

SYNTHESIS, CHARACTERIZATION AND CATALYTIC BEHAVIOR OF DIMERIC Co(II) AND Ni(II) COMPLEXES CONTAINING *N,N'*-(PHENYL-2-PYRIDINYLMETHYLENE)-3,3',5,5'-TETRAMETHYLBENZIDINE

Yong Cui, Shu Zhang and Wen-hua Sun*

Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Abstract The *N,N'*-(phenyl-2-pyridinylmethylene)-3,3',5,5'-tetramethylbenzidine and its dimeric Co(II) and Ni(II) complexes were synthesized. The organic compound was characterized by elemental analyses, IR and NMR spectra, while the bimetal complexes were determined by elemental analyses, IR spectra as well as the single-crystal X-ray diffraction. The nickel complex showed high activity for ethylene polymerization and its cobalt analogue showed negligible activity in ethylene activation.

Keywords: Bis-pyridinylimino ligand; Nickel complex; Cobalt complex; Ethylene polymerization.

INTRODUCTION

The nickel complex was evidentially proved as good catalyst for ethylene oligomerization in SHOP process^[1]. In 1995, the pioneering work by Brookhart's group on α -diimino nickel complexes for high molecular weight polyethylene broke out the silence of late-transition metal catalysts for polyolefins^[2], and resulted in the remarkable increase of academic publications and patents about polyolefins obtained with Group VIII metal complexes as catalysts^[3–5]. The various Schiff-base ligands such as bidentate N-donors' ligands^[2, 6–8] have been extensively studied based on their easy preparation and the promising catalytic properties of their late-transition metal complexes. Involved in the exploring alternative nickel complexes as catalysts for ethylene activation, the bidentate and tridentate pyridinylimino^[9–17] and phenanthroline^[18–20] derivatives are also generally considered. Pyridinylimino nickel complexes were observed as the centrosymmetric dimers with two bridging bromine atoms around each five-coordination nickel center^[6–8] or the monomers with one acetonitrile molecule around five-coordination nickel center^[21] in different solvents, all these nickel complexes showed good activities for ethylene polymerization. Though the bridged bis(pyridinylimino) ligands and their nickel complexes were reported^[22], the investigating the scope of such nickel complexes and their exaltation will be helpful in data cumulating and finding practicable catalyst. The *N,N'*-(phenyl-2-pyridinylmethylene)-4,4'-tetramethylbenzidine and its Co(II) and Ni(II) complexes are synthesized and characterized. In the presence of methylaluminoxane (MAO), the nickel complex showed considerably good activities for ethylene polymerization. Herein the synthesis and characterization of ligand and its cobalt and nickel complexes were reported.

EXPERIMENTAL

General

Compound 2-benoxypyridine and 3,3',5,5'-tetramethylbenzidine were purchased from Acros Chemical Co and

* Corresponding author: Wen-hua Sun (孙文华), E-mail: whsun@iccas.ac.cn

Invited lecture presented at the Asian Polyolefin Workshop 2007, 2007, Hangzhou, China

Received February 13, 2008; Revised March 20, 2008; Accepted March 24, 2008

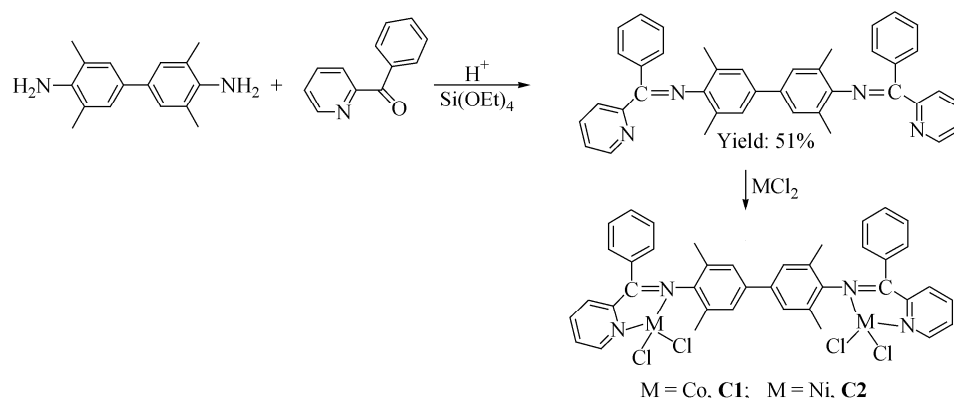
Aldrich Chemical Co. All these were used commercially without further purification unless stated otherwise. Methylaluminoxane (MAO) in toluene (10 wt%) was from the Aybemarle Co (USA). Toluene was dried by refluxing metallic sodium and distillation under nitrogen. Polymerization grade ethylene monomer, produced by Beijing Yanshan Petrochemical Co (China), was used without further purification.

IR spectra were obtained as KBr pellets on a Perkin-Elmer FTIR 2000 spectrometer; ^1H -NMR spectra were recorded on a Bruker DMX-300 spectrometer with TMS as internal standard. Mass spectra were measured on a Kratos AEI MS-50 instrument using the fast atom bombardment (FAB) technology. Melting points were taken on an electrothermal melting point apparatus without further correction. Elementary analyses were performed on a HP-MOD 1106 microanalyzer. Melting points (m.p.) were taken on a digital electrothermal melting point apparatus without further correction. ^{13}C -NMR spectra of polymers were measured on a Bruker MSL-300, in 1, 2-dichlorobenzene- d_4 at 135°C.

The branching was determined according to the method of Alexson *et al.*^[23]. GPC was performed on a Waters Alliance (USA), GPCV2000 instrument with trichlorobenzene as solvent. DSC traces were obtained on Perkin-Elmer (UK) series 7 thermal analysis systems at a heating rate of 10 K/min under N_2 and the data reported are from the second scanning run.

Preparation of the Ligand

The N,N' -(phenyl-2-pyridinylmethylene)-3,3',5,5'-tetramethylbenzidine was obtained by reacting 2-benzoyl pyridine with the 3,3',5,5'-tetramethylbenzidine using concentrated H_2SO_4 as acid catalyst and tetraethyl orthosilicate as dehydration agent at 150°C (Scheme 1) according to literature^[22, 24]. It was purified through column chromatography and afforded in acceptable isolated yield (51%). It reacted with NiCl_2 and CoCl_2 in ethanol at elevated temperature to form their complexes.



Scheme 1 Synthesis of ligand and complexes

To a mixture of diamine (10 mmol) and 2-benzoyl pyridine (22 mmol) was added two drops of concd. H_2SO_4 and $\text{Si}(\text{OEt})_4$ (23 mmol). The mixture was heated at 150°C under nitrogen for 10 h. The EtOH formed in reaction was evaporated during the reaction and the residue was dissolved in ether (100 mL) and washed with saturated NaHCO_3 solution (50 mL) and brine (2×50 mL), and dried over Na_2SO_4 . Evaporation of the volatiles afforded a residue, which was subsequently purified by column chromatography [silica gel; eluent: EtOAc-petroleum ether (from 1:5 to 1:2)] to obtain the pure diimine, N,N' -(Phenyl-2-pyridinylmethylene)-3,3',5,5'-tetramethylbenzidine as yellow crystals. Isolated yield: 51%. M.p.: 203–204°C. IR (cm^{-1}): 2965, 1632 ($\text{C}=\text{N}$), 1582, 1466, 1376, 1305, 1245, 1213, 1159, 1087, 995, 957, 889, 863, 801, 749, 697. ^1H -NMR(CDCl_3 , δ): 2.08 (s, 6H), 2.12 (s, 6H), 7.02 (d, 1H), 7.08–7.23 (m, 9H), 7.37–7.55 (m, 6H), 7.80 (d, 2H), 7.85 (t, 1H), 8.23 (d, 1H), 8.61 (d, 1H), 8.67 (d, 1H). MS (FAB, m/z): 571 ($\text{M}+1$). Anal. Calcd. for $\text{C}_{40}\text{H}_{34}\text{N}_4$: C, 84.18; H, 6.00; N, 9.82. Found: C, 84.08; H, 6.30; N, 9.46.

Preparation of the Complexes 1–2*[N,N'-(phenyl-2-pyridinylmethylene)-3,3',5,5'-tetramethylbenzidine]2CoCl₂ (C1)*

A solution of *N,N'*-(phenyl-2-pyridinylmethylene)-3,3',5,5'-tetramethylbenzidine (142.5 mg, 0.25 mmol) in ethanol (10 mL) was added dropwise at 60°C to a solution of CoCl₂·6H₂O (64.9 mg, 0.50 mmol) in ethanol (5 mL) to yield a blue solution. After stirred at 60°C for 4 h, the reaction mixture was allowed to cool to room temperature. The green precipitate was subsequently collected by filtration, washed with diethyl ether (3 × 10 mL), and dried to afford 180 mg of Co complex, yield 87%. M.p. > 320°C. IR (cm⁻¹): 3399, 2960, 1585, 1564, 1469, 1443, 1382, 1331, 1261, 1211, 1160, 1091, 1020, 985, 865, 804, 784, 753, 703. Anal. Calcd. for C₄₀H₃₄N₄·2CoCl₂: C, 57.86; H, 4.13; N, 6.75. Found: C, 57.57; H, 4.42; N, 6.30.

[N,N'-(Phenyl-2-pyridinylmethylene)-3,3',5,5'-tetramethylbenzidine]2NiCl₂ (C2)

The procedure as above, using ligand (144 mg, 0.25 mmol) and NiCl₂·6H₂O (131 mg, 0.55 mmol) give the Ni complex as dark yellow powder (200 mg, 97%). IR (cm⁻¹): 3366, 1617 (C=N), 1590, 1470, 1444, 1382, 1329, 1262, 1209, 1159, 1104, 1026, 985, 864, 801, 752, 704. Anal. Calcd. for C₄₀H₃₄N₄Ni₂Cl₄·2C₂H₅OH: C, 57.31; H, 5.03; N, 6.08. Found C, 56.90; H, 5.44; N, 6.36.

X-Ray Crystallographic Data

In general, Co complex (C1) intensity data sets were collected at 293 K on a Bruker SMART 1000 diffractometer with graphite-monochromated Mo-K α radiation (λ = 0.071073 nm), using the ω -2 θ scan mode. Cell parameters were obtained by the global refinement of the positions of all collected reflections. Intensities

Table 1. Crystal data and structure refinement of C1

Formula	C ₄₆ H ₄₈ C ₁₄ Co ₂ N ₆ O ₂
CCDC deposition	180100
Formula weight	976.56
Temperature (K)	293(2)
Wavelength (nm)	0.071073
Crystal system	Monoclinic
Space group	P2(1)/n
<i>a</i> (nm)	1.1658(4)
<i>b</i> (nm)	3.0105(10)
<i>c</i> (nm)	1.3808(4)
β (°)	98.112(6)
Volume (nm ³)	4.798(3)
<i>Z</i>	4
<i>D</i> _{calc} (mg m ⁻³)	1.352
μ (mm)	0.957
<i>F</i> (000)	2016
Crystal size (mm)	0.30 × 0.25 × 0.20
θ range (°)	1.35 – 25.03
Limiting indices	–13 ≤ <i>h</i> ≤ 13 –26 ≤ <i>k</i> ≤ 35 –14 ≤ <i>l</i> ≤ 16
Reflections collected	8465
Unique reflections	3724 [<i>R</i> _{int} = 0.0857]
Completeness to θ (%)	1.000 (θ = 25.03)
Absorption correction	MULTI-SCAN
Max./min. transmission	0.608/0.007
Data/restraints/parameters	8465/0/549
Goodness-of-fit on <i>F</i> ²	0.976
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0549, <i>wR</i> ₂ = 0.1080
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1549, <i>wR</i> ₂ = 0.1456
Largest diff peak and hole (e nm ³)	0.367 × 10 ⁻³ – 0.333 × 10 ⁻³

were corrected by Lorentz and polarization effects and empirical absorption. The structure was solved by direct method, and refined by full-matrix least square on F², using Shelxl-97 package^[25]. Final R1 value for this complex was 0.0549. Crystal Data: C₄₀H₃₄N₄·2CoCl₂·2DMF, Formula weight: 976.56, monoclinic, space group P2(1)/n, *a* = 1.1658(4) nm, *b* = 3.0105(10) nm, *c* = 1.3808(4) nm, β = 98.112(6)°, *V* = 4.798(3) nm³, *Z* = 4, *D_c* = 1.352 g/cm³, *F*(000) = 2016, Crystal size: 0.30 mm × 0.25 mm × 0.20 mm. The crystal data and refinement parameters were summarized in Table 1.

The molecular structure of the cobalt complex crystal **C1** was shown in Fig. 1.

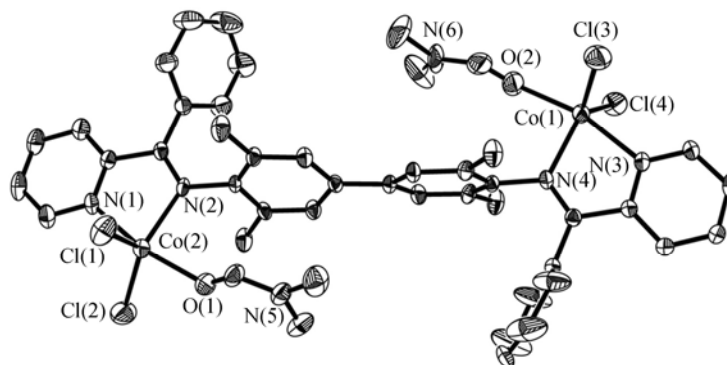


Fig. 1 Molecular structure of Co complex **C1**
Displacement ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity.

General Procedure for Ethylene Polymerization

The reactions were performed in 200 mL Schlenk-type glass reactor equipped with a magnetic stirrer. After evacuating air and moisture from the reactor for about 30 min. and replacing three times with nitrogen, the complex was weighed into the reactor under a nitrogen atmosphere. Reaction started when nitrogen in the reactor was twice replaced by ethylene monomer and toluene (50 mL) and MAO were introduced sequentially. After the desired period of time the reaction was quenched by injecting 5% HCl-acidified ethanol to precipitate white polymer. The polymer was collected by filtration, washed with anhydrous ethanol and dried under vacuum at 50°C until a constant weight was achieved.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Ligand and Complexes

As shown in Scheme 1, the ligand could be prepared by one-step condensation in moderate yield (51%) of two equivalents of benzoyl pyridine with one equivalents of 3,3',5,5'-tetramethylbenzidine when a few drops of concentrated H₂SO₄ was introduced as catalyst and Si(OEt)₄ was used to remove the water formed during the reaction. The ligand was characterized by ¹H-NMR, mass spectrometry, IR and microanalysis. According to ¹H-NMR spectrum, two set peaks give the signals of the substituted methyl group on phenyl group. Subsequent complex formation was accomplished by treatment of a slight excess of nickel(II) chloride hexahydrate or cobalt(II) chloride hexahydrate with the ligand in ethanol affording compounds **1–2** in good yields.

Molecular Structure

The cobalt complex crystal suitable for X-ray structural determination was grown by vapor diffusion of Et₂O into DMF solutions. The molecular structure is shown in Fig. 1 and the selected bond lengths and angles are listed in Table 2. In the structure of **2**, one ligand coordinates with two metal cations. The molecular is composed of two similar parts connected by the biphenyl group. The dihedral angle between the two aromatic rings is 22.14°, which is different with the methylene bridged bis-pyridinylimino dinickel complexes^[22]. Each cobalt(II) center is bound to one pyridylimino, two chloride atoms and a DMF linked by O atoms, in a distorted trigonal-bipyramidal geometry. The nitrogen of imino and the two chlorides form an equatorial plane while the axial plane consists of one nitrogen atom from pyridine and one oxygen atom from DMF and the cobalt core.

The cobalt atom deviates from the equatorial plane by 0.0156 nm for Co1 and 0.0122 nm for Co2. The equatorial plane is nearly perpendicular to the axial plane with a dihedral angle of 89.80° for Co1 and 88.06° for Co2.

Table 2. Selected bond lengths (nm) and angles (°) for **C1**

Bond lengths			
Co(1)—N(4)	0.2095(4)	N(2)—C(13)	0.1443(6)
Co(1)—O(2)	0.2119(5)	N(3)—C(34)	0.1332(6)
Co(1)—N(3)	0.2151(4)	N(3)—C(30)	0.1337(6)
Co(1)—Cl(3)	0.2274(2)	N(4)—C(29)	0.1284(6)
Co(1)—Cl(4)	0.2276(2)	N(4)—C(25)	0.1461(6)
Co(2)—O(1)	0.2088(4)	N(5)—C(41)	0.1317(7)
Co(2)—N(2)	0.2096(4)	N(5)—C(42)	0.1442(7)
Co(2)—N(1)	0.2142(4)	N(5)—C(43)	0.1445(8)
Co(2)—Cl(2)	0.2273(2)	N(6)—C(45)	0.1243(2)
Co(2)—Cl(1)	0.2305(2)	N(6)—C(44)	0.1276(1)
N(1)—C(1)	0.1339(6)	N(6)—C(46)	0.1546(2)
N(1)—C(5)	0.1344(6)	O(1)—C(41)	0.1204(7)
N(2)—C(6)	0.1284(6)	O(2)—C(44)	0.1252(9)
Bond angles			
N(4)—Co(1)—O(2)	91.29(2)	O(1)—Co(2)—N(2)	91.89(2)
N(4)—Co(1)—N(3)	75.29(2)	O(1)—Co(2)—N(1)	165.52(2)
O(2)—Co(1)—N(3)	166.11(2)	N(2)—Co(2)—N(1)	75.08(2)
N(4)—Co(1)—Cl(3)	114.37(1)	O(1)—Co(2)—Cl(2)	91.63(1)
O(2)—Co(1)—Cl(3)	95.70(2)	N(2)—Co(2)—Cl(2)	125.56(1)
N(3)—Co(1)—Cl(3)	93.16(1)	N(1)—Co(2)—Cl(2)	90.96(1)
N(4)—Co(1)—Cl(4)	123.47(1)	O(1)—Co(2)—Cl(1)	96.23(1)
O(2)—Co(1)—Cl(4)	95.11(2)	N(2)—Co(2)—Cl(1)	108.22(1)
N(3)—Co(1)—Cl(4)	89.52(1)	N(1)—Co(2)—Cl(1)	93.88(1)
Cl(3)—Co(1)—Cl(4)	120.68(8)	Cl(2)—Co(2)—Cl(1)	125.30(9)

Polymerization of Ethylene

Upon treatment with MAO, the nickel complex activates ethylene for polymerization in toluene while the cobalt complex produced no polyethylene under the same conditions. Their ethylene activities for polymerization along with the properties of the products were listed in Table 3. The molecular weights (M_w) of the polymers produced by nickel complexes were in the range of 12000–66000, and the molecular weight distributions were from 1.4 to 5.4.

Table 3. The activities for ethylene polymerization of the complexes 1–2 ^a

Complex	T (°C)	Activity ^b	M_w	M_w/M_n	T_m (°C)	Branches/1000C
2	–15	0.948	66400	5.34	128.26	
2	0	4.527	18700	2.69	119.57	32
2	15	1.495	12000	1.42	117.33	
2	40	No				
1	15	No				

^a Cocat: MAO, Al/Ni = 500, reaction time: 1 h; ^b gPE/(molNi·h·Pa)

The nature of the metal center had a large influence on catalyst productivity. Treating of nickel complex with MAO produced quite effective catalyst for ethylene polymerization while the cobalt complex, in turn, showed nearly negligible activity under the same reaction conditions indicating improper electronic environment provided by the cobalt center as well as lacking enough steric bulk of the ligand.

The reaction conditions (such as temperature) greatly influenced their productivities and the nature of the

polymeric products. The nickel complex lost activity with decreasing or increasing reaction temperature: the highest catalytic activities were obtained at 0°C while lowering the temperature to -15°C led to a significant decline in polymer production because of lack of enough active sites. Reduced polymer yields with increasing reaction temperature could be attributed to lower monomer concentrations at higher temperature or catalyst deactivation. It was worthy of noting that nickel complex showed distinctly low tolerance for reaction temperature because it deactivated at 40°C. Moreover, as the temperature increase, the molecular weight, the molecular weight distributions and the melting point of polyethylene produced by the nickel complex decreased simultaneously. A likely explanation to account for it was that higher temperature favors the chain transfers and β -H elimination and resulted in low molecular weight and low melting point.

¹³C-NMR of the Polyethylenes

Analysis of the polymer microstructure by ¹³C-NMR spectroscopy (Fig. 2) indicated that the polyethylene had high degree of branching with a little methyl of the chain ends can be seen from ¹³C-NMR spectroscopy. Moreover, the side chains are all C4 according to the ¹³C-NMR. This could be explained by considering that chain isomerization occurs during the course of ethylene polymerization.

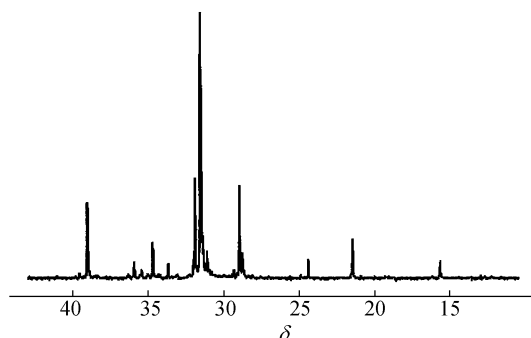


Fig. 2 The ¹³C-NMR of PE produced by the Ni complex [Al]/[Ni] = 500, *T* = 0°C

CONCLUSIONS

Dimeric cobalt(II) and nickel(II) complexes containing *N,N'*-(phenyl-2-pyridinylmethylene)-3,3',5,5'-tetramethylbenzidine were prepared and characterized. The nickel complex showed high catalytic activity towards ethylene polymerization for branched polyethylenes. The cobalt complex, however, showed no activity for ethylene polymerization.

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