Syntheses of Chiral Nonracemic Half-Sandwich Cobalt Complexes with Menthyl-Derived Cyclopentadienyl, Indenyl, and Fluorenyl Ligands

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Several optically active (Cp^R)Co(L) (L = 1,5-cyclooctadiene, norbornadiene) complexes were prepared. The complex (−)-(menthylCp)Co(COD) (**1**) was synthesized by the direct treatment of (−)-menthylcyclopentadiene with highly reactive "atomic" cobalt in the presence of COD. The other examples, (+)-*pR*-(1-neomenthylindenyl)Co(COD) (**2**) and (+)-*pR*-(1-neomenthylindenyl)Co(NBD) (**3**) were prepared by deprotonation of (−)-3-neomenthylindene with BuLi and the metathetic reaction of the corresponding lithium salt with tris(triphenylphosphine)-cobalt(I) chloride, followed by replacement of PPh_3 with COD or NBD, respectively. The diastereoselectivity of the complexation was as high as 74.5% de, and the major diastereomers were separated chromatographically. Optically pure complex (−)-*pS*-(1-neomenthylindenyl)-Co(COD) (**4**) was prepared similarly, starting from (+)-3-neomenthylindene, and the diastereomeric excess of the major diastereomer was 74.4% de. The (+)-neomenthylfluorene **5** was prepared by the alkylation of fluorenyllithium with (−)-menthyltosylate, and the complex (+)-(*pseudo*-neomenthylfluorenyl)Co(COD) (**6**) was synthesized by the metathetic reaction of the corresponding lithium salt with $(PPh_3)_3CoCl$ and COD, in which an inversion of the cyclohexane ring of the terpene moiety was observed upon complexation. The structures of the compounds **1**, **2**, **3**, **4**, **5**, and **6** were determined by single-crystal X-ray diffractometry. Structural features of the complexes are also discussed on the basis of ^{1}H, ^{13}C NMR, and MS spectra.

Introduction

A menthyl moiety attached to the cyclopentadienyl ring of metallocenes is a powerful tool for the amplification of chiral information. Chiral menthyl-derived cyclopentadienyl and indenyl complexes of various transition metals are being widely exploited in different stoichiometric and catalytic asymmetric reactions and asymmetric structural effects. Complexes of rhodium,[1] ruthenium,[2] iridium,[1b,c] palladium,[2a] iron,[2b] nickel,[2b] cobalt,[1b,c,4a] molybdenum,[1b,c] zirconium,[3,2b] titanium,[3a,4] and numerous lanthanides[5] are among them. As a part of our ongoing investigations of the Co(I)-photocatalyzed cycloaddition of acetylenes and nitriles into a pyridine core,[6] we report the syntheses of several chiral nonracemic menthyl-derived (Cp^R)Co(COD/NBD) complexes, which are suitable for the elaboration of asymmetric versions of the reaction.

As reported earlier,[6c] (Cp^R)Co(COD) complexes are more effective precatalysts for the [2 + 2 + 2] photocycloaddition of acetylenes and nitriles than are analogous (Cp^R)Co(CO)$_2$ and (Cp^R)Co(PR$_3$)$_2$ complexes from

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the viewpoint of the reaction rate and the yield of pyridine. A preliminary survey of the literature has shown that, surprisingly, only one example of a chiral (Cp^R)Co(COD) complex has been reported so far,[7a] but the compound was not resolved optically. Recently we reported the first example of such complexes prepared on the basis of tartaric acid.[7b] In general, there is a noticeable lack of a uniform, reliable method for the preparation of the complexes, which are difficult compounds. There are several methods described for producing achiral (Cp^R)Co(COD) complexes: (a) complexation of $Co_2(CO)_8$ to substituted cyclopentadienes giving (Cp^R)$Co(CO)_2$ complexes (the latter can also be produced by treatment of $Cp^RLi(Na)$ with $(CO)_2CoI$)[8a] followed by replacement of CO with COD;[8b−d] (b) treatment of $Cp^RLi(Na)$ with $(PR_3)_3CoX$ followed by replacement of phosphine (phosphite) ligands with COD;[9] (c) direct complexation of highly reactive "atomic" cobalt powder (generated in situ from $Co(acac)_3$ and anthracene-activated magnesium) in the presence of COD;[10] (d) reduction of bis(Cp^R)Co complexes with lithium sand in the presence of COD.[11] Each of these methods has specific advantages and shortcomings and should be chosen in each case for the particular Cp^R ligand.

Experimental Section

All operations involving organometallic compounds were carried out in 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. Only characteristic fragments containing the isotopes of highest abundance are listed. Relative intensities in percentages are given in parenthesese. $(PPh_3)_3CoCl$, (−)-menthylcyclopentadiene,[3a,5d] (+)-3-neomenthylindene,[3c] (−)-menthyltosylate, and (+)-menthyltosylate[3c] were prepared according to published procedures. (−)-3-Neomenthylindene was prepared by analogy with its (+)-enantiomer. Cobalt(III) acetylacetonate (Merck), magnesium dust (50 mesh), methyliodide, anthracene, COD, and NBD were carefully dried and degassed prior to use. *n*-Butyllithium and fluorene were used as purchased.

(−)-(η^4-Cycloocta-1,5-diene)(η^5-1-menthylcyclopentadienyl)cobalt, 1. Magnesium dust (1.822 g, 75 mmol) was placed in a three-necked flask (250 mL) provided with an inlet, a condenser (with an outlet on the top), and a magnetic stirrer. The system was vacuumized, filled with argon, and carefully flame-dried with special attention to the magnesium. Anthracene (0.2763 g, 1.55 mmol) was introduced after cooling as a fine powder. Freshly distilled THF (75 mL) was then added followed by methyl iodide (100 μL). A yellow-green color appeared after 30 min of stirring, which then turned orange because of the strong precipitation of an anthracene−magnesium complex. The flask was placed in a water bath at a temperature of 55 °C, and COD (6.77 mL, 55.9 mmol) was added followed by (−)-menthylcyclopentadiene (5.5 mL, 24.46 mmol). The temperature of the bath was raised to 75 °C, and powdered $Co(acac)_3$ (8.9 g, 25 mmol) was added in portions for 30 min to maintain a gentle reflux. The reaction mixture was then refluxed for 1 h. The brown mixture was filtered through a G3 filter to remove solids and washed with THF. The solvent was removed in vacuo, and the residue was dried in a high vacuum for 1 h, then dissolved in 50 mL of pentane. The resulting white precipitate (magnesium acetylacetonate) was filtered off using a G4 filter and washed with pentane. The filtrate was concentrated to the volume of 20 mL and plunged into degassed silica (3 × 15 cm column), an orange band being eluted with pentane. The fraction was concentrated to a volume of 20 mL and cooled to −78 °C. Precipitated red-orange crystals were filtered off to give 3.7 g (40.8% yield) of the title compound **1**: mp 99 °C; $[\alpha]^{20}_D$ −229.6° (*c* 0.055, toluene); ^{1}H NMR (C_6D_6, δ) 5.42−5.41 (m, 1H), 4.22−4.21 (m, 2H), 3.75−3.7 (m, 2H), 3.63−3.58 (m, 2H), 3.49−3.43 (m, 2H), 2.86−2.67 (m, 4H), 2.38−2.32 (m, 1H), 2.1−1.76 (m, 9H), 1.39 (d, J = 5.94 Hz, 3H), 1.31−1.21 (m, 3H), 1.03 (d, J = 7.13 Hz, 3H), 0.93 (d, J = 6.94 Hz, 3H); ^{13}C NMR (C_6D_6, δ) 109.92, 84.50, 84.06, 82.13, 81.75, 64.61, 64.22, 51.59, 44.91, 40.23, 35.96, 34.13, 33.20, 32.40, 27.70, 25.55, 23.50, 22.07, 16.07; MS (250 °C, 70 eV, *m/z*) 370 (M^+, 50), 260 (100), 231 (21), 137 (10), 113 (15), 59 (8). Anal. Calcd for $C_{23}H_{35}Co$ (mol wt 370.46): C, 74.57; H, 9.52. Found: C, 74.78; H, 9.69.

(+)-(*pR*)-(η^4-Cycloocta-1,5-diene)(η^5-1-neomenthylindenyl)cobalt, 2. BuLi (2 mL of 2.5 M solution in hexanes, 5 mmol) was added in one portion to the solution of (−)-3-neomenthylindene (1.27 g, 5 mmol) in THF (15 mL) at −78 °C. The mixture was stirred for 5 min, the temperature was allowed to rise to +20 °C for 30 min, and stirring continued for 2 h at rt. The solution of 1-neomenthylindenyllithium was again cooled to −78 °C, and $(PPh_3)_3CoCl$ (4.41 g, 5 mmol) was added. The stirred solution was allowed to warm to rt for a period of 1 h and was stirred for an additional hour. COD (0.92 mL, 7.5 mmol) was added to the dark red reaction mixture, which was then brought to reflux and kept so for 0.5 h. The color soon changed to red-orange, and the solution was cooled and filtered through a thin pad of degassed silica (2 × 3 cm), being eluted with THF. The solvent was removed in vacuo, and the oily residue was dried for 1 h in high vacuum and purified by column chromatography (1.5 × 30 cm) on degassed silica. Elution with pentane allowed the separation of the main diastereomer as the first red-orange fraction, and the more slowly moving second minor fraction was set aside. The eluate was evaporated in vacuo to a volume of 5 mL. Cooling to −78 °C caused the precipitation of the complex **2** as a dark red crystalline compound. The yield of this compound after filtration and drying in high vacuum was 1.11 g (52.7%): mp 89 °C; $[\alpha]^{20}_D$ +1568° (*c* 0.06, toluene); ^{1}H NMR (C_6D_6, δ) 7.87 (d, J = 8.2 Hz, 1H), 7.19 (t, J = 7.0 Hz, 1H), 7.12 (t, J = 7.0 Hz, 1H), 6.80 (d, J = 8.5 Hz, 1H), 5.17 (d, J = 2.4 Hz, 1H), 3.89 (d, J = 2 Hz, 1H), 3.5−3.44 (m, 2H), 3.20−3.17 (m, 1H), 3.01 (m, 1H), 2.8 (m, 2H), 2.63−2.54 (m, 2H), 2.48 (m, 1H), 2.35−2.26 (m, 2H), 2.09−2.02 (m, 2H), 1.78−1.61 (m, 5H), 1.52−1.48 (m, 3H), 1.42 (d, J = 6.5 Hz, 3H), 1.34−1.28 (m, 1H), 0.75 (d, J = 6.4 Hz, 3H), 0.64 (d, J = 6.6 Hz, 3H); ^{13}C NMR (C_6D_6, δ) 126.07, 125.35, 122.06, 121.10, 103.10, 102.67, 99.37, 89.97, 73.14, 70.63, 67.18, 47.01, 40.07, 34.09, 33.44, 32.76, 31.19, 28.83, 28.67, 24.22, 23.70, 22.56, 20.50; MS (250 °C, 70 eV, *m/z*) 420 (M^+, 100), 310 (81), 281 (21), 175 (31), 141 (23), 113 (35), 59

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(14). Anal. Calcd for $C_{27}H_{37}Co$ (mol wt 420.52): C, 77.12; H, 8.87. Found: C, 77.29; H, 8.54.

(+)-(*pR*)-(η^4-Norbornadiene)(η^5-1-neomenthylindenyl)-cobalt, 3. The reaction (in analogy with **2**) of (−)-3-neomenthylindene (1.27 g, 5 mmol) in THF (15 mL), BuLi (2 mL of 2.5 M solution in hexanes, 5 mmol), $(PPh_3)_3CoCl$ (4.41 g, 5 mmol), and NBD (1.1 mL, 10 mmol) gave 1.23 g (60.8%) of the compound **3** as red-orange crystals: mp 99 °C; $[\alpha]^{20}_{D}$ +623° (*c* 0.12, toluene); ^1H NMR (C_6D_6, δ) 7.35−693 (m, 4H), 5.12 (m, 1H), 4.26 (m, 1H), 3.08−2.92 (m, 3H), 2.51−2.25 (m, 5H), 1.85 (m, 1H), 1.54−0.75 (m, 9H), 1.09 (m, 3H), 0.63 (m, 3H), 0.44 (m, 3H); ^{13}C NMR (C_6D_6, δ) 124.71, 122.98, 122.45, 101.25, 100.97, 96.02, 88.50, 70.98, 55.39, 48.34, 43.92, 42.10, 35.04, 34.13, 31.51, 30.48, 29.63, 28.57, 24.83, 23.3, 23.14, 20.49; MS (250 °C, 70 eV, *m*/*z*) 404 (M^+, 84), 361 (38), 312 (2), 265 (100), 239 (11), 201 (14), 187 (14), 175 (28), 150 (46), 141 (14), 115 (12), 91 (11), 59 (11). Anal. Calcd for $C_{26}H_{33}Co$ (mol wt 404.47): C, 77.21; H, 8.22. Found: C, 77.45; H, 8.39.

(−)-(*pS*)-(η^4-Cycloocta-1,5-diene)(η^5-1-neomenthylindenyl)cobalt, 4. The reaction (in analogy with **2**) of (+)-3-neomenthylindene (1.27 g, 5 mmol) in THF (15 mL), BuLi (2 mL of 2.5 M solution in hexanes, 5 mmol), $(PPh_3)_3CoCl$ (4.41 g, 5 mmol), and COD (0.92 mL, 7.5 mmol) gave 1.14 g (54.3%) of the title compound **4** as dark red crystals: mp 89 °C; $[\alpha]^{20}_{D}$ −1600° (*c* 0.15, toluene); ^1H NMR (C_6D_6, δ) 7.88 (d, $J = 8.4$ Hz, 1H), 7.19 (t, $J = 7.1$ Hz, 1H), 7.12 (t, $J = 6.9$ Hz, 1H), 6.79 (d, $J = 8.4$ Hz, 1H), 5.17 (d, $J = 2.4$ Hz, 1H), 3.9 (d, $J = 2$ Hz, 1H), 3.5−3.45 (m, 2H), 3.21−3.17 (m, 1H), 3.01 (m, 1H), 2.8 (m, 2H), 2.64−2.55 (m, 2H), 2.48 (m, 1H), 2.35−2.25 (m, 2H), 2.09−2.01 (m, 2H), 1.78−1.62 (m, 5H), 1.51−1.48 (m, 3H), 1.41 (d, $J = 6.6$ Hz, 3H), 1.34−1.28 (m, 1H), 0.75 (d, $J = 6.4$ Hz, 3H), 0.64 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (C_6D_6, δ) 126.07, 125.35, 122.06, 121.10, 103.10, 102.67, 99.37, 89.97, 73.14, 70.63, 67.18, 47.01, 40.07, 34.09, 33.44, 32.76, 31.19, 28.83, 28.67, 24.22, 23.70, 22.56, 20.50; MS (250 °C, 70 eV, *m*/*z*) 420 (M^+, 100), 310 (76), 281 (19), 175 (28), 141 (24), 113 (35), 59 (16). Anal. Calcd for $C_{27}H_{37}Co$ (mol wt 420.52): C, 77.12; H, 8.87. Found: C, 76.89; H, 8.51.

(+)-9-Neomenthylfluorene, 5. A solution of fluorene (20 g, 0.12 mol) in THF (150 mL) was treated dropwise with BuLi (52 mL of 2.5 M solution in hexanes, 0.12 mol) at room temperature. The reaction mixture was cooled to −78 °C, and the solution of (−)-menthyltosylate (36.9 g, 0.12 mol) in THF (100 mL) was then added dropwise to the deep red solution of fluorenyllithium. The reaction mixture was brought to rt for 30 min, then was stirred for 30 h under reflux. Water (200 mL) was added to quench the reaction, and the mixture was extracted with 100 mL of ether. The organic phase was separated, dried with Na_2SO_4, and filtered through a thin pad of silica. The solvents were removed in vacuo, and the remaining residue was purified by column chromatography using hexane as an eluent; the first fraction was collected. The solvent was evaporated to dryness, and the pale yellow oily residue was dissolved in hot MeOH to crystallize the product as white crystals. The yield was 9.6 g (26.2%): mp 76 °C; $[\alpha]^{25}_{D}$ +60.8° (*c* 0.2, heptane); ^1H NMR ($CDCl_3$, δ) 7.99−7.46 (m, 8H), 4.53 (d, $J = 2.8$ Hz, 1H), 3.05 (m, 1H), 2.44−2.35 (m, 1H), 2.12−1.93 (m, 2H), 1.83−1.79 (m, 1H), 1.66−1.58 (m, 1H), 1.5 (d, $J = 6.5$ Hz, 3H), 1.4 (d, $J = 6.5$ Hz, 3H), 1.15−1.12 (m, 1H), 1.0−0.73 (m, 3H), 0.62 (d, $J = 6.1$, 3H); ^{13}C NMR (C_6D_6, δ) 150.0, 147.10, 142.82, 141.90, 128.35, 126.34, 124.13, 120.18, 119.78, 77.79, 77.48, 77.15, 48.47, 47.98, 40.97, 36.23, 36.14, 30.77, 27.95, 26.87, 23.40, 22.35, 22.18; MS (250 °C, 70 eV, *m*/*z*) 304 (M^+, 24), 165 (100), 139 (49), 97 (24), 83 (71), 69 (45), 57 (32), 55 (42), 41 (21). Anal. Calcd for $C_{23}H_{28}$ (mol wt 304.47): C, 90.73; H, 9.27. Found: C, 91.01; H, 9.25.

(+)-(η^4-Cycloocta-1,5-diene)(η^5-9-neomenthylfluorenyl-)cobalt, 6. A solution of (+)-9-neomenthylfluorene (1.012 g, 3.325 mmol) in THF (10 mL) was treated with BuLi (1.35 mL of 2.5M solution in hexanes, 3.35 mmol) at −78 °C. The mixture was stirred for 5 min, the temperature raised to +20 °C for 30 min, and the mixture finally stirred for 10 h at rt. The red solution of 9-neomenthylfluorenyllithium was cooled to −78 °C, and $(PPh_3)_3CoCl$ (2.93 g, 3.325 mmol) was added. The stirred solution was allowed to warm to rt for a period of 1 h and stirred for an additional hour. COD (0.62 mL, 5 mmol) was added to the dark red reaction mixture, which was then brought to reflux and kept so for 0.5 h. After cooling it was filtered through a thin pad of degassed silica (2 × 3 cm), a red-orange fraction being eluted with THF. The solvent was removed in vacuo, and the oily residue was dried for 1 h in high vacuum and dissolved in pentane (30 mL). The solution was allowed to stand overnight at 0 °C. The precipitated crystals of PPh_3 were filtered off, and the solution was evaporated. The residue was purified chromatographically on degassed SiO_2 using a 1.5 cm × 15 cm column and pentane as an eluent. A red fraction was collected, and the solution was evaporated to the volume of 20 mL and cooled to −78 °C to crystallize the cobalt complex **6** as a black crystalline compound (0.69 g; 44.1%): mp 127 °C; $[\alpha]^{20}_{D}$ +1148.3° (*c* 0.06, toluene); ^1H NMR (400 MHz, C_6D_6) δ 8.07 (m, 1H), 7.48−7.06 (m, 8H), 2.96−2.83 (m, 3H), 2.56 (m, 3H), 2.16−1.15 (m, 15H), 1.23 (d, $J = 4.1$ Hz, 3H), 0.68 (d, $J = 4.6$ Hz, 3H), 0.01 (d, $J = 4.2$ Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 128.15, 126.46, 124.90, 124.25, 123.74, 123.32, 122.68, 122.62, 107.32, 107.17, 98.12, 95.29, 80.13, 72.94, 71.08, 44.96, 35.76, 32.43, 31.25, 30.75, 28.5, 28.08, 25.86, 25.07, 23.76, 22.21, 18.79; MS (250 °C, 70 eV, *m*/*z*) 470 (M^+, 100), 358 (36), 314 (19), 237 (17), 225 (43), 191 (42), 178 (18), 165 (63), 113 (44), 59 (14). Anal. Calcd for $C_{31}H_{39}Co$ (mol wt 470.57): C, 79.12; H, 8.35. Found: C, 79.38; H, 8.56.

X-ray Structure Determination. Single crystals of **1**, **2**, **3**, **4**, **5**, and **6** were 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.

Crystallographic data for the structures (excluding structure factors) reported in this paper have been deposited at the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-203413 for **1**, CCDC-203414 for **2**, CCDC-203415 for **3**, CCDC-203416 for **4**, CCDC-203417 for **5**, and CCDC-203418 for **6**. 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).

Results and Discussion

The preparation of the complex (−)-(menthylCp)Co-(COD) (**1**) is described. Our synthesis follows the method of Bogdanovič,[10] in which elemental cobalt reacts with a number of conventional cyclopentadienyl ligands. The finely powdered “atomic” cobalt was generated in situ by reduction of cobalt(III) acetylacetonate with anthracene-activated magnesium in THF, and (−)-menthylcyclopentadiene was added to the reaction mixture together with COD. The procedure was slightly modified, and filtration through a thin pad of degassed silica

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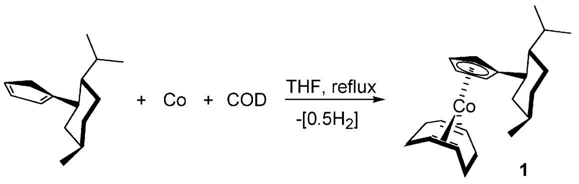
[12] Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997.

[13] Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

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

	1	**2**	**3**	**4**	**5**	**6**
empirical formula	$C_{23}H_{35}Co$	$C_{27}H_{37}Co$	$C_{26}H_{33}Co$	$C_{27}H_{37}Co$	$C_{23}H_{28}$	$C_{31}H_{39}Co$
fw	370.44	420.50	404.45	420.50	304.45	470.55
cryst size (mm)	0.6 × 0.6 × 0.4	0.4 × 0.3 × 0.2	0.6 × 0.4 × 0.4	0.5 × 0.3 × 0.3	0.4 × 0.4 × 0.2	0.4 × 0.3 × 0.3
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.855(2)	9.391(2)	9.723(2)	6.897(2)	8.684(2)	8.813(2)
b (Å)	8.514(2)	9.953(2)	12.278(3)	9.916(2)	12.540(3)	18.115(4)
c (Å)	13.253(3)	24.078(5)	17.230(3)	32.649(7)	17.167(3)	30.780(6)
α (deg)	90	90	90	90	90	90
β (deg)	96.98(3)	90	90	90	90	90
γ (deg)	90	90	90	90	90	90
V (Å^3)	991.8(3)	2250.5(8)	2056.9(7)	2232.9(8)	1869.4(6)	4914.0(17)
D_{calcd} (Mg/m^3)	1.240	1.241	1.306	1.251	1.082	1.272
Z	2	4	4	4	4	8
μ(Mo Kα) (mm^{-1})	0.866	0.772	0.842	0.778	0.060	0.715
F(000)	400	904	864	904	664	2016
diffractometer radiation	STOE-IPDS graphite monochromated, λ(Mo Kα) = 0.71073 Å					
temp (K)	200	200	200	200	293	200
θ range for data collecn (deg)	2.32−23.00	2.21−23.00	2.04−23.00	2.15−22.99	2.01−22.50	1.74−22.25
index range (h, k, l)	−9 to +9, −8 to +9, −14 to +14	−10 to +10, −10 to +10, −23 to +23	−10 to +10, −13 to +13, −18 to +18	−7 to +7, −10 to +10, −35 to +35	−9 to +9, −13 to +13, −18 to +18	−9 to +9, −19 to +19, −32 to +32
no. of reflns collected	4816	10 610	9912	10142	8507	21 520
no. of indep reflns	2666	3109	2863	3105	2454	6224
no. of obsd reflns	2470	2720	2636	2808	1847	5501
no. of refined params	217	253	244	253	208	577
R1 (2$\sigma(I)$)	0.0303	0.0333	0.0245	0.0391	0.0395	0.0287
R1 (all data)	0.0337	0.0399	0.0278	0.0437	0.0573	0.0356
wR2 (all data)	0.0727	0.0766	0.0597	0.0960	0.0855	0.0607
goodness of fit	0.982	0.914	0.881	0.980	0.908	0.946
largest diff peak and hole (e/Å^3)	0.289/−0.190	0.250/−0.206	0.152/−0.223	0.793/−0.298	0.119/−0.094	0.250/−0.275

Scheme 1



was used to remove magnesium acetylacetonate, this being the most efficient method for such removal. Cooling of the *n*-pentane solution to −78 °C gave the complex **1** in 41% yield (Scheme 1).

A crystal of the complex **1** suitable for single-crystal X-ray diffraction analysis was grown from pentane by the gradual cooling of the solution to −78 °C (Figure 1).

3-Substituted indenyl ligands have two enantiotopic π-faces and therefore can form two enantiomeric half-sandwich complexes upon complexation with transition metals. Diastereoselective complexation of various transition metals to 3-menthylindenes is well documented.[14] However, a recent example of cobalt complexation is worth mentioning. Treatment of (−)-(1-menthyl-4,7-dimethylindenyl)potassium with (dppe)$CoCl_2$ in THF led to a mixture of two diastereomers of the corresponding (1-menthylindenyl)Co(dppe) complex in 33% yield and ratio 6.0:1 (71% de).[1b] Utilization of 2 equiv of the ligand was necessary for in situ reduction of Co(II) to Co(I) species. The major diastereomer was purified by additional crystallization; however, no X-ray investigation was reported, and an absolute configuration of the complex was not established. The source of such diastereoselective recognition was supposed to be the particular stereoarrangement of the menthyl group, whose 4′-isopropyl group is more sterically demanding than the corresponding 1′-methyl group, and thus favors the preferable formation of one of the two diastereomers.

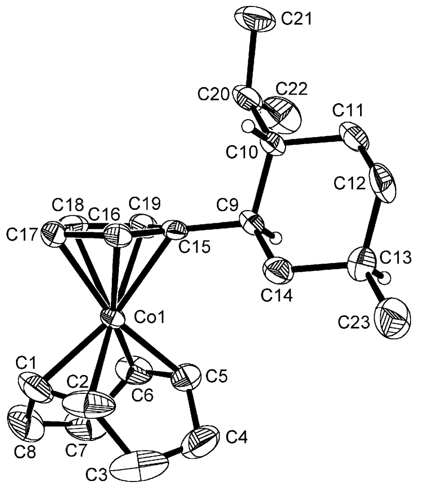


Figure 1. ORTEP plot of **1** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (Å): C(15)−C(16) = 1.398(6), C(16)−C(17) = 1.418(5), C(17)−C(18) = 1.392(6), C(18)−C(19) = 1.421(6), C(19)−C(15) = 1.442(5), Co(1)−C(15) = 2.139(3), Co(1)−C(16) = 2.118(3), Co(1)−C(17) = 2.073(3), Co(1)−C(18) = 2.073(4), Co(1)−C(19) = 2.051(4), Co(1)−C(COD) = 1.999−2.018(4).

We have discovered that utilization of $(PPh_3)_3CoCl$ as a source of cobalt is more attractive for the preparation of various (1-menthylindenyl)Co(L_x) complexes from the viewpoint of chemical yield and diastereoselectivity. The

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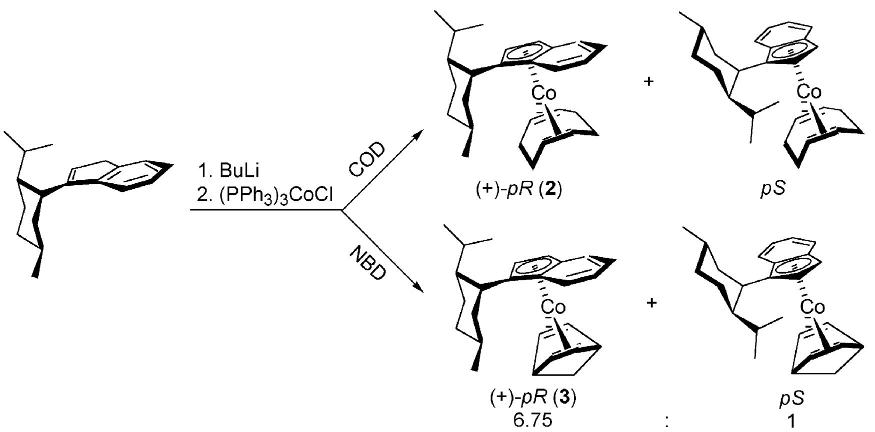
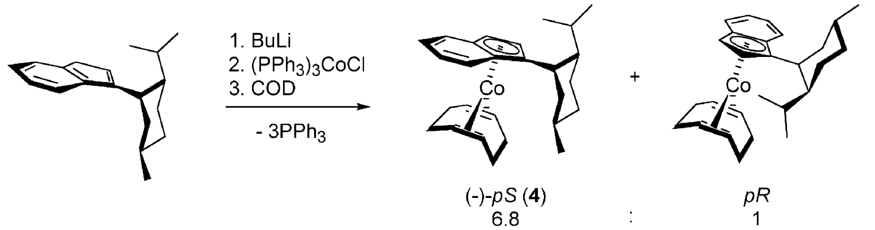
[14] For an exhaustive survey see: Paley, R. S. *Chem. Rev.* **2002**, *102*, 1493.

Scheme 2. Diastereomeric Complexation to (−)-3-Neomenthylindene



Scheme 3. Diastereomeric Complexation to (+)-3-Neomenthylindene



procedure generally involves deprotonation of ligands with BuLi in THF solution followed by treatment of the lithium salts with $(PPh_3)_3CoCl$ at −78 °C with the temperature rising gradually to 20 °C. The (1-menthylindenyl)$Co(PPh_3)_2$ complexes can easily replace both PPh_3 ligands after treatment in situ with a small excess of COD or NBD and a short reflux to give corresponding (1-menthylindenyl)Co(bisalkene) complexes (a sample for ^1H and ^{13}C NMR investigations is taken at this point; spectra are analyzed for two sets of signals of the diastereomeric complexes, a ratio being calculated on the basis of the integral intensities). The diastereomeric complexes have been easily separated from one another using column chromatography on degassed silica followed by crystallization from pentane or ethanol. Once isolated in such a way, the optically pure crystalline complexes can henceforth be purified by simple recrystallization of the crude mixture of diastereomeric complexes. Minor diastereomers were not separated in a pure state because of their insufficient concentration in the reaction mixture and reasonable decomposition on silica, probably due to higher thermodynamic instability.

The cobalt complexation to (−)-3-neomenthylindene led thus to the (+)-*pR* complex **2** in 52.7% yield, with diastereoselectivity being 74.2% de. If NBD was taken as a replacing ligand in the latter reaction, the corresponding (+)-*pR* complex **3** was prepared in 60.8% yield and the same diastereoselectivity (Scheme 2).

The analogous complexation using (+)-3-neomenthylindene furnished (−)-*pS* complex **4**, which is an enantiomer of the complex **2**, with nearly the same diastereoselectivity (74.4% de) and chemical yield (Scheme 3).

Crystals of **2** and **3** were grown from pentane, and ethanol was used to crystallize the complex **4**. The solid-state structures were determined by X-ray diffraction methods. The ORTEP plots of these molecules are shown in Figures 2−4.

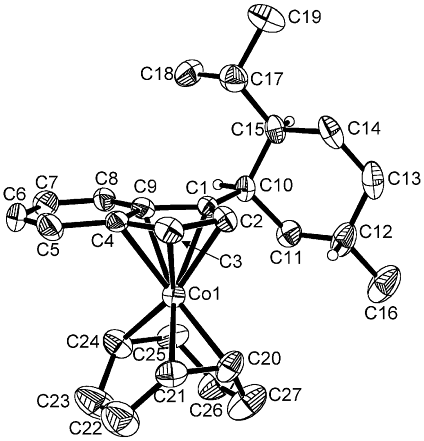


Figure 2. ORTEP plot of **2** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (Å): C(1)−C(2) = 1.399(5), C(2)−C(3) = 1.435(5), C(3)−C(4) = 1.410(4), C(4)−C(9) = 1.445(5), C(9)−C(1) = 1.451(5), Co(1)−C(1) = 2.174(4), Co(1)−C(2) = 2.117(4), Co(1)−C(3) = 2.075(4), Co(1)−C(4) = 2.118(4), Co(1)−C(9) = 2.137(4), Co(1)−C(COD) = 2.007−2.034(4).

It is worth mentioning that attempts to apply an “atomic” cobalt procedure for the complexation to the indenyl ligands gave only traces of the desired complexes.

To our surprise, we discovered that no synthesis of menthyl-derived fluorenyl ligands has been described in the literature, in contrast to corresponding well-studied cyclopentadienyl and indenyl compounds. However, a simple alkylation of fluorenyllithium with (−)-menthyltosylate in THF solution gave us the (+)-9-neomenthylfluorene **5** in a satisfactory yield of 26.2% (Scheme 4).

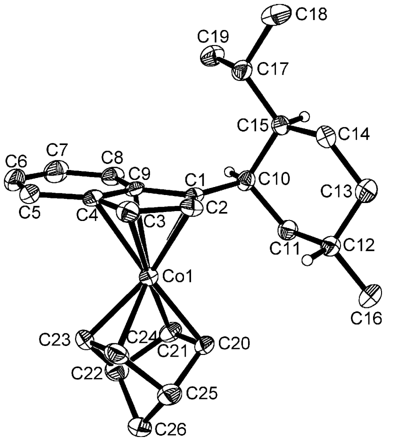


Figure 3. ORTEP plot of **3** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (Å): C(1)–C(2) = 1.430(4), C(2)–C(3) = 1.407(4), C(3)–C(4) = 1.434(4), C(4)–C(9) = 1.435(4), C(9)–C(1) = 1.449(4), Co(1)–C(1) = 2.118(3), Co(1)–C(2) = 2.080(3), Co(1)–C(3) = 2.068(3), Co(1)–C(4) = 2.158(3), Co(1)–C(9) = 2.170(4), Co(1)–C(COD) = 2.010–2.025(4).

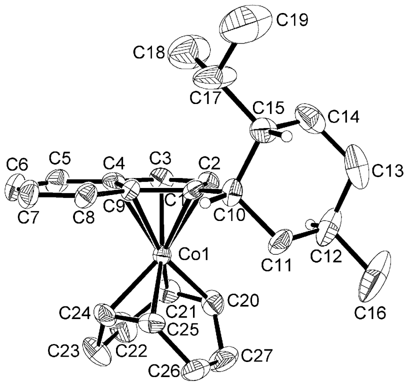
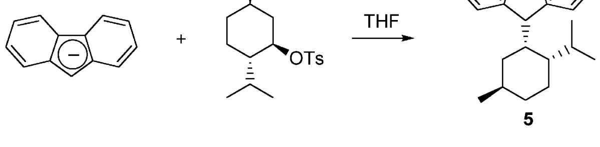


Figure 4. ORTEP plot of **4** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (Å): C(1)–C(2) = 1.409(6), C(2)–C(3) = 1.424(6), C(3)–C(4) = 1.409(6), C(4)–C(9) = 1.450(5), C(9)–C(1) = 1.460(6), Co(1)–C(1) = 2.148(4), Co(1)–C(2) = 2.098(5), Co(1)–C(3) = 2.072(4), Co(1)–C(4) = 2.136(4), Co(1)–C(9) = 2.128(4), Co(1)–C(COD) = 1.994–2.013(5).

Scheme 4. Preparation of (+)-9-Neomenthylfluorene, 5



A single-crystal X-ray structure determination confirmed the expected neomenthyl stereochemistry of the terpene moiety (Figure 5).

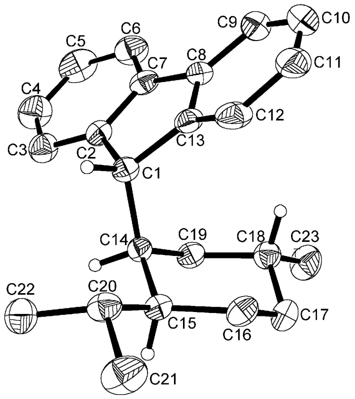


Figure 5. ORTEP plot of **5** with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (Å): C(1)–C(2) = 1.527(4), C(2)–C(7) = 1.392(4), C(7)–C(8) = 1.456(4), C(8)–C(13) = 1.393(4), C(13)–C(1) = 1.512(3).

Although unsubstituted (η^5-fluorenyl)Co(η^4-COD) is easily available through the reaction of fluorenylsodium with [((*i*-PrO)$_3$P)$_3$CoBr] followed by replacement of phosphite ligands with COD at 100 °C, a substituted 9-carboxymethylfluorene failed to react in the same way.[9] There are also some reports that (fluorenyl)Mn(CO)$_3$[15a] and (fluorenyl)ZrCpCl$_2$[15b] are inclined to so-called "ring-slippage" reactions, an irreversible change of Cp^R–metal binding from η^5 to η^1 form, followed by total elimination of the metal to give bisfluorenyl derivatives, particularly in the media of donor solvents (for example, THF).

An initial attempt failed to deprotonate the ligand **5** with BuLi in a benzene medium. Fortunately, THF appeared to be the solvent of choice for the deprotonation and subsequent treatment with (PPh$_3$)$_3$CoCl and COD to give the desired complex **6** in 44.1% yield (Scheme 5). Although the reaction proceeded smoothly enough, a considerable cobalt deposition (as a mirror) was observed at a longer reflux of the reaction mixture, proving that some elimination of the metal is still possible.

Results of single-crystal X-ray structure determination of the complex **6** grown from pentane are presented in Figure 6.

The main feature of the structure **6** is the inverted configuration of the terpene moiety. In the original ligand **5** it has adopted a classical neomenthyl arrangement with isopropyl and methyl groups in equatorial positions, and an axial (fluorenyl)Co(COD) group attached to the cyclohexyl ring in the chair conformation. In comparison, the isopropyl and methyl groups have appeared to be in axial positions in the complex **6**, and the metallocene residue has moved to the equatorial position. The axial isopropyl group has adopted a more sterically favorable orientation, with a methine proton pointing toward the inner space of the cyclohexyl molecule to minimize steric interactions with axial protons at C(19) and C(17). The rearrangement of the cyclohexyl structure can be rationalized as a tendency of the whole molecule to avoid unfavorable 1,3-diaxial interactions of the protons at C(12) and C(3) of the fluorenyl moiety with axial protons at C(16) and C(17) of cyclohexane, which became stronger after the complexation and made the conventional neomenthyl arrangement apparently impossible. Such pseudorotation of the neomenthyl unit to something that could be called a "*pseudo*-neomenthyl" group was already observed in several cases after complexation of (+)-neomenthyl-

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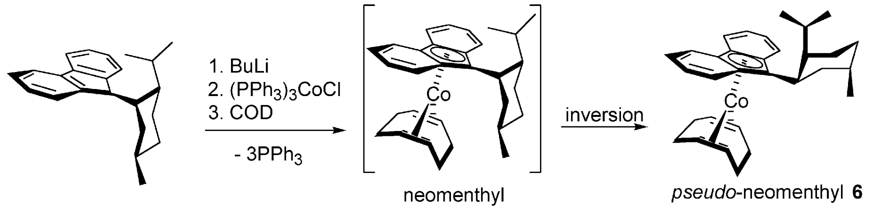
(15) (a) Biagioni, R. N.; Larkovich, I. M.; Skelton, J.; Hartung, J. B. *Organometallics* **1990**, *9*, 547. (b) Schmid, M. A.; Alt, H. G.; Milius, W. *J. Organomet. Chem.* **1996**, *525*, 15.

Scheme 5. Preparation of (+)-(η^4-Cycloocta-1,5-diene)(η^5-1-*pseudo*-neomenthylfluorenyl)cobalt, 6



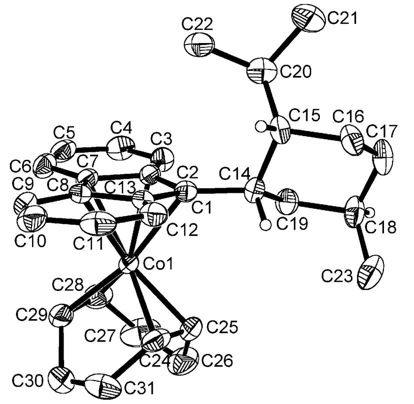


Figure 6. ORTEP plot of **6** (one of the two molecules in the asymmetric unit) with crystallographic numbering. Thermal ellipsoids are shown at the 50% probability level for non-hydrogen atoms. Selected distances (molecule A/molecule B) (Å): C(1)−C(2) = 1.428/1.444(5), C(2)−C(7) = 1.458/1.434(5), C(7)−C(8) = 1.445/1.440(5), C(8)−C(13) = 1.432/1.430(5), C(13)−C(1) = 1.465/1.464(5), Co(1)−C(1) = 2.109/2.098(3), Co(1)−C(2) = 2.106/2.130(3), Co(1)−C(7) = 2.121/2.151(3), Co(1)−C(8) = 2.195/2.215(3), Co(1)−C(13) = 2.201/2.215(3), Co(1)−C(COD) = 1.998−2.039(3).

diphenyphosphine with some chiral areneruthenium(II) complexes,[16a,b] (1,3-butadienyl)Fe(CO)$_3$ complexes,[16c] (isopropyloxycarbonylmethyl)Co(CO)$_4$ complex,[16d] and (benzylideneacetone)Fe(CO)$_3$ complex.[16e] In all cases, the addition of a new bulky stereochemical ligand to the phosphorus atom caused an inversion of the cyclohexane ring, which became obvious from X-ray observations. Another remarkable example of the inversion was found for a complexation of the [Rh(COD)Cl]$_2$ to the (+)-1-neomenthyl-2,3,4,5-tetraphenylcyclopentadiene.[1a] The enormously increased steric pressure of two phenyl groups adjacent to the neomenthyl group also caused the rearrangement of the terpene ring after the complexation. However, despite the new stereoarrangement, the terpene moiety was still referred to as a “neomenthyl group” in all mentioned papers.

The pure crystalline cobalt complexes **1**, **2**, **3**, **4**, and **6** are reasonably air-stable (up to 10 min) and can be briefly handled outside an inert atmosphere. In contrast to the behavior in the solid state, contact of their solutions with even traces of oxygen during the purification processes leads to the immediate decomposition of the complexes accompanied by a color change from the red-orange of Co(I) to the dirty green of Co(II). The paramagnetic nature of the latter makes ^{1}H NMR spectra undecipherable if even small quantities of the species are present in the solution. The complexes are well soluble in most organic solvents such as THF, benzene, diethyl ether, dioxane, pentane, and hot absolute ethanol and less soluble in cold absolute ethanol. They can be conveniently recrystallized from this solvent, but they are insoluble in water.

Table 2. Selected X-ray Parameters of the Complexes 1, 2, 3, 4, and 6

	distance C_{Cp}−Co[a] (Å)	bite angle C_{db1}−Co−C_{db2}[b] (deg)	dihedral angle of the Cp plane to the terpene moiety[c] (deg)	dihedral angle of the Cp plane to plane of the diolefin[d] (deg)
1	1.710	90.8	68.1	3.6
2	1.743	91.0	85.1	4.4
3	1.735	74.9	83.1	6.4
4	1.732	91.7	87.9	2.8
6	1.766	91.0	53.0	1.5
	1.775	91.5	44.4	4.8

[a] C_{Cp} = centroid of the cyclopentadienyl ring. [b] C_{db1}, C_{db2} = centroids of the diolefin double bonds. [c] Best plane of the six-membered ring. [d] Best plane of the four atoms of the diolefin double bonds.

According to X-ray investigations, all five complexes are monomeric, free of solvents, and diastereomerically pure. They clearly show the characteristic three stereocenters of menthyl moieties.

The average bond distances from cobalt to the five-membered Cp^R ring increase from 1.710 (**1**) to 1.775 Å (**6**) along with the steric hindrance of the Cp^R unit (Table 2). The average bond lengths from cobalt to the diene system of COD or NBD units are nearly identical and occupy a range of 1.994−2.039 Å. The bite angle defined by the center of COD−olefin bonds and the cobalt atom in the complexes **1**, **2**, **4**, and **6** is 90.3 ± 0.5°, much larger than the corresponding bite angle in the NBD complex **3** (74.9°).

The dihedral angle between the Cp^R cycle and the plane defined by double bonds of the diolefins in the complexes **1**, **2**, **3**, **4**, and **6** varies a little in the range 1.4−6.4°. Thus it is almost parallel, as in other known half-sandwich diolefin transition metal complexes.

In the case of indenyl−neomenthyl complexes **2**, **3**, and **4** the terpene moiety adopts a conformation more or less perpendicular to the Cp^R plane, with each of the isopropyl groups pointing away from the metal. The alignment is similar to that in the isostructural (+)-(*pS*)-(η^4-cycloocta-1,5-diene)(η^5-1-neomethylindenyl)rhodium(I) complex.[1b] In the case of Cp^{menthyl} complex **1** the angle decreases to 68.1°, probably due to the less strained equatorial position of the metallocene. Also, for the fluorenyl complex **6** the shift of metallocenyl residue to a more favorable equatorial position in the *pseudo*-

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neomentyl steric group leads to a substantially smaller dihedral angle (53.0° and 44.4°) when compared with those for the complexes **2**, **3**, and **4**, where the metallocene adopts a tense axial position in the neomenthyl terpene configuration.

All of these cobalt complexes exhibited C_1 symmetry in NMR spectra in solution, and each diastereomeric compound gave only one set of signals at room temperature. This is consistent with the absence of rotation of the menthyl groups along the $C^1-C^{3'}$ axis, since the rotation would lead to a new rotamer in which all the atoms would be in a new chemical environment with potentially different chemical shifts. The alkene ligands do not seem to rotate around the cobalt−indenyl axis on the ^{1}H NMR time scale. The signals of COD and NBD show no broadening but give complicated coupling patterns, as all their protons are chemically inequivalent. In the ^{13}C NMR spectra, only four of the eight chemically nonequivalent carbon atoms of COD and four of the seven chemically nonequivalent carbon atoms of NBD are detected. This may be caused by an empirically low induction of the chiral indenyl ligand on the COD or NBD moiety or by a rotating COD or NBD ligand on the ^{13}C NMR time scale. For all indenyl complexes **2**, **3**, and **4** ^{13}C NMR spectra have failed to recognize clearly the number of carbon atoms of indenyl ligand to which the cobalt atom is anchored in benzene solution. It is usually determined according to characteristic shifts of the carbon atoms at the junction of fused five- and six-membered rings. Chemical shifts of the carbon atoms C(8) and C(9) of our complexes have values in the range δ 100.97−105.10 ppm, which are intermediate between the average values observed for the two basic bonding situations established for unsubstituted indenyl complexes: δ 75.10−98.30 ppm in the case of η^5-indenyl complexes characterized by a high π-electron delocalization and δ 134.30 ppm in the case of a 1−3-η^3-indenyl binding.[17] The shifts obtained are comparable to those determined for unsubstituted (indenyl)Co(COD) complex (δ 104.70 ppm) in $CDCl_3$ solution.[11] On the other hand, the complex **4** (δ 103.10 ppm, C(8); δ 102.67 ppm, C(9)) shows a definitely weaker tendency toward the intermediate $\eta^2+\eta^3$ coordination in benzene solution than the analogous rhodium compound (δ 112.30 ppm, C(8); δ 110.70 ppm, C(9)), and it looks more like a η^5-indenyl complex.[1b]

The fragmentation of cobalt complexes **1**, **2**, **3**, **4**, and **6** under electron strike (MS) showed that only the cyclopentadienyl complex **1** forms a (Cp^R)Co molecular ion as the peak of highest intensity, and the molecular peak of (Cp^R)Co(COD) is at 50% intensity. Indenyl complexes **2** and **4** formed corresponding (Cp^R)Co peaks with 81% and 76% of intensity, respectively. The ions of (Cp^R)Co(COD) are at the highest intensity in the spectra. Fluorenyl complex **6** retains COD most tightly ((Cp^R)Co − 36%, (Cp^R)Co(COD) − 100%). In the case of (indenyl)Co(NBD) complex **3** the intensity of the (Cp^R)-Co peak is only 2% of the intensity of the entire molecular ion. This indicates a very strong complexation of cobalt to NBD in the complex **3** and predicts a low activity of such (Cp^R)Co(NBD) complexes in [2 + 2 + 2] cyclotrimerisation reactions. As it was established by previous investigations, the dissociation of the COD ligand from the (Cp^R)Co(COD) precatalyst is a key step in launching the catalytic cycle, and the addition of COD to the reaction mixture slows down or even suppresses the reaction.[6b] A direct relationship was observed between the binding power of the removable alkene ligand and the temperature of the catalyst activation.[18]

Conclusion

The direct complexation of "atomic" cobalt to (−)-menthylcyclopentadiene in the presence of COD provides a convenient method for the preparation of (−)-(1-menthylCp)cobalt(COD) complex **1**. Metathetic reactions of lithium salts of 3-menthylindenyl ligands with $(PPh_3)_3CoCl$ and COD (or NBD) lead to a number of planar-chiral, nonracemic half-sandwich (neomenthylindenyl)cobalt (COD/NBD) complexes **2**, **3**, and **4**. The diastereomeric excess of the complexation is 74.3±0.1% de. A new ligand, (+)-9-neomenthylfluorene **5**, is synthesized. A similar reaction of its lithium salt with $(PPh_3)_3CoCl$ and COD gives corresponding fluorenyl complex **6**, and an inversion of the cyclohexyl ring of the terpene moiety has been observed upon the complexation. X-ray diffraction analyses of the complexes **1**, **2**, **3**, **4**, and **6** confirm the enantiomeric purity of all stereogenic centers in the complexes.

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

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