



Synthesis, characterization and butadiene polymerization studies of cobalt(II) complexes bearing bisiminopyridine ligand

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ABSTRACT

A series of 2,6-bis(imino)pyridyl Co(II) complexes of the general formulas $[2,6-(\text{ArN}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}]\text{CoCl}_2$ (Ar = $-\text{C}_6\text{H}_5$, **3a**; $2\text{-MeC}_6\text{H}_4$, **3b**; $2\text{-EtC}_6\text{H}_4$, **3c**; $2\text{-}^i\text{PrC}_6\text{H}_4$, **3d**; $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$, **3e**; $4\text{-}^i\text{PrC}_6\text{H}_4$, **3f**; $4\text{-FC}_6\text{H}_4$, **3g**; $4\text{-CF}_3\text{C}_6\text{H}_4$, **3h**; $2\text{-FC}_6\text{H}_4$, **3i**; $2,6\text{-F}_2\text{C}_6\text{H}_3$, **3j**; $2\text{-Me-4-FC}_6\text{H}_3$, **3k** and $2,6\text{-Me}_2\text{-4-FC}_6\text{H}_2$, **3l**) and $[2,6-(\text{ArN}=\text{CH})_2\text{C}_5\text{H}_3\text{N}]\text{CoCl}_2$ (Ar = $-\text{C}_6\text{H}_5$, **3m**; $2\text{-EtC}_6\text{H}_4$, **3n** and $4\text{-}^i\text{PrC}_6\text{H}_4$, **3o**) have been synthesized and characterized. The structures of new complexes **3a**, **3f–3h** and **3m–3o** are further confirmed by X-ray crystallography. All complexes adopt distorted trigonal bipyramidal configuration with the equatorial plane formed by the pyridyl nitrogen atoms and the two chlorine atoms. In the complexes **3m** and **3o**, three aromatic rings are essentially coplanar, which is in sharp contrast to the other complexes, where three rings are almost orthogonal to each other. With methylaluminoxane (MAO) as cocatalyst in toluene at room temperature, the complexes show moderate to high conversion (42–99%) in butadiene polymerization, producing polybutadiene with tunable *cis*-1,4 structure (77.5–97%) and controllable molecular weight and molecular weight distribution. The catalytic activity, selectivity as well as the molecular weight and molecular weight distribution of the resultant polymer are found to be dependent on the size and nature of substituents on iminoaryl rings and their positions located. By deliberately tuning the ligand structure, more efficient catalyst in terms of high activity and high selectivity can be obtained.

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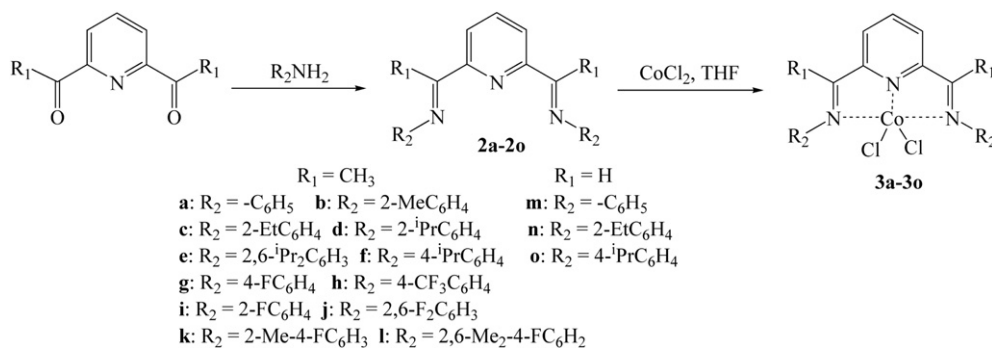
1. Introduction

The past decades have experienced the rapid development of the catalysts for regio- and/or stereoselective polymerization of butadiene, because the resultant polybutadienes have been found extensive and diverse applications in rubber industry. Thus, numerous catalyst systems have been invented in past decades, especially those based on transition metals, which under the presence of aluminum alkyls, aluminum chlorides, MAO or borates, provide polybutadiene in high *cis*-1,4 [1–11], *trans*-1,4 [12–16] or 1,2 configuration [17–23] used as important synthetic rubbers and thermal plastic elastomers. Numerous metal systems, including lithium/sodium, rare earth metal and transition metal recipes have been explored, particular attentions have been paid to the late transition metals such as iron-, nickel- and cobalt-based catalysts, due to the high activity and high selectivity in some systems, particularly the remarkable functional-group tolerance, rendering them competitive in industrial application. Among the systems,

versatile cobalt-based catalysts are much highlighted for initiating regio- and/or stereoselective polymerization of butadiene, especially those for high *cis*-1,4 selectivity, because the resulted polymer is the most important elastomer used for tires and other elastic materials. As a result, a large number of complexes [1,24–34] have been designed to initiate *cis*-1,4 selective polymerization, such as CoCl_2/MAO [33], $\text{CoCl}_2(\text{PR}_3)_2/\text{AlEt}_2\text{Cl}$ [24] and $\text{Co}(\text{salen})_2/\text{MAO}$ [29], while some of them are either heterogeneous, leading to slow initiation and gel formation [25–27], or suffering from comparatively low *cis*-1,4 selectivity [31]. Meanwhile, for some of cobalt catalyst recipes [24,30,33,34], the active species are generated in situ by mixing the components (cobalt compound, donor and activator), therefore, little is known about the structure of precursor and catalyst–polymer correlation, hindering mechanism study and catalyst design for screening more efficient candidates. Thus, investigation of new cobalt catalyst that is homogeneous, well-defined, straightforward and high yielding in synthesis, and providing highly *cis*-1,4 oriented catalysis has still been one of the most fascinating and challenging subjects.

Tridentate ligands such as N,N,N [35–43], N,X,N (X = C, O, S) [44–50] and X,N,X (X = O, P, S) [51–54] ligated complexes have been booming in olefin polymerization over the past decade for

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Scheme 1. Syntheses of complexes (**3a–3o**).

their crucial roles in promoting catalytic activity, improving selectivity as well as controlling molecular weight of products. The impressive catalytic performance observed in 2,6-bis(imino)pyridyl ligated complexes, especially the remarkable activities of iron and cobalt derivatives for ethylene polymerization, indicates the significant scope for incorporating such kind of ligand into late transition metal-based catalysts. Recently, Chirik et al. [55–57] revealed how this ligand system is capable of accepting and donating negative charges, thereby, influencing the redox potential of the coordinated metals. More significantly, a single site active iron-alkyl species bearing bisiminopyridine has been firstly isolated and characterized, which even in the absence of MAO, displayed comparable catalytic properties as compared to the corresponding $\text{FeCl}_2(\text{bisiminopyridine})/\text{MAO}$ systems [55]. A surprising finding of such ligand set in olefin polymerization may also be extrapolated to the area of conjugated diene polymerization. Reports on transition metals bearing such kind of ligands for butadiene polymerization, however, have only started to emerge in the literature [1,14,15,58]. We have reported 2,6-bis(imino)pyridyl ligated transition metal complexes for selectivity-controlled polymerization of butadiene [59], finding the selectivity can be tuned within a wide range from high *cis*-1,4 (97.0%) to high *trans*-1,4 (95.4%) just by altering the metal center. We assume that, the large π -system, featuring all 2,6-bis(imino)pyridyl ligands, to accommodate negative charge has been believed to increase the Lewis-acidity of coordinated metal centers, facilitating interaction with butadiene molecule, therefore,

exerting a positive impact on polymerization activity. More importantly, high regio- and/or stereoselectivity can also be achieved, due to the specified coordination mode from the rigidity of the pincer framework around the metal center [59]. In this report, we present coordination chemistry of new cobalt dichlorides supported by 2,6-bis(iminoaryl)pyridyl ligands and their catalytic behaviors in butadiene polymerization activated by MAO. The substituents on the ligand backbones of the complexes varying from alkyl-free to bulky groups, from electron-donating alkyl groups to electron-withdrawing groups, provide an insight into both electronic and steric effects on their butadiene polymerization performances, which, in turn, renders more powerful catalyst accessible by designing ligand structure.

2. Results and discussions

2.1. Synthesis and characterization of ligands and complexes

A general synthetic route for cobalt complexes used in this study is shown in Scheme 1. The reaction of CoCl_2 with 1 equiv of 2,6-bis(imino)pyridines in THF at room temperature affords cobalt(II) complexes with high yields. The obtained complexes are identified by FTIR and elemental analysis. The IR of the free ligands show that the $\text{C}=\text{N}$ stretching frequencies appear at $1642\text{--}1624\text{ cm}^{-1}$, while in complexes, that shifts toward lower frequencies by $5\text{--}19\text{ cm}^{-1}$ and the intensities are greatly reduced, indicating the occurrence of

Table 1
Crystal data and structure refinements of complexes **3f–3h** and **3m–3o**.

	3f	3g	3h	3m	3n	3o
Formula	$\text{C}_{27}\text{H}_{31}\text{N}_3\text{CoCl}_2$	$\text{C}_{21}\text{H}_{17}\text{F}_2\text{N}_3\text{CoCl}_2$	$\text{C}_{23}\text{H}_{17}\text{F}_6\text{N}_3\text{CoCl}_2$	$\text{C}_{38}\text{H}_{30}\text{N}_6\text{Co}_2\text{Cl}_4$	$\text{C}_{23}\text{H}_{23}\text{N}_3\text{CoCl}_2$	$\text{C}_{25}\text{H}_{27}\text{N}_3\text{CoCl}_2$
Molecular weight	527.38	479.22	579.23	830.36	471.27	499.33
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)2(1)2(1)$	$P-1$	$P21/n$	$P2(1)/n$	$C2/c$	$P2(1)/n$
<i>a</i> (Å)	12.3543(18)	8.9684(5)	13.189(5)	16.8014(14)	11.9187(11)	12.2538(9)
<i>b</i> (Å)	14.073(2)	12.7985(7)	15.525(5)	13.5413(12)	8.9839(8)	9.3736(7)
<i>c</i> (Å)	15.343(2)	22.9214(12)	14.798(5)	18.4366(16)	19.9946(18)	20.8322(15)
α (°)	90.000	101.2960(10)	90.000(5)	90	90	90
β (°)	90	91.6320(10)	111.709(5)	97.624(2)	92.9290(10)	94.0020(10)
γ (°)	90	95.5380(10)	90.000(5)	90	90	90
<i>V</i> (Å ³)	2667.5(7)	2564.9(2)	2815.1(17)	4157.5(6)	2138.2(3)	2387.0(3)
<i>Z</i>	4	2	4	8	4	4
<i>D</i> _{calcd} (Mg/m ³)	1.313	1.571	1.567	1.509	1.464	1.389
Absorp coeff (mm ⁻¹)	0.863	1.222	1.048	1.222	1.067	0.960
<i>F</i> (000)	1100	1224	1332	1924	972	1036
Crystal size (mm)	0.29 × 0.17 × 0.09	0.13 × 0.10 × 0.08	0.18 × 0.12 × 0.09	0.25 × 0.14 × 0.08	0.24 × 0.15 × 0.08	0.22 × 0.11 × 0.11
θ Range (deg)	1.96–25.03	1.63–25.68	1.77–26.06	1.54–25.08	2.04–26.03	1.87–26.03
No. of reflns collected	13,981	14,055	15,468	21,191	5825	12,959
No. of indep reflns	4723 (<i>R</i> _{int} = 0.0361)	9500 (<i>R</i> _{int} = 0.0129)	5571 (<i>R</i> _{int} = 0.0266)	7339 (<i>R</i> _{int} = 0.0678)	2110 (<i>R</i> _{int} = 0.0264)	4679 (<i>R</i> _{int} = 0.0257)
No. of data/restraint/params	4723/0/304	9500/0/604	5571/0/343	7339/2/497	2110/0/143	4679/0/284
GOF on <i>F</i> ²	1.010	1.026	1.047	0.992	0.963	1.027
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0386	0.0344	0.0479	0.0601	0.0364	0.0364
<i>wR</i> ₂	0.0786	0.0828	0.1280	0.1475	0.0886	0.0866

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