Synthesis, Characterization, and Mechanism Studies of Bis(imino)pyridine Ligands and Their Cr(III) Compounds¹

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Abstract—Two new bis(imino)pyridine ligands L^1 , L^2 ($L^1 = 2,6$ -bis[1-(4-bromophenylimino)]pyridine, $L^2 = 2,6$ -bis[1-(4-methylphenylimino)]pyridine) have been prepared. Their compounds [CrCl₃L¹] (I) and [Cr(Cl)(μ -Cl)(L^2 ')]₂ (II) ($L^{2'} = 6$ -bis(6-methylquinoline)pyridine) for olefin oligomerization were obtained by hydrothermal methods, during which L^2 was appeared from L^2 , and characterized by elemental analysis, single-crystal X-ray analysis (CIF files CCDC nos. 1025448 (I),1025447 (II)), IR spectra and melting point test. Compound I is a mononuclear compound, while compound II, bridged with the chlorine atoms, is a binuclear compound. The transformation mechanism between L^2 and L^2 ' is also studied, and the possible reason is due to the presence of the electron-donating groups as substituents on L^2 . The subsequent studies on that will be carried on.

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INTRODUCTION

Recently, there has been considerable interest in the use of metal compounds for olefin oligomerization, which are important reactants used in the preparation of plasticizers, lubricants, detergents, oil field chemicals, and monomers for copolymerization. In the past decade, late transition metal compounds are the most attractive candidates toward ethylene activation both in academic and industrial research [1-5]. However, until the middle of 20th century, only few reports introduced these compounds as catalysts, which major due to β -hydrogen elimination occurring in competition with ethylene insertion and chain propagation of the polymer [6-8]. Based on the principle, which the use of bulky substituents on the aryl groups of the diimine ligands blocks associative olefin exchange, so retarding the chain transfer reactions and leading to high molecular weight polymers. Brookhart et al. and Gibson et al. reported a new class of iron and cobalt compounds bearing bis(imino)pyridine ligands [9-11].

As an important class of N-N ligands, pyridine-Schiff based imines have drawn increasing attention recently due to their flexible coordination behavior associated with steric and electronic properties. The presence of a pyridine N-donor could significantly affect the way a ligand compound to the central metal, which in turn would lead to dramatic changes in the reactivity and enantioselectivity of the catalytic reaction.

Steric effects and the electronic factor of ligands affect the catalytic behavior of ethylene poly- or oligomechanism, and characteristics of the polymer product. Furthermore the changing of substituents on the ligands only causes the transfer of iron catalyst from oligomerize ethylene to linear α -olefins with high activity [12–14]. Halogens are a family of interesting substituents, which mainly lead to the electronic effects. Compared to the small difference in electronic effect origination from changing the alkyl groups, the electronic effect from varying halogens is much more significant due to the large difference in their electrongativities. The halogens are generally electron-attracting, while the alkyls are electron-donating.

In this paper, we have synthesized two new 2,6bis(imino)pyridine ligands L^1 and L^2 , and their compounds, namely [CrCl₃L¹] (I) and [Cr(Cl)(μ -Cl)($L^{2'}$)]₂ (II) under hydrothermal conditions [15– 18]. The two new ligands and their compounds were well confirmed by elemental analysis, while the singlecrystal X-ray analysis was only applied to the compounds. In addition, the transformation mechanism between L^2 and $L^{2'}$ has been studied, which possibly due to the presence of the electron-donating groups as substituents.

¹ The article is published in the original.

EXPERIMENTAL

Materials and measurements. All manipulations of air- and/or moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques. Starting chemicals and solvents were of reagent grade and were used as received. Elemental analyses were performed by the VARIOEL III. ¹H and ¹²C NMR were recorded on INOVA-400 MHz spectrometers. The FT–IR spectra were obtained from KBr pellets on a Bruker Vectorm 22 spectrometer in the 400–4000 cm⁻¹ region.

Synthesis of the 2,6-pyridine-dimethylformate. A solution of 2,6-pyridinedicarboxylic acid (15.0 g), SOCl₂ and *N*,*N*-dimethylformamide was refluxed for 10 h, cooled and then added 100 mL absolute methanol carefully under stirring in ice baths. The reaction mixture was refluxed for 1 h and then diluted with methanol. The white crystal was collected, washed with cold methanol and dried in vacuum (the yield was 85.1%, m.p. = $41.0-42.5^{\circ}$ C).

Synthesis of the 2,6-bis(hydroxymethyl)pyridine. A solution of 2,6-pyridinedicarboxylic acid (3.30 g) in absolute ethyl alcohol (60 mL) was added NaBH₄ (4.01 g) dropwise under stirred in ice-salt baths. After 2 h, refluxed for 10 h following stirred at the room temperature for 3 h, the reaction mixture was evaporated under reduced pressure. Then, acetone was added (20 mL), and solution was refluxed and evaporated again. After cooling to room temperature, potassium carbonate solution (20 mL) and water were added, and the reaction mixture was extracted with CHCl₃. The collected organic layers were dried over NaSO₄, filtered and evaporated under reduced pressure to give a pale white acicular crystal (the yield was 1.20 g (51.1%); m.p. = 115.6–116.7°C).

Synthesis of the 2,6-bis(methanal)pyridine. The new-made MnO_2 (10 g) was added into the stirred solution of 2,6-bis(hydroxymethyl)pyridine (1.39 g) in CHCl₃ (90 mL). After cooling to room temperature, the reaction mixture was filtered, and MnO_2 was watered several times with CHCl₃. The combined organic layers were evaporated under reduced pressure to give a pale acicular crystals (the yield was 0.706 g (52.3%); m.p. = 114.0-115.1°C).

For C₇H₅NO₂

anal. calcd., %:	C, 62.22;	Н, 3.73;	N, 10.37.
Found, %:	C, 62.39;	Н, 3.19;	N, 10.61.

IR (v, cm⁻¹): 3085, 2865, 1720, 620. ¹H NMR (400 MHz; CDCl₃; δ , ppm): 10.22 (s., 2H), 8.49(d., J = 7.5 Hz, 2H), 8.22 (t., J = 7.7 Hz, 1H).

Synthesis of the L¹. An ethanol solution of 4-bromaniline (0.6397 g, 5.0 mmol) and glacial acetic acid was added to an ethanol solution of 2,6-bis(methanol)pyridine (0.3313 g, 2.5 mmol). The mixture solution was refluxed for 4 h. After cooling to room temperature, the precipitate was filtered and washed successively with *n*-hexane. The product was dried under vacuum, and obtained light yellow powder (the yield was 0.814 g (76.1%); m.p. = $203.7-204.4^{\circ}$ C).

For $C_{19}H_{13}N_3B_1$	r ₂		
anal. calcd., %:	C, 51.50;	Н, 2.96;	N, 9.48.
Found, %:	C, 50.37;	Н, 2.97;	N, 9.16.

IR (KBr; v, cm⁻¹): 1621 v(C=N). ¹H NMR (400 MHz; CDCl₃; δ , ppm): 8.28 (d., J = 7.7 Hz, 2H), 8.19 (t., J = 7.6 Hz, 1H), 7.75(s., 2H), 7.55(d., J = 8.4 Hz, 4H), 7.31 (d., 4H).

Synthesis of the L^2 was carried out by the same synthetic procedure as that for L^1 , except that *p*-toluidine was used instead of 4-bromaniline. A light yellow acicular crystal was obtained (the yield was 0.814 g (69.7%); m.p. = 178.8–179.3°C).

For C₂₁H₁₉N₃

anal. calcd., %:	C, 80.48;	Н, 6.11;	N, 13.41.
Found, %:	C, 79.62;	H, 6.09;	N, 13.34.

IR (KBr; v, cm⁻¹): 1620 v(C = N). ¹H NMR (400 MHz; CDCl₃; δ , ppm): 8.68 (d., J = 7.3 Hz, 2H), 8.28 (t., J = 7.6 Hz, 1H), 7.75 (s., 2H), 7.55 (d., J = 8.4 Hz, 8H), 6.96 (d., J = 7.4 Hz, 4H), 6.62 (d., J = 7.8 Hz, 4H), 2.42 (s., 6H).

Synthesis of compound I. $CrCl_3 \cdot 6H_2O(0.0139 \text{ g})$ was added to an ethanol solution, which contained L^1 (0.0226 g) and distilled water. Then mixture was put into a stainless-steel reactor with Teflon liner, heated to 180°C and kept at constant temperature for 72 h. Dark green crystals of compound I were obtained after cooling to room temperature.

For C ₁₉ H ₁₃ N ₃ C	l ₃ Br ₂ Cr		
anal. calcd., %:	C, 37.93;	H, 2.8;	N, 6.99.
Found, %:	C, 37.89;	Н, 2.357;	N, 6.768.

Synthesis of compound II was carried out by the same synthetic procedure as that for compound I, except that L^2 was used instead of L^1 . Reddish brown crystals of compound II were obtained.

For $C_{50}H_{38}N_6Cl_4Cr_2$ anal. calcd., %: C, 62.12; H, 3.95; N, 8.68. Found, %: C, 62.05; H, 3.876; N, 8.54.

X-ray crystallography. Single-crystal X-ray diffraction measurements were performed on Brucker Smart Apexccd diffractometer with a graphite-monochromated Mo K_{α} radiation at 296(2) K. Absorption corrections were applied to the date using SADABS program. The hydrogen atoms were assigned with com-

	Value		
Parameter	Ι	II	
M	601.49	966.07	
Description	Block	Block	
Color	Green	Brown	
Crystal size, mm	$0.20\times0.13\times0.09$	$0.30\times0.19\times0.09$	
Crystal system	Monoclinic	Triclinic	
Space group	$P2_1/n$	PĪ	
a, Å	13.722(3)	10.646(16)	
b, Å	18.905(2)	11.114(16)	
c, Å	9.3530(3)	12.160(18)	
α , deg	90	91.039(19)	
β, deg	124.702(12)	110.219(18)	
γ, deg	90	99.676(19)	
<i>V</i> , Å ³	2156.4(7)	1326(3)	
Ζ	4	2	
$ ho_{calcd}, g \ cm^{-3}$	1.853	1.456	
<i>F</i> (000)	1172	594	
θ Range, deg	2.18-25.94	1.79–25.10	
Number of data collected	11189	6515	
Number of unique data	4177	4625	
Number of parameters	254	317	
Goodness-of-fit on F^2	0.967	1.045	
R indices $(I > 2\sigma(I))$	$R_1 = 0.0466, wR_2 = 0.1147$	$R_1 = 0.1274, wR_2 = 0.3312$	
<i>R</i> indices (all data)	$R_1 = 0.1043, wR_2 = 0.1534$	$R_1 = 0.2310, wR_2 = 0.3960$	
$\Delta ho_{min} / \Delta ho_{max}$, $e \text{\AA}^{-3}$	-0.413/0.3614	-0.998/0.928	

Table 1. Crystallographic data and refinement parameters for complexes I and II

mon isotropic displacement factors and included in the final refinement by use of geometrical restrains, while the non-hydrogen atoms were treated with common anisotropic displacement factors and included in the final refinement with geometrical restrains. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELX-97 program. The details of the crystal parameters, data collections and refinements for compounds I and II are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 1025448 (I), 1025447 (II)); deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The structure of I is shown in Fig. 1a. The unit contains one Cr^{3+} ion, one L^1 ligand, and three Cl^- ions. The coordination geometry of the Cr³⁺ ion is a distorted octahedron, coordinated by three nitrogen atoms from L¹ and three Cl⁻ ions. The lengths of two bonds (Cr(1)-N(1) 2.170(5) Å and Cr(1)-N(3))2.105(5) Å) are slightly longer than that of Cr(1)–N(2) bond (1.997(4) Å). The bond lengths of N(1)-C(7)(1.283(7) Å) and N(3)–C(13) (1.277(7) Å) show the typical double bond properties, while the bond angles N(2)Cr(1)N(1), of N(2)Cr(1)N(3), and N(3)Cr(1)N(1) (77.86(11)°, 76.68(18)°, 153.84(18)°) indicate that the Cr³⁺ ion occupies at a serious distorted octahedral coordination environment.

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No. 2

Bond	$d, \mathrm{\AA}$	Bond	d, Å
		I	
Cr(1)–N(2)	1.997(4)	Cr(1)–N(3)	2.105(5)
Cr(1)–N(1)	2.170(5)	Cr(1)–Cl(1)	2.2959(17)
Cr(1)–Cl(2)	2.3025(19)	Cr(1)–Cl(3)	2.3042(19)
I		II	
$Cr(1) - Cl(1)^{\#1}$	2.303(3)	Cr(1)–Cl(1)	2.2960(17)
Cr(1)–N(2)	1.994(9)	Cr(1)–N(3)	2.130(9)
Cr(1)–N(1)	2.162(8)	Cr(1)–Cl(2)	2.296(4)
Angle	ω, deg	Angle	ω, deg
		I	
N(2)Cr(1)N(3)	76.68(18)	N(2)Cr(1)N(1)	77.86(11)
N(3)Cr(1)N(1)	153.84(18)	N(2)Cr(1)Cl(1)	174.56(14)
N(3)Cr(1)Cl(1)	97.97(13)	N(1)Cr(1)Cl(1)	108.18(14)
N(2)Cr(1)Cl(2)	87.19(14)	N(3)Cr(1)Cl(2)	87.05(14)
N(1)Cr(1)Cl(2)	91.55(14)	Cl(1)Cr(1)Cl(2)	91.60(7)
N(2)Cr(1)Cl(3)	87.83(14)	N(3)Cr(1)Cl(3)	89.83(14)
N(1)Cr(1)Cl(3)	89.31(14)	Cl(1)Cr(1)Cl(3)	93.18(7)
Cl(2)Cr(1)Cl(3)	174.62(7)		
I		II	
$Cl(1)^{#1}Cr(1)Cl(1)$	77.6(3)	$Cl(1)^{#1}Cr(1)N(2)$	165.2(3)
Cl(1)Cr(1)N(2)	87.6(3)	$Cl(1)^{#1}Cr(1)N(3)$	104.1(3)
Cl(1)Cr(1)N(3)	92.3(3)	N(2)Cr(1)N(3)	76.4(4)
$Cl(1)^{#1}Cr(1)N(1)$	102.3(3)	Cl(1)Cr(1)N(1)	93.1(3)
N(2)Cr(1)N(1)	77.9(3)	N(3)Cr(1)N(1)	153.5(4)
$Cl(1)^{#1}Cr(1)Cl(2)$	96.8(2)	Cl(1)Cr(1)Cl(2)	174.4(2)
N(2)Cr(1)Cl(2)	98.0(3)	N(3)Cr(1)Cl(2)	88.2(3)
N(1)Cr(1)Cl(2)	89.0(3)		

 Table 2. Selected bond distances (Å) and angles (deg) for complexes I and II*

* Symmetry codes: ${}^{\#1}-x+1, -y+1, -z; {}^{\#2}-x+1, -y+2, -z+1$ (II).

X-ray diffraction analysis reveals that the basic centrosymmetric unit of compound **II** contains two Cr^{3+} ions, which have the same coordinated environment and bridged with the chlorine atoms. The molecular structure **II** is shown in Fig. 1b. The new C–C bonds have formed under the oxidative coupling of ethanol and L² in hydrothermal method, which is 2,6-bis(6methylquinolin-2-yl)pyridine. In compound **II**, each Cr^{3+} ion is coordinated by three nitrogen atoms, one of which from pyridine and two from quinolines, and three Cl⁻ ions. Two Cr³⁺ ions are bridged by two Cl⁻ ions. The equatorial sites are occupied by three nitrogen atoms (N(1), N(2), N(3)) and one Cl⁻ ion (Cl(1*A*)), while the axial sites are formed by two Cl⁻ ions (Cl(1), Cl(2)).

The new C–C bonds have formed under the oxidative coupling of ethanol and L^2 in hydrothermal method, which is different from L^1 , this may due to the electron withdrawing of bromine atoms on the phenyl groups [19–21]. The possible reaction mechanism of synthesis of 2,6-bis(6-methylquinolin-2-yl)pyridine are below:



Losing one water molecule, the methylene carbon cations have been formed under the acidic condition, attacked to the phenyl rings, and the intermediate 1 was obtained, which cannot react in L^1 . And then attack to the C=N bonds, the 2,6-bis(6-methylquino-lin-2-yl)pyridine has been produced followed by los-



(b)



Fig. 1. Coordination environment of compounds I (a) and II (b).

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ing two water molecules. The bromine atoms have more withdrawing electron ability than methyl groups, so that there are no more electrons on the phenyl groups to attack to the methylene carbon cations, which is different from the methyl groups as substituents on the L^1 . Therefore, the intermediate 1 will not been formed and nor as to the 2,6-bis(6-methylquinolin-2-yl)pyridine under the presence of the methyl groups.

In summary, two new late metal compounds for olefin oligomerization have been synthesized by using the bis(imino)pyridine ligands. These results show that compound I is a mononuclear compound, in which the Cr^{3+} ion is six-coordinated with distorted octahedral coordination geometry. Meanwhile, in compound II, the Cr^{3+} ions are bridged by two Cl^{-} ions to form a binuclear compound. The diverse structures between L^2 and L^2 may be caused by the electron withdrawing of bromine atoms on the phenyl groups in L^2 . And the subsequent studies will be focused on the influence of the halogen atoms as substituents on the ligands.

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REFERENCES

- 1. Ziegler, K., Holzkamp, E., Martin, H., et al., *Angew. Chem. Int. Ed.*, 1955, vol. 7, p. 541.
- 2. Natta, G., Angew. Chem., 1956, vol. 68, no. 12, p. 393.
- Breslow, D.S. and Newburg, N.R., J. Am. Chem. Soc., 1957, vol. 79, p. 5072.

- 4. Natta, G., Pino, P., Mazzanti, G., et al., *J. Am. Chem. Soc.*, 1957, vol. 79, no. 11, p. 2975.
- Kaminsky, W., Miri, M., Sinn, H., et al., *Chem. Rapid. Commun.*, 1983, vol. 4, no. 6, p. 417.
- Johnson, L.K., Mecking, S., Brookhart, M., et al., J. Am. Chem. Soc., 1996, vol. 118, no. 1, p. 267.
- Ittel, S.D., Johnson, L.K., Brookhart, M., et al., *Chem. Rev.*, 2000, vol. 100, no. 4, p. 1169.
- Johnson, L.K., Killian, C.M., Brookhart, M., et al., J. Am. Chem. Soc., 1995, vol. 117, p. 6414.
- 9. Britovsek, G.J.P., Gibson, V.C., Spitzmesser, S.K., et al., *Dalton Trans.*, 2002, p. 1159.
- Britovsek, G.J.P., Gibson, V.C., Kimberley, B.S., et al., *Dalton Trans.*, 2001, vol. 10, p. 1639.
- 11. Bianchini, C., Mantovani, G., Meli, A., et al., *Organometallics*, 2003, vol. 22, no. 13, p. 545.
- 12. Sun, W.H., Zhang, S., and Zuo, W.W., C. R. Chimie, 2007, p. 1.
- 13. Bianchini, C., Giambastiani, G., Rios, G.I., et al., *Coord. Chem. Rev.*, 2006, vol. 250, nos. 11–12, p. 1391.
- 14. Gibson, V.C., Redshaw, C., and Solan, G.A., *Chem. Rev.*, 2007, vol. 107, no. 5, p. 1745.
- 15. Osman, D., Dogan, F., Ismet, K., et al., *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.*, 2010, vol. 40, no. 5, p. 337.
- 16. Dotterl, M., Schmidt, R., Englmann, T., et al., WO Patent 2011003044, 2011.
- 17. Legrand, Y.M., Dumitru, F., Lee, A.V.D., et al., *Supramol. Chem.*, 2009, vol. 21, nos. 3–4, p. 230.
- 18. Barboiu, M., Dumitru, F., Legrand, Y.M., et al., *Chem. Commun.*, 2009, no. 16, p. 2192.
- 19. Liu, C.M., Gao, S., and Kou, H.Z., *Chem. Commun.*, 2001, p. 1636.
- 20. Evans, O.R. and Lin, W.B., Cryst. Growth Des., 2001, vol. 1, p. 9.
- 21. Hu, H.W., Organic Chemistry, Beijing: Higher Education, 1989.