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Copper(I)-catalyzed hydrophosphination of styrenes

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ABSTRACT

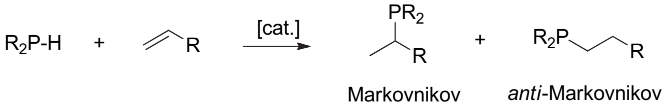
Hydrophosphination of styrenes has been accomplished with metal salts for the first time. $(CuOTf)_2\cdot$toluene complex is the catalyst of choice, but CuCl can also be used. “In-situ” EPR and NMR studies suggest Cu(I) as the catalytically active metal species, giving exclusively the *anti*-Markovnikov product. Phosphine oxides or β-ketophosphine oxides can be prepared in one-pot by oxidation with molecular oxygen.

1. Introduction

Addition of X–H bonds (X = carbon, heteroatom, semi-metallic or metallic) across unsaturated C–C bonds is a 100% atom-economical reaction that fits the requirements of modern sustainable chemistry [1–3]. In particular, phosphines R_2P-H add to alkenes to give tertiary alkyl phosphines, useful as ligands and intermediates in organic synthesis (Scheme 1) [4,5].

The addition proceeds usually in *anti*-Markovnikov way. The reaction can be carried out in the presence of a strong base in stoichiometric amount but a catalytic process is always preferred provided that acceptable conversion and selectivity are achieved. Radical initiators such as AIBN are generally used as catalyst [4a]. Lewis acids could also act as catalyst but, unfortunately, examples are scarce [6–8]. Only two metallic systems based on ytterbium [6] and nickel complexes [7] have been successfully employed for the metal-catalyzed intermolecular hydrophosphination of unactivated alkenes while organolanthanide species can act as catalysts for the intramolecular process [8]. All these metallic catalysts are quite expensive and toxic and, in some cases, operate under harsh conditions [7]. Therefore, there is not still a simple metal salt that catalyzes the hydrophosphination of alkenes. Furthermore, the use of a metal could allow designing heterogeneous catalysts for a fully sustainable system.

First-row transition metals have attracted the interest of chemists in the last years for their use in catalysis, since new or old coinage-metal-catalyzed reactions can now be accomplished. In contrast to second- and third-, first row transition metals are inexpensive, non-toxic and environmentally friendly. In particular, iron [9] and copper [10] have regained attention for their ability to activate unsaturated C–C bonds. During the course of our investigations in the iron(III)-catalyzed dimerisation of styrenes [2], we found that Fe(III) coordinates so poorly to triphenylphosphine that liquid ^{31}P NMR measurements of the complex $FeCl_3(PPh_3)_2$ only recorded the peak for free PPh_3 ($\delta = -6$ ppm), regardless the solvent used. In contrast, ^{31}P MAS-CP solid NMR of the solid gave the expected downshifted signal for the coordinated phosphine ($\delta = 336$ ppm). Although variable temperature experiments in solution should be performed to confirm the stability of the complex, results infer that Fe(III) hardly interacts with phosphines



Scheme 1. Hydrophosphination of alkenes.

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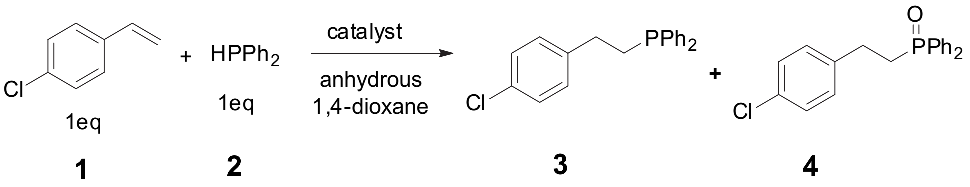


Scheme 2. Hydrophosphination of 4-chlorostyrene **1** with diphenylphosphine **2**.

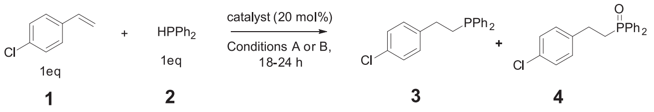
in solution and, given the high affinity of phosphines to bound (and poisoning) coinage metals, we envisage Fe(III) and, by analogy, highly cationic first-row transition metals, could act as alternative catalysts to coinage metals for those reactions were phosphines are used as reactants, it is the case for the hydrophosphination of alkenes. Therefore, we carried out an extended study on the addition of phosphines to alkenes catalyzed by different metal salts. We can anticipate that, although unfortunately Fe(III) salts do not work as catalysts, other metal salts do work. Finally Cu(I) was found the catalyst of choice in terms of activity, non-toxicity and price.

2. Results and discussion

2.1. Formation of tertiary phosphines

The hydrophosphination of 4-chlorostyrene **1** with diphenylphosphine **2** was used as reaction test (Scheme 2).

Table 1
Hydrophosphination of 4-chlorostyrene **1** with diphenylphosphine **2** in the presence of different metal species. Conditions: A) anhydrous DMF (2 M), 140 °C; B) anhydrous 1,4-dioxane (2 M), 100 °C. If not specified, the triflate salts are not preformed but pure compounds.



Entry	Conditions	Catalyst	Conversion (%)[a]	**3** (%)[a]	**4** (%)[a]
1	A	non-catalyzed	10	5	–
2		$Cu(OTf)_2$	100	95	–
3		$CuCl_2$	81	71	4
4		$Fe(OTf)_3$	60	40	–
5		$FeCl_3$	25	–	–
6	B	non-catalyzed	88	51	7
7		$Cu(OTf)_2$	81	72	9
8		$CuCl_2$	77	61	17
9[c]		**$(CuOTf)_2$·toluene**	**100**	**95**	–
10[b]			92	87	–
11[c]			96	77	6
12[d]			64	50	4
13		CuCl	100	77	6
14		$FeCl_3$	40	7	6
15[e]		$Fe(OTf)_3$	87	70[e]	5
16		$Fe(NTf_2)_2$	39	33	–
17		Ag_2CO_3	72	32	–
18		AgOTf	91	86	–
19[f]		$MnCl_2 \cdot 4H_2O + 2AgOTf$	100	80	5

[a] NMR yield, double-checked with GC-MS yield. Both techniques differentiate quantitatively **3** and **4**.

[b] Run with 10 mol% of catalyst.

[c] catalyst 5 mol%.

[d] 0.5 mol%.

[e] 26% of **3** corresponding to another isomer, assigned by GC-MS to the Markovnikov product.

[f] Catalyst pre-formed by stirring at rt during 30 min before addition of reactants.

Preliminary catalytic results for different metal salts in dioxane at 80 °C are shown in Table S1. It was found that $PdCl_2$, $Ru(OTf)_3$ and $FeCl_3$ (entries 2–4) did not give any conversion to products. However, the exchange of chlorides in $FeCl_3$ with triflate or triflimide anions significantly improves the yield to the hydrophosphination product **3** and the phosphine oxide **4** (entries 5, 6) [11,12]. Iron(III) works better than iron(II) (compare entries 5 and 7). The $Fe(OTf)_3$-catalyzed hydrophosphination of **1** with **2** (entry 5) was followed in d^8-dioxane by in-situ ^1H, ^{13}C, ^{31}P and DEPT, NMR spectroscopy. The NMR measurements showed that **3** is a primary product and **4** was formed later. However, when a high purity $FeCl_3$ (99.99%) was exchanged with triflate anions and used as catalyst, the yield to **3** and **4** dropped to the blank level (entry 8). This result suggests that iron is not the real catalyst but impurities of other metals, copper being a plausible candidate [13]. Indeed, copper(II) salts give similar or even better yields to **3** and **4** than the corresponding iron species, $Cu(OTf)_2$ in particular (entries 9–11). Brønsted acid catalysis proceeds in low extent (entry 12) but silver(I) [3,14] works well (entries 13, 14). Anyway, a second series of experiments were carried out, increasing the amount of metal catalyst, reaction temperature and reactants concentration (Table 1).

1,4-Dioxane (at 100 °C) is better reaction medium than DMF (at 140 °C) for the reaction (compare entries 1 and 6) [2] but, nevertheless, $Cu(OTf)_2$ showed complete conversion and selectivity for **3** in DMF (entry 2). $CuCl_2$ also gave a good conversion and selectivity (entry 3) and the corresponding Fe(III) catalysts worked poorly (entries 4, 5). In dioxane, a slight decrease in activity was observed

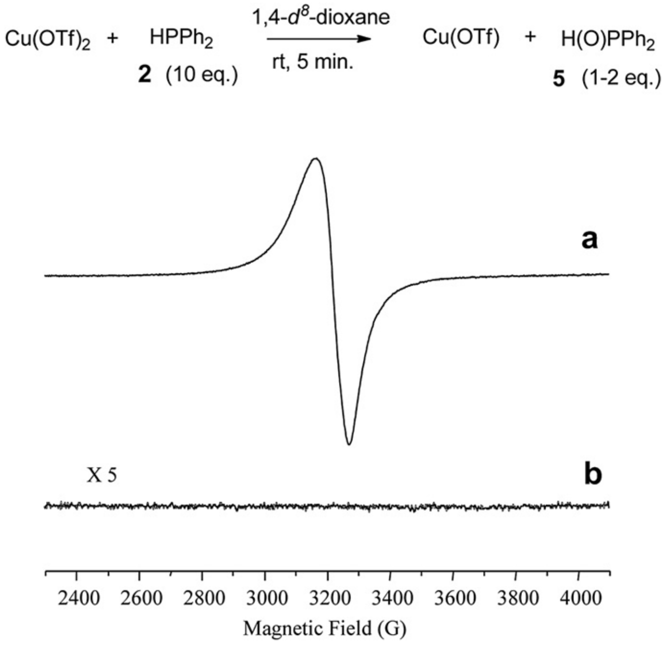


Fig. 1. EPR spectra of $Cu(OTf)_2$ in dioxane (a) before and (b) after addition of **2** at room temperature.

for the copper(II) salts (entries 7, 8). At this point, we performed in-situ EPR and NMR experiments of the catalytic system $Cu(OTf)_2$/dioxane (Fig. 1). The EPR spectrum of $Cu(OTf)_2$ shows a paramagnetic signal corresponding to Cu(II). The signal disappears after the addition of **2** at room temperature, the product **5** being concomitantly formed as indicated by ^{31}P NMR spectroscopy (signal at ~20 ppm). These data suggest that the formation of Cu(I) and **5** is the result of a redox process between $Cu(OTf)_2$ and **2**. In this sense, it has been reported that $In(C_5H_5)_3$ and **2** react to produce the corresponding $In(C_5H_5)$ complex and $Ph_2P\text{-}PPh_2$ as oxidation product [15,16]. Therefore, EPR experiments show that Cu(I) should be the true catalyst in the phosphination reaction.

Accordingly, $(CuOTf)_2 \cdot$toluene and CuCl showed an excellent activity as catalysts for the hydrophosphination of **1** with **2** (Table 1, entries 9–13) even at room temperature (entry 10) [17]. Iron salts worked poorly in general (entries 14–16) but, curiously, an isomer of **3** was obtained in significant amount (entry 15). GC-MS and ^{31}P NMR suggests that this isomer could be the Markovnikov product, in accordance with the superior ability of Fe(III) to activate benzylic positions [2,18]. Anyway, $FeCl_3$ and Fe(II) worked poorly again (entries 14 and 16) as catalyst. Although, perhaps, Fe(III) could be a real catalyst under these new reaction conditions, it cannot be concluded. Silver triflate worked well as catalyst (entry 17), although was less effective than Cu(I) (compare entries 9 and 17). Silver carbonate did not work.

ICP-AES analysis of $Fe(OTf)_3$ and $Fe(NTf_2)_2$ [2,19] were performed (Table 2) and they shows that the copper and silver impurities are extremely low in both salts. Mn(II), the main metal impurity of $Fe(OTf)_3$ by ICP-AES analysis and detected by EPR measurements (six signals with relative intensity 1:1:1:1:1:1 at $g = 2.0066$ and hyperfine coupling constant of 96G, $I_{Mn} = 5/2$), and not present in $Fe(NTf_2)_2$, also works as catalyst but worse than Cu(I) (compare entries 9 and 19). Therefore, results point out to $(CuOTf)_2 \cdot$toluene as the catalyst of choice. The amounts of **4** are low in all cases. Compounds **3** and **4** were isolated in order to assure the correctness of NMR assignations, since both products have only slight differences [20].

The scope of the Cu(I)-catalyzed hydrophosphination of alkenes was then studied (Table 3). Styrenes **1**, **6**–**11** react well with **2** to afford exclusively the *anti*-Markovnikov product in good to excellent yields, regardless their electronic nature (compare entries 1–5) or the position of the substituent on the ring (entries 6, 7). ^1H- and ^{31}P NMR yields fit, confirming that no polymerization of the styrene derivative occurs under the reaction conditions.

Disubstituted alkenes react sluggishly (entries 8 and 9) or do not react at all (entry 10). 1-Octene **15** also reacts poorly (entry 11). However, dialkyl phosphine **16** reacts with styrene derivatives in moderate yields (entries 12, 13) and no oxidized product were observed [20]. Finally, when both counterparts are alkylic, no reaction is observed (entry 14).

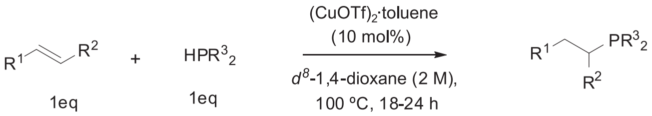
Table 2
ICP-AES analysis of the salts $Fe(OTf)_3$ and $Fe(NTf_2)_2$.

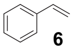
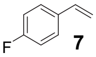
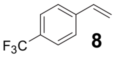
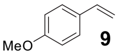
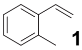
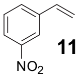
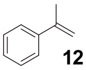
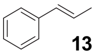
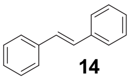
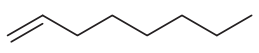
Metal	$Fe(OTf)_3$		$Fe(NTf_2)_2$	
	wt% (x 10^4)	% respect to Fe	wt% (x 10^4)	% respect to Fe
Fe	108727	100	110591	100
Mn	377	0.35	5	–
Na	294	0.27	854	0.77
In	170	0.16	246	0.22
Al	69	0.06	105	0.09
Cu	27	0.03	9	–
Ga	7	–	<1	–
Co	1	–	<1	–
Zn	<1	–	792	0.71
Ag	<1	–	<1	–
K	<1	–	1939	1.75

2.2. Formation of phosphine oxides

Shifting the selectivity from the phosphine **3** to the phosphine oxide **4** would be of interest since phosphine oxides have biological

Table 3
Scope and limitations of the hydrophosphination of alkenes catalyzed by $(CuOTf)_2 \cdot$toluene complex.



Entry	Alkene	Phosphine	Product yield (%)[a]
1[b]	**1**	Ph_2PH **2**	95 [83]
2	 **6**		92/83
3	 **7**		98/92 [72]
4	 **8**		85/88
5	 **9**		>99/>99 [80]
6	 **10**		83/89
7[b, c]	 **11**		87
8	 **12**		19
9[d]	 **13**		16
10[e]	 **14**		<5
11[e]	 **15**		16
12[b]	**1**	Cy_2PH **16**	62
13[e]	**9**		29
14[e]	**15.**		<5

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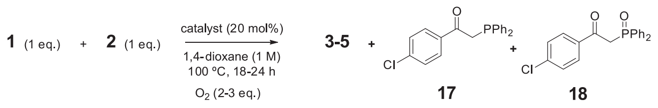
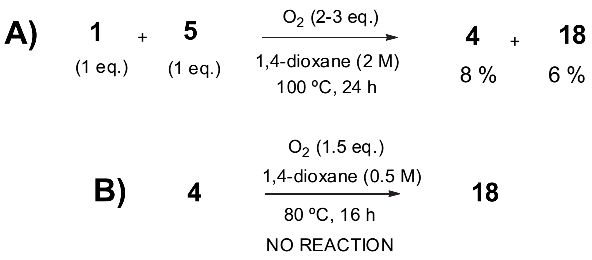
[a] ^{31}P NMR/^1H NMR yields; between brackets, isolated yields.
[b] ^{31}P NMR yield, confirmed by GC-MS.
[c] 72% phosphine oxide product.
[d] ^1H NMR yield, confirmed by GC-MS.
[e] ^{31}P NMR yield.

Table 4
Metal-catalyzed hydrophosphination of 4-chlorostyrene **1** with diphenylphosphine **2** under an oxygen atmosphere.



Entry	Catalyst	Conversion^a	**3**^{a}	**4**^{a}	**5**^{a}	**17**^{a}	**18**^{a}	Others^a
1	$(CuOTf)_2$·toluene	100	–	69	–	27	4	–
2^b	$Fe(OTf)_3$	100	20	13^b	–	20	18	29
3	non-catalyzed	100	–	5	12	13	50	20

[a] GC-MS yield.
[b] Tentatively assigned to the Markovnikov addition product.



Scheme 3. Study on the formation of the β-ketophosphine oxide **17**.

and medicinal properties [21,22]. Although secondary phosphine oxides can add directly to alkenes (hydrophosphorylation) [21,23,24], the corresponding phosphines are usually less expensive. Thus, the metal-catalyzed hydrophosphination of **1** with **2** was performed under a stoichiometric amount of O_2 to oxidise in-situ **3** to **4** (Table 4).

Indeed, the use of $(CuOTf)_2$·toluene in catalytic amount allows obtaining the phosphine oxide **4** in good yields, although benzylic oxidation to form **17** competes to some extent (entry 1). β-Ketophosphine oxide **18** is formed in the presence of $Fe(OTf)_3$ (entry 2) and also under non-catalyzed conditions (entries 2, 3), although the product distribution is different. The synthesis of β-functionalized alkyldiaryl phosphines is of interest [25] and β-ketophosphine oxides have been studied by the Warren's group and others and are useful intermediates for the preparation of ketones [26,27], asymmetric cyclopropanations [28], electrophile addition [29] and more [30]. We were wondering if **18** comes from a double oxidation of **3** (in accordance to the in-situ NMR experiments, see entry 5 in Table S1) or, alternatively, from a possible addition of $Ph_2P(O)H$ **5** to **1**, to form **4**, and later benzylic oxidation occurs, since Hirai and Han have reported an air-induced hydrophosphorylation to alkenes [23]. Phosphine oxide **5** would be formed in-situ from the oxidation of **1**. To check these hypotheses, two new experiments were carried out (Scheme 3).

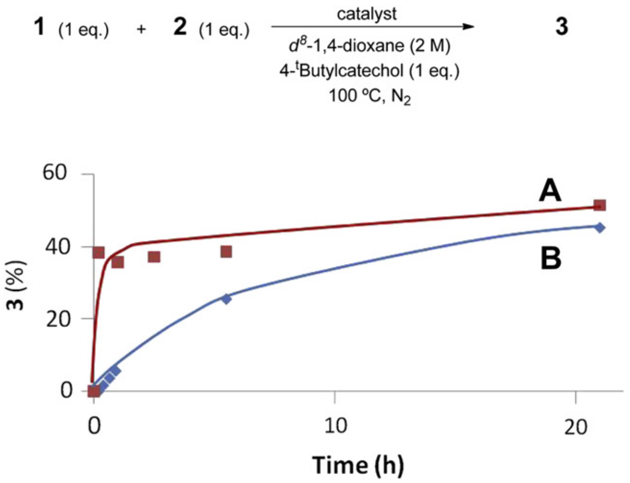
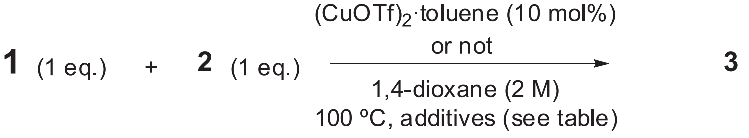


Fig. 2. Kinetic plot-yield for the hydrophosphination of **1** with **2** in the presence (A) or not (B) of $(CuOTf)_2$·toluene (20 mol%).

The reaction of **1** with **5** was performed under similar conditions to those in Table 4 (Scheme 3, A). The hydrophosphorylation of **1** only proceeds in minor extent, showing that **18** does not come from a previous addition of **5** to **1** [23]. Moreover, **4** was completely recovered after treatment with oxygen (Scheme 3, B), which also discards a benzylic oxidation of **4**. The oxidation of phosphines [31] is a more favoured process than the benzylic oxidation under non-

Table 5
Hydrophosphination of 4-chlorostyrene **1** with diphenylphosphine **2** under different reaction conditions.



Entry	$(CuOTf)_2$·toluene	Catechol (eq.)	Comments	Conversion (%)^a	Product 3 (%)^b
1	No	–	Standard conditions	77	54/62
2	Yes	–	N_2 + deaerated solvent	85	75/73
3	No	–		73	58/73
4	Yes	1	Darkness + radical inhibitor	47	36/38
5	No	1		60	40/45
6	Yes	–	Darkness + deaerated solvent	87	78/73
7	No	–		66	47/63
8	Yes	1	Radical inhibitor	94	81/90
9	No	1		53	33/36
10	Yes	3		40	24/22
11	No	3		30	16/22
12	Yes	1	D_2O (1 eq.) + radical inhibitor	82	60/57
13	No	1		62	42/38

[a] ^{31}P NMR conversion.
[b] $^{31}P/^{1}H$ NMR yields.

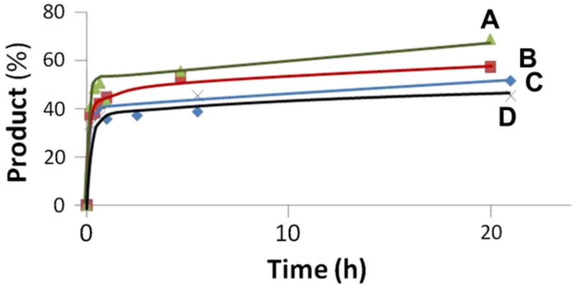


Fig. 3. Kinetic plot-yield for the hydrophosphination of the styrene derivatives **9** (A), **6** (B), **1** (C) and **8** (D) with **2** in the presence of $(CuOTf)_2$·toluene (20 mol%) For reaction conditions see Fig. 2.

catalyzed conditions, so the formation of **18** from **17** seems quite disfavoured. Thus, we can only speculate about a radical mechanism promoted by molecular oxygen.

2.3. Insights into the mechanism

In order to elucidate if copper(I) is active as a catalytic Lewis acid or is simply activating traces of O_2 for radical catalysis [23], a set of experiments were carried out (Table 5 and Figs. 2 and 3). d^8-1,4-dioxane was employed as solvent to avoid any further manipulation.

Degassing of the solvent, reaction under darkness, use of 4-tert-butylcatechol as radical inhibitor or combination of these conditions lead generally to a decrease in the conversion and product yield. Remarkably, if Cu(I) was used as catalyst, the yield is systematically 20–40% higher (compare entries 1–11). Addition of water (as D_2O) has a minor influence on the reaction (compare entries 8, 9 and 12, 13). Kinetic experiments were then carried out (Figs. 2 and 3). It can be clearly seen that the presence of Cu(I) in the reaction medium (containing the radical inhibitor) boosts the initial rate of the reaction in nearly two orders of magnitude (TOFs: 9.5 h^{-1} vs 0.3 h^{-1}), giving a better final yield.

The influence of the electronic nature of the substituent on the aryl ring of the styrene derivative was also studied (Fig. 3), showing that electron-donor groups accelerate the reaction while electron-withdrawing groups retard it.

These results suggest a charged intermediate in the transition state, which would also confirm the catalytic activity of Cu(I) as Lewis acid. When representing the initial rates in a Hammett plot the correlations are not lineal for any value of σ, which infers than contribution to the reaction state of the radical pathway occurs concomitantly.

3. Conclusions

The first metal salt-catalyzed hydrophosphination of styrenes has been accomplished. $(CuOTf)_2$·toluene is the catalyst of choice, although the more stable CuCl can also be used. The Cu(I) active species is generated from $Cu(OTf)_2$ by a redox reaction with the phosphine. Mn(II) and Ag(I) are also active catalysts. The *anti*-Markovnikov products are exclusively formed in good yields. Phosphine oxides and β-ketophosphine oxides can be formed with molecular oxygen by adding or not $(CuOTf)_2$·toluene in catalytic amounts. Kinetic studies show that the electronic density of the ring influences the rate of the reaction.

4. Experimental

Typical hydrophosphination procedure (Tables 1–3, see details in Supplementary material data). $(CuOTf)_2$·toluene complex (51.4 mg, 10 mol%) was placed in a 1.5 mL vial and anhydrous 1,4-dioxane (0.25 mL), 4-chlorostyrene **1** (60.0 μL, 0.5 mmol) and diphenylphosphine **2** (86.0 L, 0.5 mmol) were sequentially added. The vial was sealed and the mixture was placed in a pre-heated oil bath at 100 °C and magnetically stirred for 18–24 h. An aliquot was taken for GC-MS and the rest was concentrated under reduced pressure, re-dissolved in $CDCl_3$ and analysed by NMR. When d^8-1,4-dioxane was used, the mixture was directly analysed by NMR. For isolation, the mixture was passed through a pad of silica, eluted with diethyl ether and the volatiles were removed under vacuum. When the products were chromatographied on silica under nitrogen, a meaning loss of yield was observed (nearly 70% from the expected by NMR). ^{31}P assignments (δ, ppm, H_3PO_4 as reference): −41 (**2**) [32], −10.3 (**3**, isolated, see Supplementary material data) [25], +31.7 (**4**, isolated, see Supplementary material data), +18 (**5**) [33], +26.8 (**17**, isolated, see Supplementary material data) [26], +25.8 (PH_2POOH) [17], −13.6 (Ph_2P-PPh_2) [15]. For those experiments where iron or manganese catalysts were used, the mixture was passed through a pad of silica (AcOEt/ether (20 vol%) as eluent) after the reaction. *With degassed solvent*: d^8-1,4-dioxane was degassed by bubbling dry N_2 during 15 min. *Under darkness*: the vial was wrapped with aluminium foil. *With radical inhibitor*: 4-*tert*-butylcatechol was added together with the catalyst.

Under oxygen atmosphere: the reaction was performed at half-scale in a double-walled conical 2 mL vial equipped with a sealable cap and connected to a manometer. Oxygen was purged three times at room temperature and finally loaded to 5–6 atm. (0.6 mmol, 2.2 eq.). After reaction, the oxygen was removed and the mixture analysed as above.

Kinetics. $(CuOTf)_2$·toluene complex (128 mg, 20 mol%) and 4-*tert*-butylcatechol (415.5 mg, 2.5 mmol) were placed in a 10 mL round-bottomed flask. Air was evacuated under vacuum and nitrogen was introduced. A septum rubber was finally fitted with a N_2 balloon and anhydrous 1,4-dioxane (1,25 mL), the corresponding styrene derivative (2.5 mmol) and diphenylphosphine (430 μL, 2.5 mmol) were added by syrinnge. The mixture was placed in a pre-heated oil bath at 100 °C and magnetically stirred. Aliquots of 0.15 mL were periodically taken, cooled with 0.5 mL of $CDCl_3$ and analysed by ^{31}P NMR.

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Appendix A. Supplementary material data

General methods, characterisation and NMR copies of compounds **3**, **4** and **17**. Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.09.069.

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