


ORIGINAL RESEARCH PAPER
Chemistry
2-AMINOMETHYLPYRIDINE NICKEL(II) COMPLEXES-SYNTHESIS, MOLECULAR STRUCTURE AND CATALYSIS OF ETHYLENE POLYMERIZATION
KEY WORDS: 2-Aminomethylpyridine, Ethylene polymerization, 2-iminomethylpyridine.

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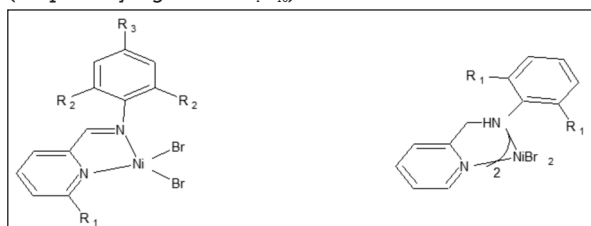
ABSTRACT

Nickel catalysts were used to oligomerize ethylene and dimerize propylene and higher olefins because nickel metal was usually thought to generally prefer H elimination followed by reductive elimination⁽¹⁾. For nickel catalysts, the salicylaldimine, diimine and diketoamine nickel complexes have been studied extensively. Yi et al. reported the ethylene polymerisation by 2-imino pyridine nickel(II) dibromide 1 (Scheme 1) and found that the product produced by 1 was composed of oligomers (the primary ingredient C₄C₁₀) with 45% olefin. Laine et al. found that these complexes could obtain solid polyethylene (M_w= 270040000) under the polymerization conditions of high ethylene pressure (P_e = 0.300.55 MPa) and high Al/Ni ratio (Al/Ni=2000). Gibson et al. found that the aminopyridine iron(II) complexes were more efficient catalysts for styrene polymerization than their unsaturated 2-iminopyridine relatives.

INTRODUCTION:

In the past, nickel catalysts were best known to oligomerize ethylene and dimerize propylene and higher olefins because nickel metal was usually thought to generally prefer H elimination followed by reductive elimination⁽¹⁾. In 1995 cationic Ni(II) and Pd(II) catalysts derived from bulky arylsubstituted diimines were reported to convert ethylene and olefins to high molecular weight polyolefins⁽²⁾. Otherwise, by comparison with early transition metal catalysis, late transition metal complexes are generally much more functional group tolerant as the result of their less oxophilic nature^(3,4). Recently, olefin polymerization and oligomerization catalyzed by late transition metal complexes have attracted great attention in both academic and industrial research⁽⁵⁾.

Earlier, for nickel catalysts, the salicylaldimine, diimine and diketoamine nickel complexes have been studied extensively. Yi et al. reported the ethylene polymerisation by 2-imino pyridine nickel(II) dibromide 1 (Scheme 1) and found that the product produced by 1 was composed of oligomers (the primary ingredient C₄C₁₀) with 45% olefin⁽⁶⁾.


 I. R₁ = H, R₂ = iPr, R₃ = H a:

 R₁ = Me

 ii. R₁ = Me, R₂ = iPr, R₃ = H B:

 R₁ = 'Pr

 iii. R₁ = H, R₂ = R₃ = Me c:

 R₁ = F

Scheme 1. 2Imino pyridine nickel(II) dibromide (1) and 2aminomethyl pyridine nickel(II) dibromide(2)
1. Experimental:
(i) Solvents and Reagents

All manipulations involving air and moisture sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard Schlenk techniques. Solvents were purified with standard procedures. 2Pyridine carboxaldehyde (99%), 2,6-dimethylaniline (98%), 2,6-diisopropylaniline (98%), 2,6-difluoroaniline (98%) and lithium aluminium hydride (LiAlH₄) were purchased from

Aldrich Chemical Co. and used without further purification. (DME)NiBr₂ was synthesized by the reaction of 1,2-dimethoxy methane with anhydrous nickel(II) bromide. MAO was prepared by the hydrolysis of trimethylaluminum with Al₂(SO₄)₃·18H₂O in toluene with the H₂O/Al ratio of 1.3:1.

(ii) Measurements

Elemental analyses were performed on a Vario EL microanalyzer. ¹H NMR spectra were carried out on an Inova instrument (300 MHz) at room temperature in CDCl₃ solution using tetramethylsilane as an internal standard for the ligands and ¹³C NMR spectra were performed on an Inova instrument (500 MHz) at 120°C in dichlorobenzene-d₂ for the polymers (15 wt%) with the chemical shift (δ = 30.00) of the main backbone methylene as an internal standard. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distributions (MWD) of the polymers were performed on a Water 2000 at 135°C based on standard polystyrene as the reference with 1,2,4-trichlorobenzene as the solvent. Gas chromatography/mass spectrometry (GCMS) of the oligomer was handled with a Voyager instrument from Finigan Co. Single crystal X-ray diffraction data of complex 2c was collected on a Bruker Smart CCD (diffractometer at 173(2) K. The structures were solved by Patterson methods followed by difference Fourier syntheses and then refined by full matrix least squares techniques against F₂ with SHELXTL⁽¹⁰⁾.

(iii) Synthesis of Complexes (2a-2c)

(DME)NiBr₂ was added to the above solution and then stirred for 10 h at room temperature. The solution was filtered and washed by 5 mL dichloromethane for three times. The solution was evaporated to a little volume in vacuo, and 20 mL n-hexane was added. The mixture was stirred for 20 min and filtered, and then the residual solid was washed with n-hexane (3×5 mL).

1. Bis[N2,6dimethylphenylaminomethyl2pyridyl] Nickel(II) dibromide (2a)

prepared with 1a 0.44 g (2.07 mmol) and 0.32 g (DME)NiBr₂ was obtained as green crystal in 0.55 g (82.7%). ¹H NMR (300 MHz, CDCl₃,): 1.321.36 (6H, d, 2CH₃), 5.33 (3H, s, CH₂, NH), 3.313.68 (2H, m, 2CH), 4.09 (2H, s, CH₂), 5.29 (1H, s, NH), 7.27 (overlapping, 7H, s, benzyl, Py). Anal. Calcd for C₂₈H₃₂N₄NiBr₂: C, 52.29%; H, 5.02%; N, 8.71%. Found: C, 52.15%, H, 5.17%; N, 8.59%.

2. Bis[N2,6diisopropylphenylaminomethyl2pyridyl]Nickel(II) dibromide (2b)

prepared with 1b 0.26 g (0.97 mmol) and 0.18 g (DME)NiBr₂ was obtained as green crystal in 0.25 g (68.3%). ¹H NMR (300 MHz, CDCl₃,): 1.291.32 (12H, d, 4CH₃), 3.263.40 (2H, m, 2CH), 4.28 (2H, s, CH₂), 5.13 (1H, s, NH), 7.18 (overlapping, 7H, s,

benzyl, Py). Anal. Calcd. For $C_{38}H_{48}N_2NiBr_2$: C, 57.25%; H, 6.41%; N, 7.42%. Found: C, 57.49%; H, 6.57%; N, 7.52%

3. Bis[N2,6difluorophenylaminomethyl2pyridyl] Nickel(II) dibromide (2c)

prepared with 1c 0.66 g (3.00 mmol) and 0.45 g (DME)NiBr₂ was obtained as green crystal in 0.52 g (52.6%). ¹HNMR (300 MHz, CDCl₃): 3.533.69 (2H, d, CH₂), 5.37 (1H, s, NH), 7.27 (overlapping, 7H, s, benzyl, Py). Anal. Calcd. For $C_{24}H_{20}N_2F_2NiBr_2$: C, 43.75%; H, 3.06%; N, 8.50%. Found: C, 43.63%; H, 3.03%; N, 8.65%.

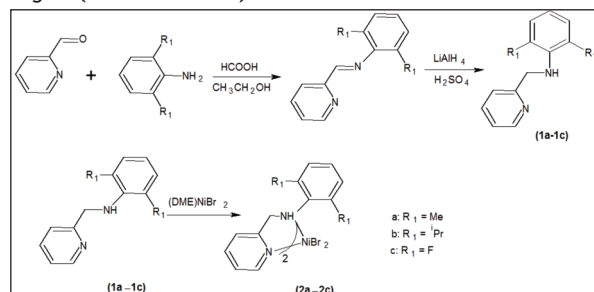
(iv) Ethylene Polymerization

Ethylene polymerization was carried out in a 50 mL glass flask equipped with magnetic stirrer or 100 mL stainless steel autoclave. In the reactor filled with ethylene, desired amounts of MAO and toluene were added and the polymerization was initiated by injecting a CH₂Cl₂ solution of the nickel complex.

2. RESULTS AND DISCUSSION:

(I) Synthesis of Ligands and Catalysts

The synthesis routes of 2aminoethylpyridine ligands and Ni(II) complexes bearing different substitution groups are shown in Scheme 2. 2Iminomethyl pyridines were synthesized based on condensation reaction of 2pyridine carboxaldehyde and the corresponding anilines. Deoxidization of the obtained 2iminomethylpyridines by LiAlH₄ resulted in the desired ligands 1alc⁽¹²⁾. In the ¹HNMR spectra of the obtained ligands 1al1b, hydrogen chemical shifts of CH₂ and NH appear at δ = 4.30 and δ = 4.20, respectively, whereas the corresponding chemical shifts of 1c move to the downfield region (δ = 4.61 and δ = 4.86).



Scheme 2 Synthesis route of ligands 1alc and nickel complexes 2a-2c

Complexes 2a-2c were synthesized directly by the coordination reaction of ligands 1alc and (DME)NiBr₂. Crystals of complexes 2c suitable for singlecrystal Xray diffraction analysis were grown from their hexane/dichloromethane solution. The ORTEP diagram of complex 2c is presented in the Fig. 1. The complex 2c exists as bisligand single molecular (monomer) structure with octahedral geometries about nickel in solid state and a crystallographic C₂ axis of symmetry that make the two ligands equivalent. The bond distance of N₂Ni (0.2270(4) nm) is little longer than that of N₂Ni (0.2063(4) nm), indicating that the binding ability of pyridine N with metal nickel is stronger than that of amino N with metal nickel.

(I) Ethylene Polymerization

The complexes 2a-2c were efficient catalysts for ethylene polymerization in the presence of MAO (Methyl aluminoxane) and the polymerization results are presented in Table 3.1. Among these complexes, 2c showed the highest catalytic activity. The products obtained by complexes 2a and 2b containing orthoalkylsubstituent were composed of solid polymer with a certain amount of oligomer, but only oligomer was obtained by 2c containing orthofluorosubstituent. of the aminoaryl bond. As reported by Zou et al., the Naryl rotation of the unsymmetrical diimine ligands could be observed by NMR analysis⁽¹⁴⁾. Aydeniz et al. had investigated the pair of rotational isomers for 3(arylyl)Smethylrhodanines using NMR spectroscopy and density functional theory (DFT) calculations⁽¹⁵⁾.

Table 1.1 also lists the results of polymerization at various polymerization conditions including ethylene pressure and polymerization temperature.

Table 1.1: Results of ethylene polymerization catalyzed by 2a-2c/MAO

Ent ry	Cata lyst	T _p °C	Polymer yield(g)	Activity (kgE/ (molNi.h))		M _n	PDI	Branc hes/ 1000C
				Polymer	Oligomer			
1	2a	20	0.16	3.20	1.00	17500	2.46	6.4
2	2a	0	0.29	5.74	2.02	6980	2.38	
3	2a	15	0.51	10.2	3.40	2030	B	98.2
4	2a	30	0.05	1.00	4.00			
5 ^a	2a	15	2.46	49.2	nd	13630	3.80	28.5
6	2b	20	0.11	2.20	0.42	25800	2.26	
7	2b	0	0.20	4.21	0.70	8500	2.36	
8	2c	20	0		7.00			
9	2c	0	0		22.6			

Conditions:

catalyst 10mol; time 30 min; toluene 20 mL; ethylene pressure 20.3 kPa; Al.Ni=800; ^aEthylene pressure 2.0 MPa; ^bThe molecular weight are too low to get correct PDI values; nd = not detected

The obtained oligomer by 2c in toluene was characterized by GCMass and the spectrum with the analysis results is presented in Fig. 3. The retention time of 1.75 and 4.97 min attached to the dichloromethane and toluene which was added as solvent for nickel complex and the reaction respectively. The oligomers of C₈H₈, C₈H₁₂, C₈H₁₆, C₁₀H₂₀, C₁₂H₂₄, C₁₄H₂₈, C₁₆H₃₂, C₁₈H₃₆, C₂₀H₄₀, C₂₂H₄₄, C₂₄H₄₈ and C₂₆H₅₂ can be distinguished in the spectrum and appear at the retention times of 1.55, 2.28, 5.81, 11.7, 17.4, 20.3, 22.3, 23.8, 25.2, 26.5, 27.6 and 28.6 min, respectively. In the oligomers obtained by 2c at 0C, C₁₂H₂₄ had the maximum content. The olefin distribution data were plotted based on the AndersonSchulz Flory (ASF) equation.

$$\lg\left(\frac{W_n}{n}\right) = n\lg a + const$$

where W_n is the mass fraction of the species with carbon number n⁽¹⁶⁾. As shown in Fig. 3, two values of the chain growth probability (i=0.95, 2=0.81) are obtained from the slopes of the plot of lg(W_n/n) against n. The bimodal ASF distribution could be interpreted by differently structured active centers.

3. CONCLUSION:

2Aminomethylpyridine nickel(II) complexes can be synthesized by the coordination reaction of 2 aminomethylpyridine ligands and (DME)NiBr₂. On the basis of singlecrystal Xray diffraction analysis, complex 2c is C₂

axis of symmetry and exists as monomer structure with octahedral geometries about nickel in solid state. Complexes 2a-2c are active catalysts for the ethylene polymerization. The orthoalkylsubstituted complexes 2a and 2b afforded high molecular weight branched polyethylenes with a certain amount of oligomer in the presence of MAO, (Methyl aluminoxane) whereas only oligomers were obtained by orthosubstituted complex 2c. The olefin content of the oligomers obtained by 2c suited approximately to bimodal ASF distribution in which C₁₂H₂₄ has the maximum content.

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