ORGANOMETALLICS
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pubs.acs.org/Organometallics

Cyclopentadienyl 1,2- and 1,3-Disubstituted Cobalt Sandwich Compounds $\{\eta^5\text{-}[MeOC(O)]_2C_5H_3\}$ $Co(\eta^4\text{-}C_4Ph_4)$: Precursors for Sterically Hindered Bidentate Chiral and Achiral Ligands

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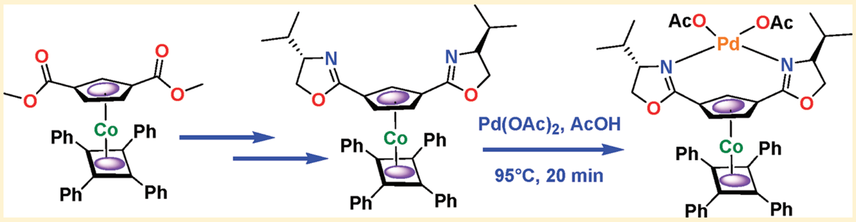
Ⓢ *Supporting Information*



ABSTRACT: Reaction of the sodium cyclopentadienyl $Na\{C_5H_4[C(O)OMe]\}$ with methyl chloroformate, ClC(O)OMe, in a 2:1 molar ratio was found to result in a mixture of sodium salts of 1,2- and 1,3-dicarbomethoxycyclopentadienyls. This mixture, on refluxing in toluene with $CoCl(PPh_3)_3$ and diphenylacetylene, resulted in the formation of cyclopentadienyl 1,3- and 1,2-diester derived cobalt sandwich compounds $\{\eta^5\text{-}[MeOC(O)]_2C_5H_3\}Co(\eta^4\text{-}C_4Ph_4)$ (**1**, **2**) in 85% yield. 1,3- and 1,2-diesters **1** and **2** were converted to the dicarboxylic acids **3** and **4** by refluxing with aqueous KOH in ethanol. The diacyl chloride of **4** was generated in situ by the reaction of **4** with oxalyl chloride and this, on further reaction with ferrocene under Friedel–Crafts conditions, yielded the novel bis-metallocenyl acenequinone **5**, having both the iron and cobalt sandwich units in the same compound. The dicarboxylic acid **3** on reaction with oxalyl chloride followed by (*S*)-2-amino-3-methyl-1-butanol, triethylamine, and mesyl chloride was converted to the novel 1,3-bis(oxazoline) cyclopentadienyl-derived bidentate chiral complex $[\eta^5\text{-}1,3\text{-}(4\text{-}i\text{Pr-}2\text{-Ox})_2C_5H_3]Co(\eta^4\text{-}C_4Ph_4)$ (**6**; Ox = oxazolinyl). Reaction of **6** with $Pd(OAc)_2$ in acetic acid at 95 °C resulted in the formation of the chiral palladium complex **7**. The utility of this palladium complex as a chiral catalyst for the asymmetric rearrangement of trichloroacetimidates to trichloroacetamides has been evaluated.

■ INTRODUCTION

Stable organometallic sandwich compounds having one sterically bulky cyclobutadienyl or cyclopentadienyl ring (e.g., C_4Ph_4, C_5Ph_5) have recently attracted considerable interest from the perspective of synthesizing novel achiral as well as chiral ligands.[1,2] Preparation of catalysts for high-yielding and highly enantioselective reactions ranging from palladium-catalyzed cross-coupling reactions to aza-Claisen rearrangements have been reported using such ligands.[3,4] Among such sandwich compounds, $(\eta^5\text{-}Cp)Co(\eta^4\text{-}C_4Ph_4)$ has been the choice for many chemists, due to the relative ease of its synthesis and excellent air and moisture stability.[5,6] Sustained interest in this compound is indicated by the fact that improved protocols are currently being reported for the synthesis of a range of its analogues.[7] Although very similar to ferrocene in stability, the relatively poor reactivity of the Cp ring makes cyclopentadienyl derivatization of $(\eta^5\text{-}Cp)Co(\eta^4\text{-}C_4Ph_4)$ quite difficult. For example, lithiation of the Cp ring required for the synthesis of the first planar chiral bidentate ligand based on this sandwich compound, $[\eta^5\text{-}1,2\text{-}(PPh_2)(SBu^t)C_5H_3]Co(\eta^4\text{-}C_4Ph_4)$, was made possible only by using the superbase t-BuLi/KOBu^t, also in poor yields.[8] However, the syntheses of palladacycles by ortho palladation of the oxazoline-derived $(\eta^5\text{-}Cp)Co(\eta^4\text{-}C_4Ph_4)$ and its cyclobutadiene linked dimer have been quite facile and excellent chiral catalysts for enantioselective aza-Claisen rearrangements have resulted from such studies.[4,9,10]

Disubstitution on a Cp ring of sandwich compounds has been an elegant route for making achiral as well as planar chiral bidentate ligands. While many such ligands are known with ferrocene,[11] only a handful of examples having 1,2- and 1,3-disubstitution on the Cp ring of $(\eta^5\text{-}Cp)Co(\eta^4\text{-}C_4Ph_4)$ have been reported so far.[12] Most of these have a methyl group as one of the Cp substituents, which limits the range of their utility. Richards and co-workers have very recently reported a reaction of $(\eta^5\text{-}Cp)Co(\eta^4\text{-}C_4Ph_4)$ with mercuric acetate followed by iodine to generate the difunctional 1,2- and 1,3-diiodo derivatives $(\eta^5\text{-}C_5H_3I_2)Co(\eta^4\text{-}C_4Ph_4)$, albeit in moderate yields, with the 1,2-isomer as the major product.[13] In this paper we report an easy and straightforward method for the synthesis of cyclopentadienyl 1,2- and 1,3-diester derivatives of $(\eta^5\text{-}Cp)Co(\eta^4\text{-}C_4Ph_4)$ in good overall yields and also report the synthesis of useful difunctional derivatives from the same. We have attempted to maximize the yields of the cyclopentadienyl 1,3-diester derivative and report herein the synthesis of a chiral

Received: January 13, 2012
Published: February 22, 2012

dx.doi.org/10.1021/om300027c | *Organometallics* 2012, 31, 2059–2065

Table 1. X-ray Crystal Structure Parameters of Compounds 1, 2, 5, and 6

param	1	2	5	6
formula	$C_{37}H_{29}CoO_4$	$C_{37}H_{29}CoO_4$	$C_{45}H_{31}CoFeO_2$	$C_{45}H_{43}CoN_2O_2$
mol wt	596.53	596.53	718.48	702.74
cryst syst	triclinic	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
a (Å)	10.440(2)	8.132(1)	11.079(3)	13.958(2)
b (Å)	11.605(2)	20.642(3)	12.484(3)	15.306(2)
c (Å)	13.574(2)	17.443(3)	13.700(3)	17.085(2)
α (deg)	91.814(3)	90	116.292(4)	90
β (deg)	102.502(3)	95.169(3)	90.592(5)	90
γ (deg)	113.468(3)	90	103.413(5)	90
V (Å^3)	1459.9(4)	2915.9(8)	1638.5(7)	3650.1(7)
Z	2	4	2	4
T/K	298	298	298	298
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g/cm^3)	1.357	1.359	1.456	1.279
μ (mm^{-1})	0.628	0.629	0.989	0.511
goodness of fit	1.199	1.317	1.018	1.184
θ range (deg)	1.55−25.0	1.53−25.00	1.67−25.00	1.79−25.50
total no. of rflns	14081	27598	15768	35049
no. of unique rflns	5124	5136	5737	6420
no. of obsd data ($I > 2\sigma(I)$)	4494	4914	3801	6203
R_{int}	0.045	0.047	0.070	0.045
R1 ($F^2 > 2\sigma(F^2)$), wR2 (F^2)[a]	0.0758, 0.1667	0.0704, 0.1454	0.0635, 0.1414	0.0435, 0.1009
Flack param				0.04(1)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(|F_o^2 - F_c^2|)^2]/\sum|w(F_o^2)^2|\}^{1/2}$.

1,3-bis(oxazoline) derivative of (η^5-Cp)Co(η^4-C_4Ph_4) which can function as a bidentate chiral ligand. We also report the synthesis of a novel chiral palladium complex based on this ligand which has shown promising catalytic activity in the asymmetric aza-Claisen rearrangement of trichloroacetimidates.

EXPERIMENTAL SECTION

General Methods. All manipulations of the complexes were carried out using standard Schlenk techniques under a nitrogen atmosphere. Tetrahydrofuran, xylene, and toluene were freshly distilled from sodium benzophenone ketyl under a nitrogen atmosphere and used. The sodium salt of carbomethoxycyclopentadiene,[14] tris(triphenylphosphine)cobalt chloride,[15] and trichloroacetimidates[16] were prepared according to literature procedures. Methyl chloroformate, ethyl chloroformate, triphenylphosphine (Spectrochem), dimethyl carbonate, L-valinol, mesyl chloride, and diphenylacetylene (Aldrich) were used as received.

Instrumentation. ^{1}H and ^{13}C{^{1}H} spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300 and 75.47 MHz, respectively. IR spectra in the range 4000−250 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 on a Bruker Micro-TOF QII quadrupole time-of-flight (Q-TOF) mass spectrometer. Optical rotations of the chiral compounds were measured on an Autopol V (Rudolph Research, Flanders, NJ) instrument. All the rotations were measured at 589 nm (sodium D line) using chloroform as solvent, and readings were cross-checked by taking measurements at two different concentrations (200 and 400 mg/100 mL). The enantiomeric excess was determined by a Shimadzu LC6AD HPLC instrument fitted with a Daicel OD-H chiral column. All HPLC analyses used to determine enantiomeric purity were calibrated with samples of the racemate.

X-ray Crystallography. Suitable crystals of compounds **1**, **2**, and **4**−**6** were obtained by slow evaporation of their saturated solutions in ethyl acetate/hexane mixtures. Single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with a Mo Kα (λ = 0.710 73 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. The crystal structures were solved and refined using the SHELXTL (version 6.12) package.[17] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. Table 1 gives the data collection and structure solution parameters for compounds **1**, **2**, **5**, and **6**. Selected bond distances and angles for compounds **1**, **2**, and **4**−**6** are given in the Supporting Information.

Synthesis of Na{[MeOC(O)]$_2$C$_5$H$_3$}. Na{[MeOC(O)]C$_5$H$_4$} (6.00 g, 41.00 mmol) was dissolved in 40 mL of THF and cooled to 0 °C using an ice bath. To this cooled solution was added MeOC(O)Cl (1.93 g, 20.50 mmol) dropwise with stirring. The ice bath was removed, and the reaction mixture was stirred for 30 min at room temperature followed by 30 min at 50 °C. After the reaction mixture was cooled, ethyl ether (100 mL) was added to precipitate the sodium salt of the diester. The dark red solvent layer was removed using a pipet after the precipitate settled down. This process was repeated three to four times until the solvent layer turned colorless. Afterward, the precipitate was dried on a hot plate at 150 °C under nitrogen. The dried precipitate was cooled and dissolved in THF (50 mL) to get a red-brown solution. The solution was filtered under nitrogen, and evaporation of the clear solution gave Na{[MeOC(O)]$_2$C$_5$H$_3$} (yield 3.56 g, 17.45 mmol, 85%). This was freshly prepared and used for the next step.

{η^5-1,3-[MeOC(O)]$_2$C$_5$H$_3$}Co(η^4-C$_4$Ph$_4$) (1) and {η^5-1,2-[MeOC(O)]$_2$C$_5$H$_3$}Co(η^4-C$_4$Ph$_4$) (2). Co(PPh$_3$)$_3$Cl (8.80 g, 10.00 mmol) was added to a solution of Na{[MeOC(O)]$_2$C$_5$H$_3$} (2.35 g, 11.50 mmol) in 10 mL of THF, and the mixture was stirred for 5 min. To the resultant solution was added diphenylacetylene (4.10 g, 23.00 mmol) in 50 mL of toluene, and the mixture was refluxed for 5 h. The reaction mixture was cooled, solvent was evaporated off, and the residue was chromatographed on a neutral alumina column. Triphenylphosphine was removed by eluting the column with hexane. When the polarity was gradually increased (5% ethyl acetate−95% hexane), the first fraction came out, which on evaporation of the solvent gave a yellow crystalline powder characterized as **1**. Yield: 2.35 g, 4.00 mmol, 40%. Mp: 182−184 °C. Anal. Found: C, 74.33; H, 4.96. Calcd for $C_{37}H_{29}O_4Co$: C, 74.49; H, 4.90. IR (ν, cm^{-1}): 1729, 1705 vs (C═O). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 3.28 (6H, s, CH_3), 5.29 (2H, s, Cp*H*), 5.84 (1H, s, Cp*H*), 7.21−7.33 (12H, m, *m*-/*p*-Ph*H*), 7.40−7.42 (8H, m, *o*-Ph*H*). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 51.38 (CH_3), 77.92 (C_4Ph_4), 85.28, 86.91, 89.49 (Cp*C*), 127.15, 128.14, 128.75, 133.93 (Ph*C*), 165.45 (CO). HRMS: calcd for $C_{37}H_{29}O_4Co$ 596.1398, found 596.1402.

On further increasing the polarity using 7% ethyl acetate−93% hexane, a second fraction was collected, which on evaporation gave a reddish yellow crystalline solid characterized as **2**. Yield: 2.68 g, 4.50 mmol, 45%. Mp: 175−177 °C. Anal. Found: C, 74.30; H, 4.80. Calcd for $C_{37}H_{29}O_4Co$: C, 74.49; H, 4.90. IR (ν, cm^{-1}): 1708 vs (C═O). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 3.26 (6H, s, CH_3), 4.86 (1H, s, Cp*H*), 5.25 (2H, s, Cp*H*), 7.23−7.30 (12H, m, *m*-/*p*-Ph*H*), 7.45−7.47 (8H, m, *o*-Ph*H*). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 51.41 (CH_3), 77.76 (C_4Ph_4), 86.39, 87.44, 89.64 (Cp*C*), 127.04, 128.12, 128.87, 134.13 (Ph*C*), 165.13 (CO). HRMS: calcd for $C_{37}H_{29}O_4Co$ 596.1398, found 596.1399.

[η^5-1,3-(COOH)$_2$C$_5$H$_3$]Co(η^4-C$_4$Ph$_4$) (3). Potassium hydroxide (0.56 g, 10.00 mmol) dissolved in 5 mL of water was mixed with **1** (0.60 g, 1.00 mmol) in 75 mL of ethyl alcohol, and the mixture was refluxed for 30 h. The reaction was quenched with 2 M HCl (25 mL). After extraction with CH_2Cl_2 (80 mL), the organic phase was washed with 100 mL of 2 M aqueous HCl, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to give the orange solid **3**. Yield: 0.55 g, 0.96 mmol, 96%. Mp: >330 °C. Anal. Found: C, 74.02; H, 4.47. Calcd for $C_{35}H_{25}O_4Co$: C, 73.94; H, 4.43. IR (ν, cm^{-1}): 3359 vs (−OH). ^{1}H NMR (δ, 300 MHz, d_6-DMSO): 4.82 (2H, s, Cp*H*), 5.26 (1H, s, Cp*H*), 7.18 (12H, br s, *m*-/*p*-Ph*H*), 7.36 (8H, bs, *o*-Ph*H*). ^{13}C NMR (δ, 75 MHz, CD_3OD): 75.67 (C_4Ph_4), 85.08, 95.76 (Cp*C*), 126.42, 128.50, 128.85, 135.74 (Ph*C*), 171.98 (CO). HRMS: calcd for $C_{35}H_{25}O_4CoK$ 607.0722, found 607.0724.

{η^5-1,2-[COOH]$_2$C$_5$H$_3$}Co(η^4-C$_4$Ph$_4$) (4). Compound **2** (0.60 g, 1.00 mmol) was taken in place of **1** in an identical reaction by which **3** was synthesized to give **4**. Yield: 0.54 g, 0.95 mmol, 95%. Mp: 265−268 °C. Anal. Found: C, 73.86; H, 4.46. Calcd for $C_{35}H_{25}O_4Co$: C, 73.94; H, 4.43. IR (ν, cm^{-1}): 3359 vs (−OH). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 4.92 (1H, s, Cp*H*), 5.52 (2H, s, Cp*H*), 7.21−7.23 (12H, br s, *m*-/*p*-Ph*H*), 7.35−7.37 (8H, bs, *o*-Ph*H*). ^{13}C NMR (δ, 75 MHz, d_6-DMSO): 77.45 (C_4Ph_4), 89.47, 91.47 (Cp*C*), 127.70, 128.49, 128.61, 133.40 (Ph*C*), 166.68 (CO). HRMS: calcd for $C_{35}H_{25}O_4CoK$ 607.0722, found 607.0676.

Ferrocene Fused Acenequinone (η^4-C$_4$Ph$_4$)Co[μ_2-η^5:η^5-1,2-C$_5$H$_3$(CO)$_2$-(1,2-C$_5$H$_3$)]Fe(η^5-Cp) (5). The 1,2-dicarboxylic acid **4** (0.15 g, 0.26 mmol) was dissolved in dry CH_2Cl_2 (10 mL). Oxalyl chloride (0.25 g, 2.00 mmol) and DMF (1 drop) were also added, and the mixture was stirred for 30 min at room temperature. The resultant reddish yellow solution was evaporated completely to dryness under high vacuum at 40 °C to give the 1,2-diacyl chloride. Without further purification, the diacyl chloride was dissolved in dry CH_2Cl_2 (5 mL). To this solution were added ferrocene (0.04 g, 0.28 mmol) and anhydrous aluminum chloride (0.15 g, 1.13 mmol) together. The reaction mixture was stirred for 30 min at room temperature and then quenched with 2 M aqueous NaOH (5 mL), and the product was extracted with ethyl ether (2 × 25 mL). Combined ether extracts were dried with $MgSO_4$ and filtered, and the volatiles were removed in vacuo. The crude product was chromatographed through alumina using an ethyl acetate/hexane (1/5) mixture as the eluent. A dark red band was eluted out that upon evaporation of the solvent gave a dark red crystalline solid, which was characterized as **5**. Yield: 0.07 g, 0.10 mmol, 38%. Mp: 235−238 °C dec. Anal. Found: C, 75.40; H, 4.29. Calcd for $C_{45}H_{31}O_2CoFe$: C, 75.22; H, 4.35. IR (ν, cm^{-1}): 1644 vs (C═O). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 4.12 (5H, s, Cp unsubstituted), 4.76−4.77 (1H, t, ^{3}J = 2.7 Hz, FeCHC*H*CH), 4.81−4.83 (1H, t, ^{3}J = 2.7 Hz, CoCHC*H*CH), 4.93−4.94 (2H, d, ^{3}J = 2.7 Hz, FeC*H*CHC*H*), 5.64−5.65 (2H, d, ^{3}J = 2.8 Hz, CoC*H*CHC*H*), 7.13−7.31 (20H, m, PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 71.38, 72.65, 77.21, 79.25, 79.58, 84.47, 92.16 (Cp*C*), 75.07 (C_4Ph_4), 127.26, 128.24, 128.46, 133.62 (Ph*C*), 189.69 (*C*═O). HRMS: calcd for $C_{45}H_{31}O_2CoFe$ 718.1005, found 718.1008.

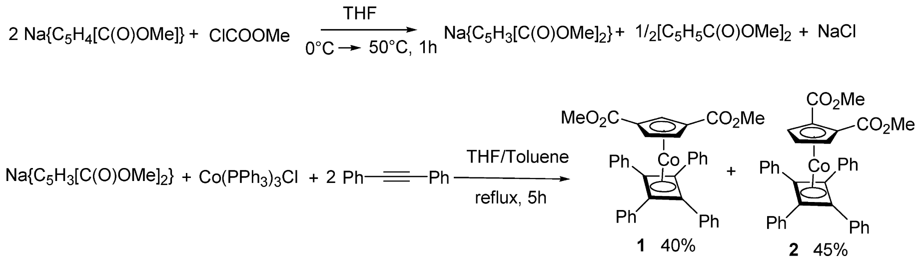
[η^5-1,3-(4-*i*Pr-2-Ox)$_2$C$_5$H$_3$]Co(η^4-C$_4$Ph$_4$) (6). The crude acid **3** (0.55 g, 0.96 mmol) was dissolved in CH_2Cl_2 (15 mL). Oxalyl chloride (0.15 g, 1.17 mmol) and DMF (1 drop) were added sequentially. Upon addition of the latter, gas evolution was observed. The resulting solution was stirred at room temperature. After 30 min, the solution was concentrated using a rotary evaporator. Byproducts and excess oxalyl chloride were removed by repeated extraction of the residue with CH_2Cl_2 (3 × 20 mL) to yield the acid chloride as a red-brown solid, which was used directly in the next step.

(*S*)-2-amino-3-methyl-1-butanol (L-valinol; 0.23 g, 2.23 mmol) was taken up in a mixture of triethylamine (4 mL) and CH_2Cl_2 (15 mL). A solution of the crude acid chloride in 20 mL of CH_2Cl_2 was also transferred to this flask. The resulting solution was stirred at room temperature and, after 2 h, was cooled to 0 °C using an ice bath. Mesyl chloride (0.35 g, 3.05 mmol) was added, and the resulting solution was warmed to room temperature. After it was stirred for 16 h, the solution was washed with 30 mL of saturated aqueous sodium bicarbonate and 30 mL of brine using a separating funnel. The organic layer was dried over Na_2SO_4, filtered, and concentrated using a rotary evaporator. The residue was purified using a silica gel column with a 7/1 hexane/ethyl acetate mixture as eluent. Evaporation of the solvent gave **5** as a yellow crystalline solid. Yield: 0.51 g, 0.73 mmol, 73%. Mp: 101−103 °C. $[\alpha]_D^{35} = -35°$ (*c* 0.20 in $CHCl_3$). Anal. Found: C, 76.79; H, 6.08; N, 4.14. Calcd for $C_{45}H_{43}O_2N_2Co$: C, 76.91; H, 6.17; N, 3.99. IR (ν, cm^{-1}): 1655 vs (C═N). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 0.73−0.76 (3H, m, $CHCH_3$), 0.83−0.90 (3H, m, $CHCH_3$), 1.48−1.53 [2H, m, $CH(CH_3)_2$], 3.36−3.42 (2H, m, $CHCH_2$), 3.45−3.49 (1H, m, $CHCH_2$), 3.56−3.65 (2H, m, $CHCH_2$), 3.73−3.82 (1H, m, $CHCH_2$), 5.16 (1H, s, Cp*H*), 5.25 (1H, s, Cp*H*), 5.79 (1H, s, Cp*H*), 7.17−7.30 (12H, m, *m*-/*p*-Ph*H*), 7.42−7.45 (8H, m, *o*-Ph*H*). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 18.08, 18.24, 19.13, 19.77 ($CH(CH_3)_2$), 32.73, 32.94 ($CH(CH_3)$), 69.34, 69.63 ($CHCH_2$), 72.53, 72.93 ($CHCH_2$), 77.05 (C_4Ph_4), 82.02, 84.41, 86.13, 86.91, 87.47 (Cp*C*), 126.60, 127.87, 128.85, 134.51 (Ph*C*), 159.73, 160.12 (*C*═N). HRMS: calcd for $C_{45}H_{43}O_2N_2CoH$ 703.2735, found 703.2723.

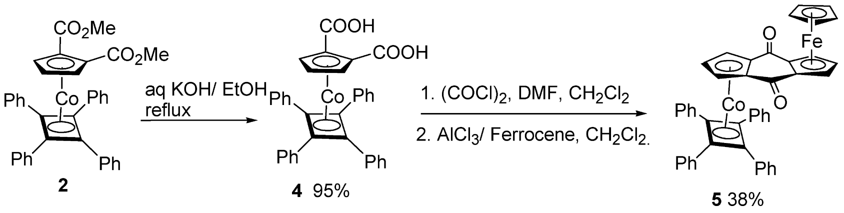
Pd(OAc)$_2${[η^5-1,3-(4-*i*Pr-2-Ox)$_2$C$_5$H$_3$]Co(η^4-C$_4$Ph$_4$)} (7). Palladium acetate (0.11 g, 0.50 mmol) was added to a solution of **6** (0.35 g, 0.50 mmol) in acetic acid (1.5 mL), and the mixture was stirred at 95 °C for 20 min. The yellow precipitate formed was filtered, washed with acetic acid, and dried under vacuum to give a yellow crystalline powder which was characterized as **7**. Yield: 0.29 g, 0.31 mmol, 62% Mp: 206−208 °C dec. $[\alpha]_D^{35} = -95°$ (*c* 0.20 in $CHCl_3$). Anal. Found: C, 63.29; H, 5.38; N, 3.05. Calcd for $C_{49}H_{49}O_6N_2CoPd$: C, 63.47; H, 5.33; N, 3.02. IR (ν, cm^{-1}): 1628. ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 0.58−0.60 (3H, d, ^{3}J = 6.0 Hz, $CHCH_3$), 0.77−0.79 (3H, d, ^{3}J = 6.0 Hz, $CHCH_3$), 1.13 (3H, s, $COCH_3$), 1.17−1.19 (3H, d, ^{3}J = 6.0 Hz, $CHCH_3$), 1.39 (3H, s, $COCH_3$), 1.74−1.76 (1H, m, $CH(CH_3)_2$), 2.70−2.76 (1H, m, $CHCH_2$), 2.90−2.98 (1H, m, $CH(CH_3)_2$), 3.43−3.57 (2H, m, $CHCH_2$), 3.68−3.74 (1H, m, CHC*H*H), 3.92−4.04 (1H, m, $CHCH_2$), 4.13−4.18 (1H, m, CHCH*H*), 5.55 (1H, s, Cp*H*), 6.85 (1H, s, Cp*H*), 7.15−7.26 (20H, Ph*H*), 7.38 (1H, s, Cp*H*). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 15.93, 18.56, 21.28, 21.55 ($CH(CH_3)_2$), 22.47, 22.96 ($COCH_3$), 29.22, 31.07 ($CH(CH_3)_2$), 67.32, 69.90 ($CHCH_2$), 72.57 ($CHCH_2$), 78.12 (C_4Ph_4), 84.46, 85.90, 87.04, 87.92, 91.54 (Cp*C*), 126.87, 128.72, 128.80, 134.18 (Ph*C*), 163.97, 167.97 (*C*═N), 177.37, 177.44 (*C*═O). HRMS: calcd for $C_{49}H_{49}CoN_2O_6PdNa$ 949.1855, found 949.1839.

General Procedure for Rearrangement of Allylic Trichloroacetimidates Catalyzed by Palladium Complex 7. A solution of the catalyst **15** (0.02 mmol) in CH_2Cl_2/CH_3CN (0.50 mL) was added to trichloroacetimidates **8a**−**c** (1.00 mmol) in an oven-dried 2 mL reaction vial having a stirring bar. The vial was capped, and the solution was stirred at 37 °C/65 °C. After 10 h, the solution was concentrated to give a semisolid. Purification by silica gel column chromatography using 2% ethyl acetate/98% hexane provided the pure allylic trichloroacetamides **9a**−**c**. Chiral HPLC analysis (Shimadzu,

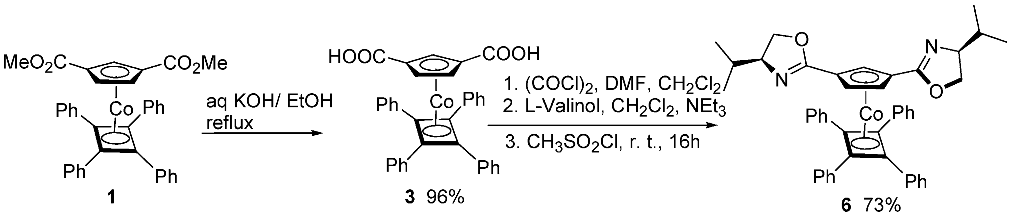
Scheme 1. Synthesis of the 1,2- and 1,3-$\{[MeOC(O)]_2C_5H_3\}Co(C_4Ph_4)$ Derivatives



Scheme 2



Scheme 3



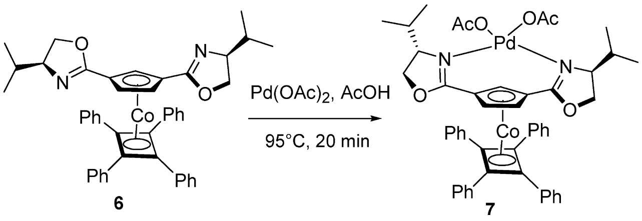
Daicel OD-H column, 0.5−1.0% IPA/*n*-hexane, 0.50 mL/min) was carried out to determine the enantiomeric excess of **9a**−**c**, details of which are provided in the Supporting Information.

■ RESULTS AND DISCUSSION

A reaction of the sodium salt of the monoester MeOC(O)-CpNa with methyl chloroformate in THF at 50 °C resulted in the formation of a mixture of the sodium salts of 1,2- and 1,3-diester-derived sodium cyclopentadienyl along with the disubstituted cyclopentadienyl dimer as a side product (Scheme 1).[18] The latter was removed by repeated extraction of the reaction mixture with ethyl ether and the sodium salt was reacted directly with $Co(PPh_3)_3Cl$ and diphenylacetylene in refluxing toluene to yield the 1,3- and 1,2-diesters $\{\eta^5\text{-}[MeOC(O)]_2C_5H_3\}Co(\eta^5\text{-}C_4Ph_4)$ (**1** and **2**) in 83−85% overall isolated yield (Scheme 1). The mixture was easily separated and purified by column chromatography. For the sake of comparison, we have also carried out a reaction of the carboethoxy sodium cyclopentadienyl $Na\{C_5H_4[C(O)OEt]\}$ with ethyl chloroformate, ClC(O)OEt, but observed that the reaction results in lower yield (28%) of the 1,3-diester.

The diesters **1** and **2** were hydrolyzed to the dicarboxylic acids **3** and **4** by refluxing with aqueous KOH in ethanol. The 1,2-diacyl chloride of the 1,2-dicarboxylic acid **4** was generated in situ by a reaction with oxalyl chloride, and it was further reacted with ferrocene under Friedel−Crafts conditions to yield the novel bis-metallocenyl acenequinone **5**, having both iron and cobalt sandwich units in the same compound (Scheme 2). A similar reaction attempted using **3** did not result in any isolable products. The 1,3-dicarboxylic acid **3** after reaction with oxalyl chloride, followed by (*S*)-2-amino-3-methyl-1-butanol, triethylamine, and mesyl chloride, was converted to the novel 1,3-bis(oxazoline)-derived bidentate chiral ligand $\{(\eta^5\text{-}1,3\text{-}[(4\text{-}i\text{Pr-}2\text{-Ox})]_2C_5H_3\}Co(\eta^4\text{-}C_4Ph_4)$ (**6**; Ox = oxazolinyl) (Scheme 3). Interestingly, an attempt to prepare an analogous 1,2-bis(oxazoline) derivative was unsuccessful. Reaction of **6** with $Pd(OAc)_2$ in acetic acid resulted in the formation of the chiral palladium complex **7** (Scheme 4). While previous reactions of chiral monodentate ligands derived from $(\eta^5\text{-Cp})Co(\eta^4\text{-}C_4Ph_4)$ with palladium acetate resulted exclusively in the formation of palladacycles,[1,9] compound **6** was found to be simply acting as a chelating bidentate ligand in the synthesis of complex **7**. The identity of the chiral complex **7** was conclusively proved by HRMS, CHN analysis, optical rotation, and NMR (^{1}H and ^{13}C) studies. Two peaks of $COCH_3$ at 1.13 and 1.39 ppm in ^{1}H NMR and two peaks of $COCH_3$ at 177.26 and 177.50 in ^{13}C NMR provided clear evidence for the two acetate groups, which was further supported by HRMS. Three peaks at 5.55, 6.85, and 7.38 ppm for the Cp protons confirmed that compound **7** is not a palladacycle.

Scheme 4



A range of 1,2- and 1,3-phenyl-substituted ligands, many of them chiral, such as phenyl bis(oxazoline) (Phebox) have shown excellent applications in homogeneous catalysis, especially enantioselective synthesis.[19] However, a search in the literature of examples of 1,2 and 1,3 symmetrically Cp disubstituted metal sandwich compounds, analogous to the (η^5-$R_2C_5H_3$)Co(η^4-C_4Ph_4) derivatives reported in the present study, indicated only a handful of examples, mostly ferrocene derivatives. These include the 1,2-methyl diester,[20] 1,2-ethyl diester,[21] 1,2- and 1,3-dialdehydes,[20] 1,3-hydroxymethyl,[20] and 1,2-diacetylene derived ferrocenes.[22] In addition, synthesis of the 1,2-phenyl diester of CpRuCp*[23] and 1,3-dialkyne of $CpMn(CO)_3$[22b] has also been reported.

In the 1,3-bis(oxazoline) derivative **6**, the hydrogen flanked by the two oxazolinyl groups was found to resonate at 5.79 ppm, which is slightly deshielded in comparison to the reported monooxazolinyl analogue.[6a] On formation of the palladium complex **7**, this hydrogen was found to be significantly deshielded (7.38 ppm), suggesting a possible C−H···Pd anagostic interaction similar to such anagostic interactions reported for cyclobutadiene linked dimeric palladacycles.[10a] The activity of **7** as chiral catalyst was evaluated in the asymmetric rearrangement of trichloroacetimidates, which is also an elegant method for the catalytic synthesis of chiral allylic amines.[9c]

Structural Studies on the New Compounds. Single-crystal structures of diesters **1** and **2**, diacid **4**, acenequinone **5**, and 1,3-bis(oxazoline) **6** were determined. Figures 1−4 show the ORTEP diagrams of compounds **1**, **2**, **5**, and **6**. ORTEP and packing diagrams of compound **4** are given in the Supporting Information. Structural analysis of the 1,2-dicarboxylic acid **4** showed both intramolecular and intermolecular OH···O hydrogen bonding between the two carboxylic acid groups. The intermolecular hydrogen bonding results in a linear chain where successive cobalt sandwich units alternate on both sides of the chain (see the Supporting Information). Crystal structures of two acenequinones having two metallocenyl units similar to acenequinone **5** have been reported.[23] These are (A) having both the metallocenyl units as CpRuCp* and (B) having one CpRuCp* and other ferrocene (Figure 5). The structures of these compounds showed some interesting variations. In the case of compound **5** and the bis-CpRuCp* acenequinone, the two Cp rings on both sides of the quinone unit are planar (angles between the mean planes of the Cp rings being 0.7(2) and 0°, respectively), while for the compound having CpRuCp* and ferrocene, the corresponding angle is 13.8(6)°, indicating that the ruthenocene unit is placed toward the carbonyl and the ferrocenyl unit is placed away from the carbonyl group (Figure 5).

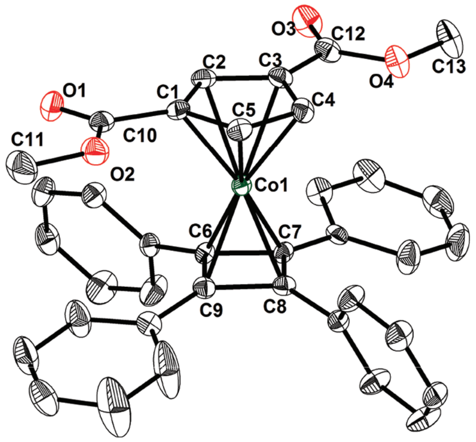


Figure 1. ORTEP diagram of **1** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

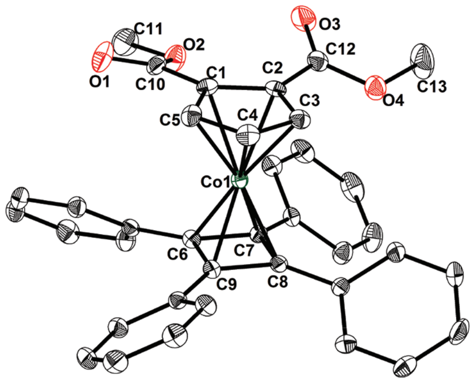


Figure 2. ORTEP diagram of **2** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

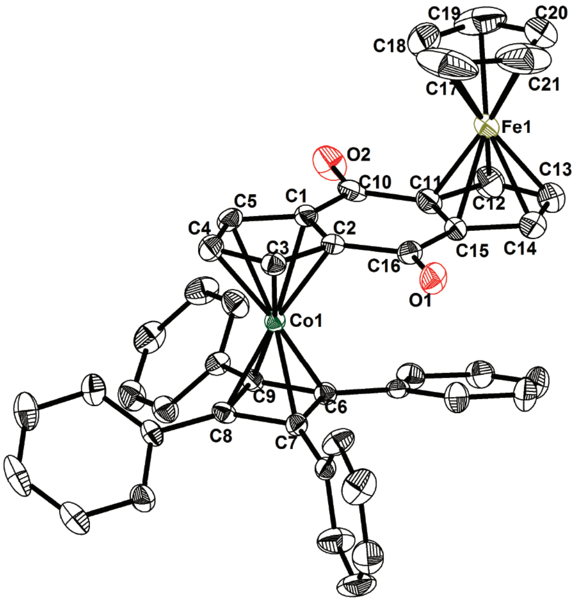


Figure 3. ORTEP diagram of **5** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

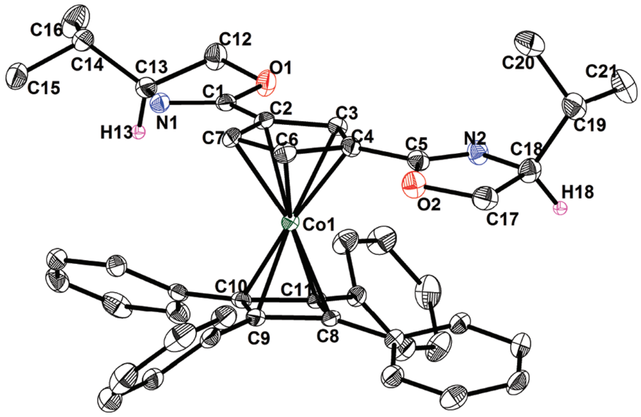


Figure 4. ORTEP diagram of **6** with thermal ellipsoids at the 30% probability level. Some hydrogen atoms have been omitted for clarity.

However, the carbonyl stretching band of the quinone groups of **5** was observed at 1643 cm^{-1}, which is the same as

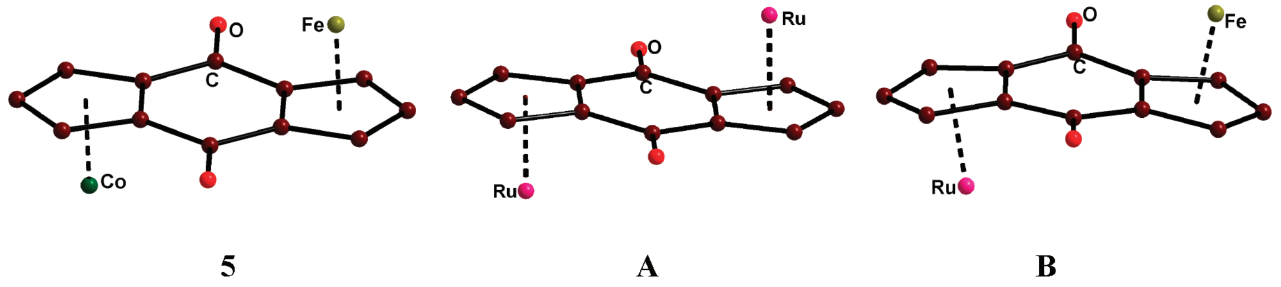
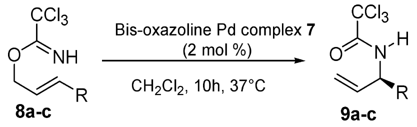


Figure 5. Comparison of ring planarity of acenequinone **5** with analogous complexes.

Table 2. Aza-Claisen Rearrangement Carried Out on Trichloroacetimidates using Bis(oxazoline) Pd Complex 7



entry	R	substrate	product	solvent	reacn temp (°C)	yield (%)[a]	ee[b] (%) (configн)
1	Me	**8a**	**9a**	CH_2Cl_2	37	82	95 (*S*)
2	Me	**8a**	**9a**	CH_3CN	65	90	83 (*S*)
3	n-Pr	**8b**	**9b**	CH_2Cl_2	37	85	96 (*S*)
4	n-Pr	**8b**	**9b**	CH_3CN	65	93	90 (*S*)
5	$PhCH_2CH_2$	**8c**	**9c**	CH_2Cl_2	37	81	94 (*S*)

[a]Isolated yield. [b]Determined by HPLC analysis using chiral ODH column.

that observed for the acenequnone having CpRuCp* and ferrocene units, possibly suggesting that the electronic effects of CoC_4Ph_4 and RuCp* units on the carbonyl groups of the acenequnone are comparable. These ν_{CO} values are lower than the 1660 cm^{-1} reported for 9,10-anthraquinone and, as suggested by Selegue and co-workers, can be rationalized by resonance-stabilized structures.[23a] The crystal structure of compound **6** (Figure 4) is the first example of the structure of a bis-oxazoline derived metal sandwich compound. The mean planes of the two oxazoline rings at the 1- and 3-positions are almost in the same plane as that of the cyclopentadiene ring with dihedral angles of 5.2(1) and 7.5(1)°.

Catalytic Studies Using the Palladium Complex 7. The catalytic asymmetric rearrangement of trichloro- or trifluoroacetimidates to the corresponding chiral allylic trichloro- or trifluoroacetamides is a well-known method utilized to evaluate the enantioselective efficiency of many chiral catalysts.[4] To explore the catalytic activity of the palladium complex **7**, we have carried out the aza-Claisen rearrangement of three selected trichloroacetimidates, $RCH{=}CHCH_2OC(NH)CCl_3$ ($R = Me$, n-Pr, CH_2CH_2Ph), in the presence of **7** as catalyst. Reactions were carried out in dichloromethane and acetonitrile over a period of 10 h with a catalyst loading of 2 mol %, and the results obtained are given in Table 2.

The chiral complex **7** was found to be quite efficient in bringing about the aza-Claisen rearrangement at ambient temperature with good enantioselectivity. The yields of the trichloroacetamides after the aza-Claisen rearrangement are in the range of 81–85% and the ee's obtained ranged from 94 to 96% when the reaction was carried out at 37 °C. An attempt to increase the yield further by increasing the reaction temperature to 65 °C resulted in improved yields (90–93%) but a decrease in ee (83–90%).

■ CONCLUSION

The first synthesis of cyclopentadienyl 1,2- and 1,3-diester derivatives of (η^5-Cp)Co(η^4-C_4Ph_4) has been described. These diesters are potential precursors for the synthesis of a range of basal bulky bidentate chiral and achiral ligands with a scope of preparing a range of catalysts. A novel ferrocene fused acenequinone of (η^5-Cp)Co(η^4-C_4Ph_4) was synthesized using the 1,2-dicarboxylic acid derivative of (η^5-Cp)Co(η^4-C_4Ph_4). Reaction of the 1,3-dicarboxylic acid derivative of (η^5-Cp)Co(η^4-C_4Ph_4) with oxalyl chloride followed by reacting with (*S*)-2-amino-3-methyl-1-butanol and ring closing by mesyl chloride resulted in the first example of a chiral bidentate 1,3-bis(oxazoline) ligand. Reaction of this chiral bidentate ligand with $Pd(OAc)_2$ yielded the chiral chelated Pd complex **7**. The utility of the palladium complex as a catalyst in the asymmetric aza-Claisen rearrangement of three different trichloroacetimidates was explored. The reaction when carried out at 37 °C in CH_2Cl_2 gave yields in the range of 81–85% and good ee's ranging from 94 to 96%. While all previous studies on aza-Claisen rearrangements of trichloro- and trifluoroacetimidates which resulted in good enantiomeric excess was reported with palladacycles, the present study has shown that chiral palladium complexes with bulky basal ligands which are not necessarily palladacycles can also bring about the rearrangement with good enantiomeric excess. This study further substantiates the finding by Overman and others that the crucial factor which enhances enantioselectivty in this rearrangement is the basal bulkiness of the chiral ligand utilized.[9a]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data for compounds **1**, **2**, and **4**–**6** and figures giving ^1H and ^{13}C NMR spectra of 1,3-oxazoline **6**, palladium complex **7**, trichloroacetimidates **8a**–**c**, their rearranged products **9a**–**c**, and HPLC plots of **9a**–**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Department of Science and Technology (DST) of India for financial assistance in the form of research grant to A.J.E. (No. SR/SI/IC-43/2010). N.S. thanks the UGC India for a research fellowship. We thank the DST-FIST and IITD for funding of the single-crystal X-ray diffraction facility at IIT Delhi.

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