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# Synthesis, characterization, and butadiene polymerization of iron(III), iron(II) and cobalt(II) chlorides bearing 2,6-bis(2-benzimidazolyl)pyridyl or 2,6-bis(pyrazol)pyridine ligand

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# ABSTRACT

Iron(III), iron(II) and cobalt(II) complexes bearing neutral N,N,N-tridentate ligand (Fe(III)L1, 1a; Fe(III)L2, 1b; Fe(III)L3, 1c; Fe(III)L4, 2a; Fe(III)L5, 2b; Fe(III)L6, 2c; Fe(II)L1, 3a; Fe(II)L2, 3b; Fe(II)L3, 3c; Fe(II)L4, 4a; Fe(II)L5, 4b; Fe(II)L6, 4c; CoL1, 5a; CoL2, 5b; CoL3, 5c; CoL5, 6b and CoL6, 6c) have been synthesized from the metal chlorides (FeCl<sub>3</sub>, FeCl<sub>2</sub>·4H<sub>2</sub>O or CoCl<sub>2</sub>) by treating the corresponding ligands (2,6-bis(benzimidazol-2-yl)pyridine, L1; 2,6-bis(1'-ethylbenzimidazol-2'-yl)pyridine, 12: bis(1'-benzylbenzimidazol-2'-yl)pyridine, L3; 2,6-bis(pyrazol)pyridine L4; 2,6-bis(3-methylpyrazol) pyridine, L5 or 2,6-bis(3,5-dimethylpyrazol)pyridine, L6. The complexes are characterized by FTIR and elemental analyses. The structures of complexes 1a, 1b, 3a, 3b, 3c, 4a, 5a, 5b, 5c and 6c are further confirmed by X-ray crystallographic analyses. Six coordination iron(III) (1a, 1b and 1c) and iron(II) (3c\*DMF) complexes adopt a distorted octahedral configuration with the equatorial plane formed by the three nitrogen atoms and one chlorine atom, while the iron(II) (3a, 3b and 4a) and cobalt complexes (5a, **5b**, **5c** and **6c**) adopt a trigonal bipyramidal configuration with the equatorial plane formed by the pyridyl nitrogen atoms and the two chlorine atoms. All complexes are evaluated as precursors for 1,3-butadiene polymerization in the presence of cocatalyst in toluene at room temperature. Iron(III) and iron(II) bearing the same ligand show comparable catalytic performance. The catalytic activity and selectivity are significantly influenced by the ligand structure, with the latter being tunable within a wide range from cis-1,4 to trans-1,4. Cobalt complexes, in combination with either MAO or aluminum chlorides shown high activity, and high cis-1,4-selectivity irrespective of the structure of ligand backbone.

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# 1. Introduction

The past half century has witnessed tremendous growth in interest of the applicable catalysts for selective polymerization of conjugated dienes (butadiene and isoprene) as their extensive and diverse applications in automobile industry [1-5]. Therefore, diversified catalyst recipes based on transition metals and lanthanides have been invented to afford polybutadiene and polyisoprene with various enchainments [6–20]. Excellent activity and selectivity, even the superior controllable features in terms of microstructures, molecular weight as well as molecular weight distribution of the resultant polymers, have been achieved, though mostly interested in fundamental researches and practical application of the catalysts have not yet been demonstrated. Considering

the potent application of the resultant polymers, attention has been particularly focused on the late transition metals such as iron and cobalt-based catalysts, the advantage of which are manifold, spanning from the ease of preparation and handling to the use of low-cost metals with negligible environmental impact.

We have been interested in iron and cobalt catalyzed butadiene polymerization over the past decades. Cobalt-based catalysts are known as the versatile recipes for initiating *cis*-1,4, *trans*-1,4 and 1,2- polymerization of butadiene, among them, much attention is paid to those for high *cis*-1,4-selectivity, because the resulted polymer is the most important elastomer used for tires and other elastic materials. Thus, a large number of systems [21–31] have been screened for initiating *cis*-1,4 selective polymerization. To understand the nature of active species of cobalt catalysts, effort has also been paid to the well-defined cobalt-based catalysts as well as exploring their catalytic performance of homogeneous model systems. Comparatively, researches on iron catalytic system have been limited mainly because of the low activity and poor

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selectivity. The activity has been improved by using 1,10phenanthroline or 2,2'-bipyridine as the supporting ligands, and high selectivity (1,2-selectivity: 91%) can also be available at -78 °C, at expense of activity [32,33]. Recently, progresses have been made since dialkylphosphite and phosphate are invented as an important additive in iron-based catalyst in our group, with which syndiotactically enriched 1.2-polybutadiene (1.2-: 87–95%, pentad rrrr: 65–95%) has been obtained under benign polymerization conditions [18,20,34-38]. To date, iron catalysts are mainly for 1,2selectivity, and those based on high 1,4-selectivity are quite few [39-43]. Meanwhile, for some of cobalt, and most iron catalyst recipes [18,20,21], the active species are generated in situ by mixing the components (cobalt or iron compound, additive and cocatalyst), therefore, little is known about the structure of precursor and catalyst-polymer correlation. Thus, investigation of new cobalt and iron catalyst that is homogeneous, well-defined, straightforward and high yielding in synthesis, and providing highly 1,4 orientated catalysis has still been the subject.

Over the past decade, the use of neutral tridentate ligands has witnessed a momentous advancement in olefin area. This ligand set has led to success in olefin polymerization catalysis due to the ability to manipulate catalytic activity, comonomer incorporation, as well as molecular weight, and stereochemistry of the polymer produced by choice of substituents, leading to rational catalyst design. Especially, the impressive catalytic performance observed in the 2,6-bis(imino)pyridyl ligated transition metal derivatives for ethylene polymerization and oligomerization, indicates the significant scope for incorporating such kind of ligand into late transition metal-based catalysts. As such, various analogous tridentate ligands such as N^N^N [44–52], N^X^N (X = C, O, S et al.) [53–59] and  $X^N^X$  (X = 0, P, S et al.) [60,61] ligated complexes have also been proved to effectively promote activity, improve selectivity, and govern the molecular weight of products. The exceptional performance of such ligand set in olefin polymerization may also be relevance to butadiene area and catalytic performance of transition metals bearing such set of ligands for butadiene polymerization, however, is less established [12,13,15,62,63]. We have reported the high active 2,6-bis(imino)pyridyl ligands ligated transition complexes for selectivity-controlled polymerization of butadiene [39,42,43], and found the selectivity could be manipulated within a wide range, from high cis-1,4 (97.0%) to high trans-1,4 (95.4%) just by either altering the metal center or modifying the ligand environments. The exceptional performance of 2,6-bis(imino)pyridyl prompts a more thorough investigation of other N,N,N-tridentate ligand derivatives. In this manuscript, we present coordination chemistry of new iron(II), iron(III), cobalt dichlorides supported by 2,6-bis(2-benzimidazolyl)pyridyl or 2,6-bis(pyrazol)pyridine ligands and their catalytic behaviors in butadiene polymerization. The combination of tunable ligand environment and metal center could also allow easy stereo and electronic modification, which are both highly desirable in the study of ligand and metal effect on both activity and selectivity, ultimately open a door to desired catalyst recipes.

#### 2. Results and discussion

# 2.1. Syntheses and characterization of ligands and complexes

2,6-bis(2-benzimidazolyl)pyridine (**L1**) could be synthesized from condensation of 1,2-phenylenediamines and pyridine-2,6-dicarboxylic acid in the presence of polyphosphoric acid (PPA) at 240 °C [52]. The 2,6-bis(2-benzimidazolyl)pyridine derivatives (**L2** and **L3**) could be readily prepared by N-alkylation of **L1** in acetone at or above room temperature. The stretching frequencies of all ligands fall within the following ranges:  $\nu_{(N-H)}$  is about 3055 cm<sup>-1</sup> for **L1**,  $\nu_{(C=C)}$  is between 1584 and 1600 cm<sup>-1</sup>, and  $\nu_{(C=N)}$  is between 1567 and 1572 cm<sup>-1</sup>. Ligands (**L4–L6**) were prepared as the reported methods [64]. The ligands synthesized were also confirmed by elemental analysis and NMR spectra.

Complexes (**1a–6c**) were synthesized in high yields by reaction of the metal chlorides (FeCl<sub>3</sub>, FeCl<sub>2</sub>·4H<sub>2</sub>O, CoCl<sub>2</sub>) with one equivalent of the corresponding ligands (L1-L6, Scheme 1) in THF at room temperature. The products were collected by filtration, washed with diethyl ether and dried under vacuum. They are stable toward oxidation and hydrolysis. The one-step complexation at room temperature, giving high yields (85–91%), represents an additional advantage. The elemental analyses results reveal that the components of all complexes are in accord with the formula MtCl<sub>x</sub>L. The IR spectra of the free ligands show that the C=N stretching frequencies appear at 1561–1577 cm<sup>-1</sup>. In complexes, the C=N stretching vibrations shift toward lower frequencies 1667–1707 cm<sup>-1</sup> and are greatly reduced in intensity, which indicated the coordination interaction between the imino nitrogen atoms and the metal ions. In order to establish the coordination mode of the complexes, complexes 1a, 1b, 2a, 3a, 3b, 3c, 5a, 5b, 5c and **6c** were selected for structural analysis by single-crystal X-ray diffraction and the crystal structures of 1b, 3c and 5a were depicted in Fig. 1, Fig. 2 and Fig. 3, respectively. Crystal data and collection parameters were collected in Table 1 and Table 2, and bond distances and angles were compiled in Table 3 and Table 4.

X-ray analysis revealed that the conformers of **1a** and **1b** (Fig. 1) have essentially identical structures, both displaying a slightly



 $Scheme \ 1. \ Synthesis \ of \ 2,6-bis(2-benzimidazolyl) pyridine \ derivatives \ (L_1-L_3) \ and \ their \ complexes \ (1a-1c, \ 3a-3c \ and \ 5a-5c).$ 



Fig. 1. ORTEP view of the complex 1b, drawn at 35% of probability. Hydrogen atoms were omitted for clarity.

distorted octahedron geometry around the iron(III) center with the equatorial plane defined by N1 and three chlorines. Complex 1a has approximate  $C_{2\nu}$  symmetry about the plane, while **1b** displays  $C_s$ symmetry. All the bond angles in the equatorial plane are very close to a right angle  $(N(1)-Fe-Cl(1), 87.49(4)^{\circ}; N(2)-Fe-Cl(2),$ 88.26(4)°; N(3)-Fe-Cl(1), 89.66(5)°; N(3)-Fe-Cl(2), 89.82(5)°). The axial angle N(2)–Fe–N(3) deviates significantly from linearity (147.91(6)° 1a; 146.16(10)° 1b). The deviations of the metal ion from the plane formed by the coordinated nitrogen atoms in 1a and 1b are 0.0786, and 0.0631 Å, respectively. The iron center is coordinated to pyridyl nitrogen atom (N1), and sp2 hybridized nitrogen atoms instead of sp3 nitrogen in the benzimidazole ring. The Fe-N(pyridyl) (Fe-N1) bond distances of complexes are about 0.027–0.077 Å longer than the Fe–N2 and Fe–N3 bond distances, sharply contrast to those found in the 2,6-bis(imino)pyridyl iron(II), iron(III) and cobalt complexes [42,43], where the bond of Fe–N(pyridyl) is unanimously shorter than that of Fe-N(iminoaryl), presumably due to the stronger interaction between iron and benzimidazole. It is notable that different N-substituents in the ligands also have certain influence on the Fe1-N bond length, though the exact reason is unclear. The Fe-N1 distance (2.1688(15) Å) in **1a** is shorter than the bond (2.204(2) Å)in the analogous 1b, while both Fe-N2 (2.1385(16) Å) and Fe-N3 (2.1419(16) Å) bonds of former complex are longer than those (2.1271(18) Å) found in the latter analog. Three chlorine ligands are



Fig. 2. ORTEP view of the complex 3c, drawn at 35% of probability. Hydrogen atoms were omitted for clarity.



Fig. 3. ORTEP view of the complex 5a, drawn at 35% of probability. Hydrogen atoms were omitted for clarity.

in a meridional geometry, where Fe–Cl bond distances located at *trans* position (Fe–Cl(3)) to pyridine are shorter than those at *cis* position to pyridine (Fe–Cl(2) and Fe–Cl(3)) in both complexes. The corresponding Fe–Cl bond distances in two complexes are comparable, suggesting little effect of the N-substitutes. The planes of the pyridyl rings are essentially coplanar to two benzimidazoyl rings in the both complexes.

Complex **3c\*DMF** (Fig. 2), with the structural features similar to **1a.** the coordination geometry around the iron center can also be described as a distorted octahedron because of the coordination of one DMF molecule, which is also observed in nickel and iron complexes, where one methanol is coordinated [65,66]. Similarly, the iron center is coordinated to nitrogen atom in pyridyl ring and sp2 hybridized nitrogen atom instead of sp3 nitrogen atom in the benzimidazole ring, forming two fused-membered rings with N-Fe-N angle of 73.36(10)° (N1-Fe1-N2, N1-Fe1-N3), in which the iron atom lies slightly out of the equatorial plane by 0.0651 Å. The two benzimidazole planes are both nearly coplanar to the pyridyl plane with a dihedral angle of about 4.8°. The benzyl ring is individually perpendicular to the pyridyl rings as angles of nearly 88.0°. As expected, the bond lengths of Fe-N are significantly different: the Fe1–N1 bond length (2.182(5) Å) is longer than those of Fe1-N2 and Fe1-N3 (2.150(3) Å), in which the differences are virtually identical to those seen in the above discussed iron(III) analogs. However, there is an unexceptional asymmetry in the two Fe-Cl linkages because of the presence of one DMF molecule, with Fe1–Cl(1) being about 0.1052 Å, significantly longer than Fe1–Cl(2) in two terminal Cl in trans-location, which is also observed in the iron(III) complex.

In the solid state of complexes 3a, X-ray analysis revealed displays a slightly distorted trigonal bipyramidal configuration, with the iron atom surrounded by a tridentate 2,6bis(benzimidazolpyridine) and two terminal chlorides, where the nitrogen atom (N(2)) of the pyridyl nitrogen and two chlorine atoms compose an equatorial plane and the central iron atom slightly deviates by 0.0567 Å from this plane. The three equatorial angles N(1)-Fe-Cl(1), N(1)-Fe-Cl(2) and Cl(1)-Fe-Cl(2) are 145.46(7)°, 102.54(6)° and 111.96(4)°, respectively, and the axial Fe–N bonds subtend an angle of  $144.67(9)^{\circ}$  (N(2)–Fe–N(3)). The dihedral angle between the equatorial plane and the pyridyl plane is 87.9°. The two benzimidazole planes are essentially coplanar to pyridyl ring, and nearly perpendicular to the equatorial plane with the dihedral angles of 89.5° and 89.1°. The iron center is coordinated to nitrogen atom in pyridyl ring (N1) and sp2 hybridized nitrogen (N2 and N3) atom, too. Iron complexes 3a and 3b shown roughly identical structures, and differ mainly in the orientation of the FeCl<sub>2</sub> moiety. In complex **3b**, the bond distance of Fe-N1

Table 1	
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Crystal data and data collection parameters of iron complexes.

	1a·2DMF	1b	<b>3a</b> · DMF	3b	<b>3c</b> · DMF
Formula	C <sub>25</sub> H <sub>25</sub> N <sub>7</sub> O <sub>2</sub> Cl <sub>3</sub> Fe	C <sub>23</sub> H <sub>21</sub> N <sub>5</sub> Cl <sub>3</sub> Fe	C22H18N6OCl2Fe	C <sub>23</sub> H <sub>21</sub> N <sub>5</sub> Cl <sub>2</sub> Fe	C <sub>36</sub> H <sub>32</sub> N <sub>6</sub> OCl <sub>2</sub> Fe
Molecular weight	617.72	529.65	509.17	494.20	691.43
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	P21/c	Pnma	P21/n	P-1	Cm
a (Å)	11.6132(4)	15.6479(7)	14.5862(6)	8.8979(6)	9.0444(7)
b (Å)	11.3896(4)	15.9379(7)	7.7262(3)	9.6977(7)	16.2526(13)
c (Å)	21.7169(7)	9.0570(4)	19.8126(9)	13.0379(9)	10.4674(8)
$\alpha$ (deg)	90	90.00	90.00	92.8820(10)	90.00
$\beta$ (deg)	103.4360(10)	90.00	102.6230(10)	103.8960(10)	96.4450(10)
$\gamma$ (deg)	90	90.00	90.00	95.7280(10)	90.00
$V(Å^3)$	2793.87(16)	2258.77(17)	2178.83(16)	1083.43(13)	1528.9(2)
Ζ	4	4	4	2	2
$D_{calcd}$ (Mg/m <sup>3</sup> )	1.469	1.557	1.552	1.515	1.502
Absorp coeff $(mm^{-1})$	0.863	1.045	0.966	0.964	0.709
F(000)	1268	1084	1040	508	1040
Crystal size (mm)	$0.32 \times 0.21 \times 0.18$	$0.33\times0.23\times0.18$	$0.33 \times 0.24 \times 0.16$	$0.33\times0.21\times0.15$	$0.23 \times 0.22 \times 0.12$
$\theta$ Range (deg)	1.80 to 26.08	2.56 to 26.09	1.58 to 26.10	1.61 to 26.02	1.96 to 26.15
No. of reflns collected	15227	11981	11775	6057	4235
No. of indep reflns	5530	2328	4322	4119	2408
	$(R_{\rm int} = 0.0218)$	$(R_{\rm int} = 0.0290)$	$(R_{\rm int} = 0.0273)$	$(R_{\rm int} = 0.0110)$	$(R_{\rm int} = 0.0196)$
No. of data/restraints/params	5530/0/347	2328/0/155	4322/0/291	4119/0/282	2408/2/216
GOF on F <sup>2</sup>	1.034	1.015	1.098	1.054	1.045
$R_1$ (I > 2sigma(I))	0.0303	0.0329	0.0424	0.0296	0.0411
wR <sub>2</sub>	0.0865	0.1182	0.1389	0.0785	0.0999

(2.1826(15) Å) is significantly longer than those of Fe–N2 (2.1460(15) Å) and Fe–N3 (2.1513(15) Å), while in the **3a**, there is an exceptional asymmetry, the corresponding distance of Fe-N1 is 2.173(2) Å, shorter by about 0.018 Å than Fe-N3 (2.191(2) Å), but longer by 0.004 A° than Fe-N2 bond (2.169(2) Å), which is also remarkably different from the previous reported tridentate N3 ligand systems [39,43]. The two Fe-Cl bond lengths in 3b just show a slight difference between the Fe1–Cl2 (2.1513(15) Å) and Fe1–Cl1 (2.3184(5) Å), but the two Fe–Cl bond lengths in **3a** are substantially different (2.2880(9) Å, 2.2880(9) Å). The oxidation state of iron on Fe-N and Fe-Cl bond distance are also observable: the Fe(III)–N distances (1a) are all shorter than those corresponding values found in the Fe(II) (3a), probably due to the much stronger interaction between iron center and nitrogen atoms in 1a, while the elongated Fe(III)-Cl bond distance are possibly resulted from a more congested environment around the iron center.

The cobalt complexes **5a** (Fig. 3), **5b** and **5c** have an essentially identical structure, differ slightly in the orientation of the CoCl<sub>2</sub> moiety. The coordination geometry around the cobalt center is a distorted trigonal bipyramid, similar to the five coordinated Fe(II) analogs, in which the pyridine-nitrogen (N(1)) and two chlorine atoms form the equatorial plane, with total value of three equatorial angles N1-Co-Cl1, N1-Co-Cl2 and Cl1-Co-Cl2 in each complex are equal to 360°, while the cobalt atom lies slightly out of the equatorial plane by 0.0356 Å in **5a**, 0.0407 Å in **5b** and 0.0343 Å in **3c**. The axial positions are occupied by the other two sp2 nitrogen atoms N(2) and N(3). The N(2)–Co–N(3) moiety deviates significantly from linearity (**5a**: N(2)-Co(1)-N(3) 146.00(7)°; **5b**: 141.8(2)°; **5c**: 144.21(7)°), a distortion as a consequence of satisfying the tridentate chelating constraints of the ligand. The equatorial planes of these two complexes are nearly perpendicular to two benzimidazole rings, with average dihedral angles of 88.4° in

#### Table 2

Crystal data and data collection parameters of 4a and cobalt complexes.

	4a	<b>5a</b> · DMF	5b	5c	<b>6c</b> · DMF
Formula	C <sub>11</sub> H <sub>9</sub> N <sub>5</sub> Cl <sub>2</sub> Fe	C22H20N6OCl2C0	C <sub>23</sub> H <sub>21</sub> N <sub>5</sub> Cl <sub>2</sub> Co	C33H25N5Cl2C0	C <sub>18</sub> H <sub>24</sub> N <sub>6</sub> OCl <sub>2</sub> Co
Molecular weight	337.98	514.27	497.28	621.41	470.26
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P21/c	P21n	P-1	P-1	P-1
a (Å)	10.6816(8)	14.6172(6)	8.902(5)	8.7617(7)	8.197(6)
<i>b</i> (Å)	8.0290(6)	7.7043(3)	9.662(5)	12.4505(10)	11.510(9)
<i>c</i> (Å)	15.1952(12)	19.6714(8)	13.109(7)	13.6184(11)	11.856(9)
$\alpha$ (deg)	90	90.00	92.846(9)	71.9870(10)	88.381(11)
$\beta$ (deg)	93.4260(10)	102.3420(10)	103.611(9)	89.4920(10)	75.101(12)
$\gamma$ (deg)	90	90.00	95.032(9)	81.5180(10)	77.556(12)
$V(Å^3)$	1300.85(17)	2164.10(15)	1088.7(10)	1396.26(19)	1055.2(13)
Ζ	4	4	2	2	2
D <sub>calcd</sub> (Mg/m <sup>3</sup> )	1.726	1.578	1.517	1.478	1.480
Absorp coeff $(mm^{-1})$	1.561	1.069	1.055	0.839	1.088
F(000)	680	1052	510	614	972
Crystal size (mm)	$0.34\times0.24\times0.16$	$0.28\times0.18\times0.12$	$0.33\times0.25\times0.23$	$0.33\times0.21\times0.18$	$0.33 \times 0.21 \times 0.15$
$\theta$ Range (deg)	1.91 to 26.04	1.58 to 26.10	1.60 to 24.97	1.57 to 26.17	1.78 to 25.99
No. of reflns collected	6966	11615	6422	7824	5787
No. of indep reflns	2562 ( $R_{int} = 0.0165$ )	$4301(R_{int} = 0.0258)$	$3785 (R_{int} = 0.0761)$	5506 ( $R_{int} = 0.0186$ )	$3999 \ (R_{\rm int} = 0.0634)$
No. of data/restraint/params	2562/0/172	4301/0/299	3785/0/282	5506/0/370	3999/0/259
GOF on F <sup>2</sup>	1.051	1.105	0.948	1.004	0.967
$R_1$ (I > 2sigma(I))	0.0243	0.0295	0.0882	0.0344	0.0890
wR <sub>2</sub>	0.0671	0.0834	0.2354	0.0837	0.2422

Table 3	
Selected bond distances (Å) and angles (°) of iron complexes	1a. 1b. 4a. 3a. 3b and 3c.

	1a 2DMF	1b	3a · DMF	3b	3c DMF	4a
Fe–N1	2.1688(15)	2.204(2)	2.173(2)	2.1826(15)	2.182(5)	2.1539(14)
Fe-N2	2.1385(16)	2.1271(18)	2.169(2)	2.1460(15)	2.150(3)	2.1833(14)
Fe-N3	2.1419(16)	2.1271(18)	2.191(2)	2.1513(15)	2.150(3)	2.1860(15)
Fe-Cl1	2.3311(6)	2.3874(9)	2.2880(9)	2.3184(5)	2.4871(15)	2.3269(5)
Fe-Cl2	2.3838(5)	2.3319(9)	2.3653(9)	2.3566(5)	2.3819(16)	2.3048(5)
Fe-Cl3	2.2686(5)	2.2500(10)	_	-	2.283(4) (Fe-O1)	_
N1-Fe-N3	73.93(6)	73.08(5)	73.14(9)	73.40(6)	73.36(10)	72.66(5)
N1-Fe-N2	73.98(6)	73.08(5)	73.73(9)	73.52(6)	73.36(10)	72.22(5)
N3-Fe-N2	147.91(6)	146.16(10)	144.67(9)	141.56(6)	145.90(19)	142.87(6)
N1-Fe-Cl1	87.49(4)	85.29(7)	145.46(7)	158.00(4)	85.89(13)	139.08(4)
N3-Fe-Cl1	89.66(5)	88.86(5)	98.31(6)	102.03(4)	92.42(9)	105.04(4)
N2-Fe-Cl1	88.22(5)	88.86(5)	101.98(7)	101.27(4)	92.42(9)	93.75(4)
N1-Fe-Cl3	177.31(5)	178.69(7)	_	_	87.78(17) (N1-Fe-O1)	_
N3-Fe-Cl3	104.39(5)	106.92(5)	-	-	85.76(9) (N3-Fe-O1)	-
N2-Fe-Cl3	107.70(5)	106.92(5)	-	-	85.76(9) (N2-Fe-O1)	-
Cl1-Fe-Cl3	94.62(2)	93.39(4)	-	-	173.67(14) (Cl1-Fe-O1)	-
N3-Fe-Cl2	89.82(5)	89.31(5)	100.24(6)	103.68(4)	106.61(10)	98.41(4)
N2-Fe-Cl2	88.26(4)	89.31(5)	98.57(7)	99.41(4)	106.61(10)	104.36(4)
N1-Fe-Cl2	85.20(4)	88.44(7)	102.54(6)	97.29(4)	179.50(13)	109.69(4)
Cl1-Fe-Cl2	172.53(2)	173.73(3)	111.96(4)	104.68(2)	94.60(6)	111.015(19)
Cl3–Fe–Cl2	92.73(2)	92.87(4)	_	_	91.73(13)	_
					(01–Fe–Cl2)	-

5a, 83.7° in 5b and 83.7° in 5c. The two benzimidazole rings lie almost coplanar to the pyridyl plane. The benzyl moiety in **3c** is almost orthogonal to the other rings, as observed in the iron(II) 2c. The effect of substituents at sp3 nitrogen (N3 and N4) is also reflected in the Co–N and Co–Cl bond lengths not in each complex but also among three complexes. Following the same trend observed in iron(II) complexes, Co-N1 distances in N-substituted **5b** and **5c** are slightly longer that Co–N1 and Co–N2, while in **3a**, that of Co-N1 is intermediate between two Co-N2 and Co-N3. The corresponding Co-N distances among the three complexes are also different and follow the trends, Co–N(1): **5b** (2.170(6) Å) > 5a(2.1358(18) Å) > 3c (2.1345(17) Å); Co-N(2): 5a (2.1360(17) Å) > 5b(2.118(6) Å) > 5c (2.1060(19) Å); Co-N(2): 5a (2.1427(17) Å) > 5b(2.122(6) Å) > **5c** (2.1069(18) Å), while average Co–Cl distance: **5b** (2.3245 Å) > 5a (2.3055 Å) > 5c (2.3031 Å) and Cl1-Co-Cl2changes in this way: **5a**  $(111.56(3)^{\circ}) > 5c$   $(107.64(2)^{\circ}) > 5b$ (104.50(8)°). Clearly the introduction of electron withdrawing substituents in the ortho-positions of the phenyl rings has a pronounced effect on the structure, and this is also likely to affect the catalytic activities. As compared with those seen in iron(II) analogs (3a, 3b), Co-N and Co-Cl (5a, 5b) are all shorted by 0.01-0.05 Å, most probably due to the reduced Co<sup>2+</sup> radius, while no significant variation regarding either N-M-N, N-Mt-Cl or Cl-Mt-Cl is found.

Table 4	
Selected bond distances (Å) and angles (°) of cobalt complexes 5a, 5b, 5c an	d <b>6c</b> .

	5a · DMF	5b	5c	6c · DMF
Co-N1	2.1345(17)	2.170(6)	2.1358(18)	2.069(5)
Co-N2	2.1360(17)	2.118(6)	2.1060(19)	2.162(5)
Co-N3	2.1427(17)	2.122(6)	2.1069(18)	2.158(5)
Co-Cl1	2.2825(6)	2.309(2)	2.2993(6)	2.282(2)
Co-Cl2	2.3284(6)	2.338(2)	2.3069(6)	2.287(2)
N1-Co-N3	74.31(6)	73.7(2)	74.79(7)	74.41(18)
N1-Co-N2	74.62(6)	74.7(2)	73.95(7)	75.00(18)
N3-Co-N2	146.00(7)	141.8(2)	144.21(7)	149.40(18)
N1-Co-C11	147.02(5)	160.27(17)	155.47(5)	124.26(17)
N3-Co-Cl1	98.38(5)	101.90(18)	100.69(5)	100.69(16)
N2-Co-Cl1	100.13(5)	100.66(17)	100.48(5)	95.99(15)
N3-Co-Cl2	101.02(5)	103.77(17)	103.49(5)	96.52(16)
N2-Co-Cl2	98.33(5)	99.82(17)	97.12(5)	99.65(17)
N1-Co-Cl2	101.41(5)	95.21(17)	96.81(5)	121.26(16)
Cl1-Co-Cl2	111.56(3)	104.50(8)	107.64(2)	114.48(7)

2.2. Butadiene polymerization behaviors of complexes activated by MMAO or aluminum chlorides

Recently, we have been engaged in the stereospecific polymerizations of 1,3-conjugated dienes [18,20,39,42,43], which is a very important process in the chemical industry to afford products that are among the most significant and widely used rubbers. Therefore these complexes have been tested as precatalysts for butadiene polymerization. The generated homogeneous catalysts showed versatile catalytic performances and the selected polymerization data were summarized in Table 5. As compared with catalytic performance of the naked cobalt chloride, the attached ligands has a significant role on promoting the catalytic activity as well as improving the selectivity as evidenced from the remarkable improved catalytic properties of the activated corresponding complexes in butadiene polymerization.

Iron(III) complex **1a**, in combination with MMAO exhibits high activity and high selectivity, reaching monomer conversion of 91% within 4 h at room temperature, affording polybutadiene with 80.2% of cis-1,4 and 11.7% of trans-1,4 regularity, however, switching to activator AlEt<sub>2</sub>Cl, the formed system shows completely no activity toward butadiene. It is evident to find the ligand effect also plays a significant role in control of both activity and selectivity, incorporation of either ethyl (1b) or benzyl group (1c), instead of the hydrogen (1a) on the nitrogen atom of the benzimidazole ligand leads to a sharply decrease in both selectivity and monomer conversion. Applying catalyst **1b**, only a small amount of polymer (polymer yield, 15%) is obtained with *cis*-1,4 moderate selectivity of 55.4%. With N-benzyl substituted catalyst 1c, comparatively, only trace polymer is obtained. Evidently, steric argument from Nsubstituent could not rationalize the difference, as they are too far to sterically affect the metal center. Tentatively, these results suggest that N-H functionality, which could be deprotonated to give anionic amide ligands when activated by MMAO, is assumed to be essential for high activity, possibly selectivity as well with this ligand system. The anionic amide ligands could be free or form N-Al species (anion-cation pair) which may act to increase catalytic activity. This observation is also consistent with the previous reports [52], although the mechanism is not clear yet. These hydrido tridentate ligands thus offer a mix of donor characters that provides the metal unique environment throughout the catalytic cycle. These features could also offer an explanation to the rare cis-

Table 5
Polymerization of 1,3-butadiene with 2,6-bis(2-benzimidazolyl)pyridine or 2,6-bis(pyrazolyl)pyridine iron and cobalt complexes.

Entry	Complex	Al	Al/Fe (Co)	Yield (%)	$M_n$	$M_w/M_n$	Microstructure (%)		
							Cis-1,4	Trans-1,4	1,2
1	1a	MMAO	200	91	153,000	2.7	80.2	11.7	8.1
2	1a	AlEt <sub>2</sub> Cl	50	0	-	_	-	_	_
3	1b	MMAO	200	15	94,000	3.3	55.4	34.3	10.3
4	1c	MMAO	200	trace	-	-	-	-	_
5	2a	MMAO	200	74	55,000	1.9	1.5	91.2	7.3
6	2b	MMAO	200	37	115,000	2.2	25.4	44.5	30.1
7	2c	MMAO	200	26	141,000	2.1	21.4	46.5	32.1
8	3a	MMAO	200	95	142,000	2.5	81.2	12.1	6.7
9	3a	AlEt <sub>2</sub> Cl	50	0	-	-	_	-	_
10	3b	MMAO	200	11	88,000	3.1	57.2	30.9	11.9
11	3c	MMAO	200	trace	_	_	_	-	_
12	4a	MMAO	200	78	42,000	1.6	1.5	90.4	8.1
13	4b	MMAO	200	38	101,000	2.5	27.1	44.5	28.4
14	4c	MMAO	200	31	144,000	2.0	19.3	47.0	33.7
15	5a	MMAO	200	32	69,000	4.0	93.6	0.6	5.8
16	5a	AlEt <sub>2</sub> Cl	50	100	102,000	2.3	95.9	0.5	3.6
17	5a	Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub>	60	100	114,000	2.6	97.2	0.3	2.5
18	5b	Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub>	60	88	89,000	2.9	97.8	0.1	2.1
19	5c	Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub>	60	85	76,000	3.5	96.4	0.3	3.3
20	6b	Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub>	60	82	114,000	2.2	96.6	1.0	2.4
21	6c	$Al_2Et_3Cl_3$	60	91	125,000	2.1	96.8	0.7	2.5

Polymerization conditions: precursor, 10 µmol; butadiene, 10 mmol; toluene, 5 mL; time, 4 h; temperature, 20 °C.

1,4-selectivity, in striking contrast to the documented FeN3 systems as well as the pyrazolyl iron complexes discussed herein, which normally give high *trans*-1,4-selectivity [13,43].

It is quite interesting to note the pyrazolyl iron complexes display distinctive trans-1,4-selectivity compared to the benzimidazolyl analogs, but consistent with the results observed from the reported symmetry N3 ligands like bisiminopyridine and terpyridine [13,43]. Here, metal environments of solvent free iron(II) 3b and 4a are compared. The neutral bulky benimidazoly moiety may hinder monomer delivery and coordination, being to blame for poor selectivity as well as activity as already observed in bulky iron bisiminopyridine systems [13,43]. Complex 4a is also demonstrated to have more free space near active center than **3b**, as evident from the shorter Fe-N1 distance as well as longer Fe-N2 and Fe-N3 bonds, and this unique structure may facilitate trans-coordination and insertion taking place synchronously, which leads to trans-1,4 unit, and such synchronicity excludes any significant errors which possibly resulted from isomerization of syn- to anti-conformation in case the insertion rate is slower than coordination rate [4].

Fe(III)-based precatalysts 2a-2c reveal that an increase of steric bulk near metal center results in decreases in monomer conversion and increases in  $M_n$ . Replacement of hydrogen by the methyl group on both 3- and 5- position of the pyrazole rings (precatalyst 2c, Table 5, entry 7) results in a decrease in monomer conversion from 74% to 26% and an increase in  $M_n$  from 55,000 to 141,000. The replacement of 3-position on pyrazole ring with a methyl group (precatalyst 2b, Table 5, entry 6) yields intermediate values of conversion and  $M_n$ . This could be explained that in this catalytic system with MMAO, the reaction speed mostly depended on the insertion of butadiene at the active species, so a more bulky group caused slower insertion reaction and consequently lower monomer conversion which might be attributed that the catalysts with less steric bulkiness facilitate the reaction of propagation not the  $\beta$ hydrogen elimination reaction. The steric bulk exerts obvious influence on the selectivity as well. The regularity of polybutadiene derived from 2a is mainly trans-1,4 enchained, which is in agreement with results observed for iron catalytic [13,43]. The methyl derivatives 2c is less trans-1,4-selectivity, and 2b gives a lower trans-1,4-selectivity than either the 2a or 2c. Clearly, steric open of the active site is also a crucial factor in controlling butadiene

coordination as well as the subsequent insertion. Thus, modifying catalyst for better catalytic performance is difficult in this system, but it may drop a clue on how to seek for suitable ligand to obtain *trans*-1,4 selective iron catalyst: neutral tridentate N3 ligand, with appropriate space for monomer access and insertion [13,43].

The corresponding iron(II) complexes 3a-3c and 4a-4c shows very similar catalytic performance with 1a-1c and 2a-2c, respectively, in terms of monomer conversion, polymer properties under the same polymerization conditions, attributable to the same cationic iron species generated from the two type of complexes, though differ in the original oxidation states.

Besides the types of co-activators and ligands, the central metal also exerts an obvious influence on the catalytic performances, and controlling of selectivity is attainable by changing the metal center. Cobalt complexes generally show higher activity and cis-1,4selectivity compared with iron analogs. Complex 5a, in combination with MMAO, exhibits moderate activity towards butadiene polymerization, providing polybutadiene with cis-1,4 incorporation about 94%, and  $M_n$  calculated to be about 80,000 with broad molecular weight distribution. The monomer conversion appears to be sensitive to the cocatalyst, while the selectivity difference is less pronounced. Alkylaluminum chlorides are found to be the better cocatalysts, for example, with diethylalumium chloride, 100% monomer conversion is achieved from complexes 3a, and cis-1,4selectivity is improved to be 96% as well, and ethyl aluminum sesquichloride initiated catalyst also shows the comparable excellent catalytic performance. For the N-alkylated (5b, N-ethyl) and (5c, N-Benzyl), high cis-1,4 enchainment in the resultant polybutadiene is maintained, albeit with marginally lower monomer conversion, 88% and 85% for 5b and 5c, respectively. The unambiguous ligand effect summarized in the cobalt complexes is similar to the trend observed in iron analogs, but less pronounced.

We extend the research with the 2,6-bis(prazolyl)pyridine into cobalt complexes. Treatment of either **6b** or **6c** with  $Al_2Et_3Cl_3$  leads to active butadiene polymerization catalyst converting butadiene to *cis*-1,4 polybutadiene with high monomer conversion. Neither the activity nor the selectivity appears to be sensitive to the ligand environment.

The selectivity of cobalt system is mainly dependent on the coordination atoms on the ligands. Cobalt complexes supported by

N, N, N tridentate ligands [12,39,42,62,63], O, N– or O, O–based anionic ligands [25,26,29] are likely to give *cis*-1,4 structure. And, such  $\pi$ -donating ligand maybe favor *cis*-1,4 coordination of butadiene with cobalt center followed by quick insertion to terminal carbon of cobalt allylic polymer chain [24]. While for those supported by  $\sigma$ -donating phosphine ligands, the mainly 1,2-selectivity [19,24,28] is generated when the coordinated monomer preferentially attacks the third carbon to the last.

The N, N, N-tridentate ligand reported here as well as previously published [12,39,42,62,63] may also serve to design appropriate new ligand framework for *cis*- and/or *trans*-1,4 selective polymer-ization of butadiene.

# 3. Conclusion

Structurally well-defined iron and cobalt homogeneous catalyst systems were developed and applied in polymerization of 1,3butadiene, polybutadiene with a broad range of controllable microstructure, which could be realized by varying a combination of the ligand, central metal and cocatalyst, is accessible.

## 4. Experimental

#### 4.1. General methods

All manipulation related to air and/or moisture sensitive compounds were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a glovebox. FeCl<sub>3</sub>. FeCl<sub>2</sub>·4H<sub>2</sub>O. CoCl<sub>2</sub> as well as pyridine-2,6-dicarboxylic acid, o-phenylenediamine, benzyl chloride and ethyl bromide were all purchased from Alfa Aesar. Methylaluminoxane (MMAO) was commercially available from AkzoNoble. Toluene and tetrahydrofuran (THF) were freshly distilled in the presence of sodium and benzophenone. Polymerization grade butadiene was supplied from Jinzhou Petrochemical Corporation and purified by passing through four columns packed with 4 Å molecular sieves and KOH. Ligands (L1–L6) were prepared according to the methods [52,64]. Other chemicals were used as received unless otherwise noted. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) were recorded on a Varian Unity spectrometer in CDCl<sub>3</sub> or DMSO- $d_6$  at room temperature. IR spectra were performed on BRUKE Vertex-70 FIR spectrophotometer. Elemental analyses were recorded on an elemental Vario EL spectrometer. The proportion of 1,2, *cis*-1,4 and *trans*-1,4 units of polymer were determined by IR spectra, <sup>1</sup>H NMR and <sup>13</sup>C NMR [67–69]. The molecular weights  $(M_n)$ and molecular weight distributions  $(M_w/M_n)$  of polymer were measured at 30 °C by gel permeation chromatography (GPC) equipped with a Waters 515 HPLC pump, four columns (HMW 7 THF, HMW 6E THF  $\times$  2, HMW 2 THF) and a Waters 2414 refractive index detector. THF was used as eluent at a flow rate of 1.0 mL/min. The molecular weight of polymer was determined using the polystyrene calibration.

#### 4.2. X-ray structure determinations

Crystals for X-ray analysis were obtained as described in the experimental section. Data collections were performed at -88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo K radiation ( $\lambda = 0.71073$  Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL program. Refinement was performed on F<sup>2</sup> anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were

placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

# 4.3. Syntheses and characterization of ligands and complexes

2,6-Bis(benzimidazol-2-yl)-pyridine  $(L_1)$ , 2,6-Bis(1'-ethylbenzimidazol-2'-yl)pyridine  $(L_2)$  and 2,6-Bis(1'-benzylbenzimidazol-2'-yl)pyridine  $(L_3)$  were prepared in according to the reported methods.

# 4.3.1. 2,6-Bis(benzimidazol-2-yl)-pyridine iron(III) chloride (1a)

2,6-Bis(benzimidazol-2-yl)-pyridine (0.31 g, 1.0 mmol) and anhydrous FeCl<sub>3</sub> (0.17 g, 1.0 mmol) were added to a flask containing THF (15 mL). The mixture was stirred at 20 °C for 12 h, during which time, a deep-red suspension was formed. Et<sub>2</sub>O was added and a suspension formed. The precipitate was collected by filtration and washed with 4  $\times$  5 mL of heptane. The desired product (0.40 g, 83.3%) was obtained after dried in *vacuo* at 40 °C.

IR (KBr, cm<sup>-1</sup>): 3051 ( $v_{N-H}$ ), 1606 ( $v_{C=C}$ ), 1591, 1577 ( $v_{C=N}$ ), 1465 ( $\delta_{N-H}$ ), 1321, 1147, 1022, 997, 764, 756 ( $\delta_{N-H}$ ). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.35 (2H, H<sub>pyr</sub>), 8.19 (1H, H<sub>pyr</sub>), 7.76 (4H, H<sub>ph</sub>), 7.32 (4H, H<sub>ph</sub>). Anal. Calcd. For C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>FeCl<sub>3</sub>: C, 48.19; H, 2.77; N, 14.79. Found: C, 49.41; H, 3.75; N, 12.47. MALDI–Tof for C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>3</sub><sup>35</sup> (relative ratio): (m/z) 437 ( $m^+$ , –Cl), 402 ( $m^+$ , –2Cl).

# 4.3.2. 2,6-bis(1'-ethylbenzimidazol-2'-yl)pyridine iron(III)Cl<sub>3</sub> (**1b**)

The procedure as above in (4.3.1) using  $L_2$  and FeCl<sub>3</sub> gave **1b** as a red powder in 85% yield.

IR (KBr, cm<sup>-1</sup>): 2974, 2931, 1599 ( $\nu_{C=C}$ ), 1573 ( $\nu_{C=N}$ ), 1485, 1460, 1441, 1337, 1132, 770, 756. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.37 (2H, H<sub>pyr</sub>), 8.25 (1H, H<sub>pyr</sub>), 7.76 (4H, H<sub>ph</sub>), 7.34 (4H, H<sub>ph</sub>), 1.32 (6H, -CH<sub>3</sub>). Anal. Calcd. for C<sub>23</sub>H<sub>21</sub>N<sub>5</sub>FeCl<sub>3</sub>: C, 52.16; H, 3.40; N, 13.22. Found: C, 52.24; H, 3.41; N, 12.70. MALDI–Tof for C<sub>23</sub>H<sub>21</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>3</sub><sup>35</sup> (relative ratio): (*m*/*z*) 493 (m<sup>+</sup>, -Cl), 458 (m<sup>+</sup>, -2Cl).

#### 4.3.3. 2,6-bis(1'-benzylbenzimidazol-2'-yl)pyridine iron(III)Cl<sub>3</sub> (1c)

The procedure as above in (4.3.1) using  $L_3$  and FeCl<sub>3</sub> gave **1c** as a red powder in 85% yield.

IR (KBr, cm<sup>-1</sup>): 1606 ( $\nu_{C=C}$ ), 1575 ( $\nu_{C=N}$ ), 1496, 1466, 1320, 763, 747, 668. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.36 (2H, H<sub>pyr</sub>), 8.21 (1H, H<sub>pyr</sub>), 7.78 (2H, H<sub>ph</sub>), 7.49 (2H, H<sub>ph</sub>), 7.28 (4H, H<sub>ph</sub>), 7.16 (8H, H<sub>ph</sub>), 6.81 (2H, H<sub>ph</sub>), 5.77 (4H,  $-CH_2$ Ph). Anal. Calcd. for C<sub>33</sub>H<sub>27</sub>N<sub>5</sub>FeCl<sub>3</sub>: C, 60.44; H, 4.15; N, 10.68. Found: C, 59.95; H, 4.08; N, 9.95. MALDI–Tof for C<sub>33</sub>H<sub>27</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>3</sub><sup>55</sup> (relative ratio): (m/z) 617 (m<sup>+</sup>, -Cl), 582 (m<sup>+</sup>, -2Cl).

# 4.3.4. 2,6-bis(pyrazoyl)pyridine iron(III)Cl<sub>2</sub> (2a)

The procedure as above in (4.3.1) using **L**<sub>4</sub> and FeCl<sub>3</sub> gave **2a** as a red powder in 86.1% yield.

IR (KBr, cm<sup>-1</sup>): 1618, 1587, 1528, 1495, 1479, 1401, 1345, 1314, 1175, 1064, 977, 800, 779. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.95 (2H, H<sub>pyr</sub>), 8.14 (t, 1H, H<sub>pyr</sub>), 7.87 (2H, H<sub>pyz</sub>), 7.82 (2H, H<sub>pyz</sub>), 6.63 (2H, H<sub>pyz</sub>). Anal. Calcd. for C<sub>11</sub>H<sub>9</sub>N<sub>5</sub>Cl<sub>3</sub>Fe: C, 35.38; H, 2.43; N, 18.75. Found: C, 37.08; H, 2.30; N, 17.58. MALDI–Tof for C<sub>11</sub>H<sub>9</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>3</sub><sup>35</sup> (relative ratio): (*m*/*z*) 337 (m<sup>+</sup>), 302 (m<sup>+</sup>, –Cl).

#### 4.3.5. 2,6-bis(3-methylpyrazoyl)pyridine iron(III)Cl<sub>2</sub> (**2b**)

The procedure as above in (4.3.1) using **L**<sub>5</sub> and FeCl<sub>3</sub> gave **2b** as a red powder in 92.4% yield.

IR (KBr, cm<sup>-1</sup>): 3095, 3051, 1614, 1587, 1534, 1485, 1369, 1320, 1237, 1177, 1062, 990, 810, 788. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.78 (2H, H<sub>pyr</sub>), 8.05 (1H, H<sub>pyr</sub>), 7.68 (2H, H<sub>pyz</sub>), 6.42 (2H, H<sub>pyz</sub>), 2.31 (6H, -CH<sub>3</sub>). Anal. Calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>5</sub>FeCl<sub>3</sub>: C, 38.89; H, 3.26; N, 17.44. Found: C, 40.09; H, 3.70; N, 15.63. MALDI–Tof for

 $C_{13}H_{13}N_5Fe^{56}Cl_3^{35}$  (relative ratio): (*m*/*z*) 365 (m<sup>+</sup>, -Cl), 330 (m<sup>+</sup>, -2Cl).

# 4.3.6. 2,6-bis(3,5-dimethylpyrazoyl)pyridine iron(III)Cl<sub>2</sub> (2c)

The procedure as above in (4.3.1) using  $L_6$  and FeCl<sub>3</sub> gave **2c** as a red powder in 91.7% yield.

IR (KBr, cm<sup>-1</sup>): 3108, 3001, 1613, 1591, 1561, 1483, 1472, 1419, 1393, 1362, 1315, 1302, 1182, 1138, 1051, 986, 813, 791, 741. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.06 (1H, H<sub>pyr</sub>), 7.67 (2H, H<sub>pyr</sub>), 6.14 (2H, H<sub>pyz</sub>), 2.21 (12H, -CH<sub>3</sub>). Anal. Calcd. for C<sub>15</sub>H<sub>17</sub>Cl<sub>3</sub>N<sub>5</sub>Fe: C, 41.94; H, 3.99; N, 16.30. Found: C, 39.89; H, 3.72; N, 17.63. MALDI–Tof for C<sub>15</sub>H<sub>17</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>3</sub><sup>35</sup> (relative ratio): (*m*/*z*) 393 (m<sup>+</sup>, -Cl), 358 (m<sup>+</sup>, -2Cl).

# 4.3.7. 2,6-bis(benzimidazol-2-yl)pyridine iron(II)Cl<sub>2</sub> (3a)

The procedure as above in (4.3.1) using  $L_1$  and FeCl<sub>2</sub> gave **3a** as a dark blue powder in 85% yield.

IR (KBr, cm<sup>-1</sup>): 3195, 3046 ( $\nu_{N-H}$ ), 1608 ( $\nu_{C=C}$ ), 1577 ( $\nu_{C=N}$ ), 1495 ( $\delta_{N-H}$ ), 1493, 1443, 1317, 1237, 1147, 994, 820, 748 ( $\delta_{N-H}$ ). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.35 (2H, H<sub>pyr</sub>), 8.19 (1H, H<sub>pyr</sub>), 7.76 (4H, H<sub>ph</sub>), 7.32 (4H, H<sub>ph</sub>). Anal. Calcd. for C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>FeCl<sub>2</sub>: C, 52.09; H, 2.99; N, 15.99. Found: C, 52.16; H, 2.98; N, 15.95. MALDI–Tof for C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>3</sub><sup>35</sup> (relative ratio): (m/z) 437 (m<sup>+</sup>), 402 (m<sup>+</sup>, -Cl).

# 4.3.8. 2,6-bis(1'-ethylbenzimidazol-2'-yl)pyridine iron(II)Cl<sub>2</sub> (3b)

The procedure as above in (4.3.1) using  $L_2$  and FeCl<sub>2</sub> gave **3b** as a dark blue powder in 85% yield.

IR (KBr, cm<sup>-1</sup>): 2933, 2872, 1600 ( $\nu_{C=C}$ ), 1570 ( $\nu_{C=N}$ ), 1507, 1460 ( $\delta_{N-H}$ ), 1484, 1460, 1441, 1417, 1349, 1335, 1135, 1095, 873, 810, 761, 748. Anal. Calcd. for C<sub>23</sub>H<sub>21</sub>N<sub>5</sub>FeCl<sub>2</sub>: C, 55.90; H, 4.28; N, 14.17. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.37 (2H, H<sub>pyr</sub>), 8.25 (1H, H<sub>pyr</sub>), 7.76 (4H, H<sub>ph</sub>), 7.34 (4H, H<sub>ph</sub>), 1.32 (6H, -CH<sub>3</sub>). Found: C, 55.21; H, 4.29; N, 14.44. MALDI–Tof for C<sub>23</sub>H<sub>21</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>2</sub><sup>35</sup> (relative ratio): (*m*/*z*) 493 (m<sup>+</sup>), 458 (m<sup>+</sup>, -Cl).

#### 4.3.9. 2,6-bis(1'-benzylbenzimidazol-2'-yl)pyridine iron(II)Cl<sub>2</sub> (**3c**)

The procedure as above in (4.3.1) using  $L_3$  and FeCl<sub>2</sub> gave **3c** as a dark blue powder in 85% yield.

IR (KBr, cm<sup>-1</sup>): 3024 ( $\nu_{N-H}$ ), 1603 ( $\nu_{C=C}$ ), 1449, 1470, 1442, 1157, 861, 734, 696. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.36 (2H, H<sub>pyr</sub>), 8.21 (1H, H<sub>pyr</sub>), 7.78 (2H, H<sub>ph</sub>), 7.49 (2H, H<sub>ph</sub>), 7.28 (4H, H<sub>ph</sub>), 7.16 (8H, H<sub>ph</sub>), 6.81 (2H, H<sub>ph</sub>), 5.77 (4H, -CH<sub>2</sub>Ph). Anal. Calcd. for C<sub>33</sub>H<sub>27</sub>N<sub>5</sub>FeCl<sub>2</sub>: C, 63.89; H, 4.39; N, 11.29. Found: C, 63.63; H, 4.48; N, 11.59. MALDI–Tof for C<sub>33</sub>H<sub>27</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>2</sub><sup>35</sup> (relative ratio): (*m*/*z*) 617 (m<sup>+</sup>), 582 (m<sup>+</sup>, -Cl).

# 4.3.10. 2,6-bis(pyrazoyl)pyridine iron(II)Cl<sub>2</sub> (4a)

The procedure as above in (4.3.1) using **L**<sub>4</sub> and FeCl<sub>2</sub> gave **4a** as a yellow powder in 76.9% yield.

IR (KBr, cm<sup>-1</sup>): 1619, 1587, 1526, 1478, 1400, 1344, 1311, 1179, 1077, 1059, 968, 782. Anal. Calcd. for  $C_{11}H_9N_5FeCl_2$ : C, 39.09; H, 2.68; N, 20.72. Found: C, 38.48; H, 2.52, N, 21.63.; MALDI–Tof for  $C_{11}H_9N_5Fe^{56}Cl_2^{35}$  (relative ratio): (*m*/*z*) 337 (m<sup>+</sup>), 302 (m<sup>+</sup>, –Cl).

#### 4.3.11. 2,6-bis(3-methylpyrazoyl)pyridine iron(II)Cl<sub>2</sub> (**4b**)

The procedure as above in (4.3.1) using **L**<sub>5</sub> and FeCl<sub>2</sub> gave **4b** as a yellow powder in 92.4% yield.

IR (KBr, cm<sup>-1</sup>): 3104, 1615, 1582, 1540, 1483, 1382, 1371, 1316, 1241, 1175, 1062, 984, 795, 776. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.78 (2H, H<sub>pyr</sub>), 8.04 (1H, H<sub>pyr</sub>), 7.68 (2H, H<sub>pyz</sub>), 6.41 (2H, H<sub>pyz</sub>), 2.30 (6H, -CH<sub>3</sub>). Anal. Calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>5</sub>FeCl<sub>2</sub>: C, 42.66; H, 3.58; N, 19.13. Found: C, 43.46; H, 3.23; N, 19.73. MALDI–Tof for C<sub>13</sub>H<sub>13</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>2</sub><sup>35</sup> (relative ratio): (*m*/*z*) 365 (m<sup>+</sup>, -Cl), 330 (m<sup>+</sup>, -2Cl).

# 4.3.12. 2,6-bis(3,5-dimethylpyrazoyl)pyridine iron(II)Cl<sub>2</sub> (4c)

The procedure as above in (4.3.1) using  $L_6$  and FeCl<sub>2</sub> gave **4c** as a yellow powder in 81.7% yield.

IR (KBr, cm<sup>-1</sup>): 3100, 2925, 1613, 1562, 1479, 1393, 1363, 1309, 1182, 1136, 1047, 985, 846, 788, 739. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.05 (1H, H<sub>pyr</sub>), 7.67 (2H, H<sub>pyr</sub>), 6.14 (2H, H<sub>pyz</sub>), 2.21 (12H, -CH<sub>3</sub>). Anal. Calcd. for C<sub>15</sub>H<sub>17</sub>N<sub>5</sub>FeCl<sub>2</sub>: C, 45.72; H, 4.35; N, 17.77. Found: C, 44.89; H, 4.12; N, 18.41. MALDI–Tof for C<sub>15</sub>H<sub>17</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>2</sub><sup>35</sup> (relative ratio): (*m*/*z*) 394 (m<sup>+</sup>, -Cl), 358 (m<sup>+</sup>, -2Cl).

## 4.3.13. 2,6-bis(benzimidazol-2-yl)pyridine cobalt(II)Cl<sub>2</sub> (5a)

The procedure as above in (4.3.1) using  $L_1$  and CoCl<sub>2</sub> gave **5a** as a green powder in 85% yield.

IR (KBr, cm<sup>-1</sup>): 3061( $v_{N-H}$ ), 1607 ( $v_{C=N}$ ), 1691( $v_{C=C}$ ), 1575, 1494, 1459 ( $\delta_{N-H}$ ), 1317, 1234, 1147, 996, 819, 744 ( $\delta_{N-H}$ ). Anal. Calcd. for C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>Cocl<sub>2</sub>: C, 51.73; H, 2.97; N, 15.87. Found: C, 51.24; H, 3.35; N, 14.10. MALDI–Tof for C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>Co<sup>58</sup>Cl<sub>2</sub><sup>35</sup> (relative ratio): (m/z) 405 ( $m^+$ , -Cl), 369 ( $m^+$ , -2Cl).

# 4.3.14. 2,6-bis(1'-ethylbenzimidazol-2'-yl)pyridine cobalt(II)Cl<sub>2</sub> (**5b**)

The procedure as above in (4.3.1) using  $L_2$  and CoCl<sub>2</sub> gave **5b** as a green powder in 85% yield.

IR (KBr, cm<sup>-1</sup>): 3020, 2987, 2935, 1600 ( $v_{C=C}$ ), 1573 ( $v_{C=N}$ ), 1512, 1485, 1460, 1443, 1349, 1335, 1154, 1094, 812, 762, 749. Anal. Calcd. for C<sub>23</sub>H<sub>21</sub>N<sub>5</sub>CoCl<sub>2</sub>: C, 55.55; H, 4.26; N, 14.08. Found: C, 54.48; H, 4.31; N, 12.94. MALDI–Tof for C<sub>23</sub>H<sub>21</sub>N<sub>5</sub>Fe<sup>56</sup>Cl<sub>2</sub><sup>35</sup> (relative ratio): (*m*/*z*) 461 (m<sup>+</sup>, –Cl).

# 4.3.15. 2,6-bis(1'-benzylbenzimidazol-2'-yl)pyridine

#### cobalt(II)Cl<sub>2</sub> (5c)

The procedure as above in (4.3.1) using  $L_3$  and CoCl<sub>2</sub> gave **5c** as a green powder in 85% yield.

IR (KBr, cm<sup>-1</sup>): 1596 ( $\nu_{C=C}$ ), 1568 ( $\nu_{C=N}$ ), 1498, 1471, 1436, 1335, 815, 781, 749, 731, 695. Anal. Calcd. for C<sub>33</sub>H<sub>27</sub>N<sub>5</sub>CoCl<sub>2</sub>: C, 63.58; H, 4.37; N, 11.23. Found: C, 63.98; H, 4.19; N, 10.82. MALDI–Tof for C<sub>33</sub>H<sub>27</sub>N<sub>5</sub>Co<sup>58</sup>Cl<sub>2</sub><sup>35</sup> (relative ratio): (m/z) 585 (m<sup>+</sup>, –Cl), 549 (m<sup>+</sup>, –2Cl).

#### 4.3.16. 2,6-bis(3-methylpyrazoyl)pyridine cobalt(II)Cl<sub>2</sub> (**6b**)

The procedure as above in (4.3.1) using **L**<sub>5</sub> and CoCl<sub>2</sub> gave **6b** as a blue powder in 95.1% yield.

IR (KBr, cm<sup>-1</sup>): 3103, 3074, 1616, 1582, 1542, 1484, 1385, 1316, 1241, 1175, 1061, 983, 795, 778, 790. Anal. Calcd. for  $C_{13}H_{13}N_5CoCl_2$ : C, 42.30; H, 3.55; N, 18.97. Found: C, 42.00; H, 3.81; N, 19.31. MALDI–Tof for  $C_{13}H_{13}N_5Co^{58}Cl_2^{35}$  (relative ratio): (*m*/*z*) 333 (m<sup>+</sup>, -Cl).

#### 4.3.17. 2,6-bis(3,5-dimethylpyrazoyl)pyridine cobalt(II)Cl<sub>2</sub> (6c)

The procedure as above in (4.3.1) using  $L_6$  and CoCl<sub>2</sub> gave **6c** as a blue powder in 91.1% yield.

IR (KBr, cm<sup>-1</sup>): 3100, 2971, 1613, 1590, 1563, 1480, 1393, 1363, 1309, 1181, 1136, 1048, 983, 842, 788, 739. Anal. Calcd. for  $C_{15}H_{17}N_5CoCl_2$ : C, 45.36; H, 4.31; N, 17.63. Found: C, 46.18; H, 4.12; N, 18.04. MALDI–Tof for  $C_{15}H_{17}N_5Co^{58}Cl_2^{35}$  (relative ratio): (m/z) 361 (m<sup>+</sup>, -Cl).

#### 4.4. Procedure for butadiene polymerization

A typical procedure for the polymerization is as follows (entry 1 in Table 5): a toluene solution of butadiene (5 mL, 2.0 mol/L) was added to a moisture free ampere bottle preloaded with complex **1a** (5.3 mg, 0.01 mmol), then MMAO (2.0 mmol) was injected to initiate the polymerization at 20 °C. After 4 h, methanol was added to the system to quench the polymerization. The mixture was

poured into a large quantity of methanol containing 2,6-di-tertbutyl-4-methylphenol (1.0 wt%) as a stabilizer. Filtered and dried under vacuum at 40 °C, polybutadiene was resulted at a constant weight (0.49 g, 91%).

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# **Appendix A. Supplementary material**

CCDCnumbers 749520 (**1a**), 740170(**1b**), 836391(**3a**), 740445(3b), 740175(3c), 740454(4a), 740172(5a), 749517(5b), 740171(5c) and 740173(6c) contains the supplementary crystallographic data for this paper., . These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data\_request/cif.

# Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.11.025.

#### References

- [1] Z.-Q. Shen, Inorg. Chim. Acta 140 (1987) 7-14.
- [2] Z.-Q. Shen, J. Ouyang, Handbook of the physics and chemistry of rare earth, in: K. Gschneidner, L. FlemingJr. (Eds.), Ch. 61 (Rare Earth Coordination Catalysts in Stereospecific Polymerization), Elsevier, Amsterdam, 1987.
- [3] W. Kuran, Principle of Coordination Polymerization, John Wiley and Sons Ltd., New York, 2001.
- L. Friebe, O. Nuyken, W. Obrecht, Adv. Polym. Sci. 204 (2006) 1-154.
- [5] A. Fischbach, R. Anwander, Adv. Polym. Sci. 204 (2006) 155-281 (and references therein).
- [6] S. Arndt, K. Beckerle, P.M. Zeimentz, T.P. Spaniol, J. Okuda, Angew. Chem. Int. Ed. 44 (2005) 7473-7477.
- S. Kaita, Z.-M. Hou, Y. Wakatsuki, Macromolecules 34 (2001) 1539-1541.
- [8] W. Gao, D.-M. Cui, J. Am. Chem. Soc. 130 (2008) 4984-4991.
- [9] A. Miyazawa, T. Kase, K. Hashimoto, Macromolecules 37 (2004) 8840–8845. [10] R. Cariou, J. Chirinos, V.C. Gibson, G. Jacobsen, A.K. Tomov, M.R.J. Elsegood,
- Macromolecules 42 (2009) 1443-1444. [11] A. Fischbach, C. Meermann, G. Eickerling, W. Scherer, R. Anwander, Macro-
- molecules 39 (2006) 6811-6816. [12] V. Appukuttan, L. Zhang, C. Ha, I. Kim, Polymer 50 (2009) 1150-1158.
- [13] Y. Nakayama, Y. Baba, H. Yasuda, K. Kawakita, N. Ueyama, Macromolecules 36 (2003) 7953-7958.
- [14] W.J. Evans, D.G. Giarikos, J.W. Ziller, Organometallics 20 (2001) 5751-5758.
- [15] E. Colamarco, S. Milione, C. Cuomo, A. Grassi, Rapid Commun. 25 (2004) 450-454.
- [16] L.-H. Cao, W.-M. Dong, L.-S. Jiang, X.-Q. Zhang, Polymer 48 (2007) 2475-2480.
- [17] G. Ricci, M. Battistella, Macromolecules 34 (2001) 5766-5769.
- [18] D.-R. Gong, W.-M. Dong, J.-C. Hu, X.-Q. Zhang, L.-S. Jiang, Polymer 50 (2009) 2826-2829
- [19] Y.C. Jang, P.S. Kim, H. Lee, Macromolecules 35 (2002) 1477-1480.
- [20] D.-R. Gong, W.-M. Dong, Y.-M. Hu, J.-F. Bi, X.-Q. Zhang, L.-S. Jiang, Polymer 50 (2009) 5980-5986
- Y.C. Jang, P.S. Kim, H.Y. Jeong, H. Lee, J. Mol. Catal. A: Chem. 206 (2003) 29-36. [21][22] D.C.D. Nath, T. Shiono, T. Ikeda, Appl. Catal. A 238 (2003) 193-199.
- [23] D.C.D. Nath, T. Shiono, T. Ikeda, Macromol. Chem. Phys. 204 (2003) 2017-2022. [24] Z.-G. Cai, M. Shinzawa, Y. Nakayama, T. Shiono, Macromolecules 42 (2009) 7642-7643
- [25] K. Endo, N. Hatakeyama, J. Polym. Sci. Part A: Polym. Chem. 39 (2001) 2793-2798.
- [26] D. Chandran, C.H. Kwak, C.S. Ha, I. Kim, Catal. Today 131 (2008) 505-512.
- [27] P. Cass, K. Pratt, T. Mann, B. Laslett, E. Rizzardo, R. Burford, J. Polym. Sci. Part A: Polym. Chem. 38 (2000) 1083-1089.

- [28] G. Ricci, A. Forni, A. Boglia, T. Motta, J. Mol. Catal. A: Chem. 226 (2005) 235-241
- [29] K. Endo, T. Kitagawa, K. Nakatani, J. Polym. Sci. Part A: Polym. Chem. 44 (2006) 4088-4094
- [30] M. Gippn, Eng. Chem. Prod. Res. Dev. 1 (1962) 32-39.
- [31] C. Longgivae, R. Castelli, G.F. Groce, Chim. Ind. 43 (1961) 625-630.
- [32] H.E. Swift, J.E. Bozik, C.-Y. Wu, J. Catal. 17 (1970) 331–340.
- [33] Z.-Y. Zhang, H.-J. Zhang, H.-M. Ma, Y. Wu, J. Mol. Catal. 17 (1982) 65–76.
- [34] C. Bazzini, A. Giarrusso, L. Porri, Macromol. Rapid Commun. 23 (2002) 922-927.
- [35] G. Ricci, D. Morganti, A. Sommazzi, R. Santi, F. Masi, J. Mol. Catal. A: Chem. (2003) 204-205 287-293.
- [36] S. Luo, Iron-based catalyst composition and process for producing syndiotactic 12-polybutadiene US Patent 2001 6284 702
- [37] J. Lu, Y.-M. Hu, X.-Q. Zhang, J.-F. Bi, W.-M. Dong, L.-S. Jiang, B.-T. Huang, J. Appl. Polym. Sci. 100 (2006) 4265–4269.
- [38] Y.-M. Hu, W.-M. Dong, L.-S. Jiang, X.-Q. Zhang, Y. Guo, L.-H. Cao, Chin. J. Catal. 8 (2004) 664-668.
- [39] D.-R. Gong, B.-L. Wang, C.-X. Bai, J.-F. Bi, F. Wang, W.-M. Dong, X.-Q. Zhang, L.-S. Jiang, Polymer 50 (2009) 6259-6264.
- [40] G. Natta, L. Porri, A. Mazzei, Chim. Ind. 41 (1959) 116-122. [41] S. Milione, C. Cuomo, C. Capacchione, C. Zannoni, A. Grassi, A. Proto, Macromolecules 40 (2007) 5638-5643.
- [42] D.-R. Gong, B.-L. Wang, H.-G. Cai, X.-Q. Zhang, L.-S. Jiang, J. Organomet. Chem. 696 (2011) 1584-1590.
- [43] D.-R. Gong, X.-Y. Jia, B.-L. Wang, F. Wang, C.-Y. Zhang, X.-Q. Zhang, L.-S. Jiang, W.-M. Dong, Inorg. Chim. Acta 373 (2011) 47-53.
- [44] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143-7144.
- [45] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049-4050
- [46] D. Takeuchi, R. Masuura, S. Park, K. Osakada, J. Am. Chem. Soc. 129 (2007) 7002-7003.
- [47] Y.-F. Chen, R.-F. Chen, C.-T. Qian, X.-C. Dong, J. Sun, Organometallics 22 (2003) 4312-4321.
- [48] D.M. Dawson, D.A. Walker, M. Thornton-Pett, M. Bochmann, J. Chem. Soc. Dalton Trans. (2000) 459-466.
- V.C. Gibson, C. Redshaw, G.A. Solan, Chem. Rev. 107 (2007) 1745-1776. [49]
- [50] G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Strömberg, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728-8740.
- [51] C. Bianchini, G. Mantovani, A. Meli, F. Migliacci, F. Laschi, Organometallics 22 (2003) 2545-2547.
- [52] W.-J. Zhang, W.-H. Sun, S. Zhang, J.-X. Hou, H.-B. Song, Organometallics 25 (2006) 1961-1969.
- [53] L.-Y. Wang, W.-H. Sun, L.-Q. Han, Z.-L. Li, Y.-L. Hu, C.-X. He, C.-H. Yan, J. Organomet. Chem. 650 (2002) 59-64.
- [54] G.J.P. Britovsek, V.C. Gibson, O.D. Hoarau, S.K. Spitzmesser, A.J.P. White, D.J. Williams, Inorg. Chem. 42 (2003) 3454-3465.
- J.S. Fossey, C.J. Richards, Organometallics 21 (2002) 5259-5264.
- Ì56] S. Nückel, P. Burger, Organometallics 19 (2000) 3305-3311.
- [57] W.J. Hoogervorst, C.J. Elsevier, M. Lutz, A.L. Spek, Organometallics 20 (2001) 4437-4440.
- [58] W.J. Hoogervorst, A.L. Koster, M. Lutz, A.L. Spek, C.J. Elsevier, Organometallics 23 (2004) 1161-1164.
- [59] J.M. Vila, M. Gayoso, T. Pereira, T.M. Lopez, A. Fernández, J.M. Ortigueira, J. Organomet. Chem. 506 (1996) 165–174.
- [60] S. Al-Benna, M.J. Sarsfield, M. Thornton-Pett, D. Ormsby, P.J. Maddox, P. Bres, M. Bochmann, J. Chem. Soc. Dalton Trans. (2000) 4247-4257.
- [61] J. Zhang, M. Gandelman, D. Herrman, G. Leitus, L.J.W. Shimon, Y. Ben-David, D. Milstein, Inorg. Chim. Acta 359 (2006) 1955–1960.
- [62] V. Appukuttan, L. Zhang, J.Y. Ha, D. Chandran, B.K. Bahuleyan, C.-S. Ha, Il Kim, J. Mol. Catal. A: Chem. 325 (2010) 84-90.
- [63] R. Cariou, J.J. Chirinos, V.C. Gibson, G. Jacobsen, A.K. Tomov, G.J.P. Britovsek, Andrew J.P. White, Dalton Trans. 39 (2010) 9039-9045.
- [64] A.R. Karam, E.L. Catarì, F. López-Linares, G. Agrifoglio, C.L. Albano, A. Dìaz-Barrios, T.E. Lehmanna, S.V. Pekerar, L.A. Albornoz, R. Atencio, T. González, H.B. Ortega, P. Joskowics, Appl. Catal. A 280 (2005) 165-173.
- [65] R. Gao, L.-W. Xiao, X. Hao, W.-H. Sun, F.-S. Wang, Dalton Trans. (2008) 5645-5651.
- [66] S.-Y. Jie, S. Zhang, W.-H. Sun, X.-F. Kuang, T.-F. Liu, J.-P. Guo, J. Mol. Catal. A: Chem. 269 (2007) 85-96.
- [67] S. Tobisch, R. Taube, Organometallics 18 (1999) 5204-5218.
- [68] S. Tobisch, Acc. Chem. Res. 35 (2002) 96-104.
- [69] A.R. O'Connor, P.S. White, M. Brookhart, J. Am. Chem. Soc. 129 (2007) 4142-4143.