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RESEARCH ARTICLE

Homonuclear Bimetallic Fe(II) or Co(II) Complexes for Selective Oligomerization Process

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ABSTRACT

Synthesis of tetrakis-bisimino pyridine ligand based Fe or Co complexes [($^{Me}Ar_2Py\text{-}N_2$)$_2M_2Cl_4$, M = Fe/Co, Ar = -C_6H_3, Py = -C_5H_2N] and their application towards ethylene oligomerization with the cocatalysts, ethyl aluminium sesquichloride and methylaluminoxane, were studied. Ligands were characterized by ^1H, ^{13}C NMR and elemental analysis. The complexes were characterized by elemental analysis and mass spectra. Both the complexes were active towards ethylene oligomerization. Fe complex showed better activity than its Co analogue to form oligomers C_6 (Fe complex) and C_4 (Co complex) as major products. Cooperative mechanism of the two adjacent metal centers during the reaction was observed. Cooperative mechanism enhanced the oligomerization activity.

Keywords: Bimetallic complexes, Ethylene oligomerization, Fe and Co complexes, Late transition metal complexes, Cooperative effect

1. Introduction

Advancement of late transition metal 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(imono)pyridyl and α-diimine ligands, in particular the investigation of highly active catalysts containing the metals like Pd, Ni, Co and Fe, that convert both ethylene and α-olefins to tailor made polymers, have been reported [4–8]. The preference of late transition metal 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 [9, 10]. In addition, their less oxophilicity and the tolerance towards the functional groups opened a door to co-polymerization of ethylene with polar monomers [11]. Oligomerization of ethylene using such organometallic complexes to provide α-olefins in highly desirable range, C_4-C_{20}, for their use in the synthesis of LLDP (linear low density polyethylene), fine chemicals and in detergent preparation, plasticizers etc, made this research area much attractive [12].

The choice of aryl-imino groups in the bis-iminopyridyl backbone cannot be considered as compulsory condition to create a ligand capable of oligomerizing ethylene to α-olefins in combination with various types of cocatalysts [13]. The substituents on the aryl-imino moiety is crucial to determine the product which can be varied from oligomer to polymer, in which tiny substituents like H, CH_3 on the aryl ring lead to the formation of oligomers having low molecular weight and bulky substituents favor high molecular weight polymers [8, 9]. According to the previous reports complexes with two or more metals showed interesting polymerization behaviors that are different from their mononuclear analogues and this may be because of the interaction between the two adjacent active centers known as ‘cooperative effect’ [14–17]. In the binuclear Ni (II) complexes, authors compared the properties

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of the product obtained by ethylene oligomerization process with the monometallic analogue and found an enhancement in the catalytic activity as well as molecular weight of the oligomers [16]. As a continuation, author was interested to the study such cooperative or multinuclearity effect of various metal catalyzed polymerization or oligomerization system. Therefore, binuclear iron and cobalt methyl substituted bipyridyl-imino derivatives were synthesized for the present study. Oligomerization studies were performed with ethyl aluminium sesquichloride (EAS), and methylaluminoxane (MAO) cocatalysts.

2. Experimental

2.1. Materials

Synthesis of ligands and corresponding organometallic Fe, Co complexes were performed under nitrogen atmosphere with Schlenk lines. Ethylene used for polymerization was purified by passing it through columns of Fisher RIDOXTM catalyst and molecular sieve 5 Å/13X. Purification of solvents were done according to reported procedures and stored over molecular sieves (4A) [18]. The reagents used in present work were purchased from Aldrich and used as received.

2.2. Characterization

^{1}H and ^{13}C NMR of the synthesized ligands were recorded on a Bruker AV500 spectrometer (500 MHz and 125 MHz for ^{1}H and ^{13}C respectively) at room temperature, indicating chemical shifts in ppm (δ 7.24 for ^{1}H with $CDCl_3$ and δ 77 for ^{13}C with $CDCl_3$). 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.

2.3. 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 by an automated experimental setup. 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.

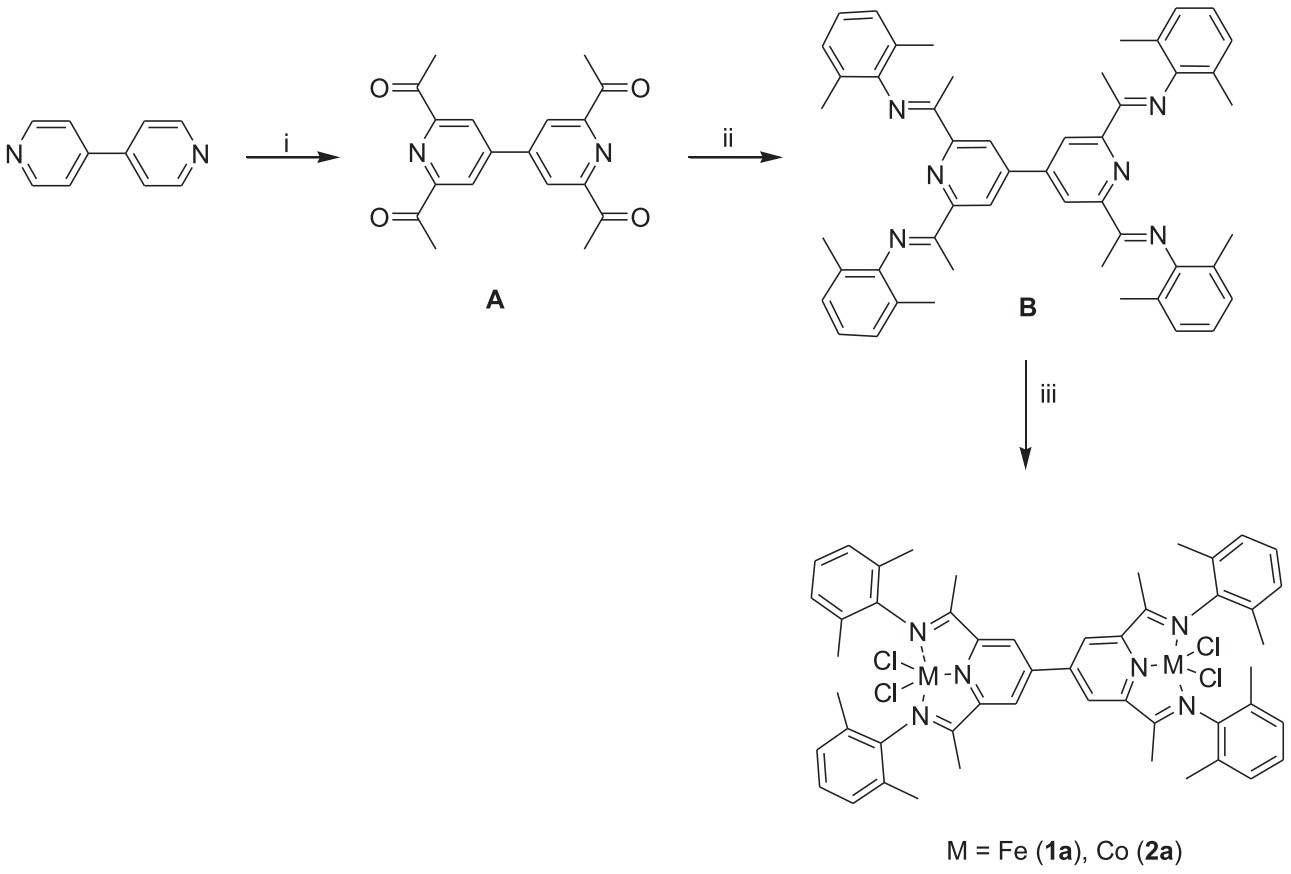
*Synthesis of 2,6,2′,6′-(2,6–dimethylphenyl) ethylideneamine[4,4′]bipyridinyl(**B**)*: Tetraacetyl bipyridyl derivative, **A** (Scheme 1) was synthesized according to the reported procedure [19]. A suspension of compound **A** in *n*BuOH was treated with 2,6-dimethylaniline and a few drops of formic 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. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 24H, CH_3^{Ar}), 2.35 (s, 12H, N=CCH_3), 6.91 (t, 4H, H_{arom}), 7.05 (d, 8H, H_{arom}), 7.11(s, 4H, H_{arom}). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 17.21, 17.79, 121.55, 124.12, 127.8, 128.05, 148.93, 149.52, 161.20, 165.34. Anal. Calcd for $C_{50}H_{52}N_6$: 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 $FeCl_2$ (0.1 mmol batch) and ligand **B** in THF was stirred 12 h at room temperature (RT). Metal to ligand ratio was 2:1. The greenish colored solid obtained was filtered, washed (ether) and dried to get **1a** in 85% yield. MS (FAB+): m/z = 988. Anal. Calcd for $C_{50}H_{52}Cl_4Fe_2N_6$: 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 $CoCl_2$ (0.1 mmol batch) and ligand **B** in THF was stirred 12 h at RT. Metal to ligand ratio was 2:1. The brown solid obtained was filtered, washed (ether) and dried to get **2a** in 86% yield. MS (FAB+): m/z = 994. Anal. Calcd for $C_{50}H_{52}Cl_4Co_2N_6$: C, 60.25; H, 5.26; N, 8.43. Found: C, 60.25; H, 5.28; N, 8.42.

3. Results and discussion

Bipyridine based ligand was prepared by the condensation of tetraacetyl bipyridyl derivative with 2,6-dimethyl aniline according to the reported procedure [19]. Fig. 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 Table 1, it is clear that the activity of the catalyst **1a** is 12.57 × 10^6 (g-oligomer/mol-Fe-h-bar, Table 1, entry 2) and for **2a** is 3.37 × 10^6 (g-oligomer/mol-Co-h-bar, Table 1, entry 7).



Scheme 1. Complex synthesis, i) *t*BuOOH, CH_3CHO; ii) 2,6-Me-aniline, HCOOH, *n*BuOH, reflux; iii) MCl_2, THF.

Table 1. Ethylene Oligomerization Results.[a]

Run	Catalyst used	Al/M[b]	T_p (°C)	R_p[c] × 10^{-5}	Oligomer distribution (%)[d]		
					C_4	C_6	C_{10-20}
1	**1a**(1 μmol)	250/EAS	30	36.3	35.2	62.6	2.2
2	**1a**(2.5 μmol)	250/EAS	30	125.7	36.1	61.2	2.7
3	**1a**(5 μmol)	250/EAS	30	126.5	36.7	60.8	2.5
4	**1a**(10 μmol)	250/EAS	30	79.4	37.4	60.5	2.1
5	**1a**(2.5 μmol)	250/EAS	50	102.4	34.6	58.4	7.0
6	**1a**(2.5 μmol)	500/MAO	30	84.2	34.1	65.4	0.5
7	**2a**(2.5 μmol)	250/EAS	30	33.7	56.3	42.7	1.0
8	**2a**(5 μmol)	250/EAS	30	22.3	55.7	42.5	1.8
9	**2a**(2.5 μmol)	500/MAO	30	11.3	53.2	41.8	5.0

[a]Conditions: toluene 80 mL, PC_2H_4 = 1 bar, and time = 30 min; [b]EAS = ethylaluminiumsesquichloride, MAO = methylaluminoxane; [c]Average rate of propagation as g-product/mol-M-h-bar; [d]Determined by GC.

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 [19, 20]. 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 [21]. Gibson and coworkers have reported that Fe complexes undergo different chain transfer mechanisms during the oligomerization reaction than compared to similar Co complexes [21].

Cocatalyst has an important role during polymerization or oligomerization to initiate the reaction. It should be noted that for conventional Ziegler-Natta catalysts the cocatalyst with halogens itself can act as a poison to the catalyst [22]. Even the quantity of alkyl aluminum affected the molecular weight and molecular weight distribution and their complete mechanism still remains as a "black box" [23]. MAO is the commonly used cocatalyst both in research and

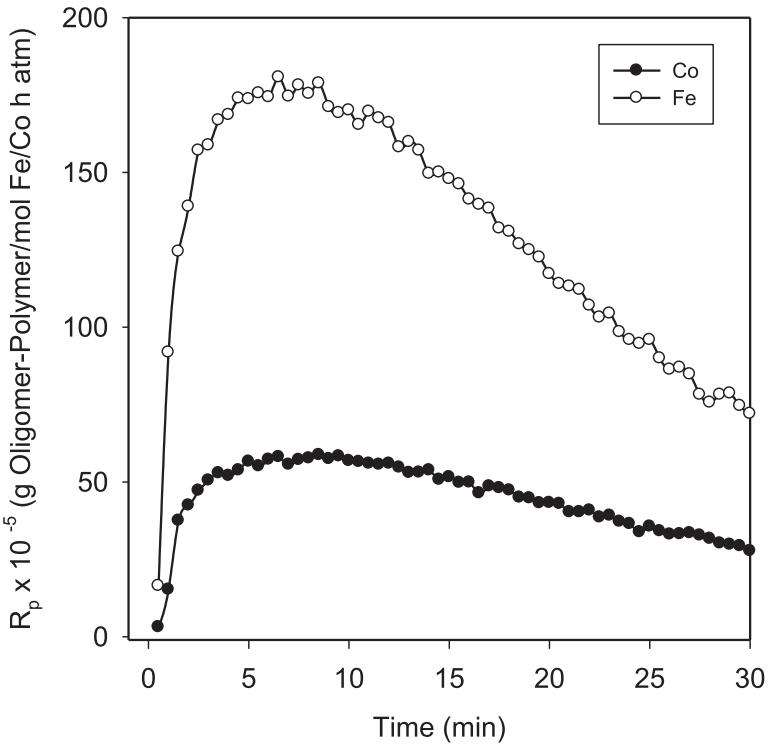


Fig. 1. Oligomerization rate versus time plot of reaction catalyzed by Fe (**1a)** and Co (**2a)** catalysts with ethylaluminium sesquichloride (Al/M = 250).

industrial sectors. In the present work, one of the less expensive cocatalysts, EAS, was preferred 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 a small amount of cocatalyst was consumed for a polymerization reaction when EAS was used [7, 16] For example 250 to 300 equivalents of EAS were enough to activate the metal complex during polymerization while 500 to 1000 or more equivalents of MAO have been used [7].

250 equivalents of EAS were used for each oligomerization reaction while catalyst amount was varied from 1 μmol to 10 μmol as shown in Table 1. Fig. 2 shows the oligomerization rate curves for various amounts of catalyst **1a** in combination with EAS. It is clear from the figure that the initial activity is highest when 5 μmol of catalyst **1a** was used. After 10 minutes of reaction, the activity decelerated steeply and the same phenomena was observed with 10 μmol of **1a** as shown in Fig. 2. With 2.5 μmol of **1a** the activity sustained without a considerable decrease for a long time and hence 2.5 micromol of catalyst was chosen for all other reactions.

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 the ortho position of the aryl ring produced high molecular weight polymers because they will provide an effective steric hindrance in the axial sites to block β-hydrogen elimination [9]. 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 low molecular weight oligomers) [24]. This phenomenon is due to the cooperative effect of the two active adjacent metal centers in a complex which can be explained by a special mechanism in which propagative species produced from one metal is consumed immediately by the nearby metal centre [17, 25]. The distance between the two adjacent metal centers is crucial to observe the cooperative interactions. Such propagative species obtained by both normal and cooperative insertion modes is responsible for the broad molecular weight distribution [26]. Similar examples were reported among Ni and Pd complexes with various monomers [16, 27]. For the binuclear Pd complexes,

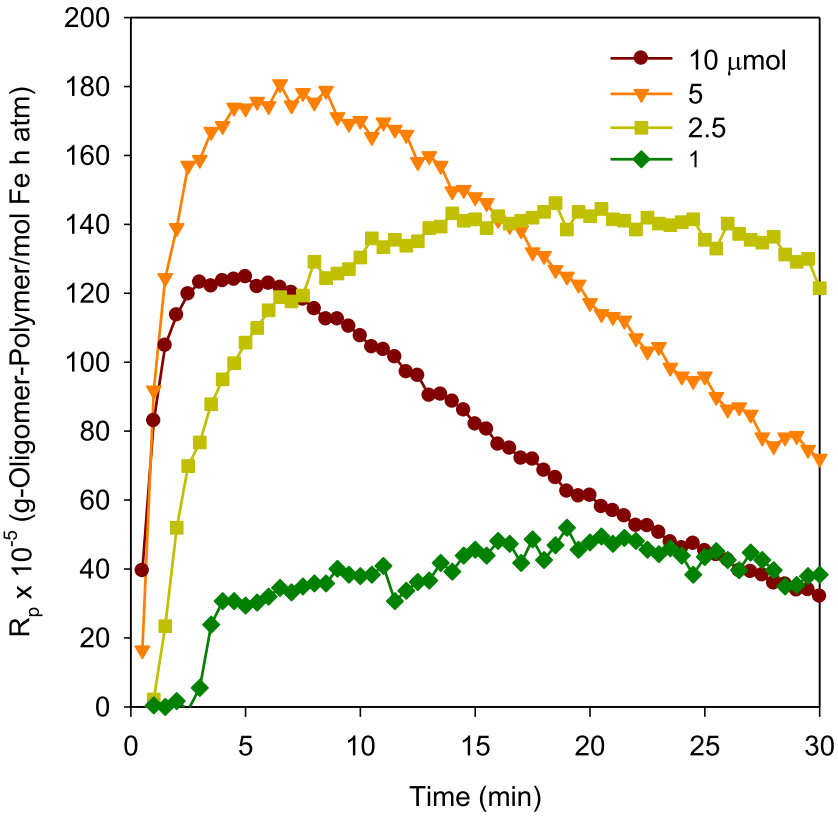


Fig. 2. Oligomerization rate versus time plot of reaction catalyzed by Fe catalyst **1a** with ethylaluminium sesquichloride (Al/Fe = 250) at different amounts of catalyst.

a mechanism based on agostic interactions by the propagative species of methyl methacrylate monomer between two metal centers was picturized along with the enhancement in the polymer properties [27]. Another trinuclear Fe/Ni complexes were reported, in which an increase in the number of adjacent metal centers in the catalyst enhanced the obtained polyethylene properties [28]. Similar trends were observed in the current study with Fe and Co metals. Polyethylene obtained by this cooperative mechanism of catalyst **1a** resulted a T_m of 131 °C, indicates a linear polymer as expected from the Fe catalyst [21].

4. Conclusion

New methyl substituted tetrakis-bisimino pyridine ligand based Fe and Co complexes were synthesized. Characterization of the complexes was carried out by elemental analysis and FAB mass spectra. These Fe and Co catalysts were screened for ethylene oligomerization studies in which iron complexes showed better catalytic activity than their cobalt analogues 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 mononuclear analogue due to the cooperative effect of two adjacent metals during the oligomerization reaction. C_4 and C_6 can be used as co-monomers for the production of various types of polyethylene like high density polyethylene, linear low density polyethylene etc.

Conflict of interest

The authors declare no conflict of interest.

Author contribution

The author confirms the responsibility for the complete study, presented results and manuscript preparation.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its supplementary materials.

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