Asymmetric hydrogenation with perfluoroalkylated monodentate phosphorus(III) ligands in supercritical CO_2 and CH_2Cl_2†

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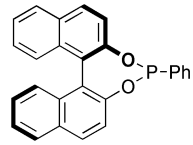
Four chiral perfluoroalkylated monodentate phosphorus(III) ligands have been prepared and characterised. These ligands have been evaluated in the rhodium-catalysed asymmetric hydrogenation of dimethyl itaconate in both dichloromethane and supercritical CO_2 ($scCO_2$) and compared with the parent, non-perfluoroalkylated, catalyst systems.

Introduction

We have been investigating the application of perfluoroalkylated phosphorus(III) ligands for catalysis under fluorous biphase conditions,[1,2] in perfluorocarbon solvents[3–5] and in $scCO_2$[6,7] as alternative media to conventional organic solvents and have now turned our attention to asymmetric catalysis. We have recently reported the synthesis of (*R*)-6,6′-bis(tridecafluorohexyl)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl and (*R*)-6,6′-bis(1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl and their application in the ruthenium-catalysed hydrogenation of dimethyl itaconate in methanol.[8] However, the requirement of >60% fluorine by weight for preferential perfluorocarbon solubility[9] and the relatively poor reactivity of catalysts including our derivatised BINAP ligands in $scCO_2$‡ indicated that it was unlikely that a viable fluorous- and $scCO_2$-compatible BINAP-based catalyst system could be prepared. Recently, however, there has been significant interest in the applications of chiral monodentate phosphonite, phosphoramidite and phosphite ligands based upon (*R*)- and (*S*)-binaphthol as cheap, easily accessible ligands for rhodium-catalysed enantioselective hydrogenation of prochiral olefins. Independently, Reetz[10] and Pringle[11] report ee's of up to 94% for the hydrogenation of dimethyl itaconate and methyl-2-acetamidoacrylate using mono- and bis-phosphonite ligands with a variety of alkyl and aryl substituents (*e.g.* **1**). Feringa and de Vries,[12] Chan[13] and Zhou[14] report comparable enantioselectivities using the *N*,*N*-dimethyl-phosphoramidite ligand (**2**), whilst Reetz[15,16] and Xiao[17] report the best asymmetric induction in this series using monodentate phosphite ligands (*e.g.* **3**) particularly those incorporating chiral alcohols. Here, we report the synthesis of four perfluoroalkylated chiral monodentate phosphorus(III) ligands and their application in rhodium-catalysed asymmetric hydrogenation in conventional solvents and supercritical CO_2.



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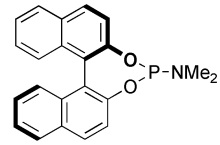

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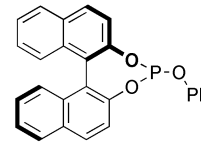

(**3**)

Experimental

Proton, ^{19}F and ^{31}P NMR spectroscopies were carried out on a Bruker ARX250 spectrometer at 250.13, 235.34 and 101.26 MHz or a Bruker DPX300 spectrometer at 300.14, 282.41 and

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Green Context

The development of catalytic processes involving metal-cented catalysts in $scCO_2$ requires the development of novel CO_2-soluble ligands for the complexes involved. This paper describes the preparation in high yield of some such ligands, as well as initial attempts to utilise them in enantioselective hydrogenations under supercritical conditions. So far, enantioselectivities were moderate and lower than in the conventional system. However, the work helps to point the way forward in this area ***DJM***

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121.50 MHz respectively and were referenced to external $SiMe_4$ (^1H), external $CFCl_3$ (^{19}F) and to external H_3PO_4 (^{31}P) using the high frequency positive convention. Elemental analyses were performed either by Butterworth Laboratories Ltd. or the Elemental Analysis Service at the University of North London. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer. The products from the catalytic experiments were analysed on a Varian CP-3380 GC equipped with a Chiraldex G-TA (40 m × 0.25 mm) column for the determination of ee values.

(*R*)-6,6′-Bis(tridecafluorohexyl)-2,2′-dihydroxy-1,1′-binaphthyl[8] and 4-tridecafluorohexylphenol[1] were prepared as described previously. Diethyl ether was dried by refluxing over sodium under dinitrogen. Dichloromethane and triethylamine were dried by refluxing over calcium hydride under dinitrogen. Each was then distilled under nitrogen, stored in closed ampoules over molecular sieves and freezed–pumped–thawed three times to remove all dissolved gases before use. Phosphorus trichloride, dichlorophenylphosphine and hexamethylphosphorus triamide (Aldrich) were distilled under nitrogen prior to use. The gases CO_2 and H_2 (BOC), used in the catalytic experiments, were used without purification.

Preparation of phenyl-(*R*)-1,1′-binaphthyl-6,6′-tridecafluorohexyl -2,2′-diyl-phosphonite, (4)

(*R*)-6,6′-Bis(tridecafluorohexyl)-2,2′-dihydroxy-1,1′-binaphthyl (759 mg, 0.823 mmol) and triethylamine (115 µl, 0.826 mmol) were dissolved in CH_2Cl_2 (10 cm³) and dichlorophenylphosphine (112 µl, 0.825 mmol) was added slowly *via* syringe. After stirring the solution for 3 h, the solvent was removed *in vacuo*, the residue dissolved in ether–dichloromethane (ratio: 1:1) and filtered. After removing the solvent, the pale yellow product was washed with acetonitrile (3 × 5 cm³) and dried for 2 h at 50 °C under vacuum to obtain the product as a white solid (0.804 g, 95%). (Found: C, 44.15; H, 1.32. $C_{38}H_{15}F_{26}O_2P$ requires C, 44.36; H, 1.46%). MS (FAB): *m*/*z* = 1028 [M⁺]. ^1H NMR (C_6D_6): δ 6.90 (1H, d, $^3J_{HH}$ = 8.7 Hz), 7.17 (3H, m), 7.36 (3H, m), 7.41 (1H, s), 7.48 (1H, d, $^3J_{HH}$ = 8.7 Hz), 7.49 (1H, d, $^3J_{HH}$ = 8.7 Hz), 7.65 (2H, m), 7.74 (1H, d, $^3J_{HH}$ = 8.9 Hz), 8.19 (1H, s), 8.27 (1H, s). ^{31}P {^1H} NMR (C_6D_6): δ 186.6 (s). ^{19}F {^1H} NMR (C_6D_6): δ −81.44 (6F, t, $^4J_{FF}$ = 10.6 Hz), −110.26 (4F, m), −121.67 (8F, m), −123.08 (4F, m), −126.50 (4F, m). $[\alpha]_D^{17}$ −77.4 (*c* 0.5, $CHCl_3$).

Preparation of (*R*)-1,1′-binaphthyl-6,6′-tridecafluorohexyl -2,2′-diyl-dimethylamino-phosphoroamidite, (5)

(*R*)-6,6′-Bis(tridecafluorohexyl)-2,2′-dihydroxy-1,1′-binaphthyl (630 mg, 0.683 mmol) was dissolved in dichloromethane (10 cm³) and $P(NMe_2)_3$ (125 µl, 0.689 mmol) added. After stirring the solution for 3 h, the solvent was removed *in vacuo*, the residue dissolved in ether–dichloromethane (ratio: 1:1) and filtered. After removing the solvent, the slight yellow product was washed with acetonitrile (5 cm³) and dried at 50 °C under vacuum to obtain the product as a white solid (0.639 g, 94%). (Found: C, 40.98; H, 1.57; N, 1.37. $C_{34}H_{16}F_{26}O_2PN$ requires C, 41.01; H, 1.61; N 1.41%). MS (FAB): *m*/*z* = 995 [M⁺]. ^1H NMR (C_6D_6): δ 2.51 (6H, d, $^3J_{PH}$ = 9.2 Hz, CH_3), 7.31 (2H, AB multiplet, $^3J_{HH}$ = 9.4 Hz), 7.38 (2H, AB multiplet, $^3J_{HH}$ = 9.4 Hz), 7.45 (1H, d, $^3J_{HH}$ = 8.7 Hz), 7.56 (1H, d, $^3J_{HH}$ = 8.7 Hz), 7.96 (1H, d, $^3J_{HH}$ = 8.7 Hz), 8.05 (1H, d, $^3J_{HH}$ = 8.7 Hz), 8.15 (1H, s), 8.17 (1H, s). ^{31}P {^1H} NMR (C_6D_6): δ 150.0 (s). ^{19}F {^1H} NMR (C_6D_6): δ −81.27 (6F, t, $^4J_{FF}$ = 10.6 Hz), −110.59 (4F, m), −121.89 (4F, m), −123.22 (4F, m), −128.14 (4F, m). $[\alpha]_D^{17}$ −225.6 (*c* 1.2, CH_2Cl_2).

Preparation of phenyl-(*R*)-1,1′-binaphthyl-6,6′-tridecafluorohexyl -2,2′-diyl-phosphite, (6)

Phosphorus trichloride (200 µl; 2.30 mmol) and triethylamine (280 µl; 2.01 mmol) were dissolved in dichloromethane (10 cm³) and a solution of (*R*)-6,6′-bis(tridecafluorohexyl)-2,2′-dihydroxy-1,1′-binaphthyl (937 mg, 1.02 mmol) in dichloromethane (10 cm³) was added slowly. After stirring the solution for 3 h, the solvent was removed *in vacuo* and the yellow solid dried for 2 h at 80 °C under vacuum. Complete removal of the excess PCl_3 *in vacuo* was followed by ^{31}P NMR spectroscopy. The yellow solid was dissolved in CH_2Cl_2 and triethylamine (125 µl; 0.899 mmol) and phenol (86 mg; 0.915 mmol) in CH_2Cl_2 (5 cm³) added. After stirring the solution for 3 h, the solvent was removed *in vacuo*, the residue dissolved in ether–dichloromethane (ratio: 1:1) and filtered. After removal of the solvent, the slight yellow product was washed with acetonitrile (2 × 5 cm³) and dried for 2 h at 50 °C under vacuum to afford the product as a white solid (0.85 g, 89%). (Found: C, 43.76; H, 1.44. $C_{38}H_{15}F_{26}O_3P$ requires C, 43.68; H, 1.44%). MS (FAB): *m*/*z* = 1044 [M⁺]. ^1H NMR ($CDCl_3$): δ 7.28 (2H, m), 7.09 (3H, m), 7.36 (2H, AB multiplet, $^3J_{HH}$ = 11.7 Hz), 7.38 (2H, AB multiplet, $^3J_{HH}$ = 11.7 Hz), 7.45 (1H, d, $^3J_{HH}$ = 8.95 Hz), 7.62 (1H, d, $^3J_{HH}$ = 8.95 Hz), 7.99 (1H, d, $^3J_{HH}$ = 8.95 Hz), 8.08 (1H, d, $^3J_{HH}$ = 8.95 Hz), 8.14 (1H, s), 8.17 (1H, s). ^{31}P {^1H} NMR (C_6D_6): δ 145.7. ^{19}F {^1H} NMR (C_6D_6): δ −81.42 (6F, t, $^4J_{FF}$ = 9.72 Hz), −110.24 (4F, t, $^4J_{FF}$ = 16.0 Hz), −121.63 (8F, m), −123.06 (4F, m), −126.48 (4F, m). $[\alpha]_D^{17}$ −96.4 (*c* 1.4, CH_2Cl_2).

Preparation of 4-tridecafluorohexylphenyl-(*R*)-1,1′-binaphthyl-6,6′-tridecafluorohexyl -2,2′-diyl-phosphite, (7)

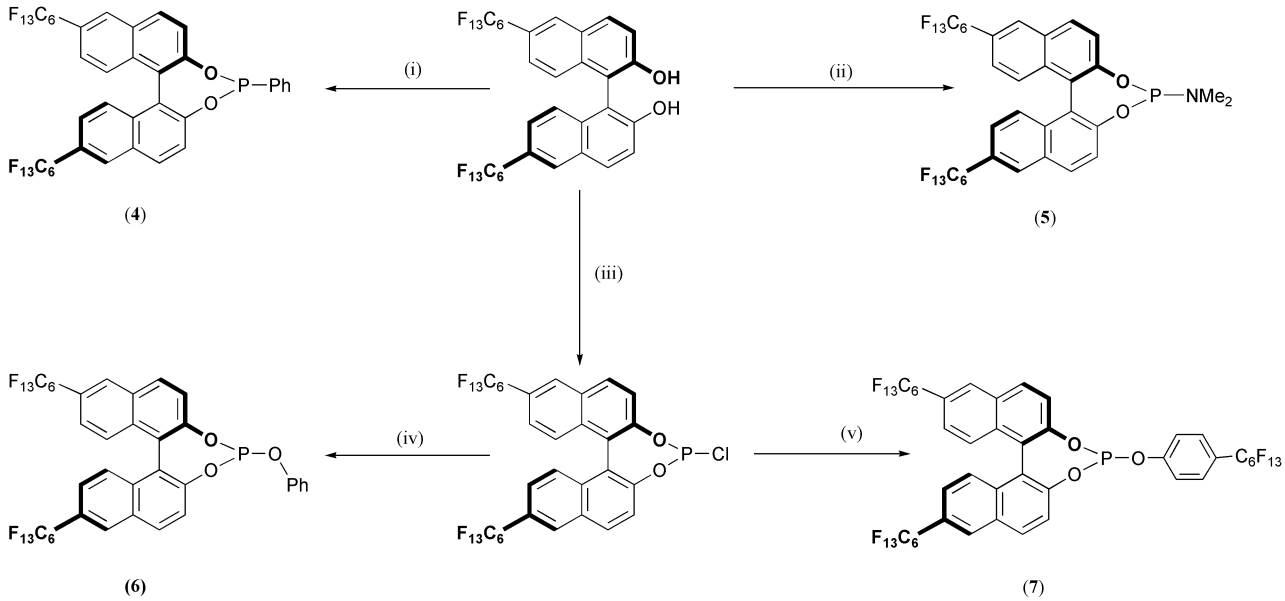
This was prepared following the method for (**6**) in 90% yield using 4-tridecafluorohexylphenol. (Found: C, 38.69; H, 0.98. $C_{44}H_{14}F_{39}O_3P$ requires C, 38.77; H, 1.03%). MS (FAB): *m*/*z* = 1362 [M⁺]. ^1H NMR ($CDCl_3$): δ 7.19 (2H, m), 7.47 (6H, m), 7.55 (1H, d, $^3J_{HH}$ = 8.78 Hz), 7.72 (1H, d, $^3J_{HH}$ = 8.78 Hz), 8.02 (1H, d, $^3J_{HH}$ = 8.78 Hz), 8.19 (1H, d, $^3J_{HH}$ = 8.97 Hz), 8.22 (1H, s), 8.28 (1H, s). ^{31}P {^1H} NMR (C_6D_6): δ 141.0 (s). ^{19}F {^1H} NMR (C_6D_6): δ −81.27 (9F, m), −110.10 (2F, m), −110.25 (4F, m), −121.62 (12F, m), −123.03 (6F, m), −126.45 (6F, m). $[\alpha]_D^{17}$ −89.1 (*c* 2.0, CH_2Cl_2).

General procedure for hydrogenation in $scCO_2$

The catalyst was prepared by adding the monodentate ligand (20.7 µmol) to a solution of $[Rh(cod)_2][BF_4]$ (10 µmol) in CH_2Cl_2 (10 cm³). The solution was stirred for 10 minutes before the solvent was removed *in vacuo*. The preformed catalyst (0.6–2.4 µmol) was placed directly into an autoclave and dimethyl itaconate (104 mg) loaded in a small glass sample tube was placed upright in the autoclave to avoid catalysis prior to pressurisation with carbon dioxide. The vessel was flushed several times with hydrogen and pressurized to 20 bar. After heating to the desired reaction temperature, carbon dioxide was pressurized to a total pressure of 200 bar. After stirring the reaction mixture for 2–24 h, the vessel was cooled in an ice bath and slowly depressurized. The reaction mixture was dissolved in CH_2Cl_2, the catalyst removed via a short silica gel column and the product(s) solution directly analyzed by GC.

General procedure for hydrogenation in CH_2Cl_2

The catalyst was prepared by adding the monodentate ligand (35.0 µmol) to a solution of $[Rh(cod)_2][BF_4]$ (17 µmol) in



Scheme 1 (i) $PhPCl_2$, Et_3N, CH_2Cl_2, rt; (ii) $P(NMe_2)_3$, CH_2Cl_2, rt; (iii) PCl_3, Et_3N, CH_2Cl_2, rt; (iv) C_6H_5OH, Et_3N, CH_2Cl_2, rt; (v) HOC_6H_4-4-C_6F_{13}, Et_3N, CH_2Cl_2, rt.

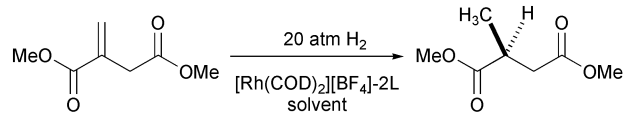
CH_2Cl_2 (10 cm^3). Dimethyl itaconate (104 mg), the required volume of the catalyst solution and dichloromethane (to a total volume of 4 cm^3) were loaded into the pressure vessel. The vessel was flushed several times with hydrogen and pressurized to 20 bar. After reaction, the vessel was depressurized, the catalyst removed *via* a short silica gel column and the product(s) solution directly analysed by GC.

Results and discussion

The synthesis of a range of chiral monodentate perfluoroalkylated phosphorus(III) ligands incorporating chelation at the phosphorus centre has been achieved by the high yielding reaction of the perfluoroalkylated-(*R*)-binaphthol[8] with phosphorus chloride reagents (in the presence of triethylamine) or hexamethylphosphorus triamide (Scheme 1). For the reaction of perfluoroalkylated-(*R*)-binaphthol with PCl_3, it is important to add the triethylamine before the derivatised binaphthol to get the desired $(ArO)_2PCl$ compound. Addition of phenol or derivatised phenol results in ligands **6** and **7**.

Whilst the phosphoramidite (**5**) is air- and moisture-stable, the phosphonite (**4**) and phosphites (**6**, **7**) are highly moisture sensitive. The ^1H NMR spectroscopic data for these ligands reveal complicated, overlapping, resonances in the aryl region of their ^1H NMR spectra associated with the binaphthyl and phenyl protons. The ligands show six or five, highly characteristic, resonances in their ^{19}F NMR spectra associated with the tridecafluorohexyl ponytails, diagnostic singlets in their $^{31}P\{^1H\}$ NMR spectra (at 187, 150, 146 and 141 ppm respectively) and parent ions in their FAB mass spectra. The optical purity of the products was confirmed by CD which, for (**5**), interestingly gave the opposite rotation to that reported for the parent, non-perfluoroalkylated phosphoramidite.[18] During the course of this work, we have remade both (*R*)- and (*S*)-1,1′-binaphthyl-2,2′-diyl-dimethylaminophosphoroamidite and measured their optical rotations. We have found that the optical rotations for these ligands also have the opposite signs to those reported in the literature which concurs with our data for (**5**).

We have evaluated the reactivity and enantioselectivity of these ligands in the rhodium-catalysed hydrogenation of dimethyl itaconate in dichloromethane and supercritical CO_2 (Scheme 2). The rhodium catalysts formed with ligands



Scheme 2

containing two perfluoroalkyl groups (**4,5,6**) are readily soluble in dichloromethane and, hence, their catalytic activities and enantioselectivities (Table 1) can be compared directly with

Table 1 Asymmetric Rh-catalysed hydrogenation of dimethyl itaconate using (*R*)-perfluoroalkylated phosphorus(III) ligands in CH_2Cl_2.[a]

Ligand	*t*/h	Substrate/ Catalyst	Conversion (%)	% ee
4	14	500	100	84
4	3	500	98	82
4	1	500	90	84
1[b]	n.r.	1000	100	29
5	3	250	100	> 99
5	3	500	100	> 99
2[c]	20	20	100	87
6	3	500	45	91
6	3	100	100	91
(*S*)-3[d]	20	1000	100	97
7	16	500	14	< 1

[a] (*R*)-ligands unless otherwise stated; Ligand:Rh = 2:1; room temperature. [b] Ref. 10; n.r. = not reported. [c] Ref. 12; % ee increases to 94.4 at 0 °C. [d] Ref. 15.

those for the parent literature, non-perfluoroalkylated, catalyst systems. Unfortunately, the tris-derivatised phosphite is not sufficiently soluble in dichloromethane, as a consequence of the perfluoroalkyl sidechains, and gave very poor conversion and asymmetric induction even after 16 hours, which is probably a result of background reaction due to unligated rhodium. Complete conversion could be achieved with the ligands **4–6** depending on the substrate : catalyst ratios and reaction times and, interestingly, the introduction of the perfluoroalkyl groups directly on to the binaphthyl backbone appears to have a significant influence on the enantioselectivities in comparison to those for the perprotio parents. Thus, ee's of 84% and > 99%

Table 2 Asymmetric Rh-catalysed hydrogenation of dimethyl itaconate using (*R*)-perfluoroalkylated phosphorus(III) ligands in supercritical CO_2.[a]

Ligand	*t*/h	*T*/°C	Substrate/ Catalyst	Conversion (%)	% ee	Additive
4	3	40	1000	9	8	
5	3	40	1000	11	10	
5	5	40	500	85	15	NaBARF (1.1 equiv)
5	3	40	250	84	31	NaBARF (1.1 equiv)
5	2	60	500	6	16	NaBARF (1.1 equiv)
5	3	80	500	9	5	NaBARF (1.1 equiv)
5	13	40	500	67	1	NaBARF (1.1 equiv) + $C_6F_{13}C_2H_4OH$ (30 mg)
6	3	40	1000	8	7	
7	13	40	250	21	34	
7	13	40	250	28	65	NaBARF (1.1 equiv)

[a] Ligand : Rh = 2 : 1.

to the (*R*) enantiomer were observed with **4** and **5** respectively. In contrast, their parental analogues were reported to give ee's at only 29% and 87% respectively.[10,12] The data indicate that, in these systems, the introduction of the perfluoroalkyl groups directly on to the binaphthyl backbone has relatively little influence on the reactivities but can result in enhanced enantioselectivities in comparison with their perprotio parents.

Previous work on the coordination properties of perfluoroalkylated phosphite ligands, has shown that the additional oxygen linker atom was not sufficient to completely insulate the phosphorus donor atoms from the electronic influence of the fluorous ponytails.[19] Here, we believe that the electron-withdrawing effects of the fluorous ponytails is having a beneficial influence on these monodentate phosphorus(III) ligands in terms of their enantioselectivities. In our previous work on the ruthenium catalysed asymmetric hydrogenation of dimethyl itaconate,[8] we found whilst a tridecafluorohexyl group imposed no detectable effect on enantioselectivity, it was necessary to introduce an additional C_2H_4 insulating spacer group between the fluorous ponytails and the binaphthyl rings in order to get reactivity comparable to that for the parent Ru-BINAP complex. The difference between the monodentate ligands described here and our derivatised BINAPs could be ascribed to the two different types of ligand systems being compared. With the BINAP system good σ donor phosphine ligands were investigated whereas, here, we are examining the applications of poor σ donor phosphonite, phosphoramidite and phosphite ligand.

Unfortunately, this level of reactivity has not been retained in supercritical CO_2 (Table 2). The reactivity and enantioselectivity in $scCO_2$ using the bis-derivatised ligands (**4,5,6**) are much lower than in CH_2Cl_2. After 3 h the conversion is around 10% and the ee value is also around 10% for all three ligands in $scCO_2$. This dramatic decrease in reactivity and selectivity is unlikely to be purely a solvent effect and is probably caused by poor solubility of the catalysts in the supercritical fluid. Following the addition of the fluorinated anion, BARF, as used by Burk and Tumas for asymmetric hydrogenation using the Et-DUPHOS ligand[20] and by Leitner *et al.* for asymmetric hydrogenation using a bisperfluoroalkylated phosphinite ligand,[21] enhanced reactivities and enantioselectivities can indeed be achieved for the phosphoramidite ligand (**5**), showing that the low reactivity of these catalysts results mainly from their low solubility in the reaction medium. To achieve a higher solubility in $scCO_2$ the catalysis was attempted at a higher temperature; but, instead of an increase in reactivity and selectivity, both values were decreased due to decomposition of the catalysts, which was visible by deposition of black metal particles after the reaction. Although reactivity can be improved by the addition of a small amount of a fluorous alcohol, this is at the expense of selectivity, probably due to decomposition of the ligand by the acidic alcohol. For a similar reason, menthyl binaphthylphosphite was shown to be ineffective in the same reaction in MeOH.[17] However, fluorous alcohols have previously been shown to enhance the enantioselectivity in Ru(II)-BINAP catalysed asymmetric hydrogenation reactions in $scCO_2$.[22] Consistent with the solubility argument, much higher enantioselectivities were observed with the tris-derivatised phosphite ligand (**7**) in the presence of the BARF counterion in $scCO_2$, 65%, and the phosphoroamidite ligand (**5**) in hexane, 92%. At 65% ee the enantioselectivity is still much lower than that for ligand **6** in CH_2Cl_2 but this could be explained by a combination of solvent effects and the potential influence of the third perfluoroalkyl chain and is not necessarily a solubility problem. Our explanation for this rests with the apolarity of carbon dioxide as a solvent which may argue against its application in asymmetric hydrogenation using binaphthyl-backboned ligands. However, it is not clear if, or to how great a degree, the solvent polarity contributes to the observed low ee's in $scCO_2$. In attempts to resolve these issues, further work on ligands with larger numbers of fluorous ponytails for enhanced solubility in $scCO_2$ and asymmetric catalysis in alternative supercritical fluids is underway.

Conclusions

The synthesis of chiral perfluoroalkylated monodentate phosphorus(III) ligands has been achieved in high yield. In the rhodium-catalysed asymmetric hydrogenation of dimethyl itaconate in dichloromethane the perfluoroalkyl substituents have a considerable influence upon the enantioselectivities of the catalyst. However, in $scCO_2$ even in the presence of the fluorinated BARF anion, activities as well as enantioselectivities in this asymmetric hydrogenation reaction are modest.

Acknowledgement

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‡ In the ruthenium-catalysed asymmetric hydrogenation of dimethyl itaconate in $scCO_2$ with (*R*)-6,6′-bis(tridecafluorohexyl)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl and (*R*)-6,6′-bis(1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, good enantioselectivities (73 and 75% ee respectively) were obtained but the reactions took 24

hours to go to 100% completion compared to just 15 minutes in methanol.

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