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Olefin oligomerization by novel catalysts prepared by oxidative addition of carboxylic acids to nickel(0) precursors and modified by phosphine ancillary ligands and organoaluminum compounds

Carlo Carlini^{a,*}, Mario Marchionna^b, Anna Maria Raspolli Galletti^a, Glauco Sbrana^a

^a *Dipartimento di Chimica e Chimica Industriale, University of Pisa, via Risorgimento 35, 56126 Pisa, Italy*

^b *Snamprogetti S.p.A., via Maritano 26, 20097 San Donato Milanese (MI), Italy*

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Abstract

Novel Ziegler–Natta-type catalysts, prepared in situ by oxidative addition of carboxylic acids to bis(cyclooctadiene)nickel(0) [Ni(cod)₂]/phosphine adducts and activated by different organoaluminum compounds, are described. These catalysts resulted very active in olefin oligomerization. When 2-nitrobenzoic acid (NBA), tricyclohexylphosphine (PCy₃) and MAO were employed in combination with Ni(cod)₂ for propylene oligomerization, a regioselectivity to 2,3-dimethylbutenes (DMB) within the C₆ cut very close to 90% was achieved with a high productivity (turnover frequency (TOF) values up to 16,400 h⁻¹). Similar results in terms of regioselectivity to DMB were obtained when trifluoroacetic acid (TFA) was adopted. However, although with a lower productivity, a higher value of overall yield to DMB (62.7%) was achieved. When these catalysts were used for ethylene oligomerization they resulted very active (TOF values up to 65,000 h⁻¹), the nature of the phosphine ligand allowing to strongly affect the chemoselectivity of the process, shifting the oligomeric composition towards specific fractions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Propylene and ethylene oligomerization; 2,3-Dimethylbutenes; C₄–C₁₂ oligomers; Homogeneous nickel catalysts; Trifluoroacetic acid; 2-Nitrobenzoic acid; Organoaluminum co-catalysts; Tricyclohexylphosphine

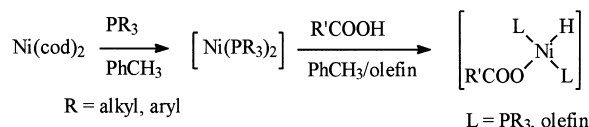
1. Introduction

It is well established that protic acids may give an oxidative addition to nickel(0) derivatives to afford nickel(II) complexes. This type of reactivity was firstly ascertained by Keim who investigated the interaction of phosphino carboxylic acids with bis(cyclooctadiene)nickel(0) [Ni(cod)₂] to give, by hydrogen transfer from the carboxylic function to the

C8 ring, a stable five-membered P^ηO metallacyclo complex [1–5].

This type of complexes have been claimed to produce very active catalysts for ethylene oligomerization at *T* > 50°C [1–3]. These catalysts, which may be called non Ziegler–Natta as they do not need any organoaluminum co-catalyst for their activation, were applied in the SHOP industrial process [6]. Indeed, this is able to afford C₄–C₃₀₊ olefinic cuts with a rather high productivity (2000–4000 mol of converted C₂H₄/(moles of Ni × time), where time is in hours), as well as an excellent content of linear components (>99%) and terminal olefins (96–98%), very useful to be applied for

* Corresponding author. Tel.: +39-50-918222;
fax: +39-50-918260.
E-mail address: carlini@dcc.unipi.it (C. Carlini).



Scheme 1.

detergents, lubricants, plasticizers, and oil additives [6].

The possibility to prepare the above nickel(II) derivatives also by using a combination of monofunctional ligands with individual carboxylic and donor moieties was also investigated. Indeed, this approach has the advantage to afford nickel complexes in which the acid strength and the coordination properties of the two ligands could be easily varied without the synthesis of the corresponding bifunctional chelate ligand. Moreover, this synthetic procedure allowed to vary independently the acid/metal and donor/metal molar ratios. Indeed, Keim claimed [7] a modest catalytic activity in ethylene oligomerization for nickel complexes prepared by oxidative addition of a carboxylic acid to Ni(cod)₂.

In this context, the studies of Wilke concerning the synthesis of nickel complexes by oxidative addition of carboxylic acids to Ni(cod)₂ in the presence of an ancillary phosphine ligand are of relevant interest (Scheme 1) [8].

It is noteworthy that the preparation in situ of the above complexes was carried out under ethylene atmosphere, because the coordination of the olefin to the metal stabilized the system, thus preventing its decomposition to metal (Scheme 2).

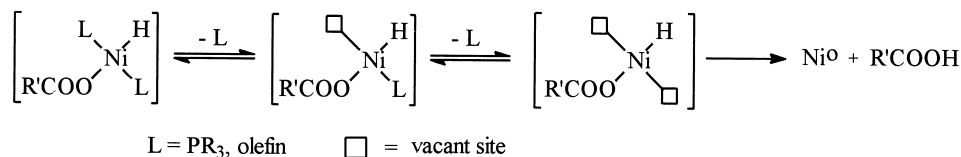
The carboxylate phosphino-modified nickel(II) complexes, in the absence of organoaluminum co-catalysts, exhibited a certain activity in ethylene oligomerization, productivity values in the 200–2000 mol of converted ethylene/(moles of Ni × time) range being obtained [9,10]. Moreover, the

catalytic activity resulted to be affected by the nature of the carboxylic acid and phosphine ligand as well as of the type of solvent used.

Quite recently, we have investigated the oxidative addition of trifluoroacetic acid to Ni(cod)₂ in the presence of a phosphine ligand, such as tricyclohexylphosphine (PCy₃) and triphenylphosphine (PPh₃), and the catalytic behavior of the resulting nickel(II) systems has been also examined [11,12]. The HNi(CF₃COO)(PR₃)₂ (R = Cy, Ph) complexes thus obtained, contrary to other non Ziegler–Natta nickel catalysts, were able to activate also higher olefins and co-oligomerize ethylene with propylene, although with rather low activities.

Finally, Sumitomo researchers reported that the addition of sulfonic acid to nickel catalysts of complex formulation, such as Ni(naph)₂/PCy₃/Et₃Al/chlorinated phenol (naph = naphthenate), improved the activity (30,000 mol of oligomers/(moles of Ni × time)) and the selectivity to 2,3-dimethylbutenes (DMB) (88%) in propylene oligomerization [13–15]. This system, even in its complexity, is the first example of phosphino-modified nickel(II) complexes activated by both a strong organic acid and an organoaluminum compound.

Therefore, in the present paper our attention will be devoted to the study of nickel catalysts of Ziegler–Natta type, based on the oxidative addition of strong carboxylic acids to Ni(cod)₂ in the presence of a phosphine ancillary ligand, when applied to the activation of C₂ and C₃ olefins. In particular, the effect of the nature of the carboxylic acid as well as of the organoaluminum co-catalyst will be investigated with the aim to orientate the oligomerization process of propylene and ethylene to valuable target products, such as DMB and C₁₀–C₂₀ cut, respectively. Indeed, whereas the former represent valuable high octane number gasoline blending components [16], the latter may be applied as high cetane gas–oil additives, provided that they are characterized by a linear structure.



Scheme 2.

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) was obtained by distillation on K/Na alloy under dry argon and stored on molecular sieves (4 Å).

Methylalumoxane (MAO) (Witco) in toluene solution (4.5 M), diethyl aluminum chloride (Aldrich) in toluene solution (1.8 M), ethyl aluminum sesquichloride ($\text{Et}_3\text{Al}_2\text{Cl}_3$) (Aldrich) in toluene solution (0.9 M), triethylaluminum (Et_3Al) (Witco, neat), tricyclohexylphosphine (PCy_3), and triphenylphosphine (PPh_3) (Aldrich) were used as received and stored under dry argon.

Bis(cyclooctadiene)Ni(0) [$\text{Ni}(\text{cod})_2$] (Strem) was used as received and stored under dry argon at -20°C .

Propylene (Ukar, 99.95%), ethylene (99%, Rivoira) trifluoroacetic acid (Aldrich) and 2-nitrobenzoic acid (Aldrich) were used as received.

2.2. Catalytic olefin oligomerization experiments

Catalytic batch experiments at room temperature were performed in a 150 ml rocking stainless-steel autoclave. The nickel precursor was previously prepared under dry argon in a Schlenk-type vessel. In a typical procedure, $\text{Ni}(\text{cod})_2$ was dissolved at 0°C in anhydrous toluene under magnetic stirring, then the ancillary phosphine ligand was added ($\text{P}/\text{Ni} = 1.5\text{--}2.0 \text{ mol mol}^{-1}$). Subsequently, the carboxylic acid was added to the $\text{Ni}(\text{cod})_2$ /phosphine adduct under olefin atmosphere ($\text{COOH}/\text{Ni} = 1\text{--}3 \text{ mol mol}^{-1}$). After aging at 0°C for 15 min, the solution of the catalyst precursor was transferred with a syringe under olefin atmosphere into the autoclave, then the proper amount of aluminum co-catalyst was added. When the olefin used was propylene, it was charged by cooling the autoclave at -15°C . The amount of olefin introduced in the autoclave was determined by weight. When ethylene was used as olefin, the autoclave was pressurized at 50 atm, and the pressure was manually maintained at that value by repeated olefin feeds. It is noteworthy

that particularly in the experiments where a larger amount of catalyst was used, due to the high reaction rate, the temperature of the reaction mixture inside the autoclave was significantly higher than room temperature.

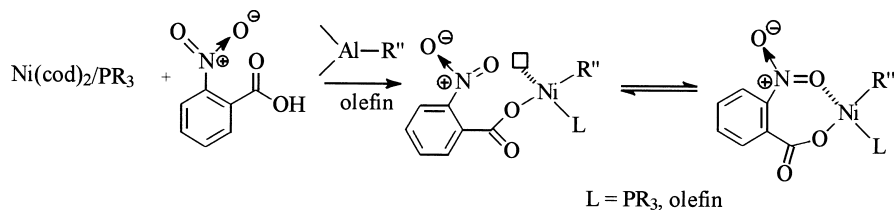
The reaction was stopped by fast-cooling the autoclave and degassing unreacted olefin through a trap cooled at -10°C , then the liquid products were collected, weighted, and analyzed by gas chromatography (GC).

Catalytic batch experiments carried out from -5 to -25°C for propylene oligomerization were performed in a 250 ml magnetically stirred Büchi glass reactor, equipped with a jacket circulating cooling fluid in order to maintain the reaction temperature at the desired value. The nickel precursor was dissolved at 0°C in toluene under dry argon in a Schlenk-type vessel in the presence of PCy_3 ($\text{P}/\text{Ni} = 1.5 \text{ mol mol}^{-1}$), then the carboxylic acid was added under olefin atmosphere. After aging at 0°C for 15 min, the solution of the catalyst precursor was transferred with a syringe under olefin atmosphere into the reactor, then the proper amount of aluminum co-catalyst was added under olefin atmosphere, the reactor was finally pressurized with propylene up to 3 atm, and the pressure manually held at the above value by repeated olefin feeds. The recovery of the reaction products and their characterization were performed as described before.

The reliability of experimental results was evaluated to be in the $\pm 5\%$ range.

2.3. Analytical procedures

Oligomers analysis was performed 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^{-1} 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 $\text{C}_4\text{--C}_{20}$ cuts. The individual components were identified by comparison with authentic samples [17].



Scheme 3.

2.4. 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 an IRDM Perkin-Elmer software.

¹H- and {¹H}-³¹P-NMR (nuclear magnetic resonance) spectra were performed by a Varian XL Gemini 200 spectrometer operating at 200 and 80.95 MHz, respectively, on samples in CDCl₃ solution. Tetramethylsilane (TMS) and 85% H₃PO₄ were used as internal and external standards, respectively.

3. Results and discussion

3.1. Propylene oligomerization by nickel catalysts obtained in situ through oxidative addition of 2-nitrobenzoic acid to the Ni(cod)₂/PCy₃ adduct and subsequent treatment with different organoaluminum co-catalysts

Taking into account that the use of a protic acid having a quite high Brønsted acid strength allowed to significantly increase both regioselectivity and productivity of Sumitomo catalysts to 2,3-dimethylbutenes (DMB) [13–15]. It appeared interesting to check if a bifunctional carboxylic acid, such as 2-nitrobenzoic acid (NBA), never applied in the preparation of nickel catalysts, when combined with the Ni(cod)₂/PCy₃ adduct and an organoaluminum compound could improve catalytic performances in propylene oligomerization as compared with those recently obtained by using homogeneous nickel catalysts based on either β-dithioketonate or α-nitroketonate ligands [17–19]. Indeed, the high acidity character of carboxylic group in NBA due to the presence of the nitro group

(pK_a = 2.2) [20] should favor the oxidative addition to a Ni(0) precursor, thus forming a nickel(II) carboxylate species further stabilized by the interaction with the –NO₂ moiety. Indeed, it is possible to imagine a hemilabile chelation where the nickel(II) center is firmly linked to the carboxylate moiety and the coordination of the nitro group, through the formation of a seven-membered metallacyclo, takes place only when a coordinative vacancy occurs on the metal site (Scheme 3).

PCy₃, a basic and bulky phosphine, was chosen as ancillary ligand, because it is known to strongly favor the formation of DMB in several nickel catalysts based on chelate ligands [17–19].

In order to check the effect of the presence of NBA in the catalytic system, a blank experiment in absence of any carboxylic acid was performed as a reference (entry 1, Table 1). Indeed, when the Ni(cod)₂/PCy₃ adduct was activated by MAO (MAO/Ni = 100 mol mol⁻¹) without any addition of carboxylic acids, a quite low activity was ascertained (TOF = 450 h⁻¹; TOF, turnover frequency), although a rather high selectivity to DMB was obtained. When an equimolar amount of NBA with respect to the nickel precursor was added (entry 2, Table 1), a sharp improvement of both activity (TOF = 2800 h⁻¹) and regioselectivity to DMB within the C₆ cut (88 versus 75.8%) were obtained. However, an increase of higher oligomers was also found, the chemoselectivity to C₆ cut being reduced from 73.2 to 55.7%. As a consequence, a decrease of the overall yield (Y) of DMB was observed (55.5 versus 49%).

It is noteworthy that, due to the scarce stirring efficiency and heat removal capability of a rocking autoclave in processes characterized by fast reaction rate, the oligomerization occurs in almost adiabatic conditions, thus preventing a good control of the temperature inside the reactor. As a consequence,

Table 1

Propylene oligomerization by homogeneous nickel catalysts obtained in situ by reacting NBA acid with the Ni(cod)₂/PCy₃ adduct and subsequent activation with organoaluminum compounds^a

Entry	NBA/Ni (mol mol ⁻¹)	Aluminum co-catalyst		Dimers ^b (%)			C ₆ (%)	C ₉ (%)	C ₁₂₊ (%)	Y ^c (%)	TOF ^d (h ⁻¹)
		Type	Al/Ni ^e	DMB	MP	HEX					
1	–	MAO	100	75.8	17.9	6.3	73.2	20.9	5.9	55.5	450
2	1	MAO	100	88.0	11.6	0.4	55.7	28.0	12.3	49.0	2800
3	1	MAO	100	87.8	11.9	0.3	55.8	28.1	16.1	49.0	7000
4	2	MAO	100	80.8	18.5	0.7	72.4	22.6	5.0	58.5	9000
5	2	MAO	100	83.7	15.9	0.4	61.0	25.9	13.1	51.1	14500
6	3	MAO	100	83.8	15.6	0.6	57.1	27.5	15.4	47.8	6700
7 ^f	2	MAO	100	86.0	13.6	0.4	65.4	25.3	9.3	56.2	16400
8	2	Et ₂ AlCl	30	49.7	44.5	5.7	96.1	3.6	0.3	47.8	1900
9	2	MAO/Et ₂ AlCl (5:1)	60	60.6	33.4	6.1	77.1	18.2	4.7	46.7	2550
10 ^g	2	MAO	100	89.2	10.4	0.4	63.1	24.4	12.5	56.3	6000
11 ^g	2	Et ₂ AlCl	30	49.8	44.5	5.7	96.2	3.8	0.0	47.9	6500

^a Reaction conditions: Ni(cod)₂: 0.1 mmol (entries 1, 3, 5, 7, and 10) and 0.2 mmol (entries 2, 4, 6, 8, 9, and 11); P/Ni = 1.5 mol mol⁻¹, if not otherwise indicated; solvent (toluene): 20 ml; charged C₃H₆: 20 g (entries 1 and 2), 50 g (entries 3, 8, and 9), and 70 g (entries 4–7); initial temperature: 25°C; time: 1 h; process carried out in a rocking stainless-steel autoclave.

^b DMB, 2,3-dimethylbutenes; MP, 2- and 4-methylpentenes; HEX, *n*-hexenes.

^c Overall yield to DMB determined as fraction of DMB in C₆ cut × percentage of C₆ cut in the oligomeric products.

^d Turnover frequency expressed as moles of converted propylene/(moles of Ni × time).

^e Molar ratio.

^f P/Ni = 2 mol mol⁻¹.

^g Process carried out in a glass Büchi reactor; P_{C₃H₆}: 3 atm; T: –5°C.

the enhancement of the temperature could cause in principle a partial catalyst deactivation. Taking into account that an increase of the catalyst concentration enhancing the reaction rate may favor deactivation processes, a further experiment (entry 3, Table 1) was accomplished by halving the amount of the nickel precursor (0.1 mmol). Moreover, it is important also to underline that due to the relative long duration of each experiment up to now described (1 h) in connection with the high reaction rate and the rather low amount of charged propylene (20 g), the productivity values achieved could be underestimated, the olefin being rapidly consumed in the first reaction period. Therefore, a larger amount of propylene was charged (50 g). The obtained data indicate that under these conditions, a further improvement of productivity was obtained in entry 3 (TOF = 7000 h⁻¹), although the selectivity and yield to DMB of the process remained substantially unvaried.

When the amount of NBA was increased (NBA/Ni = 2 mol mol⁻¹) and a further enhancement of propylene was charged (70 g; entry 4, Table 1), a significant improvement of activity was observed (TOF =

9000 h⁻¹). Moreover, the detrimental effect on the regioselectivity to DMB within the C₆ cut (80.8 versus 88%) was balanced by the formation of a lower amount of higher oligomers, the overall yield to DMB being significantly increased (Y = 58.5%). By reducing the amount of catalyst (0.1 mmol; entry 5, Table 1) again an improvement of productivity was ascertained (TOF = 14,500 h⁻¹), a slight increase of regioselectivity to DMB being also observed (83.7%), although the enhancement of higher oligomers formation caused a lowering of the overall yield to DMB (51.1%). A further increase of the relative NBA amount (NBA/Ni = 3 mol mol⁻¹; entry 6, Table 1) gave rise to a decrease of productivity, selectivity performances becoming also worse. Therefore, from the above data, it may be concluded that the best performances are obtained for a NBA/Ni molar ratio equal to 2. When the relative amount of phosphine was increased (PCy₃/Ni = 2 mol mol⁻¹), as in entry 7 (Table 1), a very high productivity was obtained (TOF = 16,400 h⁻¹) accompanied by high values of regioselectivity and yield to DMB (86 and 56.2%, respectively). When MAO was replaced by Et₂AlCl

(entry 8, Table 1), a co-catalyst usually applied with high selectivities and productivities for homogeneous nickel catalysts based on β -dithioketonate and α -nitroketonate chelate ligands [17–19], a drop of both the above performances was observed. However, the use of a MAO/ Et_2AlCl (5/1 mol mol⁻¹) co-catalyst, with a total Al/Ni molar ratio equal to 60 (entry 9, Table 1), allowed to appreciably increase the regioselectivity to DMB, although this performance was still unsatisfactory. Moreover, the productivity was only slightly increased (TOF = 2550 h⁻¹). However, an optimization of the selectivity to DMB may be foreseen, taking into account the sensitivity of this parameter to the relative content of the two co-catalyst components.

Finally, in order to study the effect of reaction temperature on the catalyst performances, few experiments were performed at lower temperature (-5°C) in a glass Büchi reactor, where it was possible to have a better control of the temperature by efficient stirring and heat removal. Indeed, it is well known that a decrease of temperature usually increases selectivity of the oligomerization process towards DMB [17,18].

However, it must be underlined that due to the different volume and geometry of this reactor as compared with the previous one and to the varied conditions in terms of olefin concentration and stirring efficiency, the productivity of the same catalyst in the two reactors is expected to be significantly different.

Indeed, when MAO was used as co-catalyst (Al/Ni = 100 mol mol⁻¹; entry 10, Table 1), a very high regioselectivity to DMB within the C₆ cut (89.2%) and a good productivity (TOF = 6000 h⁻¹) were obtained. This confirmed that a decrease of reaction temperature has a beneficial effect on selectivity of the oligomerization process. This value of regioselectivity is the highest never reached with the exception of that obtained at 0°C with the nickel catalyst prepared by oxidative addition of α -nitroacetophenone to the Ni(cod)₂/PCy₃ adduct and activated by MAO [19]. Finally, when Et_2AlCl was used in the place of MAO (entry 11, Table 1), the same selectivity data as those found in the corresponding experiment carried out in the rocking autoclave (entry 8) were obtained, although a three-fold higher productivity was achieved.

In conclusion, the oxidative addition of a bifunctional carboxylic acid, such as NBA to a nickel(0) pre-

cursor, in the presence of a bulky and basic phosphine ancillary ligand, when activated by a suitable organoaluminum compound (MAO) allows one to obtain catalysts with very high performances both in terms of selectivity and productivity to DMB.

With the aim to verify the effect of the use of a monofunctional carboxylic acid on catalyst performances in propylene oligomerization as compared with the bifunctional NBA, the oxidative addition of the strong trifluoroacetic acid (TFA) to Ni(cod)₂ in the presence of PCy₃ and an organoaluminum co-catalyst was investigated. Indeed, the high acid strength of TFA could favor the olefin coordination to the metal center and hence the oligomerization process [21].

3.2. Propylene oligomerization by nickel catalysts obtained *in situ* through oxidative addition of trifluoroacetic acid to the Ni(cod)₂/PCy₃ adduct and subsequent treatment with different organoaluminum co-catalysts

Nickel catalysts modified by TFA and in the presence of an ancillary phosphine ligand have been reported by Knudsen to be moderately active for the oligomerization of ethylene [10]. However, neither the above systems were ever used for the selective dimerization of propylene to DMB nor activation by organoaluminum co-catalysts was previously attempted. Therefore, the experiments were carried out by using in general Al/Ni and P/Ni molar ratios equal to 20–100 and 2.2, respectively, and in the presence of PCy₃ at -5°C in order to improve the selectivity to the target DMB. However, a preliminary run carried out without any co-catalyst completely failed in the activation of propylene. Even in the presence of a large excess of Et₃Al, the resulting catalyst was inactive (entry 12, Table 2).

When Et_2AlCl was used in the place of Et₃Al (entry 13, Table 2), a high activity of the resulting catalyst was found; however, the regioselectivity within the C₆ cut was unsatisfactory, analogously to what previously observed by using NBA as acid ligand. Therefore, MAO was subsequently employed as co-catalyst (entries 14–16, Table 2), and the ratio P/Ni was varied from 1.5 to 3 at a fixed MAO/Ni molar ratio equal to 100. The results obtained clearly indicate that the best performances in terms of both selectivity and productivity were achieved at a P/Ni molar ratio equal to 2.2

Table 2

Propylene oligomerization by homogeneous nickel catalysts obtained in situ by TFA acid with the Ni(cod)₂/PCy₃ adduct and subsequent activation with organoaluminum compounds^a

Entry	Aluminum co-catalyst		P/Ni ^b	Dimers ^c (%)			C ₆ (%)	C ₉ (%)	C ₁₂₊ (%)	Y ^d (%)	TOF ^e (h ⁻¹)
	Type	Al/Ni ^b		DMB	MP	HEX					
12	Et ₃ Al	100	2.2	–	–	–	–	–	–	–	0
13	Et ₂ AlCl	20	2.2	48.3	47.0	4.8	91.8	6.5	1.7	44.3	9200
14	MAO	100	1.5	87.3	12.1	0.6	60.0	24.9	15.1	52.4	2800
15	MAO	100	2.2	89.0	10.8	0.2	70.4	23.4	6.2	62.7	3500
16	MAO	100	3.0	86.4	12.8	0.8	63.2	27.9	8.9	54.6	550
17	MAO	50	2.2	87.1	12.5	0.5	67.8	23.3	8.9	59.0	1700
18 ^f	MAO	100	1.5	84.2	15.4	0.4	59.0	26.0	15.0	49.7	11300
19	MAO/Et ₂ AlCl (9:1)	100	2.2	82.9	16.3	0.8	73.6	21.6	4.8	61.0	2200
20	MAO/Et ₂ AlCl (4:1)	100	2.2	78.6	20.7	0.7	82.8	16.2	1.0	65.1	2500
21	MAO/Et ₃ Al ₂ Cl ₃ (9:1)	100	2.2	83.2	16.1	0.7	72.7	20.9	6.4	60.5	4900
22	MAO/Et ₃ Al ₂ Cl ₃ (6:1)	100	2.2	77.0	21.9	1.1	81.4	15.2	3.4	62.7	16300
23	MAO/Et ₃ Al ₂ Cl ₃ (4:1)	100	2.2	63.7	33.2	3.1	87.0	11.5	1.5	55.4	26500
24 ^g	MAO/Et ₂ AlCl (4:1)	100	2.2	82.3	16.8	0.9	74.2	20.0	5.8	61.1	1300
25 ^g	MAO/Et ₃ Al ₂ Cl ₃ (6:1)	100	2.2	83.6	15.0	1.4	73.8	19.6	6.6	61.7	3900

^a Reaction conditions: Ni(cod)₂: 0.1 mmol; TFA/Ni = 1.3 mol mol⁻¹, if not otherwise specified; solvent (toluene): 20 ml; PCy₃H₆: 3 atm; T: -5°C; time: 1 h; process carried out in a glass Büchi reactor.

^b Molar ratio.

^c DMB, 2,3-dimethylbutenes; MP, 2- and 4-methylpentenes; HEX, *n*-hexenes.

^d Overall yield to DMB determined as fraction of DMB in C₆ cut × percentage of C₆ cut in the oligomeric products.

^e Turnover frequency expressed as moles of converted propylene/(moles of Ni × time).

^f TFA/Ni = 1.0 mol mol⁻¹.

^g T: -25°C.

(entry 15). Indeed, very high regioselectivity (89%) and overall yield to DMB (62.7%) were obtained. The above values are even better than those found in entry 10 (Table 1) where NBA was employed, although the productivity value being lower (TOF = 3500 h⁻¹).

As previously reported [17], when a high content of DMB is present in the C₆ cut, the major components of the C₉ cut are represented by 2,3,5-trimethylhexenes which after hydrogenation give rise to the corresponding paraffin having a high octane number. In this context, it is noteworthy to underline that in entry 15, C₆ and C₉ cuts with a very high content of highly branched components represent almost 94%, thus supporting their potential use as high octane gasoline additives.

The reduced activity of the catalyst obtained, when a large excess of PCy₃ was used (P/Ni = 3; entry 16, Table 2), may be addressed to the fact that, under these conditions, the excess phosphine competes with propylene giving rise mainly to coordinatively saturated metal species and hence inactive for olefin coordination.

When the MAO/Ni molar ratio was lowered to 50 (entry 17, Table 2), the productivity of the resulting catalyst decreased without any improvement of selectivity to DMB.

If the amount of TFA is slightly reduced (TFA/Ni = 1.0 instead of 1.3 mol mol⁻¹; entry 18, Table 2), a sharp increase of productivity was observed (TOF = 11,300 h⁻¹) as compared with that observed in the corresponding experiment (entry 14, Table 2). However, a small detrimental effect was observed on the regioselectivity within the C₆ cut and the overall yield to DMB.

With the aim to optimize catalysts performances, several experiments were performed by using different mixtures of organoaluminum co-catalysts with modulated Lewis acidity, still maintaining constant the other reaction parameters.

The use of an increasing amount of Et₂AlCl in combination with MAO (entries 19 and 20, Table 2) gave rise to intermediate productivities with respect to entries 13 and 15, where Et₂AlCl and MAO alone were used, respectively. As far as the overall yield to

DMB is concerned, particularly in the case of entry 20 (Table 2), a very high value was achieved (65.1%). However, this result was mainly due to the drastic reduction of the content of C₁₂₊ cut (1%) in the oligomeric products rather than to an improvement of regioselectivity to DMB within C₆ cut which on the contrary was lowered (78.6 versus 89.0 in entry 15).

The use of Et₃Al₂Cl₃, an organoaluminum compound with much higher Lewis acidity as compared with Et₂AlCl, allowed to improve catalyst productivity when combined with decreasing amount of MAO (entries 21–23, Table 2). A progressive decrease of the regioselectivity to DMB was also observed. However, in the case of entry 22, where a MAO/Et₃Al₂Cl₃ equal to 4 mol mol⁻¹ was adopted, very high TOF and overall yield to DMB were achieved (16,300 h⁻¹ and 62.7%, respectively). The latter value was equal to that obtained with MAO alone (entry 15), where a much higher regioselectivity to DMB within the C₆ cut was however found.

Finally, in order to further improve the selectivity of propylene oligomerization to DMB, few experiments at -25°C were performed. In particular, experiments corresponding to entries 20 and 22 were repeated at lower temperatures and the results compared in the two cases.

As reported in entries 24 and 25 (Table 2), the experiments carried out at -25°C did not caused a significant improvement of the overall yield to DMB to justify to work at this temperature. Moreover, a sharp decrease of productivity was also observed.

In conclusion, the use of TFA in the oxidative addition to nickel(0) precursors, provided that a basic and bulky phosphine ligand as well as a suitable organoaluminum co-catalyst were adopted, appears as a very interesting approach for obtaining nickel catalysts with high activity and selectivity to DMB analogously to what described for 2-nitrobenzoic acid.

It is noteworthy that these results may be further improved by the optimization of reaction parameters, such as temperature and olefin pressure, as well as of catalytic components in terms of a better balance among the characteristics of carboxylic acid, phosphine ancillary ligands, and organoaluminum components.

3.3. Ethylene oligomerization by nickel catalysts obtained in situ through oxidative addition of carboxylic acids to Ni(cod)₂/PR₃ adducts and subsequent treatment with MAO

In order to check the performances of the above catalysts in the oligomerization of ethylene, some experiments were carried out in a rocking stainless-steel autoclave at room temperature (Table 3). In particular, both NBA and TFA acids were used, and phosphines with different bulkiness and basicity were adopted in combination with Ni(cod)₂. Acid/Ni molar ratios equal to 2 and 1 for NBA and TFA, respectively, as well as P/Ni = 1.5 mol mol⁻¹ were adopted in combination with MAO (Al/Ni = 100 mol mol⁻¹), because under the above conditions, the best values of

Table 3

Ethylene oligomerization by homogeneous nickel catalysts obtained in situ by oxidative addition of different carboxylic acids to Ni(cod)₂/PR₃ adducts and subsequent activation with MAO^a

Entry	Ni(cod) ₂ (mmol)	Acid ^b	PR ₃	Oligomers (%)				Trimers ^c (%)			TOF ^d (h ⁻¹)
				C ₄	C ₆	C ₈	C ₁₀₊	MP	EtB	HEX	
26 ^e	0.1	NBA	–	63.2	30.5	4.6	1.7	35.2	15.9	48.9	4300
27	0.1	NBA	PPh ₃	55.8	32.7	2.9	8.6	52.5	2.2	45.3	52300
28	0.03	NBA	PPh ₃	49.8	36.9	4.2	9.1	50.7	2.6	46.7	65000
29	0.1	NBA	PCy ₃	6.5	36.8	15.8	40.9	49.0	0.8	50.2	60200
30	0.1	TFA	PCy ₃	58.9	31.7	5.9	4.5	29.2	32.8	38.0	34600

^a Reaction conditions: Al/Ni = 100 mol mol⁻¹; P/Ni = 1.5 mol mol⁻¹; solvent (toluene): 20 ml; charged C₂H₄: 50 atm; initial temperature: 25°C; time: 0.25 h, if not otherwise specified; process carried out in a rocking stainless-steel reactor.

^b NBA/Ni and TFA/Ni equal to 2 and 1 mol mol⁻¹, respectively.

^c MP, 2- and 4-methylpentenes; EtB, ethylbutenes; HEX, *n*-hexenes.

^d Turnover frequency expressed as moles of converted ethylene/(moles of Ni × time).

^e Reaction time: 1 h.

productivity in the propylene oligomerization had been obtained.

When NBA was added to $\text{Ni}(\text{cod})_2$ in absence of a phosphine ancillary ligand and the resulting adduct activated by MAO (entry 26, Table 3), an appreciable activity ($\text{TOF} = 4300 \text{ h}^{-1}$) was observed higher than that previously reported in the presence of carboxylate phosphino nickel complexes in absence of organoaluminum compounds [10]. However, more than 60% of the oligomeric products consisted of butenes, and $\text{C}_4 + \text{C}_6$ cuts represented almost 94% of the total amount of oligomers. Moreover, the linearity of C_6 cut was slightly lower than 50%.

When the catalyst was prepared in the presence of PPh_3 (entry 27, Table 3), an extremely higher activity was observed. It is noteworthy that due to the high reaction rate, it was not possible to control the reaction temperature which reached inside the autoclave much higher values than 25°C , the process occurring in almost adiabatic conditions. This indicates that the catalytic system is quite stable at high temperature, as confirmed by the fact that no catalyst decomposition (metal formation) was ascertained at the end of the reaction. This catalyst stability could be addressed to the chelating character of NBA previously mentioned and depicted in Scheme 3. Even under these conditions, a TOF value higher than one order of magnitude ($52,300 \text{ h}^{-1}$), as compared with the corresponding experiment in absence of phosphine, was observed. The analysis of the reaction products allowed to conclude that a similar composition, as compared with that of entry 26, was obtained, only a slight shift towards higher oligomers being found ($\text{C}_{10+} \sim 9\%$). When the amount of the nickel precursor was reduced (0.03 versus 0.1 mmol; entry 28, Table 3), the other reaction parameters remaining constant, an even higher value of productivity was achieved ($\text{TOF} = 65,000 \text{ h}^{-1}$). In this case, due to a lower catalyst concentration, the reaction rate was slower and the heating control resulted slightly better than in entry 27, but not enough to prevent a large increase of temperature inside the autoclave. The oligomers' composition was substantially similar to that observed in entry 27. When PPh_3 was replaced by the more basic and bulky PCy_3 (entry 29, Table 3) under the same conditions as in entry 27, a certain improvement of productivity ($\text{TOF} = 60,200 \text{ h}^{-1}$) was observed. Moreover, it is noteworthy that a large shift towards higher

oligomers occurred, C_4 cut being reduced to only 6.5%, C_{10+} fraction increasing up to more than 40%, and C_{12+} oligomers representing more than 70% of C_{10+} cut. Moreover, no large effect on the linearity of the products was observed, the content of *n*-hexenes in the C_6 fraction remaining substantially similar (50.2%).

When NBA was replaced by TFA (entry 30, Table 3) and PCy_3 was adopted as ancillary ligand analogously to entry 29, the activity of the catalyst was significantly lower, although still high ($\text{TOF} = 34,600 \text{ h}^{-1}$) and the chemoselectivity deeply changed towards lower oligomers. Indeed, C_{10+} represented less than 5% of the total amount of oligomers. Finally, the linearity of oligomeric products, as evaluated on the C_6 fraction, was significantly reduced (38%).

The above results indicate that nickel catalysts prepared in situ by addition of strong acids and phosphine ligands to a nickel(0) precursor, provided that an organoaluminum co-catalyst is present, display a very high activity in the ethylene oligomerization, much higher with respect to previous experiments carried out with nickel catalysts obtained by oxidative addition of α -nitroketones to $\text{Ni}(\text{cod})_2/\text{PR}_3$ adducts and activated by MAO [22]. Moreover, by changing the nature of the acid and the characteristics of the phosphine ligand, it is possible to modulate the oligomeric products in a wide range of composition.

4. Conclusions

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

1. Novel catalytic systems of Ziegler–Natta type have been prepared by oxidative addition of carboxylic acids to different phosphine/ $\text{Ni}(\text{cod})_2$ adducts and activation with organoaluminum compounds.
2. The above catalysts revealed a much higher activity in olefin oligomerization as compared with previously reported phosphino-carboxylate nickel systems operating in absence of organoaluminum co-catalysts. It is noteworthy that these performances are obtained working at room temperature and in hydrocarbon solvents, contrarily to what reported for other nickel catalysts which need higher temperature and polar solvents for their activation.

3. When propylene oligomerization was performed by the NBA/Ni(cod)₂/PCy₃/MAO system, a very high regioselectivity to DMB within the C₆ cut (almost 90%) was obtained in a large temperature range (−5 to +25°C), even with high productivity (TOF values around 15,000 h^{−1}). Analogous results were obtained with the TFA/Ni(cod)₂/PCy₃/MAO system, although with slightly lower activity.
4. The above catalysts showed a very high activity also in ethylene oligomerization, particularly when an ancillary phosphine ligand was used (TOF values up to 65,000 h^{−1}). When the NBA/Ni(cod)₂/PR₃/MAO system was adopted, the nature of the phosphine strongly affected the chemoselectivity of the process, PCy₃ shifting the oligomeric composition towards higher oligomers.
5. Finally, it is noteworthy to conclude from these preliminary results that the optimization of reaction conditions and catalyst composition would allow one to orientate the process towards specific target products depending on the olefin submitted to the oligomerization.

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