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Journal of Molecular Catalysis A: Chemical 169 (2001) 19–25

JOURNAL OF  
MOLECULAR  
CATALYSIS  
A: CHEMICAL

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# Selective propylene dimerization to 2,3-dimethylbutenes by homogeneous catalysts obtained from bis( $\alpha$ -nitroacetophenone)nickel(II), tricyclohexylphosphine and different organoaluminum compounds

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Received 17 July 2000; accepted 9 November 2000

## Abstract

The propylene dimerization to 2,3-dimethylbutenes (DMB) by homogeneous catalysts prepared in situ by an alternative method based on the reaction of bis( $\alpha$ -nitroacetophenone)nickel(II) [Ni(naph)<sub>2</sub>] with different organoaluminum compounds, in the presence of a bulky and basic alkyl phosphine such as tricyclohexylphosphine (PCy<sub>3</sub>), was described. In particular, the influence of the nature of the organoaluminum co-catalyst as well as of the reaction temperature was studied.

The catalysts prepared according to this procedure displayed higher activity at room temperature and in hydrocarbon medium as compared with those obtained by oxidative addition of  $\alpha$ -nitroacetophenone to bis(1,5-cyclooctadiene)nickel(0) [Ni(cod)<sub>2</sub>] in the presence of the same phosphine ancillary ligand, turnover frequencies up to 24 800 h<sup>-1</sup> being achieved when methylalumoxane (MAO) was used as co-catalyst. Moreover, regio-selectivity values to DMB within the C<sub>6</sub> cut higher than 82% were observed under the above conditions. Finally, the regio-selectivity was scarcely influenced by decreasing the reaction temperature below 25°C, thus allowing to work at room temperature. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Propylene oligomerization; 2,3-Dimethylbutenes; Homogeneous catalysis; Bis( $\alpha$ -nitroacetophenone)nickel(II); Organoaluminum co-catalysts; Tricyclohexylphosphine

## 1. Introduction

The selective dimerization of propylene to 2,3-dimethylbutenes (DMB) represents an attractive process from industrial point of view, because the above target compounds may be used, after hydro-

genation, as valuable high octane number gasoline blending components [1].

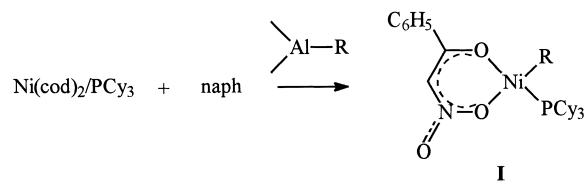
In this context, it is well established that nickel(II) complexes, based on both  $\beta$ -dithioketonate and bulky basic phosphine ligands, are able to give homogeneous catalysts with very high activity and selectivity to DMB, provided they may be activated by organoaluminum compounds of proper Lewis acidity [2,3].

Very recently [4], novel alkyl(tricyclohexylphosphino)( $\alpha$ -nitroacetophenone)nickel(II) [R(PCy<sub>3</sub>)(naph)Ni(II)] (**I**) complexes were obtained by

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Scheme 1.

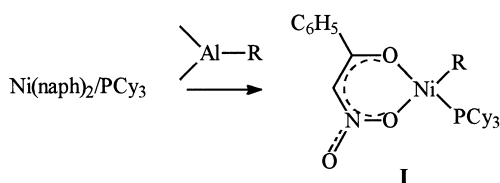
addition of an organoaluminum compound to the equimolar adduct of  $\alpha$ -nitroacetophenone ( $\text{naph}$ ) with bis(1,5-cyclooctadiene)nickel(0) [ $\text{Ni}(\text{cod})_2$ ], in the presence of tricyclohexylphosphine ( $\text{PCy}_3$ ) as ancillary ligand (Scheme 1).

The above complexes, when prepared in situ, contrarily to the  $\beta$ -dithioketonate nickel systems, resulted remarkably active in the selective dimerization of propylene to DMB, even at room temperature and in hydrocarbon solution [5]. In particular, **I** gave more than 90% of DMB in the  $\text{C}_6$  cut, when methylalumoxane ( $\text{MAO}$ ) was used as co-catalyst, and almost 70% of overall yield into DMB when activated by a  $\text{MAO}/\text{Et}_2\text{AlCl}$  (4:1) mixture. In this case the chemoselectivity to the propylene dimers was almost complete (>98%).

However, the use of  $\text{Ni}(\text{cod})_2$  as catalyst precursor, due to its high cost and extreme sensitivity to air, humidity and protic impurities, appeared a serious drawback for an industrial application. In this connection, the alternative synthesis [4] of catalysts **I**, through the addition of the organoaluminum co-catalyst to the equimolar adduct of  $\text{PCy}_3$  with the cheaper and more stable  $\text{Ni}(\text{naph})_2$  complex (Scheme 2), appeared very attractive in order to overcome the above drawback.

Moreover, catalysts **I**, prepared in situ by this alternative route, were found to display in ethylene oligomerization high activity at room temperature and in hydrocarbon solution [6].

Therefore, in this paper the propylene oligomerization catalyzed by complexes **I** will be investigated



Scheme 2.

with particular attention to the role played on catalyst performances by the nature of the organoaluminum co-catalyst and by reaction temperature.

## 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*-heptane (Carlo Erba) were obtained by distillation on  $\text{K}/\text{Na}$  alloy under dry argon and stored on molecular sieves (4 Å).

$\text{MAO}$  (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), trimethyl aluminum ( $\text{Me}_3\text{Al}$ ) (Aldrich) in toluene solution (2 M),  $\text{PCy}_3$  (Aldrich), were used as received and stored under dry argon.

$\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  ( $\text{OAc}$  = acetate) (Carlo Erba) and  $\text{naph}$  (Aldrich), were used without any further purification.

$\text{Ni}(\text{naph})_2$  was prepared by heating under vacuum ( $150^\circ\text{C}$  at 0.1 mmHg)  $\text{Ni}(\text{naph})_2 \cdot 2\text{EtOH}$ , in turn obtained from  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{naph}$  [7].

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ): 7.2 (m, 5H, aromatic protons), 6.85 (s, 1H, CH kelate ring).

Propylene (Ukar, 99.95%) and hydrogen (Rivoira, >99%) were used as received.

### 2.2. Catalytic propylene oligomerization experiments

Catalytic batch experiments at temperature  $\geq 0^\circ\text{C}$  were performed in a 150 ml rocking stainless steel autoclave. The catalyst precursor was previously prepared under dry argon in a Schlenk-type vessel. In a typical procedure  $\text{Ni}(\text{naph})_2$  was dissolved in boiling toluene under magnetic stirring. The ancillary phosphine ligand ( $\text{P}/\text{Ni} = 1.5$  mol/mol) was then added in toluene solution, after cooling at  $50^\circ\text{C}$ . Subsequently, the solution of the nickel/phosphine adduct was transferred with a syringe into the autoclave at  $25^\circ\text{C}$  and, under propylene atmosphere, the proper amount of

aluminum co-catalyst was added. Finally, propylene was charged, the introduced amount being determined by weight. The reaction temperature was then adjusted by immersing the autoclave in a oil-bath at 25°C. It is worth noting 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 usually higher than that of the corresponding oil-bath.

The reaction was stopped by fast cooling the autoclave and degassing unreacted propylene 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 at 0°C 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 catalyst precursor was prepared under dry argon in a Schlenk-type vessel in the presence of PCy<sub>3</sub> (P/Ni = 1.5 mol/mol), as above described. After the introduction of the catalyst precursor dissolved in the reaction solvent, the aluminum co-catalyst was added under propylene atmosphere and the reactor was finally pressurized with propylene up to 3 atm. The pressure was manually held at that value by repeated olefin feeds. The recovery of the reaction products and their characterization were performed as above described.

### 2.3. Analytical procedures

The oligomeric olefinic reaction mixtures were hydrogenated before their GC characterization, in order to reduce the number of components. The hydrogenation was performed in a 125 ml stainless-steel rocking autoclave by using 0.5 g of coal supported 5% palladium (Baker) for 10 ml of olefinic products. The autoclave was then charged with hydrogen up to 100 atm and heated with an oil-bath at 130°C for 12 h.

Hydrogenated 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 heating until 230°C was reached, this value was maintained constant for further 40 min. In this way it was possible to separate the paraffins of C<sub>6</sub>–C<sub>12</sub> cuts. The individual components were identified by comparison with authentic samples.

### 2.4. Physicochemical measurements

Fourier transform infrared (FT-IR) 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. <sup>1</sup>H-, and {<sup>1</sup>H}-<sup>31</sup>P-nuclear magnetic resonance (NMR) spectra were performed by a Varian XL Gemini 200 spectrometer operating at 200 and 80.95 MHz, respectively, on samples in CDCl<sub>3</sub> solution. Tetramethylsilane (TMS) and 85% H<sub>3</sub>PO<sub>4</sub> were used as internal and external standards, respectively.

## 3. Results and discussion

### 3.1. Selective propylene dimerization to DMB in toluene at 25°C by catalysts **I** prepared *in situ* from the Ni(naph)<sub>2</sub>/PCy<sub>3</sub> adduct and different organoaluminum compounds

In preliminary experiments the nickel precursor was suspended in toluene and reacted with PCy<sub>3</sub> at 0°C, before transferring the resulting adduct into the autoclave, under propylene atmosphere, and adding the organoaluminum co-catalyst. However, adopting the above procedure, when either Me<sub>3</sub>Al or Et<sub>2</sub>AlCl (entries 1 and 2, Table 1) was added (Al/Ni = 10 mol/mol) the resulting catalyst **I** appeared completely inactive or scarcely active in the propylene oligomerization, respectively. Taking into account that the insolubility of Ni(naph)<sub>2</sub> in toluene at room temperature could prevent the formation of the adduct with the phosphine ligand, in all the subsequent experiments Ni(naph)<sub>2</sub> was dissolved in boiling toluene, then PCy<sub>3</sub> was added at 50°C and the resulting adduct was transferred at room temperature into the autoclave under propylene atmosphere for the further activation with the organoaluminum co-catalyst.

Indeed, whereas adopting this procedure Me<sub>3</sub>Al again was not able to activate catalyst **I**, only traces of oligomers being produced (entry 3), Et<sub>2</sub>AlCl gave

Table 1

Propylene oligomerization at 25°C by catalysts **I** prepared in situ from the Ni(naph)<sub>2</sub>/PCy<sub>3</sub> adduct and different organoaluminum co-catalysts<sup>a</sup>

Entry	Nickel precursor (mmol)	Al co-catalyst		Dimers (%) <sup>b</sup>			C <sub>6</sub> (%)	C <sub>9</sub> (%)	C <sub>12+</sub> (%)	Y <sup>c</sup> (%)	TOF <sup>d</sup> (h <sup>-1</sup> )
		Type	Al/Ni (mol/mol)	DMB	MP	HEX					
1 <sup>e</sup>	0.15	Me <sub>3</sub> Al	10	–	–	–	–	–	–	0.0	0
2 <sup>e</sup>	0.15	Et <sub>2</sub> AlCl	10	42.1	49.2	8.8	98.3	1.7	0.0	41.3	320
3	0.15	Me <sub>3</sub> Al	10	51.5	44.6	3.9	91.3	8.7	0.0	47.0	~0
4	0.15	Et <sub>2</sub> AlCl	10	49.2	46.2	4.6	93.8	6.1	0.1	46.1	2100
5 <sup>f</sup>	0.12	Et <sub>2</sub> AlCl	10	51.2	44.3	4.5	93.3	6.3	0.4	47.8	2800
6	0.15	Et <sub>2</sub> AlCl	50	55.7	40.3	4.1	90.4	9.4	0.2	50.3	3400
7	0.075	Et <sub>2</sub> AlCl	50	55.6	40.1	4.3	90.2	9.3	0.5	50.2	7100
8	0.075	Et <sub>2</sub> AlCl	100	50.4	44.8	4.8	91.4	8.2	0.4	46.1	6900
9 <sup>g</sup>	0.075	Et <sub>2</sub> AlCl	100	41.4	52.5	6.1	92.0	6.8	1.2	38.1	4850
10	0.075	MAO	100	78.6	20.3	1.1	50.5	26.8	22.7	39.7	8400
11 <sup>f</sup> [4]	0.13	MAO	100	89.1	10.2	0.7	53.0	30.3	16.7	47.2	2000
12	0.075	MAO	100	82.1	17.2	0.7	51.1	25.9	23.0	42.0	24800
13	0.075	MAO	500	82.6	16.6	0.8	50.6	26.0	23.4	41.8	19400
14 <sup>h</sup>	0.075	MAO	100	83.4	16.1	0.5	64.7	23.8	11.5	54.0	15500
15 <sup>i</sup>	0.075	MAO	100	83.3	16.1	0.6	65.4	24.1	10.5	54.5	18500

<sup>a</sup> Reaction conditions: Ni(naph)<sub>2</sub> was dissolved in boiling toluene, then PCy<sub>3</sub> was added at 50°C and the resulting adduct was activated at room temperature by the organoaluminum co-catalyst; P/Ni = 1.5 mol/mol; solvent (toluene) = 20 ml; time: 1 h; charged C<sub>3</sub>H<sub>6</sub> = 20 g (entries 1–11) and 80 g (entries 12–15); experiments carried out in a stainless steel rocking autoclave.

<sup>b</sup> DMB: 2,3-dimethylbutenes; MP: 2- and 4-methylpentenes; HEX: *n*-hexenes.

<sup>c</sup> Overall yield to DMB, determined as: fraction of DMB in C<sub>6</sub> cut × percentage of C<sub>6</sub> cut in the oligomeric products.

<sup>d</sup> Turnover frequency expressed as: mole of converted propylene/(mole of Ni × h).

<sup>e</sup> Ni(naph)<sub>2</sub> was suspended in toluene at room temperature, then PCy<sub>3</sub> was added at 0°C and the resulting adduct was activated at room temperature by the organoaluminum co-catalyst, P/Ni = 1.5 mol/mol.

<sup>f</sup> The catalyst was prepared by oxidative addition at 0°C of naph to the Ni(cod)<sub>2</sub>/PCy<sub>3</sub> equimolar adduct and subsequently activated by the organoaluminum co-catalyst.

<sup>g</sup> P/Ni = 5 mol/mol.

<sup>h</sup> In the presence of hydrogen ( $P_{H_2} = 5$  atm).

<sup>i</sup> In the presence of hydrogen ( $P_{H_2} = 7$  atm).

(entry 4) **I** with a significant activity, a turnover frequency (TOF) of 2100 h<sup>-1</sup> being obtained. The above data, confirming previous findings obtained with nickel catalysts based on β-dithioketonate ligands [2,8], indicates that trialkylaluminum compounds are not able to activate nickel catalysts, due to their very low Lewis acidity. A more detailed examination of the results obtained in entry 4 allowed to ascertain that the oligomerization process gave rise to almost only dimeric and trimeric products, a high chemoselectivity to dimers being also obtained (C<sub>6</sub> cut > 93%). However, the regio-selectivity to DMB within the C<sub>6</sub> fraction was not too high (about 50%) with an overall yield to these branched dimers of about 46%. The above data are substantially equal to those previously obtained (entry 5, Table 1) [4] in the presence of

catalyst **I** prepared by oxidative addition of naph to the Ni(cod)<sub>2</sub>/PCy<sub>3</sub> adduct and subsequently activated with Et<sub>2</sub>AlCl, this occurrence clearly suggesting that the two synthetic routes give rise to the same active species. An increase of the Al/Ni molar ratio from 10 to 50 caused a remarkable improvement of productivity (TOF = 3400 h<sup>-1</sup>), the performances in terms of chemo- and regio-selectivity becoming also better (entry 6, Table 1). It is worth noting to underline that, due to the fast reaction rate as well as to the scarce stirring efficiency and heat removal, the oligomerization process occurred in almost adiabatic conditions, thus preventing a good control of the temperature inside the reactor. As a consequence, the enhancement of the temperature could cause a partial deactivation of the catalyst. Therefore, the amount of

nickel precursor was reduced to one half in all the subsequent experiments, thus decreasing reaction rate and, hence better controlling the temperature during the oligomerization process. Indeed, when entry 5 was repeated under the above conditions (entry 7), a remarkable improvement of productivity was observed ( $\text{TOF} = 7100 \text{ h}^{-1}$ ), the other performances remaining unvaried. A further increase of the amount of  $\text{Et}_2\text{AlCl}$  ( $\text{Al/Ni} = 100 \text{ mol/mol}$ ) (entry 8) did not caused any improvement of catalyst performances. Finally, the increase of the  $\text{P/Ni}$  molar ratio from 1.5 to 5 (entry 9) caused a decrease of activity as well as of regio-selectivity and overall yield ( $Y$ ) to DMB. Indeed, the excess phosphine ligand may compete with the olefin in the coordination step and modify the coordinative sphere of the metal sites, thus reducing olefin insertion rate and selectivity of the process. The replacement of  $\text{Et}_2\text{AlCl}$  with commercial MAO, containing about 30% of  $\text{Me}_3\text{Al}$  ( $\text{Al/Ni} = 100 \text{ mol/mol}$ , entry 10, Table 1) allowed to give a catalyst characterized by not only a higher activity ( $\text{TOF} = 8400 \text{ h}^{-1}$ ) but also a large improvement of regio-selectivity within the  $\text{C}_6$  cut (DMB  $\sim 79\%$ ). This result must be underlined because previous nickel catalysts based on  $\beta$ -dithioketonate ligands [3,8] resulted substantially inactive when obtained in the presence of commercial MAO and only moderately active when purified MAO (after removal of  $\text{Me}_3\text{Al}$ ) was used. However, a significant increase of higher oligomers was also found,  $\text{C}_6$  cut being reduced from more than 90 to about 50%, thus causing a significant decrease of the overall yield to DMB ( $<40\%$ ). A comparison of these data with those obtained [4] by using catalyst **I** prepared by the oxidative addition of naph to the  $\text{Ni}(\text{cod})_2/\text{PCy}_3$  adduct and subsequent activation with MAO (entry 11), shows that with the latter procedure higher regio-selectivity within the  $\text{C}_6$  cut and overall yield to DMB were obtained. However, the use of  $\text{Ni}(\text{naph})_2$  in the place of  $\text{Ni}(\text{cod})_2$  gave a much more active catalytic system, four-fold higher productivity being obtained in the former case. Indeed, this result may be explained considering the higher thermal stability and less sensitivity to impurities of  $\text{Ni}(\text{naph})_2$  as compared with  $\text{Ni}(\text{cod})_2$ . However, it cannot be ruled out that the higher concentration of nickel precursor (almost the double) used in entry 11 may be responsible, at least in part, of the observed phenomenon, due to a lower control of reaction tem-

perature caused by an initial increase of the reaction rate.

It is important to underline that, due to the relative long duration of each experiment up to now described (1 h) as compared with the high reaction rate and the amount of propylene charged (20 g), the productivity values achieved could be underestimated, the olefin being rapidly consumed in the first reaction period. Therefore, in the subsequent experiments (entries 12–15, Table 1) 80 g of propylene were charged. As expected, increasing the amount of charged propylene (entry 12) a very high productivity ( $\text{TOF} = 24800 \text{ h}^{-1}$ ) was obtained substantially maintaining the same selectivity performances. When MAO was used as co-catalyst, the  $\text{Al/Ni}$  molar ratio equal to 100 appeared to be the best checked value, an increase up to 500 (entry 13) causing a decrease of the catalyst productivity without any improvement of selectivity and overall yield to DMB. Even if we have recently reported [3] that, when a high content of DMB is present in the  $\text{C}_6$  cut also the  $\text{C}_9$  fraction is mainly constituted by highly branched components having high octane number values, thus allowing also to use them as valuable gasoline additives, an effort was done in order to reduce the amount of higher oligomers, particularly the  $\text{C}_{12+}$  fraction. In this context, the effect of molecular hydrogen, which is known to be one of the most effective chain transfer agents during the propylene polyinsertion catalyzed by Ziegler–Natta systems [9–11], was checked.

Indeed, when hydrogen was charged into the reactor up to 5 atm catalyst **I** activated by MAO (entry 14, Table 1) gave a significant decrease of the relative amount of  $\text{C}_{12+}$  accompanied by an appreciably increase of  $\text{C}_6$  components in the oligomeric mixture, still maintaining the same regio-selectivity to DMB within the  $\text{C}_6$  cut as in the absence of hydrogen (entry 12, Table 1). This procedure allowed to increase the overall yield to DMB up to about 55%. Moreover, the catalyst productivity, although lower, maintained a satisfactory value ( $\text{TOF} = 15500 \text{ h}^{-1}$ ).

A further increase of the hydrogen pressure (entry 15) did not substantially modify the picture. However, a more accurate analysis of reaction products allowed to ascertain the presence of a significant amount of propane, thus decreasing the interest from the industrial point of view on this approach for limiting higher oligomers formation. Finally, experiments carried out

at longer reaction times allowed also to conclude that a progressive decay of activity, as a function of the partial pressure of hydrogen applied, occurred, due to the reduction of the catalyst **I** to metal.

In order to check if a decrease of the reaction temperature below 25°C could allow a further improvement of regio-selectivity to DMB, some experiments were performed at 0°C, by using a Büchi glass reactor characterized by more efficient stirring and heat removal.

### 3.2. Selective propylene dimerization to DMB in toluene at 0°C by catalysts **I** prepared in situ from the Ni(naph)<sub>2</sub>/PCy<sub>3</sub> adduct and MAO

It is worthnoting that, the rocking stainless steel autoclave and the Büchi glass reactor, due to the different volume and geometry, as well as stirring conditions and propylene concentration adopted, are expected to give, even with the same catalytic system, different results in terms of productivity. However, as far as the catalyst selectivity is concerned, the comparison between experiments carried out into the two types of reactors should be acceptable.

As reported in Table 2, when catalyst **I** was obtained in the presence of MAO, an Al/Ni molar ratio equal to 100 was used and the experiment was carried out at 0°C (entry 16) both the regio-selectivity to DMB within the C<sub>6</sub> cut and the overall yield to these branched dimers were substantially similar to those obtained at 25°C (entry 12, Table 1). This result, contrarily to what previously observed in the propylene oligomerization catalyzed by nickel sys-

tems based on β-dithioketonate ligands [2,3], where a decrease of reaction temperature was always accompanied by a significant improvement of the selectivity to DMB, may be addressed to the stabilizing effect of naph chelate ligand on the nickel active sites. An increase of the molar ratio (MAO/Ni = 500), contrarily to what previously observed, produced (entry 17, Table 2) a detrimental effect on both activity and selectivity to DMB, thus suggesting that the interactions between the excess MAO and nickel active sites are temperature dependent.

When entry 16 is compared with the corresponding experiment carried out with catalyst **I** prepared by the oxidative addition of naph to the Ni(cod)<sub>2</sub>/PCy<sub>3</sub> adduct [4] (entry 18, Table 2), despite the lower regio-selectivity to DMB within C<sub>6</sub> cut (83.6 versus 90.4%) and the the overall yield to the same branched dimers obtained (44 versus 51.7%), again a large improvement of productivity was ascertained in the former case, as evidenced by the TOF values (5900 versus 1700 h<sup>-1</sup>) according to the higher stability of Ni(naph)<sub>2</sub> precursor as compared with Ni(cod)<sub>2</sub>.

It is worthnoting that the selectivity and productivity data obtained in entry 16 may be further improved by using balanced mixtures of organoaluminum co-catalysts having different Lewis acidity, this approach being resulted very promising when applied to the same catalysts obtained via oxidative addition of naph to the Ni(cod)<sub>2</sub>/PCy<sub>3</sub> adduct [5] as well as to nickel catalysts based on β-dithioketonate ligands [8].

In conclusion, the data reported in Tables 1 and 2 clearly indicate that catalysts **I**, prepared in situ

Table 2

Propylene oligomerization at 0°C by catalysts **I** prepared in situ from the Ni(naph)<sub>2</sub>/PCy<sub>3</sub> adduct and MAO as co-catalysts<sup>a</sup>

Entry	Nickel precursor		Dimers (%) <sup>b</sup>			C <sub>6</sub> (%)	C <sub>9</sub> (%)	C <sub>12+</sub> (%)	Y <sup>c</sup> (%)	TOF <sup>d</sup> (h <sup>-1</sup> )
	mmol	Al/Ni (mol/mol)	DMB	MP	HEX					
16	0.075	100	83.6	14.4	2.0	52.6	28.2	19.2	44.0	5900
17	0.075	500	53.6	38.2	8.3	48.4	29.6	22.0	25.9	2150
18 <sup>e</sup> [4]	0.10	100	90.4	9.4	0.2	57.2	25.3	17.5	51.7	1700

<sup>a</sup> Reaction conditions: Ni(naph)<sub>2</sub> was dissolved in boiling toluene, then PCy<sub>3</sub> was added at 50°C and the resulting adduct was activated at room temperature by MAO; P/Ni = 1.5 mol/mol; solvent (toluene) = 20 ml; time: 1 h; P<sub>C<sub>3</sub>H<sub>6</sub></sub> = 3 atm.

<sup>b</sup> DMB: 2,3-dimethylbutenes; MP: 2- and 4-methylpentenes; HEX: *n*-hexenes.

<sup>c</sup> Overall yield to DMB, determined as: fraction of DMB in C<sub>6</sub> cut × percentage of C<sub>6</sub> cut in the oligomeric products.

<sup>d</sup> Turnover frequency expressed as: mole of converted propylene/(mole of Ni × h).

<sup>e</sup> The catalyst was prepared by oxidative addition at 0°C of naph to the Ni(cod)<sub>2</sub>/PCy<sub>3</sub> equimolar adduct and subsequently activated by MAO; P/Ni = 1.5.

starting from Ni(naph)<sub>2</sub>, provided that a bulky and basic phosphine ancillary ligand and an organoaluminum compound of proper Lewis acidity are adopted, appear more suitable systems, as compared with those obtained by oxidative addition of naph to the Ni(cod)<sub>2</sub>/PCy<sub>3</sub> adduct in the presence of the same co-catalyst, for the manufacture of DMB.

#### 4. Conclusions

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

1. The reaction of bis( $\alpha$ -nitroketonate)nickel(II) complexes with organoaluminum compounds, in the presence of a bulky and basic phosphine ancillary ligand, allows one to obtain in situ catalytic systems with high productivity and regio-selectivity in the propylene dimerization to DMB.
2. The above catalysts are substantially constituted by the same active species as those produced by the oxidative addition of the free  $\alpha$ -nitroketone ligand to Ni(cod)<sub>2</sub> in the presence of the same ancillary phosphine ligand. A great advantage of these catalytic systems is that, differently from previous nickel catalysts based on other chelate ligands, they do not require to work in chlorinated solvents but more environmentally friendly hydrocarbon solvents may be adopted.
3. The catalysts obtained from Ni(naph)<sub>2</sub> are to be preferred to those prepared through oxidative addition of naph to Ni(cod)<sub>2</sub> because the former precursor is cheaper and more stable. Moreover, the slight decrease of regio-selectivity to DMB of the former systems is largely balanced by a higher activity.

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