



Acenaphthene-1-carboxylic acid methyl ester by palladium-catalyzed chemoselective hydroesterification of acenaphthylene

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Abstract

The hydroesterification of acenaphthylene with carbon monoxide and methanol, catalyzed by Pd^{II}/PR₃ systems (PR₃ = PPh₃, P(*o*-MeC₆H₄)₃, P(*p*-MeC₆H₄)₃, P(*p*-FC₆H₄)₃, P(^{*t*}Bu)₃, PEt₃, PCy₃, P(OEt)Ph₂, P(OPh)₃, P(O-*o*-MeC₆H₄)₃, P(O-*o*-^{*t*}BuPh)₃, dppm, dppe, dppp, dppb, 1,1'-bis(diphenylphosphino)ferrocene (dppf), rac-BINAP) has been studied, the reaction yields a mixture of acenaphthene-1-carboxylic acid methyl ester **1**, 1-methoxyacenaphthene **2** and polyacenaphthylene **3**. For Pd/monophosphine/*p*-TsOH precursors, only ligands with intermediate electronic and steric properties formed active catalytic systems with satisfactory chemoselectivities. These systems are highly influenced by the reaction conditions, as the methanol concentration and the Pd/*p*-TsOH ratio, yielding conversions up to 85% with a chemoselectivity in ester **1** of 93%. When diphosphines were used as auxiliary ligands, less efficient catalytic systems were produced and their characteristics can be attributed to the electronic properties of the ligands, yielding conversions up to 60% and chemoselectivities in ester **1** of 85%.

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1. Introduction

The transition metal complex catalyzed hydroesterification of arylenes with carbon monoxide and an alcohol yields esters of valuable 2-arylpropionic acids [1–4], such as ibuprofen [5] and naproxen [6,7], which belong to an important class of non-steroidal anti-inflammatory drugs (NSAIDs) [8].

Catalytic systems for alkoxyacylation of olefins based on palladium are investigated because of their activity and selectivity [9]. Several neutral and cationic palladium(II) precursors have been used in the hydroesterification of arylenes, showing that activities and selectivities are very strongly dependent on the precise catalytic system employed and the reaction conditions used [10–23]. With regard to the reaction mechanism, two different routes are considered [9]. The metal hydride route involves olefin insertion into the Pd–H bond followed by CO insertion into the Pd–alkyl bond. The nucleophilic attack of the alcohol on the metal acyl yields the ester product

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[24]. Alternatively, in the alkoxy-carbonyl mechanism the formation of a palladium–alkoxy-carbonyl complex is postulated, the olefin is then inserted into the Pd–carbon bond and protonolysis of the metal–alkyl bond gives the corresponding ester [11]. Although these two mechanisms are claimed to be operative depending on the reaction conditions and substrates [25], the metal hydride route is the most widely accepted [26–29].

Acenaphthene-1-carboxylic acid is a molecule with potential applications related to its biological activity as the acid part of amides with powerful analgesic properties or as a plant growth factor [30–32]. However, acenaphthene-1-carboxylic acid is available through stoichiometric routes in a series of synthetic steps with rather low atom economy [33–37]. Catalytic hydroformylation with rhodium has been used to obtain acenaphthene-1-carboxaldehyde, but the oxidation to the target acid required three extra steps [38–41]. We have shown catalytic hydrocarboxylation of technical acenaphthylene from coal to be the simplest and cheapest method to obtain acenaphthene-1-carboxylic acid [42]. Nevertheless, the chemoselectivity of the reaction (15–85%) is penalized by the production of polymeric byproducts. The related hydroesterification reaction should be a catalytically alternative, albeit synthetically equivalent process. Classified as a reaction analogous to the water-consuming hydrocarboxylation, hydroesterification uses alcohols. From the standpoint of the palladium center where the important steps of the reaction take place, the use of alcohols constitutes a substantial variation with practical implications, because the redox and coordinating properties of alcohols differ substantially to those of water.

2. Experimental section

2.1. Materials

PdCl_2 , $\text{Pd}(\text{OAc})_2$, PPh_3 , $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(i\text{Bu})_3$, PEt_3 , PCy_3 , $\text{P}(\text{OEt})\text{Ph}_2$, $\text{P}(\text{OPh})_3$, $\text{P}(O\text{-}o\text{-MeC}_6\text{H}_4)_3$, dppm , dppe , dppp , dppb , 1,1'-bis(diphenylphosphino)ferrocene (dppf), rac-BINAP , p -toluenesulfonic acid ($p\text{-TsOH}$) and CO (4.7) were commercially obtained and used without further purification. Reaction solvents were dried by standard

methods, distilled and deoxygenated before use. Complexes $[\text{PdCl}_2(\text{PPh}_3)_2]$ [43,44] and $[\text{PdCl}_2(\text{PhCN})_2]$ [45,46] were prepared by established procedures. Commercial technical acenaphthylene is of variable quality, containing acenaphthene (15–30%) and some tars. This acenaphthylene was recrystallized in hexane before use. Typically, the recrystallized material has an acenaphthylene content between 88 and 92%, the rest being acenaphthene and uncharacterized materials (2% by GC).

2.2. Analytical procedures

Proton NMR spectra were recorded at 400 and 200 MHz on a Bruker ARX-400 and Bruker DPX-200 spectrometers, respectively. Peak positions are relative to tetramethylsilane as internal reference. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on the Bruker DPX-200 instrument operating at 81.0 MHz. Chemical shifts are relative to external 85% H_3PO_4 , with downfield values reported as positive. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on both the instruments operating at 100.6 and 50.32 MHz, respectively. Chemical shifts are relative to tetramethylsilane as internal reference. Infrared spectra of samples in KBr pellets were recorded on a Mattson Satellite FT-IR. Elemental analyses were performed on a Fisons EA-1108 analyzer. Melting points were measured on an Electrothermal IA9100. Gas chromatography analyses were performed on a Shimadzu GC-17A with a Tracer TRB-5 capillary column (30 m length \times 0.25 mm diameter), incorporating a FID detector. The identification of GC peaks was done by GC–MS analyses on a Thermo Quest Trace GC 2000 with a J&W Scientific DB-5 capillary column (30 m length \times 0.25 mm diameter), incorporating a MS detector. Flash chromatography was performed on silica gel 60 A CC. Solvents for chromatography were distilled at atmospheric pressure prior to use.

2.3. Typical procedure for hydroesterification

A solution of acenaphthylene (4 mmol), the metal catalyst precursor (0.04 mmol), and the corresponding amount of PR_3 and $p\text{-TsOH}$ when necessary, was prepared in a mixture of methanol/1,2-dichloroethane (total solvent, 30 ml) under a nitrogen atmosphere and was introduced into an evacuated reactor *Chemipress* (Trallero & Schlee S.L.). The reactor was pressurized

with CO and heated to the reaction temperature. Once the system reached thermal equilibrium, the reaction pressure was adjusted and the stirring started. After each run, the reactor was cooled, its contents were removed and the volatile products analyzed by gas chromatography. The reaction mixture was then filtered to remove the metallic palladium and the solvents were stripped off. The residue was treated with a mixture of hexane/ethyl acetate (9/1) and the insoluble polymer was separated by filtration. The solvent was removed under vacuum to yield product **1**. A sample of purified ester **1** can be obtained by flash chromatography in a mixture of hexane/ethyl acetate (9.5/0.5).

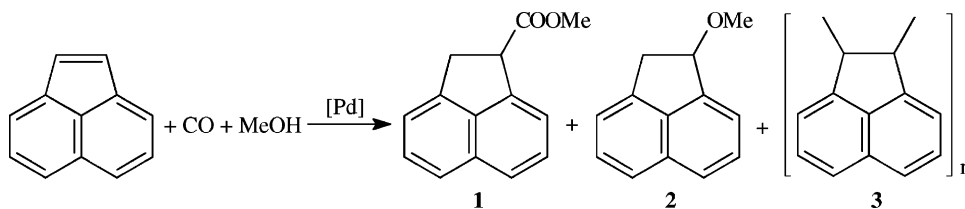
Data for **1** is in agreement with the literature [47]: ^1H NMR (200.13 MHz, CDCl_3 sol.): δ 3.58 (dd, 1H, H^b , $J_{b-a} = 17.6$ Hz, $J_{b-c} = 8.8$ Hz), 3.76 (s, 3H, CH_3), 3.86 (dd, 1H, H^a , $J_{a-b} = 17.6$ Hz, $J_{a-c} = 4.2$ Hz), 4.55 (dd, 1H, H^c , $J_{c-b} = 8.8$ Hz, $J_{c-a} = 4.2$ Hz), 7.2–7.7 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3 sol.): δ 34.16 (s, CH_2 , C_β), 48.35 (s, CH, C_α), 52.33 (s, CH_3), 119.57 (s, CH), 120.32 (s, CH), 122.64 (s, CH), 123.92 (s, CH), 127.79 (s, CH), 128.07 (s, CH), 131.55 (s, C), 138.13 (s, C), 142.11 (s, C), 143.22 (s, C), 173.31 (s, CO). IR (KBr, cm^{-1}): 1738 (ν_{CO}). Analytically found (calculated) for $\text{C}_{14}\text{H}_{12}\text{O}_2$: C, 78.89 (79.22); H, 5.77 (5.70). MS: m/e 212 (M^+ , 90%), 197 ($M^+ - 15$, 5%), 181 ($M^+ - 31$, 2%), 180 ($M^+ - 32$, 4%), 153 ($M^+ - 31-28$, 99%), 152 ($M^+ - 60$, 100%). 1-Methoxyacenaphthene **2** was identified by comparison (GC–MS) with a true sample obtained by alkylation of 1-acenaphthanol with MeI. Data for **2** is in agreement with the literature [47]: ^1H NMR (200.13 MHz, CDCl_3 sol.): δ 3.32 (dm, 1H, H^a , $J_{b-a} = 17.6$ Hz, $J_{a-c} = 2.4$ Hz, $J_{a-\text{Ar}} < 1$ Hz), 3.45 (s, 3H, CH_3), 3.62 (dd, 1H, H^b , $J_{a-b} = 17.6$ Hz, $J_{b-c} = 6.9$ Hz), 5.38 (dd, 1H, H^c , $J_{c-b} = 6.9$ Hz, $J_{c-a} = 2.4$ Hz), 7.2–7.7 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.32 MHz, CDCl_3 sol.): δ 37.79 (s, CH_2 , C_β), 55.79 (s, CH_3), 82.40 (s, CH, C_α), 119.61 (s, CH), 121.07 (s, CH), 122.67 (s, CH), 124.94 (s, CH), 127.74 (s, CH), 127.99 (s, CH), 131.32 (s, C), 137.82 (s, C), 141.86 (s, C), 143.30 (s, C). Analytically found (calculated) for $\text{C}_{13}\text{H}_{12}\text{O}$: C, 84.19 (84.75); H, 6.46 (6.57). MS: m/e 184 (M^+ , 95%), 169 ($M^+ - 15$, 10%), 153 ($M^+ - 31$, 100%). Data for **3**: polyacenaphthylene was identified by comparison (IR and mp) with a true commercial sample. It was obtained as a white ivory powder with melting point in the range of 240–270 °C.

2.4. Preparation of $P(\text{O}-o\text{-}^t\text{BuC}_6\text{H}_4)_3$ and $P(\text{O}-o\text{-MeC}_6\text{H}_4)_3$

The literature procedure for $P(\text{O}-o\text{-}^t\text{BuC}_6\text{H}_4)_3$ [48] was followed for both phosphites with very little modification. For $P(\text{O}-o\text{-MeC}_6\text{H}_4)_3$: phosphorous trichloride (0.05 mmol) was added, to a solution containing the corresponding phenol (0.15 mmol) and N,N' -dimethylaniline (0.005 mmol) in xylene (50 ml), under nitrogen atmosphere and the reaction mixture was heated to reflux for 3 h. The solvent was distilled and the residue was purified by flash chromatography (hexane/ethyl acetate, 9.75/0.25, 22% yield). Data for $P(\text{O}-o\text{-MeC}_6\text{H}_4)_3$: ^1H NMR (CDCl_3 sol.): δ 2.29 (s, 3H), 7.0–7.3 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 sol.): δ 16.59 (s), 120.29 (d, $J_{\text{C-P}} = 10.8$ Hz), 124.03 (s), 126.78 (s), 129.87 (d, $J_{\text{C-P}} = 2.6$ Hz), 131.27 (s), 150.26.53 (d, $J_{\text{C-P}} = 2.3$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 sol.): δ 131.60 (s). Analytically found (calculated) for $\text{C}_{21}\text{H}_{21}\text{O}_3\text{P}$: C, 71.64 (71.58); H, 6.05 (6.01).

3. Results and discussion

Hydroesterification of acenaphthylene with carbon monoxide and methanol catalyzed by palladium complexes yields a mixture of the desired product, acenaphthene-1-carboxylic acid methyl ester **1**, and two byproducts: 1-methoxyacenaphthene **2** and polyacenaphthylene **3** (Scheme 1). Ether **2** is a product of the direct addition of methanol to acenaphthylene and it is also observed in the absence of the catalyst precursor. Conversely, homopolymer **3** was only produced in the presence of palladium complexes, usually in low amounts (<5%), with no other polymeric products such as CO/olefin co-polymers being observed. Although most 1,2-disubstituted alkenes are reluctant to homopolymerization, acenaphthylene is an exception, and homopolymers have been reported as the products of cationic, free radical, and thermal polymerizations [49,50]. The nature of the polymerization and the factors that determine the formation of this byproduct in the tested conditions are still under study. Methanol is the alcohol of choice in hydroesterification because of its high polarity and low bulkiness [23], 1,2-dichloroethane was chosen as a solvent because of its non-coordinating properties and p -toluenesulfonic acid (p -TsOH) was used as an



Scheme 1. Hydroesterification of acenaphthylene.

acid promoter because of the low coordinating ability of its anion [23].

3.1. Pd/PPh₃/*p*-TsOH catalytic system

Preliminary results showed a lower reactivity for this internal, albeit electron-rich olefin compared to standard test substrates of the styrene type, and a high dependency of the activity of the palladium catalyst on the reaction conditions. In this line, a systematic study of the influence of the reaction parameters on the catalytic conversion and chemoselectivity of the acenaphthylene hydroesterification was undertaken. The catalytic system was formed in situ by addition of the corresponding amounts of PPh₃ and *p*-TsOH to the catalyst precursor [PdCl₂(PPh₃)₂] in a mixture of methanol/1,2-dichloroethane in the volume ratio of 1/1 unless otherwise stated.

3.1.1. Effect of *p*-toluenesulfonic acid concentration

The catalyst precursor [PdCl₂(PPh₃)₂] + 2PPh₃ showed low activity in the absence of *p*-TsOH, but high chemoselectivity in hydroesterification product **1** (Table 1). The low catalytic conversion can be related to the formation of palladium methoxycarbonyl species with low activity in the hydroesterification reaction, in the presence of excess methanol [51–53].

Addition of *p*-TsOH to the catalyst precursor up to a *p*-TsOH/Pd ratio of 2.5, caused a significant increase of catalytic activity, mainly in hydroesterification product **1**. Further increase of the *p*-TsOH concentration had an undesirable effect in the amount of side products **2** and **3**. It has been suggested that addition of *p*-TsOH to [PdCl₂(PPh₃)₂] results in the formation of cationic complexes of the type [Pd(PPh₃)_n]²⁺[*p*-TsO[−]]₂, described as the active catalytic species in the hydroesterification reaction [23]. In these cationic species, the charge of the palladium cation is counteracted by weakly coordinating anions (*p*-TsO[−]) and, therefore, the formation of free coordination sites to activate the reactant molecules is more efficient than in the chloro species, [PdCl₂(PPh₃)_n], with more strongly coordinating anions (Cl[−]). In fact, the *p*-TsOH/Pd ratio of 2.5 is, in slight excess, the stoichiometric amount necessary to formally displace all the chlorides to form the cationic species from the [PdCl₂(PPh₃)₂] precursor. In addition, it has also been proposed that *p*-TsOH plays an important role in the regeneration of the active Pd(II) species from any Pd(0) that may be formed by alcohol promoted reduction [23,53,54]. Metallic palladium was observed at the end of most reactions, suggesting that the MeOH/Pd ratio used was excessive from a redox standpoint. In reference to the formation of **2**, direct

Table 1

Effect of the *p*-TsOH/Pd ratio in the hydroesterification of acenaphthylene using [PdCl₂(PPh₃)₂] + 2PPh₃

<i>p</i> -TsOH/Pd ratio	Conversion (%)	1 (%)	2 (%)	3 (%)	Chemoselectivity (%)
0 ^a	28	25	2	1	89
2.5 ^a	40	35	4	1	88
5.0 ^a	45	36	6	3	80

Reaction conditions: acenaphthylene, 4.0 mmol; [PdCl₂(PPh₃)₂], 0.04 mmol; PPh₃, 0.08 mmol; 1,2-dichloroethane, 15 ml; methanol, 15 ml; temperature, 80 °C; CO pressure, 30 bar; reaction time, 24 h.

^a Metallic palladium was observed at the end of the reaction.

Table 2

Effect of the reaction temperature in the hydroesterification of acenaphthylene using $[\text{PdCl}_2(\text{PPh}_3)_2] + 2\text{PPh}_3 + 2.5p\text{-TsOH}$

Temperature (°C)	<i>p</i> -TsOH/Pd ratio	Conversion (%)	1 (%)	2 (%)	3 (%)	Chemoselectivity (%)
60 ^a	0	9	8	1	–	89
80 ^a	0	28	25	2	1	89
100 ^a	0	15	9	5	1	60
60 ^a	2.5	17	16	1	–	94
80 ^a	2.5	40	35	4	1	88
100 ^a	2.5	21	11	8	2	52

Reaction conditions: acenaphthylene, 4.0 mmol; $[\text{PdCl}_2(\text{PPh}_3)_2]$, 0.04 mmol; PPh_3 , 0.08 mmol; 1,2-dichloroethane, 15 ml; methanol, 15 ml; CO pressure, 30 bar; reaction time, 24 h.

^a Metallic palladium was observed at the end of the reaction.

addition of methanol to an olefin is catalyzed by acid [2,18], so that the conversion in ether **2** increased with the increase in *p*-TsOH concentration.

3.1.2. Effect of the reaction temperature and the CO pressure

For catalyst precursor $[\text{PdCl}_2(\text{PPh}_3)_2] + 2\text{PPh}_3$, with or without addition of *p*-toluenesulfonic acid, higher catalytic activity was observed when the temperature was increased from 60 to 80 °C. Further increase of the temperature to 100 °C caused an appreciable decrease in both activity and chemoselectivity (Table 2). The loss of catalytic activity at 100 °C can be related to the lower stability of palladium catalytic systems at higher temperatures [53]. Direct addition of methanol to acenaphthylene was not affected by this thermally promoted deactivation of the catalyst, consequently, the selectivity in ester **1** decreased with temperature. It has been observed that the quantity of PPh_3 present in the reaction mixture also affects the stability of the catalytic system at different reaction temperatures. The effect of CO pressure on the catalytic activity and chemoselectivity

was studied at 18, 30 and 40 bar for the catalyst precursor $[\text{PdCl}_2(\text{PPh}_3)_2] + 2\text{PPh}_3 + 2.5p\text{-TsOH}$. While the conversion in hydroesterification product **1** and the chemoselectivity increased between 18 and 30 bar, a further increase produced a small effect (Table 3). The competition between CO and acenaphthylene for coordination at high pressures can be the cause for the small increase of activity and selectivity observed when the pressure was increased from 30 to 40 bar. In these conditions, stable polycarbonylpalladium species $[\text{Pd}(\text{PPh}_3)_n(\text{CO})_m]^{2+}[p\text{-TsO}^-]_2$ lacking free coordination sites for the substrate molecules can be formed [21].

3.1.3. Effect of PPh_3/Pd ratio

The PPh_3/Pd ratio has been found to have a significant role in catalytic activity and product chemoselectivity using the $[\text{PdCl}_2(\text{PPh}_3)_2] + 2.5p\text{-TsOH}$ catalyst precursor. At 100 °C, the catalytic activity and the selectivity in hydroesterification of product **1** increased steadily with the PPh_3/Pd ratio. In contrast, at lower temperatures both activity and chemoselectivity increased with phosphine content up to a PPh_3/Pd ratio

Table 3

Effect of the CO pressure in the hydroesterification of acenaphthylene using $[\text{PdCl}_2(\text{PPh}_3)_2] + 2\text{PPh}_3 + 2.5p\text{-TsOH}$

CO pressure (bar)	Conversion (%)	1 (%)	2 (%)	3 (%)	Chemoselectivity (%)
18 ^a	22	14	3	5	64
30 ^a	40	35	4	1	88
40	47	42	3	2	89

Reaction conditions: acenaphthylene, 4.0 mmol; $[\text{PdCl}_2(\text{PPh}_3)_2]$, 0.04 mmol; PPh_3 , 0.08 mmol; *p*-TsOH, 0.1 mmol; 1,2-dichloroethane, 15 ml; methanol, 15 ml; temperature, 80 °C; reaction time, 24 h.

^a Metallic palladium was observed at the end of the reaction.

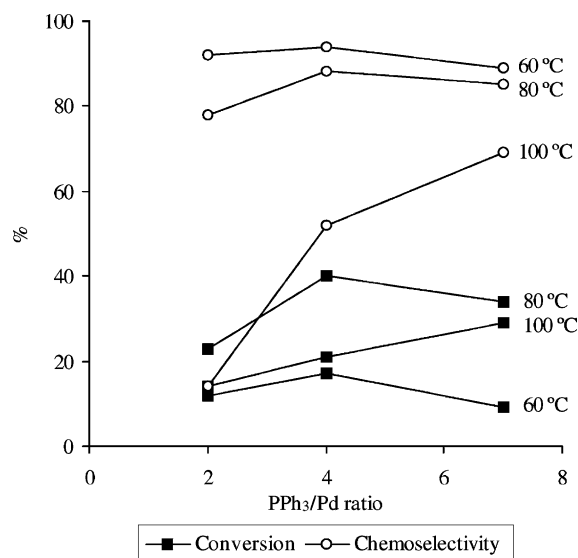


Fig. 1. Effect of the PPh₃/Pd ratio at different temperatures in the hydroesterification of acenaphthylene using [PdCl₂(PPh₃)₂] + 2.5*p*-TsOH. Reaction conditions: acenaphthylene, 4.0 mmol; [PdCl₂(PPh₃)₂], 0.04 mmol; *p*-TsOH, 0.1 mmol; 1,2-dichloroethane, 15 ml; methanol, 15 ml; CO pressure, 30 bar; reaction time, 24 h.

of four, and decreased with further increase of this ratio (Fig. 1). The presence of an excess of PPh₃ is proposed to have two different effects with opposite consequences on the catalytic activity. First, there is the stabilization of the catalytic system in front of thermal and reductive decomposition, this should cause an increase of conversion with the PPh₃/Pd ratio. Second, the use of an excess of auxiliary ligand would produce the deactivation of the catalyst by competition with the reactant molecules for coordination to the metal [23]. At 100 °C, the catalytic system seems to be rather unstable, and the main effect of an excess of PPh₃ is its stabilization. At lower temperatures, both the effects are important and a PPh₃/Pd ratio of four seems to be the best compromise for the acenaphthylene substrate. Direct reaction between acenaphthylene and methanol to give byproduct 2 is independent of the catalytic system.

3.1.4. Effect of methanol concentration

The high methanol concentration (12.3 M) used in the above experiments seems to make the catalytic systems unstable towards the decomposition by

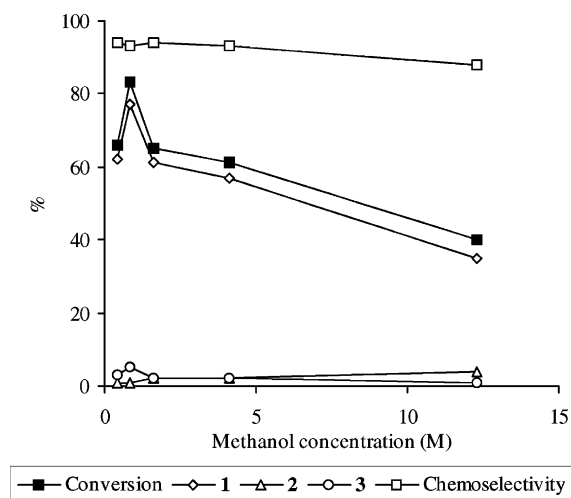


Fig. 2. Effect of the methanol concentration in the hydroesterification of acenaphthylene using [PdCl₂(PhCN)₂] + 4PPh₃ + 2.5*p*-TsOH. Reaction conditions: acenaphthylene, 4.0 mmol; [PdCl₂(PhCN)₂], 0.04 mmol; PPh₃, 0.16 mmol; *p*-TsOH, 0.1 mmol; 1,2-dichloroethane/methanol, 30 ml; temperature, 80 °C; CO pressure, 30 bar; reaction time, 24 h.

alcohol promoted reduction. For catalyst precursor [PdCl₂(PhCN)₂] + 4PPh₃ + 2.5*p*-TsOH, the catalytic activity increased with decreasing methanol concentration down to [MeOH] = 0.82 M, further decrease gave lower activity (Fig. 2). It should be noted that with methanol concentrations <4.10 M, no metallic palladium was observed at the end of the reaction. The chemoselectivity remained almost constant and only decreased slightly at high methanol concentration. The activity results can be explained by considering that an excess methanol has two opposite effects. Assuming the hydride route as the operating mechanism for this system, the reaction rate would be higher at higher methanol concentrations, as the nucleophilic attack of methanol on the acyl complex is proposed to be the rate determining step. Moreover, the catalytic activity increases with the polarity of the medium and, therefore, with the methanol concentration [23,24]. On the other hand, the activity should decrease at high methanol concentrations, because the catalyst precursor can be converted to less active or inactive species such as carbomethoxy complexes or palladium metal [51,52]. According to the results, a methanol concentration of 0.82 M seems to be the best compromise. The increase of methanol concentration

Table 4
Electronic and steric parameters of the various phosphorous ligands studied

PR ₃	ν (cm ⁻¹)	θ (°)
PEt ₃	2061.7	132
P(OEt)Ph ₂	2070.6	133
P(OPh) ₃	2085.3	128
P(^{<i>i</i>} Bu) ₃	2059.6	143
P(<i>p</i> -MeC ₆ H ₄) ₃	2066.7	145
PPh ₃	2068.9	145
P(<i>p</i> -FC ₆ H ₄) ₃	2071.3	145
P(<i>O-o</i> -MeC ₆ H ₄) ₃	2084.1	141
P(Cy) ₃	2056.4	170
P(<i>o</i> -MeC ₆ H ₄) ₃	2066.6	194
P(<i>O-o'</i> -BuC ₆ H ₄) ₃	2084.1	190

produces an increase in ether **2**, but a decrease in polymer **3** formation. Compensation of these effects justifies the practically constant selectivity in ester **1**.

3.2. Pd/PR₃/*p*-TsOH catalytic system

The effect of the properties of the phosphorous ligand was studied using monodentate phosphines, phosphites and phosphinites with different electronic and steric parameters (Table 4) [55,56]. The catalytic systems were formed in situ by addition of the corresponding amounts of PR₃ and *p*-TsOH (*p*-TsOH/Pd 2.5) to the catalyst precursor [PdCl₂(PhCN)₂] in a mixture of methanol/1,2-dichloroethane in a volume ratio of 1/1 unless otherwise stated, and the reactions were carried out at 80 °C and 30 bar of CO.

3.2.1. Effect of the electronic parameter

The effect of the electronic parameter of the phosphorous ligand on the catalytic activity and chemoselectivity was studied using auxiliary ligands with similar cone angles (141–145°) and different electronic parameters (cm⁻¹): P(^{*i*}Bu)₃, 2059.6; P(*p*-MeC₆H₄)₃, 2066.7; PPh₃, 2068.9; P(*p*-FC₆H₄)₃, 2071.3; and P(*O-o*-MeC₆H₄)₃, 2084.1. With the exception of P(^{*i*}Bu)₃ and P(*O-o*-MeC₆H₄)₃ that form practically inactive catalytic systems, conversions and chemoselectivities increase with the PR₃/Pd ratio up to a value of PR₃/Pd = 4, and decrease with a further increase of this ratio (Fig. 3), just as we have observed for the Pd/PPh₃/*p*-TsOH catalytic system in the same conditions. The catalytic activity

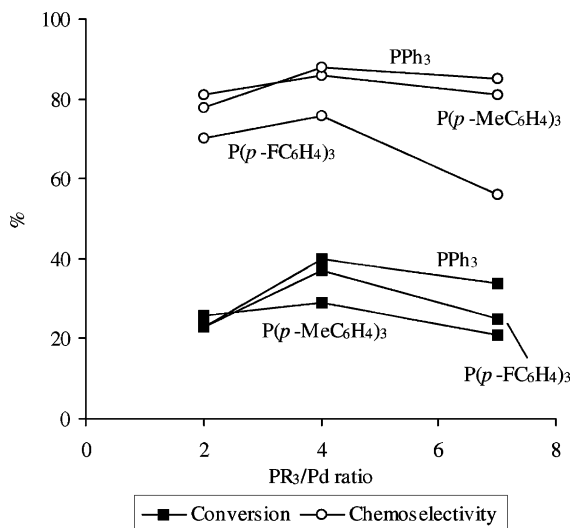


Fig. 3. Effect of the electronic parameter of the phosphorous ligands in the hydroesterification of acenaphthylene using [PdCl₂(PhCN)₂] + 2.5*p*-TsOH at different PR₃/Pd ratios. Reaction conditions: acenaphthylene, 4.0 mmol; [PdCl₂(PhCN)₂], 0.04 mmol; *p*-TsOH, 0.1 mmol; 1,2-dichloroethane, 15 ml; methanol, 15 ml; temperature, 80 °C; CO pressure, 30 bar; reaction time, 24 h.

was found to be higher for ligands with intermediate basicity and this can be related to the ligand-modified relative ability of the metal to coordinate acenaphthylene and carbon monoxide. The more basic ligands (P(^{*i*}Bu)₃), that form a stronger P–Pd bond, disfavor the coordination of acenaphthylene, while the less basic ligands (P(*O-o*-MeC₆H₄)₃) tend to allow the formation of kinetically stable olefin complexes of low reactivity. Only for the active catalytic systems the activity increases with the decrease of the methanol concentration (Fig. 4), thus the inactivity observed with P(^{*i*}Bu)₃ and P(*O-o*-MeC₆H₄)₃ can be traced to the electronic properties of the ligands, and not to the lack of stability towards decomposition of the catalytic system by alcohol promoted reduction.

3.2.2. Effect of the steric parameter

The effect of the steric parameter of the phosphorous ligand on the catalytic activity and chemoselectivity was studied using auxiliary ligands with similar electronic parameters (2066.6–2070.6 cm⁻¹) and different cone angles: P(OEt)Ph₂, 133°; PPh₃, 145°; and P(*o*-MeC₆H₄)₃, 194°. Only PPh₃, with

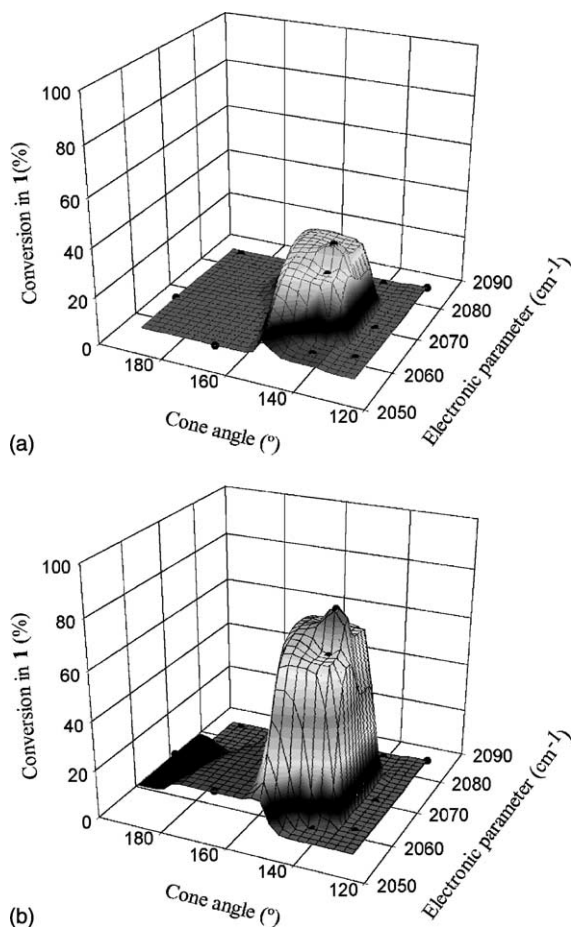


Fig. 4. Effect of the electronic (ν) and steric (θ) parameter of the phosphorous ligands at different methanol concentration in the hydroesterification of acenaphthylene using $[\text{PdCl}_2(\text{PhCN})_2] + 4\text{PR}_3 + 2.5p\text{-TsOH}$. Reaction conditions: acenaphthylene, 4.0 mmol; $[\text{PdCl}_2(\text{PhCN})_2]$, 0.04 mmol; PR_3 , 0.16 mmol; $p\text{-TsOH}$, 0.1 mmol; 1,2-dichloroethane/methanol, 30 ml; temperature, 80 °C; CO pressure, 30 bar; reaction time, 24 h. (a) $[\text{MeOH}]$, 12.3 M; (b) $[\text{MeOH}]$, 0.82 M.

an intermediate cone angle, forms active catalytic systems with appreciable chemoselectivities. This result can be explained by considering that less sterically demanding ligands ($\text{P}(\text{OEt})\text{Ph}_2$) compete with the olefin for coordination, producing species lacking the coordination sites to activate the reactant molecules [57,58], and bulkier ligands ($\text{P}(o\text{-MeC}_6\text{H}_4)_3$) do not stabilize the catalytic system. In fact, the decrease of methanol concentration produced an increase in the activity of this catalytic system yielding **1** (8%) with

low chemoselectivity (40%) due to the formation of a large amount of polymer **3** (Fig. 4).

The effect of electronic and steric properties of the auxiliary ligands was also studied using other phosphorous ligands with different electronic and steric properties: PEt_3 , $\text{P}(\text{OPh})_3$, $\text{P}(\text{Cy})_3$ and $\text{P}(\text{O}-o\text{-}^t\text{BuC}_6\text{H}_4)_3$ (Table 4). The results shown in Fig. 4 suggest that active catalytic systems are only produced by ligands with intermediate properties, both electronic and steric.

3.2.3. Effect of the catalyst precursor

The use of $\text{Pd}(\text{OAc})_2$ in the catalytic systems $\text{Pd}/\text{PR}_3/p\text{-TsOH}$ caused a decrease in activity and chemoselectivity (Table 5). However, when the reaction time was increased from 24 to 72 h using $\text{P}(p\text{-FC}_6\text{H}_4)_3$, the catalytic activity and the chemoselectivity were found to be independent of the metal precursor used. The higher TOF observed for $[\text{PdCl}_2(\text{PhCN})_2]$ can be related to the presence in the reaction mixture of chloride anions with weaker coordinating properties as compared to acetate anions, being the formation of free coordination sites to activate the reactant molecules more efficient.

3.3. $\text{Pd}/\text{P}(p\text{-FC}_6\text{H}_4)_3/p\text{-TsOH}$ catalytic system

The results obtained using $\text{P}(p\text{-FC}_6\text{H}_4)_3$ as auxiliary ligand were comparable to those observed for PPh_3 , with the advantage that no metallic palladium was observed at the end of reaction (24 h). Therefore, the systems with $\text{P}(p\text{-FC}_6\text{H}_4)_3$ seem to be more stable, although somewhat slower at the beginning of the reaction (Fig. 5), and more sensitive to the reaction conditions. The behavior of this catalytic system, with regard to the effect of $p\text{-toluenesulfonic acid}$ concentration, temperature, PR_3/Pd ratio, CO pressure and methanol concentration, can be explained in the same terms used for the $\text{Pd}/\text{PPh}_3/p\text{-TsOH}$ systems. Addition of $p\text{-TsOH}$ to the catalyst precursor (Table 6, entries 1–3), up to a $p\text{-TsOH}/\text{Pd}$ ratio of 2.5, resulted in an increase of catalytic activity owing to the formation of the cationic complexes $[\text{Pd}(\text{P}(p\text{-FC}_6\text{H}_4)_3)_n]^{2+}[p\text{-TsO}^-]_2$, previously described as the active catalytic species in the hydroesterification reaction [23]. Further increase in the $p\text{-TsOH}$ concentration has some effect on the conversion to ether **2** but total conversion decreases; this

Table 5

Effect of the catalyst precursor in the hydroesterification of acenaphthylene using [Pd] + 4 PR₃ + 2.5*p*-TsOH

Complex	PR ₃	Reaction time (h)	Conversion (%)	1 (%)	2 (%)	3 (%)	Chemoselectivity (%)
[PdCl ₂ (PhCN) ₂] ^a	PPh ₃	24	40	35	4	1	88
Pd(OAc) ₂ ^a	PPh ₃	24	29	24	3	2	83
[PdCl ₂ (PhCN) ₂]	P(<i>p</i> -FC ₆ H ₄) ₃	24	37	28	6	3	76
[PdCl ₂ (PhCN) ₂] ^a	P(<i>p</i> -FC ₆ H ₄) ₃	72	68	56	8	4	82
Pd(OAc) ₂	P(<i>p</i> -FC ₆ H ₄) ₃	24	24	16	4	4	67
Pd(OAc) ₂ ^a	P(<i>p</i> -FC ₆ H ₄) ₃	72	68	57	8	3	84
[PdCl ₂ (PhCN) ₂] ^a	P(<i>p</i> -MeC ₆ H ₄) ₃	24	29	25	3	1	86
Pd(OAc) ₂ ^a	P(<i>p</i> -MeC ₆ H ₄) ₃	24	14	10	1	3	71

Reaction conditions: acenaphthylene, 4.0 mmol; [Pd], 0.04 mmol; PR₃, 0.16 mmol; *p*-TsOH, 0.1 mmol; 1,2-dichloroethane, 15 ml; methanol, 15 ml; temperature, 80 °C; CO pressure, 30 bar.

^a Metallic palladium was observed at the end of the reaction.

was not observed in the case of PPh₃. An explanation for the different overall behavior of PPh₃ and P(*p*-FC₆H₄)₃ could be based on the competition of the direct addition of methanol to acenaphthylene with the catalytic hydroesterification. This competitive effect is more important for the slower P(*p*-FC₆H₄)₃ catalytic system than for the PPh₃ system.

When the temperature was increased from 70 to 80 °C, higher catalytic activity was observed (Table 6,

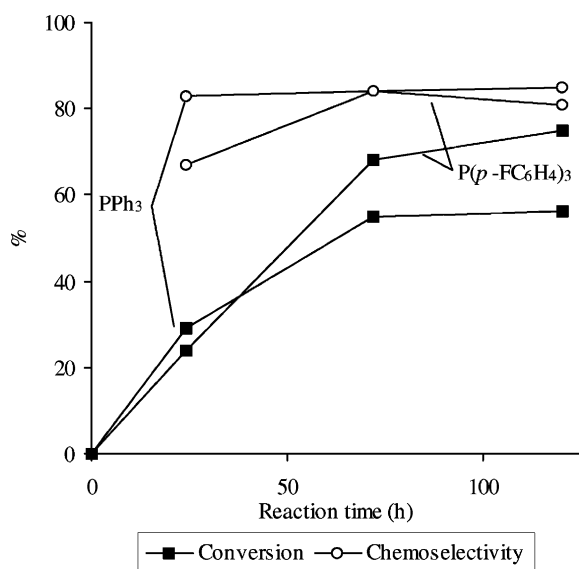


Fig. 5. Effect of the reaction time in the hydroesterification of acenaphthylene using Pd(OAc)₂ + 4PR₃ + 2.5*p*-TsOH. Reaction conditions: acenaphthylene, 4.0 mmol; Pd(OAc)₂, 0.04 mmol; PR₃, 0.16 mmol; *p*-TsOH, 0.1 mmol; 1,2-dichloroethane, 15 ml; methanol, 15 ml; CO pressure, 30 bar; temperature, 80 °C.

entries 4–6). Further increase of temperature caused a strong decrease in both activity and chemoselectivity. The loss of catalytic activity at high temperature can be related, as in the PPh₃ case, to the instability of the catalytic system [53]. Concerning the chemoselectivity, direct addition of methanol to acenaphthylene was not affected by this thermally promoted deactivation of the catalyst, and conversion in ether **2** increased with the temperature. Moreover, at 100 °C polymer **3** was the major product and, consequently, the selectivity in ester **1** decreased noticeably at high temperatures. At 80 °C, both activity and chemoselectivity increased with the P(*p*-FC₆H₄)₃/Pd ratio up to a value of P(*p*-FC₆H₄)₃/Pd equal to 4, and decrease with further increase (Fig. 3). This ligand/Pd ratio seems to be the best compromise between the stabilization of the catalytic system by the presence of an excess of phosphorous ligand and the deactivation of the catalyst by competition between the auxiliary ligand and the reactant molecules for coordination [23]. By increasing the CO pressure from 20 to 30 bar, higher conversions were observed (Table 6, entries 5, 7–10). Further increase resulted in a strong decrease of the catalytic activity, owing to the competition between CO and acenaphthylene for coordination to the metal. In comparison to PPh₃, the lower basicity of P(*p*-FC₆H₄)₃ cannot efficiently prevent the formation of the less active or inactive polycarbonylpalladium species at high CO pressures [21]. Finally, the conversion increased with the decrease of methanol concentration, due to the stabilization of the catalytic systems in front of the decomposition by alcohol promoted reduction (Fig. 4).

Table 6

Hydroesterification of acenaphthylene using $[\text{PdCl}_2(\text{PhCN})_2] + 4\text{P}(p\text{-FC}_6\text{H}_4)_3$

Entry	<i>p</i> -TsOH/Pd ratio	Temperature (°C)	Pressure (bar)	Conversion (%)	1 (%)	2 (%)	3 (%)	Chemoselectivity (%)
1 ^a	0	80	30	20	15	2	3	75
2 ^a	2.5	80	30	37	28	6	3	76
3 ^a	5.0	80	30	33	24	7	2	73
4 ^b	2.5	70	30	31	24	6	1	77
5 ^b	2.5	80	30	68	56	8	4	82
6 ^b	2.5	100	30	35	12	10	13	34
7 ^b	2.5	80	20	60	46	9	15	77
8 ^b	2.5	80	26	65	52	8	5	80
9 ^b	2.5	80	36	37	31	6	–	84
10 ^b	2.5	80	38	16	13	3	–	81

Reaction conditions: acenaphthylene, 4.0 mmol; $[\text{PdCl}_2(\text{PhCN})_2]$, 0.04 mmol; $\text{P}(p\text{-FC}_6\text{H}_4)_3$, 0.16 mmol; 1,2-dichloroethane, 15 ml; methanol, 15 ml; reaction time, 72 h.

^a Reaction time: 24 h.

^b Metallic palladium was observed at the end of the reaction.

3.4. Pd/diphosphine catalytic systems

With the purpose to explore the possibilities of an enantioselective version of the acenaphthylene hydroesterification, a preliminary study using diphosphines as auxiliary ligands has been performed. The effect of the nature of the bischelate ligands was studied using diphosphines with different electronic and steric properties. The catalytic systems were formed

in situ by addition of the diphosphine ($\text{P/Pd} = 2$) and *p*-TsOH ($p\text{-TsOH/Pd} = 2.5$) to the catalyst precursor, $[\text{PdCl}_2(\text{PhCN})_2]$ or $\text{Pd}(\text{OAc})_2$, in a mixture of methanol/1,2-dichloroethane ($[\text{MeOH}] = 0.82 \text{ M}$) and the reactions were carried out at 80 °C and 30 bar of CO.

The results shown in Table 7 indicate that only 1,1'-bis(diphenylphosphino)ferrocene (dppf) in association with $\text{Pd}(\text{OAc})_2$ forms an active catalytic system

Table 7

Hydroesterification of acenaphthylene using $[\text{Pd}] + \text{diphosphine} + 2.5p\text{-TsOH}$ catalytic systems

Entry	Complex	Diphosphine	β_n (°) ^a	Conversion (%)	1 (%)	2 (%)	3 (%)	Chemoselectivity (%)
1	$[\text{PdCl}_2(\text{PhCN})_2]$	dppm	72	2	–	2	–	–
2	$\text{Pd}(\text{OAc})_2$	dppm	72	2	–	2	–	–
3	$[\text{PdCl}_2(\text{PhCN})_2]$	dppe	85	2	–	2	–	–
4	$\text{Pd}(\text{OAc})_2$ ^b	dppe	85	1	–	1	–	–
5	$[\text{PdCl}_2(\text{PhCN})_2]$	dppp	91	3	–	3	–	–
6	$\text{Pd}(\text{OAc})_2$	dppp	91	3	1	2	–	33
7	$[\text{PdCl}_2(\text{PhCN})_2]$	BINAP	92	3	–	3	–	–
8	$\text{Pd}(\text{OAc})_2$	BINAP	92	6	3	1	2	50
9	$[\text{PdCl}_2(\text{PhCN})_2]$	dppf	96	13	2	3	8	15
10	$\text{Pd}(\text{OAc})_2$	dppf	96	24	17	2	5	71
11	$[\text{PdCl}_2(\text{PhCN})_2]$	dppb	98	2	–	2	–	–
12	$\text{Pd}(\text{OAc})_2$	dppb	98	5	3	2	–	60
13	$\text{Pd}(\text{OAc})_2$ ^c	BINAP	92	60	50	–	10	83
14	$\text{Pd}(\text{OAc})_2$ ^c	dppf	96	60	50	1	9	83

Reaction conditions: acenaphthylene, 4.0 mmol; $[\text{Pd}]$, 0.04 mmol; diphosphine, 0.04 mmol; *p*-TsOH, 0.1 mmol; 1,2-dichloroethane, 29 ml; methanol, 1 ml; CO pressure, 30 bar; reaction time, 24 h.

^a Natural bite angle β_n [59].

^b Metallic palladium was observed at the end of the reaction.

^c Toluene was used as auxiliary solvent.

giving ester **1** with poor yield and selectivity. These results are in agreement with those obtained for the hydroesterification of styrene, for which diphosphines generate less efficient catalysts than monophosphines [18]. With regard to the steric properties of the ligand, the results do not suggest a direct relationship between the activity of the catalytic system and the bite angle of the bischelate auxiliary ligand, unlike the case of styrene hydroesterification [18] or other related carbonylations [59]. It seems that the activity of the dppf system would have to be ascribed to its electronic properties. In fact, this ligand is a triaryl phosphine and compared to alkyl-diaryl phosphines it is less of an electron donor. The lack of activity of rac-BINAP systems, with electronic properties more similar to dppf than to dppe, dppe, dppp or dppb, can be related to its insolubility in the reaction mixture. When toluene was used as a solvent, both dppf and BINAP (with Pd(OAc)₂) were more soluble and gave ester **1** with higher conversions and chemoselectivities. It should be noted that in these conditions both triaryl diphosphines gave similar results. An explanation for the different behavior of triaryl and alkyl-diaryl phosphines can be the modified ability of the metal to coordinate acenaphthylene and carbon monoxide. Replacement of CO by alkene should take place more readily when phosphines having less electron donating capacity are used [59,60]. The use of the insoluble [PdCl₂(PhCN)₂] in toluene as catalyst precursor, produced ester **1** with poor yields (<25%) and selectivities (<50%) owing to the formation of a large amount of polymer **3**.

4. Conclusions

Hydroesterification of acenaphthylene with carbon monoxide and methanol catalyzed by palladium complexes has been used to obtain acenaphthene-1-carboxylic acid methyl ester **1** with good activities and high chemoselectivities. The reaction yields a mixture of desired ester **1**, 1-methoxyacenaphthene **2** and polyacenaphthylene **3**. The catalytic system, formed by addition of PPh₃ and *p*-TsOH to a palladium precursor, is highly influenced by the reaction conditions, specially the methanol concentration and the Pd/*p*-TsOH ratio yielding conversions up to 83% with chemoselectivities in ester **1** of 93%. The nature of the phosphorous ligand is found to have a significant

role in catalytic activity and product chemoselectivity. Only ligands with intermediate electronic and steric properties gave active catalytic systems with satisfactory chemoselectivities. Ligand P(*p*-FC₆H₄)₃ formed a slower catalytic system with higher stability in front of decomposition by alcohol promoted reduction. However, in long reaction time experiments, P(*p*-FC₆H₄)₃-based precursors produced higher conversions and similar selectivities to PPh₃-based systems. When diphosphines were used as auxiliary ligands, less efficient catalytic systems were formed, with conversions up to 60% and chemoselectivities in ester **1** of 85%. Only triaryl diphosphines were found to be active.

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