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Ethylene Oligomerizations by Sterically Modulated Salicylaldimine Cobalt(II) Complexes Combined with Various Alkyl Aluminum Cocatalysts

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Abstract A set of structurally modulated salicylaldimine cobalt(II) complexes have been synthesized and utilized them for ethylene oligomerizations in combination with various organoaluminum cocatalysts. All catalyst systems yielded α-olefins with butenes as major product. The catalytic activity and product distribution were affected by the catalytic structure and reaction conditions. The formation of active species in these complexes under oligomerization conditions was investigated by UV-VIS spectroscopy and the results matched well with oligomerization results.

Keywords Cocatalysts · Ethylene · Oligomerization · Homogeneous cobalt catalysis · Salicylaldimine ligands

1 Introduction

α-Olefins are one of the essential industrial feed stocks used as comonomer in polymerization of ethylene to give linear low-density polyethylene (LLDPE) or for the preparation of detergents and synthetic lubricants. Ethylene oligomerization is one of the important industrial processes through which linear α-olefins can be obtained [1]. Catalysts currently used in industry for this purpose like that used for shell higher olefin process (SHOP) contain neutral Ni(II) complexes and such complexes are well known for their high activity and capability to direct the reaction towards specific targeted products [2–7]. Recently cationic Ni(II) α-diimine complexes were reported to be highly effective as ethylene oligomerization catalysts [8]. Moreover, high-performance from Ni catalysts to selectively produce oligomers can be obtained via tailoring of the surrounding ligands [9, 10].

Compared to the extensive studies of nickel complexes, a very few number of attempts only were reported on cobalt complexes being able to oligomerize ethylene to low-carbon olefins. Investigations such as those bestowed by groups of Brookhart [11, 12], Benett [13] and Gibson [14] have made great contributions towards designing highly active ethylene polymerization catalysts based on iron(II) and cobalt(II) bearing 2,6-(imino)pyridyl ligands. Such detailed attempts to extend this effect of predesigned ligands towards the potential of cobalt metal to oligomerize ethylene are relatively few in number.

Herein, we synthesized a series of salicylaldimine cobalt(II) complexes (Fig. 1) with a modulation in the bulkiness of *ortho* substituents by one-shot protocol. We looked into the possibility of these complexes as catalysts being able to produce the target α-olefins and also investigated the steric effects of ligands on ethylene oligomerization, along with the effects of the type and the amount of cocatalyst, reaction temperature, and reaction medium.

2 Experimental

All reactions and operations were performed under a dry, oxygen-free nitrogen-atmosphere with standard Schlenk techniques. Polymerization grade of ethylene (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX^{TM} catalyst and molecular sieve 5Å/13X. Organic solvents were distilled according to the standard

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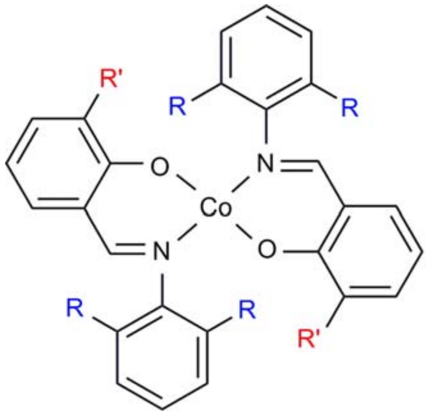


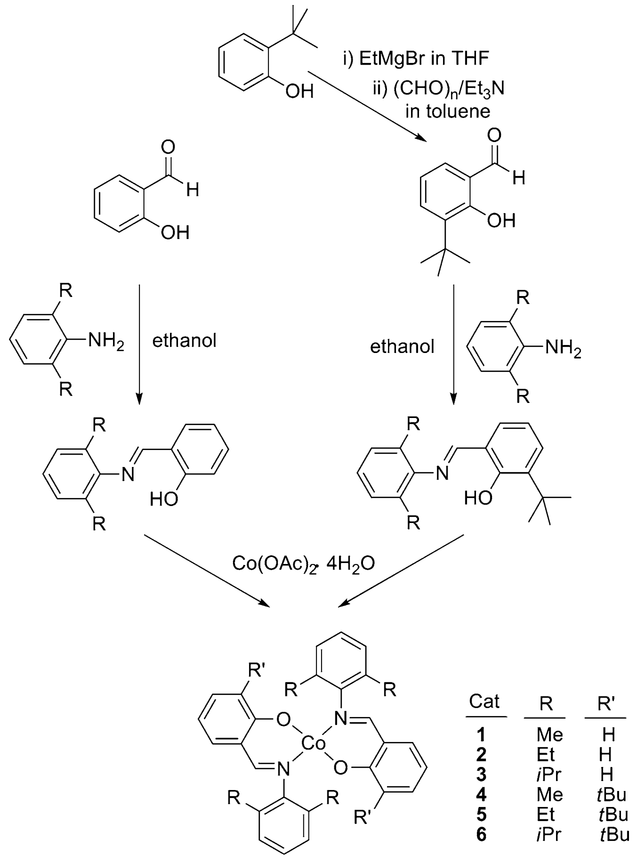
R	R'
Me	H
Et	H
*i*Pr	H
Me	*t*Bu
Et	*t*Bu
*i*Pr	*t*Bu

Fig. 1 Sterically modulated salicylaldimine cobalt(II) complexes

procedure and stored over molecular sieves (4 Å). Ethylaluminum sesquichloride (EAS, 25 wt.-% solution in toluene) and methylaluminum dichloride (MADC, 1.0 M solution in hexane), triethylaluminum (TEA, 25 wt.-% solution in toluene) were purchased from Aldrich Chemical Co. and used without further purification. All other reagents used in this study were purchased from Aldrich Chemical Co. and used without further purification. Methylaluminoxane (MAO, 8.4 wt.-% total Al solution in toluene) was purchased from Akzo Chemical.

General procedures for catalyst preparation are shown in Scheme 1. Detailed procedures for preparation and characterization of the complexes have reported earlier elsewhere [15].

Ethylene oligomerizations were performed in a 250 mL round-bottom flask equipped with a magnetic stirrer and a thermometer. High dilution techniques were adopted to reduce the monomer mass transport effect. After adding the catalyst, reactor was charged with toluene (80 mL) by using syringe and immersed in a constant temperature bath previously set to desired temperature. When reactor was equilibrated with bath temperature, ethylene was introduced into the reactor after removing nitrogen gas under vacuum. When no more absorption of ethylene into toluene was observed, required amount of cocatalyst was injected into reactor and then oligomerization was started. Oligomerization rate was determined at every 0.01 s from the rate of consumption, measured by a hotwire flow meter (model 5850 D from Brooks Instrument Div.) connected to a personal computer through an A/D converter. Oligomerization was quenched by the addition of methanol containing HCl (5 v/v %) after cooling to 0 °C. The resulting mixture was passed through an alumina column to remove Al containing species and the obtained oligomers were analyzed by gas chromatography (HP–6890), which was performed using a J&W Scientific DB608 column (30 mm × 0.53 mm) with a FID detector. The injector and detector temperature was kept constant at 250 °C. The program was set the initial temperature 40 °C (hold 2 min) and finishing temperature 220 °C (hold 10 min) with a heating rate of 10 °C/min.



Cat	R	R'
1	Me	H
2	Et	H
3	*i*Pr	H
4	Me	*t*Bu
5	Et	*t*Bu
6	*i*Pr	*t*Bu

Scheme 1 One shot synthesis of various salicylaldimine cobalt(II) complexes starting with salicylaldehyde or 3-*t*-butyl-salicylaldehyde

IR spectra of the complexes were collected on a Shimadzu Fourier Transform Infrared spectrometer IRPrestige-21 by making KBr pellets of the samples. Elemental analysis was carried out using Vario EL and UV-vis spectra were recorded on a Shimadzu UV-1650PC spectrophotometer.

3 Results and Discussion

3.1 Catalyst Preparations and Ethylene Oligomerizations

A series of cobalt(II) complexes with a modulation in bulkiness of *ortho* substituents were prepared according to the protocol described in Scheme 1. For example, 2-((2,6-dialkylphenylimino)methyl)phenol and 2-*t*-butyl-6-((2,6-dialkylphenylimino)methyl)phenol ligands (alkyl = methyl, ethyl and isopropyl) were synthesized by the condensation of 2-hydroxybenzaldehyde or 3-*t*-butyl-2-hydroxybenzaldehyde with 2,6-dialkylaniline in equimolar ratio, and at the same time on refluxing with cobalt acetate tetrahydrate in ethanol yielded cobalt complexes **1–6**. One-shot synthetic method has been adopted in order to avoid ligand purification step and hence to make the process more convenient. All compounds were obtained in high yields over 60%.

The elemental analyses of all the complexes are consistent with a 1:2 metal-ligand stoichiometry. The complexes are sufficiently soluble in $CHCl_3$, dioxane, DMSO, DMF, and pyridine for spectral measurements and stable in solution in air. The coordinating abilities of ligands bearing OH towards cobalt(II) acetate were high enough to form their cobalt(II) complexes even at one-shot synthetic conditions. In the previous study, we have shown that the resulting cobalt complexes efficiently tune the product microstructure in 1,3-butadiene polymerizations [15]. Motivated from these results, we studied the effect of their sequentially varied structure on ethylene oligomerization reactions.

When combined with EAS all the complexes **1–6** were found to be highly active in ethylene oligomerizations. Figure 2 shows the ethylene oligomerization rate profile. Under given reaction conditions (oligomerization temperature (T_o) = 30 °C, ethylene pressure (PC_2H_4) = 1.3 bar), all complexes showed high activity towards ethylene oligomerization with average rate of oligomerization ($R_{o,avg.}$) ranging from 8.13×10^4 to 17.9×10^4 g-oligomer/mol-Co h bar. The results of ethylene oligomerization are summarized in Table 1. All catalytic systems studied readily oligomerize ethylene to a mixture of linear olefins with even number of carbon atoms, from C_4 to C_{20}. The main products of the oligomerization are α-olefins which constitute from 79.8 to 89.3% of the products (Table 1).

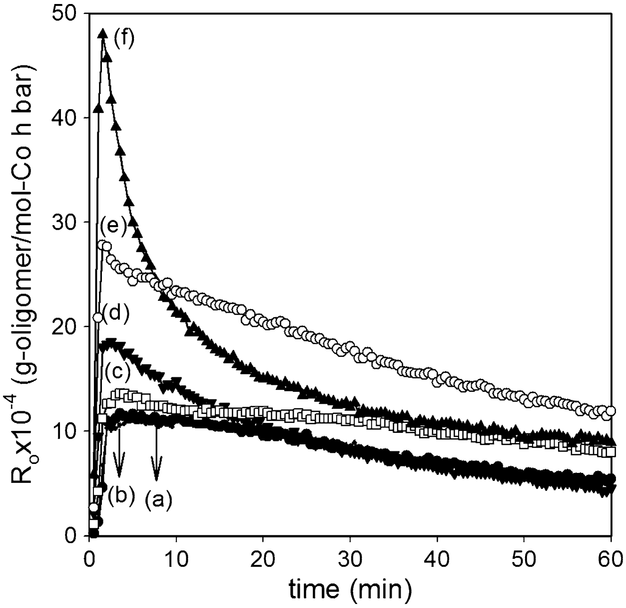


Fig. 2 Rate of oligomerization (R_o) versus time profiles of ethylene oligomerization by various salicylaldimine cobalt(II) complexes bearing sterically modulated ligands in the presence of ethylaluminu sesquichloride (EAS) with catalyst = 13.6 μmol, toluene solvent = 80 mL, PC_2H_4 = 1.3 bar, and oligomerization temperature (T_o) = 30 °C: (a) (2,6-Me_2Ar–N = C–Ar–O)$_2$Co (**1**); (b) (2,6-Et_2Ar–N = C–Ar–O)$_2$Co (**2**); (c) (2,6-*i*Pr_2Ar–N = C–Ar–O)$_2$Co (**3**); (d) (2,6-Me_2Ar–N = C-3-*t*BuAr–O)$_2$Co (**4**); (e) (2,6-Et_2Ar–N = C-3-*t*BuAr–O)$_2$Co (**5**); and (f) (2,6-*i*Pr_2Ar–N = C-3-*t*BuAr–O)$_2$Co (**6**) complex

In general, steric environment of ligands is one of the decisive factors determining the amount of termination by β-elimination [16] in olefin oligomerization/polymerization. For cationic nickel complexes steric bulk of the ligands influences the ground state energy of the resting-state species and the energy of migratory insertion transition state [17]. Theoretic investigations on Ni and Pd cationic tetrahedral complexes were revealed that strong steric interaction of atoms inserted on the metal center with bulkier substituents increases ground state energy of catalyst resting state. During the formation of transition state these inserted atoms will be brought to a single plane and hence makes the migratory insertion transition state more stable than the ground state of catalyst resting state, making the propagation easier [18]. But with a comparatively open structure, the *ortho* substituents in the N-aryl rings of cobalt salicylaldimine complexes cannot make a strong interaction with the inserted atoms as strong as the cationic nickel and palladium α-diimines, and hence cannot have a more stable migratory insertion transition state. It is evidenced from the low activity they show when compared with α-diimines. But within the salicylaldimines as the complexes become more sterically hindered, the catalytic activity increases as can be seen from Table 1, indicating that the ground state energy for the catalyst resting state is influenced by the bulkiness of *ortho* substituents on the N-aryl rings.

In the case of α-diimine complexes of Ni and Pd, the steric effect play an important role in determining the molecular weight of the resulting product [19]. The rate of associative displacement and chain transfer are generally retarded by the increase in steric bulk of the diimine ligand. The N-aryl rings lie roughly perpendicular to the plane through which the transition state is dispersed and the *ortho* substituents on them block axial approach of olefins and hence chain propagation rates are enhanced permitting the formation of high molecular weight polymers. For most of the salicylaldiminato complexes of Ni(II) reported so far, the steric bulk expected to achieve high molecular weights [17]. For these molecules the square planar transition state formed or the natural square planar structure helps the bulky *ortho* substituents on the N-aryl rings to orient roughly perpendicular to the square plane and hence towards the axial positions of the metal center increasing the catalyst productivity [17]. But the tetrahedral metal center geometry for the Co salicylaldimine complexes [20, 21] makes this inhibition of axial positions ineffective.

Table 1 Results of ethylene oligomerizations by various salicylaldimine cobalt(II) complexes bearing sterically modulated ligands in the presence of ethylaluminum sesquichloride (EAS)

Run[a]	Cat.	Yield (g)	$R_{o,avg}$[b] × 10^{-4}	α-Olefins (%)[c]	Distribution of α-olefins[d] (%)			
					C_4	C_6	C_8	C_{10-20}
1	**1**	2.32	8.13	83.2	72.4	18.4	2.3	6.9
2	**2**	2.29	8.11	89.3	72.5	20.1	0.2	7.2
3	**3**	2.45	9.12	81.7	74.1	18.0	1.8	6.1
4	**4**	2.71	10.6	79.8	73.5	19.9	3.1	3.5
5	**5**	2.98	15.3	80.4	68.6	24.3	3.6	3.5
6	**6**	3.21	17.9	81.7	70.3	20.1	0.8	8.8

[a] Reaction conditions: catalyst precursor = 13.6 μmol, [EAS]/[Co] = 200, T_o = 30 °C, toluene 80 mL, PC_2H_4 = 1.3 bar, reaction time = 1 h

[b] Average rate of oligomerization as g-oligomer/mol-Co h bar

[c] Linear olefins (α-$C^{=}_{4-20}$/Σ $C^{=}_{4-20}$)

[d] Determined by GC using calibration curves with standard solutions

Unlike the other square planar structures discussed before, bringing all atoms to a single plain may not be easy in these tetrahedral salicylaldiminato Co(II) complexes, as they are electronically different from the tetrahedral cationic complexes of Ni and Pd or the square planar neutral Ni complexes. This makes the chain transfer reaction easier than propagation and hence leading to oligomerization rather than polymerization. In addition to this, during the activation a ligand will be abstracted by cocatalyst [22], and hence only one N-aryl ring with *ortho* substituents will be remaining in the effective catalytic species. Previously Brookhart has reported that catalysts with only one substituent in the N-ring for the α-diimine do not yield polymer but instead produce oligomers [23]. It can be expected from an active species containing only one bulky N-aryl ring with *ortho* substituents that they can possibly give oligomerization rather than polymerization.

In our previous study it was found that electronic effect of substituents influences the electronic properties of metal center [15].The electron releasing inductive effect of alkyl substituents on aromatic rings increases from methyl to isopropyl. And hence electronegativity of cobalt metal will be decreased when the substituents changes from methyl to isopropyl group. This causes a weaker monomer to metal bond from catalysts bearing methyl to isopropyl substituents on their ligands in **1**–**3**. The interactions become again weaker when a *t*-butyl group is introduced in the ligand as in complexes **4**–**6**. When the metal to monomer and metal to α-olefin interaction become weaker, the chain propagation in oligomerization reactions facilitated as can be seen from the run 1–6 in Table 1.

3.2 Effect of Type and Concentration of Cocatalysts

The cocatalyst has quite complex functions in the present catalyst system. The cocatalysts are expected to alkylate catalyst after removing one of the two ligands to provide a coordinatively unsaturated complex, and stabilize the resulting cationic complexes by functioning as a non-coordinating anion [22]. Numerous studies in the recent past revealed that the influence of cocatalyst on catalytic activity, stability, polymerization kinetic profile, and polymer molecular weight and stereoregularity in cationic transition metal catalyzed olefin polymerization processes [24]. In order to check the effect of type of cocatalyst on ethylene oligomerization we carried out ethylene oligomerizations using complex **3** in combination with various cocatalysts such as MAO, TEA, MADC. The oligomerization results are summarized in Table 2.

When MAO has employed as cocatalyst ([Al]/[Co] = 200) complex **3** evidenced a very small activity which could not be measured by rate measurement system of this study; however, analysis of the resulting products identified a noticeable amount of hexenes with very high α-olefin content (89.9%). When TEA ([Al]/[Co] = 200) has used as cocatalyst the observations were closer to that obtained for MAO. It showed a negligible activity, the major product were hexenes and have shown moderately high α-olefin content (70.8%). Variations of the [Al]/[Co] ratio in a wide range with MAO and TEA showed no mentionable activity increase. With MADC ([Al]/[Co] = 200) the reaction showed a slightly higher activity than the reaction with MAO or TEA. As can be seen from Table 2, EAS was found to be the most efficient coactivator. We performed a series of ethylene oligomerizations using complex **3**/EAS system with various EAS concentrations from [EAS]/[Co] = 200–600. When [EAS]/[Co] = 400, the activity records the highest value, 22.2 × 10^4 g-oligomer/mol-Co h bar.

It is interesting to note that butene content increases and α-olefin content decreases as [EAS]/[Co] ratio increases. Chain terminations with the present catalysts should occur

Table 2 Results of ethylene oligomerizations catalyzed by salicylaldimine cobalt(II) complex (2,6-$i\mathrm{Pr}_2$Ar–N = C–Ar–O)$_2$Co (**3**)

Run[a]	Cocat.	[Al]/[Co]	T_o (°C)	Yield (g)	$R_{o,avg}$[b] × 10^{-4}	α-Olefins (%)[c]	Distribution of α-olefins[d] (%)			
							C_4	C_6	C_8	$C_{10–20}$
1	EAS	200	0	0.01	0.06	76.1	68.3	29.1	0.3	2.3
2	EAS	200	10	0.37	1.21	77.3	71.8	21.2	2.7	4.3
3	EAS	200	30	2.45	9.12	81.7	74.1	18.0	1.8	6.1
4	EAS	200	50	0.02	0.12	85.4	70.5	22.2	1.2	6.1
5[e]	EAS	200	30	2.83	13.17	91.4	77.5	16.3	2.2	4.0
6[f]	EAS	200	30	0.01	0.06	93.1	60.7	29.3	2.6	7.4
7	MAO	200	30	0.01	0.06	89.9	68.3	19.8	1.0	10.9
8	TEA	200	30	0.01	0.06	70.8	70.3	23.7	4.2	1.8
9	MADC	200	30	0.03	0.17	79.3	73.5	19.2	6.2	1.1
10	EAS	400	30	3.47	22.2	77.6	73.6	18.3	1.6	6.5
11	EAS	600	30	2.81	15.8	71.9	74.1	18.0	1.8	6.1

[a] Conditions: **3** = 13.6 μmol, toluene = 80 mL, PC_2H_4 = 1.3 bar, reaction time = 1 h

[b] Average rate of propagation as g-oligomer/mol-Co h bar

[c] Linear olefins (α-$C_{4-20}^{=}$/Σ $C_{4-20}^{=}$)

[d] Determined by GC using calibration curves with standard solutions

[e] Reaction medium = CH_2Cl_2 (80 mL)

[f] Reaction medium = n-hexane (80 mL)

predominantly by two mechanisms: *β*-hydride elimination and alkylation of the cocatalyst. Evidently the rate of *β*-hydride elimination is controlled by the catalyst, with apparent both structural and electronic contributions. However, once the catalyst is chosen, the options for control of product distribution are somewhat limited. The alkylation of the cocatalyst has normal kinetic parameters for a bimolecular reaction and therefore can be controlled by the concentration of each reactant. As the cocatalyst concentration increases, the alkylation can be more activated so that the concentration of α-olefin in the product decreases.

3.3 Effect of Oligomerization Temperature and Solvents

The effect of reaction temperature on oligomerization behavior by catalyst **3** combined with EAS was investigated and these results are also summarized in Table 2. In general catalyst life time were found sufficiently short above 60 °C [23], and hence oligomerization experiments were limited below 50 °C. For the catalytic system **3**/EAS in toluene medium, the activity was found the highest at 30 °C (9.12×10^4 g-oligomer/mol-Co h bar); however, showed low to moderate activity at 0 (0.06×10^4 g-oligomer/mol-Co h bar), 50 (0.12×10^4 g-oligomer/mol-Co h bar) and 10 °C (1.21×10^4 g-oligomer/mol-Co h bar). At low temperatures it might be difficult to attain the activation energy for oligomerization reactions, while at higher temperature catalyst deactivation and decrease in ethylene solubility reduce the activity of the catalyst [23].

The rate of termination reactions through chain transfer, especially *β*-hydride elimination, with the homogeneous catalysts are controlled by both the structural and electronic contributions of the catalysts. If the *β*-hydride elimination has high activation energy, the chain transfer reactions can be controlled by reaction temperatures. However, **3**/EAS catalyst yielded butenes as a predominant product regardless of the temperature, even though both α-olefin and butenes contents increased as the temperature increased. In addition, the catalyst system is not activated at low temperatures. These results demonstrate that the *β*-hydride elimination of **3**/EAS catalyst system has normal to low activation energy and therefore are determined by reaction temperature. Since the activation energy for this termination is slightly higher than that for propagation, the product distribution and the activation procedure can be controlled by temperature.

Catalytic activities can be affected by solvents due to the change in monomer concentration as the solubility of monomer depends on solvents or due to the solvation effect in the formation of active centers and oligomerization process. Beyond these effects the solubility of the catalysts influences the catalytic activity. Ethylene oligomerization reactions were carried out using **3**/EAS catalyst system in methylene chloride and hexane, and compared with the corresponding results in toluene (run 5, 6 and 3 in Table 2). Oligomerization rate profiles are given in Fig. 3. In all cases the rates reach maximum within a few minutes and then decrease monotonously. Under similar conditions the activity was found decreased in the order methylene

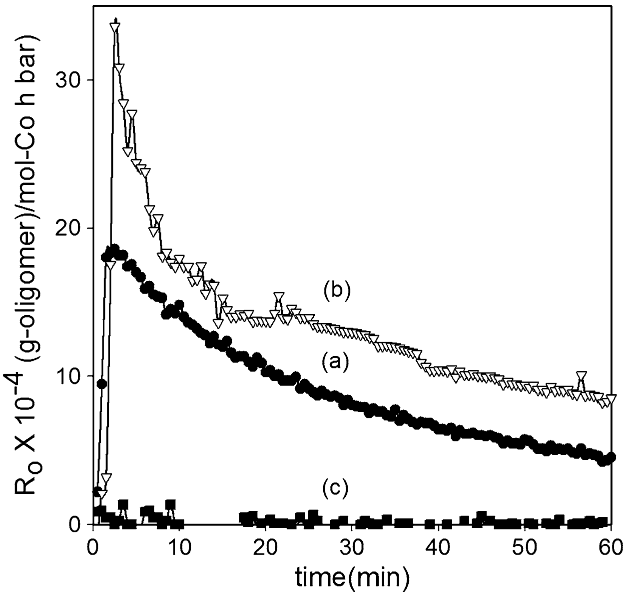


Fig. 3 Rate of oligomerization (R_o) versus time profiles of ethylene oligomerization in different reaction media of (a) toluene, (b) CH_2Cl_2, and (c) *n*-hexane with (2,6-*i*Pr_2Ar–N = C–Ar–O)$_2$Co (**3**) combined with ethylaluminu sesquichloride (EAS). Catalyst **3** = 13.6 μmol, solvent = 80 mL, PC_2H_4 = 1.3 bar, and [Al]/[Co] = 200, T_o = 30 °C

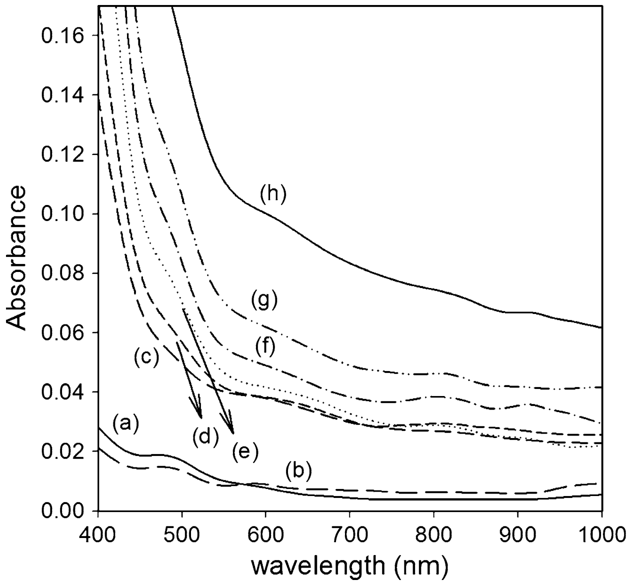


Fig. 4 UV-VIS spectra of (2,6-*i*Pr_2Ar–N = C–Ar–O)$_2$Co (**3**) and **3**/ethylene/ethylaluminum sesquichloride (EAS) in toluene solution: (a) complex **3** alone, (b) **3**/ethylene, (c) **3**/ethylene with 25 equiv. EAS, (d) **3**/ethylene with 50 equiv. EAS, (e) **3**/ethylene with 100 equiv. EAS, (f) **3**/ethylene with 200 equiv. EAS, (g) **3**/ethylene with 300 equiv. EAS, and (h) **3**/ethylene with 400 equiv. EAS

chloride > toluene ≫ hexane. The insertion of an ethylene into a coordinatively unsaturated cobalt–carbon bond is an essential step in the present catalyst system. As a result the rate of insertion reactions are dependent upon the polarity of solvent, with more polar solvent giving higher rate of reaction for **3**/EAS catalyst system. A high activity for complex **3**/EAS catalyst system in methylene chloride may be due to the initial ease of dissociation to ion pair in a solvent with high dielectric constant. The reverse is true in hexane solvent. In addition the low solubility of complex **3** in hexane is another reason for the low activity. The α-olefin content increased from 87.2% in toluene to 93.1% in *n*-hexane (Table 2). In addition product distribution including major product butene changes a lot according to solvent, demonstrating the polarity of the environment around the metal center deeply affects both propagation and termination processes.

3.4 Spectroscopic Investigation of the Formation of Active Species

There had been a considerable number of theoretic and experimental investigations on early and late transition metal complexes to elucidate their active species formed during olefin polymerizations [25–31]. These attempts on several zirconocene/MAO systems [26–30] and α-diimine-[*N,N*]$NiBr_2$/MAO system [31] for olefin polymerizations have contributed much to understand the successive elementary steps involved in the formation of cationic active species. An investigation of cobalt salicylaldimine complex **3** based on its UV-VIS spectroscopy under oligomerization conditions was carried out to get an idea about the active species involved in these oligomerization reactions. The formation of various types of cobalt species upon incremental addition of EAS has been identified in this process.

Figure 4 shows the UV-VIS spectrum of the cobalt complex **3**, and those of complexes obtained by reacting with EAS. Complex alone have an absorption maximum around 500 nm and it has no other characteristic absorptions between 400 and 1,000 nm. Addition of a small quantity of ethylene did not produce any difference in the pattern of the spectrum. An incremental addition of EAS causes absorptions at 600, 800 and 900 nm. At [EAS]/[Co] = 25, 50 and 100, the absorptions are not so pronounced, even though they are distinguishable. But when the ratio becomes 200, the absorptions become prominent. Those at 800 and 900 nm were appeared strong. But when the ratio increased further, the absorption at 600 become prominent and those at 800 and 900 nm started gradually dying out. From the oligomerization experiments it was found that at ratios below and above 200, the system is less active (Table 2). Combining with the oligomerization results it can be concluded that the absorptions at 800 and 900 nm represent the active species and that at 600 nm is deactivated species. In our previous attempt with 1,3-butadiene as monomer a similar observation was obtained with much prominent absorption for active species, where the activity of the catalysts towards 1,3-butadiene was very high [15].

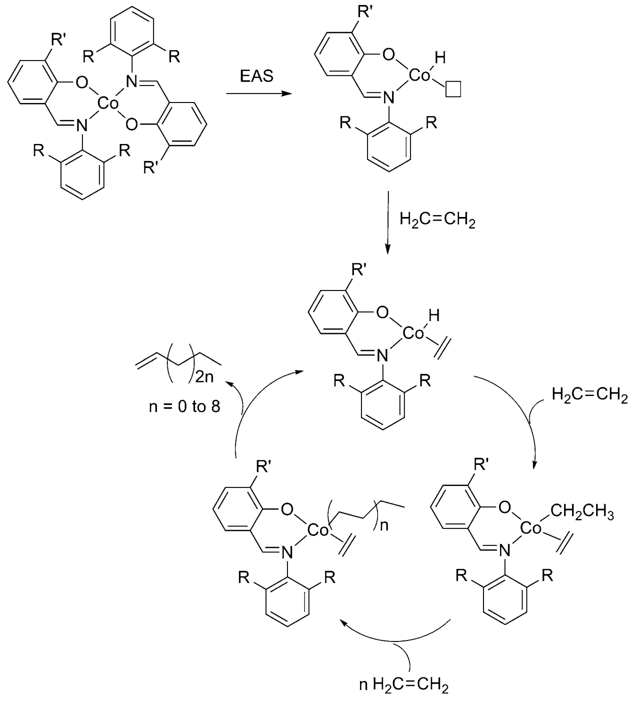


Fig. 5 Reaction mechanism for ethylene oligomerization by salicylaldimine cobalt(II) catalysts combine with ethylaluminum sesquichloride

Combining these results of UV-VIS spectroscopic investigations and the results from the previous studies, it is possible to deduce the mechanism of oligomerization at the cobalt metal center. In our previous study involving Ni metal center having same ligand environment of the current study, we have been able to conclude that on reaction with EAS the salicylaldimine Ni(II) complex transformed into an active species often involving metal having interactions with a hydride (or alkyl) and ethylene molecule [16, 32]. We expect a similar sort of mechanism (as in Fig. 5) for the salicylaldimine Co(II) complexes, as there are a lot of similarities between cobalt and nickel metal centers in the way they behave in catalysis. The alkyl ethylene complex in this mechanism constitutes the catalyst resting state and which has been identified by monitoring the ethylene chain growth at late-transition metals by low-temperature NMR spectroscopy [11, 33]. This mechanism clearly proposes the barrier to chain transfer is very low as the open and less crowded structure does not hinder the olefinic units which can axially orient to form the transition state for β-hydrogen transfer process [17]. This supports an easy chain transfer leading oligomerization reactions. For the salicylaldimine Co(II) complexes, the EAS is the most efficient Lewis acid to remove a ligand from the initial four-coordinate species (coordinatively saturated) to a three-coordinate complex that has vacant coordination site where the ethylene can bind, comparing to TEA, MADC or MAO.

4 Conclusions

A series of salicylaldimine cobalt(II) complexes with varying steric demands were prepared and used for ethylene oligomerizations. Among various combinations with alkyl aluminums, the EAS was found to be the most effective cocatalyst for salicylaldimine cobalt(II) complexes. When [EAS]/[Co] ratio is around 200, the catalyst system yields the highest activity. This result matches well with UV-VIS spectroscopic investigation on the active species formation, where the population density of active species is the most prominent when the [EAS]/[Co] is 200. Predominantly α-olefins with even number of carbon atoms up to C_{20} were produced with C_4 as the major product. The catalytic activity was dependent upon the catalyst structure with a positive influence of the increase in steric bulk. In methylene chloride solvent the activity recorded the highest and in hexane the least. By changing the parameters such as cocatalyst concentration and temperature as well as reaction medium, the product distribution could be controlled to some degree; however, they were not the sole decisive factors.

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