tive. Therefore, the Cr(III) sandwiched complexes show three unpaired electrons, while the Cr(IV) derivative is diamagnetic.[17] A detailed theoretical explanation will be reported in the near future.

Investigations of the reaction chemistry of the anionic and neutral chromacarboranes and other related sandwich complexes are currently underway in our laboratories.

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Supplementary Material Available: Tables of positional and thermal parameters, selected bond distances, bond angles, and torsion angles (5 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

C_2-Symmetric 2,2'-Dimethyl-1,1'-binaphthyl-Bridged *ansa*-Bis(1-indenyl)metal Complexes

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Summary: The use of a C_2-symmetric 2,2'-dimethyl-1,1'-binaphthyl bridge between two 1-indenyl ligands, readily obtained from known, enantiomerically pure 2,2'-bis(bromomethyl)-1,1'-binaphthyl, suppresses the formation of an undesired meso orientation of *ansa*-bis(indenyl)metal complexes of titanium and zirconium dichlorides 3 and favors the desired isolation of one of the possible two C_2-symmetric isomers in enantiomerically enriched form, avoiding the need for resolution of the metal complexes.

C_2-symmetric ethylene-bridged *ansa*-bis(indenyl)titanium and -zirconium dichlorides are well-known to behave as homogeneous catalysts for stereoregular propylene polymerizations[1] and enantioselective alkene hydrogenations[2] and as reagents for allyl additions to aldehydes.[3] Despite these successful applications and the implied great potential of these compounds in other enantioselective transformations, no practical direct synthetic route to enantiomerically pure bis(indenyl) ligands and/or their corresponding complexes has yet been developed. Current strategies involve the initial formation of an isomeric mixture of racemic (C_2-symmetric) and meso (achiral) bis(indenyl)metal complexes, which first must be separated by crystallization, followed by optical resolution of the C_2-symmetric enantiomers (via diastereomeric derivatives) and finally conversion to the enantiomerically pure dichlorides.[4,5] The introduction of a C_2-symmetric chiral bridge between the two indene moieties could potentially suppress formation of the undesired meso complex and favor the formation of one of the two possible C_2-symmetric bis(indenyl)metal diastereomers. We report here the preparation of the new chiral ligand (R)-(+)-(1,1'-binaphthyldiyl-2,2'-dimethylene)bis(1-indene) (1), which is shown to form a single C_2-symmetric stereoisomer upon coordination to titanium and zirconium.[6]

We recently have reported the conversion of (R)-(+)-2,2'-bis(bromomethyl)-1,1'-binaphthyl (2) to a binaphthyl-annulated C_2-symmetric chiral cyclopentadiene.[7] We now find that addition of dibromide (R)-(+)-2 to 2.5 equiv of indenyllithium in THF at 0 °C and warming to room temperature affords bis(indene) (R)-(+)-1 (mp 195

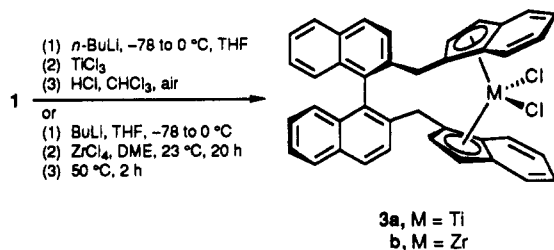(R)-(+)-2 (R)-(+)-1
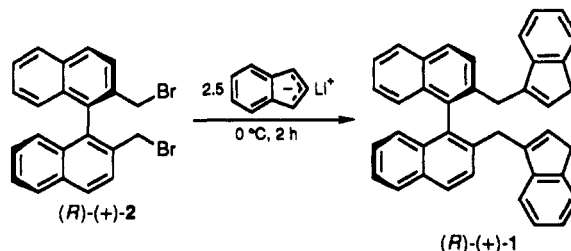
°C, $[\alpha]_D{}^{23}$ +18°)[8] as a single thermodynamically favored double-bond isomer in 71% yield after chromatography

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(SiO$_2$, 9:1 petroleum ether/methylene chloride). Performing the same reaction at -30 °C gave a mixture of double-bond isomers. The use of indenylpotassium also gave good yields of bis(indene) 1, but no alkylation with indenylsodium was observed.

Metalation of bridged bis(1-indenes) can, in principle, occur on either prochiral face of the indenyl ligands, producing a mixture of (R,R)-, (S,S)-, (R,S)-, and (S,R)-ansa-metallocenes. In contrast, metalation of the R isomer of 1 could, in principle, produce a diastereomeric mixture of C$_2$-symmetric (R,R,R and S,S,R) and identical C$_1$-symmetric (R,S,R and S,R,R) isomers. Thus, due to the additional stereogenic unit in binaphthylbis(indene) 1, the selective formation of only one C$_2$-symmetric diastereomer may be energetically possible and, even in the case of nonselective metalation, the isolation of a desired C$_2$-symmetric isomer should require no further derivatization.

(1) n-BuLi, −78 to 0 °C, THF
(2) TiCl$_3$
(3) HCl, CHCl$_3$, air

1 ———————→
or
(1) BuLi, THF, −78 to 0 °C
(2) ZrCl$_4$, DME, 23 °C, 20 h
(3) 50 °C, 2 h

3a, M = Ti
b, M = Zr

(8) All new compounds were fully characterized spectroscopically. (R)-(+)-2,2'-Bis(1-indenylmethyl)-1,1'-binaphthyl (1). Freshly distilled indene (0.680 mL, 5.82 mmol) was diluted with THF (13 mL) and cooled to −78 °C. n-Butyllithium (1.99 M in hexane, 2.92 mL, 5.82 mmol) was added dropwise to form an orange heterogeneous solution of the indenyl anion. This solution was warmed to 0 °C over 0.5 h, producing a homogeneous solution, and (R)-(+)-2,2'-bis(bromomethyl)-1,1'-binaphthyl (97% optical yield, 1.02 g, 2.33 mmol) in THF (13 mL) was added slowly at 0 °C and the mixture stirred for 1.5 h. The reaction mixture was then warmed to room temperature and stirred for 0.5 h and partitioned between NH$_4$Cl and ethyl acetate; the combined organic extracts were washed with water and brine and dried over anhydrous sodium sulfate. Concentration of the crude product gave a yellow solid, which was chromatographed (SiO$_2$, 9:1 petroleum ether/CH$_2$Cl$_2$), yielding a white powder (0.847 g, 71%): mp 195 °C; [α]$_D^{23}$ +18° (c 0.495, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (m, 4 H), 7.52 (d, J = 8.5 Hz, 2 H), 7.40 (m, 2 H), 7.33 (d, J = 7.5 Hz, 2 H), 7.20 (m, 2 H), 7.11 (m, 4 H), 7.03 (m, 2 H), 6.95 (d, J = 7.5 Hz, 2 H), 5.82 (s, 2 H), 3.63 (s, 4 H), 3.12 (d, J = 23.0 Hz, 2 H), 2.87 (d, J = 23.0 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.13, 144.30, 142.63, 136.02, 134.93, 133.15, 132.41, 130.42, 127.95, 127.90, 127.66, 126.26, 126.01, 125.73, 125.29, 124.38, 123.48, 119.18, 37.51, 32.15; IR (KBr) 3053, 2902, 1608, 1506, 1462, 1395, 1259, 962, 864, 811, 769, 740, 713, 506 cm^{-1}; MS (EI, 70 eV, relative intensity) m/z 510 (M$^+$, 100%), 395 (23), 264 (37), 128 (10); HRMS (EI, 70 eV) calcd for C$_{40}$H$_{30}$ 510.2347, found 510.2317. (R)-(−)-2,2'-Bis(1-indenylmethyl)-1,1'-binaphthyldichlorotitanium (3a). (R)-(+)-2,2'-Bis(1-indenylmethyl)-1,1'-binaphthyl (315 mg, 0.617 mmol) was dissolved in THF (4 mL) and the solution cooled to −78 °C. n-Butyllithium (2.25 M in hexane, 0.576 mL, 1.29 mmol) was added dropwise via syringe, producing a deep red solution, which was warmed to 0 °C over 0.5 h. This dianion solution was then slowly cannula-transferred to a rapidly stirred purple TiCl$_3$ (105 mg, 0.678 mmol) solution in THF (3 mL) at −10 °C. After this addition was complete, the reaction mixture was refluxed for 6 h. Removal of the solvent in vacuo provided a dark green residue, which was dissolved in CHCl$_3$ (7 mL) and the solution cooled to −78 °C. HCl (6 M, 3.5 mL) was introduced, and the reaction mixture was warmed to 23 °C with rapid stirring open to air for 2 h. The reaction mixture was transferred to a separatory funnel, the aqueous phase back-extracted with CH$_2$Cl$_2$, and the combined organic extracts dried with brine and sodium sulfate. The concentrated green solid was purified by dissolving it in CH$_2$Cl$_2$ and then slowly adding hexane to precipitate the product as a dark green powder (162 mg, 42%): mp 270 °C; [α]$_D^{23}$ −1800° (c 0.050, CHCl$_3$); ^{1}H NMR (400 MHz, C$_6$D$_6$, 70 °C) δ 7.79 (d, J = 8.5 Hz, 2 H), 7.76 (d, J = 8.5 Hz, 2 H), 7.27 (d, J = 8.5 Hz, 2 H), 7.22 (m, 6 H), 7.07 (ddd, J = 11.0, 4.0, 1.0 Hz, 2 H), 6.95 (m, 6 H), 6.12 (d, J = 3.0 Hz, 2 H), 5.12 (s, 2 H), 4.32 (d, J = 17.0 Hz, 2 H), 3.98 (d, J = 17.0 Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$, 70 °C) δ 135.40, 135.16, 133.77, 132.93, 131.07, 129.82, 128.60, 128.51, 128.30 (2 C), 128.02, 127.33, 126.77, 126.32, 125.96, 123.30, 122.76, 113.84, 33.09; IR (KBr) 3170, 2971, 1718, 1595, 1507, 1425, 1260, 1099, 1028, 869, 808, 755, 665, 509, 455 cm^{-1}; MS (EI, 40 eV, relative intensity) m/z 627 (M$^+$ + 1, 1.4%), 626 (M$^+$, 3), 625 (M$^+$ − 1, 2.6), 624 (M$^+$ − 2, 6), 508 (100), 392 (49), 276 (69); HRMS (EI, 40 eV) calcd for C$_{40}$H$_{28}$Cl$_2$Ti 626.1048, found 626.1114.

Treatment of the lithium salt of bis(indene) (R)-(+)-1 with TiCl$_3$ followed by aerobic treatment with HCl in chloroform[9] gave a green solid whose ^{1}H NMR spectrum indicated the formation of a single isomer of 3a in addition to polymeric material. Recrystallization from methylene chloride/hexane produced pure (R)-(−)-3a in 42% yield (mp 270 °C, [α]$_D^{23}$ −1800° (c 0.050, CHCl$_3$)). Likewise, the bis(indenyl)zirconium dichloride 3b was obtained in 20% yield by treatment of the dilithium salt of 1 with zirconium tetrachloride in DME.[10] Again only a single isomer of 3b was detected in the ^{1}H NMR spectrum of the crude reaction product. In both cases, there was a preference for complex formation via the metalation of a single diastereotopic face of both indenyl moieties, a result rationalized by inspection of molecular models, which indicated severe steric interactions in all but one possible bis(indenyl) complex. Although only one product was isolated, it is questionable whether the initial metalation of 1 was highly selective; initial metalation of one diastereomeric face of 1 may have led to the isolated complexes, whereas initial metalation of the other diastereomeric face of 1 may have led to the unisolable polymeric material.

The molecular structure of titanocene 3a was determined by X-ray crystallography, and the ORTEP diagram is shown in Figure 1.[11] Although the Ti−indenyl and Ti−Cl bond lengths and angles are typical,[4b] the expected C$_2$ symmetry axis is not observed for this molecule in the solid state. Instead, geometric constraints imposed by the binaphthylbis(indenyl) ligand apparently force the complex to adopt a conformation having the two chlorine atoms approximately staggered about one of the indene moieties.

In solution, the resonances for the indenyl hydrogens are also broadened in the ^{1}H NMR spectrum at 20 °C. Variable-temperature ^{1}H NMR spectroscopy indicated the presence of two equivalent frozen C$_1$-symmetrical conformations of 3a at −60 °C (Δν = 800 Hz), coalescence near 10 °C, and one rapidly equilibrating molecule exhibiting C$_2$ symmetry above 60 °C (ΔG‡ = 13 kcal/mol). In the low-temperature limit, the two equivalent C$_1$-symmetrical conformations presumably are those having the chlorines staggered over either of the two indenyl groups of 3a. This result is consistent with the solid-state structure of 3a (Figure 1) and, to our knowledge, is the first observation of hindered rotation in a bis(indenyl)metal compound. The zirconium analogue 3b also exhibited similar dynamic behavior in the ^{1}H NMR spectrum, but the coalescence temperature for this complex was near −40 °C and the signals for slow exchange were still not observed as low as −70 °C. The more facile conformational changes observed in 3b, relative to those in 3a, are probably a result of the increase in metal−indenyl bond distances (Zr > Ti), which reduces the unfavorable interactions present during bond rotation. Knowledge of the solution structures of 3a,b at various temperatures may have significance in studying stereoselective reactions using these compounds.

Given the strong interest in applications of enantiomerically pure, C$_2$-symmetric bis(indenyl)metal complexes and the facile preparation and selective metalation of our enantiomerically pure binapthyl-bridged bis(indene) 1,

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(11) X-ray data for racemic 3a: C$_{40}$H$_{28}$TiCl$_2$·C$_6$H$_{14}$, triclinic P$\bar{1}$ (No. 2), a = 14.50 (1) Å, b = 15.75 (1) Å, c = 8.463 (5) Å, α = 95.33 (6)°, β = 91.43 (6)°, γ = 69.91 (6)°, V = 1807 (2) Å^3, Z = 2, λ = 1.541 78, temp 20 °C, 2138 observed reflections (>3σ), μ = 35.8 cm^{-1}, p = 0.03, R = 8.1, R$_w$ = 8.9, GOF = 2.3. See the supplementary material for full data.
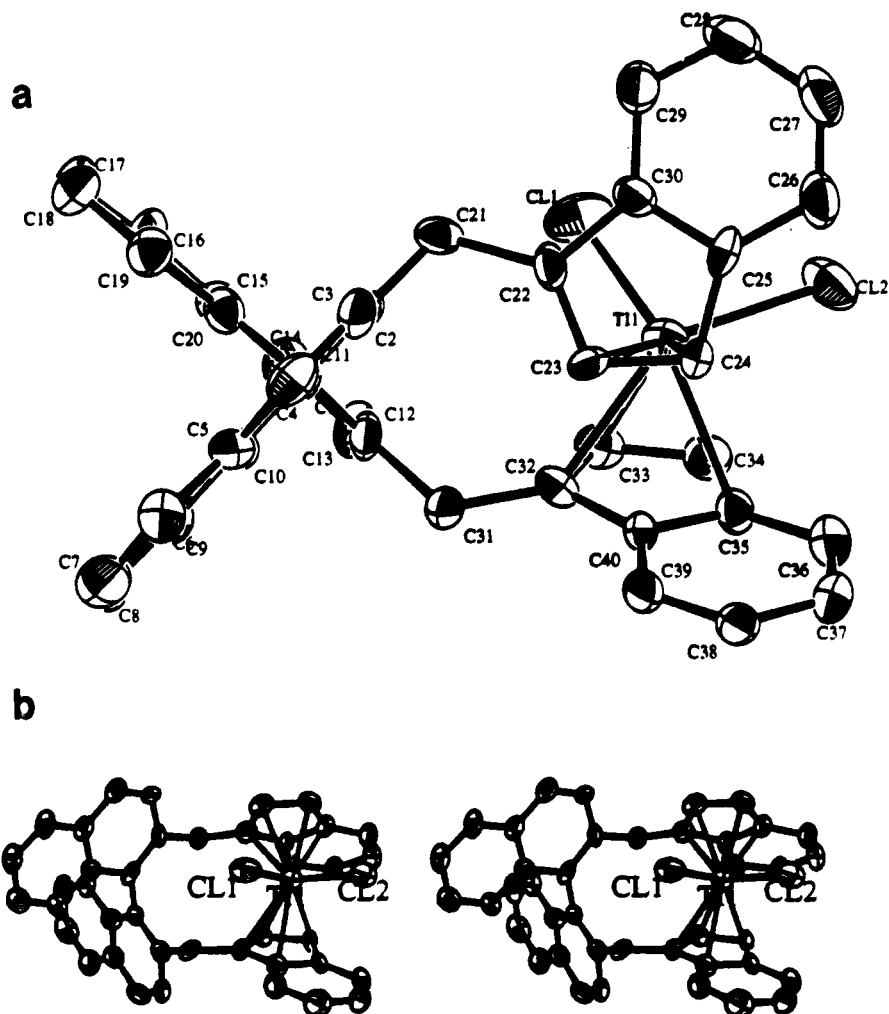
Figure 1. (a) ORTEP diagram of **3a**. (b) Stereoview of the crystal structure of **3a**.

metal complexes of this ligand promise to be useful reagents in a variety of applications.