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Fluorous Catalysts and Fluorous Phase Catalyst Separation for Hydrogenation Catalysis

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40.1

Introduction

Since the first demonstration of the technique of fluorous biphasic catalyst separation by Horváth and Rábai in 1994 [1], this separation technique has been extensively studied and is maturing into a good alternative next to other catalyst recycling methods. Several reviews have appeared within a relatively short period, underlining the growth of interest in this field [2]. This chapter focuses on the application of fluorous techniques for the separation and recycling of soluble hydrogenation catalysts. Soluble or homogeneous hydrogenation catalysts are mostly employed for the selective hydrogenation of fine chemicals where high chemoselectivity, regioselectivity and, in some cases, even enantioselectivity is required. The resulting products are usually of reasonably high-added value and, from an economical perspective, it is not always necessary to recycle the catalyst or its components. However, a high selectivity is often only obtained at the cost of activity, and consequently high catalyst loadings are needed in some cases. In addition, catalyst residues in the end product are often undesirable because of their toxicity profile or unwanted side effects in subsequent synthetic transformations. In those cases, fluorous biphasic separation can have advantages over other separation and recycling techniques:

- Because of the thermomorphic properties of fluorous organic biphasic systems, homogeneous single-phase reaction conditions are still possible, preventing the risk of liquid–liquid or liquid–solid mass transport limitations that may influence the activity or selectivity of the catalyst. Above its consolute temperature, the mixed fluorous-organic phase has generally enough “solvent power” for organic substrates and products to dissolve completely.
- The fluorocarbon component of the solvent system, preferably high-boiling to limit emission to the atmosphere, is usually inert and not reactive towards the catalyst.
- Finally – and perhaps most importantly – the fluorous tagging of the catalyst that introduces affinity for the fluorous phase can be a very mild immobilization technique, as there is no direct covalent link with a support and the sepa-

ration itself does not impose additional thermal stress on the catalyst. (Recycling of a homogeneous catalyst by distillation of the more volatile solvent and products is often not possible due to thermal degradation of the catalyst.) In this chapter it will be shown that, by using certain specific spacers between the fluorinated tags and the active site of the catalyst, it is possible to leave the selectivity and activity of the catalyst intact.

To be fair, it should be realized that if a catalyst must be recycled for economic reasons, the recycling efficiency compared to the nonfunctionalized catalyst must be higher in order to compensate for the increased price of the fluorinated catalyst itself. However, every recycling technique has its own cost that must be evaluated for each specific case.

Apart from applications in catalysis, fluorinated biphasic separation strategies are also being developed for application in (high-throughput) organic synthesis schemes [3], and even in bioorganic synthesis [4]. In some cases, the fluorinated solvent has been used advantageously for its “green” properties [5] or to enhance the rate of specific reactions [6].

In the following sections, an overview is provided of fluorinated hydrogenation catalysts that have been developed for fluorinated biphasic separation strategies, along with a discussion of their performance in hydrogenation reactions and the recycling efficiencies attained. The chapter does not include fluorinated hydrogenation catalysts for application in supercritical carbon dioxide (scCO₂), which have been described in Chapter 39.

A wide range of fluorinated phosphorus ligands have become available that are based on different spacer-units between the perfluoroalkyl tails and the remainder of the ligand. Alkylphosphines having a $-(\text{CH}_2)_n-$ moiety, triarylphosphines with a perfluoroalkyl tail directly connected to the aryl ring, and triaryl phosphines with an additional spacer unit between the perfluoroalkyl group and the aryl ring, are the most commonly applied. Additional spacers among the latter class of phosphines are $-(\text{CH}_2)_n-$, $-\text{SiMe}_{3-b}(\text{CH}_2\text{CH}_2)_b-$, and $-\text{OCH}_2-$ moieties.

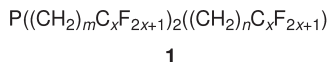
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Catalysts Based on Fluorous Alkylphosphines, -Phosphinites, -Phosphonites, and -Phosphites

The first fluorinated phosphine ligands for application in fluorinated phase catalysis were fluorinated trialkylphosphines **1** [7–9].

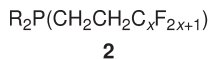
Ligands **1a** (C₆F₁₃-tail) and **1b** (C₈F₁₇-tail) were applied in the fluorinated hydrogenation of internal and terminal alkenes [10] and styrenes [10, 11]. The Wilkinson-type complexes [RhCl(**1a–b**)₃] displayed lower activities compared to [RhCl(PPh₃)₃]. Catalyst recycling resulted on average in a 1.5% lower yield after each cycle [10]. Although Rh-leaching was not measured, it is most probably comparable to the values obtained for hydroboration with the same catalyst (ca. 0.2% per cycle). The loss of yield which does not appear to match with the loss

of rhodium could be indicative of loss of dissociated ligand, which leads to the formation of less active species (*vide infra*).

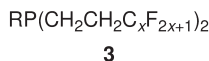


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|---------------------------------|---------------------------------|
| a: $m = n = 2; x = 6$ | f: $m = n = 3; x = 8$ |
| b: $m = n = 2; x = 8$ | g: $m = 3; n = 4; x = 8$ |
| c: $m = n = 2; x = 10$ | h: $m = 4; n = 3; x = 8$ |
| d: $m = 2; n = 3; x = 8$ | i: $m = n = 4; x = 8$ |
| e: $m = 3; n = 2; x = 8$ | j: $m = n = 5; x = 8$ |

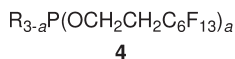
The fluorous alkylphosphines **2** [8, 12] and **3** [8, 13], containing one or two perfluoroalkyl tails, respectively, have also been prepared. Partition coefficients of the chiral fluorous monophosphines **3a–b** were found to be lower than the values measured for the corresponding phosphines **1**, which contain one extra perfluoroalkyl tail [13]. In addition, fluorous phosphinites, phosphonites and phosphites **4a–e** and diphosponite **5** have become available [8, 14].



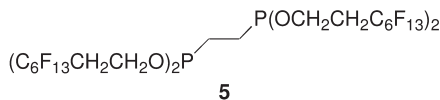
- a:** R = Cy; $x = 6$
b: R = ⁱPr; $x = 6$
c: R = Ph; $x = 6$



- a:** R = menthyl; $x = 6$
b: R = menthyl; $x = 8$
c: R = Ph; $x = 6$



- a:** $a = 3$
b: $a = 2; \text{R} = \text{Ph}$
c: $a = 1; \text{R} = \text{Ph}$



- d:** $a = 1, \text{R} = \text{}^i\text{Pr}$
e: $a = 1, \text{R} = \text{Cy}$

The ligands **2a**, **2c** and **4d–e** were used for the rhodium-catalyzed hydrogenation of 1-hexene under homogeneous conditions, using the 1-hexene itself as solvent [12, 14]. The catalysts were synthesized *in situ* by reacting $[\text{RhCl}(\text{COD})]_2$ with 6 equiv. of the ligand. As for fluorous trialkylphosphines **1**, lower activities were found compared to the catalyst based on PPh_3 . Turnover numbers (TONs) after 24 h were found to increase in the order **2a** < **4d** < **4e** \approx **2c** < PPh_3 .

In a similar fashion, **2a**, **2c**, **4a** and **4c** were also tested in the hydrogenation of 1-hexene under fluorous biphasic conditions (1-hexene/PFMCH=1:2 (v:v)) [12, 14]. Relatively low activities were found for all catalysts, with activities increasing in the order **4a** < **4c** < **2a** < **2c**.

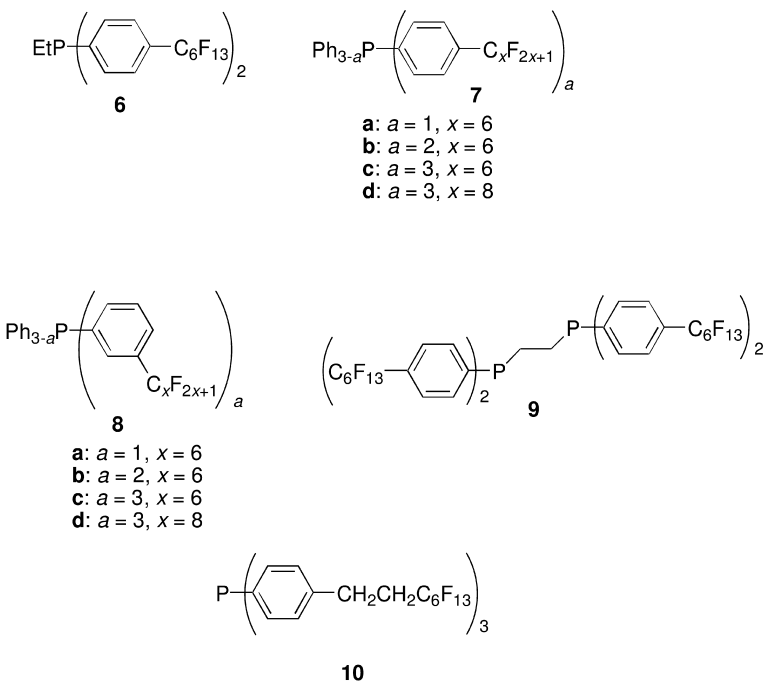
A cationic complex, formed *in situ* from **5** and $[\text{Rh}(\text{COD})_2]\text{OTf}$, was also active in biphasic hydrogenation [14]. No preference for the fluorous phase was found for ligands containing only one perfluoroalkyl tail, but neutral and cationic complexes, containing mono- and bidentate **4a** or **5**, respectively, were selectively dissolved in the fluorous phase. No leaching and recycling studies were performed.

In general, the fluorous catalysts containing fluorous alkylphosphines display good recycling efficiency, but their activity is lower compared to existing systems containing PPh_3 as ligand.

40.3

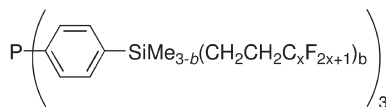
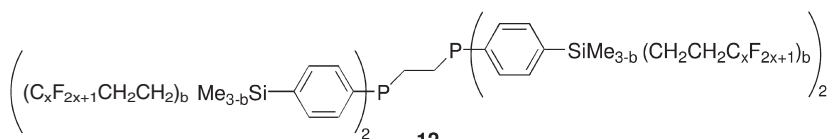
Catalysts Based on Perfluoroalkyl-Substituted Arylphosphines

A large variety of fluorous triarylphosphines that differ in the type of isolating group between the perfluoroalkyl tail and the aryl ring, has been reported. The simplest ones are arylphosphines **6–9**, with the perfluoroalkyl tail directly connected to the aryl ring. The electron-withdrawing effect of the perfluoroalkyl tails was clearly noticeable upon application of some of these fluorous compounds in homogeneous catalysis. The reaction rates that were found in fluorous hydrogenation of styrene using $[\text{RhCl}(\text{L})_3]$ ($\text{L}=\mathbf{6}, \mathbf{7c}$ [8, 15, 16] or **8** [16, 17]) or $[\text{Rh}(\mu\text{-Cl})(\mathbf{9})_2]$ [8] as catalyst were all lower compared to that of the nonfluorous analogues (based on PPh_3 , EtPPh_2 , or DPPE (DPPE=1,2-bis(diphenylphosphino)ethane)) [11]. However, the activities observed were similar to catalysts containing $\text{P}(3\text{-C}_6\text{H}_4\text{CF}_3)_3$ or $\text{P}(4\text{-C}_6\text{H}_4\text{CF}_3)_3$ as ligand, indicating that the strong electron-withdrawing character of the perfluoroalkyl tails was responsible. The reaction rates were unaffected upon recycling of the catalysts in all cases, and essentially no rhodium (i.e., <1 ppm) or free ligand could be detected in the toluene layer by inductively coupled plasma-atomic absorption spectroscopy (ICP-AAS) analysis [11].



To overcome the electron-withdrawing effect of the perfluoroalkyl tail exerted on the phosphorus atom when the tail is directly coupled to the aryl ring, extra spacers have been introduced, the most frequently used one being $-(\text{CH}_2)_n-$ units. Compound **10** was used to demonstrate in the context of styrene hydrogenation how the use of a volatile fluororous solvent can be eliminated [18]. The fluororous solvent was replaced by fluororous silica, and the fluorophilicity of the remaining organic solvent was increased by expansion with CO_2 to allow the fluororous Wilkinson-type catalyst to dissolve. Release of the CO_2 pressure causes the catalyst to re-precipitate on the fluororous silica, facilitating the recycling of the catalyst. The catalyst was recycled four times with essentially no drop in activity, and Rh leaching was below the detection limit ($<0.5\%$), although phosphine leaching was not measured.

Another solution to insulate the phosphorus donor-atom from the electron-withdrawing perfluoroalkyl tail, and to simultaneously provide easy synthetic access to the introduction of more tails to one aryl ring, is the use of the $-\text{Si}(\text{Me})_{3-b}(\text{CH}_2\text{CH}_2-)_b$ spacer. Here, the silicon atom acts as an additional insulator for the electron-withdrawing effect of the perfluoroalkyl tail, while it can simultaneously be used as a branching point for the attachment of up to three tails per aryl ring. Using this principle, phosphines **11** were prepared [19]. Similarly, highly fluororous derivatives of DPPE **12** were obtained [20].

**11****a:** $b = 0$ **b:** $b = 1; x = 6$ **c:** $b = 1; x = 8$ **d:** $b = 2; x = 6$ **e:** $b = 2; x = 8$ **f:** $b = 3; x = 6$ **g:** $b = 3; x = 8$ **12****a:** $\text{R}_f = \text{C}_6\text{F}_{13}, b = 1$ **b:** $\text{R}_f = \text{C}_6\text{F}_{13}, b = 2$ **c:** $\text{R}_f = \text{C}_6\text{F}_{13}, b = 3$ **d:** $\text{R}_f = \text{C}_8\text{F}_{17}, b = 1$ **e:** $b = 0$

The possible electronic influence of a fluororous *para*-silyl-substituent was studied in detail using a wide range of physico-chemical techniques [19–23], sug-

gesting that the electron-withdrawing effect of the perfluoroalkyl group is effectively cancelled by the ethylsilyl spacer. The partition coefficients measured for **11 b–g**, in general, are higher than values obtained for fluororous triphenylphosphine **10**, despite the larger organic part of the former [19b]. Partition coefficients in *n*-pentane/PFMCH behaved as described above for fluororous trialkyl- and triaryl-phosphines – that is, more tails as well as longer tails give higher partition coefficients. Similar behavior was observed in *n*-octane/PFMCH for **11 b–e**. Surprisingly, upon attachment of another tail ($b=3$, **11 f–g**), the partition coefficient decreased, with **12 g** ($x=8$) having a higher value than **12** ($x=6$). Even more unexpected partitioning behavior was found in toluene/PFMCH; that is, upon lengthening the tail from $x=6$ to $x=8$, the partition coefficient increased for $b=1$, remained unchanged for $b=2$, and decreased for $b=3$. Furthermore, maximum values were found for $b=2$. Interestingly, this unexpected behavior was not observed for fluororous diphosphines **13** – that is, the partition coefficient increased upon increasing the number of tails, resulting in a maximum value ($P=92$) for **13 c** containing 12 tails.

The unexpected behavior observed for fluororous, silyl-substituted monophosphines **12** was studied in further detail, using combinatorial techniques and statistical design of experiments [24]. A library of phosphines **11** (*a*, *b*, *x*, *pos*) was prepared by parallel synthesis, with *a* (1–3) being the number of silyl-substituted phenyl groups, *b* (1–3) the number of tails per Si-atom, *x* (4, 6, 8, 10) the length of the tail, and *pos* (*meta* (C3), *para* (C4) or 3,5-substituted (C3C5)) the position of the Si-atom on the aryl ring. Using this approach, the highest partition coefficient was observed for **11** (2, 3, 6, C3C5) ($P=236$).

Complexes $[\text{RhCl}(\text{L})_3]$ ($\text{L}=\mathbf{11 a–c}$) were applied in the fluororous hydrogenation of 1-octene in a fluororous biphasic system, as well as in benzonotrifluoride (BTF) [22]. The activities measured in the hybrid solvent BTF were comparable with that of Wilkinson's catalyst, $[\text{RhCl}(\text{PPh}_3)_3]$, with activities increasing in the order $\mathbf{11 c} < \text{PPh}_3 \approx \mathbf{11 b} < \mathbf{11 a}$. This was the first example of a fluororous hydrogenation catalyst with similar activity compared to the nonfluorous analogue. $[\text{RhCl}(\mathbf{12 c})_3]$ was tested for its hydrogenation activity upon recycling in a fluororous biphasic solvent system. Nine cycles were performed, with an average Rh leaching of 0.1% per cycle. The extent of rhodium leaching, as studied by ICP-AAS, turned out to be small (0.1% Rh detected), whereas leaching of dissociated ligand was substantial (2% per cycle for $\text{L}=\mathbf{11 c}$). These studies demonstrated that, when recycling of catalysts with fluororous biphasic separation techniques is applied, both leaching of the transition metal, leaching of (expensive) fluororous solvent and of free fluororous ligand should be considered.

Some of the improved fluororous arylsilylphosphines in the library **11** (*a*, *b*, *x*, *pos*) were tested in the context of hydrosilylation catalysis [24]. Rh and phosphine leaching were driven down further to non-detectable levels (<0.1%) and 0.8%, respectively, and it can be expected that even better results are possible for hydrogenation catalysis.

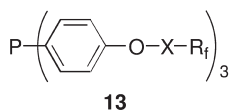
Fluorous diphosphine complexes $[\text{Rh}(\text{COD})(\mathbf{12})\text{BF}_4]$ showed amphiphilic behavior, resulting in the formation of aggregates with a size of several hundreds

of nanometers in acetone solutions [23]. When these fluorinated diphosphine rhodium complexes were applied in the hydrogenation of 1-octene and 4-octyne [23], interesting differences in catalytic performance were observed between fluorinated and nonfluorinated derivatives of $[\text{Rh}(\text{COD})(\text{DPPE})]\text{BF}_4$ – that is, the fluorinated catalyst displayed lower isomerization rate constants, resulting in higher hydrogenation activity and selectivity. This phenomenon was explained by the unique aggregation behavior of the fluorinated catalyst that was not previously observed.

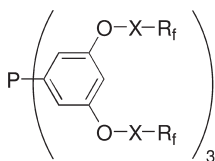
Fluorinated biphasic recycling of $[\text{Rh}(\text{COD})(\mathbf{12c})]\text{BF}_4$ was studied in two fluorinated solvent systems (acetone/PFMCH and hexane/FC-75). Recycling was possible in both systems without loss of conversion. ICP-AAS-measurements on the organic phase showed the presence of rhodium and phosphorus in a 1:2 molar ratio, indicating that diphosphines can be used to prevent leaching of free fluorinated ligand. Interestingly, no rhodium ($<0.08\%$) could be detected in the organic phase when hexane/FC-75 was used as solvent system.

Another spacer which was used to insulate the phosphorus atom from the electron-withdrawing effect of the perfluoroalkyl tail is the $-\text{O}(\text{CH}_2)_n-$ spacer that contains an electron-donating oxygen atom directly attached to the aryl ring [25]. Fluorinated derivatives of triphenylphosphine containing this ether spacer ($\mathbf{13a-c}$) were prepared, though the lower $^1J_{\text{PtP}}$ coupling constant of *cis*- $[\text{PtCl}_2(\mathbf{13a})_2]$ and higher ν_{CO} of *trans*- $[\text{MCl}(\text{CO})(\mathbf{13a})_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) compared to *cis*- $[\text{PtCl}_2\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{OMe})_3\}_2]$ and *trans*- $[\text{MCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{OMe})_3\}_2]$, respectively, indicates that the oxygen atom does not fully insulate the electron-withdrawing effect [26]. Ligands $\mathbf{13a-c}$ were found to be soluble in organic solvents (Et_2O , CHCl_3) as well as fluorinated solvents (C_8F_{18}) [25].

The oxygen-spaced derivative $\mathbf{13a}$ (along with related derivatives) was successfully employed in the Rh-catalyzed hydrogenation of (*E*)-cinnamate and 2-cyclohexen-1-one, with activities comparable to that of the corresponding PPh_3 derivative [27]. Recycling efficiency studies demonstrated a two- to three-fold drop in activity over three cycles, while leaching values were in the range 0.37 to 0.56% (Rh) and 0.94 to 0.95% (phosphine) for the last two cycles. The highly fluorinated derivative $\mathbf{14}$ displayed the lowest leaching: 0.12 to 0.23% (Rh) and 0.46 to 0.63% (phosphine), but the presence of two perfluoroalkyl tails induce an eight-fold drop in activity compared to PPh_3 .

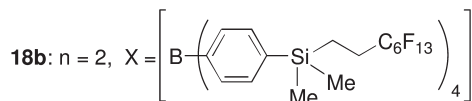
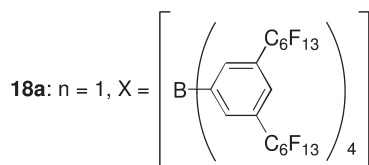
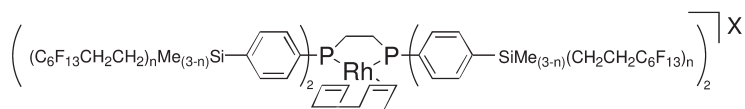
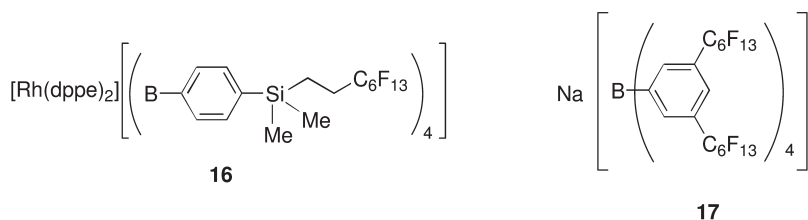


- a:** $\text{X} = \text{CH}_2$; $\text{R}_f = \text{C}_7\text{F}_{15}$
b: $\text{X} = (\text{CH}_2)_3$; $\text{R}_f = \text{C}_8\text{F}_{17}$
c: $\text{X} = \text{CH}_2\text{O}(\text{CH}_2)_2$; $\text{R}_f = \text{CF}_2(\text{O}(\text{CF}_3)\text{CF}_2)_{3.38}(\text{OCF}_2)_{0.11}\text{OCF}_3$



- 14** $\text{X} = \text{CH}_2$, $\text{R}_f = \text{C}_7\text{F}_{15}$

Today, many fluorinated borate anions are recognized [31], the most well-known being $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $[\text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)_4]^-$ (BARF). Furthermore, it is known that the attachment of (short) perfluoroalkyl groups increases the lipophilicity of these anions [32]. With these considerations in mind, fluoros derivatives of tetraphenylborate containing $-\text{C}_6\text{F}_{13}$ or $-\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{13}$ groups were prepared [33]. It was found that attachment of a long (1*H*,1*H*,2*H*,2*H*-perfluoroalkyl)dimethylsilyl group to the anion in complex **16** considerably increases the solubility in apolar solvents. The sodium salt **17** of a fluoros derivative of tetraphenylborate containing eight tails even dissolved in a fluoros solvent [34]. The fluoros borate anions were successfully used to boost the fluorophilicity of complexes of the type $[\text{Rh}(\text{COD})(\text{Ar}_2\text{PCH}_2\text{CH}_2\text{PAr}_2)]\text{X}$ (*Ar*=aryl, *X*=weakly coordinating anion) that were previously shown to be not sufficiently fluorophilic for fluoros biphasic separation protocols unless the aryl groups were very heavily perfluoroalkylated. By employing highly fluoros borate anions resulting in complexes **18a, b**, only lightly fluoros diphosphines were needed to obtain good recycling efficiencies [35]. In addition, the use of these fluoros anions as counterions in butane-bridged $[\text{Rh}(\text{COD})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]\text{X}$ (*X*= BF_4^- , or fluoros tetraarylborate) led to significantly enhanced reaction rates under nonfluorous conditions.



40.5

Catalysts Based on Nonphosphorus Ligands

To date, fluororous hydrogenation catalysts have been mainly based on phosphorus ligands with one exception. This is a system consisting of fluororous dendrimer-encapsulated Pd(0) nanoparticles that is active for the hydrogenation of alkenes and conjugated alkenes, and can be recovered by fluororous biphasic separation [36]. Recently, the same system was demonstrated in CO₂-induced phase switching of a fluororous biphasic solvent system, offering an alternative to temperature-induced mixing and demixing strategies [37].

40.6

Enantioselective Hydrogenation Catalysts

Although fluororous derivatives of DPPE were successfully employed in catalytic hydrogenation (*vide supra*), chiral fluororous diphosphines have had limited success in enantioselective hydrogenation. For example, ethylene-spaced and nonethylene-spaced 6,6'-perfluoroalkylated BINAP-type phosphines based on the 1,1'-binaphthyl unit have been investigated in Ru-mediated hydrogenation [38]. Enantioselectivities obtained in methanol and dichloromethane were comparable with that of the nonfunctionalized Ru-BINAP system, with the nonethylene-spaced ligand showing the lowest activity [38, 39]. Recycling became possible only by chromatography over fluororous silica gel. The challenge remains to render the large organic core – that is often needed to induce enantioselectivity – sufficiently fluorophilic for preferential solubility in perfluorocarbon solvents.

40.7

Conclusions

Based on the content of this chapter, it can be concluded that several phosphorus ligand systems are now available for the efficient fluororous biphasic recovery of hydrogenation catalysts. In most cases, the perfluoroalkyl tail exerts an electron-withdrawing effect on the ligand system and the catalytically active metal center. This leads to lower activity in hydrogenation reactions, though selectivity is usually not an issue. Only fluororous catalysts containing the $-\text{SiMe}_{3-b}(\text{CH}_2\text{CH}_2)_b-$ and $-\text{OCH}_2-$ spacers display similar or higher activity in hydrogenation catalysis compared to their nonfluorous analogues. For hydrogenations by cationic metal complexes that are difficult to render fluorophilic by perfluoroalkylation of the ligand system alone, highly fluororous borate counterions have been developed.

Recently, the fluororous biphasic separation technique has been enriched with two new developments, both of which were demonstrated in hydrogenation. The need for a fluororous solvent can be eliminated by using fluororous silica as a fluororous catalyst scavenger. In liquid–liquid biphasic systems, reversible expan-

sion with CO₂, as an alternative to temperature shuttling, has been employed to switch between biphasic and monophasic conditions. Asymmetric hydrogenation combined with fluorous biphasic separation strategies remains a field that is relatively underdeveloped, and represents a clear challenge for future studies.

Abbreviations

BTF	benzotrifluoride (<i>a,a,a</i> -trifluorotoluene)
FC-75	perfluoro-2-butyltetrahydrofuran
ICP-AAS	inductively coupled plasma-atomic absorption spectroscopy
NBD	norbornadiene
PFMCH	perfluoromethylcyclohexane
scCO ₂	supercritical carbon dioxide
TON	turnover number

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