DOI: 10.1002/ejoc.200900697

Novel, Highly Efficient and Selective Ruthenium Catalysts for the Synthesis of Vinyl Esters from Carboxylic Acids and Alkynes

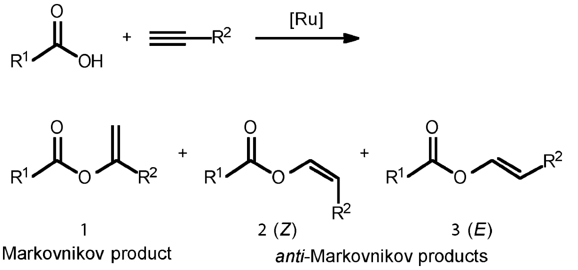
François Nicks,[a] Rosario Aznar,[b] Daniel Sainz,[b] Guillermo Muller,[b] and Albert Demonceau*[a]

Keywords: Alkynes / Carboxylic acids / Homogeneous catalysis / Microwave chemistry / Ruthenium / Vinyl esters

An efficient and highly selective synthesis of vinyl esters was developed that employed carboxylic acids and terminal alkynes as reagents, and novel tethered (η^1:η^6-phosphanoarene)ruthenium complexes as catalyst precursors. With these catalyst systems, the reactions were somewhat slower than when using the best catalysts reported to date, but the selectivities were excellent with up to 98 % of the Markovnikov isomer. In addition, with a turnover number (TON) of 5000, these catalysts greatly outperformed their competitors. Minute amounts of water had a beneficial impact on the reaction rates, while maintaining the same selectivities. Furthermore, microwave heating at 160 °C also considerably accelerated the reactions, albeit to the detriment of the selectivity. Finally, it should also be noted that formation of dimerization products of 1-alkynes was completely suppressed by using these tethered (η^1:η^6-phosphanoarene)ruthenium catalytic systems.

Introduction

Vinyl esters are structural motifs that are present in natural and bioactive compounds, such as basiliolides,[1] transtaganolides,[2] xerulins,[3] and lissoclinolide,[4,5] but they are mainly used as monomers (e.g., vinyl acetate) in olefin polymerization and as intermediates in organic synthesis. Vinyl esters are quite efficient reagents for acylation reactions.[6a–6d] They can, indeed, react with amines and alcohols under neutral or nearly neutral conditions,[6e–6o] or in the presence of enzymes,[7] and release a ketone to afford the corresponding *N*- and *O*-acylated products in high yields. Enol esters can also be converted into vinyl arenes through decarbonylative Heck–Mizoroki olefination.[8] Accordingly, a vast range of protocols for the synthesis of vinyl esters have been developed.[9] The most straightforward and atom-economic way is the 1:1 condensation of 1-alkynes and carboxylic acids (Scheme 1), a process where the C–C triple bond is activated by means of a catalyst, which may be either an electrophile or a transition-metal complex.[10] In this respect, the method of Kita is especially powerful as it involves ethoxyacetylene as reaction partner and provides thereby 1-ethoxyvinyl esters, which upon acylation of amines and alcohols release ethyl acetate.[11] Recent years have witnessed increasing efforts in developing efficient and highly selective catalysts for the synthesis of vinyl esters.[12] Of particular significance are ruthenium-based catalysts[13] and, in this regard, the contribution of Gooßen is especially noteworthy,[14] as it disclosed a highly efficient and selective, in situ-generated catalyst system consisting of easy-to-handle, commercially available components: $[RuCl_2(p\text{-cymene})]_2$ (*p*-cymene = 4-isopropyltoluene), $P(Fur)_3$ (Fur = 2-furyl), and Na_2CO_3.



Scheme 1. Synthesis of vinyl esters through addition of terminal alkynes to carboxylic acids.

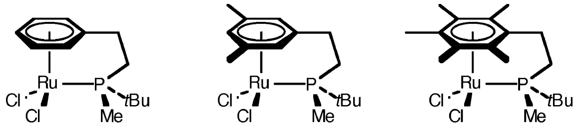
In the course of our studies toward the synthesis of P-chiral, functionalized η^6-arene ruthenium complexes,[15] we recently reported a general, high-yielding method for the preparation of new tethered phosphanoarene ruthenium complexes,[16] such as compounds **4**–**6** represented on Scheme 2. To examine their catalytic activity, we considered

---

[a] Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège,
Sart-Tilman (B.6a), 4000 Liège, Belgium
Fax: +32-43663497
E-mail: A.Demonceau@ulg.ac.be
[b] Departament de Química Inorgànica, Universitat de Barcelona,
Martí i Franquès 1–11, 08028 Barcelona, Spain
Fax: +34-93-4907725
E-mail: guillermo.muller@qi.ub.es

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900697.

first the addition of alkynes to carboxylic acids as an attractive synthetic goal. Our preliminary results in this field form the subject of the present communication.



4 **5** **6**

Scheme 2. The ruthenium complexes under investigation.

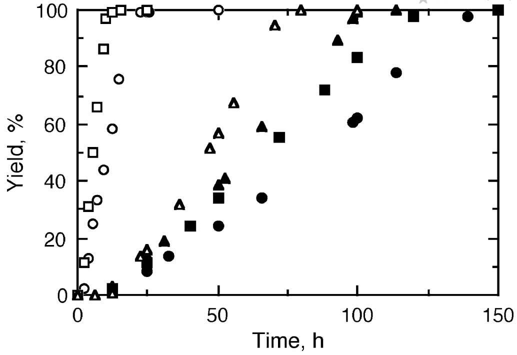
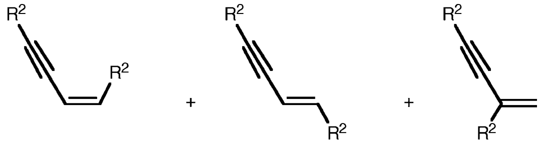


Figure 1. Variation in enol ester yield with respect to time for reactions between 4-acetoxybenzoic acid and 1-hexyne catalyzed by complexes **4** (filled circles, open circles), **5** (filled squares, open squares), and **6** (filled triangles, open triangles), and performed in dry toluene (filled circles, squares, and triangles) or in water-saturated toluene (open circles, squares, and triangles). Reaction conditions: 4-acetoxybenzoic acid, 1.15 mmol; 1-hexyne, 1.725 mmol; catalyst, 9.2×10^{-3} mmol; Na_2CO_3, 18.4×10^{-3} mmol; toluene, 6 mL; T = 60 °C under nitrogen.

Results and Discussion

Our investigation started thus with the evaluation of the catalytic activity of ruthenium complexes **4**–**6** for the synthesis of vinyl esters. For this purpose, 4-acetoxybenzoic acid and 1-hexyne were used as reaction partners (Scheme 1, R^1 = 4-$AcOC_6H_4$, R^2 = n-C_4H_9), employing experimental conditions that proved previously to be quite satisfactory.[14,17] Accordingly, the reactions were performed at 60 °C with dry toluene as solvent and sodium carbonate (2 equiv. relative to the ruthenium complex) as additive (Table 1). Under these conditions, the synthesis of vinyl esters proceeded quantitatively, although catalysts **4**–**6** were significantly less active than [$RuCl_2$(p-cymene)(PPh_3)] and [$RuCl_2$(p-cymene)($PFur_3$)] (see Supporting Information, Figure SI1).[14,17] Furthermore, the reaction rate was found to be considerably faster with complex **6** bearing the pentamethylphenyl moiety than with the less-substituted derivatives **5** and **4** (Table 1 and Figure 1). Also of particular interest is the selectivity of the synthesis of vinyl esters. In this respect, with 96–98% selectivity for the Markovnikov isomer **1**, catalysts **4**–**6** outperformed those used in previous works.[13,17] Additionally, the dimerization products of 1-hexyne (Scheme 3, R^2 = n-C_4H_9) were observed in only trace amounts.

In the course of this preliminary study, we also serendipitously found that the synthesis of vinyl esters was accelerated when the reaction was performed in commercial toluene. For the sake of both comparison and reproducibility, all the previous catalytic reactions were then repeated in degassed water-saturated toluene (Table 1 and Figure SI1). Thus, when the test reaction was performed using catalyst **5** in moist toluene the reaction was complete after only 1 d, against 5–6 d in dry toluene. Noteworthily, in moist toluene catalyst **5** was more efficient than **4** and **6**, whereas in dry toluene the reactivity sequence **6** > **5** > **4** was observed. In addition, in water-saturated toluene, the selectivity of the addition remained at a level of 97–98% in favor of the Markovnikov isomer.



7 **8** **9**

Scheme 3. Dimerization products of terminal alkynes.

The reaction conditions developed above were found to be broadly applicable to a wide variety of carboxylic acids (Table 2 and Figure SI2). Substitution at the 4-position of benzoic acid was well tolerated and, in agreement with the literature,[13b,13c] the stronger the carboxylic acid, the higher the reactivity. 4-(Trifluoromethyl)benzoic acid (pK_a = 3.67), for instance, required only 8 h for complete conversion, against 40 h for 4-methoxybenzoic acid (pK_a = 4.46) (Figure 2). 4-Formylbenzoic acid, however, was less reactive than expected from its pK_a value (Figure SI3), presumably because of its very low solubility in toluene. Notably, for all the carboxylic acids under investigation, the vinyl esters could be isolated in excellent 96–99% yields after distil-

Table 1. Influence of the catalyst on the synthesis of enol esters.

Catalyst	Conditions A[a,b]							Conditions B[a,c]						
	% Yield[d]				% Selectivities[e]			% Yield[d]				% Selectivities[e]		
	25 h	50 h	100 h	150 h	**1**	**2**	**3**	12 h	25 h	50 h	100 h	**1**	**2**	**3**
4	8	24	62	100	96.5	3	0.5	58	99	100		97.5	2	0.5
5	11	34	83	100	96.5	3	0.5	99	100			97.5	2	0.5
6	14	39	99	100	97.5	2	0.5	1	16	57	100	97.5	2	0.5

[a] Reaction conditions: 4-acetoxybenzoic acid, 1.15 mmol; 1-hexyne, 1.725 mmol; catalyst, 9.2 10^{-3} mmol; Na_2CO_3, 18.4 10^{-3} mmol; toluene, 6 mL; T = 60 °C under nitrogen. [b] Dry toluene. [c] Water-saturated toluene. [d] Determined by GC using dodecane as internal standard. [e] Selectivities obtained at 100% conversion, determined by GC.

Table 2. Influence of the carboxylic acid on the synthesis of enol esters.

Carboxylic acid	pK_a	Conditions A[a,b]						Conditions B[a,c]					
		% Yield[d]			% Selectivities[e]			% Yield[d]			% Selectivities[e]		
R^1		12 h	25 h	50 h	**1**	**2**	**3**	12 h	25 h	50 h	**1**	**2**	**3**
4-CF_3-C_6H_4	3.67	100			96.5	2.5	1						
4-HCO-C_6H_4	3.76	24	67	100	96	3	1						
4-AcO-C_6H_4	4.14	81	100		97.5	2	0.5	51	86	100	96.5	2.5	1
C_6H_5	4.19	92	100		97.5	2	0.5	61	98	100	97	2	1
4-CH_3-C_6H_4	4.34	56	96	100	97	2	1	47	79	100	96	2.5	1.5
4-CH_3O-C_6H_4	4.46	38	82	100	96	2.5	1.5	27	67	100	96	2.5	1.5

[a] Reaction conditions: 1-hexyne, 1.15 mmol; carboxylic acid, 1.15 mmol; catalyst **5**, 9.2×10^{-3} mmol; Na_2CO_3, 18.4×10^{-3} mmol; water-saturated toluene, 6 mL; T = 60 °C. [b] Under nitrogen. [c] Under air. [d] Determined by GC using dodecane as internal standard. [e] Selectivities obtained at 100% conversion, determined by GC.

lation. With respect to the selectivity, the Markovnikov adduct (**1**) predominated again, leveling up to 96–98% in all cases (Table 2).

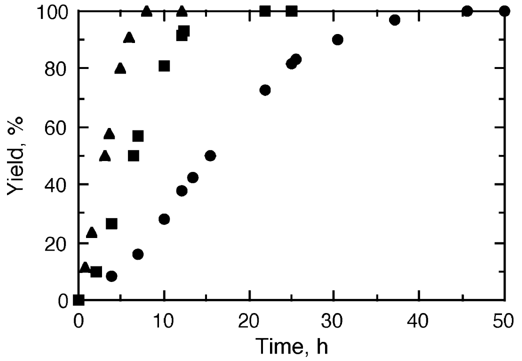


Figure 2. Variation in enol ester yield with respect to time for reactions between 1-hexyne and 4-trifluoromethylbenzoic acid (filled triangles), benzoic acid (filled squares), and 4-methoxybenzoic acid (filled circles) catalyzed by complex **5**. Reaction conditions: 1-hexyne, 1.15 mmol; carboxylic acid, 1.15 mmol; catalyst, 9.2×10^{-3} mmol; Na_2CO_3, 18.4×10^{-3} mmol; water-saturated toluene, 6 mL; T = 60 °C under nitrogen.

After having established that the synthesis of vinyl esters was considerably accelerated in moist toluene, we next examined the effect of air. As can be seen in Table 2 (Conditions B), reactions performed under air were still quantitative, although appreciably slower than those conducted under nitrogen, and the selectivities were unchanged (Figure SI2).

The high efficiency of the reactions described above prompted us to extend the reaction to other terminal alkynes. The results of this study are summarized in Table 3 (See also Figure SI4). Not surprisingly, 1-octyne exhibited the same reactivity as 1-hexyne with the Markovnikov adduct as the major isomer (97%). The bulky *tert*-butylacetylene participated also in the reaction, but required longer reaction times than its linear counterpart. Furthermore, the selectivity was somewhat lower with 92% in favor of the Markovnikov isomer (**1**). Interestingly, no dimerization product was found with these alkyl-substituted acetylenes. Phenylacetylene, on the contrary, was a very poor substrate, at least at 60 °C (Table 3 and SI2). At that temperature, indeed, the formation of vinyl esters was extremely slow with less than 10% yield after 5 d of reaction. Instead dimerization of the substrate was observed, although in modest yield (50% after 5 d of reaction), with a distinct preference for the tail-to-tail (Z)-enyne **7** (**7**, 90%; **8**, 6%; **9**, 4%). Interestingly, the outcome of the reaction was reversed at 110 °C and the synthesis of vinyl esters (98% yield) took precedence over dimerization (2%). Again, the Markovnikov adduct was the preferred isomer, with a decent 85% selectivity (Table 3 and SI2).

Table 3. Influence of the alkyne on the synthesis of enol esters.[a]

Alkyne	% Yield[b]				% Selectivities[c]		
	12 h	25 h	50 h	100 h	**1**	**2**	**3**
1-Hexyne	81	100			97.5	2	0.5
1-Octyne	82	100			97	2	1
tert-Butylacetylene	22	45	85	100	92	8	t[d]
Phenylacetylene	–	3	4.5	7	90	7.5	2.5
	98[e]				85[e]	10[e]	5[e]

[a] Reaction conditions: 4-acetoxybenzoic acid, 1.15 mmol; alkyne, 1.15 mmol; catalyst **5**, 9.2 10^{-3} mmol; Na_2CO_3, 18.4 10^{-3} mmol; water-saturated toluene, 6 mL; T = 60 °C under nitrogen. [b] Determined by GC using dodecane as internal standard. [c] Selectivities obtained at 100% conversion, determined by GC. [d] $<$ 0.2%. [e] Reaction performed in a sealed tube at 110 °C for 4 h.

In recent years, microwave heating has received increasing attention as a powerful tool for accelerating chemical reactions.[18] As part of our research program,[19] we carried out previously[17] the synthesis of vinyl esters in a sealed vessel heated at 160 °C in a CEM Discover monomode microwave reactor, and found that−as expected−microwave-assisted syntheses (MW) catalyzed by [$RuCl_2$(*p*-cymene)-(PR_3)] (R = Ph, 4-Cl-C_6H_4, and 2-furyl) were faster than related experiments performed under conventional heating (Δ) at 60 °C. Furthermore, we suggested that microwave irradiation and conventional heating using otherwise identical conditions (concentration, temperature, etc.) were equipotent methods.[17] In the present study, microwave irradiation was applied to the test reaction using as solvent either dry toluene (*without* base) or water-saturated toluene in the presence of Na_2CO_3 (2 equiv. relative to the catalyst) (Table 4 and Figure SI5). It was found that, under both experimental conditions, microwave-assisted reactions at 160 °C were significantly faster than those carried out under conventional convective heating at 60 °C. Because of the ongoing debate over non-thermal microwave effects,[20] we decided to perform similar reactions in sealed tubes immersed in a thermostatically controlled silicon oil heating bath kept at 160 °C. Contrary to our previous observations,[17] we found that reactions were slightly faster under conventional heating than under microwave heating (Figure SI5, Supporting Information). Oddly enough, at 160 °C, whatever the heating mode and the state of the solvent (dry or moist toluene) (Table 4), the relative rate of product formation, **5** < **4** < **6**, was different from that observed at 60 °C in dry toluene (**4** < **5** < **6**) or in water-saturated toluene (**6** < **4** < **5**). Finally, in all cases, performing the reactions at 160 °C appreciably decreased the selectivity, with only 88% of the Markovnikov isomer.

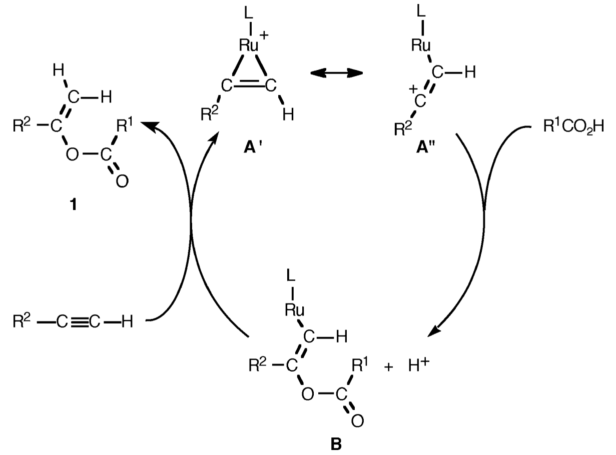
Table 4. Thermal vs. microwave-assisted addition of 4-acetoxybenzoic acid to 1-hexyne.[a]

Catalyst	Reaction time [min]	% Yield[b]		
		Conditions A[a,c]	Conditions B[a,d]	
		MW	MW	Δ
4	30	32	56	94
5	30	21	36	54
6	10	16	85	97
	30	65	100	100

[a] Reaction conditions: 4-acetoxybenzoic acid, 0.5 mmol; 1-hexyne, 0.75 mmol; catalyst, 4 10^{-3} mmol; T = 160 °C under nitrogen. [b] Determined by GC using dodecane as internal standard. [c] Dry toluene, 2.6 mL (*without* base). [d] Water-saturated toluene, 2.6 mL; Na_2CO_3, 8 10^{-3} mmol.

Given the faster rates at 160 °C, lower catalyst loadings were then examined (Table SI3). To this aim, a mixture of the ruthenium complex and Na_2CO_3 in a 1:2 molar ratio was finely dispersed in Celite (2 wt.-%)[21] in order to introduce a precise amount of the catalyst system to the reaction mixture. When the reaction in water-saturated toluene was carried out at 160 °C under conventional heating using 0.1 mol-% of complex **6**, the desired products were obtained in 58% yield after 30 min of reaction, but required a longer time (90 min) for the reaction to go to completion. Further reduction of **6** to 0.05 and 0.02 mol-% proved less satisfactory, giving the corresponding vinyl esters in 79 and 28% yield, respectively, after 1.5 h of reaction. Nevertheless, extending the reaction time to 2.5 and 14 h, respectively, led to quantitative yields in vinyl esters (Figure SI6). Interestingly, for lower catalyst loadings, such as 0.015 and 0.01 mol-%, the final yields were no more quantitative (52 and 15%, respectively) and the turnover numbers dropped to 3500 and 1500, respectively (Figure SI6). Finally, blank experiments performed in sealed tubes at 160 °C in the *absence* of catalyst demonstrated that the starting compounds were unchanged after the reaction, even after 50 h of heating. Thus, with a maximum turnover number of 5000, complex **6** greatly outperforms [$RuCl_2$(*p*-cymene)(PPh_3)], which culminated in 1000 turnovers.[17] Complex **6** is therefore the most active catalyst precursor described so far for the synthesis of vinyl esters from carboxylic acids and alkynes. This statement is mitigated, however, by the observation that the selectivity not only decreased with the temperature, but also with the catalyst loading (Figure SI7), seemingly indicating that the Markovnikov isomer (**1**) is the kinetically controlled reaction product while the anti-Markovnikov isomers, **2** and **3**, may be viewed as the thermodynamically preferred products. This assumption was refuted after having observed that the isomer distribution of several reaction mixtures was not affected by an extended heating for 50 h at 160 °C,[13b] suggesting thereby that the decrease of the selectivity might merely be due to a (partial?) transformation of the primary catalytic species into less selective ones.

In recent years, particular attention has been paid to the use of (arene)ruthenium complexes as catalysts or catalyst precursors for a wide range of reactions including transfer hydrogenation of ketones and imines,[22] hydrogenation of alkenes,[23] Diels–Alder reactions,[24] olefin metathesis,[25] olefin cyclopropanation,[26] and atom transfer radical reactions.[27] In most cases, the catalytic performances have been shown to be strongly affected by the nature of the arene ligand, although its role remains totally or partially unanswered. For instance, in the hydrogen transfer reactions to ketones, the arene species is assumed to be an ancillary ligand throughout the catalytic process, whereas in olefin metathesis and atom transfer radical reactions, the catalytic activity apparently results from arene disengagement. The situation is less clear for the synthesis of enol esters from carboxylic acids and terminal alkynes. A plausible mechanism has been outlined (Scheme 4), which however ignores the role of the arene ligand.[13a] Interestingly, it has been shown that the nature of the arene ligand was not important as [(arene)$RuCl_2(PMe_3)$] [arene = C_6Me_6, 1,3,5-(iPr)$_3$-C_6H_3, *p*-cymene] gave essentially the same results, suggesting that the catalytic species were likely devoid of the arene ligand.[13a]



Scheme 4. Proposed mechanism for the synthesis of Markovnikov-type enol esters through addition of carboxylic acids to 1-alkynes.[13a]

Owing to the chelate effect, the stability of the (arene)-ruthenium moiety in tethered (arene)ruthenium complexes containing a phosphorus donor atom is greatly increased.[15,28] In order to get some insight into the catalyst's structure, we investigated by ^{31}P NMR spectroscopy a reaction mixture using complex **4** as catalyst precursor, moist toluene, and Na_2CO_3. After two hours of reaction, which corresponds approximately to the end of the induction period, the signal at δ = 61.9 ppm of the chelating phosphane in complex **4**[16] vanished and was not balanced by the appearance of new signals (Figure 3). After completion of the reaction (24 h), the ^{31}P NMR spectrum was quite different, exhibiting a sharp signal at δ = 36.26 ppm along with several extremely small peaks between 15 and 35 ppm. Noteworthily, the free phosphane PMe(*t*Bu)(CH_2CH_2Ph) (δ = –15.5 ppm in CH_2Cl_2/[D_6]acetone), the protonated phosphane (δ = 24.96 ppm in $CDCl_3$), and the phosphane oxide (δ = 51.7 ppm in $CDCl_3$) were not detected in the reaction mixture. Thus, these results clearly demonstrate that the initial ruthenium complex **4** was transformed in the course of the reaction into a multitude of phosphorus-containing species, rendering nowadays highly speculative any discussion on the mechanism of the reaction. Nevertheless, given the importance of the arene fragment on the outcome of the reactions, it seems obvious that the phosphanoarene ligand is involved throughout the catalytic process.

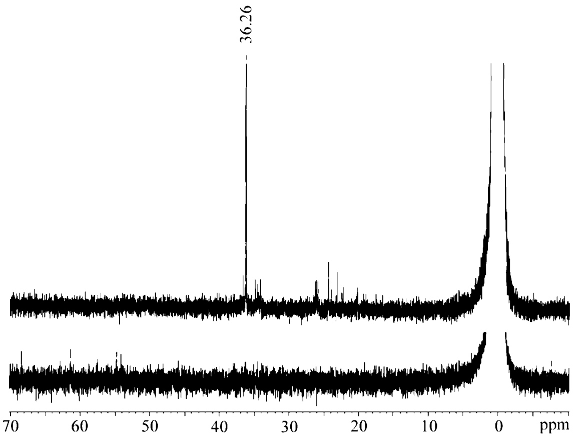
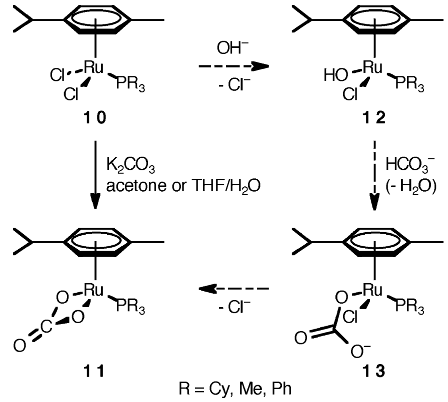


Figure 3. ^{31}P NMR spectra of crude reaction mixtures with complex **4** as the catalyst precursor after 2 and 24 h of reaction [aqueous H_3PO_4 (85%) as reference]. Reaction conditions: 4-acetoxybenzoic acid, 0.75 mmol; 1-hexyne, 1.125 mmol; complex **4**, 6 10^{-3} mmol; Na_2CO_3, 12 10^{-3} mmol; water-saturated toluene, 4 mL; *T* = 60 °C under nitrogen.

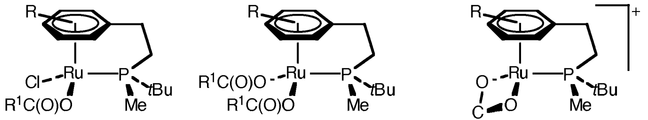
As reported previously by Gooβen,[14] addition of 2 equiv. of Na_2CO_3 relative to the ruthenium complex significantly increases the catalytic activity. Because the proposed catalytic cycle involves attack of the carboxylic acid onto the alkyne coordinated to the ruthenium (Scheme 4), the presence of catalytic amounts of base should increase the amount of carboxylate ions and might thus facilitate the reaction more effectively.[14] On another note, addition of a higher amount of Na_2CO_3 resulted in the evolution of CO_2, as indicated by bubbling of the solution, and to a lower yield in enol esters. Thus, when 1 equiv. of Na_2CO_3 relative to the carboxylic acid was added (125 equiv. relative to the ruthenium complex), no enol ester formation was observed. On the other hand, it is also known that the carbonate anion can enter into the coordination sphere of the ruthenium center.[29] Thus, [$RuCl_2$(*p*-cymene)(PR_3)] complexes (**10**) react with K_2CO_3 in the presence of water to afford carbonato–ruthenium(II) derivatives (**11**) (Scheme 5).[30] Although this reaction is quite slow at room temperature (2–10 days are indeed necessary for the reaction to reach completion), we might expect that at 60 °C or at the higher temperatures used in the present study, formation of ruthenium carbonate should be significantly faster. It should also be noted that the synthesis of ruthenium carbonates **11** requires the presence of water, suggesting that the addition of water might result in the additional presence of the more reactive hydroxide anion and hence in the formation of Ru–OH (**12**) and Ru–OCO_2^- (**13**) intermediates (Scheme 5).[30] On the basis of these results, the involvement of hydroxy-, η^1- and η^2-carbonato–ruthenium species cannot be excluded a priori during the synthesis of enol esters from carboxylic acids and terminal alkynes.



Scheme 5. Proposed mechanism for the synthesis of ruthenium carbonates **11** catalyzed by water.[30]

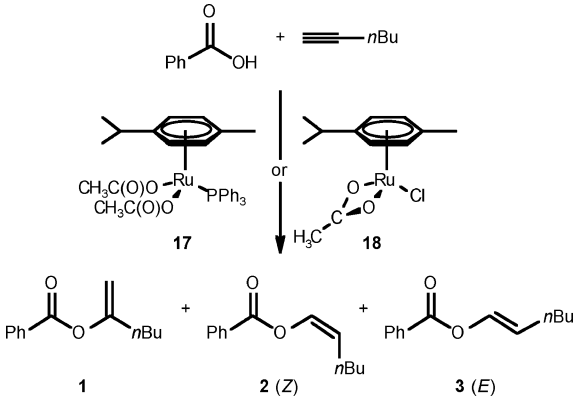
We have also shown that the use of water-saturated toluene resulted in improved catalytic activity. Based on the solubility of water in toluene (0.0460 wt.-% at 20 °C and 0.0615 wt.-% at 30 °C),[31] standard reaction mixtures with 9.2 10^{-3} mmol of ruthenium complex and 18.4 10^{-3} mmol of Na_2CO_3 in 6 mL of toluene contain ca. 17–19 equiv. of water relative to the catalyst (i.e. ca. 9 equiv. relative to Na_2CO_3). A simple explanation for the beneficial effect of water on the course of the reaction is that water facilitates the solubilization of the base. However, compared with Na_2CO_3, water clearly takes a secondary part in the catalytic process as reactions conducted *without sodium carbonate* proceeded similarly in anhydrous and moist toluene. Furthermore, as stated above, water could also promote the formation of hydroxy-, η^1- and η^2-carbonato–ruthenium species (**11**–**13**, Scheme 5). Finally, over the past few years, aqueous and especially aqueous–organic biphasic systems have provided new prospects in organometallic catalysis,[32] and thereby interest in aqua complexes of ruthenium has increased.[33] In light of these results, coordination of water to ruthenium may also be a plausible event in the synthesis of enol esters. Consequently, the slight decrease of the selectivity with the catalyst loading (Figure SI7) might find a plausible explanation. Thus, as the catalyst loading decreases, the initial molar ratios [H_2O]/[ruthenium complex] and [H_2O]/[Na_2CO_3] increase, which might result in the formation of various oxygenated ruthenium species, presumably active in the synthesis of enol esters and displaying an overall selectivity that is somewhat lower than that of the primary catalytic species.

In principle, the carboxylic acid substrate could also interact with the ruthenium center. To the best of our knowledge, however, the direct synthesis of ruthenium carboxylates from [$RuCl_2$(arene)(PR_3)] and carboxylic acids, alkali metal carboxylates, or mixtures thereof has never been reported.[34] The use of silver carboxylates, however, proved successful, with precipitation of AgCl acting as the driving force of the substitution reaction. Thus, [$Ru(O_2CCF_3)_2$(*p*-cymene)(PPh_3)] could easily be obtained upon treatment of [$RuCl_2$(*p*-cymene)(PPh_3)] with 2 equiv. of CF_3CO_2Ag.[35] It is also worth noting that application of the same protocol to [$RuCl_2$(*p*-cymene)(PCy_3)] bearing the bulky and basic tricyclohexylphosphane ligand (PCy_3) afforded a new molecular scaffold in which the [$CF_3CO_2Ag{\cdot}PCy_3$] adduct was connected to a [$Ru(O_2CCF_3)_2$(*p*-cymene)] fragment through three trifluoroacetato bridges.[35] In light of these observations, the direct formation of ruthenium–carboxylates, such as **14**–**16** (Scheme 6), during the synthesis of enol esters is hardly credible. However, would such ruthenium–carboxylate complexes be formed during the reaction, the insertion of the alkyne into a R^1C(O)O–Ru bond has been ruled out. It has been shown indeed that the reaction between benzoic acid and 1-hexyne in the presence of η^1-acetato– (**17**) or η^2-acetato–ruthenium complexes **18** afforded only hexenyl benzoates. Not even a trace of the hexenyl acetates was observed, demonstrating that coordinated carboxylate groups do not add to the alkyne, but only an external carboxylic acid (Scheme 7).[13a]



14 **15** **16**

Scheme 6. Hypothetical ruthenium–carboxylate complexes.



Scheme 7. Stoichiometric reactions between benzoic acid, 1-hexyne, and ruthenium carboxylates **17** and **18**.[13a]

To summarize, owing to the chelate effect of the 8-electron phosphanoarene ligand, the arene moiety is believed to be coordinated throughout the catalytic process, although variation in hapticity cannot be excluded a priori. This is consistent with the experimental observations that the arene fragment greatly influences the outcome of the reaction. In addition, the presence of small quantities of both Na_2CO_3 and water might lead to a variety of ruthenium species including hydroxy, η^1- and η^2-carbonato, and aqua complexes, which might explain the presence of several peaks in the ^{31}P NMR spectrum of a reaction mixture (Figure 3).

Conclusions

We have shown that tethered (η^1:η^6-phosphanoarene)ruthenium complexes **4**–**6** are highly efficient catalyst precursors for the selective synthesis of Markovnikov-type vinyl esters from carboxylic acids and terminal alkynes. The efficiency of the catalyst systems can be improved further by using moist toluene as solvent. Consequently, TON's as high as 5000 were achieved, which makes complexes **4**–**6** attractive additions to the repertoire of catalysts for the synthesis of vinyl esters. Further investigations on related catalyst systems bearing variously substituted arene moieties are underway.

Experimental Section

General Information: All reactions were carried out under an inert atmosphere, using reagents (Aldrich) and solvents (Aldrich, Labotec) dried and purified by standard techniques.[36] Microwave-assisted syntheses were performed using a single-mode Discover reactor from CEM Corp. (Matthews, NC) where the temperature was monitored with an IR sensor. GC analyses were performed on a Varian Star 3400 CX gas chromatograph equipped with an RSLM-150 capillary column (25 m × 0.25 mm; film thickness, 0.25 µm) and a flame ionization detector. The enol esters were purified by distillation under high vacuum and characterized by ^1H and ^{13}C NMR spectroscopy, according to the literature.[12,13]

Typical Procedure for the Addition of Carboxylic Acids to Alkynes. Conventional Heating: The reaction between 4-acetoxybenzoic acid and 1-hexyne is representative of the procedure utilized. A 25-mL dry round-bottom Pyrex vessel containing a stirring bar and fitted with a three-way stopcock was charged with the catalyst (9.2×10^{-3} mmol), sodium carbonate (18.4×10^{-3} mmol, 1.9 mg), and 4-acetoxybenzoic acid (1.15 mmol, 208 mg), and then purged of air (three vacuum–nitrogen cycles). A stock solution (6 mL) containing 1-hexyne (1.725 mmol) and dodecane (internal standard) in toluene was then added under nitrogen. The resulting mixture was placed in an oil bath and treated at 60 °C. The reaction was monitored by withdrawing samples at regular time intervals from the reaction mixture and analyzing them by GC.

Conventional Heating in Sealed Tubes: A 10-mL glass tube equipped with a stirring bar was charged with the catalyst (0.004 mmol) and 4-acetoxybenzoic acid (0.5 mmol, 90 mg) and then purged of air (three vacuum–nitrogen cycles) before a stock solution (2.6 mL) containing 1-hexyne (0.75 mmol) and dodecane (internal standard) in toluene was added. The tube was sealed under vacuum and immersed in an oil bath heated at 160 °C. After a given reaction time, the ampoule was drawn out of the bath and cooled to room temperature.

Microwave Heating: A 10-mL glass vial containing a Teflon®-coated stir bar was charged with the catalyst (0.004 mmol) and 4-acetoxybenzoic acid (0.5 mmol, 90 mg) and then purged of air (three vacuum–nitrogen cycles) before a stock solution (2.6 mL) containing 1-hexyne (0.75 mmol) and dodecane (internal standard) in toluene was added. The vial was capped under nitrogen, heated to 160 °C (monitored by IR sensor), and then held at that temperature in a CEM Discover instrument with 150-W microwave power. No ramp and no simultaneous cooling were applied. After rapid air-cooling by the unit, the reaction mixture was analyzed by GC.

Supporting Information (see also the footnote on the first page of this article): Experimental section and additional results.

Acknowledgments

The Belgian team thanks the Fonds pour la Formation à la Recherche dans l'Industrie et dans l'Agriculture (FRIA) for a fellowship to F. N. and the Fonds National de la Recherche Scientifique (FNRS), Brussels for financial support of this work (grants FRFC 2.4565.07 and 2.4645.07) and for the purchase of major instrumentation. The Barcelona team thanks the Spanish Ministerio de Educación y Ciencia (MEC) (project CTQ2007-61058/BQU). R. A. thanks the Departament d'Universitats, Recerca i Societat de la Informació de la Generalitat de Catalunya (DURSI) for the award of a Ph.D. grant.

---

[1] G. Appendino, S. Prosperini, C. Valdivia, M. Ballero, G. Colombano, R. A. Billington, A. A. Genazzani, O. Sterner, *J. Nat. Prod.* **2005**, *68*, 1213–1217.

[2] A. Saouf, F. M. Guerra, J. J. Rubal, F. J. Moreno-Dorado, M. Akssira, F. Mellouki, M. López, A. J. Pujadas, Z. D. Jorge, G. M. Massanet, *Org. Lett.* **2005**, *7*, 881–884.

[3] a) E. Negishi, A. Alimardanov, C. Xu, *Org. Lett.* **2000**, *2*, 65–67; b) R. Rossi, F. Bellina, A. Catanese, L. Mannina, D. Valensin, *Tetrahedron* **2000**, *56*, 479–487.

[4] F. C. Görth, R. Brückner, *Synthesis* **1999**, 1520–1528.

[5] a) N. B. Carter, A. E. Nadany, J. B. Sweeney, *J. Chem. Soc. Perkin Trans. 1* **2002**, 2324–2342. See also: b) G. R. Flematti, E. L. Ghisalberti, K. W. Dixon, R. D. Trengove, *Science* **2004**, *305*, 977; c) K. Sun, Y. Chen, T. Wagerle, D. Linnstaedt, M. Currie, P. Chmura, Y. Song, M. Xu, *Tetrahedron Lett.* **2008**, *49*, 2922–2925; d) Y. Demydchuk, Y. Sun, H. Hong, J. Staunton, J. B. Spencer, P. F. Leadlay, *ChemBioChem* **2008**, *9*, 1136–1145; e) L. Commeiras, J. Thibonnet, J.-L. Parrain, *Org. Biomol. Chem.* **2009**, *7*, 425–427; f) L. Commeiras, J. Thibonnet, J.-L. Parrain, *Eur. J. Org. Chem.* **2009**, 2987–2997.

[6] a) Y. Kita, S. Akai, N. Ajimura, M. Yoshigi, T. Tsugoshi, H. Yasuda, Y. Tamura, *J. Org. Chem.* **1986**, *51*, 4150–4158; b) Z. Kabouche, C. Bruneau, P. H. Dixneuf, *Tetrahedron Lett.* **1991**, *32*, 5359–5362; c) M. Neveux, C. Bruneau, S. Lécolier, P. H. Dixneuf, *Tetrahedron* **1993**, *49*, 2629–2640; d) C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1997**, 507–512. See also: ; e) B. M. Trost, J. D. Chisholm, *Org. Lett.* **2002**, *4*, 3743–3745; f) B. M. Trost, J. D. Chisholm, S. T. Wrobleski, M. Jung, *J. Am. Chem. Soc.* **2002**, *124*, 12420–12421; g) B. M. Trost, P. E. Harrington, J. D. Chisholm, S. T. Wrobleski, *J. Am. Chem. Soc.* **2005**, *127*, 13598–13610; h) Y.-G. Wang, M. Wachi, Y. Kobayashi, *Synlett* **2006**, 481–483; i) P. Va, W. R. Roush, *Tetrahedron* **2007**, *63*, 5768–5796; j) H. H. Jung, J. R. Seiders II, P. E. Floreancig, *Angew. Chem. Int. Ed.* **2007**, *46*, 8464–8467; k) P. A. Roethle, I. T. Chen, D. Trauner, *J. Am. Chem. Soc.* **2007**, *129*, 8960–8961; l) G. Ehrlich, J. Hassfeld, U. Eggert, M. Kalesse, *Chem. Eur. J.* **2008**, *14*, 2232–2247; m) C. H. Kim, H. J. An, W. K. Shin, W. Yu, S. K. Woo, S. K. Jung, E. Lee, *Chem. Asian J.* **2008**, *3*, 1523–1534; n) D. K. Mohapatra, B. Chatterjee, M. K. Gurjar, *Tetrahedron Lett.* **2009**, *50*, 755–758; o) W. Tu, P. E. Floreancig, *Angew. Chem. Int. Ed.* **2009**, *48*, 4567–4571.

[7] See for instance: a) M. Shoji, S. Kishida, M. Takeda, H. Kakeya, H. Osada, Y. Hayashi, *Tetrahedron Lett.* **2002**, *43*, 9155–9158; b) G. Mehta, S. S. Ramesh, *Tetrahedron Lett.* **2004**, *45*, 1985–1987; c) G. Mehta, K. Islam, *Tetrahedron Lett.* **2004**, *45*, 3611–3615; d) G. Mehta, K. Islam, *Tetrahedron Lett.* **2004**, *45*, 7683–7687; e) E. Pinot, A. Guy, A. Fournial, L. Balas, J.-C. Rossi, T. Durand, *J. Org. Chem.* **2008**, *73*, 3063–3069; f) N. Li, M.-H. Zong, D. Ma, *Eur. J. Org. Chem.* **2008**, 5375–5378; g) J. Stambasky, A. V. Malkov, P. Kocovsky, *J. Org. Chem.* **2008**, *73*, 9148–9150; h) A. Träff, K. Bogár, M. Warner, J.-E. Bäckvall, *Org. Lett.* **2008**, *10*, 4807–4810; i) D. Özdemirhan, S. Sezer, Y. Sönmez, *Tetrahedron: Asymmetry* **2008**, *19*, 2717–2720; j) N. Li, M.-H. Zong, D. Ma, *Tetrahedron* **2009**, *65*, 1063–1068; k) C. Quirin, U. Kazmaier, *Eur. J. Org. Chem.* **2009**, 371–377.

[8] L. J. Gooßen, J. Paetzold, *Angew. Chem. Int. Ed.* **2004**, *43*, 1095–1098.

[9] See for instance: a) H. H. Wasserman, P. S. Wharton, *J. Am. Chem. Soc.* **1960**, *82*, 661–665; b) P. F. Hudrlik, A. M. Hudrlik, *J. Org. Chem.* **1973**, *38*, 4254–4258; c) R. C. Larock, K. Oertle, K. M. Beatty, *J. Am. Chem. Soc.* **1980**, *102*, 1966–1974; d) R. D. Bach, R. A. Woodard, T. J. Anderson, M. D. Glick, *J. Org. Chem.* **1982**, *47*, 3707–3712; e) B. C. Söderberg, M. J. Turbeville, *Organometallics* **1991**, *10*, 3951–3953; f) B. C. Söderberg, J. Liu, T. W. Ball, M. J. Turbeville, *J. Org. Chem.* **1997**, *62*, 5945–5952; g) H. Imagawa, Y. Fujikawa, A. Tsuchihiro, A. Kinoshita, T. Yoshinaga, H. Takao, M. Nishizawa, *Synlett* **2006**, 639–641; h) A. Duchêne, J. Thibonnet, J.-L. Parrain, E. Anselmi, M. Abarbri, *Synthesis* **2007**, 597–607; i) K. Komeyama, K. Takahashi, K. Takaki, *Org. Lett.* **2008**, *10*, 5119–5122.

[10] F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* **2004**, *104*, 3079–3159.

[11] a) Y. Kita, H. Maeda, K. Omori, T. Okuno, Y. Tamura, *Synlett* **1993**, 273–274; b) Y. Kita, H. Maeda, K. Omori, T. Okuno, Y. Tamura, *J. Chem. Soc. Perkin Trans. 1* **1993**, 2999–3005; c) Y. Ohba, M. Takatsuji, K. Nakahara, H. Fujioka, Y. Kita, *Chem. Eur. J.* **2009**, *15*, 3526–3537.

[12] See for instance: a) Y. Ishino, I. Nishiguchi, S. Nakao, T. Hirashima, *Chem. Lett.* **1981**, 641–644; b) C. Lambert, K. Utimoto, H. Nozaki, *Tetrahedron Lett.* **1984**, *25*, 5323–5326; c) C. Bianchini, A. Meli, M. Peruzzini, F. Zanobini, C. Bruneau, P. H. Dixneuf, *Organometallics* **1990**, *9*, 1155–1160; d) E. Genin, P. Y. Toullec, S. Antoniotti, C. Brancour, J.-P. Genêt, V. Michelet, *J. Am. Chem. Soc.* **2006**, *128*, 3112–3113; e) E. Marchal, P. Uriac, B. Legouin, L. Toupet, P. van de Weghe, *Tetrahedron* **2007**, *63*, 9979–9990; f) F. Neatu, V. I. Pârvulescu, V. Michelet, J.-P. Genêt, A. Goguet, C. Hardacre, *New J. Chem.* **2009**, *33*, 102–106; g) H. Harkat, A. Yénimégué Dembelé, J.-M. Weibel, A. Blanc, P. Pale, *Tetrahedron* **2009**, *65*, 1871–1879.

[13] See for instance: a) C. Bruneau, M. Neveux, Z. Kabouche, C. Ruppin, P. H. Dixneuf, *Synlett* **1991**, 755–763; b) M. Rotem, Y. Shvo, *J. Organomet. Chem.* **1993**, *448*, 189–204; c) H. Doucet, B. Martin-Vaca, C. Bruneau, P. H. Dixneuf, *J. Org. Chem.* **1995**, *60*, 7247–7255; d) S. Ye, W. K. Leong, *J. Organomet. Chem.* **2006**, *691*, 1117–1120; e) S. Costin, N. P. Rath, E. B. Bauer, *Adv. Synth. Catal.* **2008**, *350*, 2414–2424.

[14] L. J. Gooβen, J. Paetzold, D. Koley, *Chem. Commun.* **2003**, 706–707.

[15] B. Therrien, *Coord. Chem. Rev.* **2009**, *253*, 493–519.

[16] R. Aznar, G. Muller, D. Sainz, M. Font-Bardia, X. Solans, *Organometallics* **2008**, *27*, 1967–1969.

[17] a) F. Nicks, L. Libert, L. Delaude, A. Demonceau, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **2008**, *49*(2), 944–945; b) F. Nicks, L. Libert, L. Delaude, A. Demonceau, *Aust. J. Chem.* **2009**, *62*, 227–231.

[18] a) L. Perreux, A. Loupy, *Tetrahedron* **2001**, *57*, 9199–9223; b) P. Lidström, J. Tierney, B. Wathey, J. Westman, *Tetrahedron* **2001**, *57*, 9225–9283; c) M. Larhed, C. Moberg, A. Hallberg, *Acc. Chem. Res.* **2002**, *35*, 717–727; d) C. O. Kappe, *Angew. Chem. Int. Ed.* **2004**, *43*, 6250–6284; e) B. Desai, C. O. Kappe, *Top. Curr. Chem.* **2004**, *242*, 177–208; f) C. O. Kappe, A.

Stadler, *Microwaves in Organic and Medicinal Chemistry*, Wiley-VCH, Weinheim, **2005**; g) D. Dallinger, C. O. Kappe, *Chem. Rev.* **2007**, *107*, 2563–2591; h) C. O. Kappe, *Chem. Soc. Rev.* **2008**, *37*, 1127–1139; i) D. M. Ide, M. P. Eastlund, C. L. Jupe, R. A. Stockland Jr., *Curr. Org. Chem.* **2008**, *12*, 1258–1278; j) P. Appukkuttan, E. Van der Eycken, *Eur. J. Org. Chem.* **2008**, 1133–1155.

[19] a) A. Aidouni, A. Demonceau, L. Delaude, *Synlett* **2006**, 493–495; b) S. Delfosse, Y. Borguet, L. Delaude, A. Demonceau, *Macromol. Rapid Commun.* **2007**, *28*, 492–503; c) Y. Borguet, A. Richel, S. Delfosse, A. Leclerc, L. Delaude, A. Demonceau, *Tetrahedron Lett.* **2007**, *48*, 6334–6338; d) A. Aidouni, S. Bendahou, A. Demonceau, L. Delaude, *J. Comb. Chem.* **2008**, *10*, 886–892; e) F. Nicks, Y. Borguet, S. Delfosse, D. Bicchielli, L. Delaude, X. Sauvage, A. Demonceau, *Aust. J. Chem.* **2009**, *62*, 184–207.

[20] a) J. G. P. Binner, N. A. Hassine, T. E. Cross, *J. Mater. Sci.* **1995**, *30*, 5389–5393; b) A. de la Hoz, Á. Díaz-Ortiz, A. Moreno, *Chem. Soc. Rev.* **2005**, *34*, 164–178; c) J. D. Moseley, P. Lenden, A. D. Thomson, J. P. Gilday, *Tetrahedron Lett.* **2007**, *48*, 6084–6087; d) J. P. Gilday, P. Lenden, J. D. Moseley, B. G. Cox, *J. Org. Chem.* **2008**, *73*, 3130–3134; e) K. R. Seipel, Z. H. Platt, M. Nguyen, A. W. Holland, *J. Org. Chem.* **2008**, *73*, 4291–4294; f) C. K. Lombard, K. L. Myers, Z. H. Platt, A. W. Holland, *Organometallics* **2009**, *28*, 3303–3306.

[21] In control experiments, we checked that Celite was inert, even under extended reaction times with heating to 160 °C; see ref.[17b]

[22] a) M. C. Carrión, F. A. Jalón, B. R. Manzano, A. M. Rodríguez, F. Sepúlveda, M. Maestro, *Eur. J. Inorg. Chem.* **2007**, 3961–3973; b) O. Hamelin, M. Rimboud, J. Pécaut, M. Fontecave, *Inorg. Chem.* **2007**, *46*, 5354–5360; c) L.-I. Rodríguez, O. Rossell, M. Seco, G. Muller, *J. Organomet. Chem.* **2007**, *692*, 851–858; d) W. Tan, X. Zhao, Z. Yu, *J. Organomet. Chem.* **2007**, *692*, 5395–5402; e) A. Bacchi, M. Balordi, R. Cammi, L. Elviri, C. Pelizzi, F. Picchioni, V. Verdolino, K. Goubitz, R. Peschar, P. Pelagatti, *Eur. J. Inorg. Chem.* **2008**, 4462–4473; f) X. Wu, J. Liu, D. Di Tommaso, J. A. Iggo, C. R. A. Catlow, J. Bacsa, J. Xiao, *Chem. Eur. J.* **2008**, *14*, 7699–7715; g) N. A. Cortez, G. Aguirre, M. Parra-Hake, R. Somanathan, *Tetrahedron: Asymmetry* **2008**, *19*, 1304–1309; h) Y. Chen, Y. Tang, S. Liu, M. Lei, W. Fang, *Organometallics* **2009**, *28*, 2078–2084.

[23] A. B. Chaplin, P. J. Dyson, *Organometallics* **2007**, *26*, 2447–2455.

[24] a) J. W. Faller, A. Lavoie, *J. Organomet. Chem.* **2001**, *630*, 17–22; b) A. E. Díaz-Álvarez, P. Crochet, M. Zablocka, V. Cadierno, L. Vendier, J. Gimeno, J.-P. Majoral, *Polyhedron* **2007**, *26*, 933–940.

[25] a) A. W. Stumpf, E. Saive, A. Demonceau, A. F. Noels, *J. Chem. Soc., Chem. Commun.* **1995**, 1127–1128; b) A. Demonceau, A. W. Stumpf, E. Saive, A. F. Noels, *Macromolecules* **1997**, *30*, 3127–3136; c) L. Delaude, A. Demonceau, A. F. Noels, *Macromolecules* **1999**, *32*, 2091–2103; d) L. Delaude, A. Demonceau, A. F. Noels, *Chem. Commun.* **2001**, 986–987; e) L. Delaude, A. Demonceau, A. F. Noels, *Macromolecules* **2003**, *36*, 1446–1456; f) M. Ahr, C. Thieuleux, C. Copéret, B. Fenet, J.-M. Basset, *Adv. Synth. Catal.* **2007**, *349*, 1587–1591; g) X. Sauvage, Y. Borguet, G. Zaragoza, A. Demonceau, L. Delaude, *Adv. Synth. Catal.* **2009**, *351*, 441–455; h) L. Delaude, X. Sauvage, A. Demonceau, J. Wouters, *Organometallics* **2009**, *28*, 4056–4064.

[26] a) F. Simal, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **1998**, *39*, 3493–3496; b) N. E. Leadbeater, K. A. Scott, L. J. Scott, *J. Org. Chem.* **2000**, *65*, 3231–3232; c) A. Tudose, A. Demonceau, L. Delaude, *J. Organomet. Chem.* **2006**, *691*, 5356–5365.

[27] a) F. Simal, A. Demonceau, A. F. Noels, *Angew. Chem. Int. Ed.* **1999**, *38*, 538–540; b) F. Simal, S. Sebille, L. Hallet, A. Demonceau, A. F. Noels, *Macromol. Symp.* **2000**, *161*, 73–85; c) F. Simal, D. Jan, L. Delaude, M.-R. Spirlet, A. F. Noels, *Can. J. Chem.* **2001**, *79*, 529–535; d) L. Delaude, S. Delfosse, A. Richel, A. Demonceau, A. F. Noels, *Chem. Commun.* **2003**, 1526–1527; e) A. Richel, S. Delfosse, C. Cremasco, L. Delaude, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **2003**, *44*, 6011–6015; f) X. Sauvage, Y. Borguet, A. F. Noels, L. Delaude, A. Demonceau, *Adv. Synth. Catal.* **2007**, *349*, 255–265.

[28] a) P. D. Smith, A. H. Wright, *J. Organomet. Chem.* **1998**, *559*, 141–147; b) F. Simal, D. Jan, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **1999**, *40*, 1653–1656; c) D. Jan, L. Delaude, F. Simal, A. Demonceau, A. F. Noels, *J. Organomet. Chem.* **2000**, *606*, 55–64; d) K. Umezawa-Vizzini, T. R. Lee, *Organometallics* **2003**, *22*, 3066–3076; e) P. Pinto, A. W. Götz, G. Marconi, B. A. Hess, A. Marinetti, F. W. Heinemann, U. Zenneck, *Organometallics* **2006**, *25*, 2607–2616.

[29] a) J. F. Hartwig, R. G. Bergman, R. A. Andersen, *Organometallics* **1991**, *10*, 3344–3362; b) L. Maurette, B. Donnadieu, G. Lavigne, *Angew. Chem. Int. Ed.* **1999**, *38*, 3707–3710; c) T. J. Geldbach, P. S. Pregosin, *Eur. J. Inorg. Chem.* **2002**, 1907–1918; d) G. Henig, M. Schulz, B. Windmüller, H. Werner, *Dalton Trans.* **2003**, 441–448; e) J.-B. Sortais, L. Brelot, M. Pfeffer, L. Barloy, *Acta Crystallogr., Sect. E* **2008**, *64*, m483–m484; f) I. Özdemir, S. Demir, B. Çetinskaya, C. Gourlaouen, F. Maseras, C. Bruneau, P. H. Dixneuf, *J. Am. Chem. Soc.* **2008**, *130*, 1156–1157; g) O. R. Allen, S. J. Dalgarno, L. D. Field, P. Jensen, A. C. Willis, *Organometallics* **2009**, *28*, 2385–2390.

[30] B. Demerseman, M. D. Mbaye, D. Sémeril, L. Toupet, C. Bruneau, P. H. Dixneuf, *Eur. J. Inorg. Chem.* **2006**, 1174–1181.

[31] B. A. Énglin, A. F. Platé, V. M. Tugolukov, M. A. Pryanishnikova, *Khim. Tekhn. Topliv Masel* **1965**, *9*, 42–46.

[32] a) P. A. Grieco, *Organic Synthesis in Water*, Blackie, London, **1998**; b) F. Joó, *Aqueous Organometallic Catalysis*, Kluwer, Dordrecht, **2001**; c) D. J. Adams, P. J. Dyson, S. J. Tavener, *Chemistry in Alternative Reaction Media*, Wiley, Chichester, **2004**; d) F. Joó, Á. Kathó, *Aqueous Phase Organometallic Catalysis* (Eds.: B. Cornils, W. A. Herrmann), 2nd ed., Wiley-VCH, **2004**; e) B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt (Eds.), *Multiphase Homogeneous Catalysis*, Wiley-VCH, Weinheim, **2005**.

[33] a) E. Garcia Fidalgo, L. Plasseraud, G. Süss-Fink, *J. Mol. Catal. A* **1998**, *132*, 5–12; b) P. V. Grundler, G. Laurenczy, A. E. Merbach, *Helv. Chim. Acta* **2001**, *84*, 2854–2867; c) A. Rossin, G. Kovács, G. Ujaque, A. Lledós, F. Joó, *Organometallics* **2006**, *25*, 5010–5023; d) G. Kovács, G. Ujaque, A. Lledós, F. Joó, *Eur. J. Inorg. Chem.* **2007**, 2879–2889; e) T. Campos-Malpartida, M. Fekete, F. Joó, Á. Kathó, A. Romerosa, M. Saoud, W. Wojtków, *J. Organomet. Chem.* **2008**, *693*, 468–474.

[34] D. A. Tocher, R. O. Gould, T. A. Stephenson, M. A. Bennett, J. P. Ennett, T. W. Matheson, L. Sawyer, V. K. Shah, *J. Chem. Soc., Dalton Trans.* **1983**, 1571–1581.

[35] M. R. Buchmeiser, D. Wang, Y. Zhang, S. Naumov, K. Wurst, *Eur. J. Inorg. Chem.* **2007**, 3988–4000.

[36] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon, Oxford (UK), **1988**.

Received: June 22, 2009