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Novel nickel catalysts based on perfluoroalkyl-β-diketone ligands for the selective dimerization of propylene to 2,3-dimethylbutenes

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Abstract

The propylene dimerization to 2,3-dimethylbutenes (DMB) by novel homogeneous catalysts prepared in situ by two alternative routes was described. The former synthetic procedure was based on the oxidative addition of hexafluoro-2,4-pentandione (hfacac) to bis(1,5-cyclooctadiene)nickel(0) [Ni(cod)$_2$] in the presence of an ancillary phosphine ligand and an organoaluminium compound. The latter route consisted in the reaction of bis(perfluoroalkyl-β-diketonato)nickel(II) complexes with the organoaluminium compound in the presence of the phosphine ligand. In this context the novel bis(tetradecafluoro-4,6-nonandionato)nickel(II)·2 dimethylformamide complex [Ni(tdfnd)$_2$(dmf)$_2$] was synthesized and its crystal and molecular structures were determined. The catalytic systems obtained with both procedures resulted highly active in the oligomerization of propylene (TOF > 20000 h^{-1}). In particular, when Ni(hfacac)$_2$ was combined with the bulky and basic tricyclohexylphosphine (PCy$_3$) and MAO was adopted as co-catalyst a very high regioselectivity to DMB within the C$_6$ cut was achieved (ca. 90%). The use of Ni(tdfnd)$_2$(dmf)$_2$ in the place of Ni(hfacac)$_2$ gave similar results under the same reaction conditions. Changing the type of phosphine ligand and the nature of the organoaluminium co-catalyst it was possible to deeply modify both regio- and chemo-selectivity of the process, thus allowing to orientate the reaction towards specific target oligomeric products. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Propylene oligomerization; 2,3-Dimethylbutenes; Homogeneous catalysis; bis(Hexafluoro-2,4-pentandionato)nickel(II); bis(Tetradecafluoro-4,6-nonandionato) nickel(II)·2dmf; Organoaluminium co-catalysts; Phosphine ligands

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1. Introduction

It is well known that chelated nickel complexes without added organoaluminium co-catalysts are highly active in the ethylene oligomerization. In particular, nickel complexes based on differently substituted β-diketone chelate ligands have been reported [1–5]. The above complexes have been prepared by oxidative addition of the β-diketone to a nickel(0) complex, such as bis(1,5-cyclooctadiene)nickel [Ni(cod)$_2$]. This reaction provides [1] as a first step the transfer of an acidic hydrogen from the diketone enol form to the coordinated cod ligand, thus allowing the displacement from the metal of the other cod ligand and the formation of the (η^1,η^2-cyclooctenyl)(β-diketonato)nickel complex (**I**) (Scheme 1).

In this way a nickel complex with a square planar structure is obtained, whose activity and selectivity depend on the nature of the ligands around the metal. Indeed, a substantially linear dependence of catalytic activity on the acidity of the β-diketone ligand was observed [2], the highest being found for the system modified by the 1,1,1,5,5,5-hexafluoro-2,4-pentandione (hfacac) ligand [6]. This may be addressed to the fact that the substituents on the β-diketone moiety with electron withdrawing characteristics, such as CF$_3$ groups, reduce the electron density on the metal centre,

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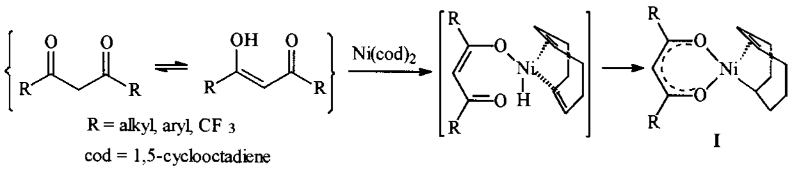


Scheme 1.

thus favouring the olefin coordination and hence the activity of the catalytic system [7]. Although the presence of a co-catalyst is not necessary for the activation of the catalytic systems modified by β-diketone ligands, the activity was enhanced when an organoaluminium compound was used [8,9].

In this context, it appeared of considerable interest to study the activity of nickel catalysts based on fluorinated β-diketone ligands in the presence of organoaluminium co-catalysts in the oligomerization of propylene, never investigated up to now. However, in order to drive the selectivity of the process towards 2,3-dimethylbutenes (DMB), valuable gasoline high octane blending components [10], the presence of a basic and bulky ancillary phosphine ligand was essential, as previously reported for nickel catalysts based on different chelate ligands [11–14]. Analogous effects were reported in the propylene dimerization by phosphine modified η^3-allyl nickel complexes [15,16].

Therefore, in the present paper the activity and selectivity of different perfluoroalkyl-β-diketonato nickel catalysts in the propylene oligomerization to DMB will be studied, with particular attention to the influence played by the nature of both the β-diketone and ancillary phosphine ligands as well as the type of the organoaluminium co-catalyst on their performances.

2. Results and discussion

2.1. Molecular structure of Ni(tdfnd)$_2$(dmf)$_2$

A perspective view of the molecular structure of Ni(tdfnd)$_2$(dmf)$_2$ is shown in Fig. 1 and significant bond distances and angles are listed in Table 1.

The nickel is placed on the inversion centre at 1/2, 1/2, 0 which is the only operation symmetry for the whole molecule. The coordination geometry is almost exactly octahedral, the main distortion being represented by the O(1)–Ni–O(3) and O(2)–Ni–O(3) angles, both 87.9° instead of the ideal 90°.

The Ni–O distances, 2.04 Å mean value, compare very well with those found for the analogous *trans*-diaqua-bis(2,4-pentanedione)nickel(II) diperchlorate [17,18], where, however, being the pentadione ligands uncharged, the angles within the dioxanickelacyclohexane rings are not exactly the same. A closer analogy may be found with the nickel environment in the crystal structure of bis(1-ethyl-1,4-dihydro-4-oxo(1,3)dioxolo-(4,5-g)cinnoline-3-carboxylato)-bis(dimethylsulfoxide)-nickel tetrahydrate [19]. In this case the dioxanickelacyclohexane rings are forced to be almost plane by the delocalization of π electrons in the ligands. In fact either in the last compound or in Ni(tdfnd)$_2$(dmf)$_2$ the

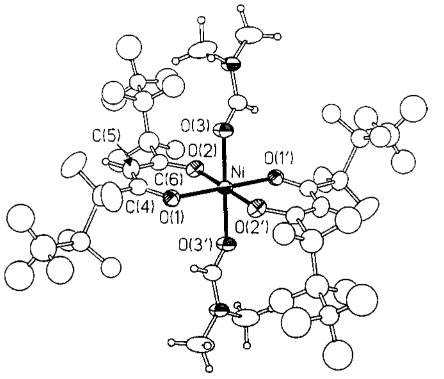
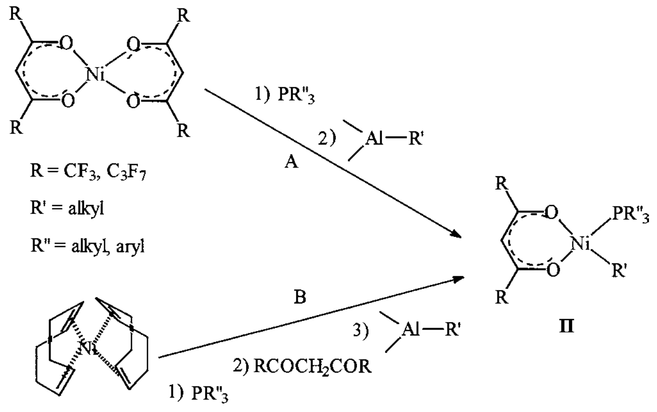


Fig. 1. Perspective view of the molecular structure of Ni(tdfnd)$_2$(dmf)$_2$. Only the most populated positions of the disordered {C_3F_7} groups, corresponding to an occupancy factor 0.55, are represented for clarity. The thermal ellipsoids are at 30% probability. The apexes in the atom labels have the same meaning as in Table 1.

Table 1
Bond lengths (Å) and bond angles (°) around the nickel in the molecular structure of Ni(tdfnd)$_2$(dmf)$_2$ [a]

Bond lengths			
Ni–O(1)	2.033(5)	C(4)–C(5)	1.38(1)
Ni–O(2)	2.035(6)	C(5)–C(6)	1.38(1)
Ni–O(3)	2.054(6)	C(6)–O(2)	1.26(1)
C(4)–O(1)	1.24(1)		
Bond angles			
O(1′)–Ni–O(1)	180	O(2)–Ni–O(3)	87.9(2)
O(1)–Ni–O(2′)	89.4(2)	O(3′)–Ni–O(3)	180
O(1)–Ni–O(2)	90.6(2)	O(1)–C(4)–C(5)	128.5(9)
O(2′)–Ni–O(2)	180	C(4)–O(1)–Ni	124.1(6)
O(1)–Ni–O(3′)	92.1(2)	C(4)–C(5)–C(6)	123.8(9)
O(2)–Ni–O(3′)	92.1(2)	O(2)–C(6)–C(5)	128.6(9)
O(1′)–Ni–O(3)	92.1(2)	C(6)–O(2)–Ni	123.3(6)
O(1)–Ni–O(3)	87.9(2)		

[a] Symmetry transformation used to generate equivalent atoms: $' = -x+1,\ -y+1,\ -z$.



Scheme 2.

rings are very few puckered and the maximum deviation from the planarity is only 0.14 Å for C(5) in Ni(tdfnd)$_2$(dmf)$_2$.

2.2. Propylene oligomerization by homogeneous nickel catalysts based on perfluoroalkyl-β-diketone ligands

In principle, alkyl(β-diketonato)(phosphine)nickel(II) complexes (**II**) may be obtained by two alternative routes A and B, as described in Scheme 2.

Indeed, the formation of **II** through the synthetic procedure A, involving the interaction of Ni(acac)$_2$ with aluminium alkyls in the presence of a tertiary phosphine ligand, was proved to occur by FT-IR and ^{1}H-NMR [20,21] as well as by UV–vis studies [22]. A further confirmation to this type of reactivity was obtained by electrochemical investigations [23]. On the other hand, the synthesis of **II** by route B was reported to occur when β-dithioketones [24] or α-nitroketones [25] chelate ligands, very similar to substituted β-diketones, were reacted with a Ni(cod)$_2$/phosphine adduct and subsequently treated with an organoaluminium compound.

Therefore, both procedures were adopted for obtaining in situ the complexes **II**, whose activity was checked in the propylene oligomerization.

It was previously ascertained that the performances of nickel catalysts based on β-dithioketone ligands are solvent dependent and much higher activity was found when halogenated solvents, such as chlorobenzene, were used [11–14]. On the contrary, nickel catalysts based on α-nitroketone ligands, due to their higher acidity with respect to β-diketones and β-dithioketones, display high activity even in aromatic hydrocarbon solvents [25]. Therefore, taking into account that fluorinated β-diketones, such as hfacac and tdfnd, have an acid strength higher than that of α-nitroketones [2], all the experiments have been performed in toluene solution. Finally, the majority of the experiments were carried out by using as co-catalyst the MAO/Et$_3$Al$_2$Cl$_3$ (6:1) mixture because this was found to promote the conversion of propylene to DMB with high activity and selectivity, when nickel catalysts were prepared by oxidative addition of a strong carboxylic acid to Ni(cod)$_2$ in the presence of PCy$_3$ [26].

Indeed, when catalyst **II** (R = CF$_3$) was prepared by oxidative addition of hfacac to the Ni(cod)$_2$/PCy$_3$ adduct and the resulting intermediate treated with MAO/Et$_3$Al$_2$Cl$_3$ (6:1) mixture, according to route B of Scheme 2, (entry 1, Table 2) almost 78% of DMB was obtained in the C$_6$ cut with a high activity (TOF = 9800 h^{-1}).

It is also noteworthy that a high content of C$_6$ fraction (> 81%) and a very low amount of higher oligomers (C$_{12+}$ = 3.5%) were found, the overall yield of DMB (Y) being more than 63%. When an almost double amount of nickel precursor was used (entry 2, Table 2) similar performances, in terms of chemo- and regio-selectivity were obtained. However, a higher activity was ascertained (TOF = 11300 h^{-1}), probably due to a lower effect of protic impurities in the reaction medium. Indeed, the above difference cannot be addressed to the scarce reproducibility of the data because the reliability of our experiments in terms of activity was evaluated to be in the ± 5% range [27].

Subsequently, route A of Scheme 2 was used for the preparation in situ of catalysts **II** (R = CF$_3$) (entries 3–6, Table 2) starting from the Ni(hfacac)$_2$/PCy$_3$ adduct and successive treatment with MAO/Et$_3$Al$_2$Cl$_3$ (6:1) co-catalyst mixture. When entry 3 is compared with the corresponding experiment carried out via the alternative route B (entry 2), a significant improvement of regioselectivity to DMB within the C$_6$ cut was observed (83.9%). Moreover, also an improvement of the overall yield to DMB was found. However, a decrease of activity was ascertained (TOF = 5300 h^{-1}). When the concentration of the nickel precursor was reduced progressively (entries 4–6), a different behaviour was observed as compared with that previously found in entries 1 and 2, starting from the more labile Ni(cod)$_2$. Indeed, on decreasing the concentration of Ni(hfacac)$_2$, an improvement of activity was observed until a maximum (TOF = 22500 h^{-1}) was reached (entry 5). This behaviour may be explained assuming that, when the concentration of the nickel precursor is too small, as in entry 6, the protic impurities may cause a detrimental effect on the catalyst activity. It is also noteworthy that a significant decrease of regioselectivity to DBM within the C$_6$ cut (from 83.9 to 67.3%) was observed on decreasing the catalyst concentration. When only MAO was used as co-catalyst (entry 7, Table 2) still maintaining the same Al/Ni molar ratio (100), a remarkable increase of regioselectivity to DMB within the C$_6$ cut was observed (88.9%), although a larger amount of higher oligomers was produced and a significant decrease of activity was found (TOF = 2900 h^{-1}). The above combined performances represent almost the

Table 2
Propylene oligomerization at −5°C by catalysts **II** prepared in situ from different nickel precursors, ancillary phosphine ligands and organoaluminium co-catalysts [a]

Entry	Nickel precursor		PR_3 [b]	Co-catalyst [c]	Dimers (%) [d]			C_6 (%)	C_9 (%)	C_{12+} (%)	Y [e] (%)	TOF [f] (h^{-1})
	Type	mmol			DMB	MP	HEX					
1 [g]	$Ni(cod)_2$	0.047	Cy	$MAO/Et_3Al_2Cl_3$ (6:1)	77.9	21.0	1.1	81.2	15.3	3.5	63.3	9800
2 [g]	$Ni(cod)_2$	0.091	Cy	$MAO/Et_3Al_2Cl_3$ (6:1)	75.8	22.7	1.5	76.4	19.7	3.9	57.9	11300
3	$Ni(hfacac)_2$	0.100	Cy	$MAO/Et_3Al_2Cl_3$ (6:1)	83.9	15.2	0.9	73.1	16.8	10.1	61.3	5300
4	$Ni(hfacac)_2$	0.042	Cy	$MAO/Et_3Al_2Cl_3$ (6:1)	77.6	21.2	1.2	82.9	14.8	2.3	64.0	14200
5	$Ni(hfacac)_2$	0.021	Cy	$MAO/Et_3Al_2Cl_3$ (6:1)	70.7	27.3	2.0	82.9	14.8	2.3	58.6	22500
6	$Ni(hfacac)_2$	0.015	Cy	$MAO/Et_3Al_2Cl_3$ (6:1)	67.3	29.8	2.9	79.7	16.6	3.7	53.6	9900
7	$Ni(hfacac)_2$	0.100	Cy	MAO	88.9	10.6	0.5	62.8	26.1	11.1	55.8	2900
8	$Ni(tdfnd)_2$	0.029	Cy	$MAO/Et_3Al_2Cl_3$ (6:1)	70.5	27.1	2.4	77.4	17.5	5.1	54.6	23200
9	$Ni(tdfnd)_2$	0.039	^{i}Pr	$MAO/Et_3Al_2Cl_3$ (6:1)	67.7	29.8	2.5	81.3	16.0	2.7	55.1	28500
10	$Ni(tdfnd)_2$	0.039	Ph	$MAO/Et_3Al_2Cl_3$ (6:1)	19.5	67.1	13.5	96.2	3.7	0.1	18.8	14000
11	$Ni(tdfnd)_2$	0.039	Ph	MAO	7.6	74.0	18.5	93.8	6.2	0.0	7.1	6300

[a] Reaction conditions: the catalyst was prepared according to route A of Scheme 3 (see Section 4), unless otherwise indicated; solvent (toluene): 20 ml; $P_{C_3H_6} = 3$ atm; time = 1 h.

[b] P/Ni = 2.2 mol/mol.

[c] Al/Ni = 100 mol/mol.

[d] DMB, 2,3-dimethylbutenes; MP, methylpentenes, HEX, *n*-hexenes.

[e] Yield in DMB, determined as: fraction of DMB in C_6 cut ×% of C_6 cut in the oligomeric products.

[f] Turnover frequency expressed as: moles of converted propylene/(moles of Ni × h).

[g] The catalyst was prepared according to route B of Scheme 2 (see Section 4); hfacac/Ni = 1.3 mol/mol.

highest values up to now achieved, the only comparable case being obtained with the α-nitroacetophenone/$Ni(cod)_2/PCy_3$/MAO catalytic system (Al/Ni = 100 mol/mol) [25]. When $Ni(tdfnd)_2(dmf)_2$ was adopted as catalyst precursor (entry 8, Table 3) similar results in terms of activity and regioselectivity to DMB were obtained by **II** ($R = C_3F_7$) under the same conditions as for $Ni(hfacac)_2$ (entry 5). The use of P^iPr_3 (entry 9, Table 2), a more basic phosphine as compared with PCy_3 [28,29], allowed to increase the catalyst activity although it did not improve the regioselectivity to DMB (compare entry 9 with entry 4). These results are in agreement with those previously obtained by using homogeneous nickel catalysts based on β-dithioketonate ligands [12]. Moreover, when a less basic phosphine, such as PPh_3, was adopted in combination with $Ni(tdfnd)_2(dmf)_2$ (entry 10) a dramatic change of regioselectivity to DMB within the C_6 cut was observed (19.5%), accompanied by a much higher chemoselectivity to dimers (> 96%), analogously to what previously found in the case of homogeneous nickel catalysts based on β-dithioketonate [11] and α-nitroketonate ligands [30].

Finally, when MAO was used in the place of the $MAO/Et_3Al_2Cl_3$ (6:1) mixture (entry 11, Table 2) adopting the same reaction conditions as in entry 10, a further decrease of regioselectivity to DMB (7.6%) was found.

These results indicate that it is possible to orientate the propylene oligomerization towards specific target products by choosing the ancillary phosphine ligand with the appropriate bulkyness and basicity as well as the co-catalyst with the suitable Lewis acidity.

3. Conclusions

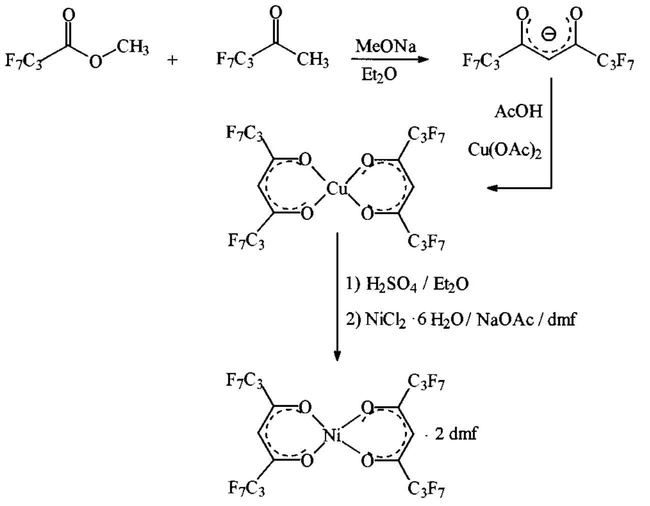
On the basis of the obtained results the following concluding remarks can be drawn:

Table 3
Crystal data and structure refinement of $Ni(tdfnd)_2(dmf)_2$

Empirical formula	$C_{24}H_{16}F_{28}N_2NiO_6$
Formula weight	1019.10
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbcn* (no. 60)
Unit cell dimensions	
a (Å)	10.643(3)
b (Å)	13.786(5)
c (Å)	25.560(8)
V ($Å^3$)	3750(2)
Z	4
D_{calc} (g cm^{-3})	1.805
μ (mm^{-1})	0.697
Data/restraints/parameters	3294/0/216
$R(F_o)$ [a] [$I > 2\sigma(I)$]	0.0970
$Rw(F_o^2)$ [b] [$I > 2\sigma(I)$]	0.2717

[a] $R(F_o) = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$.

[b] $Rw(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$, where $Q = [\max(F_o^2, 0) + 2F_c^2]/3$.



Scheme 3.

(1) A new bis(perfluoroalkyl-β-diketonato)nickel(II) complex, such as $Ni(tdfnd)_2(dmf)_2$, was synthesized and its crystal and molecular structures determined.

(2) Novel catalytic systems in situ prepared either by oxidative addition of perfluoroalkyl-β-diketones to Ni(0) complexes or by the corresponding bis(perfluoroalkyl-β-diketonato)nickel(II) complexes both in the presence of an ancillary phosphine ligand and an organoaluminium co-catalyst were found to display high activity in the propylene oligomerization.

(3) When a bulky and basic phosphine, such as PCy_3, and an organoaluminium co-catalyst with suitable Lewis acidity were adopted, regioselectivity values to DMB up to almost 90% within the C_6 cut were achieved with good productivity. Moreover, the above performances were achieved in aromatic hydrocarbon medium, thus avoiding the use of chlorinated solvents, less environmentally appealing in industrial applications.

(4) It was possible to modulate both regio- and chemo-selectivities of these nickel catalysts, by choosing the appropriate phosphine ligand and the suitable organoaluminium co-catalyst, in order to orientate the propylene oligomerization towards specific target products.

(5) Finally, the extensive fluorination of these catalyst species makes them suitable candidates for their application to biphasic catalytic olefin oligomerization processes carried out in perfluorinated solvents as reaction medium. Work is in progress in order to evaluate this possible goal.

4. Experimental

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

4.1. 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.

$Ni(cod)_2$ (Strem) was stored at −20°C under dry argon and used without any further purification.

1,1,1,5,5,5-Hexafluoro-2,4-pentandione (Aldrich) (hfacac) and bis(1,1,1,5,5,5-hexafluoro-2,4-pentandionato)Ni [$Ni(hfacac)_2$] (Aldrich), sodium methoxide (MeONa) (Aldrich), cupric acetate $Cu(OAc)_2$ (Carlo Erba), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) (Carlo Erba), tricyclohexylphosphine (PCy_3) (Aldrich), triphenylphosphine (PPh_3) (Aldrich), triisopropylphosphine (P^iPr_3) (Fluka), *n*-butyllithium (BuLi) (Aldrich) in *n*-hexane solution (2.5 M), ethylaluminium sesquichloride ($Et_3Al_2Cl_3$) (Aldrich), in toluene solution (0.91 M), and methylalumoxane (MAO) (Witco), in toluene solution (4.5 M), were stored under dry argon and used as received.

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

Propylene (Ucar) was used as received.

Bis(1,1,1,2,2,3,3,7,7,8,8,9,9,9 - tetradecafluoro - 4,6-nonandionato)nickel(II)·2dmf [$Ni(tdfnd)_2(dmf)_2$] was prepared according to a general synthetic procedure previously reported for the obtainement of nickel complexes with other perfluorinated ligands [31] (Scheme 3).

Indeed, $Cu(tdfnd)_2$ was prepared as follows: 0.71 g (13.2 mmol) of MeONa, dissolved in 15 ml of anhydrous Et_2O, were introduced at 0°C and under dry argon into a 100 ml flask, equipped with a reflux condenser and a dropping funnel. Subsequently, 2.74 g (11.8 mmol) of MHFB in Et_2O (5 ml) were added dropwise. After 1 h of reaction under vigorous stirring 2.5 g (11.8 mmol) of MHFPK were added dropwise. The mixture was reacted for 12 h at 0°C and subsequently for additional 12 h at room temperature. Finally, 0.87 g (14 mmol) of acetic acid in water solution (4 ml) and 1.76 g (84 mmol) of cupric acetate in 15 ml of water were added. Et_2O was evaporated under vacuum and a light green solid product was precipitated. After filtration the solid was dried to give 4.35 g (5.0 mmol) of $Cu(tdfnd)_2$ (85% yield).

M.p. = 87–88°C; Calc. for $C_{22}H_2O_4F_{28}Cu$: C, 28.5; H, 0.4; Cu, 7.1; F, 57.5; O, 6.9. Found: C, 28.8; H, 0.7; F, 57.5%. FT-IR (KBr disc): 1640 (ν_{CO}), 1350 (νas_{CF_3}), 1227 (νas_{CF_2}), 1191 (νs_{CF_3}), 1120(νs_{CF_2}) cm^{-1}. ^{19}F-NMR: $\delta = -80.5$ (s, 3F, $-CF_3$), -121 (s, 4F, $-CF_2$).

The corresponding nickel complex was obtained as follows: 0.5 g (0.57 mmol) of $Cu(tdfnd)_2$ were treated under magnetic stirring with 3 ml of aq. H_2SO_4 (15%) and 3 ml of Et_2O. The ethereal layer was added rapidly to 135.4 mg (0.57 mmol) of $NiCl_2 \cdot 6H_2O$ dissolved in 12 ml of dmf. Subsequently, 93.5 mg (1.14 mmol) of AcONa dissolved in 2 ml of water were added. After Et_2O evaporation the residual solution was dropped into excess water at 0°C. The precipitated light green solid was filtered, washed with water and finally dried under vacuum. 0.47 g (0.46 mmol) of pure $Ni(tdfnd)_2(dmf)_2$ was obtained (81% yield) as confirmed by elemental, ^{19}F-NMR and FT-IR analyses.

M.p. = 76°C. Calc. for $C_{28}H_{14}O_6N_2F_{28}Ni$: C, 31.6; H, 1.3; F, 49.9; N, 2.6; Ni, 5.5; O, 9. Found: C, 31.8; H, 1.5; F, 50.3%. FT-IR (KBr disc): 1651 (ν_{CO}), 1380 (νas_{CF_3}), 1345 (νas_{CF_2}), 1260 (νs_{CF_3}), 1245(νs_{CF_2}) cm^{-1}. ^{19}F-NMR: $\delta = -80$ (s, 3F, $-CF_3$), -120 (s, 4F, $-CF_2$).

4.2. 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 (−5°C). When the catalyst precursor was prepared by oxidative addition of the perfluoroalkyl-β-diketone to a nickel(0) complex, the solvent (toluene, 15 ml) and the desired amount of $Ni(cod)_2$ (ca. 0.05–0.1 mmol) were introduced at 0°C under dry argon in a Schlenk-type vessel in the presence of PCy_3 (P/Ni = 2.2 mol/mol). Subsequently, the suitable amount of the perfluoroalkyl-1,3-diketone (diketone/Ni = 1.3 mol/mol), dissolved in toluene (5 ml) was slowly added under vigorous stirring. On the addition of the ligand a sharp colour change from light yellow to red–brown was observed. The reaction mixture was maintained at 0°C for 15 min, then it was transferred into the reactor and the aluminium co-catalyst (Al/Ni = 100 mol/mol) was added under propylene atmosphere. The reactor was finally pressurized with propylene up to 3 atm. The pressure was manually held at that value by repeated olefin feeds. When $Ni(hfacac)_2$ or $Ni(tdfnd)_2(dmf)_2$ were used as precursors, the proper amount of the complex (0.015–0.1 mmol) was introduced under dry argon into a Schlenk-type vessel and dissolved in toluene (15 ml) at the reflux temperature. After cooling at 50°C, the phosphine ligand (P/Ni = 2.2 mol/mol) was slowly added in toluene solution (5 ml). Subsequently, the solution of the nickel/phosphine adduct was transferred into the reactor at room temperature and, under propylene atmosphere, the proper amount of aluminium co-catalyst (Al/Ni = 100 mol/mol) was added. Finally, the reactor was pressurized with propylene as above described. In all cases the reaction was stopped by degassing unreacted propylene through a trap cooled at −10°C, then the liquid products were collected, weighted and analyzed by gas-chromatography (GC).

4.3. 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_6–C_{12} cuts. The individual components were identified by comparison with authentic samples.

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

4.4. 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.

^1H-, ^{19}F-, $\{^1H\}$-^{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 (Me_4Si) was used as internal standard for ^1H-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 by X-ray diffractometry as follows: a light green prismatic crystal of $Ni(tdfnd)_2(dmf)_2$, obtained by slow evaporation of its dmf solution, was glued at the end of a glass fibre and was mounted on a Bruker P4 diffractometer, equipped with a graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The X-ray diffraction measurements were carried out at room temperature ($T = 293$ K). The crystal sample had $0.66 \times 0.44 \times 0.21$ mm^3 dimensions. The cell parameters, calculated from the setting angles of 35 reflections having $5.34 < \theta < 12.73°$, are listed in Table 3, together with some other structural details.

The intensity data collection was carried out with the $\omega/2\theta$ scan mode, collecting a redundant set of data in order to check the diffraction symmetry and the reliability of the absorption correction procedure. Three standard reflections were measured every 97 measurements to check sample decay and equipment stability. The 4172 collected intensities, having $2.4° < \theta < 25.0°$, were corrected for Lorentz and polarisation effects and for absorption by means of a gaussian method based on the crystal shape [32]. The equivalent reflections were then merged ($R_{\text{int}} = 0.0457$) giving 3294 independent intensities, among which only one half (1791) had $I > 2\sigma(I)$. The structure solution was obtained by means of the automatic direct methods and the refinement, based on full-matrix least-squares on F^2, were done by means of SHELXTL programme [33]. A marked conformational disorder was found to be present in the perfluorinated propyl groups. The model was then modified as resulting from the superposition of two different conformations for each $\{C_3F_7\}$group, by imposing the total population of each disordered moiety equal to 1. The ordered and the disordered atoms have been refined anisotropically and isotropically, respectively. The hydrogen atoms have been introduced in calculated positions and refined according to the riding model. The final refinement cycles gave the reliability factors listed in Table 1. The residual peaks in the final difference Fourier map were less than 0.77 e Å^{-3}.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149605. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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