# Iron(II)- and Cobalt(II) Complexes with Tridentate Bis(imino)pyridine Nitrogen Ligands Bearing Chiral Bulky Aliphatic and Aromatic Substituents: Crystal Structure of [CoCl<sub>2</sub>{2,6-bis[R-(+)-(bornylimino)methyl]pyridine}]

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**Abstract.** Iron(II) and cobalt(II) complexes (**7-15**) based on new aldimine 2,6-bis[(imino)methyl]pyridine (**1,2,4,6**) and ketimine (2,6-bis[(imino)ethyl]pyridine (**3,5**) ligands with bulky chiral aliphatic or aromatic terminal groups have been prepared and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR-, mass spectroscopy (EI), and elemental analysis. The complex [CoCl<sub>2</sub>(BBoMP)]<sup>-1</sup>/<sub>2</sub> CHCl<sub>3</sub> (**13**) (BBoMP:

# **1** Introduction

Until the middle of 90's few reports were introduced about utilizing late transition metal based complexes as catalyst precursors for polymerization of  $\alpha$ -olefins and ethylene [1]. This is probably because these catalysts generally exhibit reduced activities for olefin polyinsertion [2]. However, in 1995 new nickel(II) and palladium(II) based catalysts bearing bulky diimine ligands were reported for ethylene polymerization [3]. A few years later, late transition metal based catalysts have attracted increasing attention in the field homo- and copolymerization of  $\alpha$ -olefin [4, 5], especially after *Brookhart's* and *Gibson's* reports on new Fe<sup>II</sup>-based complexes containing 2,6-bis(imino)pyridyl ligands as efficient catalyst precursors for ethylene polymerization. After MAO activation these complexes are highly active and produce strictly linear polyethylene (PE) [6, 7].

Recently we reported on highly active 2,6-bis(arylimino)pyridine iron(II)- and cobalt(II)-based ethylene polymerization catalysts which lack the *ortho* alkyl substituents on the aryl groups [8]. Modifications of the steric bulkiness of

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2,6-bis{(R-(+)-(bornylimino)-methyl}pyridine) crystallizes in monoclinic space group P2<sub>1</sub> with cell dimensions: a = 7.6603(11) Å, b = 28.3153(14) Å, c = 13.537(2) Å,  $V = 2908.1(6) \text{ Å}^3$ , Z = 4. The coordination sphere around Co is distorted trigonal bipyramidal.

Keywords: Iron; Cobalt; Imines, Tridentate nitrogen ligands

the aromatic groups in the tridentate ligands influenced not only the catalytic activity but also the molecular weight and the microstructure of the resulted polymer material. Therefore, there is still a great interest to discover and develop new families of polymerization catalysts that can allow further control of the polymer microstructure, material properties and, if possible, capable to polymerize polar vinylic monomers. The late transition metals are less oxophilic than the early transition metals, and are therefore supposed to be more tolerant toward Lewis bases.

As an extension to our studies on both the coordination chemistry of heteroatom-containing ligands and the catalytic application of their metal complexes [9-12] we report here the synthesis and characterization of new 2,6-bis(imino)pyridyl ligands bearing myrtanyl-, bornyl, benzyl or naphthyl terminals and their corresponding iron(II) and cobalt(II) complexes. The new compounds were characterized by elemental analysis, IR-, MS-, <sup>1</sup>H-, and <sup>13</sup>C-NMR spectroscopy. Furthermore, the complex  $[CoCl_2\{2,6-bis[R-(+)-(bornylimino)methyl]pyridine\}]$  was a subject to X-ray structural analysis.

# 2 Results and Discussion

# 2.1 Ligands and complexes

Ligand synthesis was based on a classical condensation reaction where a primary amine is allowed to react with 2,6pyridinedicarboxaldehyde or 2,6-diacetylpyridine to form the corresponding aldimines (2,6-bis[(imino)methyl]pyridines) (1, 2, 4, and 6) or ketimines (2,6-bis[(imino)ethyl]pyriddine) (3, and 5), respectively (Scheme 1). In the case of ketimines the reaction requires a catalytic amount of formic acid while the aldimines form without the acid. The products precipitated nicely from the reaction solution as yellow or white powder. The reaction can easily be followed by IR



Scheme 1

spectroscopy as the strong aldehyde and ketone absorption bands disappear and new bands appear between 1620 to  $1642 \text{ cm}^{-1}$  which are due to the stretching vibration of the imine C=N bond. The <sup>13</sup>C-NMR spectra of the 2,6-bis(imino)pyridine ligands exhibit a singlet signal at about 160-169 ppm which can be assigned to the imine (C=N) carbon. The ketimine ligands showed also a singlet at 13.9 -17.5 ppm which can be ascribed to the methyl groups in the backbone of the ligand. The iron(II) aldimine with penta-coordinated metal atoms (7, 8, 10, and 12) and ketimine (9 and 11), as well as cobalt(II), aldimine (13, 14, and 15) complexes were synthesized by treatment of FeCl<sub>2</sub> or CoCl<sub>2</sub> with the corresponding 2,6- bis(imino)pyridine ligand in THF (Scheme 1). Also the complex synthesis can be followed by IR spectroscopy as the imine bands shift to the region of  $1530 - 1593 \text{ cm}^{-1}$  because of the coordination [13]. To further confirm the identity of the complexes, a variety of complimentary techniques including elemental analysis and mass spectroscopy (EI) were applied.

# 2.2 Crystal structure of [CoCl<sub>2</sub>(BBoMP)]·<sup>1</sup>l<sub>2</sub>CHCl<sub>3</sub> (13)

The compound **13** crystallizes with two discrete cobalt(II) complex units and one solvent molecule in the asymmetric unit. Both complex units are highly similar. The coordination sphere around the cobalt atom can be roughly classified as a distorted trigonal bipyramid, in which the imino nitrogen atoms of the ligand occupy the axial positions and the two chloride ligands and the nitrogen atom at the pyridine form the trigonal plane (Figure 1). Axial angles (N8a-Co1a-N8a and N8b-Co1b-N8b (149.93(9))°) show a clear

distortion from the linear arrangement in both molecules. But, on the other hand, the trigonal plane is fairly regular having all angles close to  $120^{\circ}(\pm 3)$  (Table 1). Similar coordination arrangement was found in a dichloro Fe<sup>II</sup> complex bearing bis[(2,4,6-trimethylphenyl-imino)ethyl]pyridine (BMeEP) [14]. In the same study a dichloro cobalt(II) complex **BPEP-Co(II)** (**BPEP** = 2,6-bis[(2,6-diisopropylphenylimino)ethyl]pyridine) bearing similar ligand with bulkier arvlimino substituents, however, crystallized in a square pyramidal coordination around the metal atom. The solid state structure of 13 shows that the N-bornyl substituents do not displace the CoCl<sub>2</sub> from the N<sub>3</sub>Co plane to the square pyramidal arrangement as was seen in the case of BPEP-Co(II). Instead, the cobalt atom deviates from the N<sub>3</sub>-plane much less (0.0706(3) Å and 0.0278(3) Å in molecules A and B, respectively) than in BPEP-Co(II) (0.56 Å).

The trigonal bipyramid configuration in 13 fits well to the C<sub>2</sub>-symmetry, when the pyridine nitrogen and the cobalt atom are chosen for a rotation axis. The Co1-N1 (pyridine) distances (2.031(2) Å and 2.027(2) Å in mol A and B, respectively) are only slightly shorter than reported for **BPEP-Co(II)**, (2.051(3) Å), while the Co-N (imino) distances (molecule A. 2.309(3), 2.350(2) and molecule B 2.260(3) and 2.436(3) are significantly longer than those in **BPEP-Co(II)** (2.211(3) and 2.211(3) Å). We assume that this difference is due to the change of the imino substituents from aromatic to aliphatic ones. In addition, the ligand framework is twisted as shown in the side view picture in Figure 1.b. The imino nitrogen atoms are shifted opposite sides of the mean plane, which is established by the pyridine and the cobalt atom. The chloride ions locate on both sides of the ligand plane and the Cl-Co-Cl angles (121.21(3)° and

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# Figure 1b

Figure 1a

118.47(4)°) are wider than observed for **BPEP-Co(II)** (116.5(1)°) (Table 1).

Table 1 Selected bond lengths/Å and angles/°.

Co1A-N1A	2.031(2)	Cl2A-Co1A-8A	95.06(7)
Co1A-Cl1A	2.2493(9)	N1A-Co1A-N20A	74.56(10)
Co1A-Cl2A	2.2696(9)	Cl1A-Co1A-N20A	91.05(7)
Co1A-N8A	2.309(3)	Cl2A-Co1A-N20A	98.18(6)
Co1A-N20A	2.350(2)	N8A-Co1A-N20A	149.93(9)
Co1B-N1B	2.027(2)	N1B-Co1B-Cl2B	121.90(7)
Co1B-Cl2B	2.2426(9)	N1B-Co1B-Cl1B	119.38(7)
Co1B-Cl1B	2.2521(9)	Cl2B-Co1B-Cl1B	118.47(4)
Co1B-N20B	2.260(3)	N1B-Co1B-N20B	76.74(10)
Co1B-N8B	2.436(3)	Cl2B-Co1B-N20B	102.93(7)
N1A-Co1A-Cl1A	117.34(7)	Cl1B-Co1B-N20B	95.32(7)
N1A-Co1A-Cl2A	121.11(7)	N1B-Co1B-N8B	73.20(9)
Cl1A-Co1A-Cl2A	121.21(3)	Cl2B-Co1B-N8B	92.18(6)
N1A-Co1A-N8A	75.47(10)	Cl1B-Co1B-N8B	100.12(6)
Cl1A-Co1A-N8A	104.91(7)	N20B-Co1B-N8B	149.93(9)

# **3** Experimental

# 3.1 General

All reactions were carried out under dry argon using standard Schlenk techniques. All chemicals were commercial and used as such. Hydrocarbon solvents were purified by refluxing over  $\text{LiAlH}_4$  or sodium followed by distillation under argon. Methanol was treated with sodium methoxide/ dimethylterphthalate and subsequently distilled. Solvents were stored under argon atmosphere.

Elemental analyses were performed at the Faculty of Pharmacy, University of Helsinki (EA 1110 CHNS-O CE instrument). <sup>1</sup>Hand <sup>13</sup>C-NMR spectra (CDCl<sub>3</sub>) were recorded on a Varian Gemini 200 spectrometer operating at 200 MHz and at 50.286 MHz, respectively. Infrared spectra were measured on a BIO-RAD FTS-7 FT-IR spectrometer using KBr pellet. Mass spectra (EI) were acquired with a JEOL JMS-SX102 mass spectrometer.

### 3.2 Synthesis of ligands

# 3.2.1 2,6-bis[(R)-(+)-bornylimino)methyl]pyridine (BBoMP) (1)

A solution of 2,6-pyridinedicarboxaldehyde (0.22 g, 1.63 mmol) in MeOH (15 mL) was added to a solution of (R)-(+)-bornylamine (0.5 g, 3.26 mmol) in the same solvent (20 mL) and 3 drops of 97 % formic acid was added. After 4 h of stirring at room temperature, a white precipitate was formed which was collected, washed with cold methanol (2×10 ml) and dried in vacuum. Yield: 0.35 g (52 %), m. p. 141 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.82 (s, 2H, CH= N.), 8.12-7.70 (m, 3H, H<sub>arom</sub>), 3.53-3.48 (m, 4H, N-CH<sub>2-Born</sub>), 0.96 (s, 6H, head), 0.90 (s, 6H, head), 0.71 (s, 6H, Born.). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 160.1 (C=N). IR: v(cm<sup>-1</sup>) = 1642 m (C=N). Anal. Calcd. for C<sub>27</sub>H<sub>39</sub>N<sub>3</sub>: C, 79.95; H, 9.69; N, 10.4. Found: C, 79.36; H, 9.93; N, 10.3 %.

# *3.2.2 2,6-bis[(-)-cis-myrtanylimino)methyl]pyridine* (*BMyMP*) (**2**)

A solution of 2,6-pyridinedicarboxaldehyde (0.29 g, 2.15 mmol) in MeOH (15 mL) was to add a solution of (-)-(cis)-myrtanylamine (0.72 g, 4.72 mmol) in the same solvent (20 mL) and 3 drops of 97 % formic acid was added. The reaction mixture was stirred at 50 °C for 3 days after which the brown oil product was, washed with pentane (2×50 ml) and dried in vacuum. Yield: 0.60 g (70 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.49$  (s, 2H, CH=N). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta = 161.5$  (C=N). IR: v(cm<sup>-1</sup>) = 1636 m (C=N). Anal. Calcd. for C<sub>27</sub>H<sub>39</sub>N<sub>3</sub>: C, 79.95; H, 9.69; N, 10.4. Found: C, 79.53; H, 9.82; N, 10.2 %.

### 3.2.3 2,6-bis[(cyclohexanemethylimino)ethyl]pyridine (BChEP) (3)

2,6- Diacetylpyridine (0.92 g, 5.7 mmol) and three drops of formic acid (97 %) was to added to cyclohexanemethylamine (1.50 g, 13.2 mmol). After two days the reaction mixture was put in vacuumat 65 °C for 5 hours to remove excess of amine and water formed in reaction. Yield 1.91 g (96 %) <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.00-1.90 (m, 12H, H<sub>cyclohex</sub>), 2.39 (s, 6H, CH<sub>3</sub>), 3.35 (d, 4H, CH<sub>2</sub>), 7.69 (t, 1H, H<sub>arom</sub>), 8.10 (d, 2H, H<sub>arom</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 166.41 (C=N). IR: v(cm<sup>-1</sup>) 1635 m (C=N). Anal. Calcd. for C<sub>23</sub>H<sub>35</sub>N<sub>3</sub>. 0.5 H<sub>2</sub>O: C 76.19, H 10.01, N 11.59. Found: C 77.03, H 10.11, N 11.55 %.

# 3.2.4 2,6-bis[(benzylimino)methyl]pyridine (BBzMP) (4)

The ligand was prepared following the same procedure described above (3.2.3).

1.63 g (15.2 mmol) of the benzylamine was allowed to react with 0.85 g (6.3 mmol) of 2,6-pyridinedicarboxaldehyde. Yield 1.89 g, (96 %), <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.81 (s, 4H, CH<sub>2</sub>), 7.16-7.29 (m, 10H, H<sub>arom</sub>), 7.70 (t, 1H, H<sub>arom</sub>), 8.15 (d, 2H, H<sub>arom</sub>), 8.45 (s, 2H, CH). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 162.61 (C=N). IR v(cm<sup>-1</sup>) = 1630 m (C=N). Anal. calcd. for C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>: C 80.48; H 6.11; N 13.41. Found: C 79.77; H 6.25; N 13.25 %.

# 3.2.5 2,6-bis[(benzylimino)ethyl]pyridine (BBzEP) (5)

The ligand was prepared following the same procedure described above (3.2.3).

1.46 g (13.7 mmol) of the benzylamine was allowed to react with 0.97 g (5.9 mmol) of 2,6-diacetylpyridine. Yield 1.93 g, (96 %), <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 2.43 (d, 6H, CH<sub>3</sub>), 4.69 (s, 4H, CH<sub>2</sub>), 7.13-7.38 (m, 10H, H<sub>arom</sub>), 7.66 (t, 1H, H<sub>arom</sub>), 8.14 (d, 2H, H<sub>arom</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 167.70 (C=N). IR v(cm<sup>-1</sup>) = 1638 m (C=N). Anal. Calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>. 0.5 H<sub>2</sub>O: C 78.83, H 6.90, N 11.99. Found: C 79.24, H 6.50, N 12.43 %.

# 3.2.6 2,6-bis[(1-naphthylimino)methyl]pyridine (BNaMP) (6)

A solution of 2,6-pyridinedicarboxaldehyde (1.0 g, 7.4 mmol) in MeOH (25 mL) was added to a solution of 1-naphthylamine (2.12 g, 14.8 mmol) in the same solvent (25 mL) and 3 drops of 97 % formic acid was added. After 3 h of stirring at room temperature, a yellow precipitate was filtered, washed with cold methanol (2×5 ml) and dried in vacuum. Yield: 2.7 g (93 %), m. p. 172 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.81-7.19 (m, 19H, H<sub>arom</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 160.45 (C=N). IR v(cm<sup>-1</sup>) = 1620 m (C=N). Anal. Calcd. for C<sub>27</sub>H<sub>19</sub>N<sub>3</sub>: C, 84.13; H, 4.96; N, 10.9. Found: C, 83.83; H, 4.86; N, 10.4 %.

# 3.3 Synthesis of complexes

3.3.1 2,6-bis[(R)-(+)-bornylimino)methyl]pyridine iron(II) chloride (7) and 2,6-bis[(R)-(+)bornylimino)methyl]pyridine cobalt(II) chloride (13)

A filtered solution of the ligand **1** 0.30 g, (0.74 mmol) in THF (30 ml) was added to FeCl<sub>2</sub> or CoCl<sub>2</sub> (0.67 mmol) powder under continuous stirring at room temperature. Upon addition a precipitate started to form. After 3 h, the solid was filtered, washed with ether (2×5 mL), n-pentane (2×5 mL) and dried in vacuum. 7, Yield: 0.22 g (62 %). M.p.(dec) 155 °C. IR: v [cm<sup>-1</sup>] = 1581 m (C= N). Anal. Calcd. for C<sub>27</sub>H<sub>39</sub>N<sub>3</sub>FeCl<sub>2</sub>. 5H<sub>2</sub>O: C, 59.90; H, 7.44; N, 7.76. Found: C, 59.90; H, 7.42; N, 7.39. **13**, Yield: 0.25 g (70 %), green. M.p. (dec) 207 °C. IR: v(cm<sup>-1</sup>) = 1582 m (C=N). Anal. Calcd. for C<sub>27</sub>H<sub>39</sub>N<sub>3</sub>CoCl<sub>2</sub>: C, 60.56; H, 7.34; N, 7.85. Found: C, 60.45; H, 7.34; N, 7.28 %. Suitable crystals of compound **13** were grown from chloroform.

3.3.2 2,6-bis[(-)-cis-myrtanylimino)methyl]pyridine iron(II) chloride (8) and 2,6-bis[(cis-myrtanylimino)methyl]pyridine cobalt(II) chloride (14)

The complexes were prepared following the same procedure described above (3.3.1).

0.59 g (1.5 mmol) of the ligand **2** was allowed to react with (1.32 mmol) of FeCl<sub>2</sub> or CoCl<sub>2</sub>. **8**, Yield: 0.29 g (41 %), purple. M.p.(dec) 289 °C. (MS, EI) :m/z (%) 531 (10 %), 496 (10 %), 407 (80 %). IR: v(cm<sup>-1</sup>) = 1567 m (C=N). Anal. Calcd. for C<sub>27</sub>H<sub>39</sub>N<sub>3</sub>FeCl<sub>2</sub>: C, 60.92; H, 7.38; N, 7.89. Found: C, 60.73; H, 7.02; N, 7.38. **14**, Yield: 0.35 g (50 %), green. M.p.(dec) 293 °C. IR: v [cm<sup>-1</sup>] = 1587 m (C=N). Anal. Calcd. for C<sub>27</sub>H<sub>39</sub>N<sub>3</sub>CoCl<sub>2</sub>: C, 60.56; H, 7.34; N, 7.84. Found: C, 59.15; H, 6.99; N, 6.96 %.

# 3.3.3 2,6-bis[(cyclohexanemethylimino)ethyl]pyridine iron(II) (9)

Solid iron(II) chloride 0.29 g (2.3 mmol) was added to a stirred solution of ligand 3 1.0 g, (2.9 mmol) in THF (25 ml). Stirring was continued for 24 hours. Dark blue product was filtered off and washed with THF (10 ml) and Et<sub>2</sub>O (10 ml) and dried in vacuum. Yield: 1.0 g (92 %), blue. (MS,EI): m/z 479. IR: v [cm<sup>-1</sup>] = 1562 m (C=N). Anal. Calcd. for  $C_{23}H_{35}N_3FeCl_2$ : C, 57.52; H, 7.34; N, 8.75. Found: C, 57.42; H, 7.33; N, 8.82 %.

# 3.3.4 2,6-bis[(benzylimino)methyl]pyridine iron(II) (10)

The complex was prepared following the same procedure described above (3.3.3).

0.78 g (2.5 mmol) of the ligand **4** was allowed to react with 0.25 g (2.0 mmol) of FeCl<sub>2</sub>. **12**, Yield: 0.80 g (91 %), blue. (MS,EI): m/z 439. IR: v(cm<sup>-1</sup>) = 1585 m (C=N). Anal. Calcd. for  $C_{21}H_{20}N_3FeCl_2$ : C, 57.30; H, 4.35; N, 9.55. Found: C, 56.87; H, 4.59; N, 9.25 %.

### 3.3.5 2,6-bis[(benzylimino)ethyl]pyridine iron(II) (11)

The complex was prepared following the same procedure described above (3.3.3).

1.1 g (3.1 mmol) of the ligand **5** was allowed to react with 0.31 g (2.5 mmol) of FeCl<sub>2</sub> Yield: 0.9 g (77 %), blue. (MS, EI) :m/z (%) 468 (5 %), 341 (15 %), 250 (80 %). IR:  $v(cm^{-1}) = 1585 \text{ w}$  (C=N). Anal. Calcd. for C<sub>23</sub>H<sub>23</sub>N<sub>3</sub>FeCl<sub>2</sub>: C, 59.00; H, 4.95; N, 8.98. Found: C, 58.98; H, 5.18; N, 8.10 %.

### 3.3.6 2,6-bis[(1-naphthylimino)methyl]pyridine iron (II) chloride (12) and 2,6-bis[(1-naphthylimino)methyl]pyridine cobalt (II) chloride (15)

A filtered solution of the ligand **6** (0.50 g, 1.32 mmol) in THF (50 ml) was added to FeCl<sub>2</sub> or CoCl<sub>2</sub> (0.15 g 1.2 mmol) powder under continuous stirring at room temperature. Upon addition a precipitate started to form gradually. After 18 h, the solid was filtered, washed with THF (2×25 mL), n-pentane (2×25 mL) and dried in vacuum. **12**, Yield: 0.39 g (63 %), dark green. M.p. (dec) °C. IR: v(cm<sup>-1</sup>) = 1585 s (C=N). Anal. Calcd. for C<sub>27</sub>H<sub>19</sub>N<sub>3</sub>FeCl<sub>2</sub> 0.5 H<sub>2</sub>O: C, 62.21; H, 3.86; N, 8.06. Found: C, 61.93; H, 4.23; N, 7.59. **15**, Yield: 0.68 g (68 %), brown. M.p. (dec) 186 °C. IR: v(cm<sup>-1</sup>) = 1586 s (C=N). Anal. Calcd. for C<sub>27</sub>H<sub>19</sub>N<sub>3</sub>CoCl<sub>2</sub>. H<sub>2</sub>O: C, 60.80; H, 3.96; N, 7.87. Found: C, 61.05; H, 3.99; N, 7.51 %.

### 3.4 Crystal structure determination for 13 · 112 CHCl<sub>3</sub>

Crystal data for  $C_{27}H_{39}Cl_2N_3Co \cdot 1/2$  CHCl<sub>3</sub> Data were collected on a Nonius KappaCCD diffractometer. Structure was solved and the non-hydrogen atoms were refined with full-matrix least-squares on  $F^2$  using SHELXTL 97 program package at T = 173(2) K,  $\lambda$ (Mo  $K\alpha$ ) = 0.71073 Å, and  $\mu$ (Mo  $K\alpha$ ) = 0.933 mm<sup>-1</sup>. The crystal data, cell parameters and specific data collection parameters are summarized in table 2. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 229490 for compound **13**. Copies of this infor**Table 2** Crystallographic data parameters for data collection andrefinementfor $[CoCl2{2,6-bis[R-(+)-(bornylimino)methyl]}-pyridine}] \cdot \frac{1}{2}$  CHCl<sub>3</sub> (13).

Entry	[CoCl <sub>2</sub> (BBoMP)] (13)	
Chemical formula	C <sub>27</sub> H <sub>39</sub> N <sub>3</sub> CoCl <sub>2</sub> ·1/ <sub>2</sub> CHCl <sub>3</sub>	
Formula weight	595.13	
T /K	173(2)	
Crystal system	monoclinic	
Space group	$P2_1$	
a /Å	7.6603(11)	
b /Å	28.3153(14)	
c /Å	13.5365(18)	
βΙ°	97.927(9)	
V /Å <sup>3</sup>	2908.1(6)	
Z	4	
$D_{calc}/g \text{ cm}^{-3}$	1.359	
Absorption coefficient /mm <sup>-1</sup>	0.933	
Crystal dimensions /mm	0.18 x 0.10 x 0.08	
$\theta$ range /°	5.02 to 27.52	
Scan mode		
Number of data collected	40410	
Number of unique data	$13134 [R_{int} = 0.0559]$	
Number of data refined	13134	
Number of parameters	631	
$R^{\rm a}$ [I > $2\sigma(\hat{\rm I})$ ]	0.0432	
$wR_2^{(b)}$	0.0769	
Residual density /eA <sup>-3</sup>	0.295 and -0.376	

a)  $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ .

<sup>b)</sup>  $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}.$ 

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