

Novel nickel(II) and cobalt(II) catalysts based on poly-salen type ligands for the dimerization of propylene

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Abstract

A series of poly-salen type Ni(II) and Co(II) complexes were prepared, and the catalytic behavior in the dimerization of propylene has been studied in combination with aluminum co-catalysts and phosphine ligands. The effects of various reaction factors, such as the type of phosphine ligand and the P/Ni ratio, the type of aluminum co-catalyst and its quantity, particularly the nature of the nickel and cobalt complexes, were also examined. The results indicated that the productivity of the catalytic system was strongly dependent on the steric character of poly-salen ligand in the Ni(II) and Co(II) complexes. It was also found that reaction temperature deeply affected the performance of the catalytic system in the presence of phosphine ligand and alkyl aluminum promoter, and higher regioselectivities to 2,3-dimethylbutenes (2,3DMB) in the dimers were observed with incorporation of bulky and basic PCy₃ into the nickel and cobalt catalysts. An extremely high activity in the propylene dimerization (TOF up to 221,000 h⁻¹) was obtained with the **2b** system under suitable conditions, which was much higher than that obtained with the corresponding monomeric salen system. However, it seemed difficult to realize recycling of the catalysts owing to the restrict dependence of catalytic activity with its solubility, at least under the adopted conditions.

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1. Introduction

The salen ligand (salen: *N,N'*-bis(salicylaldehyde)-ethylenediamine) and its metal complexes were discovered since 19th century, the synthesis and chemistry of the salen type transition metal complexes have been extensively studied for decades [1,2]. Moreover, the potential catalytic behavior of the salen type species, especially in the areas of asymmetric catalysis [3], was gradually recognized on the basis of wide research work. There also appeared several reports concerning

application of the salen type iron and cobalt complexes in the oligomerization of ethylene with appreciable activity [4,5].

Currently, an interesting class of salen type metal complexes—poly-(salen-metal) complexes—have received much attention owing to their conducting character [6–13] as well as the electrocatalytic behavior [14–17]. More recently, a novel poly-salen Mn(III) complex containing chiral group was claimed to have application in the enantioselective epoxidation of olefin [18], which exhibited slightly lower activity and selectivity as compared with the corresponding monomeric salen system [19]. In addition, it was likely to recycle the catalysts in appropriate reaction systems.

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Dimerization of propylene is one of the important processes to convert low carbon olefin (e.g. C_2^{2-} , C_3^{2-} and C_4^{2-}) to useful value-added oligomers, such as fuel additives and monomeric starting material. Great efforts have been devoted to the dimerization of propylene since 1960s [20,21], and a large number of transition metal catalysts, particularly various types of nickel-based species in combination with Lewis acid activators and phosphine ligands, were successfully employed in such fields [22,23].

To the best of our knowledge, no reports appeared about the use of poly-salen nickel(II) and cobalt(II) complexes in olefin oligomerization up to now. In this contribution, several poly-salen type Ni(II) and Co(II) complexes were synthesized, and the catalytic performance in propylene oligomerization in the presence of aluminum co-catalysts and phosphine ligand was tested. The effects of various reaction factors, such as phosphine ligands, aluminum co-catalysts, the nature of poly-salen ligand in the precursor as well as the reaction temperature, were also checked.

An attempt to recycle the catalyst was also undertaken by changing the reaction medium, in which poly-salen species exhibited different solubility.

2. Experimental

All manipulations were performed under dry argon using standard Schlenk techniques. Chlorobenzene was dried and deoxygenated with P_2O_5 under atmosphere of argon after being treated with anhydrous $CaCl_2$ for a week. Anhydrous toluene was obtained by distillation on Na metal under dry argon and stored

on molecular sieves (4A). The other chemicals were used as received.

5,5'-Methylenebis(salicylaldehyde) and 5,5'-methylenebis(3-Bu^tsalicylaldehyde) were prepared according to literatures [24,25]. Poly-salen ligands were obtained by polycondensation of 1,2-diamine (ethylenediamine for poly-schiff base ligand **1**, 1,2-diaminocyclohexane for poly-schiff base ligand **2** and *o*-phenylenediamine for poly-schiff base ligand **3**) with equimolar amount of the corresponding disalicylaldehyde in ethanol or methanol [18,25,26]. The structure of poly-salen type ligands was characterized by 1H NMR, ^{13}C NMR and VPO analysis according to the procedures described in literatures [18,25]. The poly-salen type Ni(II) and Co(II) complexes (**1–3**, Fig. 1) were obtained according to the reported methods [18,25,26]. Ethylaluminumoxane (EAO) was prepared by partial hydrolysis of Et_3Al in toluene at -15 to -10 °C with finely ground $CuSO_4 \cdot 5H_2O$ as water source ($Al/H_2O = 1$, molar ratio) [27].

Catalytic batch experiments were carried out in a 250 ml stainless steel autoclave or a 500 ml rocking stainless steel autoclave equipped with magnetic stirring and jacket circulator cooling bath in order to maintain the reaction temperature. The appropriate amount of precursor suspended in solvent in a 50 ml Schlenk tube in the presence of desired phosphine ligands under argon, and transferred into the autoclave under propylene atmosphere, then the suitable Al co-catalyst was added. The internal temperature of the autoclave was adjusted to that of 3–5 °C lower than the desired value in advance because of the highly exothermic character of propylene dimerization. The autoclave was finally pressurized with propylene up to

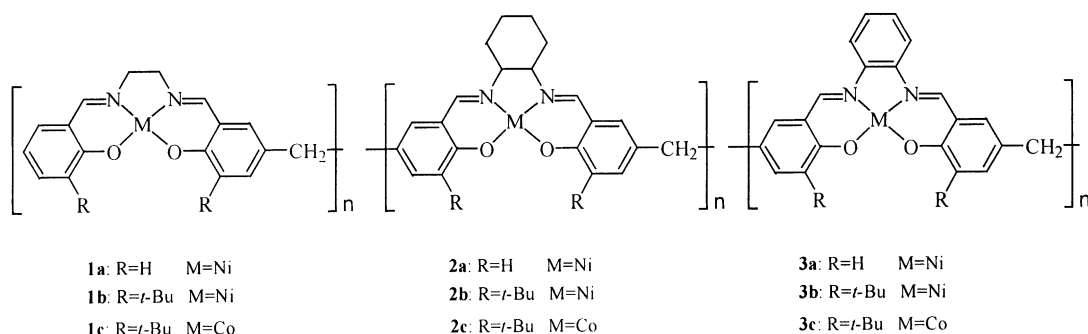


Fig. 1. The structures of poly-salen type nickel(II) and cobalt(II) complexes.

0.4 MPa. The pressure was manually held at that value by repeated propylene feeds. After 60 min the reaction was stopped by carefully degassing unreacted propylene and the liquid products were collected, weighted and analyzed by gas chromatography (GC). The reliability of the data in the dimerization experiments was evaluated to be in a range of $\pm 5\%$.

The oligomeric mixture was analyzed by GC on HP-4890D, equipped with FID and a 30 m SE-54 capillary column. *n*-Heptane was used as an internal standard. The distribution of the dimers was analyzed by GC-910 equipped with a 4 m \times 3 mm stainless steel column, with a stationary of 30% DMS. The column temperature stayed at 30 °C.

3. Results and discussion

3.1. Effect of the PPh_3/Ni molar ratio on the catalytic performance

Primarily, experiments were carried out to examine the catalytic performance under propylene atmosphere by the poly-salen type nickel complexes activated with organoaluminum co-catalyst. As evidenced in entry 1, poor activity in the dimerization of propylene was obtained by the nickel precursor **2a** in

combination with $Et_3Al_2Cl_3$, which characterized by strong Lewis acidity and good alkylating capability in the metal-catalyzed olefins activation process. This result indicated that it is rather difficult to activate of the poly-salen type nickel precursor only treated with alkyl aluminum promoter in the absence of phosphine ligand at the ambient temperature. It is well known that the catalytic behavior in propylene dimerization by transition metal system based on chelating ligands is remarkably modified by phosphine ligands, thus some experiments were carried out catalyzed by the nickel precursors **2a** and **3a** when PPh_3 was used as an additive in the presence of $Et_3Al_2Cl_3$ co-catalyst.

As demonstrated in Table 1, when a minor quantity of PPh_3 was used in the **2a** system ($P/Ni = 2$, entry 2), the catalytic system displayed a low productivity close to that of in the absence of phosphine ligands. When the P/Ni molar ratio was increased from 2 to 4, 10 and 20 (entries 3–5), certain improvement of the activity in the order was obtained as compared with that of entry 1. When the P/Ni molar ratio was raised up to 30 and 40 (entries 6 and 7), turnover frequency as high as $147,000 h^{-1}$ was observed in the system. However, the productivity of the catalytic process did not increase any more when the P/Ni ratio was higher than 40 (entry 8). Similar results were detected in the **3a** system in the presence of PPh_3 ancillary ligand (entries 9–13).

Table 1

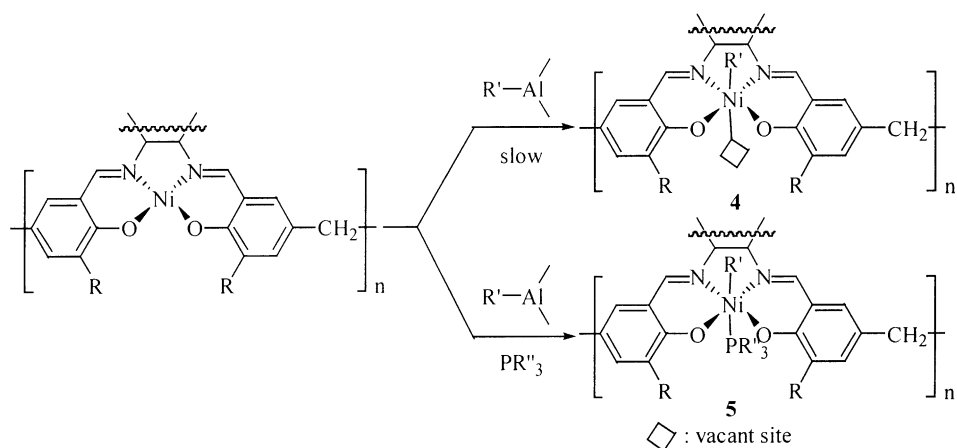
Effect of the PPh_3/Ni ratio on the catalytic performance with the **2a** and **3a** systems in the presence of PPh_3

Entry	Precursor	P/Ni (molar ratio)	TOF ^a (h^{-1})	C_6^{2-} (wt.%)	Dimers distribution (wt.%) ^b			
					4MP	2MP	Hex	2,3DMB
1	2a	0	10700	70.1	69.4	9.7	20.8	0.1
2	2a	2	11900	71.6	68.6	10.2	20.8	0.4
3	2a	4	44500	72.4	64.7	10.2	21.3	3.8
4	2a	10	45200	74.5	56.6	21.7	20.0	1.7
5	2a	20	48300	81.4	39.0	36.5	17.7	6.8
6	2a	30	138000	84.5	23.7	51.3	15.5	9.5
7	2a	40	140000	87.2	21.6	53.5	15.3	9.6
8	2a	60	120000	86.7	23.1	52.1	15.4	9.4
9	3a	2	121000	71.0	64.6	14.6	19.6	1.2
10	3a	4	23600	72.5	59.7	17.1	17.8	5.4
11	3a	10	43600	78.3	35.7	39.4	16.0	8.9
12	3a	20	63100	84.1	28.4	46.7	15.3	9.6
13	3a	40	130000	86.6	23.9	51.7	15.3	9.1

Reaction conditions: a 250 ml autoclave; 0.008 mmol precursor; $Et_3Al_2Cl_3$ as co-catalyst; Al/Ni (molar ratio) = 300; 18 ml $PhCl$; 0.4 MPa C_3^{2-} ; 20 °C; 60 min.

^a Turnover frequency expressed as moles of propylene converted/(moles of Ni \times h).

^b 4MP: 4-methylpentenes; 2MP: 2-methylpentenes; Hex: hexenes; and DMB: 2,3-dimethylbutenes.



Scheme 1.

It is well known that the formation of nickel hydride or alkyl nickel, which generally is the catalytically active nickel species, is required in nickel-catalyzed propylene dimerization. The outcome in entry 1 indicated that it was rather difficult to activate the poly-salen nickel complex with organoaluminum to give catalytically active intermediates (**4**, Scheme 1), the observation may be addressed to the structural character of rigid plane formed by nickel center. When large excess phosphine ligands were added, the strong bonding of Ni–X (X = N, O) might be weakened in some degree through coordinative interaction between phosphine ligand and nickel center. Hence it became easier to give active nickel species (**5**), which was stabilized by phosphine ligand, as demonstrated in Scheme 1.

As shown in Table 1, the selectivity of dimers was slightly increased by raising the relative amount of PPh₃ with respect to the nickel species. The regioselectivity towards 4-methylpentenes (4MP) in the C₆ cut declined steadily by increasing the P/Ni molar ratio, whereas a contrary tendency concerning the content of 2-methylpentene (2MP) was observed. However, the composition of the dimers was not substantially altered by varying the PPh₃/Ni ratio.

3.2. Effect of the relative amount and the type of Al co-catalyst on the catalytic performance

The above data showed that the catalytic productivity in the propylene dimerization by the poly-salen

nickel precursor and Et₃Al₂Cl₃ was remarkably improved when a large excess PPh₃ ligands were added. Herein, the effects of the type of aluminum co-catalyst and its quantity were tested on the catalytic process in the **2a** system.

When the Al/Ni molar ratio was increased from 100 to 300 (entries 13–15), as summarized in Table 2, the catalytic productivity was also enhanced steadily. However, a slight drop of activity was observed when the Al/Ni molar ratio higher than 300 was employed (entry 16). These data indicated that the proper value of Al/Ni molar ratio was at around 300. When Et₂AlCl and AlEt₃ were used as co-catalyst in the place of Et₃Al₂Cl₃ (entries 17 and 18), the catalytic activities were sharply declined. These results confirmed that strong Lewis acidity of aluminum co-catalyst was necessary for activation of the poly-salen nickel precursors even in the presence of phosphine ligands. No activity at all was obtained when EAO was adopted as co-catalyst, it may be due to its poor Lewis acidity not enough to generate the active nickel species. It was noteworthy that an extremely low activity was found when Al(*i*-Bu)₃ was used, the behavior was probably connected with the bulkiness of the *iso*-butyl group besides its poor Lewis acidity.

Higher selectivities to the dimers were observed in the case of Et₂AlCl and AlEt₃ co-catalysts (entries 17 and 18) compared to that obtained with Et₃Al₂Cl₃. The outcome may be attributed to a higher propensity of β-elimination to give the dimers rather than further insertion of propylene molecule in the catalytic

Table 2

Effect of the Al/Ni ratio and type of organoaluminum on the catalytic performance with **2a** in the presence of PPh₃

Entry	Al co-catalyst		TOF (h ⁻¹)	C ₆ ²⁻ (wt.%)	Dimers distribution (wt.%)			
	Type	Al/Ni (molar ratio)			4MP	2MP	Hex	2,3DMB
14	Et ₃ Al ₂ Cl ₃	100	12400	79.3	38.6	36.5	16.0	8.9
15	Et ₃ Al ₂ Cl ₃	200	60700	82.9	29.1	46.4	15.5	9.0
13	Et ₃ Al ₂ Cl ₃	300	130000	86.6	23.9	51.7	15.3	9.1
16	Et ₃ Al ₂ Cl ₃	500	95000	82.9	25.8	46.9	15.4	11.9
17	Et ₂ AlCl	300	28300	95.0	27.6	47.2	16.8	8.4
18	AlEt ₃	300	5900	92.5	30.6	46.7	15.9	6.8
19	Al(<i>i</i> -Bu) ₃	300	4500	92.0	34.2	43.5	15.6	6.7
20	EAO	300	0	–	–	–	–	–

Reaction conditions: a 250 ml autoclave; 0.008 mmol precursors; P/Ni (molar ratio) = 40; 18 ml PhCl; 0.4 MPa C₃²⁻; 20 °C; 60 min.

cycle. However, distribution of the dimers was essentially unaffected with changing the type of aluminum co-catalysts and its relative amount with respect to nickel species, at least under the adopted conditions.

3.3. Effect of the nature of Ni(II) and Co(II) precursors on the catalytic performance

It is well known that the structural property and the stability of salen type transition metal complexes are closely dependent on the nature of salen ligands, in terms of both the structural and the electronic character. Thus it is likely to modify the catalytic performance of the propylene dimerization through carefully tuning the nature of poly-salen ligands. Therefore, a

series of poly-salen type Ni(II) and Co(II) complexes characterized by different structural behavior were prepared and the catalytic behavior were also checked when treated with Et₃Al₂Cl₃ and PPh₃.

As shown in Table 3, when **2b** containing a bulky *tert*-butyl group on the phenolic ring was used as a precursor (entry 24), a marked increase of catalytic productivity was detected as compared with **2a** (entry 7). The productivities were also improved in the **1b** and **3b** systems (entries 22 and 30) comparable to the corresponding non-substituted parent species **1a** and **3a** (entries 21 and 13). It should be pointed out that a rather high catalytic activity was achieved even at the low P/Ni ratio equal to 2 (entries 24 and 25). All the above data could be explained that the steric

Table 3

Effect of the type of Ni(II) and Co(II) precursors on the catalytic performance in the presence of Et₃Al₂Cl₃ and PPh₃

Entry	Precursor	P/M (molar ratio)	TOF (h ⁻¹)	C ₆ ²⁻ (wt.%)	Dimers distribution (wt.%)			
					4MP	2MP	Hex	2,3DMB
21	1a	40	98800	84.0	26.1	49.3	15.7	8.9
22	1b	40	195000	91.0	21.2	54.5	14.9	9.4
23	1c	40	99100	85.5	27.2	49.6	14.9	8.3
7	2a	40	144000	87.2	21.6	53.5	15.3	9.6
24	2b	1	103000	80.4	59.2	23.4	16.4	1.0
25	2b	2	126000	78.6	49.3	29.4	17.4	3.9
26	2b	30	186000	82.7	37.9	40.2	14.8	7.1
27	2b	40	221000	89.1	20.3	55.7	14.5	9.5
28	2c	40	140000	86.2	28.1	47.9	14.4	9.6
13	3a	40	130000	86.6	23.9	51.7	15.3	9.1
30	3b	40	174000	85.5	25.7	44.7	14.3	15.3
31	3c	40	89000	85.5	27.0	48.9	15.2	8.9

Reaction conditions: a 250 ml autoclave; 0.008 mmol precursor; Et₃Al₂Cl₃ as co-catalyst; Al/M (molar ratio, M = Ni and Co) = 300; 18 ml PhCl; 0.4 MPa C₃²⁻; 20 °C; 60 min.

hindrance of *tert*-butyl group, which considered probably leading to a slight distortion of the N_2O_2 plane bound to nickel center, hence weaken the bonding of Ni–X (X = N, O). Therefore, it became easier to generate catalytically active species in situ from the metal precursors activated with aluminum co-catalyst even at low PPh_3/Ni molar ratio under the propylene atmosphere. It was also found that the **2** series of systems characterized by 1,2-cyclohexyl group in the diimine moiety displayed higher activity compared to the analogous **1** and **3** systems. The observation may be originated from a chair conformation of the cyclohexyl group existed in the nickel complexes exhibiting a “bulkiness effect” on the catalytic behavior similar to that of the *tert*-butyl group on the phenolate fragment. In contrast to the nickel systems, lower catalytic productivities by the corresponding poly-salen type cobalt species were detected under the same reaction parameters (entries 23, 28 and 31).

The selectivity of catalytic process, in terms of selectivity to dimers and distribution of the dimers, seemed essentially unaffected with tuning the nature of the poly-salen ligands in precursors, at least under the adopted conditions.

3.4. Effects of the nature of phosphine ligands and the reaction temperature on the catalytic performance

According to all the above results, high productivity and good selectivity to the dimers in the propylene dimerization by the poly-salen type Ni(II) and Co(II) complexes were ascertained in combination with aluminum co-catalyst and PPh_3 ligand. However, no significant modification of the regioselectivity of the dimers was obtained even by changing the nature of poly-salen ligands. Taking into account that the catalytic activity was enhanced remarkably by adding excess phosphine ancillary ligands, thus the influence of the type of phosphine ligands on the catalytic performance was also investigated. In addition, the effect of the reaction temperature on the dimerization process was examined as well. The results are listed in Table 4.

As evidenced in entry 36, when PCy_3 was used at the P/Ni molar ratio equal to 30 in the **2b** system, the activity was moderately decreased, whereas the regioselectivity to 2,3-dimethylbutenes (2,3DMB) in the C_6 fraction was raised from 9.5 to 50.3%

Table 4
Effect of the type of phosphine ligands on the catalytic performance at controlled temperatures^a

Entry	Precursor	Phosphine		T (°C)	TOF (h ⁻¹)	C ₆ ²⁻ (wt.%)	Dimers distribution (wt.%)			
		Type	P/M ^b				4MP	2MP	Hex	2,3DMB
32	1a	PCy ₃	30	20	54000	87.9	29.0	23.1	3.6	44.3
33	1b	PCy ₃	30	20	149000	95.2	25.8	22.6	3.5	48.1
34	1c	PCy ₃	30	20	62000	90.6	27.6	20.9	3.2	48.3
35	2a	PCy ₃	30	20	60000	82.0	27.6	18.7	3.3	50.4
36	2b	PCy ₃	30	20	160000	84.0	29.7	15.2	4.8	50.3
37	2c	PCy ₃	30	20	92800	86.6	25.4	20.9	3.5	50.2
38	3a	PCy ₃	30	20	46000	84.5	32.9	15.3	5.3	46.5
39	3b	PCy ₃	30	20	95500	88.2	28.2	16.4	4.0	51.4
40	3c	PCy ₃	30	20	42200	80.2	20.6	23.4	5.8	50.2
41	2b	PCy ₃	4	20	118000	80.2	50.9	20.5	8.7	19.9
42	2b	PCy ₃	4	5	134000	79.0	42.0	13.5	10.0	34.5
43	2c	PBu ₃ ^d	4	5	219000	90.1	41.2	32.2	6.2	20.4
44	2c	PEt ₃	4	5	127000	83.0	59.7	16.8	13.4	10.1
45	2d	PPh ₃	4	5	133000	71.8	48.7	24.4	14.0	12.9
46	2b ^c	PCy ₃	2	-5	140000	78.0	38.8	8.9	3.6	48.7
47	2b ^c	PCy ₃	4	-5	157000	90.0	21.1	18.3	3.3	57.3
48	2b ^c	PCy ₃	8	-5	176000	89.6	19.6	18.6	2.8	59.0

^a A 250 ml autoclave; 0.008 mmol precursor; Et₃Al₂Cl₃ as co-catalyst; Al/M (molar ratio) = 300; 18 ml PhCl; 0.4 MPa C₃²⁻; 60 min.

^b Molar ratio, M = Ni and Co.

^c A 500 ml autoclave; 0.016 mmol precursor; 36 ml PhCl, the other procedures are the same as in footnote a except for the temperature.

Table 5
Effect of recycle of the catalysts on the catalytic performance^a

Entry	Precursor	Cycle	TOF (h ⁻¹)	C ₆ ²⁻ (wt.%)	Dimers distribution (wt.%)			
					4MP	2MP	Hex	2,3DMB
27	2b	First	221000	89.1	20.3	55.7	14.7	9.3
49	2b	Second ^b	0	–	–	–	–	–
50	2b	Second ^c	16200	70.6	30.5	46.8	16.2	6.5
51	2b	First ^d	109000	80.6	23.1	51.5	16.3	9.1
52	2b	Second ^e	10800	71.2	28.6	49.7	15.1	6.6
53	6^f	First	129000	83.7	22.5	52.9	15.0	9.6

^a Reaction conditions in the first cycle: a 250 ml autoclave; 0.008 mmol precursor; Et₃Al₂Cl₃ as co-catalyst (Al/Ni = 300, molar ratio); PPh₃ (P/Ni = 40, molar ratio); 18 ml PhCl; 0.4 MPa C₃²⁻; 20 °C; 60 min, the other experiments in the first cycle were carried out with the same process as the entry 27 except for specified.

^b It became almost impossible to separation of catalysts by the traditional procedures of filtration and washing owing to the minimal amount of catalyst and its good solubilities in the catalytic system. Thus following procedure was adopted: adding 18 ml fresh PhCl to the autoclave after the first batch reaction in entry 27, 0.4 MPa C₃²⁻, 20 °C, 60 min.

^c Adding 18 ml fresh PhCl, PPh₃ (P/Ni = 40, molar ratio) and Et₃Al₂Cl₃ (Al/Ni = 300, molar ratio) after the first batch reaction in entry 27, the other reaction conditions are the same as in footnote b.

^d 18 ml PhMe used as solvent.

^e Adding 18 ml fresh PhMe, PPh₃ (P/Ni = 40, molar ratio) and Et₃Al₂Cl₃ (Al/Ni = 300, molar ratio) after the batch reaction in entry 50, other reaction conditions are the same as in footnote b.

^f (N,N'-bis(3-*tert*-Butylsalicylidene)-1,2-cyclohexanediaminato)nickel(II) complex.

compared to that obtained with PPh₃ in entry 26. Similar modification of the regioselectivity to 2,3DMB in the dimers was obtained in the other poly-salen systems in the presence of PCy₃ (entries 32–35, 37–40). Indeed, the distribution of the dimers was mainly determined by the direction of the nickel hydride (or alkyl nickel) addition to the propylene (Ni → C₁ or Ni → C₂) in the dimerization process. In the poly-salen system, in the first step the nickel hydride inserted the propylene molecule in the mode of Ni → C₁, which was unaffected by the type of phosphine ligands. The behavior could be explained in terms of the polarity of Ni–C, Ni–H and C=C bonds as the most nickel-based catalysts [22,23,29]. However, in the second step the mode of insertion was steadily altered from Ni → C₁ to Ni → C₂ as the bulky and basic PCy₃ was adopted, in which the steric interference played a decisive role through the axial coordination position of the N₂O₂ plane (5, Scheme 1). Hence, the regioselectivity to 2,3DMB in the dimers was preferred in the dimerization process. The outcome was consistent with what was observed for the π-allyl nickel system [28,29], in which incorporation of highly basic phosphine (except for the PBu₂^{*t*}Pr^{*i*}) into nickel catalysts led to improved selectivities to 2,3DMB.

As reported in Tables 4 and 5, when changing the reaction temperature from 20 °C over 5 to –5 °C with the PCy₃/Ni molar ratio equal to 4 (entries 41, 42 and 47), a continuous enhancement of regioselectivity to 2,3DMB in the C₆ cut was obtained, accompanied with a definite improvement of the catalytic activity. The results concerning the correlation between the regioselectivity and the reaction temperature may be explained as the difference of activation energies between the primary and secondary insertion of the second propylene molecule into alkyl nickel intermediates increased by lowering the temperature, hence the influence of bulky and basic PCy₃ ligand on the catalytic behavior became stronger in the second insertion step [30]. On the other hand, the solubility of propylene in the reaction medium substantially increased by lowering the reaction temperature, thus promoted the insertion rate of propylene molecule into nickel species and resulted in higher productivities. However, the influence of the reaction temperature at the adopted range in the poly-salen system was not pronounced as that of the NiBr(η-C₃H₅)(PCy₃) system at the range of –55 to –75 °C, in which the activity almost doubled as raising 10 °C [31].

When PPh₃, PEt₃ and P(*n*-Bu)₃ were employed as additives, respectively (entries 43–45), no significant

modification of selectivity like to PCy₃ was observed (entry 42). In the case of P(*n*-Bu)₃ system (entry 43), a drastically high activity was obtained, however, no remarkable modulation of the product distribution was achieved relative to that of PCy₃. It may be originated from the lower bulkiness and higher flexibility of *n*-butyl group, although P(*n*-Bu)₃ displayed slightly lower basicity as PCy₃ [32,33]. All the above results concluded that the presence of phosphine ligands with high basicity and large bulkiness was necessary to obtain a predominant regioselectivity to 2,3DMB in the C₆ fraction. The variation of catalytic productivity possibly resulted from the different effects of various phosphine ligands on the rate of both formation of active nickel species and β-elimination of nickel intermediates to give the dimers in the catalytic process.

Unfortunately, it should be underlined that the precursor exhibited good solubility in the reaction medium when chlorobenzene was used as a solvent in the presence of aluminum co-catalysts and phosphine ligands. Thus it seemed difficult to realize recycling of the poly-salen catalysts through simply adding fresh solvent and promoters after the first batch reaction (entries 49 and 50, Table 5). When the reaction medium was changed from chlorobenzene to toluene (entry 51), in which the nickel precursor exhibited lower solubilities, the catalytic activity also considerably decreased compared to that of entry 27. Poor productivity was obtained as well when reusing the catalyst by adding fresh solvent and aluminum co-catalysts as well as phosphine ligands (entry 52). The total outcome recycling the catalyst in toluene (entries 51 and 52) seemed not as good as the results using the catalyst one time in chlorobenzene (entry 27), at least under the adopted reaction conditions in Table 5.

However, the poly-salen type system displayed much higher productivities in the propylene dimerization relative to that obtained with the corresponding monosalen system (entry 53). There does not appear significant difference between the structure of poly-salen ligand and that of salen monomer. However, a large number of nickel species existed in the polymeric chain in the poly-salen type complexes, whereas the discrete nickel species generated in the reaction medium in the latter. Therefore, it is probably that a “concerto effect” between the individual salen ligands in the poly-salen complexes system occurred.

4. Conclusions

On the basis of all the above results, the following conclusions can be made:

1. For the first time, the catalytic behavior of the poly-salen type Ni(II) and Co(II) complexes for propylene dimerization has been investigated in combination with aluminum co-catalysts and phosphine ligands.
2. The catalytic performance might be modified by changing reaction parameters, such as the type of phosphine ligands and P/Ni ratio, the type and relative amount of aluminum promoters as well as the reaction temperature. Greater selectivities to 2,3DMB in the dimers were obtained by incorporation of basic PCy₃ in the nickel and cobalt catalysts, especially at a lower temperature.
3. The nature of Ni(II) and Co(II) precursors also deeply affected the activity in the catalytic system. It was found that higher bulky character of the poly-salen ligands led to higher productivity. An extremely high activity was obtained by the **2b** system under appropriate conditions, which is much higher as compared with the analogous monosalen nickel species.
4. It was difficult to realize recycling of the poly-salen catalysts due to the close relationship between the catalytic activity and the solubilities of catalysts in reaction medium, at least under the adopted conditions.

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