



Propylene dimerization using bis(salicylaldehyde)nickel(II) complexes in the presence of organoaluminum and phosphine ligands

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Abstract

Dimerization of propylene was studied with several bis(salicylaldehyde)nickel(II) complexes in combination with aluminum co-catalysts, eventually in the presence of ancillary phosphine ligands. The effects of the type and relative amount of aluminum co-catalyst as well as the nature of nickel precursors were examined. The results clearly indicated that the nickel precursors characterized by the presence of either bulky substituents or electron-withdrawing groups on the salicylaldehyde ligands displayed high activity. The catalytic performance was also remarkably modified in the presence of phosphine ligand, and the regioselectivity in the dimers was directed to 2,3DMB with incorporation of basic and bulky PCy₃ into the nickel catalysts, especially at the temperature below 0 °C. A preliminary UV-Vis study was performed in order to detect the variation of nickel species involved in the dimerization process. The bis(2-hydroxy-1-naphthaldehyde)nickel (**1d**) system exhibited an extremely high productivity (TOF up to 262,000 h⁻¹) as well as a moderate regioselectivity to 2,3DMB (65.6%) in the dimerization of propylene under appropriate reaction parameters.

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1. Introduction

Considerable interests have been devoted to bis(salicylaldehyde)nickel(II) complexes in the past decades, owing to their easy preparation and modification of the steric and electronic properties by using different substituents on the phenolic ring [1,2]. The potential catalytic performance of bis(salicylaldehyde)nickel(II) complexes was also progressively explored on the basis of extensive research

work. Recently, there appeared some reports regarding use of Group 4 metal catalysts based on salicylaldehyde ligands in the activation of olefin [3,4], and few concerning the nickel species.

The nickel catalysts based on β-diketonate chelating ligands have been studied in the dimerization of propylene when treated with aluminum co-catalysts and phosphine ligands since the sixties [5]. For decades, a wide variety of β-diketonate nickel systems and their analogous species have been investigated in order to develop more effective catalytic systems for olefin oligomerization [6–17]. In most cases, the active species are in situ prepared from various bis(β-diketonate)nickel(II) species in the presence of

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appropriate Lewis acid activators, which is generally called Ziegler–Natta catalysts [6,7]. Thus it becomes more convenient to modulate the catalytic system, and the correlation between the catalytic performance and various reaction parameters in the β -diketonate nickel systems has been extensively investigated, such as the linear relationship between productivity and acidity of the β -diketonate ligands [10,13,15,16], the dependence of content of *n*-hexene and the property of Al co-catalysts used in propylene dimerization [12,13,17]. Moreover, the mechanistic aspects, in terms of kinetic consideration and thermochemistry [13,18–20] as well as the active intermediates involved in the oligomeric process [16,18,20,21], have been also discussed through various analytical methods in the diketonate systems.

Indeed, the bis(salicylaldehyde)nickel(II) complexes displayed an analogous chelating environment around nickel center based on oxygen–oxygen bidentate coordination as compared with that of bis(β -diketonate)nickel(II) species [1,2]. Thus it is likely to activate bis(salicylaldehyde)nickel(II) complexes with proper promoters under propylene atmosphere. Herein, dimerization of propylene with several bis(salicylaldehyde)nickel(II) complexes combined with aluminum co-catalyst and/or phosphine ligand was undertaken. Particular attention was devoted to effect of the nature of salicylaldehyde ligands on the catalytic behavior.

Furthermore, currently it again appears of great interest in the regioselective dimerization of propylene to 2,3DMB. Due to the products it might be used as an additive to raise the octane value of gasoline after its hydrogenation ([6,7,23–26] and references therein). Therefore, influence of the type of phosphine ligands and its relative amount with respect to nickel metal would be also discussed, especially at a controlled temperature. In addition, a preliminary investigation of UV-Vis spectrum would be performed to clarify the change of nickel species involved in the catalytic process.

2. Experimental

All manipulations were carried out under purified argon using standard Schlenk techniques. Anhydrous toluene was obtained by distillation on Na under dry

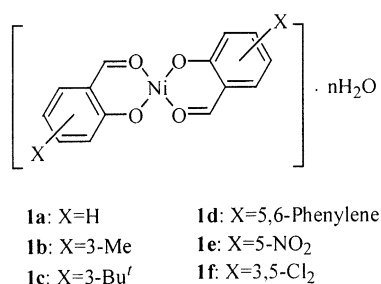


Fig. 1.

argon and stored on molecular sieves (4A). Chlorobenzene was dried and deoxygenated with P₂O₅ under atmosphere of argon after being treated with anhydrous CaCl₂ for a week. The other chemicals were used as received.

3-Mesalicylaldehyde and 3-Bu^t salicylaldehyde were prepared according to literature [27]. Bis(salicylaldehyde)nickel(II) complexes (**1a–1f**, Fig. 1) were obtained according to reported methods [28]. Ni(acac)₂ was achieved by reacting of NiCl₂·6H₂O with acetylacetone in the presence of anhydrous NaAc followed by dehydrated in vacuum. Ethylaluminumoxane (EAO) was prepared by partial hydrolysis of Et₃Al carefully in toluene at –15 to –10 °C with finely ground CuSO₄·5H₂O as water source (Al/H₂O = 1, molar ratio) [29].

Catalytic batch experiments were performed in a 100 ml stainless steel autoclave or a 500 ml stainless steel autoclave equipped with a high-rate magnetic stirring and jacket circulator cooling bath in order to maintain the reaction temperature. The proper amounts of nickel precursor dissolved in chlorobenzene in a 50 ml Schlenk tube in the presence of desired phosphine ligands under argon, and transferred into the autoclave under propylene atmosphere, the proper Al co-catalyst was added. Then the temperature was adjusted to that of 3–5 °C lower than the desired value owing to the highly exothermic character of propylene dimerization, especially in the case of a larger amount of catalysts being used in Table 5. The autoclave was finally filled with propylene up to 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, weighed and analyzed by gas chromatography (GC).

The reliability of experimental data was evaluated to be in the 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 internal standard. The distribution of 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 was 30 °C.

Analysis of UV-Vis spectra was carried out on a V-550 UV-Vis double-ray spectrophotometer (JASCO) operating between 300 and 800 nm with a scanning rate of 120 nm/min.

3. Results and discussion

3.1. Influence of the relative amount of aluminum co-catalyst on catalytic performance

Preliminary experiments were run to examine the catalytic performance under propylene atmosphere by nickel precursor **1c** in the presence of $\text{Et}_3\text{Al}_2\text{Cl}_3$ co-catalyst, and the effect of Al/Ni molar ratio was also discussed. The results were illustrated in Table 1.

It was found that the bis(3-Bu^t salicylaldehyde)-nickel(II) complex (**1c**) displayed no activity at all in the activation of propylene in the absence of aluminum co-catalyst (entry 1). Significant activity was detected in the presence of a low amount of $\text{Et}_3\text{Al}_2\text{Cl}_3$ with respect to nickel metal (Al/Ni = 50, entry 2). When the Al/Ni molar ratio was raised from 50 over 100–200 (entries 2–4) the productivity progressively increased

as well. As further increasing the Al/Ni molar ratio higher than 200 (entries 5–7), no improvement of activity was achieved any more. The results indicated that the proper value of Al/Ni molar ratio was around 200 when $\text{Et}_3\text{Al}_2\text{Cl}_3$ was adopted as a co-catalyst.

The results in Table 1 also turned out that the dimers selectivity in oligomeric mixtures slightly enhanced with raising the relative concentration of aluminum co-catalyst, whereas the distribution of dimers was essentially unaffected in the adopted range.

It is well developed that the active nickel species was in situ generated by treatment of bis(β -diketonate)nickel(II) [22,30] or bis(α -nitroketonate)nickel(II) complexes [31] with organoaluminum under ethylene atmosphere, which has been confirmed by UV-Vis, IR and NMR analysis. Herein, UV-Vis analysis of the bis(salicylaldehyde)nickel(II) system in dimerization of propylene was also carried out with the aim to detect the variation of nickel species involved in the catalytic process. A band at 341 nm with a molar extinction coefficients equal to 8000 l/(mol cm) was detected in the UV-Vis spectroscopy of the bis(3-Bu^t salicylaldehyde)nickel(II) complex (**1c**) in chlorobenzene (curve a, Fig. 2). However, when $\text{Et}_3\text{Al}_2\text{Cl}_3$ was added with a Al/Ni molar ratio equal to 100 (curve b), the band at 341 nm absolutely vanished and a new band centered at 400 nm appeared. At the same time, the color of the nickel solution was changed from yellow green to light brown. On increasing the Al/Ni molar ratio up to 200 (curve c), the spectrum did not substantially altered except for the molar extinction coefficients. A spectroscopy analogous to curve c, except that a further reduction of

Table 1
Influence of the Al/Ni ratio on catalytic performance by precursor **1c**

Entry	Al/Ni (molar ratio)	TOF ^a (h ⁻¹)	C ₆ ²⁻ (wt.%)	Distribution of dimers (wt.%) ^b			
				4MP	2MP	Hex	2,3DMB
1	0	0	–	–	–	–	–
2	50	69000	72.5	59.7	19.9	15.6	4.8
3	100	109000	78.1	56.8	24.4	15.0	3.8
4	200	120000	82.0	50.9	29.0	15.9	4.2
5	300	115000	89.0	44.9	34.3	16.0	4.8
6	400	96700	80.3	59.7	19.9	15.6	4.8
7	600	87600	72.5	58.6	20.3	16.4	4.7

Reaction conditions: 0.008 mmol nickel precursor, 10% $\text{Et}_3\text{Al}_2\text{Cl}_3$ in toluene, 18 ml PhCl, 0.4 MPa C₃²⁻, 20 °C, 60 min.

^a TOF, turnover frequency determined as moles of propylene converted/(moles of Ni \times h).

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

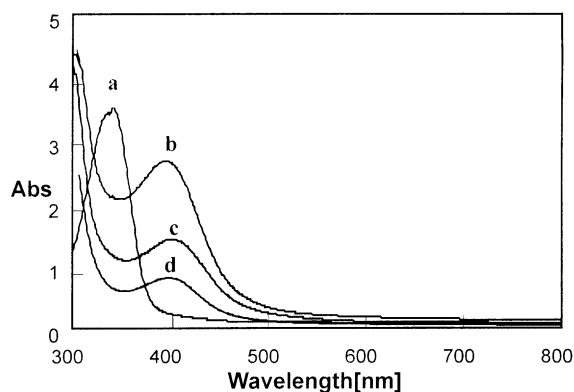
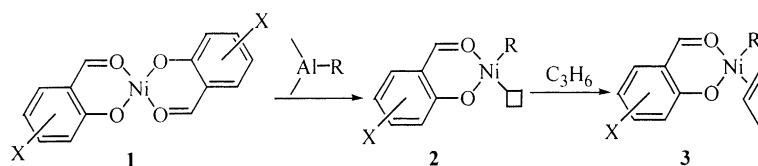


Fig. 2. Interaction of bis(3-Bu^t salicylaldehyde)nickel(II) with Et₃Al₂Cl₃ in chlorobenzene solution at different Al/Ni molar ratio, as checked by UV-Vis analysis: (a) Al/Ni = 0, (b) Al/Ni = 100, (c) Al/Ni = 200 and (d) Al/Ni = 200 under propylene atmosphere.

the absorption intensity occurred, was observed under propylene atmosphere with the Al/Ni molar ratio at 200. All the above observation indicated that the pristine bis(3-Bu^t salicylaldehyde)nickel(II) complex did not exist in chlorobenzene solution any more when alkylaluminum was added with a Al/Ni molar ratio higher than 100. According to what is known for the interaction of bis(β-diketone)nickel(II) complexes and bis(α-nitroketone)nickel(II) complexes with organoaluminum under ethylene atmosphere [6,7,30,31], it allowed to suggest that, when treatment of bis(salicylaldehyde)nickel(II) complex with aluminum co-catalyst, it led to release one of the two salicylaldehyde ligands and afford an alkyl nickel intermediate (**2**) which constantly coordinated with propylene molecule to give **3** due to the presence of a vacant site, as shown in Scheme 1.

3.2. Influence of the type of aluminum co-catalyst on catalytic performance

It was confirmed that the presence of aluminum activators was required in the activation of propylene by



Scheme 1.

the bis(salicylaldehyde)nickel(II) precursor. Here, effect of the type of aluminum promoters on the catalytic behavior was also checked.

As demonstrated in Table 2, when Et₃Al₂Cl₃ was used as a co-catalyst in the place of Et₃Al₂Cl₃ in the **1b** system, it led to a remarkable reduction of activity (entry 8). Lower catalytic productivity was observed when AlEt₃ was adopted as an alkylating agent instead of Et₂AlCl (entry 9). In the case of EAO system (entry 11), it gave a rather poor productivity. All the above data turned out that, in addition to intermediate alkylating capability, proper Lewis acidity of aluminum co-catalyst was necessary to activate bis(salicylaldehyde)nickel(II) species for the propylene dimerization. The catalytic system also displayed a low activity when treated with Al(*i*-Bu)₃ co-catalyst, probably due to its scarce Lewis acidity as well as the bulkiness of *iso*-bulky group.

Although some variation of the selectivity to the dimers occurred with changing the type of aluminum co-catalyst, and the regioselectivity of the catalytic process was essentially unaffected, at least under the adopted conditions.

3.3. Influence of the nature of nickel precursors on catalytic performance

It is well established that the property of bis(salicylaldehyde)nickel(II) complexes was closely dependent on the type of salicylaldehyde ligand [1,2]. Hence, it is likely to modify catalytic behavior of the dimerization reaction by varying the nature of ligands. Therefore, the catalytic performance of several bis(salicylaldehyde)nickel(II) complexes characterized by differently substituted salicylaldehyde ligands was described.

As shown in Table 3 when bis(3-*tert*-butylsalicylaldehyde)nickel(II) complex (**1c**) was adopted as a precursor (entries 4 and 18), activity of the catalytic system was substantially increased as compared

Table 2
Influence of Al co-catalyst on catalytic performance by precursor **1c**

Entry	Al co-catalyst	TOF (h ⁻¹)	C ₆ ²⁻ (wt.%)	Distribution of dimers (wt.%)			
				4MP	2MP	Hex	2,3DMB
4	Et ₃ Al ₂ Cl ₃	120000	82.0	50.9	29.0	15.9	4.2
8	Et ₂ AlCl	68400	95.6	52.0	28.7	17.2	2.1
9	AlEt ₃	53000	89.7	51.3	27.9	16.5	4.3
10	Al(<i>i</i> -Bu) ₃	21500	87.3	55.4	26.8	16.1	1.7
11	EAO	8600	88.2	52.7	27.5	16.8	3.0

Reaction conditions: 0.008 mmol nickel precursor, Al/Ni (molar ratio) = 200.18 ml PhCl, 0.4 MPa C₃²⁻, 20 °C, 60 min.

with those of **1a** in entries 12 and 17 whenever either Et₃Al₂Cl₃ or Et₂AlCl was employed as a co-catalyst. The productivity with precursor **1b**, characterized by a methyl group on three-position of the phenolic ring (entry 13), was lower than that of **1c**, although it exhibited higher activity than **1a**. Rather high productivity was obtained as well by the bis(2-hydroxy-1-naphthaldehyde)nickel(II) complex (**1d**) system (entries 14 and 19). From all the above results, it could be concluded that steric characteristics of salicylaldehyde ligands enhanced the activity of catalytic system. This behavior was likely addressed to the fact that the highly bulkiness of ligands allowed to improve the rate of formation of active nickel intermediate in the catalytic process through weakening the bonding of ligands with nickel center. It was noteworthy that rather high activities were detected as well with both the bis(5-nitrosalicylaldehyde)nickel(II) complex (**1e**)

and bis(3,5-dichlorosalicylaldehyde)nickel(II) complex (**1f**) (entries 15, 16 and 20). The observation might be originated from the fact that the electron-withdrawing character of nitro group in the phenolic ring reduced the electron density of nickel center, hence increased the insertion rate of propylene molecule and improved the activity of the catalytic system. In fact, almost a linear correlation between the catalytic activity and the acidity of diketone ligands was detected as well in the β-diketone nickel systems [10,13,15,16]. Thus, the catalytic behavior of Ni(acac)₂ in the propylene dimerization was also discussed here in order to compare difference of the two systems. As reported in entries 21 and 22, notwithstanding the Ni(acac)₂ species exhibited slightly higher productivity than **1a**, and the value was much lower than those of the nickel systems with either highly bulky substituents (**1c**, **1d** and **1f**) or

Table 3
Influence of the nature of nickel precursors on catalytic performance

Entry	Precursor	Co-catalyst	TOF (h ⁻¹)	C ₆ ²⁻ (wt.%)	Distribution of dimers (wt.%)			
					4MP	2MP	Hex	2,3DMB
12	1a	Et ₃ Al ₂ Cl ₃	87000	75.0	54.9	23.8	16.2	5.1
13	1b	Et ₃ Al ₂ Cl ₃	104000	82.1	64.5	14.9	18.2	2.4
4	1c	Et ₃ Al ₂ Cl ₃	120000	82.0	50.9	29.0	15.9	4.2
14	1d	Et ₃ Al ₂ Cl ₃	117000	82.9	51.7	26.7	14.8	6.8
15	1e	Et ₃ Al ₂ Cl ₃	132000	83.7	63.2	16.1	17.8	2.9
16	1f	Et ₃ Al ₂ Cl ₃	112000	81.3	61.1	16.2	19.7	3.0
17	1a	Et ₂ AlCl	31500	89.7	55.6	25.0	16.1	3.3
18	1c	Et ₂ AlCl	68400	95.6	52.0	28.7	17.2	2.1
19	1d	Et ₂ AlCl	70200	91.2	51.2	27.4	15.8	5.6
20	1e	Et ₂ AlCl	71000	89.5	60.1	20.6	14.8	4.5
21	Ni(acac) ₂	Et ₃ Al ₂ Cl ₃	92000	81.7	57.4	22.9	15.1	4.6
22	Ni(acac) ₂	Et ₂ AlCl	41000	90.8	56.9	20.4	17.4	5.3

Reaction conditions: 0.008 mmol nickel precursor, Al/Ni (molar ratio) = 200.18 ml PhCl, 0.4 MPa C₃²⁻, 20 °C, 60 min.

electron-withdrawing groups (**1e**) on the salicylaldehyde ligands.

However, the results in Table 1 showed that the product composition was relatively unaffected with varying the substituents of ligands, at least under the adopted reaction conditions.

3.4. Influence of the type and relative amount of phosphine ligand on catalytic performance

From all the above data, high activity by bis(salicylaldehyde)nickel(II) precursors combined with aluminum activator was assured in the propylene dimerization. However, no significant modification of the dimers distribution was achieved even tuning the nature of ligands. It is well known that the catalytic performance of various nickel catalysts in the dimerization of propylene, in terms of both activity and selectivity, is substantially influenced by the presence of phosphine ligands [6,7,32,33]. Herein, experiments were run to examine the effect of the presence of PCy₃ on the bis(salicylaldehyde)nickel(II) and organoaluminum system at ambient temperature.

The results in Table 4 indicated that, when PCy₃ was added in the **1c** system, the regioselectivity of 2,3-dimethylbutene (2,3DMB) in the C₆ cut was en-

hanced in the order with increasing the P/Ni ratio in the range from 2 to 30 through 3, 10 and 20 (entries 23–27), whereas the catalytic productivity was slightly varied. On further increasing the P/Ni ratio higher than 30 (entries 28 and 29), no further improvement of selectivity of 2,3DMB occurred any more. Similar results were detected in the other nickel systems (**1a**, **1b**, **1d–1f**; entries 30–34). According to what is known for the effect of phosphine ligands on the catalytic behavior in π -allyl nickel system [32,33], it allowed to suggest that, in the first step, nickel hydride (or alkyl nickel) inserts into propylene molecule in the Ni \rightarrow C₂ mode, which is essentially unaffected by the nature of phosphine ligands. In the second step, the presence of highly hindered and basic PCy₃ would direct the dimerization process to formation of 2,3DMB within the C₆ cut through steric interference. When Pet₃, PPh₃ and P(*n*-Bu)₃ were employed as additives (entries 36–38) no remarkable modification of products distribution was obtained as compared with PCy₃. Although a drastic activity was achieved in the case of P(*n*-Bu)₃ system (entry 37), and a lower content of 2,3DMB in the C₆ cut was detected compared to that of entry 27. The behavior might be connected with lower bulkiness and more flexibility of *n*-butyl group of P(*n*-Bu)₃ ligand although

Table 4

Effect of the type of phosphine ligand and the P/Ni ratio on the catalytic performance

Entry	Precursor	Phosphine		TOF (h ⁻¹)	C ₆ ²⁻ (wt.%)	Distribution of dimers (wt.%)			
		Type	P/Ni ^a			4MP	2MP	Hex	2,3DMB
23	1c	PCy ₃	2	102000	74.2	50.7	20.0	15.7	13.6
24	1c	PCy ₃	5	109000	76.0	58.8	15.9	12.1	18.2
25	1c	PCy ₃	10	116000	83.5	46.9	17.0	11.7	24.4
26	1c	PCy ₃	20	124000	88.8	34.1	19.5	6.2	40.2
27	1c	PCy ₃	30	125000	91.6	25.5	20.8	4.4	49.3
28	1c	PCy ₃	40	123000	83.2	20.6	26.0	4.3	49.1
29	1c	PCy ₃	60	18000	85.4	24.1	23.9	4.6	47.4
30	1a	PCy ₃	30	117000	88.1	25.3	23.7	5.0	46.0
31	1b	PCy ₃	30	124000	88.0	26.9	20.9	5.3	46.9
32	1d	PCy ₃	30	131000	86.9	24.9	21.1	4.7	49.3
33	1e	PCy ₃	30	157000	89.3	31.7	16.4	5.6	46.3
34	1f	PCy ₃	30	136000	88.6	29.1	19.5	6.1	45.3
35	Ni(acac) ₂	PCy ₃	30	112000	89.1	18.5	29.4	4.3	47.8
36	1c	PCy ₃	30	121000	82.3	57.6	21.3	10.8	10.3
37	1c	PBu ^{<i>n</i>} ₃	30	226000	82.9	31.2	37.5	5.6	25.7
38	1c	Pet ₃	30	111000	80.5	32.0	39.8	8.1	20.1

Reaction conditions: 0.008 mmol precursor, 10% Et₃Al₂Cl₃ in toluene, Al/Ni (molar ratio) = 200.18 ml PhCl, 0.4 MPa C₃²⁻, 20 °C, 60 min.

^a Molar ratio.

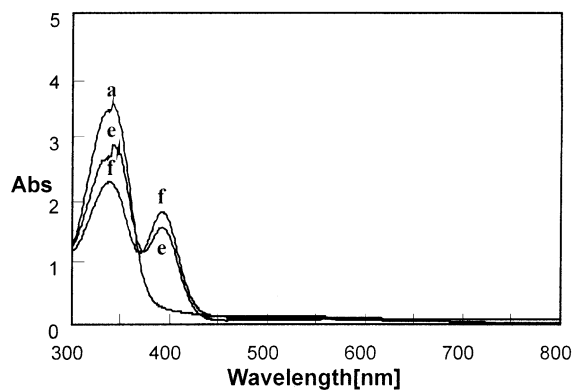


Fig. 3. Interaction of bis(3-Bu^t salicylaldehyde)nickel(II) with PCy₃ in the absence of organoaluminum in chlorobenzene solution at different P/Ni molar ratio, as checked by UV-Vis analysis: (a) P/Ni = 0, (e) P/Ni = 4 and (f) P/Ni = 30.

it exhibited slightly lower basicity than PCy₃ ligand [34,35].

The UV-Vis spectroscopy of the bis(salicylaldehyde)nickel system in the presence of PCy₃ was also studied here in order to detect the interaction of phosphine ligand with nickel species during the catalytic process. As shown in Fig. 3, when PCy₃ was added with a P/Ni molar ratio equal to 4 in the absence of aluminum co-catalyst (Fig. 3, curve e), a new band centered at 392 nm with a molar extinction coefficients equal to 5.101 l/(mol cm) was observed, whereas the absorption band of the pristine nickel complex **1c** (341 nm) still existed. On further raising the relative amount of PCy₃ with a P/Ni ratio up to 30 (curve f), a similar spectrum to that of the curve e was observed with two bands at 392 and 339 nm, respectively. The observation indicated that, despite its high basicity, PCy₃ is able to only partially displace salicylaldehyde ligand from the nickel metal even under extreme condition (P/Ni = 30) [23,36]. Indeed, no activity at all was achieved in the above nickel system (relative to that of curve f) under propylene atmosphere by GC analysis. Therefore, a further UV-Vis study concerning the interaction of the **1c**/PCy₃ with an alkyl aluminum promoter was performed as well. As evidenced in curve g (Fig. 4), when Et₃Al₂Cl₃ was added to the **1c**/PCy₃ adduct (P/Ni = 4, Al/Ni = 200), a novel band centered at 408 nm appeared with a molar extinction coefficients equal to 1.919 l/(mol cm) and the original band of the bis(salicylaldehyde)nickel(II)

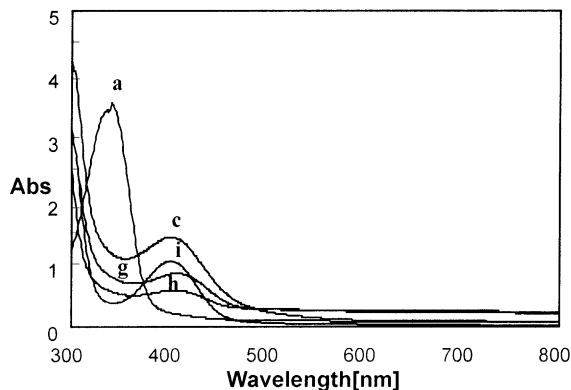
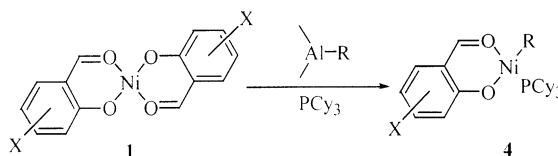


Fig. 4. Interaction of bis(3-Bu^t salicylaldehyde)nickel(II) with PCy₃ in the presence of Et₃Al₂Cl₃ (Al/Ni = 200) in chlorobenzene solution at different P/Ni molar ratio, as checked by UV-Vis analysis: (c) P/Ni = 0, (g) P/Ni = 4, (h) P/Ni = 30 and (i) P/Ni = 300 under propylene atmosphere.

complex at 341 nm thoroughly disappeared. In the case of PCy₃/Ni ratio equal to 30 (Al/Ni = 200, curve h), no novel bands were observed, accompanied with a certain reduction of the absorption intensity of the band at 341 nm. A band at 396 nm with increasing intensity related to curve h was detected under propylene atmosphere (P/Ni = 30, Al/Ni = 200, curve i). These results might be explained that, when treatment of bis(salicylaldehyde)nickel(II) with excess PCy₃ ligands and Et₃Al₂Cl₃ promoters, it caused the formation of the nickel precursor **4** (Scheme 2), which stabilized by coordination with phosphine ligand. Under propylene atmosphere, the intermediate **4** would coordinate with propylene molecule to afford novel alkyl nickel species, then the dimerization reaction began to occur. Indeed, when Et₃Al₂Cl₃ was added to the **1c**/PCy₃ mixture, the color of the solution was sharply changed from yellow green to red brown. Moreover, the red brown color of the resulting nickel species was immediately faded as propylene was bubbled into the solution. Similar observation concerning



Scheme 2.

the UV-Vis spectra has been reported for the corresponding bis(β -diketonate)nickel(II), bis(salicylaliminate)nickel(II) and bis(α -nitroketonate)nickel(II) systems [36–39].

The outcome obtained with the Ni(acac)₂ catalyst was similar to that of **1a**, as shown in entry 35.

3.5. The effect of reaction temperature on catalytic performance in the presence of phosphine ligand

From the above results, certain modification of regioselectivity to 2,3DMB in the C₆ cut was obtained in the presence of PCy₃ at ambient temperature. Here, experiments were carried out at a controlled temperature in the presence of phosphine ligands.

As evidenced in Table 5, when the reaction temperature decreased from 15 °C over 5 to –5 °C in **1d** system (entries 39, 40 and 46), significant enhancement of productivity was observed accompanied by a significant increase of regioselectivity towards 2,3DMB in the C₆ cut. When further lowering the reaction temperature to –15 °C (entry 48), slightly higher selectivity of 2,3DMB was given whereas a certain drop of productivity occurred. The results also indicated that the catalytic behavior, in terms of activity and

regioselectivity to 2,3DMB, was improved with increasing the P/Ni ratio from 1 to 8 at –5 °C (entries 44–47). Similar results were obtained by other bis(salicylaldehyde)nickel species (such as **1a**, **1b**, **1c**, **1e** and **1f**; entries 49–53) under the identical reaction conditions as entry 46. It should be noteworthy that an extremely high productivity (up to 270,000 h^{–1}) with a moderate regioselectivity of 2,3DMB within the dimers (62.3%) was achieved with the catalyst **1e** characterized by the presence of nitro group of the salicylaldehyde ligand (entry 52). In addition, from all the above results in Table 5, it was concluded that the effects of various reaction parameters, such as the nature of nickel complexes and the type of phosphine ligands, became stronger on the catalytic performance compared to those obtained at ambient temperature.

All the above results may be interpreted that the difference of activation energies between the two insertion fashions of second propylene molecule into nickel carbon bond was increased as lowering the reaction temperature, thus it became more effective of the modification of phosphine ligands and the type of salicylaldehyde ligands on the catalytic behavior [40,41]. Furthermore, the solubility of propylene in the reaction medium was substantially enhanced with

Table 5

Influence of the reaction temperature on catalytic performance in the presence of phosphine ligands^a

Entry	Precursor	Phosphine		T (°C)	TOF (h ^{–1})	C ₆ ^{2–} (wt.%)	Distribution of dimers (wt.%)			
		Type	P/Ni ^b				4MP	2MP	Hex	2,3DMB
39	1d	PCy ₃	4	15	109000	79.8	40.1	19.0	12.2	28.7
40	1d	PCy ₃	4	5	162000	73.5	33.6	11.2	4.7	50.5
41	1d	PCy ₃	4	5	137000	90.2	59.3	19.4	15.8	5.5
42	1d	PBu ^u ₃	4	5	280000	82.9	30.6	38.8	4.5	26.1
43	1d	Pet ₃	4	5	110000	78.6	31.1	40.2	7.5	21.2
44	1d^c	PCy ₃	1	–5	174000	71.7	40.5	11.9	6.2	41.4
45	1d^c	PCy ₃	2	–5	176000	87.8	25.5	14.2	1.7	58.6
46	1d^c	PCy ₃	4	–5	221000	86.7	23.2	13.6	2.3	60.9
47	1d^c	PCy ₃	8	–5	262000	82.9	24.0	9.3	1.1	65.6
48	1d^c	PCy ₃	4	–15	152000	82.0	22.3	14.0	1.5	62.2
49	1a^c	PCy ₃	4	–5	171000	72.9	29.4	12.2	11.7	46.7
50	1b^c	PCy ₃	4	–5	192000	90.7	26.8	13.9	1.6	57.7
51	1c^c	PCy ₃	4	–5	192000	91.6	21.1	16.1	2.2	60.6
52	1e^c	PCy ₃	4	–5	270000	90.2	21.6	14.1	2.0	62.3
53	1f^c	PCy ₃	4	–5	232000	85.6	24.7	13.6	2.7	59.0
54	Ni(acac) ₂ ^c	PCy ₃	4	–5	168000	80.4	25.1	15.8	3.9	55.2

^a 0.008 mmol nickel precursor, Et₃Al₂Cl₃ as co-catalyst, Al/Ni (molar ratio) = 300.18 ml PhCl, 0.4 MPa C₃^{2–}, 60 min.

^b Molar ratio.

^c 0.016 mmol nickel precursor, 36 ml PhCl, other reaction parameters are the same as in footnote 'a' except for the temperature.

lowering the temperature, and improved, the rate of dimerization reaction. On the other hand, the nickel intermediates probably became more stable at lower temperatures.

Both the catalytic activity and the selectivity of 2,3DMB in the dimers obtained with the Ni(acac)₂ system (entry 54) were lower than those bis(salicylaldehyde)nickel(II) species, characterized by the presence of either bulky substituents or electron-withdrawing groups on the salicylaldehyde ligands.

4. Conclusions

On the base of all the above results, the following conclusions can be drawn:

1. For the first time, the catalytic behavior of the bis(salicylaldehyde)nickel(II) complexes for propylene dimerization was studied in combination with aluminum co-catalyst, eventually in the presence of phosphine ligand.
2. The results indicated that the catalytic activity was remarkably affected by the nature of nickel precursors as well as the type of phosphine ligands used. Incorporation of bulky and basic PCy₃ into the nickel catalysts resulted in preferred formation of 2,3DMB in the C₆ cut, particularly at lower temperatures.
3. A preliminary study of the UV-Vis spectrum of the bis(salicylaldehyde)nickel(II) system has been performed, and several nickel intermediates were supposed to afford in the catalytic process based on the results of UV-Vis analysis.
4. The bis(salicylaldehyde)nickel catalysts, characterized by the presence of either highly bulky substituents or strongly electron-withdrawing groups on the salicylaldehyde ligands, exhibited much higher catalytic behavior than the corresponding Ni(acac)₂ system, although the latter displayed a similar catalytic performance to the **1a** system.

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