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Editor's Choice paper

Unsymmetrical (pyrazolylmethyl)pyridine metal complexes as catalysts for ethylene oligomerization reactions: Role of solvent and co-catalyst in product distribution

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ABSTRACT

Reactions of 2-(chloromethyl)-6-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (**L1**) and 2-(chloromethyl)-6-((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine (**L2**) with $NiCl_2$, $NiBr_2$, $CoCl_2$ and $FeCl_2$ led to the formation of their respective metal complexes [$NiCl_2$(**L1**)] (**1**), [$NiBr_2$(**L1**)] (**2**), [$CoCl_2$(**L1**)] (**3**), [$FeCl_2$(**L1**)] (**4**), [$NiBr_2$(**L2**)] (**5**), and [$CoCl_2$(**L2**)] (**6**) in moderate to high yields. The complexes were characterized by elemental analyses, mass spectrometry and single-crystal x-ray diffraction for 5 and 6. Solid state structures of **5** and **6** confirmed the bidentate coordination modes of **L1** and **L2** and formation of monometallic compounds. Complexes **1**-**6** formed active catalysts for the oligomerization of ethylene reactions when activated with either $EtAlCl_2$ or methylaluminoxane (MAO). The catalytic activities of **1**-**6** and products formed largely depended on the co-catalyst and solvent system. While activation with $EtAlCl_2$, in toluene produced Friedel-Crafts toluene-alkylated products, the use of hexane and chlorobenzene gave predominantly C_4 and C_6 oligomers. On the other hand, activation with MAO in toluene led to the formation of mainly C_4, C_6 and C_8 oligomers. The complex structure and reaction conditions such as co-catalyst/complex ratio, time and pressure also influenced the catalytic behaviour of these pre-catalysts.

1. Introduction

Late-transition metal complexes containing nitrogen donor ligands have continued to receive attention as α-olefin oligomerization and polymerization catalysts [1] since the discovery by Brookhart's and co-workers that α-diimine late transition metal complexes form active catalysts for olefin oligomerization and polymerization reactions [2–6]. Significant amount of research has been directed towards the design and development of other late transition metal nitrogen–donor complexes as ethylene polymerization [7–9] and oligomerization catalysts [10–13]. The role of ligands in transition metal catalyzed ethylene oligomerization reactions is reaching new frontiers with recent discoveries of Dyer et al. [14] that nickel(II) complexes of *N*-phosphino guanidine ligands and $EtAlCl_2$ as a co-catalyst promote *in situ* Friedel–Crafts alkylation of toluene solvent by the preformed oligomers. Until then, most ethylene oligomerization reactions catalyzed by nickel(II) complexes were reported to give mostly ethylene oligomers irrespective of the co-catalysts and solvent used. Well known examples include Shell Higher Olefin process PÔ nickel(II) catalysts [15–17], α-diimine complexes discovered by Brookhart and co-workers [2,3] and nitrogen and phosphine donor nickel(II) catalysts developed by Braunstein [18–21].

As a follow up to the Dyer report, Song et al. [22] reported the oligomerization of ethylene to butene, hexene and octene followed by subsequent Friedel–Crafts alkylation of the toluene solvent using nickel(II) complexes and $EtAlCl_2$ or MAO as co-catalysts. Our first reports of this phenomenon were using (pyrazol-1-ylmethyl)pyridine [23] and (pyrazolylmethyl)benzene nickel(II) complexes [24] that catalyze ethylene oligomerization to mainly C_4 and C_6 fractions followed by subsequent Friedel–Crafts alkylation of the toluene solvent. More recently, Obuah et al. reported [25] that pyrazolylamine nickel(II) complexes when activated with $EtAlCl_2$ in toluene oligomerize ethylene to butenes and hexenes accompanied by selective Friedel–Crafts alkylation of toluene solvent by butenes to butyltoluene, dibutyltoluene and tributyltoluene products. On the other hand, reactions in chlorobenzene solvent using $EtAlCl_2$ as a co-catalyst produced butenes, hexenes as well as branched polyethylene. In these findings, the use of MAO as a co-catalyst in toluene solvent afforded exclusively higher density

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polyethylene. From these accounts, it is clear that Friedel–Crafts alkylation of the pre-formed oligomers is more complex than initially thought to be initiated by use of excess $EtAlCl_2$ co-catalyst and toluene solvent. It is therefore apparent that in addition to the solvent and co-catalyst used, the identity of the ligand might also play a major role in these Friedel–Crafts reactions.

As part of our continued study of pyrazolyl transition metal complexes as catalysts in ethylene oligomerization and polymerization reactions, we report here a simple modification of the bis(pyrazolylmethyl)pyridine ligand, which we had previously investigated [23]. The aim was to further gain insight into the role of the pyrazolyl unit in controlling the catalytic activities of these metal complexes. Herein, we describe the synthesis of 2-(chloromethyl)-6-(pyrazol-1-ylmethyl)pyridine nickel(II), cobalt(II) and iron(II) complexes and their catalytic behaviour in ethylene oligomerization reactions. The effects of co-catalyst and solvent have been investigated using $EtAlCl_2$ and MAO co-catalysts and toluene, hexane and chlorobenzene solvents.

2. Experimental

2.1. Materials and methods

All synthetic manipulations were performed under nitrogen atmosphere using standard Schlenk line techniques. All solvents were of analytical grade and were dried and distilled prior to use. Tetrabutylammonium bromide, ethylaluminium dichloride ($EtAlCl_2$, 1.8 M in toluene), ethylaluminium dichloride ($EtAlCl_2$, 1.0 M in hexane), methylaluminoxane (10 wt. % in toluene), 3,5-dimethylpyrazole, dibenzoylmethane, hydrazine hydrate, thionyl chloride, 2,6-bis(hydroxymethyl)pyridine, and metal halides were obtained from Sigma–Aldrich and used as received. The starting materials 2,6-bis(chloromethyl)pyridine [26], and 3,5-diphenylpyrazole [27] were synthesized following literature procedures. ^{1}H NMR and ^{13}C $\{^1$H$\}$ NMR were recorded on a Bruker Ultrashield 400 (^{1}H NMR 400 MHz, ^{13}C $\{^1$H$\}$ NMR 100 MHz) in $CDCl_3$ solution at room temperature and chemical shifts (δ) were determined relative to internal TMS and are given in ppm. Elemental analyses were performed on a Thermal Scientific Flash 2000 while mass spectra were recorded on an LC premier micro-mass spectrometer. Magnetic moments of the complexes were determined using Evans balance. GC analyses were performed on a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 μm film thickness) CP-Sil 5 CB capillary column while GC–MS analyses were performed on a Shimadzu GC–MS-QP2010 fitted with a quadrupole mass detector.

2.2. Syntheses of (pyrazolylmethyl)pyridine ligands and their metal complexes

2.2.1. 2-(chloromethyl)-6-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine (*L1*)

Ligand **L1** was prepared by dissolving 2, 6-bis(chloromethyl) pyridine (1.83 g, 10.4 mmol) and 3,5-dimethylpyrazole (1.00 g, 10.4 mmol) in toluene (30 mL) followed by addition of 40% aqueous NaOH (12 mL) and 40% aqueous tetrabutylammonium bromide (5 drops). The reaction mixture was refluxed for 24 h after which the organic layer was separated from the aqueous layer and washed three times with deionised water. The organic layer was dried over anhydrous Na_2SO_4 and reduced under vacuum. Purification was done by column chromatography using hexane/diethyl ether (3:2) solvent mixture to afford **L1** as a white solid. Yield: 0.64 g (26%). ^{1}H NMR ($CDC1_3$): δ 2.19 (s, 3H, CH_3, pz); 2.24 (s, 3H, CH_3, pz); 4.64 (s, 2H, CH_2); 5.33 (s, 2H, CH_2); 5.88 (s, 1H, pz); 6.72 (d, 1H, py, $^3J_{HH}$ = 7.61 Hz); 7.34 (d, 1H, py, $^3J_{HH}$ = 7.72 Hz); 7.61(t, 1H, py, $^3J_{HH}$ = 7.73 Hz). ^{13}C NMR ($CDC1_3$): δ 11.08, 13.43, 46.54, 54.18, 105.80, 120.30, 121.4, 138.12, 139.96, 148.10, 156.20, 157.20. ESI-MS: *m/z* (%) 258 [(M + Na,)$^+$, (^{35}Cl) 100%], 260 [(M + Na,)$^+$, (^{37}Cl) 49%]. Anal. Calcd. for $C_{12}H_{14}ClN_3 \cdot 0.5CH_2Cl_2$: C, 53.97; H, 5.44; N, 15.11. Found: C, 53.41; H, 5.21; N, 15.00.

2.2.2. 2-(chloromethyl)-6-((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine (*L2*)

Ligand **L2** was prepared from 2,6-bis(chloromethyl)pyridine (3.0 g, 17.04 mmol) and 3,5-diphenylpyrazole (3.75 g, 17.04 mmol) following the procedure described for **L1.** The crude product was purified by column chromatography on silica gel using petroleum ether to diethyl ether (2:1) to give **L2** as an analytically pure white solid. Yield: 1.7 g (28%). ^{1}H NMR ($CDC1_3$): δ 4.65 (s, 2H, Cl-CH_2); 5.54 (s, 2H, CH_2); 6.73 (s, 1H, pz); 6.93 (d, 1H, py, $^3J_{HH}$ = 7.82 Hz); 7.46–7.34 (m, 9H, Ar, $^3J_{HH}$ = 7.72 Hz); 7.65 (t, 1H, Ar, $^3J_{HH}$ = 7.82 Hz); 7.88 (d, 2H, Ar, $^3J_{HH}$ = 7.32 Hz). ^{13}C NMR ($CDC1_3$): δ 46.60, 54.92, 103.84, 120.61, 121.46, 125.75, 127.89, 128.83, 130.24, 133.35, 138.09, 146.08, 151.51, 156.16, 157.53. ESI-MS: *m/z* (%) 282 [(M + Na,)$^+$, (^{35}Cl) 100%], 284 [(M + Na,)$^+$, (^{37}Cl) 56%]. Anal. Calcd for $C_{22}H_{18}ClN_3$: C, 73.43; H, 5.04; N, 11.68. Found: C, 73.94; H, 4.60; N, 11.92.

2.2.3. [{2-(chloromethyl)-6-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine}$NiCl_2$] (*1*)

Complex **1** was prepared by adding a solution of $NiCl_2$ (0.11 g, 0.85 mmol) in dichloromethane (15 mL) to a solution of **L1** (0.20 g, 0.85 mmol) in dichloromethane (15 mL). The resultant solution was stirred for 24 h to give green precipitate which was isolated by filtration, washed with ethanol and diethyl ether to afford complex **1** as a green solid. Yield: 0.12 g (65%). ESI-MS: *m/z* (%) 329 (M^+–Cl, 88%). Anal. Calcd for $C_{12}H_{14}ClN_3NiCl_2 \cdot CH_2Cl_2$: C, 34.68; H, 3.58; N, 9.33. Found: C, 34.95; H, 3.66; N, 10.06. μ_{eff} = 3.64 BM.

Complexes **2**-**4** were prepared following the procedure described for **1**.

2.2.4. [{2-(chloromethyl)-6-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine}$NiBr_2$] (*2*)

[$NiBr_2$] (0.19 g, 0.85 mmol) and **L1** (0.20 g, 0.85 mmol). Pale purple solid. Yield: 0.30 g (78%). ESI-MS: *m/z* (%) 373 (M^+–Br, 97%). Anal. Calcd for $C_{12}H_{14}ClN_3NiBr_2 \cdot CH_2Cl_2$: C, 28.96; H, 2.99; N, 7.79. Found: C, 29.26; H, 3.35; N, 8.37. μ_{eff} = 3.92 BM.

2.2.5. [{2-(chloromethyl)-6-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine}$CoCl_2$] (*3*)

[$CoCl_2$] (0.06 g, 0.42 mmol) and **L1** (0.10 g, 0.42 mmol). Recrystallisation from CH_2Cl_2-hexane solution gave **3** as an analytically pure blue solid. Yield: 0.13 g (84%). ESI-MS: *m/z* (%) 328 (M^+–Cl, 68%). Anal. Calcd for $C_{12}H_{14}ClN_3CoCl_2$: C, 39.43; H, 3.86; N, 11.49. Found: C, 39.09; H, 3.91; N, 11.00. μ_{eff} = 4.27 BM.

2.2.6. [{2-(chloromethyl)-6-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)pyridine}$FeCl_2$] (*4*)

[$FeCl_2 \cdot 4H_2O$] (0.08 g, 0.42 mmol) and **L1** (0.10 g, 0.42). Brown solid. Yield: 0.13 g (82%). ESI-MS: *m/z* (%) 326 (M^+–Cl, 32%). Anal. Calcd for $C_{12}H_{14}ClN_3FeCl_2 \cdot 1.5CH_2Cl_2$: C, 33.10; H, 3.50; N, 8.58. Found: C, 33.58; H, 3.35; N, 9.40. μ_{eff} = 5.28 BM.

2.2.7. [{2-(chloromethyl)-6-((3,5-diphenyl-1H-pyrazol-1-yl)methyl)pyridine}$NiBr_2$] (*5*)

To a solution of $NiBr_2$ (0.12 g, 0.56 mmol) in dichloromethane (15 mL) was added a solution of **L2** (0.20 g, 0.56 mmol) in dichloromethane (15 mL). The resultant solution was stirred for