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Journal of Organometallic Chemistry 689 (2004) 2614–2623

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Novel neutral arylnickel(II) phosphine catalysts containing 2-oxazolinylphenolato N–O chelate ligands for ethylene oligomerization and propylene dimerization

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Received 28 January 2004; accepted 18 May 2004
Available online 6 July 2004

Dedicated to Professor Yanlong Qian

Abstract

A series of new neutral arylnickel(II) phosphine complexes **1** bearing 2-oxazolinylphenolato ligands [2-(4-R^1-5-R^2-C$_3$H$_2$NO)–C$_6$H$_4$O]Ni(2-R^4-4-R^3-C$_6$H$_3$)(PPh$_3$) were synthesized by reactions of sodium salts of 2-(4,5-dihydro-2-oxazolyl)phenol derivatives with *trans*-Ni(Ar)(Cl)(PPh$_3$)$_2$ or by direct reactions of the ligands with *trans*-Ni(Ar)(Cl)(PPh$_3$)$_2$ in the presence of NEt$_3$. These neutral Ni(II) complexes **1** exhibited high activities and selectivities in ethylene oligomerization and propylene dimerization. The catalytic activities and the product distributions were dependent on the selection of various organoaluminum cocatalysts and phosphine scavenger (Ni(COD)$_2$). The effects of various reaction conditions on ethylene oligomerization were also examined. The highest activity of 5.51×10^5 g oligomers/(mol Ni·h) and 83% selectivity of C$_6$ internal olefins were obtained in **1a**/MAO catalytic system in ethylene oligomerization. The oligomers consisted mainly of lower carbon olefins in the range of C$_4$–C$_8$. Complexes **1** showed the moderate tolerance of polar additives in ethylene oligomerization. The highest activity of **1a**/MAO in propylene dimerization reached to 1.32×10^5 g oligomers/(mol Ni·h).

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Keywords: Nickel complexes; Oxazoline ligand; Ethylene oligomerization; Propylene dimerization

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1. Introduction

Late transition metal catalysts attracted considerable attentions in both scientific and commercial fields in transforming α-olefins to more valuable oligomers or polymers [1–4]. Because of their less oxophilic nature, late transition metal complexes generally had more tolerance of polar media than early transition metal complexes did. Nickel and palladium complexes containing α-diimine ligands as olefin polymerization catalysts had been reported by Brookhart and co-workers [5]. These complexes could not only polymerize ethylene to high-branched polymers but also copolymerize ethylene and polar-functionalized α-olefins [6]. Grubbs and co-workers [7,8] described the neutral salicylaldiminato nickel complexes, which exhibited high catalytic activity and good tolerance of polar functional group in ethylene polymerization [9]. In addition, Brookhart [10] and Gibson [11] groups, reported highly active cationic iron and cobalt olefin polymerization catalysts with bulky pyridine diimine

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0022-328X/$ - see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.jorganchem.2004.05.021

ligands independently, whose activities were up to 10^7 TOF. At the same time, Mecking [12–14] and Claverie [15–17] groups, successfully applied Ni(P^O), Ni(N^O), and Pd(N^N) chelating complexes in aqueous emulsion ethylene polymerization with the coming out of the stable polymer latices.

Furthermore, late transition metal complexes could act as better candidates for olefin oligomerization because of their facile β-hydrogen elimination [18]. The researches could go back to the prominent SHOP catalytic systems of α-keto-ylide nickel catalysts [(P^O)Ni(R)(L)] reported by Keim and co-workers [19–21]. Later, many neutral and cationic late transition metal complexes with chelating ligands have been successfully applied in the field of olefin oligomerization [22]. Recently, Brookhart and co-workers [23–25] reported that nickel and iron complexes bearing diimine ligands with MMAO together showed high activities in ethylene oligomerization by decreasing the steric hindrance of aniline. He [26] and Qian [27] groups, revealed the catalytic property of diimine pyridyl iron complexes when EAO or MMAO were employed in ethylene oligomerization. Bianchini et al. [28] also reported that cobalt complexes with pyridylimino ligands could act as efficient catalysts for ethylene oligomerization. More recently, Carlini and co-workers [29–34] investigated that many olefin oligomerization catalytic systems based on neutral nickel complexes bearing anionic [N^O] and [O^O] chelate ligands showed high activities and selectivities for ethylene or propylene oligomerization. So, the design and selection of ligand's backbone of catalysts were of current interest in the field of olefin oligomerization and polymerization by late transition metal catalysts.

2-Oxazolinylphenolato ligands had extensive applications in the catalytic reaction fields [35–40]. In contrast to salicyaldimine ligands, the basicity of the nitrogen atom of 2-oxazolinylphenolato ligand was a litter stronger, because the oxygen in the oxazoline ring was conjugated with C=N. So, it could be deduced that the strong coordination of the nitrogen with metal centers was in existence. If the ligands were introduced to arylnickel phosphine complexes, it was speculated that the neutral nickel complexes might serve as olefin oligomerization catalysts. With this in mind, we designed and synthesized neutral nickel complexes **1** bearing 2-oxazolinylphenolato ligands. We have reported the short communication about the synthesis of complex **1a** and the application in catalyzing olefin oligomerization [41]. In this paper, the synthesis of oxazoline–nickel complexes **1a**–**1f** and their catalytic behavior in ethylene and propylene oligomerizations were studied in detail when complexes **1** were activated by methylaluminoxane (MAO), diisobutylaluminum hydride (DIBAL-H), triethylaluminum ($AlEt_3$), and di(1,5-cyclooctadiene)nickel ($Ni(COD)_2$).

2. Results and discussion

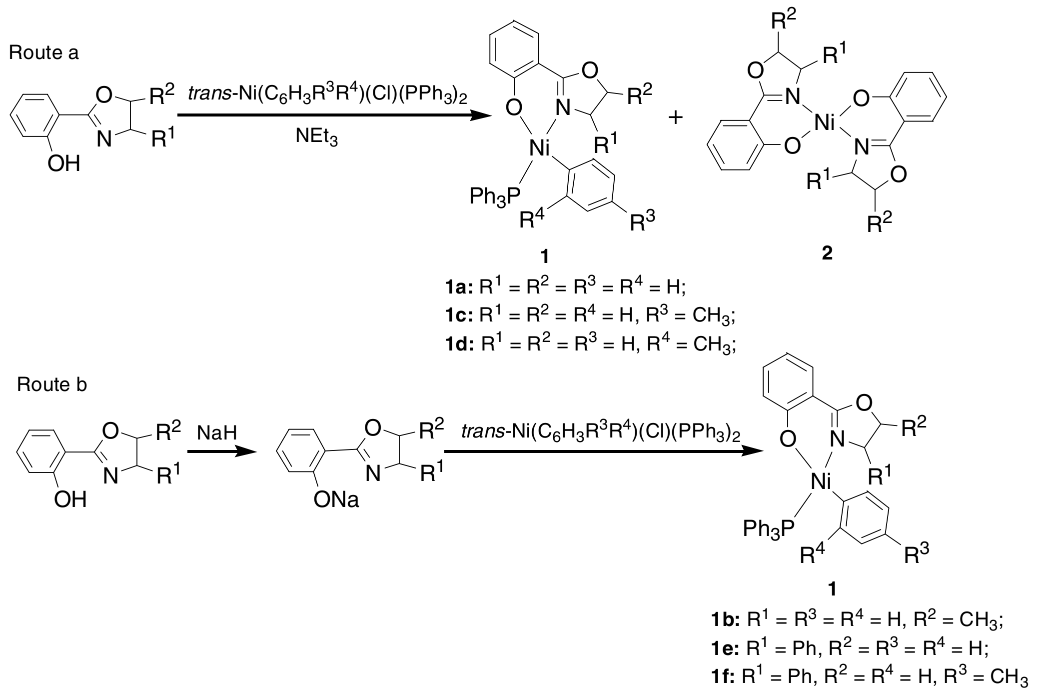
2.1. Synthesis and structure characterization

Two synthetic routes of neutral nickel complexes **1** are shown in Scheme 1. In route b, similarly to the synthesis of salicylaldiminato nickel complexes [7], the reaction of the sodium salt of 2-(5-methyl-4,5-dihydro-2-oxazolyl)phenol or 2-(4-phenyl-4,5-dihydro-2-oxazolyl)-phenol with *trans*-Ni(Ar)(Cl)$(PPh_3)_2$ results in the formation of complexes **1b**, **1e** and **1f**. However, the solubility of sodium salt obtained by the reaction of 2-(4,5-dihydro-2-oxazolyl)phenol with NaH is very poor, which leads to lower yield. In view of the high acidity of the hydroxyl proton, route a is adopted to obtain target complexes **1a**, **1c** and **1d** in the presence of NEt_3. Although there are some by-products of bis(2-oxazolinylphenolato)nickel complexes **2**, the separation of these two kinds of complexes **1** and **2** is very easy according to their different solubility in toluene.

The IR spectra of the free oxazoline ligands show a very strong absorption band at 1642 cm^{-1} attributed to $\nu_{C=N}$, while the $\nu_{C=N}$ of complexes **1** is in 1608–1617 cm^{-1}. The shift of the C=N stretching absorption band to lower frequency indicates the decrease of the C=N stretching force constant as a consequence of the coordination through the nitrogen atom, which is in agreement with the results of X-ray diffraction [41]. The strong absorption bands in about 1435 (ν_{P-C}) and 693 (ν_{Ni-P}) cm^{-1} can confirm the existence of PPh_3 [42]. The weak absorption bands of **1** in 572–576 cm^{-1} and 460–464 cm^{-1} may be attributed to ν_{Ni-N} and ν_{Ni-O}, respectively [43]. The X-ray diffraction reveals that complexes **1** have a square-planar arrangement and the ligand, phenyl, triphenylphosphane coordinate with nickel atom, and triphenylphosphane is in the *trans*- position to the N atom [41].

2.2. Ethylene oligomerization

The neutral nickel complexes **1** with 2-oxazolinylphenolato ligands exhibit considerable activities and selectivities in ethylene oligomerization. The highest activity up to 5.51×10^5 g oligomers/(mol Ni·h) can be obtained by **1a**/MAO catalytic system (Table 1). The products provided by complexes **1** consist mainly of dimer, trimer and tetramer. For example, in **1**/MAO, only low-molecular-weight oligomers (C_4–C_8 olefins) are formed, and the proportion of the trimer (C_6 olefins) is relatively high. No other oligomers such as C_{10} and higher carbon olefins are detected by GC analysis. In order to study the effects of the cocatalysts and phosphine scavenger on the catalytic properties, another two sets of experiments are performed: one using DIBAL-H and $AlEt_3$ as organoaluminum cocatalysts, whose results are listed in Tables 2 and 3; and the other using

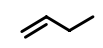
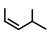
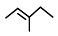


1a: $R^1 = R^2 = R^3 = R^4 = H$;
1c: $R^1 = R^2 = R^4 = H, R^3 = CH_3$;
1d: $R^1 = R^2 = R^3 = H, R^4 = CH_3$;

1b: $R^1 = R^3 = R^4 = H, R^2 = CH_3$;
1e: $R^1 = Ph, R^2 = R^3 = R^4 = H$;
1f: $R^1 = Ph, R^2 = R^4 = H, R^3 = CH_3$

Scheme 1. Synthetic routes of complexes **1**.

Table 1
Ethylene oligomerization with complexes **1**/MAO[a]

Run	Reaction conditions			Activity (×10^5 g (mol Ni·h)$^{-1}$)	Distribution of oligomers (%)			Distribution of C_4 (%)	Distribution of C_6 (%)		
	Catalyst	Cocatalyst	Al:Ni		C_4	C_6	C_8				
1	**1a**	MAO	1000	5.51	9.0	82.9	8.1	100	17.5	20.3	62.2
2	**1b**	MAO	1000	4.59	13.9	73.8	12.3	100	21.1	27.1	51.8
3	**1c**	MAO	1000	4.42	7.9	80.9	11.2	100	14.0	36.0	50.0
4	**1d**	MAO	1000	3.65	5.4	77.9	16.7	100	15.9	40.5	43.6
5	**1e**	MAO	1000	5.43	7.0	83.0	10.0	100	19.1	29.1	51.8
6	**1f**	MAO	1000	4.57	7.0	87.3	5.7	100	21.4	30.5	48.1
7[b]	**1a**	MAO	1000	1.82	45.8	27.3	26.9	100	72.4	Trace	27.6
8[c]	**1a**	MAO	1000	1.47	78.1	21.9	Trace	100	100	Trace	Trace
9[d]	**1a**	MAO	1000	2.09	28.0	48.1	23.9	100	31.2	Trace	68.8

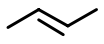
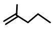
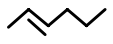
[a] Conditions: 1.5 μmol of complexes **1**; solvent: toluene; total volume: 30 ml; ethylene pressure: 12 atm; temperature: 25 °C; reaction time: 0.5 h.
[b] Polar additive: 1.5 ml Et_2O.
[c] Polar additive: 1.5 ml THF.
[d] Polar additive: 1.5 ml CH_2Cl_2.

$Ni(COD)_2$ as phosphine scavenger, whose results are listed in Table 4.

It is noted that oxazoline–nickel complexes **1** are highly active catalysts for ethylene oligomerization when activated by MAO, DIBAL-H, and $AlEt_3$ (Tables 1–3). The activities of **1**/organoaluminum catalytic systems are almost 10 times as high as those of **1**/$Ni(COD)_2$ (Table 4). In any organoaluminum cocatalytic system, higher activities can be shown by complex **1a**, which has no any substituent on its oxazoline ring and Ni-aryl. In **1**/MAO and **1**/$AlEt_3$, **1c**, **1d** and **1f** show slightly lower activities than the corresponding complexes **1a** and **1e**, because of the methyl substituent on Ni-aryl (*ortho*- or *para*-position). Especially, **1d** with the *ortho*-substituent on the aryl shows the lowest catalytic activity among all six complexes **1** when activated by any one of three organoaluminum cocatalysts, because of the effects of Ni-aryl steric bulkiness on the formation of Ni-hydride active species. In contrast, no oligomers are detected by GC analysis when cocatalysts or phosphine scavenger are absent in the catalytic system (Table 4, run 24).

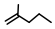
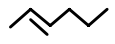
Keim and Schulz [21] summarized that the limitation of ligand backbone flexibility could bring higher catalytic activities in the known Ni(P^N) complexes. In this

Table 2
Ethylene oligomerization with complexes **1**/DIBAL-H[a]

Run	Reaction conditions			Activity (×10^5 g (mol Ni·h)$^{-1}$)	Distribution of oligomers (%)			Distribution of C_4 (%)		Distribution of C_6 (%)		
	Catalyst	Cocatalyst	Al:Ni		C_4	C_6	C_8					
10	**1a**	DIBAL-H	500	4.87	54.0	28.7	17.3	54.8	45.2	25.5	31.1	43.4
11	**1b**	DIBAL-H	500	3.28	56.5	32.0	11.5	46.5	53.5	24.2	Trace	75.8
12	**1c**	DIBAL-H	500	5.10	49.8	31.6	18.6	36.7	63.3	18.1	26.5	55.4
13	**1d**	DIBAL-H	500	2.40	33.0	59.9	7.1	100	Trace	14.8	30.0	55.2
14	**1e**	DIBAL-H	500	2.95	57.7	33.8	8.5	44.7	55.3	26.3	Trace	73.7
15	**1f**	DIBAL-H	500	3.41	53.1	35.2	11.7	42.1	57.9	25.7	Trace	74.3

[a] Conditions: 1.5 μmol of complexes **1**, solvent: toluene, total volume: 30 ml, ethylene pressure: 12 atm, temperature: 25 °C, reaction time: 0.5 h.

Table 3
Ethylene oligomerization with complexes **1**/$AlEt_3$[a]

Run	Reaction conditions			Activity (×10^5 g (mol Ni·h)$^{-1}$)	Distribution of oligomers (%)			Distribution of C_4 (%)	Distribution of C_6 (%)		
	Catalyst	Cocatalyst	Al:Ni		C_4	C_6	C_8				
16	**1a**	$AlEt_3$	500	3.64	61.8	11.1	27.1	100	46.0	28.5	25.5
17	**1b**	$AlEt_3$	500	1.50	60.6	13.8	25.6	100	22.7	47.8	29.4
18	**1c**	$AlEt_3$	500	1.09	47.5	36.9	15.6	100	22.1	66.9	11.0
19	**1d**	$AlEt_3$	500	1.36	79.8	5.1	15.1	100	36.9	32.9	30.2
20	**1e**	$AlEt_3$	500	2.35	68.1	14.3	17.6	100	48.4	35.7	15.9
21	**1f**	$AlEt_3$	500	2.00	75.9	6.5	17.6	100	33.9	38.3	27.8

[a] Conditions: 1.5 μmol of complexes **1**, solvent: toluene, total volume: 30 ml, ethylene pressure: 12 atm, temperature: 25 °C, reaction time: 0.5 h.

Table 4
Ethylene oligomerization with complexes **1**/$Ni(COD)_2$[a]

Run	Reaction conditions			Activity (×10^5 g (mol Ni·h)$^{-1}$)	Distribution of oligomers (%)		
	Catalyst	Phosphine scavenger	$Ni(COD)_2$:catalyst		C_4	C_6	C_8
22	**1a**	$Ni(COD)_2$	2	0.56	–	15.1	84.9
23	**1b**	$Ni(COD)_2$	2	0.62	–	47.2	52.8
24	**1a**	–	–	0	–	–	–

[a] Conditions: 1.5 μmol of complexes **1**, solvent: toluene, total volume: 30 ml, ethylene pressure: 12 atm, temperature: 25 °C, reaction time: 0.5 h.

system, the oxygen atom in the oxazoline ring is conjugated with C=N, so it is possible that the π-conjugated system is composed of the phenyl ring and the oxazoline ring, which makes the structure of ligands more rigid. Thus, the structural factor makes the ethylene insertion into the active center accelerated and the catalytic activities improved.

Tables 1–3 also shows that the selectivities of **1**/MAO, **1**/DIBAL-H, and **1**/$AlEt_3$ are excellent in obtaining only lower carbon olefins (C_4–C_8 olefins). As reported in cationic Ni α-diimine catalytic system, the axial steric hindrance on metal has a more pronounced effect on the selectivity of ethylene polymerization and oligomerization [23–25,44]. In order to obtain lower carbon oligomers, lower steric demand should be satisfied in the molecular structure of complexes **1** to speed up the occurrence of chain transfer (*β*-H elimination).

Most of ethylene oligomerization catalytic systems reported show the good selectivity of linear α-olefins. Surprisingly, in **1**/MAO, the oligomers formed are exclusive branched C_6 internal olefins ranging from 74% to 87% (wt%). The major components of C_6 olefins are *cis*-4-methyl-2-pentene, *cis*-3-methyl-2-pentene, and *trans*-3-methyl-2-pentene. Babik and Fink [45] reported that higher steric demand of bisiminepyridine iron complexes could promote the formation of linear α-olefins. As to the **1**/MAO catalytic system, lower steric hindrance of oxazoline ligands may cause the formation of internal olefins, especially of 2-olefins. Svejda and Brookhart [24] proposed the mechanism of chain isomerization and chain transfer with diimine nickel complexes in ethylene oligomerization. By analogy, we suppose the possible mechanism of ethylene oligomerization with complexes **1** (Scheme 2). After ethylene insertion and chain propagation occurs to (Scheme 2, Path A), if chain transfer (β-H elimination) takes place, α-olefins can be formed. On the contrary, if chain isomerization takes place, the formation of internal olefins is inevitable (Scheme 2, Path B).

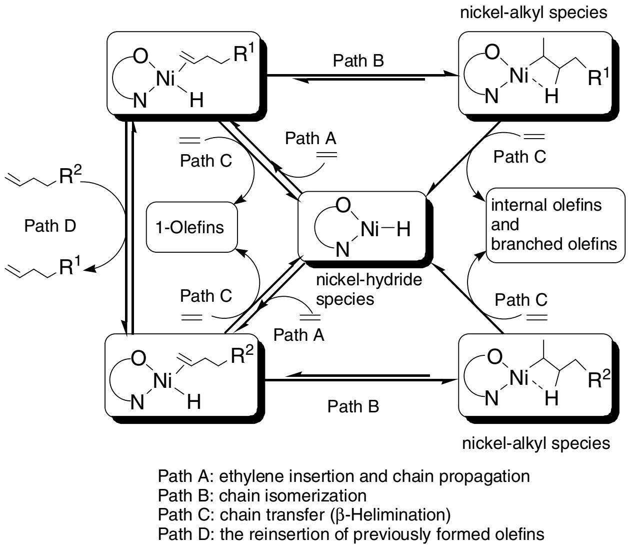
Upon activation with both DIBAL-H and $AlEt_3$, complexes **1** show the excellent selectivities to C_4 fraction. In **1**/DIBAL-H, the content of C_4 olefins composed by 1-butene and 2-butene is about 51% (wt%); while in **1**/$AlEt_3$, 1-butene is about 66% (wt%) of the total amount of oligomers produced. For both cases above, three kinds of C_6 olefins are obtained, which are 2-methylpentene, 1-hexene, and 2-hexene. We note that the dependence of the selectivity on the nature of the cocatalysts seems to correlate with the bulk of cocatalysts in ethylene oligomerization [46]. The MAO molecule is much larger than $AlEt_3$ and is favor to the formation of C_6 fraction. It is possible that these activators acting as ligands attach to the nickel center, making chain propagation faster than chain transfer (*β*-H elimination) and affecting the catalytic performance. In recent studies, the XAS spectroscopy supports this assumption that the alkylaluminum activator bonds to the metal active center [47,48].

In analogy with **1**/organoaluminum catalytic system, lower carbon olefins, C_6 and C_8 olefins, are also obtained in **1**/Ni(COD)$_2$. However, C_8 fraction is major product rather than C_6 and C_4 fractions. It is well known that phosphine scavengers, such as Ni(COD)$_2$, plays a important role of the removal of PPh_3 in the course of olefin oligomerization or polymerization [7,49]. In combining with Ni(COD)$_2$, SHOP-type oligomerization catalysts could also convert ethylene to polyethylene with molecular weights over 1,000,000. Interestingly, when phosphine scavenger is applied to the neutral oxazoline–nickel catalytic system, the molecular weights of oligomers slightly increase, and polymer can not be obtained. Although **1**/Ni(COD)$_2$ show moderate activity to produce olefin oligomers, being a non-organoaluminum activator, Ni(COD)$_2$ plays a crucial role in the stabilization of the catalytic active site.

In view of higher activity of **1a**/MAO catalytic system, some further studies are performed aiming at evaluating the influence of ethylene pressure, reaction temperature, and Al/Ni molar ratio as well as oligomerization in the presence of polar additives on the activity and selectivity.

In **1**/MAO, Fig. 1 demonstrates clearly that the higher ethylene pressure, the higher the catalytic activity. For example, the enhancement of ethylene pressure (from 4 to 12 atm) gives a proportional promotion of the activities from 2.32×10^5 to 5.51×10^5 g oligomers/(mol Ni·h) in **1a**/MAO. In the meantime, the selectivity of trimer (C_6 fraction) increases and the selectivity of dimer (C_4 fraction) decrease (Fig. 2). However, the enhancement of ethylene pressure has no dramatic effect either on the distribution of C_4 olefin (100% 1-butene) or on the distribution of C_6 olefins. The other five complexes **1b**–**1f** follow the same general tendency in activity and distribution as observed on **1a**.

Higher ethylene pressure means to the enhancement of ethylene concentration in toluene. As explained above, Scheme 2 illustrates that ethylene concentration affects not only on the steps of ethylene insertion and



Scheme 2. Proposed mechanism of ethylene oligomerization with complexes **1**.

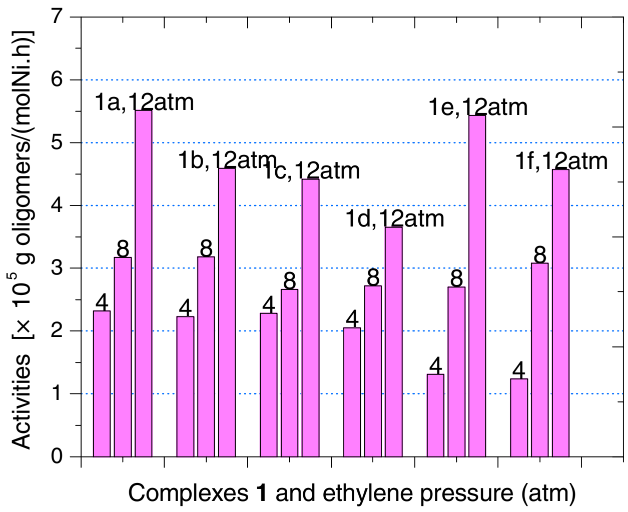


Fig. 1. The effects of ethylene pressure on activities with complexes **1**/MAO.

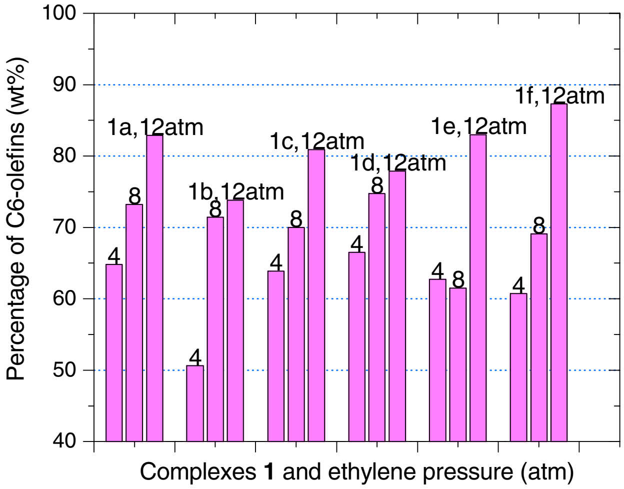


Fig. 2. The effects of ethylene pressure on product distribution with complexes **1**/MAO.

chain propagation (Path A) but also on the step of chain transfer (Path C) [50]. Therefore, in principle, higher ethylene pressure improves the catalytic activities and the content of C_6 fraction. However, as shown in Path B, ethylene pressure should have less influence on the step of chain isomerization. As a result, the distribution of both C_6 olefins and C_4 olefin does not be changed.

In **1a**/MAO, Fig. 3 shows that the catalytic activities decrease with the enhancement of reaction temperatures for ethylene oligomerization. As explained the effects of ethylene pressure, the solubility of ethylene in toluene decreases dramatically while increasing the temperature [51], similar conclusions can be drawn. When temperature is raised from 25 to 40 °C, with ethylene pressure held constant at 12 atm and Al/Ni molar ratio being 1000, the activities of **1a**/MAO rapidly decrease from 5.51×10^5 to 1.71×10^5 g oligomers/(mol Ni·h), and the proportion of C_6 olefins decreases from 82.9% to 34.9%. However, when temperature is further increased, the activities go down smoothly. Furthermore, temperature has almost no effect on the distribution of trimers, in analogy with the results of the influence of ethylene pressure.

In **1a**/MAO, the effects of Al/Ni molar ratio on ethylene oligomerization are investigated and the results are shown in Fig. 4. The catalytic activities are enhanced dramatically as the ratio of Al/Ni (mol/mol) increase from 250 to 1000. However, when the Al/Ni ratio improves further, the activities go down smoothly. The activity of **1a**/MAO reaches a maximum at 700–1000 Al/Ni molar ratio under 25 °C, 12 atm ethylene pressure. The percentage of C_6 olefins also follows the rule. When the ratio is lower than 700, the product distribution tends to be dimer (C_4 olefin). When the ratio is higher than 1000, the proportion of C_8 olefin slightly increases. The fact that a large excess of MAO does not significantly increase the activity suggests that catalytic active species (Ni-alkyl species) could be possibly deactivated by the reaction with excess MAO, or the envelope of excess MAO on the surface of active species [26].

To test the compatibility of complexes **1** toward functional groups, the effects of polar additive on **1a**-catalyzed ethylene oligomerization are also studied. Besides catalytic activity decreasing in **1a**/MAO, runs 7–9 (Table 1) also shows that ethylene oligomerization can be carried out in the presence of three kinds of 5% polar additives, which make early transition metal catalysts deactivate, e.g., Et_2O, THF, and CH_2Cl_2. The polar additives affect not only the catalytic activities but also the product distribution. The percentage of dimer (C_4 olefin) increases, while the percentage of trimer (C_6 olefins) decreases. The most remarkable are that the amount of *cis*-4-methyl-2-pentene is strikingly higher than that of

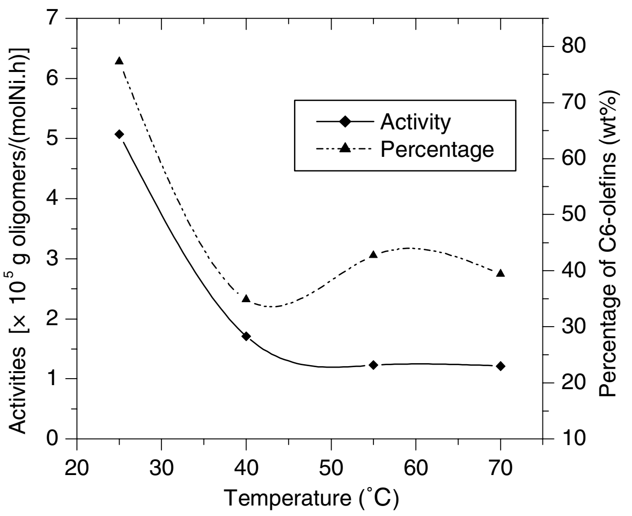


Fig. 3. The effects of reaction temperature with complex **1a**/MAO.

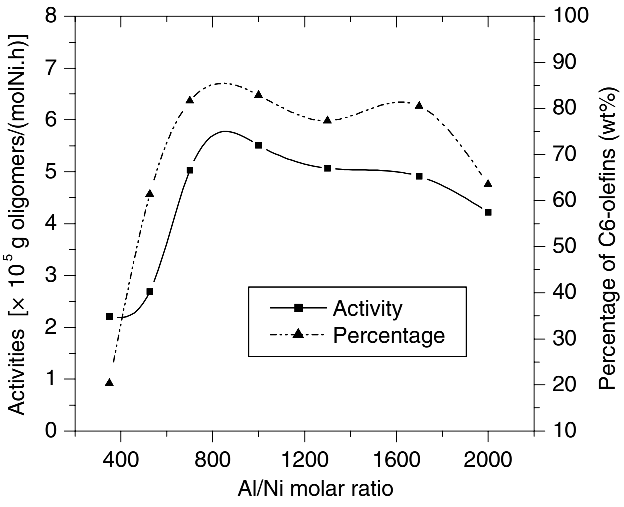


Fig. 4. The effects of Al/Ni molar ratio with complex **1a**/MAO.

Table 5
Propylene dimerization with complexes **1**[a]

Run	Reaction conditions			Activity ($\times 10^4$ g $(\text{mol Ni}\cdot\text{h})^{-1}$)	Distribution of dimers (%)		
	Catalyst	Cocatalyst	Cocatalyst:catalyst		DMB[b]	2MP[b]	HEX[b]
25	**1a**	MAO	1000	13.24	Trace	48.0	52.0
26	**1b**	MAO	1000	9.82	11.9	27.7	60.4
27	**1c**	MAO	1000	8.08	Trace	39.1	60.9
28	**1d**	MAO	1000	2.37	Trace	43.8	56.2
29	**1e**	MAO	1000	6.36	9.3	41.5	49.2
30	**1f**	MAO	1000	2.78	Trace	34.0	66.0
31	**1a**	DIBAL-H	500	8.68	Trace	19.9	80.1
32	**1b**	DIBAL-H	500	9.26	Trace	19.1	80.9
33	**1c**	DIBAL-H	500	6.25	Trace	15.3	84.7
34	**1d**	DIBAL-H	500	8.41	Trace	16.3	83.7
35	**1e**	DIBAL-H	500	11.13	Trace	18.5	81.5
36	**1f**	DIBAL-H	500	9.76	Trace	16.9	83.1
37	**1a**	$AlEt_3$	500	3.81	73.5	Trace	26.5
38	**1b**	$AlEt_3$	500	3.26	56.6	4.1	39.3
39	**1c**	$AlEt_3$	500	1.82	45.8	15.5	38.7
40	**1d**	$AlEt_3$	500	1.61	39.1	16.2	44.7
41	**1e**	$AlEt_3$	500	3.08	38.6	18.4	43.0
42	**1f**	$AlEt_3$	500	1.42	44.9	15.7	39.4
43	**1a**	$Ni(COD)_2$	2	2.43	Trace	76.0	24.0

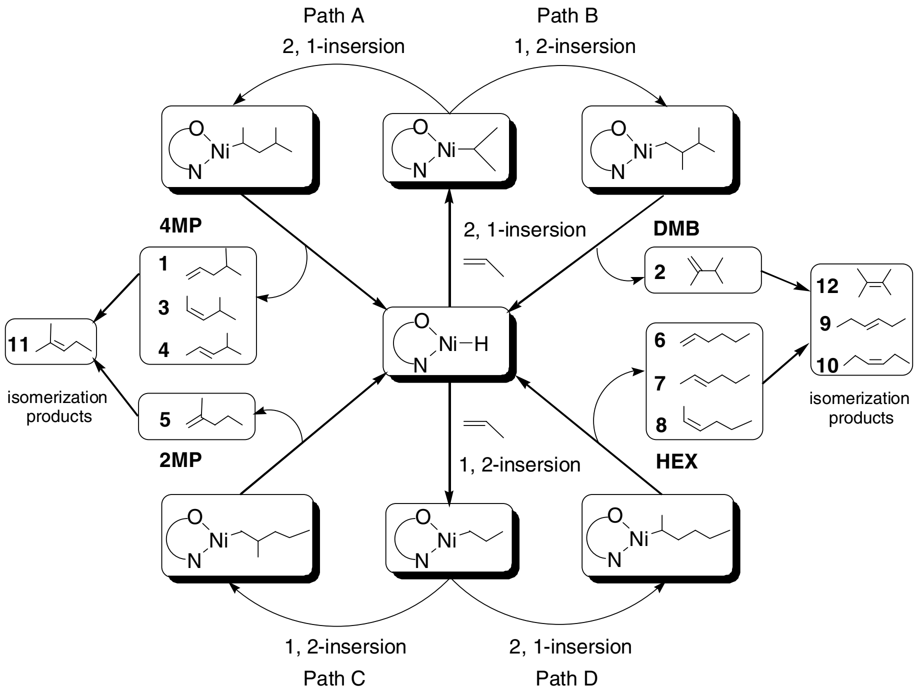
[a] Conditions: 1.5 μmol of complexes **1**, solvent: toluene, total volume: 30 ml, propylene pressure: 1 atm, temperature: 25 °C, reaction time: 0.5 h.
[b] DMB, 2,3-dimethyl-1-butene; 2MP, 2-methyl-1-pentene; HEX, hexene; 4MP, 4-methyl-pentene.

3-methyl-2-pentene when employing Et_2O and THF as additives.

2.3. Proylene dimerization

The catalytic performance of neutral nickel complexes **1** is also evaluated in propylene oligomerization at 25 °C and 1 atm of propylene pressure, when three organoaluminum cocatalysts and phosphine scavenger are employed. The results are summarized in Table 5.

Firstly, complexes **1** exhibit high activities and excellent selectivities in propylene dimerization. Only dimers (C_6 olefins) are produced, higher carbon olefins are not found by GC analysis. Secondly, **1a** shows the highest ac-



Scheme 3. Proposed mechanism of propylene dimerization with complexes **1**.

tivity up to 1.32×10^5 g oligomers/(mol Ni·h) in **1**/MAO. The conclusion of propylene dimerization is similar to that of ethylene oligomerization aforementioned. Under identical reaction conditions, **1c**, **1d** and **1f** with the methyl group on Ni-aryl show slightly lower activities than the corresponding complexes with no substituent on Ni-aryl. Thirdly, **1**/organoaluminum catalytic systems have the excellent selectivities on hexene (HEX), and the content of HEX is 80–85% in **1**/DIBAL-H. However, in **1a**/Ni(COD)$_2$, the content of 2-methyl-1-pentene (2MP) is up to 76% of the product mixtures.

Babik and Fink [45] proposed the mechanism of propylene oligomerization involving the iron alkyl activated species. They believed that the propylene oligomerization catalytic system was a very complicated process of insertion and subsequent elimination. By analogy, a possible mechanism proposed in this case is shown in Scheme 3.

In **1**/MAO and **1**/DIBAL-H, because of the unique mechanism of propylene dimerization in which the regiochemistry of propylene insertion changes from 1,2 to 2,1 between the first and second steps (Scheme 3, Path D), the major products are HEX comprising up to 85% of the product mix. Another product in the reaction is 2MP resulting from two successive 1,2 insertions followed by chain termination (Scheme 3, Path C). In addition, trace product is 2,3-dimethyl-1-butene (DMB), which is formed by the route of 2,1 and 1,2 insertions (Scheme 3, Path B). In **1a**/Ni(COD)$_2$, the major product is 2MP, which can be formed by two successive 1,2 insertions and subsequent β-H elimination. Because of the lower steric hindrance of 2-oxazolinylphenolato ligands, the first propylene insertion step tends to undergo 1,2 insertion pathway. Thus, the proportion of HEX and 2MP is higher than that of DMB and 4MP in catalytic systems. Recently, Fink found that such relation also existed in the iron complexes with bisiminopyridine ligands. The more bulky the ligand, the more frequent 2,1 propylene insertion, and thus the higher molecular mass of the oligomers.

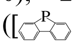
3. Experimental

3.1. General methods

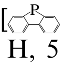
All operations were carried out under argon atmosphere using standard Schlenk techniques. All solvents were distilled from sodium wire prior to use, and chemicals were obtained from commercial suppliers. The 2-(4,5-dihydro-2-oxazolyl)phenol derivatives, *trans*-Ni(Ar)(Cl)(PPh$_3$)$_2$, and Ni(COD)$_2$ were prepared according to the literatures [52–54]. ^{1}H NMR spectra were recorded on a Bruker Advance 500 spectrometer in d_6-C$_6$D$_6$. Elemental (C, H, N) analysis data were obtained with an EA-1106 spectrometer. Infrared spectra using KBr pellets were collected on a Nicolet Magna-IR 550 spectrophotometer. EI-MS and EI-HRMS (*m*/*z*, 70 eV) were recorded on a Micromass GCT mass spectrometer. GC analysis of oligomers was performed on Shimadazu GC-14B equipped with a Simplicity-1 column (30 m×0.25 mm).

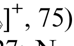
3.2. Synthesis of complexes *1a*, *1c* and *1d*

To a suspension of *trans*-Ni(Ar)(Cl)(PPh$_3$)$_2$ (1.5 mmol) and NEt$_3$ (1.78 mmol) in toluene (20 ml) was dropwise added the toluene solution (10 ml) of 2-(4,5-dihydro-2-oxazolyl)phenol (1.66 mmol). This reaction mixture was allowed to stir for 20 h at ambient temperature. After filtered, the reaction products were separated into two parts: the dark red filtrate and the green solid. The filtrate was reduced to 5 ml under vacuum, and *n*-hexane (30 ml) was added to it. A yellow solid precipitated from solution was isolated by filtration. The crude product was recrystallized from toluene and *n*-hexane to give brown–yellow needle crystals as complexes **1** in 57–66% yields. The green solid separated from the reaction mixture was washed with toluene (3×10 ml), and recrystallized from THF and *n*-hexane to give green solid as complex **2** [55].

1a – M.p.: 149–150 °C. ^{1}H NMR (d_6-C$_6$D$_6$, 500 MHz): $\delta=2.30$ (s, 1.5H, CH_3 Ph), 2.89 (t, $J=9.5$ Hz, 2H, NCH_2), 3.40 (t, $J=9.5$ Hz, 2H, OCH_2), 6.61 (d, $J=8.5$ Hz, 1H, Ar–H), 6.73 (t, $J=7.4$ Hz, 1H, Ar–H), 6.90–6.96 (m, 3H, Ar–H), 7.15–7.24 (m, 10H, Ar–H), 7.25–7.32 (m, 2.5H, Ar–H), 7.67 (d, $J=7.4$ Hz, 2H, Ar–H), 7.92 (t, $J=9.9$ Hz, 6H, Ar–H), 8.10 (dd, $J=8.0$, 1.6 Hz, 1H, Ar–H). ^{13}C NMR (d_6-C$_6$D$_6$, 300 MHz): $\delta=55.0$ (NC_2), 65.9 (OC_2), 110–138 (Ar–C). ^{31}P NMR (d_6-C$_6$D$_6$, 300 MHz): $\delta=31.4$ (PPh$_3$). IR (KBr pellet): 3044m, 2986m, 2908m, 1617vs, 1586m, 1539m, 1475vs, 1433s, 1399m, 1349m, 1260s, 1242m, 1153m, 1096m, 1075m, 928m, 851m, 733s, 695vs, 572w, 463w cm^{-1}. MS (*m*/*z*, %): 262 ([PPh$_3$]$^{+\cdot}$, 100), 220 (M$^{+\cdot}$ – PPh$_3$ – Ph, 1), 185 ([PPh$_2$]$^+$, 8), 183 ([]$^+$, 62), 154 ([Ph–Ph]$^+$, 89). Anal. Calc. for 2C$_{33}$H$_{28}$NNiO$_2$P·C$_6$H$_5$CH$_3$: C, 72.30; H, 5.32; N, 2.31; Found: C, 72.58; H, 5.33; N, 2.15%. HRMS calcd for C$_{33}$H$_{28}$NNiO$_2$P: 559.1211, found: 559.1162.

1c – M.p.: 148–149 °C. ^{1}H NMR (d_6-C$_6$D$_6$, 500 MHz): $\delta=2.36$ (s, 3H, CH_3PhNi), 2.92 (t, $J=9.5$ Hz, 2H, NCH_2), 3.41 (t, $J=9.5$ Hz, 2H, OCH_2), 6.61 (d, $J=8.3$ Hz, 1H, Ar–H), 6.73 (t, $J=7.4$ Hz, 1H, Ar–H), 6.78 (d, $J=7.7$ Hz, 1.5 H, Ar–H), 6.91–6.95 (m, 1H, Ar–H), 7.17–7.26 (m, 9H, Ar–H), 7.27–7.29 (m, 1H, Ar–H), 7.52 (d, $J=6.7$ Hz, 1.5H, Ar–H), 7.92 (t, $J=9.9$ Hz, 6H, Ar–H), 8.10 (dd, $J=8.0$, 1.8 Hz, 1H, Ar–H). IR (KBr pellet): 3055m, 2960m, 2906m, 1615vs, 1585s, 1539s, 1471vs, 1436s, 1397s, 1355s, 1257s, 1242m, 1153m, 1093m, 1074m, 927m, 745m, 693s, 573w, 460w cm^{-1}. MS (*m*/*z*, %): 262 ([PPh$_3$]$^{+\cdot}$, 100), 220

($M^{+\cdot} - PPh_3 - Ph$, 1), 185 ($[PPh_2]^+$, 6), 183 ([]$^+$, 64). Anal. Calc. for $C_{34}H_{30}NNiO_2$ P: C, 71.11; H, 5.27; N, 2.44; Found: C, 71.24; H, 5.20; N, 2.43%.

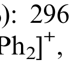
1d – M.p.: 152–153 °C; ^{1}H NMR (d_6-C_6D_6, 500 MHz): $\delta = 2.79-2.90$ (m, 2H, NCH_2), 3.00 (s, 3H, CH_3PhNi), 3.36–3.47 (m, 2H, OCH_2), 6.57 (d, $J = 8.6$ Hz, 1H, Ar–*H*), 6.73 (t, $J = 7.5$ Hz, 1H, Ar–*H*), 6.81 (d, $J = 7.3$ Hz, 1H, Ar–*H*), 6.99 (t, $J = 7.2$ Hz, 1H, Ar–*H*), 7.15–7.19 (m, 6H, Ar–*H*), 7.21–7.24 (m, 3H, Ar–*H*), 7.27 (t, $J = 7.8$ Hz, 1H, Ar–*H*), 7.84 (s, 1H, Ar–*H*), 7.87 (t, $J = 7.3$ Hz, 1H, Ar–*H*), 7.88 (t, $J = 8.9$ Hz, 6H, Ar–*H*), 8.10 (dd, $J = 8.1$, 1.3 Hz, 1H, Ar–*H*). IR (KBr pellet): 3046m, 2973m, 2901m, 1612vs, 1584s, 1540m, 1471s, 1435s, 1401m, 1351m, 1260m, 1245s, 1154m, 1095m, 1077m, 928w, 740m, 693s, 574w, 460w cm^{-1}. MS (*m*/*z*, %): 262 ($[PPh_3]^{+\cdot}$, 100), 220 ($M^{+\cdot} - PPh_3 - Ph$, Ph, 2), 185 ($[PPh_2]^+$, 6), 183 ([]$^+$, 75). Anal. Calc. for $C_{34}H_{30}NNiO_2$ P: C, 71.11; H, 5.27; N, 2.44; Found: C, 71.10; H, 5.48; N, 2.27%.

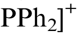
3.3. Synthesis of complexes **1b**, **1e** and **1f**

To a suspension of sodium hydride (3 mmol) in THF (5 ml) was added a solution of 2-(5-methyl-4,5-dihydro-2-oxazolyl)phenol or 2-(4-phenyl-4,5-dihydro-2-oxazolyl)- phenol (1.8 mmol) in THF (10 ml). The resulting mixture was stirred for 2 h at ambient temperature. After filtered, the filtrate was reduced in vacuum. The solid residue was washed with *n*-hexane (10 ml) and dried in vacuum. The salt was immediately used in the next step without further purification.

The sodium salt of ligands and *trans*-Ni(Ar)(Cl)$(PPh_3)_2$ (1.4 mmol) were dissolved in toluene (30 ml) and stirred for 8 h at room temperature. After filtered, the filtrate was reduced in vacuum to 5 ml, and *n*-hexane (30 ml) was added to the solution. A yellow solid precipitated from solution was isolated by filtration. The crude product was recrystallized from toluene and *n*-hexane to give brown–yellow needle crystals as complexes **1** in 65–73% yields.

1b – M.p.: 134–135 °C. ^{1}H NMR (d_6-C_6D_6, 500 MHz): $\delta = 0.79$ (d, $J = 6.2$ Hz, 3H, CH_3), 2.30 (s, 3H, C$H_3$$C_6H_5$), 2.76 (dd, $J = 13.9$, 8.1 Hz, 1H, NCH_2), 3.19 (dd, $J = 13.9$, 9.4 Hz, 1H, NCH_2), 3.99–4.03 (m, 1H, OC*H*), 6.61 (d, $J = 8.6$ Hz, 1H, Ar–*H*), 6.73 (t, $J = 7.5$ Hz, 1H, Ar–*H*), 6.93–6.96 (m, 3H, Ar–*H*), 7.16–7.24 (m, 12H, Ar–*H*), 7.25–7.32 (m, 3H, Ar–*H*), 7.71 (t, $J = 6.7$ Hz, 2H, Ar–*H*), 7.93 (t, $J = 9.0$ Hz, 6H, Ar–*H*), 8.12 (dd, $J = 8.1$, 1.4 Hz, 1H, Ar–*H*). IR (KBr pellet): 3047m, 2975m, 1608vs, 1582s, 1536m, 1471vs, 1435s, 1352m, 1242m, 1153m, 1096m, 1075m, 1059m, 734s, 693vs, 575w, 463w cm^{-1}. MS (*m*/*z*, %): 262 ($[PPh_3]^{+\cdot}$, 100), 234 ($M^{+\cdot} - PPh_3 - Ph$, 1), 185 ($[PPh_2]^+$, 6), 183 ([]$^+$, 52). Anal. Calc. for $C_{34}H_{30}NNiO_2$-$P \cdot C_6H_5CH_3$: C, 73.89; H, 5.75; N, 2.10; Found: C, 73.73; H, 5.62; N, 1.92%.

1e – M.p.: 152–153 °C; ^{1}H NMR (d_6-C_6D_6, 500 MHz): $\delta = 3.74$ (dd, $J = 8.4$, 3.1 Hz, 1H, OCH_2), 3.82 (t, $J = 8.5$ Hz, 1H, NC*H*), 4.33 (dd, $J = 9.0$, 3.0 Hz, 1H, OCH_2), 6.44 (s, 1H, Ar–*H*), 6.65 (d, $J = 8.4$ Hz, 2H, Ar–*H*), 6.76 (t, $J = 7.2$ Hz, 1H, Ar–*H*), 6.85 (t, $J = 7.3$ Hz, 1H, Ar–*H*), 6.94 (s, 1H, Ar–*H*), 7.11–7.19 (m, 12H, Ar–*H*), 7.25–7.27 (m, 3H, Ar–*H*), 7.30–7.32 (m, 1H, Ar–*H*), 7.85 (t, $J = 10.0$ Hz, 6H, Ar–*H*), 8.18 (dd, $J = 8.0$, 1.8 Hz, 1H, Ar–*H*). IR (KBr pellet): 3050m, 3022m, 2960w, 2909w, 1612vs, 1578s, 1536s, 1469s, 1435s, 1399m, 1355m, 1267s, 1234m, 1156m, 1095m, 1083m, 931m, 858m, 737s, 693vs, 576w, 463w cm^{-1}. MS (*m*/*z*, %): 296 ($M^{+\cdot} - PPh_3 - Ph$, 1), 262 ($[PPh_3]^{+\cdot}$, 54), 185 ($[PPh_2]^+$, 4), 183 ([]$^+$, 33), 154 ([Ph–Ph]$^+$, 100). Anal. Calc. for $C_{39}H_{32}NNiO_2P$: C, 73.61; H, 5.07; N, 2.20; Found: C, 73.62; H, 5.13; N, 2.05%.

1f – M.p.: 150–151 °C; ^{1}H NMR (d_6-C_6D_6, 500 MHz): $\delta = 2.31$ (s, 3H, CH_3), 3.75 (dd, $J = 8.2$, 3.0Hz, 1H, OCH_2), 3.83 (t, $J = 8.8$ Hz, 1H, NC*H*), 4.37 (dd, $J = 8.9$, 2.9 Hz, 1H, OCH_2), 6.44 (s, 1H, Ar–*H*), 6.66 (t, $J = 8.5$ Hz, 2H, Ar–*H*), 6.76 (t, $J = 7.7$ Hz, 1H, Ar–*H*), 6.85 (t, $J = 7.2$ Hz, 1H, Ar–*H*), 6.95 (s, 1H, Ar–*H*), 7.11–7.21 (m, 12H, Ar–*H*), 7.25–7.27 (m, 3H, Ar–*H*), 7.85 (t, $J = 9.5$ Hz, 6H, Ar–*H*), 8.18 (dd, $J = 8.1$, 1.7 Hz, 1H, Ar–*H*). IR (KBr pellet): 3052m, 3024m, 2960w, 2910w, 1612vs, 1577s, 1535s, 1468s, 1444m, 1435s, 1398m, 1355m, 1266s, 1234m, 1156m, 1094m, 1081m, 930m, 857m, 737s, 692vs, 575w, 464w cm^{-1}. MS (*m*/*z*, %): 296 ($M^{+\cdot} - PPh_3 - Ph$, 10), 262 ($[PPh_3]^{+\cdot}$, 33), 185 ($[PPh_2]^+$, 3), 183 ([]$^+$, 20). Anal. Calc. for $C_{40}H_{34}NNiO_2P$: C, 73.87; H, 5.27; N, 2.15; Found: C, 73.45; H, 5.07; N, 2.10%.

3.4. Oligomerization procedure

A 100 ml autoclave, equipped with a magnetic stir bar, was preheated at 100 °C under vacuum for 30 min and then cooled to the required temperature. Toluene was injected into the reactor and pressured with ethylene (or propylene) to 1 atm. After equilibrating for 20 min, the appropriate volume of catalysts solution and cocatalysts were injected to start the reaction. The ethylene pressure was kept constant during the reaction. After the desired run time, the reactor was vented and the reaction mixture was terminated by ethanol. *n*-Heptane was added to the mixture as internal standard for GC analysis. An upper-layer clear solution was separated from the reaction mixture to analyze and quantify the soluble components by GC. The individual products of oligomerization were identified by GC–MS.

Acknowledgement

We gratefully acknowledge financial support from the Special Funds for Major State Basic Research

Projects (1999064801), the National Natural Science Foundation of China (NNSFC) (20072004 and 20372022), and the Research Fund for the Doctoral Program of Higher Education (RFDP) (20020251002).

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