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Synthesis and structure of *ansa*-metallocene complexes ($M = ZrCl_2$, $TiCl_2$, YCl, and LuCl) containing the bis(2-methyl-4,5,6,7-tetrahydroinden-yl)dimethylsilane ligand☆

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Abstract

The three step synthesis of 2-methyl-4,5,6,7-tetrahydro-1*H*-indene from cyclohexyl methacrylate is described [(a) PPA cyclization; (b) $LiAlH_4$ reduction; (c) HCl dehydration]. This annelated trisubstituted cyclopentadiene was bridged selectively to form ethylene- or dimethylsilyl-bridged bis(2-methyl-4,5,6,7-tetrahydro-1*H*-inden-1-yl) ligands. Metal complexes ($M = ZrCl_2$, $TiCl_2$, YCl, and LuCl) of the bis(2-methyl-4,5,6,7-tetrahydroinden-1-yl)dimethylsilane ligand were formed as *meso*/*dl* stereoisomeric mixtures in ratios from 1:1 to 2:1 *dl*:*meso*. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Tetrahydroindenyl ligand; *ansa*-Bis(tetrahydroindenyl)metal; Chiral metallocenes; Zirconocene dichloride; Titanocene dichloride; Bis(tetrahydroindenyl)yttrium chloride; Bis(tetrahydroindenyl)lutetium chloride

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1. Introduction

The reactivities and physical properties of *ansa*-bis(indenyl)- or *ansa*-bis(tetrahydroindenyl)zirconium dichlorides can be readily compared since the hydrogenation of easily-prepared *ansa*-bis(indenyl)zirconium dichlorides gives the corresponding *ansa*-bis(tetrahydroindenyl)zirconium dichlorides [1]. For example, the dimethylsilyl bridged *ansa*-bis(2-methylindenyl)zirconium dichloride (**1**) was converted into the bis(tetrahydroindenyl) derivative **2**. Complex **2** was found to be more active and selective for producing high molecular weight isotactic polypropylene [2]. The ability to efficiently hydrogenate the six-membered ring in indenylmetal complexes is, however, not general and has not been reported for any indenyllanthanide complexes [3]. Since indenyllanthanides tend to have low solubility, we desired to produce the presumably more soluble *ansa*-bis(tetrahydroindenyl)lanthanum chlorides directly from 'pre-reduced' bis(tetrahydroindenyl) ligands.

Only a limited number of bridged bis(tetrahydroindenes) have been reported in the literature due to their generally difficult synthesis. Without the coordinated metal to protect the five-membered ring, hydrogenation of indene itself does not occur on the benzene ring, but rather it occurs at the styrenyl double bond, leaving the benzene ring intact. A limited number of achiral unbridged ligands such as tetrahydroindene [4], isodicyclopentadiene [5] and bicyclooctane-annelated cyclopentadienes [6] have been known for some time. Attempts to bridge annelated cyclopentadienes such as tetrahydroindenes are complicated, however, by the nearly equivalent reactivity in the alkylation or silylation of the 1- and 2-positions in these cyclopentadienes — in contrast with the electronic preference for alkylating only at the 1-position of indene. Thus, efforts to form bridged bis(tetrahydroindenes) have focused on establishing the bridging position before forming the cyclopentadiene moiety. Recently, we have reported the application of the Pauson–Khand cyclization for the preparation of the first bis(tetrahydroindenes) containing either the ethylene bridge in **3** or the 1,2-phenylene bridge in **4** [7]. This general method has been nicely extended to a bridged chiral variation [8]. Herein we

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☆ See Ref. [1].

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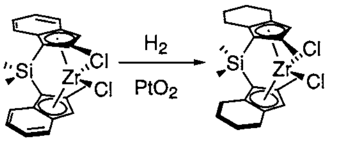
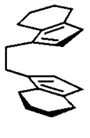
present an efficient method for the synthesis of the dimethylsilyl bridged bis(2-methyltetrahydroindene) **5** and its application in the formation of *ansa*-zirconocene and titanocene dichloride and yttrium and lutetium chloride complexes.



1 **2**



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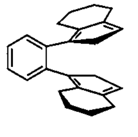

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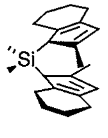

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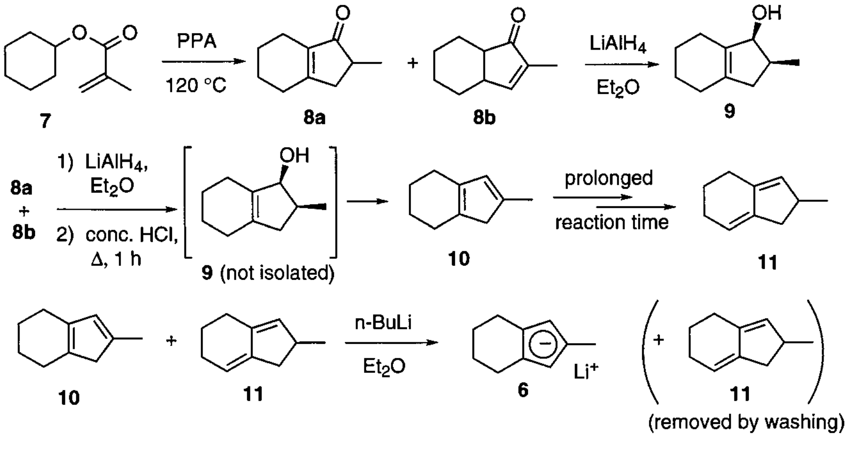
2. Results and discussion

2.1. Synthesis of 2-methyl-4,5,6,7-tetrahydroindenyllithium (6)

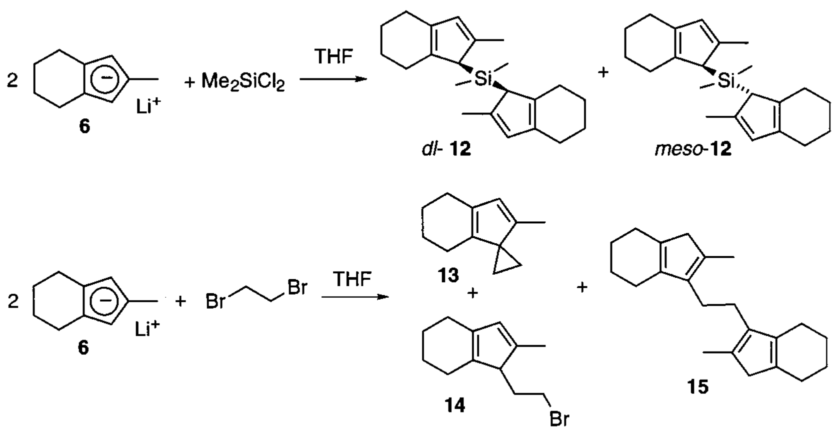
In order to overcome the normally unselective reactivity of alkylation at the various unsubstituted sites in tetrahydroindenes, we chose to block the 2-position by utilizing 2-methyltetrahydroindene **6** for forming the bridged ligands. The synthesis of 2-methyltetrahydroindene **6** is illustrated in Scheme 1. A modification of Conia's procedure [9,10] for the rearrangement and PPA-promoted Nazarov cyclization of cyclohexyl methacrylate **7** at 120°C, followed by vacuum distillation gave isomeric 2-methyltetrahydroindenones **8** in an improved yield of 30%. Under our conditions, cyclization to give the more substituted double bond isomer **8a** was favored over the trisubstituted double bond isomer **8b** in a ratio of 85:15. The presence of the methyl doublet in the ^{1}H-NMR spectrum of **8a** was diagnostic for this isomer, while **8b** exhibited a vinyl hydrogen signal at 6.55 ppm. Reduction of the cyclopentenone mixture **8** with excess $LiAlH_4$ in diethyl ether gave the allylic alcohol **9** as the major stereoisomer in 85% yield. Attempts to dehydrate this cyclopentenol with p-TsOH in benzene or methylene chloride led only to polymeric material. Alternatively, the reaction mixture of enone **8** and $LiAlH_4$ in diethyl ether could be directly acidified with concentrated HCl and this solution heated under reflux for 1 h [11] to give crude 2-methyltetrahydroindene **10** in good yield. If the reaction time was prolonged or if the product was stored for several days, the rearranged diene **11** formed as the predominant species. MM2 calculations showed diene **11** to be 1.84 Kcal mol^{-1} more stable than diene **10** [12]. Chromatographic separation of these isomers was not feasible and the crude mixture was taken on to the next step. Deprotonation of the mixture of **10** and **11** with n-BuLi in hexane gave 2-methyl-4,5,6,7-tetrahydroindenyllithium (**6**) in 44% yield as an insoluble white solid after purification by washing with hexane to remove any unreacted or isomerized tetrahydroindenes.

2.2. Bridging of 2-methyl-4,5,6,7-tetrahydroindene

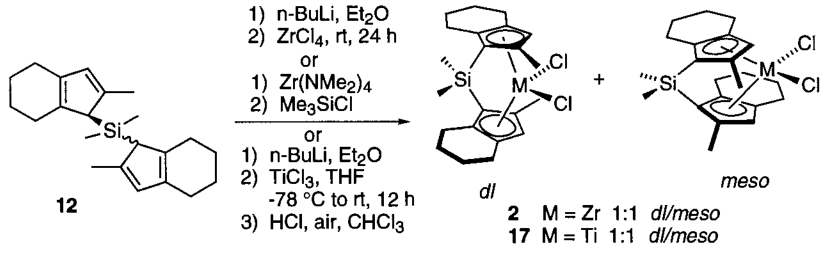
With the preparation of 2-methyl-4,5,6,7-tetrahydroindenyllithium (**6**), we had a ligand that we could selectively bridge at the equivalent 1- or 3-positions. Since ethylene and silylene groups are particularly common bridging groups in *ansa*-metallocenes, we focused on their incorporation as one- or two-atom bridges [13]. As shown in Scheme 2, treatment of 2-methyl-4,5,6,7-tetrahydroindenyllithium (**6**) with dichlorodimethylsilane in THF gave the silyl-bridged bis(tetrahydroindene) **12** in 59% yield as an inconsequential stereoisomeric mixture of *dl* and *meso* forms. Attempts at carrying out the silyl bridging in diethyl or dimethyl ether resulted mainly in the formation of a monosilylindene.



Scheme 1.



Scheme 2.



Scheme 3.

The incorporation of the ethylene bridge in ethylene bis(tetrahydroindene) **15** proved to be much more troublesome due to a competing intramolecular cyclization to form the spiro-cyclopropane side product **13**. Under typical conditions [14], the lithium salt **6** was treated with 1,2-dibromoethane to give a mixture of monotetrahyroindenylethyl bromide **14**, spiro-annelated tetrahydroindene **13** and traces of the desired bridged ligand **15**. The formation of the spiro side product in the synthesis of bis(indenes) and bis(cyclopentadienes) is well known and the reported methods for avoiding it were attempted [14]. The most successful method for avoiding spiro-annelation has been to alkylate the magnesium salt generated by deprotonating cyclopentadienes by alkylmagnesium halides [14b]. Unfortunately during the prolonged period in refluxing THF needed for the deprotonation by Grignard reagents, tetrahydroindene **10** isomerized into the thermodynamically more stable diene isomer **11**, which was the major isolated product of this treatment. The best method for the preparation of **15** was an ultimately unsatisfactory compromise involving the use the isolated lithium salt **6** (freed of any isomerized diene) in an alkylation with 1,2-ethylene ditosylate. As expected, less isomerization to **11** was observed by deprotonating with *n*-BuLi, but rather large amounts of the spiro product **13** were formed. The desired ethylene bridged bis(tetrahydroindene) **15** was ultimately isolated in only 14% yield after chromatographic purification. Given the poor yields in our attempts to form ethylene-bridged **15**, we were not able to carry this ligand forward to metal complexes.

2.3. Preparation of [bis(2-methyl-4,5,6,7-tetrahydroindenyl)dimethylsilane]metal complexes

2.3.1. Preparation of [bis(2-methyl-4,5,6,7-tetrahydroindenyl)dimethylsilane]zirconium dichloride (2)

The dimethylsilylene bridged bis(2-methyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride (**2**) has been prepared previously through the hydrogenation of the corresponding bis(indenyl)zirconium dichloride complex and the ^{1}H-NMR spectrum, and polymerization characteristics of this complex were reported [2]. In our case (Scheme 3), deprotonation of the *dl* and *meso* mixture of silyl-bridged bis(tetrahydroindene) **12** by *n*-BuLi in Et_2O was followed by treatment of the resulting yellow suspension of the dilithio salt with $ZrCl_4$ at room temperature (r.t.). The solvent was removed in vacuo and the residue was taken up in methylene chloride and filtered. Removal of the solvent from this filtrate provided zirconocene **2** as a 1:1 mixture of *dl* and *meso* forms in 95% yield. The *meso* isomer of **2** was more soluble than the *dl* isomer in hexane. Washing the initial 0.9 g of the mixture with hexane (3 × 40 ml) gave 0.28 g of pure *dl*-**2**. The spectroscopic characterization of this complex is discussed below.

Metalation of the silyl bridged bis(tetrahydroindene) **12** with tetrakis(dimethylamido)zirconium under equilibrating conditions in toluene, followed by chlorotrimethylsilane treatment [15] gave a 96% yield of the zirconocene dichloride **12** but again with a 1:1 ratio of the *dl* and *meso* isomers. The ^{1}H-NMR spectrum of the intermediate bis(dimethylamido)bis(2-methyl-4,5,6,7-tetrahydroindenyl)dimethylsilane]zirconium (**16**) also indicated a 1:1 ratio of *dl* and *meso* isomers. The frequently observed improvement of the *dl*:*meso* ratios through this amido elimination method was not realized in our case.

*2.3.2. Preparation of [bis(2-methyl-4,5,6,7-tetrahydroindenyl)dimethylsilane]titanium dichloride (**17**)*

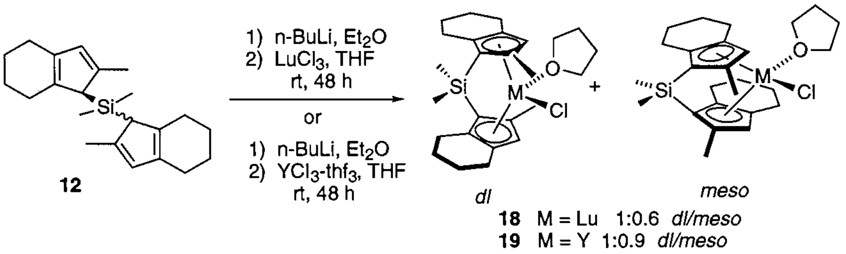
The dilithio salt of silyl-bridged bis(tetrahydroindene) **12** was treated with $TiCl_3$ in THF, followed by air oxidation in chloroform [16] to give the bis(tetrahydroindenyl)titanium dichloride **17** as a brown, air stable solid as a 1:1 mixture of *dl* and *meso* isomers in 78% yield. These isomers were not separated and were characterized as the mixture.

*2.3.3. Preparation of [bis(2-methyl-4,5,6,7-tetrahydroindenyl)dimethylsilane]lanthanide chlorides (**18**) and **19***

The silyl-bridged bis(tetrahydroindene) **12** did prove to be a suitable starting material for forming bis(tetrahydroindenyl)lanthanide chloride complexes of lutetium and yttrium, as shown in Scheme 4. Deprotonation of **12** as above, followed by metalation with either $LuCl_3$ or YCl_3–THF_3 in THF solvent led to the isolation of a *dl*/*meso* mixture of the metal complexes **18** (M = Lu, 90% yield, 1:0.6 *dl*:*meso*) and **19** (M = Y, 78% yield, 1:0.9 *dl*:*meso*) as light yellow THF adducts. The coordination of the solvent in either the lutetium or yttrium complexes could potentially give rise to two *meso* diastereomers, but the ^{1}H-NMR spectra evidenced only one, possibly averaged *meso* structure. Although the *dl* isomer in the lutetium case was favored by almost a 2:1 ratio, the *dl* isomer could not be isolated by fractional recrystallization. Complexes of both metals were characterized as the diastereomeric mixtures.

2.4. NMR spectra of the metallocenes

In the case of zirconocene **2** where the *meso* and *dl* isomers could be separated, the assignments of the ^{1}H-NMR signals could be assigned unambiguously due to the presence of the two diastereotopic silylmethyl groups lying in the mirror plane of the *meso* isomer. In *dl*-**2**, the two silylmethyl groups are equivalent and give rise to only one signal. In the two lanthanide cases **18** and **19**, where the *dl*:*meso* ratios were not unity, the major signals (with only one silylmethyl signal) corresponded to the *dl* isomers. The remaining titanium



Scheme 4.

Table 1
^{1}H-NMR data for the metal complexes

Complex	Metal	Chemical shift (ppm)					
		Cp–H		$Cp–CH_3$		$Si–CH_3$	
		rac	*meso*	*rac*	*meso*	*rac*	*meso*
2	Zr	6.45	6.27	2.11	2.23	0.90	0.82/0.96
17	Ti	6.71	6.49	2.00	2.16	0.93	0.87/1.00
16	Zr	6.34	6.26	2.19	2.29	0.72	0.70/0.74
18	Lu	6.18	6.07	2.45	2.56	0.98	0.96/1.01
19	Y	6.29	6.21	2.46	2.57	1.04	1.01/1.05

complex **17** and the bis(amido)zirconium complex **16** were assigned by analogy to give the assignments shown in Table 1. In each case, the Cp–H signal in the *meso* isomers appeared at higher field, while the Cp–Me signal for the *meso* isomers appeared at lower field.

2.5. Summary

2-Methyl-4,5,6,7-tetrahydroindene could be bridged by dimethylsilane and the bridged bis(indene) could be converted directly into dimethylsilyl-bridged bis(tetrahydroindenyl)metal chloride complexes of zirconium, titanium, yttrium and lutetium in *dl*:*meso* ratios of 1:0.6–1:1.

3. Experimental

3.1. General

All operations involving air sensitive compounds were performed in a nitrogen glove box or under argon using standard Schlenck glassware techniques. See Refs. [7] and [14b] for a more complete description of general techniques and instrumentation used.

3.2. 1H-2-Methyl-2,3,4,5,6,7-hexahydroindan-1-one (8a) [9]

In a three neck flask equipped with an overhead stirrer and reflux condenser, polyphosphoric acid (500 g) was heated to 100°C. Cyclohexyl methacrylate (130 ml, 0.72 mol) was added to give a deep red solution. After 1 h, the hot solution was poured into ice water (500 ml) and the mixture was stirred until the polyphosphoric acid completely dissolved. To the resulting brown mixture was added NH_4Cl (10.0 g, 0.19 mol) and after 30 min the solution was extracted with Et_2O (3×100 ml). The combined organic portion was washed with 10% aqueous $NaHCO_3$ (100 ml) and saturated aqueous NaCl, and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the viscous black–red residue was distilled under vacuum (0.01 mbar, 55°C) to give **8a** as a yellow oil (33.0 g, 30% yield). ^{1}H-NMR (400 MHz, C_6D_6, δ): 1.01 (d, $J = 7.6$ Hz, 3H, 10-H_3), 1.37 (m, 4H, 6-H_2/7-H_2),1.67 (dm, $J = 17$ Hz, 1H, 3-H), 1.88 (m, 2H, 8-H_2), 2.01 (m, 2H, 5-H_2), 2.06 (qd, $J = 7.6/3.3$ Hz, 1H, 2-H), 2.27 (dm, $J = 17$ Hz, 1H, 3-H); ^{13}C-NMR (100.57 MHz, C_6D_6, δ): 16.56 (C_{10}), 20.57, 22.01, 22.49, 28.21, 38.94 ($C_{3, 5, 6, 7, 8}$), 39.88 (C_2), 137.35 (C_9), 169.76 (C_4), 208.95 (C_1), MS (70 eV DIP): 150 (56) [M^+] 135 (100) [$M^+ - CH_3$], 122 (30), 79 (91) [$M^+ - C_2H_4$–CO], 77 (62); IR (NaCl, thin layer, cm^{-1}): 2929, 2868, 1699, 1652, 1277, 1252, 1230, 935.

3.3. 1H-2-Methyl-2,3,4,5,6,7-hexahydroindan-1-ol (9)

To a suspension of $LiAlH_4$ (0.80 g, 21.0 mmol; six equivalents) in Et_2O (200 ml) at 0°C, was added dropwise a solution of 2-methyl-4,5,6,7-tetrahydroindan-1-one (**3**) (2.20 g, 14.6 mmol) in Et_2O (20 ml). After 3 h at r.t., the suspension was cooled to 0°C and saturated aqueous potassium sodium tartrate (Rochelle's salt) was added dropwise until the evolution of gas stopped. This mixture was stirred for 30 min, then filtered. The filtrate was concentrated by rotary evaporation to give **9** as a yellow liquid (1.86 g, 84% yield). ^{1}H-NMR (200 MHz, C_6D_6, δ): 1.07 (d, $J = 6.6$ Hz, 3H, 10-H_3), 1.45–2.45 (m, 11H, 2-H, 3-/5-/6-/7-/8-H_2), 3.45 (br-s, 1H, OH), 4.11 (br-s, 1H, 1-H); ^{13}C-NMR (75.42 MHz, C_6D_6, δ): 19.18 (C_{10}), 22.67, 25.79, 41.56, 41.77 ($C_{2, 3, 5, 6, 7, 8}$), 86.61 (C_1), 135.74 (C_9), 137.34 (C_4); MS (70 eV DIP): 152 (47) [M^+], (36) [$M^+ - CH_3$], 135 (90) [$M^+ -$ OH], 109 (48), 107 (40), 79 (100) [$M^+ - CH_3$–C_2H_4–H_2CO); IR (NaCl, thin layer in cm^{-1}): 3322, 2926, 2836, 1446, 1277, 1032.

3.4. 1H-2-Methyl-4,5,6,7-tetrahydroindene (10)

To a suspension of $LiAlH_4$ (7.80 g, 0.20 mol, four equivalents) in Et_2O (700 ml) at 0°C was added dropwise a solution of 2-methyl-4,5,6,7-tetrahydroindan-1-one (**3**) (30.9 g, 0.20 mol) in Et_2O (100 ml). After heating for 1 h under reflux, water (100 ml) was added to the cooled suspension, followed by the addition of enough concentrated HCl to dissolve all of the aluminum hydroxide precipitate. The resulting solution was then heated under reflux for 1 h. After cooling to r.t., the phases were separated and the organic portion was washed with water and saturated aqueous $NaHCO_3$, and dried over $MgSO_4$. The solvent was removed by rotary evaporation to give indene **10** as a yellow liquid (26.5 g, 98% yield), which darkens upon standing. ^{1}H-NMR (300 MHz, C_6D_6, δ): 1.67 (m, 4H, 6-/7-H_2), 1.99 (s, 3H, 10-H_3), 2.25 (m, 4H, 5-/8-H_2), 2.60 (s, 2H, 3-H_2), 6.01 (s, 1H, 1-H); ^{13}C-NMR (75.42 MHz, $CDCl_3$, δ in ppm): 17.80 (C_{10}), 22.50, 23.10, 24.20, 25.20 ($C_{5, 6, 7, 8}$), 46.40 (C_3), 129.20 (C_2), 135.60 (C_4), 137.80 (C_9), 140.80 (C_1); MS (70 eV DIP, 63°C): 135 (100) [MH^+], 133 (25) [$M^+ - H$], 119 (22) [$M^+ - CH_3$], 105 (27) [$M^+ - H$–C_2H_4], 79 (26) [$C_6H_7^+$], 77 (30) [$C_6H_5^+$], IR (NaCl, thin layer in cm^{-1}): 3036, 2928, 2864, 2836, 1446, 1050.

3.5. (2-Methyl-4,5,6,7-tetrahydroindenyl)lithium (6)

To 2-methyl-4,5,6,7-tetrahydroindene (**10**) (15.9 g, 0.12 mol) in hexanes (180 ml) under argon was added *n*-butyllithium (2.5 M in hexane, 0.14 mol; 1.2 equivalents) at r.t. to give a brighter yellow solution, which slowly produced a white precipitate. After 12 h at r.t., the precipitate was filtered under argon, washed with hexane and dried under vacuum to give lithium salt **6** as a white powder (7.20 g, 44% yield). The filtrate contained isomerized diene **11**.

*3.6. 1,2-Ethylenebis(2-methyl-4,5,6,7-tetrahydroinden-1-yl) (**15**)*

To a yellow suspension of [2-methyl-4,5,6,7-tetrahydroindenyl]lithium (**6**) (0.80 g, 5.70 mmol) in THF (15 ml) at r.t. was added ethylene-1,2-bis(tosylate) (0.85 g, 2.28 mmol). After stirring for 48 h at r.t., the mixture was hydrolyzed with saturated aqueous NH_4Cl (40 ml) and extracted with petroleum ether (60 ml total). The combined organic portion was washed with 10% aqueous $NHCO_3$ and saturated aqueous NaCl, dried over $MgSO_4$ and concentrated by rotary evaporation. The yellow residue was purified by column chromatography (H_2O–deactivated SiO_2, pet ether) to give recovered indene **10**, spiro-annelated **11** and the desired bis(indene) **15** as a colorless oil (93 mg, 14% yield). ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.05 (m, 4H, 11-H_2), 1.20–1.80 (m, 12H, 5-/6-/7-/8-H_2), 1.90 (m, 6H, 10-H_3), 2.00–2.70 (m, 6H, 5-/8-H_2, 3-H), 5.60–5.90 (m, 4H, 1-H); ^{13}C-NMR (75.42 MHz, $CDCl_3$, δ): 14.59; 15.32 (C_{10}), 21.42, 23.33, 24.09, 24.40, 25.49, 29.12, 53.79, 55.13, 55.32, 55.73, 55.84 ($C_{3, 5, 6, 7, 8, 11}$), 124.33, 124.48, 128.88 (C_2), 137.34, 137.43, 139.16, 139.27, 139.67, 139.80, 139.84, 156.49 ($C_{1, 4, 9}$); MS (70 eV DIP, 63°C): 294 (10) [M^+], 161 (10) [$M^+ - C_{10}H_{13}$], 160 (100) [$M^+ - C_{10}H_{14}$], 145 (66) [$M^+ - C_{10}H_{14}$–CH_3], 135 (39) [$C_{10}H_{15}^+$], 117 (54) [$M^+ - C_{10}H_{14}$–CH_3–C_2H_4], 105 (96) [$C_8H_9^+$]; IR (NaCl, thin layer in cm^{-1}): 3042, 2849, 2243, 1699, 1661, 1652, 1634, 1446, 1418, 907, 728.

*3.6.1. 1H-1-(2-Bromoethyl)-2-methyl-4,5,6,7-tetrahydroindene (**14**)*

When the ethylene-1,2-bis(tosylate) in the preceding experiment was replaced by 1,2-dibromoethane, the monoalkylated product **14** was also obtained. ^{1}H-NMR (300 MHz, $CDCl_3$, δ in ppm): 1.68 (m, 4H, 6-/7-H_2), 1.94 (s, 3H, 10-H_3), 2.20 ($s_{br,}$ 4H, 5-/8-H_2), 2.25 (m, 2H, 11-H_2), 2.80 (s_{br}, 1H, 3-H), 3.05 (t, $^3J(^1H,^1H) = 8.0$ Hz, 2H, 12-H_2), 5.90 (s, 1H, 1-H); MS (70 eV DIP, 36°C): 240/242 (5/6) [M^+], 161 (10) [$M^+ - Br$], 146 (100) [$M^+ - Br$–CH_3] 133 (91) [$M^+ - Br$–C_2H_4], 117 (22) [$M^+ - HBr$–C_2H_4–CH_3], 105 (78) [$M^+ -$ Br–C_2H_4–C_2H_4], IR (NaCl, thin layer in cm^{-1}): 2932, 2858, 1699, 1652, 1446, 1352, 1087, 839, 648.

*3.6.2. 1H-1,1-Ethano-2-methyl-4,5,6,7-tetrahydroindene (**13**)*

In both of the preceding experiments, a substantial amount of spiro compound **13** was isolated. ^{1}H-NMR (300 MHz, $CDCl_3$, δ in ppm): 1.25 (m, 4H, 11-/12-H_2), 1.70 (m, 7H, 6-/7-H_2, 10-H_3), 1.88 (s_{br}, 2H, 8-H_2), 2.30 (m, 2H, 5-H_2), 6.07 (s, 1H, 1-H), ^{13}C-NMR (75.42 MHz, $CDCl_3$, δ in ppm): 11.80 ($C_{11, 12}$), 12.50 (C_{10}), 21.00, 22.80, 2380, 25.10 ($C_{5, 6, 7, 8}$), 37.70 (C_3), 127.40 (C_2), 136.10 (C_4), 138.70 (C_9), 144.10 (C_1); MS (70 eV DIP, 60°C): 160 (45) [M^+], 145 (95) [$M^+ - CH_3$], 117 (100) [$M^+ - CH_3$–C_2H_4], 77 (20) [$M^+ -$ C_2H_4–C_2H_4–CH_3–C]; IR (NaCl, thin layer in cm^{-1}) 3080, 3044, 3002, 2928, 2854, 2834, 1439, 993, 845.

*3.7. Bis(2-methyl-4,5,6,7-tetrahydroinden-1-yl)-dimethylsilane (**12**)*

To a yellow suspension of [2-methyl-4,5,6,7-tetrahydroindenyl]lithium (**6**) (1.31 g, 9.30 mmol) in THF (15 ml) at r.t. was added dichlorodimethylsilane (0.45 g, 3.50 mmol, 0.75 equivalents). After 24 h at r.t., the mixture was hydrolyzed with saturated aqueous NH_4Cl (40 ml) and extracted with petroleum ether (60 ml total). The combined organic portion was washed with 10% aqueous $NHCO_3$ and saturated aqueous NaCl, dried over $MgSO_4$ and concentrated by rotary evaporation. The yellow residue was purified by column chromatography (H_2O–deactivated SiO_2, pet ether) to give **12** as a colorless oil (0.67 g, 59% yield). No desired reaction was observed when diethyl ether was used as the reaction solvent. Anal. Calc. for $C_{22}H_{32}Si$: C, 81.41; H, 9.94. Found: C, 78.14; H, 9.79%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ in ppm): -0.272, -0.255, -0.245 (s, 6H, 11-/12-H_3), 1.55 (m, 4H, 6-/7-H_2), 1.78 (m, 4H, 6-/7-H_2), 2.07, 2.09 (s, 6H, 10-H_3), 2.32 (m, 8H, 5-/8-H_2), 3.19 (s, 2H, 3-H), 6.03 (s, 2H, 1-H), ^{13}C-NMR (75.42 MHz, $CDCl_3$, δ in ppm): -6.19 ($C_{11, 12}$), 17.36, 17.49 (C_{10}), 23.29, 23.85, 24.58, 27.20, 27.36 ($C_{5, 6, 7, 8}$), 52.30 (C_3), 129.83 (C_2), 137.55 (C_4), 137.90 (C_9), 141.97 (C_1); MS (70 eV DIP, 63°C): 324 (22) [M^+], 191 (100) [$M^+ - C_{10}H_{13}$], 131 (55) [$C_{10}H_{11}^+$], 79 (91) [$M^+ -$ C_2H_4–CO], 59 (12) [$HSi(CH_3)_2^+$], IR (NaCl, thin film in cm^{-1}): 3037, 2926, 2854, 2836, 1631, 1248, 1001, 830.

*3.8. [ansa-Dimethylsiladiyl-bis(2-methyl-4,5,6,7-tetrahydroinden-1-yl)]zirconium dichloride (**2**) [2]*

To bis[2-methyl-4,5,6,7-tetrahydroindenyl]dimethylsilane (**12**) (0.66 g, 2.00 mmol) in diethyl ether (10 ml) was added *n*-butyllithium (2.5 M in hexane, 4.90 mmol, 1.2 equivalents) at 0°C. The mixture was then stirred for 24 h at r.t. to give a yellow, oily precipitate. Solid $ZrCl_4$ (0.76 g, 3.20 mmol, 1.6 equivalents) was added at r.t. to give a yellow suspension. After 24 h at r.t., the volatiles were removed under high vacuum and CH_2Cl_2 (20 ml) was added. The resulting suspension was filtered through a glass frit to remove LiCl and concentration of the filtrate gave zirconocene dichloride **2** as a yellow–brown solid (0.92 g, 95% yield). The *dl*:*meso* diastereomeric ratio was determined by ^{1}H-NMR spectroscopy to be 1:1. Repeated extraction of the solid with hexane could be used to remove the more soluble *meso* isomer. Stirring the crude reaction product with hexane (40 ml), decanting the hexane and repeating twice more gave a yellow residue of *dl*-**2** (0.28 g, 29%). Recrystallization from dichloromethane and hexane gave nearly colorless crystals of pure *dl*-**2** (m.p. 212°C). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 6.45 (s, 2H, *H-3*), 2.40–3.05 (m, 8H, *H-4*, *H-7*), 2.11 (s, 6H, =CCH_3), 1.40–1.95 (m, 8H, *H-5*, *H-6*), 0.90 (s, 6H, SiCH_3); ^{13}C-NMR (50.28 MHz, $CDCl_3$): δ 138.9, 129.0, 128.8, 127.7, 97.5, 26.7, 24.4, 22.8, 22.0, 17.3, 2.06; IR (KBr pellet) 2939, 2858, 1259, 1097, 1024, 844 cm^{-1}; MS (12 eV DIP) 484 (11), 482 (10, M^+), 448 (7), 324 (2), 192 (2), 134 (100, $C_{10}H_{14}^+$), 132 (21), 119 (25); Anal. Calc: C, 54.52; H, 6.24. Found: C, 51.27; H, 6.58%.

A sample enriched in the *meso*-**2** isomer was obtained by concentrating the above hexane fractions. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 6.27 (s, 2H, *H-3*), 2.30–3.18 (m, 8H, *H-4*, *H-7*), 2.23 (s, 6H, =CCH_3), 1.40–1.95 (m, 8H, *H-5*, *H-6*), 0.96 (s, 3H, SiCH_3), 0.82 (s, 3H, SiCH_3); ^{13}C-NMR (50.28 MHz, $CDCl_3$): δ 140.0, 130.4, 128.1, 127.4, 97.5, 26.4, 24.5, 23.0, 22.1, 18.2, 2.12, 1.94.

*3.9. [Bis(dimethylamido)][ansa-dimethylsiladiyl-bis(2-methyl-4,5,6,7-tetrahydroinden-1-yl)]zirconium **(16)***

To tetrakis(dimethylamido)zirconium (0.24 g, 0.89 mmol; 1.2 equivalents) in toluene (5 ml) at r.t. was added a solution of bis[2-methyl-4,5,6,7-tetrahydroindenyl]dimethylsilane (**12**) (0.25 g, 0.77 mmol) in toluene (15 ml). While stirring at 100°C for 14 h, gas was evolved and the solution deepened from yellow to orange. The solvent was removed under vacuum to give **16** as an orange pasty solid. The *dl*:*meso* ratio was found to be 1:1. ^{1}H-NMR (200 MHz, C_6D_6): δ 6.26 (s, 2H, *H-3 meso*), 6.34 (s, 2H, *H-3 rac*), 3.18 (br, 6H, NMe_2 *meso*), 3.07 (br, 6H, NMe_2 *meso*), 3.14 (br, 12H, NMe_2 *rac*), 2.30–2.95 (m, 16H, *H-4*, *H-7 rac* + *meso*), 2.29 (s, 6H, =CCH_3 *meso*), 2.19 (s, 6H, =CCH_3 *rac*), 1.20–1.95 (m, 16H, *H-5*, *H-6 rac* + *meso*) 0.74 (s, 3H, SiCH_3 *meso*), 0.70 (s, 3H, SiCH_3 *meso*), 0.72 (s, 6H, SiCH_3 *rac*); ^{13}C-NMR (50.28 MHz, C_6D_6): δ 134.5, 130.8, 124.2, 122.6, 122.2, 121.9, 119.8, 117.1, 106.9, 105.9, 52.0, 49.7, 48.6, 26.6, 26.4, 25.5, 25.1, 24.7, 24.2, 22.9, 17.1, 16.7, 2.29, 2.21.

The crude reaction product was dissolved in benzene (5 ml) and chlorotrimethylsilane (0.42 g, 3.85 mmol, 1.5 equivalents) was added to the resulting orange solution. After 14 h at r.t., the volatiles were removed under vacuum and the yellow solid residue was taken up in methylene chloride (20 ml). Filtration of the solid LiCl and concentration of the filtrate gave **2** (0.36 g, 96% yield) as a yellow powder. The spectroscopic characteristics matched those reported above.

*3.10. [ansa-Dimethylsiladiyl-bis(2-methyl-4,5,6,7-tetrahydroinden-1-yl)]titanium dichloride **(17)***

To a solution of bis[2-methyl-4,5,6,7-tetrahydroindenyl]dimethylsilane (**12**) (0.25 g,0.77 mmol) in diethyl ether (8 ml) at 0°C was added a solution of *n*-butyllithium (2.5 M in hexane, 1.84 mmol, 1.2 equivalents). The mixture was then stirred at r.t. for 24 h to give a yellow oily precipitate. The solvent was removed under vacuum and the residue was taken up in THF (10 ml). After cooling this solution to −78°C, $TiCl_3$ (0.19 g, 1.23 mmol, 1.6 equivalents) was added and the resulting mixture was stirred at r.t. for 12 h to give a dark purple solution, which when heated under reflux for 4 h turned black–green. The solvent was removed under vacuum and the residue taken up at 0°C in chloroform (8 ml). Air was bubbled through the solution for 4 h and the solution was then stirred with 2 N HCl (5 ml) for 10 min. The phases were separated and the aqueous phase extracted with dichloromethane (total of 40 ml). The combined organic portion was washed with 1 N HCl and water, dried over magnesium sulfate and concentrated by rotary evaporation to give **17** as a waxy solid (0.26 g, 78% yield). Washing with hexane gave an air-stable brown solid in a *dl*:*meso* ratio of 1:1. M.p. 216°C. ^{1}H-NMR (200 MHz, $CDCl_3$); δ 6.71 (s, 2H, *H-3 rac*), 6.49 (s, 2H, *H-3 meso*), 2.30–3.45 (m, 16H, *H-4*, *H-7 rac* + *meso*), 2.16 (s, 6H, =CCH_3 *meso*), 2.00 (s, 6H, =CCH_3 *rac*), 1.30–1.95 (m, 16H, *H-5*, *H-6 rac* + *meso*) 1.00 (s, 3H, SiCH_3 *meso*), 0.87 (s, 3H, SiCH_3 *meso*), 0.93 (s, 6H, SiCH_3 *rac*); ^{13}C-NMR (50.28 MHz, $CDCl_3$): δ 147.1, 145.8, 137.2, 135.9, 135.2, 133.7, 132.1, 131.8, 96.1, 95.9, 27.4, 27.0, 25.7, 25.5, 22.7, 22.6, 21.7, 21.6, 19.3, 18.5, 1.86 (SiCH_3 *meso*), 1.51 (SiCH_3 *meso*), 1.66 (SiCH_3 *rac*); IR (KBr pellet) 2939, 2864, 1497, 1455, 1435, 1259, 1036, 816 cm^{-1}; MS (12 eV DIP) 442 (21), 441 (13), 440 (29, M^+), 405 (17), 404 (46, $M^+ - Cl$), 368 (100, $M^+ - 2Cl$); Anal. Calc: C, 59.87; H, 6.85. Found: C, 58.90; H, 7.36%.

*3.11. [ansa-Dimethylsiladiyl-bis(2-methyl-4,5,6,7-tetrahydroindenyl)]lutetium chloride **(18)***

To a solution of **12** (0.40 g, 1.23 mmol) in diethyl ether (8 ml) was added at 0°C *n*-butyllithium in hexane (2.71 mmol). The solution was allowed to warm to r.t. and it was stirred for 24 h to form a yellow precipitate. The solvent was removed in vacuo and the yellow solid was taken up in THF (10 ml). The solution was cooled to −78°C and lutetium trichloride (1.47 mmol, 0.41 g) was added. After 30 min, the mixture was allowed to warm to r.t. and it was stirred for an additional 48 h. The solvent was removed in vacuo and the residue was extracted with diethyl ether (20 ml). The voluminous LiCl precipitate was removed by filtration and the filtrate evaporated in vacuo to give **18** as a light yellow solid (0.72 g, 90%) in a diastereomeric *rac*:*meso* ratio of 1:0.6. Attempts to isolate a single diastereomer by recrystallization were unsuccessful. The NMR spectra indicated the presence of coordinated THF, but the presence of a C_2- and only one *meso*-symmetrical isomer was indicated. Anal. Calc. for $C_{22}H_{30}SiLuCl$: C, 49.58; H, 5.67. Found: C, 52.13; H, 6.68%. Calc. with 1.5 equivalents of THF: C, 52.45; H, 6.60%. *rac*:*meso* 2:1 by NMR spectra. ^{1}H-NMR (200 MHz, C_6D_6): δ 6.18 (s, 2H, *H-3 rac*), 6.07 (s, 2H, *H-3 meso*), 3.58 (br, THF), 2.65–3.15 (m, 16H, *H-4*, *H-7 rac* + *meso*), 2.56 (s, 6H, $=CCH_3$ *meso*), 2.45 (s, 6H, $=CCH_3$ *rac*), 1.36 (br, THF), 1.50–2.20 (m, 16H, *H-5*, *H-6 rac* + *meso*) 1.01 (s, 3H, Si*CH*$_3$ *meso*), 0.96 (s, 3H, Si*CH*$_3$ *meso*), 0.98 (s, 6H, Si*CH*$_3$ *rac*); ^{13}C-NMR (50.28 MHz, C_6D_6): δ 129.4, 128.3, 127.8, 125.4, 124.1, 123.4, 123.1, 119.4, 104.6, 27.6, 27.4, 25.4, 25.3, 24.9, 24.5, 24.3, 24.2, 17.7, 16.9, 3.40 (Si*C*H$_3$ *meso*), 3.26 (Si*C*H$_3$ *meso*), 3.33 (Si*C*H$_3$ *rac*); MS (70 eV DIP) 1064 (55%, M_2^+), 932 [12, $M_2^+ - C_{10}H_{12}$], 874 [100, $M_2^+ - C_{12}H_{18}Si$], 532 [80, M^+], 497 [57, $M^+ - Cl$], 401 (16), 191 (15), 132 (11, $C_{10}H_{12}$), 59 (32, $HSi(CH_3)_2^+$).

3.12. [ansa-Dimethylsiladiyl-bis(2-methyl-4,5,6,7-tetrahydroindenyl)]yttrium chloride ***(19)***

Following the procedure described for the formation of the lutetium complex **18** using **12** (0.40 g, 1.23 mmol) in diethyl ether (8 ml), *n*-butyllithium in hexane (2.71 mmol) and yttrium trichloride–THF_3 (0.61 g, 1.47 mmol) gave **19** (0.43 g, 78%) as a light yellow solid in a diastereomeric *rac*:*meso* ratio of 1:0.9. ^{1}H-NMR (200 MHz, C_6D_6): δ 6.29 (s, 2H, *H-3 rac*), 6.21 (s, 2H, *H-3 meso*), 3.66 (br, THF), 2.60–3.29 (m, 16H, *H-4*, *H-7 rac* + *meso*), 2.57 (s, 6H, $=CCH_3$ *meso*), 2.46 (s, 6H, $=CCH_3$ *rac*), 1.47 (br, THF), 1.25–2.35 (m, 16H, *H-5*, *H-6 rac* + *meso*) 1.05 (s, 3H, Si*CH*$_3$ *meso*), 1.01 (s, 3H, Si*CH*$_3$ *meso*), 1.04 (s, 6H, Si*CH*$_3$ *rac*).

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