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Nickel-based ethylene oligomerization catalysts

supported by PNSiP ligands

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Abstract: A series of nickel (II) complexes bearing silicon bridged diphosphines ligands (PNSiP) have been synthesized and characterized. All nickel precatalysts, activated with ethylaluminum dichloride (EtAlCl₂), exhibited moderate to high activities for ethylene dimerization to butylene. The *in situ* nickel precatalysts formed by mixing

N-cyclopentyl-N-((diphenylphosphanyl)dimethylsilyl)-1,1-diphenylphosphanamine (L2) with NiBr₂(DME) showed high catalytic activity (2.40×10^8 g/(mol_{Ni}•h)) and high product selectivity (88.6%) towards butene using methylcyclohexane as solvent at

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1.0MPa ethylene pressure and 45°C temperature, no polyethylene(PE) was observed.

Ligand backbone tuning of PNSiP-based catalytic systems help in precise

understanding of steric bulk variation effects on catalytic performance.

Keywords: ethylene dimerization; butene; nickel complexes; ethylaluminum dichloride

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1. Introduction

Worldwide butene availability, especially as crude mixture, is enormous. 1-Butene is mainly used as a comonomer in the production of polyethylene, polypropylene, butene oxide and butanone.^[1] 2-Butene is mainly used in the production of gasoline, butadiene and butanone. Ethylene oligomerization or dimerization can produce high purity 1-butene.^[2] Since the pioneering work of Keim and co-workers,^[3] nickel(II)-based precatalysts played important function in the development of alkene oligomerization process. Due to the commercial success, nickel-catalyzed ethylene oligomerization was studied in detail at the fundamental level.^[4-9] Nickel precatalysts based on bi- and tridentate ligands with various combinations of donor atoms (N, P, O, and S) have been extensively studied. Bi-dentate ligands (N^N, N^O, N^P, P^O and P^P) based nickel complexes gained much interest in their synthesis. Extensive research on ethylene polymerization using bi-dentate Ni-based precatalysts bearing P^P type ligation has been reported.^[10] Nickel precatalysts of symmetric carbon-bridge diphosphines ligands show high activity toward oligomer/polymer products.^[11-13] In addition, the groups of Le Floch ^[14] and Matt^[15], reported ethylene dimerization (butene>90%) from nickel precatalysts based on xanthene-calixarene associated with methylaluminoxane (MAO) activator. Symmetrical diphosphinoamine Ph₂P-NR-PPh₂ nickel complexes [with R = Ph, CH₂-C₆H₅, CH₂-(C₄H₃O), CH₂-(C₄H₃S), $CH_2-(C_5H_4N)$, $CH_2-CH_2-(C_4H_3S)$ can catalyze ethylene oligomerization to light olefins with

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moderate activity when activated by MAO.^[10, 16] High active neutral nickel(II) complexes with non-symmetrical P,O ligands, are successfully used in the Shell Higher Olefin Process (SHOP) ^[17-19] to produce linear α -olefins. Recently, new varieties of pincer ligands with non-symmetrical backbones and/or ligating groups, have been reported and their application in transition metal complexes has been explored in a variety of catalytic transformations.^[20] This approach proved beneficial in a variety of ways, such as the use of a single weakly coordinating moiety, capable of dissociating and thereby creating a vacant coordination site to increase catalyst activity. Silyl groups, as large electropositive substituents, have a substantial effect in the complex structure and can hence control the stereochemistry of the reaction. Our group reported the synthesis of a series of Ni (II) complexes with diphosphine ligand (PCSiP),^[21] and achieved a high activity and selectivity towards ethylene dimerization to butene. In this paper, we have designed and synthesized a series of novel silicon-bridged diphosphine ligands (PNSiP). The results showed that it has greatly improved catalytic activity from 3.12×10^6 g/(mol_{Ni}·h) to 2.40×10^8 g/(mol_{Ni}·h).

2. Results and discussion

The target PNSiP ligands **L1–L3** were prepared by convenient salt metathesis (**Figure 1**). Deprotonation by *n*-butyllithium and subsequent dropwise addition of chlorodiphenylphosphine converted primary amines to N,P-based units. Diphenylphosphanide was obtained from the diphenylphosphine and butyllithium treatment and was added to dichlorodimethylsilane to

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produce Si,P-based units. The designed ligands were obtained by reacting the N,P-based units with *n*-butyllithium, followed by dropwise addition of Si, P-based units. These ligands were coordinated with NiBr₂(DME) to produce precatalysts **C1–C3** as brown powders (**Figure 2**).





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2.1 Effect of precatalyst loading on catalytic activity and product selectivity

Table 1 displays the influence of catalyst loading on catalytic activity and product selectivity. C2 was firstly synthesized for the ethylene oligomerization test. Reducing the catalyst dosage from 2.4µmol to 0.1µmol, the catalytic activity and 1-butene selectivity increased significantly. It showed that precatalyst with large quantity was unable to activate completely and to form active species, which is consistent with the spectral study results reported by Do.^[22] When the catalyst loading is low, the ethylene can contact faster with the catalytic active center to generate catalytically active species. Moreover when the catalyst loading is too high, the diffusion velocity of ethylene molecules into solvent is slow, the ethylene can not coordinate with nickel complex in time, which reduce the catalytic activity of C2 catalyst. The proportion of 1-butene in butene fraction decreases rapidly with increasing catalyst dosage. These results indicate that 1-butene is the primary product during ethylene oligomerization. The rising and uncontrollable temperature caused by the exothermicity of increasing amount of nickel precatalyst speed up the 1-butene isomerization.^[23]

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Catalyst	Catalyst	Activity	Product selectivity (%)									
Catalyst	mass(µmol)	$[10^7 \text{ g/(mol_{Ni} \cdot h)}]$	C_4	$1 - C_4^{=}$	trans-C ₄	cis-C ₄	C_6	$1 - C_6^{=}$	$\geq 1 - C_8^{=}$			
C2	2.4	0.7	76.2	7.2	61.7	31.1	23.8	1.3	Nd			
	1.2	1.8	84.1	13.7	56.3	30.0	15.9	3.1	Nd			
	0.4	6.3	80.2	19.8	53.2	26.9	19.8	4.0	Nd			
	0.1	9.4	83.8	34.4	36.8	28.8	16.2	8.0	Nd			

Reaction conditions: n(Al)/n(Ni)=500; solvent, 20 mL (methylcyclohexane); time, 30 min; T,

45°C; EADC used as co-catalyst.

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2.2 Effect of reaction temperature on catalytic activity and product selectivity

From **Table 2** we found that the catalytic activity of **C1**, **C2** and **C3** initially increased upon increasing the reaction temperature, reached maximum at 45°C and then decreased significantly with further increase in temperature. It indicates that reaction temperature is an important parameter that affects the catalytic activity of C1, C2 and C3 complexes. The decrease in activity attributed to the lower concentration of ethylen in methylcyclohexane at high temperature.^[24] On the other hand, elevated temperature increases the deactivation rate of active sites which also lowers the catalytic activity of the complex. In most cases, a steady increase in 1-butene selectivity was observed with a decrease of temperature from 60 °C to 30 °C, suggesting that the selectivity of the complexes was substantially affected with temperature. These results indicate that 1-butene is the initial product of ethylene oligomerization and that its catalyzed isomerization to cis/trans 2-butene becomes prominent when the reaction temperature increases. The catalytic activity and 1-butene selectivity were also profoundly affected by the ligand environment. Higher catalytic and lower 1-butene selectivity of C1 and C2 compared to C3 also made confirm the existence of a general correlation between catalytic performance and N atom substituent. On the other hand, butene selectivity remains unaffected, showing its independent selectivity from N atom substitution. The effect of the steric hindrance of ortho-position substituent on the catalytic activity of (a-diimine)nickel(II) complexes is evident. The different activities obtained using diphosphines

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with C1, C2 and C3 suggest that ligand rigidity and/or steric hindrance play an important role in catalyst performance.

	т	Activity	Product selectivity (%)									
Catalyst	1 (°C)	[10 ⁷ g/(mol _{Ni} ·h)]	C_4	$1 - C_4^{=}$	trans-C ₄	cis-C ₄	C ₆	$1 - C_6^{=}$	$\geq 1 - C_8^{=}$			
	60	8.6	83.5	30.1	36.6	33.3	16.5	7.9	Nd			
C1	45	9.2	86.2	30.4	37.7	31.9	13.8	10.1	Nd			
	30	2.6	67.5	67.6	19.6	12.9	32.5	12.0	Nd			
	60	9.2	81.9	34.9	37.4	33.9	18.1	9.9	Nd			
	45	9.4	83.8	34.4	36.8	28.8	16.2	8.0	Nd			
C2	30	9.0	83.7	34.1	36.7	29.2	16.3	7.4	Nd			
	15	1.6	84.6	32.9	35.9	31.2	15.4	6.5	Nd			
	60	3.2	86.7	52.4	25.9	21.7	13.3	11.3	Nd			
C3	45	6.6	86.3	54.1	26.5	19.4	13.7	10.2	Nd			
	30	2.4	86.9	58.2	23.5	18.3	13.1	6.9	Nd			

Table2 Effect of reaction temperature on catalytic activity and product selectivity

Reaction conditions: n(Cat), 0.1µmol; n(Al)/n(Ni), 500; solvent, 20 mL (methylcyclohexane); P,

1.0 MPa; time, 30 min; EADC used as co-catalyst.

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2.3 Effect of Al/Ni molar ratio on catalytic activity and product selectivity

Table 3 displays the influence of Al/Ni molar ratio on the catalytic activity and product selectivity. Upon increasing Al/Ni molar ratio from 100 to 700, the catalytic activity increased significantly, but selectivity toward butene decreased. This trend can be attributed to less dosage of EADC, in which some of its amount is consumed and the remaining amount is not enough to form catalytic active species with nickel and other catalyst components. Therefore, an optimal amount of EDAC is needed to activate catalyst effectively.

Catalant	n(Al)/n(Ni)	Activity	Product selectivity (%)							
Catalyst		$[10^7 \text{ g/(mol_{Ni} \cdot h)}]$	C_4	$1 - C_4^{=}$	trans-C ₄	cis-C ₄	C_6	$1 - C_6^{=}$	$\geq 1 - C_8^{=}$	
<u>C1</u>	700	11.4	82.1	32.6	37.8	29.6	17.9	6.7	Nd	
CI	500	9.2	86.2	30.4	37.7	31.9	13.8	10.1	Nd	
	700	10.8	82.2	33.2	39.2	27.6	17.8	7.3	Nd	
	500	9.4	83.8	34.4	36.8	28.8	16.2	8.0	Nd	
C2	300	8.2	84.1	41.2	32.1	26.7	15.9	10.1	Nd	
	100	1.2	88.6	66.8	16.9	16.3	11.4	12.3	Nd	
C 2	700	7.6	85.9	35.9	32.4	31.7	14.1	9.2	Nd	
03	500	6.6	86.3	54.1	26.5	19.4	13.7	10.2	Nd	

Table 3 Effect of Al/Ni molar ratios on catalytic activity and product selectivity

Reaction conditions: n(Cat), 0.1µmol; P, 1.0 MPa; solvent, 20 mL (Methylcyclohexane); T, 45°C;

time, 30 min; EADC used as co-catalyst.

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2.4 Effect of the ethylene pressure on catalytic activity and product selectivity

As shown in **Table 4**, the catalytic activity increased with increasing ethylene pressure, while selectivity toward butene did not change obviously. Ethylene solubility changed with ethylene pressure in liquid phase reaction which affected catalytic activity.

Ethylene		Activity	Product selectivity (%)								
Catalyst	pressure(M Pa)	$\frac{\text{Activity}}{[10^7 \text{ g/(mol_{Ni}} \cdot h)]}$	C_4	$1 - C_4^{=}$	trans-C ₄	cis-C ₄	C ₆	$1 - C_6^{=}$	$\geq 1 - C_8^{=}$		
	1	9.4	83.8	34.4	36.8	28.8	16.2	8.0	Nd		
C 2	0.8	6.4	83.9	34.3	36.7	29.0	16.1	8.1	Nd		
C2	0.4	3.8	83.7	34.1	36.7	29.3	16.3	7.4	Nd		
	0.1	1.6	84.6	32.9	35.9	31.2	15.4	6.5	Nd		

Table 4 Effect of ethylene pressure on catalytic activity and product selectivity

Reaction conditions: *n*(Cat), 0.1µmol; *n*(Al)/*n*(Ni), 500; solvent, 20 mL (Methylcyclohexane);

time, 30 min; T, 45°C; EADC used as co-catalyst.

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2.5 Effect of the reaction time on catalytic activity and product selectivity

Table 5 reveals that the reaction time has a slightly greater effect on the activity of the catalysts, while the selectivity toward butene remained relatively stable. These results again suggest that the catalyst can be easily deactivated if treated for long time.

Table 5 Effect of reaction time on catalytic activity and product selectivity

Catalant	Reaction	Activity	Product selectivity (%)							
Catalyst	time (min)	$[10^7 \text{ g/(mol_{Ni} \cdot h)}]$	C_4	$1 - C_4^{=}$	trans-C ₄	cis-C ₄	C_6	$1 - C_6^{=}$	$\geq 1 - C_8^{=}$	
	30	9.4	83.8	34.4	36.8	28.8	16.2	8.0	Nd	
C2	20	13.2	82.3	35.7	35.1	29.2	17.7	8.5	Nd	
	10	24.0	81.8	35.0	32.8	32.2	18.2	8.8	Nd	

Reaction conditions: n(Cat), 0.1µmol; n(Al)/n(Ni), 500; P, 1.0 MPa; solvent, 20 mL

(Methylcyclohexane); T, 45°C; EADC used as co-catalyst.

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3. Experimental

3.1 Materials and methods

Bis(phenyl)phosphorus chloride, diphenylphosphine, dichlorodimethylsilane, n-butyllithium (2.4 mol/L in n-hexane) and NiBr₂(DME) were purchased from Aldrich and were used as received. Lithium diphenylphosphine was prepared using the method reported by Peterson^[25]. Polymerization-grade ethylene was obtained from Tianjin Summit Specialty Gases (China). EADC (1.4 mol/L in toluene) was purchased from Albemarle Corp (USA). Methylcyclohexane, tetrahydrofuran(THF) and n-hexane were dried and degassed prior to use. ¹H, ¹³C, and ³¹P NMR spectra of the products were recorded at 25 °C using a Fourier 400 NMR spectrometer (Bruker, Billerica, MA) with tetramethylsilane (TMS) as an internal reference. Elemental analysis were performed using an Elemental Vario EL analyzer. Mass spectra were recorded using a MALDI-TOF mass spectrometer. Gas chromatography (GC) was performed using Agilent 7890A GC system.

3.2 Synthesis of ligands

3.2.1 Synthesis of N-(2,6-diisopropylphenyl)-N-((diphenylphosphanyl)dimethylsilyl)-1,1diphenylphosphanamine (L1)

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1. n-BuLi (4.2 mL, 2.4 mol/L in n-hexane, 9.96 mmol) was added dropwise to a solution of 2,6-diisopropylaniline (1.791 g, 10.00 mmol) in n-hexane (20 mL) at -20°C. The mixture was stirred over night at room temperature, followed by addition of chlorodiphenylphosphine (2.207 g, 10.00 mmol). The precipitated LiCl was filtered and the faint yellow solution was concentrated to give yellow residue, which was recrystallized in n-hexane to give N-(2, 6-diisopropylpenyl)-1-dipenylphosphanamine (**L1a**) (**Table 6**) (2.207g, 6.10mmol) in 68% yield.

2. n-BuLi (4.2 mL, 9.96 mmol, 2.4 mol/L in n-hexane) was added dropwise to n-hexane solution of diphenylphosphine (1.900 g, 10.00 mmol) in n-hexane (10 mL) at -20°C. The mixture was stirred over night at room temperature. After filtration and washing twice with n-hexane (2 mL), lithium diphenylphosphanide (L1b) (Table 6) (1.928 g, 10.00 mmol) was obtained in nearly 100% yield after drying in a vacuum. The above product was added by multiple-low-dose to a solution of dichlorodimethylsilane (2.581 g, 20.00 mmol) in n-hexane (20 mL) at -20°C followed by stirring at room temperature for 8h. After filtration, the volatiles were removed in vacuum, giving yellow oily product. The colorless oil (chlorodimethylsilyl)diphenylphosphine (L1c) (Table 6) was obtained by vacuum distillation (155 °C~160 °C, 10 mmHg, 1.087 g, 3.90 mmol, 39% yield).

3. n-BuLi (2.8 mL, 2.4 mol/L in n-hexane, 6.80 mmol) was added dropwise to n-hexane solution of above **L1a**. The mixture was stirred at room temperature for 5h. After filtration and washing twice with n-hexane (2 mL), lithium

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(2,6-diisopropylphenyl)(diphenylphosphanyl)amide (L1d) (Table 6) (2.447 g, 6.10 mmol) was obtained in approximately 100% yield after drying in a vacuum. A solution of L1c (0.224 g, 1.00 mmol) in toluene (20 mL) was added dropwise to a solution of L1d (0.368 g, 1.00 mmol) in toluene (5 mL) at -20 °C. After stirring overnight and filtration, a yellow oil was obtained by removing the volatiles in vacuum. Recrystallization from n-hexane produced ligand L1 (0.411 g. 0.68 mmol) of 68% yield. ¹H NMR (400 MHz, C_6D_6) δ 7.98 (t, J = 7.5 Hz, 4H), 7.58 (dd, J = 10.4, 4.9Hz, 4H), 7.14–6.96 (m, 15H), 3.58–3.46 (m, 2H), 1.11 (d, J = 6.7 Hz, 6H), 0.43 (d, J = 6.7 Hz, 6H), 0.41 (d, J = 2.0 Hz, 6H). ³¹P NMR (162 MHz, C₆D₆) δ 52.2 (d), -43.2 (d, J = 25.9 Hz). ¹³C NMR (101 MHz, C₆D₆) δ 148.4, 142.5, 142.4, 139.1, 138.9, 137.7, 137.7, 137.6, 137.6, 136.2, 136.2, 136.1, 136.0, 136.0, 135.9, 135.9, 129.7, 128.9, 128.9, 128.9, 126.6, 125.2, 29.4, 29.4, 26.7, 26.6, 24.1, 2.8, 2.7, 2.6. Anal. Calcd for C₃₈H₄₃NP₂Si: C, 75.59; H, 7.18; N, 2.32. Found: C, 75.55; H, 7.16; N, 2.28.

L1a L1b L1c L1d Li Ph₂P^{_N}-R $Ph_2P \sim R$ LiPPh₂ Structure $C1^{2}$ PPh₂ R=2,6-diisopropylphenyl R=2,6-diisopropylphenyl

Table 6 structure of L1a-d

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3.2.2 Synthesis of N-cyclopentyl-N-((diphenylphosphanyl)dimethylsilyl)-1,1diphenylphosphanamine (L2)

Similarly for L1a, the preparation of N-cyclopentyl-1,1-diphenylphosphanamine (L2a) was achieved by using cyclopentanamine (0.852 g, 10.00 mmol), n-BuLi (4.2 mL, 9.96 mmol, 2.4 mol/L in n-hexane) and chlorodiphenylphosphine (2.207 g, 10.00 mmol). Vacuum distillation gave a colorless oil L2a (150 °C ~160 °C, 2.725 g, 10.11 mmol, 50% yield). The preparation of L2b was conducted by the same method as described for L1b with n-BuLi (2.2 mL, 5.22 mmol, 2.4 mol/L in n-hexane) and L2a (0.276 g, 1.00 mmol) and achieved in nearly 100% yield (1.436 g, 5.22 mmol). 0.322 g L2 (1.34 mmol, 63% yield) was obtained, as for L1, by using L2b (0.276 g, 1.00 mmol) and **L1d** (0.279 g, 1.00 mmol). ¹H NMR (400 MHz, C_6D_6) δ 7.56 (t, 4H), 7.14 (t, 4H), 7.05 (m, 12H), 3.69–3.78 (m, 1H), 1.78 (m, 2H), 1.44 (m, 4H), 1.23 (m, 2H), 0.53 (s, 6H). ³¹P NMR (162 MHz, C_6D_6) δ 51.9 (br), -53.7 (d, J = 53.8 Hz). ¹³C NMR (101 MHz, C_6D_6) δ 140.9, 140.9, 140.7, 140.7, 137.3, 137.3, 137.2, 137.1, 135.5, 135.4, 135.3, 133.1, 132.9, 128.9, 128.8, 128.8, 128.7, 128.6, 128.3, 128.2, 128.1, 63.1, 34.6, 34.6, 32.3, 23.8, 3.2, 3.1, 3.0. Anal. Calcd for C₃₁H₃₅NP₂Si: C, 72.77; H, 6.90; N, 2.74. Found: C, 72.72; H, 7.11; N, 2.52.

3.2.3 Synthesis of N-((diphenylphosphanyl)dimethylsilyl)-N-isopropyl-1,

1-diphenylphosphanamine (L3)

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N-((diphenylphosphanyl)dimethylsilyl)-N-isopropyl-1,1-diphenylphosphanamine (L3): N-isopropyl-1,1-diphenylphosphanamine (L3a) was synthesized by the method as L1a using isopropylamine (0.591 g, 10.00 mmol), n-BuLi (4.2 mL, 9.96 mmol, 2.4 mol/L in n-hexane) and chlorodiphenylphosphane (2.206 g, 10.00 mmol). Colorless oil L3a was obtained by vacuum distillation at 10 mmHg (140 °C ~150 °C, 1.314 g, 5.40 mmol, 54% yield). Similarly to L1, 0.325 g L3 (0.65 mmol, 65% yield) was obtained by using L3a (0.243 g, 1.00 mmol), n-BuLi (0.4 mL, 0.96 mmol, 2.4 mol/L in n-hexane) and L1d (0.279 g, 1.00 mmol). ¹H NMR (400 MHz, C_6D_6 δ 7.73–7.65 (m, 4H), 7.57–7.52 (m, 4H), 7.16–7.00 (m, 12H), 3.75 (m, J = 13.4, 6.7 Hz, 1H), 1.08 (d, J = 6.7 Hz, 6H), 0.48 (m, 6H). ³¹P NMR (162 MHz, C₆D₆) δ 50.4 (br), -53.0 (d, J =54.7 Hz). ¹³C NMR (101 MHz, C₆D₆) δ 140.8, 140.7, 140.6, 140.5, 137.3, 137.3, 137.1, 137.1, 135.6, 133.3, 133.1, 128.9, 128.8, 128.7, 128.7, 128.6, 128.3, 128.1, 32.3, 25.9, 25.8, 25.8, 3.5, 3.4, 3.3. Anal. Calcd for C₂₉H₃₃NP₂Si: C, 71.73; H, 6.85; N, 2.88. Found: C, 71.72; H, 6.83; N, 2.75.

3.3 Synthesis of metal complexes

All complexes (Figure 2) were synthesized under dry N_2 atmosphere in oven-dried flasks using standard Schlenk techniques. We tried to grow all the complexes into single crystals, but failed.

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Figure 2 Structures of complex C1, C2 and C3

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3.3.1 L1/NiBr₂ complex

A tetrahydrofuran solution (20 mL) of L1 (0.127 g, 0.21 mmol) was added to a tetrahydrofuran dispersion liquid (30 mL) of [NiBr₂DME] (0.062 g, 0.2 mmol). The reaction mixture was turned dark brown immediately and was allowed to stir for 24 h. The solvent was evaporated using a cold trap and vacuum pump and then the solid residue was washed three times with *n*-hexane. Drying *in vacuo* provided a dark brown powder. Yield: 0.157 g (85%). Anal. Calcd for $C_{38}H_{43}Br_2NNiP_2Si$: C, 55.50; H, 5.27; N, 1.70. Found: C, 55.37; H, 5.13; N, 1.48.

 $3.3.2 L2 / NiBr_2 complex$

L2 (0.107 g, 0.21 mmol) and [NiBr₂(DME)] (0.062 g, 0.2 mmol) were dispersed in tetrahydrofuran (20 mL), the mixture was allowed to stir for 24 h. After evaporation and purification, a brown powder was obtained. Yield: 0.137 g (84%). Anal. Calcd for $C_{31}H_{35}Br_2NNiP_2Si: C, 50.99; H, 4.83; N, 1.92.$ Found: C, 50.65; H, 5.11; N, 1.57. 3.3.3 L3/ NiBr₂ complex

L3 (0.102 g, 0.21 mmol) and [NiBr₂(DME)] (0.062 g, 0.2 mmol) were dispersed in tetrahydrofuran (20 mL), the mixture was allowed to stir for 24 h. After evaporation and purification a brown powder was obtained. Yield: 0.129 g (81%). Anal. Calcd for $C_{29}H_{33}Br_2NNiP_2Si$: C, 49.47; H, 4.72; N, 1.99. Found: C, 49.36; H, 4.58; N, 1.64.

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3.4 General oligomerization procedure

A 140-mL transparent glass reactor was heated in a high temperature drying oven for 2 h at 105 °C prior to use. Subsequently a magneton was placed inside the reactor, and then the reactor was heated in an oil bath at required tempereture for the oligomerization reaction. The reactor was equipped with a thermocouple, a pressure meter, and needle valves for injections. The reactor was vacuumed and then charged with high-purity N₂, this process was repeated three times. Then repeated the above operation with ethylene. After that Methylcyclohexane solution of the catalyst precursor and the co-catalyst EADC were introduced into the reactor, consequently the reactor was charged with 1.0 MPa of ethylene. The reaction was run for the required time (generally 30 min) and then the ethylene feed was turned off. The products of oligomerization were cooled an in ice ethanol bath and the reaction was quenched by slow addition of acidic ethanol (2 mL). Once venting was complete, the products of oligomerization were analyzed by an Agilent 7890A gas chromatography. The heptane was used as the internal standard.

4. Conclusion

We synthesized and characterized three new nickel complexes based on silicon bridged PNSiP ligands and evaluated for ethylene oligomerization upon EADC activation. All nickel complexes catalyzed ethylene oligomerization to butene and hexene. The ligand structure with different N atom substituents was an important parameter to influence the catalytic activity. The

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catalytic activity and product selectivity increased with decreasing catalyst mass, which shows that the presence of a large amount of catalyst tends to prevent the precatalyst from complete activation into active species. With an increase in temperature, ethylene solubility decreases in methylcyclohexane, and the deactivation rate of active sites increases which results in lower catalytic activity and product selectivity. Furthermore, ethylene pressure also greatly influences the catalytic activity. We found that our systems showed good catalytic performance at optimum conditions $(45^{\circ}C, n(Al)/n(Ni) = 500, 10 min)$.

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