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PAPER

Highly active and stereospecific polymerization of 1,3-butadiene catalyzed by dinuclear cobalt(II) complexes bearing 3-aryliminomethyl-2-hydroxybenzaldehydes†

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A series of cobalt(II) complexes bearing 3-aryliminomethyl-2-hydroxybenzaldehydes (tridentate [NOO] ligands) was prepared and characterized by FT-IR and elemental analysis along with single-crystal X-ray diffraction. The X-ray diffraction analysis revealed that a dinuclear centrosymmetrical structure formed, in which each cobalt atom is surrounded by two bridged ligands and two acetate groups as a distorted octahedron. These dinuclear cobalt complexes displayed high catalytic activities for the polymerization of 1,3-butdiene on activation with organoaluminum cocatalysts to yield *cis*-1,4-polybutadiene with high selectivity. Ethylaluminum sesquichloride (EASC) was found to be the most efficient cocatalyst resulting in high conversion of butadiene and *cis*-1,4 content in the polymers with moderate molecular weight. The high catalytic activity and stereoselectivity could be achieved in a wide range of reaction conditions. All the dinuclear cobalt complexes (**C1–C6**) yielded predominantly *cis*-1,4-polybutadienes ($> 96\%$) with negligible amounts of *trans*-1,4 ($< 2.4\%$) and 1,2-vinyl ($< 1.5\%$) products under the Al/Co molar ratio of 80 at 25 °C. The ligand modification by varying the substituents at the 4-position of phenol and on the imino-N aryl ring showed slight influence on the catalytic activity and microstructure of the resulting polymers.

Introduction

The metal-catalyzed stereospecific polymerization of 1,3-butadiene is of considerable interest from both an academic and industrial point of view.[1] Among the different isomeric polybutadienes, *cis*-1,4-polybutadiene (PBD) has gained much industrial importance, especially for tire production, due to its natural-rubber-like properties. The large-scale technical synthesis of *cis*-1,4-polybutadiene is currently carried out by solution polymerization with organometallic complex catalysts of the Ziegler–Natta type containing $TiC1_4/I_2/Al(i\text{-}Bu)_3$,[2] $CoCl_2/AlEt_2Cl$,[1b,3] $Ni(OOCR)_2/BF_3{\cdot}OEt_2/AlEt_3$,[4] or $Nd(OOCR)_3/Et_3Al_2Cl_3/Al(i\text{-}Bu)_2H$[5] in aromatic or aliphatic hydrocarbon solvents at 50–70 °C. The cobalt-based catalysts play a very important role in the butadiene polymerization, depending on the reaction conditions and catalyst formulation, since they can produce polymers with different microstructures, including *cis*-1,4-PBD and syndiotactic 1,2-PBD, which are the only two kinds of polybutadienes produced on an industrial scale.[1a,1d] The halides and carboxylates of cobalt are stereoselective to high *cis*-1,4-PBD when activated with methylaluminoxane (MAO).[6] However, the cobalt halides when combined with alkylphosphines and pyridyl adducts produced predominantly 1,2-PBD.[7]

In order to gain better control over catalytic activity, molecular weight and more importantly stereoselectivity of the polymerization, academic and industrial research has focused on well-defined organometallic single-site catalysts, mainly based on rare earth metals and first-row transition metals.[1c,1d,8] The discovery of 2,6-bis(imino)pyridine ligands for iron and cobalt catalysts in the field of olefin polymerization[9] has extended a large number of tridentate ligands based on either derivatives of bis(imino)pyridine or designing new organic compounds especially consisting of heterocycles.[10] Although their complexes of transition metals were extensively studied for the oligomerization and/or polymerization of olefins, the cobalt-based complexes bearing these ligands as catalysts in the polymerization of butadiene are few in number. For example, four-coordinated (Salen)cobalt(II) (**A**, Chart 1) or bis(salicylaldiminate)cobalt(II) complexes (**B**, Chart 1) achieved high activity and high *cis*-1,4 selectivity in the polymerization of butadiene in combination with MAO or EASC.[11] Tridentate ligands (especially [NNN]) have also featured in the cobalt-based catalyst systems for the polymerization of butadiene, mainly producing high *cis*-1,4-PBDs upon activation with MAO or EASC, such as bis(imino)pyridine ligands (**C**, Chart 1),[12] bis(benzimidazolyl)amine ligands (**D**, Chart 1),[13] bis(benzimidazolyl)pyridine ligands (**E**, Chart 1).[14]

With the view of exploring new suitable chelate cobalt(II) complexes effective for the stereospecific polymerization of

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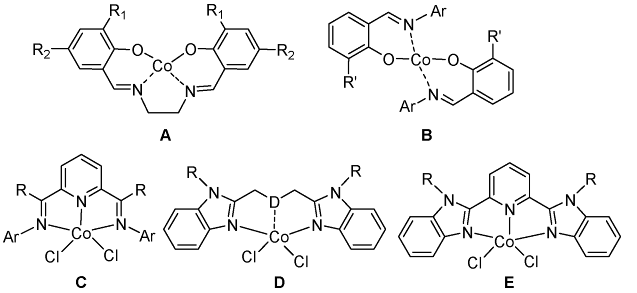


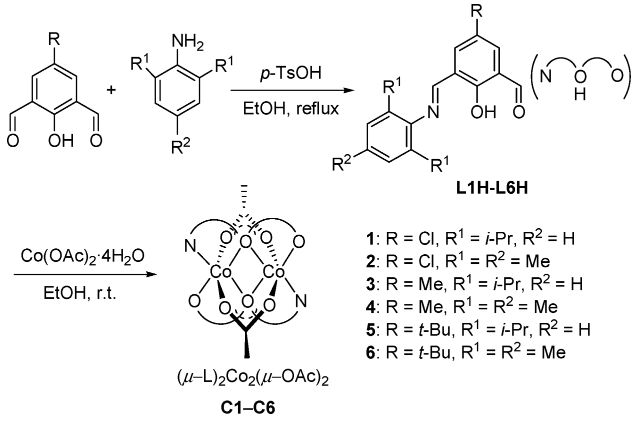
Chart 1 Cobalt(II)-based catalysts for the *cis*-polymerization of 1,3-butadiene

butadiene, we chose 3-aryliminomethyl-2-hydroxybenzaldehydes for cobalt(II) complexes, two of which have been used as asymmetric bidentate [NO] ligands for neutral arylnickel(II) phosphine complexes, showing high activities for ethylene oligomerization in conjunction with MAO.[15] Herein we are reporting the synthesis and characterization of dinuclear cobalt(II) complexes bearing 3-aryliminomethyl-2-hydroxybenzaldehydes as tridentate [NOO] ligands and their application in the stereospecific polymerization of 1,3-butadiene to produce high contents of *cis*-1,4-PBD by using low amounts of EASC as cocatalyst.

Results and discussion

Synthesis and characterization

The starting materials, 2,6-diformylphenols, were prepared from the corresponding 4-substituted phenols *via* the Dull reaction.[16] The titled 3-aryliminomethyl-2-hydroxybenzaldehyde ligands **L1H–L6H** were then synthesized as yellow or orange solids in moderate yields through the Schiff-base condensation reaction of 4-substituted 2,6-diformylphenols with one equivalent of appropriate aniline in the presence of a catalytic amount of toluene-*p*-sulfonic acid (*p*-TsOH) in refluxing ethanol (Scheme 1). All the ligands were identified on the basis of FT-IR, elemental analysis, ^{1}H and ^{13}CNMR spectra, and the results of **L1H** and **L2H** were compared with the reference data.[15]



Scheme 1 Synthesis of ligands **L1H–L6H** and cobalt complexes **C1–C6**.

The cobalt complexes **C1–C6** were readily prepared by combining ethanol solutions of $Co(OAc)_2 \cdot 4H_2O$ and one equivalent of the corresponding ligand at room temperature (Schemes 1). Except for complex **C4**, the resulting cobalt complexes had good solubility in ethanol. All the complexes were isolated as orange or reddish orange air-stable powders in good yields and high purities by adding diethyl ether to the concentrated ethanol solutions. The structures of these complexes were determined by FT-IR spectra and elemental analysis. It was unexpected that all these cobalt complexes possessed dinuclear centrosymmetrical structure with bridged phenolate ligands and acetate groups, as was established by single-crystal X-ray diffraction (see below). In the IR spectra, the stretching vibration bands of C=N double bonds of these cobalt complexes (1618–1621 cm^{-1}) shifted to lower wave number and the peak intensity greatly reduced, as compared to the corresponding ligands (1624–1630 cm^{-1}), indicating the coordination interaction between the imino-N atom and the metal center; and so did the carbonyl groups from 1672–1686 cm^{-1} (free ligands) shifting to 1645–1653 cm^{-1} (cobalt complexes). The elemental analysis results revealed that the components of these complexes were in accordance with the formula of $(\mu\text{-L})_2Co_2(\mu\text{-OAc})_2$. The molecular structure of complex **C2** was further confirmed by the single-crystal X-ray diffraction analysis (Fig. 1).

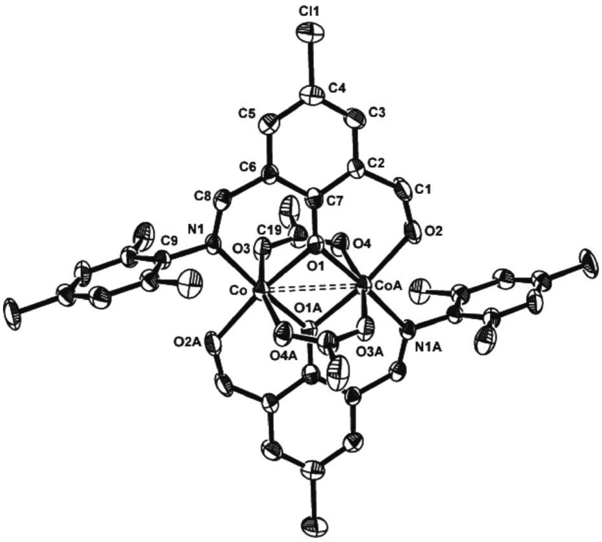


Fig. 1 ORTEP drawing of complex **C2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Crystal structure of complex C2

Single crystals of complex **C2** suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into its dichloromethane solution. Analysis of X-ray crystallography revealed that complex **C2** displays a dinuclear centrosymmetrical structure as shown in Fig. 1, in which each cobalt metal center is coordinated to the [*N*,O] atoms of one ligand, the [*O*,O] atoms of the other ligand, and two oxygen atoms from two bridged acetate groups forming a distorted octahedron. The phenoxy-O atoms of two ligands bridge the two cobalt atoms in such a way that a planar $Co_2(\mu\text{-O})_2$ core forms and the two μ-acetate groups symmetrically locate in either side of this plane, respectively. The dihedral angles between $Co_2(\mu\text{-O})_2$ plane and phenoxy plane, N-aryl ring are 153.3° and 72.0°, respectively, while the phenoxy plane and N-aryl ring are nearly perpendicular with the dihedral angle of 96.8°.

Table 1 Selected bond lengths [Å] and angles [°] of complex **C2**

Bond lengths		Bond angles	
Co–O1	2.078(5)	O1–Co–O1A	92.4(2)
Co–O1A	2.096(5)	O1–Co–O2A	171.5(3)
Co–O2A	2.095(6)	O1–Co–O4A	83.7(2)
Co–O3	2.068(6)	O1–Co–O3	85.2(2)
Co–O4A	2.048(6)	O1–Co–N1	85.4(2)
Co–N1	2.085(6)	O3–Co–N1	93.2(2)
C8–N1	1.274(9)	O3–Co–O1A	82.0(2)
C1–O2	1.236(10)	O3–Co–O2A	101.5(2)
C19–O3	1.268(9)	O3–Co–O4A	162.2(2)
C19–O4	1.269(10)	O1A–Co–N1	174.9(2)
Co···CoA	2.888(2)	O1A–Co–O2A	83.5(2)
		O1A–Co–O4A	84.6(2)
		O2A–Co–N1	99.2(2)
		O2A–Co–O4A	88.5(3)
		O4A–Co–N1	99.8(2)
		O3–C19–O4	125.3(8)

Around each cobalt center, an equatorial plane is composed by O1, O2A, O3, and O4A atoms and the two axial bonds nearly form a straight angle (O1A–Co–N1, 174.9(2)°). All the bond angles in the equatorial plane are close to a right angle (O1–Co–O4A, 83.7(2)°; O1–Co–O3, 85.2(2)°; O3–Co–O2A, 101.5(2)°; O2A–Co–O4A, 88.5(3)°) and the central cobalt atom deviates by 0.1666 Å from this plane (Table 1). The Co–O3 and Co–O4A bond lengths between cobalt atom and two acetate ligands from both sides of $Co_2(\mu\text{-}O)_2$ core are 2.068(6) Å and 2.048(6) Å, respectively. Both Co–N1 and Co–O1(A) bond lengths between cobalt atom and phenolate ligand are slightly longer than those in the neutral arylnickel(II) phosphine complexes with the same ligand,[15] or those in the 2,6-bis(imino)phenoxy cobalt complexes.[17] The imino C8–N1 bond length (1.274(9) Å) is consistent with the typical characters of C═N double bond although it is relatively shorter than those in the literature.[15,17] The carbonyl C1–O2 bond length is 1.236(10) Å and slightly longer than the non-coordinated C═O bond (1.212(4) Å in arylnickel(II) phosphine complexes).[15] The two C–O distances in the electron-delocalized acetate groups are almost equal (1.268(9) Å and 1.269(10) Å). The Co–Co distance of 2.888(2) Å is longer than those found in some dicobalt complexes[18] and carbonyl cobalt compounds.[19]

Solution polymerization of butadiene

The solution polymerization of 1,3-butadiene was carried out in toluene under various reaction conditions. The effects of different type and amount of cocatalysts on the polymerization of butadiene were firstly investigated with complex **C2** and the results are summarized in Table 2. The **C2**/MAO catalytic system showed relatively lower conversion of butadiene (25.4% in 30 min, entry 1 in Table 2) under the Al/Co molar ratio of 100 with 5.0 μmol of precatalyst load. When both precatalyst and butadiene concentrations increased, much higher conversions of butadiene were obtained (entries 2 and 3 in Table 2); however, the polybutadienes produced showed similar molecular weights and microstructures with high contents of the *cis*-1,4 isomer (*ca.* 94%). The conversion of butadiene with the **C2**/$AlEt_2Cl$ system reached 96.4% in 60 min and the *cis*-1,4 content (92.8%) and molecular weight of the polymers were relatively low when compared to those obtained by other cocatalysts (entry 4 in Table 2). Ethylaluminum sesquichloride (EASC) was found to afford high catalytic activity and the highest *cis*-1,4 content in the resulting polymers by using 40 equivalents of EASC to precatalyst. The higher molecular weight was also achieved by the **C2**/EASC system (entry 5 in Table 2). Therefore, EASC was employed for the following investigations under various reaction parameters.

With the **C2**/EASC catalytic system, a series of reaction parameters such as Al/Co molar ratio, reaction temperature, and reaction time were varied in order to investigate the effects of polymerization conditions on the catalytic activities and polymer microstructure. Although no conspicuous variation of microstructure was observed according to the Al/Co molar ratio, the conversion of butadiene changed greatly. The conversion of butadiene increased considerably as the increase of Al/Co molar ratio from 10 to 80 (entries 1–5 in Table 3) and a complete consumption of butadiene was observed under the Al/Co molar ratio of 80, as usually observed in transition metal catalyzed olefin polymerizations in combined with alkylaluminum cocatalysts. However, the influence of Al/Co molar ratio on the molecular weight and molecular weight distribution of polymers didn't exhibit an obvious regularity, from which we could infer that the chain transfer to aluminum was not as significant for butadiene polymerization as in the case of olefin polymerization.[20]

The butadiene polymerization behavior with the **C2**/EASC catalytic system was highly sensitive to reaction temperature. The catalytic system was nearly inactive at 0 °C and the optimum activity was gained at 25 °C with the complete conversion of butadiene (entries 5 and 6 in Table 3). The **C2**/EASC catalytic system showed remarkable thermal stability affording the 81.8% conversion of butadiene even at 90 °C (entries 7–9 in Table 3), whereas the decrease in polymerization rate at the elevated reaction temperature was common in olefin polymerization catalyzed by

Table 2 Effects of different cocatalysts on the polymerization of 1,3-butadiene with complex **C2**[a]

								Microstructure[e] (mol%)		
Entry	Cocat.	Al/Co	t (min)	Conv (%)	M_{calcd}[c] (10^4 g mol^{-1})	M_n[d] (10^4 g mol^{-1})	M_w/M_n[d]	*cis*-1,4-	*trans*-1,4-	1,2-
1	MAO	100	30	25.4	2.75	15.1	1.69	94.9	3.2	1.9
2[b]	MAO	100	60	63.3	6.85	17.5	1.95	94.3	3.5	2.2
3[b]	MAO	100	120	72.4	7.83	15.4	2.05	93.6	4.2	2.2
4	$AlEt_2Cl$	40	60	96.4	10.4	9.45	2.92	92.3	5.3	2.4
5	EASC	40	60	90.7	9.81	23.6	2.39	96.6	2.2	1.2

[a] Polymerization conditions: precatalyst: 5.0 μmol, solvent: 20 mL of toluene, [BD]/[Co]: 2000, reaction temperature: 25 °C. MAO: methylaluminoxane; EASC: ethylaluminum sesquichloride. [b] precatalyst: 10.0 μmol, solvent: 30 mL of toluene, [BD]/[Co]: 2000. [c] $M_{calcd} = 2000 \times 54.09 \times X$ (X = conversion). [d] Determined by GPC against polystyrene standards and reported uncorrected. [e] Determined by ^1H and ^{13}C NMR spectroscopies.

Table 3 Effects of various reaction parameters on the polymerization of 1,3-butadiene with complex **C2**/EASC[a]

								Microstructure[d] (mol%)		
Entry	Al/Co	T/°C	t (min)	Conv (%)	M_{calcd}[b] (10^4 g mol^{-1})	M_n[c] (10^4 g mol^{-1})	M_w/M_n[c]	*cis*-1,4-	*trans*-1,4-	1,2-
1	10	25	60	12.2	1.32	29.8	2.00	97.1	0	2.9
2	20	25	60	83.2	9.00	16.7	2.84	97.1	1.7	1.2
3	40	25	60	90.7	9.81	23.6	2.39	96.6	2.2	1.2
4	60	25	60	96.5	10.4	17.8	3.18	95.1	3.2	1.7
5	80	25	60	100	10.8	20.5	2.39	95.0	3.6	1.4
6	80	0	60	trace	—	—	—	—	—	—
7	80	50	60	97.4	10.5	14.3	3.13	92.1	6.1	1.8
8	80	70	60	95.1	10.3	9.46	3.84	85.7	11.5	2.8
9	80	90	60	81.8	8.85	10.6	3.00	83.6	13.0	3.4
10	80	25	10	63.4	6.86	25.8	1.42	97.5	1.5	1.0
11	80	25	20	84.8	9.17	20.9	2.16	96.9	2.0	1.1
12	80	25	30	92.9	10.0	23.0	2.19	96.6	1.9	1.5
13	80	25	40	96.5	10.4	23.9	2.54	96.5	2.3	1.2

[a] Polymerization conditions: precatalyst: 5.0 μmol, cocatalyst: EASC, solvent: 20 mL of toluene, [BD]/[Co]: 2000. [b] $M_{\text{calcd}} = 2000 \times 54.09 \times X$ (X = conversion). [c] Determined by GPC against polystyrene standards and reported uncorrected. [d] Determined by ^{1}H and ^{13}C NMR spectroscopies.

late transition metal catalysts.[10] The molecular weights of PBDs decreased and the molecular weight distributions became broader at the elevated reaction temperature. The most distinguished feature was the obvious change of polymer microstructure induced by the variation of reaction temperature. The *trans*-1,4 content of PBDs increased gradually along with the elevation of reaction temperature, producing 13.0% content of *trans*-1,4 isomer at 90 °C and *cis*-1,4 content reducing to 83.6%; however, the content of 1,2-inserted isomer had a slight increase from 1.4% to 3.4%. The formation of increased *trans*-1,4 content at elevated temperature was probably ascribed to the facilitated *anti-syn* isomerization because the higher reaction temperature might supply the needed energy requirement.[21]

The plots of conversion of butadiene and $\ln([\text{BD}]_0/[\text{BD}]_t)$ *vs.* the reaction time initiated by **C2**/EASC system are depicted in Fig. 2, where $[\text{BD}]_0$ and $[\text{BD}]_t$ are the initial monomer concentration and the monomer concentration at time t, respectively. A good linear relationship between $\ln([\text{BD}]_0/[\text{BD}]_t)$ and reaction time was observed from Fig. 2, indicating that first-order dependency of polymerization rate on monomer concentration. The molecular weights and molecular weight distributions tended to increase with reaction time up to 10–40 min. The formation of polymers with similar stereoregularity indicated the identical nature of the active center.

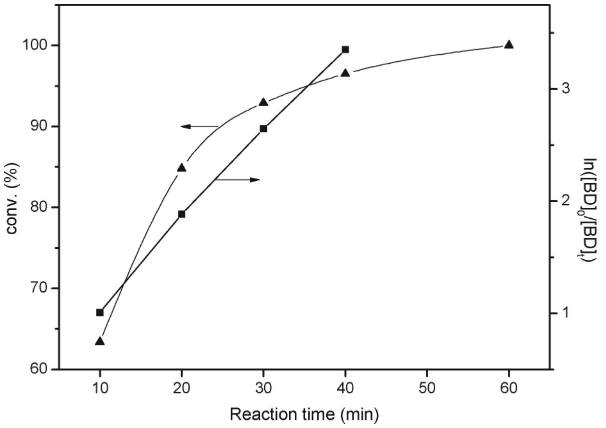


Fig. 2 The plots of conversion (%) of BD (▲) and $\ln([\text{BD}]_0/[\text{BD}]_t)$ (■) against reaction time for BD polymerization with **C2**/EASC system. Polymerization conditions: precatalyst: 5.0 μmol, [Al]/[Co]: 80, solvent: 20 mL of toluene, [BD]/[Co]: 2000, reaction temperature: 25 °C.

The dinuclear cobalt complexes (**C1–C6**) with different ligand environments were applied in butadiene polymerization for examining steric and electronic effects on catalytic activity and properties of resulting polymers (Table 4). When comparing the complexes bearing the same substituents on the imino-N aryl ring, complexes **C1** and **C2** with the electron-drawing Cl group at the 4-position of phenol (R = Cl) had slightly higher conversions than the corresponding complexes **C3**, **C4** (R = Me) and **C5**, **C6** (R = *t*-Bu) with the electron-donating methyl and *tert*-butyl groups, respectively; furthermore, the bulkier *tert*-butyl group also resulted in a little higher conversion than the methyl group (that is, conversion orders: **C1** > **C5** > **C3**; **C2** > **C6** > **C4**). Concerning the complexes with the same R group at the 4-position of the phenol, the Cl-substituted complexes **C1** and **C2** obtained similar conversion, whereas the molecular weight of resulting polymers had large difference and the bulkier isopropyl groups on the imino-N aryl ring led to lower molecular weight (M_n = 155 kg mol^{-1}) than methyl groups (M_n = 230 kg mol^{-1}). As for the Me-substituted complexes **C3** and **C4**, the bulkier isopropyl groups yielded relatively higher conversion and lower molecule weight of PBDs than methyl groups. The *t*-Bu-substituted complexes **C5** with bulkier isopropyl groups also had higher conversion than **C6** with methyl groups; however, they produced the PBDs with the same molecular weight. The PBDs produced by complexes **C1–C6** had very high *cis*-1,4 contents (96.4%–98.0%) and relatively narrow molecular weight distributions (2.19–2.70) albeit with their different molecular weights.

The microstructure of the resulting polymers was analyzed by FT-IR and NMR spectra and found to be predominantly *cis*-1,4-PBD together with small amounts of *trans*-1,4 and 1,2-vinyl isomers by all the cobalt complexes. Characterized by FT-IR spectra recorded in the range 4000–400 cm^{-1}, the polymers can be confirmed to be mainly *cis*-1,4-PBD from the characteristic vibration absorption bands at 740 cm^{-1} of =C–H bonds.[22] The ^{1}H and ^{13}C NMR spectra of PBDs obtained by the **C1**/EASC

Table 4 Polymerization of 1,3-butadiene with complexes **C1–C6**/EASC[a]

						Microstructure[d] (mol%)		
Entry	Cat.	Conv (%)	M_{calcd}[b] (10^4 g mol^{-1})	M_n[c] (10^4 g mol^{-1})	M_w/M_n[c]	*cis*-1,4-	*trans*-1,4-	1,2-
1	**C1**	92.1	9.96	15.5	2.70	96.4	2.4	1.2
2	**C2**	92.9	10.0	23.0	2.19	96.4	2.1	1.5
3	**C3**	89.5	9.68	21.7	2.42	97.3	1.6	1.1
4	**C4**	86.8	9.39	24.4	2.60	98.0	0.8	1.2
5	**C5**	90.4	9.78	20.0	2.28	97.2	1.7	1.1
6	**C6**	88.6	9.58	20.0	2.50	97.1	1.8	1.1
7[e]	**C1**	98.4	10.6	15.1	2.67	95.8	2.9	1.3
8[f]	**C1**	98.2	10.6	13.4	2.62	94.9	3.0	2.1

[a] Polymerization conditions: precatalyst: 5.0 μmol, cocatalyst: EASC, [Al]/[Co]: 80, solvent: 20 mL of toluene, [BD]/[Co]: 2000, reaction temperature: 25 °C; reaction time: 30 min. [b] $M_{calcd} = 2000 \times 54.09 \times X$ (X = conversion). [c] Determined by GPC against polystyrene standards and reported uncorrected. [d] Determined by ^{1}H and ^{13}C NMR spectroscopies. [e] Addition of 0.5 equiv. of PPh_3/Co. [f] Addition of 1.0 equiv. of PPh_3/Co.

system are shown in Fig. 3 as a representative example, and the assignments and contents of isomers were determined according to the literature.[23] The ^{13}C NMR spectra further demonstrated that *cis*-1,4-PBD was predominant in the polymers, and the single peaks at δ 129.6 and 27.4 ppm corresponded to =CH- and -CH_2- carbon atoms in *cis*-1,4-PBD, respectively. In all the cases at 25 °C, the molecular weight of the resulting PBDs was higher than the theoretic values, which probably attribute to the rapid propagation rather than initiation, leading to the reduction of catalyst efficiency (M_{calcd}/M_{measd}).[24]

The addition of phosphines to butadiene polymerization reactions catalyzed by Ziegler–Natta type of cobalt-based catalytic systems had been previously shown to increase the 1,2-vinyl content in the resulting polymers,[25,26] which was also proved by bis(benzimidazole)-based cobalt catalysts.[13b,13c] Therefore, the butadiene polymerizations were carried out in the presence of 0.5 and 1.0 equivalent of PPh_3/Co by using the **C1**/EASC system. As shown in Table 4 (entries 7 and 8), the addition of PPh_3 resulted in the increased conversions of butadiene. The molecular weights and molecular weight distributions of the resulting polymers were slightly lower than those obtained in the PPh_3-free system, indicating that PPh_3 induced the chain transfer reactions. However, unexpectedly, the microstructure didn't show an important change and 1,2-vinyl content was still present in negligible amounts.

Conclusions

In summary, a series of dinuclear cobalt(II) complexes bearing 3-aryliminomethyl-2-hydroxybenzaldehyde ligands was synthesized and characterized. Single crystal X-ray analysis revealed that a dinuclear centrosymmetrical structure formed, in which each cobalt atom is surrounded by two bridged ligands and acetate groups. Upon activation with EASC, all the complexes could catalyze the polymerization of 1,3-butdiene with high activity to give predominantly *cis*-1,4-polybutadiene with high selectivity. The increase of Al/Co molar ratio enhanced the catalytic activity but only slightly decreased the *cis*-1,4 content in the polymers. The catalytic system was rather thermally stable at 25–90 °C. However, the reaction temperature could alter the microstructure of resulting polybutadienes importantly. The ligand environment was not found to significantly influence the catalytic activity and the microstructure of resulting polymers. The addition of PPh_3 could improve the conversion of butadiene in some extent, but it didn't greatly increase the 1,2-vinyl content of polymers produced by the current system.

Experimental

All manipulations of air- or moisture-sensitive compounds were carried out under an atmosphere of argon using standard Schlenk

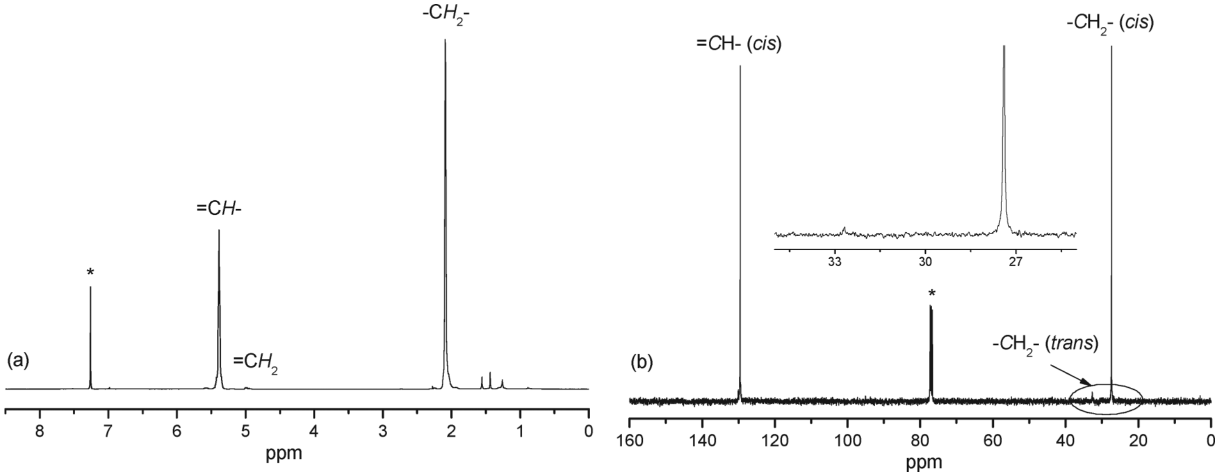


Fig. 3 NMR spectra of the polybutadiene obtained by **C1**/EASC system (entry 1 in Table 4). (a) ^{1}H NMR; (b) ^{13}C NMR; *, $CDCl_3$.

techniques. IR spectra were recorded on a Perkin–Elmer FT-IR 2000 spectrometer by using KBr disks or liquid films for polybutadienes in the range 4000–400 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX-400 instrument in $CDCl_3$ with TMS as the internal standard. Elemental analysis was performed on a Flash EA1112 microanalyzer. The molecular weight and molecular weight distribution of polybutadienes were measured by GPC using Waters 2414 series system in THF at 25 °C calibrated with polystyrene standards.

Toluene was refluxed over sodium-benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M in toluene) was purchased from Akzo Nobel Corp. Diethylaluminium chloride (0.9 M in toluene), ethylaluminum sesquichoride (0.4 M in hexane) and all the anilines were purchased from Acros Chemicals and used directly without further purification. Polymerization grade butadiene was purified by passing it through columns of KOH and molecular sieves. All other chemicals were obtained commercially and used without further purification unless otherwise stated. The compounds, 4-methyl-2,6-diformylphenol and 4-chloro-2,6-diformylphenol, 4-*tert*-butyl-2,6-diformylphenol,[16,27] and the ligands, 3-(2,6-Diisopropylphenylimino)methyl-5-chloro-2-hydroxybenzaldehyde (**L1H**) and 3-(2,4,6-Trimethylphenylimino)methyl-5-chloro-2-hydroxybenzaldehyde (**L2H**)[15] were prepared according to the literature.

Synthesis of 3-(2,6-diisopropylphenylimino)methyl-2-hydroxy-5-methylbenzaldehyde (L3H)

To a solution of 4-methyl-2,6-diformylphenol (0.328 g, 2.0 mmol) and a few drops of glacial acetic acid in absolute ethanol (20 mL), 2,6-diisopropylaniline (0.337 g, 1.9 mmol) in absolute ethanol (10 mL) was added dropwise. The reaction mixture was stirred at 50 °C for 24 h. After the evaporation of ethanol, the resulting mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (40/1) as an eluent. The ligand **L3H** was obtained as a yellow solid in 48% yield (0.312 g). FT-IR (KBr disk, cm^{-1}): 2961, 2922, 2865, 1680 ($\nu_{C=O}$), 1630 ($\nu_{C=N}$), 1590, 1465, 1402, 1361, 1306, 1233, 1180, 1027, 969, 861, 794, 756, 740, 684, 582, 463. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 13.82 (s, 1 H, Ar–O*H*), 10.57 (s, 1 H, C*H*=O), 8.33 (s,1 H, C*H*=N), 7.79 (s, 1 H, Ar–*H*), 7.43 (s, 1 H, Ar–*H*), 7.21 (s, 3 H, Ar–*H*), 2.98 (sept, 2 H, J = 6.8 Hz, C*H*(CH_3)$_2$), 2.38 (s, 3 H, Ar–C*H*$_3$), 1.20 (d, 12 H, J = 6.8 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 189.4 (*C*H=O), 165.9 (*C*H=N), 162.2 (aromatic-*C*–OH), 145.6, 138.6, 132.4, 128.3, 125.8, 124.0, 123.4, and 119.8 (aromatic-*C*), 28.2 (*C*H(CH_3)$_2$), 23.5 (CH(*C*H$_3$)$_2$), 20.2 (Ar–*C*H$_3$). Anal. Calcd. for $C_{21}H_{25}NO_2$ (323.43): C, 77.98; H, 7.79; N, 4.33. Found: C, 78.42; H, 7.49; N, 4.58.

Synthesis of 3-(2,4,6-trimethylphenylimino)methyl-2-hydroxy-5-methylbenzaldehyde (L4H)

In a manner similar to that described for **L3H**, the ligand **L4H** was prepared as a yellow solid in 56% yield. FT-IR (KBr disk, cm^{-1}): 2965, 2915, 2856, 1672 ($\nu_{C=O}$), 1625 ($\nu_{C=N}$), 1592, 1466, 1386, 1307, 1261, 1202, 1142, 1092, 1025, 967, 858, 803, 625, 586. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 14.02 (s, 1 H, Ar–O*H*), 10.56 (s, 1 H, C*H*=O), 8.36 (s,1 H, C*H*=N), 7.76 (s, 1 H, Ar–*H*), 7.40 (s, 1 H, Ar–*H*), 6.94 (s, 2 H, Ar–*H*), 2.36 (s, 3 H, Ar–C*H*$_3$), 2.31 (s, 3 H, Ar–C*H*$_3$), 2.19 (s, 3 H, Ar–C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 189.4 (*C*H=O), 166.0 (*C*H=N), 162.4 (aromatic-*C*–OH), 144.9, 138.5, 135.0, 132.1, 129.1, 128.2, 128.1, 124.0, and 119.9 (aromatic-*C*), 19.8, 20.1, and 18.4 (Ar–*C*H$_3$). Anal. Calcd. for $C_{18}H_{19}NO_2$ (281.35): C, 76.84; H, 6.81; N, 4.98. Found: C, 76.48; H, 6.82; N, 4.84.

Synthesis of 3-(2,6-diisopropylphenylimino)methyl-2-hydroxy-5-*tert*-butylbenzaldehyde (L5H)

In a manner similar to that described for **L3H**, the ligand **L5H** was prepared as a yellow solid in 55% yield. FT-IR (KBr disk, cm^{-1}): 2962, 2928, 2869, 1686 ($\nu_{C=O}$), 1627 ($\nu_{C=N}$), 1596, 1585, 1463, 1398, 1364, 1307, 1264, 1236, 1223, 1180, 1099, 993, 863, 755, 726, 578, 498. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 13.94 (s, 1 H, Ar–O*H*), 10.60 (s, 1 H, C*H*=O), 8.38 (s, 1 H, C*H*=N), 8.02 (s, 1 H, Ar–*H*), 7.62 (s, 1 H, Ar–*H*), 7.21 (s, 3 H, Ar–*H*), 2.99 (sept, 2 H, J = 6.8 Hz, C*H*(CH_3)$_2$), 1.37 (s, 9 H, C(C*H*$_3$)$_3$), 1.20 (d, 12 H, J = 6.8 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 189.5 (*C*H=O), 166.3 (*C*H=N), 162.2 (aromatic-*C*–OH), 145.4, 141.9, 138.6, 135.1, 129.1, 125.8, 123.8, 123.3, and 119.5 (aromatic-*C*), 34.2 (*C*(CH_3)$_3$), 31.2 (C(*C*H$_3$)$_3$), 28.2 (*C*H(CH_3)$_2$), 23.5 (CH(*C*H$_3$)$_2$). Anal. Calcd. for $C_{24}H_{31}NO_2$ (365.51): C, 78.86; H, 8.55; N, 3.83. Found: C, 78.73; H, 8.51; N, 3.84.

Synthesis of 3-(2,4,6-trimethylphenylimino)methyl-2-hydroxy-5-*tert*-butylbenzaldehyde (L6H)

In a manner similar to that described for **L3H**, the ligand **L6H** was prepared as a yellow solid in 60% yield. FT-IR (KBr disk, cm^{-1}): 2955, 2915, 2866, 1676 ($\nu_{C=O}$), 1628 ($\nu_{C=N}$), 1591, 1464, 1407, 1365, 1308, 1264, 1228, 1203, 1145, 1122, 1034, 995, 852, 844, 794, 758, 636, 589, 580. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 14.09 (s, 1 H, Ar–O*H*), 10.60 (s, 1 H, C*H*=O), 8.40 (s, 1 H, C*H*=N), 8.00 (s, 1 H, Ar–*H*), 7.59 (s, 1 H, Ar–*H*), 6.94 (s, 2 H, Ar–*H*), 2.31 (s, 3 H, Ar–C*H*$_3$), 2.20 (s, 6 H, Ar–C*H*$_3$), 1.36 (s, 9 H, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 189.5 (*C*H=O), 166.3 (*C*H=N), 162.4 (aromatic-*C*–OH), 144.9, 141.7, 135.0, 134.9, 129.1, 128.7, 128.2, 123.8, and 119.6 (aromatic-*C*), 34.2 (*C*(CH_3)$_3$), 31.2 (C(*C*H$_3$)$_3$), 20.8 (Ar–*C*H$_3$), 18.4 (Ar–*C*H$_3$). Anal. Calcd. for $C_{21}H_{25}NO_2$ (323.43): C, 77.98; H, 7.79; N, 4.33. Found: C, 79.68; H, 7.81; N, 4.38.

Synthesis of cobalt(II) complexes C1–C6

To a stirred solution of the ligand (0.5 mmol) at room temperature, an ethanol solution containing one equiv. of $Co(OAc)_2 \cdot 4H_2O$ (0.5 mmol) was added. The reaction mixture was stirred at room temperature for 6 h. Thereafter the solution was concentrated to *ca.* 3 mL and diethyl ether was added. The resulting precipitate was filtered, washed with diethyl ether and dried *in vacuo* to afford an orange or reddish orange powder. All the cobalt complexes were prepared in good yield in this manner.

Complex C1. Obtained as an orange powder in 85% yield. FT-IR (KBr disk, cm^{-1}): 2966, 2925, 2867, 1652, 1620, 1479, 1534, 1643, 1441, 1410, 1384, 1335, 1320, 1218, 1178, 1032, 786, 777, 716, 662. Anal. Calcd. For $C_{44}H_{48}Cl_2Co_2N_2O_8$ (921.63): C, 57.34; H, 5.25; N, 3.04. Found: C, 56.99; H, 5.30; N, 2.98.

Complex C2. Obtained as an orange powder in 78% yield. FT-IR (KBr disk, cm^{-1}): 2973, 2919, 1653, 1621, 1565, 1531, 1481, 1444, 1421, 1200, 1144, 1028, 860, 786, 775, 665. Anal. Calcd. For $C_{38}H_{36}Cl_2Co_2N_2O_8$ (837.47): C, 54.50; H, 4.33; N, 3.34. Found: C, 54.09; H, 4.51; N, 3.21.

Complex C3. Obtained as an orange powder in 67% yield. FT-IR (KBr disk, cm^{-1}): 2965, 2924, 2865, 1647, 1618, 1600, 1588, 1572, 1533, 1465, 1409, 1360, 1334, 1229, 1178, 1049, 997, 876, 829, 802, 775, 717, 662. Anal. Calcd. For $C_{46}H_{54}Co_2N_2O_8$ (880.80): C, 62.73; H, 6.18; N, 3.18. Found: C, 62.45; H, 6.24; N, 3.03.

Complex C4. Obtained as an orange powder in 75% yield. FT-IR (KBr disk, cm^{-1}): 2974, 2952, 2917, 1645, 1620, 1599, 1567, 1536, 1483, 1454, 1410, 1203, 1145, 1051, 998, 852, 777, 712, 664. Anal. Calcd. For $C_{40}H_{42}Co_2N_2O_8$ (796.64): 60.31; H, 5.31; N, 3.52. Found: C, 59.93; H, 5.58; N, 3.17.

Complex C5. Obtained as an orange powder in 75% yield. FT-IR (KBr disk, cm^{-1}): 2963, 2866, 1649, 1618, 1585, 1572, 1532, 1440, 1415, 1362, 1335, 1238, 1222, 1177, 1042, 1020, 839, 776, 665. Anal. Calcd. For $C_{52}H_{66}Co_2N_2O_8$ (964.96): C, 64.72; H, 6.89; N, 2.90. Found: C, 64.57; H, 6.93; N, 2.84.

Complex C6. Obtained as a reddish orange powder in 77% yield. FT-IR (KBr disk, cm^{-1}): 2956, 2918, 2868, 1646, 1618, 1594, 1571, 1530, 1480, 1452, 1411, 1361, 1244, 1223, 1199, 1146, 1045, 1019, 852, 781, 715, 664. Anal. Calcd. For $C_{46}H_{54}Co_2N_2O_8$ (880.80): C, 62.73; H, 6.18; N, 3.18. Found: C, 62.56; H, 6.23; N, 3.20.

X-ray crystallography for complex C2

Single-crystal X-ray diffraction studies for complex **C2** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 Package.[28]

Crystal data for C2. $C_{38}H_{36}Cl_2Co_2N_2O_8$, $M_w = 837.45$ g mol^{-1}, $T = 293(2)$K, tetragonal crystal system, space group I4(1)/a, $a = 23.979(3)$ Å, $b = 23.979(3)$ Å, $c = 13.130(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 7549.8(16)$ Å^3, $Z = 8$, $D_c = 1.474$ Mg m^{-3}, $\mu = 1.074$ mm^{-1}, $F(000) = 3440$, crystal size = $0.04 \times 0.04 \times 0.02$ mm^3, 15500 reflections collected, 3330 unique which were used in all calculations. Empirical absorption correction made, T_{min} and T_{max} 0.9586 and 0.9790 respectively. GOF = 0.908, Final R indices [$I > 2\sigma(I)$] $R_1 = 0.0616$, w$R_2 = 0.1342$, R indices (all data) $R_1 = 0.2046$, w$R_2 = 0.1857$. Largest diff. peak and hole 0.350 and –0.509 e Å^{-3}.

Polymerization of 1,3-butadiene

Solution polymerizations of 1,3-butadiene in toluene were carried out in a sealed glass reactor (100 mL) with a rubber septum and a connection to a vacuum system. The reactor was charged with the desired amounts of precatalyst and cocatalyst solutions, followed by the addition of PPh_3 when required. The mixture was stirred for 2 min at the desired temperature and followed by the addition of a solution of 1,3-butadiene in toluene. The polymerization reaction was carried out by vigorous stirring of the reaction mixture at the various temperature. After the polymerization, the resulting solution was poured into a large amount of acidified ethanol (5% v/v solution of HCl) containing 2,6-di-*tert*-butyl-4-methylphenol as a stabilizer. The precipitated polymers were filtered, washed with ethanol and dried under vacuum at 50 °C overnight.

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