Palladium-catalyzed arylation of bis(4-bromo-2-methylinden-1-yl)dimethylsilane and related compounds

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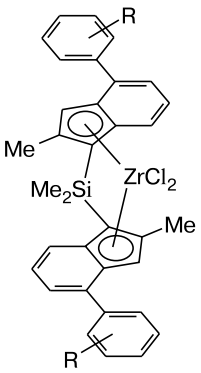
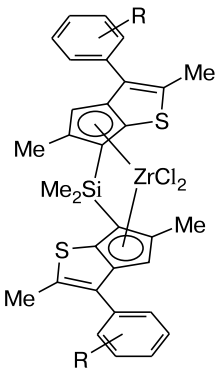
A new procedure was developed for the synthesis of a broad range of *ansa*-zirconocenes containing bis(2-methyl-4-arylindenyl)dimethylsilane ligands. The method is based on the palladium-catalyzed reaction of halogen-substituted bis(indenyl)dimethylsilanes with various organozinc compounds. The aryl-substituted bridging ligands thus prepared serve as the starting compounds for the synthesis of *ansa*-zirconocenes, which can be used as components of promising catalysts for propylene polymerization.

Key words: *ansa*-zirconocenes, cross-coupling, Negishi reaction, organozinc compounds, organosilicon compounds, bis(4-bromo-2-methylinden-1-yl)dimethylsilane.

Recent extensive research into the relationship between the structures of *ansa*-metallocenes and the activity and stereoselectivity of the corresponding catalysts for propylene polymerization showed that the best results were achieved for catalysts based on the so-called improved *ansa*-zirconocenes **A** containing bis(2-methyl-4-arylindenyl)dimethylsilane ligands, as well as on related complexes **B** containing 3-aryl-2,5-dimethylcyclopenta[*b*]thienyl moieties.[1—4]



A



B

The main method for the synthesis of *ansa*-zirconocenes is based on the reaction of the dilithium salt of the bis-indenyl ligand with zirconium tetrachloride.[5] In turn, bis(indenyl)dimethylsilanes are prepared by the reaction of 2 equiv. of the lithium salt of the corresponding indene with dichlorodimethylsilane. This synthesis has drawbacks. Since the indenyl moiety in the intermediate of this reaction, *i.e.*, in indenyldimethylchlorosilane, is more acidic than the starting indene,[6] the synthesis of the bridging ligand is accompanied by transmetallation of this intermediate with the starting lithium salt of indene as the side reaction. This results in a decrease in the yield of the target product and the formation of large amounts of polymeric and oligomeric by-products. If it is necessary to prepare a series of different zirconium *ansa*-complexes of the **A** (or **B**) type according to the above-mentioned procedure, the corresponding aryl-substituted indenes (or cyclopenta[*b*]thiophenes) must first be synthesized. Earlier, we have shown that in this case, the approach based on the palladium-catalyzed arylation of halogen-substituted indenes and related substrates is the method of choice.[7] In the next step, it is necessary to synthesize the corresponding bridging ligands by the reaction of the salt of indene with dimethylchlorosilane. Hence, the synthesis of a number of *ansa*-complexes **A** (or **B**) involves a series of similar reactions, in particular, the introduction of the dimethylsilylene bridge giving rise to the target products in rather low yields. In this connection, a more convenient approach can be suggested based on the synthesis of a single halogen-substituted bis(indenyl)dimethylsilane as the precursor. In the next step, this compound can be used as the template for the catalytic cross-coupling involving various aryl-substituted organometallic derivatives. This allows the simultaneous synthesis of a number of bridging ligands and then of the corresponding *ansa*-metallocenes. Therefore, the aims of the present study were to synthesize bis(4-bromo-2-methylinden-1-yl)dimethylsilane and related com-

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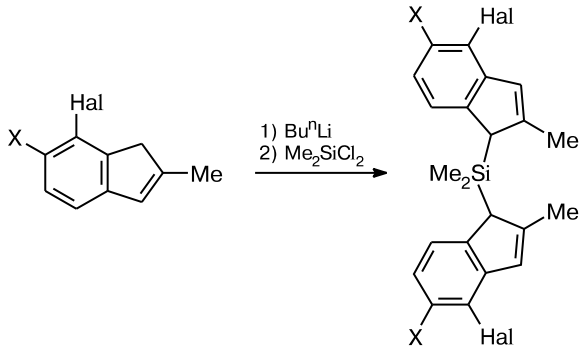
pounds and to develop a procedure for the palladium-catalyzed arylation of these substrates. It should be noted that, when designing this study, the success was not evident. This is associated with two facts. First, silyl derivatives of indenes are not completely inert in the presence of palladium catalysts. These compounds containing olefin and allylsilyl moieties are potential substrates for the Heck[6,7] and Hiyama reactions,[10,11] respectively. Second, the silicon—cyclopentadienyl bond in bis(indenyl)-dimethylsilanes is known to be sensitive to alkalis and particularly to acids.[6] Hence, rather strict limitations were initially placed on the conditions of catalytic arylation. In particular, the reactions in the presence of bases in protic solvents (for example, in water) were completely excluded. The use of strongly basic reagents (for example, of ArMgX), which are substrates in the Kumada reaction, was also impractical, because these reactions can be accompanied by metallation of the indenyl moieties and a decrease in the yields of the target compounds.

Scheme 1



1—3

Compound	**1**	**2**	**3**
Hal	Br	Cl	Br
X	H	H	Me

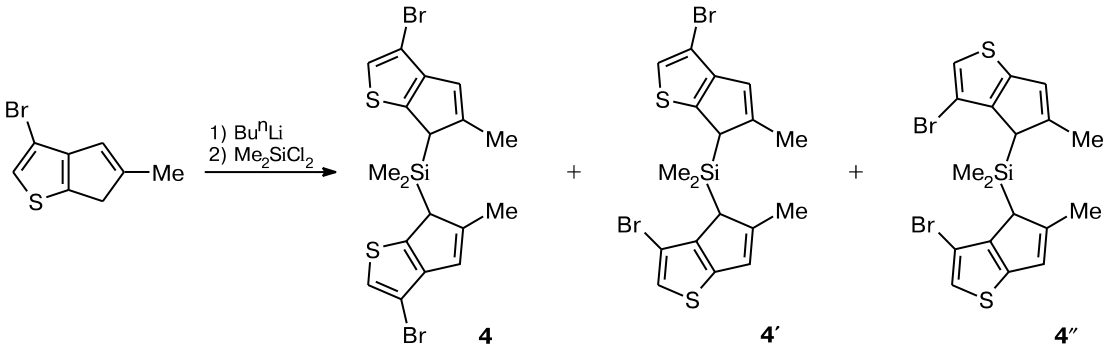
Results and Discussion

In the first step, we synthesized halogen-substituted bridging ligands. For this purpose, 4(7)-bromo-2-methyl-1(3)*H*-indene, 4(7)-bromo-2,5(6)-dimethyl-1(3)*H*-indene, or 4(7)-chloro-2-methyl-1(3)*H*-indene were metallated with *n*-butyllithium in diethyl ether, and then 0.5 equiv. of dimethyldichlorosilane was added (Scheme 1). Analytically pure samples of compounds **1** and **3** were obtained in 47 and 61% yields, respectively, by washing the organic reaction products with hexane. Ligand **2** was isolated in 69% yield by recrystallization from hexane.

It appeared that the analogous reaction with the lithium salt of 3-bromo-5-methyl-4(5)*H*-cyclopenta[*b*]thiophene is not regioselective. This reaction affords the target 6,6′-substituted bis(3-bromo-5-methylcyclopenta[*b*]-thien-6-yl)dimethylsilane (**4**) along with isomeric 4,6′- and 4,4′-substituted compounds **4′** and **4″** containing the 3-bromo-5-methylcyclopenta[*b*]thien-4-yl moiety (Scheme 2). These three compounds have similar solubilities, which makes difficult the isolation of analytically pure isomer **4** by crystallization. A mixture of three compounds was isolated in 42% yield by silica gel flash chromatography. The content of 6,6′-isomer **4** in this mixture was 60%.

The observed difference in the regioselectivity of the reactions involving indenyl and cyclopenta[*b*]thienyl derivatives is apparently attributed to the fact that the bromine atom in 3-bromo-5-methylcyclopenta[*b*]thiophene is spatially remote from the cyclopentadienyl moiety and, consequently, this bromine atom cannot provide sufficient steric shielding of the nearest carbon atom in the cyclopentadienyl ring. A radically different situation is observed for analogous indene derivatives. In these compounds, the halogen atom is substantially closer to one of the carbon atoms of the cyclopentadienyl ring. It is known that organosilyl substituents in cyclopentadiene and its derivatives can be involved in the 1,3-sigmatropic

Scheme 2



rearrangement even at room temperature.[6] Therefore, the bridging bis-indenyl ligands, in which the halogen atom is adjacent to the organosilicon moiety, even if are produced, should undergo the rearrangement to form sterically less hindered bis(4-bromoinden-1-yl)dimethylsilanes, and that is the case. This conclusion is not true for compounds containing the 3-bromo-5-methylcyclopenta[*b*]-thienyl moiety. In the latter case, the thermodynamic stabilities of isomeric silyl-substituted products are rather similar, due to which the complete stereocontrol in the synthesis of the corresponding bridging ligands cannot be performed.

It should be noted that, according to NMR spectroscopic data, the double bonds in the cyclopentadienyl rings in all the ligands synthesized in the present study are in allylic positions with respect to the bridging dimethylsilylene moiety.

Bridging ligands **1—4** (ligand **4** was obtained in a mixture with isomers **4´** and **4´´** as impurities) were used as the starting substrates in the cross-coupling reactions catalyzed by palladium complexes. In our studies, the main attention was paid to bridging ligand **1** containing the 4-bromo-2-methylinden-1-yl moieties. The investigation of the transformations of ligand **2** is important from the viewpoint of the development of a procedure employing cheaper and more readily available but less reactive chlorine-containing substrates. Ligand **3** is the sterically hindered substrate. The choice of ligand **4** was determined by the fact that *ansa*-zirconocenes **B** are apparently promising compounds, as well as by the necessity of evaluating the applicability of the methods developed for the cross-coupling to sulfur-containing substrates, which are by themselves or their transformation products can, in some cases, serve as catalytic poisons for systems based on transition metals.[7,12]

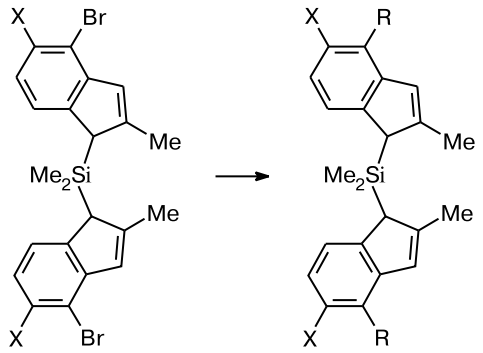
We used the Negishi reaction with organozinc compounds as the main method for the synthesis of aryl-substituted bridging ligands.[12] The starting arylzinc chlorides were synthesized *in situ* by the reaction of zinc chloride with the corresponding Grignard reagent in THF. The cross-coupling reaction was carried out at 70 °C for several hours. The $Pd(PBu^t_3)_2$ complex, whose high activity was demonstrated in the study[13] and was confirmed in our studies performed with halogen-substituted indenes,[7] was used as the catalyst. The experimental results are presented in Table 1. In the case of bromine-substituted substrate **1**, the cross-coupling products were obtained in nearly quantitative yields (Scheme 3, X = H), which is indicative of the applicability of this method to the synthesis of a broad range of aryl-substituted bridging ligands, including ligands containing sterically crowded (see Table 1, example *3*), electron-withdrawing (examples *4* and *8*), or electron-donating (examples *6* and *9*) aryl groups at position 4 of the indenyl moiety. In addition, this method allows the synthesis of the corresponding products containing alkyl (example *5*) or hetaryl (example *7*) groups and can also be used for the cross-coupling with sterically crowded substrates, for example, with bromine-substituted ligand **3** (see Scheme 3, X = Me; see Table 1, examples *10* and *11*).

Table 1. Yields of ligands **5—7** synthesized by the Negishi reaction

Run	Starting compound	Product	Yield (%)
1	**1**	**5a**	97
2	**1**	**5b**	96
3	**1**	**5c**	94
4	**1**	**5d**	97
5	**1**	**5e**	98
6	**1**	**5f**	92
7	**1**	**5g**	95
8	**1**	**5h**	97
9	**1**	**5i**	98
10	**3**	**6a**	95
11	**3**	**6b**	95
12	**2**	**5b**	82
13	**4** + **4´** + **4´´**	**7a**	97
14	**4** + **4´** + **4´´**	**7b**	93
15	**4** + **4´** + **4´´**	**7c**	88

In the next step, we studied the reactivity of chlorine-substituted compound **2**. Initially, we used the $Pd(PBu^t_3)_2$ complex as the catalyst for the cross-coupling reactions with the involvement of this substrate. The reaction with phenylzinc chloride was carried out in THF at 70 °C for 5 h. The analysis of the reaction mixture showed that the desired product was absent when the ~40% conversion of the starting compound was achieved. This indicates that,

Scheme 3



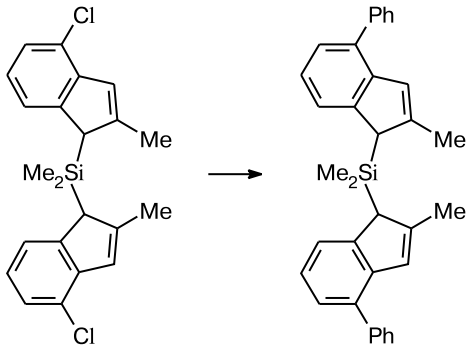
1, 3 **5a—i, 6a,b**

X = H (**1, 5**), Me (**3, 6**); R = Ph (**5a, 6a**), 4-MeC_6H_4 (**5b**), 2,4,6-$Me_3C_6H_2$ (**5c**), 3-$F_3CC_6H_4$ (**5d**), Me (**5e**), 4-$Me_2NC_6H_4$ (**5f**), 1-benzothien-2-yl (**5g**), 2-$F_3CC_6H_4$ (**5h**), 4-$Bu^tC_6H_4$ (**5i**), 3,5-$(F_3C)_2C_6H_3$ (**6b**).

Reagents and conditions: RZnCl, $Pd(PBu^t_3)_2$, THF, 70 °C.

under the conditions used, either the slow decomposition of the starting substrate occurs or the cross-coupling proceeds only at one of the chlorine atoms of the starting substrate. Hence, we developed an alternative procedure[14] for the Negishi reaction with the involvement of aryl chlorides. Thus, we used the $Pd(dba)_2$—2-(di-*tert*-butylphosphino)biphenyl system as the catalyst. It appeared that the reaction of substrate **2** with *p*-tolylzinc chloride in the presence of this catalyst in THF at 70 °C for 15 h afforded double cross-coupling product **5b** in 82% yield (Scheme 4, see Table 1, run *12*). Therefore, the reactions in the presence of this catalyst for cross-coupling can be performed with cheaper chlorine-containing substrates, due to which the target *ansa*-metallocenes also become more readily available.

Scheme 4



2 **5b**

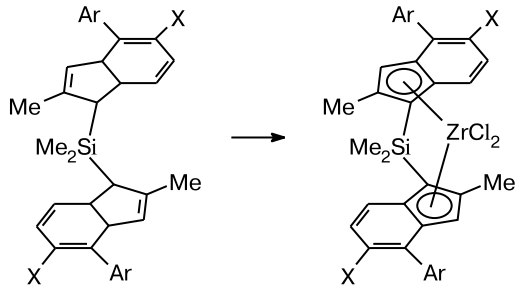
Reagents and conditions: PhZnCl, $Pd(dba)_2$, 2-$PhC_6H_4PBu^t_2$, THF, 70 °C.

Runs *13—15* (see Table 1) show that the approach under consideration can be used to synthesize related cyclopenta[*b*]thiophene derivatives (Scheme 5).

When studying this reaction, we obtained unexpected results. Thus, the reaction starting from a mixture of isomers **4** + **4′** + **4″** afforded individual compounds **7a—c** rather than mixtures of the corresponding isomeric aryl-substituted products. This is attributed to the fact that organosilicon derivatives of cyclopentadienes and related compounds readily undergo the 1,3-sigmatropic rearrangement,[6] as well as to the lower thermodynamic stability of isomers, in which the bulky aryl moiety is in the immediate vicinity of the $SiMe_2$ bridge. As a result, the arylation products of the isomeric bridging ligands containing the 3-aryl-5-methylcyclopenta[*b*]thienyl moieties with the silyl substituent at position 4 are rearranged into sterically less hindered products containing the silyl substituent at position 6. Due to the observed isomerization of the products in the course of cross-coupling, the labor-consuming isolation of isomers with similar properties is not required and a series of interesting compounds for the subsequent synthesis of *ansa*-metallocenes can be rather easily prepared.

Aryl-substituted bridging ligands **5e**, **5f**, **6a**, **7a**, and **7c** were used to synthesize *ansa*-zirconocenes **8a, 8b, 9, 10a,** and **10b**, respectively (Schemes 6 and 7).

Scheme 6

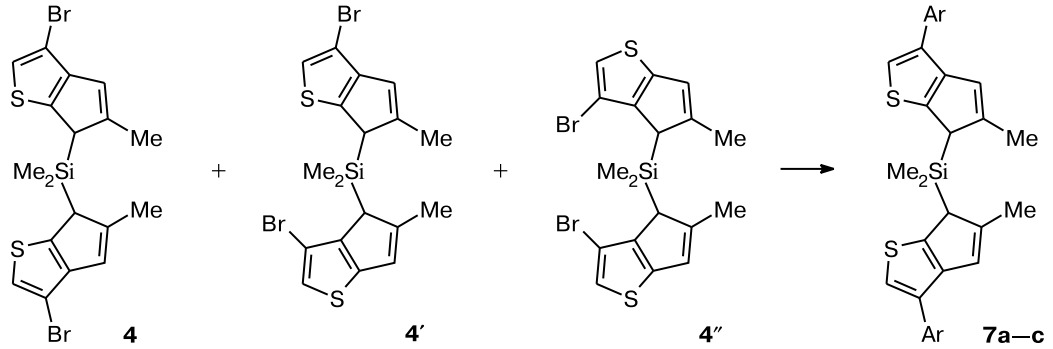


5e, 5f, 6a **8a,b, 9**

Compound	**5e, 8a**	**5f, 8b**	**6a, 9**
Ar	$CF_3C_6H_4$	4-$Me_2NC_6H_4$	Ph
X	H	H	Me

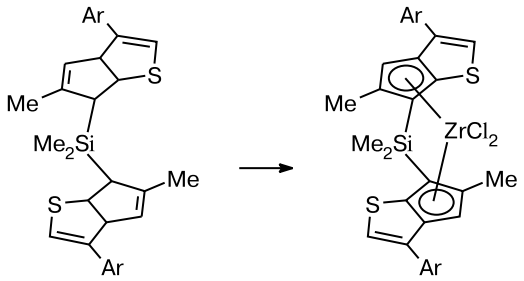
Reagents and conditions: 1) Bu^nLi; 2) $ZrCl_4 \cdot 2$ THF.

Scheme 5



Ar = Ph (**7a**), 4-$Bu^tC_6H_4$ (**7b**), 1-naphthyl (**7c**).
Reagents and conditions: RZnCl, $Pd(PBu^t_3)_2$, THF, 70 °C.

Scheme 7



7a,c **10a,b**

Ar = Ph (**7a, 10a**), 1-naphthyl (**7c, 10b**).
Reagents and conditions: 1) Bu^nLi; 2) $ZrCl_4 \cdot 2$ THF.

The complexes were synthesized according to the conventional procedure,[7] which involves the metallation of the starting ligand with *n*-butyllithium in diethyl ether followed by the reaction of the dilithium salt of the ligand with zirconium tetrachloride tetrahydrofuranate. Analytically pure racemic complexes **8a**, **8b**, **9**, and **10a** were isolated in 22, 23, 29, and 25% yields, respectively, by crystallization of the reaction products, *i.e.*, mixtures of the *rac* and *meso* complexes, from dichloromethane. The *rac* isomer of complex **10b** was obtained by recrystallization of the reaction product from toluene.

To summarize, we developed a new approach to the synthesis of aryl-substituted bis(indenyl)dimethylsilanes and related compounds based on the palladium-catalyzed Negishi arylation of the corresponding halogen-substituted substrates. In spite of the fact that the starting halogen-substituted bridging ligands containing cyclopenta[*b*]-thienyl moieties are mixtures of regioisomers as to the position of the bridging fragments with respect to the halogen atoms, the products of the Negishi reaction are rearranged to give the only isomer required for the synthesis of *ansa*-metallocenes. The new approach allows the preparation of a library of aryl-substituted ligands starting from a single parent compound. The aryl-substituted ligands can be used for the synthesis of aryl-substituted *ansa*-metallocenes serving as components of promising catalysts for propylene polymerization.

Experimental

All experiments with the use of atmospheric oxygen- and moisture-sensitive compounds were carried out under argon using the standard Schlenk techniques or in a glove box under a nitrogen-controlled atmosphere. The solvents were purified according to standard procedures. Tetrahydrofuran and diethyl ether were stored over potassium hydroxide and then distilled over sodium metal in the presence of benzophenone. Toluene and *n*-hexane were stored and then distilled over sodium metal. Dichloromethane was distilled over P_4O_{10}. *n*-Butyllithium (Aldrich), $ZnCl_2$ (Acros), 2-bromotoluene (Acros), $ZrCl_4 \cdot 2$ THF, $Pd(PBu^t_3)_2$ (Aldrich), and other reagents were used without addition purification, unless otherwise mentioned. 4(7)-Bromo-2-methyl-1(3)*H*-indene, 4(7)-bromo-2,5(6)-dimethyl-1(3)*H*-indene, and 4(7)-chloro-2-methyl-1(3)*H*-indene were synthesized according to known procedures.[7] 5-Methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one was prepared from thiophene and methacrylic acid according to a known procedure.[15] 3-Bromo-5-methyl-4(5)*H*-cyclopenta[*b*]thiophene was synthesized by bromination of 5-methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one followed by reduction and dehydration according to a known procedure.[5] The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 DPX spectrometer operating at 400 and 100 MHz, respectively; the chemical shifts are given with respect to $SiMe_4$. The elemental analysis was carried out on a CHN-O-Rapid analyzer (Heraeus).

Bis(4-bromo-2-methyl-1*H*-inden-1-yl)(dimethyl)silane (1). A 1.6 *M* solution of MeLi (29.9 mL, 47.8 mmol) in diethyl ether was added to a solution of 4(7)-bromo-2-methylindene (10.0 g, 47.8 mmol) in diethyl ether (250 mL) at 10 °C. The reaction mixture was stirred at room temperature for 1 h and cooled to 0 °C. Then Me_2SiCl_2 (2.89 mL, 3.08 g, 23.9 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. Then water (100 mL) was added, the organic layer was separated and dried over K_2CO_3, and the solvent was distilled off on a rotary evaporator. After evaporation, the residue was washed with hexane (3S30 mL) and dried *in vacuo*. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 5.37 g (47%). Calculated (%): C, 55.71; H, 4.68. $C_{22}H_{22}Br_2Si$. Found (%): C, 56.02; H, 4.77. ^1H NMR ($CDCl_3$), δ: 7.36 and 7.34 (both d, 2 H each, 5,5′-H in *meso* and *rac* isomers, $J = 8.5$ Hz); 7.32 and 7.23 (both d, 2 H each, 7,7′-H in *meso* and *rac* isomers, $J = 7.6$ Hz); 6.95 and 6.93 (both t, 2 H each, 6,6′-H in *meso* and *rac* isomers, $J = 8.1$ Hz); 6.70 (br.s, 4 H, 3,3′-H in *rac*- and *meso* isomers); 3.74 and 3.73 (both s, 2 H each, CHSiCH in *meso* and *rac* isomers); 2.23 and 2.17 (both d, 6 H each, 2,2′-Me in *meso* and *rac* isomers, $J = 1.2$ Hz); −0.19 (s, 3 H, SiMe in *meso* isomer); −0.24 (s, 6 H, $SiMe_2$ in *rac* isomer); −0.27 (s, 3 H, SiMe′ in *meso* isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 148.4, 148.3, 145.9, 145.1, 145.0, 128.4, 126.5, 124.2, 124.1, 121.8, 114.1, 48.6, 48.5, 17.9, −5.4, −5.6.

Bis(4-chloro-2-methyl-1*H*-inden-1-yl)(dimethyl)silane (2). A 1.6 *M* solution of MeLi (23.4 mL, 37.4 mmol) in diethyl ether was added to a solution of 4(7)-chloro-2-methylindene (6.15 g, 37.4 mmol) in diethyl ether (200 mL) at 0 °C. The reaction mixture was stirred at room temperature for 2 h and cooled to 0 °C. Then Me_2SiCl_2 (2.26 mL, 2.41 g, 18.7 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. Then water (100 mL) was added, the organic layer was separated and dried over K_2CO_3, and the solvent was distilled off on a rotary evaporator. After evaporation, the residue was recrystallized from hexane (30 mL). The precipitate was filtered off, washed with hexane (2×10 mL), and dried *in vacuo*. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 4.97 g (69%). Calculated (%): C, 68.56; H, 5.75. $C_{22}H_{22}Cl_2Si$. Found (%): C, 68.70; H, 5.88. ^1H NMR ($CDCl_3$), δ: 7.18 and 7.15 (both m, 2 H each, 5,5′-H in *meso* and *rac* isomers); 7.09 and 7.07 (both d, 2 H each, 7,7′-H in *meso* and *rac* isomers, $J = 7.9$ Hz); 6.90 and 6.88 (both m, 2 H each, 6,6′-H in *meso* and *rac* isomers); 6.63 (m, 4 H, 3,3′-H in *rac*- and *meso* isomers); 3.59 and 3.58 (both m, 2 H each, CHSiCH in *meso* and *rac* isomers); 2.11 and 2.06 (both d, 6 H

each, 2,2′-Me in *meso* and *rac* isomers, J = 1.0 Hz); −0.33 (s, 3 H, SiMe in *meso* isomer); −0.38 (s, 6 H, $SiMe_2$ in *rac* isomer); −0.40 (s, 3 H, SiMe′ in *meso* isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 148.31, 148.24, 146.1, 143.15, 143.05, 128.0, 126.3, 125.3, 124.6, 123.88, 123.82, 121.3, 48.3, 48.2, 17.9, −5.52, −5.59, −5.8.

Bis(4-bromo-2,5-dimethyl-1*H*-inden-1-yl)(dimethyl)silane (3). A 2.5 *M* solution of *n*-BuLi (17.9 mL, 44.8 mmol) in hexane was added to a solution of 4(7)-bromo-2,5(6)-dimethylindene (10.0 g, 44.8 mmol) in diethyl ether (400 mL) at 10 °C. The reaction mixture was stirred at room temperature for 12 h and cooled to 0 °C. Then Me_2SiCl_2 (2.72 mL, 2.89 g, 22.4 mmol) was added. The reaction mixture was stirred at room temperature for 24 h. Then water (50 mL) was added, the organic layer was separated and dried over Na_2CO_4, and the solvent was distilled off on a rotary evaporator. After evaporation, the residue was washed with hexane (3×30 mL) and dried *in vacuo*. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 7.02 g (61%). Calculated (%): C, 57.38; H, 5.22. $C_{24}H_{26}Br_2Si$. Found (%): C, 57.55; H, 5.34. ^1H NMR ($CDCl_3$), δ: 7.53 (d, 2 H, 7,7′-H in *rac* isomer, J = 7.5 Hz); 7.41 (d, 2 H, 7,7′-H in *meso* isomer, J = 7.5 Hz); 7.25 (d, 2 H, 6,6′-H in *rac* isomer, J = 7.5 Hz); 7.22 (d, 2 H, 6,6′-H in *meso* isomer, J = 7.5 Hz); 7.02 (m, 4 H, 3,3′-H in *rac*- and *meso* isomers); 4.02 (s, 2 H, 1,1′-H in *rac* isomer); 3.99 (s, 2 H, 1,1′-H in *meso* isomer); 2.74 (s, 6 H, 5,5′-Me in *rac* isomer); 2.72 (s, 6 H, 5,5′-Me in *meso* isomer); 2.51 (m, 6 H, 2,2′-Me in *meso* isomer); 2.46 (m, 6 H, 2,2′-Me in *rac* isomer); 0.08 (s, 3 H, SiMe in *meso* isomer); 0.015 (s, 3 H, SiMe′ in *meso* isomer); 0.006 (s, 6 H, $SiMe_2$ in *rac* isomer).

Bis(3-bromo-5-methyl-6*H*-cyclopenta[*b*]thien-6-yl)-(dimethyl)silanes (4, 4′, and 4″). A 1.6 *M* solution of MeLi (16.0 mL, 25.6 mmol) in diethyl ether was added to a solution of 3-bromo-5-methylcyclopenta[*b*]thiophene (5.50 g, 25.6 mmol) in diethyl ether (250 mL) at −60 °C. The reaction mixture was stirred at room temperature for 1 h and cooled. Then Me_2SiCl_2 (1.55 mL, 1.65 g, 12.8 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. Then water (50 mL) was added, the organic layer was separated and dried over K_2CO_3, and the solvent was distilled off on a rotary evaporator. The product was isolated by silica gel flash chromatography (40—63 μm, *d* 40 mm, *l* 500 mm, hexane as the eluent), which afforded a mixture of the 6,6′ isomer (~60%) along with the 4,4′- and 4,6′-isomeric compounds (~40%) in a total yield of 2.61 g (42%). The analytically pure product was isolated by recrystallization of the reaction mixture from a hexane—diethyl ether mixture (3 : 1, v/v). Calculated (%): C, 44.45; H, 3.73. $C_{18}H_{18}Br_2C_2Si$. Found (%): C, 44.90; H, 3.87. ^1H NMR ($CDCl_3$), δ, *rac* isomer: 7.11 (s, 2 H, 2,2′-H); 6.52 (m, 2 H, 4,4′-H); 3.84 (s, 2 H, 6,6′-H); 2.25 (s, 6 H, 5,5′-Me); −0.25 (s, 6 H, $SiMe_2$); *meso* isomer, 7.09 (s, 2 H, 2,2′-H); 6.52 (m, 2 H, 4,4′-H); 3.76 (s, 2 H, 6,6′-H); 2.26 (s, 6 H, 5,5′-Me); −0.21 (s, 3 H, SiMe); −0.26 (s, 3 H, SiMe′).

Negishi reaction (general procedure). A 1.0 *M* solution of the Grignard reagent (26.0 mL, 26.0 mmol) in THF was added to a 0.50 *M* solution of $ZnCl_2$ (58.0 mL, 29.0 mmol) in THF at room temperature. The reaction mixture was stirred for 1 h. Then aryl bromide (10.0 mmol) and a 0.02 *M* solution of $Pd(PBu^t_3)_2$ (20.0 mL, 0.40 mmol) in THF were added. The reaction mixture was stirred at 70 °C for 5 h, cooled, and passed through a layer of silica gel (*d* 30 mm, *l* 50 mm, THF as the eluent). The solvent was distilled off on a rotary evaporator. The product was isolated by silica gel flash chromatography (40—63 μm, *d* 30 mm, *l* 100 mm, hexane as the eluent).

Bis(2-methyl-4-phenyl-1*H*-inden-1-yl)(dimethyl)silane (5a). Compound **5a** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **1** and phenylmagnesium bromide. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 4.54 g (97%). Calculated (%): C, 87.13; H, 6.88. $C_{34}H_{32}Si$. Found (%): C, 87.30; H, 6.93. ^1H NMR ($CDCl_3$), δ: 7.60—7.16 (m, 18 H, 5,5′,6,6′,7,7′-H in indenyl and Ph in *rac* and *meso* isomers); 6.84 (m, 2 H, 3,3′-H in indenyl of *rac* or *meso* isomer); 6.82 (m, 2 H, 3,3′-H in indenyl of *meso* or *rac* isomer); 3.83 (s, 4 H, 1,1′-H in indenyl of *rac* and *meso* isomers); 2.27 (d, 6 H, 2,2′-Me in *rac* or *meso* isomer, J = 0.9 Hz); 2.19 (d, 6 H, 2,2′-Me in *meso* or *rac* isomer, J = 0.9 Hz); −0.150 (s, 3 H, SiMe in *meso* isomer); −0.152 (s, 6 H, $SiMe_2$ in *rac* isomer); −0.17 (s, 3 H, SiMe′ in *meso* isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 147.7, 147.6, 145.52, 145.48, 143.0, 142.9, 141.40, 141.36, 134.2, 128.9, 128.4, 126.7, 126.05, 126.00, 125.60, 125.58, 123.11, 123.05, 122.19, 122.14, 47.7, 47.6, 18.0, 17.9, −5.57, −5.60.

Bis[4-(4-methylphenyl)-2-methyl-1*H*-inden-1-yl]-(dimethyl)silane (5b). ***A.*** Compound **5b** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **1** and *p*-tolylmagnesium bromide. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 4.76 g (96%). Calculated (%): C, 87.04; H, 7.30. $C_{36}H_{36}Si$. Found (%): C, 87.22; H, 7.39. ^1H NMR ($CDCl_3$), δ: 7.45—7.51 (m, 6 H, 7,7′-H in indenyl *rac* isomer and 3,3′,5,5′-H in *p*-tolyl of *rac* and *meso* isomers); 7.38 (m, 2 H, 7,7′-H in indenyl of *meso* isomer); 7.27—7.32 (m, 12 H, 5,5′-H in indenyl and 2,2′,6,6′-H in *p*-tolyl of *rac* and *meso* isomers); 7.16—7.22 (m, 4 H, 6,6′-H in indenyl of *rac* and *meso* isomers); 6.84 (m, 2 H, 3,3′-H in indenyl of *meso* isomer); 6.82 (m, 2 H, 3,3′-H in indenyl of *rac* isomer); 3.82 (s, 4 H, 1,1′-H in indenyl of *rac* and *meso* isomers); 2.46 (s, 6 H, 4,4′-Me in *p*-tolyl of *rac* isomer); 2.45 (s, 6 H, 4,4′-Me in *p*-tolyl of *meso* isomer); 2.27 (d, 6 H, 2,2′-Me in indenyl of *meso* isomer, J = 0.9 Hz); 2.19 (d, 6 H, 2,2′-Me in indenyl of *rac* isomer, J = 0.9 Hz); −0.15 (s, 9 H, $SiMe_2$ in *rac* isomer and SiMe in *meso* isomer); −0.17 (s, 3 H, SiMe′ in *meso* isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 147.6, 147.4, 145.47, 145.42, 143.0, 142.9, 136.46, 136.41, 136.39, 136.35, 134.1, 129.1, 128.8, 126.1, 126.0, 125.49, 125.46, 123.1, 123.0, 122.0, 121.9, 47.6, 47.5, 21.2, 18.0, 17.9, −5.7.

B. A 1.0 *M* solution of *p*-tolylmagnesium bromide (10.1 mL, 10.1 mmol) in THF was added to a 0.50 *M* solution of $ZnCl_2$ (22.7 mL, 11.3 mmol) in THF at room temperature. The reaction mixture was stirred for 1 h. Then aryl chloride **2** (1.85 g, 3.91 mmol), $Pd(dba)_2$ (86.3 mg, 0.15 mmol), and 2-di-(*tert*-butyl)phosphinobiphenyl (89.5 mg, 0.30 mmol) were added. The reaction mixture was stirred at 70 °C for 15 h, cooled, and passed through a layer of silica gel (*d* 30 mm, *l* 50 mm, THF as the eluent). The solvent was distilled off on a rotary evaporator. The product was isolated by silica gel flash chromatography (40—63 μm, *d* 30 mm, *l* 100 mm, hexane as the eluent). The white solid compound as an equimolar mixture of the *rac* and *meso* isomers, which is identical to that prepared according to the method *A*, was obtained in a yield of 1.59 g (82%). Calculated (%): C, 87.04; H, 7.30. $C_{36}H_{36}Si$. Found (%): C, 87.14; H, 7.25.

Bis[4-(2,4,6-trimethylphenyl)-2-methyl-1*H*-inden-1-yl]-(dimethyl)silane (5c). Compound **5c** was synthesized according

to the general procedure by the Negishi reaction starting from aryl bromide **1** and mesitylmagnesium bromide. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 5.20 g (94%). Calculated (%): C, 86.90; H, 8.02. $C_{40}H_{44}Si$. Found (%): C, 87.17; H, 8.10. ^{1}H NMR ($CDCl_3$), δ: 7.72 and 7.49 (both d, 2 H each, 7,7′-H in indenyl of *meso* and *rac* isomers, J = 7.5 Hz); 7.29 and 7.24 (both t, 2 H each, 6,6′-H in indenyl of *meso* and *rac* isomers, J = 7.5 Hz); 7.05—7.13 (m, 12 H, 6,6′-H in indenyl and 3,3′,5,5′-H in mesityl of *rac* and *meso* isomers); 6.31 (s, 4 H, 3,3′-H in indenyl of *rac* and *meso* isomers); 4.03 (s, 2 H, 1,1′-H in indenyl of *rac* and *meso* isomers); 4.00 (s, 2 H, 1,1′-H in indenyl of *meso* and *rac* isomers); 2.45 (s, 12 H, 2,6-Me in mesityl of *rac* and *meso* isomers); 2.34 (d, 6 H, 2,2′-Me in indenyl of *rac* and *meso* isomers, J = 0.9 Hz); 2.23 (d, 6 H, 2,2′-Me in indenyl of *meso* and *rac* isomers, J = 0.9 Hz); 2.11 and 2.10 (both s, 6 H each, 4,4′-H in mesityl of *meso* and *rac* isomers); 2.07 (s, 12 H, 2,6-Me in mesityl of *meso* and *rac* isomers); –0.22 (s, 3 H, SiMe of *meso* isomer); –0.246 (s, 3 H, SiMe′ of *meso* isomer), –0.252 (s, 6 H, $SiMe_2$ of *rac* isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 147.01, 146.97, 144.75, 144.70, 144.0, 143.9, 137.5, 136.28, 136.23, 132.9, 132.8, 127.93, 127.89, 126.0, 123.0, 122.9, 121.6, 47.63, 47.61, 21.1, 20.5, 18.0, 17.8, –6.3, –6.8.

Bis[4-(3-trifluoromethylphenyl)-2-methyl-1*H*-inden-1-yl]-(dimethyl)silane (5d). Compound **5d** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **1** and 3-trifluoromethylphenylmagnesium bromide. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 5.92 g (98%). Calculated (%): C, 71.50; H, 5.00. $C_{36}H_{30}F_6Si$. Found (%): C, 71.69; H, 5.13. ^{1}H NMR ($CDCl_3$), δ: 7.39—7.84 (m, 24 H, 5,5′,7,7′-H in indenyl and $CF_3C_6H_4$ of *rac* and *meso* isomers); 7.29 (m, 2 H, 6,6′-H in indenyl of *rac* isomer); 7.23 (t, 2 H, 6,6′-H in indenyl of *meso* isomer, J = 7.5 Hz); 6.76 (s, 4 H, 3,3′-H in indenyl of *rac* and *meso* isomers); 3.85 (s, 2 H, 1,1′-H in indenyl of *rac* isomer); 3.82 (s, 2 H, 1,1′-H in indenyl of *meso* isomer); 2.28 (s, 12 H, 2,6-Me in mesityl of *meso* isomer); 2.23 (d, 6 H, 2,2′-Me in indenyl of *rac* isomer, J = 0.9 Hz); –0.11 (s, 3 H, SiMe of *meso* isomer); –0.15 (s, 3 H, SiMe′ of *meso* isomer); –0.16 (s, 6 H, $SiMe_2$ of *rac* isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 148.60, 148.55, 145.7, 142.95, 142.88, 142.12, 142.10, 132.63, 132.57, 132.2, 130.9 (q, $^1J(^{13}C—^{19}F)$ = 32.2 Hz), 128.8, 125.65, 125.62, 125.57, 125.53, 125.37, 125.34, 123.50, 123.47, 123.43, 122.9, 122.78, 122.75, 47.80, 47.74, 18.0, –5.33, –5.39, –5.6.

Bis(2,4-dimethyl-1*H*-inden-1-yl)(dimethyl)silane (5e). Compound **5e** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **1** and methylmagnesium chloride. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 3.34 g (97%). Calculated (%): C, 83.66; H, 8.19. $C_{24}H_{28}Si$. Found (%): C, 83.70; H, 8.26. ^{1}H NMR ($CDCl_3$), δ: 7.32—7.38 (m, 4 H, 7,7′-H in *rac* and *meso* isomers); 7.19—7.25 (m, 4 H, 5,5′-H in *rac* and *meso* isomers); 6.96—7.06 (m, 4 H, 6,6′-H in *rac* and *meso* isomers); 6.71 (m, 4 H, 3,3′-H in *rac* and *meso* isomers); 3.75 (s, 2 H, 1,1′-H in *rac* isomer); 3.72 (s, 2 H, 1,1′-H in *meso* isomer); 2.45 (s, 6 H, 4,4′-Me in *rac* isomer); 2.44 (s, 6 H, 4,4′-Me in *meso* isomer); 2.26 (d, 6 H, 2,2′-Me in *rac* isomer, J = 1.0 Hz); 2.21 (d, 6 H, 2,2′-Me in *meso* isomer, J = 1.0 Hz); –0.28 (s, 3 H, SiMe in *meso* isomer); –0.325 (s, 6 H, $SiMe_2$ in *rac* isomer); –0.334 (s, 3 H, SiMe′ in *meso* isomer). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 146.6, 146.5, 144.61, 144.55, 144.26, 144.20, 129.04, 129.01, 126.0 , 124.98, 124.95, 122.81, 122.74, 120.71, 120.67, 47.49, 47.42, 18.8 , 18.0 , –5.7, –5.9, –6.1.

Bis[4-(4-dimethylaminophenyl)-2-methyl-1*H*-inden-1-yl]-(dimethyl)silane (5f). Compound **5f** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **1** and 4-dimethylaminophenylmagnesium bromide. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 5.10 g (92%). Calculated (%): C, 82.26; H, 7.63. $C_{38}H_{42}N_2Si$. Found (%): C, 82.41; H, 7.58. ^{1}H NMR ($CDCl_3$), δ: 7.45—7.51 (m, 6 H, 7,7′-H in indenyl of *rac* isomer and 3,3′,5,5′-H in C_6H_4 of *rac* and *meso* isomers); 7.34 (d, 2 H, 7,7′-H in indenyl of *meso* isomer, J = 7.5 Hz); 7.29 (m, 2 H, 6,6′-H in indenyl of *rac* isomer); 7.26 (m, 2 H, 6,6′-H in indenyl of *meso* isomer); 7.18 (dd, 2 H, 6,6′-H in indenyl of *meso* isomer, J = 7.5 Hz, J = 5.9 Hz); 7.16 (dd, 2 H, 6,6′-H in indenyl of *rac* isomer, J = 7.5 Hz, J = 5.9 Hz); 6.85—6.90 (m, 12 H, 3,3′-H in indenyl and 2,2′,6,6′-H in C_6H_4 of *rac* and *meso* isomers); 3.82 (s, 4 H, 1,1′-H in indenyl of *rac* and *meso* isomers); 3.04 (s, 12 H, 4,4′-NMe_2 of *rac* isomer); 3.03 (s, 12 H, 4,4′-NMe_2 of *meso* isomer); 2.27 (d, 6 H, 2,2′-Me in indenyl of *meso* isomer, J = 0.9 Hz); 2.18 (d, 6 H, 2,2′-Me in indenyl of *rac* isomer, J = 0.9 Hz); –0.16 (s, 6 H, $SiMe_2$ in *rac* isomer); –0.17 (s, 3 H, SiMe in *meso* isomer); –0.19 (SiMe′ in *meso* isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 149.5, 147.1, 146.9, 145.51, 145.46, 142.84, 142.76, 134.3, 129.8, 129.6, 126.35, 126.30, 125.18, 125.14, 123.02, 122.97, 121.38, 121.32, 112.6, 47.6, 47.5, 40.7, 17.94, 17.85, –5.67.

Bis[4-(1-benzothien-2-yl)-2-methyl-1*H*-inden-1-yl]-(dimethyl)silane (5g). A 2.5 *M* solution of *n*-BuLi (5.24 mL, 13.0 mmol) in hexane was added to a solution of benzothiophene (1.74 g, 13.0 mmol) in THF (30 mL) at room temperature. The reaction mixture was stirred for 2 h. Then a 0.50 *M* solution of $ZnCl_2$ (29.0 mL, 14.5 mmol) in THF was added. The reaction mixture was stirred for 1 h. Then compound **1** (2.37 g, 5.0 mmol) and a 0.02 *M* solution of $Pd(PBu^t_3)_2$ (10.0 mL, 0.20 mmol) in THF were added. The reaction mixture was stirred at 70 °C for 5 h, cooled, and passed through a layer of silica gel (d = 30 mm, l = 50 mm, THF as the eluent). The solvent was distilled off on a rotary evaporator. The product was isolated by silica gel flash chromatography (40—63 μm, d 30 mm, l 100 mm, hexane as the eluent). The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 2.76 g (95%). Calculated (%): C, 78.57; H, 5.55. $C_{38}H_{32}C_2Si$. Found (%): C, 78.70; H, 5.46. ^{1}H NMR ($CDCl_3$), δ: 6.96—7.82 (m, 36 H, 3,3′,5,5′,6,6′,7,7′-H in indenyls and benzothienyls of *rac* and *meso* isomers); 3.70 and 3.66 (both s, 2 H each, 1,1′-H in indenyls of *meso* or *rac* isomer); 2.22 and 2.07 (both m, 6 H each, 2,2′-Me in indenyls of *meso* or *rac* isomer); –0.11 (s, 3 H, $SiMe_2$ of *rac* isomer), –0.14 (s, 3 H, SiMe of *meso* isomer); –0.18 (s, 6 H, SiMe′ of *meso* isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 148.7, 148.5, 145.8, 143.83, 143.81, 143.0, 142.8, 140.5, 139.77, 149.76, 126.57, 126.55, 126.2, 126.1, 126.0, 125.9, 124.3, 123.9, 123.39, 123.35, 123.07, 123.04, 122.9, 122.05, 122.03, 121.5, 47.8, 47.7, 18.0, 17.8, –4.9, –5.1, –5.2.

Bis[4-(2-trifluoromethylphenyl)-2-methyl-1*H*-inden-1-yl]-(dimethyl)silane (5h). Compound **5h** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **1** and 2-trifluoromethylphenylmagnesium

bromide. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 5.86 g (97%). Calculated (%): C, 71.50; H, 5.00. $C_{36}H_{30}F_6Si$. Found (%): C, 71.66; H, 5.12. ^{1}H NMR ($CDCl_3$), δ: 7.21—7.94 (m, 28 H, 5,5′,6,6′,7,7′-H in indenyl and 3,3′,4,4′,5,5′,6,6′-H in C_6H_4 of *rac* and *meso* isomers); 6.40 (m, 4 H, 3,3′-H in indenyl of *rac* and *meso* isomers); 3.92—4.07 (m, 4 H, 1,1′-H in indenyl of *rac* and *meso* isomers); 2.21—2.39 (m, 12 H, 2,2′-Me in indenyl of *rac* and *meso* isomers); –0.04—0.24 (m, 12 H, Me_2Si in indenyl of *rac* and *meso* isomers).

Bis[4-(4-*tert*-butylphenyl)-2-methyl-1*H*-inden-1-yl]-(dimethyl)silane (5i). Compound **5i** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **1** and 4-*tert*-butylphenylmagnesium bromide. The white solid compound was obtained as a 1 : 1 mixture of the *rac* and *meso* isomers in a yield of 5.70 g (98%). Calculated (%): C, 86.84; H, 8.33. $C_{42}H_{48}Si$. Found (%): C, 86.90; H, 8.39. ^{1}H NMR ($CDCl_3$), δ: 7.52—7.57 (m, 18 H, 7,7′-H in indenyl of *rac*- and *meso* isomers and 2,2′,3,3′,5,5′,6,6′-H in C_6H_4 of *rac*- and *meso* isomers); 7.39—7.43 (m, 2 H, 7,7′-H in indenyl of *meso* and *rac* isomers); 7.31—7.36 (m, 4 H, 5,5′-H in indenyl of *rac* and *meso* isomers); 7.19—7.26 (m, 4 H, 6,6′-H in indenyl of *rac* and *meso* isomers); 6.92 (m, 4 H, 3,3′-H in indenyl of *rac* and *meso* isomers); 3.88 and 3.85 (both m, 2 H each, 1,1′-H in indenyl of *meso* and *rac* isomers); 2.30 and 2.24 (both m, 6 H each, 2,2′-Me in indenyl of *meso* and *rac* isomers); 1.46 and 1.45 (both s, 18 H each, Bu^t of *meso* and *rac* isomers); –0.13 (s, 3 H, MeMe′Si of *meso* isomer); –0.15 (s, 3 H, MeMe′Si of *meso* isomer), –0.16 (s, 6 H, Me_2Si of *rac* isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 149.6, 147.5, 147.4, 145.52, 145.50, 143.00, 142.95, 138.49, 138.45, 134.09, 134.04, 128.6, 126.3, 126.2, 125.63, 125.58, 125.3, 123.14, 123.06, 122.05, 122.00, 47.7, 47.6, 34.6, 31.5, 18.03, 18.01, –5.58, –5.59, –5.8.

Bis(2,5-dimethyl-4-phenyl-1*H*-inden-1-yl)(dimethyl)silane (6a). Compound **6a** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **3** and phenylmagnesium bromide. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 4.72 g (95%). Calculated (%): C, 87.04; H, 7.30. $C_{36}H_{36}Si$. Found (%): C, 87.91; H, 7.38. ^{1}H NMR ($CDCl_3$), δ: 7.28—7.50 (m, 24 H, 7,7′-H and 4,4′-Ph in indenyl of *rac* and *meso* isomers); 7.07 and 7.04 (both d, 2 H each, 6,6′-H in indenyl of *meso* and *rac* isomers, J = 7.5 Hz); 6.34 (m, 4 H, 3,3′-H in *rac*- and *meso* isomers); 3.80 and 3.79 (both s, 2 H each, 1,1′-H in indenyl of *meso* and *rac* isomers); 2.254 and 2.246 (both s, 6 H each, 5,5′-Me in indenyl of *meso* and *rac* isomers); 2.21 and 2.14 (both d, 6 H each, 2,2′-Me in indenyl of *meso* and *rac* isomers, J = 0.9 Hz); –0.21 (s, 3 H, SiMe *meso* isomer); –0.22 (s, 9 H, SiMe′ *meso* isomer and $SiMe_2$ *rac* isomer). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 147.17, 147.05, 144.58, 144.53, 142.27, 142.23, 140.4 , 133.89, 133.84, 132.05, 132.01, 129.9, 129.7, 128.0 , 126.6 , 126.38, 126.33, 124.88, 124.81, 122.04, 122.01, 47.32, 47.26, 20.1 , 17.89, 17.85, –5.9, –6.0, –6.1.

Bis[4-(3,5-bis(trifluoromethyl)phenyl)-2,5-dimethyl-1*H*-inden-1-yl](dimethyl)silane (6b). Compound **6b** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **3** and 3,5-bis(trifluoromethyl)phenylmagnesium bromide. The white solid compound was obtained as a mixture of the *rac* and *meso* isomers in a ratio of ~1 : 2 in a yield of 7.30 g (95%). Calculated (%): C, 62.49; H, 4.20. $C_{40}H_{32}F_{12}Si$. Found (%): C, 62.55; H, 4.28. ^{1}H NMR ($CDCl_3$), δ: 8.02 (m, 4 H, 4,4′-H in aryl of *rac* and *meso* isomers); 7.93 and 7.89 (both m, 4 H each, 2,2′,6,6′-H in aryl of *meso* and *rac* isomers); 7.57 and 7.46 (both m, 2 H each, 7,7′-H in indenyl of *meso* and *rac* isomers); 7.20 and 7.17 (both m, 2 H each, 6,6′-H in indenyl of *meso* and *rac* isomers); 6.36 (m, 4 H, 3,3′-H in indenyl of *rac*- and *meso* isomers); 3.92 and 3.91 (both m, 2 H each, 1,1′-H in indenyl of *meso* and *rac* isomers); 2.34 (m, 6 H, 2,2′-Me of *rac*- and *meso* isomers); 2.33 and 2.32 (both s, 6 H each, 5,5′-Me of *meso* and *rac* isomers); 2.28 (m, 6 H, 2,2′-Me of *meso* and *rac* isomers); –0.05 (s, 3 H, SiMeMe′ of *meso* isomer); –0.08 (s, 3 H, SiMeMe′ of *meso* isomer); –0.09 (s, 6 H, $SiMe_2$ of *rac* isomer).

Bis(5-methyl-3-phenyl-6*H*-cyclopenta[*b*]thien-6-yl)-(dimethyl)silane (7a). Compound **7a** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **4** and phenylmagnesium bromide. The white solid compound was obtained as an equimolar mixture of the *rac* and *meso* isomers in a yield of 4.61 g (96%). Calculated (%): C, 74.95; H, 5.87. $C_{30}H_{28}S_2Si$. Found (%): C, 75.20; H, 5.99. ^{1}H NMR ($CDCl_3$), δ, *rac*-**7a**: 7.63—7.67 (m, 4 H, 2,2′,6,6′-H in C_6H_4); 7.39—7.46 (m, 4 H, 3,3′,5,5′-H in C_6H_4), 7.30—7.34 (m, 2 H, 4,4′-H in C_6H_4); 7.29 (d, 2 H, 5-H in cyclopenta[*b*]thienyl, J = 0.6); 6.80 (m, 2 H, 3,3′-H in cyclopenta[*b*]-thienyl); 3.94 (m, 2 H, 1,1′-H in cyclopenta[*b*]thienyl); 2.19 (d, 6 H, 2,2′-Me in cyclopenta[*b*]thienyl, J = 1.4 Hz); –0.23 (s, 6 H, $SiMe_2$); *meso*-**7a**: 7.62—7.66 (m, 4 H, 2,2′,6,6′-H in C_6H_4); 7.39—7.46 (m, 4 H, 3,3′,5,5′-H in C_6H_4); 7.30—7.34 (m, 2 H, 4,4′-H in C_6H_4); 7.26 (d, 2 H, 5-H in cyclopenta[*b*]thienyl, J = 0.6); 6.81 (m, 2 H, 3,3′-H in cyclopenta[*b*]thienyl); 3.83 (m, 2 H, 1,1′-H in cyclopenta[*b*]thienyl); 2.32 (d, 6 H, 2,2′-Me in cyclopenta[*b*]thienyl, J = 1.4 Hz); –0.20 (s, 3 H, SiMe), –0.21 (s, 3 H, SiMe′).

Bis[3-(4-*tert*-butylphenyl)-5-methyl-6*H*-cyclopenta[*b*]thien-6-yl](dimethyl)silane (7b). Compound **7b** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **4** and 4-*tert*-butylphenylmagnesium bromide. The white solid compound was obtained as a mixture of the *rac* and *meso* isomers in a ratio of ~1 : 3. in a yield of 5.52 g (93%). Calculated (%): C, 76.97; H, 7.48. $C_{38}H_{44}S_2Si$. Found (%): C, 77.21; H, 7.56. ^{1}H NMR ($CDCl_3$), δ, *rac*-**7b**: 7.57—7.61 (m, 4 H, 3,3′,5,5′-H in C_6H_4); 7.42—7.46 (m, 4 H, 2,2′,6,6′-H in C_6H_4); 7.26 (m, 2 H, 5-H in cyclopenta[*b*]thienyl); 6.81 (m, 2 H, 3,3′-H in cyclopenta[*b*]thienyl); 3.93 (m, 2 H, 1,1′-H in cyclopenta[*b*]thienyl); 2.19 (d, 6 H, 2,2′-Me in cyclopenta[*b*]-thienyl, J = 1.3 Hz); 1.367 (s, 18 H, Bu^t), –0.26 (s, 6 H, $SiMe_2$); *meso*-**7b**: 7.55—7.59 (m, 4 H, 3,3′,5,5′-H in C_6H_4); 7.43—7.47 (m, 4 H, 2,2′,6,6′-H in C_6H_4); 7.23 (m, 2 H, 5-H in cyclopenta[*b*]thienyl); 6.81 (m, 2 H, 3,3′-H in cyclopenta[*b*]thienyl); 3.82 (m, 2 H, 1,1′-H in cyclopenta[*b*]thienyl); 2.31 (d, 6 H, 2,2′-Me in cyclopenta[*b*]thienyl, J = 1.3 Hz); 1.363 (s, 18 H, Bu^t), –0.23 (s, 3 H, SiMe); –0.24 (s, 3 H, SiMe′).

Bis[5-methyl-3-(1-naphthyl)-6*H*-cyclopenta[*b*]thien-6-yl]-(dimethyl)silane (7c). Compound **7c** was synthesized according to the general procedure by the Negishi reaction starting from aryl bromide **4** and 1-naphthylmagnesium bromide. The white solid compound was obtained as a mixture of the *rac* and *meso* isomers in a ratio of ~1 : 2 in a yield of 5.12 g (88%). Calculated (%): C, 78.57; H, 5.55. $C_{38}H_{32}S_2Si$. Found (%): C, 78.79; H, 5.66. ^{1}H NMR ($CDCl_3$), δ, *rac*-**7c**: 7.25—7.96 (m, 14 H, naphthyl); 7.20 (s, 2 H, 5,5′-H in cyclopenta[*b*]thienyl); 6.26 (s, 2 H, 3,3′-H in cyclopenta[*b*]thienyl); 3.96 (s, 2 H, 1,1′-H in

cyclopenta[*b*]thienyl); 2.06 (s, 6 H, 2-Me in cyclopenta[*b*]-thienyl); –0.22 (s, 6 H, $SiMe_2$); *meso*-**7c**: 7.25—7.96 (m, 14 H, naphthyl); 7.17 (s, 2 H, 5,5′-H in cyclopenta[*b*]thienyl); 6.26 (s, 2 H, 3,3′-H in cyclopenta[*b*]thienyl); 3.84 (s, 2 H, 1,1′-H in cyclopenta[*b*]thienyl); 2.19 (s, 6 H, 2-Me in cyclopenta[*b*]-thienyl); –0.18 (s, 3 H, SiMe); –0.22 (s, 3 H, SiMe′).

Synthesis of *ansa*-zirconocenes (general procedure). A 2.5 *M* solution of *n*-BuLi (7.92 mL, 20.0 mmol) in hexane was added to a solution of the ligand (10.0 mmol) in diethyl ether (220 mL) at room temperature. The reaction mixture was stirred for 24 h and cooled to –78 °C. Then $ZrCl_4(THF)_2$ (10.0 mmol) was added. The reaction mixture was stirred at room temperature for 24 h, and the solvent was distilled off to dryness. Toluene (220 mL) was added to the residue, the reaction mixture was stirred at 90 °C for 8 h, and the hot solution was filtered through a G4 filter. The residue was additionally washed with hot toluene (3S100 mL). The combined extracts were dried to dryness. The product was isolated by crystallization of the residue from dichloromethane (for all zirconocenes, except for **10b**) or toluene (for **10b**).

***rac*-1,1′-Dimethylsilylenebis[η^5-2-methyl-4-(3-trifluoromethylphenyl)inden-1-ide]zirconium dichloride (8b).** Compound **8b** was synthesized according to the general procedure starting from ligand **5f**. The orange solid compound was obtained in 22% yield. Calculated (%): C, 56.53; H, 3.69. $C_{36}H_{28}Cl_2F_6SiZr$. Found (%): C, 56.70; H, 3.75. ^{1}H NMR (CD_2Cl_2), δ: 7.81—7.90 (m, 4 H, 2,2′,6,6′-H C_6H_4); 7.69—7.74 (m, 2 H, 7,7′-H of indenyl); 7.51—7.63 (m, 4 H, 5,5′,4,4′-H C_6H_4); 7.37 (dd, 2 H, 5,5′-H of indenyl, J = 7.0 Hz, J = 0.6 Hz); 7.12 (dd, 2 H, 6,6′-H of indenyl, J = 8.7 Hz, J = 7.0 Hz); 6.84 (s, 2 H, 3,3′-H of indenyl); 2.22 (s, 6 H, 2,2′-Me of indenyl); 1.33 (s, 6 H, $SiMe_2$).

***rac*-1,1′-Dimethylsilylenebis[η^5-2-methyl-4-(4-dimethylaminophenyl)inden-1-ide]zirconium dichloride (8a).** Compound **8a** was synthesized according to the general procedure starting from ligand **5e**. The orange solid compound was obtained in 23% yield. Calculated (%): C, 63.84; H, 5.64. $C_{38}H_{40}Cl_2N_2SiZr$. Found (%): C, 64.05; H, 5.77. ^{1}H NMR (CD_2Cl_2), δ: 7.54—7.70 (m, 6 H, 7,7′-H in indenyl and 2,2′,6,6′-H in C_6H_4); 7.27—7.40 (m, 6 H, 5,5′-H in indenyl and 3,3′,5,5′-H in C_6H_4); 7.09 (dd, 2 H, 6,6′-H in indenyl, J = 8.7 Hz, J = 7.2 Hz); 6.87 (s, 2 H, 3,3′-H in indenyl); 3.15 (s, 12 H, 4,4′-NMe_2 in C_6H_4); 2.20 (s, 6 H, 2,2′-Me in indenyl); 1.32 (s, 6 H, $SiMe_2$).

***rac*-1,1′-Dimethylsilylenebis[η^5-2,5-dimethyl-4-phenylinden-1-ide]zirconium dichloride (9).** Compound **9** was synthesized according to the general procedure starting from ligand **3a**. The orange solid compound was obtained in 29% yield. Calculated (%): C, 65.83; H, 5.22. $C_{36}H_{34}Cl_2SiZr$. Found (%): C, 65.95; H, 5.31. ^{1}H NMR (CD_2Cl_2), δ: 7.51 (d, 2 H, 7,7′-H in indenyl, J = 8.9 Hz); 7.40 (m, 4 H, 2,2′,6,6′-H in Ph); 7.35 (m, 4 H, 3,3′,5,5′-H in Ph); 7.20 (m, 2 H, 4,4′-H in Ph); 6.95 (d, 2 H, 6,6′-H in indenyl, J = 8.9 Hz); 6.35 (m, 2 H, 3,3′-H in indenyl); 2.23 (s, 6 H, 5,5′-Me); 2.14 (s, 6 H, 2,2′-Me); 1.26 (s, 6 H, $SiMe_2$).

***rac*-6,6′-Dimethylsilylenebis(η^5-5-methyl-3-phenylcyclopenta[*b*]thiophen-6-ide)zirconium dichloride (10a).** Compound **10a** was synthesized according to the general procedure starting from ligand **7a**. The orange solid compound was obtained in 25% yield. Calculated (%): C, 56.22; H, 4.09. $C_{30}H_{26}Cl_2C_2SiZr$. Found (%): C, 56.41; H, 4.15. ^{1}H NMR ($CDCl_3$), δ: 7.54—7.62 (m, 4 H, 2,2′,6,6′-H Ph); 7.49 (s, 2 H, 3,3′-H cyclopenta[*b*]-thienyl); 7.34—7.43 (m, 4 H, 3,3′,5,5′-H Ph); 7.25—7.34 (m, 2 H, 4,4′-H Ph); 6.86 (s, 2 H, 3,3′-H cyclopenta[*b*]thienyl); 2.32 (s, 6 H, 2,2′-Me cyclopenta[*b*]thienyl); 1.09 (s, 6 H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 144.7, 137.7, 136.2, 135.7, 130.8, 130.4, 129.4, 128.6, 121.4, 120.4, 72.5, 20.7, 0.7.

***rac*-6,6′-Dimethylsilylenebis[η^5-3-(1-naphthyl)-5-methylcyclopenta[*b*]thiophen-6-yl]zirconium dichloride (10b).** Compound **10b** was synthesized according to the general procedure starting from ligand **7c**. The red solid compound was obtained in 22% yield. Calculated (%): C, 61.59; H, 4.08. $C_{38}H_{30}Cl_2C_2SiZr$. Found (%): C, 61.68; H, 4.15. ^{1}H NMR (CD_2Cl_2), δ: 8.06 (d, 2 H, 4,4′-H in naphthyl, J = 8.4 Hz); 7.87 (m, 2 H, 8,8′-H in naphthyl); 7.83 (d, 2 H, 2,2′-H in naphthyl, J = 8.4 Hz); 7.72 (dd, 2 H, 5,5′-H in naphthyl, J = 7.2 Hz, J = 0.9 Hz); 7.53 (s, 2 H, 5,5′-H in cyclopenta[*b*]thienyl); 7.37—7.52 (m, 6 H, 3,3′,6,6′,7,7′-H in naphthyl); 6.58 (s, 2 H, 3,3′-H in cyclopenta[*b*]thienyl); 2.34 (s, 6 H, 2,2′-Me in cyclopenta[*b*]thienyl); 1.14 (s, 6 H, $SiMe_2$).

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