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Iron-Salt-Promoted Highly Regioselective α and β Hydrophosphination of Alkenyl Arenes

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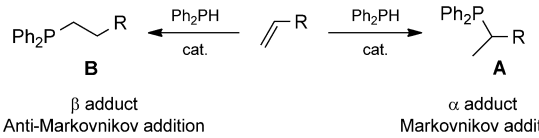
Dedicated to Professor Irina Petrovna Beletskaya

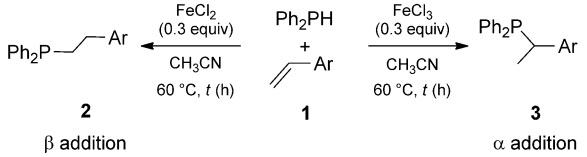
The catalytic addition of phosphines to alkenes (hydrophosphination) is an attractive process (Scheme 1).[1] It is a 100% atom-economical reaction that uses widely available and inexpensive starting materials. It offers an access to alkylphosphines, which are useful ligands,[2] organocatalysts,[3]



Scheme 1. Formation of Markovnikov and anti-Markovnikov regioisomers by catalytic addition of phosphines to alkenes.

and reagents in organic synthesis.[4] However, due to the high energy of the P–H bond ($E = 77$ kcal mol^{-1}),[5] the reaction usually requires activation by radical initiators.[1c,6] Thermal-,[7] acid-,[8] and base-promoted[9] reactions have also been applied, although less frequently. Metal- and lanthanide-catalyzed processes were also reported recently.[1c,10] Whatever the method, the addition usually proceeds in an anti-Markovnikov way leading to the β adduct **B** (addition of the phosphorus atom to the terminal carbon atom of a terminal alkene). In contrast, the selective formation of the valuable α adduct **A**, with formation of a stereogenic centre, is still a challenging problem.[11] In addition, examples of styrenic hydrophosphination are scarce. Addition to styrene was reported under basic,[9b,c,d] and radical[12] conditions and more recently by using transition-metal catalysts (Ni, Cu).[13] All these procedures afforded anti-Markovnikov adducts.

Inexpensive and environmentally friendly iron salts[14] have recently emerged as powerful tools in organic synthesis.[15] Their efficiency has been demonstrated in several addition reactions to carbon–carbon double bonds (hydroamination,[16] hydrothiolation,[17] hydroboration,[18] hydrosilylation,[19] hydroarylation,[20] and oxyphosphorylation[21]) and during the course of our studies in the double hydrophosphination of terminal arylacetylenes.[22] As part of our ongoing studies of the control of the regioselectivity of hydrophosphination reactions,[7a,b,23] herein we report the iron-promoted hydrophosphination reaction of styrenes, which offers selective access to either the β adduct **B** or the α adduct **A** (Schemes 1 and 2).[24]



Scheme 2. Regioselective iron-catalyzed hydrophosphination of alkenyl arenes.

As a model reaction, we investigated the iron-catalyzed addition of diphenylphosphine to styrene (**1a**) (Scheme 2, Ar = Ph). A preliminary set of experiments was arbitrarily carried out at 60 °C in acetonitrile. Without catalyst, the reaction was very slow (18% conversion of Ph_2PH after 5 h) leading to the formation of the β adduct (11%) along with a mixture of unidentified byproducts (Table 1, entry 1). Use of 0.3 equivalents of $FeCl_2$ afforded 46% of the β adduct **2a**[13b] with a 47% conversion of Ph_2PH after 5 h at 60 °C (Table 1, entry 2). Finally, running the reaction for 12 h led to full conversion of Ph_2PH and to 97% of the corresponding phosphine **2a** (Ar = Ph)[25] (Table 1, entry 3). No trace of the

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hypothetical α adduct **3a** could be detected. When the catalyst loading was decreased to 0.1 equivalents an incomplete conversion of 68% was observed after 12 h. The full conversion was not reached, even after an extended reaction time of 24 h. Other iron salts such as $[Fe(acac)_3]$ and $K_3[Fe(CN)_6]$ also led to the selective formation of the anti-Markovnikov β adduct **2a**, but the best promoter remains $FeCl_2$.

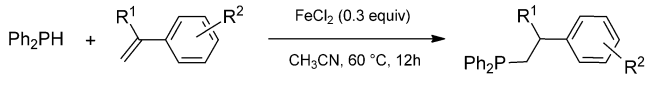
A different result was observed when $FeCl_3$ was the catalyst. Indeed, a new signal was observed in the ^{31}P NMR spectrum of the crude medium. Isolation and full characterization suggested the formation of the α adduct **3a** (Scheme 2 and Table 1, entry 6), by comparison with an authentic sample prepared by an alternative route.[20] This preliminary result led us to investigate the possibility of tunable control of the regioselectivity of hydrophosphination by careful selection of the iron catalyst (Scheme 2).

Table 1. Screening of iron catalysts for the hydrophosphination of styrene (**1a**, Ar = Ph) with diphenylphosphine.[a]

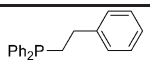
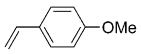
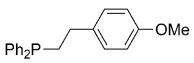
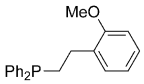
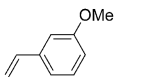
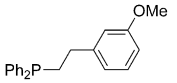
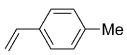
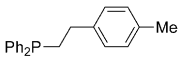
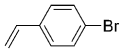
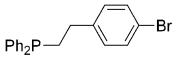
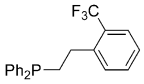
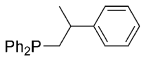
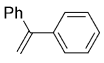
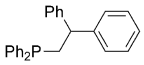
	Catalyst	Time [h]	Ph_2PH Conv. [%][b]	β adduct **2a** [%][c]	α adduct **3a** [%][c]
1	none	5	18	11	–
2	$FeCl_2$	5	47	46	–
3	$FeCl_2$	12	99	97	–
4	$Fe(acac)_3$	12	66	66	–
5	$K_3Fe(CN)_6$	12	70	68	–
6	$FeCl_3$	12	100	–	92

[a] Reaction conditions: Iron salt (0.3 equiv), CH_3CN, Ph_2PH (1 equiv), styrene (2 equiv), 60 °C. [b] Conversion (consumption of Ph_2PH) determined by ^{31}P NMR spectroscopy. [c] ^{31}P NMR spectroscopic yield.

Table 2. Regioselective $FeCl_2$-mediated β hydrophosphination of various alkenyl arenes with diphenylphosphine.[a]

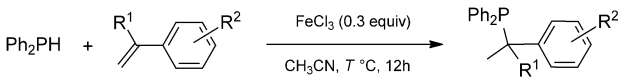


1a–i **2a–i**

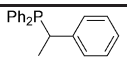
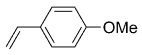
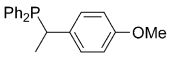
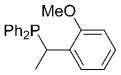
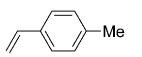
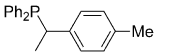
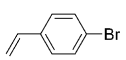
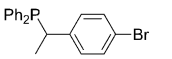
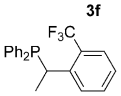
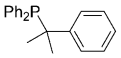
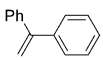
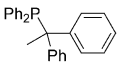
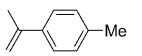
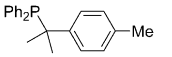
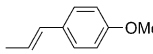
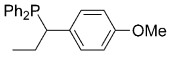
	Alkenyl arene	Product	Yield [%] ^{31}P[b]	Yield [%] Isolated[c]
1		 **2a**	97	87
2		 **2b**	95	85
3		 **2c**	100	84
4		 **2d**	100	84[d]
5		 **2e**	100	87
6		 **2f**	100	82
7		 **2g**	90	74
8		 **2h**	47	30[e]
9		 **2i**	17	–[e]

[a] Reaction conditions: $FeCl_2$ (99% purity, 0.3 equiv), CH_3CN, Ph_2PH (1 equiv), alkenyl arene (2 equiv), 60 °C. [b] ^{31}P NMR yield. [c] Isolated yield of the corresponding **2**·BH_3. [d] Reaction performed for 48 h. [e] Reaction performed at 90 °C.

Table 3. Regioselective $FeCl_3$-mediated α hydrophosphination of various alkenyl arenes with diphenylphosphine.[a]



1a–c, e–k **3a–c, e–k**

	Alkenyl arene	Product	Yield [%] T [°C]	Yield [%] ^{31}P[b]	Yield [%] Isolated[c]
1		 **3a**	60	85	73
2		 **3b**	60	92	85
3		 **3c**	60[d]	84	74
4		 **3e**	60	62	44
5		 **3f**	60	<5	<5
6		 **3g**	60	<5	<5
7		 **3h**	90	96	76
8		 **3i**	90	100	76
9		 **3j**	90	90	72
10		 **3k**	90	79	53

[a] Reaction conditions: $FeCl_3$ (0.3 equiv), CH_3CN, Ph_2PH (1 equiv), alkenyl arene (2 equiv), 60–90 °C. [b] ^{31}P NMR yield. [c] Isolated yield of the corresponding **3**·BH_3. [d] Heating was performed by microwave irradiation (3 × 10 min). A lower ^{31}P NMR yield of 55% was obtained by classical heating.

The scope of these processes for different alkenyl arenes is shown in Tables 2 and 3. $FeCl_2$ was selected for the preparation of the anti-Markovnikov β adducts **2a–i** and $FeCl_3$ for the Markovnikov α adducts **3a–c** and **3e–k**.

With $FeCl_2$ (Table 2), all of the alkenyl arenes tested afforded the expected β adduct with 0.3 equivalents of $FeCl_2$ at 60 °C in acetonitrile. The scope of the reaction ranges from electron-rich to electron-poor derivatives (Table 2, entries 2–5 and 6–7). Substrates bearing *ortho* substituents also reacted in high yields (Table 2, entries 3 and 7). Addition to a 1,1-disubstituted double bond proved to be more difficult (Table 2, entries 8 and 9), even at higher temperature (90 °C).[1c,27]

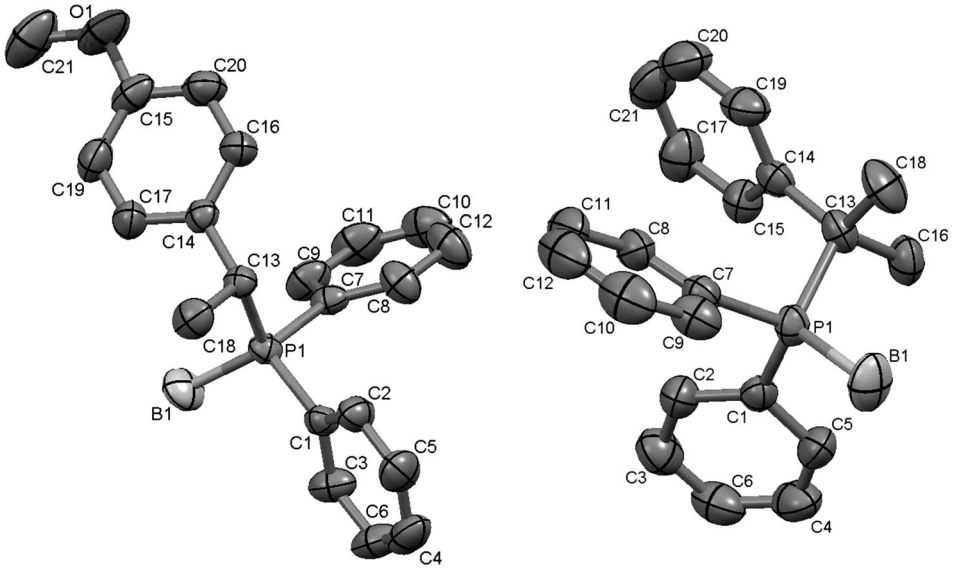


Figure 1. X-ray structures of **3b**·BH_3 (left) and **3h**·BH_3 (right).

The scope of the $FeCl_3$-catalyzed α-hydrophosphination process was evaluated (Table 3) at temperatures between 60 and 90 °C. Compared to the $FeCl_2$ promoted formation of β-adducts, the substituents of double bond play a less important role in the α addition. Indeed, the hydrophosphination adducts of α-methylstyrene, 1,1-diphenylethene and α-methyl-*p*-methylstyrene were formed in very good yields (90 to 100 % ^{31}P NMR yield; Table 3, entries 7–9). On the other hand, the electronic effects play a major role. Whereas electron-donating groups are well tolerated (entries 2–4), electron-withdrawing groups seem to inhibit the hydrophosphination process (conversion < 5 %, entries 5–6). This tendency is in agreement with the results reported for the hydroamination of styrenes with $FeCl_3$.[16c] Interestingly, when monosubstituted alkenes were used (entries 1–4), the temperature could be lowered to 60 °C. The possibility of lowering the catalyst loading to 0.1 equiv was checked with substrate **1b**. After 12 h, the conversion to **3b** was only 42 %. Because extending the reaction time may favor the thermal formation of the β adduct (Table 1, Entry 1), a catalyst loading of 0.3 equivalents appears more convenient for the formation of the α adduct.

Single-crystals of the addition products **3b**·BH_3 and **3h**·BH_3 obtained with *p*-methoxystyrene and α-methylstyrene, respectively, were grown by slow diffusion of pentane into a CH_2Cl_2 solution. X-ray structures furnished the definitive proof of the α addition (Figure 1).

The difference encountered in the scope and limitation of the two processes clearly indicates a potential difference in mechanism. From a general point of view, the observation of the α regioisomer in the hydrophosphination process is rare in the literature, regardless of the substrates involved. Only stoichiometric amounts of a strong acid (CH_3SO_3H) in harsh conditions were reported to allow the formation of the α adduct.[8] By analogy, HCl, which could be released by $FeCl_3$, may be responsible for the transformation. However, replacing $FeCl_3$ by HCl[28] under other similar conditions led to poor conversion of the alkenyl arenes (as an example, with 1,1-diphenylethene, less than 7 % of the expected α adduct was formed).

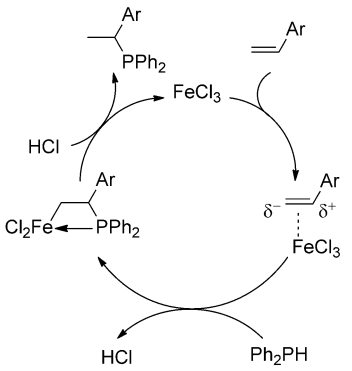
Impurities in $FeCl_3$ could also be suspected to promote the addition reaction, notably copper oxide traces.[29] Thus, metal contaminants ($MnCl_2$, $ZnCl_2$, $CuCl_2$, Cu_2O) commonly found in $FeCl_3$ were tested in the reaction under the optimized conditions and none are efficient promoters of the formation of the α adduct (see Table 4, entry 1 and the Supporting Information). Moreover, whatever the quality of $FeCl_3$ (Table 4, entries 2–4), similar results were obtained.

Table 4. Influence of the quality of $FeCl_3$ on the α hydrophosphination of 1,1 diphenylethene[30] to form compound **3i**.[a]

	Catalyst	Ph_2PH Conv. [%][b]	α adduct[b]
1	Cu_2O	25	1
2	$FeCl_3$ (98 %)	100	94
3	$FeCl_3$ (99.99 %)	100	92
4	$FeCl_3 \cdot 6\,H_2O$	93	81

[a] Reaction conditions: $FeCl_3$ (0.3 equiv), CH_3CN, Ph_2PH (1 equiv), 1,1-diphenylethene (2 equiv), 60 °C, 20 h. [b] ^{31}P NMR yield.

Although the mechanism of the original α addition is still under investigation, the scope of the reaction can give some clues. A likely catalytic cycle would start from the initial activation of the double bond of the alkenyl arene by the Lewis acid ($FeCl_3$) leading to a polarized π complex (or transient carbocation), which is stabilized by electron-donating substituents. Subsequent addition of diphenylphosphine to the activated double bond and release of hydrogen chloride could be the next step. Lastly, protonation of the carbon



Scheme 3. Plausible reaction mechanism for the $FeCl_3$ catalyzed α hydrophosphination of alkenyl arenes.

metal bond would lead to the formation of the final product and would release the initial iron complex (Scheme 3).

The fact that only $FeCl_3$ and not $FeCl_2$ is able to promote the α addition is not clear. Nevertheless, the difference in Lewis acidity of these iron salts can probably account for this difference.[31] With regard to the formation of the β adduct, iron(II) could simply favor a radical process through activation of traces of O_2.[21] Addition of a radical inhibitor such as *tert*-butylcatechol or performing the reaction in the dark lowered the yield by 20 to 30%, but did not fully suppress the reaction. Similar tests performed in the presence of $FeCl_3$ did not affect the course of the reaction. Thus, at this stage, it is difficult to draw concrete conclusions. Rationalization of these experimental results is currently in progress.

In conclusion, we have developed an iron-promoted hydrophosphination of alkene derivatives with diphenylphosphine as the phosphinating agent. Compared to other hydrophosphination methodologies, our approach uses a low-cost and low-toxicity transition metal and offers highly selective access to both the α and the β adducts just by selecting the nature of the iron salt ($FeCl_3$ or $FeCl_2$ respectively). Unprecedented access to the α adduct through substrate independent regioselectivity has also been achieved. Extension of this methodology to various substrates other than styrenes and to asymmetric reactions is currently under investigation, as well as a deeper study of the mechanism of the two processes.

Experimental Section

Typical procedure: $FeCl_3$-catalyzed α hydrophosphination of styrene (**1a**) with diphenylphosphine (Table 3, entry 1): Styrene (**1a**, 120 μL, 1.04 mmol) and diphenylphosphine (100 μL, 0.57 mmol) were successively added to a solution of $FeCl_3$ (30 mg, 0.18 mmol) in acetonitrile (150 μL). The reaction mixture was then heated at 60°C for 12 h. After cooling to 0°C, $BH_3{\cdot}SMe_2$ (63 μL, 0.7 mmol) was added dropwise and the reaction mixture stirred at RT for 30 min. Volatiles were eliminated under reduced pressure then the crude product was purified by silica gel chromatography with a CH_2Cl_2/pentane mixture (2:3) as eluent. Diphenyl-(1-phenyl-ethyl)phosphine borane (**3a**·BH_3) was isolated as a colorless oil (129 mg, 0.42 mmol) in 73% yield.

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Keywords: alkenes · hydrophosphination · homogeneous catalysis · iron · phosphanes · regioselectivity

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Hydrophosphination

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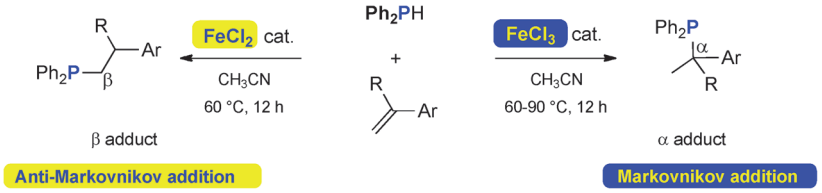
Iron-Salt-Promoted Highly Regioselective α and β Hydrophosphination of Alkenyl Arenes



Iron(ic) phosphination: The iron-promoted hydrophosphination of alkenyl arenes with diphenylphosphine as phosphinating agent has been established. This method provides efficient access to diarylalkylphosphines. The regioselectivity of the reaction can be fine-tuned by the choice of the iron salts, offering highly selective access to both the β and the α adducts (see scheme).