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Effects of the ponytails of arylphosphines on the hydroformylation of higher olefins in supercritical CO_2

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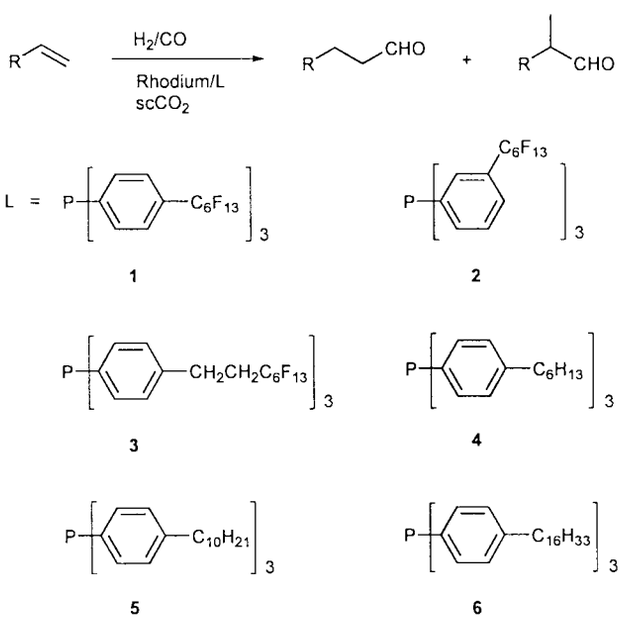
A series of ponytail-appended arylphosphines $P(C_6H_4R\text{-}m)_3$ ($m = 4$, R = n-C_6F_{13} **1**, n-$CH_2CH_2C_6F_{13}$ **3**, n-C_6H_{13} **4**, n-$C_{10}H_{21}$ **5** or n-$C_{16}H_{33}$ **6**; $m = 3$, R = n-C_6F_{13} **2**) have been studied in the rhodium-catalysed hydroformylation of higher olefins in supercritical CO_2 ($scCO_2$), with the perfluoroalkylated ligands exhibiting the highest and the alkylated one the lowest activities. The high rates derived from **1** and **2** probably originate from the strong electron-withdrawing effect of their ponytails, while the slow rates observed with **4**–**6** are mainly due to the low solubility of these ligands in $scCO_2$.

Modification of phosphines with fluorinated ponytails is an elegant solution to the immobilization of organometallic complexes in such non-traditional solvents as supercritical (sc) CO_2 and perfluorocarbons for catalytic applications.[1–7] Indeed, phosphines bearing fluorinated ponytails such as $P(CH_2CH_2C_6F_{13})_3$ and $P(C_6H_4CH_2CH_2C_6F_{14}\text{-}4)_3$ have been shown, when combined with a metal precursor compound, to be effective and recyclable in hydroformylation,[8–12] hydrogenation,[13–15] hydroboration,[16,17] and C–C bond formation reactions[18–20] in perfluorocarbons or $scCO_2$. Owing to the strong electron-withdrawing effect of the perfluoroalkyl substituents, a spacer group such as methylene is normally employed to insulate the phosphorus from the perfluoroalkylated ponytails. This approach was used in the seminal work of Horváth *et al.* and Leitner *et al.* on hydroformylation in fluorous phases and $scCO_2$.[1,2] However, insulating space groups may not be necessary for a hydroformylation reaction, as previous investigations have shown that triarylphosphines and related bidentate ligands bearing electron-withdrawing substituents tend to give higher rates and better regioselectivities to linear aldehydes in rhodium-catalysed hydroformylation in normal organic solvents.[21,22] In our previous report it was found that the perfluorinated ponytail-modified phosphine $P(C_6H_4C_6F_{13}\text{-}4)_3$ **1**, when combined with $[Rh(acac)(CO)_2]$, affords a highly active catalyst for the hydroformylation of higher olefins in $scCO_2$.[23] We therefore thought that it would be of interest to compare the effects of the ponytail-bearing phosphines **1**–**6** on the same reaction in this medium (Scheme 1). The results obtained would demonstrate whether electron-withdrawing fluorinated ponytails are necessary for fast and regioselective hydroformylation in $scCO_2$ and whether less expensive alkylated phosphines such as **4**–**6** could be used to replace the more expensive **1**–**3**. We report here that the rates of hydroformylation in $scCO_2$ vary markedly with the nature of the ponytails of the triarylphosphines and the reaction does benefit from electron-withdrawing perfluorinated ponytails. While this work was in progress a paper by Palo and Erkey appeared, mainly describing the effects of CF_3-substituted triphenylphosphines on the rhodium-catalysed hydroformylation of 1-octene in $scCO_2$.[12]

Hydroformylation of higher olefins is an important industrial process. The resulting long chain aldehydes can be converted into plasticizer alcohols (C_{6-11}) and biodegradable detergent alcohols (C_{12-20}), of which the latter are of high commercial value.[24,25] Long chain aldehydes also find applications in perfumery and fragrance industries. A number of publications concerned with this reaction have appeared, in the search for more active and selective rhodium catalysts coupled with easy catalyst separation and reuse.[24–30] The difficulty in catalyst separation encountered in the hydroformylation of higher olefins lies in the thermolability of conventional rhodium–phosphine catalysts, the high boiling points of the aldehyde product, and the limited solubility of higher olefins in water, which could otherwise be employed to immobilize aqueous soluble catalysts. $scCO_2$ offers an attractive alternative to the known approaches for the hydroformylation of higher olefins. The reaction can easily be conducted in a homogeneous phase, thereby eliminating problems of interfacial gas and



Scheme 1 Rhodium-catalysed hydroformylation of 1-alkenes in the presence of ponytail-bearing arylphosphines in $scCO_2$.

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olefin mass transfer, and the separation of the catalyst from the product can be induced by simple variation of pressure or temperature.

Results and discussion

Attaching electron-donating or -withdrawing ponytails to an arylphosphine will affect the σ donor/π acceptor properties of the ligand.[31] This effect is attenuated by the phenyl rings, however, and so is expected to be less significant than observed with trialkylphosphines when the alkyl groups are fluorinated or partly fluorinated.[9,32] To gain further insight into the effect, single point energy calculations were performed for ligands **1**–**4** using the semi-empirical PM3 method implemented in GAUSSIAN 94 following geometry optimization.[33] The phosphorus lone pair energies and charges assigned to the phosphorus atom following Mulliken population analysis are given in Table 1. As was discussed previously, the lone pair energy levels and the charges associated with the phosphorus measure approximately the σ donor capability of the phosphine ligands.[9] Together with the carbonyl stretching frequencies observed for the complexes [RhCl(CO)L_2] (L = **1**–**4**), which are also included in Table 1, the calculation shows that the electronic properties of the *para* fluoroalkylated **1** and *meta* fluoroalkylated **2** are approximately the same. This is in line with previous structural and spectroscopic studies of metal complexes containing CF_3-substituted arylphosphines, showing the electronic effects of the CF_3 group to be cumulative and felt equally at the *ortho*, *meta* or *para* position.[36] Both the lone pair eigenvalue of **4** and the corresponding ν(CO) value indicate that **4** is a better σ donor than either **1** or **2**. Insertion of an ethylene spacer diminishes, but does not eliminate, the electron-withdrawing effect of the perfluorohexyl group on the phosphorus lone pair of **3**. However, the similar ν(CO) values, which presumably reflect both the σ donor and π acceptor capabilities of the phosphines,[31] suggest that electronically **3** and **4** have only marginal differences.

Table 1 Electronic properties of *para* substituted arylphosphines

Ligand	P lone-pair level/eV	P Mulliken population	$\tilde{\nu}$(CO)[a]/cm^{-1}
1	−9.8	0.71	1993[b]
2	−9.5	0.72	1992[b]
3	−9.2	0.69	1972
4	−8.7	0.67	1975[c]

[a] For the complex *trans*-[RhCl(CO)L_2] (L = **1**–**4**). [b] Ref. 34. [c] Ref. 35.

As mentioned earlier, our previous work has shown that ligand **1** in combination with rhodium is highly active in the hydroformylation of 1-hexadecene in $scCO_2$. To investigate the effect of ponytails on the rhodium–arylphosphine catalysed hydroformylation of higher olefins in $scCO_2$, we again chose 1-hexadecene as a model for higher olefins. In addition, the reaction of 1-decene was studied. The hydroformylation reactions in $scCO_2$ were performed using a combination of [Rh(acac)$(CO)_2$] and 10 equivalents of a phosphine ligand as catalyst precursor in an autoclave at 80 °C, 20 bar H_2–CO (1 : 1) and 180 bar CO_2. To minimize the effects of possible induction periods on the comparison, each reaction was preceded by heating the mixture of [Rh(acac)$(CO)_2$] and the phosphine ligand under 20 bar syngas (H_2–CO) in $scCO_2$ (150 bar CO_2) at 80 °C for 1 h. Precatalysts such as [RhH(CO)L_3] (L = **1**–**6**) are expected to form under such conditions. Hydroformylation was started by introducing the olefin *via* an injection valve followed by topping the reactor with CO_2 to 200 bar. All the reactions were carried out for 1 h. Tables 2 and 3 summarize the results obtained with ligands **1**–**4** for hydroformylation of 1-hexadecene and 1-decene, respectively. For most of the reactions, selectivity to aldehyde is over 95%. The only by-products, as revealed by GC and NMR analysis, are the isomers of the starting olefins. The relatively electron-deficient **1** and **2** afford significantly more isomerization product than their more electron-rich counterparts **3** and **4**, which is reminiscent of the observation made by Moser *et al.* on the rhodium-catalysed hydroformylation of 1-hexene in dichloromethane using P(C_6H_4X-4)$_3$ (X = CF_3, Cl, F, H, OMe or NMe_2) as ligand.[21] Somewhat surprisingly, however, the regioselectivity of both reactions, as measured by the linear : branched aldehyde (L : B) ratios, does not increase with the increasing electron-withdrawing power of the ponytails. This is in contrast with the results obtained by Moser *et al.*[21] in liquid solvents but consistent with those by Palo and Erkey in $scCO_2$.[12]

The most significant effect of the ponytails is on the activity of rhodium, as indicated by the average turnover frequency (TOF) to aldehyde shown in Tables 2 and 3. Thus, on going from the perfluoroalkylated ligand **1** to the ethylene-spaced **3**,

Table 2 Hydroformylation of 1-hexadecene by [Rh(acac)$(CO)_2$]–L in $scCO_2$[a]

Ligand	Olefin : Rh	Conversion (%)[b]	Aldehyde (%)[c]	Isomerization (%)[d]	L : B[e]	TOF[f]
1	4393	71	95	5	3.6	2963
2	4499	73	93	7	3.6	2998
3	4393	22	99	1	3.6	957
4	3789	4	99	1	4.5	150

[a] General reaction conditions: 1.5–3.0 μmol [Rh(acac)$(CO)_2$], 10 equivalents of L (L = **1**–**4**), olefin concentration 0.15 M, 20 bar H_2–CO (1 : 1), 180 bar CO_2, 80 °C for 1 h. The product was analysed by ^{1}H NMR and the results were confirmed by GC. [b] Conversion of 1-hexadecene. [c] Selectivity to aldehyde. [d] Selectivity to internal olefins. [e] Linear : branched aldehyde ratio. [f] Average turnover frequency: mol of aldehyde formed per mol of catalyst per hour.

Table 3 Hydroformylation of 1-decene by [Rh(acac)$(CO)_2$]–L in $scCO_2$[a]

Ligand	Olefin : Rh	Conversion (%)	Aldehyde (%)	Isomerization (%)	L : B	TOF
1	5940	49	96	4	3.8	2794
2	5920	50	97	3	3.7	2871
3	5614	28	99	1	3.8	1556
4	6513	3	>99	<1	3.7	195

[a] For general reaction conditions, see Table 2.

the rates of hydroformylation of 1-hexadecene and 1-decene decreased *ca*. 2–3 times. Since both ligands are soluble and form a homogeneous solution in $scCO_2$ under the reaction conditions and because they are sterically similar, the observed decrease in rates can only be attributed to an increase in the electron richness of the phosphorus in **3**. More remarkably, the rates observed for **1** and the electron-rich, alkylated ligand **4** differ more than 20-fold in the case of 1-hexadecane. The same trend also holds for 1-decene, albeit to a lesser degree. Whilst our results corroborate previous findings that electron-deficient triarylphosphines afford faster rates in the rhodium-catalysed hydroformylation in both liquid solvents and $scCO_2$,[12,21] the dramatic, 20-fold difference in rates between **1** and **4** cannot solely be explained by the electronic effect imposed by the ponytails. For example, in the hydroformylation of 1-hexene in dichloroethane, Moser *et al.* observed that the rate with $P(C_6H_4CF_3\text{-}4)_3$ is only 5 times faster than that with $P(C_6H_4\text{-}NMe_2\text{-}4)_3$, although the amino group is even more electron donating than an alkyl group.[21] Likewise, for the hydroformylation of 1-octene in $scCO_2$, the initial rates measured by Palo and Erkey differ only 4–5 fold with the ligands $P[C_6H_3(CF_3)_2\text{-}3,5]_3$, $P(C_6H_4CF_3\text{-}4)_3$ and $P(C_6H_4(CH_2)_3C_4F_9\text{-}4)_3$, the last of which is expected to display similar electronic properties to those of **4**.[12] Careful inspection of the reaction mixture containing **4** using a window reactor revealed the presence of tiny liquid droplets, indicating that **4** is probably only partly soluble in $scCO_2$ under the reaction conditions. Thus, while the decrease in rate from **1** to **3** can reasonably be ascribed to ligand electronic effects, the dramatic fall in rate with **4** is more likely to be a result of decreased solubility of the ligand in $scCO_2$. This also explains the significant difference in rates between **3** and **4**, which, as mentioned previously, have similar electronic properties. As may be expected on the base of electronic effects, ligands **1** and **2** show no significant difference in terms of rates and regioselectivities (Tables 2 and 3).

In an attempt to increase the solubility of triarylphosphines modified with alkyl ponytails in $scCO_2$, ligands **5** and **6** with longer alkyl chains were prepared and examined in the hydroformylation of 1-hexadecene in $scCO_2$ under conditions similar to those used for **1**–**4**. A slight increase in TOF (350 h^{-1}) was indeed observed with **5**, but the TOF (*ca*. 20 h^{-1}) value for **6** became even lower. Low solubility of the ligands appears again to be the major factor responsible for the low activity of the rhodium catalyst. The slightly higher activity associated with **5** is reminiscent of a previous study, which shows that alkylated organophosphorus reagents with an alkyl chain length of approximately eight carbons have the most favorable properties for high solubility in $scCO_2$. When the alkyl chain length is further increased, as is the case with **6**, the increase in ligand solubility in $scCO_2$ caused by the decrease in the ligand solubility parameter will be counterbalanced by the negative effect of the increasing molar volume of the ligand on solubility.[37]

Further to examine whether the low rates observed with compounds **4**–**6** result from low solubility of the ligands in $scCO_2$, we compared the hydroformylation of 1-hexadecane in toluene (0.42 M) at 80 °C and 20 bar H_2–CO using the ligands **1**, **3**, **4** and PPh_3, all of which show high solubility in toluene. The observed TOF values for the four ligands are 580, 480, 390 and 530 h^{-1}, respectively. Although the electron-deficient **1** does give a higher rate than the other three ligands including the relatively electron-rich **4**, the difference in rates between **1** and **4** is much less significant than that observed in $scCO_2$, reinforcing the argument made above that the low rates associated with the alkyl ponytail-modified **4**–**6** are due mainly to their low solubility in $scCO_2$. It is interesting that the average TOFs for **1** and **3** in toluene are markedly lower than those in $scCO_2$. The higher rates in $scCO_2$ may be accounted for by a higher concentration of syngas in the supercritical fluid as compared with that in toluene under the same syngas pressure. Previous studies have established that the hydroformylation of 1-alkenes in liquid solvents is first order in H_2 pressure and positive order in CO pressure when the latter is not higher (*ca*. <10 bar).[25,38] Under the conditions employed in this study (20 bar H_2–CO) a high syngas concentration may be expected to lead to a high rate in $scCO_2$.

In summary, we have demonstrated that the ponytails that are attached to arylphosphines exert remarkable effects on the rhodium-catalysed hydroformylation of olefins in $scCO_2$, with the more electron-withdrawing fluoro-ponytails affording faster rates in comparison with the more electron-donating ones. However, the regioselectivity of the reaction, as measured by the L : B ratios, varies little with respect to change in the ponytails. Furthermore, electronic effects alone cannot explain the drastic difference in rates observed with the perfluoroalkylated and alkylated ligands. The low rates in association with the latter are mainly due to their low solubility in $scCO_2$, with the phosphines bearing longer alkyl ponytails giving even slower rates. The results are in line with previous studies on substituted diketones, where fluoroalkylated substituents are shown to be more effective for conferring solubility in $scCO_2$ on the diketones than analogous alkylated groups.[39] Thus, while alkylated arylphosphines are attractive in terms of cost, their application in reactions in $scCO_2$ will be limited. In the particular case of hydroformylation, where electron-deficient phosphines are favored, fluorinated ponytails represent one of the best solutions to the effective adaptation of the established rhodium–arylphosphine catalysts to $scCO_2$.

Experimental

CO_2 (99.995%) and syngas (H_2–CO, 1 : 1) were obtained from BOC Gases and used without further purification. The 1-alkenes and $[Rh(acac)(CO)_2]$ were purchased from Aldrich and the former were degassed before use. Toluene was distilled over CaH_2 under nitrogen. The phosphines tris[4-(perfluorohexyl)-phenyl]phosphine **1**, tris[3-(perfluorohexyl)phenyl]phosphine **2**, tris[4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phenyl]phosphine **3**, tris[4-hexylphenyl]phosphine **4**, tris[4-decylphenyl]phosphine **5** and tris[4-hexadecylphenyl]phosphine **6** were prepared according to published procedures.[32,40]

Hydroformylation reactions were carried out in a Parr 71 mL high-pressure stainless steel reactor equipped with a glass liner (actual reactor volume = 56 mL) and a magnetic stirrer. In a typical experiment, $[Rh(acac)(CO)_2]$ (1.5–3.0 μmol) and 10 equivalents of a phosphine ligand were added. The autoclave was then sealed, degassed and heated to the reaction temperature (80 °C). After the introduction of H_2–CO (20 bar), liquid CO_2 was transferred into the autoclave using a head-cooled HPLC pump to give a total pressure of 150 bar. The mixture was stirred for 1 h. An olefin (1-hexadecene, 8.34 mmol or 1-decene, 12.62 mmol) was then added to the autoclave through an injection valve, and finally the autoclave was pressurized with more CO_2 to a total pressure of 200 bar. After reaction for 1 h, the autoclave was allowed to cool in a solid CO_2 bath. The CO_2 was then carefully vented. The product was collected and analysed by ^1H NMR and the results were confirmed by GC.

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