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# Iron/Cobalt Binuclear Complexes and their Application as Oligomerization Catalysts

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## Abstract

Synthesis of tetrakis-bisimino pyridine ligand based Fe/Co complexes and their application towards ethylene oligomerization with the cocatalysts, ethyl aluminium sesquichloride and methylaluminumoxane cocatalysts, are described. Fe complex showed better activity than its Co analogue to form oligomers C<sub>6</sub> and C<sub>4</sub> as major products respectively. Cooperative mechanism of the two adjacent metal centers during the reaction was also studied.

## Introduction

Advancement of postmetallocene catalysts for polymerization and oligomerization of olefins has generated special interest in industrial and academic sectors from decades [1-3]. Studies on late transition metal complexes incorporating bis(imino)pyridyl and  $\alpha$ -diimine ligands, in particular the investigation of highly active catalysts containing the metals like Pd, Ni, Co and Fe, that convert both ethylene and  $\alpha$ -olefins to tailor made polymers, have been reported [4,5]. The preference of post metallocene complexes over other single site polymerization complexes lies in their ease of synthesis, promising catalytic activities and handling along with the utilization of low cost metals under negligible environmental impact [1]. In addition, their less oxophilicity and the tolerance towards the functional groups opened a door to co-polymerization of ethylene with polar monomers [1]. Oligomerization of ethylene using such organometallic complexes to provide  $\alpha$ -olefins in highly desirable range, C<sub>4</sub>-C<sub>20</sub>, for their use in the synthesis of LLDPE (linear low density polyethylene), fine chemicals and in detergent preparation, plasticizers etc, made this research area much attractive. The presence of arylimino groups in the bis(imino)pyridyl backbone is not a mandatory condition to generate a ligand capable of oligomerizing ethylene to  $\alpha$ -olefins in combination with various types of cocatalysts [6]. The substituents on the arylimino moiety is crucial to determine the product which can be varied from oligomer to polymer, in which small aryl substituents result in the formation of low molecular weight oligomers. According to the previous reports complexes with two metals showed interesting polymerization behaviors that are different from their mononuclear analogues due to the cooperative interactions between the two active centers [7]. It is our special interest to study such cooperative effect of late transition metals during oligomerization reaction and hence we synthesized binuclear iron and cobalt methyl substituted bipyridylimino derivatives for the present study. Oligomerization studies were performed with ethyl aluminium sesquichloride (EAS), and methylaluminumoxane (MAO) cocatalysts.

## Experimental

### Materials

Synthesis of ligands and complexes were carried out under inert atmosphere using Schlenk lines. Purification of solvents and ethylene were done according to reported procedures. The reagents used in present work were used as received.

### Characterization

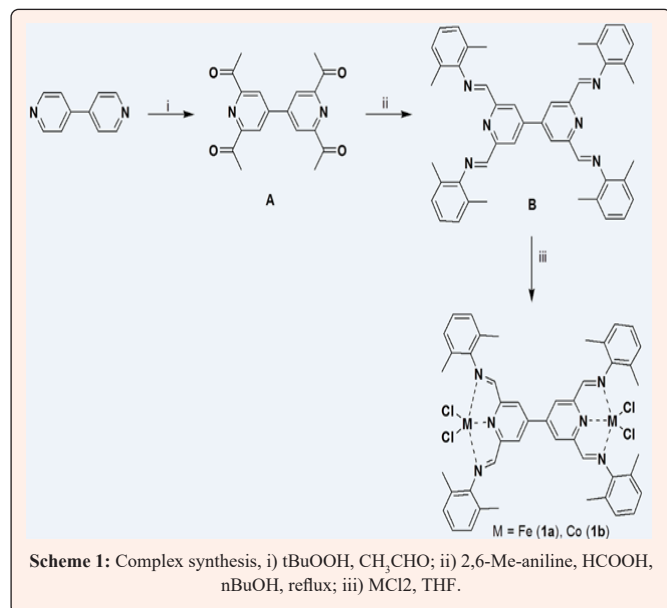
<sup>1</sup>H and <sup>13</sup>C NMR of the synthesized ligands were recorded on a Bruker AV500 spectrometer (500 MHz and 125 MHz for <sup>1</sup>H and <sup>13</sup>C respectively) at room temperature, indicating chemical shifts in ppm ( $\delta$  7.24 for <sup>1</sup>H with CHCl<sub>3</sub> and  $\delta$  77 for <sup>13</sup>C with CDCl<sub>3</sub>). Elemental analyses were carried out using an EAI CE-440 CHN/O/S Elemental Analyzer. Mass spectra of the complexes were recorded on JEOL-JMS-AX505WA, HP 5890 Series spectrometer using positive FAB (fast atom bombardment) methods. SHIMADZU GC-2025AF gas chromatograph (Shimadzu Co. Ltd.) containing a flame ionization detector was used for GC analysis.

### Oligomerization Reaction

A 500 mL flask was used to perform ethylene oligomerization reaction with a magnetic stirrer and digital thermometer. Prescribed amount of the catalyst was added to the reactor followed by 80 mL of toluene at constant temperature bath and ethylene was introduced in to the reactor. Required amount of cocatalyst was added when the system was saturated with ethylene to start the oligomerization. Reaction rate was monitored at every 0.01 s. At a desired oligomerization time the reaction was quenched using methanol and HCl. It was then filtered to collect the polymer if any and washed with excess methanol. The filtrate was analyzed by GC methods to find the oligomer distribution.

### Synthesis of 2,6,2',6'-(2,6-Dimethylphenyl) ethylideneamine[4,4']bipyridinyl (B):

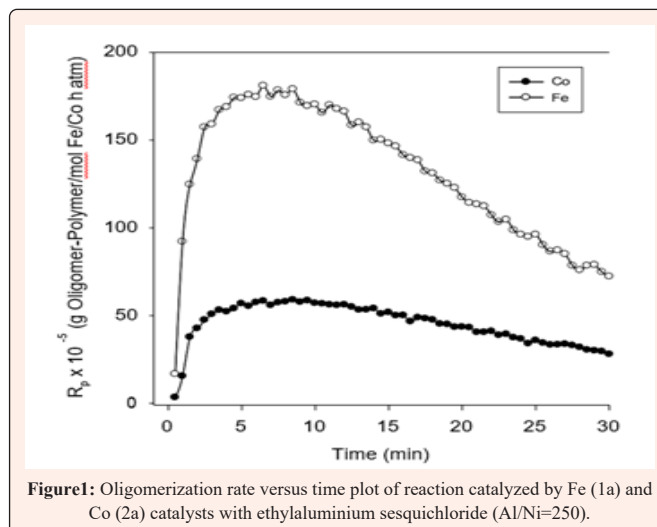
Tetraacetyl bipyridyl derivative, A (Scheme 1) was synthesized according to the reported procedure [8]. A suspension of compound A in nBuOH was treated with 2,6-dimethylaniline and a few drops of formic acid as catalyst. It was then refluxed for 1 day. Then the reaction mixture was cooled to get a light yellow crystalline solid. It was then washed with cold methanol to obtain B in 90 % yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.31 (s, 24H, CH<sub>3</sub>Ar), 2.35 (s, 12H, N=CCH<sub>3</sub>), 6.91 (t, 4H, H<sub>arom</sub>), 7.05 (d, 8H, H<sub>arom</sub>), 7.11 (s, 4H, H<sub>arom</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  17.21, 17.79, 121.55, 124.12, 127.8, 128.05, 148.93, 149.52, 161.20, 165.34. Anal. Calcd for C<sub>30</sub>H<sub>32</sub>N<sub>6</sub>: C, 81.49; H, 7.11; N, 11.40. Found: C, 81.47; H, 7.10; N, 11.39.



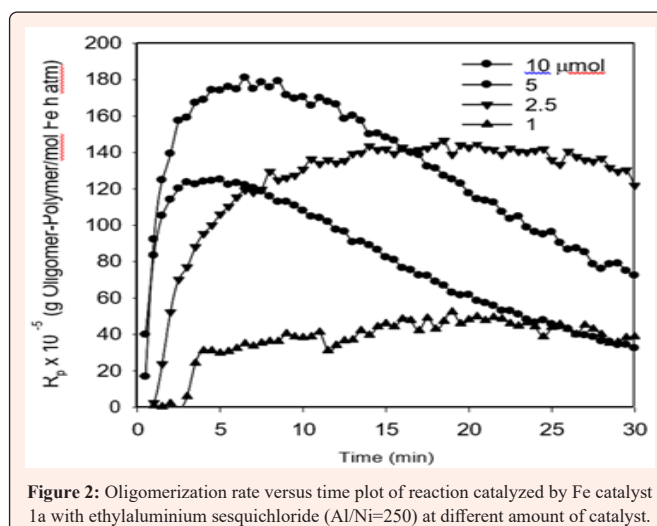
- Synthesis of Fe (1a) catalyst:** A mixture of FeCl<sub>2</sub> (0.1 mmol batch) and ligand B in THF was stirred 12 h at room temperature (RT). The greenish colored solid obtained was filtered, washed (ether) and dried to get 1a in 85% yield. Anal. Calcd for C<sub>50</sub>H<sub>32</sub>C<sub>14</sub>Co<sub>2</sub>N<sub>6</sub>: C, 60.63; H, 5.29; N, 8.48. Found: C, 60.62; H, 5.30; N, 8.49.
- Synthesis of Co catalyst (2a):** A mixture of CoCl<sub>2</sub> (0.1 mmol batch) and ligand B in THF was stirred 12 h at RT. The brown solid obtained was filtered, washed (ether) and dried to get 2a in 86% yield. Anal. Calcd for C<sub>50</sub>H<sub>32</sub>C<sub>14</sub>Co<sub>2</sub>N<sub>6</sub>: C, 60.25; H, 5.26; N, 8.43. Found: C, 60.25; H, 5.28; N, 8.42.

## Results and Discussion

Bipyridine based ligand was prepared by the condensation of tetraacetyl bipyrindyl derivative with 2,6-dimethyl aniline according to the reported procedure [8]. (Figure 1) indicates the oligomerization rate (rate vs time curves) for Fe and Co complexes with the cocatalyst (EAS) and the ethylene oligomerization results are given in (Table 1). Fe complex 1a showed better catalytic activity than its cobalt congener 2a. From the (Table 1), it is clear that the activity of the catalyst 1a is 12.57x10<sup>6</sup> (g-oligomer/mol-Fe-h-bar, Table 1, entry 2) and for 2a is 3.37x10<sup>6</sup> (g-oligomer/mol-Co-h-bar, Table 1, entry 7). Bianchini & co-workers reported the isopropyl analogue of 1a and 2a in which both Fe and Co catalysts showed almost similar catalytic activity with MAO cocatalyst [8]. In the present study with methyl substituted complexes, Fe complex showed better activity than Co complex towards ethylene oligomerization in combination with EAS or MAO. These results are in agreement with the most studied monometallic bisiminopyridyl Fe and Co complexes [6]. Cocatalyst has an important role during polymerization or oligomerization to initiate the reaction. It shall be noted that for conventional Ziegler-Natta catalysts the cocatalyst with halogens itself can act as a poison to the catalyst [9]. Even the quantity of alkyl aluminum affected the molecular weight and molecular weight distribution and their complete mechanism still remains as a “black box” [10]. MAO is the commonly used cocatalyst both in research and industrial sectors. In the present work we preferred one of the less expensive cocatalysts, EAS, and found that this is better than MAO as it is clear from the (Table 1). These results are in agreement with the previous reports in which small amount of cocatalyst was consumed for a polymerization reaction when EAS was used [11]. For eg. 250 to 300 equivalents of EAS was enough to activate the metal complex during polymerization while 500 to 1000 or more equivalents of MAO have been used [11]. We used 250 equivalents of EAS for each oligomerization reaction while catalyst amount was varied from 1 mmol to 10 mmol as shown in (Table 1). (Figure 2) shows the oligomerization rate curves for various amount of catalyst 1a in combination with EAS. It is clear from the figure that the initial activity is highest when 10 mmol of catalyst 1a was used. After 10 minutes of reaction, the activity decelerated steeply and the same phenomena was observed with 5 mmol of 1a as shown in (Figure 2). With 2.5 mmol of 1a the activity sustained without considerable decrease for long time and hence we chose 2.5 mmol of catalyst for all other reactions.



**Figure 1:** Oligomerization rate versus time plot of reaction catalyzed by Fe (1a) and Co (2a) catalysts with ethylaluminum sesquichloride (Al/Ni=250).



**Figure 2:** Oligomerization rate versus time plot of reaction catalyzed by Fe catalyst 1a with ethylaluminum sesquichloride (Al/Ni=250) at different amount of catalyst.

**Table 1:** Ethylene Oligomerization Results. aConditions: toluene 80 mL, PC2H4=1 bar, and time=30 min; bEAS=ethylaluminiumsesquichloride, MAO=methylaluminioxane; cAverage rate of propagation as g-product/mol-M-h-bar; dDetermined by GC.

Run	Catalyst Used	Al/Ni <sup>b</sup>	T <sub>p</sub> (°C)	R <sub>p</sub> × 10 <sup>-5</sup>	α-Olefins Distribution (%) <sup>d</sup>		
					C <sub>4</sub>	C <sub>6</sub>	C <sub>10-20</sub>
1	1a(1 mmol)	250/EAS	30	36.3	35.2	62.6	2.2
2	1a(2.5 mmol)	250/EAS	30	125.7	36.1	61.2	2.7
3	1a(5 mmol)	250/EAS	30	126.5	36.7	60.8	2.5
4	1a(10 mmol)	250/EAS	30	79.4	37.4	60.5	2.1
5	1a(2.5 mmol)	250/EAS	50	102.4	34.6	58.4	7.0
6	1a(2.5 mmol)	500/MAO	30	84.2	34.1	65.4	0.5
7	2a(2.5 mmol)	250/EAS	30	33.7	56.3	42.7	1.0
8	2a(5 mmol)	250/EAS	30	22.3	55.7	42.5	1.8
9	2a(2.5 mmol)	500/MAO	30	11.3	53.2	41.8	5.0



From the GC analysis it was found that the binuclear Fe and Co catalysts generated  $C_4$  and  $C_6$  as major products. Complex 1a showed a slight selectivity towards  $C_6$  and 2a favored  $C_4$  under all experimental conditions. In addition a small amount of polymer was obtained along with oligomers in the form of wax, indicating the presence of low molecular weight polymers. Generally complexes with bulky substituents at ortho position of aryl ring produced high molecular weight polymers because they will provide an effective steric hindrance in the axial sites to block  $\beta$ -hydrogen elimination [1]. Lack of such steric bulk on catalysts will lead to the formation of oligomers when they interact with alkyl aluminums. The molecular weight of PE obtained from 1a and 2a was 2500 and 1800 with a broad molecular weight distribution of 5.2 and 6.1 respectively. Compared to the previous reports the molecular weight of the polymer obtained with 1a is higher than monometallic system ( $M_w=2500$  versus 540), but lower than pyridyl imino binuclear catalysts [12]. This phenomenon is due to the cooperative effect of the two active metal centers which can be explained by a special mechanism in which propagative species produced from one metal is consumed immediately by the nearby metal centre [7]. Such propagative species obtained by both normal and cooperative insertion modes is responsible for the broad molecular weight distribution. Polyethylene obtained by this cooperative mechanism of catalyst 1a resulted a  $T_m$  of 131 °C, indicates a linear polymer as expected from a Fe catalyst [6].

## Conclusion

New methyl substituted binuclear Fe and Co complexes were synthesized and characterized well. These complexes were screened for ethylene oligomerization studies in which both complexes showed good catalytic activity in combination with EAS and MAO cocatalysts. EAS was found to be the suitable cocatalyst under all experimental conditions. Both Fe and Co catalysts favored  $C_6$  and  $C_4$  as the major products. Molecular weight of the resulting polyethylene was higher than polymer obtained by the corresponding monometallic analogue due to the cooperative effect.

## References

1. Reinhart ED, Jordan RF (2020) Synthesis and ethylene reactivity of dinuclear iron and cobalt complexes supported by macrocyclic bis(pyridine-diimine) ligands containing o-terphenyl linkers. *Organometallics* 39: 2392-2404.
2. Gibson VC, Spitzmesser SK (2003) Advances in non-metallocene olefin polymerization catalysis. *Chem Rev* 103: 283-316.
3. Semikolenova NV, Sun WH, Soshnikov IE, Matsko MA, Kolesova OV, et al. (2017) Origin of "multisite-like" ethylene polymerization behavior of the single-site nonsymmetrical bis(imino)pyridine iron(II) complex in the presence of modified methylaluminumoxane. *ACS Catal* 7: 2868-2877.
4. Johnson K, Killian CM, Brookhart M (1995) New Pd(II)- and Ni(II)-based catalysts for polymerization of ethylene and  $\alpha$ -olefins. *J Am Chem Soc* 117: 6414-6415.
5. Britovsek GJP, Baugh SPD, Hoarau O, Gibson VC, Wass DF, et al. (2003) *Inorg Chem Acta* 345: 279.
6. Britovsek GJP, Bruce MI, Gibson VC, Kimberley BS, Maddox PJ, et al. (1999) *J Am Chem Soc* 121: 8728.
7. Bahuleyan BK, Lee U, Ha CS, Kim I (2008) *Appl Cat A: Gen* 36: 351.
8. Barbaro P, Bianchini C, Giambastiani G, Rios IG, Meli A, Oberhauser W, Segarra AM, Sorace L, Toti A, (2007) *Organometallics* 26: 4639.
9. Caunt AD (1964) *J Polym Sci C* 4: 49.
10. Chen EYX, Marks TJ (2000) Cocatalysts for metal-catalyzed olefin polymerization: activators, activation processes, and structure-activity relationships. *Chem Rev* 100: 1391-1434.
11. Bahuleyan BK, Son GW, Park DW, Ha CS, Kim I (2008) *J Polym Sci Part A: Polym Chem* 46: 1066.
12. Britovsek GJP, Baugh SPD, Hoarau O, Gibson VC, Wass DF, White AJP, Williams DJ (2003) *Inorg Chem Acta* 345: 279.