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## Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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### Synthesis and Characterization of Novel Pyrazole-Based Ligands of $[\eta^5$ -Cyclopentadiene] $[\eta^4$ -Tetraphenylcyclobutadiene]Cobalt

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# Synthesis and Characterization of Novel Pyrazole-Based Ligands of $[\eta^5$ -Cyclopentadiene] $[\eta^4$ -Tetraphenylcyclobutadiene]Cobalt

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 $(\eta^{5}\text{-N},N\text{-dimethylaminomethylcyclopentadienyl})(\eta^{4}\text{-tetraphenylcyclobutadiene}) cobalt was prepared by the Mannich reaction of the metallocene (<math display="inline">\eta^{5}\text{-Cp})Co(\eta^{4}\text{-Ph}_{4}C_{4})$  with tetramethylmethylenediamine and phosphoric acid. The methyl iodide salt of this compound was reacted with 3,5-dimethylpyrazole and 3-methyl-5-trifluoromethylpyrazole to prepare the pyrazole derived metallocenes, [ $\eta^{5}\text{-}(C_{5}H_{4}CH_{2})\text{-}3,5\text{-}(CH_{3})_{2}(C_{3}HN_{2})]Co[\eta^{4}\text{-}(Ph_{4}C_{4})]$ (1) and [ $\eta^{5}\text{-}(C_{5}H_{4}CH_{2})\text{-}3\text{-}CH_{3}\text{-}5\text{-}CF_{3}(C_{4}H_{2}N)]Co[\eta^{4}\text{-}(Ph_{4}C_{4})]$ (2). Compounds 1 and 2 were structurally characterized.

Keywords dimethylpyrazole, methyltrifluoromethylpyrazole, metallocene, cobalt, dimethylaminomethylcyclopentadienyl, tetraphenylcyclobutadiene

#### INTRODUCTION

Pyrazole as such or as part of a molecule has been used extensively as ligands in coordination chemistry.<sup>[1]</sup> The stability and electronic properties of such ligands has helped in the design of a host of metal complexes and metal clusters, some of which has shown potential use as light emitting devices and display devices.<sup>[2]</sup> Examples of organometallic compounds known so far having pyrazole moieties has been mostly centered on ferrocene based molecules (Figure 1).<sup>[3–5]</sup> The stability and electroactivity of these ferrocene based

pyrazole ligands has been utilized in the preparation of many novel metal complexes with interesting electrochemical properties. In addition, ferrocene-based ligands having pyrazolyl and substituted pyrazolyl groups having planar chirality and central chirality has been used in the design of catalysts useful in asymmetric synthesis.<sup>[6]</sup>

Among organometallic sandwich compounds, there are only few compounds whose chemical properties match that of ferrocene. Among these, ( $\eta^5$ -cyclopentadienyl) ( $\eta^4$ -tetraphenylcyclobutadiene)cobalt has been very promising in its stability and reactivity.<sup>[7]</sup> Recent work carried out on carboxylic acid derivatives of this metallocene has shown its potential as a substrate whose functional group chemistry can be utilized in the design of novel chiral organometallic catalysts<sup>[8–10]</sup> as well as clusters.<sup>[11]</sup> Herein we report the synthesis and structural characterization of the first examples of pyrazolyl derivatives of this metallocene, which are potential ligands similar to their ferrocene analogues.

#### **RESULTS AND DISCUSSION**

Two examples of pyrazole-derived  $(\eta^5$ -cyclopentadienyl)  $(\eta^4$ -tetraphenylcyclobutadiene)cobalt  $\{\eta^5$ -[3,5-(CH<sub>3</sub>)<sub>2</sub>C<sub>3</sub>HN<sub>2</sub>] CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>}-Co[ $\eta^4$ -(Ph<sub>4</sub>C<sub>4</sub>)] (1) and  $\{\eta^5$ -[3-(CH<sub>3</sub>) 5-(CF<sub>3</sub>)C<sub>3</sub>HN<sub>2</sub>] CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>}-Co[ $\eta^4$ -(Ph<sub>4</sub>C<sub>4</sub>)] (2) were prepared in this study. We have attempted to vary the basicity of the pyrazolyl group by introducing, on the ring, two methyl groups and also by replacing one of the methyl groups by a trifluoromethyl group. The incorporation of one trifluoromethyl group is expected to decrease the electron-donating property of 2 in comparison to 1 and increase the ligand-centered  $\pi\pi^*$  energy gap.

The reaction of Co(PPh<sub>3</sub>)<sub>3</sub>Cl with NaCp and diphenylacetylene resulted in the formation of the metallocene ( $\eta^{5}$ cyclopentadienyl)( $\eta^{4}$ -tetraphenylcyclobutadiene) cobalt in around 50% yield (Scheme 1). The compound is purified by column chromatography on silica gel. Reaction of ( $\eta^{5}$ -Cp) Co( $\eta^{4}$ -Ph<sub>4</sub>C<sub>4</sub>) with tetramethylmethylenediamine and phosphoric acid as catalyst in acetic acid medium resulted in the formation of ( $\eta^{5}$ -N,N-dimethylaminomethylcyclopentadienyl) ( $\eta^{4}$ -tetraphenylcyclobutadiene)cobalt in 70% yield (Scheme 2).

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Dedicated to Prof. Dr. Herbert W. Roesky on the occasion of his  $70^{\text{th}}$  birthday.

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FIG. 1. Examples of ferrocene-derived pyrazole ligands.

The synthesis of this compound was reported previously by Rausch et al.<sup>[12]</sup> However we have utilized a relatively inexpensive and carbonyl-free method for the synthesis of  $(\eta^{5}-(Cp)Co(\eta^{4}-Ph_{4}C_{4}))$  by slightly modifying the procedure reported for the preparation of  $\{\eta^{5}-C_{5}H_{4}[C(O)OMe]\}Co(\eta^{4}-Ph_{4}C_{4}))$  by Richards and coworker.<sup>[13]</sup> The methyliodide salt of the dimethylaminomethyl metallocene, which was prepared by reaction of  $[\eta^{5}-C_{5}H_{4}CH_{2}N(CH_{3})_{2}]Co[\eta^{4}-(Ph_{4}C_{4})]$  cobalt and iodomethane (Scheme 3).

This methyliodide salt reacts directly with 3,5-dimethylpyrazole and 3-methyl-5-trifluoromethylpyrazole to yield the pyrazole derived metallocenes 1 and 2 in 45 and 33% yields, respectively (Scheme 4). Compounds 1 and 2 were purified by column chromatography over silica gel using a hexaneethylacetate mixture as eluent and are quite stable under air and moisture over extended periods of time.

#### Spectral Studies

The <sup>1</sup>H-NMR spectra of compounds **1** and **2** differ considerably from each other. Even though there is no difference in the chemical shift values of cyclopentadienyl protons of compounds **1** and **2**, the CH proton of the pyrazole ring and CH<sub>2</sub> protons show downfield shifts in the case of compound **2** (6.15–6.40 and 4.36 ppm, respectively) compared to



SCH. 2.



compound **1** (5.65 and 4.29 ppm). This may be due to the presence of a strongly electron-withdrawing CF<sub>3</sub> group in compound **2**. Further, the signal of the CH proton is split into a multiplet due to long-range coupling with the CF<sub>3</sub> group. <sup>1</sup>H-NMR spectra of compound **1** gave two different signals for the methyl groups (2.05 and 2.12 ppm). This was further confirmed by the <sup>13</sup>C-NMR spectra, which gave two different signals for the CH<sub>3</sub> carbon atoms (11.28 and 13.50 ppm). The <sup>13</sup>C-NMR spectra of compound **2** gave a signal at 29.71 ppm for the -CF<sub>3</sub> carbon and at 11.35 ppm for the CH<sub>3</sub> carbon atom. <sup>1</sup>H-NMR spectra of compound **2** gave one signal for the CH<sub>3</sub> proton (2.07 ppm) which was shifted to the upfield region compared to 3-methyl-5-trifluoromethylpyrazole (2.43 ppm).

#### Structural Studies

The crystal structure of compounds 1 and 2 showed many similarities (Figures 2 and 3). The pyrazole rings of 1 and 2are oriented at angles of 112.34° and 112.62° respectively with respect to the cyclopentadienyl rings. The CF<sub>3</sub> group present in compound 2 is oriented away from the cyclopentadiene ring. The plane containing the pyrazole ring bisects the plane containing the cyclopentadienyl ring at an angle of  $71.98^{\circ}$  in the case of compound **1** and  $70.09^{\circ}$  in case of compound 2. The four phenyl rings present in the cyclobutadiene ring are oriented at almost equal angles with respect to the cyclobutadiene ring in both the compounds 1 and 2(Table 1). This is in contrast to the observation of the  $(\eta^5$ carboxycyclopentadienyl)( $\eta^4$ -tetraphenylcyclobutadiene)cobalt where the four phenyl rings of the tetraphenyl cyclobutadiene ring of 4 are displaced at different angles 37.39, 48.44, 29.25, and 60.49° with respect to the cyclobutadiene ring. Further the  $-CF_3$  group present in compound 2 involved in weak C-F...H interaction (2.585(6) Å) with -CH<sub>3</sub> hydrogen of the adjacent molecule (Figure 4). The cyclopentadienyl ring and cyclobutadienyl ring are planar.



SCH. 4. Where  $R_1$ ,  $R_2 = CH_3$  (1)  $R_1 = CH_3$ ,  $R_2 = CF_3$  (2).



FIG. 2. Thermal ellipsoid view of compound **1** with 30% probability factor (H atoms are omitted for clarity).

In conclusion, we have prepared and structurally characterized the first examples of pyrazole-based ligands of  $[\eta^5$ -cyclopentadiene][ $\eta^4$ -tetraphenylcyclobutadiene]cobalt having different electronic properties. Further study on the use of these organometallic ligands in synthesis of metal complexes is in progress.

#### **EXPERIMENTAL**

All manipulations were carried out using standard Schlenk techniques under nitrogen atmosphere. THF and toluene were freshly distilled from sodium benzophenone ketyl under nitrogen atmosphere and used. Sodium salt of cyclopentadiene, tris(triphenylphosphine)cobalt chloride,<sup>[13]</sup> 3,5-dimethylpyrazole and 3-methyl-5-trifluoromethylpyrazole were prepared according to the literature procedures.<sup>[14]</sup> Diphenylacetylene and triphenylphosphine (Aldrich) were used as such. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300 and 75.47 MHz

FIG. 3. Thermal ellipsoid view of compound **2** with 30% probability factor (H atoms are omitted for clarity).

TABLE 1								
Selected bond	distances	and	angles	of	compounds	1	and 2	

	Compound	Compound 2
	I	2
Bond lengths (Å)		
Co(1)-C(7)	2.058 (3)	2.020 (3)
Co(1)-C(12)	1.981 (3)	1.984 (3)
Co(1)-C(15)	1.987 (3)	1.987 (3)
C(12)-C(16)	1.473 (4)	1.469 (4)
N(1)- N(2)	1.364 (5)	1.343 (4)
N(2)-C(2)	1.334 (5)	1.335 (5)
Bond angles ( $^{\circ}$ )		
N(1)-C(6)-C(7)	112.3 (3)	112.6 (2)
C(12)-C(16)-C(17)	119.9 (2)	120.3 (0)
C(13)-C(22)-C(23)	121.9 (8)	122.1 (9)
C(14)-C(28)-C(29)	121.6 (0)	121.7 (7)
C(15)-C(34)-C(35)	120.9 (4)	121.6 (5)

respectively. IR spectra in the range  $4000-250 \text{ cm}^{-1}$  were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer. Mass spectra were recorded in the EI mode using a JEOL SX 102/DA-6000 mass spectrometer.

#### X-ray Crystallographic Study

Suitable crystals of compounds 1 and 2 were obtained by slow evaporation of their saturated solutions in ethyl acetate/ hexane solvent mixture. Single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with a MoK $\alpha$  ( $\lambda = 0.71073$  Å) sealed tube. All crystal structures were solved by direct methods. The program SAINT (version 6.22) was used for integration of the intensity of reflections and scaling. The program SADABS was used for absorption correction.<sup>[15]</sup> The crystal structures were solved and refined using the SHELXTL (version 6.12) package.<sup>[16]</sup> All hydrogen atoms were included in idealized positions, and a riding model was used. Nonhydrogen atoms were refined with anisotropic displacement parameters. CCDC 626105 and 626104 contains the supplementary crystallographic data for the compounds 1 and 2, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/datarequest/cif.

#### **General Procedure**

A stoichiometric mixture of  $[\eta^5-C_5H_4CH_2N(CH_3)_3I]Co[\eta^4-(Ph_4C_4)]$ , 3,5-dimethylpyrazole (or) 3-methyl-5-trifluoromethylpyrazole and potassium carbonate were taken in 20 ml of dry acetonitrile. The mixture was heated to reflux for several hours and the progress of the reaction was monitored



FIG. 4. View of compound  $\mathbf{2}$  with 30% probability factor showing weak C-F...H interaction.

by thin layer chromatography. After completion of the reaction, the solvent was evaporated by rotary evaporator and the compound was separated by a silica gel column using ethylacetate-hexane mixture as the eluent. A small amount of the compound was recrystallized using the same solvent mixture to give red-colored, block-like crystals (Table 2).

#### { $\eta^{5}$ -[3,5-(CH<sub>3</sub>)<sub>2</sub>C<sub>3</sub>HN<sub>2</sub>]CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>}-Co[ $\eta^{4}$ -(Ph<sub>4</sub>C<sub>4</sub>)] (1)

 $[\eta^{5}-C_{5}H_{4}CH_{2}N(CH_{3})_{3}I]Co[\eta^{4}-(Ph_{4}C_{4})]$  (0.20 g, 0.3 mmol), 3,5-dimethylpyrazole (0.03 g, 0.3 mmol), and potassium carbonate (0.04 g, 0.3 mmol). Reaction time: 33 hours. Yield: 0.08 g, 45%. MP: 195°C; IR ( $\nu$ , cm<sup>-1</sup>): 3048w, 2922w, 2358w, 1596s, 1545s, 1496vs, 1453s, 1327w, 1064w, 1025s, 772s, 698vs, 572s; H<sup>1</sup>-NMR: 2.05 (s, 3H, CH<sub>3</sub>), 2.12 (s, 3H, CH<sub>3</sub>), 4.29 (s, 2H, CH<sub>2</sub>), 4.59 (d, 2H, Cp-H), 4.74 (d, 2H, Cp-H), 5.65 (s, 1H, Py-H), 7.23-7.26 (m, 12H, Ar-H), 7.45–7.49 (m, 8H, Ar-H); <sup>13</sup>C-NMR: 11.28 (-CH<sub>3</sub>), 13.50 (-CH<sub>3</sub>), 46.07 (Cp-CH<sub>2</sub>), 75.19 (C<sub>4</sub>Ph<sub>4</sub>), 76.59 (C<sub>4</sub>Ph<sub>4</sub>), 83.43 (CpC), 83.96 (CpC), 92.68 (ipso-CpC), 105.12 (Py-CH), 126.43 (PhC), 128.12 (PhC), 128.81 (PhC), 136.02 (ipso-PhC), 138.07 (py C-CH<sub>3</sub>), 147.19 (py N-C); MS (ES<sup>+</sup>)  $[m/e \text{ (species)}]: 589 (M+1)^+, 493 (M-Py)^+, 415$  $(Co(C_4Ph_4)^+$ . Anal. calcd. for  $C_{39}H_{33}CoN_2$ : C 79.58, H 5.65; Found: C 79.43, H 5.51.

#### { $\eta^{5}$ -[3-(CH<sub>3</sub>) 5-(CF<sub>3</sub>)C<sub>3</sub>HN<sub>2</sub>]CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>}-Co[ $\eta^{4}$ -(Ph<sub>4</sub>C<sub>4</sub>)] (2)

 $[\eta^{5}-C_{5}H_{4}CH_{2}N(CH_{3})_{3}I]Co[\eta^{4}-(Ph_{4}C_{4})]$  (0.22 g, 0.33 mmol), 3-methyl-5-trifluoromethylpyrazole (0.06, 0.4 mmol), and potassium carbonate (0.056 g, 0.4 mmol). Reaction time 48 hours. Yield: 0.07 g, 33%; MP: 210°C; IR ( $\nu$ , cm<sup>-1</sup>): 3051bs, 2925w, 2358bs, 1601s, 1549w, 1492vs, 1446w, 1389s, 1335w, 1228vs, 1168vs, 1119vs, 1028s, 974s, 812s, 782s, 699w, 559s, 458w; <sup>1</sup>H-NMR: 2.07 (3H, d, -CH<sub>3</sub>), 4.36 (d, 2H, CH<sub>2</sub>), 4.55 (2H, s, Cp-CH<sub>2</sub>), 4.70 (2H, d, Cp-CH<sub>2</sub>), 6.27 (1H, d, Py-CH), 7.17 (12H, brs, m + p-PhH), 7.39 (8H, brs, o-PhH); <sup>13</sup>C-NMR:

 TABLE 2

 Data collection and structure solution parameters of compounds 1 and 2

	I I I I I I I I I I I I I I I I I I I	
Empirical formula	C <sub>39</sub> H <sub>33</sub> CoN <sub>2</sub> (1)	$C_{39}H_{30}CoF_{3}N_{2}$ (2)
Formula mass	588.60	642.58
Crystal system	Triclinic	Monoclinic
Space group	P-1	P21/c
<i>T</i> (K)	298 (2)	298 (2)
A (Å)	9.841 (5)	11.2529 (18)
<i>B</i> (Å)	11.087 (6)	19.914 (3)
<i>c</i> (Å)	14.651 (8)	14.255 (2)
$\alpha$ (°)	86.746 (9)	90.00
$B(^{\circ})$	75.803 (8)	95.029 (3)
$\Gamma$ (°)	79.410 (9)	90.00
$V(\text{\AA}^3)$	1523.2 (14)	3182.0 (9)
Ζ	2	4
$D_{\rm calcd}~({\rm g/cm^3})$	1.283	1.341
$M (\mathrm{mm}^{-1})$	0.593	0.587
$T_{max}/T_{min}$	0.503/0.206	0.939/0.907
$\theta$ range (°)	2.17-25.49	2.23-28.26
Index ranges	$-11 \le h \le 11$	$-13 \le k \le 13$
	$-13 \le k \le 13$	$-24 \le k \le 24$
	$-17 \le l \le 17$	$-17 \le l \le 17$
Refl. collected	12124	30841
Refl. unique	5223	5930
Refl. observed	3768	4832
$Rl(I > 2\sigma(I))$	0.0534	0.0578
wR2 (all data)	0.1510	0.1341
$(\Delta \rho)_{\rm max}, (\Delta \rho)_{\rm min}$	0.557/-0.671	0.520/-0.275
$\Lambda$ (Å)	0.71073	0.71073

11.35 (-CH<sub>3</sub>), 29.71 (-CF<sub>3</sub>), 47.32 (Cp-CH<sub>2</sub>), 75.46 (C<sub>4</sub>Ph<sub>4</sub>), 76.59 (C<sub>4</sub>Ph<sub>4</sub>), 83.42 (CpC), 84.17 (CpC), 91.43 (ipso-CpC), 103.92 (PyC-CH), 126.59 (PhC), 128.19 (PhC), 128.81 (PhC), 135.80 (ipso-PhC), 139.12 (py N-C); MS (ES<sup>+</sup>) [m/e(species)]: 642 (M)<sup>+</sup>, 493 (M-Py)<sup>+</sup>; Anal. calcd. for C<sub>39</sub>H<sub>30</sub>CoF<sub>3</sub>N<sub>2</sub>: C 72.89, H 4.71; Found: C 72.78, H 4.61.

#### REFERENCES

1. (a) Chandrasekhar, V.; Azhakar, R.; Krishnan, V.; Athimoolam, A.; Pandian, B. M. Cyclocarbophosphazenecontaining tetrameric assemblies formed by the mediation of P-O-P and P-O-Cu linkages. J. Am. Chem. Soc. 2006, 128, 6802-6803; (b) Chandrasekhar, V.; Athimoolam, A.; Srivatsan, S. G.; Sundaram, P. S.; Verma, S.; Steiner, A.; Zachcini, S.; Butcher, R. Pyrazolylcyclotriphosphazene containing pendant polymers: synthesis, characterization, and phosphate ester hydrolysis using a Cu(II)-metalated cross-linked polymeric 2002, 41, catalyst. Inorg. Chem. 5162-5173; (c) Chandrasekhar, V.; Kingsley, S.; Rhatigan, B.; Lam, M. K.; Rheingold, A. L. New structural forms in molecular metal phosphonates: novel tri- and hexanuclear zinc(II) cages containing phosphonate and pyrazole ligands. Inorg. Chem. 2002, 41, 1030–1032; (d) Sharma, S.; Barooah, N.; Baruah, J. B. Tris(3,5dimethylpyrazole)copper(II) nitrate as an oxidation catalyst. *J. Mol. Cat. A Chem.* **2005**, *229*, 171–176.

- (a) Yang, C.-H.; Li, S.-W.; Chi, Y.; Cheng, Y.-M.; Yeh, Y. S.; Chou, P.-T.; Lee, G.-H.; Wang, C.-H.; Shu, C.-F. Heteroleptic cyclometalated iridium(III) complexes displaying blue phosphorescence in solution and solid state at room temperature. *Inorg. Chem.* 2005, 44, 7770–7780; (b) Li, J.; Djurovich, P. I.; Alleyne, B. D.; Yousufuddin, M.; Ho, N. N.; Thomas, J. C.; Peters, J. C.; Bau, R.; Thompson, M. E. Synthetic control of excited-state properties in cyclometalated Ir(III) complexes using ancillary ligands. *Inorg. Chem.* 2005, 44, 1713.
- Barranco, E. M.; Gimeno, M. C.; Antonio, L.; Villacampa, M. D. Gold and silver complexes with the ferrocenyl-pyrazolate ligand FcCH2pz. *Inorg. Chim. Acta* 2005, *358*, 4127–4182.
- Tang, L.-F.; Jia, W.-L.; Wang, Z.-H.; Chai, J.-F.; Wang, J.-T. Synthesis, structures and electrochemical properties of Group 6 metal carbonyl complexes containing ferrocenylpyrazole ligands. J. Organomet. Chem. 2001, 637–639, 209–215.
- Reger, D. L.; Brown, K. J.; Gardiner, J. R.; Smith, M. D. Syntheses and structural characterizations of rhenium carbonyl complexes of a bitopic ferrocene-linked bis(pyrazolyl)methane ligand. J. Organomet. Chem. 2005, 690, 1889–1900.
- Burckhardt, U.; Drommi, D.; Togni, A. Synthesis, structure, and reactivity of new chiral ferrocenyl pyrazole ligands. *Inorg. Chim. Acta* 1999, 296, 183–194.
- (a) Varela, J. A.; Saa, C. Construction of pyridine rings by metalmediated [2+2+2] cycloaddition. *Chem. Rev.* 2003, 103, 3787-3801; (b) MacFarland, D. K.; Gorodetzer, R. Rotorshaped cyclopentadienyltetraphenylcyclobutadienecobalt. An advanced inorganic experiment. *J. Chem. Educ.* 2005, 82, 109-110; (c) Goswami, A.; Meier, C.-J.; Pritzkow, H.; Siebert, W. Cobalt-mediated cyclooligomerization reactions of borylacetylenes. *Eur. J. Inorg. Chem.* 2004, 13, 2635-2645; (d) Schaefer, C.; Gleiter, R.; Rominger, F. Isolation of bis(η<sup>2</sup>nitrato) (η<sup>4</sup>-cyclobutadiene)cobalt(II) complexes from the oxidation of sterically hindered CpCo-stabilized cyclobutadiene complexes. *Organometallics* 2004, 23, 2225-2227.
- (a) Jones, G.; Richards, C. J. (S)-Serine derived N-O and N-P oxazoline ligands for asymmetric catalysis. *Tetrahedron: Asymmetry* 2004, *15*, 653–664; (b) Butler, D. C. D.; Richards, C. J. Synthesis of 1'-substituted derivatives of 1,2,3,4,5-pentaphenylferrocene. *Organometallics* 2002, *21*, 5433–5436; (c) Jones, G.; Richards, C. J. Metallocene-appended imidazoles displaying virtual planar chirality. *Organometallics* 2001, *20*, 1251–1254.
- (a) Anderson, C. E.; Overman. L. E. Catalytic asymmetric rearrangement of allylic trichloroacetimidates. A practical method for preparing allylic amines and congeners of high

enantiomeric purity. J. Am. Chem. Soc. 2003, 125, 12412-12413; (b) Kirsch, S. F.; Overman, L. E.; Watson, M. P. Monomeric cobalt oxazoline palladacycles (COP). Useful catalysts for catalytic asymmetric rearrangement of allylic trichloroa-2004, 69, 8101-8104; cetimidates. J. Org. Chem. (c) Kirsch, S. F.; Overman, L. E. Catalytic asymmetric synthesis of chiral allylic esters. J. Am. Chem. Soc. 2005, 127, 2866-2867; (d) Prasad, R. S.; Anderson, C. E.; Richards, C. J.; Overman, L. E. Synthesis of *tert*-Leucine-derived cobalt oxazoline palladacycles. Reversal of palladation diastereoselectivity and application to the asymmetric rearrangement of N-Aryl trifluoroacetimidates. Organometallics 2005, 24, 77-81.

- 10. Gupta, H. P.; Kumar, M. S.; Upreti, S.; Elias, A. J. Synthesis of metallocene carboxylate esters  $[\eta^4-Ph_{4-n}(SiMe_3)_nC_4][\eta^5-MeOC(O)C_5H_4]Co (n = 1, 2) and their desilylation reactions: structural studies and conversion to metallocene carboxylic acids and alcohols.$ *Eur. J. Inorg. Chem.***2006**, 5022–5032.
- 11. Kumar, M. S.; Upreti, S.; Gupta, H. P.; Elias, A. J. Reactions of  $[\eta^5$ -carboxycyclopentadiene] $[\eta^4$ -tetraphenylcyclobutadiene]cobalt with alkyl and aryl tin oxides: Synthesis, characterization and electrochemistry of novel monomeric and dimeric  $[\eta^5$ -carboxycy-clopentadiene] $[\eta^4$ -tetraphenylcyclobutadiene]cobalt based stannoxanes. J. Organomet. Chem. **2006**, 691, 4708–4816.
- (a) Rausch, M. D.; Genetti, R. A. Organometallic π-complexes. XXII. Chemistry of π- cyclopentadienyltetraphenylcyclobutadie necobalt and related compounds. J. Org. Chem. 1970, 35, 3888;
   (b) Izumi, T.; Maemura, M.; Endoh, K.; Oikawa, T.; Zakozi, S.; Kasahara, A. The σ bonded palladium(II) complex of [-(dimethylaminomethyl)cyclopentadienyl]tetraphenylcyclobutadienecoblat(II). Bull. Chem. Soc. Jpn. 1981, 54, 836–839.
- Stevens, A. M.; Richards, C. J. Synthesis highly diastereoselective palladation of (η<sup>5</sup>-(S)-2-[4-(isopropyl)oxazolinylcyclopentadienyl](η<sup>4</sup>-tetraphenylcyclobutadiene)cobalt. Organometallics 1999, 18, 1346–1348.
- (a) Furnis, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Textbook of Practical Organic Chemistry*, 4th edn.; Addison-Wesley: Essex, 1989, p. 1149; (b) Zelenin, K. N.; Tugusheva, A. R.; Yakimovich, S. I.; Alekseev, V. V.; Zerova, E. V. 5-Hydroxy-2-pyrazolines and some of their 1-substituted analogs. *Chemistry of Heterocyclic Compounds* 2002, 38, 668–676.
- Sheldrick, G. M. Unpublished work based on the method described in: Blessing, R. H. Acta Crystallogr. Sect. A 1995, S1–S33.
- (a) Sheldrick, G. M. Acta Crystallogr. 1990, A46, 467–473;
  (b) Sheldrick, G. M. SHELXTL-NT 2000, Version 6.12, Reference Manual; University of Göttingen: Göttingen, Germany.