

# Fluorous soluble polymer catalysts for the fluorous biphase hydroformylation of olefins

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**Fluorous soluble polymer ligands have been prepared and shown to be active and selective catalysts when combined with rhodium for the fluorous biphase hydroformylation of various olefins.**

One of the most interesting recent developments in homogeneous catalysis is the concept and application of fluorous biphase catalysis (FBC).<sup>1</sup> The principle of FBC is based on the limited miscibility of common organic solvents with perfluorinated compounds. A very attractive aspect of FBC is that it provides, by means of phase separation, an elegant solution to the catalyst/product separation problem associated with homogeneous catalysis. Undoubtedly, successful application of FBC depends on rational design of catalysts that show high affinities to the fluorous phase. Until now, all the fluorous soluble metal catalysts have been based on molecular metal complexes containing conventional ligands modified with fluorinated groups.<sup>2,3</sup> The best known such catalysts are perhaps rhodium trialkylphosphine complexes appended with fluorous ponytails such as  $[\text{RhH}(\text{CO})\{\text{P}(\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13})_3\}_3]$ . The applicability of these complexes has been convincingly demonstrated by Horváth and Gladysz in the fluorous biphase hydroformylation,<sup>4</sup> hydrogenation<sup>5</sup> and hydroboration<sup>6</sup> of olefins. As with their nonfluorinated counterparts, however, the rhodium fluoroalkylphosphine catalysts exhibit lower activity in the reactions studied in comparison with complexes containing arylphosphine ligands. Fluorinated, low molecular weight arylphosphines are less useful in FBC, on the other hand, owing to their solubility in common organic solvents such as toluene and hexane.<sup>2,7</sup> Herein we describe fluorous soluble fluoropolymer-supported arylphosphine ligands as an alternative to fluorous soluble low molecular weight ligands for FBC and the application of the new ligands in fluorous biphase hydroformylation of higher and functionalised olefins. We anticipated that by incorporating an arylphosphine into a fluoropolymer the solubility of the former in normal solvents would be minimised. A fluorous soluble copolymer has recently been reported by Bergbreiter and Franchina.<sup>8</sup>

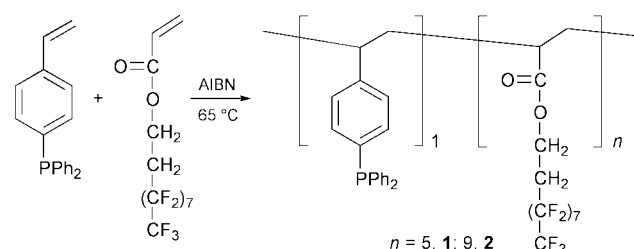
Hydroformylation of higher olefins has been addressed in a number of publications.<sup>9</sup> The focal point is to search for more active and selective rhodium catalysts in conjunction with easy catalyst separation and reuse. The difficulty in catalyst separation encountered in the hydroformylation of higher olefins lies in the thermolability of conventional rhodium phosphine catalysts, high boiling points of the aldehyde product, and limited solubility of higher olefins in water, which could otherwise be employed to immobilise aqueous soluble catalysts. Polymer-supported rhodium catalysts including those that are water soluble have been investigated for the hydroformylation of olefins.<sup>10–13</sup> These catalysts, while potentially having the advantages of both homogeneous and heterogeneous catalysts, often display low catalytic activities.

The poly(fluoroacrylate-*co*-styryldiphenylphosphine) ligands **1** and **2** were prepared by free radical copolymerisation of 1*H*,1*H*,2*H*,2*H*-perfluorodecylacrylate with styryldiphenylphosphine at 65 °C in the presence of AIBN in  $\alpha,\alpha,\alpha$ -trifluorotoluene (Scheme 1).<sup>14</sup> For the fluoropolymer **1**, an

acrylate to styryldiphenylphosphine molar ratio of 5:1 was used. For **2**, the ratio was 9:1. After removing the solvent, the resultant solid was washed with hot toluene, affording the polymers as white powders in >90% yields. As expected, the polymers are not soluble in normal organic solvents such as toluene, acetone or alcohols but highly soluble in fluorinated solvents such as  $\alpha,\alpha,\alpha$ -trifluorotoluene and perfluoromethylcyclohexane. The IR spectrum of both polymers showed the disappearance of the absorption due to C=C stretching, in line with the lack of resonances from olefinic protons in <sup>1</sup>H NMR spectra. The C=O absorption appeared at 1738 cm<sup>-1</sup> for **1** and 1740 cm<sup>-1</sup> for **2** in the IR spectra. The <sup>31</sup>P NMR spectrum of each polymer in  $\alpha,\alpha,\alpha$ -trifluorotoluene (CDCl<sub>3</sub> external lock) displayed a relatively sharp singlet at  $\delta$  ca. -6.2. The phosphorus content of the polymers was estimated to be 1.2% for **1** and 0.8% for **2** by <sup>31</sup>P NMR spectroscopy using bis(diphenylphosphino)methane as an internal standard. These values are close to the values of 1.1 and 0.6% calculated on the basis of the monomer ratios, and are consistent with the high yields of polymer synthesis.

To demonstrate the feasibility of phase separation when using the two polymers as ligands in catalysis,  $[\text{Rh}(\text{CO})_2(\text{acac})]$  was added to a mixture of hexane (2 mL), toluene (1 mL) and perfluoromethylcyclohexane (2 mL) containing 100 mg of **1** (P/Rh = 6). The fluorous phase attained a yellow colour immediately, while the organic phase remained colourless and phase-separated from the perfluoro solvent at ambient temperature. Upon heating the solvent mixture to ca. 50 °C, a single homogeneous yellow phase formed and on cooling, the coloured fluorous phase separated quickly from the colourless organic phase. However, in the absence of hexane, the phase boundary remained even at reflux.

The catalytic performance of the fluoropolymer ligands **1** and **2** was tested in the fluorous biphase hydroformylation of alkenes, styrene and *n*-butyl acrylate. The reaction was conducted in a batch reactor in a hexane-toluene-perfluoromethylcyclohexane (40:20:40, v/v) solvent mixture (10 mL). The catalyst was formed *in situ* by adding  $[\text{Rh}(\text{CO})_2(\text{acac})]$  (5  $\mu\text{mol}$ , P/Rh = 6) to the polymer-containing solvent mixture followed by introduction of syngas (30 bar, CO-H<sub>2</sub> = 1:1). Table 1 summarises the results obtained. The salient features of the results are (i) the activity of the fluorous soluble polymer catalysts are significantly higher than those reported for solid polymer- and aqueous soluble polymer-supported rhodium catalysts.<sup>10–13</sup> For example, the average turnover frequency



Scheme 1 Preparation of fluorocopolymer-supported arylphosphines.

**Table 1** Fluorous biphasic hydroformylation of olefins by soluble polymer catalysts<sup>a</sup>

| Olefin                   | Polymer | Olefin/Rh | Conversion (%) | Selectivity <sup>b</sup> (%) | L/B <sup>c</sup> |
|--------------------------|---------|-----------|----------------|------------------------------|------------------|
| Dec-1-ene                | 1       | 2120      | 97             | 99                           | 4.8/1            |
|                          | 2       | 2120      | 90             | 99                           | 5.9/1            |
| Hexadec-1-ene            | 1       | 2100      | 78             | 98                           | 4.8/1            |
|                          | 2       | 2100      | 59             | 99                           | 5.0/1            |
| Styrene                  | 1       | 3500      | 85             | >99                          | 1/6.2            |
|                          | 2       | 3500      | 80             | >99                          | 1/5.4            |
| <i>n</i> -Butyl acrylate | 1       | 2800      | 100            | >99                          | B <sup>d</sup>   |
|                          | 2       | 2800      | 100            | >99                          | B <sup>d</sup>   |

<sup>a</sup> Reaction conditions: 5  $\mu\text{mol}$   $[\text{Rh}(\text{CO})_2(\text{acac})]$  (P/Rh = 6), 30 bar CO–H<sub>2</sub> (1:1), 100 °C for dec-1-ene and hexadec-1-ene, 80 °C for styrene and *n*-butyl acrylate, hexane–toluene–perfluoromethylcyclohexane = 4:2:4 (mL), 15 h reaction time. The products were analysed by <sup>1</sup>H NMR and the conversion and selectivity confirmed by GC. <sup>b</sup> To aldehyde, olefin isomerisation accounts for the product balance. <sup>c</sup> Linear to branched aldehyde ratio, determined by <sup>1</sup>H NMR. <sup>d</sup> The branched product was a 1:1 mixture of enol and aldehyde, the linear aldehyde was <1%.

(TOF) for the fluororous biphasic hydroformylation of dec-1-ene is 136 mol aldehyde h<sup>-1</sup> per mol of rhodium catalyst with an aldehyde selectivity of 99%. In comparison, a rhodium catalyst supported on the water soluble polymer poly(enolate-*co*-vinyl alcohol-*co*-vinyl acetate) gave a TOF of 56 (100 °C, 41 bar) with an aldehyde selectivity <70% in the aqueous hydroformylation of oct-1-ene.<sup>13</sup> As might be expected, ligand **1**, which has a higher phosphine loading, gave higher turnovers. (ii) As with solid polymer-supported catalysts,<sup>10</sup> the linear/branched (L/B) ratio is markedly higher than achievable with similar P/Rh ratios when using homogeneous rhodium phosphine catalysts, *e.g.*  $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ , which yielded a L/B ratio of 2.9 only in the presence of an excess of PPh<sub>3</sub> (P/Rh = 19) in the hydroformylation of pent-1-ene in benzene (100 °C, 27 bar).<sup>15</sup> (iii) Smaller olefins appear to give higher turnovers, probably owing to better miscibility of the olefins with the fluororous phase. In fact, when hex-1-ene was hydroformylated under conditions identical to those for dec-1-ene, a conversion of 70% with an aldehyde selectivity of 98% and a L/B ratio of 4.4 was obtained in 1 h reaction time, corresponding to a remarkable TOF of 1454. Again, a low olefin isomerisation selectivity of 1.7% was observed.

The activity and stability of the soluble fluoropolymer catalysts may also be judged by the hydroformylation of hex-1-ene when the olefin/Rh ratio was increased to 200 000. At 100 °C and 50 bar syngas with polymer **1** as the supporting ligand, the catalyst afforded a turnover number (TON, mole of aldehyde per mol of rhodium) of *ca.* 140 000 with a 98% selectivity to aldehyde (L/B = 4.4; 2% isomerisation) for 58 h reaction time. We also examined the recyclability of the fluoropolymer catalysts taking the reaction of hex-1-ene as a

model example. The other substrates and related products should be easier to separate under the fluororous biphasic conditions as they are less miscible with the perfluoro solvent. At 100 °C and 50 bar with olefin/Rh = 48 000, three consecutive hydroformylation reactions were run, giving a combined TON of 70 000 and an average aldehyde selectivity of 99%. A 1 ppm loss of rhodium accompanied with a 6% decrease in conversion in each recycle experiment was measured. This loss in rhodium and in catalyst activity appears to be largely due to the finite miscibility of the substrate/product with the perfluorinated solvent. At the end of the third run, all the perfluoromethylcyclohexane had leached to the product phase, thus making the polymer catalyst partially soluble in the product. By optimising the operating conditions, *e.g.* by varying the organic solvent, the problem of rhodium leaching can be minimised.

In conclusion, we have introduced a fluororous soluble polymer ligand for FBC and shown the arylphosphine-containing ligand, when combined with rhodium, to be highly active and selective in the fluororous biphasic hydroformylation of various olefins. Given the easy availability of various vinyl monomers that can be used for fluoropolymer synthesis and the variability in FBC conditions, better performing soluble polymer catalysts coupled with efficient phase separation could be envisioned not only for FBC but also for fluororous combinatorial chemistry.

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