Propylene oligomerization by nickel catalysts in biphasic fluorinated systems

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Abstract

In the present paper, the dimerization of propylene to 2,3-dimethylbutenes (DMB) with fluorinated nickel precursors, such as bis(tetradecafluoro-4,6-nonandionate)nickel(II)·2dmf [Ni(tdfnd)$_2$(dmf)$_2$] and bis(hexafluoro-2,4-pentandionate)nickel(II) [Ni(hfacac)$_2$], in combination with phosphine ligands and aluminium alkyl promoters, was investigated in fluorous solvents as reaction medium with the aim of realizing a catalytic process operating in a fluorinated biphasic system (FBS). The role of the nature of the perfluorinated medium was carefully examined and significant productivities (TOF up to ∼25,000 h^{-1}) were ascertained. Also fluorinated phosphine ligands were used with the aim of improving catalyst solubility in the fluorinated phase. Finally, with the aim to reach the same goal, tris(pentafluorophenyl)borane [B(C$_6$F$_5$)$_3$], was also employed in the place of organoaluminium co-catalysts. However, in all the catalytic experiments a progressive migration of the catalyst towards the hydrocarbon phase, generated by the formation of the oligomeric products, was observed, thus evidencing the difficulty of realizing a FBS olefin oligomerization catalytic process, at least under the adopted conditions. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Reactions in homogeneous phase catalyzed by transition metal complexes have always focused the research interest due to their high activity and selectivity. However, the main drawback of these processes is represented by the catalyst recovery from the reaction products and its recycle. With the aim to combine the advantages of the homogeneous catalysis with those of the heterogeneous one, the anchorage of the metal complexes on solid supports, both organic and inorganic, has been largely applied [1–5].

However, this approach suffers of severe limitations, particularly in terms of metal leaching and lower activity of the resulting heterogenized catalytic systems [6,7].

An alternative route is to work in a liquid–liquid biphasic medium, frequently applied in separation procedures and synthetic catalytic processes [8], where it is essential for the success of the operation

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that catalyst and reagents may be soluble in one phase and the reaction products in the other one. In fact, in this way the catalytic process may occur in homogeneous phase and at the same time the catalyst may be easily recovered by separation of the two phases.

The concept of catalysis in a double layer was firstly industrially applied in the SHOP process for the production of α-olefins from ethylene [9], where the nickel catalyst is soluble at high temperature and pressure in 1,4-butandiol, whereas the reaction products generate another phase which may be easily separated. Another example is represented by Hoechst olefin hydroformylation processes which operate with a proper phosphino-modified rhodium catalyst soluble in water phase, where the aldehyde products are completely insoluble [8–11]. More recently, an increasing attention was devoted to the possibility to use perfluorinated solvents for generating a liquid phase where the catalyst may work, the reaction products being collected in another phase [12,13]. In principle, this would be realized quite easily because perfluorohydrocarbons are usually non-polar compounds having very low intermolecular interactions which prevent them to be compatible with the most common organic products. Of course, it is essential that in this picture both the catalytic system and the reagents may be appreciably soluble in the fluorinated phase. This may be approached by introducing in the metal catalyst precursor one or more ligands characterized by long perfluorinated alkyl chains. This novel technique operating in a "fluorinated biphasic system" (FBS)

complexes which, contrarily to the reaction products, are soluble in perfluorinated solvents [15]. More recently, Keim studied the oligomerization of olefins in FBS catalysis by the use of the β-diketonate nickel complex (**I**) (Chart 1) modified by a long perfluorinated alkyl chain [16]. However, the activity of the system in ethylene oligomerization resulted rather low (TOF up to $2500\,h^{-1}$) and a certain metal release towards the hydrocarbon phase was observed.
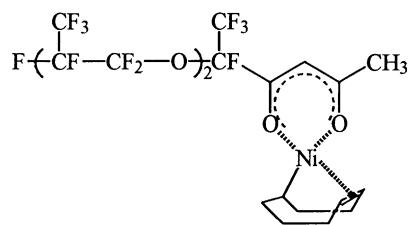
I

Chart 1

In this context, very recently we succeeded to prepare the bis(tetradecafluoro-4,6-nonandionate)-nickel(II)·2dmf [Ni(tdfnd)$_2$(dmf)$_2$] (**II**) (Chart 2) which was found to be very active in the oligomerization of propylene in the presence of phosphine ancillary ligands and organoaluminium co-catalysts [17]. Therefore, in the present paper the activity and selectivity of nickel catalysts based on **II** as well as on bis(hexafluoro-2,4-pentandionate)nickel(II) [Ni(hfacac)$_2$] (**III**) precursors (Chart 2) will be studied in the dimerization of propylene to 2,3-dimethylbutenes (DMB) with the aim of realizing a FBS catalytic process.
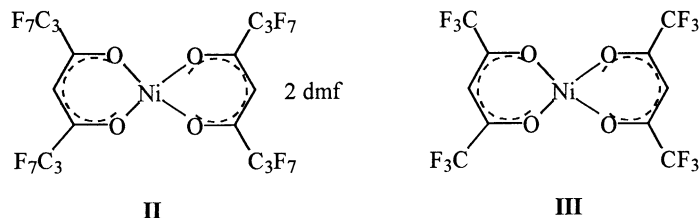
II   **III**

Chart 2

may be considered as the most recent approach in the biphasic catalysis [14]. An interesting example of FBS catalysis is represented by the oxidation of aldehydes to the corresponding acids by nickel catalysts based on bis(perfluorinated-β-diketonate)nickel(II)

Particular attention will be devoted to the nature of the perfluorinated medium adopted for the reaction process. The use of fluorinated phosphine ligands for improving catalyst solubility in the fluorinated phase will be also considered. Finally,

tris(pentafluorophenyl)borane [B(C$_6$F$_5$)$_3$], recently used for the activation of Brookhart-type nickel catalysts in ethylene polymerization [18], will be also checked as co-catalyst in the place of organoaluminium compounds with the aim of improving catalyst solubility in the fluorinated phase and hence readily obtaining its separation from the reaction products as well as its recyclability.

2. Experimental

All manipulations were carried out under dry argon in Schlenk-type vessels, using anhydrous, air free, reagents and solvents.

2.1. Materials

Anhydrous toluene (Baker) and *n*-hexane (Carlo Erba) were obtained by distillation on K/Na alloy under dry argon and stored on molecular sieves (4 Å). *N,N*-dimethylformamide (dmf) (Aldrich) was purified by distillation at reduced pressure.

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentandionate)Ni [Ni(hfacac)$_2$] (**III**) (Aldrich), sodium methoxide (MeONa) (Aldrich), cupric acetate Cu(OAc)$_2$ (Carlo Erba), nickel chloride hexahydrate (NiCl$_2$·6H$_2$O) (Carlo Erba), tricyclohexylphosphine (PCy$_3$) (Aldrich), triisopropylphosphine (P^{i}Pr$_3$) (Fluka), tris(pentafluorophenyl)phosphine [P(C$_6$F$_5$)$_3$] (Aldrich), monochlorodiisopropylphosphine (ClP^{i}Pr$_2$) (Aldrich), pentafluorobromobenzene (Aldrich), *n*-butyllithium (BuLi) (Aldrich) in *n*-hexane solution (2.5 M), ethylaluminium sesquichloride (Et$_3$Al$_2$Cl$_3$) (Aldrich) in toluene solution (0.91 M), methylalumoxane (MAO) (Witco) in toluene solution (4.5 M) and tris(pentafluorophenyl)borane (Aldrich) were stored under dry argon and used as received.

Perfluorohexane (Aldrich), perfluorodecalin (Aldrich) and perfluorobenzene (Aldrich) were degassed by several freeze-thaw cycles and stored under dry argon.

Methyl heptafluorobutanoate (MHFB) (Fluorochem Ltd.) and methyl-heptafluoropropyl-ketone (MHFPK) (Fluorochem Ltd.) were stored at −20 °C and used as received.

The perfluoroether Galden HT110$^®$, kindly supplied by Ausimont and having an average molecular weight of 580, was distilled and stored under dry argon. Its molecular structure is represented as follows: CF$_3$–{[O–CF(CF$_3$)–CF$_2$]$_n$–[O–CF$_2$]$_m$}–O–CF$_3$. Propylene (Ucar) was used as received.

Bis(1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonandionate)nickel(II)·2dmf [Ni(tdfnd)$_2$(dmf)$_2$] (**II**) was prepared as previously described [17], according to a general procedure reported for the synthesis of nickel complexes with other perfluorinated ligands [19]. mp = 76 °C. Calc. for C$_{28}$H$_{14}$O$_6$N$_2$F$_{28}$Ni: C 31.6%, H 1.3%, O 9%, N 2.6%, F 49.9%, Ni 5.5%. Found: C 31.8%, H 1.5%, F 50.3%. FT-IR (KBr disc): 1651 (ν_{CO}), 1380 ($\nu_{as_{CF_3}}$), 1345 ($\nu_{as_{CF_2}}$), 1260 ($\nu_{s_{CF_3}}$), 1245 ($\nu_{s_{CF_2}}$) cm^{-1}. ^{19}F NMR: $\delta = -80$ (s, 3F, -CF$_3$), -120 (s, 4F, -CF$_2$).

Pentafluorophenyldiisopropylphosphine [(C$_6$F$_5$)P^{i}Pr$_2$] was prepared according to a general procedure described for other differently substituted phosphines [20]. In particular, 5 ml (40 mmol) of pentafluorobromobenzene in 500 ml of anhydrous *n*-hexane were introduced under dry argon in a 1 l flask equipped with a dropping funnel, a condenser and a magnetic stirrer and then cooled at −78 °C. Subsequently, 40 mmol of BuLi in *n*-hexane solution were added dropwise. After 1 h under vigorous stirring, 3.07 g (20 mmol) of ClP^{i}Pr$_2$ were added at −78 °C. The reaction mixture was warmed up to room temperature and the liquid phase, after separation from the solid LiBr by siphoning off, was evaporated under vacuum to give a liquid residue. This was distilled (bp = 120 °C/1 mmHg) to afford 4.2 g (14.8 mmol) (74% yield) of pure C$_6$F$_5$P^{i}Pr$_2$ which was characterized by gas chromatography–mass spectrometry (GC–MS), FT-IR, ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR.

FT-IR (liquid between two KBr discs): 2962 ($\nu_{as_{CH_3}}$), 2930 ($\nu_{as_{CH}}$), 2893 ($\nu_{s_{CH_3}}$), 2870 ($\nu_{s_{CH}}$), 1638 ($\nu_{C=C}$, aromatic), 1466 ($\delta_{cis\,CH_3}$), 1386 and 1368 ($\delta_{gem\,CH_3}$), 1087 (ν_{CF}, aromatic) cm^{-1}. ^{1}H NMR: $\delta = 2.45$ (hept, 1H, CH), 1.32 (hept, 1H, CH), 1.14 (dd, 6H, CH$_3$) and 0.96 (dd, 6H, CH$_3$) ppm. ^{13}C NMR: $\delta = 20.4$ (m, CH$_3$), 23.4 (dt, $^1J_{P-C} = 12$ Hz, $^4J_{C-F} = 4$ Hz), 134.7, 139.9, 146.4, 151.2 (m, aromatic) ppm. ^{19}F NMR: $\delta = -128.0$ (dt, 2F, *ortho*-aromatic), -151.3 (t, 1F, *para*-aromatic), -161.2 (dt, 2F, *meta*-aromatic) ppm. ^{31}P NMR: $\delta = 2.0$ (t, $^3J_{P-F} = 35$ Hz) ppm. GC–MS: $m/z = 284$ ($M^{•+}$, 62.3%), 242 ($M^{•+} - C_3H_6$, 36.1%), 200 (($M^{•+} - 2C_3H_6$, 34.4%), 43 (C$_3$H$_7$, 100%).

2.2. Catalytic propylene oligomerization experiments

Catalytic batch experiments were performed in a 250 ml mechanically stirred Büchi glass reactor, equipped with a jacket circulating cooling fluid in order to maintain the reaction temperature at the desired value. The proper amount of $Ni(hfacac)_2$ or $Ni(tdfnd)_2(dmf)_2$ (0.02–0.042 mmol) was introduced under dry argon into a Schlenk-type vessel and dissolved in the appropriate solvent at the reflux temperature. When either MAO or its mixtures with $Et_3Al_2Cl_3$ were used as co-catalyst, after cooling at 50 °C, the desired amount of PR_3, dissolved in the reaction solvent, was slowly added. Subsequently, the solution of the nickel/phosphine adduct was transferred into the reactor at room temperature and, under propylene atmosphere, the suitable amount of aluminium co-catalyst (Al/Ni = 100 mol/mol) was added. When $B(C_6F_5)_3$ was used as co-catalyst, the nickel precursor was introduced in the Schlenk vessel as previously mentioned, then Et_3Al and the borane were added (Al/Ni and B/Ni = 5 and 1.5 mol/mol, respectively) eventually in the presence of PCy_3 as ancillary ligand; then the catalytic system was heated at 40 °C for 1 h under propylene (1 atm) and subsequently transferred into the glass reactor. In all cases the temperature was adjusted to the desired value and the reactor was finally pressurized with propylene up to 3 atm. The pressure was manually held at that value by repeated olefin feeds. In all cases the reaction was stopped by degassing the unreacted propylene through a trap cooled at −10 °C, then the liquid products were collected, weighted and analyzed by gas-chromatography (GC).

2.3. Catalytic ethylene oligomerization experiments

Catalytic batch experiments were performed in a 150 ml rocking stainless steel autoclave. In a typical procedure $Ni(hfacac)_2$ (0.042 mmol) was introduced under ethylene atmosphere into a Schlenk-type vessel and dissolved in toluene at room temperature. Then the proper amount of Et_3Al and/or $B(C_6F_5)_3$ were added and the resulting mixture was transferred into the autoclave under ethylene atmosphere. Finally ethylene was charged up to 80 atm and the reaction temperature adjusted at the desired value by immersing the autoclave in a thermostatted oil-bath.

The pressure was manually held by repeated ethylene feeds. The reaction was stopped by fast cooling the autoclave and degassing unreacted ethylene through a trap cooled at −10 °C, then the liquid products were collected, weighted and analyzed by GC.

2.4. Analytical procedures

The oligomeric olefin mixtures were analyzed by GC on a Hewlett-Packard 5890 chromatograph equipped with a flame ionization detector, a HP PONA 50 m capillary column with a stationary phase based on poly(methyl-phenyl-siloxane) and a HP 3396 integrator. *n*-Heptane was used as internal standard. The following temperature program of the oven was adopted: 25 °C for 45 min, then the temperature was increased by a 8 °C/min heating until 230 °C was reached; this value was maintained constant for further 40 min. In this way it was possible to separate the olefins of C_4–C_{12} cuts. The individual components were identified by comparison with authentic samples.

Elemental analysis (C, H, F) of the samples was performed at Enitecnologie SpA laboratories, S. Donato Milanese (MI).

2.5. Physicochemical measurements

FT-IR (Fourier transform infrared) spectra were carried out on KBr pressed pellets of the samples by using a Perkin-Elmer 1750 spectrophotometer. The spectral data were processed by a IRDM Perkin-Elmer software.

^{1}H, ^{19}F, {^{1}H}–^{31}P NMR (nuclear magnetic resonance) spectra were performed by a Varian XL Gemini 200 spectrometer operating at 200, 188.16 and 80.95 MHz, respectively, on samples in $CDCl_3$ solution. Tetramethylsilane (TMS) was used as internal standard for ^{1}H NMR spectrometry, whereas $CFCl_3$ and 85% H_3PO_4 were used as external standards for ^{19}F- and ^{31}P NMR spectrometry, respectively.

Melting points were determined by a Kofler Model Reichter Thermovar.

The structure of $Ni(tdfnd)_2(dmf)_2$ was determined on a single crystal mounted on a Bruker P4 diffractometer as previously described [17].

3. Results and discussion

In order to check if it is possible to work in FBS mode when propylene oligomerization is carried out in the presence of homogeneous nickel catalysts based on fluorinated β-diketonate precursors, preliminary experiments were performed in several perfluorinated solvents by using $Ni(hfacac)_2$ in combination with the basic and bulky PCy_3 as ancillary ligand as well as with different organoaluminium co-catalysts.

3.1. Propylene oligomerization by Ziegler–Natta-type catalysts based on bis(fluorinated-β-diketonate)nickel(II) precursors in perfluorinated solvents

Taking into account that the $Ni(hfacac)_2$(**III**)/PCy_3/ $MAO/Et_3Al_2Cl_3$ system was found to be highly active and selective in the dimerization of propylene to DMB in toluene solution [17] (entry 1, Table 1), some experiments were performed with the above catalytic

system, under the same conditions as in entry 1, by progressively increasing the amount of perfluorohexane with respect to toluene (entries 2–6, Table 1).

When the toluene/perfluorohexane volume ratio was changed from 3 to 0.5, only a slight decrease of regioselectivity to DMB within the C_6 cut was observed (entries 2–5). This behaviour was accompanied by a similar trend as far as the yield of DMB (*Y*) is concerned. The activity of the catalyst did not changed very much; however, on increasing the relative amount of perfluorohexane, the productivity of the process slightly decreased, except for the toluene/perfluorohexane volume ratio equal to one, where a maximum was obtained. Finally, when perfluorohexane was used as unique reaction solvent an appreciable decrease of the catalyst performances was obtained (entry 6), regioselectivity, overall yield to DMB as well as productivity values being significantly lower than those found in toluene solution [17] (entry 1). However, these data clearly indicate that perfluorohydrocarbons do not kill the catalytic

Table 1

Propylene oligomerization by the $Ni(hfacac)_2$ (**III**)/$PCy_3/MAO/Et_3Al_2Cl_3$ catalytic system: influence of the nature and of the relative amount of perfluorinated solvent on the catalyst performances[a]

Entry	Reaction solvent				Dimers (%)			C_6 (%)	C_9 (%)	C_{12+} (%)	Y[b] (%)	TOF[c] (h^{-1})
	Type	Volume (ml)	Type	Volume (ml)	DMB	MP[d]	HEX[e]					
1[f]	Toluene	20	–	–	77.6	21.2	1.2	82.9	14.8	2.3	64.0	14200
2	Toluene	30	C_6F_{14}[g]	10	72.1	26.0	1.9	80.5	16.1	3.4	58.0	14500
3	Toluene	20	C_6F_{14}[g]	10	70.6	27.2	2.2	78.0	17.7	4.3	55.1	12700
4	Toluene	10	C_6F_{14}[g]	10	72.8	26.0	1.2	70.3	22.6	7.1	51.2	16200
5	Toluene	7	C_6F_{14}[g]	14	74.4	23.8	1.8	74.9	20.4	4.7	55.7	12400
6	–	–	C_6F_{14}[g]	20	60.0	35.1	4.9	81.9	14.9	3.2	49.1	8900
7	Toluene	9	$C_{10}F_{18}$[h]	3	64.1	33.4	2.5	83.3	13.7	3.0	53.4	24100
8	Toluene	10	$C_{10}F_{18}$[h]	10	65.8	32.5	1.7	73.6	19.6	6.8	48.4	18800
9	Toluene	14	C_6F_6[i]	7	66.6	30.5	2.9	78.7	17.1	4.2	52.4	14900
10	Toluene	10	C_6F_6[i]	10	72.4	25.8	1.8	76.3	18.7	5.0	55.2	24800
11[j]	–	–	C_6F_6[i]	15	81.3	17.3	1.4	56.0	25.6	18.4	45.5	1500

[a] Reaction conditions—**III**: 0.042 mmol; $MAO/Et_3Al_2Cl_3 = 6$ mol/mol; Al/Ni = 100 mol/mol; P/Ni = 2.2 mol/mol; $P_{C_3H_6} = 3$ atm, time: 1 h; temperature: $-5\,^{\circ}C$.

[b] Overall yield to DMB, evaluated as percentage of DMB in the C_6 cut × percentage of C_6 cut in the oligomeric products.

[c] Turnover frequency, determined as mole of converted propylene/(mole of Ni × h).

[d] Methylpentenes.

[e] *n*-Hexenes.

[f] See [17].

[g] *n*-Perfluorohexane.

[h] Perfluorodecalin

[i] Perfluorobenzene.

[j] MAO was used as unique co-catalyst (Al/Ni = 100 mol/mol) and $0\,^{\circ}C$ was adopted as reaction temperature.

system, the TOF value being still rather high. Moreover, it is noteworthy that in all cases where a mixture toluene/perfluorohexane was used as reaction medium only the toluene phase resulted coloured during the reaction process, thus indicating that the catalyst, despite the presence around the nickel of a perfluorinated diketonate ligand, was mostly soluble in the aromatic hydrocarbon phase. This was confirmed by the data obtained in entry 6 where only perfluorohexane was used as solvent. In fact, as the reaction proceeded and the oligomeric products were formed, the hydrocarbon phase generated by the formation of the oligomeric products progressively became coloured, thus, suggesting that the catalyst migrated from the perfluorinated to the hydrocarbon phase. With the aim to approach a catalytic FBS process, perfluorohexane was substituted by perfluorodecalin (entries 7 and 8, Table 1) and perfluorobenzene (entries 9–10, Table 1). The replacement of perfluorohexane by perfluorodecalin, although improved the productivity of the catalyst, did not increased its performances in terms of regioselectivity and overall yield to DMB. Moreover, also in these cases the catalyst remained substantially soluble only in the hydrocarbon phase, thus preventing its recycle by means of the separation and recovery of the perfluorinated phase. An analogous trend was observed by using toluene/perfluorobenzene mixtures as reaction medium, although the comparison of entries 4, 8 and 10, where equal relative amounts of toluene and perfluorinated solvents were used, clearly indicates that the best performances were obtained when perfluorobenzene was adopted. However, when this was used as unique solvent and MAO was employed as co-catalyst (entry 11), a drop of productivity was observed. Moreover, notwithstanding a significant improvement of regioselectivity to DMB within the C_6 cut (81.3%), a decrease of the overall yield to DMB, due to the shift of the reaction products to higher oligomers, was ascertained.

Taking into account that the $Ni(tdfnd)_2(dmf)_2$ complex (**II**) is characterized by diketonate ligands with longer perfluoroalkyl chains, nickel catalysts based on this precursor were checked for propylene oligomerization with the aim to confine them in the perfluorinated phase more firmly with respect to those prepared from **III**, thus allowing to realize a BFS process.

As reported in Table 2, the catalyst **II**/PCy$_3$/MAO/Et$_3$Al$_2$Cl$_3$ displayed in toluene solution (entry 12)

a higher activity with respect to the corresponding catalyst from **III** (entry 1, Table 1) [17], although lower regioselectivity and overall yield to DMB were observed. However, when a toluene/perfluorohexane mixture (1/1, v/v) was adopted (entry 13, Table 2) a halved activity was observed as compared with entry 2 (Table 1) where the **III**/PCy$_3$/MAO/Et$_3$Al$_2$Cl$_3$ catalyst was used. When perfluorohexane was adopted as unique reaction solvent (entry 14, Table 2) similar activity and overall yield to DMB were observed as compared with entry 13, although an improvement of regioselectivity to DMB within the C_6 cut occurred. The increase of the relative amount of the phosphine ancillary ligand with respect to the nickel precursor from 2.2 to 3 mol/mol (entry 15, Table 2) caused an improvement of catalyst productivity, the other performances remaining substantially unchanged. However, in all these experiments, despite the increased length of the perfloroalkyl chain in the diketonate ligand of **II** as compared with **III**, no evidence of a FBS process occurred, the catalyst still being mainly soluble in the oligomers hydrocarbon phase.

With the aim to check if even the very low amount of toluene (<1 ml) introduced in the reactor with the organoaluminium co-catalysts, would be responsible for the preferential solubility of the catalyst in the hydrocarbon phase, an analogous experiment as in entry 15 was done, but using a toluene free MAO sample as unique co-catalyst (entry 16, Table 2). This was made possible by precipitating MAO from its toluene solution with *n*-hexane. This procedure allowed also to eliminate trimethylaluminium (Me$_3$Al) which always accompanies MAO in the commercial product. The similar performances obtained in entry 16 with respect to the corresponding entry 15, may be explained assuming that the detrimental effect of Me$_3$Al in MAO is balanced by the co-presence of Et$_3$Al$_2$Cl$_3$. Indeed, the negative effect of Me$_3$Al, alone or as component of MAO, was previously evidenced for homogeneous and heterogenized nickel catalysts based on β-dithioketonate ligands [21,22].

However, when the P/Ni molar ratio was increased up to 4 (entry 17, Table 2) a decrease of productivity was observed, the other performances remaining almost unchanged, owing to an increased coordinative competition between the excess phosphine ligand and the olefin. The use of perfluorobenzene alone as

Table 2

Propylene oligomerization by Ni(tdfnd)$_2$ (**II**)/PCy$_3$/organoaluminium catalytic systems: influence of the nature of organoaluminium co-catalyst and perfluorinated solvent on the catalyst performances[a]

Entry	**II** (mmol)	P/Ni (mol/mol)	Solvent		Dimers (%)			C$_6$ (%)	C$_9$ (%)	C$_{12+}$ (%)	Y[b] (%)	TOF[c] (h^{-1})
			Type	Volume (ml)	DMB	MP[d]	HEX[e]					
12	0.029	2.2	Toluene[f]	20	70.5	27.1	2.4	77.4	17.5	5.1	54.6	23200
13	0.020	2.2	C$_6$F$_{14}$[g,h]	10	63.9	31.7	4.4	75.6	17.5	6.9	48.3	7100
14	0.023	2.2	C$_6$F$_{14}$[g]	20	75.7	22.4	1.9	70.9	19.5	9.6	53.7	6700
15	0.039	3.0	C$_6$F$_{14}$[g]	20	71.2	27.0	1.8	75.2	18.0	6.8	53.5	11400
16[i]	0.039	3.0	C$_6$F$_{14}$[g]	30	64.1	34.0	1.8	82.9	15.1	2.0	53.1	11300
17[i]	0.039	4.0[j]	C$_6$F$_{14}$[g]	20	67.0	30.6	2.4	78.7	17.1	4.2	52.7	8800
18	0.023	2.2	C$_6$F$_6$[k]	10	72.3	25.6	2.1	74.3	19.2	6.5	53.7	20100
19	0.039	2.2	Galden[l]	20	58.8	37.9	3.3	84.9	13.2	1.9	49.9	6800

[a] Reaction conditions—MAO/Et$_3$Al$_2$Cl$_3$: 6 mol/mol unless otherwise specified; Al/Ni = 100 mol/mol; $P_{C_3H_6}$ = 3 atm; time: 1 h; temperature: −5 °C.

[b] Overall yield to DMB, evaluated as percentage of DMB in the C$_6$ cut × percentage of C$_6$ cut in the oligomeric products.

[c] Turnover frequency, determined as mole of converted propylene/(mole of Ni × h).

[d] Methylpentenes.

[e] *n*-Hexenes.

[f] See [17].

[g] *n*-Perfluorohexane.

[h] A toluene/perfluorohexane mixture (1/1, v/v) was used.

[i] MAO free of toluene and Me$_3$Al, obtained by precipitation with *n*-hexane, was used as unique co-catalyst (Al/Ni = 100 mol/mol).

[j] Carried out by using three equivalents of phosphine with respect to Ni during the preparation of the catalytic system and one additional equivalent in the reactor.

[k] Perfluorobenzene.

[l] Perfluoroether (see Section 2).

reaction medium (entry 18, Table 2) did not substantially modified the chemo- and regioselectivity of the catalyst, although a significant increase of productivity was observed. Finally, the use of the Galden perfluoroether as reaction solvent (entry 19, Table 2) appreciably reduced both the regioselectivity to DMB and catalyst productivity. It is noteworthy that in entries 16 and 17, carried out in rigorous absence of toluene, the catalyst once again was preferentially solubilized by the hydrocarbon phase progressively formed by the oligomeric products.

With the aim to increase the solubility in the perfluorinated phase of the catalytic system based on **II**, some experiments were done by adopting as ancillary ligand the properly synthesized P^{i}Pr$_2$(C$_6$F$_5$) which in turn contains a perfluorinated phenyl moiety.

As reported in Table 3, when toluene as solvent and a MAO/Et$_3$Al$_2$Cl$_3$ (6:1) mixture as co-catalyst were used (entry 20), the resulting catalyst displayed

in toluene modest productivity (TOF = 1100 h^{-1}) and quite low regioselectivity to DMB (∼50%).

Better performances were obtained when the same catalytic system was allowed to work in Galden as solvent (entry 21, Table 3). Finally, when MAO was adopted as unique aluminium co-catalyst (entry 22, Table 3) a quite low activity was achieved in toluene solution (TOF = 850 h^{-1}), although a better regioselectivity to DMB was obtained (67.8%). It is noteworthy that, despite the presence of partially fluorinated phosphine and perfluoroalkyl-β-diketonate ligands around the nickel sites, no evidence of a preferential solubility of the catalyst system occurred in a perfluorinated solvent such as Galden (entry 21).

Therefore, the addition of a perfluorinated phosphine, such as P(C$_6$F$_5$)$_3$, to **II** in the presence of different organoaluminium co-catalysts was checked in order to improve catalyst solubility in perfluorinated solvents and hence to realize a BFS catalysis.

Table 3
Propylene oligomerization by Ni(tdfnd)$_2$ (**II**)/PR$_3$/organoaluminium catalytic systems: influence of the nature of catalyst components as well as of the perfluorinated solvent on their performances[a]

Entry	PR$_3$	Al co-catalyst	Solvent	Dimers (%)			C$_6$ (%)	C$_9$ (%)	C$_{12+}$ (%)	Y^b (%)	TOF[c] (h^{-1})
				DMB	MP[d]	HEX[e]					
20	P^{i}Pr$_2$(C$_6$F$_5$)	MAO/Et$_3$Al$_2$Cl$_3$[f]	Toluene	50.8	44.4	4.9	77.4	17.4	5.2	39.3	1100
21	P^{i}Pr$_2$(C$_6$F$_5$)	MAO/Et$_3$Al$_2$Cl$_3$[f]	Galden[g]	57.0	40.3	2.8	82.7	14.0	3.3	47.1	2400
22	P^{i}Pr$_2$(C$_6$F$_5$)	MAO	Toluene	67.8	30.0	2.2	55.2	26.3	18.5	37.4	850
23	P(C$_6$F$_5$)$_3$	MAO	Toluene	7.6	74.0	18.5	93.8	6.2	0.0	7.1	6300
24	P(C$_6$F$_5$)$_3$	MAO/Et$_3$Al$_2$Cl$_3$[f]	C$_6$F$_{14}$[h]	7.5	74.1	18.5	93.2	6.8	0.0	7.0	4900
25	P(C$_6$F$_5$)$_3$	MAO	C$_6$F$_{14}$[h]	9.5	65.3	25.2	89.0	9.2	1.8	8.5	2900
26	P(C$_6$F$_5$)$_3$	MAO[i]	Galden[g]	8.1	74.2	17.8	91.7	7.7	0.6	7.4	2700

[a] Reaction conditions—**II**: 0.04 mmol; Al/Ni = 100 mol/mol; P/Ni = 2.2 mol/mol; solvent: 20 ml; $P_{C_3H_6}$ = 3 atm; time: 1 h; temperature: −5 °C.

[b] Overall yield to DMB, evaluated as percentage of DMB in the C$_6$ cut × percentage of C$_6$ cut in the oligomeric products.

[c] Turnover frequency, determined as mole of converted propylene/(mole of Ni × h).

[d] Methylpentenes.

[e] n-Hexenes.

[f] MAO/Et$_3$Al$_2$Cl$_3$ = 6 mol/mol.

[g] Perfluoroether (see Section 2).

[h] n-Perfluorohexane

[i] MAO free of toluene and Me$_3$Al, obtained by precipitation with n-hexane, was used as unique co-catalyst (Al/Ni = 100 mol/mol).
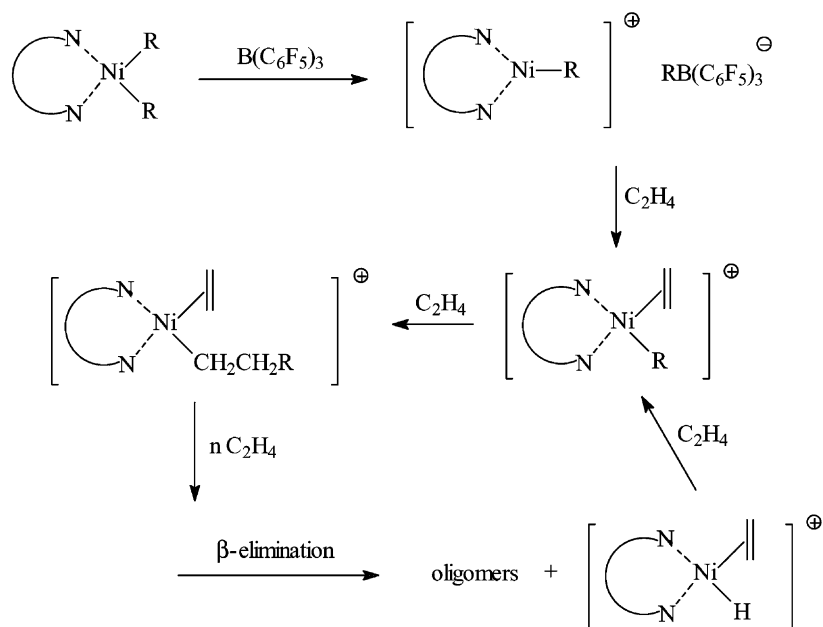
A preliminary experiment carried out in toluene (entry 23, Table 3) allowed to check that, adopting MAO as co-catalyst, the resulting catalytic system displayed a significant activity (TOF = 6300 h^{-1}). However, as expected considering the less basic character of P(C$_6$F$_5$)$_3$, a very low regioselectivity to DMB was achieved (7.6%). When the experiment was repeated by using a MAO/Et$_3$Al$_2$Cl$_3$ (6:1) mixture as co-catalyst and n-perfluorohexane as solvent (entry 24, Table 3), similar results in terms of regioselectivity and overall yield (Y) to DMB were obtained, although a certain decrease of productivity was observed (TOF = 4900 h^{-1}). Also the use of MAO either in toluene solution or as solid (precipitated with n-hexane) in n-perfluorohexane and Galden (entries 25 and 26, respectively) did not substantially modify the catalytic performances in terms of selectivity to DMB, although a further decrease of productivity was observed.

However, in entries 24–26, where a fluorinated solvent was used as reaction medium, again no evidence of preferential solubility of the catalyst in the fluorinated phase was observed, the hydrocarbon layer being progressively coloured, so as to prevent any realization of a BFS catalysis.

3.2. Olefin oligomerization by Ni(hfacac)$_2$ activated by B(C$_6$F$_5$)$_3$

Taking into account that all attempts to realize a nickel catalytic system steadily fixed in the perfluorinated phase failed, notwithstanding both the β-diketonate and the phosphine ligands around the metal were modified by introducing long perfluoroalkyl and perfluorophenyl moieties, respectively, an alternative approach could consist into the use of an alkylating perfluorinated agent, such as tris(pentafluorophenyl)borane [B(C$_6$F$_5$)$_3$], as co-catalyst.

Indeed, B(C$_6$F$_5$)$_3$, a Lewis acid of intermediate strength in between BCl$_3$ and BF$_3$ [23–26], has been widely applied in combination with titanocenes and zirconocenes for the obtainement of very active olefin polymerization catalysts [27–31]. Recently, it was also used in stoichiometric amount with α-diimine nickel complexes for ethylene activation [18]. Indeed, an alkyl (hydride) nickel cationic species is expected to be formed from dihalo- or dialkyl-α-diimine nickel derivatives [18,32], analogously to what reported for IV group metallocenes. (Scheme 1).

Scheme 1.

In order to check the activity of the catalytic systems based on perfluorinated β-diketonate nickel complexes, preliminary experiments were carried out in ethylene oligomerization (Table 4).

When Ni(hfacac)$_2$ (**III**) was reacted in toluene solution with a slight excess of B(C$_6$F$_5$)$_3$ (B/Ni = 1.5 mol/mol) under ethylene atmosphere (entry 27), a completely inactive catalyst was obtained, as expected for a precursor employed in absence of an alkylating species. Therefore, a subsequent experiment was performed (entry 28, Table 4) by adding, under ethylene atmosphere, an excess of Et$_3$Al to

III (Al/Ni = 5 mol/mol) before the addition of B(C$_6$F$_5$)$_3$. In this case, no ethylene oligomerization was observed until a temperature of 40 °C was reached, thus indicating that B(C$_6$F$_5$)$_3$ is essential to generate the active species, although a temperature threshold is required for promoting this activation process. Indeed, under these conditions and a $P_{C_2H_4}$ equal to 80 atm, a significant activity to C$_4$–C$_{10}$ oligomeric products was observed (TOF = 3800 h^{-1}).

Indeed, Et$_3$Al should transform **III** into an alkyl nickel derivative [33] which would be subsequently

Table 4
Ethylene oligomerization by the Ni(hfacac)$_2$ (**III**)/Et$_3$Al/B(C$_6$F$_5$)$_3$ catalytic system[a]

Entry	Co-catalyst		Time (h)	T (°C)	Oligomerization products (%)					TOF[b] (h^{-1})
	Al/Ni[c]	B/Ni[c]			C$_4$	C$_6$	C$_8$	C$_{10}$	C$_{12+}$	
27	0	1.5	1	20	–	–	–	–	–	0
28	5	1.5	0.5	40	89.0	8.5	2.4	0.0	0.0	3800
29	5	0	1	40	–	–	–	–	–	0

[a] Reaction conditions—**III**: 0,042 mmol; solvent: toluene (20 ml); $P_{C_2H_4}$ = 80 atm.
[b] Turnover frequency, determined as mole of converted ethylene/(mole of Ni × h).
[c] Molar ratio.
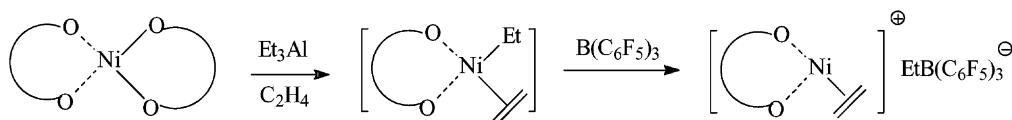
Scheme 2.

activated by the borane with the formation of a cationic nickel species (Scheme 2).

A confirmation to the above picture is based on the fact that when Et_3Al was added to **III** as unique co-catalyst (Al/Ni = 5 mol/mol) (entry 29, Table 4) the system resulted completely inactive.

Therefore, the same catalytic system was adopted in propylene oligomerization (Table 5).

When the **III**/Et_3Al/$B(C_6F_5)_3$ catalyst was used in toluene solution (Al/Ni = 5 and B/Ni = 1.5 mol/mol) in the 40–80 °C range (entries 30–32) a significant activity was observed, TOF values in the 1100–2800 h^{-1} range being found, the maximum corresponding to a 60 °C reaction temperature. As expected, when the catalytic experiment was performed below 0 °C (entry 33) the catalyst was substantially inactive (TOF = 50 h^{-1}). It is noteworthy that the analysis of C_6 cut clearly shows that less than 5% of the target DMB product was formed, independently from the temperature adopted. This may be addressed to the fact that no basic and bulky ancillary phosphine ligands were

used in these experiments. When propylene oligomerization was carried out under the same conditions as those adopted in entry 31 (60 °C), but introducing PCy_3 (P/Ni = 2 mol/mol) before the addition of the borane (entry 34), a drop of activity was observed, thus suggesting that the basic PCy_3 behaves as a borane scavenger. However, the regioselectivity within the C_6 cut strongly increased moving from 4.6 to 59.8%, although this value is still not satisfactory. The addition of PCy_3 after the formation of the active nickel species, (evidenced by the occurring of an orange coloured solution), by introducing **III**, Et_3Al and $B(C_6F_5)_3$ in that order (entry 35), seems to confirm this picture, an improvement of productivity being observed notwithstanding a higher temperature was adopted (80 °C). A further confirmation comes from entry 36 where the use of a higher relative amount of borane favoured the process productivity subtracting the phosphine ligand from the metal centre, although strongly reducing the regioselectivity to DMB (22.2 versus 59.8% of entry 36, Table 5).

Table 5
Propylene oligomerization by Ni(hfacac)$_2$ (**III**)/Et_3Al/$B(C_6F_5)_3$ catalytic systems, eventually in the presence of PCy_3 as ancillary ligand[a]

Entry	B/Ni[b]	P/Ni[b]	T (°C)	Dimers (%)			C_6 (%)	C_9 (%)	C_{12+} (%)	Y^c (%)	TOF[d] (h^{-1})
				DMB	MP[e]	HEX[f]					
30	1.5	–	40	3.9	40.1	55.9	94.8	4.1	1.1	3.7	1100
31	1.5	–	60	4.6	53.4	42.1	80.7	16.6	2.7	3.7	2800
32	1.5	–	80	3.7	36.0	60.4	86.4	10.4	3.1	3.2	1500
33	1.5	–	−5	4.8	61.9	33.4	56.2	22.4	21.4	2.7	50
34	1.5	2.2	60	59.8	31.9	8.3	81.1	18.9	0.0	48.5	50
35	1.5	2.2	80	50.7	34.9	14.4	91.8	8.2	0.0	46.5	140
36	3.0	2.2	60	22.2	60.9	16.9	81.4	18.6	0.0	18.1	350

[a] Reaction conditions—**III**: 0.042 mmol; Al/Ni: 5 mol/mol; solvent (toluene): 20 ml; time: 1 h; P_{C3H6}: 3 atm.
[b] Molar ratio.
[c] Overall yield to DMB, evaluated as percentage of DMB in the C_6 cut × percentage of C_6 cut in the oligomeric products.
[d] Turnover frequency, determined as mole of converted propylene/(mole of Ni × h).
[e] Methylpentenes.
[f] *n*-Hexenes.

All these experiments proved for the first time that it is possible to prepare active catalysts for oligomerization of olefins from β-diketonate nickel complexes by reacting them with an almost stoichiometric amount of $B(C_6F_5)_3$ in the presence of a slight excess of a trialkylaluminium.

Unfortunately, we have to underline that when this catalytic system was employed in propylene oligomerization by adopting as reaction medium perfluorinated solvents, no activity at all was observed, due to the fact that the catalyst formed in situ was not soluble in the fluorinated phase.

4. Conclusions

On the basis of the obtained results the following conclusive remarks may be drawn:

1. Nickel catalysts based on perfluorinated β-diketonate nickel(II) precursors, when activated by aluminium co-catalysts, display a rather high activity in propylene dimerization to DMB in a wide range of perfluorinated solvents, no significant poisoning being ascertained.
2. Due to the high complexity of these phosphino-modified Ziegler–Natta-type catalysts, the active species do not remain "anchored" to the fluorous layer, a progressive migration towards the hydrocarbon phase being observed.
3. Several modifications of the catalysts, in order to increase their compatibility with the fluorous phase, were performed by introducing both fluorinated phosphine ligands and borane co-catalyst.
4. For the first time active catalysts were prepared by reacting perfluorinated β-diketonate nickel(II) precursors with $B(C_6F_5)_3$, provided that a slight amount Et_3Al as alkylating agent was employed.

All the efforts up to now carried out did not allow to realize a catalytic oligomerization process in FBS. However, propylene dimerization is a very severe test for this approach, due to the polar character of the active species, likely constituted by an ion-pair involving a cationic nickel complex and an anionic counterion, resulting in a remarkable preference for the hydrocarbon phase rather than the non-polar fluorinated layer [14]. Other approaches, for example the use of ionic liquids [34], seem to be more promising in order to achieve a real biphasic catalytic system for this reaction process.

Acknowledgements

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