Pergamon

Tetrahedron 58 (2002) 3877–3888

TETRAHEDRON

Hydroformylation of higher olefins by rhodium/tris-((1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl)phosphites complexes in a fluorocarbon/hydrocarbon biphasic medium: effects of fluorinated groups on the activity and stability of the catalytic system

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Received 5 November 2001; accepted 16 January 2002

Abstract—The synthesis of three fluorous triarylphosphites in which an 'insulating' ethylene segment separates the perfluoroalkylgroup from the aryl group is described. The stabilities, solubilities and partition coefficients of these new compounds are reported. The complexes generated in situ from these fluorous triarylphosphites and $Rh(acac)(CO)_2$ have been tested as catalysts for the hydroformylation of various olefins under fluorous biphasic conditions. The activities and the selectivities were found to vary markedly with the position of the perfluoroalkylgroup on the aromatic ring. The possibility to recover the catalytic system was also investigated from consecutive recycling experiments. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Hydroformylation of higher olefins is an important industrial process where unselective cobalt-based catalysts have to be employed because the more reactive and selective rhodium-based catalysts cannot be separated from the long chain aldehyde products without decomposition.[1–3] To circumvent this problem, four major strategies have been developed: (i) anchoring of rhodium catalysts to resins, polymeric, dendrimeric or inorganic materials;[4–7] (ii) the use of amphiphilic ligands which allows the extraction of the rhodium catalyst in another phase at the end of the reaction;[8–10] (iii) the use of supercritical fluids as reaction medium,[11–15] and (iv) the use of two-phase system where the catalyst is dissolved in a phase which contains neither the substrate nor the products. In this biphasic approach, the rhodium catalyst can be dissolved in a molten salt,[16,17] in a fluorocarbon phase[18–21] or aqueous phase containing generally a mass transfer promotor.[22–27]

The fluorous biphasic catalysis is a particularly elegant concept as the two phases are generally well separated at room temperature and can become homogeneous at higher temperatures.[28–33] Obviously, this behavior allows to combine the activity of homogeneous catalysts with the simplicity of product isolation. The hydroformylation of olefins in a fluorocarbon phase was first reported by Horvath and Rabai in 1994.[18] The rhodium catalyst was dissolved in the fluorous phase by using a trialkylphosphine $P[CH_2CH_2(CF_2)_5CF_3]_3$ prepared by hydrophosphinylation of the corresponding fluorinated alkene. The ethylene spacer was necessary to insulate the phosphorus atom from the strong electron-withdrawing perfluoroalkyl group. This catalyst displays satisfactory activities in a perfluoromethylcyclohexane/toluene solvent system and the normal to branched aldehyde ratio (*n*/*i*) was comparable to that obtained in a conventional solvent with $HRh(CO)(PPh_3)_3$ (*n*/*i*=2.9). In 1998, Horvath and co-workers have reported a detailed study of the hydroformylation of 1-decene and ethylene using the same catalytic system under batch and semi-continuous fluorous biphasic conditions.[19] In this study, it was demonstrated that the long-term stability of the fluorous catalyst was greater than that of the Rh/PPh_3 catalyst. During nine consecutive reaction/separation cycles, a total turnover of more than 35,000 was reported with only a loss of 1.8 ppm of Rh/mol of product. Hydroformylation in fluorous biphasic condition with fluorous triarylphosphites was first investigated by Hope and co-workers.[20,21] The authors reported the hydroformylation

Keywords: fluorocarbons; fluorous triarylphosphites; rhodium; hydroformylation; catalyst recovery.

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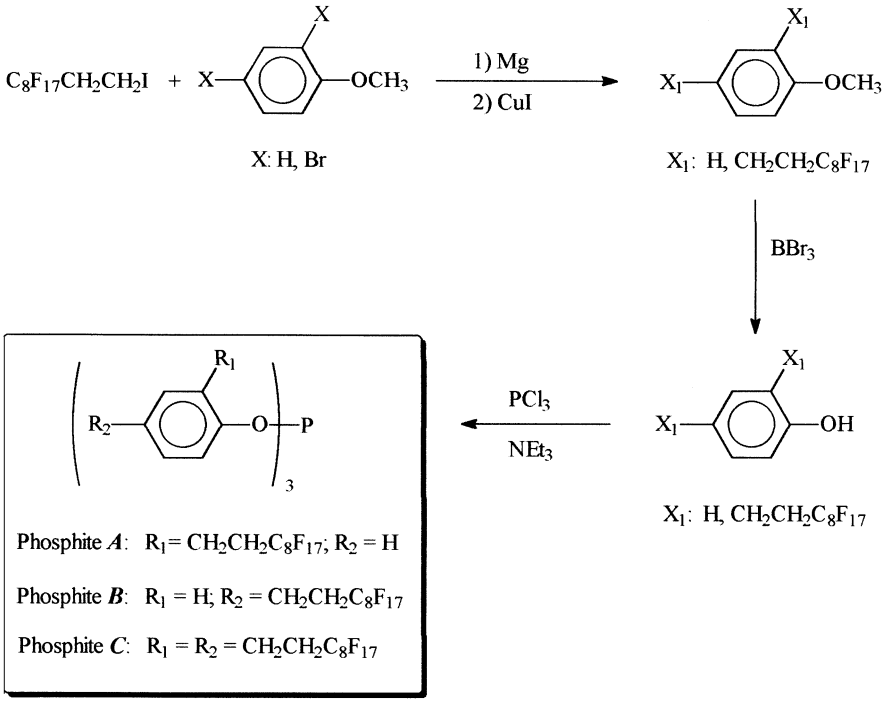
PII: S0040-4020(02)00211-9



Scheme 1. Synthesis of phosphites A, B and C.

of 1-hexene under 20 atm syngas at 70°C using tris(4-perfluorohexylphenyl)phosphite as ligand. Interestingly, it was found that the *n*/*i* ratio was higher than that observed with the Rh/$P(OPh)_3$ catalyst and that the catalytic system was also active for the hydroformylation of internal alkenes.[34]

We report herein our efforts to develop a hydroformylation process of higher olefins in the presence of fluorous-soluble triarylphosphites modified rhodium catalysts.[35] We will describe in a first time the synthesis, the stability, the solubility and the partition coefficient of fluorous triphenylphosphites in which an insulating ethylene segment separates the perfluoroalkylgroup from the phenyl group and, in a second time, the activity, selectivity and stability of catalysts generated in situ from these phosphites and $Rh(acac)(CO)_2$.

2. Results

2.1. Synthesis of new fluorinated analogues of $P(OPh)_3$

In order to minimize the effect of perfluoroalkyl group, we decided to synthesize fluorous analogues of $P(OPh)_3$ where aromatic rings are insulated of the perfluoroalkyl groups by two methylene groups. Indeed, is was clearly demonstrated that the insertion of a spacer group between phosphorus atom and perfluoroalkyl group reduces greatly the electron-withdrawing effect of fluorous ponytails.[19,36–38] For instance, Hope and co-workers have reported that tris(4-(1*H*,1*H*,2*H*,2*H*-fluorooctyl)phenyl)phosphine and tris-(4-hexylphenyl)phosphine have similar σ donor/π acceptor properties, suggesting that two-methylene groups are enough to lower the electron-withdrawing effect of fluorous ponytails in the case of fluorinated analogues of triphenylphosphine.[14] In order to obtain higher fluorous solubilities, the attachment of two perfluoroalkyl groups per aromatic ring was also investigated.

As shown in Scheme 1, the route developed for the synthesis of fluorinated analogues of $P(OPh)_3$ is based on a copper-catalyzed coupling of the Grignard reagents from bromoanisoles with 1*H*,1*H*,2*H*,2*H*-perfluorodecanyl iodide, followed by cleavage of methoxy group by BBr_3 and reaction of the corresponding phenol with phosphorus trichloride.

Using this route, tris(2-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-phenyl)phosphite (A) and tris(4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl) phosphite (B) were easily obtained on multigrams scales with overall isolated yields of 35–45%. The synthesis of a phosphite bearing two perfluoroalkyl groups per aromatic ring was more tedious (overall isolated yield of 3%). Indeed, the coupling of 2,4-dibromoanisole with 1*H*,1*H*,2*H*,2*H*-perfluorodecanyl iodide provided a complex mixture consisting of 4-bromo-2-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole (7%), 2-bromo-4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole (30%), dimerized and unreacted 1*H*,1*H*,2*H*, 2*H*-perfluorodecanyl iodide and unidentified products. Despite longer reaction times, higher temperatures and amounts of iodide derivatives have been used, all attempts to obtain directly in one step the 2,4-di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole from 2,4-dibromoanisole have failed. However, we found that the coupling of pure isolated 2-bromo-4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole with a new charge of 1*H*,1*H*,2*H*,2*H*-perfluorodecanyl iodide can afford the target 2,4-di(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-anisole in 11% yield. Cleavage of the methoxy group of this compound could be easily achieved with BBr_3 in 1,1,2-trichlorotrifluoroethane (85% yield) and reaction of the corresponding phenol with phosphorus trichloride in an ether/1*H*-perfluorooctane mixture gave

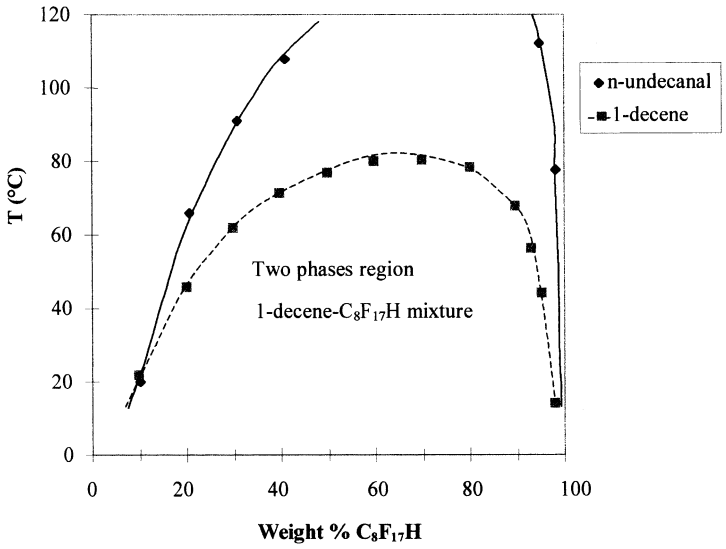


Figure 1. Miscibility diagrams of 1-decene/$C_8F_{17}H$ and *n*-undecanal/$C_8F_{17}H$.

tris(2,4-bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl)phosphite (C) in 93% yield.

2.2. Stability, solubility and partition coefficient of phosphites A, B and C

Phosphites A, B and C proved to be air stable and appeared less sensitive to hydrolysis than the perfluoroalkylated triphenylphosphites that we have previously synthesized.[39,40] For example, when phosphite A or B was dissolved in a water–tetrahydrofuran mixture (50/50; v/v) under nitrogen, no appreciable hydrolysis was observed within 48 h. Under the same conditions, the hydrolysis of tris(4-(perfluorooctyl)phenyl)phosphite (D) or 2-(perfluorooctyl)phenylphosphite into H_3PO_3 and the corresponding phenol derivative was complete after 24 h. The higher hydrolytic stability of the P–O bond of phosphites A, B or C compared to perfluoroalkylated triphenylphosphites can probably be attributed to the lower electronic influence of the perfluoroalkyl solubilizers. In line with this hypothesis, we found that the IR $\nu_{C=O}$ value is significantly lower for complex $HRh(CO)(B)_3$ than that $HRh(CO)(D)_3$ (2036 vs 2066 cm^{-1}). Surprisingly, the $^{31}P\{^1H\}$ NMR signals for complexes $HRh(CO)(B)_3$ and $HRh(CO)(P(OC_6H_5)_3$ were different: δ 142.68 and 140.98 ppm, respectively. Furthermore, the IR spectrum of $HRh(CO)(B)_3$ showed an IR $\nu_{C=O}$ value higher than that of $HRh(CO)(P(OC_6H_5)_3$ (2036 vs 2010 cm^{-1}). These data suggest strongly that the ethylene spacer does not completely insulate the fluorinated alkyl chain from the aromatic ring in terms of electronic properties.

Phosphines A, B and C are, at room temperature, highly soluble in commercially available solvents namely: perfluoroperhydrophenanthrene (PFPP), perfluoromethyldecalin (PFMD), perfluoromethylcyclohexane (PFMC) and perfluorooctyl bromide (PFOB) and in 1*H*-perfluorooctane; slightly soluble in tetrahydrofuran and ether; very slightly soluble in chloroform, toluene, and insoluble in dimethylsulfoxide and higher hydrocarbons such as *n*-decane, *n*-undecane and *n*-pentadecane. Quantitative data on their relative solubilities were also sought. Thus, partition coefficients in a 1-decene/$C_8F_{17}H$ mixture were determined by GC at room temperature. Phosphites A, B, and C gave a 5/95, 5/95 and 1/99 distribution in a 1-decene/$C_8F_{17}H$ mixture. As expected, these compounds are largely more soluble in the fluorous phase than in organic phase. However, the partition coefficients of phosphites A and B are too low to be considered as totally 'immobilized' ligands. Indeed, they should slowly leach during consecutive reaction/separation cycles. The partition coefficient of phosphite C is more suitable for a fluorous biphasis catalysis.

2.3. Hydroformylation of heavy olefins

2.3.1. Mutual miscibility of heavy olefins and aldehydes with fluorous solvents. Efficient fluorous biphasic hydroformylation process requires low mutual miscibility of the reaction products (aldehydes) and the fluorous phase in order to avoid the loss of the expensive perfluorous compounds and catalyst. Thus, accurate knowledge of the phase equilibrium relationships between the different components of the system is needed for the design of the process.

For the first time, *n*-undecanal, 1-decene and 1*H*-perfluorooctane were chosen as model components of the hydroformylation process. Fig. 1 depicted the variation of the complete solubility temperature as a function of the composition of pairs undecanal/$C_8F_{17}H$ and 1-decene/$C_8F_{17}H$. As expected, the chemical nature of the components, the composition of the mixture and the temperature have a great influence on the miscibility. For example a solution of $C_8F_{17}H$ saturated with 1-decene contains 5 wt% of decene at 46°C and 10 wt% at 60°C. Interestingly, the heavier and more polar aldehyde is more efficiently expelled from the fluorous phase than the parent olefin. Indeed, saturation of a solution of $C_8F_{17}H$ by undecanal is reached with only 0.5 and 1 wt% at 46 and 75°C, respectively. Conversely, the solubility of $C_8F_{17}H$ in 1-decene and in undecanal is roughly the same at ambient temperature and

Table 1. Upper critical solution temperature of different olefins and aldehyde in $C_8F_{17}H$

Olefin[a]	Temperature (°C)	Aldehyde[b]	Temperature (°C)
1-Hexene	<20	*n*-Heptanal	37
1-Octene	47	*n*-Nonanal	84
1-Decene	81	*n*-Undecanal	>120
1-Dodecene	>100	*n*-Tridecanal	⩾120

[a] Weight% of olefin in the mixture at maximum of the solubility curves: 1-hexene: 20%; 1-octene: 25%; 1-decene: 30% and 1-dodecene: 33%.
[b] Weight% of aldehyde in the mixture: 30%.

is much higher (10 wt%) than the one of the latter in $C_8F_{17}H$. However at higher temperature a solution of undecanal saturated with $C_8F_{17}H$ contains a much lower quantity of $C_8F_{17}H$ than the one of 1-decene. Thus the pair undecanal/$C_8F_{17}H$ exhibits an 'upper critical solution temperature' (above which phase separation cannot occur) much higher (>120°C) than the one of the pair 1-decene-/$C_8F_{17}H$ (80°C).

The miscibility of 1*H*-perfluorooctane with other higher olefins and the corresponding aldehydes resulting from their hydroformylation, was also studied. A similar behavior was observed in each case i.e. the aldehyde and the fluorous compound are always less soluble than the couple olefin–$C_8F_{17}H$. It appears also that the solubility is largely influenced by the size of the organic species. For example, Table 1 shows that 1-hexene is miscible with $C_8F_{17}H$ in all proportions at ambient temperature whereas the upper critical solution temperature of the pair 1-dodecene–$C_8F_{17}H$ is above 100°C. Olefins smaller than 1-octene seem pour candidate for fluorous biphasic hydroformylation.

Finally, the influence of the nature of the perfluorous solvent was also investigated. Fig. 2 shows the miscibility diagrams of 1-decene with various perfluorous solvents such as perfluoroperhydrophenanthrene (PFPP), perfluoromethyldecalin (PFMD), perfluoromethylcyclohexane (PFMC), perfluorooctyl bromide (PFOB) and 1*H*-perfluorooctane (1H-PFO).

The shapes of the curves of temperature solubility as function of composition are similar to the one obtained with $C_8F_{17}H$. All of them exhibit a maximum for about 75–80 wt% of the fluorous component. Moreover, except that of PFOB, the miscibility decreases and thus the upper critical solution temperature increases upon increasing the number of carbon atoms of the fluorous compound. Interestingly, at ambient temperature, the quantity of fluorous compound in the saturated organic phase is much lower with PFPP (5 wt%) and PFMD (8 wt%) than with $C_8F_{17}H$. On the other hand at 80°C (usual reaction temperature of hydroformylation) the pair PFPP/1-decene and PFMD/1-decene are only partially miscible with a low content of the olefin in the fluorous phase. Surprisingly, substitution of the H atom of $C_8F_{17}H$ by bromine in PFOB has the effect to largely shift down the curve of solubility and the two phases domain dramatically decreases. Thus, PFOB does not appear as a good solvent for fluorous biphasic hydroformylation of higher olefins.

2.3.2. Hydroformylation of 1-decene. The phosphites A, B and C were tested in fluorous biphasic hydroformylation of 1-decene under standard reaction conditions (80°C, 40 bar CO/H_2 1/1) with $Rh(acac)(CO)_2$ as catalyst precursor and a phosphite/Rh ratio of 5 (see Scheme 2). Different fluorous solvents were used in the absence of any other organic solvent or in the presence of toluene.

The progress of the reaction was monitored by GC and the results obtained are listed in Table 2. In the absence of organic solvent (pure 1-decene) and with $C_8F_{17}H$ as fluorous solvent, all phosphites induced high catalytic activities (entries 1–3). Nevertheless the bulky *ortho* substituted phosphites A and C differ from the para substituted B by much higher activities (TOF>10,000 vs 3900 h^{-1},

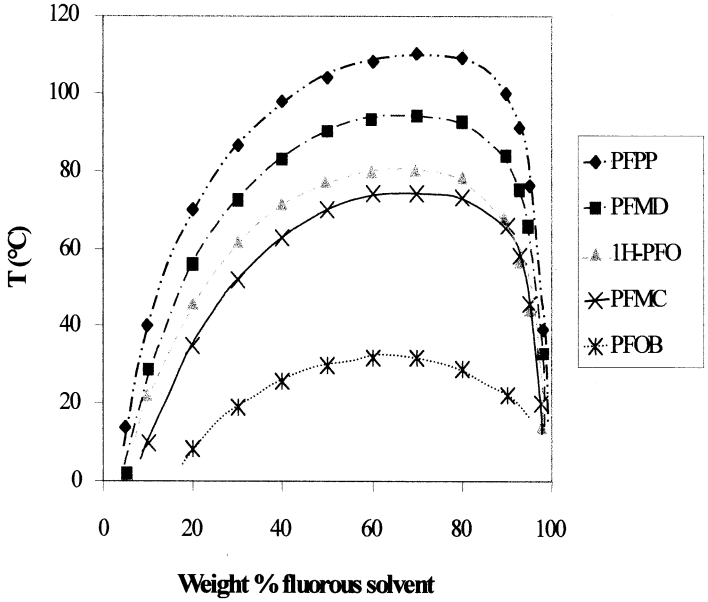
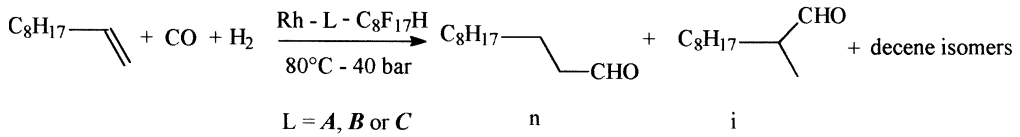


Figure 2. Miscibility diagrams of 1-decene with various fluorous solvents. PFPP: perfluoroperhydrophenanthrene; PFMD: perfluoromethyldecalin; PFMC: perfluoromethylcyclohexane, PFOB: perfluorooctyl bromide, 1*H*-PFO: 1*H*-perfluorooctane.



Scheme 2. Hydroformylation of 1-decene in fluorous biphasic medium using phosphites A, B and C as ligand.

Table 2. Hydroformylation of 1-decene under fluorous biphasic conditions

Entry	Phosphite	Perfluorous solvent	Organic solvent	t^a (min)	TOF[b] (h^{-1})	n/i[c]	Aldehyde selectivity[c] (mol%)
1	A	$C_8F_{17}H$	None	15	10000	2.0	85
2	B	$C_8F_{17}H$	$C_8F_{17}H$	30	3900	3.5	95
3	C	$C_8F_{17}H$	$C_8F_{17}H$	12	11000	2.0	85
4	B	$C_8F_{17}H$	Toluene	60	3500	3.0	98
5	B	PFMC	$C_8F_{17}H$	60	3800	3.0	98
6	B	PFMD	$C_8F_{17}H$	90	2500	3.3	95
7	B	PFPP	$C_8F_{17}H$	90	2300	3.6	95

Experimental conditions: 1-decene: 10.86 g (77.4 mmol); $Rh(acac)(CO)_2$: 10 mg (0.039 mmol, olefin/Rh=2000); phosphite: 0.194 mmol (P/Rh=5); fluorous solvent: entries 1–3: 15 ml, entries 4–7: 10 ml; toluene: 10 ml; *n*-undecane (internal standard for GC analysis): 1.21 g; *T*: 80°C; P: 40 bar CO/H_2 (1/1).

[a] Time required to reach 100% conversion.

[b] TOF: turn over frequencies defined as the number of moles of substrate transformed per hour and per moles of catalyst calculated from the slope at $t=0$ of the curve conversion=$f(t)$.

[c] n/i and aldehyde selectivity calculated at 70% conversion. The ratio of the products that are formed (both aldehydes and internal decenes) is constant at the beginning of the reaction. On the other hand when the reaction of 1-decene begins to slow down, the internal decenes previously formed are hydroformylated resulting in the production of several branched aldehydes. Thus to compare the results properly we decided to present in the table the data obtained at the same conversion (70%).

respectively), by lower normal to iso ratio of aldehydes (n/i=2.0 with A or C and 3.5 with B) and a lower aldehyde selectivity (85% vs 95%). Addition of an organic co-solvent (toluene) led to little changes in the results. The reaction proceeded with slightly lower activity and n/i ratio and a slightly higher aldehyde selectivity (compare entries 2 and 4). In the same way, the substitution of $C_8F_{17}H$ by other fluorous compounds had practically no effect on the n/i ratio and the aldehyde selectivity. On the other hand, the nature of the fluorous phase had a great influence on the activity since the TOF dropped from 3800 h^{-1} with PFMC to 2500 and 2300 h^{-1} with PFMD and PFPP, respectively.

2.3.3. Hydroformylation of various internal or terminal olefins under fluorous biphasic conditions. In order to determine the scope and limitation of the process, the hydroformylation of various heavy linear olefins and cyclohexene has been studied with phosphite B as ligand and $C_8F_{17}H$ as fluorous phase.

From Table 3, it appears that terminal olefins behave similarly as 1-decene giving a n/i ratio of 3.0 and an aldehyde selectivity of 95 mol% but the activity markedly drops with 1-dodecene.

As expected the reactivity falls again with internal olefins. Indeed the activity observed with 2-octene is three fold smaller than the one of 1-octene under the same conditions and the activity is again divided by a factor two when going from 2-octene to 4-octene. The aldehyde distribution is also markedly different with 2-octene and 4-octene. In the case of 2-octene, 2-methyloctanal and 2-ethylheptanal resulting directly from the hydroformylation of the substrate without isomerization, are the main reaction products (90 mol%). On the other hand with 4-octene isomerization markedly occurs particularly at the beginning of the reaction (about 50 mol% of isomerization at 20 min) and leads to a large extent of 2-methyloctanal and 2-ethylheptanal.

Finally, cyclic alkenes such as cyclohexene are practically inactive under these reaction conditions since its conversion reaches only 25 mol% after 6 h.

Table 3. Hydroformylation of various higher olefins under fluorous biphasic conditions

Entry	Olefin	t (min)[a]	TOF[b] (h^{-1})	n/i	Aldehyde selectivity[c] (mol%)
1	1-Octene	60	3600	3.0	95
2	1-Decene	60	3500	3.0	98
3	1-Dodecene	60	2600	3.0	94
4	2-Octene	90	1200	–[d]	82
5	4-Octene	150	440	–[e]	77
6	Cyclohexene		45	–	100

Experimental conditions: olefin: 77.4 mmol; $Rh(acac)(CO)_2$: 10 mg (0.039 mmol, olefin/Rh=2000); phosphite B: 0.194 mmol (P/Rh=5); $C_8F_{17}H$: 10 ml, toluene: 10 ml, *n*-undecane (internal standard for GC analysis):1.21 g; *T*: 80°C; P: 40 bar CO/H_2 (1/1).

[a] Time required to reach 100% conversion.

[b] Defined as in Table 2.

[c] Calculated at 70% conversion as in Table 2.

[d] Aldehyde distribution (mol%): *n*-nonanal: 5%; 2-methyloctanal: 60%; 2-ethylheptanal: 30%; 2-propylhexanal: 5%.

[e] Aldehyde distribution (mol%): *n*-nonanal: 8%; 2-methyloctanal: 28%; 2-ethylheptanal: 26%; 2-propylhexanal: 38%.

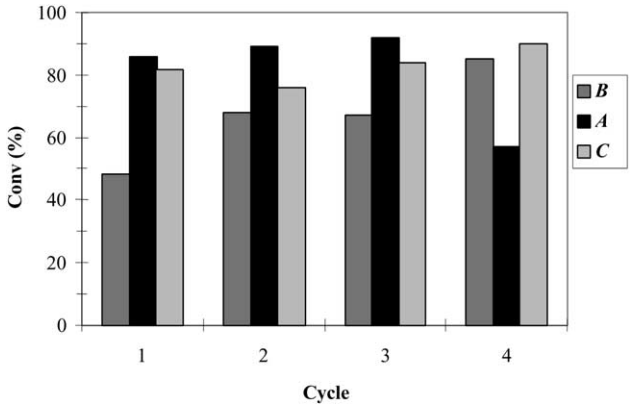


Figure 3. Conversion of 1-decene during recycle experiments with phosphites A, B and C. Experimental condition: $Rh(acac)(CO)_2$: 0.038 mmol, phosphite: 0.193 mmol; 1*H*-perfluorooctane: 15 ml; 1-decene: 77.4 mmol; undecane: 7.74 mmol (GC internal standard); *T*: 80°C. *P*: 40 atm of CO/H_2 (1/1); Reaction time: 10 min.

2.3.4. Catalyst recovery and reuse. 1-Decene and $C_8F_{17}H$ have been chosen as model to investigate the recovery and reuse of the catalytic system with phosphites A–C. The reaction was conducted as described above except that the duration of each test was fixed to 10 min in order to avoid the leveling of performances that could occur when total conversion is reached. As illustrated in Fig. 3, the activity was maintained during the three first cycles with phosphites A and C and even slightly increased in the case of B. On the other hand, the conversion dramatically dropped during the course of the fourth cycle with phosphite A. Moreover, in this last case, whereas in the first recycles the organic phases were colorless, the yellow color at the end of the last test revealed an important leaching of the Rh from the fluorous to the organic phase.

Finally, Figs. 4 and 5 show that the *n*/*i* ratio and the aldehyde selectivity regularly decreased after each cycle and the effect of the recycle on the *n*/*i* ratio was more marked in the case of phosphite B.

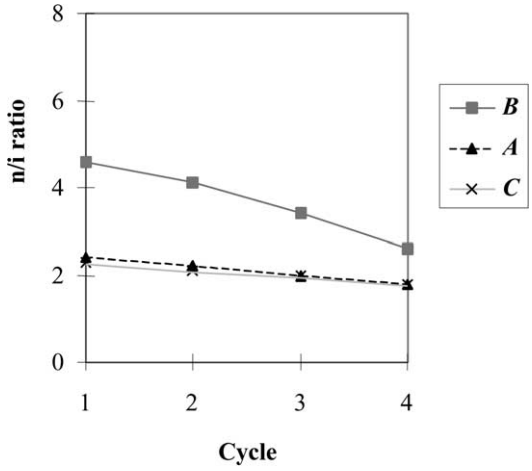


Figure 4. Hydroformylation of 1-decene—variation of the *n*/*i* ratio during recycle experiments with phosphites A, B and C. Experimental condition: $Rh(acac)(CO)_2$: 0.038 mmol, phosphite: 0.193 mmol; 1*H*-perfluorooctane: 15 ml; 1-decene: 77.4 mmol; undecane: 7.74 mmol (GC internal standard); *T*: 80°C. *P*: 40 atm of CO/H_2 (1/1); Reaction time: 10 min.

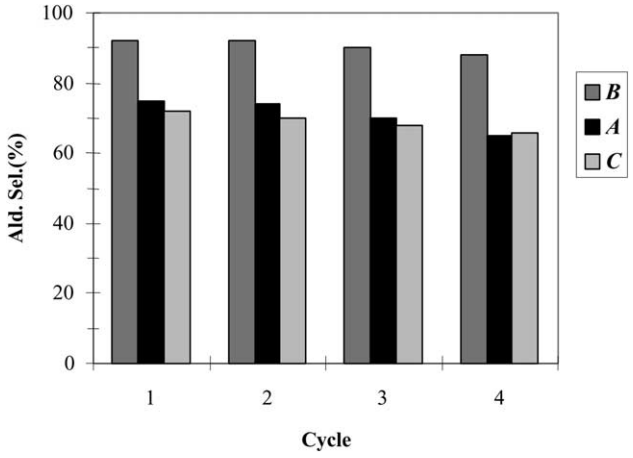
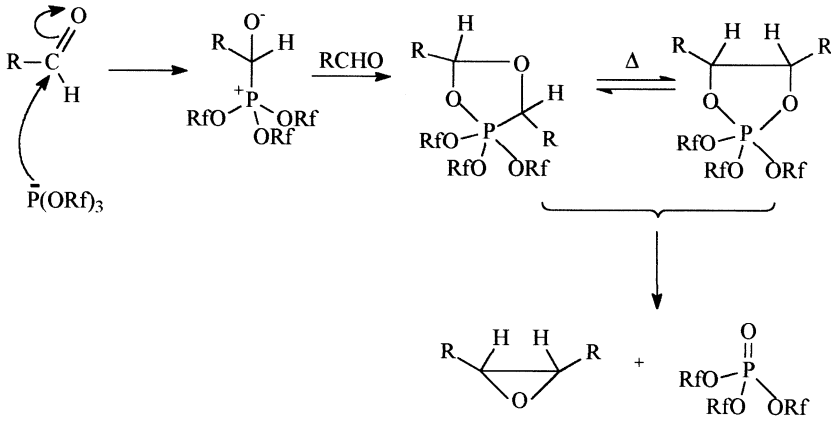


Figure 5. Hydroformylation of 1-decene—variation of the aldehyde selectivity during recycle experiments with phosphites A, B and C. Experimental condition: $Rh(acac)(CO)_2$: 0.038 mmol, phosphite: 0.193 mmol; 1*H*-perfluorooctane: 15 ml; 1-decene: 77.4 mmol; undecane: 7.74 mmol (GC internal standard); *T*: 80°C. *P*: 40 atm of CO/H_2 (1/1); Reaction time: 10 min.

3. Discussion

The results obtained with phosphites A and C differ from whose of B by a remarkably higher initial rate of hydroformylation of 1-decene. Concomitantly they lead to more modest *n*/*i* ratio and aldehyde selectivity. This difference is probably due to the fact that with the bulky orthosubstituted phosphite A and C only one phosphite coordinates to the Rh center in competition with CO to give the active species $HRhL(CO)_3$ (L=A or C).[41–42] In contrast with phosphite B, as in classical triphenyl phosphine modified catalyst, two phosphites bond to the rhodium. This assertion is in agreement with the fact that the catalyst precursor $Rh(acac)(CO)_2$ reacts with these phosphites in the absence of *syn* gas, to give Rh(acac)(CO)L (L=A or C) with phosphites A or C whereas $Rh(acac)L_2$ (L=B) is obtained with B. The complex $HRhL(CO)_3$ has, similar to $HRh(CO)_4$, a strong aptitude to CO dissociation compared with $HRh(CO)L_2$. With only one phosphite bonded to Rh the complex easily binds to the olefin initiating a very fast reaction cycle. Due to the large space available in comparison with the $HRh(CO)_2L_2$ system and the easy CO dissociation the reaction giving the branched aldehyde as well the β-H elimination proceed with relative ease resulting in a modest linearity and aldehyde selectivity.

It is also noteworthy that, even if B leads to a lower activity in hydroformylation of 1-decene in $C_8F_{17}H$ than A and C this activity is similar to the one observed with $P(OPh)_3$ in homogeneous medium and under the same reaction conditions. On the other hand, the activity markedly drops when PFMD or PFPP are used instead of $C_8F_{17}H$ as fluorous solvents. In the same way, whereas 1-octene and 1-decene are hydroformylated with about the same activity, this one is much lower with 1-dodecene. These observations are probably in connection with the fact that at the reaction temperature (80°C), as above mentioned, the miscibility of PFMD or PFPP with 1-decene (see Fig. 2) as well as the one of 1-dodecene with $C_8F_{17}H$ (see Table 1) are not total. Consequently, the reaction occurs in these cases in



Scheme 3. Proposed mechanism for the reaction of phosphites with aldehydes.

three-phase-system (two liquid phases and a gas phase) and the concentration of the olefin in the fluorous phase that contains the catalyst is much lower than in the case of a two-phase system (a liquid phase and a gas phase). As the order with respect of the substrate in the hydroformylation reaction of heavy olefins is positive at low olefin concentration,[42–43] the decrease in concentration of the olefin in the catalytic phase induces a decrease in the rate of the reaction.

From this, it may be deduced that the use of an organic fluorous biphasic system induces little change in the hydroformylation reaction in comparison with the classical homogeneous system as long as the reaction medium becomes homogeneous at the reaction temperature and provided that the fluorous pony tail of the ligand does not lead to a modification of the catalytic species.

From a recycling viewpoint, it appears that the catalytic system obtained with phosphites B and C possesses in contrast with the one resulting of phosphite A, a good reuse fitness since the activity remained constant or slightly increased after the different recycles. However the decrease in the *n*/*i* ratio and in the aldehyde selectivity after each cycle (even with phosphites B and C) indicate that a modification of the catalytic system occurs during each reuse presumably by a decrease in the P/Rh ratio. This decrease could be due in the case of A and B to a leaching of the phosphite (A and B have a modest partition coefficient) and/or to a decay of the phosphite. Actually, the attack of triphenylphosphites by aldehydes in organic medium is a known reaction which proceeds via the formation of dioxophospholanes that evolve to give a phosphite oxide and an epoxide (see Scheme 3).[44–47]

In order to confirm this hypothesis, we sought to determine the stability of the different phosphites A, B and C under the reaction conditions. A sample of each phosphite was heated at 80°C in mixtures of $C_8F_{17}H$/1-decene (1/1, v/v) or $C_8F_{17}H$/1-decene/undecanal (1/1/1, v/v/v). In the absence of undecanal all the phosphites remained unchanged after 1 h. In contrast, with undecanal, 50% of B was converted into oxidation products. Ortho substituted phosphite A and C appeared more stable but during the same time 20% decomposition again occurred. Blank experiment conducted with $P(OPh)_3$ under the same conditions ($C_8F_{17}H$/1-decene/undecanal mixture) led to 40% of decomposition, suggesting that the decay of phosphites A–C is not due to their perfluorous group. On the other hand, the steric hindrance due to the fluorous ponytail in the case of A and C has the effect to reduce their reactivity that explains their better stability. The fact that, at 80°C under the reaction conditions, undecanal is slightly soluble in $C_8F_{17}H$ (see Fig. 1) is also a favorable factor that should limit the decomposition of the different phosphites dissolved in $C_8F_{17}H$. However, the solubility is still obviously too high to prevent the reaction between undecanal and the phosphites A–C.

Thus, the decrease in the *n*/*i* ratio as well as the decrease in the aldehyde selectivity and the increase in the activity during the different recycles, are probably ascribable to the decrease in the ligand/Rh ratio due to the leaching of the phosphites and to the decomposition of phosphites. In connection with that, it is noteworthy that the effect on the *n*/*i* ratio and on the activity are more marked with phosphite B which is the less stable.

From the coloration of the organic phase with phosphite A at the end of the last recycles, it is obvious that there is an important leaching of the rhodium during these tests in contrast with phosphites B or C. However, the partition coefficient of A is not lower than the one of B and phosphite A has a better stability. To explain this apparent contradiction, it should be noticed that the main catalytic species are different with phosphite A and C, on the one hand, and B on the other hand ($HRh(CO)_3L$ and $HRh(CO)_2L_2$, respectively; L=A, B or C). Complex $HRh(CO)_3$(A) with only three perfluorous groups per Rh is probably less fluorophilic than $HRh(CO)_3$(C) or $HRh(CO)_2(B)_2$ which have six perfluorous groups per Rh. Thus $HRh(CO)_3$(A) is less retained in the fluorous phase than its counterparts particularly when the ratio P/Rh begins to decrease due to the decomposition and/or the leaching of the ligand.

4. Conclusion

Although the rhodium complexes associated with phosphites A, B and C can catalyze the hydroformylation of higher olefins in a fluorocarbon/hydrocarbon biphasic medium, this work demonstrates that ‘simple’ fluorinated analogues of $P(OPh)_3$ are not stable in the hydroformylation conditions. The synthesis of more stable fluorous-soluble

triarylphosphites and the use of phosphite C in others transition metal catalyzed reactions are currently under way in our laboratories.

5. Experimental

5.1. General

All synthesis and catalytic reactions were performed under nitrogen using standard Schlenk techniques. All solvents and liquid reagents were degassed by bubbling nitrogen for 15 min before each use or by two freeze-pump-thaw cycles before use.

5.2. Solvents and materials

Solvents were employed as follows: THF distilled from sodium/benzophenone; Et_2O: distilled from sodium/potassium; toluene, distilled from sodium; NEt_3, CH_2Cl_2, distilled from CaH_2. Petroleum ether (PE, bp 60–80°C) was distilled before use. Dicarbonylacetylacetonato rhodium(I), 2,4-bromoanisole, copper(I) iodide, magnesium turnings, phosphorus trichloride and 4-octene were purchased from Aldrich Chemicals in their highest purity and used without further purification. Perfluoromethylcyclohexane was obtained from Aldrich Chemicals and distilled from CaH_2. Cyclohexene, 1-hexene, 1-octene, 2-octene, 4-octene, 1-decene, 1-dodecene, 4-bromoanisole, 2-bromoanisole and BBr_3 were purchased from Acros Chemicals and used as received. 1*H*,1*H*,2*H*,2*H*-perfluorodecyl iodide was generously supplied by Atofina and was used as received. 1*H*-perfluorooctane, perfluorooctyl bromide and 1,1,2-trichlorotrifluoroethane were generously supplied by Atofina and were distilled from CaH_2. Perfluoromethyldecaline and perfluoroperhydrophenanthrene were supplied by Fluorochem and distilled from CaH_2. Carbon monoxide/hydrogen mixture (1/1) was used directly from cylinders (>99.9% pure; Air Liquide). Tris(4-(perfluorooctyl)phenyl)phosphite was prepared according to published procedures.[39]

5.3. Product analysis

All ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded at ambient probe temperature at 300.13, 75.5, 282.4 and 121.49 MHz on Bruker Avance DRX, respectively. Chemical shifts (δ) are given in ppm and are referenced to internal tetramethylsilane (^1H and ^{13}C NMR), external $CFCl_3$ (^{19}F NMR) and external 85% H_3PO_4 (^{31}P NMR). Abbreviations for NMR spectral multiplicities are as follows: br=broad, s=singlet, d=doublet, t=triplet, tt=triplet of triplets, dd=doublet of doublets, td=triplet of doublets, m=multiplet. The coupling constants (J) are in Hertz. Infrared spectra were obtained from NaCl plates or Nujol mulls using a Nicolet 510 FTIR spectrophotometer and wavelengths (ν) are reported in cm^{-1}. Abbreviations for IRFT spectra are as follows: w=weak, m=medium, s=strong, vs: very strong. Microanalyses were conducted by Wolff laboratories (Clichy, France). The EI mass spectra were recorded on a Nermag R10-10B mass spectrometer. The MALDI-TOF mass spectra were performed on a Finnigan MAT VISION 2000 spectrometer using 3,5-dihydroxybenzoic acid or 2,3,4-trihydroxyacetophenone as matrix. Gas chromatography was performed on Chrompack CP-9001 gas chromatograph equipped with a CPSil-5CB column (25 m×0.32 mm) and FID detector. Nirogen was the carrier gas and the temperature program was from 80 to 200°C at a heating rate of 5°C/min.

5.4. Synthesis of phosphites and precursors

5.4.1. 2-(1*H*,1*H*,2*H*,2*H*-Perfluorodecyl)anisole. To a suspension of magnesium (0.44 g, 18.06 mmol, 1.0 equiv.) in 25 ml of THF was introduced the 2-bromoanisole (9.03 mmol, 0.5 equiv.). After few min, the reaction began and 9.03 mmol of the 2-bromoanisole (0.5 equiv.) in THF (10 ml) was added dropwise. The reaction mixture was vigorously stirred at room temperature for 1 h. The reaction mixture was then filtered and added dropwise at 0°C over 1 h to a stirred suspension of 1*H*,1*H*,2*H*,2*H*-perfluorodecanyl iodide (18.06 mmol, 1.0 equiv.) and CuI (1.8 mmol, 0.1 equiv.) in 20 ml of anhydrous THF. The mixture was slowly warmed to room temperature and stirred for 24 h. Then, hydrochloric acid solution (60 ml, 2N) and ether (50 ml) were added. After 15 min, the two phases were separated and the aqueous phase was extracted with ether (3×30 ml). The combined organic layers were washed with 10% $Na_2S_2O_3$ solution (100 ml), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed on a rotary evaporator and the resulting residue was purified by column chromatography on silica gel (PE until elution of unreacted 1*H*,1*H*,2*H*,2*H*-perfluorodecanyl iodide, then PE/CH_2Cl_2 (80/20); v/v). Yield: 4.50 g (45%) of a colorless oil (Rf=0.73; PE/CH_2Cl_2 (90/10) v/v); NMR ^1H ($CDCl_3$) δ (ppm): 7.23 (td, 1H, J=7.8 and 1.6 Hz, 5-ArH), 7.15 (dd, 1H, J=7.4 and 1.6 Hz, 3-ArH), 6.91 (td, 1H, J=7.4 and 1.0 Hz, 4-ArH), 6.87 (d, 1H, J=7.8 Hz, 6-ArH), 3.84 (s, 3H, $-OCH_3$), 2.90 (m, 2H, $^3J_{HH}$=8.2 Hz, $-CH_2-CH_2-C_8F_{17}$), 2.35 (m, 2H, $^3J_{HF}$=18.6 Hz, $^3J_{HH}$=8.2 Hz, $-CH_2-CH_2-C_8F_{17}$); NMR $^{19}F\{^1H\}$ ($CDCl_3$) δ (ppm): −81.04 (t, 3F, $^3J_{FF}$=9.7 Hz, $-CF_3$), −115.04 (t, 2F, $^3J_{FF}$=11.8 Hz, CF_2- in α of $-CH_2-$), −121.98 (m, 2F, $-CF_2-$), −122.15 (m, 4F, 2×$-CF_2-$), −122.97 (m, 2F, $-CF_2-$), −123.76 (m, 2F, $-CF_2-$), −126.36 (m, 2F, $-CF_2-$); NMR $^{13}C\{^1H\}$ ($CDCl_3$) δ (ppm): 157.61 (s, 1-C arom), 130.08 (s, 3-CH arom), 128.19 (s, 5-CH arom), 127.69 (s, 2-C arom), 120.73 (s, 4-CH arom), 110.45 (s, 6-CH arom), 55.23 (s, $-OCH_3$), 31.14 (t, $^2J_{CF}$=21.8 Hz, $-CH_2-CH_2-C_8F_{17}$), 21.94 (t, $^3J_{CF}$=4.3 Hz, $-CH_2-CH_2-C_8F_{17}$), 105–120 (complex signals of $-CF_2-$ and $-CF_3$); MS (EI) *m/z*: 554 (M^+, 67.7), 535 (M^+-F, 8.9), 515 (M^+-2F-H, 2.2), 135 ($M^+-C_8F_{17}$, 2.0), 121 ($M^+-CH_2C_8F_{17}$, 100), 91 ($[C_5H_3-C_2H_4]^+$, 32.3), 69 (CF_3^+, 8.9); IRFT (KBr) ν (cm^{-1}): 3073 (w), 3009 (w), 2953 (w), 2843 (w), 1605 (w), 1592 (w), 1497 (s), 1469 (m), 1441 (w), 1370 (w), 1331 (w), 1287 (m), 1244 (vs), 1206 (vs), 1150 (vs), 1114 (m), 1083 (m), 1051 (m), 1033 (w), 972 (w), 752 (m), 704 (w), 656 (w).

5.4.2. 4-(1*H*,1*H*,2*H*,2*H*-Perfluorodecyl)anisole. The titled compound was prepared in a fashion similar to 2-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole from 4-bromoanisole (9.03 mmol). After addition of Grignard reagent to suspension of 1*H*,1*H*,2*H*,2*H*-perfluorodecanyl iodide and CuI, the mixture was stirred at room temperature for 4 h instead of 24 h. After an identical workup, chromatography yielded

6.52 g (65%) of a white solid mp: 35°C (*Rf*=0.67; PE/CH_2Cl_2 (80/20) v/v); NMR ^{1}H ($CDCl_3$) δ (ppm): 7.13 (m, 2H, *J*=8.6 and 2.5 Hz, 3.5-ArH), 6.86 (m, 2H, *J*=8.6 and 2.5 Hz, 2.6-ArH), 3.79 (s, 3H, $-OCH_3$), 2.86 (m, 2H, $^3J_{HH}$=8.4 Hz, $-CH_2-CH_2-C_8F_{17}$), 2.33 (m, 2H, $^3J_{HF}$= 18.3 Hz, $^3J_{HH}$=8.4 Hz, $-CH_2-CH_2-C_8F_{17}$); NMR ^{19}F{^{1}H} ($CDCl_3$) δ (ppm): −81.13 (t, 3F, $^3J_{FF}$=9.5 Hz, $-CF_3$), −114.99 (t, 2F, $^3J_{FF}$=12.9 Hz, $-CF_2-$ in α of $-CH_2-$), −122.02 (m, 2F, $-CF_2-$), −122.24 (m, 4F, 2×$-CF_2-$), −123.04 (m, 2F, $-CF_2-$), −123.82 (m, 2F, $-CF_2-$), −126.45 (m, 2F, $-CF_2-$); NMR ^{13}C{^{1}H} ($CDCl_3$) δ (ppm): 154.32 (s, 1-C arom), 131.51 (s, 4-C arom), 129.57 (s, 3,5-CH arom), 114.30 (s, 2,6-CH arom), 55.21 (s, $-OCH_3$), 33.41 (t, $^2J_{CF}$=22.0 Hz, $-CH_2-CH_2-C_8F_{17}$), 25.69 (t, $^3J_{CF}$=3.9 Hz, $-CH_2-CH_2-C_8F_{17}$); 105–120 (complex signals of $-CF_2-$ and $-CF_3$); MS (EI) *m/z*: 554 (M^+, 17.3), 535 (M^+-F, 6.3), 134 ($M^+-H-C_8F_{17}$, 1.6), 121 ($M^+-CH_2C_8F_{17}$, 100), 91 ($[C_5H_3-C_2H_4]^+$, 1.9), 77 ($[C_5H_3-CH_2]^+$, 1.3), 69 (CF_3^+, 2.0); IRFT (KBr) ν (cm^{-1}): 3024 (w), 2967 (w), 2840 (w), 1613 (w), 1585 (w), 1516 (s), 1454 (w), 1374 (w), 1336 (m), 1287 (m), 1245 (s), 1202 (s), 1146 (s), 1115 (m), 1102 (m), 1075 (w), 1026 (m), 986 (w), 961 (w), 832 (w), 812 (w), 714 (w), 659 (m). Anal. Calcd for $C_{17}H_{11}F_{17}O$: C, 36.85; H, 1.98; found: C, 38.11; H, 2.14.

5.4.3. 2,4-Bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole. The titled compound was synthesized in two steps. The first step was similar to that described for 4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole except than 2,4-dibromoanisole was used as starting material. After an identical workup, chromatography on silica gel (PE/CH_2Cl_2 (80/20) v/v) yielded 1.03 g (9%) of 4-bromo-2-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole as a colorless oil (*Rf*=0.85) and 3.431 g (30%) of 2-bromo-4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole as a white solid (*Rf*=0.59). The second step was analogous to that reported for 4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole except than 2-bromo-4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-anisole that was isolated in the first step was the starting material. The crude product was purified by column chromatography to afford 2,4-bis(1*H*, 1*H*,2*H*,2*H*-perfluorodecyl)anisole as a colorless oil. Yield: 1.95 g (11%) (*Rf*= 0.75; PE/CH_2Cl_2 (90/10) v/v); NMR ^{1}H ($CDCl_3$) δ (ppm): 7.06 (dd, 1H, *J*=8.3 and 2.2 Hz, 5-ArH), 6.99 (d, 1H, *J*=2.2 Hz, 3-ArH), 6.80 (d, 1H, *J*=8.3 Hz, 6-ArH), 3.82 (s, 3H, $-OCH_3$), 2.86 (m, 4H, $^3J_{HH}$=8.6 Hz, $-CH_2-CH_2-C_8F_{17}$), 2.33 (m, 4H, $^3J_{HF}$=18.6 Hz, $^3J_{HH}$=8.6 Hz, $-CH_2-CH_2-C_8F_{17}$); NMR ^{19}F{^{1}H} ($CDCl_3$) δ (ppm): −81.09 (t, 6F, $^3J_{FF}$=9.3 Hz, 2×$-CF_3$), −115.08 (m, 4F, 2×$-CF_2-$ in α of $-CH_2-$), −122.03 (m, 4F, 2×$-CF_2-$), −122.24 (m, 8F, 4×$-CF_2-$), −123.04 (m, 4F, 2×$-CF_2-$), −123.80 (m, 4F, 2×$-CF_2-$), −126.44 (m, 4F, 2×$-CF_2-$); NMR ^{13}C{^{1}H} ($CDCl_3$) δ (ppm): 156.45 (s, 1-C arom), 131.35 (s, 4-C arom), 130.13 (s, 3-CH arom), 128.12 (s, 2-C arom), 127.79 (s, 5-CH arom), 110.70 (s, 6-CH arom), 55.34 (s, $-OCH_3$), 33.39 (t, $^2J_{CF}$=22.0 Hz, $-CH_2-CH_2-C_8F_{17}$ in β of 4-C arom), 31.11 (t, $^2J_{CF}$=21.8 Hz, $-CH_2-CH_2-C_8F_{17}$ in β of 2-C arom), 25.66 (br s, $-CH_2-CH_2-C_8F_{17}$ in α of 4-C arom), 22.02 (t, $^3J_{CF}$=4.3 Hz, $-CH_2-CH_2-C_8F_{17}$ in α of 2-C arom), 105–120 (complex signals of $-CF_2-$ and $-CF_3$); MS (EI) *m/z*: 1000 (M^+, 0.3), 981 (M^+-F, 0.1), 581 ($M^+-C_8F_{17}$, 0.5), 567 ($M^+-CH_2C_8F_{17}$, 100), 162 ($M^+-2C_8F_{17}$, 8.8), 148 ($M^+-2CH_2C_8F_{17}$, 8.1), 91 ($[C_5H_3-C_2H_4]^+$, 2.3), 77 ($[C_5H_3-CH_2]^+$, 1.3), 69 (CF_3^+, 1.5); IRFT (KBr) ν (cm^{-1}): 3013 (w), 2952 (w), 2918 (w), 2878 (w), 2845 (w), 1615 (w), 1506 (s), 1494 (s), 1469 (m), 1457 (w), 1370 (m), 1330 (m), 1242 (vs), 1205 (vs), 1150 (vs), 1113 (s), 1088 (s), 1034 (m), 975 (w), 808 (w), 705 (m), 656 (m).

5.4.4. 2-(1*H*,1*H*,2*H*,2*H*-Perfluorodecyl)phenol. A solution of BBr_3 (11.73 mmol, 1.3 equiv.) in anhydrous toluene (10 ml) was added dropwise at room temperature over 15 min to a stirred solution of 2-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole (9.02 mmol, 1.0 equiv.) in anhydrous toluene (40 ml). The reaction mixture was vigorously stirred under N_2 flow at room temperature for 24 h. Then, the reaction mixture was poured into a mixture of water (50 ml) and ether (30 ml). The two phases were separated and the aqueous phase was extracted with ether (3×30 ml). The combined organic layers were washed with water (2×50 ml), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed on a rotary evaporator and the resulting residue was purified by column chromatography on silica gel (CH_2Cl_2). Yield: 3.946 g (81%) of a white solid mp: 67°C (*Rf*=0.74; CH_2Cl_2); NMR ^{1}H ($CDCl_3$) δ (ppm): 7.14 (d, 1H, *J*=7.7 Hz, 3-ArH), 7.12 (td, 1H, *J*=7.7 and 1.7 Hz, 5-ArH), 6.89 (td, 1H, *J*=7.7 and 1.0 Hz, 4-ArH), 6.73 (d, 1H, *J*=7.7 Hz, 6-ArH), 4.75 (s, 1H, –OH), 2.92 (m, 2H, $^3J_{HH}$=8.3 Hz, $-CH_2-CH_2-C_8F_{17}$), 2.40 (2m, H,$^3J_{HF}$=18.9 Hz, $^3J_{HH}$=8.3 Hz, $-CH_2-CH_2-C_8F_{17}$); NMR ^{19}F{^{1}H} ($CDCl_3$) δ (ppm): −81.02 (t, 3F, $^3J_{FF}$=9.9 Hz, $-CF_3$), −115.14 (t, 2F, $^3J_{FF}$=12.2 Hz, $-CF_2-$ in α of $-CH_2-$), −121.98 (m, 2F, $-CF_2-$), −122.19 (m, 4F, 2× $-CF_2-$), −122.98 (m, 2F, $-CF_2-$), −123.79 (m, 2F, $-CF_2-$), −126.38 (m, 2F, $-CF_2-$); NMR ^{13}C{^{1}H} ($CDCl_3$) δ (ppm): 153.56 (s, 1-C arom), 130.61 (s, 3-CH arom), 128.19 (s, 5-CH arom), 125.89 (s, 2-C arom), 121.35 (s, 4-CH arom), 115.40 (s, 6-CH arom), 31.02 (t, $^2J_{CF}$= 21.8 Hz, $-CH_2-CH_2-C_8F_{17}$), 21.65 (t, $^3J_{CF}$=4.1 Hz, $-CH_2-CH_2-C_8F_{17}$); 105–120 (complex signals of $-CF_2-$ and $-CF_3$); MS (IE) *m/z*: 540 (M^+, 49.0%), 521 (M^+-F, 6.1%), 501 (M^+-2F-H, 2.9%), 121 ($M^+-C_8F_{17}$, 2.2%), 120 ($M^+-H-C_8F_{17}$, 2.6%), 107 ($M^+-CH_2C_8F_{17}$, 100%), 91 ($[C_5H_3-C_2H_4]^+$, 3.0%), 77 ($[C_5H_3-CH_2]^+$, 7.5%), 69 (CF_3^+, 7.2%); IRFT (KBr) ν (cm^{-1}): 3504 (s), 3402 (s), 3044 (w), 2996 (w), 2948 (w), 1595 (m), 1509 (m), 1460 (m), 1373 (m), 1356 (m), 1336 (s), 1242 (vs), 1218 (vs), 1205 (vs), 1148 (vs), 1116 (s), 1078 (m), 1043 (w), 1025 (w), 972 (w), 954 (w), 765 (m), 746 (m), 655 (m).

5.4.5. 4-(1*H*,1*H*,2*H*,2*H*-Perfluorodecyl)phenol. The titled compound was prepared in a fashion similar to 2-(1*H*, 1*H*,2*H*,2*H*-perfluorodecyl)phenol from 4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)anisole (9.02 mmol). The reaction mixture was vigorously stirred under N_2 flow at room temperature for 4 h instead of 24 h. Yield: 4.286 g (88%) of a white solid mp: 88°C (*Rf*=0.48; CH_2Cl_2); NMR ^{1}H ($CDCl_3$) δ (ppm): 7.08 (m, 2H, *J*=8.5 and 2.5 Hz, 3,5-ArH), 6.78 (m, 2H, *J*=8.5 and 2.5 Hz, 2,6-ArH), 4.75 (s, 1H, –OH), 2.84 (m, 2H, $^3J_{HH}$=8.4 Hz, $-CH_2-CH_2-C_8F_{17}$), 2.32 (tt, 2H, $^3J_{HF}$= 18.3 Hz, $^3J_{HH}$=8.4 Hz, $-CH_2-CH_2-C_8F_{17}$); NMR ^{19}F{^{1}H} ($CDCl_3$) δ (ppm): −81.08 (t, 3F, $^3J_{FF}$=9.7 Hz, $-CF_3$), −114.93 (t, 2F, $^3J_{FF}$=12.5 Hz, $-CF_2-$ in α of $-CH_2-$), −121.99 (m, 2F, $-CF_2-$), −122.21 (m, 4F, 2×$-CF_2-$), −123.00 (m, 2F, $-CF_2-$), −123.78 (m, 2F, $-CF_2-$),

−126.41 (m, 2F, $-CF_2-$); NMR $^{13}C\{^1H\}$ ($CDCl_3$) δ (ppm): 154.32 (s, 1-C arom), 131.51 (s, 4-C arom), 129.57 (s, 3,5-CH arom), 115.69 (s, 2,6-CH arom), 33.31 (t, $^2J_{CF}$=21.8 Hz, $-CH_2-CH_2-C_8F_{17}$), 25.67 (t, $^3J_{CF}$=3.9 Hz, $-CH_2-CH_2-C_8F_{17}$); 105–120 (complex signals of $-CF_2-$ and $-CF_3$); MS (IE) *m/z*: 540 (M^+, 4.7), 521 (M^+-F, 2.5), 120 ($M^+-H-C_8F_{17}$, 3.1), 107 ($M^+-CH_2C_8F_{17}$, 100), 91 ($[C_5H_3-C_2H_4]^+$, 0.8), 77 ($[C_5H_3-CH_2]^+$, 0.8%), 69 (CF_3^+, 0.5) Anal. Calcd for $C_{16}H_9F_{17}O$: C, 35.58; H, 1.66; found: C, 36.63; H, 1.80; IRFT (KBr) ν (cm^{-1}): 3274 (w), 3026 (w), 2949 (w), 2876 (w), 1615 (m), 1602 (m), 1517 (vs), 1458 (m), 1373 (m), 1336 (m), 1294 (m), 1239 (vs), 1217 (vs), 1202 (vs), 1147 (vs), 1116 (m), 1080 (m), 1032 (w), 973 (w), 958 (m), 822 (m), 719 (m), 705 (m), 657 (m).

5.4.6. 2,4-Bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenol. A solution of BBr_3 (1.35 mmol, 1.3 equiv.) in toluene (4 ml) was added dropwise at room temperature over 15 min to a stirred solution of 2,4-bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-anisole (1.036 g, 1.04 mmol, 1.0 equiv.) in CF_2ClCCl_2F (10 ml). The reaction mixture was vigorously stirred under N_2 flow at room temperature for 24 h. Then, the reaction mixture was poured into a mixture of water (30 ml) and ether (30 ml). The two phases were separated and the aqueous phase was extracted with ether (3×30 ml). The combined organic layers were washed with water (2×50 ml), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed on a rotary evaporator and the resulting residue was purified by column chromatography on silica gel (CH_2Cl_2). Yield: 0.869 g (85%) of a white solid mp: 63°C (*Rf*=0.75; CH_2Cl_2); NMR ^1H ($CDCl_3$) δ (ppm): 6.98 (d, 1H, *J*=2.2 Hz, 3-ArH), 6.95 (dd, 1H, *J*=8.0 and 2.2 Hz, 5-ArH), 6.68 (d, 1H, *J*=8.0 Hz, 6-ArH), 4.73 (s, 1H, −OH), 2.90 (m, 2H, $^3J_{HH}$=8.2 Hz, $-CH_2-CH_2-C_8F_{17}$ in α of 2-C arom), 2.83 (m, 2H, $^3J_{HH}$=8.2 Hz, $-CH_2-CH_2-C_8F_{17}$ in α of 4-C arom), 2.34 (m, 4H, $^3J_{HF}$=19.7 Hz, $^3J_{HH}$=8.2 Hz, $2\times-CH_2-CH_2-C_8F_{17}$); NMR $^{19}F\{^1H\}$ ($CDCl_3$) δ (ppm): −81.04 (t, 6F, $^3J_{FF}$=9.6 Hz, 2×$-CF_3$), −114.91 (t, 2F, $^3J_{FF}$=11.4 Hz, $-CF_2-$ in γ of 4-C arom), −115.08 (t, 2F, $^3J_{FF}$=12.2 Hz, $-CF_2-$ in γ of 2-C arom), −121.98 (m, 4F, 2×$-CF_2-$), −122.20 (m, 8F, 4×$-CF_2-$), −122.99 (m, 4F, 2×$-CF_2-$), −123.78 (m, 4F, 2×$-CF_2-$), −126.39 (m, 4F, 2×$-CF_2-$); NMR $^{13}C\{^1H\}$ ($CDCl_3$) δ (ppm): 152.28 (s, 1-C arom), 131.95 (s, 4-C arom), 130.54 (s, 3-CH arom), 127.84 (s, 5-CH arom), 126.20 (s, 2-C arom), 115.65 (s, 6-CH arom), 33.32 (t, $^2J_{CF}$=21.6 Hz, $-CH_2-CH_2-C_8F_{17}$ in β of 4-C arom), 30.96 (t, $^2J_{CF}$=22.5 Hz, $-CH_2-CH_2-C_8F_{17}$ in β of 2-C arom), 25.67 (t, $^3J_{CF}$=3.6 Hz, $-CH_2-CH_2-C_8F_{17}$ in α of 4-C arom), 21.75 (t, $^3J_{CF}$=3.9 Hz, $-CH_2-CH_2-C_8F_{17}$ in α of 2-C arom), 105–120 (complex signals of $-CF_2-$ and $-CF_3$); MS (EI) *m/z*: 986 (M^+, 16.2), 967 (M^+-F, 6.9), 567 ($M^+-C_8F_{17}$, 11.0), 553 ($M^+-CH_2C_8F_{17}$, 100), 134 ($M^+-2C_8F_{17}$, 3.2), 120 ($M^+-2CH_2C_8F_{17}$, 21.1), 91 ($[C_5H_3-C_2H_4]^+$, 3.3), 77 ($[C_5H_3-CH_2]^+$, 1.9), 69 (CF_3^+, 2.5); IRFT (KBr) ν (cm^{-1}): 3489 (m), 3431 (m), 2958 (w), 2876 (w), 1509 (m), 1457 (w), 1373 (m), 1335 (s), 1236 (vs), 1202 (vs), 1149 (vs), 1115 (s), 1079 (m), 980 (w), 968 (w), 704 (w), 658 (m).

5.4.7. Tris(2-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl)phosphite (A). The 2-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenol (5.55 mmol, 3.0 equiv.) was azeotropically distilled with toluene (50 ml) and dissolved in THF (30 ml). Triethylamine (1.0 ml, 7.23 mmol, 4.0 equiv.) was added to this solution. Phosphorus trichloride (0.2 ml, 2.42 mmol, 1.3 equiv.) dissolved in 15 ml of THF was added dropwise at 0°C for 1.5 h under N_2 to the stirred solution of 2-(1*H*, 1*H*, 2*H*, 2*H*-perfluorodecyl)phenol. Subsequently the reaction mixture was stirred for 4 h at room temperature. The amine salts formed were removed by filtration over dried silica gel under N_2 with further 40 ml of THF. The solvent was removed in vacuo to afford the pure phosphite (A). Yield: 2.95 g (97%) of a white solid mp: 68°C NMR $^{31}P\{^1H\}$ ($CDCl_3$) δ (ppm): +132.71 (s); NMR ^1H ($CDCl_3$) δ (ppm): 7.22 (br d, 3H, *J*=8.0 Hz, 3×3-ArH), 7.18 (m, 6H, 3×4 and 5-ArH), 7.09 (m, 3H, *J*=8.0 Hz, 3×6-ArH), 2.85 (m, 6H, $^3J_{HH}$=8.2 Hz, $3\times-CH_2-CH_2-C_8F_{17}$), 2.26 (tt, 6H, $^3J_{HF}$=18.4 Hz, $^3J_{HH}$=8.2 Hz, $3\times-CH_2-CH_2-C_8F_{17}$); NMR $^{19}F\{^1H\}$ ($CDCl_3$) δ (ppm): −81.39 (t, 9F, $^3J_{FF}$=9.8 Hz, 3×$-CF_3$), −115.49 (m, 6F, 3×$-CF_2-$ in α of $-CH_2-$), −122.28 (m, 6F, 3×$-CF_2-$), −122.49 (m, 12F, 6×$-CF_2-$), −123.29 (m, 6F, 3×$-CF_2-$), −123.97 (m, 6F, 3×$-CF_2-$), −126.71 (m, 6F, 3×$-CF_2-$); NMR $^{13}C\{^1H\}$ ($CDCl_3$) δ (ppm): 149.93 (d, $^2J_{CP}$=3.0 Hz, 1-C arom), 130.79 (s, 3-CH arom), 130.60 (d, $^3J_{CP}$=1.9 Hz, 2-C arom), 128.27 (s, 5-CH arom), 124.79 (s, 4-CH arom), 119.86 (d, $^3J_{CP}$=13.3 Hz, 6-CH arom), 31.15 (t, $^2J_{CF}$=22.0 Hz, $-CH_2-CH_2-C_8F_{17}$), 21.57 (t, $^3J_{CF}$=3.8 Hz, $-CH_2-CH_2-C_8F_{17}$), 105–120 (complex signals of $-CF_2-$ and $-CF_3$); MS (MALDI) *m/z*: 1648 (M^+); IRFT (KBr) ν (cm^{-1}): 1490 (m), 1458 (w), 1373 (w), 1332 (w), 1244 (vs), 1221 (vs), 1202 (vs), 1176 (s), 1150 (vs), 1135 (s), 1116 (m), 1080 (m), 1039 (w), 1026 (w), 973 (w), 889 (m), 819 (w), 770 (w), 656 (m).

5.4.8. Tris(4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl)phosphite (B). The titled compound was prepared in a fashion similar to tris(2-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl)-phosphite from 4-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenol. Yield: 2.969 g (97%) of a white solid mp: 83°C NMR $^{31}P\{^1H\}$ ($CDCl_3$) δ (ppm): +127.95 (s); NMR ^1H ($CDCl_3$) δ (ppm): 7.16 (m, 6H, *J*=8.7 and 2.5 Hz, 3×3,5-ArH), 7.10 (m, 6H, *J*=8.7 Hz, 3×2,6-ArH), 2.89 (m, 6H, $^3J_{HH}$=8.4 Hz, $3\times-CH_2-CH_2-C_8F_{17}$), 2.34 (tt, 6H, $^3J_{HF}$=18.1 Hz, $^3J_{HH}$=8.4 Hz, $3\times-CH_2-CH_2-C_8F_{17}$); NMR $^{19}F\{^1H\}$ ($CDCl_3$) δ (ppm): −81.61 (t, 9F, $^3J_{FF}$=9.7 Hz, 3×$-CF_3$), −115.19 (t, 6F, $^3J_{FF}$=12.8 Hz, 3×$-CF_2-$ in α of $-CH_2-$), −122.24 (m, 6F, 3×$-CF_2-$), −122.49 (m, 12F, 6×$-CF_2-$), −123.32 (m, 6F, 3×$-CF_2-$), −124.02 (m, 6F, 3×$-CF_2-$), −126.82 (m, 6F, 3×$-CF_2-$); NMR $^{13}C\{^1H\}$ ($CDCl_3$) δ (ppm): 150.46 (d, $^2J_{CP}$=2.9 Hz, 1-C arom), 135.35 (s, 4-C arom), 129.69 (s, 3,5-CH arom), 121.16 (d, $^3J_{CP}$=6.7 Hz, 2,6-CH arom), 33.16 (t, $^2J_{CF}$=22.0 Hz, $-CH_2-CH_2-C_8F_{17}$), 25.92 (s, $-CH_2-CH_2-C_8F_{17}$), 105–120 (complex signals of $-CF_2-$ and $-CF_3$); MS (MALDI) *m/z*: 1648 (M^+). Anal. Calcd for $C_{48}H_{24}F_{51}O_3P$: C, 34.98; H, 1.45; found: C, 35.67; H, 1.60; IRFT (KBr) ν (cm^{-1}): 1506 (m), 1372 (w), 1334 (w), 1236 (s), 1204 (vs), 1149 (vs), 1114 (m), 1082 (w), 871 (w), 657 (w).

5.4.9. Tris(2,4-bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl)-phosphite (C). The 2,4-bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-phenol (0.87 mmol, 3.0 equiv.) was azeotropically distilled three times with toluene (3×50 ml) and dissolved in a mixture of Et_2O (5 ml) and perfluorooctyle (5 ml). Triethylamine (0.2 ml, 1.16 mmol, 4.0 equiv.) was added to this

solution. Phosphorus trichloride (0.03 ml, 0.40 mmol, 1.3 equiv.) dissolved in 5 ml of Et_2O was added dropwise at 0°C for 1 h under N_2 to the stirred solution of 2,4-bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenol. Subsequently the reaction mixture was stirred for 4 h at room temperature. The amine salts formed were removed by filtration over dried silica gel under N_2 with further 40 ml of Et_2O. The solvent was removed in vacuo to afford the pure phosphite (C). Yield: 0.801 g (93%) of a white solid mp: 54°C NMR $^{31}P\{^1H\}$ (CF_2ClCCl_2F, external lock on $CDCl_3$) δ (ppm): +129.87 (s); NMR ^1H (CF_2ClCCl_2F, external lock on $CDCl_3$) δ (ppm): 7.22 (d, 3H, J=8.3 Hz, 3×6-ArH), 7.09 (d, 3H, J=1.8 Hz, 3×3-ArH), 7.06 (dd, 3H, J=8.3 and 1.8 Hz, 3×5-ArH), 2.87 (m, 12H, 6×–C*H*$_2$–CH$_2$–C_8F_{17}), 2.32 (m, 12H, 6×–CH$_2$–C*H*$_2$–C_8F_{17}); NMR $^{19}F\{^1H\}$ (diethylether, external lock on $CDCl_3$) δ (ppm): −81.06 (t, 18F, $^3J_{FF}$=9.3 Hz, 6×–CF_3), −114.92 (m, 6F, 3×–CF_2– in γ of 4-C arom), −115.15 (m, 6F, 3×–CF_2– in γ of 2-C arom), −122.22 (m, 36F, 18×–CF_2–), −123.04 (m, 6F, 3×–CF_2–), −123.22 (m, 6F, 3×–CF_2–), −123.91 (m, 12F, 6×–CF_2–), −126.40 (m, 6F, 3×–CF_2–), −126.64 (m, 6F, 3×–CF_2–); NMR $^{13}C\{^1H\}$ (CF_2ClCCl_2F, external lock on $CDCl_3$) δ (ppm): 149.35 (s, 1-C arom), 136.68 (s, 4-C arom), 131.70 (br s, 2-C arom), 131.26 (s, 3-CH arom), 128.55 (s, 5-CH arom), 120.92 (d, $^3J_{CP}$=12.5 Hz, 6-CH arom), 33.71 (t, $^2J_{CF}$=22.1 Hz, –CH$_2$–*C*H$_2$–C_8F_{17} in β of 4-C arom), 31.93 (t, $^2J_{CF}$=22.1 Hz, –CH$_2$–*C*H$_2$–C_8F_{17} in β of 2-C arom), 26.41 (br s, –*C*H$_2$–CH$_2$–C_8F_{17} in α of 4-C arom), 22.32 (br s, –*C*H$_2$–CH$_2$–C_8F_{17} in α of 2-C arom), 105–120 (complex signals of CF_2– and –CF_3); MS (MALDI) *m*/*z*: 2986 (M^+); IRFT (KBr) ν (cm^{-1}): 1496 (m), 1457 (w), 1373 (w), 1333 (m), 1240 (vs), 1205 (vs), 1148 (vs), 1135 (s), 1115 (s), 1084 (m), 971 (w), 871 (w), 704 (w), 656 (w).

5.5. Miscibility diagrams

The data needed to draw the miscibility diagrams of the different binary mixtures were collected as follow. A mixture of defined composition (obtained after weighing each component) was heated until it became homogeneous. The solution was then slowly cooled. The temperature for which the mixture began to visually turn cloudy was carefully measured by mean of a thermocouple dipping in the mixture and was considered as the temperature limit of solubility for the mixture studied.

5.6. Hydroformylation experiments

All the high pressure hydroformylation experiments were carried out in a 50 ml stainless steel microclave supplied by Parr. The reactor was fitted with arrangements for liquid sampling, automatic temperature control, and variable stirring with precise speed measurement by tachometer display and pressure gauge. A safety rupture disk was also fitted to the reactor. Rh(acac)$(CO)_2$ (0.038 mmol), phosphite (0.193 mmol) were dissolved in 15 ml of 1*H*-perfluorooctane and the solution was stirred for 2 h. The resulting fluorous phase and an organic phase composed of olefin (77.4 mmol) and undecane (7.74 mmol–GC internal standard) were charged under an atmosphere of N_2 into the 50 ml reactor which was heated at 80°C. Mechanical stirring equipped with a multipaddle unit was then started (1500 rpm) and the autoclave was pressurized with 40 atm of CO/H_2 (1/1) from a gas reservoir connected to the reactor through a high pressure regulator valve allowing to keep constant the pressure in the reactor throughout the whole reaction. The reaction medium was sampled during the reaction for GC analyses of the organic phase after decantation. For kinetic measurements the time corresponding to the addition of CO/H_2 was considered as the beginning of the reaction.

5.7. Recycling experiments

The first batch was carried out as described above. After 10 min of reaction time, the autoclave was cooled rapidly to room temperature and carefully depressurized. The reaction solution was transferred to nitrogen filled Schlenk tube. After 30 min, the fluorous and organic phases were separated and a new carefully deoxygenated solution of olefin (77.4 mmol) and undecane (7.74 mmol) was introduced in the Schlenk tube. The resulting mixture was charged under an atmosphere of N_2 into the autoclave and used in another hydroformylation run as described above.

Acknowledgements

This research was supported by funds from the Centre National de la Recherche Scientifique (CNRS) and Atofina. We would like also to thank Atofina for kind gifts of fluorinated chemicals.

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