

# Dimerisation of butadiene catalyzed by nickel–tris[(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl]phosphites complexes in fluorocarbon–hydrocarbon biphasic medium

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## Abstract

Cyclodimerisation of butadiene into 1,5-cyclooctadiene can be efficiently performed under fluoruous–organic biphasic conditions using Ni(COD)<sub>2</sub> as catalytic precursor and triarylphosphites bearing long perfluorinated alkyl chain separated from the aromatic ring by an ethylene spacer group as ligand. As found earlier under homogeneous conditions, phosphites with *ortho* substituent are much more active than their *para*-substituted counterpart and a remarkable enhancement of the activity was found when the reaction was carried out in pure fluoruous solvent. Catalyst recovery and reuse were also studied.

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## 1. Introduction

Fine-tuning of the metal environment in homogeneous catalysis allows to obtain high activity and selectivity under much milder conditions than in heterogeneous catalysis. However, the difficulty of the catalyst recovery from the reaction products and its recycle represents the major problem of the homogeneous catalysis. The anchorage of the metal complexes on solid supports both organic and inorganic in order to combine the advantages of both homogeneous and heterogeneous catalysis has been largely studied [1–4]. However, the resulting heterogenized catalytic systems often exhibit lower activity than the corresponding homogenous systems and suffer from severe limitations due to metal leaching [5,6].

An alternative route is to work in a liquid–liquid biphasic medium [7]. Since, the commercial establishment of the two-phase hydroformylation process of propene by Ruhr–Chemie–Rhône–Poulenc, the use of metal complex catalysts with water-soluble ligands has been recognized as an effective method for catalyst product separation [8–10].

Actually, aqueous biphasic catalysis has the advantage to use more safety and environment friendly medium than usual organic solvents, that explains, combined with the easy separation of the catalytic phase by decantation, its increasing importance both for industrial applications and for new reactions and products. Nevertheless, the main drawback of this process is the low reaction rates exhibited by substrates poorly soluble in the water phase (the reaction rate may become economically unviable for example in the case of producing aldehydes from higher olefins) [10].

To overcome this problem, several attempts have been developed to increase the reaction rate in aqueous biphasic catalysis (including for example addition of co-solvents [11], surfactants [12,13], inverse phase transfer catalysts [14,15], amphiphilic ligands [16–20] or supported aqueous phase catalysts [21], ...).

Another way, that has recently aroused increasing interest, has been to perform biphasic catalytic reactions in non-conventional media such as ionic liquids [22] or perfluorocarbons [23,24]. The use of this last class of compounds in liquid–liquid biphasic catalytic reactions is based on the fact that higher perfluorocarbons are usually non-polar compounds, having very low intermolecular interactions, which

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prevents them to be compatible with the most common hydrocarbon products at low temperature. On the other hand, at high temperature, generally the miscibility markedly increases [25]. So, if a catalyst is designed to be selectively soluble in the fluoruous phase, any product that will be in the organic phase can be easily separated after cooling at the end of the reaction, by simple decantation. A strategy to make metal complexes soluble in fluoruous solvents is to modify their ligands by attaching long perfluoroalkyl chains. The temperature dependence of the solubility between the fluoruous and the organic phase has the advantage over other biphasic systems to allow to combine the activity of homogeneous catalysis (at the reaction temperature) with the simplicity of product isolation.

As a part of our ongoing studies in this field, we have recently reported the synthesis of various triarylphosphites modified by long perfluorinated alkyl chains [26,27] and the use of these ligands in rhodium-catalyzed hydroformylation reaction of higher olefins conducted under fluoruous biphasic conditions [28,29]. Among the phosphites synthesized, phosphite **A** and **B** (see Scheme 1) in which an ethylene spacer group between the perfluoroalkyl group and the aromatic ring has been introduced in order to reduce the strong electron withdrawing effect of the fluoruous ponytails, have been found as the more stable, giving the best results in term of catalytic reuse. Thus, in order to determine their scope and limitation, these ligands have been tested in other reactions known to be advantageously catalyzed by transition metal complexes with phosphite ligands.

We now report here our results on a study of nickel-catalyzed cyclodimerisation of butadiene under fluoruous biphasic conditions. The cyclooligomerisation of dienes on nickel catalysts has been extensively studied under homogeneous conditions in particular by Wilke et al. [10,30,31]. It is well-established that the degree of oligomerisation and the distribution of isomers depend on the nature of the ligand used and of its ratio toward the metal.

In the absence of ligand, 1,5,9-cyclododecatrienes (CDT) are selectively formed (mainly the all *trans* isomer) [32]. On the other hand, in the presence of phosphites as ligand, 1,5-

cyclooctadiene (COD) is the main product whereas phosphines direct the reaction toward the formation of vinylcyclohexene (VCH) (with a total selectivity for ligand to metal ratios equal to two or higher)[32,33].

## 2. Experimental

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

### 2.1. Solvents and materials

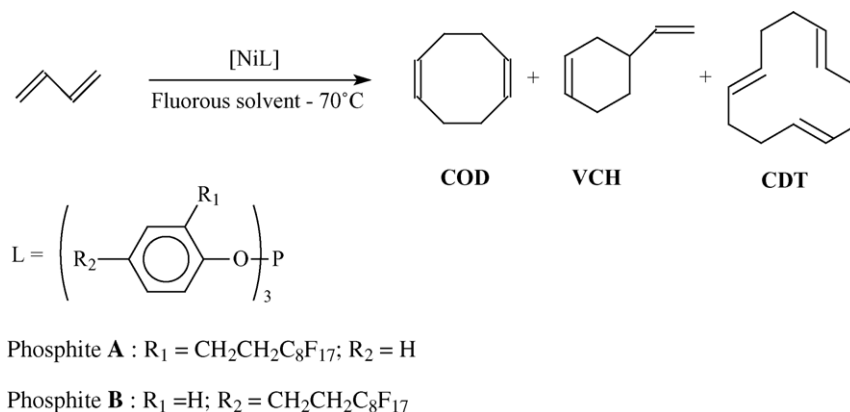
Unless otherwise noted, all materials were obtained from commercial suppliers. 1*H*,1*H*,2*H*,2*H*-perfluorodecyl iodide and 1*H*-perfluorooctane were generously supplied by ATOFINA. All solvents were dried and distilled using standard procedures. Butadiene was used directly from cylinder (>99.9% pure, Air Liquid). 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 prepared following previously described procedure [28]. Ni(COD)<sub>2</sub> was purchased from Strem Chemicals and used without purification.

### 2.2. Product analysis

Gas chromatographies were performed on Chrompack CP9001 gas chromatograph equipped with a CPSil-5CB column (25 m × 0.32 mm) (Chrompack) and a FID detector. Nitrogen was the carrier gas.

### 2.3. Typical cyclodimerisation experiment

Cyclodimerisation experiments were carried out in a glass reactor equipped with a screw cap and PTFE valve. The phosphite used (94 mg,  $5.7 \times 10^{-2}$  mmol) and Ni(COD)<sub>2</sub>



Scheme 1.

(15.7 mg,  $5.7 \times 10^{-2}$  mmol) were introduced into the reactor under nitrogen. Then a well-defined volume of cold liquid butadiene was added. The whole was mixed at low temperature ( $-4^\circ\text{C}$ ) during 15 min (time required to dissolve  $\text{Ni}(\text{COD})_2$  and the ligand in butadiene). After that, 8 mL of cold solvent were added and the solution was stirred for two additional hours at room temperature. The resulting mixture was then heated at  $70^\circ\text{C}$  under stirring. After reaction, the reactor was cooled down to room temperature and depressurized. The two phases were separated and analyzed by gas chromatography.

#### 2.4. Recycling experiments

The first run was carried out as described above with the quantity indicated in Table 6. After 2.5 h of reaction, the reactor was rapidly cooled to  $0^\circ\text{C}$  (ice bath) and carefully depressurized. After 30 min of decantation, the fluoruous and organic phase were separated. The fluoruous phase was reintroduced in the reactor. This one was cooled to  $-20^\circ\text{C}$ ; a new portion of liquid butadiene was added and used in another cyclodimerisation run as described above.

### 3. Results

#### 3.1. Influence of the nature of the solvent

Preliminary experiments were performed in order to check the possibility to use the readily available  $\text{Ni}(\text{COD})_2$  as catalyst precursor for the cyclodimerisation of butadiene under fluoruous biphasic conditions with phosphite **A** (chosen as representative of this class of ligand). In a first time, the reaction was directly carried out after addition of all the components in the reactor. After heating under stirring, only low conversion was observed due to the catalyst decomposition into nickel black. In the same way, various attempts to synthesize the catalyst in perfluorous solvents by displacement of the cyclooctadiene ligands by phosphite **A** before addition of butadiene and reaction, resulted in the decomposition of the nickel complex and once again to modest conversion.

On the other hand, when an organic solvent was used in place of the fluoruous solvent, the reaction took place with good yield whatever the procedure had been used. These observations induced us to pre-form the catalyst using only cold butadiene as solvent, i.e. in the absence of perfluorous compound this one being only added to the reaction medium before starting the reaction. This procedure allowed the reaction to go to completion and, therefore, was applied in all further experiments.

Table 1 shows the influence of the nature of solvent in terms of conversion and selectivity. As expected with nicked catalyst and phosphite ligands, cyclooctadiene was the main product and vinylcyclohexene together with cyclododecatriene, which are formed in small quantities always accompanied it. The selectivity into COD within VCH and CDT did

not change very much according to the solvent used; however, in the case of perfluoromethylcyclohexane, a slight increase in CDT was observed.

On the other hand, the activity markedly varied with the solvent. Actually, in pure organic media, the activity was much lower than in pure fluoruous solvents although in the presence of butadiene, phosphite **A** and, therefore, the catalytic species were soluble in the organic media tested. Nevertheless for a same class of solvent, we found high differences in terms of reactivity. The most effective catalyst was obtained in 1*H*-perfluorooctane where after 1 h the conversion reached 91%; whereas, in perfluoromethylcyclohexane, 2 h were needed to obtain 98% conversion. These differences of behavior according to the nature of the solvent do not seem to be ascribable to a difference of solubility and phase transfer limitation (especially at the reaction temperature where there is only one phase) but rather to a difference of stability of the catalytic species. In this way, when the reaction was conducted in 1*H*-perfluorooctane, precipitation of nickel black was observed at the end of the reaction. This fact, in connection with the decomposition observed when  $\text{Ni}(\text{COD})_2$  was mixed in pure perfluorous solvents with phosphite **A** (vide supra), seems to indicate that in this medium the catalyst with only one phosphite as ligand was only stable in the presence of butadiene, the latter playing the role of ligand to stabilize the catalytic species. When the concentration of butadiene becomes too low, the catalyst decomposes but the beginning of the decomposition depends also on the nature of the fluoruous solvent (in PMCH the catalyst remains stable up to 98% conversion). Conversely, the activity decreases with an increase in the stability of the catalyst species. It is also noteworthy that when the reaction was performed with perfluorous solvent, at the end of the reaction, a good separation of the two phases was only obtained at low temperature ( $0^\circ\text{C}$ ) particularly with PMCH. Moreover, after separation the organic phase formed of the oligomeric products was always colored suggesting that part of the catalyst migrates from the perfluorinated to the hydrocarbon phase, preventing its efficient recycle by means of separation and recovery of the perfluorinated phase. In order to make the demixing of the two phases easier and thus limit the catalyst leaching,

Table 1  
Influence of the nature of solvent in the cyclodimerisation of butadiene catalyzed by  $\text{Ni}(\text{COD})_2$ /phosphite **A** system

Entry	Solvent	Time (h)	Conv. (%)	Selectivity (mol%)		
				COD	VCH	CDT
1	Toluene	4	66	95.8	2.9	1.3
2	Isooctane	4	89	95.4	3.9	0.7
3	PMCH	2	98	93.1	2.7	4.2
4	1 <i>H</i> -PO	1	91	95.2	3.1	1.7
5	Isooctane/PMCH	4	87	95.8	3.5	0.7

Conditions:  $\text{Ni}(\text{COD})_2 = 5.7 \times 10^{-2}$  mmol, phosphite **A** =  $5.7 \times 10^{-2}$  mmol, butadiene = 11.9 mmol (1 mL), solvent = 8 mL,  $70^\circ\text{C}$ ; conv. = conversion, PMCH = perfluoromethylcyclohexane, 1*H*-PO = 1*H*-perfluorooctane.

Table 2

Influence of the nature of solvent in the cyclodimerisation of butadiene catalyzed by Ni(COD)<sub>2</sub>/phosphite **B** system

Entry	Solvent	Time (h)	Conversion (%)	Selectivity (mol%)		
				COD	VCH	CDT
1	Toluene	20	45.5	86.6	10.1	3.3
2	PMCH	2	31	86.3	7.8	5.9
3	1H-PO	2	45	87.3	7.3	5.4

Conditions: Ni(COD)<sub>2</sub> = 5.7 × 10<sup>-2</sup> mmol, phosphite **B** = 5.7 × 10<sup>-2</sup> mmol, butadiene = 11.9 mmol (1 mL), solvent = 8 mL, 70 °C.

an experiment was carried out with a mixture of PMCH and isooctane (1/1, v/v). In this case, the activity was about the same than in pure isooctane (Table 1, entry 5) (i.e. markedly lower than in pure PMCH), thus, the activating effect of the fluoros solvent disappeared.

### 3.2. Influence of the nature of the ligand

All of the catalytic systems obtained with the two fluoros phosphites **A** and **B** exhibited catalytic activity in cyclodimerisation reaction. Nevertheless, there was a great difference of reactivity between the different catalytic systems according to the position of substituent on the aromatic ring of the phosphite used.

As it can be seen in Table 2, the activity, overall yield and selectivity into COD are significantly lower for systems with *para*-substituted ligand **B**, than those found for the bulky *ortho*-substituted ligand **A**. As in the case of **A**, the most active catalytic systems were obtained using pure fluorocarbons as solvents and with the same order of reactivity. However, the systems with ligand **B** were always unstable and during the reaction, precipitation of nickel black was observed leading to limited conversions that did not exceed 50%.

### 3.3. Influence of the phosphite to nickel ratio

The decomposition of the catalytic system in particular with phosphite **B** and the fact that at the end of the reaction under biphasic conditions the organic phases were colored in the case of **A**, prompted us to increase the phosphite to Ni ratio with the aim to increase the solubility of the catalytic species in the fluoros phase at the end of the reaction (by increasing the number of perfluorous chains per nickel) and to stabilize the catalyst.

Table 3

Cyclodimerisation of butadiene catalyzed by Ni(COD)<sub>2</sub>/phosphite **A** system: influence of the P/Ni ratio

Entry	P/Ni	Time (h)	Conversion (%)	Selectivity (mol%)		
				COD	VCH	CDT
1	1	1	60	93.7	2.4	3.9
2	2	1	52	95.1	4.4	0.5
3	3	1	45	92.1	7.1	0
4	4	1	35	91.8	8.2	0

Conditions: Ni(COD)<sub>2</sub> = 5.7 × 10<sup>-2</sup> mmol, butadiene = 11.9 mmol (1 mL), perfluoromethylcyclohexane = 8 mL, 70 °C.

Table 4

Cyclodimerisation of butadiene catalyzed by Ni(COD)<sub>2</sub>/phosphite **B** system: influence of the P/Ni ratio

Entry	P/Ni	Time (h)	Conversion (%)	Selectivity (mol%)		
				COD	VCH	CDT
1	1	2	45	87.3	7.3	5.4
2	2	2	25	88.8	7.6	3.6
3	3	2	19	89.0	7.8	3.2

Conditions: Ni(COD)<sub>2</sub> = 5.7 × 10<sup>-2</sup> mmol, butadiene = 11.9 mmol (1 mL), perfluoromethylcyclohexane = 8 mL, 70 °C.

Tables 3 and 4 show the influence of this ratio on the conversion and selectivity with phosphites **A** and **B**, respectively.

In both cases, a decrease in activity was observed when the ligand/Ni molar ratio increased up to 1. However, this effect was more marked with phosphite **B**.

Using phosphite **A**, the formation of CDT decreased when the P/Ni ratio increased and for a ratio up to 2, CDT was not observed. Concurrently, the quantity of VCH significantly increased and; thus, the COD selectivity remained almost unchanged. Interestingly, at the end of the reaction for P/Ni ratios of 2 or higher, only the fluorinated phase resulted colored, thus indicating that under these conditions the catalyst was stable and only soluble in the fluoros solvent.

In the case of systems with *para*-substituted ligand, the P/Ni ratio had practically no effect on the selectivity of the different products. Moreover, even using a P/Ni ratio of 3, precipitation of nickel black occurred and in spite of the excess of ligand, an orange color of the organic phase was observed, preventing to anticipate an efficient recycling of this catalytic system.

### 3.4. Influence of the butadiene concentration

As the catalytic system with phosphite **A** proved to be more efficient in terms of activity and stability than the one with phosphite **B**, the limitations toward the concentration of butadiene were only studied with this ligand.

Table 5 shows the influence of the butadiene to nickel ratios on the conversion, the selectivity and the turnover frequencies of the catalyst (TOF) at constant quantity of fluoros solvent. As expected, when the quantity of butadiene

Table 5

Cyclodimerisation of butadiene: influence of the quantity of butadiene charged on the catalyst performance

Entry	But/[Ni]	Conversion (%)	Selectivity (mol%)			TOF (h <sup>-1</sup> )
			COD	VCH	CDT	
1	210	80	93.1	2.7	4.2	168
2	420	62				260
3	630	60	93.7	2.4	3.9	378
4	2600	29	94.8	2.3	2.9	740

Conditions: Ni(COD)<sub>2</sub> = 5.7 × 10<sup>-2</sup> mmol, phosphite **A** = 5.7 × 10<sup>-2</sup> mmol, perfluoromethylcyclohexane = 8 mL, t = 1 h, 70 °C.

initially charged increased the conversion after one hour decreased. On the other hand, interestingly the selectivity in COD slightly increased. It also appeared that the concentration of butadiene had a great influence on the TOF (defined as the number of moles of butadiene transformed per hour and per mole of catalyst calculated after 1 h of reaction). Actually, when the butadiene to nickel ratio increased from 210 to 2600, the TOF increased from 168 to 754. Fig. 1 shows that this variation of the TOF expressed as a function of the initial concentration of the butadiene in the reaction medium, was almost linear, which is in accordance with a reaction order of one toward the substrate.

### 3.5. Catalyst recovery and reuse

For the same reasons as those mentioned in the above paragraph, the system with phosphite **A** has been chosen to investigate the recovery and reuse of the catalyst. The ligand/[Ni] ratio was fixed at 4 in order to increase the stability of the catalyst and to retain it more efficiently in the fluorous phase as indicated above. Each run was conducted as previously described and with a high butadiene concentration. The duration of a run was fixed to 2.5 h in order to stop the reaction at about 70% conversion and; thus, to avoid the levelling of performances that could occur when total conversion is reached. Moreover, this procedure has also the advantage to avoid the total consumption of butadiene that proved to be detrimental to the stability of the system. At the end of each test, the two layers were separated by decantation after cooling and a new portion of liquid butadiene was added and the mixture again allowed to react.

During the first three recycle experiments, the activity remained almost unchanged (see Table 5) and at the end of each test the organic phase was colorless. However, at the end of the fourth run, the conversion significantly dropped from 70% to 50% and precipitation of small amounts of nickel black was observed. It also appears from Table 5 that the selectivity only slightly changed during the different recycles. The lowest selectivity in COD (91.1%) was observed after the first run. During the next run, the COD selectivity significantly increased to reach 94.8% and then slowly

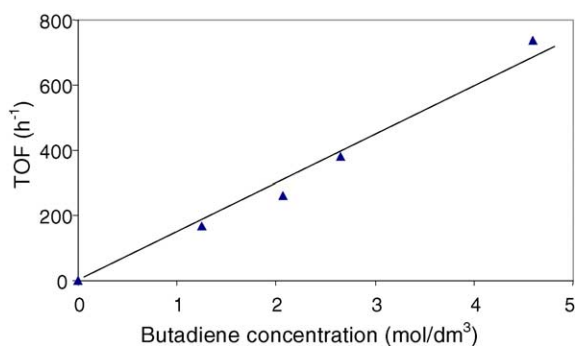


Fig. 1. Cyclodimerisation of butadiene under biphasic conditions: influence of the butadiene concentration on the TOF.

Table 6  
Cyclodimerisation of butadiene under fluorous biphasic conditions: catalyst recovery and reuse

Cycle	Conversion (%)	Selectivity		
		COD	VCH	CDT
1	70.5	91.1	8.9	0
2	71.2	94.8	5.2	0
3	70.5	93	6.8	0
4	50	92.9	7.1	0

Conditions: Ni(COD)<sub>2</sub> = 5.7 × 10<sup>-2</sup> mmol, phosphite **A** = 22.8 × 10<sup>-2</sup> mmol, butadiene = 35.7 mmol, perfluoromethylcyclohexane = 8 mL, t = 2.5 h, 70 °C.

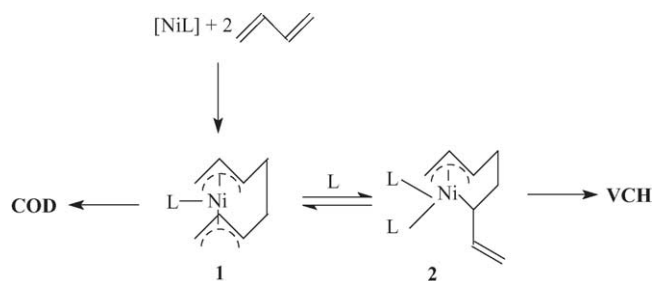
decreased during the third and fourth runs. Due to the high ligand/Ni ratio, CDT was only observed in a trace level after each run.

## 4. Discussion

The results obtained with phosphite **A** differ from those of **B** by a much higher initial rate of the reaction, a better selectivity into COD and a better stability of the catalytic system under fluorous biphasic conditions. Concomitantly, the two phosphites lead to a remarkably higher activity in pure fluorous media than in classical organic solvents or in a mixture of fluorous and hydrocarbon solvents.

The superiority of the catalytic system with phosphite **A** is not surprising since the influence of the steric and electronic properties of the ligand on the activity and selectivity of butadiene dimerisation is well-established under standard homogeneous conditions. Actually, among a series of arylphosphites, bulky *ortho*-substituted phosphites proved to be much more efficient than their *meta* or *para* isomers. For instance, Heimbach et al. have reported that the use of P(OC<sub>6</sub>H<sub>4</sub>-*o*-Ph)<sub>3</sub> allowed to convert 780 g butadiene g<sup>-1</sup> Ni h<sup>-1</sup> with a COD selectivity of 96% whereas using its homologous P(OC<sub>6</sub>H<sub>4</sub>-*p*-Ph)<sub>3</sub> the conversion and selectivity dramatically dropped, respectively, to 75 g butadiene g<sup>-1</sup> Ni h<sup>-1</sup> and 65%. A similar drop in both reactivity and selectivity was also observed going from P(OC<sub>6</sub>H<sub>4</sub>-*o*-Me)<sub>3</sub> to P(OC<sub>6</sub>H<sub>4</sub>-*m*-Me)<sub>3</sub> and finally to P(OC<sub>6</sub>H<sub>4</sub>-*p*-Me)<sub>3</sub> or from P(OC<sub>6</sub>H<sub>4</sub>-*o*-OMe)<sub>3</sub> to P(OC<sub>6</sub>H<sub>4</sub>-*p*-OMe)<sub>3</sub>. The results found in our case are in the same order of magnitude [10,32,33].

As phosphites **A** and **B**, on one hand, and the phosphites bearing organic substituents, on the other hand, behave similarly with respect to activity and selectivity, the cyclodimerisation process under fluorous conditions probably follows a reaction mechanism identical to the one that take place in classical homogeneous conditions. This one initially proposed by Wilke et al. is well-known and recently theoretical investigations (based on density functional theory (DFT) and molecular mechanics (QM/MM)) have provided further insight on the factors that are decisive for the selectivity [34,35]. Thus, the catalytic cycle will not be further discussed here.



It is nevertheless noteworthy that in the presence of an excess of ligand, the equilibrium depicted in Scheme 2 is shifted to the right that corresponds to a higher concentration of the nickel species **2**, which leads selectively to VCH; whereas, the intermediate **1** is the precursor of COD. However, steric hindrance acts in opposite way preventing a significant shifting toward **2** and, therefore, the selectivity into VCH only slightly increases (in contrast with an excess of a small ligand such as CO for which total selectivity in VCH was reported [36]).

The difference of stability in fluoruous solvent between the catalytic systems with phosphites **A** and **B** is difficult to explain since the electronic properties of these two ligands are similar. The instability of the system with **B** is probably due to the decomposition of this phosphite by hydrolysis under the reaction conditions. Indeed the condensation of butadiene prior to use and the cooling of the reactor before introduction of butadiene can induce the condensation of a small quantity of water in the reaction medium in spite of the care taken to avoid this phenomenon. The steric hindrance due to the fluoruous ponytail in the case of phosphite **A** has the effect to reduce the reactivity of its P–O bond that can explain its better stability.

The difference of reactivity observed with both fluoruous phosphite, depending on whether the reaction takes place in pure fluoruous media or in organic solvents, is also surprising and the reason for this higher rate is not clear at the present time since phosphites **A** or **B** are soluble in the organic solvents tested in the presence of butadiene specially at the reaction temperature. However, this finding is not unprecedented: for instance, a similar enhancement of the activity has been reported by Cole-Hamilton et al. [37] in the case of 1-octene hydroformylation using  $P(O-4-C_6H_4C_6F_{13})_3$  as ligand. This behavior was attributed to a difference of solubility of the gases in the liquid phase and/or to a difference of solvation of the various complexes in the different solvent systems. In our case, the difference in activity is probably related to this last explanation.

Finally, catalyst recycle and reuse experiments under biphasic conditions were only partially successful since the activity and selectivity remained unchanged during the three first runs but the conversion dramatically fell during the fourth run. The partial decomposition of the catalyst proved by the formation of some nickel black during the fourth run (al-

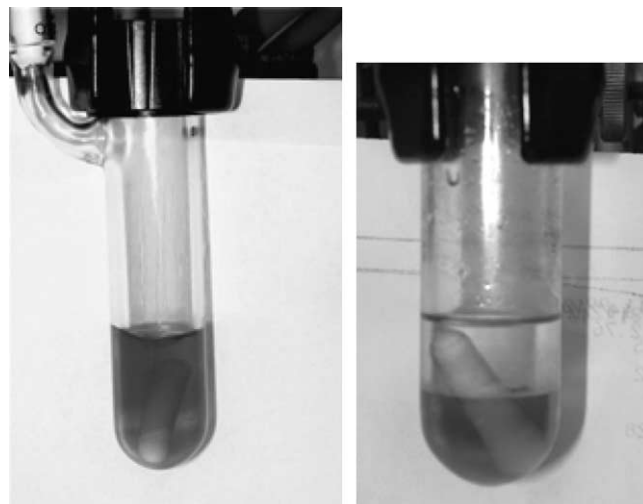


Fig. 2. Catalyst recovery and reuse: reaction mixture before experiment after adding all the components (left picture) and after four runs (right picture).

though, the fluoruous phase remained colored, see Fig. 2), accounts probably for the decrease of the activity. Even with an excess of ligand the catalyst is only stable during the first runs. Due to the solubility of phosphite **A** in butadiene, it is likely that there is a leaching of a part of the ligand during the different recycles (and probably also a leaching of the catalyst but at a lower extent since the organic phase is practically colorless). The leaching of the ligand should give rise to a decrease of its concentration during the next recycle and then to an increase of the activity. However, concomitantly the leaching of the catalyst acts in the reverse sense, thus, the apparent activity remains almost unchanged. Nevertheless, when the concentration of phosphite **A** becomes too low, the catalytic system starts to decompose leading to a drop of the activity.

## 5. Conclusion

The cyclodimerisation of butadiene into cyclooctadiene under fluoruous biphasic conditions can be successfully carried out using  $Ni(COD)_2$  as catalytic precursor and a system that consists of a fluoruous solvent and a triarylphosphite bearing a long fluoruous ponytail on each three aryl groups. Surprisingly, the use of pure fluoruous solvent leads to much higher activities than in classical hydrocarbon solvents or in mixtures of fluoruous and hydrocarbon solvents.

As in standard homogeneous conditions, the position of the substituent on the aryl ring has a great influence on the activity but more unexpected also on the stability of the catalyst; the systems with *ortho*-substituted phosphite being both the more active and the more stable.

This behavior is tentatively assigned to a better stability of the P–O bonds due to steric hindrance towards some side reactions such as hydrolysis, and is in line with the same observation made during our work using the same ligand in

hydroformylation where a reaction involving phosphite ligands and aldehydes was found to be responsible for a decrease in the ligand metal ratio after several runs [28].

We have also shown with catalytic systems obtained from *ortho*-substituted phosphite that some recycles of the catalyst can be made without loss of its efficiency. However, the lack of long-term stability of the catalytic system resulting probably from the leaching of the ligand, limits the number of recycles that can be carried out.

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