



Nickel complexes incorporating pyrazole-based ligands for ethylene dimerization to 1-butylene



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ABSTRACT

In this study we synthesized and characterized bis(3,5-dimethylpyrazolyl)dimethylsilane (**L1**) and bis(3,5-dimethylpyrazolyl)phenylphosphine (**L2**) and then prepared bidentate (N,N) nickel complexes by reacting **L1** or **L2** with NiBr₂(DME). In combination with methylaluminoxane, diethylchloroaluminum or ethyldichloroaluminum (EADC) as co-catalyst, **L1**/Ni and **L2**/Ni complexes exhibited moderate catalytic activities (240–1310 kg/mol_{Ni} h) and high selectivities (up to 93.2%) for ethylene dimerization toward 1-butylene. The catalytic performance was substantially affected by the co-catalyst type and ligand environment, especially the bridge atom.

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Introduction

Linear α -olefins are normally used for the preparation of branched polyethylene and other chemicals, such as detergents, synthetic lubricants and plasticizer alcohols. Oligomerization of ethylene to linear α -olefin have played an important role in the industrial process. Ethylene dimerization and oligomerization reactions were typically carried out using homogeneous late-transition-metal catalysts, particularly nickel-based catalysts [1–6]. A number of selective ethylene dimerization catalysts based on nickel complexes have been extensively studied and developed [7–9]. Nickel complexes that based on various chelating-ligand topologies were studied most frequently [10–14]. Besides the choice of the metal center, the desired catalytic selectivity can be tuned by designing ancillary ligands with the desired structural and electronic properties to assist the generation and stabilization of active species for selective ethylene oligomerization [15–18]. Usually, pyrazole-based ligands are used as either terminal or bridging ligands with bidentate chelation at each metal center. Currently, pyrazole ligands research mainly focus on bridging pyrazole atoms (such as carbon, silicon and boron on bridging the bridge bidentate or tridentate ligands) or changing the substituents of the ligands. It

will change the space structure of ligand, coordination ability and influence the metal central atoms, changing the catalytic performance [19–21]. Oliveira and his coworkers have reported that the tridentate catalyst which was formed with pyrazol ligand (NNN or NSN) and Ni gave high activity and selectivity for ethylene dimerization to 1-butene. They also found that changing the substituent of pyrazole would change the catalyst performance effectively, increasing the electronic properties of substituents could effectively increase the activity of the catalyst [22]. Ainooson and his coworkers reported that catalysts that consisted of 3,5-dimethyl pyrazole bidentate ligands with iron, cobalt, nickel or palladium in the ethylene oligomerization showed different catalytic activities. The nickel complexes with ethyldichloroaluminum (EADC) possessed the highest catalytic activity and selectivity for the ethylene oligomerization to butenes and hexenes [9]. We are interested in the design of new pyrazole ligands used in Ni-based catalysts for ethylene dimerization to 1-butylene with high catalytic activity, selectivity and long lifetime. Like S, C and B atom, phosphine or silicon were often used in the design of novel ligands as connecting heteroatoms [23]. However, corresponding bidentate pyrazole ligands featuring Si and P bridging atoms have never been explored previously in conjunction with transition metals for preparing catalysts used for ethylene oligomerization.

Herein, we report the synthesis and characterization of nickel complexes with bidentate bis(3,5-dimethylpyrazolyl)dimethylsilane (**L1**) or bis(3,5-dimethylpyrazolyl)phenylphosphine (**L2**) ligands, as well as their catalytic behavior for ethylene dimerization

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toward 1-butene. We also discuss the effects of the reaction temperature, the Al-to-Ni molar ratio and the co-catalysts types on the catalytic activity and selectivity of these complexes.

Experimental

Materials

3,5-Dimethylpyrazole, dichlorodimethylsilane, dichlorophenyl phosphine, *n*-butyllithium (2.4 mol/L in hexanes), and NiBr₂(DME) were purchased from Aldrich and used as received. Polymerization-grade ethylene was obtained from Tianjin Summit Specialty Gases (China). Methylaluminoxane (MAO, 1.4 mol/L in toluene), diethylchloroaluminum (DEAC, 1.4 mol/L in toluene), EADC (1.4 mol/L in toluene), triethylaluminum (TEAL, 1.4 mol/L in toluene), trimethylaluminum (TMAL, 1.4 mol/L in toluene), triisobutylaluminum (TIBA, 1.4 mol/L in toluene) were purchased from Albemarle (USA). Toluene, tetrahydrofuran (THF), dichloromethane and *n*-hexane were dried and degassed prior to use.

Synthesis of ligands

All air- and/or water-sensitive reactions were conducted under a dry N₂ atmosphere in oven-dried flasks using standard Schlenk techniques or in a glove box.

Bis(3,5-dimethylpyrazolyl)dimethylsilane (L1)

2.4 M *n*-BuLi solution in hexanes (0.44 mL, 1.05 mmol) was added dropwise to a solution of 3,5-dimethylpyrazole (96.1 mg, 1.0 mmol) in *n*-hexane (50 mL) at -78 °C. The mixture was stirred for 4 h, resulting in a light-yellow cloudy solution. Dichlorodimethylsilane (60.28 μL, 0.5 mmol) was added to the above solution, and then the mixture was stirred for 24 h. The precipitated LiCl salt was filtered off and the filtrate was concentrated to give a white residue. Recrystallization (benzene/*n*-hexane) provided **L1** in 90% yield. ¹H NMR (δ, ppm, CDCl₃, TMS): 0.939 (s, 6H, CH₃Si), 1.890 (s, 6H, (CH₃)₂pz), 2.250 (s, 6H, (CH₃)₂pz), 5.869 (s, 2H, H-4 in (CH₃)₂pz). ¹³C NMR (δ, ppm, CDCl₃): 1.65, 16.11, 17.88, 27.52, 28.55, 108.58, 109.88, 136.62, 137.49, 145.81, 147.07.

Bis(3,5-dimethylpyrazolyl)phenylphosphine (L2)

Triethylamine (3.05 mL, 22 mmol) was added to a solution of 3,5-dimethylpyrazole (1.9226 g, 20 mmol) in THF (100 mL). Then dichlorophenylphosphine (1.4 mL, 10 mmol) was added dropwise to the solution at 0 °C. The mixture was stirred for 12 h, resulting in a white cloudy solution, and then the mixture was stirred for 12 h at 50 °C. The precipitate was filtered off and the filtrate was concentrated to give white oil. The resulting oil was redissolved in petroleum ether and filtered. The solvent was removed in vacuo giving the resulting product as an oil which provided **L2** in 94% yield. ¹H NMR (δ, ppm, CDCl₃, TMS): 2.216 (s, 6H, CH₃), 2.387 (s, 6H, CH₃), 5.898 (s, 2H, CH), 7.208–7.355 (m, 5H, Ph). ¹³C NMR (δ, ppm, CDCl₃): 12.99, 13.98, 108.75, 128.44, 128.49, 129.53, 129.54, 130.69, 130.89, 135.38, 148.60, 148.76, 153.45, 153.52. ³¹P NMR (δ, ppm, CDCl₃, H₃PO₄): 59.74.

Synthesis of metal complexes

Nickel complexes were prepared by mixing equimolar amounts of the metal halide and the ligands in THF; they were isolated as diamagnetic solids in yields of 76.9% and 72.0%. These complexes are insoluble in nonpolar solvents (e.g., *n*-hexane, cyclohexane), but can be dissolved in polar solvents (e.g., toluene, THF).

L1/NiBr₂ complex

A freshly prepared solution of **L1** (273.2 mg, 1.1 mmol) in toluene was added to a solution of NiBr₂(DME) (308.6 mg, 1.0 mmol) in THF (10 mL). After the resulting dark blue solution had been stirred 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 blue powder. Yield: 428.8 mg, 0.77 mmol, 76.9%. EI-MS: *m/z* 465 [M⁺]. C₁₂H₂₀Br₂N₄NiSi: Calcd. C 30.87, H 4.32, N 12.00; Found: C 30.59, H 4.44, N 12.25. The structure of **L1**/Ni is listed in the Scheme 1.

L2/NiBr₂ complex

A freshly prepared solution of **L2** (328.2 mg, 1.1 mmol) in THF was added to a solution of NiBr₂(DME) (308.6 mg, 1.0 mmol) in THF (10 mL). After the resulting purple solution had been stirred 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 blue powder. Yield: 437.0 mg, 0.72 mmol, 72.0%. EI-MS: *m/z* 515 [M⁺]. C₁₆H₁₉Br₂N₄PNi: Calcd. C 37.18, H 3.71, N 10.84; Found: C 37.35, H 3.66, N 10.69. The structure of **L2**/Ni is listed in the Scheme 1.

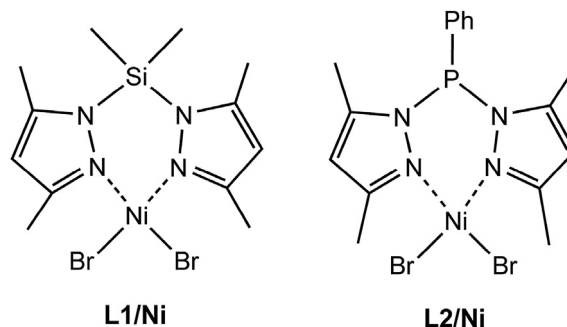
General oligomerization procedure

Ethylene oligomerization runs were performed in the Lab of Grest transparent glass reactor. Reactor heated in an oil bath, which was equipped with a magnetic stirrer bar, a thermocouple, a pressure meter, and needle valves for injections. The glass reaction vessel was dried in an oven at 105 °C for 2 h prior to each run, purged under vacuum to remove air, and then brought back to atmospheric pressure using high-purity N₂ and ethylene; this cycle was repeated three times. The reactor was then charged with solvent and stirred magnetically under an atmosphere of ambient ethylene. After the desired reaction temperature had been established, the co-catalyst and metal complexes were injected into the reactor. With stirring, the reactor was brought to the working pressure and fed continuously with ethylene until the end of each reaction was reached (generally after 30 min). The reactor was cooled to 0 °C and the excess ethylene was bled off. The samples of the organic layer were taken and analyzed through Agilent gas chromatography (GC) with flame-ionization detection (FID). The polymer was isolated by filtration, washed with ethanol and then dried at 50 °C in a vacuum oven.

Results and discussion

Effect of reaction temperature on catalytic properties for the oligomerization of ethylene

From the Table 1 we can see that the catalytic activity of the both of the catalysts initially increased upon increasing the reaction



Scheme 1. Structures of complex **L1**/Ni and **L2**/Ni.

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