Rhodium-Catalyzed Hydrogenation of Alkenes by Rhodium/Tris(fluoroalkoxy)phosphane Complexes in Fluorous Biphasic System

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Abstract: The reaction of $[Ir(\mu\text{-}Cl)(COD)]_2$ with various fluorous derivatives of triphenylphosphane containing a *para*-, *meta*-, or *ortho*-(1*H*,1*H*-perfluoroalkoxy)-substituted fluorous phosphane $P(C_6H_4\text{-}ORf)_3$ ($Rf = CH_2C_7F_{15}$, $CH_2CH_2CH_2C_8F_{17}$) and CO (1 atm) gives the corresponding *trans*-$[Ir(\mu\text{-}Cl)(CO)\{P(C_6H_4ORf)_3\}_2]$. The IR ν_{CO} values of these complexes give some information on the donor/acceptor properties of the phosphanes. These fluorous derivatives of triphenylphosphane, as well as a phosphane bearing two (1*H*,1*H*-perfluoroalkyloxy) chains at the 3,5-positions, were used in association with $[Rh(\mu\text{-}Cl)(COD)]_2$ or $[Rh(COD)_2]PF_6$ in the reduction of methyl cinnamate, 2-cyclohexen-1-one, cinnamaldehyde, and methyl α-acetamidocinnamate in a two-phase system D-100/ethanol under 1 bar hydrogen at room temperature. Some differences in catalytic activity were observed in the reduction of methyl cinnamate, the most active catalyst being the rhodium complex containing the phosphane with the *p*-fluorous ponytail. Recycling of the fluorous catalyst was possible, particularly using the *p*-substituted phosphane, where no significant loss of catalyst or activity was observed, and generally with very low leaching of rhodium or phosphane in the organic phase.

Keywords: biphasic catalysis; catalyst recycling; fluorous; hydrogenation; iridium; rhodium

Introduction

In the field of homogeneous organometallic catalysis, many efforts have been devoted in the past decade to the recycling of the expensive and often toxic catalyst. One way to immobilize the catalyst for its recovery and its eventual reuse is the use of a biphasic system. One of the most used and studied biphasic systems is the aqueous-organic system.[1–4] Recently, "ionic liquids"[5,6] as well as "fluorous biphase catalysis"[7–14] have emerged as new concepts for this immobilization.

Since the early report of Horváth et al.[7] related to the fluorous biphase catalysis, a large number of fluorous phosphanes have been prepared and used as ligands in organometallic catalysis. Although a number of catalytic reactions based on FBS (fluorous biphase systems) have been achieved, the advantages of the easy recovery of the metal catalysts have been less or more emphasized, depending strongly on the nature of the ligand and particularly its fluorine content.

In the case of hydrogenation using molecular hydrogen, fluorous triaryl- and trialkylphosphanes have been used in the reduction of some alkenes.[15–20] However, hydrogenation of terminal and cyclic alkenes using fluorous trialkylphosphanes as ligands is slow, the activity of the catalyst being generally lower than the Wilkinson's catalyst analogue $[RhCl(PPh_3)_3]$. Van Koten and coworkers[18–20] used fluorous triarylphosphanes, bearing $–CH_2CH_2Si(CH_3)_2–$ as a spacer, as ligands of rhodium catalyst in the reduction of 1-octene and found catalytic activities remarkably close to that of Wilkinson's catalyst. We recently reported the preparation of *o*-, *m*-, and *p*-substituted fluorous triarylphosphanes using the $–OCH_2–$ or $–O(CH_2)_3–$ fragments as a spacer.[21] In this paper we present the application of these fluorous phosphanes as ligands in the Wilkinson's catalyst in the hydrogenation of various unsaturated substrates under fluorous conditions; moreover, their recycling using fluorous biphasic separation was also investigated.

Results and Discussion

The synthesis of fluorous phosphanes **4** – **8** (Scheme 1) has already been described.[21] In order to increase the

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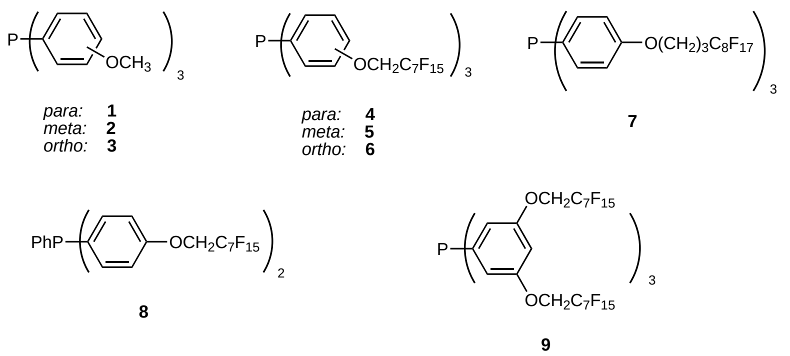
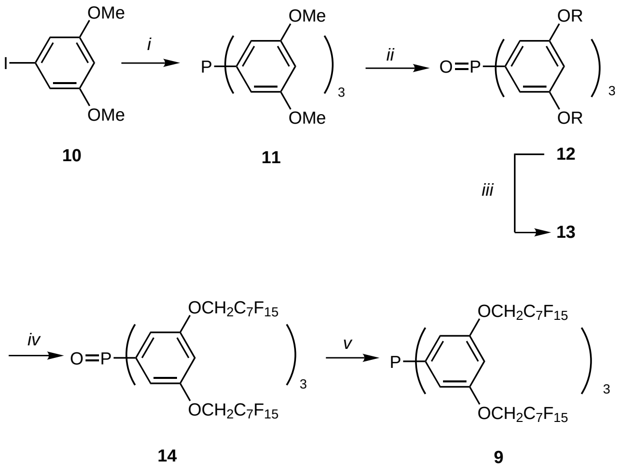


Scheme 1.



Reagents and conditions: *i*: *n*-BuLi, Et_2O, -60 °C, then PCl_3, Et_2O; *ii*: H_2O_2 30%; *iii*: BBr_3, CH_2Cl_2; *iv*: $C_7F_{15}CH_2OSO_2C_4F_9$, Cs_2CO_3, DMF; *v*: $HSiCl_3$, Et_3N, toluene

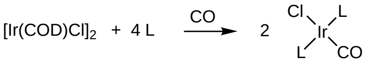
Scheme 2. Synthesis of fluorous phosphane **9**.

fluorophilicity of the phosphane, the fluorous phosphane **9** bearing two fluorous ponytails on each phenyl ring, and so containing up to 6 fluorous tails per molecule, was also prepared according to Scheme 2. The starting tris(3,5-dimethoxyphenyl)phosphane (**11**) was prepared by condensation of 3,5-dimethoxyphenyllithium, obtained by reaction of 3,5-dimethoxyiodobenzene (**10**)[22] with *n*-BuLi, and PCl_3. The phosphane oxide **12** was obtained in 97% yield by standard oxidation of phosphane **11** with hydrogen peroxide. Deprotection of the phosphane oxide **12** was performed using boron tribromide in dichloromethane,[23] affording the crude hydroxyphosphane oxide **13** in 88% yield. Coupling of this hydroxyphosphane oxide **13** with pentadecafluorooctyl nonafluorobutanesulfonate $C_7F_{15}CH_2OSO_2C_4F_9$[21] in DMF at 80 °C in the presence of cesium carbonate, provided the fluorophosphane oxide **14** in 32% yield. Reduction of oxide **14** with trichlorosilane in toluene in the presence of triethylamine[24] gave the fluorophosphane **9** in 81% yield. It is to be noticed that the ^{31}P chemical shift of phosphanes **9** and **11** are quite close ($\delta = 1.4$ and 1.3 ppm, respectively) indicating that the introduction of the $-CH_2-$ spacer seems to be very effective in minimizing the strong electron-withdrawing effect of the fluorinated tail on the phosphorus atom.

Before performing hydrogenation reactions using the above mentioned fluorous phosphanes as ligands, we studied the electronic properties of these ligands. For this purpose, we prepared the carbonyliridium complexes containing ligands **4–7** of the type *trans*-$[Ir(\mu\text{-}Cl)(CO)(PAr_3)_2]$ **18–21**, analogues of Vaska's complex, since it is known that the IR ν_{CO} values of these complexes measure the donor/acceptor properties of the metal fragment and the other ligands. This approach has already been applied to fluorous phosphanes.[16,25–27] These complexes were easily obtained by mixing $[Ir(\mu\text{-}Cl)(COD)]_2$ with the corresponding fluorous phosphane, and then adding carbon monoxide at atmospheric pressure (Scheme 3).[28] For comparative purposes, complexes **15–17** containing the corresponding *p*-, *m*-, and *o*-methoxyphosphane **1**–**3** were also prepared. These complexes were characterized by IR, ^1H, and ^{31}P NMR spectroscopy; the IR ν_{CO} values and the ^{31}P NMR signals of these complexes are summarized in Table 1, together with the values corresponding to Vaska's complex.[29]

The IR spectra of complexes **18** and **21** containing the *para*-substituted fluorous phosphanes showed a ν_{CO} value at higher wavenumber to that of complex **15**: 1961 cm^{-1} *vs.* 1950 cm^{-1}, respectively. For complexes **19** and **16** containing the *meta*-substituted phosphanes, the IR ν_{CO} values are 1962 cm^{-1} and 1959 cm^{-1}, and for complexes **20** and **17**, containing the *ortho*-substituted phosphanes, 1950 cm^{-1} and 1941 cm^{-1}, respectively. The observed differences as well as the direction of the IR shift is consistent with a small residual electron-withdrawing effect, particularly for ligands **4**, **6**, and **7**.[16] In the case of the *para*- and *meta*-substituted perfluorophosphanes, the spacer did not completely insulate the iridium from the electron-withdrawing fluoroalkyl group, although the effect is very small.

The reaction of $[Rh(\mu\text{-}Cl)(COD)]_2$, dissolved in toluene, with 6 equivalents of fluorous phosphane **4**,



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15: L = **1**; **16**: L = **2**; **17**: L = **3**; **18**: L = **4**;
19: L = **5**; **20**: L = **6**; **21**: L = **7**

Scheme 3. Synthesis of iridium complexes.

Table 1. IR and ^{13}P NMR data for iridium complexes.

Complex	ν_{CO} cm^{-1} (KBr)	^{31}P NMR δ (ppm)
$IrCl(CO)(PPh_3)_2$	1952	25.0
15	1950	20.8
18	1961	21.6
21	1961	21.0
16	1959	12.6
19	1962	26.8
17	1941	14.6
20	1950	14.5

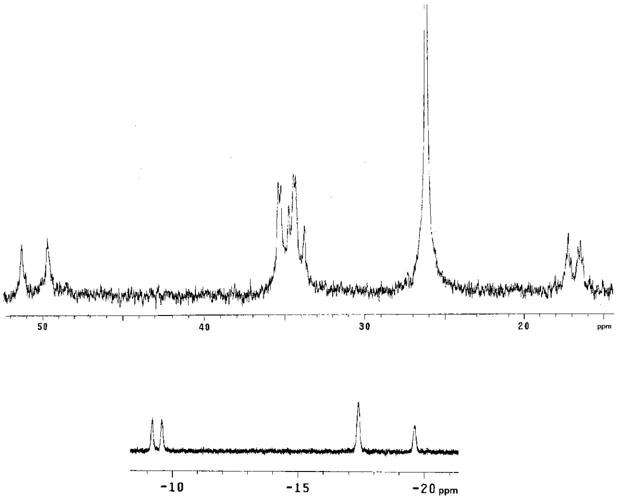
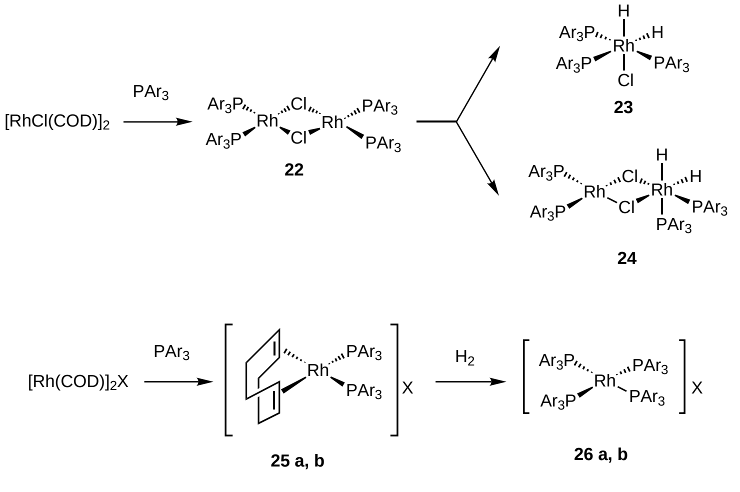


Figure 1. Representative ^{31}P (upper spectrum) and ^{1}H (lower spectrum) NMR spectra of $[Rh(\mu\text{-}Cl)(COD)]_2$ + phosphane **4** under hydrogen.

dissolved in perfluoromethylcyclohexane, was monitored by ^{31}P NMR of the perfluorous phase. After 24 h reaction, the fluorous phase became intense red. The ^{31}P{^{1}H} NMR of this fluorous phase showed a broad doublet at δ = 49.9 ppm ($^{1}J_{Rh,P}$ = 194.6 Hz) which was attributed to the complex $[Rh(\mu\text{-}Cl)(\mathbf{4})_2]_2$ by comparison with published data.[15,16,19,30] A very important singlet at δ = 26.4 ppm remained unassigned as depicted previously.[16] It is to be noticed that when perfluoromethylcyclohexane was used as the only solvent for the reaction between $[Rh(\mu\text{-}Cl)(COD)]_2$ and ligand **4**, the complex was not completely dissolved and the only signal observed in the ^{31}P-{^{1}H} NMR spectrum was this unassigned signal.

The NMR tube containing the fluorous phase obtained in the toluene/perfluoromethylcyclohexane system was charged with 3 atm of H_2 and was shaken at room temperature for 12 h. The ^{31}P{^{1}H} NMR spectrum of the orange solution (Figure 1a) showed signals at δ = 35.3 ppm (dd, $^{1}J_{Rh,P}$ = 115.4 Hz, $^{2}J_{P,P}$ = 20.4 Hz) and δ = 16.7 ppm (dt, $^{1}J_{Rh,P}$ = 89.9 Hz, $^{2}J_{P,P}$ = 20.4 Hz) which were assigned to the *cis*-dihydride monomer $[RhClH_2(\mathbf{4})_3]$; the corresponding hydride signals for $[RhClH_2(\mathbf{4})_3]$ appeared in the ^{1}H NMR spectrum (Figure 1b) at δ = – 9.4 ppm (broad d, $^{1}J_{H,P}$ = 158.1 Hz) and at δ = – 17.4 ppm (broad singlet). Related compounds are well-known for PPh_3[30] and for fluorous phosphanes.[15,19] The ^{31}P{^{1}H} NMR spectrum showed also two other broad doublets at δ = 51.0 ppm ($^{1}J_{Rh,P}$ = 194.8 Hz) and δ = 34.6 ppm ($^{1}J_{Rh,P}$ = 116.3 Hz) that were attributed to the dinuclear *cis*-dihydride $[(\mathbf{4})_2Rh(\mu\text{-}Cl)_2RhH_2(\mathbf{4})_2]$; effectively in the ^{1}H NMR



PAr_3 = **4**; **a**: X = BF_4 ; **b**: X = PF_6

Scheme 4.

another broad signal was also observed at $\delta = -19.6$ ppm. Such a complex has been reported in the literature to be formed by reaction of the Wilkinson complex $RhCl[P(C_6H_4\text{-}p\text{-}CH_3)_3]_3$ with H_2 without addition of any free ligand.[30]

The reaction of the cationic complex $[Rh(COD)_2]BF_4$ or $[Rh(COD)_2]PF_6$ with 2 equivalents of fluorous phosphane **4** in perfluorocyclohexane was also monitored in an NMR tube; the $^{31}P\{^1H\}$ NMR spectra showed a doublet at $\delta = 13.2$ ppm ($^1J_{Rh,P} = 139.8$ Hz) or $\delta = 21.3$ ppm ($^1J_{Rh,P} = 152$ Hz) corresponding to the complex $[Rh(COD)(\mathbf{4})_2]BF_4$ or $[Rh(COD)(\mathbf{4})_2]PF_6$, respectively,[31] together with some remaining free phosphane at $\delta = -20$ ppm. When the same sequence was performed using $[Rh(COD)_2]PF_6$ in the presence of 2 equivalents of fluorous phosphane **5**, a similar doublet appeared at $\delta = 26.5$ ppm ($^1J_{Rh,P} = 151$ Hz) corresponding to the complex $[Rh(COD)(\mathbf{5})_2]PF_6$.

Pressurization of the tube containing the complexes $[Rh(COD)(\mathbf{4})_2]PF_6$ or $[Rh(COD)(\mathbf{5})_2]PF_6$ with H_2 (3 atm) caused the appearance of a new doublet at $\delta = 19.6$ ppm ($^1J_{Rh,P} = 133.5$ Hz) or $\delta = 24.3$ ($^1J_{Rh,P} = 130.6$ Hz), respectively; since the ^1H NMR spectrum of these solutions showed no signal in the hydride region, this doublet was attributed to the tetraphosphane species $[Rh(\mathbf{4})_4]PF_6$ and $[Rh(\mathbf{5})_4]PF_6$ by comparison of the coupling constant of the ^{31}P data with the literature values.[31] Moreover, stirring $[Rh(COD)_2]PF_6$ for 24 h in perfluoromethylcyclohexane with 4 equivalents of **4** gave a $^{31}P\text{-}\{^1H\}$ NMR spectrum showing a broad doublet at $\delta = 20.0$ ppm ($^1J_{Rh,P} = 134.7$ Hz).

We then examined the hydrogenation of representative alkenes such as methyl *(E)*-cinnamate, cinnamaldehyde, 2-cyclohexen-1-one, and methyl *(Z)*-α-acetamidocinnamate under biphasic conditions using the analogous Wilkinson's catalyst generated *in situ* by reacting $[Rh(\mu\text{-}Cl)(COD)]_2$ or $[Rh(COD)_2]PF_6$ with the corresponding fluorous monophosphane **4**. We also compared the rates of hydrogenation of methyl *(E)*-cinnamate for *p*-, *m*-, and *o*-fluoroalkyl derivatives of phosphanes.

Before starting our experiments, we determined the average partition coefficients of the phosphanes **4**–**9**, as well as of the unsaturated and saturated substrates used, in the two-phase system D-100/C_2H_5OH (Table 2). The observed values clearly showed that the unsaturated and saturated substrates are both practically insoluble in the fluorous phase. Concerning the fluorous phosphanes, only phosphane **8** gave a low partition coefficient in favor of the fluorous phase, which precluded a very important leaching of this ligand, and so of the corresponding rhodium complex, in the organic phase; as expected the new fluorophosphane **9**, bearing 6 fluoroponytails and having 64.4% fluorine content, has the highest partition coefficient for the fluorous phase.

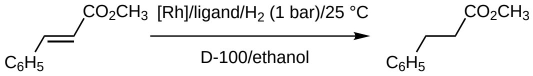
Table 2. Partition coefficients of phosphanes and unsaturated and saturated substrates in D-100/EtOH (25 °C).[a]

Compound	F-content [wt %]	Partition [% D-100/% EtOH]
4	58.7	96.1 : 3.9[b]
5	58.7	88.9 : 11.1[b]
6	58.7	88.5 : 11.5[b]
7	57.3	94.9 : 5.1[b]
8	53.9	62.0 : 38[b]
9	64.5	97.2 : 2.8
$C_6H_5CH{=}CH\text{-}CO_2CH_3$		0.1 : 99.9
$C_6H_5CH_2CH_2CO_2CH_3$		0.3 : 99.7
2-Cyclohexen-1-one		0.5 : 99.5
Cyclohexanone		1.4 : 98.6
$C_6H_5CH{=}CH\text{-}CHO$		0 : 100
$C_6H_5CH_2CH_2CHO$		0.1 : 99.9
$C_6H_5CH{=}C(CO_2CH_3)NHAc$		0 : 100
$C_6H_5CH_2CH(CO_2CH_3)NHAc$		0 : 100

[a] The partition coefficients were determined by gravimetry or by GC (see experimental section).

[b] Ref.[22]

The hydrogenation of methyl cinnamate (Equation 1) in the two-phase system D-100/C_2H_5OH was used as a model reaction in order to compare the catalytic reactivity of the different catalysts $[Rh(\mu\text{-}Cl)(COD)]_2$ + ligand **1** or **4** – **7**. The resulting conversions *vs.* time plots are shown in Figure 2.



(1)

Rhodium complexes obtained from $[Rh(\mu\text{-}Cl)COD)]_2$ and fluorous phosphanes **4** – **9** were found to be active catalysts for the reduction of methyl cinnamate at 25 °C using the two-phase system D-100/C_2H_5OH (Table 3 and Figure 2). Cooling of the reaction

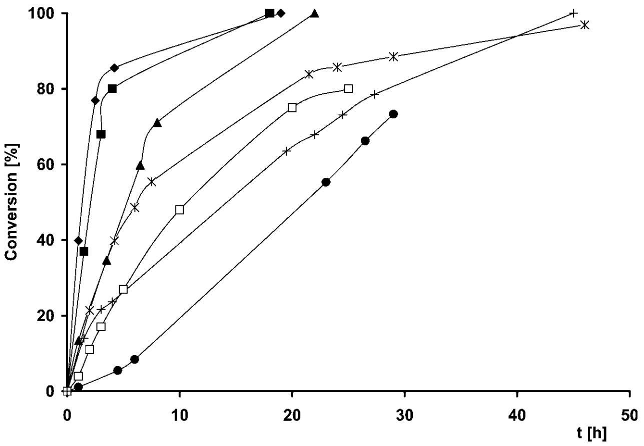


Figure 2. Conversion *vs.* time plots of the hydrogenation of methyl cinnamate using $[Rh(\mu\text{-}Cl)(COD)]_2$ + ligands **4** – **9** (Legend: ◆ = **1**, ■ = **4**, ▲ = **5**, + = **6**, ✳ = **7**, ● = **8**, □ = **9**).

Table 3. Hydrogenation of methyl *(E)*-cinnamate catalyzed by rhodium complexes[a]

Entry	Catalyst	Rh [%]	Run	Time [h]	Conversion [%]	$t_{1/2}$ [h]	Leaching	
							Rh [%]	P [%]
1	$[Rh(COD)Cl]_2 + \mathbf{1}$[b]	1		10	100	1.3		
2	$[Rh(COD)Cl]_2 + \mathbf{4}$	1	1	12	100	2.0	0.37	1.24
			2	15	100	2.8	0.37	0.94
			3	17	100	3.2	0.56	0.95
3	$[Rh(COD)Cl]_2 + \mathbf{4}$[c]	1	1	7	91			
			2	29	88			
4	$[Rh(COD)Cl]_2 + \mathbf{4}$	0.5	1	20	100	7.2		
			2	20	100	6.0		
			3	40	100	13.3		
5	$[Rh(COD)_2]PF_6 + \mathbf{4}$	1	1	6	100	2.2		
			2	10	100	3		
			3	24	96	6.3		
6	$[Rh(COD)Cl]_2 + \mathbf{4}$[d]	1	1	10	100	2.7		
			2	15	100	4.5		
			3	20	100	6.0		
			4	47	95	8.0		
7	$[Rh(COD)Cl]_2 + \mathbf{5}$	1	1	18	100	5.5	0.37	1.55
			2	45	100	13.6	0.19	1.26
			3	25	48		0.19	0.95
8	$[Rh(COD)_2]PF_6 + \mathbf{5}$	1		24	61[e]			
9	$[Rh(COD)Cl]_2 + \mathbf{6}$	1	1	45	100	15	2.78	5.57
			2	30	100	12	0.95	4.91
10	$[Rh(COD)_2]PF_6 + \mathbf{6}$	1		47	84[e]			
11	$[Rh(COD)Cl]_2 + \mathbf{7}$	1		50	100	7		
12	$[Rh(COD)Cl]_2 + \mathbf{8}$	1		29	74	21		
13	$[Rh(COD)Cl]_2 + \mathbf{9}$	1		25	80	10	1.13	0.39
				21	84	6.5	0.12	0.46
				26	77	12.9	0.23	0.63

[a] Conditions: [substrate] = 0.15 M; [substrate]:[Rh]:[phosphane] = 100:1:2; 25 °C; $p_{H2} = 1$ bar; conversion was determined by GC; leaching of rhodium and phosphorous was determined by ICP-AES.

[b] Ethanol only was used as the solvent.

[c] $[Rh(\mu\text{-}Cl)(COD)]_2$:**4** = 1:6.

[d] FC-77 was used as the fluorous solvent.

[e] Formation of colloidal rhodium.

mixture below 5 °C allows the easy isolation of the ethanolic phase, containing the hydrogenated product, from the fluorous phase. The highest activity was observed for the complex $[Rh(\mu\text{-}Cl)(COD)]_2$ + ligand **4**. It is to be noted that this activity is quite close to that of the catalyst obtained from $[Rh(\mu\text{-}Cl)(COD)]_2$ and the non-fluorous phosphane **1**, although it is a true two-phase system compared to the later one which is a homogeneous one. Comparison of the activities of the phosphanes **4–6** bearing three $-OCH_2C_7H_{15}$ ponytails gave the sequence *ortho* < *meta* < *para* (Table 3, entries 2, 7, and 9); this is probably related to some steric hindrance of the fluorous chain. Finally the activities of catalysts containing phosphanes **7** and **9** are a little lower than those observed for ligands **4–6** (Figure 2, and Table 3, entries 11 and 13).

We prepared also *in situ* the corresponding cationic complexes by mixing $[Rh(COD)_2]PF_6$ and ligands **4–7**. Since strong solvent-solute interactions needed for the separation of ion pairs are lacking in fluorous solvents having low dielectric constants, neutral and ionic complexes could have quite different behaviors due to their different solubilities. While the catalyst $[Rh(COD)_2]PF_6$ + **4** showed no difference in activity compared to the neutral analogue, the two other catalysts $[Rh(COD)_2]PF_6$ + **5** and $[Rh(COD)_2]PF_6$ + **6** gave lower activities, with the fast formation of colloidal rhodium (Table 3, entries 5, 8, and 10).

Recycling experiments were performed using complexes containing ligands **4–6** and **9** in D-100/ethanol (1:1) as solvent systems. The most active catalyst $[Rh(\mu\text{-}Cl)(COD)]_2$ + **4** can be efficiently recycled twice, since no significant drop in conversion was observed (Figure 3, and Table 3, entry 2); moreover leaching of both rhodium and phosphorus into the organic phase was low, as determined by ICP-AES: 0.37%, 0.37%, and 0.56% of the amount of rhodium was lost in the organic phase, and 1.24%, 0.94%, and 0.95% of the amount of

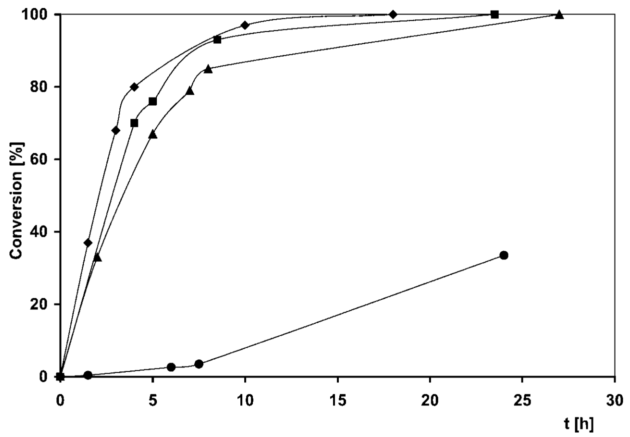


Figure 3. Conversion *vs.* time plots of the cycles in hydrogenation of methyl cinnamate using $[Rh(\mu\text{-}Cl)(COD)]_2 + \mathbf{4}$ (Legend: ◆ = run 1, ■ = run 2, ▲ = run 3, ● = run in the presence of benzaldehyde).

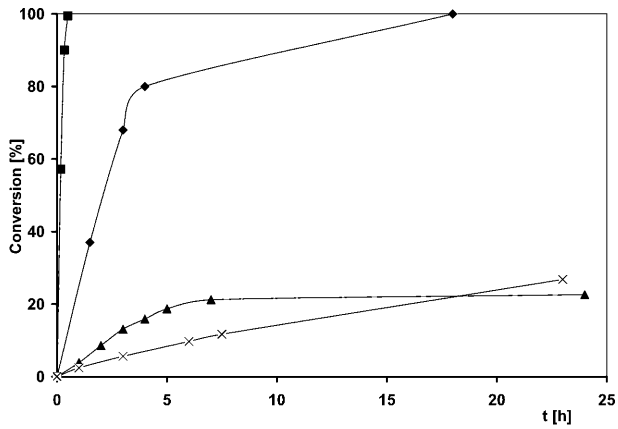


Figure 4. Conversion *vs.* time plots of the cycles in hydrogenation of various substrates using $[Rh(COD)Cl]_2 + \mathbf{4}$ (Legend: ◆ = methyl cinnamate, ■ = cyclohexenone, ▲ = cinnamaldehyde, X = methyl α-acetamidocinnamate).

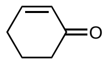
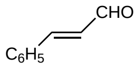
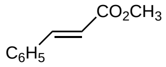
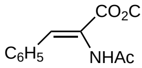
phosphane, for each cycle. It is to be noticed that the cationic catalyst $[Rh(COD)_2]PF_6 + \mathbf{4}$ can be also recycled efficiently (Table 3, entry 5), although the rhodium and the phosphorus leaching were not determined in this case. Four recycling experiments were also successfully performed using another two-phase system FC-77/ethanol (1:1) in the presence of the catalyst $[Rh(\mu\text{-}Cl)(COD)]_2 + \mathbf{4}$ (Table 3, entry 6) with only a very small loss of activity for the two first recyclings.

The catalyst $[Rh(\mu\text{-}Cl)(COD)]_2 + \mathbf{5}$ was also recycled twice (Table 3, entry 7). Over 3 cycles, only 0.37%, 0.19%, and 0.19% of the amount of rhodium, and 1.55%, 1.26%, and 0.95% of phosphane, were lost in the organic phase, respectively. In the case of the catalyst $[Rh(\mu\text{-}Cl)(COD)]_2 + \mathbf{6}$, only one recycling was performed (Table 3, entry 9); for this system, a very important loss of rhodium and phosphane was observed (2.78 and 0.95%, and 5.57 and 4.91%, respectively), and this could be due to the difficulty of preforming the Wilkinson catalyst, particularly for the first cycle.

Finally recycling experiments were also performed using the catalyst $[Rh(\mu\text{-}Cl)(COD)]_2 + \mathbf{9}$. The second cycle showed a slightly higher activity than the first one, that could be related to the difficulty to generate quantitatively the fluorous Wilkinson catalyst in the first experiment; effectively, a loss of 1.13% rhodium was observed for the first cycle, and only 0.12% and 0.23% for the two next cycles, the loss of fluorous phosphane in the organic phase being 0.39%, 0.46%, and 0.63%, respectively.

One experiment was also conducted using only 0.5% catalyst (Table 3, entry 4); although the reaction time for

Table 4. Hydrogenation of various unsaturated substrates catalyzed by rhodium complexes associated with fluorous phosphane **4**.[a]

Entry	Substrate	Catalyst	Run	Time [h]	Conv. [%]
1		$[Rh(COD)Cl]_2 + \mathbf{4}$	1	0.5	100
			2	0.5	99
2		$[Rh(COD)Cl]_2 + \mathbf{4}$		24	23
3	“	$[Rh(COD)_2]PF_6 + \mathbf{4}$		53	54
4	 + C_6H_5CHO	$[Rh(COD)Cl]_2 + \mathbf{4}$		31	41[b]
5		$[Rh(COD)Cl]_2 + \mathbf{4}$		78	51

[a] Conditions: [substrate] = 0.15 M; [substrate]:[Rh]:[phosphane] = 100:1:2; 25 °C; $p_{H2} = 1$ bar; conversion was determined by GC.

[b] Reduction of methyl cinnamate only.

the complete conversion of methyl cinnamate was higher the catalyst was efficiently recycled.

The reduction experiments were extended to three other unsaturated substrates using **4** as the fluorous ligand (Figure 4 and Table 4). 2-Cyclohexen-1-one was quantitatively reduced to cyclohexanone in 0.5 h using 1% catalyst generated from $[Rh(\mu\text{-}Cl)(COD)]_2 + \mathbf{4}$ (Table 4, entry 1). The recycled catalyst exhibited the same activity. The conversion of cinnamadehyde was very low, whatever the precursor used (Table 4, entries 2 and 3). Since we suspected some poisoning of the catalyst by the aldehyde, we reduced a 1/1 mixture of methyl cinnamate and cinnamaldehyde using 1% of the catalyst $[Rh(\mu\text{-}Cl)(COD)]_2 + \mathbf{4}$; effectively only methyl cinnamate was reduced, but very slowly, in 41% after 31 h as shown in Figure 3 (Table 4, entry 3). Finally the reduction of methyl α-acetamidocinnamate was very slow: 51% conversion was obtained after 78 h.

Conclusion

In conclusion, we have shown that the rhodium complexes obtained from $[Rh(\mu\text{-}Cl)(COD)]_2$ and various tris(fluoroalkoxy)monophosphanes are active in the hydrogenation of various functionalized alkenes such as methyl cinnamate and 2-cyclohexen-1-one. Some differences were observed in the catalytic performances using the *o*-, *m*-, and *p*-substituted fluorous phosphanes, the *p*-substituted being the most active. However, the unsaturated aldehyde was reduced very slowly, due to the poisoning of the catalyst. Recycling efficiencies are high for the catalysts associated with the phosphane having the *p*-fluorous ponytail or the 3,5-fluorous ponytails using a two-phase system D-100/ethanol, very low leaching of both rhodium and phosphane in the organic phase being detected.

Experimental Section

General Remarks

All experiments were performed in a dry nitrogen atmosphere using standard Schlenk techniques. Fluorous solvents Galden D-100 (mainly perfluorooctane) (Ausimont) and FC-77 (Acros) were degassed and stored under a dinitrogen atmosphere. PCl_3, BBr_3, Cs_2CO_3, $C_7F_{15}CH_2OH$, $C_4F_9SO_2F$, $HSiCl_3$, $[Rh(\mu\text{-}Cl)(COD)]_2$, methyl *(E)*-cinnamate, *(E)*-cinnamadehyde, and 2-cyclohexen-1-one were used as received and stored under nitrogen. $C_7F_{15}CH_2OSO_2C_4F_9$,[21] phosphanes **4** – **8**,[21] 3,5-dimethoxyiodobenzene (**10**),[22] and $[Rh(COD)_2]PF_6$[32] were prepared according to previously reported procedures. Complexes **15**[33] and **16**[34] were described previously.

NMR spectra were recorded with a Bruker AM 300 spectrometer at ambient probe temperature and references as follows:^{1}H (300 MHz), residual $CHCl_3$ at δ = 7.27 ppm; ^{13}C (75 MHz), internal $CDCl_3$ at δ = 77.23 ppm; ^{31}P (80 and 121 MHz), external 85% H_3PO_4 (δ = 0.00 ppm); ^{19}F (282 MHz), external $CFCl_3$ (δ = 0.00 ppm).

Tris(3,5-dimethoxyphenyl)phosphane (11)

A solution of 3,5-dimethoxyiodobenzene (**10**)[22] (4 g, 15.1 mmol) in diethyl ether (30 mL) was slowly added at – 60 °C to a solution of *n*-BuLi (1.6 M in hexane; 9.4 mL, 15.0 mmol) and diethyl ether.(10 mL). The solution was stirred at – 60 °C for 1 h, and a solution of PCl_3 (436 μL, 5 mmol) in diethyl ether (10 mL) was slowly added. After 1 h at – 60 °C, the solution was stirred for 15 h at room temperature. A saturated aqueous solution of NH_4Cl (50 mL) was added, and the solution was extracted with a 1/1 solution of diethyl ether/CH_2Cl_2 (3 × 35 mL). The organic phase was washed with water (2 × 25 mL) and dried over Na_2SO_4. The solvent was removed on a rotatory evaporator to give a residue that was purified by flash chromatography on silica gel using petroleum ether/CH_2Cl_2 (2:3) as the eluent to give phosphane **11**; yield: 1.55 g (70%); $R_f = 0.23$ (petroleum ether/CH_2Cl_2, 2:3); m.p. 131 – 132 °C; ^{1}H NMR ($CDCl_3$): δ = 3.72 (s, 18H, OCH_3), 6.42 (t, $^4J_{H,H} = 2.2$ Hz, 3H, H_{arom}), 6.48 (dd, $^4J_{H,H} = 2.2$, $^3J_{H,P} = 8.1$ Hz, 6H, H_{arom}); ^{31}P NMR ($CDCl_3$): δ = 1.3 (s); anal. calcd. for $C_{24}H_{27}O_6P$ (442.45): C 65.15, H 6.15; found: C 65.20, H 6.14. These values are in agreement with the literature.[22]

Tris(3,5-dimethoxyphenyl)phosphane Oxide (12)

Water (1 mL) and 30% H_2O_2 (0.5 mL) were slowly added to a solution of phosphane **11** (1.55 g, 3.5 mmol) in acetone (25 mL). After stirring for 1 h, the acetone was evaporated and CH_2Cl_2 (30 mL) was added. The organic phase was washed with a saturated aqueous solution of NaCl (3 × 30 mL), the aqueous solution was extracted with CH_2Cl_2 (2 × 30 mL), and the combined organic solutions were dried over Na_2SO_4. The solvent was removed on a rotatory evaporator to give phosphane oxide **12**; yield: 1.55 g (97%); m.p. 139 – 140 °C; ^{1}H NMR ($CDCl_3$): δ = 3.73 (s, 18H, OCH_3), 6.55 (t, $^4J_{H,H} =$ 2.2 Hz, 3H, H_{arom}), 6.76 (dd, $^4J_{H,H} = 2.2$, $^3J_{H,P} = 13.2$ Hz, 6H, H_{arom}); ^{13}C NMR ($CDCl_3$): δ = 55.6 (s), 104.2 (s), 109.7 (d, $^2J_{P,C} = 11.3$ Hz), 134.1 (d, $^1J_{P,C} = 106.2$ Hz), 160.8 (d, $^3J_{P,C} =$ 18.1 Hz); ^{31}P NMR ($CDCl_3$): δ = 31.7 (s); anal. calcd. for $C_{24}H_{27}O_7P$ (458.45): C 62.88, H 5.94; found: C 62.49, H 5.94.

Tris(3,5-dihydroxyphenyl)phosphane Oxide (13)

A solution of BBr_3 (1 M in CH_2Cl_2; 20.1 mmol, 21 mL) was slowly added at – 10 °C to a solution of phosphane **12** (922 mg, 2.0 mmol) in CH_2Cl_2 (20 mL) under argon. After being stirred for 24 h at room temperature, the solution was slowly poured into cold water (60 mL). The solid was eliminated by filtration, and the solution was extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with a saturated aqueous solution of NaCl (2 × 10 mL), and dried. Evaporation of the solvent gave the hydroxyphosphane **13** that was directly used in the next step; yield: 659 mg (88%); m.p. >300 °C; ^{1}H NMR (DMSO-d_6): δ = 6.35 (t, $^4J_{H,H} = 1.8$ Hz, 3H, H_{arom}), 6.39 (dd, $^4J_{H,H} = 1.8$, $^3J_{H,P} = 12.9$ Hz, 6H, H_{arom}), 9.63 (s, 6H, OH); ^{13}C NMR (DMSO-d_6): δ = 105.6 (s), 109.3 (d, $^2J_{P,C} =$

11.3 Hz), 134.5 (d, $^1J_{P,C} = 101.7$ Hz), 158.4 (d, $^3J_{P,C} = 16.9$ Hz); ^{31}P NMR (DMSO-d_6): $\delta = 28.5$ (s).

Tris[3,5-di(1*H*,1*H*-perfluorooctoxy)phenyl]phosphane Oxide (14)

A mixture of crude hydroxyphosphane oxide **13** (530 mg, 1.41 mmol), 1*H*,1*H*-perfluorooctyl nonabutanesulfonate (7.71 g, 11.3 mmol), and Cs_2CO_3 (4.63 g, 14.2 mmol) in DMF (30 mL) was stirred at 80 °C under N_2 for 16 h. The suspension was then cooled at room temperature, the solution was treated with H_2O (15 mL) and diethyl ether (25 mL). D-100 was added (5 mL) and the solution was vigorously stirred for 5 min. The ether and fluorous layers were separated, and the aqueous layer was extracted with a 5:1 mixture of diethyl ether/D-100 (2 × 25 mL). The combined organic phases were washed with a saturated aqueous solution of NaCl (4 × 10 mL), and dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified by column chromatography on silica gel using a 2:1 mixture of CH_2Cl_2/diethyl ether as the eluent to give the perfluorophosphane oxide **14**; yield: 1.2 g (32%); $R_f = 0.7$ (CH_2Cl_2/diethyl ether, 2:1); m.p. 89 – 91 °C; ^{1}H NMR ($CDCl_3$): $\delta = 4.46$ (t, $^3J_{H,F} = 12.6$ Hz, 12H, CH_2), 6.78 (t, $^4J_{H,H} = 2.2$ Hz, 3H, H_{arom}), 6.92 (dd, $^4J_{H,H} = 2.2$, $^3J_{H,P} = 13.2$ Hz, 6H, H_{arom}); ^{31}P NMR ($CDCl_3$): $\delta = 29.1$ (s); ^{19}F NMR ($CDCl_3$): $\delta = -126.8$ (bs, 12F), -123.7 (bs, 12F), -123.4 (bs, 12F), -122.6 (bs, 24F), -120.0 (bs, 12F), -81.6 (t, $^3J_{F,F} = 10.3$ Hz, 18F); HRMS (FAB): calcd. for $C_{66}H_{22}F_{90}O_7P$ $[M+H]^+$: 2666.9666; found: 2666.9667

Tris[3,5-di(1*H*,1*H*-perfluorooctoxy)phenyl]phosphane (9)

$HSiCl_3$ (30 μL, 300 μmol) was cautiously added under argon at 0 °C to a mixture of phosphane oxide **14** (200 mg, 75 μmol) and freshly distilled triethylamine (44 μL, 0.32 mmol) in dry toluene (5 mL). The mixture was warmed to 130 °C and stirred for 5 h. After being cooled to 0 °C, the solution was treated with precooled deaerated 2 N NaOH (10 mL). The aqueous layer was extracted with deaerated Et_2O (2 × 15 mL), and the combined organic layers were washed with deaerated water (20 mL) and dried over Na_2SO_4. Evaporation of the solvent gave fluorous phosphane **9** as a white solid; yield: 160 mg (81%); m.p. 78 – 80 °C; ^{1}H NMR ($CDCl_3$): $\delta = 4.37$ (t, $^3J_{H,F} = 12.7$ Hz, 12H, CH_2), 6.55 (t, $^4J_{H,H} = 2.1$ Hz, 3H, H_{arom}), 6.58 (dd, $^4J_{H,H} = 2.1$, $^3J_{H,P} = 8.1$ Hz, 6H, H_{arom}); ^{31}P NMR ($CDCl_3$): $\delta = 1.4$ (s); ^{19}F NMR ($CDCl_3$): $\delta = -127.0$ (bs, 12F), -124.0 (bs, 12F), -123.6 (bs, 12F), -122.8 (bs, 24F), -120.3 (bs, 12F), -81.8 (t, $^3J_{F,F} = 9.9$ Hz, 18F); HRMS (FAB): calcd. for $C_{66}H_{22}F_{90}O_6P$ $[M+H]^+$: 2650.9894; found: 2650.9716.

Synthesis of Iridium Complexes 15 – 21

A Schlenk tube was charged with $[Ir(\mu\text{-}Cl)(COD)]_2$ (15 mg, 22.3 μmol), phosphane (89.2 μmol), and $C_6H_5CF_3$ (4 mL) under argon. The solution was stirred at room temperature for 15 min, and CO was added. After 2 h, the solvent was removed, the residue was washed with hexane (3 mL). After removing of the upper phase, the solid was collected and dried under vacuum to give the corresponding iridium complex.

***trans*-[IrCl(CO){P(C$_6$H$_4$-*p*-OCH$_3$)$_3$}$_2$] (15):** yield: 90%; m.p. 178 – 180 °C; IR (KBr): $\nu_{CO} = 1950$ cm^{-1} (s); ^{1}H NMR ($CDCl_3$): $\delta = 3.83$ (s, 18H, CH_3), 6.93 (d, $J = 8.4$ Hz, 12H, H_{arom}), 7.64 – 7.70 (m, 12H, H_{arom}); ^{31}P NMR ($CDCl_3$): $\delta = 20.8$ (s); FAB-MS: $m/z = 960$ $[M]^+$, 932 $[M - CO]^+$, 895 $[M - CO - Cl - H]^+$.

***trans*-[IrCl(CO){P(C$_6$H$_4$-*m*-OCH$_3$)$_3$}$_2$] (16):** yield: 93%; m.p. 146 – 148 °C; IR (KBr): $\nu_{CO} = 1959$ cm^{-1} (s); ^{1}H NMR ($CDCl_3$): $\delta = 3.75$ (s, 18H, CH_3), 6.97 – 7.01 (m, 12H, H_{arom}), 7.25 – 7.29 (m, 6H, H_{arom}), 7.33 – 7.36 (m, 6H, H_{arom}), ^{31}P NMR ($CDCl_3$): $\delta = 12.6$ (s); FAB-MS: $m/z = 960$ $[M]^+$, 932 $[M - CO]^+$.

***trans*-[IrCl(CO){P(C$_6$H$_4$-*o*-OCH$_3$)$_3$}$_2$] (17):** yield: 86%; m.p. 205 – 207 °C. – IR (cm^{-1}, KBr): $\nu_{CO} = 1941$ cm^{-1} (s); ^{1}H NMR ($CDCl_3$): $\delta = 3.50$ (s, 18H, CH_3), 6.78 – 6.80 (m, 6H, H_{arom}), 6.86 – 6.90 (m, 9H, H_{arom}), 7.29 – 7.33 (m, 9H, H_{arom}); ^{31}P NMR ($CDCl_3$): $\delta = 14.6$ (s); FAB-MS: $m/z = 925$ $[M - Cl]^+$, 895 $[M - CO - Cl - H]^+$.

***trans*-[IrCl(CO){P(C$_6$H$_4$-*p*-OCH$_2$C$_7$F$_{15}$)$_3$}$_2$] (18):** yellow powder; yield: 84%; m.p. 167 – 169 °C; IR (KBr): $\nu_{CO} = 1961$ cm^{-1} (s); ^{1}H NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = 4.50$ (t, $J_{H,F} = 13$ Hz, 12H, CH_2), 6.94 – 7.20 (m, 12H, H_{arom}), 7.60 – 7.70 (m, 12H, H_{arom}); ^{31}P NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = 21.6$ (s); ^{19}F NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = -127.0$ (s, 12F), -123.8 (s, 12F), -123.6 (s, 12F), -122.9 (s, 24F), -120.3 (s, 12F), -82.4 (t, $J_{F,F} = 9.4$ Hz, 18F); FAB-MS: $m/z = 3102$ $[M - Cl - CO - H]^+$.

***trans*-[IrCl(CO){P(C$_6$H$_4$-*m*-OCH$_2$C$_7$F$_{15}$)$_3$}$_2$] (19):** green powder; yield: 85%; m.p. 106 – 108 °C; IR (KBr): $\nu_{CO} = 1962$ cm^{-1} (s); ^{1}H NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = 4.39$ (t, $J_{H,F} = 12.8$ Hz, 12H, CH_2), 7.03 – 7.08 (m, 6H, H_{arom}), 7.31 – 7.40 (m, 12H, H_{arom}), 7.44 – 7.48 (m, 6H, H_{arom}); ^{31}P NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = 26.8$ (s); ^{19}F NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = -126.9$ (s, 12F), -123.7 (s, 12F), -123.4 (s, 12F), -122.7 (s, 24F), -120.1 (s, 12F), -82.1 (t, $J_{F,F} = 9.9$ Hz, 18F); FAB/MS: $m/z = 3190$ $[M + Na]^+$, 3102 $[M - Cl - CO - H]^+$.

***trans*-[IrCl(CO){P(C$_6$H$_4$-*o*-OCH$_2$C$_7$F$_{15}$)$_3$}$_2$] (20):** green powder; yield: 71%; m.p. 111 – 113 °C; IR (KBr): $\nu_{CO} = 1950$ cm^{-1} (s); ^{1}H NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = 4.40$ (t, $J_{H,F} = 14.0$ Hz, 12H, CH_2), 6.82 – 6.86 (m, 6H, H_{arom}), 7.00 – 7.08 (m, 12H, H_{arom}), 7.35 – 7.41 (m, 6H, H_{arom}); ^{31}P NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = 14.5$ (s); ^{19}F NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = -126.9$ (s, 12F), -123.9 (bs, 12F), -123.4 (s, 12F), -122.7 (s, 12F), -122.5 (s, 12F), -119.8 (bs, 12F), -81.1 (t, $J_{F,F} = 9.2$ Hz, 18F); FAB-MS: $m/z = 3131$ $[M - Cl]^+$, 3102 $[M - Cl - CO - H]^+$, 1674 $[M - Cl - \mathbf{2c}]^+$, 1456 $[\mathbf{2c}]^+$.

***trans*-[IrCl(CO){P(C$_6$H$_4$-*p*-OCH$_2$CH$_2$CH$_2$C$_8$F$_{17}$)$_3$}$_2$] (21):** yellow powder; yield: 78%; IR (KBr): $\nu_{CO} = 1961$ cm^{-1} (s); ^{1}H NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = 2.10 – 2.16$ (m, 12H, CH_2), 2.26 – 2.36 (m, 12H, CH_2), 4.05 (t, $J = 5.6$ Hz, 12H, OCH_2), 6.89 (d, $J = 8.0$ Hz, 12H, H_{arom}), 7.43 – 7.48 (m, 6H, H_{arom}), 7.62 – 7.66 (m, 6H, H_{arom}); ^{31}P NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = 21.0$ (s); ^{19}F NMR ($CDCl_3/Cl_2CFCF_2Cl$): $\delta = -126.6$ (s, 12F), -123.9 (s, 12F), -123.2 (s, 12F), -122.4 (s, 24F), -122.2 (s, 12 F), -115.0 (s, 12 F), -81.7 (t, $J_{F,F} = 9.4$ Hz, 18 F); FAB-MS: $m/z = 3609$ $[M - CO]^+$, 3573 $[M - CO - Cl - H]^+$, 1908 $[M - CO - \mathbf{3}]^+$.

Determination of the Partition Coefficients

The partition coefficients were determined by dissolving 20 mg of the phosphane, the unsaturated substrate, or the saturated substrate, in a biphasic system consisting of Galden D-100 (1 mL) and ethanol (1 mL). The resulting solution was stirred at 50 °C for 0.5 h, and then cooled at room temperature. After 0.5 h, the two phases were separated. For phosphane 7, the solvents were evaporated to dryness, and the residues were weighed. For the unsaturated and saturated substrates, the two phases and the amount of substrate in each phase were analyzed by GC.

Catalytic Reactions and Recycling

The catalytic experiments were carried out in a 50-mL flask equipped with a tap under a dihydrogen atmosphere (1 bar). In a typical reaction, $[Rh(COD)Cl]_2$ (3 mg, 6.15 μmol) or $[Rh(COD)_2]PF_6$ (5.7 mg, 12.3 μmol) and the fluorous phosphane (24.6 μmol) were dissolved in 4 mL of the fluorous solvent under a dinitrogen atmosphere. After being stirred for 1 h, the inert atmosphere was replaced by hydrogen, and subsequently the unsaturated substrate (1.23 mmol) and ethanol (4 mL) were added. The mixture was vigorously stirred at room temperature; samples taken at regular time intervals were analyzed by GC. In recycling experiments, the reaction was cooled , stirring was stopped, and the hydrogen atmosphere was maintained. The organic layer was removed and new substrate as solution in ethanol was added. The reaction mixture was stirred and a new cycle was started. The resulting organic phases from the different cycles were analyzed by ICP-AES.

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