Tartrate-Derived Cyclopentadienes for the Synthesis of Chiral Substituted (η^5-Cyclopentadiene)(η^4-cycloocta-1,5-diene)cobalt(I) Complexes

Andrey Gutnov, Barbara Heller,* Hans-Joachim Drexler,
Anke Spannenberg, and Günther Oehme

Leibniz-Institut für Organische Katalyse an der Universität Rostock e.V.,
Buchbinderstrasse 5-6, 18055 Rostock, Germany

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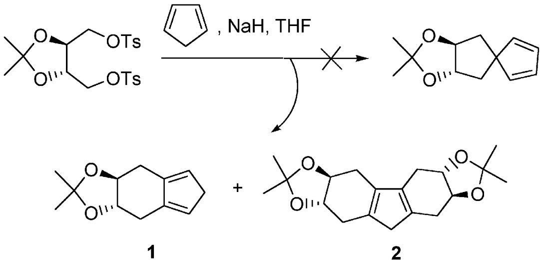
Summary: Two chiral tartrate-derived ligands, the disubstituted cyclopentadiene ***1*** *and the new tetrasubstituted cyclopentadiene* ***2****, are obtained. The corresponding (η^5-cyclopentadiene)(η^4-cycloocta-1,5-diene)cobalt(I) complexes* ***3*** *and* ***4*** *are prepared through the deprotonation of the ligands with lithium diisopropylamide followed by the metathetic reaction of the lithium salts with tris(triphenylphosphine)cobalt(I) chloride and 1,5-cyclooctadiene. The complexes are isolated in an enantiomerically pure state after chromatography with dried silica under argon. The structures of* ***2***−***4*** *have been determined by single-crystal X-ray diffractometry. The dynamic behavior of complexes* ***3*** *and* ***4*** *in solution is discussed on the basis of ^{1}H and ^{13}C NMR spectra.*

Introduction

Chiral cyclopentadiene derivatives and the corresponding metallocenes make up a widely investigated subject of modern organometallic chemistry, with strong relevance to asymmetric catalysis.[1] Those that are derived from chiral carbohydrates are of special interest for catalysis in aqueous media.[2] Herewith we wish to report the synthesis of some chiral substituted (η^5-cyclopentadienyl)Co(1,5-COD) complexes, which are potential catalysts for [2 + 2 + 2] cycloaddition of acetylenes and nitriles into a pyridine core. Recently we reported an improved photochemical procedure for such cycloaddition, which can be now conducted in water at ambient temperature and pressure.[3] Our present goal is to find chiral substituted (η^5-cyclopentadienyl)Co(1,5-COD) complexes suitable for elaboration of asymmetric versions of the reaction. It is noteworthy that only one example of such a chiral complex has been reported so far, but the compound was not optically resolved.[4]

Scheme 1



Results and Discussion

The chiral annelated cyclopentadiene **1** was first isolated by Halterman after alkylation of CpNa with 2,3-*O*-isopropylidene-(*S*,*S*)-threitol ditosylate. The compound was found to be suitable for complexation with $Co_2(CO)_8$ to give the corresponding (η^5-cyclopentadienyl)$Co(CO)_2$ complex, which was further applied for diastereoselective cyclizations of diynes and enediynes.[2a−c]

Following Halterman's procedure, we have found that another tetraalkylated cyclopentadiene, **2**, can be isolated from the extremely complicated mixture of products along with the previously mentioned bis-alkylated product **1** (Scheme 1).

No spiro-compound[5] formation has been observed in the reaction mixture (NMR control), in accordance with previous investigations. Although the yield of the cyclopentadiene **2** is low (4.1%), the loading of inexpensive starting materials can be easily increased to give multigram amounts of the compound. Moreover, the bis-alkylated cyclopentadiene **1** can be subjected to further alkylation under the same reaction conditions (1 mol of the threitol ditosylate, NaH, THF) to give the ligand **2** in 67% yield (25% of overall yield after two steps). ^{1}H and ^{13}C NMR spectra have revealed C_2 symmetry of the compound **2**. A single crystal of **2** is grown by evaporation of pentane solution, and the structure has been unambiguously confirmed by X-ray analysis (Figure 1).

Initial attempts to apply "atomic" cobalt procedures[6] for the preparation of appropriate substituted (η^5-cyclopentadienyl)Co(1,5-COD) complexes have been suc-

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* To whom correspondence should be addressed. E-mail: barbara.heller@ifok.uni-rostock.de. Fax: +49-0-381-46693-24.

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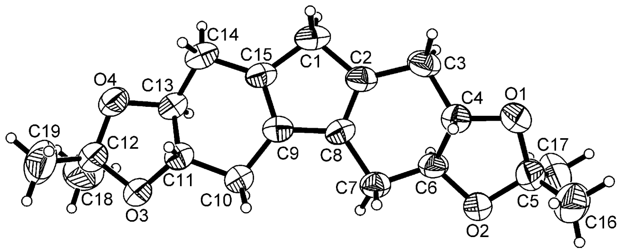
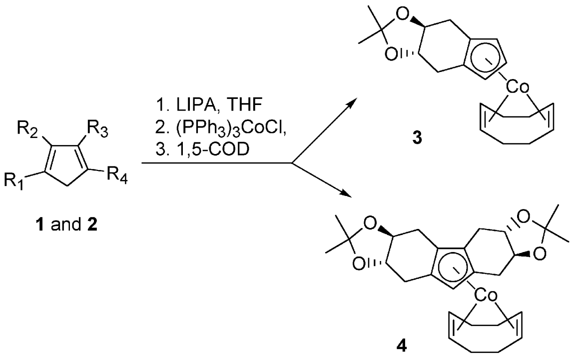


Figure 1. ORTEP plot of **2** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (Å): C(1)−C(2) = 1.510(4), C(2)−C(8) = 1.339(4), C(8)−C(9) = 1.470(4), C(9)−C(15) = 1.344(4), C(15)−C(1) = 1.504(4).

Scheme 2



cessful only in part. The highly reactive cobalt powder is generated by the reduction of cobalt(III) acetylacetonate with anthracene-activated magnesium and subjected to direct complexation with cyclopentadienyl ligands in the presence of 1,5-COD. The monoannelated complex **3** is thus obtained in a yield of 52%, but the cyclopentadiene **2** has given only traces of the complex **4**. This is generally consistent with the observations that bulky ligands are bad substrates for this method of complexation.[7]

(η^5-cyclopentadienyl)Co(1,5-COD) complexes **3** and **4** can be more conveniently prepared (in 67% and 65% yields) by using the metathetic reaction of lithium salts of both ligands **1** and **2** with tris(triphenylphosphine)cobalt(I) chloride, followed by replacement of the two remaining PPh_3 molecules with 1,5-COD (Scheme 2). The procedure was first reported by Radermacher for other ligands.[8]

As ligands **1** and **2** have only one homotopic face for complexation, a single diastereomeric complex has been isolated in both cases. Crystals of **3** and **4** have been grown from pentane, and the structures have been investigated by X-ray diffraction methods (Figures 2 and 3 and Table 1). The cobalt atom of both complexes interacts with the substituted cyclopentadienyl ring in an expected η^5 manner and completes the coordination through two η^2 interactions with the double bonds of the 1,5-COD ligand. The distance from cobalt to the center of the cyclopentadienyl ring is 1.706−1.711(9) Å for **3** and 1.717(4) Å for **4**, which generally corresponds to known substituted (η^5-cyclopentadienyl)Co(1,5-COD) complexes.[9] The dihedral angle between the cyclopentadienyl cycle and the plane defined by double bonds of the 1,5-COD ligand are 0.1−1.8° for **3** and 4.2° for **4**. In **3** as well as in **4** the double bonds of the 1,5-COD ligand are arranged nearly perpendicular to those bonds of the cyclopentadienyl ring to which chiral side rings are annelated: e.g. C(2)−C(8) (cf. ref 9a). In the case of **3** there are four independent molecules in the asymmetric unit, where the latter angle varies from 84.1 to 96.4°, and this is the major difference in the conformations.

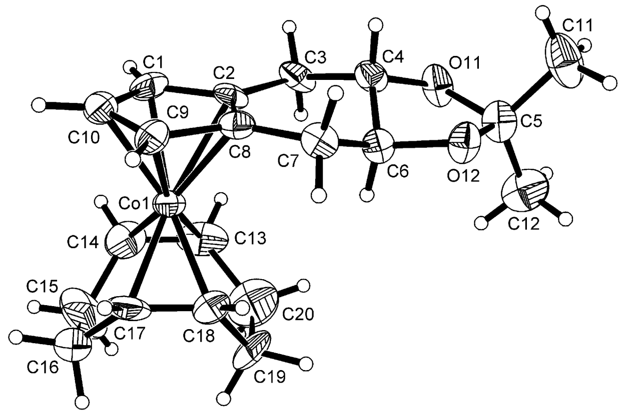


Figure 2. ORTEP plot of **3** (one of the four molecules in the asymmetric unit) with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (Å): C(1)−C(2) = 1.411−1.442(12), C(2)−C(8) = 1.401−1.426(10), C(8)−C(9) = 1.406−1.443(15), C(9)−C(10) = 1.398−1.431(13), C(10)−C(1) = 1.374−1.406(12), Co(1)−C(1) = 2.055−2.082(9), Co(1)−C(2) = 2.119−2.129(9), Co(1)−C(8) = 2.106−2.129(9), Co(1)−C(9) = 2.033−2.082(9), Co(1)−C(10) = 2.072−2.097(9), Co(1)−C(COD) = 1.973−2.030(10).

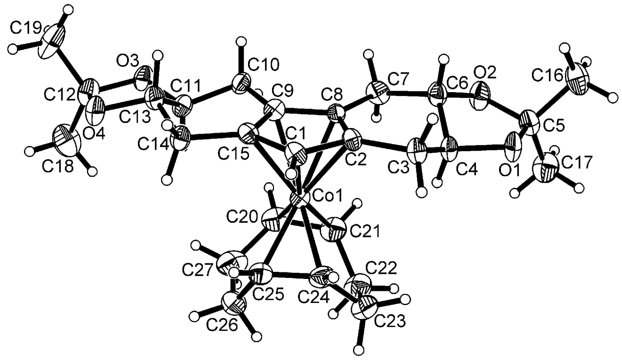


Figure 3. ORTEP plot of **4** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (Å): C(1)−C(2) = 1.445(5), C(2)−C(8) = 1.414(5), C(8)−C(9) = 1.441(4), C(9)−C(15) = 1.415(5), C(15)−C(1) = 1.415(5) Co(1)−C(1) = 2.042(3), Co(1)−C(2) = 2.098(4), Co(1)−C(8) = 2.131(4), Co(1)−C(9) = 2.134(4), Co(1)−C(15) = 2.107(4), Co(1)−C(COD) = 2.008−2.020(4).

NMR spectra of **3** and **4** have revealed an interesting dynamic behavior of the cobalt complexes in solution. The 1,5-COD ligand does not seem to rotate around the Cp−Co axis on the ^{1}H NMR time scale. The 1,5-COD signals show no broadening but give complicated coupling patterns in ^{1}H NMR spectra, as all of their 12 protons are chemically inequivalent. Only four of the

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Table 1. Experimental X-ray Diffraction Parameters and Crystal Data

	2	**3**	**4**
empirical formula	$C_{19}H_{26}O_4$	$C_{20}H_{37}CoO_2$	$C_{27}H_{37}CoO_4$
fw	318.40	358.35	484.50
cryst size (mm)	0.5 × 0.5 × 0.3	0.6 × 0.5 × 0.3	0.8 × 0.3 × 0.3
cryst syst	orthorhombic	triclinic	orthorhombic
space group	$P2_12_12_1$	$P1$	$P2_12_12$
a (Å)	5.493(1)	7.674(2)	9.283(2)
b (Å)	10.448(2)	13.879(3)	11.200(2)
c (Å)	29.985(6)	17.695(4)	23.057(5)
α (deg)	90	67.67(3)	90
β (deg)	90	83.66(3)	90
γ (deg)	90	89.81(3)	90
V (Å^3)	1720.9(6)	1731.1(6)	2397.2(8)
D_{calcd} (Mg/m^3)	1.229	1.375	1.342
Z	4	4	4
μ(Mo Kα) (mm^{-1})	0.08	1.00	0.75
F(000)	688	760	1032
diffractometer	STOE-IPDS		
radiation	graphite monochromated, λ(Mo Kα) = 0.710 73 Å		
temp (K)	293	200	200
θ range for data collecn (deg)	1.55−21.00	2.37−23.00	2.02−23.00
index range (h, k, l)	−5 to +5 −10 to +10 −32 to +32	−8 to +8 −15 to +15 −19 to +19	−10 to +10 −11 to +11 −25 to +25
no. of rflns collected	7646	8381	11 435
no. of indep rflns	2190	8381	3280
no. of obsd rflns	1496	6623	2804
no. of refined params	208	829	289
R1 (2σ(I))	0.0339	0.0328	0.0286
R1 (all data)	0.0571	0.0445	0.0348
wR2 (all data)	0.0675	0.0778	0.0661
goodness of fit	0.832	0.888	0.939
largest diff peak and hole (e/Å^3)	0.118/−0.125	0.241/−0.324	0.202/−0.245

eight chemically inequivalent carbon atoms of 1,5-COD are detected in the ^{13}C NMR spectra. This may be caused by an empirically low induction of the chiral cyclopentadienyl ligand on the 1,5-COD moiety or by a rotating 1,5-COD ligand on the ^{13}C NMR time scale.

The cobalt complexes are reasonably stable in the crystalline state and can be briefly handled in air, but they are very sensitive to oxygen in solution.

Experimental Section

All operations involving organometallic compounds were carried out under an argon atmosphere using standard Schlenk techniques in dry, oxygen-free solvents. Melting points were measured in sealed capillaries with a Büchi 540 melting point determination apparatus. Optical rotations were determined on a Gyromat-HP polarimeter. The NMR spectra were recorded on a Bruker ARX 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer at 298 K. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residue of the deuterated solvents. Mass spectra were obtained by using a Varian AMD-402 instrument. Relative intensities in percent are given in parentheses. Tris(triphenylphosphine)cobalt(I) chloride[10] and threitol ditosylate[11] were prepared according to published procedures. Lithium diisopropylamide was used as purchased.

Bis-Annelated Ligand 2. (a) The preparation and isolation are exactly as described previously, starting from CpNa and threitol ditosylate,[2b] but further elution with pentane−ether (9:1) produces **2** as a white crystalline compound (285 mg; 4.1%), which can be recrystallized from hexane: mp 155−156 °C; $[\alpha]^{20}_D = +235.85°$ (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, δ) 3.90 (m, 4H), 2.95−2.83 (m, 6H), 2.63 (m, 2H), 2.51 (m, 2H), 1.63 (s, 12H); ^{13}C NMR ($CDCl_3$, δ) 136.39, 110.72, 78.53, 44.17, 30.79, 27.56, 28.19; MS (250 °C, 70 eV, m/z) 318 (M$^+$, 100), 205 (27), 147 (26), 117 (40), 55 (43), 43 (42). Anal. Calcd for $C_{19}H_{26}O_4$ (mol wt 318.41): C, 71.67; H, 8.23. Found: C, 71.80; H, 8.41.

(b) A solution of ligand **1** (1.92 g; 10 mmol) in THF (30 mL) was treated with NaH (0.480 g, 20 mmol) and stirred for 1 h. A solution of threitol ditosylate (4.7 g, 10 mmol) in THF (20 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 1 h followed by heating at reflux for 4 h. Aqueous workup and subsequent flash chromatography with pentane−ether (9:1) yielded compound **2** (2.1 g, 67%). Analytical data are the same as those described above.

Mono-Annelated Complex 3. A solution of **1** (1.44 g, 7.5 mmol) in THF (20 mL) was treated with lithium diisopropylamide (0.8 g, 7.5 mmol; as a 10% suspension in hexane). The mixture was stirred for 5 min, and a suspension of tris(triphenylphosphine)cobalt(I) chloride (6.35 g, 7.2 mmol) and 1,5-COD (1.29 mL, 10.5 mmol) in toluene (40 mL) was added. After it was stirred for 1 h at room temperature, the dark red mixture was heated to 80 °C for 1 h, resulting finally in a clear orange solution. The reaction mixture was cooled and filtered through a short column of silica (1.5 cm × 3 cm) degassed by three argon−vacuum pump cycles, 1 h each. Volatiles were removed in vacuo, and the residue was dissolved in pentane (20 mL) and left overnight at 0 °C. Precipitated PPh_3 was filtered off, and the solution was filtered through a column of degassed silica (1.5 cm × 20 cm), an orange band being eluted with pentane. The solution was evaporated to a volume of 10 mL and cooled to −78 °C to crystallize **3** as orange needles (1.816 g, 67.6%): mp 102 °C; $[\alpha]^{20}_D = +5.5°$ (c 0.17, toluene); ^{1}H NMR (C_6D_6, δ) 5.1 (t, $J = 2.8$ Hz, 1H), 4.79−4.72 (m, 1H), 3.78−3.71 (m, 1H), 3.48−3.45 (m, 2H), 3.23−3.16 (m, 4H), 2.85−2.7 (m, 3H), 2.63−2.37 (m, 5H), 1.84−1.69 (m, 4H), 1.72 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (C_6D_6, δ) 110.89, 96.96, 95.91, 82.92, 82.32, 81.41, 79.29, 78.64, 68.49, 67.94, 32.87, 32.54, 28.58, 28.02, 27.85, 27.75. Anal. Calcd for $C_{20}H_{27}CoO_2$ (mol wt 358.36): C, 67.03; H, 7.59; Co, 16.45. Found: C, 67.29; H, 7.42; Co, 16.31.

Bis-Annelated Complex 4. The experimental procedure is as described for **3**, but the pentane−ether mixture (9:1) was used as an eluent for chromatography. Under these conditions the ligand **2** (1.46 g, 4.59 mmol) gave the compound **4** as orange needles (1.45 g, 65.3%): mp 158 °C; $[\alpha]^{20}_D = +29.6°$ (c 0.25, toluene); ^{1}H NMR (C_6D_6, δ) 7.4 (s, 1H), 4.99 (m, 1H), 4.8 (m, 1H), 3.91−3.83 (m, 2H), 3.52−3.42 (m, 2H), 3.05−2.82 (m, 5H), 2.8−2.66 (m, 2H), 2.56 (m, 4H), 2.44−2.39 (m, 1H), 2.29−2.44 (m, 1H), 2.18−2.12 (m, 1H), 2.01−1.94 (m, 1H), 1.86 (m, 3H), 1.81 (s, 3H), 1.79 (s, 3H), 1.72 (s, 3H), 1.7 (s, 3H); ^{13}C NMR (C_6D_6, δ) 110.9, 96.59, 95.51, 93.09, 90.93, 79.14, 78.88, 78.49, 78.39, 73.27, 70.74, 32.94, 32.25, 29.39, 28.88, 27.86, 27.79, 26.55, 25.53. Anal. Calcd for $C_{27}H_{37}CoO_4$ (mol wt 484.51): C, 66.93; H, 7.70; Co, 12.16. Found: C, 67.03; H, 7.83; Co, 11.89.

X-ray Structure Determinations on 2−4. Single crystals of **2**−**4** were recrystallized from pentane, mounted in inert oil, and transferred to the cold gas stream of the diffractometer.

Diffraction data were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXS-97)[12] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[13] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in theoretical positions and were refined by using the riding model.

Selected crystal data and details of the structure solutions are summarized in Table 1.

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Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-198202 for **2**, CCDC-198201 for **3**, and CCDC-198200 for **4**. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, int. code + (1223) 336−033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates for all structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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