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Preparation of 1,1′-binaphthyl-2,2′-diyl bridged *ansa*-bis(annulated cyclopentadienyl) titanium and -zirconium dichloride complexes

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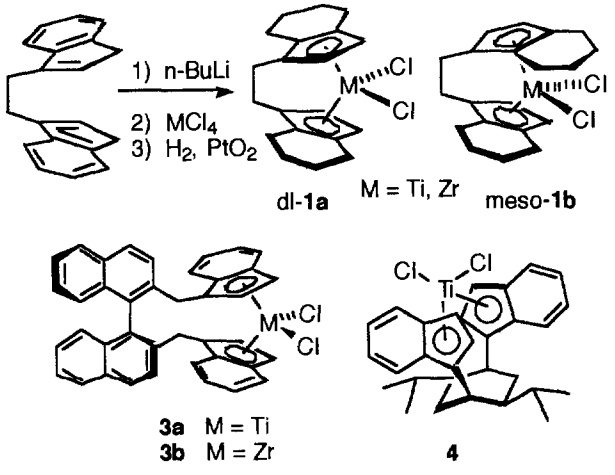
Abstract

The coupling of enantiomerically enriched 2,2′-dilithio-1,1′-binaphthyl with various annulated cyclopentenones or 2-indanone proves to be a facile route for the preparation of a series of annulated bis(cyclopentadienes) or bis(indenes) bridged at a symmetrical cyclopentadienyl position. The six- or seven-membered annulated bis(tetrahydroindene) **6** or bis(hexahydroazulene) **7** ligands could readily be converted to titanium or zirconium dichloride complexes. Owing to the symmetry of the ligands, only a single C_2-symmetrical isomer of the metallocene dichloride could form. Although the faces of the cyclopentadienyl moieties are homotopic, the chiral bridge enforces a chiral conformation of the metallocene complexes. The bis(indenyl) **5** or five-membered annulated bis(tetrahydropentalene) **8** ligands could not be metalated. Unbridged 2-methyl and 2-phenyl substituted tetrahydropentalenes **27** and **28** were prepared and could readily be converted to titanium dichloride complexes.

Keywords: Chiral cyclopentadiene; Zirconocene; Titanocene; *ansa*-Metallocene; C_2-symmetry

1. Introduction

The application of chiral metallocenes as catalysts for asymmetric catalytic and stoichiometric reactions has led to an increase in the number and variety of enantiomerically enriched metallocene complexes [1]. An early and widely applied chiral metallocene dichloride is Brintzinger's ethylene bridged *ansa*-bis(tetrahydroindenyl)metal dichloride **1**, synthesized from an achiral bis(indenyl) ligand **2** as a mixture of *meso* **1a** and racemic **1b** metallocenes [2]. Although the preparation of the necessary bridged indene is very simple, a significant synthetic drawback to obtaining enantiomerically pure **1** is that the isolation of enantiomerically pure metallocenes requires an initial separation of the *meso* and racemic isomers followed by a resolution of the racemic C_2-symmetric isomers via diastereomeric complexes [2]. By having chirality already installed in the ligand, selective formation of a single enantiomerically pure product is possible and additional resolution steps are unnecessary. We have previously utilized chiral bridging groups to facilitate the isolation of single, enantiomerically pure C_2-symmetric *ansa*-bis(indenyl)metal complexes such as **3a**, **3b** [3] and **4** [4].



Examples of resolved *ansa*-metallocenes

While only one C_2-symmetrical stereoisomer of **3a** or **3b** was isolated in their synthesis, the yields of these

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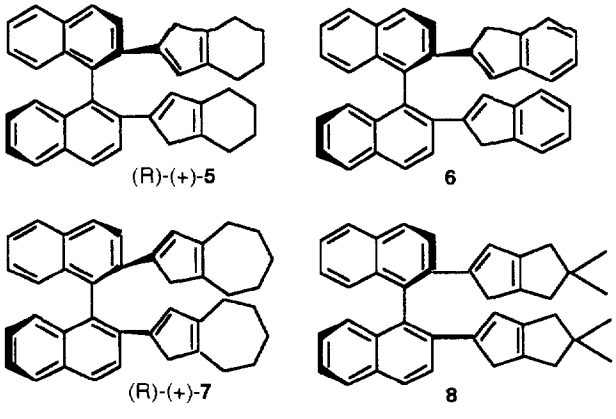
metalations were low. Presumably one diastereomeric complex of the prochiral ligands can form, while the other possible diastereomeric is not stable and forms oligimers. A conceptually different ligand has an indenyl-type ligand bridged at the 2-position by a chiral moiety. The faces of such ligands are homotopic and can inherently provide only a single isomeric metallocene with axially dissymmetric orientation of the indenyl ligands relative to the asymmetry near the metal center. We have previously published a preliminary report on the preparation and metalation of enantiomerically enriched 1,1′-binaphthyl-2,2′-bis(tetrahydroinden-2-yl) (**5**) [5], and the preparation of related enantiomerically enriched and racemic biaryl bridged metallocene dihalides has also been published by Brintzinger and coworkers [6] and Bosnich and coworkers [7]. Herein we report details of the preparation of a range of binaphthyl bridged bis(cyclopentadienes) **5–8** and the formation of titanium and zirconium dichloride complexes of **5** and **8**.



Target binaphthyl bridged bis(cyclopentadienes)

2. Results and discussion

To investigate the influence of substitution and aromatic annulation [8] on the reactivity of *ansa*-metallocenes, we undertook the preparation of a series of 1,1′-binaphthyl-2,2′-diyl bridged bis(cyclopentadienes). By varying the annulation size from five- to six- to seven-membered rings, we could hope to demonstrate an ability to fine-tune the structure and reactivity of a family of *ansa*-metallocenes. Furthermore, the comparison of the analogous indenyl and tetrahydroindenyl complexes could be of interest.

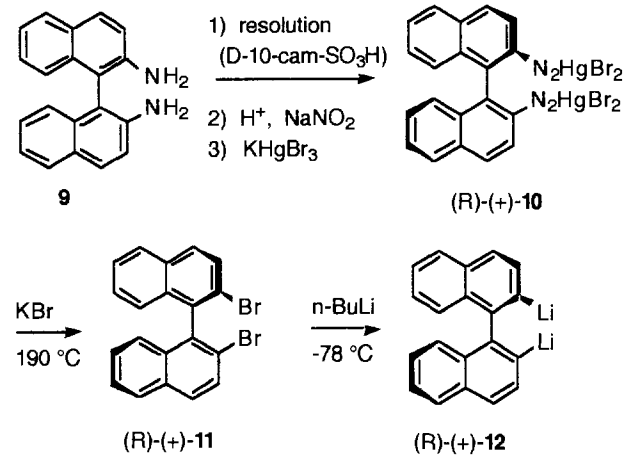
2.1. Ligand synthesis

We based our synthesis of the desired cyclopentadienyl ligands on Murdoch and coworkers' method for the synthesis of enantiomerically enriched 2,2′-dilithio-1,1′-binaphthyl (**12**) [9], as illustrated in Scheme 1, and the ability of **12** to react with chlorodiphenylphosphine without racemization. By adding **12** to the appropriate cyclopentenone or 2-indanone, we should be able to produce enantiomerically enriched ligands **5** to **8** in a nicely convergent synthesis.

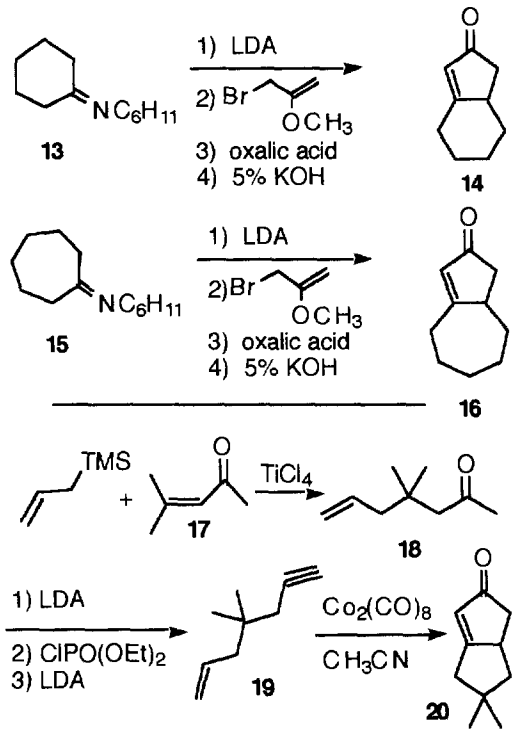
Coupling inexpensive 2-naphthol in the presence of hydrazine hydrate provided racemic 2,2′-diamino-1,1′-binaphthyl (**9**) which could be efficiently resolved with *d*-camphorsulfonic acid (*d*-CSA) [9]. The resolved diamine (R)-(+)-**9** was then converted into the bis(diazonium) salt (R)-(+)-**10** and pyrolyzed under vacuum with excess KBr, resulting in dibromide (R)-(+)-**11** with no racemization (ca. 35% yield from 2-naphthol). Lithium halogen exchange on dibromide (R)-(+)-**11** produced the 2,2′-dilithio species (R)-(+)-**12**, which is reported to be configurationally stable between −130 and −45 °C [9].

Of the several methods for preparation of annulated cyclopentenone **14** [10,11], we found the method of Jacobson et al. [10] most convenient. As shown in Scheme 2, alkylation of imine **13** with 2-methoxy-3-bromopropene followed by hydrolysis with oxalylic acid and cyclization with 5% aqueous KOH delivered the desired enone **14** in 31% overall yield. In a similar manner, the known seven-membered annulated cyclopentadiene **16** was prepared from imine **15** [7].

The known five-membered annulated cyclopentenone **20** was prepared by a Pauson–Khand cyclization [12]. 1,4-Addition of allyltrimethylsilane with mesityl oxide **17** in the presence of $TiCl_4$ gave 4,4-dimethyl-6-hepten-2-one (**18**) in 87% yield. The enol phosphate of ketone



Scheme 1. Synthesis of 2,2′-dilithio-1,1′-binaphthyl **12** [9].



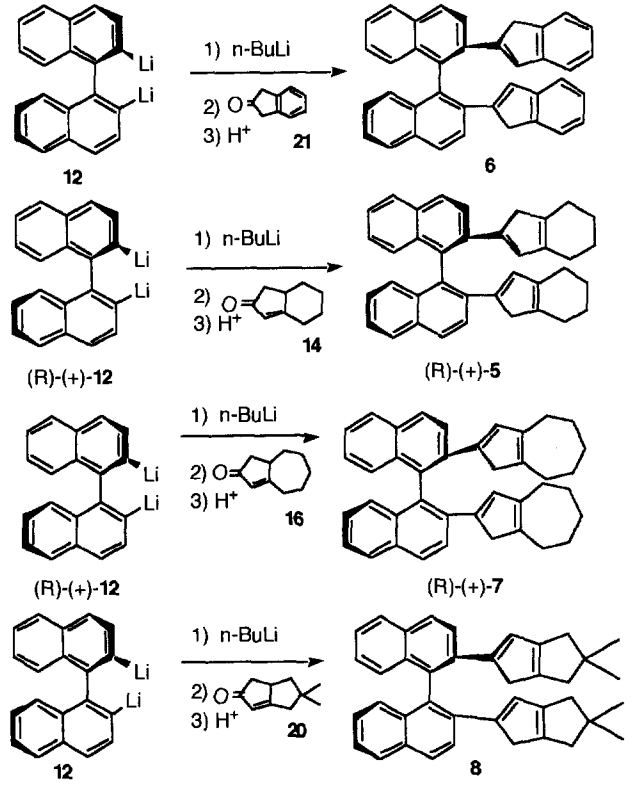
Scheme 2. Preparation of annulated cyclopentenones.

18 was dehydrophosphonylated with 2 equiv. LDA [13] to form enyne **19** in 61% yield. Intramolecular cyclization of enyne **19** was effected with $Co_2(CO)_8$ in CH_3CN, rather than heptane [13], at reflux for 8 h to provide **20** in 70% yield (41% overall yield from **17**).

The syntheses of binaphthyl bridged ligands **5–8** are illustrated in Scheme 3. In each case 2,2′-dilithio-1,1′-binaphthyl (**12**) was generated at −78 °C and directly reacted with the appropriate carbonyl compound. Slow addition of 2-indanone (**21**) to (±)-**12** provided, upon work-up, a crude diol which was dehydrated with *p*-TsOH in benzene to give **6** in 39% yield after chromatography. Spectral data are in agreement with the proposed C_2-symmetrical structure. The ^{1}H NMR spectrum of **6** exhibits an AB set of doublets at 3.05 ppm indicative of the two diastereotopic benzylic protons and a singlet at 6.65 ppm for the single vinyl proton. Presumably the yield was lowered through proton transfer from the indanone to the dilithiobinaphthyl [14]. In related additions to enones the yield could be improved through the use of added cerium chlorides [15]. In the reaction of **12** with **21** no significant change was observed in the yield and, for experimental simplicity, the lithium salt was used directly.

Addition of cylcopentenone **14** to (R)-(+)-**12** followed by acid promoted dehydration gave the binaphthyl bridged bis(tetrahyroindene) (R)-(+)-**5** in 37% yield. The purification of **5** had to be conducted carefully to remove the suspected monocyclopentadiene side product, since traces of this impurity resulted in poor metalation. This C_1-symmetrical impurity could be formed by the protonation of one basic site in **12** by the acidic methylene protons in **14**. Although not isolated, its structure is supported by the abundance of signals in the ^{1}H NMR spectrum due to the non-equivalent binaphthyl protons. The ^{1}H NMR spectrum of the desired bis(cyclcopentadiene) (R)-(+)-**5** exhibited a singlet at 6.19 ppm which indicates the presence of only the one isomer shown of the diene units. To determine the enantiomeric purity of **5**, a complex chiral lanthanide shift reagent was used in an NMR experiment [16]. A mixture of Ag(fod) and (+)-Yb(tfc)$_3$ in $CDCl_3$ was injected incrementally into a $CDCl_3$ solution of (±)-**5** and a series of ^{1}H NMR spectra taken. Resolution of the cyclopentadiene signal originally at 6.19 ppm resulted in new signals at 6.32 and 6.46 ppm. Based on the integration of these peaks for (R)-(+)-**5**, the resolved ligand appeared to be about 90% enantiomerically pure. Attempts to determine the enantiomeric purity of (R)-(+)-**5** by chiral gas chromatography (cyclodextrin coated capillary column) failed. If the reaction temperature was not carefully maintained, or if the addition of **14** to (R)-(+)-**12** was too fast, a much lower enantiomeric enrichment was observed for **5**, indicating some ability for the dilithiobinaphthyl **12** to racemize at higher temperatures.

As in the syntheses of the two preceding ligands, the addition of **20** to a −78 °C solution of 2,2′-dilithio-1,1′-binaphthyl ((R)-(+)-**12**) followed by dehydration pro-



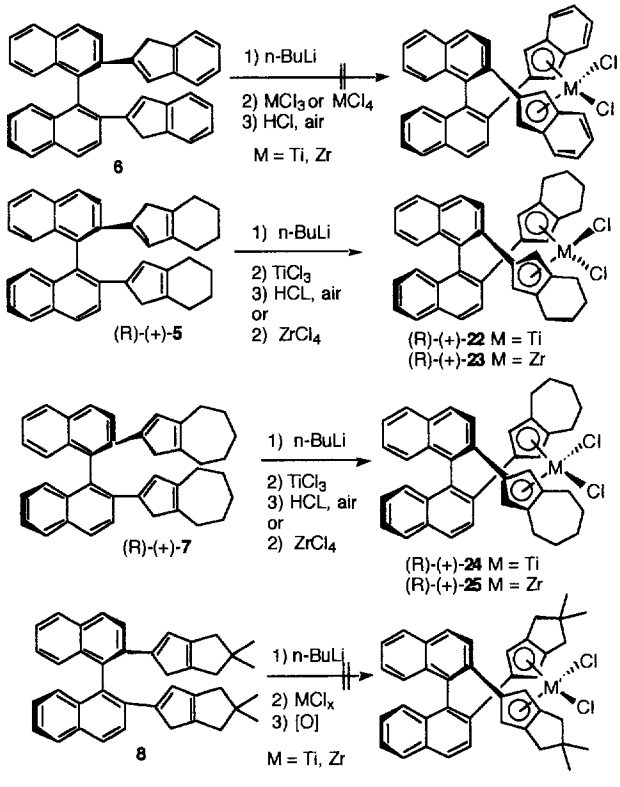
Scheme 3. Formation of binaphthyl bridged ligands.

vided the five-membered annulation analog (R)-(+)-**7**, but in just 19% yield. Again the low yield could be due to the expected partial protonation of the dilithio salt **12**. The one singlet at 6.26 ppm in the ^{1}H NMR spectrum of **7** indicated the presence of only one double bond isomer.

Slow addition of cyclopentenone **16** to dilithio binaphthyl (R)-(+)-**12** followed by acid promoted dehydration resulted in the formation of the seven-membered annulation analog (R)-(+)-**8** in 40% yield as a single double bond isomer. Attempted ^{1}H NMR spectral analysis of racemic **8** with Ag(fod) and (+)-Yb(tfc)$_3$ in $CDCl_3$ failed to produce any distinguishable signals and the enantiomeric purity of (R)-(+)-**8** could not be confirmed.

2.2. *Metalation of 1,1'-binaphthyl-2,2'-diyl bridged bis(cyclopentadienes)*

We investigated the ability of ligands **5–8** to form titanium or zirconium dichloride complexes using established methodology [17,18]. The results are illustrated in Scheme 4. The reaction of the in situ ^{n}BuLi-generated dianion or the isolated dilithio salt of bis(indene) **6** with a THF suspension of $TiCl_3$ at −78 °C, followed by heating under reflux and oxidation at −78 °C to room temperature, resulted only in the partial isolation of starting material. Attempts to perform the metalation with $TiCl_4 \cdot 2THF$, $TiCl_3 \cdot 3THF$, $ZrCl_4$, $ZrCl_4 \cdot 2THF$ also failed to produce an isolable metal complex. Given that the tetrahydroindenyl ligand **5** metalated in good yield (vide infra), the penalty for the disruption of aromaticity of the indene was too great to allow a stable metal complex to form from bis(indene) **6**.



Scheme 4. Metalation of binaphthyl bridged ligands.

In contrast to the binaphthyl bridged bis(indene) **6**, the metalation of bis(tetrahydroindene) **5** was quite successful. Deprotonation of (R)-(+)-**5** with ^{n}BuLi at −78 °C in THF resulted in a deep red solution which was added to a THF slurry of $TiCl_3$ at −78 °C. After heating under reflux for 6 h, the solvent was removed and replaced with $CHCl_3$ before the addition of 6 M HCl at −78 °C [18]. The red suspension was stirred at room temperature in the presence of air for 2 h then extracted with dichloromethane to yield a tan solid upon solvent evaporation. After recrystallizing from dichloromethane and hexanes, titanocene dichloride **22** was isolated as a tan powder in 81% yield, an improvement over our initial report of 68% [5]. The use of preformed complexes $TiCl_3 \cdot 3THF$ or $TiCl_4 \cdot 2THF$ led to lower yields (42% and 26% respectively). Owing to the symmetrical site of attachment of the bridging group to the cyclopentadienyl ligand, the faces of the ligand are homotopic and metalation could inherently only lead to a single C_2-symmetrical stereoisomer.

The signals arising from the two diastereotopic cyclopentadienyl protons H_a and H_b in **22** (Scheme 4) have an impressive 2.2 ppm chemical shift difference. Proton H_a projects away from the bridge and gives rise to a signal within the normal range for titanocene dichlorides at 6.51 ppm. Proton H_b, however, is tucked into the shielding cone of the binaphthyl bridge and exhibits a strong upfield shift to 4.33 ppm. The presence of enantiomeric enrichment was established for metallocene (R)-(+)-**22** by optical rotation, although the exact extent could not be confirmed. Attempts to determine the enantiomeric excess of titanocene dichloride **22** via ^{1}H NMR spectroscopy in the presence of chiral lanthanide shift reagents (+)-Eu(tfc)$_3$, (+)-Eu(hfc)$_3$, (+)-Yb(tfc)$_3$, or (+)-Yb(hfc)$_3$ gave only partial, non-useful resolution of signals – even in conjunction with Ag(fod) [16]. We assume that the high enantiomeric excess determined by ^{1}H NMR spectroscopic methods of the ligand is preserved in the metalation.

Racemic C_2-symmetric binaphthyl tetrahydroindenyl zirconium dichloride **25** was prepared by deprotonation of **5** in ether at 0 °C to room temperature followed, 3 h later, by the addition of $ZrCl_4$. After 15 h the crude product was dissolved in benzene and filtered to remove any LiCl. After evaporation of the solvent and trituration with hexanes, **25** was isolated as a pale yellow powder in 78% yield. Metalations performed with $ZrCl_4 \cdot 2THF$ decreased the yield and the use of DME as a solvent resulted in somewhat lower yields of a DME adduct of **25**. The spectral characteristics of **25** nearly coincided with those of the titanocene dichloride ana-

logue (R)-(+)-**24**. The signals arising from the cyclopentadienyl protons appeared at 6.89 and 4.23 ppm in the ^{1}H NMR spectrum.

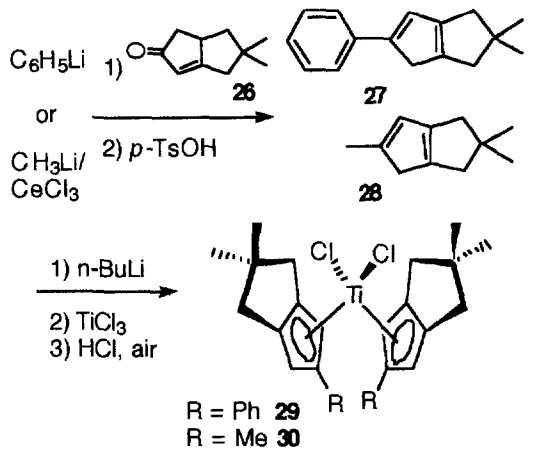
The analogous bis(hexahydroazulene) **7** could also be converted to its titanium and zirconium dichloride complexes. Deprotonation of (R)-(+)-**7** with ^{n}BuLi, metalation with $TiCl_3$ and air oxidation in chloroform afforded the titanium dichloride complex (R)-(+)-**24** as a tan solid in 81% yield. As in the case of (R)-(+)-**22**, the ^{1}H NMR spectrum of (R)-(+)-**24** exhibited cyclopentadienyl proton signals at 6.52 and 4.33 ppm. The presence of an excess of one enantiomer was confirmed by optical rotation. The ^{n}BuLi generated dianion of bis(hexahydroazulene) **7** was metalated with $ZrCl_4$ and purified as above to afford binaphthyl bridged zirconocene dichloride **25** as a pale yellow powder in 67% yield. The ^{1}H NMR spectrum displayed cyclopentadienyl signals at 6.50 and 4.27 ppm.

To complete our investigation of varying the annulation size of bis(cyclopentadienyl) ligands, we attempted to metalate the five-membered ring annulated bis(tetrahydropentalene) **8**. Attempts to metalate the dianion of **8** under several conditions (see Section 3) with various titanium and zirconium chloride complexes afforded only partial recovery of the ligand and no stable metal complex.

2.3. Preparation and metalation of 2-substituted tetrahydropentalenes

From the few reports in the literature describing the formation of pentalenyl Group 4 metallocene dichlorides [19], it was known that the yields were generally low (less than 10%), but nothing was known regarding the metalation of 2-substituted pentalenes. In order to determine the ability of such unbridged pentalenes to form metal complexes, phenyl substituted and methyl substituted tetrahydropentalenes **27** and **28** were synthesized and metalated according to Scheme 5.

Phenyllithium or methyllithium in the presence of $CeCl_3$ [15] could add to tetrahydropentalenone **20** with subsequent acid promoted elimination to give the tetrahydropentalenes **27** or **28** in 52% or 25% yields respectively. Treatment of the ^{n}BuLi generated dianions of **27** or **28** with a THF slurry of $TiCl_3$ as above followed by oxidation by air in chloroform and recrystallization with methylene chloride and hexane afforded titanocene dichlorides **29** and **30** as deep red powders in 67% and 70% yields respectively. The ^{1}H NMR spectrum of the phenyl substituted titanocene dichloride **29** displayed a signal at 6.47 ppm corresponding to the equivalent hydrogens on the cyclopentadienyl ring, methyl proton signals at 0.86 and 1.24 ppm, allylic doublet proton signals at 2.73 and 1.95 ppm and phenyl proton signals ranging from 7.35 to 7.62 ppm. The ^{1}H NMR spectrum of the methyl substituted complex **30** displayed a singlet



Scheme 5. Preparation of bis(tetrahydropentalenyl)titanium dichlorides.

at 6.12 ppm for the cyclopentadienyl protons, doublets at 2.82 and 2.34 ppm corresponding to the allylic protons and singlets at 2.11, 1.20 and 1.0 for the methyl protons. Since the ligand faces in cylopentadienes **27** and **28** are non-stereoisomeric, only a single achiral metallocene dichloride complex could form. These results demonstrate that the 2-substituted tetrahydropentalenes can be successfully metalated. The origin for the lack of success in the attempted metalation of the binaphthyl bridged bis(cyclopentadiene) **8** is unknown, but we suspect it may be due to increased strain.

2.4. Conclusion

In conclusion, we have found the coupling of enantiomerically enriched 2,2′-dilithio-1,1′-binaphthyl with various annulated cyclopentenones or 2-indanone to be a facile route for the preparation of a series of annulated bis(cyclopentadienes) or bis(indenes) bridged at the symmetrical 2-position. The six- or seven-membered annulated bis(tetrahydroindene) **6** or bis(hexahydroazulene) **7** ligands could readily be converted to titanium or zirconium dichloride complexes. Owing to the symmetry of the ligands, only a single C_2-symmetrical isomer of the metallocene dichloride could form. The bis(indenyl) **5** or five-membered annulated bis(tetrahydropentalene) **8** ligands could not be metalated. Unbridged 2-substituted tetrahydropentalenes **27** and **28**, however, could readily be metalated.

3. Experimental details

3.1. General

For a general description of experimental details, see Ref. [20]. Unless otherwise noted, all starting materials were obtained from commercial suppliers and used

without further purification. Transition metal chloride THF adducts, $TiCl_4 \cdot 2THF$, $TiCl_3 \cdot 3THF$ and $ZrCl_4 \cdot 2THF$ were prepared according to published procedures [17,18]. The following compounds were prepared by literature methods: 1,1'-dibromo-2,2'-binaphthylene [9], bicyclo[4.3.0]non-6(1)-en-8-one [10], bicyclo[5.3.0]dec-7(1)-en-9-one [10], 7,7-dimethyl-1(5)-en-3-one [13].

3.2. (R)-(+)-2,2'-bis(bicyclo[4.3.0]-nona-1(6),7-dien-8-yl)-1,1'-binaphthyl (5)

To a solution of (R)-(+)-2,2'-dibromo-1,1'-binaphthyl [9] (1.09 g, 2.64 mmol) in THF (17 ml) at −78 °C under nitrogen was added *sec*-butyllithium (0.88 M in hexanes, 6.3 ml, 5.5 mmol) added dropwise over a period of 0.5 h. The resulting bright yellow slurry was stirred for 1 h then a solution of bicyclo[4.3.0]-non-1(9)-en-8-one [10] (862 g, 6.34 mmol) in THF (5 ml) was added dropwise over a period of 0.5 h. The solution was stirred overnight at −78 °C and aqueous NH_4Cl was added and the solution allowed to warm to room temperature. The mixture was extracted with ether (3 × 20 ml), dried over $MgSO_4$, concentrated and purified by chromatography (SiO_2, petroleum ether) to yield **5** as a white solid (456 mg, 35%). (This product should be metalated immediately, for it readily decomposes upon standing.) M.p. 219 °C. $[\alpha]_D^{23}$ −159° (c 0.445, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 4.0 Hz, 2H), 7.83 (d, J = 4.0 Hz, 2H), 7.34 (dd, J = 7.5, 7.5 Hz, 2H), 7.13 (dd, J = 7.5, 7.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 6.21 (s, 2H), 2.67 (d, J = 22.5 Hz, 2H), 2.34 (d, J = 22.5 Hz, 2H), 2.00–2.08 (m, 8H), 1.51–1.57 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): 144.3, 134.0, 133.6, 133.5, 131.9, 130.4, 129.5, 128.0, 126.9, 126.7, 126.4, 124.7, 120.4, 113.6, 96.2, 25.6, 25.2, 21.8, 21.7 ppm. IR (thin film): 3054, 2930, 2360, 2333, 1650, 1595, 1421, 1263, 1017 cm^{-1}. MS, FAB m/z (100 mA, 8 kV, Xe) 490 (M^+, 7%).

3.3. 2,2'-Bis(1-inden-2-yl)-1,1'-binaphthyl (6)

To a solution of (±)-2,2'-dibromo-1,1'-binaphthyl (981 mg, 2.38 mmol) in THF (2 ml) under argon at −78 °C was added n-butyllithium (1.7 M in heptane, 3.08 ml, 5.20 mmol). After 1 h at −78 °C a bright yellow suspension was formed and a solution of 2-indanone (1.57 mg, 11.9 mmol) in THF (1 ml) was added dropwise. The solution was stirred at −78 °C for 3 h then at room temperature for 3 h. H_2O (5 ml) was added and the mixture was extracted with Et_2O (3 × 5 ml). After drying and concentrating, the crude product was dehydrated in benzene (10 ml) with a catalytic amount (10 mol%) of *p*-toluenesulfonic acid. After 1 h H_2O (5 ml) was added to the solution which was extracted with Et_2O (3 × 5 ml) and concentrated. Chromatography (SiO_2, petroleum ether) yielded **6** as a fluffy white solid (370 mg, 30%); m.p. 175–178 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.98 (dd, J = 8.0, 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.58 (dd, J = 8.0, 8.0 Hz, 2H), 7.51–7.42 (m, 4H), 7.33 (dd, J = 8.0, 8.0 Hz, 2H), 7.25–7.12 (m, 4H), 7.04 (dd, J = 8.0, 8.0 Hz, 2H), 6.65 (br s, 2H), 3.11 (d, J = 22.0 Hz, 2H), 3.00 (d, J = 22.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.51, 134.00, 131.42, 128.43, 128.00, 127.96, 127.65, 127.11, 127.04, 126.27, 126.14, 125.96, 125.73, 125.68, 124.40, 123.19, 120.80, 41.31. IR (thin film): 3052, 3013, 1611, 1590, 1501, 1457, 1385, 1366, 1260 cm^{-1}. MS, m/z (70 eV, rel. int.) 482 (1%), 369 (30), 368 (100), 353 (5).

3.4. (R)-(+)-2,2'-bis(bicyclo[5.3.0]-deca-1(10),7(8)-dien-9-yl)-1,1'-binaphthyl (7)

To a solution of (R)-(+)-2,2'-dibromo-1,1'-binaphthyl (445 mg, 1.08 mmol) in THF (5 ml) under argon at −78 °C was added n-butyllithium (2.68 M in heptane, 887 μl, 2.37 mmol) over a period of 0.5 h to give a bright yellow suspension. After 1 h at −78 °C, a solution of bicyclo[5.3.0]-dec-1(10)-en-9-one (373 mg, 2.48 mmol) in THF (2 ml) was added over 0.5 h and the resulting suspension stirred at −78 °C overnight. Aqueous NH_4Cl was added at −78 °C and the solution allowed to warm to room temperature. Extracting with Et_2O (3 × 10 ml), drying ($MgSO_4$) and concentrating gave a pale yellow solid which was dissolved in benzene (20 ml) along with a catalytic amount (10 mol%) of *p*-toluenesulfonic acid. The ensuing dehyration was monitored by TLC (5% CH_2Cl_2/petroleum ether) and was complete within 15 min. H_2O (5 ml) was added and the product extracted with Et_2O (3 × 5 ml), dried ($MgSO_4$) and concentrated. The crude product was chromatographed (SiO_2, petroleum ether) to give (R)-(+)-**7** as a white solid (253 mg, 37%); m.p. 259–260 °C. $[\alpha]_D^{23}$ +123° (c 0.500, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 4.0 Hz, 2H), 7.83 (d, J = 4.0 Hz, 2H), 7.35 (dd, J = 7.5, 7.5 Hz, 2H), 7.14 (dd, J = 7.5, 7.5 Hz, 2H) 7.04 (d, J = 8.5 Hz, 2H), 6.17 (s, 2H), 2.75 (d, J = 23.0 Hz, 2H), 2.41 (d, J = 23.0 Hz, 2H), 2.10–2.21 (m, 8H), 1.41–1.63 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.70, 137.00, 132.20, 127.77, 127.67, 127.54, 126.70, 126.61, 126.55, 125.90, 124.99, 113.70, 95.61, 34.13, 31.30, 30.24, 30.19, 27.80. IR (thin film): 2922, 2851, 1503, 1449, 1363, 1262, 1020 cm^{-1}. MS, m/z (12 eV, rel. int.) 519 (50%), 419 (13), 401 (100).

3.5. 2,2'-Bis(7,7-dimethylbicyclo[3.3.0]-octa-1(5),2-dien-3-yl)-1,1'-binaphthyl (8)

To a solution of (±)-2,2'-dibromo-1,1'-binaphthyl (670 mg, 1.62 mmol) in THF (5 ml) at −78 °C under argon was added n-butyllithium (2.5 M in heptane,

1.43 ml, 3.56 mmol) to gradually form a bright yellow suspension. After 1 h at −78 °C a solution of 7,7-dimethylbicyclo[3.3.0]-2-octen-3-one [13] (61 mg, 4.1 mmol) in THF (2 ml) was added dropwise. The mixture was stirred at −78 °C for 3 h then warmed to room temperature. H_2O (5 ml) was added, the mixture extracted with Et_2O (3 × 5 ml), the organic portion dried ($MgSO_4$) and concentrated. The crude product was dissolved in benzene (10 ml) and dehydrated with a catalytic amount (10 mol%) of *p*-toluenesulfonic acid. After 1 h H_2O (5 ml) was added, the mixture was extracted with Et_2O (3 × 5 ml) and the organic portion dried ($MgSO_4$) and concentrated. Chromatography (SiO_2, petroleum ether) yielded **8** as a white solid (98 mg, 12%); m.p. 200–205 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 9.0 Hz, 2H), 7.86 (d, J = 4.5 Hz, 2H), 7.83 (d, J = 4.5 Hz, 2H), 7.36 (dd, J = 7.5, 7.5 Hz, 2H), 7.15 (dd, J = 7.5, 7.5 Hz, 2H), 7.07 (d, J = 9.0 Hz, 2H), 6.27 (br s, 2H), 2.60 (d, J = 20.0 Hz, 2H), 2.37 (d, J = 20.0 Hz, 2H), 2.12 (br s, 8H), 1.06 (br s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.89, 142.83, 140.15, 136.04, 136.02, 135.81, 135.12, 134.31, 129.73, 129.54, 128.47, 128.35, 128.29, 127.12, 46.96, 31.72, 27.17, 26.09, 24.99, 24.85. IR (thin film): 3053, 2924, 1589, 1501, 1457, 1385, 1261, 1015 cm^{-1}. MS, m/z (70 eV, rel. int.) 519 (M^{+1}, 39%), 518 (M, 82), 417 (29), 411 (33), 401 (34), 387 (30).

3.6. *(R)-(+)-ansa-[2,2'-bis(bicyclo[4.3.0]-nona-1(9),6(7)-dien-8-yl)-1,1'-binaphthyl]-dichlorotitanium (22)*

To a solution of (R)-(+)-**5** (200 mg, 0.41 mmol) in THF (2 ml) at −78 °C under Ar was added dropwise n-butyllithium (1.5 M in hexanes, 0.57 ml, 0.85 mmol) and the resulting yellow solution was allowed to warm to 0 °C over 0.5 h. This solution was added to a suspension of $TiCl_3$ (81.8 mg, 0.53 mmol) in THF (2 ml) at −78 °C. The resulting dark purple mixture warmed to room temperature and was then heated under reflux for 6 h. After removing the solvent, the brown residue was dissolved in $CHCl_3$ (5 ml) and the temperature lowered to −78 °C. 6 M HCl (2 ml) was added, and the dark mixture was stirred at room temperature for 2 h in the presence of air. The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (3 × 2 ml). The organic phases were combined, dried over $MgSO_4$ and concentrated. The crude tan solid was dissolved in a minimum amount of CH_2Cl_2 and precipitated with dry hexanes to afford (R)-(+)-**23** as a tan powder (201 mg, 81%); m.p. > 280 °C; $[\alpha]_D^{23}$ +895° (c 0.009, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.47 (dd, J = 9.0, 9.0 Hz, 2H), 7.18 (dd, J = 9.0, 9.0 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 2.5 Hz, 2H), 4.29 (d, J = 2.5 Hz, 2H), 3.20 (ddd, J = 17.0, 6.5, 6.5 Hz, 2H), 2.67 (ddd, J = 17.0, 6.0, 6.0 Hz, 4H), 2.22 (ddd, J = 17.0, 6.0, 6.0 Hz, 2H), 2.01 (m, 4H), 1.53 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.31, 136.63, 133.95, 133.53, 133.49, 131.87, 130.318, 127.97, 127.93, 126.85, 126.69, 126.41, 124.71, 120.36, 113.59, 25.60, 25.12, 21.79, 21.61. IR (thin film): 2928, 2290, 1590, 1497, 1273, 1261 cm^{-1}. MS, FAB m/z (100 mA, 8 kV, Xe) 608 (M^+, 2%), 573 (M^+–Cl, 12), 537 (M^+–2Cl, 4). Anal. Found: C, 73.02; H, 5.24. $C_{38}H_{32}TiCl_2$ Calc.: C, 75.14; H, 5.31. $C_{38}H_{32}TiCl_2 \cdot H_2O$ Calc.: C, 72.97; H, 5.48%.

3.7. *ansa-[2,2'-Bis(bicyclo[4.3.0]-nona-1(9),6(7)-dien-8-yl)-1,1'-binaphthyl]dichlorozirconium (23)*

To a solution of **5** (190 mg, 0.388 mmol) in Et_2O (5 ml) at 0 °C under Ar was slowly added n-butyllithium (2.62 M in heptane, 311 μl, 0.814 mmol). After stirring for 2 h at room temperature, an orange suspension was formed and $ZrCl_4$ (99.4 mg, 0.427 mmol) was added via a side arm. The pale yellow suspension was stirred for 12 h and the solvent removed in vacuo. The crude yellow solid was dissolved in benzene (10 ml) and the suspension filtered to remove LiCl which was washed with additional benzene (2 × 5 ml). The filtrate was concentrated and the solid crude product triturated with hexanes (12 ml) to give, after filtering, **23** as a yellow solid (219 mg, 87%); m.p. > 280 °C (decomp.). The product could be recrystallized from chloroform and hexanes. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.41 (dd, J = 7.0, 7.0 Hz, 2H), 7.12 (dd, J = 7.0, 7.0 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.50 (d, J = 2.5 Hz, 2H), 4.24 (d, J = 2.5 Hz, 2H), 2.95 (ddd, J = 16.5, 6.0, 6.0 Hz, 2H), 2.56 (ddd, J = 16.5, 6.0, 6.0 Hz, 4H), 2.12 (ddd, J = 16.5, 6.0, 6.0 Hz, 2H), 1.86 (m, 4H), 1.47 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.13, 133.71, 133.29, 131.39, 130.63, 129.95, 129.38, 128.35, 127.95, 126.74, 126.55, 126.25, 125.24, 124.88, 115.55, 24.50, 24.44, 22.18, 21.86. IR (thin film): 2931, 2861, 1705, 1593 cm^{-1}. MS, m/z (12 eV, rel. int.) 650 (100%), 648 (85), 614 (14), 612 (19). Anal. Found: C, 59.76; H, 4.12. $C_{38}H_{32}ZrCl_2$ Calc.: C, 70.13; H, 4.96. $C_{38}H_{32}ZrCl_2 \cdot CHCl_3$ Calc.: C, 60.82; H, 4.32%.

3.8. *Attempted metalation of (±)-2,2'-bis(2-indenyl)-1,1'-binaphthyl (6)*

3.8.1. *$TiCl_2$ complex*

The metalation of (±)-**6** (56.9 mg, 0.118 mmol) in THF (5 ml) was attempted according to the procedure for the metalation of **5** using n-butyllithium (2.51 M in heptanes, 0.46 mmol, 184 μl) and $TiCl_3$ (38.6 mg, 0.25 mmol), $TiCl_4 \cdot 2THF$ (38.6 mg, 0.25 mmol) or $TiCl_3 \cdot 3THF$ (92.5 mg, 0.25 mmol).

3.8.2. $ZrCl_2$ complex

The metalation of (±)-**6** (56.9 mg, 0.118 mmol) in Et_2O (6 ml) was attempted according to the procedure for the metalation of **5** using n-butyllithium (2.51 M in heptanes, 0.46 mmol, 184 μl) and $ZrCl_4$ (58.2 mg, 0.25 mmol) or $ZrCl_4 \cdot 2THF$ (94.2 mg, 0.25 mmol). In each case no starting material or metal complex could be identified.

*3.9. (R)-(+)-ansa-2,2′ − bis(bicyclo[5.3.0]-deca-1(10),7(8)-dien-9-yl)-1,1′-binaphthyl]-dichlorotitanium (**24**)*

To a solution of (R)-(+)-**7** (50 mg, 0.096 mmol) in THF (1 ml) under argon at −78 °C was added n-butyllithium (2.62 M in heptane, 77 μl, 0.20 mmol). After stirring for 1 h at room temperature, the deep red solution was cooled to −78 °C, added via cannula to a −78 °C suspension of $TiCl_3$ (17.9 mg, 0.115 mmol) in THF (1 ml) and the resulting purple solution allowed to warm to room temperature before heating under reflux for 6 h. After cooling to room temperature, the solvent was removed in vacuo, the residual solid dissolved in $CHCl_3$ (6 ml) and air was gently bubbled through the solution for 1.5 h. 6 M HCl (1 ml) was added to the mixture and the aqueous layer extracted with CH_2Cl_2 (3 × 5 ml). The organic portion was dried over $MgSO_4$ and concentrated. The crude product was dissolved in CH_2Cl_2 (250 μl) and hexane added to precipitate (R)-(+)-**24** as a tan solid (46 mg, 76%); m.p. > 280 °C (decomp.). $[\alpha]_D^{23}$ +911° (c 0.009, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H), 7.40 (dd, J = 7.0, 7.0 Hz, 2H), 7.17 (dd, J = 7.0, 7.0 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 3.0 Hz, 2H), 4.35 (d, J = 3.0 Hz, 2H), 3.00 (ddd, J = 13.5, 4.5, 4.5 Hz, 2H), 2.82 (ddd, J = 13.5, 4.5, 4.5 Hz, 4H), 2.22 (dd, J = 8.5, 5.5 Hz, 2H), 0.98–1.94 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.15, 133.64, 133.49, 132.09, 130.05, 129.41, 128.18, 128.13, 126.91, 126.75, 126.58, 126.40, 124.74, 121.78, 116.66, 32.15, 31.88, 28.17, 27.70. IR (thin film): 2928, 2857, 1594, 1502, 1455, 1260, 1093 cm^{-1}. MS, m/z (70 eV, rel. int.) 634 (7%), 598 (3), 562 (3), 518 (69). Anal. Found: C, 75.00; H, 6.28. $C_{40}H_{36}TiCl_2$ Calc.: C, 75.60; H, 5.71%.

*3.10. ansa-[2,2′-Bis(bicyclo[5.3.0]-deca-1(10),7(8)-dien-9-yl)-1,1′-binaphthyl]-dichlorozirconium (**25**)*

To a solution of (±)-**7** (56 mg, 0.108 mmol) in Et_2O (2 ml) under argon at 0 °C was slowly added n-butyllithium (2.62 M in heptane, 86.6 μl, 0.227 mmol). The resulting orange solution was stirred for 2 h at room temperature. Solid $ZrCl_4$ (28.9 mg, 0.124 mmol) was added via a side arm and the pale yellow suspension was stirred for 12 h at room temperature before removing the solvent in vacuo. The crude yellow solid was dissolved in benzene (10 ml) and the suspension filtered to remove LiCl, which was washed with additional benzene (2 × 5 ml) with subsequent removal of solvent to yield **25** as a yellow solid (72 mg, 99%); m.p. > 280 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.41 (dd, J = 7.0, 7.0 Hz, 2H), 7.12 (dd, J = 7.0, 7.0 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.50 (d, J = 3.0 Hz, 2H), 4.27 (d, J = 3.0 Hz, 2H), 2.78 (ddd, J = 13.5, 4.5, 4.5 Hz, 2H), 2.61 (ddd, J = 13.5, 4.5, 4.5 Hz, 4H), 2.12 (dd, J = 8.5, 5.5 Hz, 2H), 1.74 (m, 4H), 0.98–1.89 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.52, 133.79, 133.25, 133.15, 130.06, 129.34, 128.03, 126.74, 126.60, 126.21, 124.89, 123.14, 117.04, 113.31, 32.15, 30.90, 30.46, 28.32, 27.96. IR (thin film): 2931, 2861, 1705, 1593, 1457, 1216 cm^{-1}. MS, m/z (12 eV, rel. int.) 678 (100%), 677 (65), 642 (14), 518 (34), 386 (14).

*3.11. Attempted metalation of 2,2′-bis(7,7-dimethylbicyclo[3.3.0]-octa-1(5),2-dien-3-yl)-1,1′-binaphthyl (**8**)*

3.11.1. Titanium complex

To a solution of (±)-**8** (100 mg, 0.19 mmol) in THF (2 ml) at −78 °C under argon was added n-butyllithium (2.51 M in heptanes, 169 μl, 0.42 mmol) and the solution warmed to room temperature over 0.5 h. The resulting red solution was added to a slurry of $TiCl_3$ (35.5 mg, 0.23 mmol), $TiCl_4 \cdot 2THF$ (76.7 mg, 0.23 mmol) or $TiCl_3 \cdot 3THF$ (85.1 mg, 0.23 mmol), in THF (4 ml) at −10 °C. In the experiments with Ti(III) chlorides, the mixture was heated under reflux for 6 h, concentrated, then oxidized with air or air/HCl in $CHCl_3$ as in the preparation of **22** or **24**. After extracting with CH_2Cl_2, the organic phases were combined, dried over $MgSO_4$ and concentrated to give a brown oil which was identified as partially recovered starting material and what appeared to be decomposed starting material. In the experiment with $TiCl_4$, the oxidation step was omitted, but again no metal complex could be identified.

3.11.2. Zirconium complex

To a solution of (±)-**8** (100 mg, 0.19 mmol) in diethyl ether (6 ml) at 0 °C under argon was added n-butyllithium (2.51 M in heptane, 169 μl, 0.42 mmol). After stirring for 2 h at room temperature an orange suspension had formed and $ZrCl_4$ (53.5 mg, 0.23 mmol) or $ZrCl_4 \cdot 2THF$ (86.7 mg, 0.23 mmol) was added via a side arm. The resulting pale yellow suspension was stirred for 12 h before removing the solvent in vacuo. The crude yellow solid was dissolved in benzene (9 ml) and the suspension filtered to remove LiCl and washed with benzene (2 × 5 ml). The combined filtrate was concentrated to reveal, by ^1H NMR spectroscopy, a

minor amount of starting material and what appeared to be decomposed starting material.

3.12. 7,7-Dimethyl-3-phenylbicyclo[3.3.0]-1(5),2-octadiene (27)

To a solution of 7,7-dimethylbicyclo[3.3.0]-2-octen-3-one (500 mg, 3.33 mmol) in THF (7 ml) at −78 °C under nitrogen was added phenyllithium (1.8 M in ether, 5.5 ml, 10 mmol). The resulting mixture was stirred for 0.5 h at −78 °C and the solution allowed to gradually come to room temperature. The reaction was quenched with aqueous NH_4Cl (10 ml), the mixture extracted with ether (4 × 5 ml) and the organic portion dried over $MgSO_4$. The concentrated oil was dissolved in benzene (5 ml) and a catalytic amount (10 mol%) of *p*-toluenesulfonic acid was added. After 0.5 h, H_2O (5 ml) was added and the mixture extracted with Et_2O (3 × 5 ml), the organic portion dried ($MgSO_4$) and concentrated. Chromatography (SiO_2, petroleum ether) yielded **27** as a white solid (364 mg, 52%); m.p. 120–125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, J = 7.0 Hz, 2H), 7.42 (t, J = 7.0 Hz, 2H), 7.24 (d, J = 7.0 Hz, 1H), 6.72 (br s, 1H), 3.18 (br s, 2H), 2.29–2.37 (m, 4H), 1.17 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.23, 128.72, 128.67, 126.50, 128.46, 127.22, 127.14, 126.07, 125.18, 124.49, 48.78, 45.45, 43.90, 37.89, 30.54. IR (thin film): 3256, 2963, 2835, 1455, 1387, 1256, 1190 cm^{-1}. MS, m/z (70 eV, rel. int.) 210 (55%), 195 (59), 180 (14).

3.13. 3,7,7-Trimethylbicyclo[3.3.0]-1(5),2-octadiene (28)

The procedure for the preparation of **27** was followed using $CeCl_3$ (1.38 g, 5.6 mmol), methylmagnesium bromide (3.0 M in ether, 1.87 ml, 5.6 mmol), THF (7 ml) (premixed for 2 h at room temperature), 7,7-dimethylbicyclo[3.3.0]-2-octen-3-one (700 μl, 4.67 mmol) in THF (1 ml). After work-up and dehydration as for **27**, chromatography (SiO_2, petroleum ether) yielded **28** as a white solid (171 mg, 25%); m.p. 97–99 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.98 (br s, 1H), 2.67 (br s, 2H), 2.22–2.31 (m, 4H), 2.04 (s, 3H), 1.15 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.79, 142.55, 123.51, 120.48, 48.36, 43.92, 42.63, 40.37, 29.16, 15.38. IR (thin film): 2951, 2920, 2841, 1461, 1442, 1378, 1364 cm^{-1}. MS, m/z (70 eV, rel. int.) 149 (M^+, 100%), 148 (34), 133 (11).

3.14. Bis(7,7-dimethyl-3-phenylbicyclo[3.3.0]-2,4-octadien-3-yl)dichlorotitanium (29)

To a solution of **27** (137 mg, 0.652 mmol) in THF (3 ml) at −78 °C under argon was added n-butyllithium (2.8 M in heptane, 256 μl, 0.717 mmol). After stirring for 1 h at room temperature, the resulting red solution was added to a −78 °C suspension of $TiCl_3$ (50 mg, 0.32 mmol) in THF (1 ml). The mixture was warmed to room temperature and heated under reflux for 9 h. After cooling to room temperature, the solvent was removed. $CHCl_3$ (6 ml) and 6 M HCl (1 ml) were added and the mixture stirred for 2 h at room temperature. H_2O (1 ml) was added and the aqueous layer extracted with CH_2Cl_2 (3 × 5 ml), the organic portion dried over $MgSO_4$ and concentrated. The crude product was dissolved in CH_2Cl_2 (250 μl) and precipitated with hexane to yield **29** as a purple solid (140 mg, 40%); m.p. 154–158 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, J = 7.5 Hz, 2H), 7.45 (t, J = 9.0 Hz, 2H), 7.38 (m, 1H), 6.49 (br s, 2H), 2.73 (d, J = 16.0 Hz, 2H), 1.95 (d, J = 16.0 Hz, 2H), 0.97–1.35 (m, 4H), 1.26 (br s, 3H), 1.24 (br s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.81, 34.77, 131.34, 128.77, 127.45, 125.31, 116.22, 47.80, 42.37, 31.72, 26.70. IR (thin film): 3251, 2936, 2853, 1457, 1377, 1249, 1090 cm^{-1}. MS, m/z (12 eV, rel. int.) 536 (2%), 501 (2), 329 (10), 327 (15).

3.15. Bis(3,7,7-trimethylbicyclo[3.3.0]-2,4-octadien-3-yl)dichlorotitanium (30)

Following the procedure for the preparation of **29** using **27** (193 mg, 1.3 mmol), THF (3.5 ml), n-butyllithium (2.8 M in heptane, 512 μl, 1.43 mmol), $TiCl_3$ (81 mg, 0.525 mmol) in THF (1 ml), $CHCl_3$ (6 ml) and 6 M HCl (1 ml) gave a crude product which was dissolved in CH_2Cl_2 (250 μl) and precipitated with hexane to yield **30** as a purple solid (241 mg, 45%); m.p. 122–124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.13 (s, 2H), 2.80 (d, J = 16.0 Hz, 2H), 2.34 (d, J = 16.0 Hz, 2H), 2.12 (s, 3H), 1.19 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.54, 132.86, 116.76, 47.69, 43.15, 31.18, 27.58, 17.69. IR (thin film): 2933, 2853, 1662, 1455, 1356, 1249, 1090, 1016 cm^{-1}. MS, m/z (70 eV, rel. int.) 412 (3%), 377 (4), 340 (8).

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