(−)-2-Menthylindenyl and (−)-2-Menthyl-4,7-dimethylindenyl Complexes of Rhodium, Iridium, Cobalt, and Molybdenum

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Optically active complexes of Rh, Ir, Co, and Mo containing the chiral, menthyl-substituted indenyl ligands (−)-2-menthylindene and (−)-2-menthyl-4,7-dimethylindene are described. Metathetic reaction of the chiral lithium salts of these indenyl systems (**1**, **2**) with the appropriate starting materials of Rh and Ir yielded the complexes (−)-(2-menthylindenyl)-Rh(COD) (**3**), (−)-(2-menthyl-4,7-dimethylindenyl)Rh(COD) (**4**), (−)-(2-menthylindenyl)Rh-$(C_2H_4)_2$ (**5**), (−)-(2-menthyl-4,7-dimethylindenyl)Rh$(C_2H_4)_2$ (**6**), (−)-(2-menthylindenyl)Ir(COD) (**7**), (−)-(2-menthylindenyl)Ir$(C_2H_4)_2$ (**8**), (−)-(2-menthyl-4,7-dimethylindenyl)Ir$(C_2H_4)_2$ (**9**), and (−)-(2-menthyl-4,7-dimethylindenyl)Ir$(COE)_2$ (**10**). $Co_2(CO)_8$ and $CoCl_2$(dppe) react with (−)-2-menthylindenyllithium (**1**) yielding (−)-(2-menthylindenyl)Co$(CO)_2$ (**11**) and (+)-(2-menthylindenyl)Co(dppe) (**12**). (−)-Li[(2-menthylindenyl)Mo$(CO)_3$]$(THF)_2$ (**13**), formed by transmetalation of $Mo(CO)_6$, is oxidized by I_2, yielding (−)-(2-menthylindenyl)Mo$(CO)_3$I (**14**), or by allylic chloride, yielding (allyl)(2-menthylindenyl)Mo$(CO)_2$ (**15**). All compounds were formed stereomerically pure and were obtained after chromatography by dried alumina under nitrogen. The structures of **3**, **4**, **6**, **7**, and **14** were determined by single-crystal X-ray diffractometry. Variable temperature ^{1}H NMR spectra of **5**, **6**, **8**, and **9** were recorded to determine the energy barriers for rotation of ethylene along the metal−indenyl and metal−ethylene axes.

Introduction

Chiral bis(indenyl) complexes of zirconium are catalysts for hydrogenations, carboaluminations, or polymerizations.[1] Most of the commonly used compounds of this type are only available in racemic form and thus are not suitable for enantioselective applications.[2] Furthermore, the corresponding complexes of late transition metals have only barely been exploited, even though late transition metal complexes have been shown to be active catalysts for a multitude of organic reactions,[3] even in large-scale industrial processes.[4] To improve the scope of and enantiomeric excess in such catalytic processes, we developed in our previous studies new facile synthetic methods to prepare conformationally well-defined, enantiomerically pure 2-menthyl- and 3-menthylindenes. Deprotonation and metalation resulted in their chiral lithium salts, which could be converted to chiral mono- and bis(menthylindenyl)metal complexes.[5−7] In this paper we describe how 2-menthylindene and 2-menthyl-4,7-dimethylindene ligands with homotopic ligand faces can be used to synthesize chiral monoindenyl transition metal complexes of rhodium, iridium, cobalt, and molybdenum. Although the indenyl ligands are chiral due to their menthyl substituent, they possess homotopic π-faces and can form only one chiral indenylmetal complex upon metalation. Their utilization as hydrogenation and hydroformylation catalysts will be reported in an additional paper,[8] while the activities of the corresponding bis(2-menthylindenyl)zirconium dichlorides as polymerization catalysts of propylene were recently reported by us.[9]

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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; ^{31}P, 80.94 MHz) or ARX 400 (^{1}H, 400 MHz; ^{13}C, 100.64 MHz; ^{103}Rh, 12.60 MHz) spectrometer at 298 K. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residue of the deuterated solvents. Chemical shifts for ^{31}P and ^{103}Rh measurements are given relative to phosphoric acid in D_2O and hexachlororhodate in D_2O. The IR spectra were recorded on a Nicolet Magna System 750 spectrometer. Mass spectra (EI, 70 eV) were obtained by using a Varian MAT 311 A/AMD instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Relative intensities as percentages are given in parentheses. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400. (−)-(2-Menthylindenyl)lithium (**1**),[5] (−)-(2-menthyl-4,7-dimethylindenyl)lithium (**2**),[5] di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I),[10] tetracarbonyldi-μ-chlorodirhodium(I),[11] di-μ-chlorobis(η^4-cycloocta-1,5-diene)diiridium(I),[12] tetrakis(ethylene)di-μ-chlorodiiridium(I),[13] and di-μ-chlorotetrakis(η^2-cyclooctene)diiridium(I)[12] were prepared according to published procedures. Tetrakis(ethylene)di-μ-chlorodirhodium(I), dichloro(1,2-bis(diphenylphosphino)ethane)cobalt(II), octacarbonyldicobalt(0), molybdenum hexacarbonyl(0), and allylic chloride were used as purchased.

(−)-(η^4-Cycloocta-1,5-diene)(η^5-2-menthylindenyl)rhodium(I) (3) General Procedure. To a solution of di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) (1.28 g, 2.60 mmol) in diethyl ether (45 mL) was added (−)-(η^5-2-menthylindenyl)lithium (**1**) (1.43 g, 5.49 mmol) at 0 °C. The suspension was stirred for 3 h, warmed to 25 °C, and stirred for an additional 10 h. The solvent was removed under vacuum (10^{-2} mbar), leaving a solid that was suspended in *n*-hexane (2 mL) and fractionally chromatographed under nitrogen with alumina. Elution with *n*-hexane gave colorless and finally yellow solutions. The solvents of the yellow fractions were removed under vacuum (10^{-2} mbar), yielding a yellow solid. Recrystallization from warm *n*-pentane (5 mL) gave 1.25 g (52%) of yellow crystals of **3**, mp 113 °C; $[\alpha]^{25}_D$ −66.7° (*c* 1.9, diethyl ether). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.13 (m, 1H, H^7), 7.07 (m, 1H, H^4), 7.06 (m, 1H, H^5), 7.04 (m, 1H, H^6), 4.85 (d, ^4J = 1.6 Hz, 1H, H^1), 4.81 (d, ^4J = 1.6 Hz, 1H, H^3), 4.00 (m, 4H, C*H*(COD)), 2.61 (m, 1H, H$^{2'}$), 2.25 (m, 1H, H$^{3'}$), 1.93 (m, 4H, C*H$_2$*(COD)), 1.78 (m, 1H, H$^{6'}$), 1.73 (m, 4H, C*H$_2$*(COD)), 1.68 (m, 1H, H$^{8'}$), 1.65 (m, 1H, H$^{5'}$), 1.47 (m, 1H, H$^{1'}$), 1.29 (m, 1H, H$^{2'}$), 1.11 (m, 1H, H$^{4'}$), 1.07 (d, ^3J = 6.4 Hz, 3H, H$^{7'}$), 1.02 (m, 1H, H$^{5'}$), 0.97 (m, 1H, H$^{6'}$), 0.74 (d, ^3J = 7.0 Hz, 3H, H$^{9'/10'}$), 0.71 (d, ^3J = 6.8 Hz, 3H, H$^{9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 100.64 MHz): δ 122.86 (C^5), 122.66 (d, $^1J_{CRh}$ = 5.9 Hz, C^2), 122.37 (C^6), 119.63 (C^7), 119.18 (C^4), 113.28 (d, $^1J_{CRh}$ = 2.1 Hz, C$^{8/9}$), 111.48 (d, $^1J_{CRh}$ = 2.7 Hz, C$^{8/9}$), 78.00 (d, $^1J_{CRh}$ = 3.8 Hz, C^1), 74.54 (d, $^1J_{CRh}$ = 4.3 Hz, C^3), 67.96 (d, $^1J_{CRh}$ = 13.1 Hz, *C*H(COD)), 67.81 (d, $^1J_{CRh}$ = 14.1 Hz, *C*H(COD)), 50.74 (C$^{4'}$), 46.95 (C$^{2'}$), 40.96 (C$^{3'}$), 35.49 (C$^{6'}$), 33.68 (C$^{1'}$), 31.68, 31.64 (*C*H$_2$(COD)), 27.81 (C$^{8'}$), 25.11 (C$^{5'}$), 23.04 (C$^{7'}$), 21.62, 15.62 (C$^{9'/10'}$). ^{103}Rh NMR (chloroform-d_1:diethyl ether = 1:3, 12.60 MHz): δ −136.90. IR (CsI): $\bar{\nu}$ = 3069 (w), 2992 (m), 2954 (s), 2944 (s), 2928 (s), 2867 (s), 2827 (m), 1459 (m), 1346 (m), 1324 (m), 1258 (m), 1004 (m), 957 (m), 922 (m), 863 (s), 836 (m), 734 (s), 566 (w), 486 (w), 453 (m), 439 (w), 383 (m), 278 (w). MS (100 °C); *m/z* (%): 464 (100) [M]$^+$, 421 (9) [$(C_{16}H_{18})(C_8H_{12})Rh$]$^+$, 356 (8) [$(C_{19}H_{25})Rh$]$^+$, 325 (6) [$(C_9H_6)(C_8H_{12})Rh$]$^+$. Anal. Calcd for $C_{27}H_{37}Rh$ (mol wt 464.50): C, 69.82; H, 8.03. Found: C, 69.75; H, 7.66. Mol wt cryosc in benzene: 465.

(−)-(η^4-Cycloocta-1,5-diene)(η^5-2-menthyl-4,7-dimethylindenyl)rhodium(I) (4). Reaction, in analogy with **3**, of di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) (0.50 g, 1.01 mmol) with (−)-(2-menthyl-4,7-dimethylindenyl)lithium (**2**) (0.61 g, 2.12 mmol) in diethyl ether (20 mL) gave after workup, chromatography, and recrystallization from warm *n*-pentane 0.83 g (83%) of yellow crystals of **4**; mp 125 °C dec; $[\alpha]^{25}_D$ −86.3° (*c* 6.0, *n*-pentane). ^{1}H NMR (benzene-d_6, 400 MHz): δ 6.81 (m, 1H, H$^{5/6}$), 6.79 (m, 1H, H$^{5/6}$), 5.05 (d, ^4J = 1.7 Hz, 1H, H$^{1/3}$), 4.97 (d, ^4J = 1.7 Hz, 1H, H$^{1/3}$), 4.10 (m, 2H, C*H*(COD)), 3.98 (m, 2H, C*H*(COD)), 2.68 (m, 1H, H$^{2'}$), 2.30 (m, 1H, H$^{3'}$), 2.25 (s, 3H, H$^{10/11}$), 2.20 (s, 3H, H$^{10/11}$), 1.92 (m, 4H, C*H$_2$*(COD)), 1.76 (m, 4H, C*H$_2$*(COD)), 1.80−0.97 (m, 8H, H$^{1',2',4',5',6',8'}$), 1.10 (d, ^3J = 6.5 Hz, 3H, H$^{7'/9'/10'}$), 0.78 (d, ^3J = 6.9 Hz, 3H, H$^{7'/9'/10'}$), 0.73 (d, ^3J = 7.0 Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (chloroform-d_1, 100.64 MHz): δ 125.89, 125.16 (C^{4,7}), 121.76 (C$^{5/6}$), 121.32 (d, $^1J_{CRh}$ = 5.4 Hz, C^2), 121.13 (C$^{5/6}$), 111.55 (d, $^1J_{CRh}$ = 2.6 Hz, C$^{8/9}$), 109.83 (d, $^1J_{CRh}$ = 2.5 Hz, C$^{8/9}$), 76.74 (d, $^1J_{CRh}$ = 4.2 Hz, C$^{1/3}$), 73.46 (d, $^1J_{CRh}$ = 4.0 Hz, C$^{1/3}$), 67.74 (d, $^1J_{CRh}$ = 13.8 Hz, *C*H(COD)), 66.84 (d, $^1J_{CRh}$ = 13.7 Hz, *C*H(COD)), 50.45, 40.65, 35.22, 27.29 (C$^{1',3',4',8'}$), 31.50, 31.34 (*C*H$_2$(COD)), 29.69 (2C, *C*H$_2$(COD)), 46.65, 33.49, 24.68 (C$^{2',5',6'}$), 22.82, 21.59, 19.00, 18.96, 15.29 (C$^{7',9',10,10',11}$). ^{103}Rh NMR (chloroform-d_1:diethyl ether = 1:3, 12.60 MHz): δ −144.13. IR (CsI): $\bar{\nu}$ = 2990 (s), 2956 (s), 2930 (s), 2926 (s), 2873 (s), 2870 (s), 2858 (s), 2826 (s), 1698 (s), 1693 (s), 1497 (m), 1462 (m), 1457 (m), 1452 (m), 1376 (m), 1368 (m), 866 (m), 861 (m), 808 (m), 803 (m), 558 (m), 553 (m), 504 (m), 499 (m), 493 (m), 483 (m). MS (103 °C); *m/z* (%): 492 (100) [M]$^+$, 477 (1) [$(C_8H_{12})(C_{20}H_{26})Rh$]$^+$, 449 (8) [$(C_8H_{12})(C_{18}H_{22})Rh$]$^+$, 384 (5) [$(C_{21}H_{29})Rh$]$^+$, 353 (9) [$(C_8H_{12})(C_{11}H_{10})Rh$]$^+$, 245 (2) [$(C_{11}H_{10})Rh$]$^+$. Anal. Calcd for $C_{29}H_{41}Rh$ (mol wt 492.55): C, 70.72; H, 8.39. Found: C, 70.88; H, 8.22.

(−)-Bis(η^2-ethylene)(η^5-2-menthylindenyl)rhodium(I) (5). Reaction, in analogy with **3**, of di-μ-chlorotetrakis(η^2-ethylene)dirhodium(I) (1.80 g, 4.63 mmol) with **1** (2.33 g, 8.95 mmol) in diethyl ether (40 mL) gave after workup and chromatography 3.36 g (91%) of orange oily **5**; $[\alpha]^{25}_D$ −79.0° (*c* 4.2, diethyl ether). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.12 (m, 1H, H^7), 7.04 (m, 1H, H^5), 7.03 (m, 1H, H^4), 7.00 (m, 1H, H^6), 4.70 (d, ^4J = 1.5 Hz, 1H, H^3), 4.63 (d, ^4J = 1.5 Hz, 1H, H^1), 2.49 (m, 1H, H$^{2'}$), 2.24 (m, 1H, H$^{3'}$), 2.08 (s br, 8H, C_2H_4), 1.76 (m, 1H, H$^{6'}$), 1.66 (m, 1H, H$^{5'}$), 1.63 (m, 1H, H$^{8'}$), 1.43 (m, 1H, H$^{1'}$), 1.24 (m, 1H, H$^{2'}$), 1.10 (m, 1H, H$^{4'}$), 1.02 (d, ^3J = 6.6 Hz, 3H, H$^{7'}$), 0.98 (m, 1H, H$^{5'}$), 0.92 (m, 1H, H$^{6'}$), 0.71 (d, ^3J = 6.8 Hz, 3H, H$^{9'/10'}$), 0.68 (d, ^3J = 7.1 Hz, 3H, H$^{9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 100.64 MHz): δ 123.79 (C^5), 123.15 (C^6), 121.35 (d, $^1J_{CRh}$ = 5.9 Hz, C^2), 119.54 (C^7), 118.85 (C^4), 111.92 (d, $^1J_{CRh}$ = 2.7 Hz, C$^{8/9}$), 110.17 (d, $^1J_{CRh}$ = 2.7 Hz, C$^{8/9}$), 80.34 (d, $^1J_{CRh}$ = 4.3 Hz, C^1), 77.07 (d, $^1J_{CRh}$ = 4.3 Hz, C^3), 50.72 (C$^{4'}$), 46.46 (C$^{2'}$), 44.53 (d, $^1J_{CRh}$ = 13.45 Hz, *C*$_2$H$_4$), 40.85 (C$^{3'}$), 35.51 (C$^{6'}$), 33.57 (C$^{1'}$), 27.70 (C$^{8'}$), 25.06 (C$^{5'}$), 22.96 (C$^{7'}$), 21.66, 15.61 (C$^{9'/10'}$). ^{103}Rh NMR (chloroform-d_1:diethyl ether = 1:3, 12.60 MHz): δ −264.83. IR (CsI): $\bar{\nu}$ = 3059 (s), 3019 (m), 2991 (s), 2953 (s), 2869 (s), 2845 (s), 1505 (m), 1496 (m), 1454 (s), 1444 (s), 1431 (s), 1384 (s), 1368 (s), 1346 (s), 1324 (m), 1302 (w), 1273 (m), 1259 (m), 1210 (s), 1198 (s), 1152 (m), 1005 (w), 961 (m), 922 (m), 847 (m), 738 (s), 565 (m), 511 (w), 457 (m), 401 (s). MS (68 °C); *m/z* (%): 412 (4) [M]$^+$, 384 (8) [$(C_2H_4)(C_{19}H_{25})Rh$]$^+$, 356 (3) [$(C_{19}H_{25})Rh$]$^+$, 354 (100) [$(C_{19}H_{23})Rh$]$^+$, 217 (1) [$(C_9H_6)Rh$]$^+$. Anal. Calcd for $C_{23}H_{33}Rh$ (mol wt 412.42): C, 66.98; H, 8.06. Found: C, 67.26; H, 8.47.

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(−)-Bis(η^2-ethylene)(η^5-2-menthyl-4,7-dimethylindenyl)rhodium(I) (6). Reaction, in analogy with **3**, of di-μ-chlorotetrakis(η^2-ethylene)dirhodium(I) (0.41 g, 1.05 mmol) with **2** (0.60 g, 2.08 mmol) in diethyl ether (20 mL) gave after workup, chromatography, and recrystallization from warm *n*-pentane 0.59 g (64%) of yellow crystals of **6**; mp 98 °C dec; $[\alpha]^{25}_{D}$ −64.2° (*c* 1.3, *n*-hexane). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.04 (d, $^3J = 7.1$ Hz, 1H, H$^{5/6}$), 7.00 (d, $^3J = 7.1$ Hz, 1H, H$^{5/6}$), 5.00 (d, $^4J = 1.7$ Hz, 1H, H$^{1/3}$), 4.80 (d, $^4J = 1.7$ Hz, 1H, H$^{1/3}$), 2.57 (m, 1H, H$^{2'}$), 2.29 (m, 1H, H$^{3'}$), 2.24 (s, 3H, H$^{10/11}$), 2.16 (s, 3H, H$^{10/11}$), 2.09 (s br, 8H, C_2H_4), 1.80 (m, 1H, H$^{6'}$), 1.76 (m, 1H, H$^{8'}$), 1.67 (m, 1H, H$^{5'}$), 1.47 (m, 1H, H$^{1'}$), 1.34 (m, 1H, H$^{2'}$), 1.14 (m, 1H, H$^{4'}$), 1.06 (d, $^3J = 6.4$ Hz, 3H, H$^{7'}$), 1.02 (m, 1H, H$^{5'}$), 0.96 (m, 1H, H$^{6'}$), 0.75 (d, $^3J = 7.0$ Hz, 3H, H$^{9'/10'}$), 0.71 (d, $^3J = 7.0$ Hz, 3H, H$^{9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 100.64 MHz): δ 126.43, 125.55 (C^{4,7}), 123.53, 122.96 (C^{5,6}), 120.21 (d, $^1J_{CRh} = 5.9$ Hz, C^2), 111.10 (d, $^1J_{CRh} = 2.7$ Hz, C$^{8/9}$), 109.55 (d, $^1J_{CRh} = 3.2$ Hz, C$^{8/9}$), 78.85 (d, $^1J_{CRh} = 4.3$ Hz, C$^{1/3}$), 75.69 (d, $^1J_{CRh} = 4.3$ Hz, C$^{1/3}$), 50.79 (C$^{4'}$), 46.69 (C$^{2'}$), 43.96 (d, $^1J_{CRh} = 13.5$ Hz, C_2H_4), 40.96 (C$^{3'}$), 35.51 (C$^{6'}$), 33.71 (C$^{1'}$), 27.75 (C$^{8'}$), 25.09 (C$^{5'}$), 22.92 (C$^{7'}$), 21.65 (C$^{9'/10'}$), 19.05, 19.03 (C^{10,11}), 15.59 (C$^{9'/10'}$). IR (CsI): $\bar{\nu} = 3064$ (m), 3059 (m), 3029 (m), 3009 (m), 2992 (s), 2955 (s), 2926 (s), 2916 (s), 2903 (s), 2870 (s), 2843 (s), 1938 (w), 1883 (w), 1835 (m), 1673 (m), 1618 (m), 1592 (w), 1496 (m), 1445 (m), 1430 (m), 1383 (m), 1367 (m), 1345 (m), 1307 (m), 1292 (m), 1274 (m), 1213 (s), 1204 (s), 1183 (m), 1165 (w), 1127 (w), 1085 (w), 1058 (w), 1036 (w), 1004 (w), 971 (m), 959 (w), 922 (m), 843 (s), 810 (s), 701 (m), 688 (w), 673 (m), 397 (m). MS (110 °C); *m/z* (%): 440 (6) [M]$^+$, 412 (8) [$(C_{21}H_{29})(C_2H_4)Rh$]$^+$, 384 (4) [$(C_{21}H_{29})Rh$]$^+$, 382 (100) [$(C_{21}H_{27})Rh$]$^+$. Anal. Calcd for $C_{25}H_{37}Rh$ (mol wt 440.48): C, 68.17; H, 8.47. Found: C, 68.67; H, 8.67. Mol wt cryosc in benzene: 418.

(−)-(η^4-Cycloocta-1,5-diene)(η^5-2-menthylindenyl)iridium(I) (7). Reaction, in analogy with **3**, of di-μ-chlorobis(η^4-cycloocta-1,5-diene)diiridium(I) (0.67 g, 1.00 mmol) with **1** (0.53 g, 2.04 mmol) in diethyl ether (25 mL) gave after workup, chromatography, and recrystallization from warm *n*-pentane 0.99 g (89%) of yellow crystals of **7**; mp 145 °C; $[\alpha]^{25}_{D}$ −86.2° (*c* 1.7, diethyl ether). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.14−6.98 (m, 4H, H^{4,5,6,7}), 5.28 (d, $^4J = 0.6$ Hz, 1H, H$^{1/3}$), 5.17 (d, $^4J = 0.6$ Hz, 1H, H$^{1/3}$), 3.98 (m, 4H, C*H*(COD)), 2.48−0.90 (m, 9H, H$^{1',2',4',5',6',8'}$), 2.20 (m, 1H, H$^{3'}$), 1.89 (m, 4H, C*H*$_2$(COD)), 1.70 (m, 4H, C*H*$_2$(COD)), 1.05 (d, $^3J = 6.5$ Hz, 3H, H$^{7'/9'/10'}$), 0.72 (d, $^3J = 6.9$ Hz, 3H, H$^{7'/9'/10'}$), 0.69 (d, $^3J = 7.0$ Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 100.64 MHz): δ 123.88, 123.36, 120.97, 120.39 (C^{4,5,6,7}), 114.22, 110.17, 107.98 (C^{2,8,9}), 73.74, 70.14 (C^{1,3}), 50.48, 40.47, 33.68, 28.03 (C$^{1',3',4',8'}$), 50.65, 50.62 (*C*H(COD)), 33.26, 33.17 (*C*H$_2$(COD)), 46.83, 35.45, 25.04 (C$^{2',5',6'}$), 22.96, 21.53, 15.57 (C$^{7',9',10'}$). IR (CsI): $\bar{\nu} = 3072$ (w), 2974 (s), 2956 (s), 2945 (s), 2927 (s), 2917 (s), 2866 (s), 2846 (m), 2829 (m), 1693 (w), 1676 (w), 1539 (m), 1455 (m), 1444 (m), 1432 (m), 1413 (w), 1383 (m), 1367 (m), 1351 (m), 1320 (m), 1262 (m), 1235 (m), 1157 (m), 1002 (m), 982 (m), 921 (w), 903 (s), 848 (m), 839 (m), 746 (m), 735 (s), 567 (m), 534 (w), 502 (m), 457 (m), 419 (m), 278 (m), 203 (m). MS (^{193}Ir, 70 °C); *m/z* (%): 554 (100) [M]$^+$, 511 (31) [$(C_8H_{12})(C_{16}H_{18})Ir$]$^+$, 446 (1) [$(C_{19}H_{25})Ir$]$^+$, 415 (5) [$(C_8H_{12})(C_9H_6)Ir$]$^+$. Anal. Calcd for $C_{27}H_{37}Ir$ (mol wt 553.81): C, 58.56; H, 6.73. Found: C, 58.66; H, 6.65. Mol wt cryosc in benzene: 520.

(−)-Bis(η^2-ethylene)(η^5-2-menthylindenyl)iridium(I) (8). Reaction, in analogy with **3**, of di-μ-chlorotetrakis(η^2-ethylene)diiridium(I) (0.78 g, 1.37 mmol) with **1** (0.72 g, 2.77 mmol) in diethyl ether (20 mL) gave after workup, chromatography, and recrystallization from warm *n*-pentane 1.25 g (91%) of yellow crystals of **8**; mp 135 °C; $[\alpha]^{25}_{D}$ −40.0° (*c* 0.6, diethyl ether). ^{1}H NMR (toluene-d_8, 400 MHz): δ 7.02−6.83 (m, 4H, H^{4,5,6,7}), 4.73 (m, 1H, H$^{1/3}$), 4.70 (m, 1H, H$^{1/3}$), 3.11 (m, 1H, H$^{3'}$), 2.75 (vd. br., $J = 35.4$ Hz, 4H, C_2H_4), 2.27−0.68 (m, 9H, H$^{1',2',4',5',6',8'}$), 0.92 (d, $^3J = 6.4$ Hz, 3H, H$^{7'/9'/10'}$), 0.86 (m, 4H, C_2H_4), 0.62 (d, $^3J = 6.8$ Hz, 3H, H$^{7'/9'/10'}$), 0.61 (d, $^3J = 6.8$ Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (toluene-d_8, 100.64 MHz): δ 124.14, 123.53, 120.25, 119.49 (C^{4,5,6,7}), 112.26, 107.91, 105.62 (C^{2,8,9}), 74.98, 71.48 (C^{1,3}), 49.88, 39.93, 33.07, 27.38 (C$^{1',3',4',8'}$), 45.96, 34.98, 24.47 (C$^{2',5',6'}$), 24.07 (C_2H_4), 22.30, 21.03, 15.05 (C$^{7',9',10'}$). IR (CsI): $\bar{\nu} = 3072$ (m), 3038 (s), 2955 (s), 2925 (s), 2870 (s), 2845 (s), 1925 (w), 1893 (w), 1669 (w), 1537 (m), 1454 (s), 1444 (s), 1385 (s), 1368 (s), 1350 (s), 1326 (m), 1301 (w), 1292 (w), 1273 (m), 1263 (m), 1202 (m), 1175 (s), 1163 (s), 1117 (m), 1002 (s), 977 (m), 921 (m), 856 (m), 780 (m), 737 (s), 566 (m), 446 (m), 203 (m). MS (^{193}Ir, 63 °C); *m/z* (%): 502 (17) [M]$^+$, 474 (1) [$(C_2H_4)(C_{19}H_{25})Ir$]$^+$, 446 (3) [$(C_{19}H_{25})Ir$]$^+$, 307 (1) [$(C_9H_6)Ir$]$^+$, 83 (100) [C_6H_{11}]$^+$. Anal. Calcd for $C_{23}H_{33}Ir$ (mol wt 501.73): C, 55.06; H, 6.63. Found: C, 55.40; H, 6.91.

(−)-Bis(η^2-ethylene)(η^5-2-menthyl-4,7-dimethylindenyl)iridium(I) (9). Reaction, in analogy with **3**, of di-μ-chlorotetrakis(η^2-ethylene)diiridium(I) (0.05 g, 0.09 mmol) with **2** (0.05 g, 0.17 mmol) in diethyl ether (10 mL) gave after workup, chromatography, and recrystallization from warm *n*-pentane 0.08 g (89%) of yellow crystals of **9**; mp 131 °C; $[\alpha]^{25}_{D}$ −29.3° (*c* 1.8, diethyl ether). ^{1}H NMR (toluene-d_8, 400 MHz): δ 6.91 (m, 1H, H$^{5/6}$), 6.61 (m, 1H, H$^{5/6}$), 4.99 (d, $^4J = 1.5$ Hz, 1H, H$^{1/3}$), 4.87 (d, $^4J = 1.5$ Hz, 1H, H$^{1/3}$), 2.96 (m, 1H, H$^{3'}$), 2.85 (d. br., $J = 83.1$ Hz, 4H, C_2H_4), 2.43−0.73 (m, 9H, H$^{1',2',4',5',6',8'}$), 2.16 (s, 3H, H$^{10/11}$), 2.10 (s, 3H, H$^{10/11}$), 0.96 (d, $^3J = 6.4$ Hz, 3H, H$^{7'/9'/10'}$), 0.90 (m, 4H, C_2H_4), 0.66 (d, $^3J = 6.8$ Hz, 3H, H$^{7'/9'/10'}$), 0.64 (d, $^3J = 7.0$ Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (toluene-d_8, 50.32 MHz): δ 127.62, 126.71 (C^{4,7}), 123.67, 123.41 (C^{5,6}), 111.88, 107.89, 105.63 (C^{2,8,9}), 74.55, 71.21 (C^{1,3}), 50.46, 40.53, 33.72, 27.92 (C$^{1',3',4',8'}$), 46.77, 35.47, 25.05 (C$^{2',5',6'}$), 24.64, 23.86 (C_2H_4), 22.65, 21.48, 19.54, 18.99, 15.48 (C$^{7',9',10,10',11}$). IR (CsI): $\bar{\nu} = 3043$ (m), 3032 (m), 2971 (s), 2958 (s), 2952 (s), 2930 (s), 2915 (s), 2867 (m), 2855 (m), 1497 (m), 1454 (s), 1437 (m), 1384 (s), 1368 (s), 1343 (w), 1297 (m), 1246 (w), 1172 (s), 1158 (s), 1134 (m), 1123 (m), 1025 (w), 999 (m), 981 (w), 922 (m), 862 (m), 852 (m), 781 (w), 675 (w), 450 (m), 203 (m), 158 (w). MS (^{193}Ir, 91 °C); *m/z* (%): 530 (20) [M]$^+$, 502 (1) [$(C_2H_4)(C_{21}H_{29})Ir$]$^+$, 474 (7) [$(C_{21}H_{29})Ir$]$^+$, 470 (100) [$(C_{21}H_{25})Ir$]$^+$, 307 (1) [$(C_9H_6)Ir$]$^+$. Anal. Calcd for $C_{25}H_{37}Ir$ (mol wt 529.79): C, 56.68; H, 7.04. Found: C, 56.41; H, 6.57.

(−)-Bis(η^2-cyclooctene)(η^5-2-menthyl-4,7-dimethylindenyl)iridium(I) (10). Reaction, in analogy with **3**, of di-μ-chlorotetrakis(η^2-cyclooctene)diiridium(I) (0.87 g, 0.97 mmol) with **2** (0.55 g, 1.91 mmol) in diethyl ether (50 mL) gave after workup, chromatography, and recrystallization from warm *n*-pentane 1.03 g (78%) of yellow crystals of **10**; mp 116 °C; $[\alpha]^{25}_{D}$ −29.9° (*c* 0.8, benzene). ^{1}H NMR (benzene-d_6, 200 MHz): δ 6.85 (m, 2H, H^{5,6}), 5.19 (s br, 1H, H$^{1/3}$), 5.00 (s br, 1H, H$^{1/3}$), 2.63 (m, 2H, C*H*(COE)), 2.20−0.84 (m, 10H, H$^{1',2',3',4',5',6',8'}$), 2.39 (s, 3H, H$^{10/11}$), 2.31 (s, 3H, H$^{10/11}$), 2.30 (m, 2H, C*H*(COE)), 1.78−1.21 (m, 24H, C*H*$_2$(COE)), 1.07 (d, $^3J = 6.2$ Hz, 3H, H$^{7'/9'/10'}$), 0.83 (d, $^3J = 6.8$ Hz, 3H, H$^{7'/9'/10'}$), 0.68 (d, $^3J = 6.9$ Hz, 3H, H$^{7'/9'/10'}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 125.81, 125.80 (C^{4,7}), 124.85, 124.31 (C^{5,6}), 115.81, 114.06, 112.26 (C^{2,8,9}), 77.51, 73.85 (C^{1,3}), 54.29, 53.18, 50.74, 46.35 (*C*H(COE)), 51.23, 40.47, 33.79, 28.13 (C$^{1',3',4',8'}$), 44.80, 35.71, 25.24 (C$^{2',5',6'}$), 34.40, 34.28, 33.21, 33.01, 32.79, 32.16, 30.10, 30.09, 29.93, 27.20, 27.01, 26.90 (*C*H$_2$(COE)), 23.01, 21.67, 20.21, 19.74, 15.80 (C$^{7',9',10,10',11}$). IR (CsI): $\bar{\nu} = 2956$ (s), 2921 (s), 2845 (s), 2680 (w), 1748 (w), 1595 (m), 1497 (m), 1466 (s), 1446 (s), 1385 (m), 1377 (m), 1368 (m), 1357 (m), 1242 (m), 1171 (m), 1149 (m), 1123 (m), 976 (m), 922 (m), 916 (m), 857 (m), 808 (s), 672 (m), 575 (m), 560 (m), 546 (w), 303 (w), 203 (m). MS (^{193}Ir, 160 °C); *m/z* (%): 694 (14) [M]$^+$, 584 (47) [$(C_8H_{14})(C_{21}H_{29})Ir$]$^+$, 555 (1) [$(C_8H_{14})_2(C_{11}H_{10})Ir$]$^+$, 474 (2) [$(C_{21}H_{29})Ir$]$^+$, 445 (100) [$(C_8H_{14})(C_{11}H_{10})Ir$]$^+$. Anal. Calcd for $C_{37}H_{57}Ir$ (mol wt 694.08): C, 64.03; H, 8.28. Found: C, 64.24; H, 8.46. Mol wt cryosc in benzene: 730.

(−)-Dicarbonyl(η^5-2-menthylindenyl)cobalt(I) (11). To a green suspension of octacarbonyldicobalt(0) (0.95 g, 2.78 mmol) and iodine (0.70 g, 2.76 mmol) in THF (20 mL) (gas evolution) was added **1** (0.84 g, 3.23 mmol) at 0 °C. The suspension was stirred for 1 h, warmed to 25 °C, and stirred for an additional 60 h. The solvent was removed under vacuum (10^{-2} mbar), leaving a solid that was suspended in *n*-hexane (2 mL) and fractionally chromatographed under nitrogen with alumina. Elution with *n*-hexane gave colorless, then yellow, and finally orange solutions. The solvents of the orange fractions were removed under vacuum (10^{-2} mbar), yielding 0.66 g (55%) of orange oily **11**; $[\alpha]^{25}_{D}$ −93.6° (*c* 0.2, diethyl ether). ^{1}H NMR (benzene-d_6, 200 MHz): δ 7.19−6.87 (m, 4H, $H^{4,5,6,7}$), 4.92 (m, 1H, $H^{1/3}$), 4.74 (m, 1H, $H^{1/3}$), 2.75−0.56 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 0.92 (d, $^3J = 6.0$ Hz, 3H, $H^{7'/9'/10'}$), 0.76 (d, $^3J = 7.0$ Hz, 3H, $H^{7'/9'/10'}$), 0.68 (d, $^3J = 6.9$ Hz, 3H, $H^{7'/9'/10'}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 50.32 MHz): δ 204.76, 204.65 (*C*O), 126.44, 124.28, 123.57, 122.02 ($C^{4,5,6,7}$), 119.78 (C^2), 107.89, 106.43 ($C^{8,9}$), 76.33, 72.90 ($C^{1,3}$), 50.11, 39.88, 33.60, 27.89 ($C^{1',3',4',8'}$), 46.32, 35.61, 24.88 ($C^{2',5',6'}$), 22.91, 21.97, 16.09 ($C^{7',9',10'}$). IR (CsI): $\bar{\nu} = 3019$ (w), 2955 (s), 2924 (s), 2869 (m), 2847 (m), 2018 (s), 1959 (s), 1928 (w), 1796 (w), 1606 (w), 1573 (w), 1465 (m), 1394 (w), 1386 (m), 1368 (m), 1345 (w), 1019 (w), 998 (w), 922 (w), 868 (w), 851 (w), 760 (m), 750 (m), 743 (m), 727 (m), 722 (m), 694 (w), 608 (w). MS (110 °C); *m/z* (%): 368 (37) $[M]^+$, 340 (12) $[(C_{19}H_{25})(CO)Co]^+$, 312 (29) $[(C_{19}H_{25})Co]^+$, 310 (100) $[(C_{19}H_{23})Co]^+$, 229 (10) $[(C_9H_6)(CO)_2Co]^+$. Anal. Calcd for $C_{21}H_{25}CoO_2$ (mol wt 368.36): C, 68.47; H, 6.84. Found: C, 68.01; H, 6.35.

(+)-(η^5-2-Menthylindenyl)(η^2-1,2-bis(diphenylphosphino)ethane)cobalt(I) (12). Reaction, in analogy with **3**, of dichloro(1,2-bis(diphenylphosphino)ethane)cobalt(II) (0.60 g, 1.14 mmol) with **1** (0.59 g, 2.27 mmol) in diethyl ether (35 mL) gave after workup and chromatography with diethyl ether and double recrystallization from *n*-pentane at −78 °C 0.55 g (68%) of brownish powdery **12**; mp 89 °C dec; $[\alpha]^{25}_{D}$ 65.3° (*c* 0.5, benzene). ^{1}H NMR (benzene-d_6, 200 MHz): δ 7.70−7.08 (m, 20H, C*H*(Phenyl)), 7.10−6.92 (m, 4H, $H^{4,5,6,7}$), 4.48 (m, 1H, $H^{1/3}$), 4.02 (m, 1H, $H^{1/3}$), 2.21−0.55 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 1.39 (m, 4H, PCH_2), 0.97 (d, $^3J = 6.2$ Hz, 3H, $H^{7'/9'/10'}$), 0.68 (d, $^3J = 6.8$ Hz, 3H, $H^{7'/9'/10'}$), 0.63 (d, $^3J = 7.0$ Hz, 3H, $H^{7'/9'/10'}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.64 MHz): δ 141.40−138.92 (m, C^q-(Phenyl)), 133.28−127.80 (m, *C*H(Phenyl)), 122.27, 121.68, 120.30, 119.26 ($C^{4,5,6,7}$), 113.37, 103.68, 102.67 ($C^{2,8,9}$), 70.85, 68.77 ($C^{1,3}$), 51.02, 39.65, 33.55, 27.46 ($C^{1',3',4',8'}$), 44.69, 35.54, 25.20 ($C^{2',5',6'}$), 27.19 (P*C*H$_2$), 24.65 (P*C*H$_2$), 21.68, 15.67, 14.32 ($C^{7',9',10'}$). $^{31}P\{^1H\}$ NMR (benzene-d_6, 80.94 MHz): δ 86.33, 85.60. IR (CsI): $\bar{\nu} = 3053$ (m), 3022 (m), 2954 (m), 2914 (m), 2869 (m), 2844 (m), 1711 (m), 1606 (m), 1483 (m), 1457 (m), 1437 (s), 1420 (w), 1388 (m), 1367 (m), 1188 (s), 1177 (s), 1123 (s), 1106 (w), 998 (m), 764 (m), 754 (m), 742 (s), 732 (s), 694 (s), 536 (m), 533 (s), 511 (m), 303 (m), 203 (m). MS (67 °C); *m/z* (%): 712 (100) $[M+H_2]^+$, 710 (85) $[M]^+$, 457 (1) $[(C_{26}H_{24}P_2)Co]^+$, 399 (55) $[C_{26}H_{25}P_2]^+$, 312 (1) $[(C_{19}H_{25})Co]^+$. Anal. Calcd for $C_{45}H_{49}CoP_2$ (mol wt 710.76): C, 76.04; H, 6.95. Found: C, 75.59; H, 7.17. Mol wt cryosc in benzene: 739.

(−)-Lithium Tricarbonyl(η^5-2-menthylindenyl)molybdate(0)(THF)$_2$ (13). To a solution of **1** (1.03 g, 3.96 mmol) in THF (20 mL) was added $Mo(CO)_6$ (1.04 g, 3.94 mmol) at room temperature. The mixture was stirred for 3 h and heated for 10 h to 65 °C. The solvent was removed under vacuum (10^{-2} mbar), leaving 2.14 g (93%) of yellow solid **13**; mp 71 °C; $[\alpha]^{25}_{D}$ −20.4° (*c* 0.7, diethyl ether). ^{1}H NMR (pyridine-d_5, 400 MHz): δ 7.75−7.71 (m, 2H, $H^{4,7}$), 6.87−6.78 (m, 2H, $H^{5,6}$), 5.96 (d, $^4J = 1.1$ Hz, 1H, $H^{1/3}$), 5.90 (d, $^4J = 1.1$ Hz, 1H, $H^{1/3}$), 3.66 (m, 8H, THF), 2.90−0.65 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 1.63 (m, 8H, THF), 0.89 (d, $^3J = 6.5$ Hz, 3H, $H^{7'}$), 0.77 (d, $^3J = 6.8$ Hz, 3H, $H^{9'/10'}$), 0.62 (d, $^3J = 7.0$ Hz, 3H, $H^{9'/10'}$). $^{13}C\{^1H\}$ NMR (pyridine-d_5, 50.32 MHz): δ 236.40 (*C*O), 125.68 (C^2), 123.80, 123.50, 119.46, 119.06 ($C^{4,5,6,7}$), 111.12, 110.73 ($C^{8,9}$), 78.01, 75.05 ($C^{1,3}$), 67.53 (THF), 51.26, 40.95, 33.46, 27.10 ($C^{1',3',4',8'}$), 44.44, 35.37, 24.82 ($C^{2',5',6'}$), 25.50 (THF), 22.73, 21.49, 15.40 ($C^{7',9',10'}$). MS (^{7}Li, ^{98}Mo, 260 °C); *m/z* (%): 435 (1) $[(C_{19}H_{25})(CO)_3Mo]^+$, 407 (1) $[(C_{19}H_{25})(CO)_2Mo]^+$, 379 (1) $[(C_{19}H_{25})(CO)Mo]^+$, 351 (1) $[(C_{19}H_{25})Mo]^+$, 212 (3) $[(C_9H_6)Mo]^+$, 143 (100) $[C_{11}H_{11}]^+$. Anal. Calcd for $C_{30}H_{41}LiMoO_5$ (mol wt 584.53): C, 61.64; H, 7.07. Found: C, 62.01; H, 6.72.

(−)-Tricarbonyliodo(η^5-2-menthylindenyl)molybdenum(II) (14). A solution of lithium tricarbonyl(η^5-2-menthylindenyl)molybdate(0)(THF)$_2$ (**13**) (2.00 g, 3.42 mmol) in THF (50 mL) was treated with iodine (0.87 g, 3.43 mmol) at 0 °C. Under heat evolution a red solution formed that was stirred for 24 h at room temperature. The analogous workup to **3**, chromatography with *n*-hexane:diethyl ether = 1:1, and recrystallization from *n*-pentane gave 0.75 g (39%) of red crystals of **14**; mp 130 °C dec; $[\alpha]^{25}_{D}$ −96.9° (*c* 0.3, benzene). ^{1}H NMR (benzene-d_6, 400 MHz): δ 7.06−7.02 (m, 2H, $H^{4,7}$), 6.79−6.70 (m, 2H, $H^{5,6}$), 5.48 (d, $^4J = 1.0$ Hz, 1H, $H^{1/3}$), 5.14 (d, $^4J = 1.0$ Hz, 1H, $H^{1/3}$), 1.77 (m, 1H, $H^{3'}$), 1.67 (m, 1H, $H^{2'}$), 1.58 (m, 1H, $H^{6'}$), 1.46 (m, 1H, $H^{5'}$), 1.41 (m, 1H, $H^{1'}$), 1.23 (m, 1H, $H^{8'}$), 0.91 (d, $^3J = 6.5$ Hz, 3H, $H^{7'}$), 0.88 (m, 1H, $H^{2'}$), 0.77 (d, $^3J = 6.9$ Hz, 6H, $H^{9',10'}$), 0.76 (m, 1H, $H^{5'}$), 0.75 (m, 1H, $H^{4'}$), 0.72 (m, 1H, $H^{6'}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.64 MHz): δ 240.23, 222.60, 219.67 (*C*O), 128.95 ($C^{5/6}$), 128.19 ($C^{4/7}$), 127.28 ($C^{5/6}$), 126.17 ($C^{4/7}$), 125.18 (C^2), 116.29, 108.77 ($C^{8,9}$), 84.89, 79.69 ($C^{1,3}$), 51.19 ($C^{4'}$), 44.17 ($C^{2'}$), 40.30 ($C^{3'}$), 34.70 ($C^{6'}$), 33.05 ($C^{1'}$), 27.52 ($C^{8'}$), 24.53 ($C^{5'}$), 22.41 ($C^{7'}$), 21.38, 15.32 ($C^{9',10'}$). IR (CsI): $\bar{\nu} = 3084$ (m), 2956 (s), 2930 (s), 2910 (s), 2897 (s), 2870 (m), 2861 (m), 2848 (m), 2032 (s), 2013 (m), 1962 (s), 1930 (s), 1913 (s), 1901 (m), 1703 (w), 1612 (w), 1536 (w), 1454 (m), 1443 (m), 1433 (m), 1386 (m), 1369 (m), 1349 (w), 1334 (w), 1249 (w), 1200 (w), 1117 (w), 1080 (w), 1041 (w), 998 (w), 953 (w), 926 (w), 869 (m), 852 (m), 841 (w), 752 (s), 673 (w), 603 (w), 575 (m), 548 (w), 523 (m), 493 (m), 483 (m), 469 (m), 447 (m), 424 (m). MS (^{98}Mo, 121 °C); *m/z* (%): 562 (1) $[M]^+$, 534 (34) $[(C_{19}H_{25})(CO)_2IMo]^+$, 506 (5) $[(C_{19}H_{25})(CO)IMo]^+$, 478 (24) $[(C_{19}H_{25})IMo]^+$, 474 (100) $[(C_{19}H_{21})IMo]^+$, 435 (3) $[(C_{19}H_{25})(CO)_3Mo]^+$, 351 (3) $[(C_{19}H_{25})Mo]^+$. Anal. Calcd for $C_{22}H_{25}IMoO_3$ (mol wt 560.28): C, 47.16; H, 4.50. Found: C, 47.38; H, 4.25. Mol wt cryosc in benzene: 534.

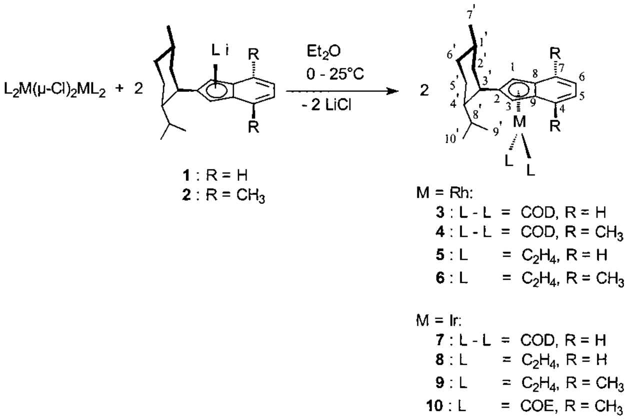
(η^3-Allyl)dicarbonyl(η^5-2-menthylindenyl)molydenum(II) (15). Reaction, in analogy with **14**, of **13** (1.78 g, 3.05 mmol) with allylic chloride (0.30 mL, 3.72 mmol) in THF (50 mL) gave after workup and chromatography 1.08 g (79%) of the *exo*- and *endo*-rotamers of **15** in the ratio 1.3:1 as a yellow oil.

Rotamer 1. ^{1}H NMR (benzene-d_6, 200 MHz): δ 6.55−6.45 (m, 4H, $H^{4,5,6,7}$), 5.62 (m, 1H, $H^{1/3}$), 5.40 (m, 1H, $H^{1/3}$), 4.96 (m, 1H, CHH′C*H*CH′H), 3.01 (m, 2H, C*H*H′CHCH′*H*), 2.60−0.61 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 2.23 (m, 2H, CH*H′*CHC*H′*H), 1.10 (d, $^3J = 6.0$ Hz, 3H, $H^{7'}$), 0.70 (d, $^3J = 6.8$ Hz, 3H, $H^{9'/10'}$), 0.62 (d, $^3J = 6.8$ Hz, 3H, $H^{9'/10'}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.64 MHz): δ 239.14, 237.76 (*C*O), 137.67, 126.36, 124.03, 121.95 ($C^{4,5,6,7}$), 121.02, 111.34, 108.48 ($C^{2,8,9}$), 83.23, 81.22, 78.71 ($C^{1,3}$, CH$_2$*C*HCH$_2$), 51.76, 41.29, 33.54, 27.55 ($C^{1',3',4',8'}$), 49.72, 47.88 (*C*H$_2$CH*C*H$_2$), 45.59, 37.28, 24.91 ($C^{2',5',6'}$), 22.77, 21.61, 15.49 ($C^{7',9',10'}$).

Rotamer 2. ^{1}H NMR (benzene-d_6, 200 MHz): δ 6.53−6.38 (m, 4H, $H^{4,5,6,7}$), 5.61 (m, 1H, $H^{1/3}$), 4.95 (m, 1H, CHH′C*H*CH′H), 4.87 (m, 1H, $H^{1/3}$), 2.93 (m, 2H, C*H*H′CHCH′*H*), 2.65−0.60 (m, 10H, $H^{1',2',3',4',5',6',8'}$), 2.28 (m, 2H, CH*H′*CHC*H′*H), 0.95 (d, $^3J = 6.1$ Hz, 3H, $H^{7'}$), 0.72 (d, $^3J = 6.8$ Hz, 3H, $H^{9'/10'}$), 0.64 (d, $^3J = 7.1$ Hz, 3H, $H^{9'/10'}$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.64 MHz): δ 239.35, 237.87 (*C*O), 137.37, 137.22, 123.25, 123.16 ($C^{4,5,6,7}$), 120.69, 110.10, 109.34 ($C^{2,8,9}$), 82.98, 80.92, 78.32 (C,^{1,3} CH$_2$*C*HCH$_2$), 51.80, 41.28, 33.51, 27.57 ($C^{1',3',4',8'}$), 49.46, 48.00 (*C*H$_2$CH*C*H$_2$), 45.62, 37.31, 35.28 ($C^{2',5',6'}$), 22.72, 21.58, 15.53 ($C^{7',9',10'}$).

Rotamers 1 and 2 in the Ratio 1.3:1. $[\alpha]^{25}_{D}$ −21.4° (*c* 0.1, diethyl ether). IR (CsI): $\bar{\nu} = 3078$ (m), 3060 (m), 2995 (m), 2953 (s), 2869 (s), 2847 (s), 2720 (w), 2417 (w), 1954 (s), 1872 (s), 1639 (m), 1617 (m), 1484 (m), 1456 (m), 1385 (m), 1368 (m), 1348 (m), 1295 (m), 1221 (m), 1200 (m), 1181 (w), 1080 (w), 993 (m), 916 (m), 873 (w), 840 (m), 808 (m), 749 (m), 618 (m), 613 (m), 602 (m), 595 (m), 583 (m), 547 (m), 530 (m), 503 (m), 482 (m), 471 (m), 439 (w), 369 (m). MS (^{98}Mo, 105 °C);

Scheme 1



m/*z* (%): 448 (11) [M]$^+$, 420 (10) [($C_{19}H_{25}$)(C_3H_5)(CO)Mo]$^+$, 392 (4) [($C_{19}H_{25}$)(C_3H_5)Mo]$^+$, 386 (100) [($C_{19}H_{19}$)(C_3H_5)Mo]$^+$, 351 (8) [($C_{19}H_{25}$)Mo]$^+$, 210 (11) [($C_{19}H_{25}$)(C_3H_5)(CO)Mo]$^{2+}$. Anal. Calcd for $C_{24}H_{30}MoO_2$ (mol wt 446.44): C, 64.57; H, 6.77. Found: C, 64.89; H, 6.96.

X-ray Structure Determination. The crystal data and details of data collection for **3**, **4**, **6**, **7**, and **14** are given in the Supporting Information.

4 crystallizes with four and **3** and **7** with two crystallographically independent molecules in the asymmetric unit. Data were collected on a Siemens SMART CCD diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å) with an area detector by use of ω scans at 173 K. The structures were solved by direct methods using SHELXS-97[14] and refined on F^2 using all reflections with SHELXL-97.[15] 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. Absolute structure parameters were determined according to the method of Flack[16] with SHELXL-97.[15] SADABS[17] was used to perform area-detector scaling and absorption corrections. The maximum and minimum transmission factors and the resulting crystallographic data are given in the Supporting Information. The geometrical aspects of the structures were analyzed by using the PLATON program.[18]

Results and Discussion

Rhodium and Iridium Complexes. (−)-2-Menthylindenyllithium (**1**) and (−)-(2-menthyl-4,7-dimethylindenyllithium (**2**) were mixed with 1 equiv of the appropriate binuclear transition metal complex [$L_2M(\mu\text{-}Cl)_2ML_2$] (M = Rh, Ir; L = COE or C_2H_4, L_2 = COD) in diethyl ether at 0 °C followed by stirring at 25 °C for 10−60 h. The crude products were isolated by removing the solvent under vacuum and purified chromatographically in an inert atmosphere with dried alumina and *n*-hexane as eluent, followed by crystallization from *n*-pentane to give **3**−**10** in 52−91% isolated yield (Scheme 1).

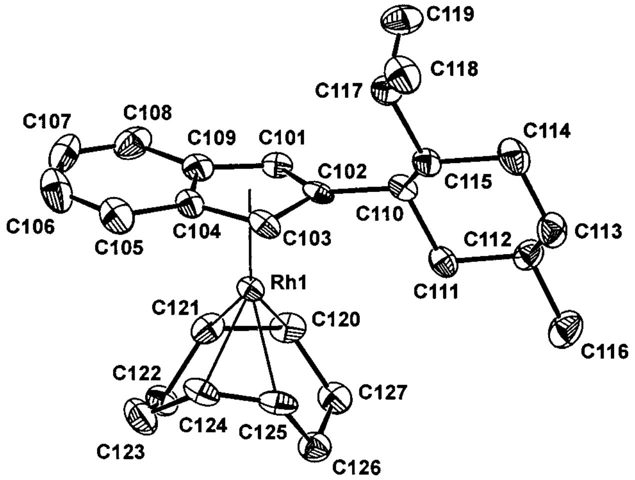


Figure 1. ORTEP plot[20] of the molecular structure and numbering scheme of **3** with 50% probability thermal ellipsoids. Only one of the two crystallographically independent molecules is shown. For clarity, all hydrogens are removed. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:[21] Rh(1)−Cg(1), 1.937(3); Rh(1)−COD(1), 2.130(6); C(101)−C(102), 1.403(8); C(102)−C(103), 1.438(7); C(103)−C(104), 1.452(9); C(104)−C(109), 1.424(8); C(101)−C(109), 1.438(8); C(120)−C(121), 1.421(9); C(124)−C(125), 1.384(10); Cg(1)−Rh(1)−C(120), 133.2(2); Cg(1)−Rh(1)−C(121), 132.5(2); Cg(1)−Rh(1)−C(124), 128.42(18); Cg(1)−Rh(1)−C(125), 138.27(18); C(120)−Rh(1)−C(121), 38.9(2); C(124)−Rh(1)−C(125), 38.0(3); C(120)−Rh(1)−C(125), 80.8(2); C(121)−Rh(1)−C(124), 81.4(2).

The contact of even traces of oxygen during this purification process led to immediate decomposition of the complexes under dimerization of the indenyl ligand, yielding 1,1′-bis(2-menthylindene) and 1,1′-bis(2-menthyl-4,7-dimethylindene), respectively.[19] In contrast to that behavior in solution, the pure crystalline complexes **3**−**10** are air- and moisture-stable. They are soluble in polar solvents such as THF, pyridine, or diethyl ether as well as in aromatic solvents such as toluene, and unpolar solvents such as *n*-hexane. As required by the symmetry of the ligand, only one complex was obtained in each case, shown by NMR spectroscopy.

Crystals of **3**, **4**, **6**, and **7** suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from *n*-pentane. Their solid-state structures were determined by X-ray diffraction methods. The menthylindenyl complexes **3**, **4**, and **7** crystallize in the same monoclinic space group $P2_1$ with two to four crystallographically independent molecules in the asymmetric unit, while the asymmetric unit of the orthorhombic **6** ($P2_12_12_1$) consists of only one crystallographically independent molecule. The iridium complex **7** is isostructural to the rhodium complex **3**. The solid-state structures of these molecules are shown in Figures 1−4.

All four complexes are monomeric, free of solvent, stereomerically pure, and clearly show the characteristic three stereocenters of the menthyl moiety. In all cases the transition metals of the formal oxidation state +1 are coordinated trigonal planar by the centroids of the cyclopentadienyl systems and the diene systems of the

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[14] Sheldrick, G. M. *SHELXS-97 Program for the Solution of Crystal Structures*; Universität Göttingen, Göttingen, Germany, 1997.

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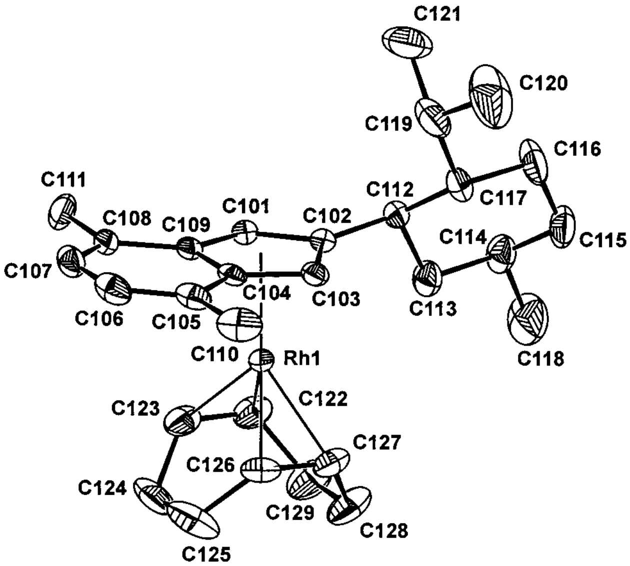

Figure 2. ORTEP plot[20] of the molecular structure and numbering scheme of **4** with 30% probability thermal ellipsoids. Only one of the four crystallographically independent molecules is shown. For clarity, all hydrogens are removed. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:[22] Rh(1)−Cg(1), 1.9442(19); Rh(1)−COD(1), 2.124(5); C(101)−C(102), 1.437(6); C(102)−C(103), 1.411(6); C(103)−C(104), 1.459(6); C(104)−C(109), 1.424(6); C(101)−C(109), 1.435(6); C(122)−C(123), 1.373(9); C(126)−C(127), 1.376(8); Cg(1)−Rh(1)−C(122), 135.31(14); Cg(1)−Rh(1)−C(123), 131.62(15); Cg(1)−Rh(1)−C(126), 130.95(13); Cg(1)−Rh(1)−C(127), 135.12(13); C(122)−Rh(1)−C(123), 37.8(2); C(126)−Rh(1)−C(127), 37.7(2); C(122)−Rh(1)−C(127), 81.0(2); C(123)−Rh(1)−C(126), 81.5(2).

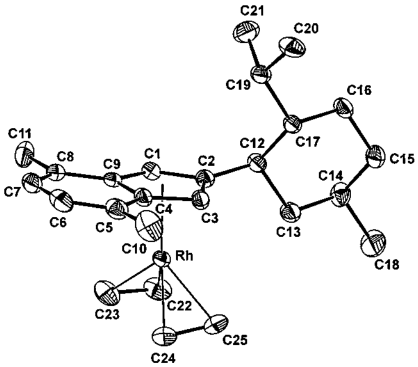

Figure 3. ORTEP plot[20] of the molecular structure and numbering scheme of **6** with 50% probability thermal ellipsoids. For clarity, all hydrogens are removed. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:[23] Rh−Cg, 1.9324(11); Rh−C(22), 2.127(3); Rh−C(23), 2.147(3); Rh−C(24), 2.145(3); Rh−C(25), 2.148(3); C(1)−C(2), 1.421(3); C(2)−C(3), 1.430(3); C(3)−C(4), 1.465(4); C(4)−C(9), 1.423(3); C(1)−C(9), 1.462(4); C(22)−C(23), 1.366(4); C(24)−C(25), 1.387(5); Cg−Rh−C(22), 131.56(11); Cg−Rh−C(23), 127.98(11); Cg−Rh−C(24), 131.67(11); Cg−Rh−C(25), 127.62(9); C(22)−Rh−C(23), 37.29(12); C(24)−Rh−C(25), 37.69(14); C(22)−Rh−C(25), 88.91(11); C(23)−Rh−C(24), 88.69(12).

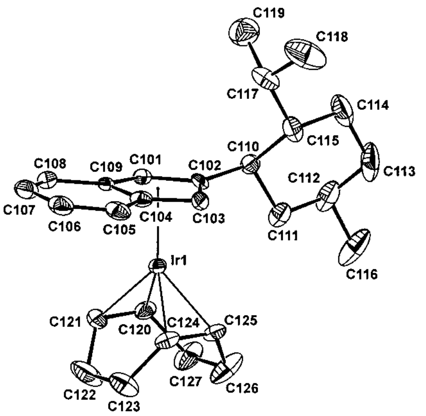

Figure 4. ORTEP plot[20] of the molecular structure and numbering scheme of **7** with 50% probability thermal ellipsoids. Only one of the two crystallographically independent molecules is shown. For clarity, all hydrogens are removed. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:[21] Ir(1)−Cg(1), 1.922(2); Ir(1)−COD(1), 2.116(6); C(101)−C(102), 1.428(7); C(102)−C(103), 1.443(8); C(103)−C(104), 1.478(8); C(104)−C(109), 1.422(8); C(101)−C(109), 1.466(8); C(120)−C(121), 1.436(10); C(124)−C(125), 1.417(9); Cg(1)−Ir(1)−C(120), 135.48(17); Cg(1)−Ir(1)−C(121), 133.65(19); Cg(1)−Ir(1)−C(124), 130.21(17); Cg(1)−Ir(1)−C(125), 132.78(18); C(120)−Ir(1)−C(121), 39.5(3); C(124)−Ir(1)−C(125), 39.3(2); C(120)−Ir(1)−C(125), 81.0(2); C(121)−Ir(1)−C(124), 80.6(2).

neutral ligands. It is particularly noteworthy that the terpene moiety adopts similar conformations, with the menthyl moiety being more or less perpendicular to the indenyl plane and that the bulky isopropyl group always is pointing away from the metal. The corresponding dihedral angles[24] are −18° and −3° for **3**, −30°, 16°, 37°, and 16° for **4**, −7° for **6**, and −16° and −1° for **7**. The average bonding distances of rhodium to the five-membered indenyl rings are 2.28 Å (**3**) and 2.29 Å (**4**, **6**), the average bond length of rhodium to the diene systems of the COD units is 2.13 Å for **3** and **4**, while the average bond length of rhodium to the ethylene ligands is 2.14 Å for **6**. These distances are in close accordance to the bond lengths given for (COD)(η^5-indenyl)rhodium (2.28 and 2.13 Å),[25] (COD)(η^5-heptamethylindenyl)rhodium (2.28 and 2.12 Å),[25] $(C_2H_4)_2$(η^5-indenyl)rhodium (2.14 Å),[26] and $(C_2H_4)_2$(η^5-1,2,3-trimethylindenyl)rhodium (2.13 Å).[27] The bent angles defined by the center of the COD−olefin bonds and the rhodium atoms of 87.2° (**3**) and 86.9° (**4**) as well as of the ethylene bonds and the rhodium atoms of 95.2° (**6**) are only insignificantly smaller than the literature value of 87.6° [25] and 96.0° [26]/96.3°,[27] respectively. The five-membered ring of the indenyl system resembles a distorted η^5-coordination to Rh. The bond lengths of the carbon atoms C(1), C(2), and C(3) to the metal are

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(21) Cg(X) defines the centroid of the ring atoms C(X01), C(X02), C(X03), C(X04), and C(X09). COD(X) defines the average bond length of the metal to the atoms C(X20), C(X21), C(X24), and C(X25).

(22) Cg(X) defines the centroid of the ring atoms C(X01), C(X02), C(X03), C(X04), C(X09). COD(X) defines the average bond length of the metal to the atoms C(X22), C(X23), C(X26), C(X27).

(23) Cg defines the centroid of the ring atoms C(1), C(2), C(3), C(4), C(9).

(24) Dihedral angle = angle between H(X01) and H(X10) or H(X01) and H(X12), respectively. Negative values correspond to H(X10) or H(X12) pointing away from the metal.

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0.09−0.16 Å shorter than the bond lengths to the bridging atoms C(4) and C(9). In general, slip distortions Δ^{28} and ring slippages RS[28] toward the C(2) atoms are found. The values for Δ and RS are 0.116 Å and 0.094 Å in **3**, 0.122 Å and 0.106 Å in **4**, and 0.168 Å and 0.182 Å in **6**. The tendency toward a slight η^3-coordination accounts for the uneven cyclopentadienyl ring and therefore to hinge angles HA[29] and fold angles FA.[29] The values for HA and FA are 8.8° and 8.4° in **3**, 8.7° and 9.0° in **4**, and 8.5° and 9.5° in **6**. The values are in the expected range for distorted η^5-coordinations such as they were found in (COD)(η^5-indenyl)rhodium[30] (Δ = 0.152 Å, HA = 8.9°, FA = 7.4°), $(C_2H_4)_2(\eta^5\text{-indenyl})$rhodium(I)[26] (Δ = 0.161 Å, HA = 8.1°, FA = 7.4°), and bis(trimethylphosphine)(η^5-indenyl)rhodium(I)[31] (Δ = 0.201 Å, HA = 8.4°, FA = 7.9°), and do not show the characteristics of η^3-coordinations such as they are found in tris(dimethylphenylphosphine)(η^3-indenyl)rhodium(I)[32] (Δ = 0.79 Å, HA = 25°, FA = 28°). Such distortions can further be detected by the differences in the C−C bond lengths in the five-membered indenyl rings. The maximum variations of 0.14 (**3**), 0.05 (**4**), and 0.18 Å (**6**) are higher than can be accounted for through the influence of the condensed six-membered ring alone. In general, the trend toward η^3-coordination is not strongly shown, although the distortions are much higher than for the asymmetrical substituted (1-menthylindenyl)metal complexes, where the substitution patterns favor not only a distortion toward C(X02) but toward C(X03) as well.[7] The ^{13}C NMR chemical shift values of the bridging carbon atoms C(X04) and C(X09) have been found to be indicative for the extent of occurring ring slippages in rhodium complexes.[30] Following this theory, the slippage from η^5- to η^3-coordination should lead to a stronger deshielding of the less coordinated atoms and therefore to a low field shift. This theory can be confirmed, as the chemical shifts of the compounds **3**, **4**, and **6** vary only between 109.6 and 113.3 ppm and all complexes show a distorted η^5-coordination as proved by X-ray diffraction. A similar distorted η^5-coordinated molecular structure can be presumed for the oily **5**, as it shows chemical shifts of the bridging atoms of 110.2 and 111.9 ppm.

The indenyliridium complex **7** shows bond lengths (average distances iridium to the five-membered indenyl ring, 2.28 Å; average bond lengths iridium to the diene systems of the COD units, 2.12 Å) that are in close accordance to the bond lengths given for the rhodium complexes as a consequence of the lanthanide contraction, causing similar ionic radii for Rh and Ir (0.67 Å for Rh^{3+} and 0.68 Å for Ir^{3+}),[33] which correspond to previously published data.[31,34,35] While the bent angle (87.3°) is only insignificantly larger than the values given earlier, the C−C bond lengths of the diene systems of COD are 0.02 Å longer than in **3** and 0.07 Å longer than in free COD.[36] This is a sign of a stronger back-bonding of the metal into antibonding orbitals of COD, which results in a stronger ligand−metal bond. **7** shows a stronger tendency toward a $\eta^2 + \eta^3$-coordination (Δ = 0.155 Å, RS = 0.150 Å, HA = 9.2°, FA = 9.3°) than the analogous rhodium complex **3**.

As the HOMO of the indenyl unit in rhodium and iridium complexes can best be stabilized at a rotation angle RA of 0° [27,37] the COD or C_2H_4 ligands are aligned parallel to the longitudinal axis of indene. In our cases values for RA of 6.9° (**3**), 1.4° (**4**), 3.3° (**6**), and 1.6° (**7**) are observed.

To study the rotational behavior in solution, variable-temperature ^{1}H NMR measurements of **5**, **6**, **8**, and **9** were performed. In all cases dynamical behavior was observed in toluene-d_8. At 292 K the ethylene protons of **5** show a broad signal at 2.08 ppm with $\nu_{1/2}$ = 30 Hz, while the signals of the indenyl ligand are unbroadened. By cooling the sample to 205 K, the rotation of the ethylene ligands around the rhodium−indenyl and rhodium−ethylene axes can be slowed, and two separated signals for the ethylene protons are detected at 3.09 und 1.06 ppm. Due to the negative anisotropy of ethylene ligands, the signal at lower field correlates to the four protons that point toward each other. Because of the asymmetric environment, all eight ethylene protons are still chemically inequivalent, but the negative anisotropy dominates their chemical shifts. That stabilization of the indenyl ligand at lower temperatures due to better border orbital overlapping occurs can be taken from the high field shift of protons H(X01) and H(X03) (292 K, 4.60 and 4.54 ppm; 200 K, 4.31 and 4.16 ppm). The high field shift correlates to a better shielding and therefore a stronger rhodium−indenyl bond.

At 292 K the ethylene protons of **6** show a broad signal at 2.05 ppm, while again the signals of the indenyl ligand show an unbroadened line width. At 205 K two separated signals for the ethylene protons are detected at 3.15 and 1.03 ppm. Even at this temperature the signals of the eight chemically inequivalent protons are still broadened and the signal at low field forms a pseudo doublet of triplets. The chemical shift of the protons H(X01) and H(X03) changes from 4.71 and 4.92 ppm (292 K) to 4.59 and 4.85 ppm (210 K).

Using the Eyring equation[38] and the observed coalescence temperatures of 247 K (**5**) and 259 K (**6**), the energy barriers of the rotation processes can be determined to be $\Delta G^\ddagger$ = 44.7 kJ/mol (**5**) and 46.9 kJ/mol (**6**). The value of **6** is higher as the indenyl ligand is higher alkylated. Both are in the expected range for this sub-

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[28] Slip distortion Δ = difference in the average metal to carbon distances: 0.5[M−C(X04) + M−C(X09)] − 0.5[M−C(X01) + M−C(X03)]; ring slippage RS = distance of the normal of the least-squares ring plane defined by C(X01), C(X02), C(X03), C(X08), and C(X09) to the metal atom and the centroid of the five-membered ring. Kakkar, A. K.; Taylor, N. J.; Marder, T., B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198*, 219.

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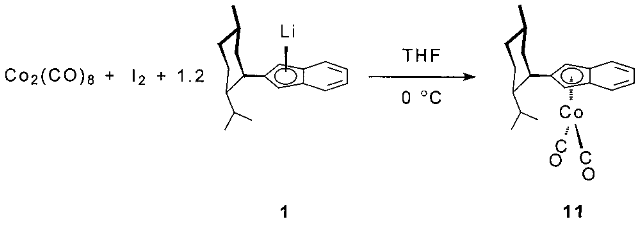
Scheme 2

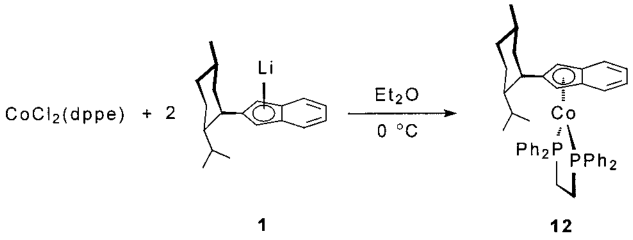


stitution pattern, as in $(C_2H_4)_2(\eta^5$-indenyl)rhodium(I) and $(C_2H_4)_2(\eta^5$-1,2,3-trimethylindenyl)rhodium(I) the barriers were calculated to $\Delta G^{\ddagger} = 43.1$ and 44.8 kJ/mol.[27] These values are significantly smaller than for $(C_2H_4)_2$-$(\eta^5$-cyclopentadienyl)rhodium(I) ($\Delta G^{\ddagger} = 65.7$ kJ/mol),[39] which can be attributed to the weaker bonded indenyl system due to the transition to a η^3-coordination.

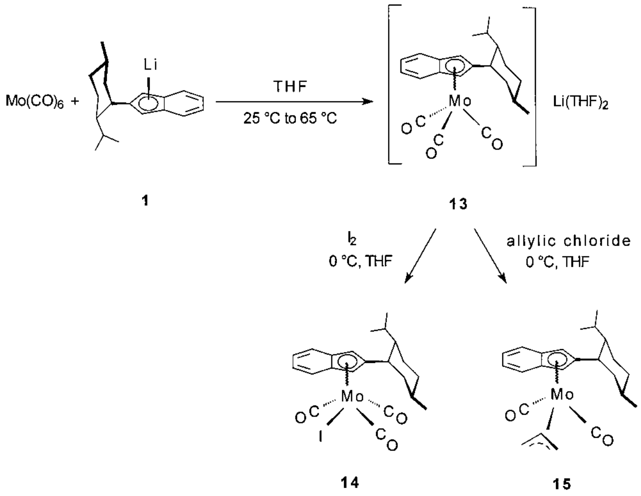
In contrast to the rhodium complexes **5** and **6**, the corresponding iridium complexes have to be heated to show coalescence of the ethylene signals in toluene-d_8. Coalescence occurs at 320 K (**8**) and 340 K (**9**), and singlets at 1.70 ppm (360 K) are detected. The energy barriers of the rotation processes are therefore $\Delta G^{\ddagger} =$ 58.4 kJ/mol (**8**) and 62.4 kJ/mol (**9**). The value for the higher alkylated compound **9** is again higher. Both are significantly higher than those for **5** and **6**, but they are still lower than for $(C_2H_4)_2(\eta^5$-cyclopentadienyl)rhodium(I). For $(C_2H_4)_2(\eta^5$-indenyl)iridium(I) and $(C_2H_4)_2(\eta^5$-cyclopentadienyl)iridium(I), barriers of $\Delta G^{\ddagger} = 59.0$ and 80.5 kJ/mol were calculated.[40] As Rh and Ir show similar ionic radii, the energy difference must be caused by orbital effects and a particularly stronger back-bonding of Ir into antibonding orbitals of ethylene.[41] This influence of the 5d orbitals of iridium is caused by relativistic effects.[42] At 230 K two separated signals for the ethylene protons of **8** are detected at 2.88 and 0.73 ppm. The signals of the eight chemically inequivalent protons are still broadened and the signal at low field forms a pseudo doublet of triplets with apparent coupling constants of $J = 37.8$ and 9.4 Hz. The further analysis of the complicated spectrum of eight chemically inequivalent protons forming two overlapping $A_1B_1X_1Y_1$- and $A_2B_2X_2Y_2$-spin systems was not performed. For the ethylene protons of **9** at 210 K, two separated signals are detected at 3.04 and 0.98 ppm. The signal at low field forms a pseudo doublet of triplets with apparent coupling constants of $J = 85.9$ and 9.4 Hz. The stabilization of the indenyl ligand at lower temperatures is again shown by the high field shift of protons H(X01) and H(X03) (**8** at 360 K, 4.83 and 4.79 ppm; at 210 K, 4.55 and 4.33 ppm. **9** at 360 K, 5.03 and 4.91 ppm; at 210 K, 4.91 and 4.77 ppm).

Cobalt and Molybdenum Complexes. The cobalt complexes **11** and **12** were synthesized in metathetic reactions under oxidation of the metal center by adding 1.2 equiv of **1** to a mixture of octacarbonyldicobalt(0) and iodine in THF at 0 °C (Scheme 2) and by adding 2 equiv of **1** to dichloro(1,2-bis(diphenylphosphino)-ethane)cobalt(II) in diethyl ether at 0 °C under reduction of the metal center, respectively (Scheme 3). Chromatography under an inert atmosphere with dried alumina and *n*-hexane as eluent gave **11** as an orange oil in 65% yield and **12** after crystallization from *n*-pentane at −78 °C as a brown, air-sensitive powder in 68% yield.

Scheme 3



Scheme 4



As shown in Scheme 4 the molybdenum complex (−)-Li[(2-menthylindenyl)Mo(CO)$_3$](THF)$_2$ (**13**) was synthesized in a transmetalation reaction by adding 1 equiv of **1** to Mo(CO)$_6$ in THF at room temperature in 93% yield by heating the reaction mixture to 65 °C. The characteristic CO resonances can be detected in the ^{13}C NMR spectrum at 236.4 ppm.

Oxidation of the anionic molybdenum tricarbonyl complex **13** with 1 equiv of iodine in THF results in the formation of (−)-(2-menthylindenyl)Mo(CO)$_3$I (**14**), while the oxidation with 1.2 equiv of allylic chloride gives (allyl)(2-menthylindenyl)Mo(CO)$_2$ (**15**). Chromatography under inert atmosphere yields 39% red crystals of **14** and 79% yellow oil of **15** as a mixture of the *exo* and *endo* rotamers in the ratio 1.3:1. The characteristic CO resonances can be detected in the ^{13}C NMR spectrum between 219.7 and 240.2 ppm for **14** and between 237.8 and 239.4 ppm for **15**. IR absorptions of the CO groups occur at $\bar{\nu} = 2032$, 1962, 1930, and 1913 cm^{-1} (**14**) and $\bar{\nu} = 1954$ and 1872 cm^{-1} (**15**).

Crystals of **14** suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from warm *n*-pentane. The menthylindenyl complex crystallizes in the orthorhombic space group $P2_12_12_1$ with one crystallographically independent molecule in the asymmetric unit. The solid-state structure is shown in Figure 5.

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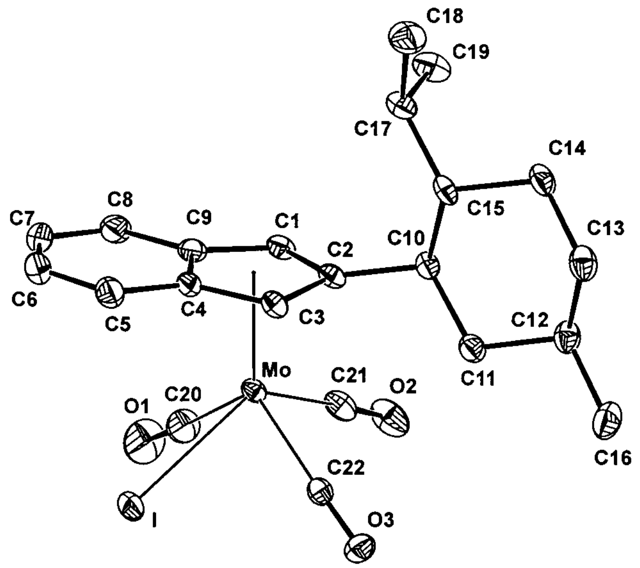

Figure 5. ORTEP plot[20] of the molecular structure and numbering scheme of **14** with 30% probability thermal ellipsoids. For clarity, all hydrogens are removed. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations:[23] Mo−Cg, 2.0229(15); Mo−I, 2.8455(4); Mo−C(20), 2.022(4); Mo−C(21), 1.972(4); Mo−C(22), 2.001(4); C(1)−C(2), 1.431(5); C(2)−C(3), 1.430(5); C(3)−C(4), 1.443(5); C(4)−C(9), 1.420(5); C(1)−C(9), 1.446(5); C(20)−O(1), 1.122(5); C(21)−O(2), 1.146(5); C(22)−O(3), 1.140(4); Cg−Mo−I, 115.01(4); Cg−Mo−C(20), 125.25(15); Cg−Mo−C(21), 114.10(13); Cg−Mo−C(22), 125.49(11); C(20)−Mo−I, 75.15(15); C(22)−Mo−I, 74.44(10); C(20)−Mo−C(21), 77.34(18); C(21)−Mo−C(22), 77.43(15); O(1)−C(20)−Mo, 176.4(5); O(2)−C(21)−Mo, 177.3(3); O(3)−C(22)−Mo, 178.3(3).

In the monomeric, solvent free, diastereomerically pure complex **14** the molybdenum metal of the formal oxidation state +2 is coordinated square pyramidal by the centroid of the cyclopentadienyl system and the four further ligands. Again the bulky isopropyl group of the menthyl moiety points away from the metal with a dihedral angle of 15°. The average bonding distance of molybdenum to the five-membered indenyl ring is 2.36 Å, the average bond lengths of molybdenum to the CO units are 2.00 Å, while the bond length Mo−I is 2.85 Å. These bond lengths are in close accordance to those in tricarbonyliodo(η^5-indenyl)molybdenum(II),[43] (η^3-allyl)dicarbonyl(η^5-indenyl)molybdenum(II),[44] and dicarbonyldi(ethanonitrile)(η^5-indenyl)molybdenum(II)tetrafluoroborate[45] (av Mo−C(ind) distances, 2.35, 2.36, and 2.34 Å; av Mo−CO distances, 1.93, 1.94, and 1.99 Å). The CO ligands are almost linearly bonded (av Mo−CO angle = 177.3°) and the average L−Mo−L angle between CO and I is 76.1°. The bond distances of the carbon atoms C(1), C(2), and C(3) to the metal are 0.10 Å shorter than the bond lengths to the bridging atoms C(4) and C(9). Overall, however, **14** shows a weaker tendency toward a η^2+η^3-coordination ($\Delta = 0.107$ Å, RS = 0.139 Å, HA = 5.7°, FA = 6.2°) than the rhodium and iridium complexes reported here.

NMR Spectra. The assignment of the ^{1}H and ^{13}C signals was based on ^{1}H,^{1}H COSY and ^{1}H,^{13}C correlated spectra as well as two-dimensional NOE experiments. All described transition metal complexes exhibited C_1-symmetry in their solution NMR spectra, which is consistent with the menthyl group not rotating on the NMR time scale along the $C^2-C^{3'}$-axis, as this would lead to a new rotamer in which all atoms are in a new chemical environment with potentially different chemical shifts. A fast rotation of the bulky menthyl moiety on the NMR time scale can be neglected, as even at 210 K no expected coalescence was detectable. The rotation of the neutral ethylene ligands was discussed above. The COD signals show no broadening but give complicated coupling patterns as all 12 of their protons are chemically inequivalent. In the ^{13}C NMR spectra only four of the eight chemically inequivalent carbon atoms of COD are detected. This gives rise to an empirical low induction of the chiral indenyl ligand on the COD moiety or to a dynamic behavior of the COD ligand on the ^{13}C NMR time scale.

Decoupled ^{103}Rh NMR spectra of **3**, **4**, and **5** in Et_2O/D_2O (3:1) were recorded and chemical shifts between −136.9 and −264.8 ppm relative to hexachlororhodate in D_2O with typical half-widths of $\nu_{1/2} = 20$ Hz were observed. The high field shift increases with higher alkylation of the indenyl ligand and stronger σ-donors bond to the metal due to an increase in electron density.[46]

Conclusion

Metathetic reactions of $L_2Rh(\mu\text{-}Cl)_2RhL_2$, $L_2Ir(\mu\text{-}Cl)_2IrL_2$, $CoCl_2(dppe)$, $Co_2(CO)_8$, and $Mo(CO)_6$ with chiral, menthyl-functionalized indenyl salts provide a convenient entry into chiral nonracemic transition metal complexes of rhodium, iridium, cobalt, and molybdenum. X-ray diffraction analyses of the monomeric, stereomerically pure complexes **3**, **4**, **6**, **7**, and **14** confirm the purity of the stereogenic centers in the ligands and the indenyl moiety being η^2+η^3-coordinated. The energy barriers for rotation of the ethylene ligands along the metal−indenyl and metal−ethylene axes were determined to $\Delta G^{\ddagger} = 44.7$ kJ/mol (**5**), 46.9 kJ/mol (**6**), 58.4 kJ/mol (**8**), and 62.4 kJ/mol (**9**).

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Supporting Information Available: Full details of the X-ray structures of complexes **3**, **4**, **6**, **7**, and **14** including complete tables of crystal data, atomic coordinates, bond lengths and angles, positional and anisotropic thermal parameters, and variable-temperature ^{1}H NMR spectra of **5**, **6**, **8**, and **9** are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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