= 11.3 Hz, J_{P-2} = 4.8 Hz, J_{12} = 1.4 Hz, J_{13} = 9.8 Hz, J_{23} = 6.2 Hz, J_{34} = 10.2 Hz, J_{45} = 10.2 Hz, J_{57} = 10.2 Hz, J_{56} = 16.9 Hz, J_{67} = 1.8 Hz. $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 20.5 (d, PCH_3, J_{PC} = 31 Hz), 20.8 (d, PCH_3', J_{PC} = 32 Hz), 33.4 (d, CH^1H^2, J_{PC} = 13 Hz), 69.0, 63.1 (s, s, CH^3 + CH^4), 91.6 (s, C_5H_5), 111.4 (s, CH^6H^7), 127.8-131.4 (PC_6H_5, overlapping with benzene-d_6 resonances), 139.4 (s, CH^5), 248.4 (d, CO, J_{PC} = 28 Hz).

Method B. This complex was also prepared by irradiation of 8 and PMe_2Ph in ether at -20 °C for 5 h, followed by purification by column chromatography; the yield was 43%.

(j) Synthesis of CpMo(CO)[$P(C_2H_5)_3$](*syn*-η^3-pentadienyl) (13). Method A. This complex was prepared similarly by irradiation of 4 in ether at -20 °C. The yield is 52%. Anal. Calcd for $C_{17}H_{27}MoOP$: C, 54.55; H, 7.22. Found: C, 54.68; H, 7.54. Mass spectrum (12 eV, ^{98}Mo, 23.78%, *m/e*): 376 (M^+), 348 (M^+ - CO), 258 (M^+-PEt_3). IR (Nujol): exo isomer, ν(CO) 1835 cm^{-1}; endo isomer, 1841 cm^{-1}; ν(C=C) 1617 cm^{-1}. ^1H NMR (400.1 MHz, benzene-d_6): exo isomer, δ -0.04 (ddd, 1 H, H^1), 0.67 (m, 9 H, PCH_2CH_3), 1.12 (m, 3 H, $PCHH'$-CH_3), 1.16 (m, 3 H, $PCHH'$-CH_3), 1.84 (ddd, 1 H, H^2), 2.43 (t, 1 H, H^4), 3.87 (td, 1 H, H^3), 4.64 (d, 5 H, C_5H_5), 4.84 (dd, 1 H, H^7), 5.52 (dd, 1 H, H^6), 5.85 (dt, 1 H, H^5), J_{P-1} = 11.7 Hz, J_{P-2} = 4.4 Hz, $J_{P-C_5H_5}$ = 1.2 Hz, J_{12} = 1.4 Hz, J_{13} = 10.2 Hz, J_{23} = 6.5 Hz, J_{34} = J_{45} = 10.2 Hz, J_{56} = 16.8 Hz, J_{57} = 10.2 Hz, J_{67} = 1.4 Hz; endo isomer, δ 0.79 (m, 9 H, PCH_2CH_3), 1.28 (m, 3 H, $PCHH'$), 1.40 (m, 3 H, $PCHH^1$), 1.53 (dd, 1 H, H^1), 1.65 (d, 1 H, H^2), 2.77 (dd, 1 H, H^4), 3.80 (td, ^1H, H^3), 4.63 (s, 5 H, C_5H_5), 4.80 (dd, 1 H, H^7), 5.00 (dd, 1 H), 6.78 (dt, 1 H, H^5), J_{P1} = 13.5 Hz, J_{23} = 6.0 Hz, J_{13} = 10.7 Hz, J_{34} = 10.7 Hz, J_{45} = 10.3 Hz, J_{56} = 16.8 Hz, J_{57} = 10.2 Hz, J_{67} = 1.0 Hz. $^{13}C\{^1H\}$ NMR (100.1 MHz, benzene-d_6): exo isomer, δ 8.3 (d, PCH_2CH_3, J_{PC} = 18 Hz), 21.26 (d, PCH_2CH_3, J_{PC} = 23 Hz), 30.0 (d, CH^1H^2, J_{PC} = 14 Hz), 63.0, 67.9 (s, s, CH^2 + CH^3), 91.2 (s, C_5H_5), 108.8 (s, CH^6H^7), 141.5 (s, CH^5), 249.7 (d, CO, J_{PC} = 38.2 Hz); endo isomer, δ 8.4 (d, PCH_2CH_3, J_{PC} = 18 Hz), 23.3 (d, PCH_2), 33.5 (d, CH^1H^2, J_{PC} = 8 Hz), 56.2, 82.6 (s, s, CH^3 + CH^4), 89.4 (s, C_5H_5), 105.5 (s, CH^6H^7), 145.6 (s, CH^5), 252.6 (d, CO, J_{PC} = 26 Hz).

Method B. This complex was also prepared by irradiation of 8 and $P(CH_2CH_3)_3$ in ether at -20 °C for 5 h, followed by purification through column chromatography; the yield was 46%.

(k) Synthesis of CpMo(CO)(PMe_3)(*syn*-η^3-pentadienyl) (14). This complex was prepared similarly by irradiation of an ether solution of 8 and PMe_3. The yield was 34%. Anal. Calcd for $C_{14}H_{21}MoOP$: C, 50.61; H, 6.32. Found: C, 50.94; H, 6.48. IR (pentane): ν(CO) 1832 cm^{-1}; ν(C=C) 1617 (w) cm^{-1}. Mass (12 eV, ^{98}Mo 23.78%, *m/e*): 334 (M^+), 306 (M^+ - CO), 258 (M^+ - PMe_3). ^1H NMR (400.1 MHz, benzene-d_6): δ -0.04 (ddd, 1 H, H^1), 1.02 (d, 3 H, CH_3), 1.82 (ddd, 1 H, H^2), 2.48 (t, 1 H, H^4), 3.86 (td, 1 H, H^3), 4.58 (d, C_5H_5), 4.81 (dd, 1 H, H^7), 5.48 (dd, 1 H, H^6), 5.83 (dt, 1 H, H^5), J_{P-CH_3} = 8.5 MHz, $J_{P-C_5H_5}$ = 1.4 Hz, J_{P-1} = 12.0 Hz, J_{P-2} = 4.6 Hz, J_{12} = 1.4 Hz, J_{13} = 10.2 Hz, J_{23} = 6.6 Hz, J_{34} = 10.2 Hz, J_{45} = 10.2 Hz, J_{57} = 16.8 Hz, J_{56} = 10.2 Hz, J_{67} = 1.2 Hz. $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 21.6 (d, PCH_3, J_{PC} = 29 Hz), 31.1 (d, CH_1H_2, J_{PC} = 14 Hz), 62.8, 68.3 (CH^3 + CH^4), 108.4 (CH^6H^7), 141.6 (CH^5), 248.0 (d, CO, J_{PC} = 22 Hz).

Acknowledgment. We wish to thank Chinese National Science Council for financial support of this work. We also wish to express gratitude to Professor R. D. Ernst for kindly informing us of his results,[13b] prior to publication.

Registry No. 1, 104293-11-0; 2, 112373-46-3; 3, 112373-48-5; 4, 112373-49-6; 5, 112373-50-9; 6, 112373-51-0; 7, 112373-47-4; 8, 104293-12-1; 9, 104293-13-2; 10 (exo isomer), 112373-52-1; 10 (endo isomer), 112455-87-5; 11, 112373-53-2; 12, 112373-54-3; 13 (exo isomer), 112457-41-7; 13 (endo isomer), 112373-58-7; 14, 112373-55-4; 15, 112373-56-5; 16, 112373-57-6; $CpMo(CO)_3Na$, 12107-35-6; PMe_2Ph, 672-66-2; PMe_3, 594-09-2; $P(CH_2CH_3)_3$, 554-70-1; (*E,E*)-1-chlorohexa-2,4-diene, 17100-75-3; tetracyanoethylene, 670-54-2; maleicanhydride, 108-31-6.

Synthesis and Asymmetric Reactivity of Enantiomerically Pure Cyclopentadienylmetal Complexes Derived from the Chiral Pool

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Starting from pulegone, camphor, and tartrate, three chiral cyclopentadienes were prepared efficiently. Metalation with $Co_2(CO)_8$ and $TiCl_3$ resulted in new chiral and enantiomerically pure substituted cyclopentadienyldicarbonylcobalt and -titanocene complexes. The latter were used in the quantitative catalytic asymmetric hydrogenation of 2-phenyl-1-butene in up to 34% optical yield. The former allowed the first asymmetric [2 + 2 + 2] cycloadditions promoted by chiral cyclopentadienylcobalt complexes to be observed.

Introduction

Organometallic compounds containing chiral ligands have recently been regarded with intense interest as potential mediators of enantioselective transformations.[1] Although transition-metal complexes attached to the most common auxiliary, chiral chelating diphosphines,[1,2] have been used successfully in several cases,[1-3] their stereodifferentiating ability can suffer due to their lability as complexing agents. In order for efficient transfer of asymmetry to a substrate to occur, the chiral ligand must be bound to the metal during the stereodifferentiating step. The relatively weak bonding ability of many such ligands is a potential drawback that can limit their applications and invites the use of a more stable system. We chose as an example the η^5-cyclopentadienyl unit because of the superior tenacity with which it attaches itself to transition metals, involving bond strengths as high as 118 kcal mol^{-1}.[4]

† University of California, Berkeley.

(1) ApSimon, J. W.; Collier, T. L. *Tetrahedron* **1986**, *42*, 5157. Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, p 455. Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876. ApSimon, J. W.; Seguin, R. P. *Tetrahedron* **1979**, *35*, 2797. Valentine, D., Jr.; Scott, J. W. *Synthesis* **1978**, 329.

(2) (a) Kagan, H. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 5, p 1. (b) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. (c) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 463.

(3) See also: (a) Koenig, K. E. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 5, p 71. (b) For a recent reference, see: Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Inoue, S.; Kasahara, I.; Noyori, R. *J. Am. Chem. Soc.* **1987**, *109*, 1596.

(4) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 7399.

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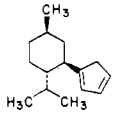
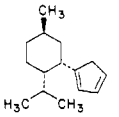
At the outset of this work,[5] there were only few examples of chiral and even fewer of optically active cyclopentadienes,[2a,6] the most commonly used being the menthol-derived dienes **1** and **2**. Although these and related compounds are readily obtained, their metal complexes have effected only modest stereoselectivity in catalytic asymmetric transformations.[6,7] Thus, in order to increase the number of potentially stereodifferentiating chiral cyclopentadienyl ligands, it was desirable to develop new expeditions and hopefully general routes to such species starting from inexpensive naturally occurring enantiomerically pure compounds. A more specific goal was to gain access to structures in which the chiral framework either was relatively bulky or was annelated to the five-membered ring, thus providing a perhaps advantageous more encumbered and/or rigid asymmetric environment to the metal. As a convenient test for their utility, applications in enantioselective titanocene-catalyzed hydrogenations[7] were envisaged, in addition to the novel exploitation of (η^5-cyclopentadienyl)cobalt complexes as mediators of similarly selective carbon–carbon bond formations in [2 + 2 + 2] cycloaddition reactions of alkynes to other unsaturated moieties.[8]

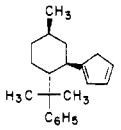


1



2

Toward these ends, we describe herein the efficient syntheses of **3** (three steps, 36% yield from phenylmenthone), **4** (five steps, 37% yield from camphor), and **5** [one step, 31% yield from threitol bis(4-methylbenzenesulfonate)]. Metalation of these ligands led to chiral titanocene dichloride and (η^5-cyclopentadienyl)dicarbonylcobalt complexes whose activity in enantioselective transformations was tested.



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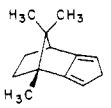

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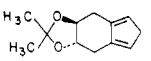
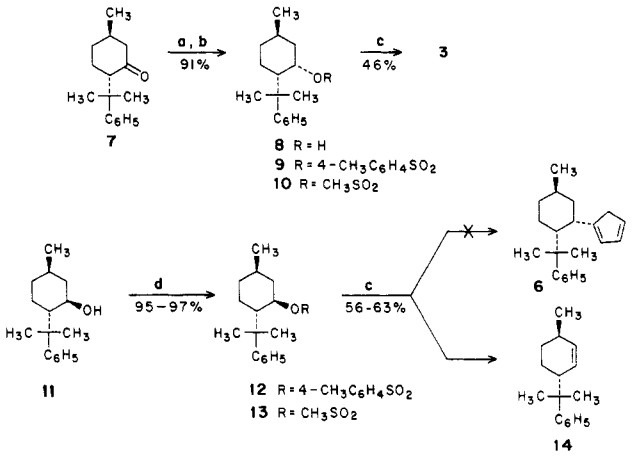


5

Results and Discussion

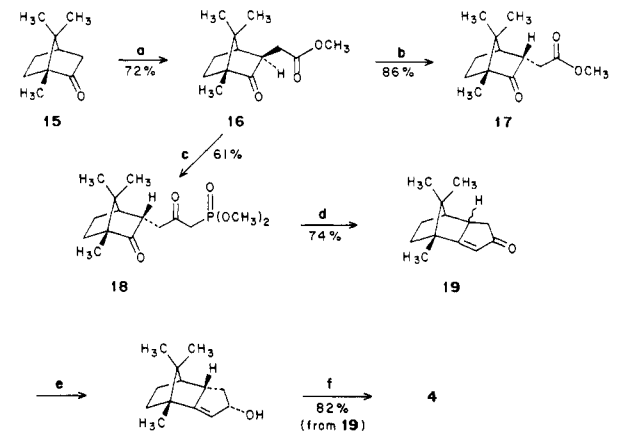
Synthesis of 3. On the basis of the report that cyclopentadienes **1** and **2** were accessible by introducing the future π ligand through alkylation of cyclopentadienyl anion by the 4-methylbenzenesulfonates of neomenthol and menthol,[6a,c-e,j,l] respectively, it was anticipated that the more bulky phenylmenthol-derived cyclopentadienes **3** and **6** would also be available by this route. These systems were chosen with the expectation that their complexes would reveal improved stereodifferentiating ability compared to **1** and **2**.[9] Phenylmenthol (**11**), the projected precursor to **6**, was prepared in three steps by literature procedures from pulegone.[10] Reduction of phenylmenthone (**7**) with K-Selectride (Aldrich) gave equivalent amounts of phenylmenthol (**11**) and neophenylmenthol (**8**), while L-Selectride (Aldrich)[11] reduction produced only the desired **8** necessary for the synthesis of **3** (Scheme I). Attempted 4-methylbenzenesulfonation of **8** to give **9** failed, perhaps due to steric congestion, whereas treatment with meth-

Scheme I[a]



[a] (a) L-Selectride, THF, 0 °C, 4 h. (b) CH_3SO_2Cl, pyr, 2 °C, 14 h. (c) NaC_5H_5, THF, 12 h, 23 °C, 2 h, Δ. (d) 4-$CH_3C_6H_4SO_2Cl$, pyr, 2 °C, 40 h or CH_3SO_2Cl, Et_3N, CH_2Cl_2, −10 °C, 40 min.

Scheme II[a]



[a] (a) 1, $[(CH_3)_2CH]_2NLi$, THF; 2, $BrCH_2CO_2CH_3$, −78 to 23 °C, 1 h. (b) $NaOCH_3$, CH_3OH, 23 °C, 16 h. (c) $LiCH_2P(O)(OCH_3)_2$, THF, −78 °C, 2 h, Δ, 18 h. (d) NaH, THF, Δ, 18 h. (e) $LiAlH_4$, Et_2O, 23 °C, 30 min. (f) 4-$CH_3C_6H_4SO_3H$, C_6H_6, 23 °C, 12 h.

(5) For a preliminary report, see: Halterman, R. L.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1986**, *27*, 1461.

(6) See, for example: (a) Cesarotti, E.; Chiesa, A.; Ciani, G. F.; Sironi, A.; Vefghi, R.; White, C. *J. Chem. Soc., Dalton Trans.* **1984**, 653. (b) Dormond, A.; El Bouadili, A.; Moise, C. *Tetrahedron Lett.* **1983**, *24*, 3087. (c) Sato, F.; Iijima, S.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1981**, 180. (d) Cesarotti, E.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1981**, *216*, 87. (e) Cesarotti, E.; Ugo, R.; Vitiello, R. *J. Mol. Catal.* **1981**, *12*, 63. (f) Couturier, S.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1980**, *195*, 291. (g) Cullen, W. R.; Einstein, F. W. B.; Huang, C.-H.; Willis, A. C.; Yeh, E.-S. *J. Am. Chem. Soc.* **1980**, *102*, 988. (h) Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett.* **1980**, *21*, 4437. (i) Tamao, K.; Hayashi, T.; Matsumoto, H.; Yamamoto, H.; Kumada, M. *Tetrahedron Lett.* **1979**, 2155. (j) Cesarotti, E.; Ugo, R.; Kagan, H. B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 779. (k) Dormond, A.; Kolavudh, T.; Tirouflet, J. *J. Organomet. Chem.* **1979**, *164*, 317. (l) Cesarotti, E.; Kagan, H. B.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1978**, *162*, 297. (m) Leblanc, J. C.; Moise, C. *J. Organomet. Chem.* **1977**, *131*, 35; **1976**, *120*, 65. (n) Marquarding, D.; Burghard, H.; Ugi, I.; Urban, R.; Klusacek, H. *J. Chem. Res., Synop.* **1977**, 82. (o) Le Plouzennec, M.; Le Moigne, F.; Dabard, R. *J. Organomet. Chem.* **1976**, *111*, C38. (p) See also: Sternbach, D. D.; Hobbs, S. H. *Synth. Commun.* **1984**, *14*, 1305 and the references therein.

(7) For other recent work, see: (a) McLaughlin, M. L.; McKinney, J. A.; Paquette, L. A. *Tetrahedron Lett.* **1986**, *27*, 5595. (b) Paquette, L. A.; McKinney, J. A.; McLaughlin, M. L.; Rheingold, A. L. *Tetrahedron Lett.* **1986**, *27*, 5599.

(8) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(9) See: Oppolzer, W.; Kurth, M.; Reichlin, D.; Moffatt, F. *Tetrahedron Lett.* **1981**, *22*, 2545.

(10) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908.

(11) The starting phenylmenthone consisted of an 85:15 mixture of diastereomers that could be separated by preparative HPLC. More conveniently, the mixture was reduced and the alcohols were separated by flash chromatography to provide pure **7** in 78% yield: Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1972**, *94*, 7159.

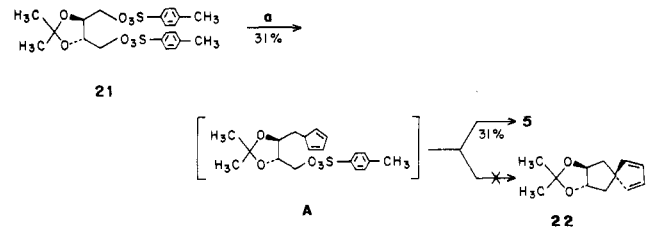
anesulfonyl chloride afforded methanesulfonate **10** quantitatively. Gratifyingly, reaction of **10** with cyclopentadienylsodium proceeded as planned to furnish the cyclopentadiene **3**, in addition to its 2-cyclopentadienyl isomer (ratio 2:1).

Unfortunately, attempts to form the (neophenylmenthyl)cyclopentadiene (**6**) proved to be unsuccessful. Both the 4-methylbenzenesulfonate **12** and the methanesulfonate **13** of phenylmenthol (**11**) were readily formed, but both failed to alkylate cyclopentadienylsodium under a variety of conditions involving changes in temperature (20 or 66 °C) and solvent (THF or THF/DMPU[12]). In all cases, only the elimination product **14** was formed. Evidently, the bulky phenyl-substituted group cis to the entering nucleophile creates too much steric hindrance for facile substitution to occur, allowing for competing elimination.

Synthesis of 4. Because the structure of the camphor-derived diene **4** incorporates a rigid chiral auxiliary fused to the cyclopentadienyl moiety, it was of particular interest to examine this ligand in potentially enantioselective CpM-mediated transformations. A synthesis of **4** had been reported previously,[13] but attempts to repeat the published preparation on a scale larger than described failed. Hence a new route to this ligand was developed. As a synthetic strategy a cyclopentannulation was chosen, involving the alkylation of camphor by a suitable three-carbon synthon, followed by ring-closure to the corresponding cyclopentenone (Scheme II).[14]

Thus, alkylation of (+)-camphor (**15**) with methyl bromoethanoate (hexane, THF, HMPA) provided keto ester **16**.[15] This product was of kinetic origin and completely epimerized to **17** in the presence of sodium methoxide. The stereochemistry of these structures was established by using difference nuclear Overhauser effect NMR spectroscopy.[16] Irradiation of one of the geminal dimethyl groups in **16** enhanced the ethanoate methylene signals while the analogous experiment with isomer **17** caused an increase in the magnitude of the tertiary hydrogen resonance. According to a published synthetic procedure,[14] the ketone carbonyl function in **16** (and/or **17**) was to be protected as the acetal before addition of the methyl phosphonate unit required for five-membered ring formation, in order to ensure reaction at the normally less reactive ester moiety. However, attempts to form the desired ethylene acetal failed, indicating steric encumbrance at that position. This finding was exploited by reaction of **16** directly with the anion of dimethyl methylphosphonate that led to phosphonate **18** as a single epimer. Deprotonation of this intermediate with sodium or potassium hydride in THF followed by heating to reflux for 18 h effected ring closure to cyclopentenone **19** as a single isomer. In contrast, the lithium salt of **18** failed to cyclize even after several days in boiling THF or THF–HMPA. However, addition of dimethyl (lithiomethyl)-phosphonate to **16** in diglyme at −78 °C followed by heating to reflux for 18 h gave **19** directly (51% mixture of epimers). Reduction of **19** with lithium aluminum hydride in ether[17] resulted in the acid-sensitive alcohol **20** in nearly quantitative yield. When this reduction was carried out in THF, a mixture of products ensued. Dehydration of **20** in benzene was accomplished overnight in the presence of 4-methylbenzenesulfonic acid to form the apparently thermodynamically favored diene **4**[13,18] as a clear oil.

Scheme III[a]



[a] (a) NaC_5H_5, NaH, 23 °C, 8 h, Δ, 2 h.

Synthesis of 5. The tartrate-derived **21** could, in principle, be convertible to the chiral cyclopentadiene **5** via double displacement of both leaving groups by the cyclopentadienyl moiety (Scheme III). However, similar transformations in the literature[19] had led to the spiro compounds related to the potential product **22** of our scheme. Fortunately, treatment of commercial **21**[20] with cyclopentadienylsodium and sodium hydride provided crystalline **5** as the only isolable product. Evidently, deprotonation of the initially formed intermediate diene A induced displacement of the second leaving group to give the annulated product **5** of a subsequent facile hydrogen migration.[21] Spiroannulation seems to be unfavorable here, perhaps because of the presence of the trans-fused bicyclo[3.3.0]octane framework in **22**.

Metalation of 3. Diene **3** was readily converted (65%) into complex **23** by treatment with octacarbonyldicobalt. The structure of this compound was evident from its spectral characteristics. The stereochemistry shown was strongly suggested by examination of the ^1H NMR spectrum. The tertiary hydrogen at the carbon bearing the cyclopentadienyl ring appears as a slightly broadened doublet of doublets (J = 11, 10.5 Hz). This finding is in agreement with the presence of two large axial–axial $^3J_{H-H}$ and a small axial–equatorial $^3J_{H-H}$ coupling, as expected for **23**.

Metalation of the anion of diene **3** with titanium trichloride (0.5 equiv) followed by addition of hydrochloric acid[22] furnished titanocene dichloride **24** (45%). Its C_2 symmetry was reflected by the observation of only 19 ^{13}C NMR signals. The stereochemistry was again indicated by ^1H NMR specroscopy; the tertiary hydrogen at C-2 bearing the cyclopentadienyl ring gave rise to the expected broad doublet of doublets (J = 10, 10 Hz).

Metalation of 4. Exposure of **4** to octacarbonyldicobalt resulted in a 3:1 mixture of the inseparable isomeric complexes **25a** and **25b**. A definitive stereochemical assign-

(12) DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone: Mukhopadhyay, T.; Seebach, D. *Helv. Chim. Acta* **1982**, *65*, 385.

(13) Compound **4** has been prepared by a bis Wittig reaction on camphor quinone in low yield and with an optical rotation at odds with our results: Burgstahler, A. W.; Boger, D. L.; Naik, N. C. *Tetrahedron* **1976**, *32*, 309.

(14) Clark, R. D.; Kozar, L. G.; Heathcock, C. H. *Synth. Commun.* **1975**, *5*, 1.

(15) House, H. O.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1971**, *36*, 2361.

(16) Becker, E. D. *High Resolution NMR, Theory and Chemical Applications*; Academic: New York, 1980. Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect*; Academic: New York, 1971.

(17) Brown, H. C.; Hess, H. M. *J. Org. Chem.* **1969**, *34*, 2206.

(18) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 7218. Bartlett, P. D.; Wu, C. *J. Am. Chem. Soc.* **1983**, *105*, 100.

(19) Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1958**, 646. Antczak, K.; Kingston, J. F.; Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 2451.

(20) Compound **21** is available from Aldrich Chemical Co. or it can be readily synthesized in three steps from diethyl tartrate: Townsend, J. M.; Blount, J. F.; Sun, R. C.; Zawoiski, S.; Valentine, D., Jr. *J. Org. Chem.* **1980**, *45*, 2995.

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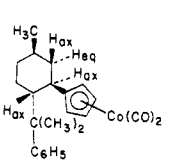
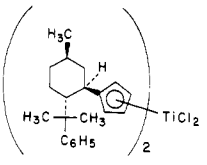
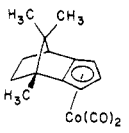


23

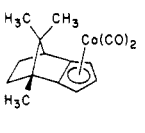


24

ment of these isomers could not be made. Since both isomers are obtained in comparable amounts, it appears that metalation of the seemingly more sterically hindered exo face may be favored electronically.[23]

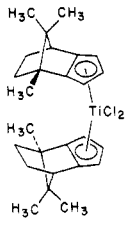


25a

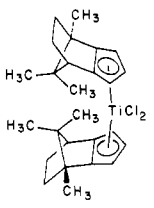


25b

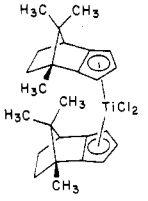
The camphor-derived titanocene dichloride **26** was synthesized in a manner analogous to that of the preparation of the phenylmethyl-derived complex **24**. The crude product was analyzed to consist of a 95:5 mixture of isomers by ^{1}H NMR spectroscopy. Recrystallization by slow evaporation of a dichloromethane–isooctane solution gave deep red crystals of the major component (11%). The minor isomer in the crude product mixture was assigned the structure **27** based on the observation of six singlets in the methyl region of its ^{1}H NMR spectrum, revealing lack of C_2 symmetry. The major isomer that exhibited such symmetry by NMR could, in principle, have the structures of either **26a** or **26b**. The arrangement depicted by **26a** is to be favored on the basis of the X-ray structural confirmation of a related system,[23] and the changes in chemical shifts in the ^{1}H NMR spectra when going from **4** to **26a**.[23]



26a

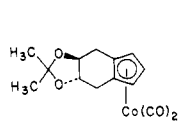


26b

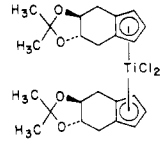


27

Metalation of 5. The problem of stereofacial differentiation encountered in the metalation of the fused camphor-derived diene **4** is avoided in the complexation of the C_2-symmetrical tartrate-derived diene **5**. Thus, treatment of **5** with dicobalt octacarbonyl produced the only possible stereoisomer of the dicarbonylcobalt complex **28** as a crystalline red solid (43%). Unfortunately, all attempts to form the corresponding titanocene dichloride **29** were unsuccessful. This failure could be due to reactivity of the acid-sensitive acetal moiety present in **5**.



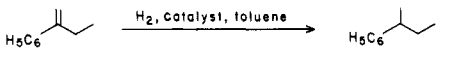
28



29

Asymmetric Hydrogenations. In order to establish whether the ligands **3**–**5** were able to transmit their asymmetry while complexed to transition metals engaged in organic reactions, hydrogenation of 2-phenyl-1-butene (**30**) was subjected to scrutiny using as catalyst precursors the titanocene dichlorides **24** and **26a**. Reduction of either **24** or **26a** by butyllithium in the presence of alkene **30** under hydrogen produced a catalytically active, gray-green solution.[22] As summarized in Table I, both species catalyzed the uptake of hydrogen after an initial induction period, producing 2-phenylbutane (**31**) quantitatively in modest optical yields.

Table I. Catalytic Hydrogenation of 30[a]



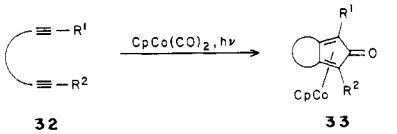
30 31

entry	cat. precursor	inductn time[b]	temp, °C	time[c]	optical yield, %
1	**24**	1 h	20	40 h	33
2	**26a**	2 min	20	20 min	22
3	**26a**	2 min	0	40 min	25
4	**26a**	2 min	−20	5 h	34

[a] Reactions were performed according to the literature with a substrate to catalyst ratio of 100:1; see ref 22. [b] Time required for the uptake of hydrogen to begin at 20 °C after addition of 4 equiv of butyllithium. The solutions were then rapidly cooled (when necessary) to the reaction temperatures shown in column 4. [c] The time required for quantitative reaction to reach completion as determined by gas chromatography.

In the reduction facilitated by **24**, hydrogen uptake began 1 h after the addition of butyllithium and the reaction reached completion after 40 h. The 2-phenylbutane so produced was purified by preparative gas chromatography and its optical rotation compared with the maximum reported value,[24] indicating the achievement of 33% optical yield in this enantioselective hydrogenation. In contrast, hydrogen uptake after reducing **26a** occurred within 2 min and alkene **30** was completely reduced within 20 min at 20 °C. The optical yield in this case was 22%. The activation of **26a** by butyllithium at 0 °C failed, necessitating 20 °C, followed by cooling of the reaction mixture to the temperature indicated in Table I for the duration of the hydrogenation. In this way, optical yields of product up to 25% and 34% were obtained after 40 min at 0 °C and 5 h at −20 °C, respectively. The results achieved here are the best yet reported and bode well for other synthetic applications of these two ligands. The lesser reactivity of the phenylmenthol-derived **24**, relative to camphor-derived **26a** and the other reported menthol-derived catalysts, may be due to increased steric hindrance encumbering both reduction of the metal and access of the substrate to the active site.

Diastereoselective Cobalt-Mediated Photolytic Alkyne Cyclizations to Complexed Cyclopentadienones. The availability of the new chiral cyclopentadienylcobalt complexes **23**, **25**, and **28** suggested an investigation of their potential in cobalt-mediated asymmetric C–C bond formations.[8] An initial exploration of this potential focused on the photolytical cyclization of unsymmetrical α,ω-diynes **32** to metal-complexed cyclopentadienones **33**.[25]



32 33

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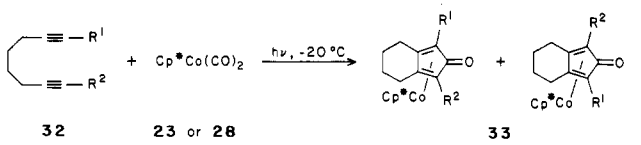
Table II. Stereoselectivity in the Formation of Cyclopentadienone Complexes 33 in the Cyclization of 32 Mediated by Cobalt Complexes 23 and 28



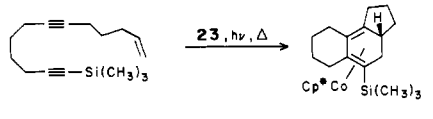
32 23 or 28 33

entry	diyne 32 R^1	diyne 32 R^2	Cp*Co-$(CO)_2$	yield of 33, %	diastereomeric ratio of 33[a]
1	$Si(CH_3)_3$	H	23	54	52:48
2	$Si(CH_3)_3$	CH_3	23	64	67:33
3	$Si(CH_3)_3$	CH_3CH_2	23	74	60:40
4	CH_3	H	23	53	61:39
5	CH_3CH_2	H	23	54	56:44
6	$Si(CH_3)_3$	CH_3CH_2	28	64	50:50

[a] Ratio determined by ^1H NMR integration of several characteristic signals.

The required diynes **32** were synthesized by standard methods.[26] A degassed THF solution of **32** and the respective cobalt complex was irradiated at −20 °C with a 450-W Hanovia mercury vapor lamp for 6 h[25] to result in the data presented in Table II. While the complex **28** gave modest diastereoselectivity in these reactions, **23** exhibited no such effect. The diastereomers of **33**, entries 1–3 and 6, could be separated by silica gel chromatography, the minor isomer eluting first. The moderate yields of **33** are due to the formation of the usual side products in these transformations, alkyne trimers and cyclobutadiene complexes[27] (not isolated in the present cases). Because of relatively low yields and modest stereoselectivities, it is hard to reach any conclusion regarding the mechanistic origin of the asymmetric induction in these transformations. Nevertheless, the results demonstrate for the first time the feasibility of achieving such selectivity.

Diastereoselective Enediyne Cyclizations to Complexed Cyclohexadienes. Prochiral α,δ,ω-enediynes cyclize to chiral tricyclic diene complexes in the presence of $CpCo(CO_2)$.[8] When enediyne **34**[28] was subjected to **23** under the usual cyclization conditions, a 58:42 mixture of the diastereomeric complexes **35** ensued, the position of the metal relative to the tertiary hydrogen tentatively assigned to be exo, based on the relatively high-field position of the ^1H NMR signals of the latter ($\delta \sim 0.45$). While again the diastereomeric excess (16%; additional stereochemistry unassigned) was only moderate (although nevertheless remarkable considering that four diastereomers could have been formed), it indicates that perhaps by appropriate fine-tuning of ligands and substrate, useful selectivities may be attained, a subject worthy of continuing investigation.[29]



34 35

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Experimental Section

General Data. Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. THF and ether were distilled from sodium benzophenone ketyl. All reactions involving air- or moisture-sensitive organometallic reagents were carried out under dry nitrogen in flame-dried glassware. Solvents for such reactions were dried by standard methods. Vacuum line operations utilized a multiple-line apparatus.

^1H and ^{13}C NMR spectra were recorded on UCB-200 MHz, UCB-250 MHz, and UCB-300 MHz instruments consisting of Cryomagnet System magnets, Nicolet 293A or 293A′ pulse programmers, and Nicolet Model 1180 or 1180E data collection systems or on a Bruker AM-500 MHz model. Data are reported as follows: chemical shifts in parts per million (ppm) relative to internal tetramethylsilane or residual solvent peaks (multiplicity, coupling constants in hertz, number of hydrogens). For ^1H NMR spectra, the peak due to residual $CHCl_3$ is listed at 7.24 ppm, and for ^{13}C NMR spectra, the central peak of the $CDCl_3$ triplet is assigned a chemical shift of 77.0 ppm. Off-resonance decoupled (off-reson decoup) ^{13}C NMR spectra were obtained for some compounds as indicated. The multiplicities observed are indicated as s (singlet), d (doublet), t (triplet), and q (quartet). DEPT ^{13}C NMR spectra[30] are also indicated for some compounds. The nature of the carbon is indicated as quat (quaternary), CH (methine), CH_2 (methylene), and CH_3 (methyl).

Infrared spectra were obtained on one of the Perkin-Elmer Models 681 or 1420 and were referenced to polystyrene (1601 cm^{-1}). Only characteristic and/or strong signals are reported. Low-resolution mass spectra [reported as m/z (relative intensity) at 70 eV], high resolution mass spectra (HRMS), and elemental analyses were provided by the Mass Spectral Service and Microanalytical Laboratory, respectively, at the University of California, Berkeley. Melting points were determined in open Pyrex capillary tubes with a Thomas-Hoover Unimelt apparatus and are uncorrected.

Column chromatography was performed on activity 3 alumina (Alfa products, activated neutral Al_2O_3, 60 mesh, deactivated with 6% w/w (water) or flash silica (E. Merck Reagents silica gel 60, 230–400 mesh ASTM). High performance liquid chromatography (HPLC) was performed on an Altex Model 330 isocratic liquid chromatographic system with a Hitachi 100-10 UV–visible detector or an Altex 153 UV detector. Two Altex 5-μm-Ultrasphere-ODS reverse phase columns were utilized in sequence. All HPLC solvents were millipore-filtered and saturated with argon prior to use.

Analytical gas chromatography was carried out on a Hewlett-Packard Model 5880 gas chromatograph equipped with a 12 m × 0.25 mm OV-101 glass capillary column or a 3 m × 2 mm 3% OV-101 on WHF 80/100 glass column. Preparative gas chromatography was executed on a Varian Model 920 instrument equipped with a stainless-stell 2 m × 7 mm 10% SE-30 on 60-80 mesh Chromosorb AW column.

Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter at 26 °C using a 1-dm quartz cell holding 1 mL.

(1*S*,2*S*,5*R*)-5-Methyl-2-(2-phenyl-2-propyl)cyclohexanol (8) and (1*R*,2*R*,5*R*)-5-Methyl-2-(2-phenyl-2-propyl)cyclohexanol. To an L-Selectride solution (75.0 mL, 1.0 M in THF, 75.0 mmol) at 0 °C was added dropwise via syringe a solution of **7** (11.52 g, 50.00 mmol, 85:15 mixture of diastereomers) in THF (50 mL). The reaction mixture was stirred for 4 h at 0 °C at which point aqueous NaOH (26.0 mL, 3.0 M, 48.0 mmol) was added dropwise followed by slow addition of 30% H_2O_2 (26.0 mL, 10 M, 260 mmol) resulting in an exothermic reaction. The solution was allowed to warm to room temperature, stirred for 30 min, and extracted with ether (5 × 20 mL). The combined organic portions were washed with water (10 mL) and dried over $MgSO_4$. The solvent was removed to give a mixture of **8** and its isomer as an oil (11.23 g, 96.7%) separated by flash chromatography (4% ether in hexanes) to yield first the minor (1*R*,2*R*,5*R*)-isomer (1.32 g, 76% based on the starting composition of **7**): IR (thin film) 3410, 2974, 2941, 1460, 1381, 1335, 1042, 707 cm^{-1}; MS, m/z (relative intensity)

(30) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323. Pegg, D. T.; Doddrell, D. M.; Bendall, M. R. *J. Chem. Phys.* **1982**, *77*, 2745.

215 (3), 119 (100), 105 (20), 91 (22), 59 (17), 57 (38); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (dd, J = 7.4, 1.0 Hz, 2 H), 7.33 (dd, J = 7.7, 7.4 Hz, 2 H), 7.21 (td, J = 7.7, 1.0 Hz, 1 H), 3.87 (br s, 1 H), 1.76–1.94 (m, 2 H), 1.46–1.66 (m, 3 H), 1.45 (s, 3 H), 1.43 (s, 3 H), 1.21 (m, 1 H), 1.16 (d, J = 7.4 Hz, 3 H), 0.92 (m, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, DEPT) δ 149.8 (quat), 127.9 (CH), 126.1 (CH), 125.4 (CH), 69.0 (CH), 52.6 (CH), 40.4 (CH_2), 40.3 (quat), 32.8 (CH_2), 27.6 (CH_3), 26.4 (CH), 25.5 (CH_3), 21.2 (CH_3), 16.4 (CH_2). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.81; H, 10.55.

A second fraction was identified as pure **8** (9.07 g, 92% based on the starting composition of **7**): IR (thin film) 3399, 2975, 2884, 1466, 1403, 1335, 1265, 1124, 1039, 973, 708 cm^{-1}; MS, m/z (relative intensity) 232 (M^+, 0.1), 214 (2), 119 (100), 105 (20), 91 (25), 77 (4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.7, 1.0 Hz, 2 H), 7.31 (dd, J = 7.7, 7.3 Hz, 2 H), 7.18 (td, J = 7.3, 1.0 Hz, 1 H), 3.86 (br s, 1 H), 1.68–1.76 (m, 2 H), 1.64 (dddd, J = 13.5, 3.5, 3.0, 2.5 Hz, 1 H), 1.48–1.57 (m, 2 H), 1.45 (ddd, J = 13.5, 3.0, 1.7 Hz, 1 H), 1.40 (s, 3 H), 1.38 (s, 3 H), 1.11 (m, 1 H), 1.02 (ddd, J = 13.5, 11.5, 2.2 Hz, 1 H), 0.87 (m, 1 H), 0.83 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, DEPT) δ 149.8 (quat), 128.0 (CH), 126.2 (CH), 125.5 (CH), 68.2 (CH), 52.2 (CH), 43.8 (CH_2), 40.2 (quat), 35.6 (CH_2), 27.6 (CH_3), 26.1 (CH), 25.8 (CH_3), 22.2 (CH_3), 21.3 (CH_2). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.76; H, 10.51.

(1*S*,2*S*,5*R*)-5-Methyl-2-(2-phenyl-2-propyl)cyclohexyl Methanesulfonate (10). To pyridine (4 mL) at −10 °C under nitrogen was added via syringe freshly distilled methanesulfonyl chloride (0.802 g, 7.00 mmol). A solution of **8** (1.162 g, 5.00 mmol) in pyridine (1 mL) was added dropwise. The mixture was stirred at this temperature for 30 min and then for 14 h at 2 °C. Aqueous workup provided **10** as a thick, thermally sensitive yellow oil (1.536 g, 99.0%): IR (thin film) 2954, 1498, 1457, 1346, 1176, 899, 704 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 4 H), 7.18 (m, 1 H), 4.90 (br s, 1 H), 2.90 (s, 3 H), 2.18 (dddd, J = 14.5, 3.5, 3.0, 2.5 Hz, 1 H), 1.79 (m, 1 H), 1.77 (br d, J = 13.0 Hz, 1 H), 1.48–1.67 (m, 3 H), 1.39 (s, 3 H), 1.35 (s, 3 H), 1.08 (ddd, J = 13.0, 13.0, 1.5 Hz, 1 H), 0.91 (m, 1 H), 0.86 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, DEPT) δ 148.9 (quat), 128.0 (CH), 126.0 (CH), 125.7 (CH), 80.7 (CH), 51.7 (CH), 40.6 (CH_2), 39.8 (quat), 39.4 (CH_3), 34.9 (CH_2), 26.6 (CH_3), 26.2 (CH), 25.1 (CH_3), 21.8 (CH_3), 21.7 (CH_2). This product was used in the next step without further purification.

(1*R*,2*R*,5*R*)-1-Cyclopentadienyl-5-methyl-2-(2-phenyl-2-propyl)cyclohexane (3). To NaH (0.160 g, 60%, 4.00 mmol), washed with pentane (3 × 10 mL) in THF (15 mL) was added freshly distilled cyclopentadiene (0.320 g, 4.00 mmol) in THF (5 mL) under nitrogen at room temperature. The solution evolved gas and was stirred for 20 min. At 0 °C **10** (0.990 g, 3.00 mmol) in THF (10 mL) was introduced dropwise into the reaction solution. This mixture was stirred at this temperature for 30 min and for 12 h at room temperature and then heated at reflux for 2 h. Acidic (HCl) aqueous workup yielded a yellow oil (0.947 g) that was purified by flash chromatography (hexanes) to provide **3** as a colorless oil (0.386 g, 45.9%) as a mixture of cyclopentadiene double-bond isomers: IR (thin film) 3060, 2952, 2915, 1603, 1497, 1456, 1370, 1034, 900, 765, 702 cm^{-1}; MS, m/z (relative intensity) 280 (M^+, 7), 154 (8), 119 (100), 105 (14), 91 (59), 79 (25), 67 (14); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.05–7.40 (m, 5 H), 6.38 (br s, 0.3 H), 6.34 (br s, 0.6 H), 6.19 (br s, 1.4 H), 5.91 (br s, 0.7 H), 2.79 (br s, 1.4 H), 2.35–2.75 (m, 1.6 H), 1.86 (m, 1 H), 1.35–1.75 (m, 4 H), 1.30 (m, 1 H), 1.27 (s, 3 H), 1.16 (s, 3 H), 0.90–1.15 (m, 2 H), 0.86 (d, J = 6.4 Hz, 3 H). Anal. Calcd for $C_{21}H_{28}$: C, 89.94; H, 10.06. Found: C, 89.71; H, 10.02.

(1*R*,2*S*,5*R*)-5-Methyl-2-(2-phenyl-2-propyl)cyclohexyl 4-Methylbenzenesulfonate (12). To 4-methylbenzenesulfonyl chloride (13.35 g, 70.0 mmol) in pyridine (40 mL) at −10 °C was slowly added phenylmenthol (**11**)[10] (11.62 g, 50.0 mmol) in pyridine (10 mL). The mixture was stirred at −10 °C for 30 min and then for 40 h at 2 °C. Acidic (H_2SO_4) aqueous workup gave a thick yellow oil that was purified by flash chromatography (10% ether in hexanes) to provide colorless crystalline **12** (18.36 g, 95.4%): mp 76.5–77.5 °C; IR (neat) 2958, 1602, 1497, 1457, 1362, 1178, 918, 870, 704, 669 cm^{-1}; MS, m/z (relative intensity) 385 (4), 214 (71), 199 (65), 172 (82), 157 (38), 143 (81), 119 (89), 91 (100); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 8.3 Hz, 2 H), 7.28 (d, J = 8.3 Hz, 2 H), 7.08–7.22 (m, 5 H), 4.77 (ddd, J = 10.6, 10.6, 4.3 Hz, 1 H), 2.42 (s, 3 H), 2.18 (br d, J = 10.6 Hz, 1 H), 1.94 (ddd, J = 10.6, 10.2, 3.4 Hz, 1 H), 1.30–1.50 (m, 3 H), 1.35 (s, 3 H), 1.28 (s, 3 H), 1.16 (m, 1 H), 0.92 (dddd, J = 13.3, 13.0, 13.0, 3.1 Hz, 1 H), 0.81 (d, J = 6.3 Hz, 3 H), 0.70 (m, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 150.6, 144.1, 135.6, 129.5, 127.9, 127.4, 125.4, 125.1, 84.3, 51.3, 42.8, 40.1, 34.1, 31.6, 28.9, 27.3, 23.6, 21.6; $[\alpha]^{26}_D$ 5.48° (*c* 0.1465, ethanol). Anal. Calcd for $C_{23}H_{30}O_3S$: C, 71.48; H, 7.82. Found: C, 71.06; H, 7.90.

Attempted Synthesis of 6 from 12. Formation of (3*R*,6*R*)-6-Methyl-3-(2-phenyl-2-propyl)cyclohexene (14). A solution of cyclopentadienylsodium–dimethoxyethane (0.991 g, 3.00 mmol) in THF (5 mL) was added at 0 °C to a solution of **12** (0.865 g, 4.5 mmol) in THF (25 mL). The reaction mixture was heated at reflux for 6 h, cooled to room temperature, and worked up with acidic (NH_4Cl) water and the residue filtered through a flash silica column (hexanes) to afford a colorless liquid (0.537 g, 56%). ^{1}H NMR analysis showed this product to be approximately 90% pure **14**: IR (thin film) 2957, 1603, 1497, 1446, 1369, 1115, 1034, 766, 702 cm^{-1}; MS, m/z (relative intensity) 214 (M^+, 1), 199 (1), 119 (100), 105 (4), 95 (5), 91 (26), 79 (7); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10–7.40 (m, 5 H), 5.57 (m, 2 H), 2.49 (m, 1 H), 2.08 (m, 1 H), 1.85 (m, 1 H), 1.61 (m, 1 H), 1.44 (m, 1 H), 1.38 (s, 3 H), 1.35 (s, 3 H), 1.17 (m, 1 H), 0.99 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 149.7, 134.9, 128.1, 127.9 (2 C), 126.1 (2 C), 125.4, 46.7, 40.2, 32.4, 30.9, 25.2, 24.9, 24.8, 22.0. Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.34. Found: C, 89.68; H, 9.99.

(1*R*,2*S*,5*R*)-5-Methyl-2-(2-phenyl-2-propyl)cyclohexyl Methanesulfonate (13). To a solution of **11**[10] (4.64 g, 20.0 mmol) and triethylamine (3.03 g, 30.0 mmol) in dichloromethane (100 mL) at −10 °C was slowly addded methanesulfonyl chloride (3.44 g, 30.0 mmol) over 10 min. Aqueous workup gave crude **13** as a pale yellow oil (6.61 g, 96.7%): IR (thin film) 2956, 1603, 1499, 1447, 1338, 1178, 918, 707 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05–7.30 (m, 5 H), 4.65 (ddd, J = 10.5, 10.5, 3.5 Hz, 1 H), 2.43 (s, 3 H), 2.28 (m, 1 H), 2.04 (ddd, J = 10.5, 10.2, 3.4 Hz, 1 H), 1.60 (m, 3 H), 1.40 (m, 1 H), 1.37 (s, 3 H), 1.19 (s, 3 H), 1.10 (m, 1 H), 0.81 (d, J = 6.4 Hz, 3 H), 0.79 (m, 1 H). This thermally sensitive product was used without further purification in the next step.

Attempted Synthesis of 6 from 13. A solution of cyclopentadienylsodium–dimethoxyethane (1.40 g, 3.62 mmol) in THF (5 mL) was added at 0 °C to a solution of **13** (1.00 g, 5.20 mmol) in THF (15 mL). The reaction mixture was heated at reflux for 6 h. Aqueous workup yielded **14** (0.492 g, 63.4%) as a colorless liquid.

(1*R*,3*R*,4*R*)-3-[(Methoxycarbonyl)methyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (16). To butyllithium (284 mL, 1.55 M in hexane, 440 mmol) in dry THF (500 mL) at −78 °C was added dropwise over 10 min distilled diisopropylamine (44.5 g, 440 mmol). After having been stirred for 15 min while the temperature was allowed to rise slightly, the solution was cooled to −78 °C and (+)-camphor (**15**) (60.88 g, 400 mmol) in THF (80 mL) was added via cannula over 30 min. After 15 min, HMPA (78.8 g, 440 mmol) and, after an additional 30 min, methyl bromoacetate (122.3 g, 800 mmol) were added via cannula as rapidly as possible (about 30 s). The solution turned yellow while it was stirred for 30 min at −78 °C. After having been warmed to room temperature over 1 h, the mixture was subjected to basic ($NaHCO_3$) aqueous workup and the resulting liquid fractionally distilled under vacuum to yield first recovered camphor (**15**) (12.3 g) and then **16** as a colorless liquid (54.74 g, 61.0%, 71.6% based on recovered camphor): bp 108–112 °C (0.05 mm): IR (thin film) 2962, 1740, 1439, 1394, 1317, 1284, 1273, 1235, 1198, 1173, 1117, 1087, 1021, 1006 cm^{-1}; MS, m/z (relative intensity) 224 (M^+, 25), 192 (47), 157 (20), 150 (26), 121 (30), 108 (52), 95 (95), 83 (100), 69 (57), 55 (50); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.70 (s, 3 H), 2.83 (dd, J = 16.0, 3.3 Hz, 1 H), 2.45 (dd, J = 9.9, 3.3 Hz, 1 H), 2.32 (dd, J = 16.0, 9.9 Hz, 1 H), 2.04 (m, 1 H), 1.97 (br d, J = 3.1 Hz, 1 H), 1.65 (m, 1 H), 1.52 (m, 2 H), 0.94 (s, 3 H), 0.91 (s, 3 H), 0.82 (3 H); ^{13}C NMR (50.8 MHz, $CDCl_3$) δ 219.3, 172.8, 57.0, 51.6, 49.9, 47.5, 46.5, 35.5, 28.8 (2 C), 21.2, 20.1, 9.2; $[\alpha]^{26}_D$ 33.3° (*c* 0.261, hexane). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.36; H, 8.78.

(1*R*,3*S*,4*R*)-3-[(Methoxycarbonyl)methyl]-1,7,7-tri-

methylbicyclo[2.2.1]heptan-2-one (17). To sodium (0.092 g, 4.00 mmol) dissolved in methanol (5 mL) under nitrogen was added **16** (0.224 g, 1.00 mmol) in methanol (1 mL) via syringe. This mixture was stirred overnight at room temperature. Aqueous acidic (HCl) workup resulted in **17** as a colorless oil (0.192 g, 86%): IR (thin film) 2962, 1741, 1439, 1312, 1275, 1234, 1170, 1047 cm^{-1}; MS, m/z (relative intensity) 224 (M^+, 26), 192 (43), 181 (13), 150 (25), 108 (56), 95 (100), 83 (76), 55 (69); ^1H NMR (300 MHz, $CDCl_3$) δ 3.62 (s, 3 H), 2.83 (ddd, J = 10.2, 5.0, 4.4 Hz, 1 H), 2.68 (dd, J = 16.3, 5.0 Hz, 1 H), 2.18 (dd, J = 16.3, 10.2 Hz, 1 H), 2.10 (dd, J = 4.4, 4.4 Hz, 1 H), 1.70 (m, 1 H), 1.65 (m, 1 H), 1.42 (ddd, J = 11, 11, 3.4 Hz, 1 H), 1.17 (m, 1 H), 0.94 (s, 3 H), 0.87 (s, 3 H), 0.85 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 218.5, 172.1, 57.9, 51.2, 46.1, 46.0, 45.4, 31.2, 30.6, 19.8, 19.1, 18.8, 9.0. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.34; H, 8.99.

(1*R*,3*S*,4*R*)-3-[3-(Dimethylphosphono)-2-oxoprop-1-yl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (18). To dimethyl methylphosphonate (0.992 g, 8.00 mmol) in THF (20 mL) at −78 °C was slowly added butyllithium (5.59 mL, 1.43 M in hexane, 8.00 mmol) via syringe. After the solution had been stirred for 30 min, **16** (0.90 g, 4.01 mmol) in THF (5 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature, stirred for 1 h, and worked up with water and the resulting oil (1.05 g, 83.0%) purified by flash chromatography (20% methanol in ethyl acetate) to yield **18** as a colorless oil (0.78 g, 61.3%): IR (thin film) 2961, 1740, 1723, 1261, 1189, 1035, 817 cm^{-1}; MS, m/z (relative intensity) 316 (M^+, 10), 288 (31), 255 (10), 205 (28), 151 (64), 124 (100), 109 (67), 55 (75); HRMS calculated for $C_{15}H_{25}O_5P$, 316.1439, found, 316.1441; ^1H NMR (200 MHz, $CDCl_3$) δ 3.80 (d, J = 11.2 Hz, 3 H), 3.79 (d, J = 11.2 Hz, 3 H), 2.9–3.2 (m, 4 H), 2.70 (dd, J = 19.0, 9.0 Hz, 1 H), 2.19 (br s, 1 H), 1.55–1.9 (m, 2 H), 1.43 (m, 1 H), 1.23 (m, 1 H), 1.00 (s, 3 H), 0.93 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR (63.1 MHz, $CDCl_3$) δ 219.8, 199.7 (d, J = 7.0 Hz), 57.9, 52.6 (d, J = 7.0 Hz), 52.5 (d, J = 7.0 Hz), 46.0, 45.6, 44.9, 40.9, 40.0 (d, J = 40.0 Hz), 30.6, 19.8, 19.1, 18.7, 9.0.

(1*R*,6*S*,7*R*)-1,10,10-Trimethyltricyclo[5.2.1.0^{2,6}]dec-2-en-4-one (19). Method A. To sodium hydride (0.660 g, 60%, 16.50 mmol) washed with pentane (3 × 5 mL) in THF (40 mL) was added at room temperature **18** (4.745 g, 15.00 mmol) in THF (10 mL) via syringe under nitrogen. Gas evolution was quite vigorous for about 10 min as the solution turned red. After having been heated to reflux for 18 h, the reaction was quenched with excess saturated aqueous $NaHSO_4$ and the resulting product purified by flash chromatography (25% ethyl acetate in pentane) to afford pure **19** as a colorless oil (2.11 g, 73.9%): IR (thin film) 2961, 1701, 1608, 1475, 1391, 1162, 1137, 842, 810, 702 cm^{-1}; MS, m/z (relative intensity) 190 (M^+, 57), 175 (18), 147 (90), 133 (39), 119 (89), 105 (36), 91 (68), 77 (49), 69 (47), 55 (48); HRMS calculated for $C_{13}H_{18}O$, 190.1358, found, 190.1353; ^1H NMR (250 MHz, $CDCl_3$) δ 5.81 (d, J = 2.5 Hz, 1 H), 3.36 (br s, 1 H), 2.48 (dd, J = 16.6, 5.9 Hz, 1 H), 2.24 (dd, J = 16.6, 4.6 Hz, 1 H), 1.98 (br dd, J = 4, 3.9 Hz, 1 H), 1.87 (m, 1 H), 1.68 (m, 1 H), 1.20 (m, 2 H), 1.19 (s, 3 H), 1.02 (s, 6 H). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.24; H, 9.50.

Method B. To dimethyl methylphosphonate (54.60 g, 440 mmol) in diglyme (600 mL, freshly distilled under vacuum from $LiAlH_4$) at −78 °C was added butyllithium (314 mL, 1.40 M in hexane, 440 mmol). After the solution had been stirred at −78 °C for 1.5 h, **16** (47.7 g, 200.0 mmol) in diglyme (50 mL) was added via cannula. The reaction mixture was stirred for 2 h at −78 °C, warmed to room temperature, heated to distill off the hexane, and subsequently stirred for another 18 h. Aqueous acidic (HCl) workup followed by flash chromatography of the resulting orange liquid (30% ethyl acetate in pentane) gave a 1:1 epimeric mixture of **19** as a clear oil (19.47 g, 51.2%), used as such in the subsequent step.

(1*R*,7*S*)-1,10,10-Trimethyltricyclo[5.2.1.0^{2,6}]deca-2,5-diene (4) and (1*R*,4*S*,7*R*)-1,10,10-Trimethyltricyclo[5.2.1.0^{2,6}]dec-2-en-4-ol (20). To $LiAlH_4$ (0.190 g, 5.00 mmol) in ether (20 mL) was added **19** (0.951 g, 5.00 mmol) in ether (5 mL) dropwise under nitrogen. The reaction mixture was stirred 30 min at room temperature, water added dropwise to quench the excess hydride, and then aqueous 1 N HCl added to neutralize the solution. The layers were separated and the aqueous portion extracted with ether (3 × 10 mL). Benzene (50 mL) and 4-methylbenzenesulfonic acid (0.019 g, 0.10 mmol) were added to the combined organic portions that were then stirred overnight at room temperature. The acid was neutralized with K_2CO_3 and the solution dried with $MgSO_4$. The solvent was removed by rotary evaporation and the resulting oil (0.870 g) passed through a short activity 3 alumina column with pentane to yield **4** as a colorless oil (0.714 g, 81.9%): IR (thin film) 2957, 1442, 1383, 1156, 893, 759 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.66 (br s, 1 H), 5.60 (s, 1 H), 3.14 (d, J = 23.0 Hz, 1 H), 3.02 (d, J = 23.0 Hz, 1 H), 2.47 (d, J = 3.5 Hz, 1 H), 1.99 (dddd, J = 11.2, 11.0, 3.8, 3.5 Hz, 1 H), 1.77 (ddd, J = 11.0, 10.5, 2.6 Hz, 1 H), 1.36 (ddd, J = 11.2, 9.6, 2.6 Hz, 1 H), 1.27 (ddd, J = 10.5, 9.6, 3.8 Hz, 1 H), 1.11 (s, 3 H), 0.94 (s, 3 H), 0.67 (s, 3 H); ^{13}C NMR (63.1 MHz, $CDCl_3$) δ 159.4, 154.5, 114.9, 113.5, 54.3, 49.1, 48.3, 44.25, 34.6, 26.9, 20.6, 18.2, 11.9; $[\alpha]^{26}_D$ 5.8° (c 0.376, hexane). The ^1H NMR spectrum of this product matched that reported[13] at lower field (60 MHz).

The intermediate allylic alcohol **20** could be obtained as a clear oil by drying and removing the solvent after the reduction. It was noted that it was unstable and a higher yield of **4** could be obtained without isolation of **20**: ^1H NMR (250 MHz, $CDCl_3$) δ 5.27 (d, J = 3.0 Hz, 1 H), 5.08 (m, 1 H), 2.95 (m, 1 H), 2.86 (br s, 1 H), 2.27 (ddd, J = 11.0, 6.1, 6.1 Hz, 1 H), 1.70 (m, 2 H), 1.50 (m, 1 H), 1.20–1.40 (m, 3 H), 1.01 (s, 3 H), 0.97 (s, 3 H), 0.95 (s, 3 H); ^{13}C NMR (63.1 MHz, $CDCl_3$) δ 165.9, 119.8, 81.7, 52.6, 50.4, 50.2, 47.7, 40.7, 40.4, 20.6, 19.8, 19.5, 11.8.

(3*S*,4*S*)-3,4-(Dimethylmethylenedioxy)bicyclo[4.3.0]-nona-6,9-diene (5). To sodium hydride (1.76 g, 60%, 44.0 mmol) washed with pentane (3 × 10 mL) in THF (70 mL) was added freshly distilled cyclopentadiene (1.32 g, 20.0 mmol) at room temperature. Gas vigorously evolved for about 2 min. After this mixture had been stirred another 10 min, **21**[20] (10.33 g, 21.9 mmol) in THF (30 mL) was added quickly via cannula. More gas evolved and the reaction solution which had turned brown stirred at room temperature for 8 h followed by heating at reflux for 2 h. Aqueous acidic (HCl) workup and subsequent flash chromatography (20% ether in pentane) yielded colorless crystalline **5** (1.20 g, 31.2%): mp 44.0–44.5 °C; IR (thin film) 2987, 2933, 2857, 1615, 1448, 1380, 1234, 1139, 1078, 857 cm^{-1}; MS, m/z (relative intensity) 192 (M^+, 34), 177 (19), 134 (25), 117 (100), 105 (68), 91 (51), 78 (45); ^1H NMR (250 MHz, $CDCl_3$) δ 6.32 (br s, 2 H), 3.77 (m, 2 H), 2.75–2.90 (m, 4 H), 2.40–2.55 (m, 2 H), 1.48 (s, 6 H); ^{13}C NMR (63.1 MHz, $CDCl_3$) δ 133.6, 132.3, 110.2, 78.3, 43.0, 30.1, 27.1; $[\alpha]^{26}_D$ 113.1° (c 0.275, 95% ethanol). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.75; H, 8.36.

{η^5-[(1*R*,2*R*,5*R*)-5-Methyl-2-(2-phenyl-2-propyl)cyclohex-1-yl]cyclopentadienyl}dicarbonylcobalt (23). A solution of **3** (1.402 g, 5.00 mmol) in 1,2-dichloroethane (10 mL) and cyclohexene (10 mL) was degassed by three freeze–pump–thaw cycles under high vacuum and added to $Co_2(CO)_8$ (1.394 g, 4.00 mmol) in a round-bottom flask equipped with a reflux condenser, and the mixture was heated at reflux under nitrogen for 16 h. The solvent was removed under vacuum and the oil taken up in degassed pentane. The product was purified by chromatography on activity 3 alumina under nitrogen with degassed solvents (pentane). A single red fraction was collected which afforded **23** as a red oil (1.255 g, 65.0%): IR (thin film) 2958, 2903, 2003, 1944, 1596, 1491, 1434, 1361, 1037, 796, 693 cm^{-1}; MS, m/z (relative intensity) 394 (M^+, 0.1), 366 (1), 338 (18), 119 (100), 105 (6), 95 (8), 91 (27), 84 (10), 81 (11); HRMS calcd for $C_{23}H_{27}CoO_2$, 394.1343, found, 394.1331; ^1H NMR (300 MHz, C_6D_6) δ 7.16 (m, 2 H), 7.03 (m, 3 H), 4.28 (br s, 3 H), 4.11 (br s, 1 H), 2.15 (br d, J = 10.5 Hz, 1 H), 1.85 (br dd, J = 11, 10.5 Hz, 1 H), 1.60 (m, 3 H), 1.28 (m, 2 H), 1.10 (s, 3 H), 1.05 (s, 3 H), 0.97 (d, J = 6.4 Hz, 3 H), 0.75–1.00 (m, 2 H); ^{13}C NMR (75.5 MHz, C_6D_6, DEPT) δ 151.8 (quat), 128.1 (CH), 126.0 (CH), 125.0 (CH), 118.9 (quat), 85.5 (CH), 83.3 (CH), 83.0 (CH), 80.6 (CH), 53.2 (CH), 51.6 (CH_2), 41.0 (quat), 38.8 (CH), 35.6 (CH_2), 33.6 (CH), 29.2 (CH_2), 28.1 (CH_3), 25.9 (CH_3), 22.3 (CH_3).

Bis{η^5-[(1*R*,2*R*,5*R*)-5-methyl-2-(2-phenyl-2-propyl)cyclohex-1-yl]cyclopentadienyl}dichlorotitanium (24). To **3** (1.402 g, 5.00 mmol) in THF (20 mL) at 0 °C was added butyllithium (3.44 mL, 1.6 M in hexane, 5.50 mmol) via syringe under nitrogen. After 30 min, $TiCl_3$ (0.424 g, 2.75 mmol), slurried in THF (5 mL), was added to the reaction solution, to be subsequently heated at reflux for 4 h. Concentrated HCl (1 mL) was added at −78 °C and the solution allowed to warm to room temperature over 1 h. Dichloromethane (20 mL) was added, and the mixture was ex-

tracted with water (2 × 4 mL) and with saturated aqueous $CaCl_2$ (1 × 4 mL) to give a red crystalline mass that was recrystallized from dichloromethane–ether to result in **24** as red crystals (0.772 g, 45.6%): mp 283–284 °C; IR (neat) 2978, 1601, 1496, 1443, 1376, 1264, 1110, 735 cm^{-1}; MS, *m/z* (relative intensity) 676 (M^+, 0.3), 641 (5), 570 (2), 397 (5), 362 (7), 280 (22), 161 (22), 141 (10), 119 (100), 115 (13), 105 (57), 91 (87), 79 (53); ^1H NMR (300 MHz, $CDCl_3$) δ 6.90–7.05 (m, 5 H), 6.20 (br s, 1 H), 6.10 (br s, 1 H), 6.03 (br s, 1 H), 5.58 (br s, 1 H), 2.65 (br dd, *J* = 10, 10 Hz, 1 H), 1.68–1.92 (m, 3 H), 1.18–1.43 (m, 3 H), 1.13 (s, 3 H), 1.07 (s, 3 H), 0.82–1.05 (m, 2 H), 0.81 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, DEPT) δ 151.2 (quat), 145.3 (quat), 127.6 (CH, 2 C), 127.1 (CH), 125.5 (CH, 2 C), 124.6 (CH), 123.1 (CH), 115.4 (CH), 108.9 (CH), 53.9 (CH), 43.7 (CH_2), 41.7 (CH), 40.6 (CH_3), 35.6 (CH_2), 32.2 (CH), 30.3 (quat), 28.7 (CH_2), 23.4 (CH_3), 22.4 (CH_3). Anal. Calcd for $C_{42}H_{54}Cl_2Ti$: C, 74.44; H, 8.03; Cl, 10.46. Found: C, 74.37; H, 8.00; Cl, 10.27.

Bis{η^5-(1*R*,7*S*)-1,10,10-trimethyltricyclo[5.2.1.0^{2,6}]dec-3,5-dien-2-yl}dichlorotitanium (26a). Into a solution of **4** (1.743 g, 10.00 mmol) in THF (15 mL) at 0 °C was injected butyllithium (7.86 mL, 1.4 M in hexane, 11.0 mmol) via syringe under nitrogen. After the solution had been stirred for 30 min, $TiCl_3$ (0.848 g, 5.5 mmol), slurried in THF (8 mL), was introduced into the reaction solution, to be heated at reflux for 4 h. After the solution had been cooled to 0 °C, concentrated HCl (1 mL) was added and the solution turned red as it was stirred for 10 min at 0 °C. Dichloromethane (20 mL) was added at room temperature, and the mixture was extracted with water (2 × 5 mL) and saturated aqueous $CaCl_2$ (1 × 5 mL) to give a thick red oil which crystallized in dichloromethane with added pentane to yield red crystals, mp 174–177 °C (0.448 g, 19.2%). ^1H NMR analysis of these crystals gave evidence of a 95:5 mixture of two isomers. Recrystallization by slow evaporation of a dichloromethane–isooctane solution gave deep red crystals of **26a** (0.258 g, 11.1%): mp 178–179 °C; IR (neat) 2958, 1481, 1455, 1391, 1374, 1080, 918, 771 cm^{-1}; MS, *m/z* (relative intensity) 429 (M^+ – Cl, 65), 394 (100), 347 (12), 293 (26), 290 (45), 256 (4), 173 (5); ^1H NMR (250 MHz, $CDCl_3$) δ 6.47 (d, *J* = 2.7 Hz, 2 H), 5.92 (dd, *J* = 2.7, 2.7 Hz, 1 H), 2.75 (d, *J* = 4.1 Hz, 1 H), 1.4–2.0 (m, 4 H), 1.23 (s, 3 H), 0.92 (s, 3 H), 0.27 (s, 3 H); ^{13}C NMR (50.8 MHz, $CDCl_3$) δ 158.5, 152.2, 122.1, 113.5, 113.0, 70.0, 54.2, 51.5, 32.2, 25.4, 21.0, 19.9, 12.8. Anal. Calcd for $C_{26}H_{34}Cl_2Ti$: C, 67.10; H, 7.36; Cl, 15.23. Found: C, 66.87; H, 7.38; Cl, 15.48. ^1H NMR analysis indicated that the isomeric purity of **26a** was at least 98%. The minor isomer, which was not purified, was assigned structure **27** because of the presence of six singlets in the methyl region of the ^1H NMR (250 MHz, $CDCl_3$) spectrum of crude material: δ 1.41, 1.25, 1.13, 0.93, 0.91, 0.85.

{η^5-(1*R*,7*S*)-1,10,10-Trimethyltricyclo[5.2.1.0^{2,6}]deca-3,5-dien-2-yl}dicarbonylcobalt (25). A solution of **4** (0.261 g, 1.50 mmol) in a mixture of 1,2-dichloroethane and 1-pentene (15 mL, 2:1) was degassed by three freeze–pump–thaw cycles and then added to $Co_2(CO)_8$ (0.283 g, 0.82 mmol). After the mixture had been heated at reflux under nitrogen for 40 h, a thick oil was obtained and purified by chromatography on activity 3 alumina (hexanes) under nitrogen to give **25** (3:1 mixture of diastereomers) as a red oil (0.240 g, 55.5%): IR (thin film) 2962, 2011, 1955, 1619, 1453 cm^{-1}; MS, *m/z* (relative intensity) 288 (M^+, 12), 260 (22), 232 (32), 188 (35), 159 (13), 131 (26), 129 (24), 115 (21); HRMS calcd for $C_{15}H_{17}CoO_2$, 288.0560, found, 288.0551; ^1H NMR (200 MHz, C_6D_6) for major isomer, δ 4.55 (br d, *J* = 2.1 Hz, 1 H), 4.50 (br d, *J* = 2.2 Hz, 1 H), 3.98 (dd, *J* = 2.2, 2.1 Hz, 1 H), 1.40–2.10 (m, 5 H), 0.86 (s, 3 H), 0.67 (s, 3 H), 0.42 (s, 3 H), for minor isomer, δ 4.54 (m, 1 H), 4.10 (m, 2 H), 1.40–2.25 (m, 5 H), 1.02 (s, 3 H), 0.65 (s, 3 H), 0.33 (s, 3 H).

Alternatively, **4** (0.523 g, 3.00 mmol) was deprotonated with butyllithium (1.94 mL, 1.55 M, 3.00 mmol) at 0 °C and then exposed to $ICo(CO)_4$ [generated by combining $Co_2(CO)_8$ (0.513 g, 1.50 mmol) and I_2 (0.380 g, 1.50 mmol) in hexane (0 °C, 1 h)]. After 16 h at room temperature, chromatography on activity 3 alumina (hexanes) under nitrogen afforded **25** (3:1 mixture of diastereomers) as a red oil (0.412 g, 47.6%). Attempted separation by reverse phase HPLC (two ODS 10 mm × 25 cm columns, 20% CH_2Cl_2 in CH_3CN) was unsuccessful.

{η^5-(3*S*,4*S*)-3,4-(Dimethylmethylenedioxy)bicyclo[4.3.0]-nona-6,8-dien-1-yl}dicarbonylcobalt (28). A solution of **5** (0.577 g, 3.0 mmol) in dichloromethane (10 mL) and 1-pentene (5 mL) was degassed by three freeze–pump–thaw cycles, added to $Co_2(CO)_8$ (0.855 g, 2.5 mmol) in a round-bottom flask equipped with a reflux condenser, and heated at reflux under nitrogen for 30 h, the solvent removed under vacuum, and the oil taken up in degassed pentane. The product was purified by activity 3 alumina chromatography under nitrogen with degassed solvents (20% ether in pentane). A single red fraction was collected which crystallized upon removal of the solvent under vacuum to provide **28** (0.394 g, 42.9%): mp 72–73 °C; IR (neat) 2989, 2928, 2859, 2024, 1960, 1449, 1381, 1236, 1142, 1087, 857 cm^{-1}; MS, *m/z* (relative intensity) 306 (M^+, 36), 278 (7), 250 (71), 208 (38), 192 (28), 164 (69), 162 (61), 138 (31), 115 (35), 105 (35), 91 (32), 59 (49); HRMS calcd for $C_{14}H_{15}CoO_4$, 306.0302, found, 306.0291; ^1H NMR (300 MHz, C_6D_6) δ 4.43 (dd, *J* = 2.6, 2.5 Hz, 1 H), 4.31 (m, 2 H), 4.08 (ddd, *J* = 10.5, 9.2, 5.1 Hz, 1 H), 3.32 (ddd, *J* = 10.3, 9.2, 7.0 Hz, 1 H), 2.65 (dd, *J* = 14.6, 5.1 Hz, 1 H), 2.54 (AB m, 2 H), 2.11 (dd, *J* = 14.6, 10.5 Hz, 1 H), 1.42 (s, 3 H), 1.40 (s, 3 H); ^{13}C NMR (75.5 MHz, C_6D_6, off-reson decoup) δ 206 (br s), 110.9 (s), 101.2 (s), 99.3 (s), 83.2 (d), 82.1 (d), 81.4 (d), 78.5 (d), 77.6 (d), 28.7 (t), 28.1 (t), 27.3 (q), 27.2 (q); $[\alpha]^{26}_D$ 70° (*c* 0.000 95, 95% ethanol).

A Typical Asymmetric Hydrogenation Catalyzed by 24. A solution of 2-phenyl-1-butene (**30**) (0.529 g, 4.00 mmol) and **24** (0.034 g, 0.05 mmol) in toluene (4 mL) was degassed by three freeze–pump–thaw cycles. The solution was placed under 1 atm of hydrogen and was stirred for 10 min at 20 °C. Butyllithium (0.090 mL, 1.62 M, 0.146 mmol) was added at room temperature causing the solution to turn dark slowly over 1 h. The uptake of hydrogen was slow, yet steady, until the reaction was complete after 40 h. Aqueous workup and distillation provided 2-phenylbutane (**31**) quantitatively as a clear liquid. The optical rotation of a sample purified by preparative GC indicated a 33% ee: $[\alpha]^{26}_D$ 7.33° (*c* 0.104, ethanol).

An analogous procedure was adopted for the asymmetric hydrogenations catalyzed by **26a**.

1-(Trimethylsilyl)-1,7-nonadiyne [32, R^1 = $Si(CH_3)_3$, R^2 = CH_3]. Butyllithium (1.50 mL, 1.80 M in hexane, 2.70 mmol) was added at −78 °C to a solution of 1-(trimethylsilyl)-1,7-octadiyne[26] (0.500 g, 2.60 mmol) in THF (10 mL). The solution was allowed to warm to 0 °C over 20 min and cooled to −78 °C and iodomethane (0.730 g, 5.14 mmol) added. After the mixture had been left standing at room temperature overnight, aqueous workup followed by Kugelrohr distillation yielded a colorless liquid (0.47 g, 87.8%): IR (thin film) 2956, 2179, 1448, 1332, 1252, 1019, 850, 763, 701 cm^{-1}; MS, *m/z* (relative intensity) 192 (M^+, 0.4), 177 (16), 135 (7), 117 (15), 109 (7), 97 (13), 83 (12), 73 (100), 59 (43); ^1H NMR (300 MHz, $CDCl_3$) δ 2.20 (t, *J* = 6.8 Hz, 2 H), 2.11 (m, 2 H), 1.74 (t, *J* = 2.5 Hz, 3 H), 1.55 (m, 4 H), 0.13 (s, 9 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 107.1, 84.5, 78.7, 75.6, 28.1, 27.7, 19.4, 18.2, 3.4, 0.1. Anal. Calcd for $C_{12}H_{20}Si$: C, 74.92; H, 10.48. Found: C, 74.74; H, 10.32.

1-(Trimethylsilyl)-1,7-decadiyne [32, R^1 = $Si(CH_3)_3$, R^2 = CH_3CH_2]. Butyllithium (2.75 mL, 1.60 M in hexane, 4.40 mmol) was added dropwise at −78 °C to a solution of 1,7-decadiyne (0.537 g, 4.00 mmol) in THF (10 mL). The solution was allowed to warm to 0 °C over 20 min and then cooled to −78 °C and chlorotrimethylsilane (0.869 g, 8.00 mmol) added. After the mixture had been left standing at room temperature overnight, aqueous workup and Kugelrohr distillation afforded a colorless liquid (0.809 g, 97.9%): IR (thin film) 2960, 2178, 1463, 1328, 1252, 1023, 844, 762, 700 cm^{-1}; MS, *m/z* (relative intensity) 206 (M^+, 1), 191 (10), 163 (8), 132 (16), 83 (12), 73 (100), 59 (54); ^1H NMR (300 MHz, $CDCl_3$) δ 2.21 (t, *J* = 6.8 Hz, 2 H), 2.14 (m, 4 H), 1.57 (m, 4 H), 1.11 (t, *J* = 7.4 Hz, 3 H), 0.12 (s, 9 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 107.2, 84.5, 81.9, 79.0, 28.2, 27.7, 19.4, 18.3, 14.3, 12.4, 0.2. Anal. Calcd for $C_{13}H_{22}Si$: C, 75.65; H, 10.75. Found: C, 75.87; H, 10.67.

Complexed Cyclopentadienones 33 [R^1 = $Si(CH_3)_3$, R^2 = H] Derived from 23. A solution of **23** (0.287 g, 0.74 mmol) and **32** [R^1 = $Si(CH_3)_3$, R^2 = H] (0.178 g, 1.00 mmol) in THF (50 mL) was irradiated for 6 h with a medium-pressure 450-W Hanovia mercury vapor lamp while being cooled by both a −20 °C bath circulating between the lamp and the reaction solution and a −30 °C external bath. The resulting red oil was purified by flash chromatography. Elution with ether removed excess diyne and the arene byproducts. Elution with 20% methanol in ether gave a red fraction whose ^1H NMR analysis showed a diastereomeric

mixture of products (0.217 g, 53.9%, ratio 52:48). These compounds were separable by flash chromatography with 10% methanol in ether to yield first the minor isomer (0.100 g) as a red oil: IR (thin film) 2958, 1597, 1251, 847, 768, 704 cm^{-1}; MS, m/z (relative intensity) 544 (M^+, 31), 471 (8), 425 (43), 338 (58), 214 (15), 205 (15), 119 (15), 111 (27), 97 (42), 91 (13), 83 (42), 73 (16), 71 (59), 57 (100); HRMS calcd for $C_{33}H_{45}CoOSi$, 544.2571, found, 544.2578; ^1H NMR (300 MHz, C_6D_6) δ 7.08 (m, 2 H), 6.99 (m, 3 H), 4.87 (br s, 1 H), 4.18 (br s, 1 H), 4.01 (s, 1 H), 3.83 (br s, 1 H), 3.64 (br s, 1 H), 2.84 (br d, J = 12.6 Hz, 1 H), 2.40–2.79 (m, 2 H), 2.05–2.30 (m, 3 H), 1.95 (m, 1 H), 1.45–1.90 (m, 7 H), 1.30–1.40 (m, 2 H), 1.26 (d, J = 6.4 Hz, 3 H), 1.15 (m, 1 H), 1.08 (s, 3 H), 1.02 (s, 3 H), 0.47 (s, 9 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 166.2, 151.7, 128.2, 125.9, 125.0, 111.3, 96.6, 94.3, 81.1, 80.5, 79.4, 79.2, 64.2, 62.5, 54.6, 44.2, 40.8, 40.4, 36.1, 33.7, 29.6, 28.8, 28.7, 25.3, 24.2, 23.4, 22.9, 22.2, 0.3. Anal. Calcd for $C_{33}H_{45}CoOSi$: C, 72.76; H, 8.33. Found: C, 72.98; H, 8.52.

The subsequent major isomer (0.109 g) was also obtained as a red oil: IR (thin film) 2961, 1597, 1450, 1374, 1251, 848, 768, 705 cm^{-1}; MS, m/z (relative intensity) 544 (M^+, 51), 471 (16), 425 (85), 338 (100), 214 (29), 203 (14), 119 (14), 97 (15), 83 (17), 71 (23), 57 (35); HRMS calcd for $C_{33}H_{45}CoOSi$, 544.2571, found, 544.2573; ^1H NMR (300 MHz, C_6D_6) δ 7.07 (m, 2 H), 6.99 (m, 3 H), 4.82 (br s, 1 H), 4.08 (s, 1 H), 3.98 (br s, 1 H), 3.73 (br s, 1 H), 3.50 (br s, 1 H), 2.90 (br dd, J = 12.8, 2.2 Hz, 1 H), 2.45 (ddd, J = 12.8, 12.5, 2.7 Hz, 1 H), 1.98–2.23 (m, 2 H), 1.78–1.95 (m, 2 H), 1.71 (m, 3 H), 1.40–1.70 (m, 5 H), 1.27–1.38 (m, 2 H), 1.22 (d, J = 6.4 Hz, 3 H), 1.10 (m, 1 H), 1.09 (s, 3 H), 1.03 (s, 3 H), 0.47 (s, 9 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 166.3, 152.0, 128.1, 126.0, 124.8, 111.3, 96.5, 94.2, 82.7, 80.7, 78.2, 78.0, 62.9, 62.8, 54.1, 44.3, 40.8, 39.5, 36.1, 33.5, 29.4, 29.1, 25.4, 25.0, 24.3, 23.4, 22.9, 22.4, 0.2. Anal. Calcd for $C_{33}H_{45}CoOSi$: C, 72.76; H, 8.33. Found: C, 73.34; H, 8.41.

Complexed Cyclopentadienones 33 [R^1 = $Si(CH_3)_3$, R^2 = CH_3] Derived from 23. A solution of **23** (0.065 g, 0.17 mmol) and **32** [R^1 = $Si(CH_3)_3$, R^2 = CH_3] (0.047 g, 0.22 mmol) in THF (50 mL) was treated as described above to give a diastereomeric mixture of products as a red oil (0.060 g, 63.8%, ratio 67:33). Separation by flash chromatography (5% methanol in ether) produced a minor isomer first (0.018 g) as a red oil: IR (thin film) 2958, 1594, 1448, 1249, 853, 767, 705 cm^{-1}; MS, m/z (relative intensity) 558 (M^+, 96), 485 (15), 439 (58), 338 (100), 214 (30), 203 (13), 138 (10), 124 (11), 119 (17), 57 (14); HRMS calcd for $C_{34}H_{47}CoOSi$, 558.2728, found 558.2734; ^1H NMR (300 MHz, C_6D_6) δ 6.95–7.15 (m, 5 H), 4.82 (br s, 1 H), 3.75 (br s, 1 H), 3.69 (br s, 1 H), 3.62 (br s, 1 H), 3.06 (br dd, J = 13.3, 2.3 Hz, 1 H), 2.26 (ddd, J = 9.9, 9.7, 2.2 Hz, 1 H), 2.17 (ddd, J = 16.6, 7.3, 6.5 Hz, 1 H), 1.82–2.05 (m, 2 H), 1.72–1.82 (m, 4 H), 1.69 (m, 1 H), 1.50–1.62 (m, 3 H), 1.45 (s, 3 H), 1.36 (d, J = 6.4 Hz, 3 H), 1.30–1.40 (m, 3 H), 1.14 (m, 1 H), 1.12 (s, 3 H), 1.06 (s, 3 H), 0.44 (s, 9 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 166.2, 151.9, 128.0, 126.9, 124.9, 110.1, 94.2, 93.4, 81.3, 81.2, 80.2, 78.0, 74.8, 61.1, 55.1, 42.6, 40.8, 40.1, 36.4, 34.2, 29.8, 28.4, 25.5, 25.2, 23.4, 22.9, 22.7, 22.1, 9.3, 0.3.

The second fraction contained the major isomer (0.037 g), also as a red oil: IR (thin film) 2960, 1594, 1451, 1248, 853, 839, 767, 707 cm^{-1}; MS, m/z (relative intensity) 558 (M^+, 100), 485 (13), 439 (50), 338 (76), 214 (19), 119 (19), 109 (27), 105 (13), 83 (39), 71 (48.3), 57 (81); HRMS calcd for $C_{34}H_{47}CoOSi$, 558.2728, found 558.2732; ^1H NMR (300 MHz, C_6D_6) δ 6.95–7.15 (m, 5 H), 4.60 (br s, 1 H), 3.83 (br s, 1 H), 3.44 (br s, 2 H), 3.18 (br dd, J = 12.9, 2.3 Hz, 1 H), 2.55 (ddd, J = 9.9, 9.7, 2.4 Hz, 1 H), 2.18 (ddd, J = 16.8, 7.2, 6.5 Hz, 1 H), 1.80–2.00 (m, 3 H), 1.60–1.80 (m, 5 H), 1.52 (m, 2 H), 1.49 (s, 3 H), 1.35 (d, J = 6.4 Hz, 3 H), 1.30 (m, 3 H), 1.13 (m, 1 H), 1.12 (s, 3 H), 1.07 (s, 3 H), 0.48 (s, 9 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 166.0, 152.1, 128.3, 126.0, 124.8, 109.4, 94.1, 93.7, 81.6, 81.0, 80.4, 79.0, 76.1, 60.0, 54.8, 42.3, 40.7, 40.4, 36.3, 33.8, 29.6, 28.5, 25.6, 25.3, 23.3, 23.2, 22.7, 22.1, 9.9, 0.2.

Complexed Cyclopentadienones 33 [R^1 = $Si(CH_3)_3$, R^2 = CH_3CH_2] Derived from 23. A solution of **23** (0.090 g, 0.23 mmol) and **32** [R^1 = $Si(CH_3)_3$, R^2 = CH_3CH_2] (0.062 g, 0.30 mmol) in THF (50 mL) was treated as described above to provide a diastereomeric mixture of products as a red oil (0.097 g, 73.6%, ratio 60:40). Separation by flash chromatography (5% methanol in ether) gave first the minor component (0.033 g) as a red oil: IR (thin film) 2958, 1588, 1448, 1249, 839, 741, 703 cm^{-1}; MS, m/z (relative intensity) 572 (M^+, 68), 557 (3), 499 (13), 453 (37), 338 (60), 216 (13), 214 (18), 119 (7), 57 (13), 43 (100) HRMS calcd for $C_{35}H_{49}CoOSi$, 572.2885, found, 572.2885; ^1H NMR (300 MHz, C_6D_6) δ 6.97–7.14 (m, 5 H), 4.58 (br d, J = 1.7 Hz, 1 H), 4.04 (br d, J = 1.7 Hz, 1 H), 3.44 (br s, 2 H), 3.18 (br d, J = 12.6 Hz, 1 H), 2.60 (m, 2 H), 2.21 (m, 1 H), 1.85–2.05 (m, 3 H), 1.70 (m, 6 H), 1.55 (m, 3 H), 1.42 (m, 1 H), 1.34 (d, J = 6.4 Hz, 3 H), 1.18 (m, 1 H), 1.12 (s, 3 H), 1.11 (m, 4 H), 1.07 (s, 3 H), 0.48 (s, 9 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 165.8, 152.1, 127.9, 126.0, 124.8, 109.5, 93.9, 93.7, 81.0, 80.9, 80.4, 80.3, 79.9, 54.9, 42.2, 40.7, 40.5, 36.3, 33.8, 29.7, 28.4, 25.6, 25.3, 23.5, 23.3, 22.8, 22.1, 18.8, 13.0, 0.2. Anal. Calcd for $C_{35}H_{49}CoOSi$: C, 73.39; H, 8.62. Found: C, 74.51; H, 8.63.

The second fraction contained the major isomer (0.053 g) as a red oil: IR (thin film) 2959, 1590, 1448, 1250, 838, 767, 738, 703 cm^{-1}; MS, m/z (relative intensity) 572 (M^+, 12), 499 (2), 453 (9), 338 (16), 214 (4), 179 (6), 71 (13), 57 (24), 43 (100); HRMS calcd for $C_{35}H_{49}CoOSi$, 572.2885, found, 572.2882; ^1H NMR (300 MHz, C_6D_6) δ 6.95–7.15 (m, 5 H), 4.82 (br s, 1 H), 3.76 (br s, 1 H), 3.72 (br s, 1 H), 3.63 (br s, 1 H), 3.06 (br d, J = 13.5 Hz, 1 H), 2.43 (m, 1 H), 2.34 (br dd, J = 10.3, 10.3 Hz, 1 H), 2.17 (m, 1 H), 1.85–2.10 (m, 3 H), 1.65–1.85 (m, 6 H), 1.36 (m, 1 H), 1.34 (d, J = 6.4 Hz, 3 H), 1.17 (m, 5 H), 1.13 (s, 3 H), 1.08 (s, 3 H), 0.43 (s, 9 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 165.8, 151.9, 128.0, 125.9, 124.9, 110.0, 94.5, 93.0, 81.2, 80.9, 80.2, 79.9, 78.5, 65.9, 55.2, 42.4, 40.8, 40.4, 36.3, 34.0, 29.8, 28.5, 25.5, 25.2, 23.3, 23.0, 22.7, 22.1, 18.5, 13.0, 0.4.

Complexed Cyclopentadienones 33 [R^1 = CH_3, R^2 = H) Derived from 23. A solution of **23** (0.076 g, 0.20 mmol) and **32** (R^1 = CH_3, R^2 = H) (0.096 g, 0.80 mmol) in THF (50 mL) was treated as described above to furnish an inseparable diastereomeric mixture of products as a red oil (0.052 g, 53.5%, ratio 61:39): IR (thin film) 2958, 1483, 1449, 1268, 1033, 808, 705 cm^{-1}; MS, m/z (relative intensity) 486 (M^+, 71), 471 (6), 367 (100), 338 (92), 216 (15), 214 (26), 177 (11), 151 (12), 138 (10), 119 (29), 105 (13), 91 (26), 69 (22), 57 (39); HRMS calcd for $C_{31}H_{39}CoO$, 486.2332, found, 486.2338; ^1H NMR (300 MHz, C_6D_6) for major isomer, δ 6.97–7.12 (m, 5 H), 4.39 (br s, 1 H), 4.23 (br s, 1 H), 4.21 (s, 1 H), 3.88 (br s, 1 H), 3.57 (br s, 1 H), 2.70 (m, 1 H), 2.25 (m, 2 H), 1.90–2.10 (m, 2 H), 1.70 (m, 5 H), 1.63 (s, 3 H), 1.50 (m, 3 H), 1.30 (m, 3 H), 1.26 (d, J = 6.4 Hz, 3 H), 1.15 (m, 1 H), 1.10 (s, 3 H), 1.02 (s, 3 H), for minor isomer, δ 6.97–7.12 (m, 5 H), 4.53 (br s, 1 H), 4.21 (s, 1 H), 3.98 (br s, 1 H), 3.72 (br s, 1 H), 3.55 (br s, 1 H), 2.70 (m, 1 H), 2.39 (m, 1 H), 2.25 (m, 1 H), 1.90–2.10 (m, 2 H), 1.70 (m, 5 H), 1.65 (s, 3 H), 1.50 (m, 3 H), 1.30 (m, 3 H), 1.19 (d, J = 6.4 Hz, 3 H), 1.17 (s, 3 H), 1.15 (m, 1 H), 1.08 (s, 3 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 157.7 (br), 152.0, 151.8, 128, 126.0, 125.9, 124.9, 124.8, 111.5, 110.3, 91.3, 89.1, 85.9, 83.0, 81.9, 81.8, 81.7, 80.6, 80.5, 78.9, 78.3, 61.4, 60.7, 60.6, 53.9, 50.1, 45.8, 44.6, 40.9, 40.8, 39.3, 38.6, 36.0, 35.9, 33.6, 33.3, 29.5, 29.3, 28.9, 28.4, 25.4, 24.9, 23.7, 23.5, 23.1, 22.9, 22.6, 22.5, 22.4, 22.3, 22.1, 9.7, 9.6.

Complexed Cyclopentadienones 33 (R^1 = CH_3CH_2, R^2 = H) Derived from 23. A solution of **23** (0.182 g, 0.47 mmol) and **39** (0.080 g, 0.60 mmol) in THF (50 mL) was treated as described above to give an inseparable diastereomeric mixture of products as a red oil (0.059 g, 54%, ratio 56:44): IR (thin film) 2954, 1602, 1455, 819, 768, 707 cm^{-1}; MS, m/z (relative intensity) 500 (M^+, 55), 471 (10), 381 (100), 353 (13), 338 (80), 214 (27), 203 (14), 177 (12), 167 (10), 137 (13), 119 (20), 105 (14), 91 (24), 83 (22), 71 (32), 57 (60); HRMS calcd for $C_{32}H_{41}CoO$, 500.2489, found, 500.2488; ^1H NMR (300 MHz, C_6D_6) for major isomer, δ 6.95–7.12 (m, 5 H), 4.48 (br s, 1 H), 4.07 (s, 1 H), 4.01 (br s, 1 H), 3.70 (br s, 1 H), 3.56 (br s, 1 H), 2.55–2.82 (m, 2 H), 2.31 (m, 1 H), 1.95–2.25 (m, 2 H), 1.45–1.90 (m, 10 H), 1.35 (m, 2 H), 1.18 (m, 7 H), 1.08 (s, 3 H), 1.05 (m, 1 H), 101 (s, 3 H), for minor isomer, δ 6.95–7.12 (m, 5 H), 4.48 (br s, 1 H), 4.11 (br s, 1 H), 4.05 (s, 1 H), 3.87 (br s, 1 H), 3.57 (br s, 1 H), 2.55–2.82 (m, 2 H), 1.95–2.25 (m, 3 H), 1.45–1.90 (m, 10 H), 1.35 (m, 2 H), 1.18 (m, 7 H), 1.08 (s, 3 H), 1.05 (m, 1 H), 0.98 (s, 3 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 159.2, 159.1, 152.0, 151.8, 127.9, 126.0, 125.9, 124.9, 124.8, 111.2, 110.2, 90.9, 89.3, 89.2, 84.9, 81.8, 81.4, 81.3, 81.2, 80.5, 80.3, 79.4, 79.0, 78.1, 61.1, 60.4, 54.1, 53.9, 50.0, 45.2, 44.4, 40.8, 40.0, 39.0, 36.0, 35.9, 33.6, 33.4, 29.5, 29.4, 28.6, 28.2, 25.5, 25.1, 23.8, 23.6, 23.1, 23.0, 22.9, 22.7, 22.6, 22.5, 22.3, 18.7, 18.6, 13.3, 13.2.

Complexed Cyclopentadienones 33 [R^1 = $Si(CH_3)$, R^2 = CH_3CH_2] Derived from 28. A solution of **28** (0.061 g, 0.20 mmol) and **32** [R^1 = $Si(CH_3)_3$, R^2 = CH_3CH_2] (0.070 g, 0.27 mmol) in

THF was treated as described above to give an inseparable diastereomeric mixture of products as a red oil (0.075 g, 69.4%, ratio 50:50): IR (thin film) 2993, 1649, 1545, 1449, 1242, 1083, 850 cm^{-1}; MS, m/z (relative intensity) 470 (M^+, 12), 455 (7), 412 (100), 395 (21), 384 (15), 339 (53), 311 (21); ^1H NMR (300 MHz, C_6D_6) δ 4.44 (br s, 2 H), 4.25 (m, 1 H), 4.22 (m, 1 H), 4.00 (br s, 1 H), 3.81 (br s, 1 H), 3.50 (br s, 2 H), 3.45 (m, 2 H), 3.16 (dd, J = 14.5, 5.0 Hz, 1 H), 2.98 (dd, J = 14.0, 13.0 Hz, 1 H), 2.63 (dd, J = 14.5, 5.0 Hz, 1 H), 2.47 (m, 3 H), 2.29 (dd, J = 14.5, 12.0 Hz, 1 H), 2.12 (m, 5 H), 1.85 (m, 8 H), 1.74 (s, 3 H), 1.68 (s, 3 H), 1.61 (m, 4 H), 1.51 (br s, 6 H), 1.38 (s, 3 H), 1.34 (s, 3 H), 0.42 (s, 9 H), 0.38 (s, 3 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 111.2, 111.1, 104.3, 96.5, 95.5, 95.3, 94.9, 94.2, 81.8, 81.6, 79.3, 78.7, 78.6, 78.4, 78.2, 78.1, 76.9, 76.8, 30.1, 27.6, 27.5, 27.3, 27.0, 26.5, 25.1, 24.8, 24.7, 24.6, 23.4, 23.3, 22.8, 22.6, 22.5, 22.2, 15.8, 7.6, 6.9, 0.3, 0.2.

Diene Complexes 35. A solution of **23** (0.153 g, 0.62 mmol) in toluene (5 mL) was degassed by three freeze–pump–thaw cycles and then added under nitrogen to **34** (0.215 g, 0.56 mmol) in a 15-mL round-bottom flask equipped with a reflux condenser. The mixture was heated at reflux and irradiated by a projector lamp (GE-ENH 250 W) for 10 h. The solvent was removed under vacuum and the residue filtered through activity 3 alumina with pentane to provide an inseparable mixture of two isomers of **35** (0.285 g, 87.3%, ratio 58:42) as a red oil (0.143 g, 69.4%): IR (thin film) 2961, 1604, 1501, 1452, 1253, 838, 707 cm^{-1}; MS, m/z (relative intensity) 584 (M^+, 9), 511 (6), 369 (17), 338 (29), 280 (8), 229 (13), 214 (3), 169 (8), 119 (25), 105 (10), 97 (17), 83 (20), 71 (30), 57 (100); HRMS calcd for $C_{37}H_{53}CoSi$, 584.3248, found, 584.3266; ^1H NMR (300 MHz, C_6D_6) for major isomer, δ 7.05–7.23 (m, 5 H), 4.87 (br s, 1 H), 3.86 (br s, 1 H), 3.61 (br s, 2 H), 2.78 (m, 1 H), 2.40–2.52 (m, 2 H), 2.33 (m, 3 H), 1.87–2.18 (m, 4 H), 1.40–1.85 (m, 12 H), 1.31 (s, 3 H), 1.11 (d, J = 6.1 Hz, 3 H), 1.10 (s, 3 H), 0.85–1.0 (m, 2 H), 0.40–0.55 (m, 2 H), 0.29 (s, 9 H), for minor isomer, δ 7.05–7.23 (m, 5 H), 4.29 (br s, 1 H), 4.27 (br s, 1 H), 4.08 (br s, 1 H), 3.97 (br s, 1 H), 2.97 (m, 1 H), 2.40–2.52 (m, 2 H), 2.33 (m, 3 H), 1.87–2.18 (m, 4 H), 1.40–1.85 (m, 12 H), 1.28 (s, 3 H), 1.07 (d, J = 6.0 Hz, 3 H), 1.03 (s, 3 H), 0.85–1.0 (m, 2 H), 0.40–0.55 (m, 2 H), 0.30 (s, 9 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 152.6, 128.2, 125.9, 125.1, 125.0, 111.9, 108.7, 93.9, 87.4, 83.0, 81.2, 80.1, 79.4, 78.7, 78.6, 56.0, 55.7, 49.1, 48.1, 41.4, 40.8, 40.6, 40.0, 39.9, 36.3, 36.1, 36.0, 35.9, 34.8, 34.1, 34.0, 33.8, 33.7, 32.9, 30.5, 30.4, 29.9, 29.4, 29.3, 29.1, 28.0, 27.6, 24.9, 24.4, 24.2, 24.1, 24.0, 23.6, 23.2, 22.9, 22.5, 22.3, 0.8, 0.7.

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Registry No. **3**, 112505-23-4; **4**, 59581-87-2; **5**, 106509-11-9; **7**, 97371-54-5; **8**, 104870-75-9; **10**, 112505-24-5; **11**, 65253-04-5; **12**, 112505-25-6; **13**, 112505-26-7; **14**, 112505-27-8; **15**, 464-49-3; **16**, 106509-10-8; **17**, 106566-51-2; **18**, 112505-28-9; **19**, 112505-29-0; **20**, 112505-30-3; **21**, 37002-45-2; **22**, 112572-77-7; **23**, 112505-34-7; **24**, 112505-35-8; **25a**, 106564-05-0; **26a**, 106564-06-1; **27**, 112505-33-6; **28**, 106563-88-6; **30**, 2039-93-2; **31**, 135-98-8; **32** (R^1 = $Si(CH_3)_3$, R^2 = H), 83182-85-8; **32** (R^1 = $Si(CH_3)_3$, R^2 = CH_3), 112505-31-4; **32** (R = $Si(CH_3)_3$, R^2 = CH_2CH_3), 112505-32-5; **32** (R^1 = Me, R^2 = H), 4116-92-1; **33** (R^1 = $Si(CH_3)_3$, R^2 = H, from **23**), 112505-38-1; **33** (R^1 = H, R^2 = $Si(CH_3)_3$, from **23**), 112572-79-9; **33** (R^1 = $Si(CH_3)_3$, R^2 = CH_3, from **23**), 112505-39-2; **33** (R^1 = CH_3, R^2 = $Si(CH_3)_3$, from **23**), 112572-80-2; **33** (R^1 = $Si(CH_3)_3$, R^2 = Et, from **23**), 112505-40-5; **33** (R = Et, R^2 = $Si(CH_3)_3$, from **23**), 112572-81-3; **33** (R^1 = H, R^2 = Me, from **23**), 112505-41-6; **33** (R^1 = Me, R^2 = H, from **23**), 112572-82-4; **33** (R^1 = H, R^2 = Et, from **23**), 112505-42-7; **33** (R^1 = Et, R^2 = H, from **23**), 112572-83-5; **33** (R^1 = $Si(CH_3)_3$, R^2 = Et, from **28**), 112572-85-7; **33** (R^1 = Et, R^2 = $Si(CH_3)_3$, from **28**), 112505-44-9; **34**, 74585-57-2; **35** (isomer 1), 112505-43-8; **35** (isomer 2), 112572-84-6; 1,7-decadiyne, 63815-29-2; $TiCl_3$, 7705-07-9; $Co_2(CO)_8$, 10210-68-1; $ICo(CO)_4$, 15976-97-3; cyclopentadiene, 542-92-7; (2*R*,4*R*)-4-methyl-2-(2-phenyl-2-propyl)cyclohexanone, 104870-79-3; (1*R*,2*R*,5*R*)-5-methyl-2-(2-phenyl-2-propyl)cyclohexanol, 104870-80-6; cyclopentadienylsodium–dimethoxyethane, 62228-16-4.

Synthesis, Reactivity, and X-ray Crystal Structure of an Anionic, Mixed-Metal Ketenylidene Cluster: [PPN][$Fe_2Co(CO)_9(CCO)$]

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The anionic mixed-metal ketenylidene cluster [PPN][$Fe_2Co(CO)_9(CCO)$] (1) can be prepared in high yield by a facile metal substitution reaction between [PPN]$_2$[$Fe_3(CO)_9(CCO)$] and $Co_2(CO)_8$ under a CO atmosphere. This cluster is structurally similar to [$Fe_3(CO)_9(CCO)$]$^{2-}$, but its reactivity more closely resembles that of the cationic cluster [$Co_3(CO)_9(CCO)$]$^+$. Compound 1 undergoes protonation at the α-carbon atom to give $Fe_2Co(CO)_{10}(CH)$ but is inert to electrophilic attack by carbocationic reagents. Nucleophilic reagents such as $LiCH_3$, $NaOCH_3$, and $KBEt_3H$ attack at the β-carbon atom to afford dinegatively charged species [$Fe_2Co(CO)_9(CC(O)R)$]$^{2-}$ (R = CH_3, OCH_3, H). Compound 1 crystallizes in the space group $C2/c$ with a = 27.231 (7) Å, b = 17.670 (6) Å, c = 23.072 (10) Å, β = 126.54 (3)°, V = 8919.9 (70) Å^3, and Z = 8.

Introduction

Ketenylidene (CCO) ligands on trinuclear metal clusters are known to undergo diverse chemistry with respect to C–C bond cleavage, C–O activation, C–C and C–O bond formation, and cluster building.[2-13] An important factor in determining the reactivity of the CCO ligand is the charge on the cluster. Ketenylidene ligands on cationic[2-4]

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