

Hydrocarboxylation of Terminal Alkenes in Supercritical Carbon Dioxide

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The catalytic hydrocarboxylation of linear alkenes to carboxylic acids using supercritical carbon dioxide as a solvent was studied. High selectivities in acids have been obtained. The best results were achieved when adding a perfluorinated surfactant to the reaction mixture (93 % conversions and ca.

80 % selectivity). Comparative multinuclear high-pressure NMR spectroscopic studies in [D₈]THF and in supercritical CO₂ show the formation of Pd⁰ species.

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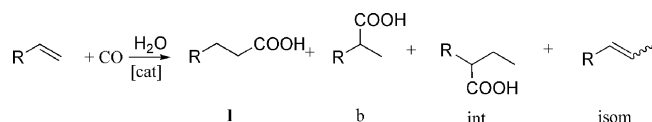
Introduction

Carbon dioxide in its liquid or supercritical state (scCO₂) has great potential as an environmentally benign reaction medium for chemical synthesis.^[1] Since the mid-1990s, rapidly increasing research efforts have shown that scCO₂ can replace conventional solvents in a wide range of processes.^[2] Replacing or reducing toxic solvents is also one of the postulates of Green Chemistry.^[3] There is also increasing evidence that the application of scCO₂ can broaden the scope of catalytic synthetic methodologies. Carbon dioxide becomes supercritical at $T_c = 31.1\text{ °C}$ and $P_c = 73.8\text{ bar}$. Beyond this point there is no distinction between the liquid or gas phase and the new supercritical phase presents properties of both states, this means higher solubility of gases than with organic solvents.^[1] Therefore it can improve the yield of homogeneous catalysis, particularly for those reactions that are first order in the concentration of the gaseous reagent. In addition, it is known that the density of CO₂ changes dramatically in the near-critical regime, therefore the solubility of the reagents suffer the same effect. Small changes in temperature or pressure cause dramatic changes in the density, viscosity and dielectric constant of supercritical CO₂, which makes it a tuneable solvent.

The mild critical data and the low cost of the material itself make carbon dioxide attractive over other solvents such as hydrocarbons or hydrofluorocarbons. Since scCO₂

is a nonpolar medium the best solubility is observed for nonpolar solutes. Organic fluorocarbons show a high solubility in scCO₂. Therefore, many works report that perfluorochains have been used to solubilize substrates, reagents or catalysts.^[1,4] The solubility of polar substances can be substantially increased by adding polar cosolvents or surfactants to form microemulsions.^[5]

Palladium-catalyzed hydrocarboxylation of alkenes^[6] (Scheme 1) is a straightforward and environmentally friendly method for obtaining carboxylic acids with an atom selectivity of 100%.^[7] Carboxylic acids have important industrial applications as large volume products and chemical intermediates such as acrylic or adipic acid derivatives.^[6] Other products of interest are 2-arylpropionic acids, which are the most important class of nonsteroidal anti-inflammatory drugs,^[8] and can be obtained by hydrocarboxylation of styrene. In this reaction (Scheme 1) two regioisomers can be formed: the branched (b) and the linear (l) isomers. Byproducts of this reaction are the isomerization products (isom) and internal carboxylic acids (int).



Scheme 1. Hydrocarboxylation reaction of alkenes.

The carbonylation of alkenes in organic solvents have been extensively studied in the last decade. There are many papers studying the effects of ligand, solvent, temperature and pressure.^[6,9] Water has been used as a solvent but when the solubility of the substrates is low the conversion decreases drastically.^[10] One efficient way to increase the affinity of water of scCO₂ is to generate water-in-CO₂ (W/C) microemulsions, which can be formed by using ammonium

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perfluoro-polyether-carboxylate surfactants.^[5c,11] These dispersions have been used to solubilize hydrophilic substances into CO₂, applied to organic reactions^[11] and used to perform aqueous/scCO₂ biphasic metal-catalyzed reactions with water-soluble catalysts.^[12] In a preliminary communication, we have recently reported that the use of a perfluoro-polyether surfactant enhances the activity and the regioselectivity to the linear acid although the selectivity decreases.^[13] In the literature there are different works on carbonylation reactions that use scCO₂,^[14,15] but none on hydrocarboxylation reactions using scCO₂.

Here, we present different aspects of the hydrocarboxylation of linear alkenes in supercritical carbon dioxide media using the catalytic precursor formed with [PdCl₂(NCPH)₂] and phosphane ligands containing fluorinated groups (**1–4**, Figure 1). Triphenylphosphane (**5**, Figure 1) is used as a reference ligand. Ligand **1** forms the rhodium CO₂ soluble complex *trans*-[Rh(CO)Cl(**1**)₂] (solubility of at least 5.5 mM in scCO₂ at 343 K and 273 atm), which was reported to be active in the hydroformylation of 1-octene in scCO₂.^[16] We also analysed the ability of perfluorinated surfactants to increase the solubility of water in scCO₂. A study of the species formed under CO pressure by HPNMR is also presented.

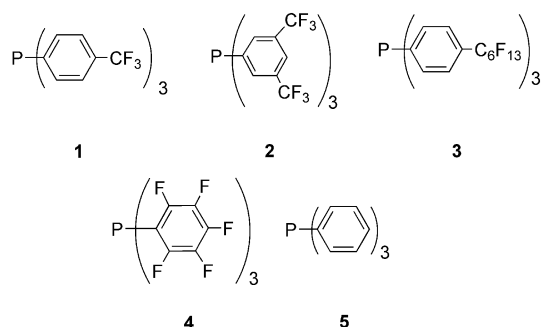
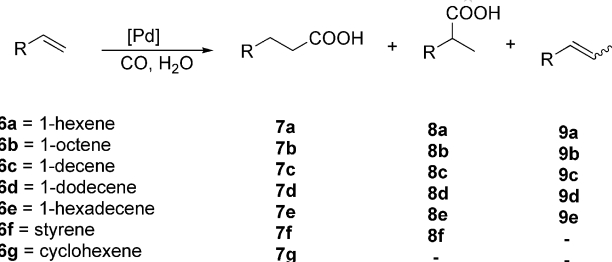


Figure 1. Fluorine containing the phosphanes **1–4** and triphenylphosphane (**5**) used as ligands in the Pd-catalysed hydrocarboxylation of 1-alkenes.

Results and Discussion

The hydrocarboxylation of alkenes **6a–g** (Scheme 2) in the presence of water was studied using supercritical carbon dioxide as the solvent and a catalyst precursor prepared in situ by the addition of the complex [PdCl₂(NCPH)₂], the corresponding ligands **1–5** (Pd/**1–5** systems) and an acid. The products obtained were the corresponding linear acids **7a–g** and branched acids **8a–f**. The internal alkenes **9a–e** formed by isomerisation were also detected in the case of the 1-alkenes (Scheme 2). For comparative purposes the reactions were also studied using a standard catalyst precursor [PdCl₂(PPh₃)₂] in an organic solvent under reaction conditions selected in previous literature studies.^[17]



Scheme 2. Products obtained in the hydrocarboxylation of different 1-alkenes.

Hydrocarboxylation in scCO₂

First we examined the solubility of the Pd/**1–5** catalyst precursor systems in scCO₂ under the reaction conditions to be used. This was carried out by placing [PdCl₂(NCPH)₂] (0.1 mmol) and the corresponding phosphane (0.4 mmol) in a 100 mL autoclave with sapphire windows, and the system was charged with liquid CO₂. Then, the pressure and temperature were gradually increased over the ranges used in the catalytic experiments. The conditions of solubility for at least 1 mM of the [PdCl₂(NCPH)₂]/PR₃ solutions (the concentration used in the reactions) are summarized in Table 1. We observed that the palladium system with the 3,5-CF₃ substituted phosphane **2** is soluble at milder conditions than the systems with the 4-substituted ones, **1** and **3**, regardless of the perfluorinated chain length. The palladium system with phosphane **4** requires a higher pressure and temperature to be solubilized and the palladium system with PPh₃ was apparently insoluble up to 250 atm and 100 °C.

Table 1. Solubility conditions of [PdCl₂(NCPH)₂]/PR₃^[a].

PR ₃	<i>P</i> _{Total} [atm]	<i>T</i> [°C]
1	175	75
2	130	90
3	160	90
4	180	90
5	insoluble up to 250	insoluble up to 100

[a] [PdCl₂(NCPH)₂] = 1 × 10^{−3} M, molar ratio Pd/PR₃ = 1:4, 30 atm of CO.

The ³¹P{¹H} NMR spectra, in deuterated chloroform, of the products obtained after the solubility tests of the systems Pd/**1** or **2** confirmed the in situ formation of the corresponding complexes [PdCl₂(**1** or **2**)₂] with signals at δ = 23.8 and 25.5 ppm, respectively.^[18,19]

Once the initial conditions in which the catalyst precursors showed solubility in scCO₂ were established, we proceeded with the catalytic studies analysing the influence of different parameters in the conversion and selectivity of the hydrocarboxylation reaction.

Initially, we studied the hydrocarboxylation reaction under standard conditions (P/Pd = 4, CO pressure 30 atm) in the presence of oxalic acid and added water, and then we studied different pressures and temperatures. With the system [PdCl₂(NCPH)₂]/**1** (Pd/**1**) we observed that at 120 atm total pressure the conversion and selectivity in acid was low

(Entry 1, Table 2). By increasing the total pressure to 150 atm, when the precatalytic system is not soluble, the conversion and selectivity increased to 55% and 90%, respectively (Entry 2, Table 2). By increasing the total pressure to 200 atm the precatalyst becomes soluble but the conversion dropped to 6% (Entry 3, Table 2) and no acids were detected at 250 atm (Entry 4, Table 2). Apparently, as the solubility in scCO_2 of the catalytic precursor increases, the reactions with a polar reagent, such as water, become less favourable. Some drops of water were always observed during the reaction period. The same behaviour in the con-

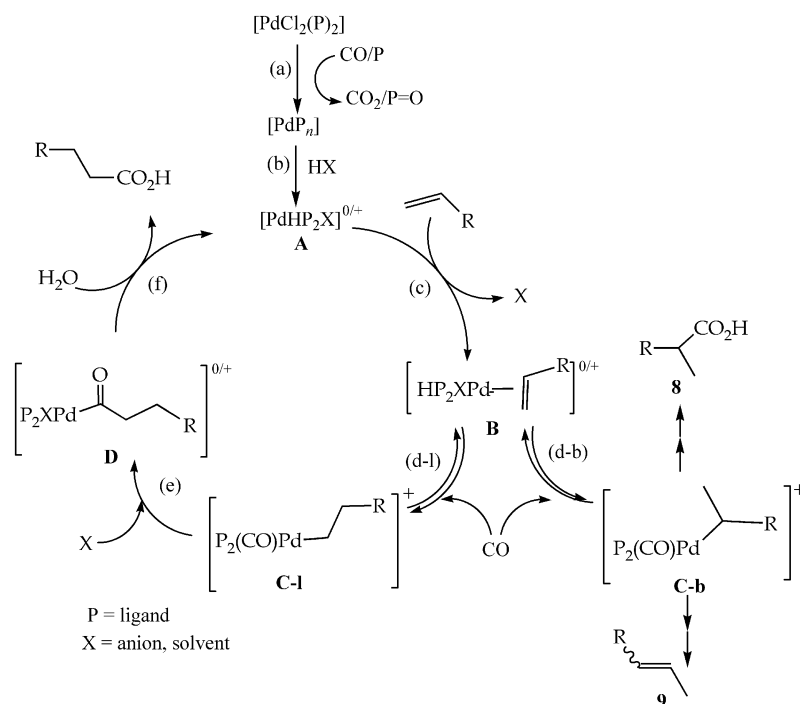
Table 2. Hydroformylation of 1-octene using $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{L}(\mathbf{1}-\mathbf{3})$ in scCO_2 .^[a]

Entry	L	P_{Total} [atm]	% C ^[b]	% S _{7,8} ^[c]	7/8 [%]	S ₉ ^[d]
1	1	120	10	61	55:45	39
2	1	150	55	90	75:25	10
3	1	200	6	75	60:40	25
4	1	250	0	—	—	—
5	2	120	57	85	41:59	15
6	2	150	2	77	34:66	—
7	3	150	11	55	73:27	45
8	3	200	1	—	—	100
9	4	120	0	—	—	—
10	4	150	0	—	—	—
11 ^[e]	1	150	16	18	58:42	82
12 ^[e]	1	200	26	83	33:67	17
13	5	150	29	33	55:45	67
14 ^[f]	5	—	89	86 ^[g]	51:49	8

[a] Reaction conditions: time = 12 h, $[\text{PdCl}_2(\text{NCPh})_2] = 1 \times 10^{-3}$ M, molar ratio $\text{Pd}/\text{L}/\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}/1\text{-octene}/\text{H}_2\text{O} = 1:4:62.5:62.5:500$, $P_{\text{CO}} = 30$ atm, $T = 90^\circ\text{C}$. [b] Total conversion. [c] Selectivity in acids. [d] Selectivity in internal alkenes. [e] $T = 120^\circ\text{C}$. [f] $[\text{PdCl}_2(\text{PPh}_3)_2]/4\text{PPh}_3$ as catalyst in dimethoxyethane as solvent. [g] 6% of oligomers also formed.

version was observed for the catalytic systems $\text{Pd}/\mathbf{2}$ (Entries 5 and 6, Table 2) and $\text{Pd}/\mathbf{3}$ (Entries 7 and 8, Table 2). The palladium catalytic system with phosphane **4** was inactive under the conditions studied (Entries 9 and 10, Table 2). At similar conditions of solubility the conversion decreased in the order $\text{Pd}/\mathbf{1} \approx \text{Pd}/\mathbf{2} > \text{Pd}/\mathbf{3} > \text{Pd}/\mathbf{4}$. This is in agreement with the observation reported in the literature for the hydrocarboxylation of acenaphthylene in organic solvent, where the $\text{Pd}/\mathbf{1}$ system gave a higher conversion than $\text{Pd}/\mathbf{4}$ under similar conditions.^[20]

Regarding the regioselectivity, the systems with the 4-substituted phosphanes **1** and **3** gave the linear product as the major product, however, with the $\text{Pd}/\mathbf{2}$ system the major product is the branched acid. In all cases the competitive reaction is the isomerisation to internal alkenes. The isomerisation products are formed from the branched alkyl intermediate (**C-b**, Scheme 3). Thus, when isomerisation is important the amount of branched acid decreases. The change in regioselectivity for the $\text{Pd}/\mathbf{1}$ and $\text{Pd}/\mathbf{2}$ systems does not seem to be related to the isomerisation side reaction since the results are similar in both cases (Entries 2 and 5, Table 2). In the styrene hydrocarboxylation it has been reported that Pd systems with PPh_3 mainly give the branched isomer, while systems with *cis*-chelated diphosphanes favour the formation of the linear isomers. This has been related to the formation of the *trans* species with the monophosphane ligands favouring the branched product and the palladium with *cis*-chelated diphosphanes favouring the linear species.^[17b] It has been reported that the formation of *cis*- or *trans*-palladium phosphane species (species **A-D**, Scheme 3) depends on the steric requirements of the phosphane.^[21] Thus, phosphanes with Tolman angles of



Scheme 3. General hydride mechanism for hydrocarboxylation.^[9b]

$\theta > 140^\circ$ favour the *trans* species while phosphanes with smaller θ values also give the *cis* species. So, phosphane **2** ($\theta = 160^\circ$)^[19] would favour the formation of the *trans* intermediate species in the catalytic cycle and therefore favours the formation of the branched acid.

The effect of the temperature has been studied with the Pd/**1** catalytic system. In Table 2 it can be observed that by increasing the temperature at 150 atm of total pressure the conversion and the selectivity decrease drastically (Entry 11 versus Entry 2, Table 2). At 200 atm, the conversion is better but still very low and the selectivity in the linear isomer decreases (Entry 12, Table 2). An increase in the branched isomer with an increase in temperature was also reported for the hydrocarboxylation of alkenes using Pd^{II}/PPh₃ as the catalytic system.^[22] The increase of isomerisation products observed in Entry 11 (Table 2) could be related to an increase of β -elimination with an increase in the temperature.^[9b]

Regarding the effect of partial pressure, at higher pressures of carbon monoxide (50 atm) the Pd/**1** system is inactive, probably because competition for the coordination to the palladium centre promotes the formation of the carbonylic Pd⁰ inactive species.^[23] At lower pressures of carbon monoxide (15 atm) no acids were detected. A decrease in the reaction conversion was also reported when the CO pressure decreased for the hydrocarboxylation of 1-octene using PdCl₂/PPh₃ as the catalytic system.^[22]

These initial experiments lead us to conclude that the best conditions of pressure and temperature for hydrocarboxylation of 1-octene are 30 atm of carbon monoxide pressure, 90 °C and 150 atm of total pressure for system Pd/**1** and 120 atm of total pressure for catalytic system Pd/**2**. In both cases the results obtained were better than the results obtained with the palladium catalytic system with PPh₃ (**5**) in scCO₂ (Entry 13, Table 2) but the conversion was lower than the one obtained in an organic solvent (dimethoxyethane) under similar conditions with the [PdCl₂(PPh₃)₂]/4PPh₃ catalytic system (Entry 14, Table 2).

The acid used also had an important effect on the results. The first evidence of this was with water only, i.e. no added acid, where the hydrocarboxylation of 1-octene using the catalyst precursor Pd/**1** did not take place in scCO₂ (Entry 1, Table 3). Presumably the palladium hydride species (species **A**, Scheme 3) is not formed in the absence of a stronger acid. Oxalic acid provided the best conversion while hydrochloric acid or a more CO₂-soluble acid such as trifluoroacetic acid gave a lower conversion and selectivity (Entries 3 and 4, Table 3). Stronger acids may favour the protonation of the phosphane, and thus decrease the formation of the active species. Furthermore, the coordinating ability of the counteranions of these acids may interfere with the coordination of the substrate and decrease the activity of the systems.

Finally, we studied the influence on the conversion of the amount of added water to the Pd/**1** system at 200 atm total pressure, 30 atm of CO pressure and 90 °C (Table 4) when the catalytic system was soluble in scCO₂. At a molar ratio of H₂O/Pd = 125 the selectivity was very low and the main

Table 3. Effect of the acid used in the hydrocarboxylation of 1-octene with Pd/**1**.^[a]

Entry	Acid	% C ^[b]	% S _{7,8} ^[c]	7/8 [%]
1	–	0	–	–
2	H ₂ C ₂ O ₄ ·2H ₂ O	55	90	75:25
3	HCl (aq.) ^[d]	18	76	73:27
4	CF ₃ COOH	3	35	75:25

[a] Reaction conditions: $P_{\text{CO}} = 30$ atm, $P_{\text{T}} = 150$ atm, $T = 90$ °C, time = 12 h, [PdCl₂(PhCN)₂] = 1×10^{-3} M, molar ratio Pd/L/acid/1-octene/H₂O = 1:4:62.5:62.5:500. [b] Total conversion. [c] Selectivity in acids. [d] 35%.

products were internal octenes. Other byproducts such as aldehydes and oligomers were also detected (Entry 1, Table 4). By increasing the molar ratio of H₂O/Pd the selectivity improved significantly but the conversion under these conditions remained low. For a Pd^{II}/PPh₃ system reported in the literature, increasing the concentration of water resulted in the conversion reaching a maximum, but a higher addition of water led to competition for coordination vacancies and decreased the conversion.^[22] In our case, the low affinity for water in the scCO₂ phase might reduce this competition, and no decrease in the conversion was observed up to a molar ratio of H₂O/Pd = 825.

Table 4. Effect of the amount of water used in hydrocarboxylation of 1-octene with Pd/**1**.^[a]

Entry	H ₂ O/Pd	% C ^[b]	% S _{7,8} ^[c]	7/8 [%]
1	125	8	8 ^[d]	62:38
2	500	6	75	60:40
3	825	26	96	67:33

[a] Reaction conditions: $P_{\text{CO}} = 30$ atm, $P_{\text{T}} = 200$ atm, $T = 90$ °C, time = 12 h, [PdCl₂(PhCN)₂] = 1×10^{-3} M, molar ratio Pd/L/H₂C₂O₄·2H₂O/1-octene = 1:4:62.5:62.5. [b] Total conversion. [c] Selectivity in acids. [d] 50% isomerisation and 42% aldehydes/oligomers.

Once the reaction conditions were optimised, we concluded that the low solubility of water in scCO₂ was the main problem to be overcome in order to achieve a higher conversion. Therefore we considered the addition of a surfactant as a mass transfer agent.

Addition of a Surfactant

We used an ammonium perfluoro-polyether-carboxylate (PFPE), Krytox[®]^[24] (**11**, Figure 2), as the surfactant. The syntheses were performed according to literature procedures.^[25] The commercially available ammonium pentadecafluorooctanoate (**12**, Figure 2) was also employed for comparative purposes.

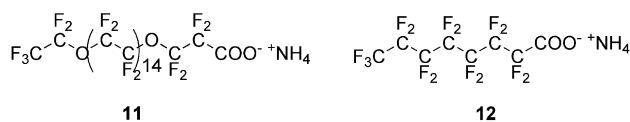


Figure 2. Perfluorinated surfactants used to form the water-scCO₂ microemulsion; Krytox[®] (**11**), ammonium pentadecafluorooctanoate (**12**).

Table 5. Hydrocarboxylation of 1-octene using surfactants (surf.) **11** and **12** and system Pd/**1** as the catalyst precursor.^[a]

Entry	<i>T</i> [°C]	<i>P</i> _{Tot} [atm]	H ₂ O/Pd (molar ratio)	H ₂ O/Surf (molar ratio)	% C ^[b]	% S ^[c]	7/8 [%]
1	90	150	500	14	93	77	82:18
2	90	150	250	14	83	78	83:17
3	120	150	250	14	11	10	66:44
4	90	150	250	28	67	78	82:18
5	90	150	500	28	80	80	80:20
6	90	200	500	14	26	42	76:24
7 ^[d]	90	150	500	28	0	—	—
8 ^[e]	90	150	500	14	0	—	—
9 ^[f]	90	150	500	14	37	45	80:20

[a] Reaction conditions: *P*_{CO} = 30 atm, time = 12 h, [PdCl₂(PhCN)₂] = 1 × 10^{−3} M, molar ratio Pd/L/H₂C₂O₄·2H₂O/1-octene = 1:4:62.5:62.5, surfactant **11**. [b] Total conversion. [c] Selectivity in acids. [d] No PR₃ addition. [e] No oxalic acid addition. [f] Surfactant **12**.

The results obtained using the catalyst precursor Pd/**1** are shown in Table 5. The addition of **11** in a H₂O/**11** molar ratio of 14 promoted an increase in the conversion of up to 93% (Entry 1, Table 5) when working at a molar ratio of H₂O/Pd = 500. The selectivity in acids was ca. 10% lower than when no surfactant was used (Entry 1 in Table 5 versus Entry 2 in Table 2). Furthermore, when the reactor was vented at pressures and temperatures above the critical point of pure CO₂ the cold trap contained detectable amounts of the acids. This indicates that, at optimised conditions, extraction of the acids from the reaction mixture is possible. At a lower H₂O/Pd molar ratio (250) the conversion was also high (83%). A general increase in the regioselectivity of the linear acid of up to ca. 80% is observed in all cases at 90 °C. This increase of linear acid could be related to the higher amount of isomerisation products that are formed from the branched alkyl intermediate. Also the coordination of the anion could increase the steric effect around the metal and favour the formation of the linear isomer. The addition of surfactant **11** did not improve the results obtained at 120 °C (Entry 3, Table 5). At lower surfactant concentrations the conversion decreased to 67% (Entry 4 versus 2 and Entry 5 versus 1, Table 5). It was observed that, like without surfactant, increasing the amount of water increased the conversion (Entry 5 versus Entry 4, Table 5). Under the conditions in which the catalyst precursor is soluble in scCO₂ (200 atm, 90 °C) the addition of surfactant promoted a higher conversion but the value was still low (Entry 6, Table 5). In the presence of the surfactant, the palladium complex [PdCl₂(NCPH)₂] without ligand **1** was an inactive catalyst (Entry 7, Table 5). Without the acid the system Pd/**1** with the surfactant was also inactive (Entry 8, Table 5). Employment of the surfactant **12** with a shorter perfluorinated chain did not improve the results (Entry 9, Table 5).

Other Substrates

The system Pd/**1** with the surfactant **11**, under the best conditions obtained for the hydrocarboxylation of 1-octene, was studied as a catalyst for substrates **6a–6g**. The results obtained are shown in Table 6. With the exception of 1-decene, the total conversions obtained using scCO₂ as the

solvent are high even for the long chain alkenes 1-dodecene and 1-hexadecene (up to ca. 90%). Although the reason is unclear, an unexpected low conversion was also reported in the hydroformylation of 1-decene in water micellar systems.^[26] The selectivities in acids are around 80%, the rest being isomerisation products. The regioselectivities in the linear acid for substrates **6b** and **6d** are around 80%, in the case of **6a** and **6e** they are lower and internal alkenes are formed (Entry 1 and 5, Table 6). When no isomerisation is possible, as in the case of styrene, no other byproducts were detected (Entry 6, Table 6). In the case of styrene, the preferred product is the branched acid, but since the addition of **11** favours the formation of the linear product it results in a low regioselectivity in the branched isomer (56%). For the hindered substrate cyclohexene only 9% of conversion was achieved (Entry 7, Table 6).

Table 6. Hydrocarboxylation with Pd/**1**/**11** of different substrates in scCO₂.^[a]

Entry	Substrate	% C ^[b]	% S _{7,8} ^[c]	7/8	% S ₉ ^[d]
1	6a	60	76	64:36	24
2	6b	93	77	82:18	23
3	6c	16	75	63:37	25
4	6d	88	86	80:20	14
5	6e	95	83	64:25 ^[e]	17
6	6f	99	>99	44:56	—
7	6g	9	—	—	—

[a] Reaction conditions: *P*_{CO} = 30 atm, time = 12 h, total pressure = 150 atm, [PdCl₂(NCPH)₂] = 1 × 10^{−3} M, molar ratio Pd/L/H₂C₂O₄·2H₂O/H₂O/substrate = 1:4:62.5:500:62.5, H₂O/**11** = 14. [b] Total conversion. [c] Selectivity in acids. [d] Selectivity in internal alkenes. [e] 11% of internal acids also formed.

Multinuclear High-Pressure NMR Experiments

In order to gain an insight into the species formed during the reaction we have performed an in situ high-pressure NMR (HP-NMR) spectroscopic study of the hydrocarboxylation of 1-octene with palladium precursors for both systems in organic solvents and in supercritical carbon dioxide. In this study the HP-NMR spectra were carried out using a palladium precursor [PdCl₂(NCPH)₂] modified with the fluorinated phosphanes **1–4**. Oxalic acid was used as the acid under CO pressure in [D₈]THF or supercritical carbon

dioxide as a solvent. Because of the detection limits in the ^{13}C experiments of the HP-NMR spectroscopy, the concentration used to record these spectra was higher than the ones used in the catalytic experiments. Selected HP-NMR spectra are presented in the Supporting Information.

HP-NMR Spectroscopy in Organic Solvents

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the palladium precursor $[\text{PdCl}_2(\text{NCPH})_2]$ (1×10^{-2} M) and the phosphane **1** (molar ratio P/Pd = 4:1) in $[\text{D}_8]\text{THF}$ at room temperature shows a singlet signal at $\delta = 23.5$ ppm, which corresponds to the complex *trans*- $[\text{PdCl}_2(\text{1})_2]$, synthesized and characterized previously,^[18] and the signal corresponding to free phosphane ($\delta = -5.6$ ppm). Oxalic acid (ratio $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}/\text{Pd} = 62.5$), deuterium oxide (0.1 mL) and 30 atm of CO were added to this solution and heated at 90 °C for 1.5 h. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature shows a broad signal centred at $\delta = 18$ ppm, a singlet at $\delta = 24.4$ ppm attributed to the Pd^{II} *trans*- $[\text{PdCl}_2(\text{1})_2]$ and a singlet corresponding to the Pd^0 species $\text{Pd}(\text{1})_3$ appears at $\delta = 19.7$ ppm. The palladium(0) species were formed by oxidation of the phosphane to the corresponding oxide [step (a) in Scheme 3], which appears at $\delta = 25.6$ ppm. The Pd^0 species with PPh_3 reported in the literature present signals at $\delta = 22.6$ ppm at 70 °C^[27] and $\delta = 21.48$ ppm at room temperature.^[28]

Upon cooling to -50 °C the broad signal splits into one at $\delta = -6.4$ ppm corresponding to the free ligand **1** and signals at $\delta = 22.7$, 25.1 and 77.6, which may correspond to Pd^0 carbonyl species in equilibrium, $\text{Pd}(\text{CO})(\text{1})_x$ ($x = 2, 3$). A similar behaviour was reported for the PPh_3 system.^[29] The Pd/**1** systems generate the expected Pd^0 species under the conditions studied.

Finally, the substrate 1-octene was added (molar ratio 1-octene/Pd = 62.5) and pressurized again at 30 atm of CO. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution at -70 °C shows the same signals as it did without the substrate, except that two more peaks at $\delta = 19.6$ and 19.1 ppm were observed with a ratio of 62:38. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra a signal appears at $\delta = 233.7$ ppm. From literature data these new signals are attributed to the acyl isomeric species $[\text{Pd}\{\text{C}(\text{O})\text{C}_8\text{H}_{17}\}\text{Cl}(\text{1})_2]$ and $[\text{Pd}\{\text{C}(\text{O})(\text{CH}_3)\text{C}_7\text{H}_{15}\}\text{Cl}(\text{1})_2]$,^[9,30] which form by migratory insertion of CO into the alkyl species C [step (e) in Scheme 3] After the reaction was completed the peaks of the acyl species disappeared and only the acid signals remained.

The same studies were carried out with the catalytic systems $[\text{PdCl}_2(\text{NCPH})_2]/\text{2}$ and **3**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the solution of the palladium precursor $[\text{PdCl}_2(\text{NCPH})_2]$ with the phosphanes **2** or **3** in $[\text{D}_8]\text{THF}$ at room temperature exhibit a major narrow singlet signal at $\delta = 26.2$, which corresponds to the complex *trans*- $[\text{PdCl}_2(\text{2})_2]$ ^[19] and a broad signal at $\delta = 23$ ppm corresponding to *trans*- $[\text{PdCl}_2(\text{3})_2]$.^[31] For the system $[\text{PdCl}_2(\text{NCPH})_2]/\text{2}$, two minor signals appear at $\delta = 20.2$ and 35.5 ppm that are attributed to cationic species resulting from the chloride exchange with the solvent, $[\text{PdCl}(\text{2})_2(\text{Solvent})]^+$ or $[\text{Pd}(\text{2})_2(\text{Solvent})_2]^{2+}$.^[32] When the acid D_2O and 30 atm of CO

were added the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the solution at room temperature shows a signal at $\delta = 19.7$ corresponding to the palladium(0) species, $\text{Pd}(\text{2})_3$, and other minor signals at 12.6, 7.2 and -4.2 ppm. When 1-octene was added to this solution no substantial changes were observed for both systems.

For all the catalytic systems studied, Pd/**1–3**, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show the corresponding singlets of the carboxylic acids, $\text{CH}_3\text{--CH}(\text{CH}_3)(\text{CH}_2)_5\text{--COOH}$ and $\text{CH}_3\text{--}(\text{CH}_2)_7\text{--COOH}$, at $\delta = 178.5$ and 174.4 ppm, respectively, confirming that the hydrocarboxylation took place.

For the palladium system $[\text{PdCl}_2(\text{NCPH})_2]/\text{3}$ no signals attributable to the Pd^0 species were detected, which may account for the low activity of the Pd/**3** system in hydrocarboxylation catalytic experiments.

HP-NMR Spectroscopy in *scCO*₂

Once the reference HP-NMR spectroscopic experiments in $[\text{D}_8]\text{THF}$ were completed the same experiments were carried out using supercritical carbon dioxide as a solvent. For this, 0.083 mmol of the complex was placed in the sapphire tube (8.2 mL) in order to obtain a 1×10^{-2} M concentration. The different components for each experiment were also placed in the tube. Then, liquid CO_2 was introduced to 1/4 of the total volume and the system was heated until the total pressure achieved 100 bar. The total pressure was measured by a digital manometer connected directly to the NMR tube. Because of CO_2 solidification no experiments were performed at low temperature. For this reason very broad signals were observed.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the palladium precursor $[\text{PdCl}_2(\text{NCPH})_2]$ with phosphane **1** (molar ratio P/Pd = 4:1) showed the signal of the free phosphane at $\delta = -5.8$ ppm and that of the *trans*- $[\text{PdCl}_2(\text{1})_2]$ at $\delta = 23.2$ ppm. After addition of oxalic acid and D_2O , and pressurizing the system with CO, the formation of the $\text{Pd}(\text{1})_3$ and phosphane oxide took place as indicated by the signals at $\delta = 19.9$ ppm and 26.6 ppm, respectively, in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. When 1-octene was added no substantial changes were observed in the ^{31}P NMR spectra although the ^{13}C NMR spectra showed the formation of the acids. The ratio of the linear/branched acid was ca. 65:35, which is close to the catalytic results (Entry 2, Table 2). In the ^{13}C NMR spectra the signal corresponding to free CO can be observed at $\delta = 182$ ppm and a small signal at $\delta = 181$ ppm could indicate the presence of species with coordinated CO, which could not be differentiated in the ^{31}P NMR spectra because of the broad signals.

When the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{PdCl}_2(\text{NCPH})_2]/\text{1}/\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}/\text{D}_2\text{O}/\text{CO}/\text{1-octene}$ is obtained in the presence of the surfactant **11** the signals of the linear and branched acids at $\delta = 177.6$ and 181 ppm, respectively, increase and a ratio of 90:10 is observed. This is a similar ratio to the one observed in the catalytic reaction (Entry 1, Table 5). Unfortunately, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 90 °C showed broad signals and no conclusions could be inferred about the species formed.

For the $[\text{PdCl}_2(\text{NCPh})_2]/2$ and **3** systems in scCO_2 the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows the signals of the *trans*- $[\text{PdCl}_2(1-2)]$ species and signals corresponding to the Pd^0 species in the range 20–21 ppm. The signals of the free ligand and the phosphane oxide are also observed. After 1-octene is added the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum confirms the formation of the acids but the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows no significant changes.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the system $[\text{PdCl}_2(\text{NCPh})_2]/4$ shows a broad small signal at $\delta = -31.2$ ppm corresponding to *trans*- $[\text{PdCl}_2(4)]$ ^[21] together with the signal of the free phosphane. After the acid addition no significant changes were observed and no acid formation was detected in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The fact that the formation of the Pd^0 species was not detected could explain the low catalytic activity of this system.

In summary, for all the systems, the major species formed by the reaction of $[\text{PdCl}_2(\text{NCPh})_2]$ with **1–4** was the *trans*- $[\text{PdCl}_2(1-4)]$ species. After the reagents and CO were added palladium(0) species were formed except with ligand **4**. According to the proposed mechanism for this reaction^[9] these Pd^0 species ($[\text{PdP}_n]$, Scheme 3) will react with the acid to form a Pd–H species (**A**, Scheme 3), which has not been detected. At the end of the experiment the formation of the acids was confirmed by ^{13}C NMR spectroscopy.

Conclusions

In conclusion, hydrocarboxylation reactions can be performed in supercritical carbon dioxide as a solvent using palladium catalysts with phosphanes containing $-\text{CF}_3$ groups. When using $[\text{PdCl}_2(\text{NCPh})_2]$ and phosphanes as catalyst precursors the conversion in the carbonylation of 1-octene is better when the catalyst is not soluble in scCO_2 . With these systems the best conversions were up to 60% with selectivities in the acid of up to 90%. The conversion in the hydrocarboxylation of 1-octene improved to 93% by adding a perfluorinated surfactant with a selectivity in acids of 77%. The regioselectivity in the linear acid increased with the use of the surfactant. Additionally this catalytic system was satisfactorily applied to the hydrocarboxylation of other long chain alkenes. The multinuclear high-pressure NMR spectroscopy allowed us to follow the formation of the Pd^0 species under CO pressure in $[\text{D}_8]\text{THF}$ and in scCO_2 .

Experimental Section

General: Compounds **1–5** are commercially available and were used without purification. The syntheses of the palladium complex $[\text{PdCl}_2(\text{NCPh})_2]$ was performed according to literature procedures.^[33] All olefins used as substrates were filtered through alumina before use. All these material were from Aldrich and Fluorochem. Carbon dioxide (SCF Grade, 99.999%) was supplied by Air Products and Linde and carbon monoxide (99.99%) was supplied by Air Liquide.

Safety Warning: Experiments involving pressurized gases can be hazardous and must only be conducted with suitable equipment and following appropriate safety conditions.

Solubility and Catalytic Studies: The solubility studies in supercritical carbon dioxide were performed in a stainless steel Thar reactor (volume 100 mL) containing sapphire windows. The palladium precursor $[\text{PdCl}_2(\text{NCPh})_2]$ (0.1 mmol) and the corresponding phosphane (0.4 mmol) were placed in the autoclave, the system was purged with nitrogen/vacuum and it was charged with liquid CO_2 . Then, the pressure and temperature were gradually increased and the solubility was examined by ocular inspection through the sapphire windows.

For catalytic experiments, the palladium precursor $[\text{PdCl}_2(\text{NCPh})_2]$ (0.025 mmol) with the acid (1.562 mmol), the phosphane (0.1 mmol), and the corresponding amount of surfactant, when used, were loaded into a stainless steel reactor vessel (25 mL). The system was purged with nitrogen/vacuum. The corresponding amount of degassed water, substrate (1.562 mmol) and undecane (97.5 mg), as GC internal standard, were mixed and charged in vacuo. Then the CO gas was charged, the reactor pressurized to the desired pressure and the liquid carbon dioxide introduced at room temperature via a syringe pump (Thar) until ca. 60 atm, and the reactor was heated to the desired temperature. The compressed carbon dioxide was introduced to attain the desired reaction pressure, adjusted by software controlling the syringe pump, and magnetically stirred (750 rpm). After the reaction was completed, the vessel was cooled with ice water to 0 °C and slowly depressurized to atmospheric pressure through a cold trap. The reaction mixture was extracted with diethyl ether and analyzed by gas chromatography using a Hewlett–Packard 5890A apparatus in an HP-5 (5% diphenyl silicone/95% dimethyl silicone) column (25 m $\times$ 0.2 mm). GC conditions: 45 °C (3.5 min), 10 °C/min, 150 °C (3 min) **8a** (*t* = 9.8 min), **7a** (10.5 min); 32 °C (7 min), 10 °C/min, 150 °C (5 min) **8b** (*t* = 19.7 min), **7b** (20.8 min); 80 °C (3.5 min), 10 °C/min, 150 °C (3 min) **8c** (*t* = 12.5 min), **7c** (13.5 min); 35 °C (3 min), 10 °C/min, 200 °C (10 min) **8d** (*t* = 18.1 min), **7d** (18.7 min); 80 °C (3 min), 20 °C/min, 200 °C (10 min) **8e** (*t* = 30.5 min), **7e** (31.8 min); 150 °C (3.5 min), 10 °C/min, 200 °C (10 min) **8f** (*t* = 5.1 min), **7f** (5.6 min); 45 °C (3.5 min), 10 °C/min, 150 °C (3 min) **7g** (*t* = 9.8 min).

1,2-Dimethoxyethane (DME) was used as the organic solvent in the comparative experiments. These were conducted with a 100 mL autoclave following the preceding procedure without the CO_2 charge.

HP-NMR Experiments in $[\text{D}_8]\text{THF}$: The high-pressure nuclear magnetic resonance spectra were performed in a 10 mm sapphire tube.^[34] The tube enables experiments to be performed with gas, liquid or supercritical fluid samples up to 100 bar pressure. The palladium precursor $[\text{PdCl}_2(\text{NCPh})_2]$ (7.7 mg, 0.02 mmol) and phosphane (0.08 mmol) were introduced into the tube under an inert atmosphere. Degassed $[\text{D}_8]\text{THF}$ (2 mL) was then introduced, and the tube was charged with ^{13}CO (1–5 atm) and with CO up to 30 atm pressure. The other reagents were introduced stepwise following the same procedure. Measurements were performed with Bruker DRX 400 MHz and Varian 300 MHz NMR spectrometers.

HP-NMR Experiments in scCO_2 : The same tube was used to carry out these experiments. The corresponding amount of palladium precursor $[\text{PdCl}_2(\text{PhCN})_2]$ (31.7 mg, 0.08 mmol) and phosphane (0.33 mmol) were introduced into the tube under an inert atmosphere. The tube was then charged with ^{13}CO (1–5 atm) and with CO up to 30 atm pressure. The tube was cooled with a dry ice/acetone bath and liquid CO_2 was introduced up to 1/4 of the total volume. The tube was heated to achieve 100 atm of pressure. The total pressure was measured by a digital manometer connected directly to the NMR tube. The other reagents were introduced step-

wise following the same procedure. Measurements were carried out with a Bruker DRX 400 MHz NMR spectrometer.

Supporting Information (see also the footnote on the first page of this article): Five figures showing $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

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- [1] P. G. Jessop, W. Leitner, *Chemical Synthesis Using Supercritical Fluids*, Wiley-VCH, Weinheim, New York, **1999**.
- [2] a) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1999**, *99*, 475–493; b) W. Leitner, *Acc. Chem. Res.* **2002**, *35*, 746–756; c) D. J. Cole-Hamilton, *Science* **2003**, *299*, 1702–1706; d) P. G. Jessop, *J. Supercrit. Fluids* **2006**, *38*, 211–231.
- [3] a) P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, **1998**; b) P. T. Anastas, M. M. Kirchhoff, *Acc. Chem. Res.* **2002**, *35*, 686–694.
- [4] a) A. V. Yazdi, E. J. Beckman, *J. Mater. Res.* **1995**, *10*, 530–537; b) A. V. Yazdi, E. J. Beckman, *J. Ind. Eng. Chem.* **1997**, *136*, 2368–2374; c) S. Kainz, D. Koch, W. Baumann, W. Leitner, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1628–1630; d) M. Giménez Pedrós, A. M. Masdeu-Bultó, J. Bayardon, D. Sinou, *Catal. Lett.* **2006**, *107*, 205–208; e) M. Giménez Pedrós, C. Tortosa-Estorch, A. Bastero, A. M. Masdeu-Bultó, M. Solinas, W. Leitner, *Green Chem.* **2006**, *8*, 875–877.
- [5] a) K. P. Johnston, K. L. Harrison, M. J. Clarke, S. M. Howdle, M. P. Heitz, F. V. Bright, C. Carlier, T. W. Randolph, *Science* **1996**, *271*, 624–626; b) M. J. Clarke, L. Kristi, L. Harrison, P. K. Johnston, S. M. Howdle, *J. Am. Chem. Soc.* **1997**, *119*, 6399–6406; c) C. T. Lee, P. A. Psathas, K. P. Johnston, J. de Grazia, T. W. Randolph, *Langmuir* **1999**, *15*, 6781–6791.
- [6] a) A. Mullen, in *New synthesis with carbon monoxide* (Ed.: J. Falbe), Springer-Verlag, Berlin, **1980**, pp. 243–258; b) B. Cornils, W. A. Hermann, *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim, **1996**; c) H. M. Colquhoun, D. J. Thompson, M. V. Twigg, *Carbonylation*, Plenum Press, New York, **1991**, 102; d) G. Kiss, *Chem. Rev.* **2001**, *101*, 3435–3456.
- [7] R. A. Sheldon, *J. Mol. Catal. A: Chem.* **1996**, *107*, 75–83.
- [8] B. Hinz, C. P. Dorn Jr, T. Y. Shen, K. Brune, in *Ullmanns Encyclopedia of Industrial Chemistry* (Ed.: W. Gerhartz), VCH, Weinheim, Germany, **2002**.
- [9] a) E. Drent, P. H. M. Budzelaar, *Chem. Rev.* **1996**, *96*, 663–681; b) I. Del Río, C. Claver, P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem.* **2001**, 2719–2738; c) D. Kruis, N. Ruiz, M. D. Janssen, J. Boersma, C. Claver, G. van Koten, *Inorg. Chem. Commun.* **1998**, *1*, 295–298; d) N. Ruiz, I. Del Río, J. L. Jiménez, C. Claver, J. Fornies-Cámer, C. J. Cardin, S. Gladiali, *J. Mol. Catal. A: Chem.* **1999**, *143*, 171–180; e) A. Ionescu, G. Laurenczy, O. Wendt, *Dalton Trans.* **2006**, *32*, 3934–3940.
- [10] a) S. Tilloy, E. Monflier, F. Bertoux, Y. Castanet, A. Morteux, *New J. Chem.* **1997**, *21*, 529–531; b) G. Verspui, J. Feiken, G. Papadogianakis, R. A. Sheldon, *J. Mol. Catal. A: Chem.* **1999**, *146*, 299–307.
- [11] G. B. Jacobson, C. T. Lee, K. P. Johnston, *J. Org. Chem.* **1999**, *64*, 1201–1206.
- [12] G. B. Jacobson, C. T. Lee, K. P. Johnston, W. Tumas, *J. Am. Chem. Soc.* **1999**, *121*, 11902–11903.
- [13] C. Tortosa, N. Ruiz, A. M. Masdeu-Bultó, *Chem. Commun.* **2006**, 2789–2791.
- [14] a) K. Nozaki, F. Shibahara, S. Elzner, T. Hiyama, *Can. J. Chem.* **2001**, *79*, 593–597; b) M. C. Chen, H. F. Jiang, J. H. Li, *Chin. J. Chem.* **2001**, *19*, 1153–1156.
- [15] a) L. Jia, H. Jiang, J. Li, *Green Chem.* **1999**, *1*, 91–93; b) C. Tortosa, A. M. Masdeu-Bultó, *Catal. Lett.* **2008**, *122*, 76–79.
- [16] a) D. R. Palo, C. Erkey, *Ind. Eng. Chem. Res.* **1998**, *37*, 4203–4206; b) D. R. Palo, C. Erkey, *Ind. Eng. Chem. Res.* **1999**, *38*, 3786–3792; c) A. C. J. Koeken, M. C. A. van Vliet, L. J. P. van de Broeke, B. J. Deelman, J. T. F. Keurentjes, *Adv. Synth. Catal.* **2006**, *348*, 1553–1559.
- [17] a) B. El Ali, H. Alper, *J. Mol. Catal. A: Chem.* **1993**, *80*, 377–381; b) I. del Río, N. Ruiz, C. Claver, L. A. van der Veen, P. W. N. M. van Leeuwen, *J. Mol. Catal. A: Chem.* **2000**, *161*, 39–48.
- [18] D. Hancu, J. Green, E. Beckman, *Ind. Eng. Chem. Res.* **2002**, *41*, 4466–4474.
- [19] M. L. Clarke, D. Ellis, K. L. Mason, A. G. Orpen, P. G. Pringle, R. L. Wingad, D. A. Zaher, R. T. Baker, *Dalton Trans.* **2005**, 1294–1300.
- [20] J. Real, E. Prat, S. González-Cabello, M. Pagès, A. Polo, *Organometallics* **2000**, *19*, 4715–4719.
- [21] A. M. Trzeciak, H. Bartosz-Bechowski, Z. Ciunik, K. Niesyty, J. J. Ziolkowski, *Can. J. Chem.* **2001**, *79*, 752–759.
- [22] D. M. Fenton, *J. Org. Chem.* **1973**, *38*, 3192–3198.
- [23] a) T. E. Kron, M. I. Terekhova, Y. G. Noskov, E. S. Petrov, *Kinet. Katal.* **2001**, *42*, 182–188; b) M. C. Bonnet, A. L. Monteiro, I. Tkatchenko, *J. Mol. Catal. A: Chem.* **1999**, *143*, 131–136.
- [24] Krytox[®] is a trademark of DuPont.
- [25] H. Kondo, Y. Hisamichi, T. Kamei, *J. Magnet. Magn. Mater.* **1996**, *155*, 332–338.
- [26] M. Giménez-Pedrós, A. Aghmiz, C. Claver, A. M. Masdeu-Bultó, D. Sinou, *J. Mol. Catal. A: Chem.* **2003**, *200*, 157–163.
- [27] B. E. Mann, A. Musco, *J. Chem. Soc., Dalton Trans.* **1975**, 1673–1677.
- [28] C. Amatore, A. Jutand, F. Lemaître, J. L. Ricard, S. Kozuch, S. Shaik, *J. Organomet. Chem.* **2004**, *689*, 3728–3734.
- [29] F. Morandini, G. Consiglio, F. Wenzinger, *Helv. Chim. Acta* **1979**, *62*, 59–61.
- [30] A. Seayad, S. Jayasree, K. Damodaran, L. Toniolo, R. V. Chaudhari, *J. Organomet. Chem.* **2000**, *601*, 100–107.
- [31] J. Fawcett, E. G. Hope, R. D. W. Kemmitt, D. R. Paige, D. R. Russell, A. M. Stuart, *J. Chem. Soc., Dalton Trans.* **1998**, 3751–3763.
- [32] V. N. Zudin, V. D. Chinakov, V. M. Nekipelov, V. A. Rogov, V. A. Likholobov, Y. I. Yermakov, *J. Mol. Catal. A: Chem.* **1989**, *52*, 27–48.
- [33] F. R. Hartley, *Org. Chem. Rev. A* **1970**, 119–137.
- [34] A. Cusanelli, U. Frey, D. Richens, A. E. Merbach, *J. Am. Chem. Soc.* **1996**, *118*, 5265–5271.

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