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Synthesis of *C7,C7′*-Ethylene- and *C7,C7′*-Methylene-Bridged *C*$_2$-Symmetric Bis(indenyl)zirconium and -titanium Dichlorides

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We have prepared several novel metallocenes bridged at the 7,7′-positions of the indenyl moiety. The new metallocenes include the methylene-bridged [*dl*-bis(4,6-dimethylinden-7-yl)methylidene]titanium dichloride **(20)** and [*dl*-bis(4,6-dimethylinden-7-yl)methylidene]zirconium dichloride **(21)**, which were prepared from *m*-xylene. In addition, [*dl*-1,2-bis(4-methylinden-7-yl)ethylidene]- and [*dl*-1,2-bis(4-isopropylinden-7-yl)ethylidene]zirconium dichlorides **(*dl*-12a** and ***dl*-12b)** and [*dl*-1,2-bis(4-isopropylinden-7-yl)ethylidene]titanium dichloride **(*dl*-13)** were synthesized from *p*-cymene and *p*-xylene, respectively. The structures of metallocene dichlorides ***dl*-12a**, ***dl*-12b**, and ***dl*-13** were determined by X-ray crystallography and found to have *C*$_1$ symmetry in the solid state but in solution exhibit *C*$_2$ symmetry, as seen in the ^{1}H NMR spectra at room temperature.

Introduction

Since the discovery of Brintzinger's complex **1**,[2] chiral *ansa*-metallocenes have drawn attention because of their utility in a number of reactions such as the reduction of carbonyls[3] and imines,[4] epoxidations,[5] isotactic propylene polymerization,[6] hydrogenations,[7] diene cyclizations,[8] and carbomagnesations.[9] Because of their many applications, numerous metallocenes possessing a variety of structures (Figure 1) have been synthesized in an attempt to find advantageous steric and electronic characteristics for the various reactions.[2,10−14]

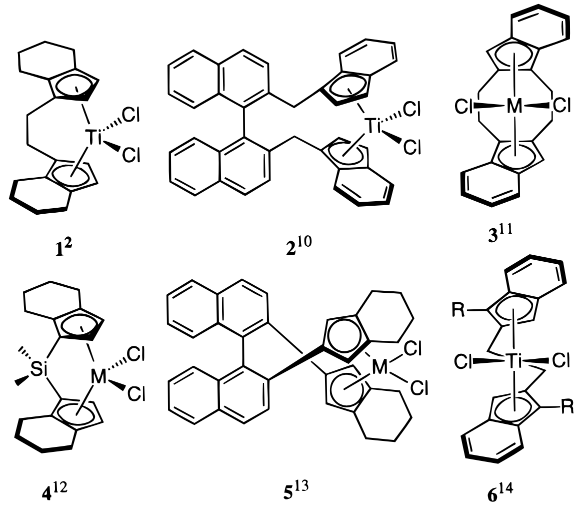

Figure 1.

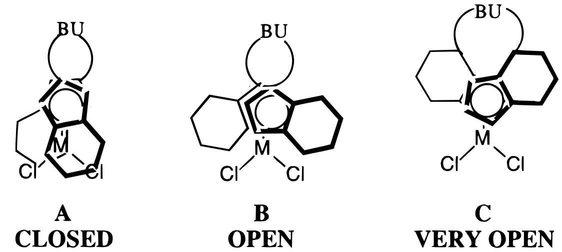

Figure 2.

Most *ansa*-bis(indenyl)titanium or -zirconium complexes such as **1**, **2**, and **4** exist in a roughly "open" conformation (structure **B** in Figure 2). A limited number of *ansa*-metallocenes such as **3** and **6** with "closed"

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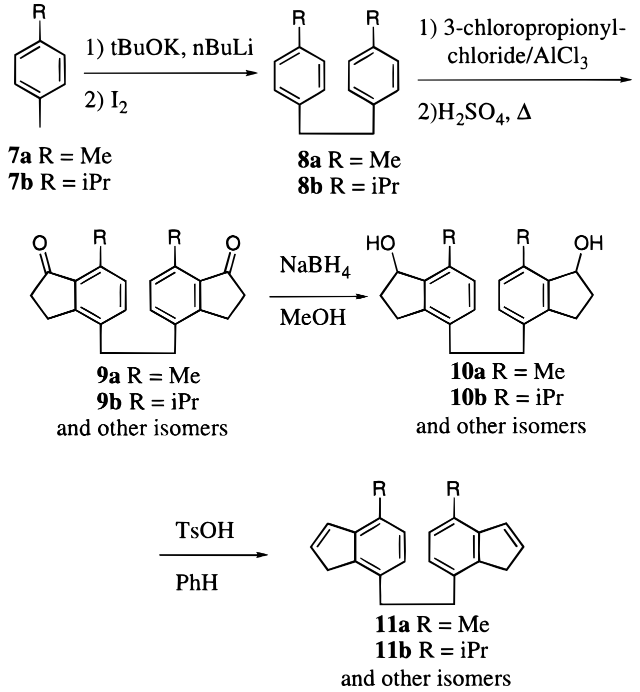
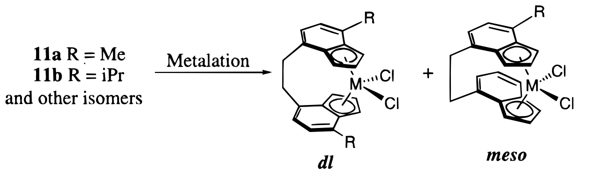
Scheme 1. Synthesis of Bis(indenyl) Ligands 11a and 11b



Scheme 2. Metalation of Bis(indenyl) Ligands 11a and 11b



Conditions	M		*dl/meso*	Yield
1) nBuLi 2) $ZrCl_4$	Zr	**12b** R = iPr	ca. 50:50	60%
1) $Zr(NMe_2)_4$ 2) Me_2NH_2Cl	Zr	**12a** R = Me **12b** R = iPr	ca. 100:0 ca. 100:0	63% 61%
1) nBuLi 2) $TiCl_3$ 3) [O]	Ti	**13** R = iPr	ca. 100:0	74%

conformations have been prepared (structure **A**). Complexes of this type have been shown to be less reactive in olefin polymerizations.[15] *ansa*-Metallocenes at the other end of the conformational spectrum would be very open. These very open complexes (structure **C**) could have a dihedral angle between the most forward Cp substituents of about 180°, as compared to 60−120° for open complexes **B** and 0−30° for closed complexes **A**.

Until now, there has been no convenient synthetic methodology for the facile preparation of very open systems having structural or conformational variations. We present herein the synthesis of five metallocenes with a one- or two-carbon bridge at the C7 and C7′ positions on the indenyl moiety. These relatively short and efficient syntheses enable access to *ansa*-metallocenes having a very open architecture. During the course of our work, some of these complexes were reported in patents.[16]

Results and Discussion

Synthesis and Properties of C7 and C7′ Ethano-Bridged Metallocenes. As shown in Scheme 1, the initial step of the synthesis begins with commercially available *p*-cymene or *p*-xylene. The selection of these starting materials was based upon the facile ability to introduce the ethano bridge using a coupling method described by Bates and Ogle.[17] The selective coupling of these para-substituted arenes could be carried out by deprotonation of the less substituted benzylic position with potassium *tert*-butoxide and *n*-butyllithium followed by the isolation of the potassium salt. The potassium salt was then treated with iodine to induce oxidative coupling to give the 1,2-diarylethanes **8a** and **8b** in excellent yields.

The cyclopentanone moieties were introduced by Friedel−Craft acylation followed by cyclization in sulfuric acid to yield an isomeric mixture of the bis(indanones) **9a** and **9b**. The carbonyls were reduced with sodium borohydride to yield the alcohols **10a** and **10b** in quantitative yields as mixtures of several stereo- and regioisomers. Dehydration with *p*-toluenesulfonic acid gave the corresponding bis(indenes) **11a** and **11b** as a greatly simplified mixture of double-bond isomers in approximately 50% yield based on bis(indanones) **9a** and **9b**.[18]

Metalation of ligands **11a** and **11b** was carried out under a variety of conditions (Scheme 2). A procedure outlined by Jordan[19] using tetrakis(dimethylamido)zirconium in chlorobenzene or toluene, followed by workup with dimethylammonium hydrochloride and purification, gave only single zirconium complexes **12a** and **12b**.

The metallocene complexes were assigned the structures of ***dl*-12a** and ***dl*-12b** based upon the unusually large chemical shift difference between indenyl H-1 (4.45 and 4.42 ppm) and H-3 (6.69 and 6.60 ppm) in the ^1H NMR spectrum, respectively. According to models of the complexes, the indenes in the *dl*-complexes are positioned so that protons at C1 and C1′ are held over the phenyl ring of the opposite indenyl group. With the position of the protons over the shielding region of the indenyl rings, the high-field shifts of 4.45 and 4.42 ppm could be readily explained. According to models of the *meso* complexes, typical indenyl shifts are expected. This was later found upon metalation of compound **11b** using *n*-butyllithium and zirconium tetrachloride to give a 1:1 mixture of ***meso*-12b** and ***dl*-12b**, which could be identified by an extra set of indenyl signals appearing at 6.65, 6.60, and 6.53 ppm in the ^1H NMR spectrum of the zirconocene complex.

Crystals of zirconium dichloride complex ***dl*-12a** suitable for X-ray diffraction could be grown by diffusion of hexanes into a solution of toluene and ***dl*-12a** at 0 °C,

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Table 1. Crystallographic Data for *dl*-12a, *dl*-12b, and *dl*-13

	***dl*-12a**	***dl*-12b**	***dl*-13**
empirical formula	$C_{22}H_{20}Cl_2Zr$	$C_{26}H_{28}Cl_2Zr$	$C_{26}H_{28}Cl_2Ti$
mol wt	446.50	502.60	698.02
temp (K)	188(2)	153(2)	188(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$P2_1/c$
a (Å)	6.7670(10)	21.671(9)	15.822(3)
b (Å)	16.921(3)	17.383(9)	17.255(3)
c (Å)	16.123(3)	12.063(6)	11.681(2)
α (deg)	90	90	90
β (deg)	95.770(10)	98.46	107.180(10)
γ (deg)	90	90	90
V (Å^3), Z	1836.8(5), 4	4495(4), 8	3046.7(9), 4
D_{calc} (Mg/m^3)	1.615	1.485	1.522
abs coeff (mm^{-1})	0.881	0.737	1.001
$F(000)$	904	2064	1424
cryst size (mm)	0.14 × 0.60 × 0.20	0.06 × 0.14 × 0.52	0.02 × 0.34 × 0.26
θ range (deg)	2.41−24.99	1.51−23.00	1.79−24.99
no. of rflns collected	3511	3213	3479
no. of indep rflns	3220 (R_{int} = 0.0331)	3089 (R_{int} = 0.0820)	3244 (R_{int} = 0.0631)
max and min transmissn	0.2765, 0.2489		0.6847, 0.4776
no. of data/restraints/params	3214/265/227	3080/305/262	3239/0/334
goodness of fit on F^2	1.011	1.058	1.039
final R1 ($I > 2\sigma(I)$)	0.0384	0.0754	0.0658
final wR2($I > 2\sigma(I)$)	0.0909	0.1730	0.1447
min and max	+0.547, −0.628	+1.699, −1.914	+0.909, −0.735
refinement method	full-matrix least squares on F^2		

and the solid-state structure of ***dl*-12a** could be solved as described in Table 1. The front and top ORTEP view of ***dl*-12a** is shown in Figure 3. The angle found between Cp_{cent}−Zr− Cp_{cent} is 130.4°. The Cp_{cent}−Zr distances are 2.221 and 2.217 Å. The dihedral angle for C6−C5−C16−C15 is 191°, confirming our design notion of creating a very open complex. Selected bond lengths and angles are shown in Table 2.

Crystals of zirconium dichloride complex ***dl*-12b** suitable for X-ray diffraction could be grown by diffusion of hexanes into a solution of dichloromethane and ***dl*-12b** at 0 °C, and the solid-state structure of ***dl*-12b** could be solved as described in Table 1. The front ORTEP view of ***dl*-12b** is shown in Figure 3. The angle found for Cp_{cent}−Zr− Cp_{cent} is 130.3°. The Cp_{cent}−Zr distances are 2.208 and 2.231 Å. This complex is also very open, having a dihedral angle for atoms C6−C5−C16−C15 of 192°.

Metalation of the isopropyl-substituted ligand **11b** with titanium trichloride followed by oxidation resulted in the isolation of only the C_2-symmetric complex of the titanocene ***dl*-13** in 74% yield. Assignment of the metallocene structure was based upon the chemical shift found for indenyl H1 at 4.21 ppm in the ^{1}H NMR for ***dl*-13**. A similar upfield shift was found for an indenyl signal in the ^{1}H NMR spectra of zirconocenes ***dl*-12a** and ***dl*-12b**. Crystals of titanocene ***dl*-13** suitable for X-ray diffraction were grown from the slow evaporation of chloroform at room temperature, and the solid-state structure was solved as described in Table 1. The top ORTEP view is shown in Figure 3. The angle Cp_{cent}−Ti− Cp_{cent} is 131.6°. The Cp_{cent}−Ti bond distances are 2.097 and 2.083 Å. The dihedral angle defined by the C5−C6 bond and the C15−C16 bond is approximately 192°, again showing a very open structure. In all cases the Cp_{cent}−M−Cp_{cent} angle is fairly wide for *ansa*-metallocenes.

Low-temperature ^{1}H NMR experiments were performed using metallocene ***dl*-12b** to see if the molecule could be constrained into the constitutional conformations indicated by molecular models. However, there was little or no change in the NMR spectra at −60 °C, suggesting the molecule continues to fluctuate between any accessible conformations.

Synthesis and Properties of C7 and C7′ Methano-Bridged Metallocenes. To increase the rigidity of the metal complexes containing bridges between the C7 and C7′ positions, the one carbon-bridged ligand **19** was prepared (Scheme 3). Much like the preparation for the ethano-bridged metallocenes, the synthesis was begun by first introducing the methylene bridge. To combat potential regioselectivity problems in forming the methylene bridge, *m*-xylene was selected as the starting material using the procedure outlined by Cornell and Gollis[20] to give **15**.

Care was required with the Friedel−Crafts acylation using aluminum trichloride and 3-propionyl chloride. It was found that the desired product from the Friedel−Crafts acylation could not be isolated, and the starting material had decomposed if the reaction mixture was warmed to room temperature or if the reaction was run for more than 30 min at 0 °C. When proper care was taken, diketone **16** was isolated and treated with sulfuric acid to promote cyclization to give bis(indanone) **17** as a single regioisomer in 49% yield. Reduction of **17** with sodium borohydride followed by dehydration promoted by *p*-toluenesulfonic acid yielded the bis(indanol) **18** and bis(indene) **19**, respectively. Bis(indene) **19** was isolated by column chromatography in 80% yield as a white solid. In contrast to ethylene-bridged bis(indenes) **11a** and **11b**, the methylene-bridged bis(indene) **19** was isolated as a single double-bond isomer.

Metalation of methylene-bridged bis(indene) **19** with *n*-butyllithium and zirconium tetrachloride or tetrakis-

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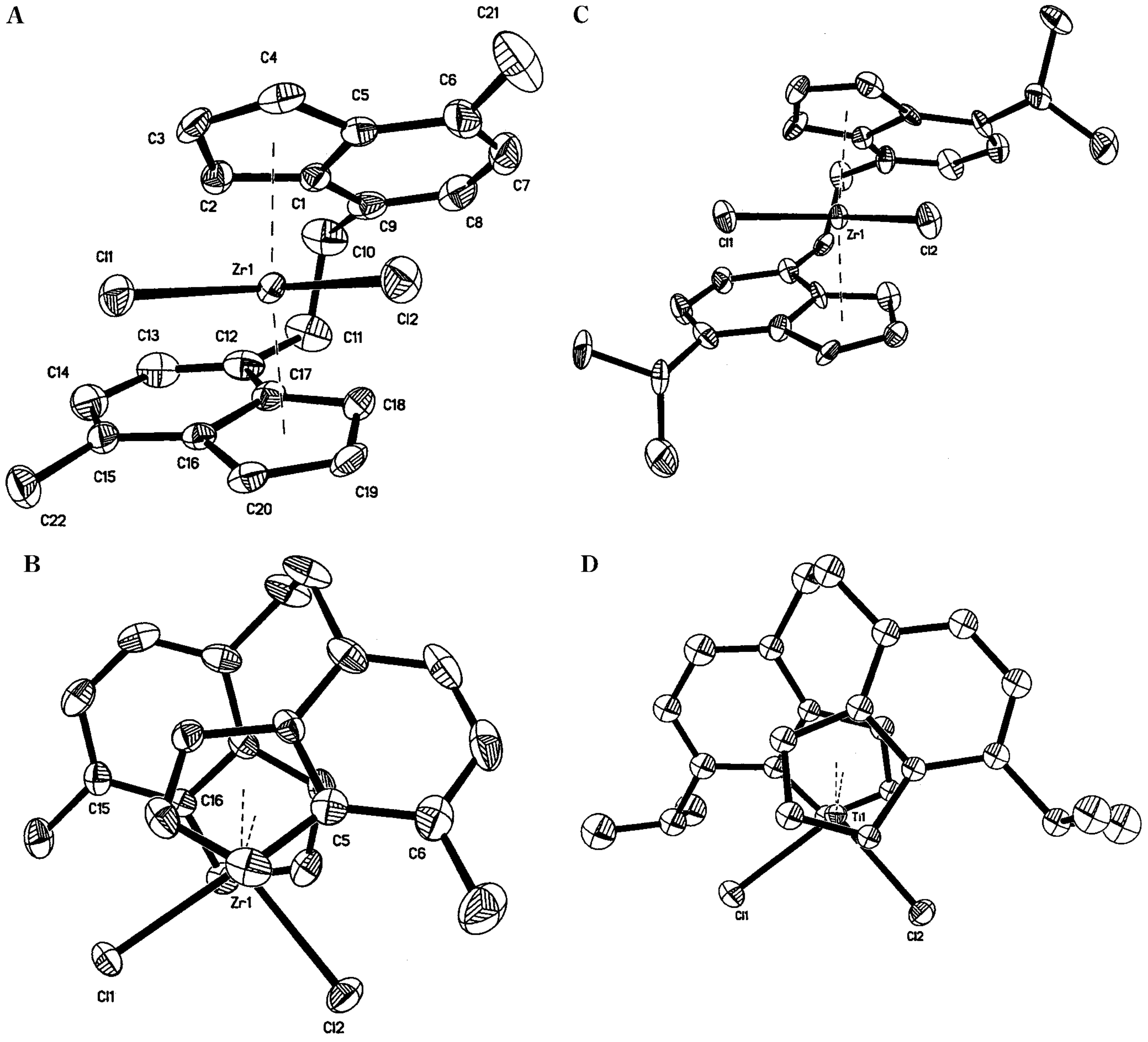


Figure 3. (a) Front view of ***dl*-12a**. (b) Top view of ***dl*-12a**. (c) Front view of ***dl*-12b**. (d) Top view of ***dl*-13**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *dl*-12a, *dl*-12b, and *dl*-13

bond lengths and angles	***dl*-12a** (M = Zr)	***dl*-12b** (M = Zr)	***dl*-13** (M = Ti)
$Cp_{cent}-M-Cp_{cent}$	130.4	130.3	131.7
$Cp_{cent}-M$	2.221 2.217	2.208 2.231	2.097 2.083
C5−C6/C15−C16 dihedral angle	191	192	192

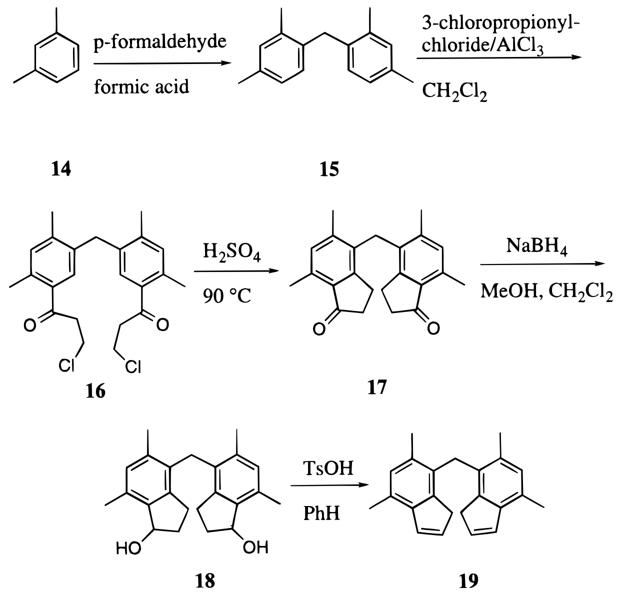
(dimethylamido)zirconium in chlorobenzene followed by workup with dimethylammonium chloride gave the C_2-symmetric zirconocene dichloride ***dl*-21** (Scheme 4). The formation of titanocene dichloride ***dl*-20** was also found to occur cleanly upon treatment with *n*-butyllithium, titanium trichloride, and oxidation. The assignment of the titanocene dichloride ***dl*-20** and zirconocene dichloride ***dl*-21** as the C_2-symmetric complexes was based upon the chemical shifts of the H1 indenyl signals in the ^{1}H NMR spectrum found at 4.02 and 4.27 ppm, respectively. The C_2-symmetric complexes ***dl*-20** and ***dl*-21** have a proton lying directly over the phenyl ring on the indenyl moiety, causing the unusual upfield shift. Unfortunately, due to the insolubility and instability of these complexes in solution neither ^{13}C NMR nor HRMS spectra could be obtained.

Experimental Section

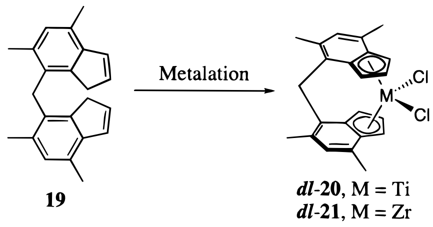
General Considerations. For general materials, techniques and equipment used, see ref 13. 1,2-Bis(4-methylphenyl)ethane **(8a)** was synthesized in one step from *p*-xylene according to the literature procedure.[15]

1,2-Bis(4-isopropylphenyl)ethane (8b). To *p*-cymene (8.99 g, 67 mmol), and potassium *tert*-butoxide (5.6 g, 50 mmol) in hexanes (50 mL) was added dropwise at room temperature *n*-butyllithium (18.6 mL, 2.69 M in hexanes, 50 mmol), resulting in an orange slurry. The slurry was stirred an additional 1 h at room temperature to yield a brick red precipitate. The precipitate was filtered, rinsed with hexanes (2 × 10 mL), and dried *in vacuo*. The solid was then transferred to an addition funnel and dissolved in tetrahydrofuran (100 mL). The tetrahydrofuran solution was then added dropwise to a solution of iodine (6.38 g, 25 mmol) in tetrahydrofuran (100

Scheme 3. Synthesis of Bis(indenyl) Ligands 19



Scheme 4. Metalation of Bis(indenyl) Ligand 19



Conditions	Product	Yield
1) nBuLi 2) ZrCl$_4$	*dl*-**21**	--
1) Zr(NMe$_2$)$_4$ 2) Me$_2$NH$_2$Cl	*dl*-**21**	43%
1) nBuLi 2) TiCl$_3$ 3) [O]	*dl*-**20**	38%

mL) at room temperature. Upon completion of the addition the reaction mixture was stirred an additional 30 min to yield a white slurry. This mixture was quenched with saturated aqueous NH$_4$Cl (50 mL), and the organic layer was separated. The aqueous layer was extracted with ether (3 × 50 mL), and the combined organic portions were washed with NaHSO$_3$, water, and brine, dried over MgSO$_4$, filtered, and concentrated to give a brown solid. The crude solid was purified by column chromatography (SiO$_2$/petroleum ether) to give **8b** (4.61 g, 17 mmol) in 69% yield as a white solid. Mp: 52−54 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.15 (bs, 8H), 2.88 (sept, J = 7.0 Hz, 2H), 2.87 (s, 4H), 1.23 (d, J = 7.0 Hz, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 146.41, 139.40, 128.28, 126.39, 37.61, 33.73, 24.10. IR (thin film) 3048, 2957, 2923, 2872, 1458, 828 cm^{-1}. MS (EI, 70 eV; *m/z* (relative intensity)): 266 (10%), 133 (100), 105 (21), 91 (12).

1,2-Bis(4-isopropylindanon-7-yl)ethane (9b). To aluminum trichloride (2.55 g, 19.1 mmol) in dichloromethane (50 mL) at 0 °C was added 3-chloropropionyl chloride (2.43 g, 19.1 mmol). The mixture was stirred for 30 min at 0 °C; then **8b** (2.29 g, 8.5 mmol) in dichloromethane (50 mL) was added dropwise. The resulting red solution was slowly warmed to room temperature and stirred for 2 h. The reaction mixture was poured over ice, separated and extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with water and sodium bicarbonate (saturated), dried over MgSO$_4$, filtered, and concentrated. The crude material was then added to concentrated sulfuric acid at 0 °C. The reaction solution was then brought to 80 °C for 2 h, cooled to room temperature, poured over ice, and extracted with ether (3 × 50 mL). The combined ether layers were washed with water, sodium bicarbonate (saturated), and brine, dried over MgSO$_4$, filtered, and concentrated. The crude white solid was purified by column chromatography (SiO$_2$/10% ethyl acetate/petroleum ether) to give ketone **9b** as a mixture of isomers (1.32 g, 3.5 mmol) in 41% yield. Mp: 121−125 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.45−7.05 (m, 4H), 3.30−2.60 (m, 10H), 3.25 (bs, 4H), 1.30−1.20 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 209.32, 209.03, 208.95, 155.74, 154.65, 154.27, 148.77, 145.20, 144.62, 141.18, 140.44, 137.59, 135.27, 134.63, 134.51, 133.71, 131.13, 130.04, 129.90, 124.87, 54.32, 37.91, 37.61, 37.56, 34.18, 33.47, 33.37, 30.59, 29.95, 27.64, 24.74, 24.67, 24.60, 24.07, 23.89. IR (thin film) 2953, 2922, 2864, 1699, 1574, 1492, 1254 1058, 846 cm^{-1}. MS (EI, 70 eV; *m/z* (relative intensity)): 374 (18%), 200 (12), 187 (100), 172 (10), 159 (14), 145 (33), 141 (10), 129 (14), 128 (29), 115 (24), 91 (13).

1,2-Bis(4-methylindanon-7-yl)ethane (9a) was prepared according to the procedure outlined for the synthesis of **9b** but using **8a** (0.500 g, 2.4 mmol) to give white solid **9a** as a mixture of isomers (0.390 g, 1.2 mmol) in 51% yield. Mp: 184−187 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.35−6.95 (m, 4H), 3.40−2.30 (m, 18H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 208.39, 208.32, 207.83, 205.88, 155.14, 154.49, 154.00, 140.18, 139.41, 136.75, 136.28, 136.01, 134.55, 134.48, 134.42, 134.25, 133.93, 133.86, 133.55, 129.50, 129.29, 128.75, 128.58, 36.76, 36.70, 36.66, 36.57, 33.18, 32.31, 32.11, 29.65, 24.33, 24.26, 23.85, 17.97, 17.87, 17.40. IR (thin film): 2955, 2924, 2857, 1703, 1580, 1492, 1446, 1248 cm^{-1}. MS (EI, 12 eV; *m/z* (relative intensity)): 318 (11%), 159 (100), 106 (14), 91 (18).

1,2-Bis(4-isopropylindanol-7-yl)ethane (10b). To **9b** (1.32 g, 3.5 mmol) in methanol (100 mL) was added at 0 °C NaBH$_4$ (0.335 g, 8.8 mmol) in four portions. The solution was then stirred for 12 h at room temperature. The solvent was removed, leaving a solid residue. The residue was added to water (100 mL) and extracted with methylene chloride (3 × 50 mL). The combined organic layers were washed with water (25 mL), dried over MgSO$_4$, filtered, and concentrated to give crude **10b** (0.997 g, 2.6 mmol) as an off-white solid. Crude **10b** (mixture of isomers) was used for characterization and carried on without further purification. Mp: 154−158 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.25−7.00 (m, 4H), 5.70−5.40 (m, 2H), 3.30−2.20 (m, 16H), 1.40−1.10 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 142.63, 142.58, 142.55, 142.39, 141.55, 141.51, 136.44, 136.21, 128.10, 127.95, 125.03, 124.87, 75.40, 75.04, 35.58, 34.87, 34.51, 34.47, 30.43, 30.38, 28.42, 28.16, 23.03, 22.30, 22.94. IR (thin film): 3327, 2958, 2925, 2869, 1701, 1492, 1456 cm^{-1}. MS (EI, 70 eV, *m/z* (relative intensity)): 360 (18%), 342 (57), 327 (16), 317 (26), 299 (32) 200, (28), 173 (100), 171 (29), 159 (9).

1,2-Bis(4-methylindanol-7-yl)ethane (10a) was prepared by following the procedure outlined for the preparation of **9b** but using **9a** (2.301 g, 7.2 mmol) to give crude **10a** as a mixture of isomers (1.69 g, 5.2 mmol). The crude white solid was used for characterization and carried on to the next step. Mp: 91−94 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.20−6.90 (m, 4H), 5.40−5.00 (m, 2H), 3.10−2.00 (m, 20H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 143.11, 143.08, 142.97, 142.92, 142.83, 142.75, 142.55, 142.48, 142.45, 142.42, 142.39, 142.25, 136.47, 136.24, 136.19, 136.09, 135.53, 135.41, 135.35, 135.31, 132.71, 131.84, 129.72, 129.70, 129.61, 129.50, 129.01, 128.87, 128.83, 128.63, 128.44, 128.37, 128.35, 127.76, 127.61, 127.39, 127.33, 35.08, 34.91, 24.83, 34.70, 34.59, 33.93, 33.15, 32.81, 29.67, 29.36, 28.88, 28.80, 28.69, 28.48, 28.45, 28.31, 18.65, 17.99. MS (EI, 70 eV; *m/z* (relative intensity)): 304 (12%), 289 (9), 386 (31), 271 (11), 160 (46), 145 (25) 143 (100), 131 (20), 128 (53), 117 (6), 115 (23) 91 (15), 77 (6).

1,2-Bis(4′-isopropylinden-7-yl)ethane (11b). To crude **10b** (0.997 g, 2.6 mmol) in benzene (75 mL) was added a few crystals of *p*-toluenesulfonic acid hydrate. The reaction vessel was then fitted with a Dean−Stark apparatus, and the solution was refluxed for 3 h. The reaction mixture was cooled to room temperature and washed with a saturated solution of sodium bicarbonate (50 mL) followed by water (25 mL). The organic layers were dried over MgSO$_4$, filtered, and concentrated to give an off-white solid. The solid was purified by column chromatography (SiO$_2$/petroleum ether) to give **11b** as a mixture of double-bond isomers (0.631 g, 1.8 mmol) as a white solid in 52% yield based on starting ketone. Mp: 54−56 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.25−7.00 (m, 6H), 6.70−6.50 (m, 2H), 3.45−3.00 (m, 10H), 1.40−1.25 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 142.94, 142.33, 143.31, 141.94 (2C), 141.61, 141.57, 141.04, 139.16, 134.55, 133.32, 133.27, 133.10, 132.16, 130.33, 130.22, 126.95, 126.93, 123.14, 121.38, 37.90, 37.84, 35.04, 34.98, 33.65, 30.86, 30.58, 29.70, 23.55, 23.06. IR (thin film): 3066, 2998, 2924, 2871, 1488, 1556, 1388 cm^{-1}. MS (EI, 70 eV; *m*/*z* (relative intensity)): 342 (10%), 299 (14), 171 (100), 156 (15), 143 (11), 141 (20), 128 (25), 115 (10).

1,2-Bis(4-methylinden-7-yl)ethane (11a) was prepared by following the procedure outlined for **11b** but using **10a** (1.34 g, 4.2 mmol) to afford **11a** as a mixture of isomers (0.671 g, 2.4 mmol) in 56% yield. Mp: 132−136 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.10−6.95 (m, 6H), 6.60−6.50 (m, 2H), 3.40−2.90 (m, 8H), 2.45−2.35 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 143.55, 142.74, 142.46, 141.74, 134.48, 133.64, 133.60, 133.17, 132.80, 132.18, 130.68, 130.52, 130.45, 130.21, 130.12, 129.51, 128.12, 128.09, 127.81, 126.69, 126.66, 125.97, 125.15, 124.70, 38.72, 38.28, 37.96, 37.92, 36.34, 35.17, 35.11, 33.86, 33.76, 29.70, 18.52, 18.35. IR (thin film): 3086, 3060, 2998, 2874, 1473, 1420 cm^{-1}. MS (EI, 70 eV; *m*/*z* (relative intensity)): 287 (6%), 286 (57), 271 (45), 256 (8), 239 (13) 143 (100), 128 (24).

[*dl*-1,2-Bis(4-isopropylinden-7-yl)ethylidene]zirconium Dichloride (*dl*-12b). To **11b** (0.292 g, 0.90 mmol) and tetrakis(dimethylamido)zirconium (0.235 g, 0.35 mmol) was added chlorobenzene (5 mL) at 0 °C. The clear yellow solution was then brought to 125 °C for 24 h, taking care that the vessel was left open to the Schlenk line to ensure the escape of dimethylamine. The resulting light orange solution was concentrated *in vacuo*, and dimethylammonium hydrochloride (0.134 g, 1.64 mmol) in dichloromethane (50 mL) was added at 0 °C. This solution was warmed to room temperature and stirred for an additional 3 h. The resulting yellow solution was concentrated to 1−2 mL total volume *in vacuo*, and hexanes were then added dropwise until a yellow precipitate began to form. This slurry was stirred for 30 min and then filtered and rinsed with hexanes (2 × 5 mL) to give pure ***dl*-12b** (0.259 g, 0.52 mmol) as a yellow powder in 61% yield. Crystals suitable for X-ray analysis were grown by diffusion of hexanes into a solution of dichloromethane and ***dl*-12b** at 0 °C. Mp: 205−215 °C dec. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.22 (d, J = 7.0 Hz, 2H), 7.12 (d, J = 7.0 Hz, 2H), 6.71 (m, 4H), 4.42 (dd, J = 3.5, 2.0 Hz, 2H), 3.68 (qq, J = 7.0, 7.0 Hz, 2H), 3.34 (d, J = 9.0 Hz, 2H), 3.02 (d, J = 9.0 Hz, 2H), 1.37 (d, J = 7.0 Hz, 6H), 1.15 (d, J = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 145.46, 136.30, 129.67, 125.76, 125.70, 124.87, 121.46, 107.51, 101.96, 36.28, 30.25, 24.19, 20.59. IR (thin film): 3111, 2962, 2844, 1461, 1448, 1257, 1076, 846, 822, 778 cm^{-1}. MS (EI, 12 eV; *m*/*z* (relative intensity)): 506 (31%), 505 (18), 504 (65), 503 (41), 502 (100), 501 (5), 500 (92), 468 (38), 467 (32), 466 (68), 465 (45), 464 (85), 342 (23), 299 (18), 171 (71). Anal. Calcd: C, 62.13; H, 5.61. Found: C, 60.60; H, 5.60.

[*dl*- and *meso*-1,2-Bis(4-isopropylinden-7-yl)ethylidene]zirconium Dichloride (12b). To **11b** (1.04 g, 3.0 mmol) in diethyl ether (20 mL) at −78 °C was added *n*-butyllithium (3.2 mL, 2.40 M in hexanes, 7.7 mmol). The resulting slurry was warmed to room temperature and stirred for an additional 5 h. The dilithio salt was Schlenk-filtered and washed twice with hexanes (2 × 5 mL). The salt was vacuum-dried and used immediately. The dilithio salt (0.309 g, 0.87 mmol) and zirconium tetrachloride (0.224 g, 0.96 mmol) were placed in a Schlenk flask. To the solid mixture was added ether (3 mL) at 0 °C, resulting in a yellow slurry. The yellow slurry was stirred for 10 h at room temperature, followed by the removal of the solvent *in vacuo*, which was replaced with dichloromethane (5 mL). The dichloromethane was then Schlenk-filtered and concentrated to 1 mL total volume followed by the addition of hexanes (5 mL) until a fine yellow precipitate formed. The precipitate was back-filtered and washed with hexanes (2 × 2 mL) to give a 1:1 mixture of ***meso*-12b** and ***dl*-12b** (0.263 g, 0.52 mmol) as a yellow powder in 60% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.22 (d, J = 7.0 Hz, 2H), 7.12 (d, J = 7.0 Hz, 2H), 7.07 (dd, J = 3.0, 2.0 Hz, 2H), 6.74−6.70 (m, 6H), 6.65 (d, J = 7.0, 2H), 6.60 (dd, J = 3.5, 2.0 Hz, 2H), 6.53 (dd, J = 3.5, 3.5 Hz, 2H), 4.42 (dd, J = 3.5, 2.0 Hz, 2H), 3.68 (qq, J = 7.0, 7.0 Hz, 2H), 3.50−3.10 (m, 8H), 3.02 (d, J = 9.0 Hz, 2H), 1.38 (d, J = 7.0 Hz, 6H), 1.23 (d, J = 7.0 Hz, 6H), 1.16 (d, J = 7.0 Hz, 6H), 1.11 (d, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.43, 142.91, 136.28, 133.66, 129.64, 129.60, 125.74, 125.67, 125.63, 124.84, 121.44, 120.91, 120.85, 107.48, 105.71, 101.95, 101.92, 98.34, 36.26, 30.51, 30.22, 24.17, 23.62, 20.57, 20.30.

[*dl*-1,2-Bis(4-methylinden-7-yl)ethylidene]zirconium dichloride (*dl*-12a). Toluene (3 mL) was added to **11a** (0.292 g, 1.02 mmol) and tetrakis(dimethylamido)zirconium (0.273 g, 1.02 mmol) at 0 °C. The clear yellow solution was then brought to 125 °C for 24 h, taking care that the vessel was left open to the Schlenk line to ensure the escape of dimethylamine. The resulting light orange solution was concentrated *in vacuo*, and dimethylammonium hydrochloride (0.162 g, 1.99 mmol) in dichloromethane (50 mL) was added at 0 °C. This solution was warmed to room temperature and stirred for an additional 3 h. The resulting yellow solution was concentrated to 1−2 mL total volume, and hexanes (5 mL) were added dropwise until a yellow precipitate began to form. This slurry was stirred for 30 min, filtered, and rinsed with hexanes (2 × 5 mL) to give pure ***dl*-12a** (0.196 g, 0.44 mmol) as a yellow powder in 63% yield. Crystals suitable for X-ray analysis were grown by diffusion of hexanes into a solution of toluene and ***dl*-12a** at 0 °C. Mp: 210−220 °C dec. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.15 (d, J = 7.0 Hz, 2H), 7.05 (dq, J = 7.0, 1.0 Hz, 2H), 6.74 (dd, J = 3.5, 3.5 Hz, 2H), 6.69 (dd, J = 3.5, 2.0 Hz, 2H), 4.45 (dd, J = 3.5, 2.0 Hz, 2H), 3.34 (d, J = 9.0 Hz, 2H), 3.02 (d, J = 9.0 Hz, 2H), 2.60 (d, J = 1.0 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 136.49, 134.84, 130.25, 126.55, 126.12, 126.00, 124.62, 108.16, 101.67, 36.28, 19.81. MS (EI, 12 eV; *m*/*z* (relative intensity)): 452.1 (4%), 451.1 (7), 450 (36), 449 (25), 447 (76), 447 (60), 446 (99), 445 (66), 444 (100), 413 (4), 412 (15), 411 (9), 410 (21), 409 (15), 408 (30) 286 (5), 92 (11). Anal. Calcd: C, 59.18; H, 4.51. Found: C, 56.57; H, 4.74.

[*dl*-1,2-Bis(4-isopropylinden-7-yl)ethylidene]titanium Dichloride (*dl*-13). To the dilithio salt isolated from the above procedure for compound **12b** (0.229 g, 4.1 mmol) was added titanium trichloride (0.070 g, 4.5 mmol). To the solid mixture at −78 °C was added tetrahydrofuran dropwise (5 mL), and after the addition the reaction slurry was brought to room temperature and refluxed for 5 h. The reaction mixture was cooled to room temperature, and the solvents were removed *in vacuo* leaving a solid green residue. The residue was dissolved in chloroform (5 mL), and 2 N hydrochloric acid (1 mL) was added at 0 °C. The mixture was then stirred while open to air for 2 h at room temperature; then the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 5 mL), and the combined organic layers were washed with water and brine, dried over MgSO$_4$, filtered, and concentrated. The solid green residue was recrystallized from dichloromethane and hexanes to give pure ***dl*-13** (0.153 g, 3.3 mmol) as a fine green precipitate in 74% yield. Crystals suitable for X-ray analysis were obtained from the slow evaporation of chloroform at room temperature. Mp: 200−210 °C dec. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 (d, J = 7.0 Hz, 2H), 7.17 (d, J = 7.0 Hz, 2H), 6.95 (dd, J = 3.5, 2.0 Hz, 2H), 6.72 (dd, J = 3.5, 3.5 Hz, 2H), 4.21 (dd, J = 3.5, 2.0 Hz, 2H), 3.86 (qq, J = 7.0, 7.0 Hz, 2H), 3.31 (d, J = 9.0 Hz, 2H), 3.01 (d, J = 9.0 Hz, 2H), 1.36 (d, J = 7.0 Hz, 6H), 1.15 (d, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 147.15, 137.25, 133.92, 127.35, 127.11, 126.48, 123.06, 116.00, 110.22, 36.59, 30.36, 24.49, 20.74. IR (thin film): 2964, 2960, 2938, 1493, 1446, 1395, 1258 cm^{-1}. MS (EI, 12 eV; m/z (relative intensity)): 462 (2%), 460 (13), 458 (18), 424 (15), 423 (16), 422 (50), 420 (7), 387 (14), 386 (100) 384 (14). Anal. Calcd: C, 67.99; H, 6.14. Found: C, 66.97; H, 6.14.

Bis[1-(3-chloropropanon-1-yl)-2,4-dimethylphen-5-yl]methane (16). To an aluminum trichloride (11.8 g, 88.5 mmol) suspension in dichloromethane (100 mL) was added slowly at 0 °C 3-chloropropionyl chloride (10.6 mL, 111 mmol). The suspension was stirred for 30 min, resulting in a clear green solution. To this solution was added dropwise **15** (10.0 g, 44.6 mmol) in dichloromethane (50 mL) at 0 °C. Upon completion of the addition the mixture was stirred an additional 30 min to give a red solution which was poured over ice, separated, and extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with sodium bicarbonate and water, dried over MgSO$_4$, filtered, and concentrated. The crude solid was purified by Soxhlet extraction (petroleum ether) to give **16** (7.39 g, 18.2 mmol) as a white solid in 41% yield. Pure **16** was obtained by chromatography (SiO$_2$; 10% ethyl acetate/petroleum ether). Mp: 112−113 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.16 (s, 2H), 7.10 (s, 2H), 3.91 (s, 2H), 3.80 (t, J = 6.5 Hz, 4H), 3.17 (t, J = 6.5 Hz, 4H), 2.48 (s, 6H), 2.26 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 199.69, 141.08, 137.16, 135.17, 134.75, 134.30, 129.53, 43.44, 39.11, 35.83, 21.03, 19.53. IR (thin film): 3014, 2966, 1674, 1549, 1443, 1343, 1206, 1090, 1032 cm^{-1}. MS (EI, 70 eV; m/z (relative intensity)): 407 (1%), 406 (6), 405 (3), 404 (9), 343 (33), 342 (24), 341 (100), 313 (9), 305 (11), 303 (4), 272 (19), 207 (16), 191 (9), 139 (20).

Bis(4,6-dimethylindanon-7-yl)methane (17). To concentrated sulfuric acid (40 mL) at 0 °C was added **16** (3.71 g, 9.1 mmol). After the addition the red solution was warmed to 80 °C for 1 h. The reaction mixture was then cooled to room temperature, poured over ice, and extracted with ether (3 × 100 mL). The combined organic layers were washed with saturated NaHCO$_3$, water, and brine, dried over MgSO$_4$, filtered, and concentrated. The crude solid was purified by column chromatography (SiO$_2$; 10% ethyl acetate/petroleum ether) to give **17** (1.33 g, 4.0 mmol) in 49% yield. Mp: 186−188 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.92 (s, 2H), 4.07 (s, 2H), 2.57 (bs, 12H), 2.64 (dt, J = 2.0, 6.0 Hz, 4H), 2.54 (dt, J = 2.0, 6.0 Hz, 4H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 207.72, 155.01, 143.20, 136.56, 133.02, 132.69, 132.35, 36.86, 29.45, 24.67, 20.61, 17.96. IR (thin film): 3007, 2949, 2920, 1701, 1574, 1479, 1439, 1253 cm^{-1}. MS (EI, 70 eV; m/z (relative intensity)): 332 (46%), 317 (12), 172 (100), 144 (36), 129 (24), 128 (17), 115 (10).

Bis(4,6-dimethylindanol-7-yl)methane (18). To **17** (0.899 g, 2.7 mmol) in methanol (50 mL) and dichloromethane (25 mL) was slowly added at 0 °C NaBH$_4$ (0.257 g, 6.8 mmol). After the addition the reaction mixture was kept at room temperature for 12 h. The solvents were removed, and the crude material was partitioned between water and dichloromethane (3 × 50 mL). The combined organic layers were washed with water, dried over MgSO$_4$, filtered, and concentrated. The crude white solid was characterized and used in the next step without purification. Mp: 144−147 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.82 (s, 2H), 5.23 (m, 2H), 3.92 (s, 2H), 2.75−2.60 (m, 2H), 2.50−2.25 (m, 2H), 2.36 (s, 6H), 2.14 (s, 6H), 2.30−1.50 (m, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 143.34, 143.30, 141.05, 141.02, 137.23, 137.16, 132.31, 132.21, 132.19, 130.78, 130.71, 75.16, 75.06, 35.04, 35.02, 31.72, 31.63, 29.20, 29.16, 20.05 (2C), 17.90. IR (thin film): 3300, 3002, 2954, 2921, 2851, 1455, 1039 cm^{-1}. MS (EI, 70 eV; m/z (relative intensity)): 336 (42%), 318 (20), 303 (18), 300 (24), 285 (10), 174 (100), 159 (18), 156 (19), 145 (18).

Bis(4,6-dimethylinden-7-yl)methane (19). Crude **18** was placed in benzene (100 mL) with a few crystals of *p*-toluenesulfonic acid hydrate. The reaction flask was fitted with a Dean−Stark apparatus and refluxed for 3 h. The reaction mixture was cooled to room temperature, and aqueous NaHCO$_3$ (50 mL) was added. The organic layers were dried with MgSO$_4$, filtered, and concentrated. The crude solid was purified by column chromatography (SiO$_2$/petroleum ether) to give **19** (0.583 g, 1.94 mmol) as a white solid in 72% yield based on starting ketone **17**. Mp: 132−133 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.93 (s, 2H), 6.89 (dt, J = 5.5, 2.0 Hz, 2H), 6.32 (dt, J = 5.5, 2.0 Hz, 2H), 4.15 (s, 2H), 2.88 (bs, 4H), 2.41 (s, 6H), 2.29 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 142.80, 141.81, 133.31, 132.68, 131.24, 129.87, 129.82, 127.82, 38.54, 31.94, 20.02, 18.23. IR (thin film): 3055, 3000, 2957, 2914, 2855, 1474, 1437, 1386 cm^{-1}. MS (EI, 70 eV; m/z (relative intensity)): 301 (6%), 300 (60), 285 (17), 157 (12), 156 (100), 142 (8), 141 (12), 128 (8), 115 (6).

[Bis(4,6-dimethylinden-7-yl)methylidene]titanium Dichloride (*dl*-20). To **19** (0.660 g, 2.19 mmol) in tetrahydrofuran (2 mL) was added at −78 °C *n*-butyllithium (1.70 mL, 2.69 M in hexanes, 4.6 mmol). After the addition the reaction mixture was warmed to room temperature and stirred for 30 min. The dilithio salt solution was then added dropwise via syringe to titanium trichloride (0.41 g, 2.64 mmol) in tetrahydrofuran (1 mL) at −78 °C. When it was warmed to room temperature, the solution went from a purple to a dark green solution. After it reached room temperature, the mixture was brought to reflux for 5 h and then cooled to room temperature. The solvents were removed *in vacuo* and replaced with chloroform (10 mL) and 1 N hydrochloric acid (2 mL). The dark green liquid was stirred for 2 h in air, during which time a precipitate formed. The layers were separated and the aqueous layer extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with water, dried over MgSO$_4$, filtered, and concentrated (note: a substantial portion of the titanocene remained with the MgSO$_4$ due to product insolubility). The solid residue was rinsed with hexanes to give ***dl*-20** (0.352 g, 0.84 mmol) as a green precipitate in 38% yield. Mp: 200−220 °C dec. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.99 (s, 2H), 6.87 (m, 2H), 6.68 (m, 2H), 4.46 (s, 2H), 4.02 (m, 2H), 2.62 (bs, 12H). MS (EI, 12 eV; m/z (relative intensity)): 420 (4%), 418 (78), 417 (36), 414 (13), 383 (5), 382 (45), 381 (24), 380 (100), 378 (18), 344 (11), 300 (7), 298 (6), 297 (10), 283 (6), 156 (8).

[Bis(4,6-dimethylinden-7-yl)methylidene]zirconium Dichloride (*dl*-21). To **19** (0.396 g, 1.32 mmol) and tetrakis(dimethylamido)zirconium (0.347 g, 1.30 mmol) was added chlorobenzene (8 mL) at 0 °C. The clear yellow solution was then brought to 125 °C for 24 h, with the vessel open to the Schlenk line to ensure the escape of dimethylamine. The resulting light orange solution was concentrated *in vacuo*, and dimethylammonium hydrochloride (0.100 g, 1.23 mmol) in dichloromethane (50 mL) was added at 0 °C. This solution was warmed to room temperature and stirred for an additional 3 h (note: precipitate forms over the 3 h period). The resulting yellow solution was concentrated to 2 mL total volume, and hexanes (5 mL) were added dropwise. This slurry was stirred for 30 min and then filtered and rinsed with hexanes (2 × 5 mL) to give ***dl*-21** (0.259 g, 0.56 mmol) as a yellow powder in 43% yield. Mp: 235−245 °C dec. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.92 (s, 2H), 6.68 (dd, J = 3.5, 3.5 Hz, 2H), 6.57 (dd, J = 3.5, 2.0 Hz, 2H) 4.46 (s, 2H), 4.27 (dd, J = 3.5, 2.0 Hz, 2H), 2.63 (s, 6H), 2.55 (s, 6H). MS (EI, 12 eV; m/z (relative intensity)): 466 (2), 465 (5) 464 (28), 463 (20), 462 (70), 461 (42), 460 (42), 459 (60), 458 (100), 426 (21) 425 (12), 424 (35), 423 (21), 422 (52), 300 (33), 156 (45).

[Bis(5,7-dimethylinden-4-yl)methylidene]zirconium Dichloride (*dl*-21). To **19** (0.198 g, 0.66 mmol) in ether (5 mL) at −78 °C was added *n*-butyllithium (0.51 mL, 2.69 M in hexanes, 1.4 mmol). The resulting slurry was warmed to room temperature and stirred for an additional 5 h. To the dilithio salt was added zirconium tetrachloride (0.231 g, 0.99 mmol) via a side arm. The yellow slurry was stirred for 12 h at room temperature, followed by the removal of the solvent *in vacuo*. Dichloromethane (5 mL) was added to the solid and stirred 30 min. The dichloromethane was Schlenk-filtered, and the solid residue was further rinsed with dichloromethane (2 × 10 mL). The residue was dried *in vacuo*, and a ^{1}H NMR spectrum revealed that the desired product remained with the lithium chloride salt and was identical with that found with the procedure described above. The yield could not be obtained due to our inability to separate the material from lithium chloride.

X-ray Structure of *dl*-12a, *dl*-12b, and *dl*-13. The data were collected on a Siemens P4 diffractometer. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scans was applied. The structure was solved by direct methods using SHELXTL (Siemens systems) and refined by full-matrix least-squares on F^2 using all reflections. All the hydrogen atoms were located and refined isotropically. Details of the crystal data and refinement are given in Table 1.

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Supporting Information Available: X-ray crystal data for ***dl*-12a**, ***dl*-12b**, and ***dl*-13**, including figures giving views of the structures and tables of atomic coordinates, anisotropic parameters, bond lengths, and angles (26 pages). Ordering information is given on any current masthead page.

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