Carbonylated Phosphines as Ligands for Catalysis in Supercritical CO_2

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Summary: This study attempts to answer if inexpensive, easily available carbonylated phosphines could be used as CO_2-philic ligands to replace the expensive, fluoroalkylated phosphines for catalysis in supercritical CO_2 ($scCO_2$). Toward this end, a series of alkoxycarbonylated arylphosphines were examined in the rhodium-catalyzed hydroformylation in $scCO_2$. The reaction rate was found to vary with the number of the carbonyl groups incorporated into the phosphines and with the nature of the olefins.

Introduction

$scCO_2$ has become one of the most attractive alternatives to common organic solvents for reaction chemistry.[1,2] For homogeneous catalysis, however, use of $scCO_2$ is met with a formidable problem; the poor solvent power of $scCO_2$ means that most of the commonly used organometallic catalysts cannot directly be employed.[3] The most successful approach to this problem is to modify ligands of the metal with CO_2-philic fluoroalkylated chains, which has been demonstrated in a number of catalytic reactions in the past few years.[2a,c−e,i,3a,4,5] A disadvantage of this approach is that the fluorous components of such ligands are expensive.[6] In fact, they are usually the most expensive of all the reagents used in preparing fluorinated ligands. Recent studies have established that incorporation of carbonyl groups can significantly enhance the solubility of polymeric materials in $scCO_2$ when the enthalpy and entropy of mixing are properly balanced.[7] In particular, Beckman and coworkers showed that addition of only one acetate group to a polyether can easily reduce the miscibility pressure in CO_2 by more than 100 bar and an ether−carbonate copolymer is even more soluble than poly(perfluoroether) in CO_2.[7a] Given that common carbonyl compounds are far less expensive than are fluorous ones, we thought that it would be of interest to examine if carbonylated ligands could indeed be used in catalysis in $scCO_2$. We report herein our results on the hydroformylation of 1-alkenes, styrene, and acrylates catalyzed by rhodium complexes containing alkoxycarbonylated phosphines in $scCO_2$. Hydroformylation is probably the most extensively studied reaction in $scCO_2$, and so comparison can readily be made with other ligands including, in particular, those bearing fluorous ponytails.[8]

Results and Discussion

Following the design principles elaborated by Beckman, the carbonylated phosphines **4**−**6** were prepared by a method similar to the one used for making **7** and **8**.[9] Briefly, the alkoxycarbonylated ligands **4**−**6** were prepared by palladium-catalyzed carbonylation of the brominated triphenlphosphine oxides **1**−**3** in the presence of methanol, followed by reduction with $HSiCl_3$ (Scheme 1), while **7** and **8** were made by the Heck olefination of **3** with acrylates followed by reduction. Addition of the carbonyl groups to the phosphines can be expected to enhance the solubility of the ligands via specific carbonyl−CO_2 donor−acceptor interaction.[7] However, increasing the number of such functional groups will also increase the solute−solute dipolar interactions and decrease the entropy of mixing, thus leading to

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Scheme 1

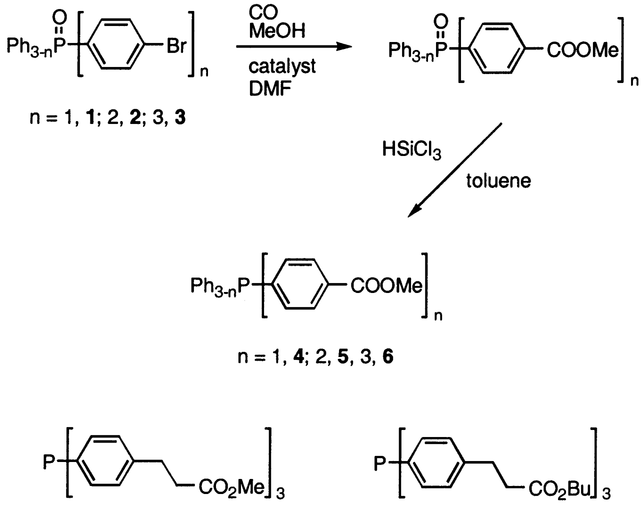

Table 1. Hydroformylation of Olefins by Rh-L Catalyst in $scCO_2$[a]

L	olefin	sel., %[b]	L/B[c]	TOF[d]
PPh_3	1-decene	>99	3.3	174
4	1-decene	>99	3.1	535
5	1-decene	99	3.4	390
6	1-decene	>99	*e*	4
7	1-decene	>99	2.7	61
8	1-decene	>99	4.2	48
4	styrene	>99	0.09	904
4	methyl acrylate	>99	B[f]	203
9	1-decene	99	3.3	803
9	styrene	>99	0.09	823
9	methyl acrylate	>99	B[f]	417

[a] Reaction conditions are given in the Experimental Section. [b] Selectivity to aldehyde. Olefin isomerization accounts for the product balance. [c] Linear/branched aldehyde ratio. [d] Average turnover frequency: mole of aldehyde formed per mole of catalyst per hour. [e] Not determined. [f] The branched product was a 1:1 mixture of enol and aldehyde; the linear aldehyde was <1%.

lower solubilities. Therefore, a point may be reached beyond which the addition of carbonyl groups decreases the solubility of the ligands in $scCO_2$. Ligands **7** and **8** contain methylene spacers, which should reduce the rigidity of the ligands, favoring the entropy of mixing.

To investigate the efficacy of the carbonyl-modified **1**−**7** in rhodium-catalyzed hydroformylation, we chose 1-decene, styrene, and methyl acrylate as models for 1-alkenes and aromatic and functionalized olefins. The hydroformylation reactions in $scCO_2$ were performed using a combination of $[Rh(acac)(CO)_2]$ and 10 equiv 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. For comparison, the hydroformylation of 1-decene using PPh_3 as ligand was also undertaken. The results are summarized in Table 1. As is expected, combining PPh_3 with rhodium does not produce an active catalyst in $scCO_2$, due to the low solubility of PPh_3. Thus, the hydroformylation of 1-decene by $Rh-PPh_3$ proceeds with an average turnover frequency (TOF) of 174 h^{-1}. The effectiveness of carbonyl groups in improving ligand solubility is evidenced by ligand **4**; the incorporation of one methoxycarbonyl unit into PPh_3 raised the TOF by 3-fold, making the reaction rate comparable to that obtained in common organic solvents (vide infra). When the reaction was run at 100 °C, the TOF rose to 1263 h^{-1}. While the TOF observed with **4** is lower than that obtained with the fluoroalkylated ligand $Ph_2P(4\text{-}C_6H_4C_6F_{13})$, **9**, which afforded a TOF of 803 h^{-1}, it is significantly higher than those (6−350 h^{-1}) observed with alkylated arylphosphines or trialkylphosphines such as $P(4\text{-}C_6H_4C_nH_{2n+1})_3$ or PEt_3.[8c,e,i] The higher activity associated with **9** could in part be due to the stronger electron-withdrawing power of the perfluoroalkylated ponytail in comparison with that of the methoxycarbonyl group. Previous studies have shown arylphosphines with electron-withdrawing substituents afford faster rates in rhodium-catalyzed hydroformylation in liquid solvents as well as $scCO_2$.[8a,e,10]

Somewhat unexpectedly, addition of two CO_2-philic carbonyl groups led to a smaller increase in TOF relative to that on going from PPh_3 to **4**, and remarkably, when three methoxycarbonyls were introduced, a drastic fall in reaction rates was observed; the TOF decreased from 174 for PPh_3 to 4 h^{-1} for **6** (Table 1). The linear-to-branched aldehyde (L/B) ratios appear to be slightly lower with these ligands than with trisfluoroalkylated arylphosphines.[8e,h]

The observed trend in rates with **4**−**6** is parallel with the phase behavior of pure **4**−**6** in $scCO_2$ and the reaction mixtures containing these ligands. Thus, when 3.1×10^{-2} mmol of each of the three ligands was pressurized with CO_2 at 80 °C in a window reactor, **4** and **5** fully dissolved at 130 and 160 bar, respectively, whereas some **6** remained as solid at 200 bar, suggesting that the solubilities of the ligands in $scCO_2$ follow the order **4** > **5** ≫ **6**. Under catalytic conditions, a homogeneous phase was formed in the case of **4**, but liquid droplets and solid precipitates were visually observed with **5** and **6**, respectively, showing that the rhodium catalysts containing **5** or **6** dissolve, at best, only partially in $scCO_2$. In fact, the observed rates indicate that the trismethoxycarbonyl-modified **6** is much less soluble than PPh_3 in $scCO_2$! Clearly, for this series of phosphines, the optimal balance between enthalpy and entropy of mixing is reached by the introduction of just one carbonyl group. Increasing the number of such functional groups leads to increasing loss in entropy and increasing ligand−ligand dipolar interaction, and thus to the eventual precipitation of the ligand out of $scCO_2$.

In an attempt to increase the solubility of trimethoxycarbonyl-substituted phosphines by increasing their structural flexibility, **7** and **8** were prepared and tested in the hydroformylation of 1-decene. As is evident from Table 1, although the TOFs associated with **7** and **8** are indeed improved, they are still far lower than that observed with **4**, indicating that the ligand−ligand interactions and the loss in entropy still override the carbonyl−CO_2 interactions. The methylene spacers, which insulate the phosphorus from the electron-withdrawing effect of the carbonyls, could also contribute to the lower rates with **7** and **8**.

Ligand **4** was also applied to the hydroformylation of styrene and acrylates (Table 1). The ligand produces an active catalyst in the hydroformylation of styrene, affording a TOF of 904 h^{-1} at 80 °C, which compares

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favorably with the value of 823 h^{-1} obtained with **9**. In contrast, for methyl acrylate, a TOF of 203 h^{-1} was obtained, which is lower than that of 417 h^{-1} when using **9** as ligand. As with liquid phase reactions involving these olefins, branched product is favored. The lower rate for the acrylate is apparently due to the precipitation of the catalyst from $scCO_2$; phase studies show the reaction mixture containing methyl acrylate to be heterogeneous. However, without the acrylate, the reaction mixture was homogeneous under conditions otherwise identical to those for the catalytic reaction and, similarly, the acrylate formed a homogeneous phase with CO_2 in the absence of $[Rh(acac)(CO)_2]$ and **4**. The appearance of liquid droplets when the acrylate is mixed with the catalyst is thus a clear indication that dipolar solute−solute interaction dominates solvent−solute interactions and prevents the dissolution of the catalyst under the reaction conditions.

To further examine if the low rate observed with **6** results from its low solubility in $scCO_2$, we compared the hydroformylation of 1-decene in toluene (0.56 M) using the ligands **4**−**6** and PPh_3, all of which show high solubility in toluene, under conditions otherwise identical to those in $scCO_2$. The observed TOF values for the four ligands are 546, 507, 501, and 530 h^{-1}, respectively, with L/B ratios ranging from 2.9 to 3.2. Thus, the activities of the catalysts containing these ligands are approximately the same in toluene, supporting the argument that the higher activity associated with **4** and the much lower activity with **6** in comparison with that observed using PPh_3 is due to enhanced and reduced ligand solubilities in $scCO_2$, respectively. The analogous TOF values for **4** in $scCO_2$ and toluene are somewhat surprising, as previous studies have shown that fluorous ponytail-attached arylphosphines afford faster hydroformylation rates in $scCO_2$ than in toluene. This may be accounted for partly by the assumption that the ligand is not completely dissolved in $scCO_2$, although the reaction mixture is visually homogeneous.

In summary, the results presented in this paper show that carbonylation can provide an inexpensive and easy alternative to fluoroalkylation for $scCO_2$-soluble ligands that are effective in promoting metal-catalyzed reactions in $scCO_2$. However, the solubility of the carbonyl-modified ligands and that of the metal complexes formed thereby depend on the number of carbonyl groups incorporated and on the nature of substrates. Hence, particular attention needs to be paid not only to ligand−CO_2 but also to possible ligand−ligand and ligand−substrate interactions in designing CO_2-philic carbonyl ligands.

Experimental Section

CAUTION: When working with high-pressure equipment, appropriate safety devices, including but not limited to pressure relief mechanisms and blast shields, should be used.

CO_2 (99.995%) and syngas (H_2/CO, 1:1) were obtained from BOC Gases and used without further purification. The olefins and $[Rh(acac)(CO)_2]$ were purchased from Aldrich, and the former was degassed before use. Toluene was distilled over CaH_2 under nitrogen. The brominated triphenylphosphine oxides $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$, **1**−**3** ($n = 1-3$),[11] and the ligands **7** and **8**[9] were prepared according to published procedures.

Preparation of Ligands. A solution of (4-bromophenyl)-diphenylphosphine oxide (3.57 g, 10 mmol), $PdCl_2(PPh_3)_2$ (175 mg, 0.25 mmol), and Et_3N (2.1 mL, 15 mmol) in DMF/MeOH (2:1, 20 mL) was placed in an autoclave. After repeatedly degassing, CO (75 bar) was introduced. The reaction mixture was stirred overnight at 125 °C. The autoclave was then allowed to cool to room temperature, and the CO was carefully released. Following removing the solvent under reduced pressure, the residue was purified by flash chromatography (SiO_2, $CHCl_3$/EtOAc, 4:1) to give methyl 4-(diphenylphosphinyl)-benzoate as a white solid (3.10 g, 92%). The oxide was reduced to give diphenyl(4-methoxycarbonylphenyl)phosphine (**4**) according to a reported method.[9] Bis(4-methoxycarbonylphenyl)-phenylphosphine (**5**) and tris(4-methoxycarbonylphenyl)-phosphine (**6**) were prepared in a similar manner. The compounds **4**−**6** and their oxides have been reported before.[12]

Hydroformylation in $scCO_2$. The 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 hydroformylation experiment, $[Rh(acac)(CO)_2]$ (3−7 μmol, olefin/Rh = 4000:1) and 10 equiv 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 (12.62 mmol of 1-decene, 20.86 mmol of styrene, or 26.29 mmol of methyl acrylate) was then added into the autoclave through an injection valve, and finally the autoclave was pressurized with more CO_2 to a total pressure of 200 bar. After reacting for 1 h for 1-decene or 2 h for styrene and methyl acrylate, the autoclave was allowed to cool in a dry ice bath. The CO_2 was then carefully vented. The product was collected, passed through a pad of silica gel, and analyzed by ^1H NMR.

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