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Journal of Organometallic Chemistry 568 (1998) 41–51

Journal of Organo metallic Chemistry

Synthesis and structure of [1,2-bis(1-indenyl)benzene]titanium and zirconium dichlorides

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Received 29 January 1998; received in revised form 27 May 1998

Abstract

The palladium-catalyzed coupling of 1,2-diiodobenzene with indenylzinc complexes obtained from indene, 4-methylindene, 4,7-dimethylindene and hydrindancene gave 1,2-bis(1-indenyl)benzenes in 29–45% yield. New phenyl-bridged *ansa*-bis(indenyl)titanium and -zirconium dichlorides were obtained from these ligands in good yield either by addition of $TiCl_3$ or $ZrCl_4$ to their lithium salts (61–92% yield) or by addition of $Zr(NMe_2)_4$ to the neutral ligands (59–67%). In each case the zirconium tetraamide metalation gave very high *dl*-selectivity. The *n*-BuLi/$ZrCl_4$ metalation of the phenyl-bridged unsubstituted indene gave a 3:2 ratio of *dl*- to *meso*- while placing substituents at the 4,7- and 5,6-positions led to 10:1 selectivity in favor of the *dl*-isomer. The *n*-BuLi/$TiCl_3$ metalation gave between 1:1 and 4:1 selectivity. The solid state structure of [1,2-bis(1-indenyl)benzene]dichlorozirconium (*dl*-**6a**) was obtained by X-ray analysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Zirconocene; Titanocene; *ansa*-Metallocene; C_2-symmetric; Palladium-coupling; *ansa*-bis(indenyl)Zirconium dichloride; *ansa*-bis(indenyl)Titanium dichloride

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1. Introduction

Chiral group 4 *ansa*-metallocene complexes constitute an important group of organometallic compounds, serving both as precatalysts and reagents for organic synthesis ([1]a–o) and for the stereoregular polymerization of propene ([2]a–e). The most widely applied types of complexes are the ethylidene-bridged or silyl-bridged *ansa*-bis(tetrahydroindenyl)metal dichlorides **1** and **2** ([3]a, b [4]a, b) which possess helical-type chirality and exhibit C_2-symmetry both in the solid state and in solution. As more has become known about the conformational structure and reactivity of these *ansa*-metallocenes, it has become evident that subtle changes in the conformation of such deceptively simple complexes can result in large changes in reactivity ([5]a, b). The ethylidene-bridged complexes **1** have been demonstrated to exhibit significant conformational mobility ([6]a–d). One can visualize the ethano-bridge together with the centroid of the Cp ring and the zirconium atom forming a five-membered ring with interconvertable λ and δ helical conformational geometries ([6]a–d), none of which exists exclusively at the NMR reading temperature of 311 K ([5]a, b). On the other hand, silyl-bridged complexes of type **2** are conformationally well-defined ([5]a, b, [7]). In addition to effects arising through conformational differences, the cyclopentadienyl-metal-cyclopentadienyl angle has been shown to strongly influence reactivity ([5]a, b, [8]). In an attempt to produce conformationally better defined *ansa*-metallocenes we have undertaken the synthesis of *ortho*-phenyl-bridged *ansa*-metallocenes. These phenyl bridges moieties should be less reactive than the isolated double bond bridges in Brintzinger's ([6]a–d) a ethylidene-bridged complexes **3**. We have recently published the preparation of 1,2-benzenediyl-bridged bis(tetrahydroindenyl) complexes **4** and **5** [9]. In this paper

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[1] Phillips Petroleum Foundation Fellow, 1995.

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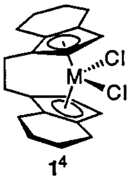
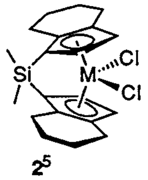
PII S0022-328X(98)00753-0

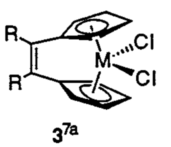
we report a more general method for preparation of 1,2-bis(1-indenyl)benzene ligands in one step from the corresponding indenes and 1,2-diiodobenzene via a palladium-catalyzed coupling reaction and we report the metalation of these ligands to form *ansa*-[1,2-bis(1-indenyl)benzene]dichlorozirconium and -titanium complexes **6** and **7**.



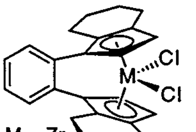
1[4]



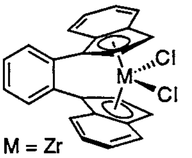
2[5]



3[7a]



4: M = Zr
5: M = Ti[10]



6: M = Zr
7: M = Ti

2. Results and discussion

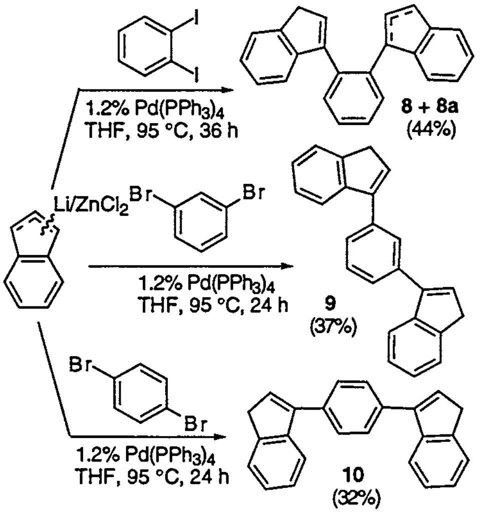
2.1. Synthesis of bis(1-indenyl)benzenes

One goal of our research was to develop a direct synthetic method that would enable the facile preparation of a variety of bis(indenyl)benzene ligands. Based on the promising applications of palladium-catalyzed coupling of cyclopentadienylmetal or indenylmetals with haloarenes ([10]a–d) we undertook the study of metal catalyzed couplings of indenylmetals with arenes. Through considerable experimentation and the screening of a wide variety of conditions ($C_6H_4X_2$, X: Br, I, OTf; IndM, M: H, $SnMe_3$, Li, MgBr, ZnCl; catalyst precursors: Pd(0), Pd(II) and Ni(II) complexes; solvents: THF, DMSO, HMPA, and ether; and temperature: room temperature to 160°C) two productive combinations of conditions were found for the coupling of indenylmetals with 1,2-dihalo-(or ditriflate-)arenes. When heated in DMSO at 110°C for 48 h, a mixture of 1,2-dibromobenzene, indenyltrimethyltin, catalytic $Pd(PPh_3)_4$ (6 mol%) and LiCl as a supporting ligand source, produced after purification the desired 1,2-bis(1-indenyl)benzene **8**, albeit in low yield (11%). A more favorable procedure involved the use of a Zn(II) species as the counter ion for the indenyl anion ([10]c). Thus, indenyllithium was prepared by the treatment of indene with *n*-BuLi in THF at −78°C. A zinc complex was formed in situ by the addition of the indenyllithium solution into a suspension of $ZnCl_2$ in THF at 0°C. A THF solution of 1,2-diiodobenzene and 1.2% of $Pd(PPh_3)_4$ was added via cannula to the indenyl-zinc chloride complex and the resulting solution was kept at 95°C in a sealable tube for 36 h. Aqueous work-up and silica gel chromatography provided bis(indene) **8** (44% yield) as a mixture of two double bond isomers (Scheme 1). Through repeated chromatography each individual isomer was isolated and characterized. Isomer **8a** having only one of the indenyl double bonds conjugated with the bridging phenyl group could be converted into the thermodynamically more stable bis-conjugated isomer **8** through a deprotonation, protonation sequence (*n*-BuLi; water) or by simply refluxing the isomeric mixture in toluene. The analogous reaction with 1,2-dibromobenzene gave the desired product in only greatly diminished yields.

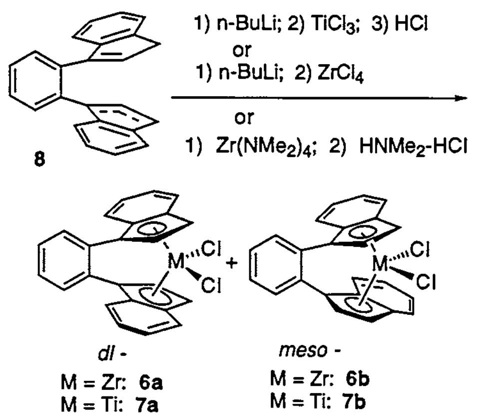
These one-step conditions (zinc chloride complex, catalytic palladium) were also successful for the coupling of 1,3-dibromobenzene or 1,4-dibromobenzene with indene to produce the known 1,3- and 1,4-bis(1-indenyl)benzenes (**9** and **10**) [11] in each case as a single double bond isomer in good yields (37 and 32%, respectively) considering the less reactive but available dibromoarenes were used. The coupling of the 1,3- or 1,4-diiodobenzenes was not investigated.

2.2. Metalation of 1,2-bis(1-indenyl)benzene *8*

The 1,2-bis(1-indenyl)benzene ligand was metalated with metal halides under ‘kinetic’ metalation conditions or with tetraamidozirconium under ‘equilibrium’conditions to form titanium dichloride and zirconium complexes (Scheme 2). Deprotonation of **8** with *n*-BuLi in THF at −78°C provided a red solution of the dianion which was added to $TiCl_3$ at −78°C. After refluxing the solution for 6 h and oxidizing with HCl in chloroform [12], a 1:1 mixture of the racemic and *meso*-isomers of *ansa*-[1,2-bis(1-indenyl)benzene]titanium dichloride **7a** + **b** was obtained in 89% overall yield. Based on the general observation that the indenyl pro-



Scheme 1. Palladium-catalyzed coupling of indene and dihalobenzenes.



Scheme 2. Metalation of 1,2-bis(1-indenyl)benzene.

ton signals for the *dl*-*ansa*-bis(indenyl)titanium dichloride isomer appear at higher field in the ^{1}H-NMR spectrum than the corresponding protons in the *meso*-isomer, the ^{1}H-NMR signals at 6.78 and 6.12 ppm were assigned to *dl*-**7a**, while those appearing at 7.01 and 6.64 ppm were assigned to *meso*-**7b**.

The zirconocene complex **6** was prepared via deprotonation of **8** with *n*-BuLi at −78°C in Et_2O, followed by the addition of solid $ZrCl_4$ at room temperature via a side arm and stirring for 24 h. After removal of the solvent, the crude product was dissolved in methylene chloride and the product was precipitated in 83% yield through addition of hexane. The ^{1}H-NMR spectrum of the crude reaction mixture showed signals which correspond to a 60:40 ratio of *dl*- to *meso*-isomers. The indenyl proton signals for the C_2-symmetric isomer appear at 6.66 and 6.23 ppm while those for the *meso*-isomer appear at 6.8 and 6.6 ppm These assignments were confirmed by the X-ray crystal structure of *dl*-**6a**. The *dl*/*meso*-selectivity in the metalation of the dilithium salt of phenyl bridged bis(indene) **8** is much lower than that observed in the analogous metalation of the ethylene bridged bis(indene) ligand. This effect may well be due to the greater conformational mobility in the ethylene bridged complex which results in increased interactions between the indenyl rings and an increased steric preference for the *dl*-isomer of the ethylene bridged complex.

To circumvent the presumably kinetic formation of the 3:2 mixture of the *dl*-and *meso*-isomers, the metalation of **8** with $Zr(NMe_2)_4$ in refluxing chlorobenzene under equilibrium conditions [13] was carried out. The resulting, more thermodynamically stable *dl*-isomer of the intermediate bis(indenyl)zirconium diamide was formed and transformed into the corresponding *ansa*-[1,2-bis(1-indenyl)benzene]zirconium dichloride (**6a**) using a solution of $Me_2NH{\cdot}HCl$ in dichloromethane (Scheme 2). In this case a single *dl*-isomer of **6a** was obtained by precipitation in 67% yield.

2.3. X-ray diffraction-derived structure of *dl*-**6a**

Crystals suitable for the X-ray diffraction were obtained by sublimation of the pure *dl*-isomer **6a**. The molecular structure of the *dl*-**6a** obtained by X-ray diffraction was derived according to the data in Table 1. Selected bond lengths and angles are given in Table 2. Fig. 1 presents two plots of this structure: (a) an ORTEP plot of the lateral view; (b) a PLUTO top view showing the approximate C_2-symmetry. The crystallographic data show that the solid state structure exhibits two noteworthy features. At 125.9°, the centroid-Zr-centroid angle is somewhat large for a two-atom bridged *ansa*-zirconocene dichloride. The related *ansa*-[1,2-bis(tetrahydroindenyl)benzene]-titanium dichloride (**5**) also has a similarly large angle (130.9°) for its class [9]. The zirconium complex *dl*-**6a** is twisted from being perfectly C_2-symmetric to a conformation having a 'tilt' angle of 8.5° between the Cl–Zr–Cl bisector and the zirconium atom to phenyl ring axis. The X-ray-derived structure of the related **5** exhibits a crystallographically imposed C_2-symmetrical conformation [9] while other 1,2-ethylene-bridged bis(indenyl)metal complexes show tilt angles of ca. 20° ([6]a).

Table 1
Crystal data and structure refinement for 6a

Identification code	RH18
Empirical formula	C_{24} H_{16} C_{12} Zr
Formula weight	466.49
Temperature (K)	230(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	6.5650(10)
b (Å)	11.7930(10)
c (Å)	12.6940(10)
α (°)	90.300(10)
β (°)	97.670(10)
γ (°)	102.800(10)
Volume (Å^3)	949.2(2)
Z	2
$D_{\mathrm{calc.}}$ (mg m^{-3})	1.632
Absorption coefficient (mm^{-1})	0.866
F(000)	468
Crystal size	0.3 × 0.3 × 0.2 mm
Theta range for data collection (°)	1.62–26.00
Index ranges	$-1\leq h\leq 8$, $-14\leq k\leq 14$, $-15\leq l\leq 15$
Reflections collected	4886
Independent reflectons	3712 [$R_{\mathrm{int}} = 0.0207$]
Refinement method	Full matrix least squares on F^2
Data/restraints/parameters	3690/0/308
Goodness of fit on $F2$	0.693
Final R indices [$I > \sigma(I)$]	$R_1 = 0.0259$, $wR_2 = 0.0678$
R indices (all data)	$R_1 = 0.0287$, $wR_2 = 0.0837$
Largest diff. Peak and hole (e Å^{-3})	0.397 and −0.650

Table 2
Bond lengths (Å) and angles (°) for 6a

Zr(1)–Cl(1)	2.4027 (6)
Zr(1)–Cl(2)	2.4107(6)
Zr(1)–CP(1)	2.237(2)
Zr(1)–CP(2)	2.247(2)
Zr(1)–C(9)	2.463(2)
Zr(1)–C(16)	2.484(2)
Zr(1)–C(17)	2.494(2)
Zr(1)–C(1)	2.506(2)
Zr(1)–C(8)	2.543(2)
Zr(1)–C(18)	2.556(2)
Zr(1)–C(2)	2.564(2)
Zr(1)–C(20)	2.591(2)
Zr(1)–C(19)	2.636(2)
Zr(1)–C(3)	2.642(2)
C(1)–C(2)	1.407(3)
C(1)–C(9)	1.414(3)
C(2)–C(3)	1.424(3)
C(3)–C(4)	1.421(3)
C(3)–C(8)	1.431(3)
C(4)–C(5)	1.361(4)
C(5)–C(6)	1.419(4)
C(6)–C(7)	1.366(3)
C(7)–C(8)	1.426(3)
C(8)–C(9)	1.443(3)
C(9)–C(10)	1.483(3)
C(10)–C(15)	1.393(3)
C(10)–C(11)	1.393(3)
C(11)–C(12)	1.398(3)
C(12)–C(13)	1.378(4)
C(13)–C(14)	1.385(4)
C(14)–C(15)	1.384(3)
C(15)–C(16)	1.492(3)
C(16)–C(17)	1.419(3)
C(16)–C(20)	1.434(3)
C(17)–C(18)	1.405(3)
C(18)–C(19)	1.424(3)
C(19)–C(24)	1.417(3)
C(19)–C(20)	1.434(3)
C(20)–C(21)	1.421(4)
C(21)–C(22)	1.360(4)
C(22)–C(23)	1.421(4)
C(23)–C(24)	1.362(4)
Cl(1)–Zr(1)–Cl(2)	97.60(2)
CP(1)–Zr(1)–CP92)	125.90(7)

2.4. Synthesis and metalation of phenyl-bridged substituted bis(indenes)

While the above equilibrium conditions selectively gave the *dl*-zirconium complex, such selective access to the *dl*-titanium complex was lacking. Examination of molecular models indicated that increased substitution on the 6- or 7-positions of *ansa*-bis(1-indenyl)metal complexes should result in sterically more crowded, less favorable *meso*-isomers, with the *dl*-complexes being less affected [5]. To establish the generality our new method of synthesizing phenyl-bridged indenes, we applied this method to the preparation the appropriately substituted phenyl-bridged ligands. As shown in Scheme 3, the one-step procedure for coupling 1,2-diiodobenzene is also successful with substituted indenes. In the coupling reaction between the unsymmetrically substituted 4-methylindene with 1,2-diiodobenzene, the only product observed, bis(indene) **11**, was a result of selective coupling at the less hindered indenyl site. A somewhat lower yield was also obtained when the indenyl group is forced to couple at a more hindered site in 4,7-dimethylindene to give **12** (29%). A good yield in the coupling reaction was obtained with the hydrindacene to give **14**. As seen from these results, the palladium-catalyzed coupling of indenyl anions with 1,2-diiodobenzene can tolorate sterically hindered substrates and shows high selectivity in the case of an unsymmetrically substituted indene.

Table 3 summarizes the metalation of the different 1,2-benzenediyl-bridged bis(indenes) with either the metal chlorides or the zirconium tetraamide. The 4-methylindene derivative **11** was only examined under the equilibrating conditions where it gave nearly the same selectivity as the indene ligand **8**. The metalation of 1,2-bis(4,7-dimethyl-1-indenyl)benzene (**12**) and 1,2-bis(hydrindacenyl)benzene (**14**) with zirconium tetrachloride gave very high selectivity for the *dl*-bis(indenyl)ziconium dichloride isomers **15a** and **17a**. Thus, the simple mixing of the dilithio-salts of **12** or **14** with solid $ZrCl_4$ in a glove-box, followed by the addition of diethyl ether at −78°C, and stirring at room temperature gave the crude products as yellow solids which could be purified to the *dl*- isomers after a simple crystallization. The use of $Zr(NMe_2)_4$ to metalate 1,2-bis(4,7-dimethyl-1-indenyl)benzene (**12**) gave nearly the same selectivity and yields as the $ZrCl_4$ metalation.

The conversion of 1,2-bis(4,7-dimethyl-1-indenyl)benzene (**12**) and 1,2-bis(hydrindacenyl)benzene (**14**) to their titanium dichloride complexes **16** and **18** was accomplished via mixing the dilithio-salt of **12** or **14** with $TiCl_3$, adding THF at −78°C, followed by refluxing for 6 h and oxidation with HCl in chloroform. The ^{1}H-NMR spectra of the solid crude reaction mixture of 4,7-dimethylindene-derived complex **16** showed signals which corresponded to a 80:20 ratio of racemic to *meso*-isomers. These isomers could be isolated by recrystallization and characterized separately. The cyclopentadienyl proton signals for the *dl*-**16a** isomer appear at 6.95 and 5.96 ppm and those of *meso*-**16b** appear at 6.98 and 6.84 ppm. The titanium complex **18** from bis(hydrindacene) was obtained as a 1:1 mixture of the *dl*- and *meso*-isomers which were not separated.

The premise for substitution at the 6- or 7-position of indene leading to higher *dl*-selectivity in the kinetic metalations with metal tetrachlorides was borne out with the zironocene complexes. While metalation of the bis(indenyl)benzene **8** with zirconium tetrachloride gave a 3:2 mixture of *dl*- and *meso*- isomers, metalation of bis(4,7-dimethylindenyl)benzene **12** and bis(hydrinda-

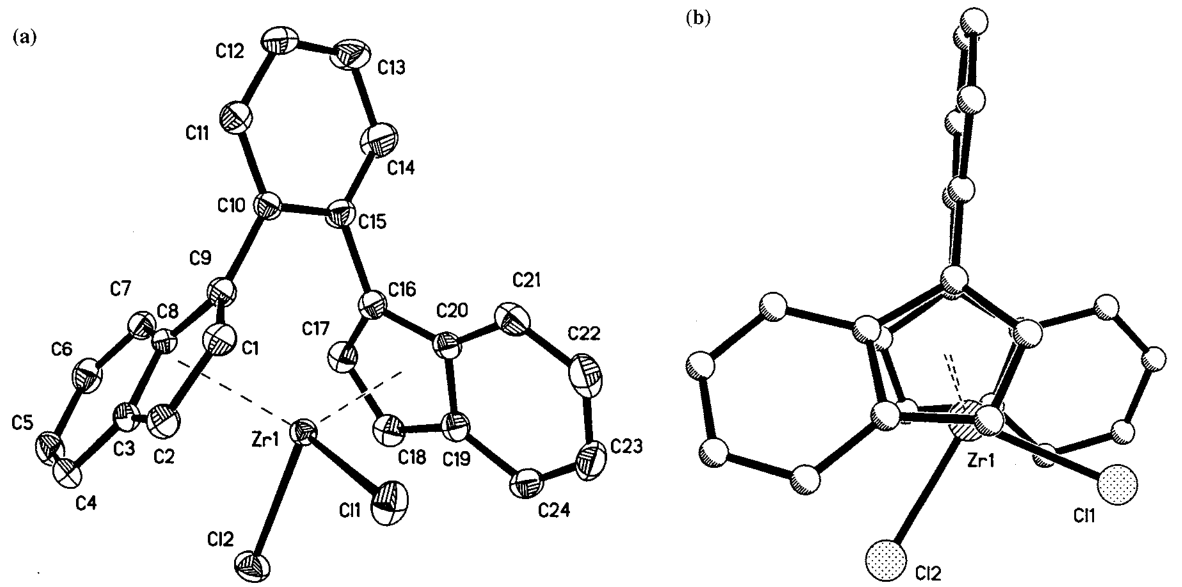


Fig. 1. X-ray structure of *dl*-**6a**: (a) ORTEP drawing with atoms drawn with 50% probability coefficients. (b) PLUTO-drawing showing approximate C_2-symmetry.

cenyl)benzene **14** both gave 10:1 selectivity in favor of the *dl*-isomers. The titanium complexes did not show the same sensitivity to indene subsitution, both the bis(indenyl)benzene **8** and bis(hydrindacenyl)benzene **14** gave 1:1 mixtures, and the metalation of bis(4,7-dimethylindenyl)benzene **12** gave an improvement to only 4:1 in favor of the *dl*-isomer. The increased *dl*/*meso* selectivity observed in these substituted indenyl complexes compensates for the selectivity lost when the conformationally more mobile ethylene bridge is replaced in the current study with the phenyl bridge.

2.5. Summary

A short and general method for the synthesis of various substituted 1,2-bis(1-indenyl)benzenes was developed using a palladium-catalyzed coupling between 1,2-diiodobenzene and various substituted indenes. The corresponding titanium and zirconium dichloride complexes of these ligands were prepared using *n*-BuLi/MCl_x or $Zr(NMe_2)_4$. Good *dl*-selectivity was observed in several cases. The solid state structure of [1,2-bis(1-indenyl)benzene]dichlorozirconium (*dl*-**6a**) was obtained.

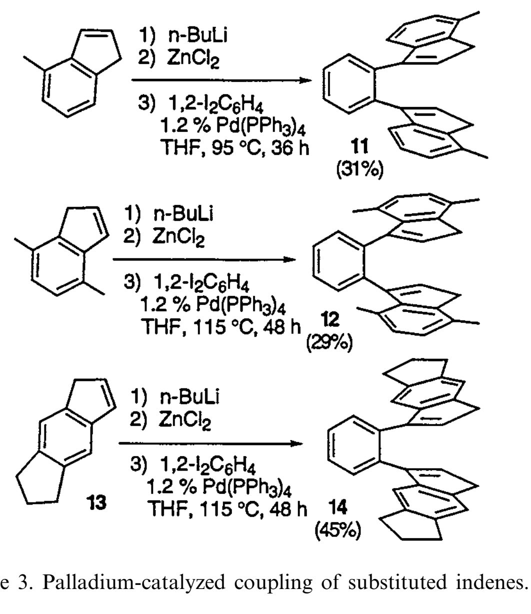
3. Experimental

3.1. General procedures

See reference [9] for standard experimental procedures and equipment used. Anhydrous $ZnCl_2$ was purchased (Aldrich) and used without further purification. Indenyltrimethyltin [14], 4-methyl-1-indene [15], 4,7-dimethyl-1-indene [15] and hydrindacen-1-one [16] were prepared according to the published procedures.

3.2. 1,2-Bis(1-indenyl)benzene (*8*) representative coupling procedure

To a solution of indene (9.64 g, 83 mmol) in THF (100 ml) at −78°C under nitrogen was added *n*-BuLi (29.5 ml, 79.7 mmol, 2.7 M in hexanes). The cooling bath was removed and the solution was allowed to warm to room temperature whereupon a deep red color developed. After 0.5 h at room temperature the solution was added dropwise via cannula to a suspension of $ZnCl_2$ (11.31 g, 83 mmol) in THF (40 ml) at 0°C and



Scheme 3. Palladium-catalyzed coupling of substituted indenes.

Table 3
Metalation of bis(indenyl)benzenes

Starting bis(indene)	[1,2-(R-Ind)$_2$benzene]ZrCl$_2$ or-TiCl$_2$		
	n-Buli/MClx (*dl*:*meso*)		Zr(NMe$_2$)$_4$ Zr
	Ti	Zr	
8, 1,2-Bis(1-indenyl)benzene	**7**, 1:1 (98%)	**6**, 3:2 (83%)	**6**, 10:1 (crude) (67%, pure)
11, 1,2-Bis(4-methyl-1-indenyl)benzene	—	—	**15**, 8:1 (crude) (59%, pure)
12, 1,2–Bis(4.7-dimethyl-1-indenyl)benzene	**16**, 4:1 (77%)	**17**, 10:1 (crude) (61%, pure)	**17**, 1 isomer only (61%)
14, 1,2-Bis(hydrindacenyl)benzene	**18**, 1:1 (92%)	**19**, 10:1 (crude) (74%, pure)	—

the pink solution was allowed to warm to room temperature and was kept at this temperature for 1 h. A solution of 1,2-diiodobenzene (10.6 g, 32.1 mmol) and Pd(PPh$_3$)$_4$ (0.43 g, 0.38 mmol) in THF (80 ml) was added via cannula to the pink solution of indenyl-zinc. The reaction tube was sealed and the resulting purple THF solution was kept at 95°C for 36 h and it gradually became black. The mixture was cooled to room temperature and the reaction was quenched with saturated aqueous NH$_4$Cl (70 ml). The mixture was extracted with petroleum ether (3×100 ml), dried with MgSO$_4$ and concentrated to a brown-red oil. The crude product was chromatographed (SiO$_2$, petroleum ether) to give **8** + **8a** as a mixture of two double bond isomers (4.35 g, 44%). Careful repeated chromatography allowed the isolation of each isomer: **8** (white solid): mp 95–97 °C. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.56 (m, 2H), 7.45 (m, 2H), 7.40 (m, 2H), 7.20 (m, 2H), 7.13 (m, 4H), 6.31 (dd, $J = 2.0$, 2.0 Hz, 2H), 3.26 (d, $J = 2.0$ Hz, 4H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 144.89, 144.47, 143.77, 135.15, 132.36, 129.89, 127.46, 125.83, 124.34, 123.57, 120.36, 38.21; IR (thin film) 3061, 3022, 2933, 1457, 1390, 1262 cm^{-1}; MS (EI, 12 eV): *m*/*e* 306 (68), 277 (8), 262 (100), 142 (36), 84 (96). **8a** (white solid): mp 135–138°C. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.54 (d, $J = 7.0$ Hz, 1H), 7.39–7.07 (m, 10H), 6.82 (dd, $J = 5.0$, 2.0 Hz, 1H), 6.70 (dd, $J = 8.0$, 1.5 Hz, 1H), 6.62 (bs, 1H), 5.52 (dd, $J = 5.0$, 2.0 Hz, 1H), 4.87 (bs, 1H), 3.59 (d, $J = 2.0$ Hz, 2H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 144.19, 145.87, 144.33, 143.95, 140.67, 137.77, 136.12, 132.43, 131.04, 129.85, 127.98, 127.33, 126.64, 126.56, 126.41, 125.16, 124.99, 123.96, 123.85, 121.07, 120.38, 53.34, 38.55; IR (thin film) 3065, 3018, 1561, 1482, 1457, 1265 cm^{-1}; MS (EI, 12 eV): *m*/*e* 306 (100), 291 (9), 215 (5).

*3.3. 1,3-Bis(1-indenyl)benzene (**9**)*

The representative procedure for the synthesis of 1,2-bis(1-indenyl)benzene (**8**) was followed using indene (0.75 g, 6.45 mmol), *n*-BuLi (2.31 ml, 6.2 mmol, 2.68 M in hexanes), ZnCl$_2$ (0.88 g, 6.45 mmol), 1,3-dibromobenzene (0.61 g, 2.58 mmol), Pd(PPh$_3$)$_4$ (0.09 g, 0.077 mmol) and THF (7 + 7 + 5 ml), 95°C, 24 h. The crude product was chromatographed (SiO$_2$, petroleum ether) to give a single isomer of **9** (0.29 g, 37%) as a colorless oil. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.84 (d, $J = 1.5$ Hz, 1H), 7.63 (dd, $J = 6.5$, 6.5 Hz, 4H), 7.55 (d, $J = 6.5$ Hz, 4H), 7.30 (m, 3H), 6.65 (dd, $J = 1.5$, 1.5 Hz, 2H), 3.54 (bs, 4H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 145.14, 144.77, 143.89, 136.48, 131.19, 128.81, 127.00, 126.97, 126.20, 124.91, 124.14, 120.35, 38.24; IR (thin film) 3016, 2877, 2766, 1603, 1479, 1457, 1389, 1299 cm^{-1}; MS (EI, 70 eV): *m*/*e* 306 (100), 289 (14), 277 (21), 191 (18), 189 (15), 152 (14), 115 (17).

*3.4. 1,4-Bis(1-indenyl)benzene (**10**)*

The representative procedure for the synthesis of 1,2-bis(1-indenyl)benzene (**8**) was followed using indene (0.75 g, 6.45 mmol), *n*-BuLi (2.31 ml, 6.2 mmol, 2.68 M in hexanes), ZnCl$_2$ (0.88 g, 6.45 mmol), 1,4-dibromobenzene (0.61 g, 2.58 mmol), Pd(PPh$_3$)$_4$ (0.09 g, 0.077 mmol) and THF (7 + 7 + 5 ml), 95°C, 24 h. The crude product was chromatographed (SiO$_2$, petroleum ether) to give a single isomer of **10** (0.253 g, 32%) as a colorless oil. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.70 (s, 4H), 7.67 (d, $J = 7.5$ Hz, 2H), 7.56 (d, $J = 7.5$ Hz, 2H), 7.32 (m, 4H), 6.65 (dd, $J = 2.0$, 2.0 Hz, 2H), 3.55 (d, $J = 2.0$ Hz, 4H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 144.80, 143.88, 135.44, 131.03, 127.88(2C), 126.19, 124.89, 124.14, 120.38, 38.25; IR (thin film) 2877, 1453, 1379, 1335 cm^{-1}; MS (EI, 70 eV): *m*/*e* 306 (100), 304 (18), 289 (14), 191 (16), 189 (17), 152 (15), 115 (9).

*3.5. [1,2-Bis(1-indenyl)benzene]dichlorotitanium (**7**)*

To a THF solution (3 ml) of 1,2-bis(1-indenyl)benzene (**8**; 0.12 g, 0.39 mmol) at 78°C under nitrogen was added *n*-BuLi (0.32 ml, 0.86 mmol, 2.7 M in hexanes) to give a red color. The cooling bath was removed and the solution was allowed to warm to room temperature. After 0.5 h at room temperature, the solution was added to a suspension of TiCl$_3$ (0.073

g, 0.47 mmol) in THF (1 ml) at −78°C, it was allowed to warm to room temperature was then refluxed for 6 h. After cooling to room temperature, the solution was concentrated in vacuo, the residue taken up in $CHCl_3$ (5 ml) and 6 M HCl (1 ml) added and allowed to stir for 1.5 h. The organic layer was separated and the water layer extracted with CH_2Cl_2 (2×5 ml), dried over $MgSO_4$ and concentrated to provide a dark brown solid. The solid was rinsed with hexanes, filtered and dried in vacuo to give **7** as a dark brown solid (0.165 g, 89%) as a 50:50 mixture of *meso*- and *dl*-isomers. ^1H-NMR (300 MHz, $CDCl_3$) δ 7.63–7.02 (m, 12H), 7.01 (d, $J = 3.0$ Hz, 1H), 6.78 (d, $J = 3.0$ Hz, 1H), 6.64 (d, $J = 3.0$ Hz, 1H), 6.12 (d, J = 3.0 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 138.91, 138.81, 130.06, 129.95, 129.88, 129.81, 129.52, 128.94, 128.90, 128.82, 128.75, 128.19, 126.38, 125.86, 125.76, 125.13, 124.98, 124.35, 123.22, 122.92, 121.80, 119.05, 118.89, 117.70; IR (thin film) 3066, 2930, 1736, 1601, 1460, 1433, 1261 cm^{-1}; MS (EI, 12 eV): *m/e* 318 (6), 306 (13), 92 (17), 84 (100), 49 (23).

3.6. [1,2-Bis(1-indenyl)benzene]dichlorozirconium (**6**)

3.6.1. $ZrCl_4$-method

To a solution of 1,2-bis(1-indenyl)benzene (**8**) (0.140 g, 0.457 mmol) in ether (10 ml) was slowly added *n*-BuLi (0.37 ml, 2.70 M) at 0°C under argon. While stirring 6 h at room temperature a white precipitate formed. $ZrCl_4$ (0.128 g, 0.549 mmol) was added via sidearm and the solution was stirred overnight at room temperature. The solvent was removed in vacuo, and the solid was dissolved in methylene chloride (2 ml). To the resulting orange solution was added hexanes dropwise until a yellow precipitate formed. The yellow precipitate was filtered and its ^1H-NMR spectrum indicated the presence of a 1.5:1 mixture of *dl*:*meso*-isomers of **6**. The characteristic signals were 6.78 and 6.12 ppm for *dl*-**6a** and 6.8 and 6.6 ppm for *meso*-**6b**. The pure *dl*-isomer was prepared by the alternate method below and fully characterized. The *meso*-isomer was not separable thus not characterized.

3.6.2. $Zr(NMe_2)_4$ method

$Zr(NMe_2)_4$ (0.17 g, 0.63 mmol) and 1,2-bis(1-indenyl)benzene (**8**) (0.195 g, 0.63 mmol) were placed in a Schlenk vessel, and chlorobenzene (4 ml) was added at 0°C under argon. The reaction mixture was refluxed for 17 h. After this time the reaction mixture was cooled to 0°C, and a solution of $Me_2NH{\cdot}HCl$ (0.095 g, 1.16 mmol) in CH_2Cl_2 (20 ml) was added dropwise over 15 min, during which time the color changed from red-orange to yellow-orange. The reaction mixture was stirred at room temperature for 3 h and then concentrated in vacuo. The solid was rinsed with hexanes, filtered and dried in vacuo to furnish the pure *dl*-isomer of **6a** as a yellow powder (0.199 g, 67%): mp: decomp. >220°C. ^1H-NMR (300 MHz, $CDCl_3$) δ 7.57–7.53 (m, 4H), 7.43–7.33 (m, 4H), 7.25 (d, $J = 6.0$ Hz, 2H), 7.13 (dd, $J = 8.5$, 6.0 Hz, 2H), 6.66 (d, $J = 2.5$ Hz, 2H), 6.23 (d, $J = 2.5$ Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 138.27, 130.91, 129.37, 128.77, 127.13, 127.11, 125.31, 124.28, 121.97, 119.97, 115.70, 110.58; IR (thin film) 3059, 1678, 1612, 1521, 1475, 1439, 1260,1210 cm^{-1}; MS (EI, 12 eV): *m/e* 472 ($M^+ + 8$, 2), 470 ($M^+ + 6$, 34), 469 ($M^+ + 5$, 12), 468 ($M^+ + 4$, 64), 467 ($M^+ + 3$, 31), 466 ($M^+ + 2$, 100), 465 ($M^+ + 1$, 34), 462 (M^+, 89), 432 (1), 432 (1), 428 (2), 306 (4), 304 (30); Anal. calculated for $C_{24}H_{16}ZrCl_2$: C, 61.79; H, 3.46. Found: C, 61.68; H, 3.39.

3.7. X-ray diffraction of **6a**

Crystals of **6a** suitable for X-ray diffraction were obtained by slow sublimation at 150°C at 10^{-3} Torr. The data were collected on a Siemens P4 diffractometer with Mo–K_α radiation. The data were corrected for Lorentz and polarization effects; absorption correction was not applied since it was judged to be insignificant. The structure was solved by the heavy atom method and refined by full-matrix least-squares on F^2 using all reflections (SHELXTL 5.03, Siemens). All the hydrogen atoms were located in the difference map and refined isotropically. Details of the crystal data and refinement are given in Table 1.

3.8. 1,2-Bis(4-methyl-1-indenyl)benzene (**11**)

The representative procedure for the synthesis of 1,2-bis(1-indenyl)benzene (**8**) was followed using 4-methyl-1-indene (8.0 g, 61.5 mmol), *n*-BuLi (22.0 ml, 59 mmol, 2.69 M in hexanes), $ZnCl_2$ (8.39 g, 61.5 mmol), 1,2-diiodobenzene (8.12 g, 24.6 mmol), $Pd(PPh_3)_4$ (0.34 g, 0.3 mmol) and THF (80 + 30 + 60 ml). The crude product was chromatographed (SiO_2, petroleum ether) to give **11** + **11a** as a mixture of two double bond isomers (2.55 g, 31%). Careful repeated chromatography allowed the isolation of each individual isomer; **11** (white solid): mp: 53–55°C; ^1H-NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, $J = 5.5$, 3.5 Hz, 2H), 5.53 (dd, $J = 5.5$, 3.5 Hz, 2H), 7.20 (d, $J = 4.0$ Hz, 4H), 7.06 (dd, $J = 4.0$, 4.0 Hz, 2H), 6.41 (dd, $J = 2.0$, 2.0 Hz, 2H), 3.26 (dd, $J = 2.0$, 2.0 Hz, 4H), 2.43 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.85, 144.84, 142.60, 135.50, 132.77, 132.03, 130.05, 127.46, 126.43, 125.74, 118.28, 37.22, 18.71; IR (thin film) 3042, 3017, 2918, 1598, 1478, 1440, 1380, 1265 cm^{-1}; MS (EI, 12 eV): *m/e* 335 (10), 334 (100), 319 (9), 229 (5), 86 (12), 84 (10); **11a** (colorless oil). ^1H-NMR (300 MHz, $CDCl_3$) δ 7.48–7.11 (m, 9H), 7.01 (dd, $J = 5.5$, 2.0 Hz, 1H), 6.81 (d, $J = 8.0$ Hz, 1H), 6.72 (bs, 1H), 6.62 (dd, $J = 5.5$, 2.0 Hz, 1H), 4.98 (bs, 1H), 3.54 (d, $J = 2.0$ Hz, 2H), 2.53 (s, 3H), 2.51 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 149.23, 145.61, 144.98, 142.68, 141.37, 140.20, 137.99, 136.35, 133.98, 133.72, 132.15, 130.49, 129.92, 128.80, 128.64, 128.55, 127.99, 126.89, 126.63, 125.33, 121.43, 118.26, 53.68, 37.50, 18.75, 18.67; IR (thin film) 3057, 3017, 2918, 1599, 1482, 1434, 1378, 1265 cm^{-1}; MS (EI, 12 eV): *m*/*e* 335 (12), 334 (100), 319 (16), 262 (79), 229 (15), 86 (17), 84 (25).

*3.9. 1,2-Bis(4,7-dimethyl-1-indenyl)benzene (**12**)*

The representative procedure for the synthesis of 1,2-bis(1-indenyl)benzene (**8**) was followed using 4,7-methyl-1-indene (4.4 g, 30.5 mmol), *n*-BuLi (10.93 ml, 29.3 mmol, 2.68 M in hexanes), $ZnCl_2$ (4.16 g, 30.5 mmol), 1,2-diiodobenzene (4.03 g, 12.2 mmol), $Pd(PPh_3)_4$ (0.166 g, 0.146 mmol) and THF (30 + 10 + 20 ml), 115°C, 48 h. The crude product was chromatographed (SiO_2, petroleum ether) to give **12** as an inseparable mixture of two double bond isomers (1.31 g, 30%). Conversion of this mixture into the dilithium salt (*n*-BuLi, THF, − 78°C), and the subsequent quenching with water resulted in the formation of a single isomer of **12** as a white solid: mp: 62–64°C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 4H), 6.41 (d, $J = 7.5$ Hz, 2H), 6.90 (d, $J = 7.4$ Hz, 2H), 6.04 (dd, $J = 2.0$, 2.0 Hz, 2H), 3.15 (dd, $J = 23.5$, 2.0 Hz, 2H), 3.97 (dd, $J = 23.5$, 2.0 Hz, 2H), 2.28 (s, 6H), 2.01 (s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 145.50, 143.33, 142.98, 138.27, 130.84, 130.22, 129.80, 129.15, 129.67, 126.64, 125.75 (2C), 36.96, 19.41, 18.28; IR (thin film) 3059, 2959, 2918, 1494, 1456, 1378, 1260 cm^{-1}; MS (EI, 12 eV): *m*/*e* 362 (100), 347 (23), 243 (9).

*3.10. Hydrindacen-1-ene (**13**)*

Hydrindacen-1-one [16] (11.5 g, 66.9 mmol) was dissolved in methanol (100 ml) and cooled to 0°C. $NaBH_4$ (2.53 g, 66.9 mmol) was added in several portions. The ice-bath was removed and the reaction mixture was stirred at room temperature for 4 h. All volatiles were removed in vacuo. Water (100 ml) was added and the resulting suspension was extracted with dichloromethane (3 × 100 ml), dried with $MgSO_4$ and concentrated to give hydrindacen-1-ol (10.95 g, 94%) as a white solid; mp: 105–108°C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.25 (bs, 1H), 7.11 (bs, 1H), 5.19 (dd, $J = 6.0$, 6.0 Hz, 1H), 3.01 (ddd, $J = 15.0$, 8.0, 5.0 Hz, 1H), 2.87 (dd, $J = 7.5$, 7.5 Hz, 4H), 2.76 (ddd, $J = 15.0$, 8.0, 5.0 Hz, 1H), 2.48 (dddd, $J = 13.0$, 8.0, 6.0, 5.0 Hz, 1H), 2.08 (ddd, $J = 15.0$, 11.0, 7.5 Hz, 2H), 1.95 (dddd, $J = 13.0$, 8.0, 6.0, 5.0 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ; IR (thin film) 3290, 2950, 2840, 1722, 1471, 1433, 1345, 1261, 1063 cm^{-1}; MS (EI, 12 eV): *m*/*e* 174 (100), 157 (10), 146 (31).

p-TsOH (0.25 g, 1.3 mmol) was added to a solution of the above hydrindacen-1-ol (10 g, 57.4 mmol) in benzene (100 ml) and the resulting mixture was refluxed with removal of water with a Dean-Stark adapter until the theoretical amount of water was collected. The solution was cooled to room temperature, rinsed once with a saturated solution of Na_2CO_3 (20 ml), dried with Na_2SO_4 and evaporated in vacuo. The crude product was chromatographed (SiO_2, petroleum ether) to give **13** (4.78 g, 53%) as a white solid; mp: 38–40°C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.28 (s, 1H), 6.85 (m, 1H), 6.50 (ddd, $J = 5.5$, 2.0, 2.0 Hz, 1H), 3.36 (s, 2H), 2.94 (dd, $J = 7.5$, 7.5 Hz, 4H), 2.12 (dddd, $J = 7.5$, 7.5, 7.5, 7.5 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 143.39, 142.32, 142.18, 140.94, 133.31, 132.00, 119.89, 116.83, 38.55, 32.70 (2C), 26.01; IR (thin film) 2949, 2927, 2842, 1635, 1462, 1440, 1390, 1348, 1274, 1213 cm^{-1}; MS (EI, 12 eV): *m*/*e* 156 (100), 141 (13), 128 (7).

*3.11. 1,2-Bis(hydrindacenyl)benzene (**14**)*

The representative procedure for the synthesis of 1,2-bis(1-indenyl)benzene (**8**) was followed using hydrindacen-1-ene (**13**) (3.6 g, 23 mmol), *n*-BuLi (8.52 ml, 22 mmol, 2.6 M in hexanes), $ZnCl_2$ (3.15 g, 23 mmol), 1,2-diiodobenzene (3.04 g, 9.23 mmol), $Pd(PPh_3)_4$ (0.128 g, 0.111 mmol) and THF (25 + 10 + 15 ml), 115°C, 48 h. The crude product was chromatographed (SiO_2, petroleum ether) to give **14** as a mixture of two double bond isomers (1.6 g, 45%). Conversion of this mixture into the dilithium salt (*n*-BuLi, THF, − 78°C), and the subsequent quenching with water resulted in the formation of a single isomer of **14** as a white solid; mp: decomp. > 240°C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, $J = 5.5$, 3.5 Hz, 2H), 7.42 (dd, $J = 5.5$, 3.5 Hz, 2H), 7.26 (s, 2H), 7.08 (s, 2H), 6.16 (dd, $J = 2.0$, 2.0 Hz, 2H), 3.19 (s, 4H), 2.89 (dd, $J = 7.0$, 7.0 Hz, 4H), 2.76 (dd, $J = 7.0$, 7.0 Hz, 4H), 2.05 (dddd, $J = 7.0$, 7.0, 7.0, 7.0 Hz, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.12, 143.98, 142.29, 141.94, 140.60, 135.62, 131.35, 129.81, 127.16, 119.86, 116.27, 37.73, 32.63, 32.56, 29.71, 25.93; IR (thin film) 3055, 2948, 2840, 1705, 1611, 1477, 1438, 1318, 1264 cm^{-1}; MS (EI, 12 eV): *m*/*e* 386 (57), 277 (42), 156 (39), 86 (22), 71 (100), 56 (23).

*3.12. [1,2-Bis(4-methyl-1-indenyl)benzene]-dichlorozirconium (**15**)*

The procedure for the synthesis of [1,2-bis(indenyl)benzene]zirconium dichloride (**7**) was followed using 1,2-bis(4-methyl-1-indenyl)benzene (**11**) (0.25 g, 0.74 mmol), $Zr(NMe_2)_4$ (0.2 g, 0.74 mmol), chlorobenzene (5 ml), $Me_2NH{\cdot}HCl$ (0.12 g, 1.45 mmol) and CH_2Cl_2 (25 ml). The crude product was purified by rinsing with hexanes, filtering and in vacuo removal of solvent to yield the yellow powder, consisting of the pure *dl*-isomer *dl*-**15a** (0.22 g, 59%) as a yellow solid: mp 292–295°C (dec.). ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.56 (dd, $J=5.5$, 3.5 Hz, 2H), 7.41 (dd, $J=5.5$, 3.5 Hz, 2H), 7.14–7.06 (m, 6H), 6.66 (d, $J=3.5$ Hz, 2H), 6.21 (d, $J=3.5$ Hz, 2H), 2.43 (s, 6H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 138.48, 135.25, 130.81, 130.7, 128.67, 127.51, 125.87, 124.08, 120.28, 119.05, 114.95. 109.28, 19.18; IR (thin film) 3022, 2925, 1596, 1477, 1460, 1380, 1268 cm^{-1}; MS (EI, 12 eV): *m/e* 498 (M$^+$ + 6, 22), 496 (M$^+$ + 4, 100), 495 (M$^+$ + 3, 49), 494 (M$^+$ + 2, 88), 493 (M$^+$ + 1, 73), 492 (M$^+$, 98), 460 (14), 458 (20), 456 (30), 334 (9).

3.13. [1,2-Bis(4,7-dimethyl-1-indenyl)benzene]-dichlorotitanium (16)

To a solution of 1,2-bis(4,7-dimethyl-1-indenyl)-benzene (**12**) (2.3 g, 6.35 mmol) in diethyl ether (25 ml) at −78°C under nitrogen was added *n*-BuLi (6.1 ml, 15.86 mmol, 2.6 M in hexanes). The cooling bath was removed and the solution was allowed to warm to room temperature. After 4 h at room temperature hexanes (50 ml) were added to the white suspension to ensure the complete precipitation of the dilithium salt of the ligand. Filtration and drying provided the dilithium salt of **12** (1.85 g, 78%) as a off-white solid. In a glove-box, TiCl$_3$ (0.625 g, 4.05 mmol) and the dilithium salt of **12** (1.32 g, 3.53 mmol) were placed inside a Schlenk tube. On the Schlenk line, this mixture was cooled to −78°C under argon and THF (20 ml) was added dropwise. The cooling bath was removed and the solution allowed to warm to room temperature developing a dark-green, brown color. The reaction mixture was kept at 95°C for 6 h. After cooling to room temperature, the solution was concentrated in vacuo, the residue taken up in CHCl$_3$ (25 ml) and 6M HCl (4 ml) added and the mixture was stirred for 1.5 h. The organic layer was separated and the water layer extracted with CH$_2$Cl$_2$ (2 × 20 ml), dried over MgSO$_4$ and concentrated to provide **16** as a dark green-brown solid (1.3 g, 77%) as a 4:1 mixture of *dl* to *meso*. Hexanes (50 ml) were added to this mixture, the resulting suspension was stirred for 1 min and filtered. Hexanes (40 ml) were added to the newly obtained solid, stirred for 1 min and filtered again. Repetition of this cycle one more time with hexanes (30 ml) resulted in nearly complete separation of the diastereomeric mixture. Evaporation of the combined hexane rinses furnished nearly isomerically pure *dl*-**16a** (1.02 g, 61%) as a green solid: mp: decomp. > 165°C. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.56 (dd, $J=5.5$, 3.0 Hz, 2H), 7.46 (dd, $J=5.5$, 3.0 Hz, 2H), 7.10 (d, $J=6.0$ Hz, 2H), 6.95 (d, $J=3.5$ Hz, 2H), 6.81 (d, $J=6.0$ Hz, 2H), 5.96 (d, $J=3.5$ Hz, 2H), 2.43 (s, 6H), 2.07 (s, 6H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 140.44, 133.49, 132.81, 131.42, 130.04, 129.50, 128.23, 128.08, 126.69, 126.22, 119.99, 116.23, 20.11, 18.96; IR (thin film) 3044, 2966, 2915, 1601, 1455, 1435, 1380, 1263 cm^{-1}; MS (EI, 12 eV): *m/e* 482 (M$^+$ + 4, 11), 481 (M$^+$ + 3, 13), 480 (M$^+$ + 2, 81), 478 (M$^+$, 100), 444 (14), 443 (29), 442 (81), 406 (19), 360 (13). Anal. Calculated for C$_{28}$H$_{24}$TiCl$_2$: C, 70.17; H, 5.05. Found: C, 69.63; H, 5.24. The brown solid left on the filter was the nearly pure *meso*-isomer **16b** (0.25 g, 14%): mp: decomp. > 225°C. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.51 (s, 4H), 6.98 (d, $J=3.5$ Hz, 2H), 6.90 (d, $J=7.5$ Hz, 2H), 6.88 (d, $J=7.5$ Hz, 2H), 6.84 (d, $J=3.5$ Hz, 2H), 2.55 (s, 6H), 1.93 (s, 6H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 140.89, 134.48, 132.36, 132.25, 131.57, 130.74, 127.82, 127.67, 127.03, 124.99, 120.19, 117.51, 20.29, 18.97; IR (thin film) 3044, 2966, 2915, 1601, 1455, 1435, 1380, 1263 cm^{-1}; MS (EI, 12 eV): *m/e* 482 (M$^+$ + 4, 11), 481 (M$^+$ + 3, 13), 480 (M$^+$ + 2, 81), 478 (M$^+$, 100), 444 (14), 443 (29), 442 (81), 406 (19), 360 (13).

3.14. [1,2-Bis(4,7-dimethyl-1-indenyl)benzene]-dichlorozirconium (17)

In a glove-box ZrCl$_4$ (0.082 g, 0.35 mmol) and the dilithium salt of **12** (0.12 g, 0.32 mmol) were placed inside a Schlenk tube. On the Schlenk line this mixture was cooled to −78°C under argon and diethyl ether (10 ml) was added dropwise. The cooling bath was removed and the solution allowed to warm to room temperature for 24 h. The yellow suspension was pumped to dryness, triturated with dichloromethane (8 ml) and filtered. The mother liquor was concentrated in vacuo to provide **17** as a yellow solid. ^{1}H-NMR spectroscopy has shown that the crude product consisted of the mixture of *dl*- and *meso*-isomers in ratio 10:1. Rinsing of that mixture with hexanes (10 ml) and back-filtration gave nearly isomerically pure *dl*-isomer **17a** (0.102 g, 61%) as a yellow solid.

Isomerically pure *dl*-**17a** was also obtained under the equilibrium conditions using **12**, Zr(NMe$_2$)$_4$ and chlorobenzene, followed by the conversion of the intermediate diamidozirconocene into the corresponding zirconium dichloride complex **17** employing Me$_2$NH·HCl in CH$_2$Cl$_2$, as described above; mp: decomp. > 280°C. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.53 (dd, $J=5.5$, 3.5 Hz, 2H), 7.44 (dd, $J=5.5$, 3.5 Hz, 2H), 7.02 (d, $J=7.0$ Hz, 2H), 6.78 (d, $J=3.5$ Hz, 2H), 6.76 (d, $J=7.0$ Hz, 2H), 6.11 (d, $J=3.5$ Hz, 2H), 2.37 (s, 6H), 2.05 (s, 6H); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 140.19, 132.81, 130.86, 130.49, 130.17, 127.93, 126.16, 123.34, 120.53, 114.68, 111.44, 20.00, 18.82; IR (thin film) 2963, 2918, 1558, 1493, 1456, 1436, 1379, 1260 cm^{-1}; MS (EI, 12 eV): *m/e*

528 (M^+ + 8, 3), 526 (M^+ + 6, 18), 525 (M^+ + 5, 17), 524 (M^+ + 4, 64), 523 (M^+ + 3, 37), 522 (M^+ + 2, 100), 521 (M^+ + 1, 50), 520 (M^+, 91), 488 (8), 485 (6), 484 (8), 362 (36), 360 (17), 243 (2), 228 (2). Anal. Calculated for $C_{28}H_{24}ZrCl_2$: C, 64.35; H, 4.63. Found: C, 63.89; H, 5.01.

*3.15. [1,2-Bis(hydrindacenyl)benzene]dichlorotitanium (**18**)*

To a solution of 1,2-bis(hydrindacenyl)benzene (**14**) (1.0 g, 2.6 mmol) in diethyl ether (10 ml) at − 78°C under nitrogen was added *n*-BuLi (2.5 ml, 6.51 mmol, 2.6 M in hexanes). The cooling bath was removed and the solution allowed to warm to room temperature. After 4 h at room temperature hexanes (20 ml) were added to the yellow-white suspention to ensure the complete precipitation of the dilithium salt of the ligand. Filtration and drying provided the dilithium salt of **14** (1.0 g, 97%) as a off-white solid. In a glove-box, $TiCl_3$ (0.08 g, 0.515 mmol) and the dilithium salt of **14** (0.17 g, 0.429 mmol) were placed inside a Schlenk tube. On a Schlenk line, this mixture was cooled to − 78°C under argon and THF (3 ml) was added dropwise. The cooling bath was removed and the solution allowed to warm to room temperature and it developed a dark green-brown color. After refluxing for 4 h, the reaction mixture was cooled to room temperature and the solution was concentrated in vacuo, the residue taken up in $CHCl_3$ (10 ml) and 6M HCl (1 ml) added and allowed to stir for 1 h. The organic layer was separated and the water layer extracted with CH_2Cl_2 (2 × 5 ml), dried over $MgSO_4$ and concentrated to provide **18** as a dark brown solid (0.2 g, 92%). ^{1}H-NMR spectroscopy has shown that the crude product consisted of the mixture of *dl*- and *meso*-isomers in ratio 1:1. This mixture was not separated. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.57–7.42 (m, 8H), 7.38 (s, 2H), 7.33 (s, 2H), 7.08 (s, 2H), 6.82 (s, 2H), 6.79 (d, $J = 3.5$ Hz, 2H), 6.55 (d, $J = 3.5$ Hz, 2H), 6.64 (d, $J = 3.5$ Hz, 2H), 5.98 (d, $J = 3.5$ Hz, 2H), 3.25–2.75 (m, 16H), 2.20–1.85 (m, 8H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 148.99, 148.25, 147.98, 147.86, 139.6, 131.66, 130.01, 129.90, 128.61, 128.32, 125.13, 123.41, 121.22, 120.78, 120.02, 119.39, 119.34, 119.08, 117.83, 117.04, 116.85, 116.45, 116.42, 32.66, 32.56, 32.45, 32.38, 26.24, 25, 62; IR (thin film) 2950, 2837, 1626, 1457, 1434, 1262 cm^{-1}; MS (EI, 12 eV): *m*/*e* 502 (3), 412 (11), 398 (36), 384 (100), 308 (7), 213 (8), 129 (10), 93 (9), 56 (11).

*3.16. [1,2-Bis(hydrindacenyl)benzene]dichlorozirconium (**19**)*

In a glove-box, $ZrCl_4$ (0.106 g, 0.454 mmol) and the dilithium salt of **14** (0.15 g, 0.378 mmol) were placed inside a Schlenk tube. On a Schlenk line, this mixture was cooled to − 78°C under argon and diethyl ether (9 ml) was added dropwise. The cooling bath was removed and the solution allowed to warm to room temperature for 24 h. The yellow suspension was pumped to dryness, triturated with dichloromethane (6 ml) and filtered. The mother liquor was concentrated in vacuo to provide **19** as a yellow solid. ^{1}H-NMR spectroscopy has shown that the crude product consisted of the mixture of *dl*- and *meso*-isomers in ratio 10:1. Rinsing that mixture with hexanes (7 ml) and back-filtration gave the pure *dl*-isomer **19a** (0.153 g, 74%) as a yellow solid; mp: dec. > 180°C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, $J = 5.5$, 3.5 Hz, 2H), 7.39 (dd, $J = 5.5$, 3.5 Hz, 2H), 7.35 (bs, 2H), 7.01 (bs, 2H), 6.55 (d, $J = 3.5$ Hz, 2H), 6.11 (d, $J = 3.5$ Hz, 2H), 3.14–2.82 (m, 8H), 2.05 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 146.35, 145.91, 138.98, 130.87, 129.61, 128.45, 124.14, 118.79, 118.64, 115.31, 114.50, 109.42, 32.51, 32.39, 26.37; IR (thin film) 2964, 2837, 1634, 1471, 1434, 1261 cm^{-1}; MS (EI, 12 eV): *m*/*e* 550 (M^+ + 6, 4), 548 (M^+ + 4, 6), 547 (M^+ + 3, 6), 542 (M^+ + 2, 15), 544 (M^+, 16), 508 (2), 440 (4), 387 (40), 386 (100), 384 (40), 357 (39), 257 (17), 187 (6), 113 (3).

Acknowledgements

We thank the National Institutes of Health (GM 42735) and the Petroleum Research Fund (25999-AC) administered by the American Chemical Society for financial support. Fellowship support for AT (Phillips Petroleum Foundation) is gratefully acknowledged. We thank David Combs for additional experimental assistance.

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