Synthesis and Characterization of (−)-1-Menthyl-4,7-dimethylindene and Its Main Group Metal Compounds with Lithium, Sodium, Potassium, and Tin

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Received December 15, 2000

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 31, 2001 on http://pubs.acs.org | doi: 10.1021/om001074m

(−)-3-Menthyl-4,7-dimethylindene and (−)-4,7-diisopropyl-3-menthylindene were prepared in 63 and 48% yield, respectively, through a 1,1′-bis(diphenylphosphino)ferrocene-palladium-catalyzed cross-coupling reaction of menthylzinc with 3-(4,7-dimethylindenyl) trifluoromethanesulfonate or 3-(4,7-diisopropylindenyl) trifluoromethanesulfonate. Several other methods including addition of menthyl Grignard to 1-indanone, addition of (indenyl)lithium to menthone, or coupling of 3-bromoindene with menthyl Grignard for preparing 1-(or 3-)-menthylindene were inferior to direct substitution of menthyl sulfonate esters by (indenyl)-lithium. (−)-3-Menthyl-4,7-dimethylindene could be deprotonated to form a single diastereomeric lithium salt that was characterized by X-ray crystallography. (−)-4,7-Diisopropyl-3-menthylindene was deprotonated to form a lithium salt. Formation of the sodium and potassium salts of (−)-3-menthyl-4,7-dimethylindene was possible, but the products were not stereochemically characterized. 1-Trialkyltin compounds with (−)-3-menthyl-4,7-dimethylindene were prepared as nearly 1:1 diastereomeric mixtures from the lithium salt.

Introduction

The study of indenylmetal complexes bearing a chiral substituent at the 1-indenyl position has been challenging not only due to the formation of diastereomeric metal complexes but also due to limited approaches to certain substituted ligands.[1,2] A selection of known chiral indenes along with the isomer ratios obtained for zirconocene dichloride complexes of these ligands are shown in Figure 1. Although these ligands were prepared by the straightforward alkylation of (indenyl)- or (4,7-dimethyl)-indenyllithium complexes with several terpene-derived sulfonate esters, the yields were not always very good.[1]

While 4,7-dimethyl-3-neomenthylindene had the highest metalation stereoselectivity,[1] the corresponding (−)-3-menthyl-4,7-dimethylindene ligand **1a** was not reported until now. Since its three equatorial substituents should render the menthyl group conformationally better defined than the neomenthyl group, we anticipated that menthyl-containing **1a** would be promising

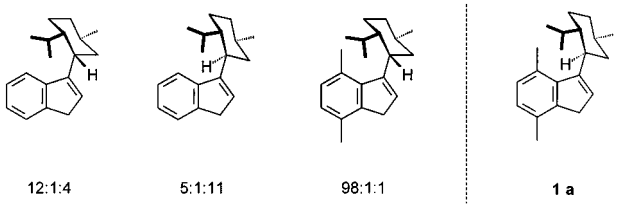

Figure 1. Chiral indenes and diastereomeric ratios for their zirconocene dichloride complexes (racem-like1:racem-like2:meso-like = (*pR*)(*pR*):(*pS*)(*pS*):(*pR*)(*pS*)).

to study. The two most favored conformational isomers of **1a** as calculated at the Becke3LYP/6-31G level are shown in Figure 2.[3] The increased steric interaction of the 4-methyl group provides a 27 kJ/mol preference for the +anticlinal conformation, whereas the energy difference for the corresponding conformation in 3-menthylindene is only 2.1 kJ/mol. Given the large preference for the +anticlinal conformation of **1a**, the isopropyl group should effectively shield the 1-*si* face of the

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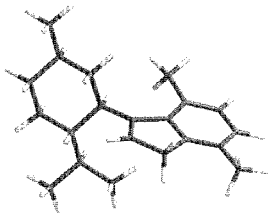
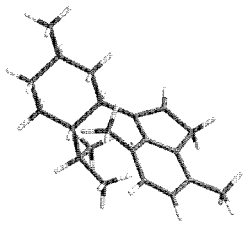
10.1021/om001074m CCC: $20.00 © 2001 American Chemical Society
Publication on Web 03/31/2001



-synclinal (Δe_{rel} = 27 kJ/mol)



+anticlinal (Δe_{rel} = 0 kJ/mol)

Figure 2. Calculated conformations of 3-menthyl-4,7-dimethylindene.

indenyl π-face and lead to selective metalation. Our attempts to form ligand **1a** through alkylation of 4,7-dimethylindene gave marginally satisfactory results and prompted us to investigate alternative synthetic methods for preparing this ligand and the related (−)-3-menthylindene and (−)-4,7-diisopropyl-3-menthylindene ligands. As part of our work on the preparation of new chiral ligands,[4] these syntheses and the formation of several main group compounds of **1a** are described in this paper.

Experimental Section

All operations involving organometallic compounds were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques in dry, oxygen-free solvents. Melting points were measured in sealed capillaries with a Büchi 510 melting point determination apparatus and are uncorrected. Optical rotations were determined on a Schmidt+Haensch Polartronic-D polarimeter. The NMR spectra were recorded on a Bruker ARX 200 (^{1}H, 200 MHz; ^{13}C, 50.32 MHz) or ARX 400 (^{1}H, 400 MHz; ^{13}C, 100.64 MHz; ^{119}Sn, 149.21 MHz) spectrometer at ambient temperatures. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residue of the deuterated solvents. Chemical shifts for ^{119}Sn measurements are given relative to tetramethyltin. The IR spectra were recorded on a Nicolet Magna System 750 spectrometer. Mass spectra (EI, 70 eV) were obtained using a Varian MAT 311 A/AMD instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Relative intensities in percent are given in parentheses. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyser 2400. (−)-Menthyl chloride,[5] (+)-neomenthyl chloride,[6] (+)-menthylmagnesium chloride,[7] (+)-neomenthylmagnesium chloride,[8] (+)-neomenthyl methanesulfonate,[9] 3-bromoindene,[10] 3-chloro-1-(2′,5′-dimethylphenyl)propanone,[11] 4,7-dimethylindanone,[11] indenylmagnesium bromide(THF)$_5$,[12] (indenyl)lithium,[13] (4,7-dimethylindenyl)lithium,[1a] (1-neomenthylindenyl)lithium,[1b] lithium bis(trimethylsilyl)amide(Et_2O),[14] and 4,7-dimethylindene[15] were prepared according to published procedures. 3-Chloropropionyl chloride, trifluoromethanesulfonic anhydride, (−)-menthone, dichloro-1,3-bis(diphenylphosphino)propanenickel(II), dichloro-1,1′-bis(diphenylphosphino)-ferrocenepalladium(II)(CH_2Cl_2), indanone, sodium amide, potassium hydride, *n*-butyllithium, trimethyltin chloride, tri-*n*-butyltin chloride, boron trifluoride(Et_2O), 4-toluenesulfonic acid(H_2O), titanium tetrachloride, cerium trichloride, copper iodide, and anhydrous aluminum trichloride were used as purchased. 1,4-Diisopropylbenzene, triethylsilane, and indene were distilled prior to use.

(−)-3-Menthyl-4,7-dimethylindene (1a) and (−)-1-Menthyl-4,7-dimethylindene (1b). A solution of (+)-neomenthyl methanesulfonate (35.79 g, 152.71 mmol) in THF (30 mL) was slowly reacted at 0 °C with a solution of (4,7-dimethylindenyl)-lithium (25.50 g, 169.83 mmol) in THF (200 mL). The purple solution was stirred 2 h at this temperature and 10 h at room temperature, before it was hydrolyzed with water (100 mL). The mixture was acidified with 1 M HCl and extracted three times with diethyl ether (200 mL). The combined organic fractions were dried with magnesium sulfate and purified by column chromatography (SiO_2, 10/1 *n*-hexane/ethyl acetate). The resulting orange oil was fractionally distilled in a vacuum (10^{-2} mbar) to yield **1b** as a yellow oil (7.79 g, 18%) at a temperature of 99 °C and the double bond isomer **1a** (12.98 g, 30%) as a yellow oil at 116 °C. **1b**: bp 99 °C (10^{-5} bar); −158.9 °C (neat). ^{1}H NMR (chloroform-d_1, 400 MHz): δ 7.00 (m, 1 H, H^6), 6.96 (d, ^3J = 1.8 Hz, 1 H, H^3), 6.90 (m, 1 H, H^5), 6.50 (dd, ^3J = 5.7 Hz, ^3J = 1.8 Hz, 1 H, H^2), 3.89 (m, 1 H, H^1), 2.47 (m, 1 H, H$^{3'}$), 2.43 (s, 3 H, H^{11}), 2.41 (s, 3 H, H^{10}), 2.3−0.75 (m, 9 H, H$^{1',2',4',5',6',8'}$), 1.08 (d, ^3J = 6.9 Hz, 3 H, H$^{9'/10'}$), 1.01 (d, ^3J = 6.9 Hz, 3 H, H$^{9'/10'}$), 0.69 (d, ^3J = 6.5 Hz, 3 H, H$^{7'}$). ^{13}C{^{1}H} NMR (chloroform-d_1, 100.64 MHz): δ 145.10, 143.73 (C^{8,9}), 135.48, 130.17, 127.45, 126.72 (C^{2,3,5,6}), 130.01, 127.49 (C^{4,7}), 51.64, 46.83, 38.85, 32.71, 26.80 (C$^{1,1',3',4',8'}$), 35.35, 33.93, 24.66 (C$^{2',5',6'}$), 22.48, 21.59, 19.16, 18.21, 15.47 (C$^{7',9',10,10',11}$). MS (59 °C): *m*/*z* 282 (100) [M]$^+$, 267 (5) [$C_{20}H_{27}$]$^+$, 239 (16) [$C_{18}H_{23}$]$^+$, 158 (62) [$C_{12}H_{14}$]$^+$, 143 (27) [$C_{11}H_{11}$]$^+$, 128 (17) [$C_{10}H_8$]$^+$. IR (CsI): $\bar{\nu}$ 3065, 2952, 2921, 2866, 1493, 1455, 718 cm^{-1}. Anal. Calcd for $C_{21}H_{30}$ (282.47 g/mol): C, 89.29; H, 10.70. Found: C, 88.95; H, 10.41. **1a**: bp 116 °C (10^{-5} bar); $[\alpha]_D^{25}$ −123.5° (*c* 5.4, diethyl ether). ^{1}H NMR (chloroform-d_1, 400 MHz): δ 7.07 (d, ^3J = 7.6 Hz, 1 H, H^5), 7.00 (d, ^3J = 7.6 Hz, 1 H, H^6), 6.29 (dd, ^3J = 2.2 Hz, ^3J = 2.2 Hz, 1 H, H^2), 3.33 (dd, ^2J = 23.5 Hz, ^3J = 2.2 Hz, 1 H, H^{1a}), 3.24 (dd, ^2J = 23.5 Hz, ^3J = 2.2 Hz, 1 H, H^{1b}), 3.04 (m, 1 H, H$^{3'}$), 2.69 (s, 3 H, H^{10}), 2.42 (s, 3 H, H^{11}), 2.23 (m, 1 H, H$^{8'}$), 2.11 (m, 1 H, H$^{2a'}$), 1.92 (m, 1 H, H$^{6a'}$), 1.87 (m, 1 H, H$^{5a'}$), 1.71 (m, 1 H, H$^{4'}$), 1.58 (m, 1 H, H$^{1'}$), 1.27 (m, 1 H, H$^{5b'}$), 1.13 (m, 1 H, H$^{6b'}$), 1.01 (d, ^3J = 7.2 Hz, 3 H, H$^{9'/10'}$), 0.99 (d, ^3J = 6.7 Hz, 3 H, H$^{7'}$), 0.96 (m, 1 H, H$^{2b'}$), 0.78 (d, ^3J = 7.2 Hz, 3 H, H$^{9'/10'}$). ^{13}C{^{1}H} NMR (chloroform-d_1, 100.64 MHz): δ 150.58 (C^3), 144.03 (C^8), 142.76 (C^9), 130.54 (C^7), 129.71 (C^5), 128.01 (C^4), 126.54 (C^2), 125.37 (C^6), 45.86 (C$^{2'}$), 45.81 (C$^{4'}$), 40.44 (C$^{3'}$), 36.58 (C^1), 35.34 (C$^{6'}$), 32.96 (C$^{1'}$), 26.65 (C$^{8'}$), 24.61 (C$^{5'}$), 22.54 (C$^{7'}$), 21.62 (C$^{10'}$), 20.33 (C^{10}), 18.30 (C^{11}), 15.88 (C$^{9'}$). IR (CsI): $\bar{\nu}$ 3059, 2953, 2917, 2868, 1493, 1457, 1383, 1368, 980, 802. MS (58 °C): *m*/*z* 282 (100) [M]$^+$, 267 (6)

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$[C_{20}H_{27}]^+$, 239 (6) $[C_{18}H_{23}]^+$, 158 (79) $[C_{12}H_{14}]^+$, 143 (16) $[C_{11}H_{11}]^+$, 128 (11) $[C_{10}H_8]^+$. Anal. Calcd for $C_{21}H_{30}$ (282.47 g/mol): C, 89.29; H, 10.70. Found: C, 88.82; H, 10.35.

1-(3′-Hydroxymenthyl)indene (4a,b) and 3-(3′-Hydroxymenthyl)indene (5). A suspension of cerium trichloride (1.25 g, 5.07 mmol) in THF (15 mL) was stirred for 72 h at room temperature, before (−)-menthone (0.58 g, 3.76 mmol) and indenylmagnesium bromide(THF)$_5$ (0.41 M solution in THF, 21.50 mL, 8.82 mmol) were added at 0 °C. The solution was stirred 1 h at this temperature and 3 h at room temperature then hydrolyzed with water (15 mL), acidified with 1 M HCl, and extracted three times with diethyl ether (20 mL) to give a 1.3:1 diastereomeric mixture of **4ab** (1.25 g, 91%) as a yellow oil. Column chromatography (SiO_2, *n*-hexane) gave **4a** as a yellow oil (0.17 g, 17%) and **4b** as a yellow oil (0.12 g, 12%). **4a**: ^{1}H NMR (chloroform-d_1, 400 MHz): δ 7.71 (d, ^3J = 6.9 Hz, 1 H, H$^{4/7}$), 7.36 (d, ^3J = 7.0 Hz, 1 H, H$^{4/7}$), 7.26 (m, 1 H, H$^{5/6}$), 7.21 (m, 1 H, H$^{5/6}$), 6.85 (m, 1 H, H$^{2/3}$), 6.35 (m, 1 H, H$^{2/3}$), 4.04 (m, 1 H, H^1), 2.58−0.59 (m, 11 H, H$^{1′,2′,3′,4′,5′,6′,8′}$,O*H*), 1.06 (d, ^3J = 7.0 Hz, 3 H, C$^{9′/10′}$), 1.04 (d, ^3J = 6.4 Hz, 3 H, C$^{7′}$), 0.65 (d, ^3J = 6.9 Hz, 3 H, C$^{9′/10′}$). **4b**: ^{1}H NMR (chloroform-d_1, 400 MHz): δ 7.39 (m, 1 H, H$^{4/7}$), 7.35 (m, 1 H, H$^{4/7}$), 7.25 (m, 1 H, H$^{5/6}$), 7.19 (m, 1 H, H$^{5/6}$), 6.87 (m, 1 H, H$^{2/3}$), 6.68 (m, 1 H, H$^{2/3}$), 3.97 (m, 1 H, H^1), 2.45−0.53 (m, 11 H, H$^{1′,2′,3′,4′,5′,6′,8′}$,O*H*), 1.09 (d, ^3J = 6.9 Hz, 3 H, C$^{9′/10′}$), 1.05 (d, ^3J = 6.6 Hz, 3 H, C$^{7′}$), 0.71 (d, ^3J = 7.0 Hz, 3 H, C$^{9′/10′}$). MS (25 °C): *m*/*z* 253 (1) $[C_{19}H_{25}]^+$, 155 (100) $[C_{10}H_{19}O]^+$, 137 (40) $[C_{10}H_{17}]^+$, 116 (29) $[C_9H_8]^+$. MS (FAB, 25 °C): *m*/*z* 270 (2) $[M]^+$, 269 (9) $[C_{19}H_{25}O]^+$, 253 (22) $[C_{19}H_{25}]^+$, 155 (54) $[C_{10}H_{19}O]^+$, 137 (54) $[C_{10}H_{17}]^+$, 115 (100) $[C_9H_7]^+$. $C_{19}H_{26}O$ (270.41 g/mol).

A solution of 1-(3′-hydroxymenthyl)indene (0.20 g, 0.74 mmol) as a mixture of the diastereomers **4a** and **4b** in the ratio 1:1 in *n*-hexane (5 mL) was reacted with *n*-butyllithium (1.6 M solution in *n*-hexane, 1.00 mL, 1.60 mmol) and stirred for 10 h at room temperature. Workup as for **4**, column chromatography (SiO_2, *n*-hexane), and evaporation of the solvent in a vacuum (10^{-2} mbar) gave **5** as a yellow oil (0.16 g, 80%). ^{1}H NMR (chloroform-d_1, 400 MHz): δ 7.54 (s br, 1 H, H$^{4/7}$), 7.48 (d, ^3J = 7.2 Hz, 1 H, H$^{4/7}$), 7.28 (m, 1 H, H$^{5/6}$), 7.20 (m, 1 H, H$^{5/6}$), 6.54 (s br, 1 H, H^2), 3.35 (m, 2 H, H^3), 2.09−0.75 (m, 11 H, H$^{1′,2′,3′,4′,5′,6′,8′}$,O*H*), 0.93−0.87 (m, 9 H, C$^{7′,9′,10′}$). MS (25 °C): *m*/*z* 270 (8) $[M]^+$, 253 (1) $[C_{19}H_{25}]^+$, 155 (100) $[C_{10}H_{19}O]^+$, 137 (42) $[C_{10}H_{17}]^+$, 116 (21) $[C_9H_8]^+$. $C_{19}H_{26}O$ (270.41 g/mol).

(−)-3-Menthylindene (3) from 1-Indanone. A suspension of cerium trichloride (1.44 g, 5.84 mmol) in THF (25 mL) was stirred 24 h at room temperature and reacted with 1-indanone (0.52 g, 3.93 mmol). The reaction mixture was stirred 30 min before (+)-menthylmagnesium chloride (0.71 M solution in THF, 8.72 mL, 6.19 mmol) was added at 0 °C. The reaction mixture was stirred 2 h at this temperature and 2 h at room temperature and was hydrolyzed with water (15 mL), acidified with 1 M HCl, and extracted three times with diethyl ether (20 mL). A yellow oil of 1-menthylindan-1-ol was obtained, which was dissolved in benzene (10 mL) and reacted with 4-toluenesulfonic acid(H_2O) (0.04 g, 0.21 mmol). The reaction mixture was stirred 6 h at room temperature, dried with magnesium sulfate, and purified by column chromatography (SiO_2, 10:1 *n*-hexane/ethyl acetate). Evaporation of the solvent in a vacuum (10^{-2} mbar) gave **3** as a yellow oil (0.09 g, 9%). $[\alpha]_D^{25}$ −61.3° (*c* 5.7, diethyl ether). ^{1}H NMR (chloroform-d_1, 400 MHz): δ 7.48−7.46 (m, 2 H, H^{4,7}), 7.29−7.16 (m, 2 H, H^{5,6}), 6.18 (m, 1 H, H^2), 3.34 (m, 2 H, H^1), 2.63 (m, 1 H, H$^{3′}$), 1.91−0.63 (m, 9 H, H$^{1′,2′,4′,5′,6′,8′}$), 0.90 (d, ^3J = 6.4 Hz, 3 H, H$^{7′/9′/10′}$), 0.88 (d, ^3J = 6.4 Hz, 3 H, H$^{7′/9′/10′}$), 0.70 (d, ^3J = 6.8 Hz, 3 H, H$^{7′/9′/10′}$). MS (30 °C): *m*/*z* 254 (8) $[M]^+$, 239 (10) $[C_{18}H_{23}]^+$, 211 (13) $[C_{16}H_{19}]^+$, 143 (17) $[C_{11}H_{11}]^+$, 128 (27) $[C_{10}H_8]^+$, 117 (100) $[C_9H_9]^+$, 115 (71) $[C_9H_7]^+$. Anal. Calcd for $C_{19}H_{26}$ (254.41 g/mol): C, 89.70; H, 10.30. Found: C, 89.36; H, 9.97.

(−)-3-Menthylindene (3) from 3-Bromoindene/Ni. To a solution of 3-bromoindene (0.70 g, 3.59 mmol) in diethyl ether (10 mL) was added dichloro-1,3-bis(diphenylphosphino)propanenickel(II) (0.16 g, 0.30 mmol) . After cooling to 0 °C (+)-menthylmagnesium chloride (0.71 M solution in THF, 9.60 mL, 6.82 mmol) was added. The brown suspension was stirred 2 h at this temperature and heated to 35 °C for 70 h. The reaction mixture was worked up and purified as before to give **3** as a yellow oil (0.14 g, 15%).

(−)-3-Menthylindene (3) from 3-Bromoindene/Pd. To a solution of 3-bromoindene (0.63 g, 3.23 mmol) in THF (20 mL) was added dichloro-1,1′-bis(diphenylphosphino)ferrocenepalladium(II)(CH_2Cl_2) (0.20 g, 0.24 mmol). After cooling to 0 °C (+)-menthylmagnesium chloride (0.71 M solution in THF, 9.10 mL, 6.46 mmol) was added. The brown suspension was stirred 2 h at this temperature and 5 h at room temperature. The reaction mixture was worked up and purified as above to give **3** (0.03 g, 4%) as a yellow oil.

(−)-3-Menthylindene (3) from 3-Bromoindene/Pd/$ZnCl_2$. To a suspension of anhydrous zinc dichloride (0.40 g, 2.93 mmol) in THF (10 mL) was added (+)-menthylmagnesium chloride (0.71 M solution in THF, 4.35 mL, 3.09 mmol) with cooling. The gray solution was stirred 10 min before a red suspension of dichloro-1,1′-bis(diphenylphosphino)ferrocenepalladium(II)(CH_2Cl_2) (0.16 g, 0.20 mmol) and 3-bromoindene (0.40 g, 2.05 mmol) in THF (10 mL) was added at 0 °C. The brown reaction mixture was stirred for 1 h at this temperature and 5 h at room temperature and was worked up and purified as above to give **3** (0.03 g, 6%) as a yellow oil.

1-Menthylinden-1-ol (8a,b). To a solution of 3-indenyl trifluoromethanesulfonate (0.53 g, 2.01 mmol) in THF (5 mL) was added dichloro-1,3-bis(diphenylphosphino)propanenickel(II) (0.02 g, 0.04 mmol). After cooling to −78 °C (+)-menthylmagnesium chloride (0.71 M solution in THF, 3.40 mL, 2.41 mmol) was added. The orange suspension was stirred for 1 h at this temperature, warmed to 25 °C over 8 h, stirred for 10 h at room temperature, and heated for 10 h to 60 °C. The red solution was hydrolyzed with water (15 mL), acidified with 1 M HCl, and extracted three times with diethyl ether (20 mL). The combined organic fractions were dried with magnesiumsulfate and purified by column chromatography (SiO_2, *n*-hexane) to give **8a** (0.14 g, 26%) and **8b** (0.21 g, 39%) with different absolute configuration at the C^1 atom as yellow oils. Furthermore (−)-3-menthylindene (**3**) (0.02 g, 4%) was obtained. **8a**: ^{1}H NMR (chloroform-d_1, 200 MHz): δ 7.60−7.11 (m, 4 H, H^{4,5,6,7}), 6.57 (d, ^3J = 5.6 Hz, 1 H, H$^{2/3}$), 6.33 (d, ^3J = 5.6 Hz, 1 H, H$^{2/3}$), 3.80−0.60 (m, 11 H, H$^{1′,2′,3′,4′,5′,6′,8′}$,O*H*), 0.86 (d, ^3J = 6.8 Hz, 3 H, C$^{7′/9′/10′}$), 0.73 (d, ^3J = 6.6 Hz, 3 H, C$^{7′/9′/10′}$), 0.50 (d, ^3J = 6.9 Hz, 3 H, C$^{7′/9′/10′}$). ^{13}C{^{1}H} NMR (chloroform-d_1, 50.32 MHz): δ 149.05, 142.66 (C^{8,9}), 141.39, 130.95, 128.24, 125.82, 122.81, 121.38 (C^{2,3,4,5,6,7}), 87.52 (C^1), 45.72, 44.24, 37.17, 35.03, 32.78, 26.75, 24.72 (C$^{1′,2′,3′,4′,5′,6′,8′}$), 22.87, 21.66, 15.69 (C$^{7′,9′,10′}$). IR (NaCl, film): $\bar{\nu}$ 3743, 3461, 3071, 2955, 2876, 1710, 1459, 758 cm^{-1}. MS (25 °C): *m*/*z* 270 (3) $[M]^+$, 227 (1) $[C_{16}H_{19}O]^+$, 153 (7) $[C_{12}H_9]^+$, 132 (100) $[C_9H_8O]^+$, 115 (27) $[C_9H_7]^+$. Anal. Calcd for $C_{19}H_{26}O$ (270.41 g/mol): C, 84.39; H, 9.69. Found: C, 84.07; H, 9.54. **8b**: ^{1}H NMR (chloroform-d_1, 200 MHz): δ 7.35−7.14 (m, 4 H, H^{4,5,6,7}), 6.63 (d, ^3J = 5.9 Hz, 1 H, H$^{2/3}$), 6.36 (d, ^3J = 5.9 Hz, 1 H, H$^{2/3}$), 3.05−0.30 (m, 11 H, H$^{1′,2′,3′,4′,5′,6′,8′}$,O*H*), 0.96 (d, ^3J = 6.9 Hz, 3 H, C$^{7′/9′/10′}$), 0.94 (d, ^3J = 6.5 Hz, 3 H, C$^{7′/9′/10′}$), 0.63 (d, ^3J = 6.8 Hz, 3 H, C$^{7′/9′/10′}$). ^{13}C{^{1}H} NMR (chloroform-d_1, 50.32 MHz): δ 150.31, 141.58 (C^{8,9}), 139.01, 132.61, 127.96, 126.47, 121.79, 121.41 (C^{2,3,4,5,6,7}), 89.03 (C^1), 48.64, 45.37, 36.81, 35.12, 32.65, 27.68, 25.16 (C$^{1′,2′,3′,4′,5′,6′,8′}$), 22.64, 21.92, 16.30 (C$^{7′,9′,10′}$). IR (NaCl, film): $\bar{\nu}$ 3541, 3461, 3069, 2956, 2927, 2876, 2859, 1705, 924, 753 cm^{-1}. MS (25 °C): *m*/*z* 270 (12) $[M]^+$, 153 (7) $[C_{12}H_9]^+$, 145 (9) $[C_{10}H_9O]^+$, 132 (100) $[C_9H_8O]^+$, 115 (9) $[C_9H_7]^+$. Anal. Calcd for $C_{19}H_{26}O$ (270.41 g/mol): C, 84.39; H, 9.69. Found: C, 83.99; H, 9.35.

(−)-3-Menthylindene (3) from 8. A solution of 1-menthylindene-1-ol (0.05 g, 0.18 mmol) in dichloromethane (5 mL) was cooled to −78 °C and reacted with triethylsilane (0.07 mL,

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Published on March 31, 2001 on http://pubs.acs.org | doi: 10.1021/om001074m

0.44 mmol) and boron trifluoride(Et_2O) (0.05 mL, 0.39 mmol). The reaction mixture was stirred 2 h at this temperature and 2 h at room temperature before sodium carbonate and then water (10 mL) was added. The mixture was extracted three times with diethyl ether (10 mL), and the combined organic fractions were dried with magnesium sulfate. After evaporation of the solvent in a vacuum (10^{-2} mbar) 0.04 g of what appeared to be the over-reduction product 1-menthylindane was obtained.

3-Indenyl Trifluoromethanesulfonate (7). A suspension of lithium bis(trimethylsilyl)amide(Et_2O) (4.80 g, 9.88 mmol) in diethyl ether (30 mL) was reacted at 0 °C with a suspension of 1-indanone (2.61 g, 19.75 mmol) in diethyl ether (20 mL). The orange solution was stirred 1 h at room temperature. After cooling to 0 °C trifluoromethanesulfonic anhydride (3.30 mL, 19.62 mmol) was added. The reaction mixture was stirred 20 h at this temperature, carefully hydrolyzed with water (20 mL), and extracted three times with diethyl ether (10 mL). The combined organic fractions were washed twice with a solution of sodium bicarbonate in water (15 mL) and twice with water (15 mL). Drying with magnesium sulfate and evaporation of the solvent in a vacuum (10^{-2} mbar) followed by column chromatography (SiO_2 deactivated with 5 vol-% H_2O, 10:1 *n*-hexane/ethyl acetate) gave **7** as an orange oil (3.28 g, 63%). The product was stored at −28 °C under nitrogen. ^{1}H NMR (chloroform-d_1, 200 MHz): δ 7.52−7.33 (m, 4 H, H^{4,5,6,7}), 6.39 (t, ^3J = 2.4 Hz, 1 H, H^2), 3.50 (d, ^3J = 2.4 Hz, 2 H, H^1). MS (25 °C): *m/z* 264 (34) $[M]^+$, 132 (4) $[C_9H_8O]^+$, 131 (100) $[C_9H_7O]^+$, 103 (8) $[C_8H_7]^+$. Anal. Calcd for $C_{10}H_7F_3O_3S$ (264.22 g/mol): C, 45.46; H, 2.67; S, 12.14. Found: C, 45.71; H, 2.98; S, 12.41.

4,7-Dimethyl-3-indenyl Trifluoromethanesulfonate (9). In analogy with 3-indenyl trifluoromethanesulfonate, lithium bis(trimethylsilyl)amide(Et_2O) (31.75 g, 131.50 mmol) in diethyl ether (200 mL) was reacted at 0 °C with a suspension of 4,7-dimethyl-1-indanone (21.07 g, 131.51 mmol) in diethyl ether (50 mL). The orange solution was stirred 1 h at room temperature before trifluoromethanesulfonic anhydride (23.00 mL, 136.71 mmol) was added at 0 °C. After stirring for 20 h at this temperature, workup, and column chromatography **9** was obtained as an orange oil (25.13 g, 65%). The product was stored at −28 °C under nitrogen. ^{1}H NMR (chloroform-d_1, 400 MHz): δ 7.04 (m, 2 H, H^{5,6}), 6.40 (t, ^3J = 2.4 Hz, 1 H, H^2), 3.32 (d, ^3J = 2.4 Hz, 2 H, H^1), 2.53 (s, 3 H, H$^{10/11}$), 2.32 (s, 3 H, H$^{10/11}$). ^{13}C{^{1}H} NMR (chloroform-d_1, 100.64 MHz): δ 149.10, 140.25, 133.60 (C^{3,8,9}), 130.98, 127.70 (C^{4,7}), 129.73, 127.96, 116.82 (C^{2,5,6}), 120.29 (*C*F$_3$), 33.09 (C^1), 17.76, 17.07 (C^{10,11}). IR (KBr, film): $\bar{\nu}$ 2963, 2960, 2929, 2892, 1426, 1142 cm^{-1}. MS (58 °C): *m/z* 292 (25) $[M]^+$, 159 (100) $[C_{11}H_{11}O]^+$, 133 (1) $[CF_3O_2S]^+$, 131 (25) $[C_9H_7O]^+$, 91 (25) $[C_7H_7]^+$. Anal. Calcd for $C_{12}H_{11}F_3O_3S$ (292.28 g/mol): C, 49.31; H, 3.79; S, 10.97. Found: C, 49.72; H, 3.46; S, 10.83.

4,7-Diisopropyl-3-indenyl Trifluoromethanesulfonate (10). In analogy with 3-indenyl trifluoromethanesulfonate, lithium bis(trimethylsilyl)amide(Et_2O) (6.70 g, 27.75 mmol) in diethyl ether (50 mL) was reacted at 0 °C with a suspension of 4,7-diisopropyl-1-indanone (5.30 g, 24.50 mmol) in diethyl ether (40 mL). The orange solution was stirred 1 h at room temperature before trifluoromethanesulfonic anhydride (5.00 mL, 29.72 mmol) was added at 0 °C. After stirring for 20 h at this temperature, workup, and column chromatography **10** was obtained as a yellow oil (5.17 g, 61%). The product was stored at −28 °C under nitrogen. ^{1}H NMR (chloroform-d_1, 200 MHz): δ 7.37 (m, 2 H, H^{5,6}), 6.53 (t, ^3J = 2.4 Hz, 1 H, H^2), 3.83 (sept, ^3J = 6.8 Hz, 1 H, H$^{10/13}$), 3.56 (d, ^3J = 2.4 Hz, 2 H, H^1), 3.15 (sept, ^3J = 6.9 Hz, 1 H, H$^{10/13}$), 1.53−1.44 (m, 12 H, H^{11,12,14,15}). ^{13}C{^{1}H} NMR (chloroform-d_1, 50.32 MHz): δ 148.85, 148.27, 142.30, 141.76, 130.43 (C^{3,4,7,8,9}), 122.50, 120.08, 116.18 (C^{2,5,6}), 121.82 (*C*F$_3$), 34.30, 28.01 (C^{10,13}), 34.00 (C^1), 24.08, 24.07, 23.86, 23.85 (C^{11,12,14,15}). IR (KBr, film): $\bar{\nu}$ 2963, 2930, 1426, 1216, 1142, 514 cm^{-1}. MS (36 °C): *m/z* 348 (17) $[M]^+$, 333 (2) $[C_{15}H_{16}F_3O_3S]^+$, 215 (100) $[C_{15}H_{19}O]^+$, 200 (4) $[C_{14}H_{16}O]^+$, 133 (1) $[CF_3O_2S]^+$. Anal. Calcd for $C_{16}H_{19}F_3O_3S$ (348.38 g/mol): C, 55.16; H, 5.50; S, 9.20. Found: C, 55.43; H, 5.71; S, 9.37.

(−)-3-Menthyl-4,7-dimethylindene (1a) from 9. A suspension of anhydrous zinc dichloride (6.47 g, 47.47 mmol) in THF (150 mL) was reacted with (+)-menthylmagnesium chloride (0.71 M solution in THF, 84.50 mL, 60.00 mmol) with cooling. The gray solution was stirred 10 min before a red suspension of dichloro-1,1′-bis(diphenylphosphino)ferrocenepalladium(II)(CH_2Cl_2) (1.63 g, 2.00 mmol) and 3-(4,7-dimethylindenyl) trifluoromethanesulfonate (11.70 g, 40.03 mmol) in THF (50 mL) was added at 0 °C. The brown reaction mixture was stirred for 1 h at this temperature, heated to 60 °C for 10 h, and worked up and purified as above for **3** to give **1a** as a yellow oil (7.13 g, 63%).

(−)-4,7-Diisopropyl-3-menthylindene (11). A suspension of anhydrous zinc dichloride (2.10 g, 15.41 mmol) in THF (30 mL) was reacted with (+)-menthylmagnesium chloride (0.71 M solution in THF, 21.55 mL, 15.30 mmol) with cooling. The gray solution was stirred 10 min before a red suspension of dichloro-1,1′-bis(diphenylphosphino)ferrocenepalladium(II)-(CH_2Cl_2) (0.07 g, 0.09 mmol) and 4,7-diisopropylindenyl trifluoromethanesulfonate (2.50 g, 7.18 mmol) in THF (30 mL) was added at 0 °C. The red reaction mixture was stirred 48 h at room temperature and worked up and purified analogously to (−)-3-menthyl-4,7-dimethylindene to give **11** as an orange oil (1.16 g, 48%): $[\alpha]_D^{25}$ −40.0° (*c* 1.2, diethyl ether). ^{1}H NMR (chloroform-d_1, 200 MHz): δ 7.23 (m, 1 H, H$^{5/6}$), 7.17 (m, 1 H, H$^{5/6}$), 6.19 (m, 1 H, H^2), 3.70 (sept, ^3J = 6.9 Hz, 1 H, H$^{10/13}$), 3.31 (m, 2 H, H^1), 2.99 (sept, ^3J = 6.9 Hz, 1 H, H$^{10/13}$), 2.89 (m, 1 H, H$^{3'}$), 2.80−1.03 (m, 9 H, H$^{1',2',4',5',6',8'}$), 1.43−1.34 (m, 12 H, H^{11,12,14,15}), 0.96 (d, ^3J = 6.7 Hz, 3 H, H$^{7'/9'/10'}$), 0.93 (d, ^3J = 6.1 Hz, 3 H, H$^{7'/9'/10'}$), 0.74 (d, ^3J = 6.9 Hz, 3 H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (chloroform-d_1, 50.32 MHz): δ 149.76, 145.98, 145.10, 142.11, 139.11 (C^{3,4,7,8,9}), 126.73, 121.64, 119.57 (C^{2,5,6}), 45.91, 41.44, 34.05, 33.03, 28.35, 26.62 (C$^{1',3',4',8',10,13}$), 45.85, 37.39, 35.38, 24.75 (C$^{1,2',5',6'}$), 25.75, 23.56, 22.74, 22.57, 21.85, 16.18, 14.15 (C$^{7',9',10',11,12,14,15}$). IR (CsI): $\bar{\nu}$ 2957, 2924, 2869, 1457, 1382, 1363 cm^{-1}. MS (69 °C): *m/z* 338 (89) $[M]^+$, 295 (14) $[C_{22}H_{31}]^+$, 214 (100) $[C_{16}H_{22}]^+$, 199 (27) $[C_{15}H_{19}]^+$. Anal. Calcd for $C_{25}H_{38}$ (338.58 g/mol): C, 88.69; H, 11.31. Found: C, 88.83; H, 11.02.

(−)-(η^5-1-Menthyl-4,7-dimethylindenyl)lithium (12). A solution of (−)-3-menthyl-4,7-dimethylindene (17.17 g, 60.79 mmol) in diethyl ether (160 mL) was cooled to −78 °C, and *n*-butyllithium (1.6 M solution in *n*-hexane, 42.00 mL, 67.20 mmol) was added. The yellow solution was stirred for 1 h at this temperature, warmed to 25 °C over 8 h, and stirred for 10 h at room temperature. After evaporation of the solvent in a vacuum (10^{-2} mbar) the residue was suspended in *n*-hexane (50 mL), stirred for 10 h, and filtered with a d4-frit. The residue was washed twice with *n*-hexane (40 mL), and the solvent was removed in a vacuum (10^{-2} mbar) to give **12** as a white solid (15.98 g, 91%): mp >240 °C; $[\alpha]_D^{25}$ −81.3° (*c* 6.3, THF). ^{1}H NMR (pyridine-d_5, 400 MHz): δ 6.82 (m, 1 H, H^3), 6.36 (m, 1 H, H^2), 6.28 (m, 2 H, H^{5,6}), 3.31 (m, 1 H, H$^{3'}$), 2.70 (s, 3 H, H^{11}), 2.46 (m, 1 H, H$^{8'}$), 2.39 (s, 3 H, H^{10}), 1.99 (m, 1 H, H$^{2a'}$), 1.66 (m, 1 H, H$^{4'}$), 1.52 (m, 1 H, H$^{6a'}$), 1.51 (m, 1 H, H$^{5a'}$), 1.26 (m, 1 H, H$^{1'}$), 1.07 (m, 1 H, H$^{2b'}$), 0.96 (m, 1 H, H$^{5b'}$), 0.76 (m, 1 H, H$^{6b'}$), 0.56 (d, ^3J = 7.1 Hz, 3 H, H$^{9'/10'}$), 0.49 (d, ^3J = 6.4 Hz, 3 H, H$^{7'}$), 0.42 (d, ^3J = 6.8 Hz, 3 H, H$^{9'/10'}$). ^{13}C{^{1}H} NMR (pyridine-d_5, 100.64 MHz): δ 130.25 (C^4), 126.11 (C^7), 124.44 (C^8), 123.90 (C^9), 114.82 (C^1), 114.06 (C^2), 114.01 (C^6), 111.30 (C^5), 91.20 (C^3), 51.51 (C$^{2'}$), 48.28 (C$^{4'}$), 41.49 (C$^{3'}$), 36.07 (C$^{6'}$), 33.40 (C$^{1'}$), 26.70 (C$^{8'}$), 25.59 (C$^{5'}$), 23.31 (C^{11}), 22.97 (C$^{7'}$), 22.06 (C$^{9'/10'}$), 20.24 (C^{10}), 15.98 (C$^{9'/10'}$). MS (254 °C): *m/z* 288 (1) $[M]^+$, 282 (100) $[C_{21}H_{30}]^+$, 158 (90) $[C_{12}H_{14}]^+$, 143 (16) $[C_{11}H_{11}]^+$. Anal. Calcd for $C_{21}H_{29}Li$ (288.40 g/mol): C, 87.46; H, 10.13. Found: C, 86.99; H, 9.65. Cryoscopically determined molecular weight in benzene: 271 g/mol.

(+)-(4,7-Diisopropyl-1-menthylindenyl)lithium (13). In analogy with the synthesis of (−)-(η^5-1-menthyl-4,7-dimethylindenyl)lithium a solution of (−)-4,7-diisopropyl-3-men-

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Published on March 31, 2001 on http://pubs.acs.org | doi: 10.1021/om001074m

thylindene (0.97 g, 2.86 mmol) in diethyl ether (20 mL) was cooled to −78 °C, and *n*-butyllithium (1.6 M solution in *n*-hexane, 2.00 mL, 3.20 mmol) was added. After the reaction and workup **13** was isolated as a yellow powder (0.76 g, 77%): mp 153 °C (dec); $[\alpha]_D^{25}$ 34.3° (*c* 0.5, diethyl ether). ^{1}H NMR (pyridine-d_5, 400 MHz): δ 7.54 (d, ^3J = 1.5 Hz, 1 H, H$^{5/6}$), 7.21 (d, ^3J = 3.2 Hz, 1 H, H$^{2/3}$), 6.83 (d, ^3J = 1.5 Hz, 1 H, H$^{5/6}$), 6.72 (d, ^3J = 3.2 Hz, 1 H, H$^{2/3}$), 4.23 (sept, ^3J = 6.8 Hz, 1 H, H$^{10/13}$), 4.08 (m, 1 H, H$^{3'}$), 3.17 (sept, ^3J = 6.8 Hz, 1 H, H$^{10/13}$), 3.52−0.78 (m, 9 H, H$^{1',2',4',5',6',8'}$), 1.62 (d, ^3J = 6.8 Hz, 3 H, H$^{11/12/14/15}$), 1.58 (d, ^3J = 6.8 Hz, 3 H, H$^{11/12/14/15}$), 1.49 (d, ^3J = 6.8 Hz, 3 H, H$^{11/12/14/15}$), 1.48 (d, ^3J = 6.8 Hz, 3 H, H$^{11/12/14/15}$), 0.95 (d, ^3J = 7.0 Hz, 3 H, H$^{7'/9'/10'}$), 0.86 (d, ^3J = 6.4 Hz, 3 H, H$^{7'/9'/10'}$), 0.81 (d, ^3J = 6.8 Hz, 3 H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (pyridine-d_5, 100.64 MHz): δ 138.53, 131.46, 130.73, 124.28 (C^{4,7,8,9}), 115.39, 114.05, 107.66 (C^{2,5,6}), 112.67 (C^1), 91.93 (C^3), 51.65, 36.44, 29.90 (C$^{2',5',6'}$), 48.94, 42.48, 35.29, 33.95, 30.11, 27.09 (C$^{1',3',4',8',10,13}$), 25.94, 25.89, 25.73, 24.73, 23.25, 22.65, 16.74 (C$^{7',9',10',11,12,14,15}$). MS (61 °C): *m*/*z* 344 (2) $[M]^+$, 338 (88) $[C_{25}H_{38}]^+$, 286 (1) $[C_{21}H_{27}Li]^+$, 205 (4) $[C_{15}H_{18}Li]^+$, 83 (100) $[C_6H_{11}]^+$. Anal. Calcd for $C_{25}H_{37}Li$ (344.51 g/mol): C, 87.16; H, 10.82. Found: C, 86.84; H, 10.41.

(1-Menthyl-4,7-dimethylindenyl)sodium(THF) (14). A solution of (−)-3-menthyl-4,7-dimethylindene (0.70 g, 2.48 mmol) in THF (20 mL) was cooled to −78 °C, and sodium amide (0.10 g, 2.56 mmol) was added. The orange suspension was stirred for 3 h at this temperature, warmed to 25 °C over 8 h, and stirred for 10 h at room temperature. The mixture was filtered with a d4-frit, and the residue was extracted with diethyl ether (10 mL) before the solvent of the filtrate was removed in a vacuum (10^{-2} mbar). The orange residue was suspended in *n*-hexane (10 mL), stirred for 10 h, and filtered with a d4-frit. The residue was washed twice with *n*-hexane (5 mL), and the solvent was removed in a vacuum (10^{-2} mbar) to give **14** as a white powder (0.63 g, 67%): mp 137 °C (dec). ^{1}H NMR (pyridine-d_5, 200 MHz): δ 6.73 (m, 2 H, H^{5,6}), 6.71 (m, 2 H, H^{2,3}), 3.64 (m, 4 H, THF), 3.59 (m, 1 H, H$^{3'}$), 2.97 (s, 3 H, H$^{10/11}$), 2.61 (s, 3 H, H$^{10/11}$), 2.55−0.90 (m, 9 H, H$^{1',2',4',5',6',8'}$), 1.60 (m, 4 H, THF), 0.88 (d, ^3J = 7.1 Hz, 3 H, H$^{9'/10'}$), 0.78 (d, ^3J = 6.4 Hz, 3 H, H$^{7'}$), 0.74 (d, ^3J = 6.9 Hz, 3 H, H$^{9'/10'}$). ^{13}C-{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 129.00, 125.00, 124.96, 124.55 (C^{4,7,8,9}), 114.92 (C^1), 114.93, 113.55, 112.22 (C^{2,5,6}), 90.46 (C^3), 67.45 (THF), 51.09, 35.91, 25.40 (C$^{2',5',6'}$), 48.37, 41.17, 33.32, 26.76 (C$^{1',3',4',8'}$), 25.42 (THF), 23.03, 22.81, 21.95, 19.89, 15.93 (C$^{7',9',10,10',11}$). Anal. Calcd for $C_{25}H_{37}NaO$ (376.56 g/mol): C, 79.74; H, 9.90. Found: C, 79.37; H, 9.43.

(−)-(1-Menthyl-4,7-dimethylindenyl)potassium (15). In analogy with the synthesis of (1-menthyl-4,7-dimethylindenyl)-sodium(THF) a solution of (−)-3-menthyl-4,7-dimethylindene (22.00 g, 77.88 mmol) in THF (200 mL) was cooled to −78 °C, and potassium hydride (3.45 g, 86.01 mmol) was added. The orange suspension was stirred 3 h at this temperature, warmed to 25 °C over 8 h, and stirred 10 h at room temperature. After the reaction and workup **15** was obtained as a green powder (24.47 g, 98%): mp 116 °C; $[\alpha]_D^{25}$ −35.2° (*c* 0.6, THF). Evidence for two sets of NMR signals was seen: *1. signal set:* ^{1}H NMR (pyridine-d_5, 400 MHz): δ 7.06 (d, ^3J = 3.2 Hz, 1 H, H^2), 6.68 (m, 2 H, H^{5,6}), 6.59 (d, ^3J = 3.2 Hz, 1 H, H^3), 3.56 (m, 1 H, H$^{3'}$), 2.93 (s, 3 H, H$^{10/11}$), 2.18 (m, 1 H, H$^{8'}$), 2.67 (s, 3 H, H$^{10/11}$), 1.99 (m, 1 H, H$^{2a'}$), 1.95 (m, 1 H, H$^{4'}$), 1.75 (m, 1 H, H$^{6a'}$), 1.66 (m, 1 H, H$^{5a'}$), 1.33 (m, 1 H, H$^{1'}$), 1.07 (m, 1 H, H$^{2b'}$), 1.02 (m, 1 H, H$^{5b'}$), 0.86 (m, 1 H, H$^{6b'}$), 0.96 (d, ^3J = 6.9 Hz, 3 H, H$^{7'/9'/10'}$), 0.93 (d, ^3J = 6.4 Hz, 3 H, H$^{7'/9'/10'}$), 0.78 (d, ^3J = 6.9 Hz, 3 H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (pyridine-d_5, 100.64 MHz): δ 129.29, 124.89, 124.71, 124.26 (C^{4,7,8,9}), 114.93 (C^1), 114.27 (C^2), 114.90, 112.19 (C^{5,6}), 91.84 (C^3), 50.66 (C$^{2'}$), 48.03 (C$^{4'}$), 41.06 (C$^{3'}$), 35.31 (C$^{6'}$), 32.92 (C$^{1'}$), 26.38 (C$^{8'}$), 24.55 (C$^{5'}$), 22.87 (C$^{10/11}$), 21.78, 21.52, 15.14 (C$^{7',9',10'}$), 19.78 (C$^{10/11}$). *2. signal set:* ^{1}H NMR (pyridine-d_5, 400 MHz): δ 6.78 (m, 1 H, H^2), 6.69 (m, 2 H, H^{5,6}), 6.70 (m, 1 H, H^3), 2.57 (m, 1 H, H$^{3'}$), 4.39 (s, 3 H, H$^{10/11}$), 2.65 (s, 3 H, H$^{10/11}$), 2.19 (m, 1 H, H$^{2a'}$), 1.88 (m, 1 H, H$^{6a'}$), 1.78 (m, 1 H, H$^{8'}$), 1.69 (m, 1 H, H$^{5a'}$), 1.42 (m, 1 H, H$^{4'}$), 1.28 (m, 1 H, H$^{1'}$), 1.18 (m, 1 H, H$^{2b'}$), 1.06 (m, 1 H, H$^{6b'}$), 1.00 (d, ^3J = 6.8 Hz, 3 H, H$^{7'/9'/10'}$), 0.96 (m, 1 H, H$^{5b'}$), 0.95 (d, ^3J = 6.4 Hz, 3 H, H$^{7'/9'/10'}$), 0.78 (d, ^3J = 6.9 Hz, 3 H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (pyridine-d_5, 100.64 MHz): δ 129.53, 128.75, 128.69, 123.60 (C^{4,7,8,9}), 117.19 (C^1), 114.89, 112.18 (C^{5,6}), 113.46 (C^2), 93.35 (C^3), 45.05 (C$^{4'}$), 40.70 (C$^{2'}$), 35.80 (C$^{6'}$), 33.62 (C$^{1'}$), 26.99 (C$^{8'}$), 26.80 (C$^{10/11}$), 26.70 (C$^{3'}$), 25.06 (C$^{5'}$), 22.90, 22.69, 15.62 (C$^{7',9',10'}$), 19.86 (C$^{10/11}$). MS (278 °C): *m*/*z* 320 (1) $[M]^+$, 282 (37) $[C_{21}H_{30}]^+$, 181 (6) $[C_{11}H_{10}K]^+$, 158 (54) $[C_{12}H_{14}]^+$, 143 (100) $[C_{11}H_{11}]^+$. Anal. Calcd for $C_{21}H_{29}K$ (320.56 g/mol): C, 78.68; H, 9.12. Found: C, 78.40; H, 9.20. Cryoscopically determined molecular weight in benzene: 891 g/mol.

(η^1-1-(3-Menthyl-4,7-dimethylindenyl))trimethylstannane (16a,b). A solution of (−)-(η^5-1-menthyl-4,7-dimethylindenyl)lithium (0.35 g, 1.21 mmol) in *n*-hexane (10 mL) was cooled to −78 °C and was reacted with trimethyltin chloride (2 M solution in diethyl ether, 0.68 mL, 1.36 mmol). The suspension was stirred for 3 h at this temperature, warmed to 25 °C over 8 h, and stirred for 10 h at room temperature. The solvent was removed in a vacuum (10^{-2} mbar), and the residue was suspended in *n*-hexane (15 mL). The mixture was filtered with a d4-frit, and the residue was extracted twice with *n*-hexane (5 mL) before the solvent of the filtrate was removed in a vacuum (10^{-2} mbar), giving 0.34 g (63%) orange oil of the diastereomers **16a,b** in the ratio 1.2:1. **16a**: ^{1}H NMR (pyridine-d_5, 400 MHz): δ 7.00 (m, 2 H, H^{5,6}), 6.51 (m, 1 H, H^2), 4.07 (m, 1 H, H^1), 3.13 (m, 1 H, H$^{3'}$), 2.69 (s, 3 H, H$^{10/11}$), 2.35 (s, 3 H, H$^{10/11}$), 2.25−0.70 (m, 9 H, H$^{1',2',4',5',6',8'}$), 0.95 (d, ^3J = 6.9 Hz, 3 H, H$^{7'/9'/10'}$), 0.88 (d, ^3J = 6.4 Hz, 3 H, H$^{7'/9'/10'}$), 0.77 (d, ^3J = 6.9 Hz, 3 H, H$^{7'/9'/10'}$), 0.05 (s, 9 H, Sn(CH_3)$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 147.12, 144.24, 140.01, 130.23, 128.34 (C^{3,4,7,8,9}), 129.55, 126.53, 123.84 (C^{2,5,6}), 45.13, 43.47, 37.84, 33.70, 29.78 (C$^{1,1',3',4',8'}$), 40.77, 35.39, 25.71 (C$^{2',5',6'}$), 22.96, 22.77, 22.02, 21.85, 15.23 (C$^{7',9',10,10',11}$), −7.98 (Sn(*C*H$_3$)$_3$). ^{119}Sn{^{1}H} NMR (pyridine-d_5, 149.21 MHz): δ −127.04. **16b**: ^{1}H NMR (pyridine-d_5, 400 MHz): δ 7.01 (m, 2 H, H^{5,6}), 6.59 (m, 1 H, H^2), 4.12 (m, 1 H, H^1), 3.18 (m, 1 H, H$^{3'}$), 2.73 (s, 3 H, H$^{10/11}$), 2.33 (s, 3 H, H$^{10/11}$), 2.25−0.70 (m, 9 H, H$^{1',2',4',5',6',8'}$), 0.93 (d, ^3J = 6.8 Hz, 3 H, H$^{7'/9'/10'}$), 0.86 (d, ^3J = 6.4 Hz, 3 H, H$^{7'/9'/10'}$), 0.78 (d, ^3J = 6.8 Hz, 3 H, H$^{7'/9'/10'}$), 0.06 (s, 9 H, Sn-(CH_3)$_3$). ^{13}C{^{1}H} NMR (pyridine-d_5, 50.32 MHz): δ 143.55, 143.28, 142.89, 130.57, 127.81 (C^{3,4,7,8,9}), 129.89, 127.07, 125.49 (C^{2,5,6}), 48.51, 47.35, 34.72, 32.87, 27.07 (C$^{1,1',3',4',8'}$), 44.06, 34.59, 25.24 (C$^{2',5',6'}$), 23.10, 22.93, 22.43, 21.59, 15.69 (C$^{7',9',10,10',11}$), −7.91 (Sn(*C*H$_3$)$_3$). ^{119}Sn{^{1}H} NMR (pyridine-d_5, 149.21 MHz): δ −124.36. **16a**:**16b** *in the ratio 1.2:1:* $[\alpha]_D^{25}$ −84.4° (*c* 1.8, diethyl ether). Anal. Calcd for $C_{24}H_{38}Sn$ (445.27 g/mol): C, 64.74; H, 8.60. Found: C, 65.13; H, 9.03.

Tri-*n*-butyl(η^1-1-(3-menthyl-4,7-dimethylindenyl))stannane (17a,b). In analogy with the synthesis of (η^1-1-(3-menthyl-4,7-dimethylindenyl))trimethylstannane a solution of (−)-(η^5-1-menthyl-4,7-dimethylindenyl)lithium (0.68 g, 2.36 mmol) in diethyl ether (30 mL) was cooled to −78 °C and reacted with tri-*n*-butyltin chloride (0.65 mL, 2.40 mmol). After the reaction and workup red oily **17a**,**b** was obtained as a 1:1 mixture of diastereomers (0.74 g, 55%). **17a**: ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.01 (m, 2 H, H^{5,6}), 6.70 (d, ^3J = 2.0 Hz, 1 H, H^2), 4.16 (d, ^3J = 2.0 Hz, 1 H, H^1), 3.23 (m, 1 H, H$^{3'}$), 2.77 (s, 3 H, H$^{10/11}$), 2.63−0.70 (m, 9 H, H$^{1',2',4',5',6',8'}$), 2.42 (s, 3 H, H$^{10/11}$), 1.60−0.86 (m, 27 H, Sn((CH_2)$_3$CH_3)$_3$), 1.08 (d, ^3J = 6.9 Hz, 3 H, H$^{7'/9'/10'}$), 0.87 (d, ^3J = 6.5 Hz, 3 H, H$^{7'/9'/10'}$), 0.71 (d, ^3J = 6.8 Hz, 3 H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (pyridine-d_5, 100.64 MHz): δ 147.34, 143.66, 140.55, 128.33, 128.01 (C^{3,4,7,8,9}), 129.44, 127.31, 124.17 (C^{2,5,6}), 47.30, 35.65, 24.74 (C$^{2',5',6'}$), 46.35, 42.57, 41.00, 33.11, 27.03 (C$^{1,1',3',4',8'}$), 29.09, 28.69, 28.49, 27.50, 27.36, 27.17, 20.59, 16.62, 11.76 (Sn((*C*H$_2$)$_3$CH$_3$)$_3$), 22.73, 21.68, 21.07, 19.16, 15.78 (C$^{7',9',10,10',11}$), 13.87, 13.81, 13.80 (Sn-((CH$_2$)$_3$*C*H$_3$)$_3$). ^{119}Sn{^{1}H} NMR (pyridine-d_5, 149.21 MHz): δ 5.08. **17b**: ^{1}H NMR (pyridine-d_5, 200 MHz): δ 7.03 (m, 2 H, H^{5,6}), 6.61 (d, ^3J = 2.0 Hz, 1 H, H^2), 4.21 (s br, 1 H, H^1), 3.12

Table 1. Crystallographic Data for 12

empirical formula	$C_{29}H_{45}LiO_2$
fw	432.61
cryst syst	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a (Å), α (deg)	8.6505(2), 90
b (Å), β (deg)	15.3157(4), 90
c (Å), γ (deg)	20.4145(5), 90
volume (Å^3)	2704.69(12)
Z	4
D(calc) (g/cm^3)	1.062
μ(Mo Kα) (mm^{-1})	0.063
F(000)	952
cryst size (mm^3)	0.54 × 0.18 × 0.16
θ_{min}, θ_{max} (deg)	1.66, 27.50
index ranges	$-11 \le h \le 11$ $-19 \le k \le 19$ $-12 \le l \le 26$
no. of reflns collected	20 377
no. of ind reflns	6183 [$R_{int} = 0.1091$]
GOF on F^2	1.003
R indices [$I > 2\sigma(I)$]	R1 = 0.0813 wR2 =0.1650
R indices (all data)	R1 = 0.1768 wR2 = 0.2050
abs structure param.	7(2)
residual electron density (e/Å^3)	max. 0.403 min. −0.492

(m, 1 H, H$^{3'}$), 2.73 (s, 3 H, H$^{10/11}$), 2.63−0.70 (m, 9 H, H$^{1',2',4',5',6',8'}$), 2.44 (s, 3 H, H$^{10/11}$), 1.60−0.90 (m, 27 H, Sn((CH_2)$_3$CH_3)$_3$), 1.19 (d, ^3J = 7.0 Hz, 3 H, H$^{7'/9'/10'}$), 0.97 (d, ^3J = 6.5 Hz, 3 H, H$^{7'/9'/10'}$), 0.86 (d, ^3J = 6.8 Hz, 3 H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (pyridine-d_5, 100.64 MHz): δ 147.41, 143.01, 140.36, 128.28, 128.08 (C^{3,4,7,8,9}), 129.67, 127.37, 124.17 (C^{2,5,6}), 47.58, 35.47, 24.91 (C$^{2',5',6'}$), 46.30, 41.87, 40.59, 33.19, 27.00 (C$^{1,1',3',4',8'}$), 29.52, 29.15, 28.69, 27.62, 27.55, 27.16, 20.58, 11.80, 8.92 (Sn((*C*H_2)$_3$CH$_3$)$_3$), 22.83, 21.85, 21.08, 19.22, 15.86 (C$^{7',9',10,10',11}$), 13.88, 13.75, 13.71 (Sn((CH$_2$)$_3$*C*H$_3$)$_3$). ^{119}Sn{^{1}H} NMR (pyridine-d_5, 149.21 MHz): δ 2.99. **17a**:**17b** *in the ratio 1:1:* $[\alpha]_D^{25}$ −31.9° (*c* 1.3, diethyl ether). Anal. Calcd for $C_{33}H_{56}Sn$ (571.52 g/mol): C, 69.35; H, 9.88. Found: C, 69.01; H, 9.69.

X-ray Structure Determination of 12. Colorless crystals of **12** suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from a mixture of 5/1 *n*-hexane/THF at −78 °C. The crystal data and details of data collection are given in Table 1. Data were collected on a Siemens SMART CCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) with area-detector by use of ω scans at 173 K for **12**. The structures were solved by direct methods using SHELXS-97[16] and refined on F^2 using all reflections with SHELXL-97.[17] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. The idealized methyl groups were allowed to rotate about their C−C bond. SADABS[18] was used to perform area-detector scaling and absorption corrections. The resulting crystallographic data are summarized in Table 1. The geometrical aspects of the structures were analyzed by using the PLATON program.[19]

Results and Discussion

Synthesis of 1-(or 3-)Menthylindenes. Although sulfonate esters of menthol can be displaced in good yield by (4,7-dimethylindenyl)lithium,[1] the analogous substitution using the less available and more expensive neomenthyl mesylate (**2**) was less satisfactory (Scheme 1). The reactivity of neomenthyl derivative **2** is lower than the menthyl derivative, and prolonged reaction times were required to obtain a mixture of (−)-1- and (−)-3-menthyl-4,7-dimethylindene. Elimination was a major competing reaction pathway,[20] and we desired to find a more efficient preparation of this ligand.

We initiated our search for better methods of attaching a menthyl group to indenes by examining the formation of the parent (−)-3-menthylindene (**3**). Once established, we could then extend the more promising methods to the preparation of 4,7-substituted indenyl derivatives. Several attempted syntheses of **3** are shown in Scheme 2. To provide a more reactive electrophilic site for the indenyl anion, additions to the carbonyl in menthone were investigated; reduction of the resulting tertiary allylic alcohol **5** would then provide menthylindene **3**. Addition of indenylmagnesium bromide with or without added $ZnCl_2$ gave only recovered menthone, presumably through a precedented deprotonation of the ketone followed by protonation of the resulting enolate upon aqueous workup. Only in the case of using $CeCl_3$ as an additive in the Grignard addition was the tertiary allylic alcohol **4a,b** obtained as a mixture of epimers. Isomerization provided allylic alcohol **5**, but all attempts to reduce this compound with Et_3SiH/BF_3 failed to give the desired ligand **3**. The polarity of the bond formation could be reversed by adding known (+)-menthylmagnesium chloride (**6**)[7] either to 1-indanone or 3-bromoindene.[10] Addition of this Grignard reagent to 1-indanone in the presence of $CeCl_3$ gave an intermediate indanol, which was dehydrated by 4-toluenesulfonic acid(H_2O), to the desired ligand **3**, albeit in poor yield. The major side reactions were enolization of the indanone and Grignard reduction of the indanone. The metal-catalyzed cross-coupling reaction of Grignard **6** with 3-bromoindene gave low yields of **3** under all conditions studied, while the analogous reaction with 1-bromoindene gave no product. The reaction of 3-indenyl triflate (**7**) with Grignard **6** led cleanly to the novel diastereomeric 1-menthyl-1-indenols **8**. This reaction evidently proceeded through an initial elimination to give indenone, to which the excess Grignard **6** added. Attempts at reducing **8** with Et_3SiH/BF_3 failed to give indene **3**.

A satisfactory and general approach to (−)-3-menthylindene ligands was developed using a palladium-catalyzed cross-coupling reaction between 3-indenyl triflates and an in situ-generated menthylzinc complex. Known (−)-3-menthylindene **3** could be isolated in 3% yield. Previously unreported 4,7-substituted indenes **1a** and **11** were prepared in 63% and 48% yield, respectively, by coupling **6** with 4,7-dimethyl-3-indenyl triflate (**9**) and 4,7-diisopropyl-3-indenyl triflate (**10**) (Scheme 3). The triflates were prepared from the available substituted 1-indanones in good yields. With multigram quantities of (−)-3-menthyl-4,7-dimethylindene now conveniently available, we studied the formation of its main group metal compounds as a preamble to looking at its transition metal complexes.[21]

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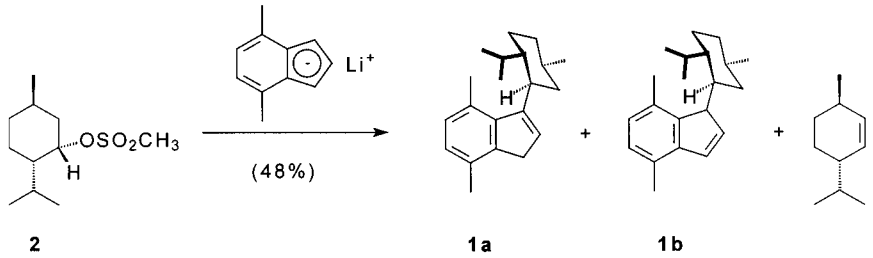
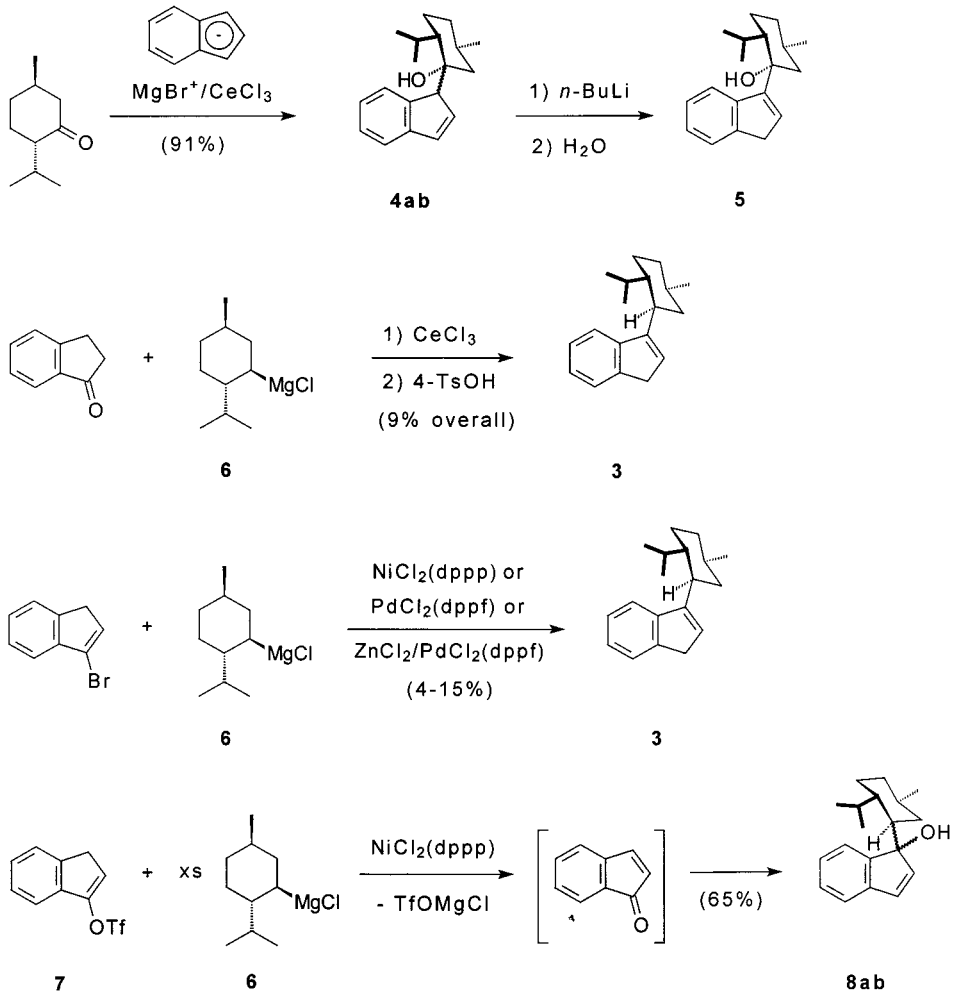
Scheme 1

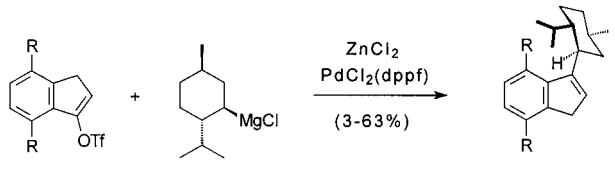


2 1a 1b

Scheme 2



Scheme 3



7 R = H
9 R = Me
10 R = *i*-Pr

6

3 R = H
1a R = Me
11 R = *i*-Pr

Formation of Metal Compounds with 1. Deprotonation of (−)-3-menthyl-4,7-dimethylindene (**1a**) by *n*-butyllithium in diethyl ether gave a 91% isolated yield of the (indenyl)lithium salt **12** as colorless crystals. One set of signals was evident in the ^{1}H and ^{13}C NMR spectra in pyridine, indicating either that only one diastereomeric form of the lithium salt was present or that the lithium was uncoordinated or rapidly exchanging coordination to both π-faces. Cryoscopic measurements in benzene gave a molecular weight of 271 g/mol, reasonably close to the expected monomeric complex molecular weight of 288 g/mol. Crystals of lithium salt **12** suitable for X-ray diffraction were obtained by recrystallization from THF/*n*-hexane. The X-ray acquisition and refinement parameters for **12** are listed in Table 1, and an ORTEP plot of this complex is shown in Figure 3. The lithium atom adopts a trigonal planar coordination with the indenyl ligand and two tetrahydrofuran molecules. The η^5-bonding is slightly slipped toward the two unsubstituted carbons (2.26 and 2.29 Å) away from the C(1) and ring fusion carbons (2.35,

(21) (a) Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Halterman, R. L. *Organometallics*, in press. (b) Schumann, H.; Stenzel, O.; Dechert, S.; Halterman, R. L. *Organometallics*, in press.

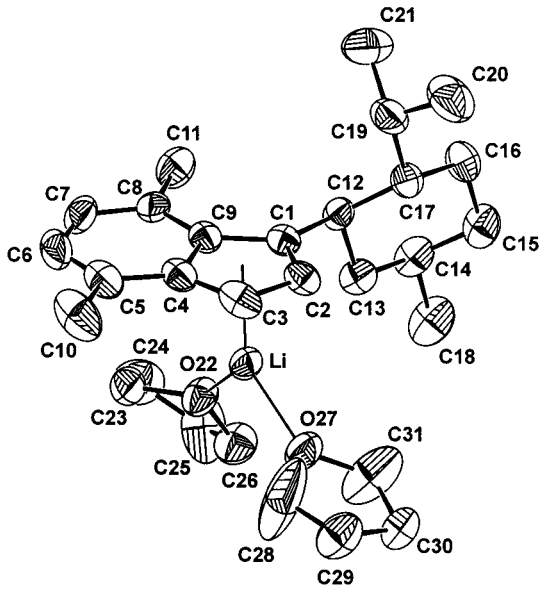


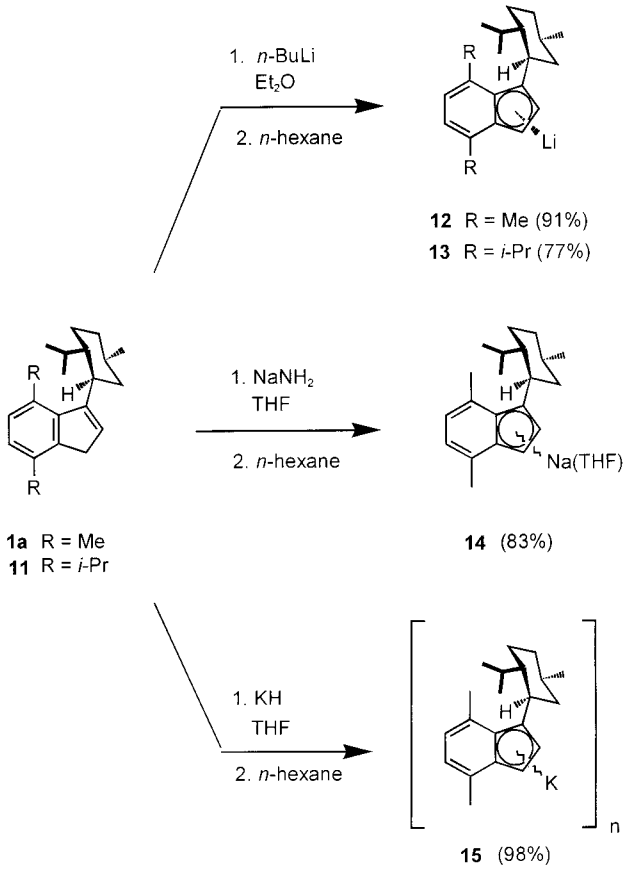
Figure 3. ORTEP drawing for **12**.

2.37, and 2.42 Å). Noteworthy is that the lithium atom is diastereoselectively coordinated to the π-face opposite the isopropyl group of the menthyl moiety in the +anticlinal conformation predicted by calculations (see Figure 2 above). Deprotonation of the analogous (−)-4,7-diisopropyl-3-menthylindene ligand **11** with *n*-butyllithium gave lithium salt **13**. The NMR spectra of this (diisopropylindenyl)lithium derivative **13** were similar to that of the (dimethylindenyl)lithium compound **12** (Scheme 4).

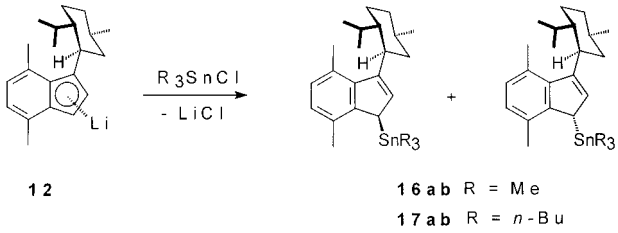
Deprotonation of (−)-3-menthyl-4,7-dimethylindene (**1a**) by $NaNH_2$ or KH in THF led to the formation of the sodium and potassium salts **14** and **15**. The sodium complex **14** gave a single set of signals in the NMR spectra, indicating behavior similar to the lithium complex. The potassium complex **15**, however, gave rise to a complex set of NMR signals. Cryoscopic molecular mass determination results in approximately a trimer of the potassium complex, which along with preliminary unrefinable X-ray data on this substance indicate the formation of an oligomeric structure. While we have strong evidence for selective coordination of the lithium atom to the expected π-face in complex **12**, we cannot specify any π-facial selectivity for the sodium or potassium complexes **14** or **15**.

The (−)-(1-menthyl-4,7-dimethylindenyl)lithium complex **12** could be readily converted by treatment with chlorostananes to the 1-trimethylstannyl or 1-(tri-*n*-butylstannyl) compounds **16** and **17** (Scheme 5). The trimethylstannane derivative **16** was isolated as a 1.2:1 mixture of diastereomers, while the tri-*n*-butylstannane compound **17** was isolated as a 1:1 mixture of diastereomers. The essentially equal formation of the epimers at C(1) of the indenyl group indicates the lack of a controlling influence of the menthyl group at the 3-indenyl position. This result may indicate that the distance between the σ-bonded stannyl group at C(1) is too remote from the stereodirecting influence of the menthyl group. In the case of the lithium complex above, the η^5-bonding would bring the metal into closer contact with the chiral substituent at C(3) and lead to the observed stereoselectivity in that case.

Scheme 4



Scheme 5



Conclusion

We have developed an efficient palladium-catalyzed cross-coupling reaction between 3-indenyl triflates and a menthylzinc complex to give (−)-3-menthylindene, (−)-3-menthyl-4,7-dimethylinden, and (−)-4,7-diisopropyl-3-menthylindene. The benzylic methyl groups in (−)-3-menthyl-4,7-dimethylindene were expected to provide an +anticlinal conformational preference to the menthyl group and selectivity in the formation of its metal compounds. This selectivity was demonstrated for the η^5-bonded lithium salt, but was completely absent for the σ-bonded tin compounds.

Acknowledgment. We thank the Partnerschaftsprogramm TU Berlin-University of Oklahoma (Erwin-Stephan-Scholarship for O.S.), the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysator-

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en"), the Alexander von Humboldt-Stiftung (Research Fel-lowship for R.L.H.), the Oklahoma Center for the Advancement of Science and Technology (AR7-11), and the Phillips Petroleum Company for support of this work. We thank Dr. Ilona Kretzschmar for the calculations concerning the geometry optimization.

Supporting Information Available: Full details of the X-ray structures of complex **12** including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters are available free of charge via the Internet at http://pubs.acs.org.

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