

# General and Selective Iron-Catalyzed Transfer Hydrogenation of Nitroarenes without Base

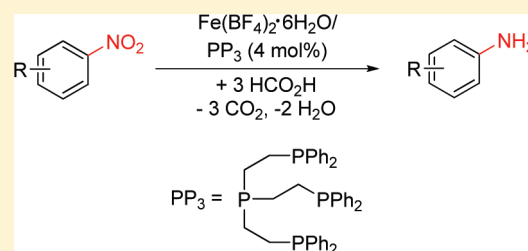
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 Supporting Information

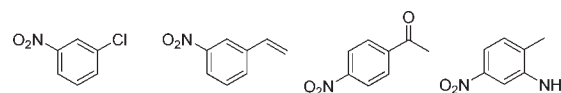
**ABSTRACT:** The first well-defined iron-based catalyst system for the reduction of nitroarenes to anilines has been developed applying formic acid as reducing agent. A broad range of substrates including other reducible functional groups were converted to the corresponding anilines in good to excellent yields at mild conditions. Notably, the process constitutes a rare example of base-free transfer hydrogenations.



## INTRODUCTION

Aromatic amines are widely used as intermediates in the synthesis of dyes, pigments, agrochemicals, and pharmaceuticals.<sup>1</sup> While primary aliphatic amines are produced by reductive amination,<sup>2</sup> reduction of nitriles,<sup>3</sup> and direct amination of alcohols,<sup>4</sup> the most important method to obtain primary anilines is based on the selective reduction of nitroarenes. In past years, for many nitroarenes stoichiometric reduction procedures such as the Béchamp process were replaced by more benign catalytic protocols. Today, noble metals are frequently used as heterogeneous catalysts for the direct hydrogenation of nitroarenes. However, a drawback of commercially available Ni or Pt catalysts is their missing chemoselectivity, and it is generally accepted that these catalysts cannot be applied for hydrogenation of substituted nitrobenzenes.<sup>5</sup> Because of this lack of selectivity, for more functionalized substrates the sulphide reductions prevail in industry.<sup>6</sup> Although remarkable advancements have been achieved in the selective catalytic hydrogenation of nitroarenes via tuning of the corresponding heterogeneous catalysts,<sup>7</sup> still the development of novel catalysts with broad functional group tolerance and high activity represents an important challenge. In this respect, the use of homogeneous catalysts based on inexpensive biorelevant metals offers interesting opportunities especially for more challenging substrates such as the ones shown in Figure 1.

In addition to catalytic hydrogenations, also transfer hydrogenation provides an attractive option for the reduction of nitroarenes.<sup>8</sup> For example, by applying formates as reducing agents, no autoclaves are required, and the handling of hydrogen is avoided.<sup>9,10</sup> So far, Rh,<sup>9</sup> Pd,<sup>9</sup> Ru,<sup>9–11</sup> Cu,<sup>12</sup> and Co<sup>12</sup> complexes are known as catalysts for such transformations. However, relatively long reaction times, high temperatures, and/or the price of the metal are drawbacks of these protocols.



**Figure 1.** Demanding substrates for selective nitro reductions.

Iron as an abundant, cheap, and less-toxic element is an ideal candidate to replace precious metals if comparable activities and selectivities are achieved.<sup>13,14</sup> To the best of our knowledge, iron-catalyzed transfer hydrogenations of nitroarenes are only known using toxic and hazardous 1,1-dimethyl-hydrazine.<sup>15</sup> On the basis of our recent report on the iron-catalyzed hydrosilylation of nitroarenes,<sup>16</sup> we became interested in related transfer hydrogenations, which obviously do not require the expensive silane and might work at milder conditions.

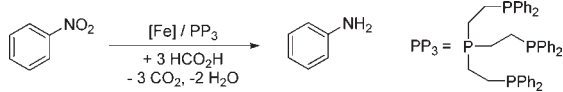
## RESULTS AND DISCUSSION

At the start of this project, we tested different iron, ruthenium, copper, and cobalt salts in the presence of various commercially available mono- and bidentate phosphines for the reduction of nitrobenzene with formic acid at low temperature (40 °C). Unfortunately, none of the *in situ*-generated complexes catalyzed the formation of aniline to any extent (see Table 1). However, using a combination of Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and the so-called tetraphos ligand tris[(2-diphenylphosphino)-ethyl]phosphine [P(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>; (PP<sub>3</sub>)] led to significant activity and gave aniline in 71% yield (Table 1, entry 10).

Notably, it was demonstrated that related catalyst systems are able to generate hydrogen directly from formic acid or can be

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Table 1. Catalytic Reduction of Nitrobenzene<sup>a</sup>


entry	catalyst	conv. (%) <sup>b</sup>	yield (%) <sup>b</sup>
1	RuCl <sub>3</sub> ·H <sub>2</sub> O/PP <sub>3</sub>	<1	<1
2	Ru(acac) <sub>3</sub> /PP <sub>3</sub>	<1	<1
3	RuCl <sub>2</sub> (cod)/PP <sub>3</sub>	<1	<1
4	FeCl <sub>3</sub> ·6H <sub>2</sub> O/PP <sub>3</sub>	<1	<1
5	Fe(acac) <sub>3</sub> /PP <sub>3</sub>	<1	<1
6	FeSO <sub>4</sub> ·7H <sub>2</sub> O/PP <sub>3</sub>	<1	<1
7	Cu(BF <sub>4</sub> ) <sub>2</sub> ·xH <sub>2</sub> O/PP <sub>3</sub>	<1	<1
8	Co(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/PP <sub>3</sub>	<1	<1
9	FeF <sub>2</sub> /PP <sub>3</sub>	19	12
10	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/PP <sub>3</sub>	78	71
11	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	<1	<1
12	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/tdme <sup>g</sup>	<1	<1
13	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/BINAP	<1	<1
14	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/dppe	<1	<1
15	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/dppp	<1	<1
16	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/tdme/PP <sub>3</sub> <sup>h</sup>	<1	<1
17 <sup>c</sup>	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/PP <sub>3</sub>	<1	<1
18 <sup>d</sup>	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/PP <sub>3</sub>	>99	95
19 <sup>d,e</sup>	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/PP <sub>3</sub>	>99	93
20 <sup>d,f</sup>	Fe(BF <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O/PP <sub>3</sub>	>99	93

<sup>a</sup> Reaction conditions: 40 °C, 1 h, 0.5 mmol of nitrobenzene, 0.01 mmol of catalyst (M/L ratio 1:1), 4.5 equiv of formic acid, 3 mL of EtOH. <sup>b</sup> Determined by GC using *n*-hexadecane as an internal standard. <sup>c</sup> M/L ratio 1:4. <sup>d</sup> 0.02 mmol of catalyst. <sup>e</sup> Room temperature, 8 h. <sup>f</sup> 70 °C, 5 min. <sup>g</sup> 1,1,1-Tris(diphenylphosphino-methyl)ethane. <sup>h</sup> 1.5 mol% of each ligand.

applied for hydrogenation with molecular hydrogen.<sup>17,18</sup> Apparently, not only hydrogen can be generated in the presence of iron, but it is also possible to transfer hydrogen to organic substrates with this catalyst system. As compared to all other tested precatalysts, the behavior of the catalyst is unique: As shown in Table 1, only the combination with Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O exhibited promising conversion toward the reduction of the nitro group, while FeF<sub>2</sub> led to slight conversion (Table 1, entry 9). Remarkably, also ruthenium precursors in combination with tetraphos did not exhibit any reactivity under these conditions.

Next, the reaction conditions for the active catalyst system were further optimized to allow for full conversion and up to 95% yield of aniline (Table 1, entries 18–20). In contrast to other protocols, this catalytic reduction can be performed even at room temperature (Table 1, entry 19), while at 70 °C only 5 min reaction time is necessary to complete the reduction without any loss of selectivity (Table 1, entry 20).

The influence of the solvent was also investigated and is shown in Table 2. Beside tetrahydrofuran, protic solvents are most suitable for this reaction (Table 2, entries 5–9).

To ensure that the nitro group is reduced via a transfer hydrogenation process and not by hydrogen generated from dehydrogenation of the formic acid, we performed the iron-catalyzed reduction of nitrobenzene at 5 bar of hydrogen pressure. Notably, when no formic acid was present, no reactivity

Table 2. Influence of the Solvent<sup>a</sup>

entry	solvent	conv. (%) <sup>b</sup>	yield (%) <sup>b</sup>
1	DCM	10	3
2	acetonitrile	<1	<1
3	DMF	14	14
4	Et <sub>2</sub> O	8	2
5	MeOH	48	35
6	EtOH	89	81
7	<i>n</i> BuOH	92	73
8	<i>i</i> PrOH	82	63
9	THF	74	67
10	toluene	9	2

<sup>a</sup> Reaction conditions: 40 °C, 1 h, 0.5 mmol of nitrobenzene, 0.01 mmol of catalyst, 4.5 equiv of formic acid, 3 mL of EtOH. <sup>b</sup> Determined by GC using *n*-hexadecane as an internal standard.

Table 3. Influence of the Reducing Agent<sup>a</sup>

entry	reducing agent	conv. (%) <sup>b</sup>	yield (%) <sup>b</sup>
1		<1	<1
2	formic acid	>99	86
3	sodium formate	16	4
4	ammonium formate	<1	<1
5	sodium formate/water (1:1)	8	2
6	formic acid/triethylamine	<1	<1
7	acetic acid	<1	<1

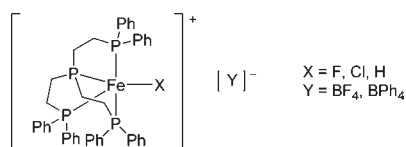
<sup>a</sup> Reaction conditions: 40 °C, 1 h, 0.5 mmol of nitrobenzene, 0.03 mmol of catalyst, 4.5 equiv of reducing agent, 3 mL of THF. <sup>b</sup> Determined by GC using *n*-hexadecane as an internal standard.

at all is observed. After that, we run the same reaction in the presence of 5 equiv of formic acid (with respect to the catalyst) and an excess of nitrobenzene (100 equiv). In this experiment, we examined if the active catalyst is formed by reaction with formic acid and subsequently is able to use hydrogen as the “true” reducing agent. However, under these conditions, only traces of aniline (1%) were detected, showing that the substrate is not reduced by an iron-catalyzed direct hydrogenation.

To study the unproductive decomposition of the reductant, we analyzed the gas phase of the reaction mixture. Here, the ratio of carbon dioxide to hydrogen was 3.2:1, demonstrating that about 31% of the consumed formic acid was decomposed to hydrogen. This finding explains the necessity of using 4.5 equiv of formic acid for complete reduction of the substrate. In addition, we advise for larger scale experiments to use appropriate safety measures similar to reactions with hydrogen.

The reducing agent was also the subject of further investigations (see Table 3). Surprisingly, formic acid is superior in comparison to various formates (Table 3, entries 2–5). Hence, the addition of base, for example, triethylamine, which is usually required for transfer hydrogenation, is not necessary but causes even lower reactivity (Table 3, entry 6). This is a rare example of base-free transfer hydrogenations and to the best of our knowledge the first example of a base-free catalytic transfer hydrogenation of nitro compounds.<sup>19</sup>

After that, we investigated the catalytic performance of defined iron complexes with the general formula [FeX(PP<sub>3</sub>)]<sub>2</sub>[Y] (X = H, H(H<sub>2</sub>), F, Cl; Y = BF<sub>4</sub>, BPh<sub>4</sub>). These complexes were tested also for the reduction of nitrobenzene as shown in Table 4. While the

**Table 4. Reduction of Nitrobenzene Applying Well-Defined Fe-Complexes<sup>a</sup>**

entry	catalyst	conv. (%) <sup>b</sup>	yield (%) <sup>b</sup>
1	[FeCl(PP <sub>3</sub> )] [BPh <sub>4</sub> ]	<1	<1
2	[FeF(PP <sub>3</sub> )] [BPh <sub>4</sub> ]	78	73
3	[FeH(PP <sub>3</sub> )] [BPh <sub>4</sub> ]	<1	<1
4	[FeH(H <sub>2</sub> )(PP <sub>3</sub> )] [BPh <sub>4</sub> ]	14	11
5	[FeF(PP <sub>3</sub> )] [BF <sub>4</sub> ]	72	63
6	Fe(BF <sub>4</sub> ) <sub>2</sub> · 6H <sub>2</sub> O/PP <sub>3</sub>	78	71
7 <sup>c</sup>	[FeH(PP <sub>3</sub> )] [BPh <sub>4</sub> ]	53	46

<sup>a</sup> Reaction conditions: 40 °C, 1 h, 0.5 mmol of nitrobenzene, 0.01 mmol of catalyst, 4.5 equiv of formic acid, 3 mL of EtOH. <sup>b</sup> Determined by GC using *n*-hexadecane as an internal standard. <sup>c</sup> Addition of 2 mol % CsF.

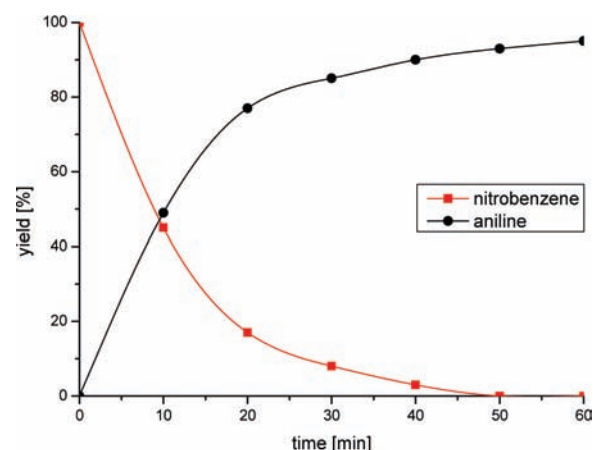
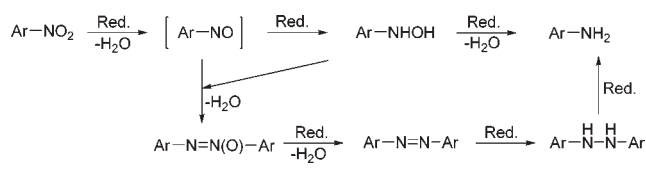
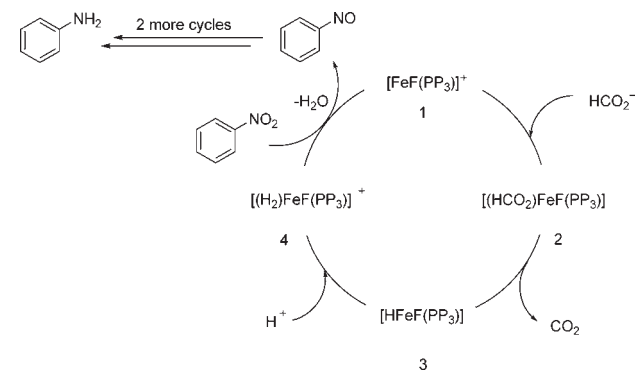
corresponding chloride and hydride species exhibit little or no reactivity (Table 4, entries 1, 3, 4), the cationic [FeF(PP<sub>3</sub>)]<sup>+</sup> complexes gave similar results as compared to the *in situ*-generated system (Table 4, entries 2, 5, and 6). Interestingly, the addition of CsF to the [FeH(PP<sub>3</sub>)] [BPh<sub>4</sub>] complex enhances the reactivity dramatically (Table 4, entry 7), probably due to the formation of the highly active [FeF(PP<sub>3</sub>)]<sup>+</sup> cation. To exclude the possibility of active copper or cobalt traces often present in iron salts, we tested Cu(BF<sub>4</sub>)<sub>2</sub> · *x*H<sub>2</sub>O and Co(BF<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O as catalysts.<sup>20</sup> However, again no reactivity is observed at all (Table 1, entries 7, 8). Additionally, atomic absorption spectroscopy was performed on the active iron complexes, showing no traces of Ni, Cu, Co, Ru, Pt, and Pd.

An important issue of the reduction of nitroarenes at larger scale is the formation of unwanted hydroxylamines. This intermediate is often less reactive as compared to the starting nitroarene, which is a critical factor especially at lower temperature.<sup>21</sup> These compounds are known carcinogens and potentially explosive at higher concentration due to their thermal instability. To our delight, in the presence of our iron-catalyzed system, no hydroxylamines (<1%) are observed during catalysis (Figure 2). Hence, taking samples from a catalytic experiment, no intermediates (>1%) are detected.

Beside the direct reduction of the nitro group, a second pathway via condensation of the initially formed nitrosoarene and the hydroxylamine is possible (Scheme 1). In this case, the resulting condensation product is further reduced via azobenzene and 1,2-diphenyl-hydrazine to give aniline.

However, in the reaction mixture of the model reaction, only small quantities of azobenzene are observed (<<1%) as side-products. Furthermore, direct iron-catalyzed reduction of azobenzene resulted only in 48% conversion. Here, about 40% of phenylhydrazine is formed, and aniline is detected in minor amounts (5%). This led us to the conclusion that the direct reduction pathway is favored in the presence of the active iron catalyst system.

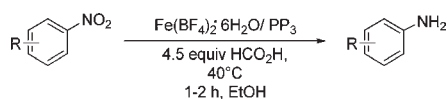
In Scheme 2, the proposed mechanism of our Fe-catalyzed transfer hydrogenation is shown. On the basis of the experiments with isolated iron complexes (see Table 4), we propose the [FeF(PP<sub>3</sub>)]<sup>+</sup> cation as active catalyst. Coordination of formate


















**Figure 2.** Concentration/time diagram for the reduction of nitrobenzene to aniline.**Scheme 1. Possible Pathways for the Reduction of Nitrobenzene****Scheme 2. Proposed Catalytic Cycle**

will lead to the neutral complex 2.  $\beta$ -Hydride elimination from 2, which is well-known in other formate decomposition reactions,<sup>22</sup> liberates carbon dioxide and results in complex 3.

Subsequent protonation from formic acid leads to the corresponding iron dihydride complex 4, which will reduce nitrobenzene to nitrosobenzene and water. Subsequent reduction of the latter intermediate in a similar catalytic cycle leads to phenyl hydroxylamine and finally to aniline. As mentioned above, these intermediates are not observed in the reaction mixture and should be therefore faster reduced as compared to the initial nitrobenzene.

Finally, to demonstrate the general applicability of this catalyst system, various nitroarenes were tested (Table 5). Easy alkyl-substituted nitroarenes are reduced in excellent yields up to 99% (Table 5, entries 1, 2). More importantly, for halogenated nitrobenzenes, full conversion is achieved, giving yields of

Table 5. Iron-Catalyzed Reduction of Nitroarenes<sup>a</sup>

entry	substrate	time (h)	conv. (%) <sup>b</sup>	yield (%) <sup>b</sup>
1		2	>99	95 (92) <sup>c</sup>
2		2	>99	99 (93) <sup>c</sup>
3		2	>99	89 (83) <sup>c</sup>
4		1	>99	88
5		1	>99	88 (83) <sup>c</sup>
6		1	>99	88 (84) <sup>c</sup>
7		1	>99	89
8		2	>99	92
9		2	>99	90
10		2	>99	95
11 <sup>d,e</sup>		2	>99	86 (81) <sup>c</sup>
12 <sup>f</sup>		2	>99	87 (87) <sup>c</sup>
13 <sup>f</sup>		2	96	78
14 <sup>f</sup>		2	87	77
15 <sup>g</sup>		2	>99	89 (85) <sup>c</sup>
16		1	>99	99 (92) <sup>c</sup>
17		1	>99	99 (93) <sup>c</sup>

<sup>a</sup> Reaction conditions: 40 °C, 0.5 mmol of substrate, 0.02 mmol of catalyst (M/L ratio 1:1), 4.5 equiv of formic acid, 3 mL of EtOH.

<sup>b</sup> Determined by GC using *n*-hexadecane as an internal standard. <sup>c</sup> Up scaling by factor 4 and isolated yields given in brackets. <sup>d</sup> Addition of 0.02 mol % CsF. <sup>e</sup> Second addition of 0.02 mol % catalyst and 4.5 equiv of formic acid after 1 h. <sup>f</sup> 0.03 mmol of catalyst. <sup>g</sup> 1.5 mol% catalyst and second addition of 1.5 mol% catalyst after 1 h.

88–92% (Table 5, entries 3–9). The position of the halide substituent did not induce any significant differences in reactivity,

and dihalogenated nitroarenes exhibit reactivity similar to that of the monohalogenated derivatives. For all substrates, no dehalogenation processes are observed.<sup>23</sup>

From a synthetic point of view, it is useful that reducible moieties such as olefins (*meta*-nitrostyrene) and ketones (*para*-nitroacetophenone) remained unaffected by the iron catalyst (Table 5, entries 10, 11). Vinylaniline was obtained in 95%, giving a yield comparable to the results of supported gold catalysts reported from the Corma group.<sup>7a</sup> Other functional groups such as esters, ethers, thioethers, and amines on the nitrobenzene are also well tolerated to give the corresponding anilines in good to very good yield without further optimization (Table 5, entries 12–15). For substrates bearing the functional moiety not directly attached, also excellent yields are achieved (Table 5, entries 16, 17).

## SUMMARY

We have developed a novel transfer reduction of industrially important nitroarenes. In the presence of well-defined iron complexes or the in situ combination of Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and P(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>, selective transfer hydrogenation of various functionalized substrates to the corresponding anilines occurred in good to excellent yields. The catalytic system already works at room temperature, and this catalytic process proceeds without any additional base, which is a common requirement for other transfer hydrogenations.

## EXPERIMENTAL SECTION

The general procedure for the reduction of nitrobenzene is as follows. In a Schlenk tube under argon atmosphere, Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (6.75 mg, 0.02 mmol) and P(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub> (13.41 mg, 0.02 mmol) were dissolved in 3 mL of dry EtOH, leading to the formation of a deep purple solution. Dry nitrobenzene (51.5 μL, 0.5 mmol) and dry *n*-hexadecane (100 μL) as internal standard were added. The reaction mixture was heated to 40 °C, and formic acid (85 μL, 4.5 equiv) was injected. The solution immediately turned brown. After 1 h, the mixture was cooled, and a sample was taken from the slight yellow solution. All catalytic reactions were performed at least twice to ensure reproducibility. To determine the isolated yield of the anilines, the general procedure was scaled up by the factor of 4, and no internal standard was added. After completion, the solution was washed with a saturated NaHCO<sub>3</sub> solution. The mixture was then extracted with ethyl acetate (three times), the combined organic layers were dried over MgSO<sub>4</sub>, and the solvent was removed *in vacuo*. The anilines were purified by column chromatography (silica; *n*-hexane/ethyl acetate mixture = 10:1 → 5:1).

The molecular defined complexes [FeH(PP<sub>3</sub>)<sub>3</sub>]BPh<sub>4</sub>, [FeH(H<sub>2</sub>)(PP<sub>3</sub>)<sub>3</sub>]<sup>+</sup>X<sup>-</sup> (X<sup>-</sup> = BF<sub>4</sub>, BPh<sub>4</sub>), [FeCl(PP<sub>3</sub>)<sub>3</sub>]BF<sub>4</sub>, and [FeF(PP<sub>3</sub>)<sub>3</sub>]<sup>+</sup>X<sup>-</sup> (X<sup>-</sup> = BF<sub>4</sub>, BPh<sub>4</sub>) were synthesized according to literature protocols.<sup>24</sup> All complexes were characterized via elemental analysis and HR-MS, in the case of [FeH(H<sub>2</sub>)(PP<sub>3</sub>)<sub>3</sub>]<sup>+</sup>X<sup>-</sup> (X<sup>-</sup> = BF<sub>4</sub>, BPh<sub>4</sub>), via NMR spectroscopy.

## ASSOCIATED CONTENT

**S Supporting Information.** Extended version of Table 1, preparation of the defined complexes, and references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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