunctionalized olefins at low iron loadings (as low as 0.3 mol%) and ambient temperature. Since this initial discovery, our group has been interested in the functional group tolerance of this catalyst class<sup>21</sup> as well as improving

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Supporting Information. Experimental procedures, including full characterization of all new compounds and crystallographic data for (Me<sup>c</sup>CNC)Fe(N<sub>2</sub>)<sub>2</sub> and (Me<sup>s</sup>CNC)Fe(N<sub>2</sub>)<sub>2</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

overall performance through rational ligand manipulation. Bis(imino)pyridine ligands are ideally suited for exploration of structure-reactivity relationships as numerous variants are accessible through relatively straightforward synthetic routes.<sup>22</sup>

Various positions are available on the bis(imino)pyridine for substitution. Our laboratory has previously reported that reduction of the size of the 2,6-aryl substituents from isopropyl to ethyl or methyl resulted in dimeric iron dinitrogen complexes,  $[(^R\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$ <sup>10</sup> ( $^R\text{PDI} = 2,6\text{-}(2,6\text{-R}_2\text{-C}_6\text{H}_3\text{-N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$ ; R = Me, Et), with dramatically improved activity for alkene hydrogenation<sup>23</sup> and hydrosilylation.<sup>24</sup> Substitution of the imine position has also been explored. Introduction of phenyl substituents, as in the case of  $(^i\text{PrBPDI})\text{Fe}(\text{N}_2)_2$  ( $^i\text{PrBPDI} = 2,6\text{-}(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3\text{-N}=\text{CPh})_2\text{C}_5\text{H}_3\text{N}$ ), resulted in high turnover frequency for 1-hexene hydrogenation but overall reduced catalyst lifetime due to competing formation of intramolecular  $\eta^6$ -arene complexes.<sup>25</sup> Replacement of the ketamine chelates with aldimine variants complicates isolation of iron dinitrogen compounds, however evaluation of iron butadiene pre-catalysts demonstrated reduced turnover frequencies and lifetimes as compared to ketamine-based iron complexes.<sup>26</sup>

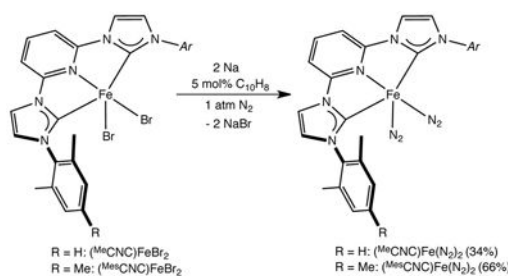
The established redox non-innocence and activity<sup>27,28</sup> of bis(imino)pyridine ligands in reduced iron complexes,<sup>29,30</sup> suggested that in-plane modifications of the chelate, particularly in the *para*-pyridine position, may have a profound impact on catalytic performance. Our laboratory has recently reported the synthesis of a series of 4-substituted bis(imino)pyridine iron dinitrogen complexes,  $(4\text{-X-}^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$  (X = <sup>t</sup>Bu, Bn, NMe<sub>2</sub>), and evaluation of the electronic influences of each group.<sup>31</sup> While no gross change in electronic structure of the iron compound was observed, more electron rich iron centers arose from introduction of alkyl or [NMe<sub>2</sub>] substituents. Here we describe evaluation of the performance of these compounds in the catalytic hydrogenation of alkenes, begin to establish structure-reactivity relationships and report that replacement of the imine fragments with *N*-heterocyclic carbenes results in highly active iron pre-catalysts for the hydrogenation of sterically hindered, unfunctionalized alkenes.

Our group has previously used the hydrogenation of ethyl 3,3-dimethylacrylate to benchmark the catalytic activity of iron catalysts.<sup>21,23</sup> Under standard conditions (5 mol % [Fe], 0.915 M substrate, 23 °C, 4 atm H<sub>2</sub>)<sup>23</sup> with  $(^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$ , only 65% conversion to alkane was observed. Completion of the catalytic reaction was impeded by competitive deactivation of the iron compound by C-O bond cleavage of the ester.<sup>32</sup> By contrast, catalysis with  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$  resulted in complete conversion to alkane in under 1 hour, highlighting the dramatic impact of aryl group substituent effects.<sup>23</sup> Introduction of a [NMe<sub>2</sub>]-substituent into the 4-position of the chelate while maintaining the steric environment imparted by the 2,6-diisopropyl groups dramatically increases the hydrogenation activity of the iron compound. Complete conversion to alkane was observed with  $(4\text{-NMe}_2\text{-}^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$  in 7 hours (Table 1).

The improved hydrogenation activity observed with  $(4\text{-NMe}_2\text{-}^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$  prompted the synthesis of more electron rich iron dinitrogen compounds. Danopoulos and coworkers have reported a related iron dinitrogen complex,  $(^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$  ( $^i\text{PrCNC} = 2,6\text{-}(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3\text{-imidazol-2-ylidene})_2\text{-C}_5\text{H}_3\text{N}$ ), where the imine groups of the bis(imino)pyridine have been

replaced by *N*-heterocyclic carbenes.<sup>33</sup> As evidenced by the toluene solution infrared stretching frequencies of the N<sub>2</sub> ligands (2104, 2037 cm<sup>-1</sup>), (iPrCNC)Fe(N<sub>2</sub>)<sub>2</sub> is more electron rich than (4-NMe<sub>2</sub>-iPrPDI)Fe(N<sub>2</sub>)<sub>2</sub> (2117, 2055 cm<sup>-1</sup>), raising the possibility of improved hydrogenation activity. Indeed, (iPrCNC)Fe(N<sub>2</sub>)<sub>2</sub> promotes the complete (>95% conversion) hydrogenation of ethyl 3,3-dimethylacrylate over the course of 1 hour at 23 °C, a significant improvement over two of the bis(imino)pyridine iron catalysts.

The remarkable catalytic hydrogenation activity of (iPrCNC)Fe(N<sub>2</sub>)<sub>2</sub> prompted synthesis of bis(arylimidazol-2-ylidene)pyridine iron dinitrogen complexes with smaller 2,6-aryl substituents. Using standard synthetic methods to access compounds of this type, reduction of (MeCNC)FeBr<sub>2</sub> (MeCNC = 2,6-(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-imidazol-2-ylidene)<sub>2</sub>-C<sub>5</sub>H<sub>3</sub>N) or (MesCNC)FeBr<sub>2</sub> (MesCNC = 2,6-(2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>-imidazol-2-ylidene)<sub>2</sub>-C<sub>5</sub>H<sub>3</sub>N) with 2 equiv of sodium metal in the presence of 5 mol% of naphthalene under an N<sub>2</sub> atmosphere furnished the desired iron bis(dinitrogen) complexes, (MeCNC)Fe(N<sub>2</sub>)<sub>2</sub> and (MesCNC)Fe(N<sub>2</sub>)<sub>2</sub> as dark brown, diamagnetic solids in 34 and 66% yields, respectively (eq 1). Isolation and characterization of the 2,6-dimethyl substituted compounds proved challenging due to the limited solubility of these species in hydrocarbon and ethereal solvents and accounts for the higher isolated yield for (MesCNC)Fe(N<sub>2</sub>)<sub>2</sub>.



(1)

Both new iron dinitrogen complexes were characterized by single crystal X-ray diffraction (Figure 1). The dimethyl-substituted compound, [(MeCNC)Fe(N<sub>2</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>), is dimeric in the crystal selected for the diffraction experiment. However, infrared data indicated that both monomers and dimers are present in the solid state (KBr). In contrast, the crystal structure of (MesCNC)Fe(N<sub>2</sub>)<sub>2</sub> established a monomeric iron compound in the solid state. Solution infrared spectroscopy on both compounds revealed that only monomers are present in toluene solution at 23 °C (see SI).

Initial assays of the catalytic hydrogenation activity of (MeCNC)Fe(N<sub>2</sub>)<sub>2</sub> and (MesCNC)Fe(N<sub>2</sub>)<sub>2</sub> were conducted with ethyl 3,3-dimethylacrylate under standard conditions. In both cases only 35% conversion to the desired alkane was observed after one hour at 23 °C. To probe whether catalytic deactivation was resulting with the less sterically protected iron dinitrogen compounds, the hydrogenation of ethyl 3,3-dimethylacrylate was repeated in the presence of *trans*-methylstilbene, a substrate that was known to undergo complete conversion with these compounds (*vide infra*). The competitive hydrogenation was performed for one hour at 23 °C with (MesCNC)Fe(N<sub>2</sub>)<sub>2</sub>; only 24% and 6.5% conversion of

3,3-dimethylacrylate and the stilbene were observed, suggesting that the carboxylated alkene is an inhibitor for hydrogenation activity with the more open iron compounds.

To further explore the possibility of inhibition, addition of ethyl 3,3-dimethylacrylate to  $(^R\text{CNC})\text{Fe}(\text{N}_2)_2$  compounds was studied in the absence of  $\text{H}_2$ . No change in the  $^1\text{H}$  NMR spectrum was observed upon addition of one equivalent of ethyl 3,3-dimethylacrylate to  $(^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$ , indicating no coordination of the substrate to this iron compound. Performing the analogous experiment with  $(^{\text{Mes}}\text{CNC})\text{Fe}(\text{N}_2)_2$  resulted in coordination of the ester likely through the carbonyl oxygen and possibly the  $\text{C}=\text{C}$  bond. Addition of 4 atm of  $\text{H}_2$  to a benzene- $d_6$  solution of the compound resulted in gradual liberation of the alkane, demonstrating that substrate coordination was reversible and not a source of deactivation by  $\text{C}-\text{O}$  bond cleavage.<sup>32</sup> Thus, the steric protection imparted by the 2,6-isopropyl groups serves to generate a more active hydrogenation catalyst by preventing formation of inactive O-bound iron ester complexes.

The scope and performance of both the bis(imino)pyridine and bis(arylimidazol-2-ylidene)pyridine iron dinitrogen complexes have been studied for unactivated tri- and tetrasubstituted alkenes. This class of substrate remains a significant challenge for precious metal catalysts.<sup>34</sup> Buchwald and coworkers have reported titanocene<sup>35</sup> and zirconocene<sup>36</sup> catalysts for the asymmetric hydrogenation of these substrates although the complexity of the pre-catalyst synthesis and the high hydrogen pressures are limitations. The previously reported bis(imino)pyridine iron dinitrogen compounds,  $(^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$  and  $[(^{\text{Me}}\text{PDI})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$  exhibit minimal activity for these types of hydrogenations. For example, the hydrogenation of *trans*-methyl stilbene proceeded with only 12% ( $\text{R} = ^i\text{Pr}$ ) and 4% ( $\text{R} = \text{Me}$ ) conversion after 24 hours. Similar results were obtained for the hydrogenation of 2-methyl-2-butene where 32% ( $\text{R} = ^i\text{Pr}$ ) and 15% ( $\text{R} = \text{Me}$ ) conversion was observed. The higher conversions observed with  $(^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$  are believed to be a result of longer catalyst lifetimes during slower substrate hydrogenations. Essentially no activity was observed for the hydrogenations of methylcyclohexene, 2,3-dimethyl-1*H*-indene or 2,3-dimethyl-2-butene with these two bis(imino)pyridine iron compounds.

Use of the more electron rich bis(imino)pyridine iron dinitrogen complex,  $(4\text{-NMe}_2\text{-}^i\text{PrPDI})\text{Fe}(\text{N}_2)_2$ , overcomes some of these limitations. The hydrogenation of *trans*-methyl stilbene proceeded to 76% conversion in 24 hours with quantitative (> 95%) formation of alkane occurring after 60 hours at 23 °C. Unfortunately, little activity was observed for the hydrogenation of methylcyclohexene or tetrasubstituted alkenes.

The bis(arylimidazol-2-ylidene)pyridine iron dinitrogen complexes are also effective for the hydrogenation of unfunctionalized, hindered alkenes. Complete hydrogenation of *trans*-methyl stilbene was accomplished in 24 hours with  $(^i\text{PrCNC})\text{Fe}(\text{N}_2)_2$ . Introduction of smaller aryl rings resulted in even more active hydrogenation catalysts as complete hydrogenation of *trans*-methyl stilbene was observed in less than one hour with both  $(^{\text{Me}}\text{CNC})\text{Fe}(\text{N}_2)_2$  and  $(^{\text{Mes}}\text{-CNC})\text{Fe}(\text{N}_2)_2$ . The improved activity observed with the less hindered compounds with unfunctionalized olefins also supports the carbonyl functional group inhibiting the hydrogenation activity of ethyl 3,3-dimethylacrylate.

The success in *trans*-methyl stilbene hydrogenation prompted further study of substrate scope with the bis(arylimidazol-2-ylidene)pyridine iron compounds. The more hindered compound, (<sup>i</sup>PrCNC)Fe(N<sub>2</sub>)<sub>2</sub>, is an effective pre-catalyst for the hydrogenation of 2-methyl-2-butene reaching quantitative conversion in 15 hours. Only modest activity was observed for the hydrogenation of methylcyclohexene and essentially no turnover was obtained for the hydrogenation 2,3-dimethyl-1*H*-indene or 2,3-dimethyl-2-butene, identifying both endocyclic tri- and tetrasubstituted alkenes as limitations for this specific catalyst.

To improve substrate scope and activity, hydrogenations with the more open iron dinitrogen compounds, (<sup>Me</sup>CNC)Fe(N<sub>2</sub>)<sub>2</sub> and (<sup>Mes</sup>CNC)Fe(N<sub>2</sub>)<sub>2</sub>, were studied. With (<sup>Me</sup>CNC)Fe(N<sub>2</sub>)<sub>2</sub>, the hydrogenation of methylcyclohexene was complete in 12 hours; with (<sup>Mes</sup>CNC)Fe(N<sub>2</sub>)<sub>2</sub> a significantly improved turnover frequency was observed with complete conversion after only 1 hour. The difference in hydrogenation activity between the two compounds is attributed to the improved solubility of (<sup>Mes</sup>CNC)Fe(N<sub>2</sub>)<sub>2</sub> in hydrocarbon solvents. For hydrogenations with (<sup>Me</sup>CNC)-Fe(N<sub>2</sub>)<sub>2</sub>, the metal complex was not completely dissolved under standard conditions<sup>25</sup> thereby reducing the concentration of the active iron compound. For less challenging trisubstituted alkenes such as 2-methyl-2-butene this complication is less evident as complete conversion to alkane was observed in one hour with both iron dinitrogen compounds.

The successful hydrogenation of unfunctionalized trisubstituted alkenes prompted exploration of even more challenging tetrasubstituted olefins.<sup>36</sup> While neither (<sup>Me</sup>CNC)Fe(N<sub>2</sub>)<sub>2</sub> or (<sup>Mes</sup>CNC)Fe(N<sub>2</sub>)<sub>2</sub> was active for the hydrogenation of 2,3-dimethyl-2-butene at 23 °C, 68 and 60 % conversion was observed with 2,3-dimethyl-1*H*-indene after 48 hours. In both cases, a 3:1 ratio of *cis* : *trans* diastereomers of the alkane was observed.

To gain insight into the origin of the *trans* isomer, a deuterium labeling experiment was conducted (Scheme 1). Exposure of a benzene solution of 2,3-dimethyl-1*H*-indene to D<sub>2</sub> gas in the presence of 5 mol% of (<sup>Me</sup>CNC)Fe(N<sub>2</sub>)<sub>2</sub> resulted in catalytic deuteration. The fate of the deuterium atoms was determined using a combination of <sup>1</sup>H, <sup>2</sup>H and <sup>13</sup>C NMR spectroscopies. No isotopic label was detected in the 3-position as would be expected for the direct hydrogenation (or deuteration) of the tetrasubstituted olefin. Deuterium was instead observed in both the 1- and 2-positions of the alkane product suggesting olefin isomerization before hydrogenation. In addition, analysis of the substrate during turnover revealed deuterium incorporation into the 1-position, consistent with C-H catalytic activation that is competitive with hydrogenation.

In summary, we have discovered that more electron rich iron dinitrogen complexes are effective for the catalytic hydrogenation of unactivated alkenes. The origin of these profound electronic influences as well as elucidation of mechanistic pathways, including the role of redox-activity, is currently under investigation. These results provide important insight for catalyst design efforts for evolution into asymmetric variants.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

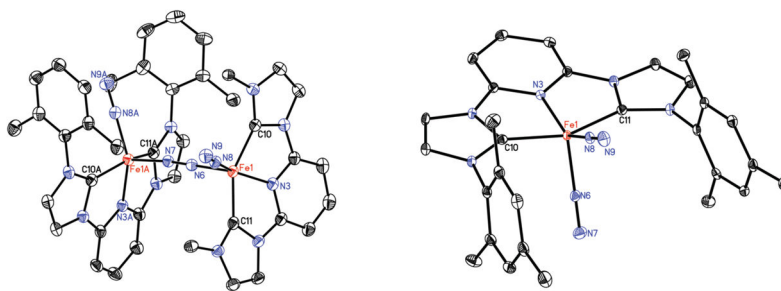
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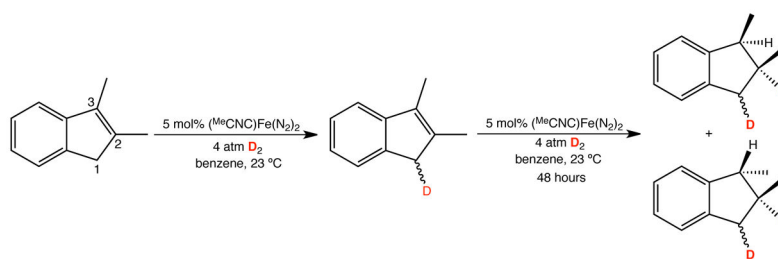
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**Figure 1.** Solid state molecular structures of  $[(^{\text{Me}}\text{CNC})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$  and  $(^{\text{Mes}}\text{CNC})\text{Fe}(\text{N}_2)_2$  at 30% probability ellipsoids. Hydrogen atoms and aryl groups on Fe1 of  $[(^{\text{Me}}\text{CNC})\text{Fe}(\text{N}_2)]_2(\mu\text{-N}_2)$  omitted for clarity.

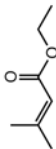
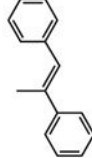
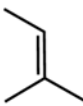
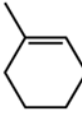
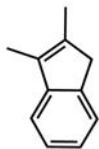





**Scheme 1.**  
Catalytic deuteration of 2,3-dimethyl-1*H*-indene with 5 mol% of  $(\text{MeCNC})\text{Fe}(\text{N}_2)_2$  in benzene and 4 atm of  $\text{D}_2$ .

Table 1

Catalytic hydrogenation of unfunctionalized alkenes with bis(imino)pyridine and bis(arylimidazol-2-ylidene)pyridine iron dinitrogen complexes.

Entry	Substrates	$(\text{IPr})\text{PDDlFe}(\text{N}_2)_2$	$[\text{C}^{\text{Me}}\text{PDDl}]_2\text{Fe}(\text{N}_2)_2$ ( $\mu\text{-N}_2$ )	(4-NMe <sub>2</sub> -IPr)PDDlFe(N <sub>2</sub> ) <sub>2</sub>	(IPr <sup>Ar</sup> CNC)Fe(N <sub>2</sub> ) <sub>2</sub>	( <sup>Me</sup> CNC)Fe(N <sub>2</sub> ) <sub>2</sub>	( <sup>Me</sup> CNC)Fe(N <sub>2</sub> ) <sub>2</sub>
1 <sup>b</sup>		65 (24 h)	> 95 (1 h)	> 95 (7 h)	> 95 (1 h)	35 (1 h) <sup>e</sup>	35 (1 h)
2 <sup>b</sup>		12 (24 h)	4 (24 h)	76 <sup>d</sup> (24 h)	89 (12 h)	> 95 (1 h)	> 95 (1 h)
3 <sup>c</sup>		32 (24 h)	15 (24 h)	15 (24 h)	> 95 (15 h)	> 95 (1 h)	> 95 (1 h)
4 <sup>b</sup>		0 (24 h)	2 (24 h)	3 (24 h)	20 (24 h)	> 95 (12 h)	> 95 (1 h)
5 <sup>b</sup>		3 (48 h)	< 1 (48 h)	3 (48 h)	4 (48 h)	68 (48 h) 3:1 <i>cis</i> : <i>trans</i>	60 (48 h) 3:1 <i>cis</i> : <i>trans</i>
6 <sup>c</sup>		0 (24 h)	0 (24 h)	0 (24 h) <sup>f</sup>	0 (24 h)	0 (24 h)	0 (24 h)

<sup>a</sup> All catalytic reactions carried out with 5 mol% [Fe] (0.032 mmol on basis of Fe), 0.633 mmol substrate, 0.915 M substrate, 4 atm H<sub>2</sub>, 23 °C.

<sup>b</sup> Conversions were determined by GC.

<sup>c</sup> Benzene-*d*<sub>6</sub> used as solvent, conversions were determined by <sup>1</sup>H NMR.

<sup>d</sup> Quantitative conversion (> 95%) observed after 60 hours.

<sup>e</sup> 45% conversion observed after 24 hours.

$f_{25\%}$  conversion observed after 24 hours at 45 °C; significant decomposition of the iron compound was also observed.

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