Hydrophosphination of Unactivated Alkenes and Alkynes using Iron(II): Catalysis and Mechanistic Insight

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KEYWORDS: alkenes, alkynes, phosphines, homogeneous catalysis, heterofunctionalization, P–C bond formation

ABSTRACT: The catalytic addition of phosphines to alkenes and alkynes is a very attractive process that offers access to phosphines in a 100% atom-economic reaction using readily available and inexpensive materials. The products are potentially useful ligands and organocatalysts. Herein we report the first example of intramolecular hydrophosphination of a series of non-activated phosphino-alkenes and phosphino-alkynes with a simple iron β-diketiminate complex. Kinetic studies suggest that this transformation is first order with respect to both the phosphine and the catalyst. A mechanistic interpretation of the iron-catalyzed hydrophosphination is presented, supported by the experimental evidence collected.

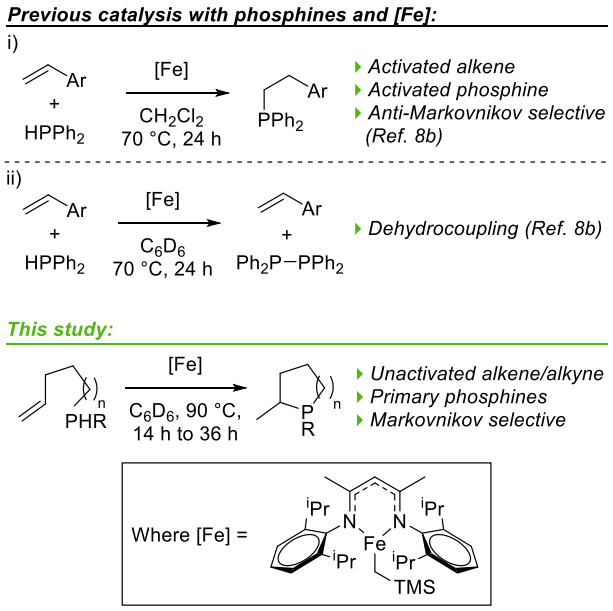
KEYWORDS: iron, phosphines, radicals, hydrofunctionalization, phospholanes, phosphinanes, phosphinines

INTRODUCTION

Phosphines have received much attention because of their essential role in various fields of chemistry. For instance, they can be used as synthetic reagents, ligands in transition metal complexes, biologically active molecules, polymers and building blocks of supramolecular assemblies.[1]

Among the large number of methods to synthesize phosphines, transition metal complex catalyzed hydrophosphination can be considered an ideal way of creating carbon-phosphorus bonds because it provides a unique opportunity to combine high-atom efficiency and exceptional selectivity.[2] The limited availability, high cost and often significant toxicity of precious metal catalysts makes the development of new, more economical and environmentally benign alternatives of increasing importance. In this context, iron is the most abundant transition metal and is the fourth most abundant element in the earth's crust; it is inexpensive and offers sustainable long-term commercial availability. In addition, iron benefits from low toxicity and from being environmentally benign.

Although there has been a great development in the use of alkali, alkaline earth metals, transition metals and f-block metals to achieve hydrophosphination,[2c,3] limitations in substrate remain,[4] and transition metal catalyzed hydrophosphination of non-activated olefins with primary phosphines continues to be a challenging task. To the best of our knowledge there are only a handful examples in the literature of hydrophosphination reactions of unactivated alkenes or alkynes using a primary phosphine. On one hand, and most recently, Waterman and co-workers disclosed the zirconium catalyzed intermolecular hydrophosphination of ethylene and 1-hexene with phenyl phosphine.[5] On the other hand, Marks and co-workers reported the first and only example of intramolecular hydrophosphination of simple non-activated alkenes and alkynes, which is catalyzed by lanthanocene complexes.[6] These studies not only achieved highly desirable intramolecular hydrophosphination to form phospholanes and phosphinanes/phosphinines, but did so in an enantioselective fashion.[6] Marks also investigated the intermolecular hydrophosphination/polymerisation of ethylene with phenylphosphine.[7] Taking these precedents into account, we questioned whether, using iron, an intramolecular substrate could lead to the kinetically favored hydrophosphination of non-activated phosphino-alkenes and alkynes. In this manuscript we report the successful intramolecular cyclization of phosphino-alkenes and –alkynes. This constitutes the first example of hydrophosphination of such substrates using an iron pre-catalyst (Scheme 1).



Scheme 1. Catalytic transformations of phosphines achieved using iron(II) β-diketiminate complexes ([Fe]).

RESULTS AND DISCUSSION

Three different iron β-diketiminate complexes were evaluated as pre-catalysts for the cyclization of phosphine **4a** (Figure 1). These pre-catalysts, although moderately air-sensitive requiring synthesis under a nitrogen atmosphere, can be readily prepared in high yield on a multigram scale.[8] Pre-catalysts **1-Fe** and **3-Fe**[8c] give poor conversions to the Markovnikov phospholane product, **5a**, after 24 h at 90 °C with a catalyst loading of 10 mol%, while the classic 2,6-diisopropyl motif, **2-Fe**, gives 100% spectroscopic yield of product after 17 h (Table 1, Entry 1). Based upon the good results we had obtained in phosphine dehydrocoupling and the report by Hannedouche on intramolecular hydroamination,[9,8b] benzene was used as the reaction solvent. Although their synthesis is not trivial, the reaction substrates (**4a** to **4h**) can be prepared on a large scale (up to 1 g) in two to three steps.[10] Following the work of Marks,[6] all catalytic reactions along with the synthesis of **4f** are performed in the dark to avoid light-induced anti-Markovnikov cyclization of the phosphino-alkenes. The 6-membered phosphinane is not a thermal product where at 90 °C the exclusion of light and catalyst does not increase the yield of this side-product.[11] These optimized conditions are in-line with those reported by Hannedouche for intramolecular hydroamination which uses a co-catalytic amount of cyclopentylamine to facilitate catalysis.[9] However, in our case this type of additive is not necessary, geminal substitution is not needed to force hydrophosphination and side-products (from reduction of the double bond or the formation of 3,4-dihydro-2H-phosphole) are not observed. Decreasing the temperature to 80 °C leads to a significant reduction in the activity of **2-Fe** and only trace amounts of **5a** are obtained. Attempts to reduce the catalyst loading to 5 mol% incurs a similar drop-off in reactivity; it is clear that both the temperature and catalyst loading are crucial for the reaction to take place. In our previous studies intermolecular hydrophosphination of styrenes does not take place in C_6D_6 and instead competitive dehydrocoupling is observed (Scheme 1);[8b] clearly intramolecular reactivity is more favorable than intermolecular processes for these substrates.

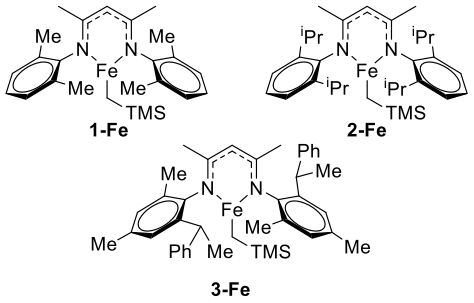
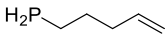
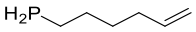
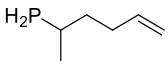
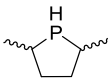
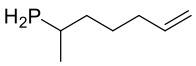
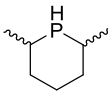
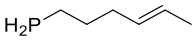
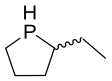
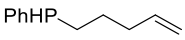
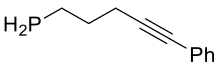
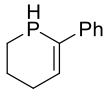
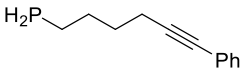
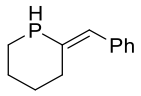


Figure 1. Pre-catalysts used for intramolecular hydrophosphination.

With optimized reaction conditions in hand (10 mol% **2-Fe**, 90 °C) we proceeded to investigate the reactivity of other phosphino-alkenes. Catalytic hydrophosphination of a substrate with a longer aliphatic chain necessitates an increased reaction time, but the formation of the six-membered phosphinane, **5b**, is accomplished in 36 h cleanly and in high yield (Table 1, Entry 2). Branched phosphines **4c** and **4d** also undergo Markovnikov hydrophosphination with good conversion (**5c** and **5d**, Entries 3 and 4). Catalysis is limited to terminal alkenes: very little reactivity is observed when **4e** is used in catalysis (Entry 5). However, the use of a secondary phosphine as the substrate yields 1-phenylphospholane with complete conversion after 14 h (**5f**, Entry 5).

Catalysis is possible for phosphino-alkynes (**4g** and **4h**, Entries 6 and 7), which show similar levels of reactivity to the simplest phosphinoalkene, **4a**. Interestingly, **4g** only needs heating at 50 °C for 14 h to form **5g** exclusively. There is no evidence for the formation of the 5-membered ring, which contains an exocyclic-double bond analogous to **5h**. When **4g** is heated to 90 °C for four days in the absence of catalyst and in the light, no reaction is observed: **5g** is not the thermal or the light cyclized product. Heating above 50 °C or using a higher catalyst loading leads to decomposition of **5g**. Catalyst-free experiments using **4a**, **4c** and **4h** also fail to yield any of the desired Markovnikov products after heating for several days at 90 °C.

Table 1. Iron mediated intramolecular hydrophosphination of alkenyl and phosphino-alkynes.

Entry	Substrate	Product	Time (h)	Isomer ratio	Conversion[a] [Yield][b] %
1	 **4a**	 **5a**	17	63 : 37	100 [86]
2	 **4b**	 **5b**	36	83 : 17	91 [69]
3	 **4c**	 **5c**	36	58 : 42	90 [72]
4	 **4d**	 **5d**	36	68 : 20 : 12	74 [20]
5[c]	 **4e**	 **5e**	36	-	~ 20 [not isolated]
6	 **4f**	 **5f**	14	62 : 38	100 [44]
7[d]	 **4g**	 **5g**	14	-	95 [57]
8	 **4h**	 **5h**	17	81 : 19	100 [90]

General reaction conditions: **4a-4g** (0.25 mmol), **2-Fe** (14 mg, 0.025 mmol) in C_6D_6 (0.5 mL), 90 °C. [a] Based on the consumption of phosphine from integration of signals in the ^1H and ^{31}P. [b] For characterization purposes, at the end of the reaction, the solution was passed through a plug of silica to remove **2-Fe**, eluting with C_6D_6. In order to accurately determine how much product had been isolated (**5a** to **5d** are volatile) 1,3,5-trimethoxybenzene was then added as an analytical standard. If undertaken on a larger scale, isolation by vacuum distillation or flash chromatography under argon is possible. [c]This conversion was obtained with both 10 and 25 mol% **2-Fe**. [d]50 °C.

All the products are formed as a mixture of isomers, depending on the starting phosphine.[10] For example, in the case of **5a**, there are two different products generated in a 3:2 ratio, but **4b** and **4h** form one isomer more selectively (4:1 ratio in both cases). In an attempt to develop enantiocontrol in the hydrophosphination reaction, chiral pro-ligands were synthesized, **6** and **7** (Figure 2). β-Diketimine pro-ligand **6**[12] has been used by Schaper to carry out lactide polymerizations with high levels of tacticity control.[13] Ligation of both the *R,R*- and *S,S*-enantiomers to iron using the simple one-pot procedure developed by Hessen[8a] is successful, but produces **6-Fe**$_{R,R}$ and **6-Fe**$_{S,S}$ as dark yellow oils that, although clean by ^1H NMR, could not be crystallized. Nevertheless cyclization of **4a** with these pre-catalysts was attempted but fails to show appreciable amounts of product. This lack of activity is postulated to be due to the benzylic functionality which does not have the same resonance stabilizing effect as a phenyl group. Similarly, although pro-ligand **7** can be synthesized in good yield and has been shown to be active for the asymmetric aziridination of al-

kenes,[14] our resulting iron complex shows no catalytic activity in intramolecular hydrophosphination.

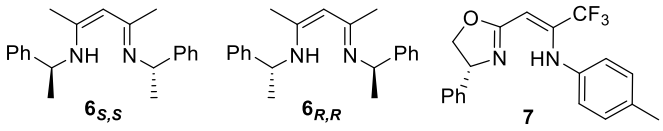
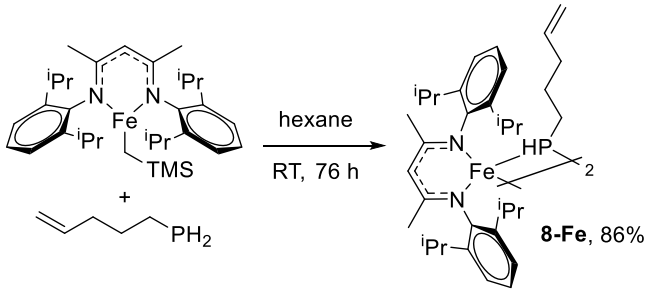


Figure 2. Chiral pro-ligands which were tested in enantioselective intramolecular hydrophosphination.

To investigate the mechanism of reaction, we synthesized iron phosphido complex **8-Fe**, which is crystallized from hexane as a dark brown solid in 86% yield (Scheme 2).



Scheme 2. Stoichiometric reaction of the pre-catalyst **2-Fe** with phosphine **4a**.

X-ray diffraction analysis of a single crystal reveals a centrosymmetric dimer in the solid state, in which two iron atoms are bridged by phosphido ligands generated by **4a** (Figure 3).[15] Each iron atom has a distorted tetrahedral geometry and the iron–phosphido bond lengths (Fe-P(1) 2.4552(4) Å, Fe-P(1) 2.4419(4) Å) are similar to those encountered in the only related iron β-diketiminate complex described by Stephan and co-workers.[16]

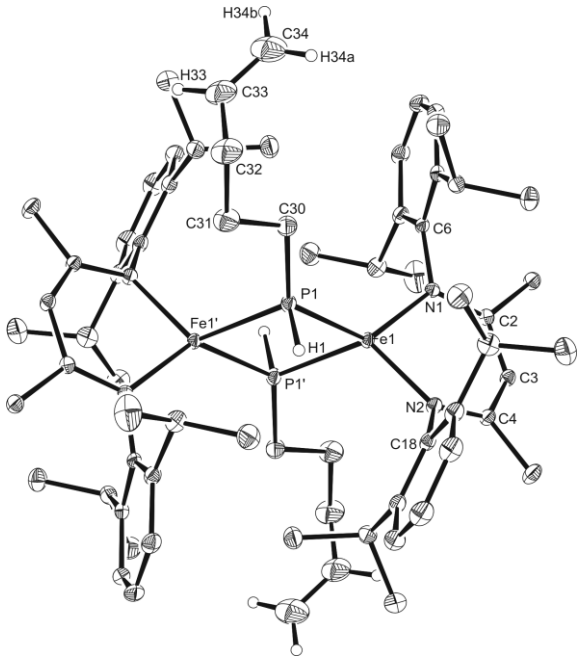


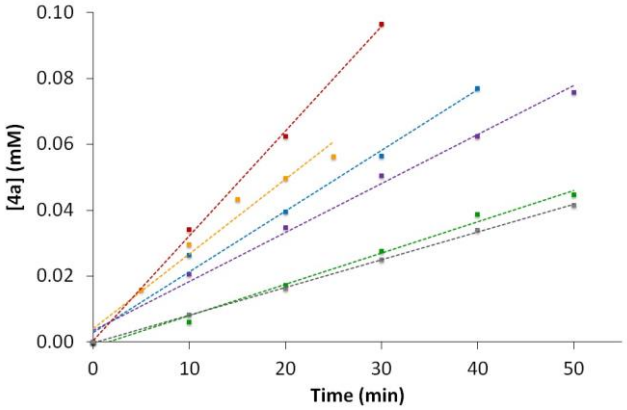
Figure 3. Ortep drawing of complex **8-Fe**. Thermal ellipsoids are set at 50% probability. Selected bond lengths (Å): Fe1–P1, 2.4419(6); Fe1–N1 2.018(1); Fe1–N2 2.026(1); Fe1–P1' 2.4553(5); P1–C30 1.847(2). Selected bond angles (°): Fe1–P1–Fe1' 94.21(2); P1–Fe1–P1' 85.79(2); N1–Fe1–N2 93.91(5).

This stoichiometric reactivity would suggest that the pre-catalyst **2-Fe** is basic enough to deprotonate the primary phosphino alkene, releasing tetramethylsilane in order to activate the catalyst. Diffusion-ordered spectroscopy (DOSY) experiments were used to establish whether this complex is a dimer (existing as **8-Fe**) or a monomer (**9-Fe**) in solution. Although somewhat limited by the paramagnetic nature of **2-Fe** and **8-Fe**, 2D solution spectra of both **2-Fe** and **8-Fe** show very similar diffusion coefficients suggesting that both species have similar molecular weights.[10,17] Therefore, knowing that the pre-catalyst (**2-Fe**) is monomeric, we can conclude that **8-Fe** splits into a monomer in solution and that the active complex involved in the catalytic cycle is likely to be a mononuclear phosphido complex analogous to **9-Fe**. The DOSY NMR spectrum of **8-Fe** in C_6D_6 does show some anomalous peaks that we attribute to an equilibrium between **8-Fe** and **9-Fe** in solution at room temperature, with monomeric **9-Fe** being the dominant species. NMR studies of a benzene solution of **8-Fe** at 90 °C is severely limited by paramagnetism and although the dimer chemical shifts disappear, we cannot rule out loss due to broadening and/or loss under another shifting signal at this high temperature. We do not observe the dimer (**8-Fe**) in the catalytic mixture. Therefore, under the reaction conditions it is believed that a mononuclear iron complex is present which is depicted as three-coordinate **9-Fe**, but a 4-coordinate phosphido/phosphine or phosphido/phospholane species, analogous to those reported by Marks,[6b] cannot be ruled out. Study of this is limited by paramagnetism: when phosphorus is directly coordinated to the metal center there is complete loss of all ^{31}P NMR signals, preventing investigation of the coordination environment at iron or the catalyst resting state.

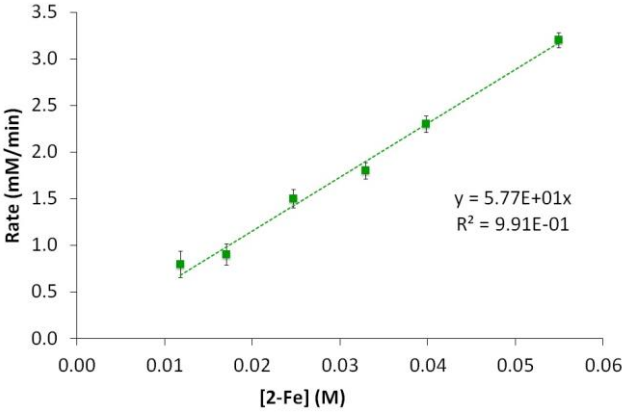
Kinetic experiments were also conducted by varying the loading of the iron pre-catalyst (**2-Fe**) and the concentration of phosphine, using **4a** as a model compound for hydrophosphination (Figure 4). Although the reaction mixture is paramagnetic, rates of reaction can be obtained *via in situ* NMR spectroscopy by monitoring the loss of alkene signals relative to an internal standard (1,3,5-trimethoxybenzene) in the ^1H NMR (Figure 4a and Table 2). A plot of concentration of **2-Fe** against initial rate shows a first order relationship (Figure 4b). A kinetic run using a solution of **8-Fe** shows a half order relationship, substantiating the monomeric nature of this complex in solution and suggesting the monomer is an active catalytic intermediate (Figure 4c). When 10 mol% **2-Fe** and 5 mol% **8-Fe** are added to reactions containing 0.25 mmol **4a**, similar initial rates of reaction are obtained (3.43×10^{-3} $mmolmL^{-1}min^{-1}$ and 3.39×10^{-3} $mmolmL^{-1}min^{-1}$ respectively), this is reflected throughout the kinetic studies when comparing **2-Fe** to **8-Fe** and further hints at the role of the monomer of **8-Fe** (*e.g.* **9-Fe**) as an on-cycle intermediate. By varying the concentration of **4a**, a first order relationship in reagent is also observed (Figure 4d and Table 3).[10] However, there may be some evidence for substrate/product inhibition at higher substrate

concentrations, as a drop-off in rate is observed. When the catalytic hydrophosphination of **4a** is spiked with 0.2 mmol of **5a**, in comparison to the standard reaction, a lower yield of product is obtained, consistent with the product inhibiting catalysis (Figure 4e).

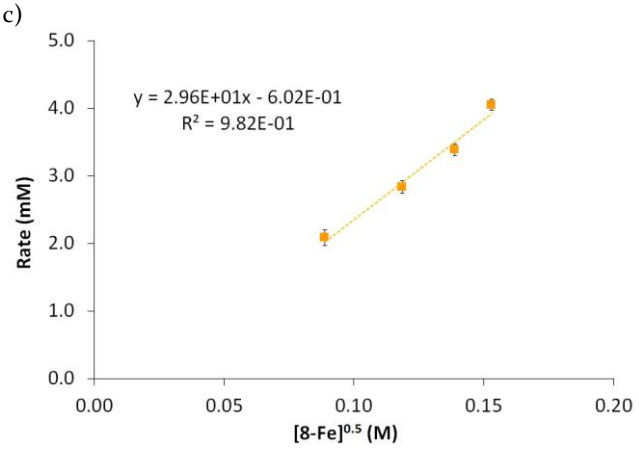
a)



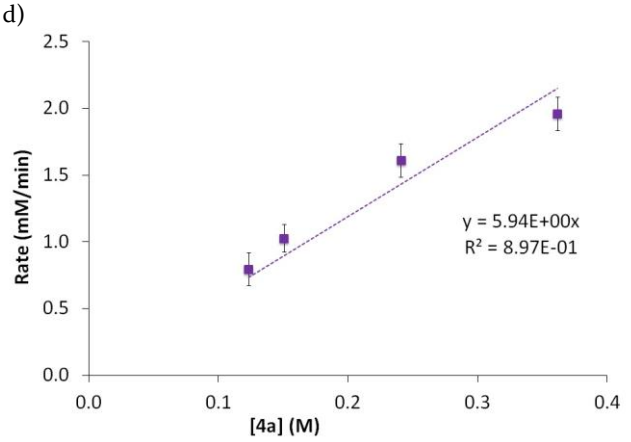
b)



c)



d)



e)

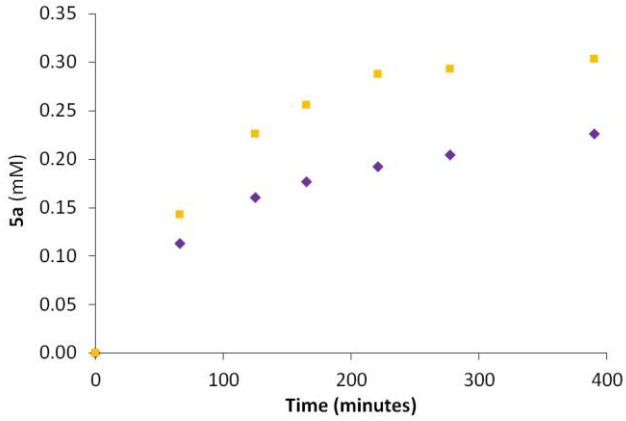


Figure 4. a) Initial rates obtained when the catalyst loading (**2-Fe**) is varied (see Table 2 for details). b) First-order fit of product concentration for different initial concentrations of **2-Fe**. c) Half order relationship obtained with complex **8-Fe**. d) First order relationship when **4a** is varied. e) Addition of **5a** (0.2 mmol) to the catalytic reaction (0.25 mmol **4a**, 10 mol% **2-Fe**) results in a reduced yield of product (73%,◆): less **4a** undergoes hydrophosphination compared to a reaction that is not spiked with **5a** where 98% product is obtained over the same time period (■).

Table 2. Rates obtained when [**2-Fe**] is varied.

Entry	**2-Fe** (mol%)	[**2-Fe**] (M)	Rate (mM min^{-1})	R^2 ($\times 10^{-2}$)
1	**30**	0.055	3.18 ± 0.08	99.9
2	**22**	0.040	2.26 ± 0.09	96.9
3	**18**	0.033	1.84 ± 0.09	98.9
4	**14**	0.025	1.49 ± 0.10	99.2
5	**9.4**	0.017	0.95 ± 0.11	99.2
6	**6.5**	0.012	0.84 ± 0.14	99.9

Conditions: **4a** (12 mg, 0.12 mmol), C_6D_6 (0.65 mL), 363 K.

Table 3. Rates obtained when [**4a**] is varied.[10]

Entry	[**4a**] (M)	Rate (mM min^{-1})	R^2 (×10^{-2})
1	0.362	1.96 ± 0.13	98.1
2	0.241	1.61 ± 0.13	99.9
3	0.151	1.03 ± 0.10	99.6
4	0.124	0.80 ± 0.12	96.7

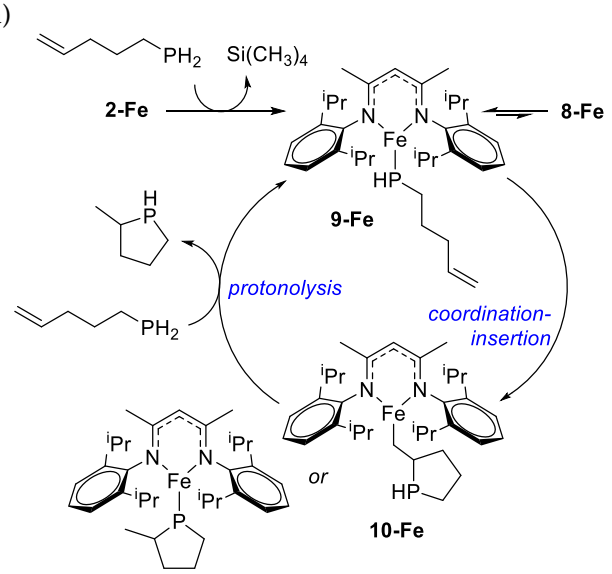
Conditions: **2-Fe** (14 mg, 0.025 mmol), C_6D_6 (0.65 mL), 363 K.

The isolation and catalytic activity of **8-Fe** along with DOSY data has allowed us to postulate a catalytic cycle. We propose that the reaction proceeds *via* a very simple redox neutral process whereby the iron pre-catalyst **2-Fe** is activated by one equivalent of phosphino-alkene (for example **4a**) to form an iron phosphido intermediate (**9-Fe**, Scheme 3a). Significantly, adding one equivalent of (chloromethyl)cyclopropane as a radical clock to the hydrophosphination of **4a** after 75 minutes, when the reaction is 48% complete, slows the reaction.[18] After 17 h the reaction contains only 78% **5a**, whereas a reaction run in parallel in the absence of the radical clock is complete. The reaction containing (chloromethyl)cyclopropane also shows the formation of 1-butene, a product that can only form in the presence of radicals. Reaction of **8-Fe** with 20 equivalents of (chloromethyl)cyclopropane and 20 equivalents of **4a** also results in the formation of 1-butene. When **4a** is reacted with (chloromethyl)cyclopropane in the absence of **2-Fe** under the standard reaction conditions, no reaction is observed *i.e.* **4a** does not form side-products *via* S_N-type reactions.

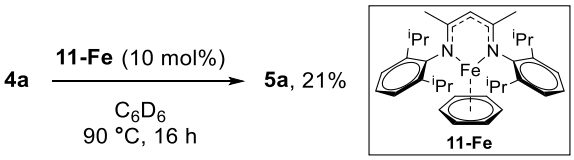
We believe that once formed **9-Fe** undergoes coordination-insertion to form iron alkyl intermediate **10-Fe** (although a proton shift and coordination through phosphorus cannot be ruled out) followed by protonolysis mediated by phosphino-alkene to release the product and regenerate **9-Fe**. The first order relationship in **4a** is potentially aligned with Marks' intramolecular hydrophosphination[19] and Hannedouche's iron catalyzed hydroamination,[9] where protonolysis is turnover-limiting. We postulate that radicals are involved in the bond making and breaking processes during the catalytic cycle, although it is difficult to ascertain the precise role of the iron[20] and the ligand[21] and whether these radicals are P-centered.[22]

To explore all possible avenues we have also considered whether the reaction proceeds *via* an iron(I)[23] species, which could be stabilized by the solvent and the non-innocent β-diketiminate ligand. Although our catalysis involves no obvious reductant, the potential of a reduced iron catalyst was highlighted by the solvent dependent reactivity we have already observed with pre-catalyst **2-Fe**.[8b] Synthesis and subsequent application of iron(I)-benzene complex **11-Fe**[24] in the hydrophosphination of **4a** is slow and fails to give an appreciable amount of product over the standard reaction time (Scheme 3b). When the reaction mixture is heated for a further 5 days, no further product is formed. This would suggest that an iron(I) complex of the form **11-Fe** is not involved as an on-cycle intermediate.

a)



b)



Scheme 3. a) Proposed mechanism for intramolecular hydrophosphination using **4a** as a model substrate. b) Poor reactivity is observed with Fe(I) complex **11-Fe**.

CONCLUSION

We have shown for the first time that a simple β-diketiminate iron(II) complex is an efficient pre-catalyst for the hydrophosphination of non-activated unsaturated C–C bonds. The active catalyst is believed to be a phosphido complex, which in solid state is a dimer bearing two bridged phosphido ligands. We have developed an in-depth study of the mechanism and all the experiments suggest that this transformation proceeds *via* a radical pathway in which one iron species and a phosphine molecule are involved. However, greater research is needed to ascertain the catalyst resting state and the exact nature of the radicals involved in catalysis.

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SUPPORTING INFORMATION

SUPPORTING INFORMATION

Experimental procedures, analysis data and spectra for starting materials and catalysis products. Details of mechanistic studies, DOSY and X-ray data.

ACKNOWLEDGMENT

We thank the EPSRC UK National Mass Spectrometry Facility at Swansea University for MS analysis, the EPSRC for funding (EP/M019810/1) and the University of Bath for a DTA studentship (AKK).

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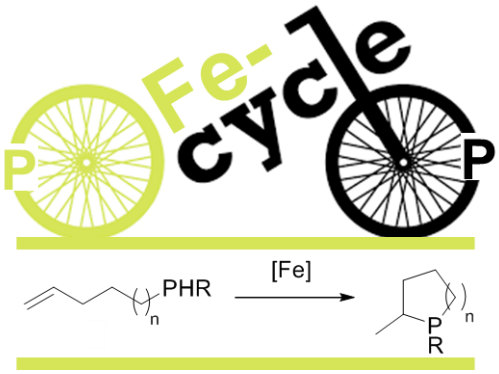
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