Articles

Zirconium Complexes with Cyclopentadienyl Ligands Involving Fused a Thiophene Fragment

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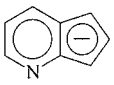
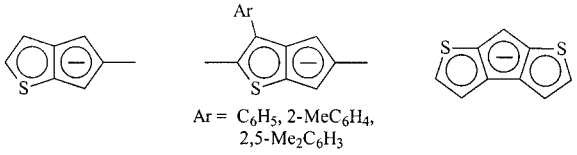
The following cyclopentadienes (Cp′H) with fused thiophene and benzothiophene fragments were synthesized: 4,5-dimethyl-6*H*-cyclopenta[*b*]thiophene (**2**), 5,6-dimethyl-4*H*-cyclopenta[*b*]thiophene (**4**), 1,3,5-trimethyl-4*H*-cyclopenta[*c*]thiophene (**6**), 2-methyl-1(and 3)*H*-cyclopenta[*b*][1]thiophenes (**9**), 2,3-dimethyl-1*H*-cyclopenta[*b*][1]benzothiophene (**11**), 1,2-dimethyl-3*H*-cyclopenta[*b*][1]benzothiophene (**14**). After a deprotonation of **2**, **4**, **11**, and **14** with n-BuLi, followed by treatment of the resulting lithium salts with (η^5-C_5Me_5)$ZrCl_3$, complexes (η^5-Cp′)(η^5-C_5Me_5)$ZrCl_2$ were obtained. The ligand **6** gave a mixture of undesirable products instead of the respective metallocene. Two of them were isolated and turned out to be the polynuclear hydride complex {(Cp*Zr)(μ-H)(μ-Cl)$_2$(Cp*ZrCl)}$_2$(μ-Cl)$_6$$Li_2$ and a binuclear complex containing an unusual bridged bis[1,5-dimethyl-3-methylene-1,3-dihydro-η^5-cyclopenta[*c*]thien-1-yl] ligand. Starting from the cyclopentadienes **2**, **4**, **11**, and **14**, several bis(cyclopentadienyl)dimethylsilanes were obtained and further used for the synthesis of the respective *ansa*-zirconocenes, which were isolated and unambiguously characterized either as pure diastereomeres or as *rac*/*meso* mixtures. Unbridged complex Cp′$_2$$ZrCl_2$ was prepared in a similar manner from the ligand **9**.

Introduction

The group 4 metallocenes including η^5-cyclopentadienyl ligands with fused heterocyclic fragments are regarded as new promising olefin polymerization catalysts.[1,2] Quite recently we described zirconium complexes including a η^5-cyclopenta[*b*]pyridinyl ligand with a cyclopentadienyl fused to the pyridine ring:[3]

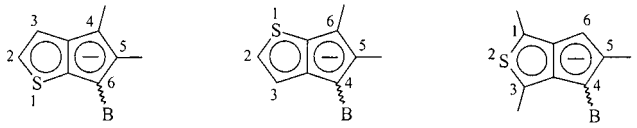


The other important metallocene family is based on Cp fused to a five-membered thiophene ring. Ewen et al.[1,2] described several zirconium complexes of this type involving the following ligands:

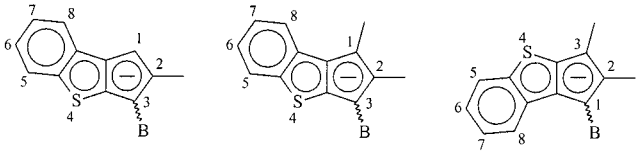


Some of these complexes have unprecedented catalytic activity in propene polymerization. For instance, *rac*-dimethylsilylbis(2,5-dimethyl-3-phenyl-6*H*-cyclopenta[*b*]thiophenyl)zirconium dichloride in the presence of MAO and H_2 produces 5004 kg isotactic PP/(mmol Zr h).

In the present paper we extended this thiophene-based ligand family to new zirconocenes. We have developed selective synthetic methods for *ansa*-metallocenes containing sulfur in different positions (with respect to bridge B) of the fused thiophene fragment, e.g., as in the following ligands:



The second problem under investigation is the synthesis of various zirconocenes with a fused benzo[*b*]-thiophene fragment, such as



(1) Ewen, J. A.; Jones, R. L.; Elder, M. J.; Rheingold, A. L.; Liable-Sands, L. M. *J. Am. Chem. Soc.* **1998**, *120*, 10786.

(2) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Rheingold, A. L.; Liable-Sands, L. M.; Sommer, R. D. *J. Am. Chem. Soc.* **2001**, *123*, 4763.

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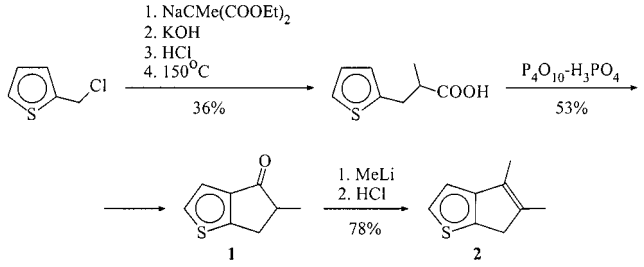
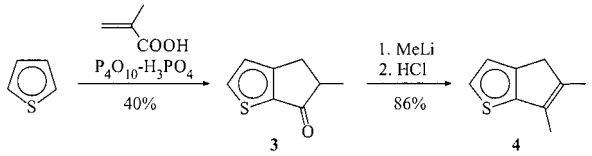
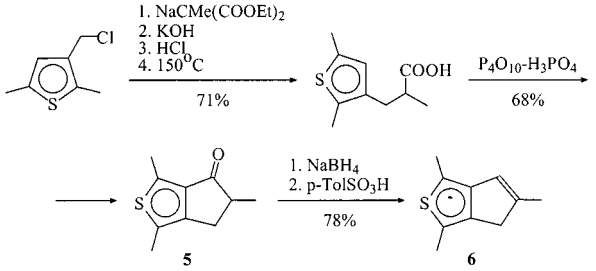
Scheme 1



Scheme 2



Scheme 3



The knowledge of accurate structure is an important key to the understanding of catalytic properties.[4] We have therefore performed a detailed crystallographic study for several zirconocenes synthesized.

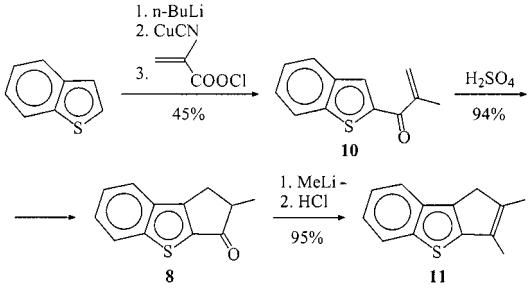
Results and Discussion

Synthesis of Cyclopentadienes with Fused Thiophene and Benzo[*b*]thiophene Fragments. 5-Methyl-5,6-dihydro-4*H*-cyclopenta[*b*]thiophen-1-one (**1**) was prepared as shown in Scheme 1, with 2-(chloromethyl)-thiophene as starting material, by a procedure described by Sam and Thompson.[5] Under treatment of this ketone with MeLi, followed by HCl, 4,5-dimethyl-6*H*-cyclopenta-[*b*]thiophene (**2**) was obtained.

The isomeric ketone 5-methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one (**3**) was prepared using the one-pot reaction (Scheme 2) developed by Gronowitz and Meth-Cohn.[6] Then, 5,6-dimethyl-4*H*-cyclopenta[*b*]thiophene (**4**) was isolated using the above-mentioned approach for the synthesis of **2**.

1,3,5-Trimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophen-4-one (**5**) was prepared as shown in Scheme 3, with 3-(chloromethyl)-2,5-dimethylthiophene as starting material, by a procedure described by Merle and coworkers[7] and involving intermolecular acylation of the respective 3-(thienyl)propionic acid. Reduction of **5** with sodium borohydride and successive H_2O elimination gave 1,3,5-trimethyl-4*H*-cyclopenta[*c*]thiophene (**6**).

Scheme 5



Whereas the one-pot acylation−Nazarov-like cyclization reaction for thiophene (Scheme 2) is selective, an analogous reaction between benzo[*b*]thiophene and methacrylic acid was found to give a ca. 5:1 mixture of 2-methyl-2,3-dihydro-1*H*-cyclopenta[*b*][1]benzothiophen-1-one (**7**) and 2-methyl-1,2-dihydro-3*H*-cyclopenta[*b*][1]-benzothiophen-3-one (**8**) (Scheme 4), which is due to a different regioselectivity of acylation of thiophene[8] and benzo[*b*]thiophene.[9] Then, a mixture of 2-methyl-1*H*- and 2-methyl-3*H*-cyclopenta[*b*][1]thiophenes (**9**) was prepared as shown in Scheme 4.

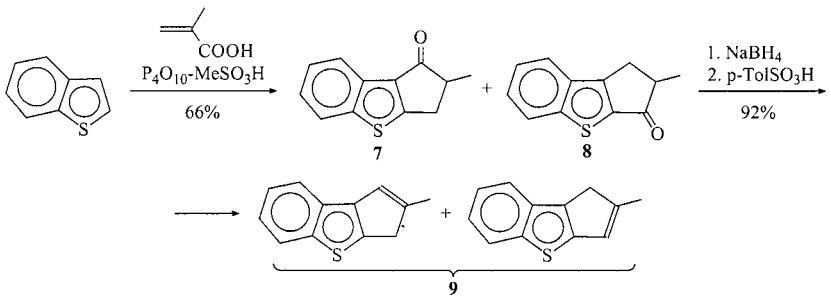
Pure cyclic ketone **8** was synthesized in a different manner (Scheme 5). Cuprate derived from benzo[*b*]-thiophene[10] reacts with methacryloyl chloride to give vinyl ketone **10**. The desired cyclic ketone was obtained in almost quantitative yield via the Nazarov-like cyclization.[11−13] This ketone was used for the synthesis of 2,3-dimethyl-1*H*-cyclopenta[*b*][1]benzothiophene (**11**), as shown in Scheme 5.

Analogously, vinyl ketone **12** and cyclic ketone **13**, as well as a mixture of 1,2-dimethyl-1*H*- and 1,2-dimethyl-3*H*-cyclopenta[*b*][1]benzothiophenes (**14**), were prepared as outlined in Scheme 6.

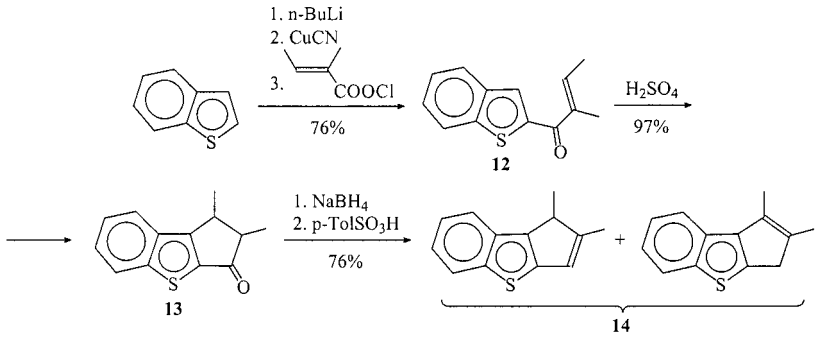
Synthesis and Molecular Structures of Unbridged Zirconocenes. Ligand **9** was deprotonated with 1 equiv of n-BuLi, then treated with 0.5 equiv of $ZrCl_4$ in toluene, to give the respective metallocene **15** as a mixture of *rac* and *meso* versions (Scheme 7).

Starting from Cp*$ZrCl_3$ and the ligands (Cp′) **2**, **4**, **11**, and **14**, several unsymmetrical unbridged metallocenes Cp′Cp*$ZrCl_2$ were prepared in moderate yield as outlined in Scheme 8. These complexes were unambiguously characterized by NMR spectroscopy (see Experimental Section).

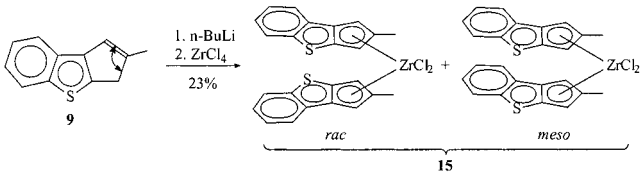
Scheme 4



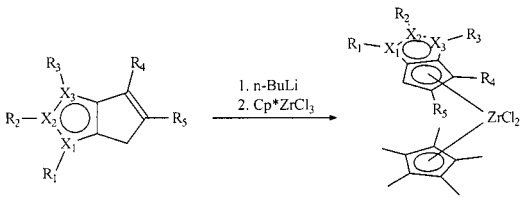
Scheme 6



Scheme 7



Scheme 8



2	**16**: $R_1X_1 = S, R_2X_2 = R_3X_3 = HC, R_4 = R_5 = Me$	45%
4	**17**: $R_3X_3 = S, R_1X_1 = R_2X_2 = HC, R_4 = R_5 = Me$	54%
11	**18**: $R_3X_3 = S, R_1X_1, R_2X_2 = C_4H_4, R_4 = R_5 = Me$	35%
14	**19**: $R_1X_1 = S, R_2X_2, R_3X_3 = C_4H_4, R_4 = R_5 = Me$	36%

Molecular structures of **16** and **17** determined by X-ray crystal structure analysis are shown in Figures 1 and 2, respectively.

Both compounds crystallize with two molecules in the asymmetric unit. Whereas the unit cell of **16** contains two molecules of the same enantiomers, the unit cell of **17** contains both enantiomers. Each isomeric molecule has the same bent sandwich geometry, with two Cl ligands in the bisecting plane. The angle between the σ-bonds is equal to 97°; the angle centroid-Cp′−Zr−centroid-Cp* is equal to 132°. The dihedral angle between the planar η^5-Cp fragments is equal to 53.5°. The Zr−Cp_{cent}(1) distances are the following: 2.240 and 2.247 Å in **16** and 2.238 and 2.241 Å in **17** (average 2.242 Å), whereas for the second molecule in the unit the Zr−Cp_{cent}(2) distances are equal to 2.219 and 2.210 Å in **16** and 2.227 and 2.225 Å in **17** (average 2.220 Å). The distance Cl···S is in **17** rather short (3.314 and 3.323 Å). In both molecules of the unit cell of **17** one Cl atom is located in the space between two Me groups of the Cp′ ligand, whereas the position of the second Cl atom is constrained by the Cl1−Zr−Cl2 angle (95.6−97.1°). Thus, in **17** this chlorine atom is located near the S atom to give the close Cl···S contact observed.

An attempt to obtain Cp′Cp*$ZrCl_2$ starting from 1,3,5-trimethyl-4*H*-cyclopenta[*c*]thiophene (**6**) failed. The reaction mixture (Scheme 9) turned dark brown, and a specific mercaptane-like smell appeared.

On the evidence of NMR spectroscopy, the resulting mixture included several new zirconium compounds. One of them, complex **20**, is crystallized slowly from toluene solution to give yellowish blocks. The molecular structure of this unusual compound was established by X-ray crystal structure analysis shown in Figure 3.

The centrosymmetric complex consists of two binuclear zirconium units $(Cp^*Zr)_2(\mu\text{-H})(\mu\text{-Cl})_2Cl_4$ bridged by two lithium atoms. To the best of our knowledge, this

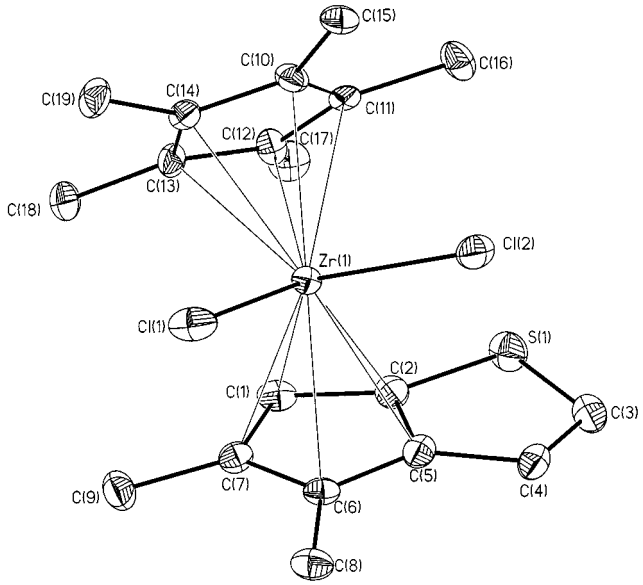


Figure 1. Structure of **16**, showing the 50% thermal ellipsoids and atom-labeling scheme for one of the independent molecules. Selected bond lengths (Å): Zr(1)−Cl(1) 2.4391(13), Zr(1)−Cl(2) 2.4467(12), Zr(1)−C(1) 2.457(4), Zr(1)−C(2) 2.509(4), Zr(1)−C(5) 2.617(4), Zr(1)−C(6) 2.620(4), Zr(1)−C(7) 2.524(4), S(1)−C(2) 1.738(5), S(1)−C(3) 1.746(5), C(1)−C(7) 1.415(6), C(1)−C(2) 1.428(6), C(2)−C(5) 1.420(6), C(3)−C(4) 1.340(7), C(4)−C(5) 1.424(6), C(5)−C(6) 1.429(6), C(6)−C(7) 1.418(6).

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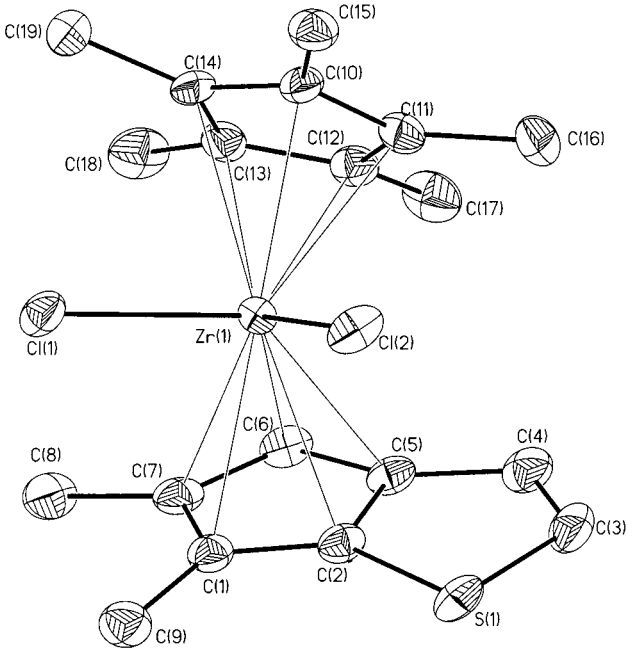
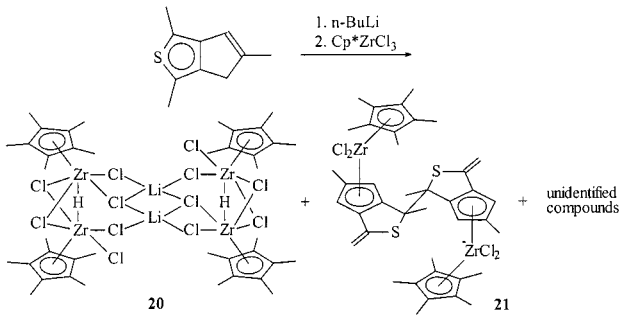


Figure 2. Structure of **17**, showing the 50% thermal ellipsoids and atom-labeling scheme for one of the independent molecules. Selected bond lengths (Å): Zr(1)−Cl(1) 2.4442(16), Zr(1)−Cl(2) 2.4359(15), Zr(1)−C(1) 2.604(6), Zr(1)−C(2) 2.610(6), Zr(1)−C(5) 2.513(6), Zr(1)−C(6) 2.455(6), Zr(1)−C(7) 2.528(6), S(1)−C(2) 1.727(6), S(1)−C(3) 1.750(7), C(1)−C(2) 1.419(9), C(1)−C(7) 1.406(9), C(2)−C(5) 1.425(9), C(3)−C(4) 1.330(10), C(4)−C(5) 1.449(9), C(5)−C(6) 1.439(9), C(6)−C(7) 1.411(9).

Scheme 9



structure is the first example of two monocyclopentadienyl zirconium centers linked by two chlorine and one hydrogen atom. However, the systems $(CpZr^{IV})_2(\mu\text{-}X)_3$ (where X = Cl,[14−16] H[17]) were previously reported. Both independent Zr(1) and Zr(2) atoms possess a distorted octahedral coordination assuming that the Cp* ligands occupy one site. The pentahapto cyclopentadienyl rings and bridging hydrogen atoms lie in apical positions, while the Cl atoms occupy equatorial ones. The deviations of both Zr atoms from the equatorial planes toward the Cp* ligands are 0.70 Å. In the structure of **20** the $Zr-Cp_{cent}$ distances (2.20 and 2.22 Å) are somewhat longer than the respective distances in the parent double-bridged structure $(Cp^*ZrCl_2)_2(\mu\text{-}Cl)_2$, 2.18 Å.[18] Zr(1) and Zr(2) centers are not structurally similar. Zr(1) bears four bridging chlorine ligands, while Zr(2) is linked to one terminal Cl(5) and three bridging Cl atoms. Four structurally different chlorine atoms were found in the structure of **20**: (a) Cl(1) and Cl(2) represent Zr−Cl−Zr bridges; (b) Cl(3) and Cl(6) represent Zr−Cl−Li bridges; (c) Cl(4) coordinates Zr(1) and two lithium atoms; (d) Cl(5) is terminally connected to Zr(2). The $Zr-Cl_a$ bond lengths show noticeable asymmetry. Thus, the Zr(1)−Cl(1) and Zr(1)−Cl(2) distances (2.5651(7) and 2.5696(6) Å) are shorter than the Zr(2)−Cl(1) and Zr(2)−Cl(2) distances (2.6124(6) and 2.6249(6) Å, respectively). It should be noticed that the Zr(2)−H(1M) distance is also slightly longer than Zr(1)−H(1M) (2.01(2) and 1.92(2) Å, respectively). The $Zr-Cl_b$ distances (Zr(1)−Cl(3), 2.4804(6), Zr(2)−Cl(6), 2.5082(7) Å) are comparable with the values for Zr−Cl(−Li) found in the related structure of $Zr_2(Cp^{=})_2Cl_4(\mu\text{-}Cl_3)Li(dme)$, 2.474(6) and 2.478(6) Å.[14] However, the Cl_b-Li bond lengths in **20** (2.304(4) and 2.432(5) Å) are significantly shorter than in $Zr_2(Cp^{=})_2Cl_4(\mu\text{-}Cl_3)Li(dme)$ (2.74(8) and 2.79(8) Å) due to a different type of coordination environment of the Li atoms. The hydride−zirconium bond lengths (2.01(2) and 1.92(2) Å) are comparable with the values observed for $Zr-H_{ap}$ in $Zr_2(Cp^*)_2(\mu\text{-}H_3)Cl_3(PMe_3)$ (2.00(3) and 2.04(4) Å).[17] In the structure of complex **20** the Zr(1)−Zr(2) distance is 3.4148(5) Å. This value is regularly shorter than in $Zr_2(Cp^{=})_2Cl_4(\mu\text{-}Cl_3)Li(dme)$ (3.880(1) Å) due to the shorter Zr−H−Zr bridge.[14] In the structure of **20** the coordination polyhedron of the Li atom represents a highly distorted tetrahedron with Cl−Li−Cl angles ranging from 90.21(14)° to 127.02(19)°. The Li(1)−Li(1A) distance is 3.101(9) Å. To the best of our knowledge, compound **20** is the first example of a structure containing two transition metal centers bridged by a tetrahedral $LiCl_4$ moiety. On the other hand, octahedral $LiCl_4(OR)_2$ bridges are well known.[14,19] In addition, the asymmetric unit in the structure of **20** contains two solvent toluene molecules.

In the $^1H\{^{13}C\}$ NMR spectrum of compound **20** in C_6D_6 appears two resonances at 2.16 and 0.76 ppm (in a ratio of integral intensivities equal to 30:1) attributed to Cp* and a bridging hydride ligand,[20] respectively. Additionally, in the IR spectrum of **20** (in Nujol emulsion) a broad absorption band appears at 1390 cm^{-1}, which is characteristic for many zirconium complexes involving bridging hydrides.[20,21] Additional evidence for this hydride was obtained from a protonolysis experiment. A sample of **20** in argon was decomposed by *i*-PrOH, and GC analysis of the resulting gas phase was performed. This analysis gave 0.10(2) wt % of hydride hydrogen in **20** (calculated for $\mathbf{20}\cdot(C_7H_8)_4$: 0.117%).[22]

While complex **20** was isolated in an analytically pure form, only several colorless crystals of the other product, complex **21**, were obtained (Scheme 9). This compound turned out to be binuclear complex **21** involving bridged

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(22) Anal. Calcd for $\mathbf{20}\cdot(C_7H_8)_4$, $C_{68}H_{94}Cl_2Li_2Zr_4$: C, 47.60; H, 5.52; Cl, 24.80; Li, 0.81. Found: C, 47.35; H, 5.40; Cl, 24.93; Li, 0.84.

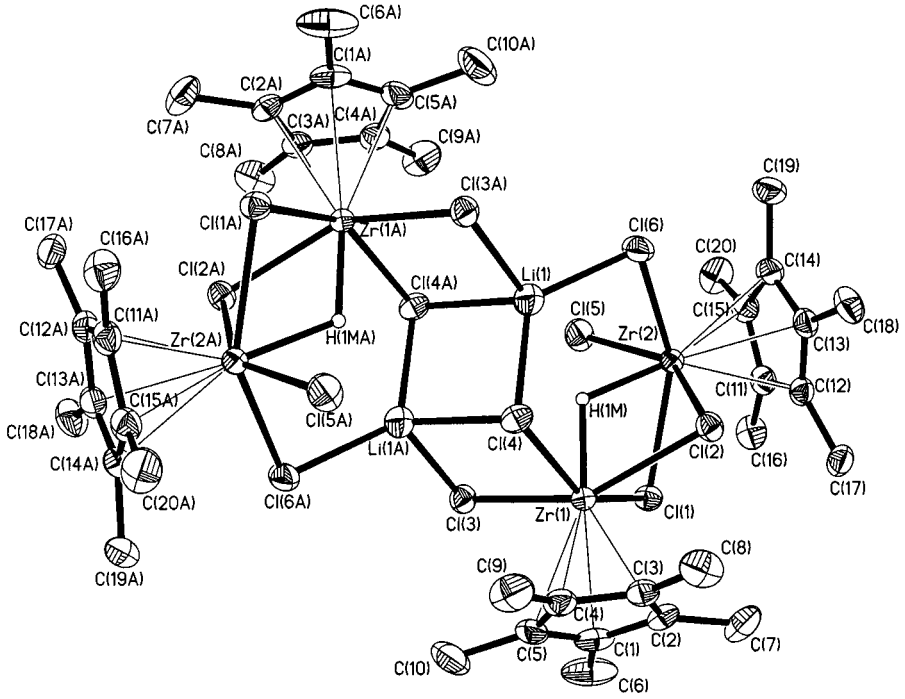


Figure 3. Structure of **20**, showing the 50% thermal ellipsoids and atom-labeling scheme. Selected bond lengths (Å): Zr(1)−C(1) 2.495(2), Zr(1)−C(2) 2.490(2), Zr(1)−C(3) 2.506(2), Zr(1)−C(4) 2.546(2), Zr(1)−C(5) 2.538(2), Zr(2)−C(11) 2.504(2), Zr(2)−C(12) 2.504(2), Zr(2)−C(13) 2.511(2), Zr(2)−C(14) 2.546(2), Zr(2)−C(15) 2.551(2), Zr(1)−H(1M) 1.92(2), Zr(2)−H(1M) 2.01(2), Zr(1)−Cl(1) 2.5651(7), Zr(1)−Cl(2) 2.5696(6), Zr(1)−Cl(3) 2.4804(6), Zr(1)−Cl(4) 2.5145(6), Zr(2)−Cl(1) 2.6124(6), Zr(2)−Cl(2) 2.6249(6), Zr(2)−Cl(5) 2.4208(7), Zr(2)−Cl(6) 2.5082(7).

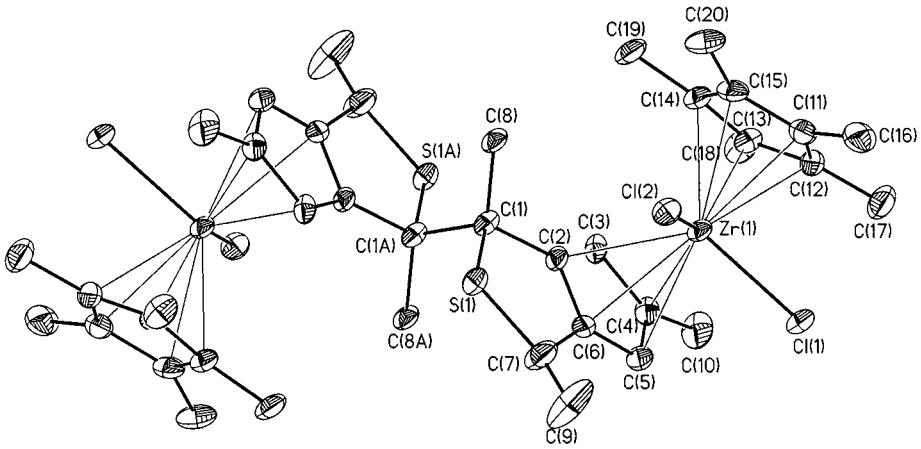
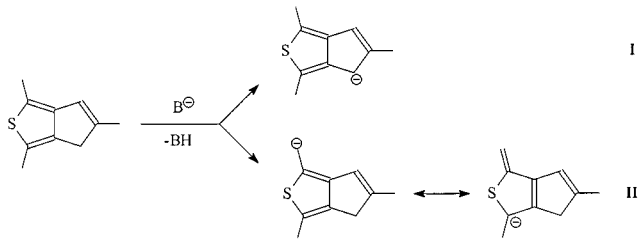


Figure 4. Structure of **21**, showing the 50% thermal ellipsoids and atom-labeling scheme. Selected bond lengths (Å): Zr(1)−Cl(2) 2.416(3), Zr(1)−Cl(1) 2.427(2), Zr(1)−C(3) 2.498(4), Zr(1)−C(4) 2.507(4), Zr(1)−C(5) 2.562(4), Zr(1)−C(2) 2.563(4), Zr(1)−C(6) 2.611(4), S(1)−C(7) 1.783(5), S(1)−C(1) 1.859(5), C(1)−C(2) 1.509(5), C(1)−C(8) 1.521(5), C(1)−C(1)#1 1.576(8), C(2)−C(6) 1.402(6), C(2)−C(3) 1.419(6), C(3)−C(4) 1.415(6), C(4)−C(5) 1.412(7), C(5)−C(6) 1.386(6), C(6)−C(7) 1.464(6), C(7)−C(9) 1.341(8).

a bis[1,5-dimethyl-3-methylene-1,3-dihydro-η^5-cyclopenta[*c*]thien-1-yl] ligand. The molecular structure of this compound (Figure 4) was determined by X-ray crystal structure analysis.

The symmetrical dimer **21** consists of two equivalent Cp*−Zr(Cl_2)−Cp′ fragments bonded via a C−C′ bridge (1.575 Å). The dihedral angle between the planar η^5-Cp fragments is equal to 50.4°; the angle centroid-Cp′−Zr−centroid-Cp*, 132°. The 1,5-dimethyl-3-methylene-1,3-dihydro-η^5-cyclopenta[*c*]thien-1-yl fragment includes a nonplanar C_4S cycle. The displacements of sulfur and C(9) are 0.282 and 0.413 Å, respectively. The dihedral angle between C1−C2−C6−C7 and Cp′ planes is equal to 10.9°. This geometry corresponds to a loss of aromacity of the thiophene system in **21**.

Scheme 10



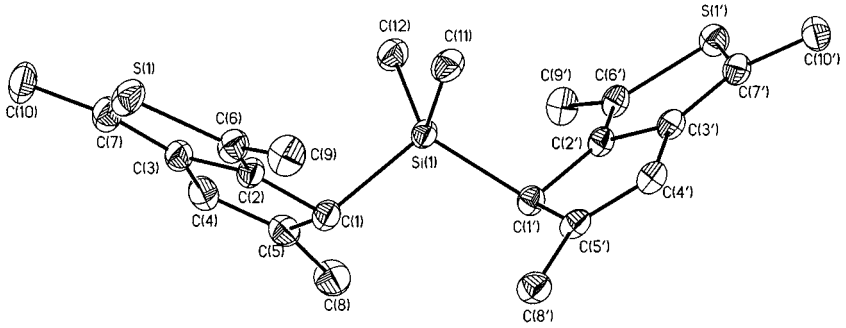
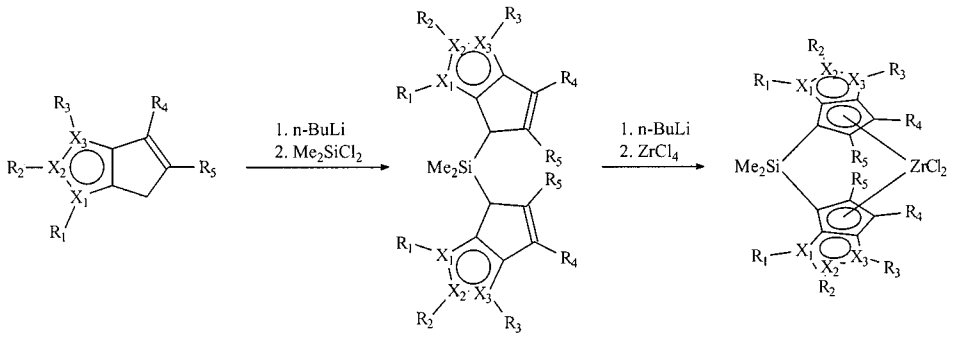


Figure 5. Structure of **24**, showing the 50% thermal ellipsoids and atom-labeling scheme. Selected bond lengths (Å): Si(1)−C(1) 1.9241(15), S(1)−C(7) 1.7356(18), S(1)−C(6) 1.7418(16), C(1)−C(2) 1.506(2), C(1)−C(5) 1.530(2), C(2)−C(6) 1.365(2), C(2)−C(3) 1.432(2), C(3)−C(7) 1.363(2), C(3)−C(4) 1.463(2), C(4)−C(5) 1.340(2).

Scheme 11



2	**22**: R_1X_1 = S, R_2X_2 = R_3X_3 = HC, R_4 = R_5 = Me	18%	**28**: 16% *rac*
4	**23**: R_3X_3 = S, R_1X_1 = R_2X_2 = HC, R_4 = R_5 = Me	71%	**29**: 10% *rac*
6	**24**: R_2X_2 = S, R_1X_1 = R_3X_3 = MeC, R_4 = H, R_5 = Me	56%	
9	**25**: R_1X_1 = S, R_2X_2,R_3X_3 = C_4H_4, R_4 = H, R_5 = Me	15%	**30**: 29% *meso*
11	**26**: R_3X_3 = S, R_1X_1,R_2X_2 = C_4H_4, R_4 = R_5 = Me	83%	**31**: 33% *rac*/*meso* 1:1
14	**27**: R_1X_1 = S, R_2X_2,R_3X_3 = C_4H_4, R_4 = R_5 = Me	23%	**32**: 36% *rac*/*meso* 1:1

To understand the mechanism of formation of **20** and **21**, the deprotonation of **6** can be supposed to proceed by two different pathways. Pathway I (Scheme 10) gives the traditional cyclopentadienyl-like anion. Pathway II should include deprotonation of the Me substituent in the thiophene ring to form the CH_2= fragment. The formation of the symmetrical dimer of **6** can result from the dimerization of the respective radicals rather than from any heterolytic transformations. These radicals can be formed by homolytic cleavage of an alkyl zirconium complex involving sulfur in the α-position to the zirconium atom. On the other hand, the only pathway for hydride−zirconium bond formation (in **20**) seems to be *β*-H elimination in this alkyl zirconium complex formed.

Synthesis of Me_2Si-Bridged Ligands. To synthesize the respective bis(cyclopentadienyl)dimethylsilanes, the above-mentioned cyclopentadienes with fused heterocyclic fragments were deprotonated with n-BuLi and, then, treated with 0.5 equiv of Me_2SiCl_2 as shown in Scheme 11.

Ligands **22**−**25** and **27** were isolated as 1:1 mixtures of *rac* and *meso* diastereomers; ligand **26** was obtained as a 1:4 *rac*/*meso* mixture. The low yield of **22** was due to problems in chromatographic separation, rather than low chemical yield. Pure ligand **27** was obtained by a low-temperature crystallization, which explains its low isolated yield. The low yield of *rac*-/*meso*-dimethyl[bis(2-methyl-3*H*-cyclopenta[*b*][1]benzothien-3-yl)]silanes (**25**) is likely to result from a possible formation of (2-methyl-1*H*-cyclopenta[*b*][1]benzothien-1-yl)silanes.

Side reactions involving a loss of aromacity of the thiophene ring were observed during the synthesis of **24** (see above). Evidence for this is a specific strong mercaptane-like smell of the reaction mixture. The molecular structure of *rac*-dimethyl[bis(1,3,5-trimethyl-4*H*-cyclopenta[*c*]thien-4-yl)]silane (*rac*-**24**) as determined by X-ray crystal structure analysis is shown in Figure 5.

Synthesis and Molecular Structures of *ansa*-Zirconocenes. The bridged ligands listed above, **22**, **23**, **25**−**27**, were deprotonated with 2 equiv of n-BuLi, and the resulting dilithium bis(cyclopentadienyl)s were treated with $ZrCl_4$ in toluene to give the respective zirconium dichlorides **28**, **29**, and **30**−**32** (Scheme 11). Complexes **28** and **29** were isolated from toluene solution as pure racemates, but compound **30** was obtained as a pure *meso* isomer. Complexes **31** and **32** were prepared and isolated as mixtures of *rac* and *meso* diastereoisomers. We were not able to separate the diastereoisomers of **31** and **32** because of the very low solubility of these compounds in all common solvents. An attempt to prepare the *ansa*-zirconium complex starting from **24** failed. This can be a result of metalation of Me groups of **24** by n-BuLi (see above).

We obtained single crystals of *rac*-**28**, *rac*-**29**, *meso*-**31**, and *meso*-**32** and carried out their X-ray crystal-

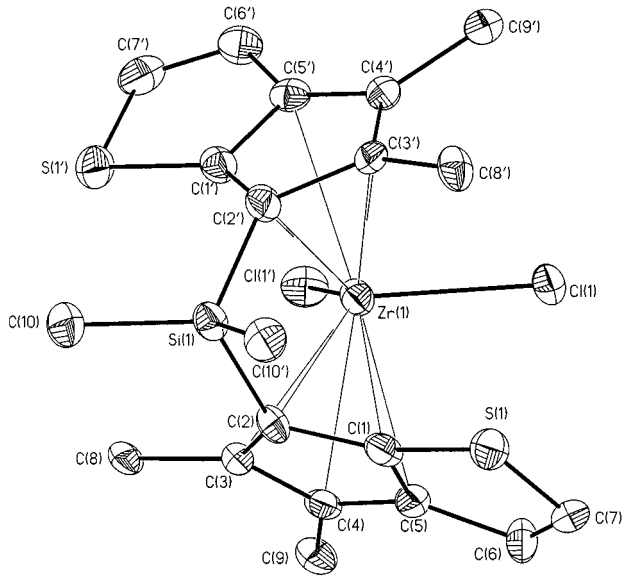


Figure 6. Structure of *rac*-**28**, showing the 50% thermal ellipsoids and atom-labeling scheme. Selected bond lengths (Å): Zr(1)−Cl(1) 2.414(7), Zr(1)−Cl(1′) 2.422(6), Zr(1)−C(1) 2.483(10), Zr(1)−C(2) 2.455(10), Zr(1)−C(3) 2.521(10), Zr(1)−C(4) 2.652(9), Zr(1)−C(5) 2.655(9), Si(1)−C(2) 1.900(10), S(1)−C(7) 1.736(10), S(1)−C(1) 1.752(8), C(1)−C(5) 1.377(13), C(1)−C(2) 1.419(13), C(2)−C(3) 1.416(12), C(3)−C(4) 1.432(14), C(4)−C(5) 1.424(11), C(5)−C(6) 1.440(12), C(6)−C(7) 1.347(13).

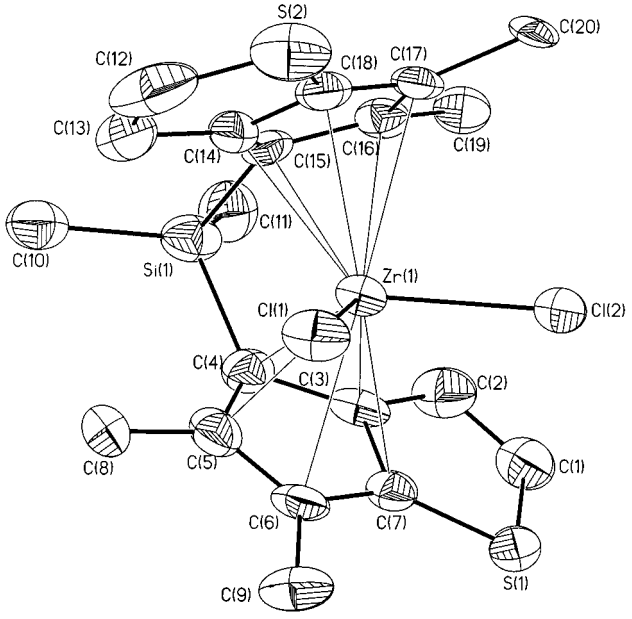


Figure 7. Structure of *rac*-**29**, showing the 50% thermal ellipsoids and atom-labeling scheme. The unit includes both *rac* and *meso* isomeric molecules in a ratio of ca. 4:1. Selected bond lengths (Å): Zr(1)−Cl(1) 2.419(2), Zr(1)−Cl(2) 2.412(2), Zr(1)−C(3) 2.500(5), Zr(1)−C(4) 2.446(5), Zr(1)−C(5) 2.492(5), Zr(1)−C(6) 2.609(5), Zr(1)−C(7) 2.639(5), S(1)−C(7) 1.681(6), S(1)−C(1) 1.758(8), Si(1)−C(4) 1.867(6), C(1)−C(2) 1.312(10), C(2)−C(3) 1.449(8), C(3)−C(7) 1.443(8), C(3)−C(4) 1.443(8), C(4)−C(5) 1.425(8), C(5)−C(6) 1.392(8), C(6)−C(7) 1.425(8).

lographic study. Molecular structures of these complexes are shown in Figures 6−9, respectively.

All molecules display a normal coordination environment for Me_2Si-bridged *ansa*-metallocenes with two chlorine atoms in the bisecting plane. All structures are centrosymmetric. Structure **28** includes the respective *racemate*, whereas structures **31** and **32** contain *meso* isomers only. Alternatively, structure **29** consists of both isomeric molecules in *rac* to *meso* ratio equal to 4:1. Similar cocrystallization of *rac*/*meso* isomers was observed recently for a Me_2Si-bridged *ansa*-zirconocene including methylcyclopentadienyl fused to a thiophene fragment.[1] Although, in the latter case, a ca. 3:1 *rac*/*meso* ratio was found, actually, the detailed analysis of the crystallographic data show that this crystal includes isomeric 5-methyl-6*H*-cyclopenta[*b*]thien-6-yl and 5-methyl-4*H*-cyclopenta[*b*]thien-4-yl fragments; that is, the Me_2Si substituent cannot be localized during the synthesis of the respective bridging ligand. So, the only reason we used double methylated Cp′ ligands is to localize the position of the Me_2Si bridge in the metallocenes synthesized.

The angles centroid-Cp′1−Zr−centroid-Cp′2 in complexes **28**, **29**, **31**, and **32** are equal to 128.8°, 120.2°, 130.1°, and 128.8°, respectively. The corresponding dihedral angles between the planar η^5-Cp fragments are 67.1°, 65.5°, 61.6°, and 61.1°. The Zr−Cp_{cent} distances are equal to 2.254 and 2.242 Å for **28**, 2.219 and 2.232 Å for **29**, 2.247 and 2.258 Å for **31**, and 2.234 and 2.236 Å for **32**. Close contacts S···Cl were found in the case of **29** (3.379−3.390 Å) and **31** (3.378−3.436 Å). These two molecules have similar structures with sulfur and silicon atoms in *trans* positions with respect to the C−C bond connecting cyclopentadienyl and thiophene rings.

In conclusion we elaborated selective synthetic procedures for zirconocenes involving cyclopentadienyl ligands with fused thiophene and benzo[*b*]thiophene fragments. Several complexes were characterized by X-ray crystal structure analysis. These metallocenes should be promising catalyst precursors for Ziegler−Natta olefin polymerization. Variable structure of the complexes obtained is expected to allow for the elucidation of trends in the structure−catalytic efficiency relationship in olefin polymerization. In the near future, we plan to study olefin polymerization catalyzed by the zirconium complexes synthesized.

Experimental Section

General Procedure. All manipulations with compounds, which are sensitive to both moisture and air, were performed either on a high-vacuum line in all-glass apparata equipped with PTFE stopcocks or in an atmosphere of thoroughly purified argon using a standard Schlenk technique. Tetrahydrofuran was purified by distillation over $LiAlH_4$ and kept over sodium benzophenone ketyl. Hydrocarbon solvents were distilled and stored over CaH_2 or Na/K alloy. Methylene chloride (and CD_2Cl_2) was distilled and stored over CaH_2. Chloroform-*d* was distilled over P_4O_{10} and stored over molecular sieves (3 Å). Thiophene (Aldrich), 2,5-dimethylthiophene (Aldrich), 1-benzothiophene (Aldrich), diethylmethylmalonate (Acros), and methacrylic acid were distilled before use. Anhydrous $ZrCl_4$ (Aldrich), CuCN (Merck), $NaBH_4$ (Aldrich), methanesulfonic acid (Aldrich), n-BuLi in hexanes (Chemetall), and MeLi in ether (Merck) were used as obtained. 2-Chloromethylthiophene,[23] methacryloyl chloride (analogously, (2*E*)-2-methyl-2-butenoyl chloride from tiglic acid),[24] and $ZrCl_4$-

(23) Wiberg, K. B.; McShane, H. F. *Org. Synth.* **1955**, *3*, 197.
(24) Stempel, G. H.; Cross, R. P.; Mariella, R. P. *J. Am. Chem. Soc.* **1950**, *72*, 2299.

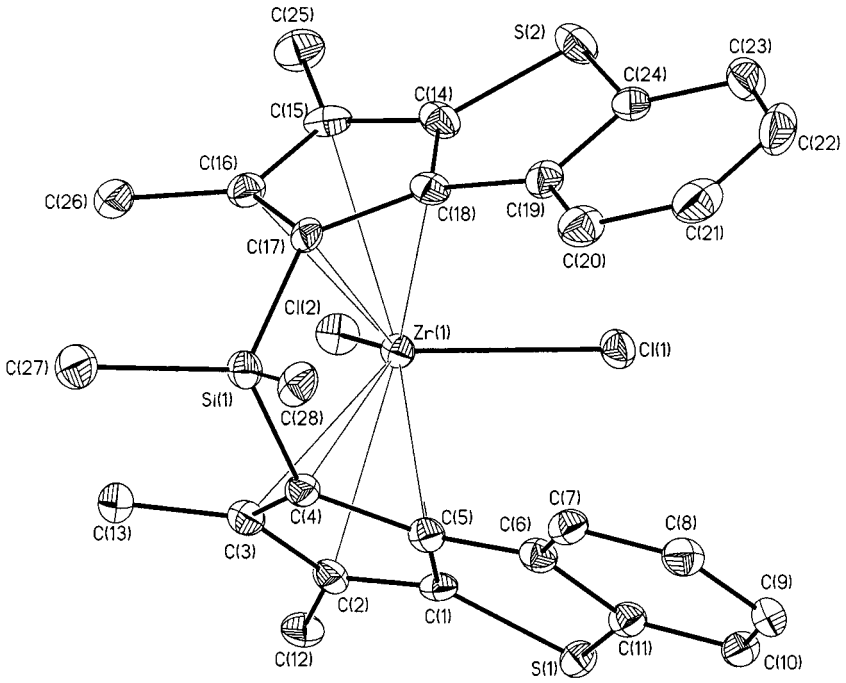


Figure 8. Structure of *meso*-**31**, showing the 50% thermal ellipsoids and atom-labeling scheme for one of the independent molecules. Selected bond lengths (Å): Zr(1)−Cl(1) 2.4131(10), Zr(1)−Cl(2) 2.4334(10), Zr(1)−C(4) 2.467(3), Zr(1)−C(3) 2.498(4), Zr(1)−C(5) 2.534(3), Zr(1)−C(2) 2.632(4), Zr(1)−C(1) 2.634(3), Zr(2)−Cl(3) 2.3991(10), Zr(2)−Cl(4) 2.4404(10), S(1)−C(1) 1.743(4), S(1)−C(11) 1.758(4), Si(1)−C(4) 1.888(4), C(1)−C(2) 1.392(5), C(1)−C(5) 1.420(5), C(2)−C(3) 1.427(5), C(3)−C(4) 1.451(5), C(5)−C(6) 1.469(5), C(6)−C(7) 1.397(5), C(6)−C(11) 1.423(5), C(7)−C(8) 1.393(5), C(8)−C(9) 1.394(5), C(9)−C(10) 1.386(5), C(10)−C(11) 1.377(5),

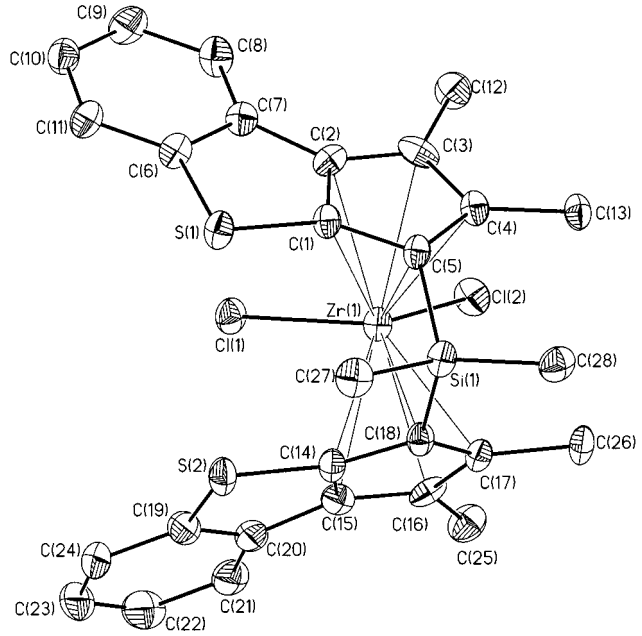


Figure 9. Structure of *meso*-**32**, showing the 50% thermal ellipsoids and atom-labeling scheme. Selected bond lengths (Å): Zr(1)−Cl(1) 2.4159(13), Zr(1)−Cl(2) 2.4216(12), Zr(1)−C(1) 2.511(4), Zr(1)−C(2) 2.625(4), Zr(1)−C(3) 2.622(4), Zr(1)−C(4) 2.506(4), Zr(1)−C(5) 2.475(4), S(1)−C(1) 1.743(4), S(1)−C(6) 1.767(4), Si(1)−C(5) 1.875(4), C(1)−C(2) 1.416(5), C(1)−C(5) 1.429(5), C(2)−C(3) 1.382(5), C(2)−C(7) 1.454(5), C(3)−C(4) 1.431(5), C(4)−C(5) 1.454(5), C(6)−C(11) 1.383(5), C(6)−C(7) 1.413(5), C(7)−C(8) 1.382(6), C(8)−C(9) 1.378(6), C(9)−C(10) 1.388(6), C(10)−C(11) 1.373(6).

$(THF)_2$[25] were prepared according to the published methods. Silica gel 60 (230−400 mesh, Fluka) was used for flash chromatographic separation. Analytical and semipreparative liquid chromatography was performed using a Waters Delta 600 HPLC system including a 996 photodiode array detector and Nova-Pack C18 or HR silica columns (60 Å, 6 μm, 3.9 and 19 × 300 mm). IR spectra were recorded using an UR-20 instrument. The content of H_2 in argon was measured using GLC analysis on a Tsvet 101 (Russia) chromatograph (3 m × 3 mm column packed with charcoal). ^{1}H and ^{13}C spectra were recorded with Brucker AM 360 and Varian VXR 400 instruments for 1−10% solutions in deuterated solvents. Chemical shifts for ^{1}H and ^{13}C were measured relative to TMS. C, H microanalyses were done using a CHN-O-Rapid analyzer (Heracus).

(C_5Me_5)$ZrCl_3$. Toluene (150 mL) was added to a mixture of 21.5 g (92.0 mmol) of freshly sublimed $ZrCl_4$ and 11.9 g (84.0 mmol) of C_5Me_5Li. The slurry was refluxed and stirred for 2 days. Then, the pale yellow precipitate was filtered off (G4) and washed with toluene (50 mL). The crude product was treated with hot decane (3 × 100 mL) using a special thick wall filtering (G4 frit) funnel equipped with a thermostated (165−170 °C) oil jacket. A yellowish precipitate was formed as soon as the filtrate was cooled to room temperature. This precipitate was filtered off (G4), washed with pentane (3 × 50 mL), and dried in vacuo for 3 h. Yield: 20.5 g (73%). Anal. Calcd for $C_{10}H_{15}Cl_3Zr$: C, 36.09; H, 4.54. Found: C, 36.13; H, 4.50. ^{1}H NMR ($C_6D_5CD_3$): δ 2.17 (s, $\Delta\nu_{1/2}$ = 12.0 Hz, C_5Me_5). $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$): δ 130.45 (C_5Me_5), 13.31 (C_5Me_5).

2-Methyl-3-(2-thienyl)propanoic Acid. Sodium metal (30.0 g, 1.30 mol) was dissolved in 600 mL of dry ethanol. To the resulting solution was added dropwise 240 mL (217 g, 1.27 mol) of diethylmethylmalonate for 10 min; then, a solution of 167.5 g (1.26 mol) of 2-chloromethylthiophene in 250 mL of dry ethanol was added dropwise. This mixture was refluxed for 3.5 h and cooled to room temperature. A solution of 253 g (4.5 mol) of KOH in 600 mL of water was added. This mixture was refluxed for 4 h to saponificate the ester formed. Ethanol

(25) Manzer, L. E. *Inorg. Synth.* **1982**, *22*, 135.

was distilled off. To this mixture was added 2 L of water and, then, 1 M HCl was added to pH 1. The substituted methylmalonic acid precipitated at 5 °C was separated, washed with 3 × 200 mL of cold water, and dried. Crude product was obtained after decarboxylation at 150 °C. Fractional distillation gave 2-methyl-3-(2-thienyl)propanoic acid as a white solid, bp 112−120 °C/1 mmHg. Yield: 76 g (36%). Anal. Calcd for $C_8H_{10}O_2S$: C, 56.44; H, 5.92. Found: C, 56.58; H, 6.02. ^{1}H NMR ($CDCl_3$): δ 11.88 (br s, 1H, COOH), 7.13 (m, 1H, 5-H in C_4H_3S), 6.92 (m, 1H, 4-H in C_4H_3S), 6.82 (m, 1H, 3-H in C_4H_3S), 3.25 (dd, J = 14.7 Hz, J = 6.7 Hz, 1H, C*H*H′), 2.93 (dd, J = 7.4 Hz, J = 14.7 Hz, 1H, CH*H*′), 2.93 (m, 1H, CH), 1.25 (d, J = 7.0 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$): δ 182.3, 141.2, 126.8, 125.7, 123.8, 41.6, 33.1, 16.5.

5-Methyl-5,6-dihydro-4*H*-cyclopenta[*b*]thiophen-4-one (1). To polyphosphoric acid (prepared from 750 g of P_4O_{10} and 540 g of 85% H_3PO_4) was added a solution of 76 g (0.45 mol) of 2-methyl-3-(2-thienyl)propanoic acid in 300 mL of chlorobenzene for 15 min by vigorous stirring. This mixture was left for 10 min and, then, immersed in 2 kg of ice. The product was extracted with 5 × 200 mL of ether. The extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. Fractional distillation gave pinkish crystalline **1**, bp 100−120 °C/1 mmHg. Yield: 36 g (53%). Anal. Calcd for C_8H_8OS: C, 63.13; H, 5.30. Found: C, 63.22; H, 5.38. ^{1}H NMR ($CDCl_3$): δ 7.34 (d, J = 5.6 Hz, 1H, 2-H), 7.14 (d, J = 5.6 Hz, 1H, 3-H), 3.43 (dd, J = 17.6 Hz, J = 6.8 Hz, 1H, 6-H), 3.05 (m, 1H, 5-H), 2.78 (dd, J = 17.6 Hz, J = 3.2 Hz, 1H, 6′-H), 1.35 (d, J = 7.2 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$): δ 200.7, 168.6, 144.8, 130.7, 119.5, 47.8, 32.9, 16.5.

4,5-Dimethyl-6*H*-cyclopenta[*b*]thiophene (2). To 123 mL (0.20 mol) of a 1.62 M solution of MeLi in ether was added dropwise a solution of 25.0 g of **1** in 175 mL of ether at −80 °C. This mixture was stirred at room temperature for 1.5 h and, then, 25 mL of 40% HCl was added dropwise at −10 °C. The resulting mixture was stirred for 40 min at room temperature. The organic layer was separated; the aqueous layer was extracted by 2 × 100 mL of methyl-*tert*-butyl ether. The combined organic extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. Fractional distillation gave a white solid of **2**, bp 62 °C/2 mmHg. Yield: 19,1 g (77,6%). Anal. Calcd for $C_9H_{10}S$: C, 71.95; H, 6.71. Found: C, 72.13; H, 6.80. ^{1}H NMR ($CDCl_3$): δ 7.20 (d, J = 4.8 Hz, 1H, 2-H), 6.87 (d, J = 4.8 Hz, 1H, 3-H), 3.19 (br s, 2H, 6-H), 2.00 (br s, 6H, 4,5-Me). ^{13}C NMR ($CDCl_3$): δ 152.8, 138.1, 137.8, 129.7, 126.3, 117.4, 39.4, 13.7, 11.2.

Complex 16. To a solution of 1.12 g (7.4 mmol) of **2** in 70 mL of toluene was added 2.96 mL (7.4 mmol) of 2.5 M n-BuLi in hexanes at room temperature. The reaction mixture was stirred for 10 h. Then, 2.47 g (7.4 mmol) of Cp*$ZrCl_3$ was added at −70 °C. The resulting mixture was stirred for 24 h at room temperature and refluxed for 5 h. The hot solution was filtrated (G4). The crystals that precipitated from the filtrate at −30 °C were separated, washed with 3 × 20 mL of cold toluene, and dried in vacuo. Yield: 1.48 g (45%) of yellow crystals of **16**. Anal. Calcd for $C_{19}H_{24}Cl_2SZr$: C, 51.10; H, 5.42. Found: C, 50.98; H, 5.33. ^{1}H NMR (CD_2Cl_2): δ 7.16 (d, J = 5.4 Hz, 1H, 2-H in C_9H_9S), 6.94 (d, J = 5.4 Hz, 1H, 3-H in C_9H_9S), 5.77 (s, 1H, 6-H in C_9H_9S), 2.22 (s, 3H, 4-Me in C_9H_9S), 1.94 (s, 15H, C_5Me_5), 1.93 (s, 3H, 5-Me in C_9H_9S). ^{13}C NMR (CD_2Cl_2): δ 133.6, 131.5, 125.6, 121.9, 121.2, 118.9, 107.3, 99.0, 16.1, 13.6, 13.3.

Bis(4,5-dimethyl-6*H*-cyclopenta[*b*]thien-6-yl)(dimethyl)silane (22). To a solution of 19.1 g (0.127 mol) of **2** in 250 mL of toluene/THF (10:1) mixture was added dropwise 105 mL (0.127 mol) of 1.21 M n-BuLi in hexanes at −80 °C. This mixture was stirred for 10 h at room temperature. Then, 7.72 mL (8.22 g, 63.7 mmol) of Me_2SiCl_2 was added at −40 °C, and the resulting reaction mixture was stirred for 48 h at room temperature. Cold water (100 mL) was added dropwise. The organic layer was separated, dried over K_2CO_3, and evaporated to dryness. The bridged ligand was isolated using flash chromatography over silica gel with hexanes as eluents. Yield: 4.07 g (18%) of a yellow oil of a *rac*/*meso* mixture of **22**. Anal. Calcd for $C_{20}H_{24}S_2Si$: C, 67.36; H, 6.78. Found: C, 67.50; H, 6.84. ^{1}H NMR ($CDCl_3$): *rac* δ 7.24 (d, J = 5.0 Hz, 2H, 3,3′-H), 6.98 (d, J = 5.0 Hz, 2H, 2,2′-H), 3.75 (m, 2H, C*H*Si), 2.11 (s, 6H, 4,4′-Me), 2.09 (s, 6H, 5,5′-Me), −0.35 (s, 6H, Me_2Si); *meso* δ 6.97 (d, J = 5.0 Hz, 2H, 3,3′-H), 6.96 (d, J = 5.0 Hz, 2H, 2,2′-H), 3.63 (m, 2H, C*H*Si), 2.14 (s, 6H, 4,4′-Me), 2.00 (s, 6H, 5,5′-Me), −0.31 (s, 3H, MeSi), −0.38 (s, 3H, Me′Si). ^{13}C NMR ($CDCl_3$): *rac* and *meso* δ 151.9, 139.7, 139.2, 129.7, 128.2, 125.7, 125.4, 123.6, 120.8, 117.6, 117.3, 117.2, 45.2, 44.9, 15.2, 15.0, 11.7, 11.6, −6.8, −7.4, −8.5.

Complex *rac*-28. To a solution of 4.07 g (11.4 mmol) of **22** in 100 mL of hexane was added 14.3 mL (22.8 mmol) of 1.6 M n-BuLi in hexanes at −40 °C. This mixture was stirred for 24 h at room temperature. The formed precipitate was filtered, washed with 3 × 40 mL of hexane, and dried in vacuo. To the suspension of this dilithium salt in 120 mL of toluene was added 2.66 g (11.4 mmol) of $ZrCl_4$ at −40 °C. This mixture was stirred for 48 h at room temperature, 5 h at 60 °C, and then, this hot mixture was filtered (G4). The filtrate was evaporated to ca. 40 mL. The yellow crystals that precipitated from the filtrate at −30 °C were separated and dried in vacuo. Yield: 0.92 g (16%) of pure *rac*-**28**. Anal. Calcd for $C_{20}H_{22}Cl_2S_2SiZr$: C, 46.49; H, 4.29. Found: C, 46.32; H, 4.35. ^{1}H NMR (CD_2Cl_2): δ 7.37 (d, J = 5.6 Hz, 2H, 3,3′-H), 6.89 (d, J = 5.6 Hz, 2H, 2,2′-H), 2.17 (s, 6H, 4,4′-Me), 1.98 (s, 6H, 5,5′-Me), 1.02 (s, 6H, Me_2Si).

5-Methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one (3). To polyphosphoric acid (prepared from 660 g of P_4O_{10} and 460 g of 85% H_3PO_4) was added a mixture of 62.5 mL (65.7 g, 0.78 mol) of thiophene and 65.6 mL (66.6 g, 0.77 mol) of methacrylic acid in 100 mL of CH_2Cl_2 at 50 °C. This mixture was stirred at this temperature for 2 h and, then, immersed in 1 kg of ice. The product was extracted by 4 × 150 mL of methyl-*tert*-butyl ether. The combined extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. Fractional distillation gave white solid **3**, bp 110 °C/5 mmHg. Yield: 47.8 g (40%). Anal. Calcd for C_8H_8OS: C, 63.13; H, 5.30. Found: C, 63.20; H, 5.36. ^{1}H NMR ($CDCl_3$): δ 7.91 (d, J = 4.7 Hz, 1H, 2-H), 7.03 (d, J = 4.7 Hz, 1H, 3-H), 3.28 (dd, J = 17.1 Hz, J = 6.9 Hz, 1H, 4-H), 3.03 (m, 1H, 5-H), 2.61 (dd, J = 17.1 Hz, J = 3.0 Hz, 1H, 4′-H), 1.34 (d, J = 7.7 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$): δ 200.3, 167.2, 140.7, 140.2, 124.1, 47.5, 32.9, 17.0.

5,6-Dimethyl-4*H*-cyclopenta[*b*]thiophene (4). To 243 mL (0.40 mol) of 1.62 M MeLi in ether was added a solution of 47.8 g (0.31 mol) of **3** in 350 mL of ether for 30 min at −80 °C. This reaction mixture was stirred for 1.5 h at room temperature. Then, 50 mL of 40% HCl was added dropwise at −10 °C. The resulting mixture was stirred for 40 min at room temperature. The organic layer was separated, and the aqueous one was extracted by 2 × 100 mL of methyl-*tert*-butyl ether. The combined extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. Fractional distillation gave **4** as a colorless liquid, bp 100 °C/13 mmHg. Yield: 40.4 g (86%). Anal. Calcd for $C_9H_{10}S$: C, 71.95; H, 6.71. Found: C, 72.09; H, 6.66. ^{1}H NMR ($CDCl_3$): δ 7.05 (d, J = 4.7 Hz, 1H, 2-H), 6.97 (d, J = 4.7 Hz, 1H, 3-H), 3.09 (s, 2H, 4-H), 2.02 (br s, 6H, 5,6-Me). ^{13}C NMR ($CDCl_3$): δ 149.0, 143.3, 138.3, 129.5, 122.5, 122.0, 39.4, 14.1, 11.7.

Complex 17. To a solution of 1.12 g (7.45 mmol) of **4** in 70 mL of toluene was added 3.0 mL of 2.5 M n-BuLi in hexanes. This mixture was stirred 10 h at room temperature and 1 h at 100 °C. Then, 2.49 g (7.48 mmol) of Cp*$ZrCl_3$ was added at −70 °C. The reaction mixture was stirred for 24 h at room temperature and refluxed for 5 h. The hot mixture was filtered

(G4). The crystals that precipitated from the filtrate at −30 °C were separated, washed with 3 × 20 mL of cold toluene, and dried in vacuo. Yield: 1.83 g (54%) of yellow crystals of **17**. Anal. Calcd for $C_{19}H_{24}Cl_2SZr$: C, 51.10; H, 5.42. Found: C, 51.00; H, 5.47. ^{1}H NMR (CD_2Cl_2): δ 7.09 (d, J = 5.4 Hz, 1H, 2-H in C_9H_9S), 6.81 (d, J = 5.4 Hz, 1H, 3-H in C_9H_9S), 5.80 (s, 1H, 4-H in C_9H_9S), 2.16 (s, 3H, 5-Me in C_9H_9S), 1.95 (s, 3H, 6-Me in C_9H_9S), 1.93 (s, 15H, C_5Me_5). ^{13}C NMR (CD_2Cl_2): δ 133.7, 131.8, 128.7, 125.4, 119.0, 118.4, 107.3, 98.6, 16.4, 13.8, 13.7.

Bis(5,6-dimethyl-4*H*-cyclopenta[*b*]thien-4-yl)(dimethyl)silane (23). To a solution of 20.0 g (133 mmol) of **4** in 300 mL of a toluene/THF (5:1) mixture was added 53.2 mL (133 mmol) of 2.5 M n-BuLi in hexanes at −80 °C. This mixture was stirred for 10 h at room temperature, then cooled to −40 °C, and 8.07 mL (8.58 g, 66.5 mmol) of Me_2SiCl_2 was added. The resulting mixture was stirred for 36 h at room temperature and 4 h at 60 °C. Cold water (50 mL) was added dropwise. The organic layer was separated, dried over K_2CO_3, and evaporated to dryness. The bridged ligand was isolated using flash chromatography over silica gel. First, **4** was separated with hexanes as eluent. The product **23** as a mixture of *rac* and *meso* isomers was obtained with a hexanes/methyl-*tert*-butyl ether (10:1) mixture as eluent. Yield: 16.7 g (71%) of a yellow solid. Anal. Calcd for $C_{20}H_{24}S_2Si$: C, 67.36; H, 6.78. Found: C, 67.51; H, 6.85. ^{1}H NMR ($CDCl_3$): *rac* δ 7.13 (m, 4H, 2,2′,3,3′-H), 3.46 (m, 2H, C*H*Si), 2.09 (s, 6H, 5,5′-Me), 2.01 (s, 6H, 6,6′-Me), −0.33 (s, 6H, Me_2Si); *meso* δ 7.09 (d, J = 4.7 Hz, 2H, 2,2′-H), 6.96 (d, J = 4.7 Hz, 2H, 3,3′-H), 3.50 (m, 2H, C*H*Si), 2.16 (s, 6H, 6,6′-Me), 2.12 (s, 6H, 5,5′-Me), −0.33 (s, 3H, MeSi), −0.40 (s, 3H, Me′Si). ^{13}C NMR ($CDCl_3$): *rac* and *meso* δ 147.5, 147.4, 144.2, 144.1, 139.4, 139.3, 129.3, 129.1, 122.4, 122.3, 121.8, 121.7, 45.7, 45.4, 15.2, 15.0, 11.8, 11.7, −6.3, −6.5, −6.7.

Complex *rac*-29. To a solution of 16.7 g (46.9 mmol) of **23** in 470 mL of toluene was added 37.5 mL of 2.5 M n-BuLi in hexanes at −40 °C. This mixture was stirred for 10 h at room temperature, then 10.9 g (46.9 mmol) of $ZrCl_4$ was added at −40 °C. The resulting mixture was stirred for 48 h at room temperature and refluxed for 5 h. The hot mixture was filtered (G4); the precipitate was washed with 5 × 150 mL of hot toluene. The crystals that precipitated from the combined filtrate at −30 °C were separated, washed with 5 × 40 mL of cold CH_2Cl_2, and dried in vacuo. Yield: 2.43 g (10%) of yellow crystals of pure *rac*-**29**. Anal. Calcd for $C_{20}H_{22}Cl_2S_2SiZr$: C, 46.49; H, 4.29. Found: C, 46.55; H, 4.37. ^{1}H NMR (CD_2Cl_2): δ 7.17 (d, J = 5.38 Hz, 2H, 3,3′-H), 6.83 (d, J = 5.38 Hz, 2H, 2,2′-H), 2.16 (s, 6H, 6,6′-Me), 1.88 (s, 6H, 5,5′-Me), 1.06 (s, 6H, Me_2Si).

3-(Chloromethyl)-2,5-dimethylthiophene. A mixture of 84.3 g (0.75 mol) of 2,5-dimethylthiophene and 46 mL of 40% HCl was prepared in a small vessel. While dry HCl gas was bubbled through this mixture at 0 °C, 22.6 g (0.75 mol) of paraform was slowly added during 2 h. Then, this mixture was purged in 400 mL of cold water. The organic layer was separated, and the aqueous one was extracted by 4 × 200 mL of methyl-*tert*-butyl ether. The combined organic extracts were washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. Fractional distillation gave the title product as a colorless liquid, bp 77−90 °C/6 mmHg. Yield: 57.7 g (48%). Anal. Calcd for C_7H_9ClS: C, 52.33; H, 5.65. Found: C, 52.49; H, 5.60. ^{1}H NMR ($CDCl_3$): δ 6.59 (m, 1H, 4-H), 4.43 (s, 2H, CH_2), 2.35 (m, 3H, 5-Me), 2.34 (s, 3H, 2-Me).

3-(2,5-Dimethyl-3-thienyl)-2-methylpropanoic Acid. To a solution of sodium ethylate (prepared from 8.42 g (0.366 mol) of sodium metal and 200 mL of dry ethanol) was added 61.7 mL (62.5 g, 0.359 mol) of diethylmethylmalonate at room temperature. This mixture was stirred for 15 min, then 57.7 g (0.359 mmol) of 2-chloromethylthiophene in 65 mL of dry ethanol was added. This mixture was stirred for 3.5 h, then a solution of 72 g (1.28 mol) of KOH in 200 mL of water was added. This mixture was refluxed for 4 h to saponificate the ester formed. Ethanol was distilled off. To this mixture was added 800 mL of water and, then, 1 M HCl was added to pH 1. The substituted methylmalonic acid precipitated at 5 °C was separated, washed with 3 × 200 mL of cold water, and dried. Crude product was obtained after decarboxylation at 180 °C. Fractional distillation gave 3-(2,5-dimethyl-3-thienyl)-2-methylpropanoic acid as a white solid, bp 158 °C/5 mmHg. Yield: 50.5 g (71%). Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12. Found: C, 60.64; H, 7.03. ^{1}H NMR ($CDCl_3$): δ 11.3 (s br, 1H, COOH), 6.44 (s, 1H, 4-H), 2.87 (dd, J = 13.8 Hz, J = 6.4 Hz, 1H, C*H*H′), 2.67 (m, 1H, CH), 2.53 (dd, J = 13.8 Hz, J = 8.1 Hz, 1H, CH*H*′), 2.37 (s, 3H, 2-Me), 2.29 (s, 3H, 5-Me), 1.17 (d, J = 7.0 Hz, 3H, CH*Me*). ^{13}C NMR ($CDCl_3$): 183.2, 135.6, 134.4, 132.1, 127.1, 40.9, 31.9, 16.8, 15.4, 13.2.

1,3,5-Trimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophen-4-one (5). To polyphosphoric acid (prepared from 220 g of P_4O_{10} and 160 g of 85% H_3PO_4) was added a solution of 24.6 g (0.124 mol) of 3-(2,5-dimethyl-3-thienyl)-2-methylpropanoic acid in 90 mL of chlorobenzene for 15 min by vigorous stirring. This mixture was left for 10 min and, then, immersed in 600 cm^3 of ice. The product was extracted with 5 × 200 mL of ether. The extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. The ketone was isolated using flash chromatography over silica gel with a hexanes/methyl-*tert*-butyl ether (2:1) mixture as eluent. Yield: 16.0 g (68%) of sandy solid. Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71. Found: C, 66.49; H, 6.70. ^{1}H NMR ($CDCl_3$): δ 2.98 (m, 2H, 6-H), 2.60 (s, 3H, 1-Me), 2.32 (m, 1H, 5-H), 2.29 (s, 3H, 3-Me), 1.28 (d, J = 7.2 Hz, 3H, 5-Me). ^{13}C NMR ($CDCl_3$): δ 201.3, 146.8, 140.1, 138.6, 126.3, 49.1, 29.0, 16.5, 12.9, 12.0.

1,3,5-Trimethyl-4*H*-cyclopenta[*c*]thiophene (6). To a solution of 16.0 g (89 mmol) of **5** in 130 mL of a THF/methanol (2:1) mixture was slowly added 5.37 g (143 mmol) of $NaBH_4$ for 1 h at 0 °C. This mixture was stirred for 10 h at room temperature. To the resulting mixture was added 170 mL of water, and then, 10% HCl was added to pH 1. 1,3,5-Trimethyl-5,6-dihydro-4*H*-cyclopenta[*c*]thiophen-4-ol was extracted by 4 × 100 mL of CH_2Cl_2. The combined extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. A mixture of this product and a catalytic quantity of *p*-toluenesulfonic acid in 700 mL of toluene was refluxed for 10 min, passed through a short column with silica gel, and evaporated to dryness. Yield: 11.3 g (78%) of a beige solid. Anal. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.36. Found: C, 73.30; H, 7.44. ^{1}H NMR ($CDCl_3$): δ 6.15 (m, 1H, 6-H), 2.91 (m, 2H, 4-H), 2.32 (s, 3H, 1-Me), 2.27 (m, 3H, 3-Me), 2.01 (m, 3H, 5-Me). ^{13}C NMR ($CDCl_3$): δ 148.9, 146.9, 142.0, 124.8, 121.7, 118.5, 36.0, 17.7, 13.2, 13.0.

Dimethyl[bis(1,3,5-trimethyl-4*H*-cyclopenta[*c*]thien-4-yl)]silane (24). To a solution of 12.6 g (77 mmol) of **6** in 170 mL of toluene/THF (10:1) was added 62 mL (77 mmol) of 1.24 M of n-BuLi in hexanes at −80 °C. This mixture was stirred for 1 h at room temperature, then 4.65 mL (4.95 g, 38 mmol) of Me_2SiCl_2 was added at −40 °C. The mixture was stirred for 48 h at 20 °C and filtered (G4); toluene from the filtrate was evaporated. The crude product was isolated using flash chromatography over silica gel with hexanes as eluent. Yield: 4.41 g (30%) of a white solid. Anal. Calcd for $C_{22}H_{28}S_2Si$: C, 68.69; H, 7.34. Found: C, 68.81; H, 7.39. ^{1}H NMR ($CDCl_3$): *rac* δ 6.13 (m, 2H, 6,6′-H, *rac*), 2.94 (m, 2H, 4,4′-H), 2.35 (s, 6H, 1,1′-Me), 2.32 (s, 6H, 3,3′-Me), 2.05 (s, 6H, 5,5′-Me), −0.05 (s, 6H, Me_2Si); *meso* δ 6.18 (m, 2H, 6,6′-H), 2.94 (m, 4H, 4,4′-H), 2.34 (s, 6H, 1,1′-Me), 2.30 (s, 6H, 3,3′-Me), 2.03 (s, 6H, 5,5′-Me), 0.02 (s, 3H, MeSi), −0.02 (s, 3H, Me′Si). ^{13}C NMR ($CDCl_3$): *rac* δ 150.2, 147.1, 144.1, 123.0, 120.5, 118.1, 41.4, 19.1, 15.0, 13.2, 3.5; *meso* δ 151.3, 147.6, 145.1, 122.6, 119.9, 117.8, 42.2, 18.9, 15.2, 13.5, 2.4, 2.7.

Mixture of 2-Methyl-2,3-dihydro-1*H*-cyclopenta[*b*][1]-benzothiophen-1-one (7) and 2-Methyl-1,2-dihydro-3*H*-cyclopenta[*b*][1]benzothiophen-3-one (8). To a solution of 19.6 g (138 mmol) of P_4O_{10} in 130 mL of methanesulfonic acid was added 19.1 mL (112 mmol) of methacrylic acid at room temperature, then 15.0 g (143 mmol) of melted 1-benzothiophene was added dropwise for 15 min under vigorous stirring at room temperature. This mixture was stirred additionally for 30 min at this temperature, then for 30 min at 40 °C. The resulting mixture was poured in a cold solution of 261 g (1.89 mol) of K_2CO_3 in 1100 mL of water. The products were extracted by 4 × 200 mL of CH_2Cl_2. The combined extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. Fractional distillation gave a white solid, bp 132°C/0.3 mmHg. Yield: 14.8 g (66%) of 5:1 mixture of **7** and **8**. Anal. Calcd for $C_{12}H_{10}OS$: C, 71.25; H, 4.98. Found: C, 71.27; H, 5.09. ^{1}H NMR ($CDCl_3$): δ 8.23 (m), 7.86 (m), 7.78 (m), 7.47 (m), 7.43 (m), 7.36 (m), 3.51 (dd, J = 17.9 Hz, J = 7.0 Hz), 3.45 (dd, J = 17.4 Hz, J = 6.7 Hz), 3.08 (m), 2.86 (dd, J = 17.9 Hz, J = 2.6 Hz), 2.77 (dd, J = 17.4 Hz, J = 2.6 Hz), 1.41 (s), 1.39 (s), 1.37(s).

Mixture of 2-Methyl-1*H*-cyclopenta[*b*][1]benzothiophene and 2-Methyl-3*H*-cyclopenta[*b*][1]benzothiophene (9). To a solution of 14.8 g (73 mmol) of the above-mentioned mixture of **7** and **8** in 100 mL of a THF/methanol (2:1) mixture was slowly added 4.15 g (110 mmol) of $NaBH_4$ at 0 °C. This mixture was stirred for 10 h at room temperature, then 800 mL of water and 10% HCl (to pH 1) were added. A mixture of the cyclopentanols was extracted by 3 × 50 mL of CH_2Cl_2. The combined extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. A mixture of the resulting yellow oil, 500 mL of toluene, and a catalytic quantity of *p*-toluenesulfonic acid was refluxed for 20 min. The product was isolated using flash chromatography over silica gel with a hexanes/methyl-*tert*-butyl ether (10:1) mixture as eluent. Yield: 12.6 g (92%) of white crystals of **9**. Anal. Calcd for $C_{10}H_{12}S$: C, 77.37; H, 5.41. Found: C, 77.14; H, 5.50. ^{1}H NMR ($CDCl_3$): δ 7.79 (m), 7.77 (m), 7.73 (m), 7.59 (m), 7.33 (m), 7.29 (m), 7.23 (m), 7.15 (m), 6.64 (m), 3.33 (d, J = 1.25 Hz), 3.26 (d, J = 1.24 Hz), 2.19 (d, J = 1.74 Hz), 2.17 (d, J = 1.74 Hz). ^{13}C NMR ($CDCl_3$): δ 148.3, 146.3, 144.4, 144.3, 139.9, 132.2, 128.0, 126.5, 124.0, 123.9, 123.7, 123.4, 123.1, 123.0, 122.7, 122.3, 121.7, 121.5, 121.0, 119.8, 40.7, 38.8, 16.9, 16.8.

Complex 15. To a solution of 5.00 g (26.8 mmol) of **9** in 260 mL of toluene was added 16.3 mL (26.8 mmol) of 1.64 M n-BuLi in hexanes. This mixture was stirred for 1 h at room temperature and 3 h at 60 °C. Then, 3.13 g (13.4 mmol) of $ZrCl_4$ was added at −40 °C. The resulting mixture was stirred for 24 h at 20 °C, refluxed for 2 h, and filtered (G4). The precipitate was washed with 5 × 100 mL of hot toluene. The crystals that precipitated from the combined filtrate at −30 °C were separated and dried in vacuo. Yield: 1.60 g (23%) of yellow crystals of **15** as a mixture of *rac* and *meso* versions. Anal. Calcd for $C_{24}H_{18}Cl_2S_2Zr$: C, 54.12; H, 3.41. Found: C, 54.01; H, 3.36. ^{1}H NMR (CD_2Cl_2): δ 7.83 (m), 7.79 (m), 7.71 (m), 7.70 (m), 7.44−7.35 (m), 6.47 (m), 6.27 (m), 5.82 (m), 5.44 (m), 2.01 (s), 1.98 (s). ^{13}C NMR (CD_2Cl_2): δ 138.1, 137.0, 135.0, 134.4, 133.6, 133.5, 133.4, 133.1, 132.9, 131.6, 131.2, 128.2, 128.1, 126.8, 126.6, 125.1, 125.0, 124.8, 124.6, 109.1, 107.3, 106.3, 18.5, 18.3.

Dimethyl[bis(2-methyl-3*H*-cyclopenta[*b*][1]benzothien-3-yl)]silane (25). To a solution of 15.0 g (80.6 mmol) of **9** in 230 mL of a toluene/THF (10:1) mixture was added dropwise 39.0 mL (80.6 mmol) of 2.05 M n-BuLi in hexanes at 0 °C. This mixture was stirred for 1 h at room temperature and 1 h at 70 °C. Then, 4.89 mL (40.3 mmol) of Me_2SiCl_2 was added at −30 °C. The resulting mixture was stirred for 10 h at room temperature and 1 h at 60 °C. Then, 100 mL of water was added. The organic layer was separated, dried over K_2CO_3, and evaporated to dryness. The product was isolated using flash chromatography over silica gel with a hexanes/CH_2Cl_2 (20:1) mixture as eluent. Yield: 5.33 g (15%) of a yellow solid of **25** as a mixture of *rac*/*meso* versions. Anal. Calcd for $C_{26}H_{24}S_2Si$: C, 72.85; H, 5.64. Found: C, 72.80; H, 5.55.

Complex *meso*-30. To a solution of 5.33 g (12.4 mmol) of **25** in 100 mL of toluene was added 17.7 mL (24.9 mmol) of 1.40 M n-BuLi in hexanes at −40 °C. This mixture was stirred for 10 h at room temperature, then 2.90 g (12.4 mmol) of $ZrCl_4$ was added at −30 °C. The resulting mixture was stirred for 12 h at room temperature and 2 h at 70 °C. The crystals that precipitated from the combined filtrate at −30 °C were separated, washed with 2 × 10 mL of cold hexane, and dried in vacuo. Yield: 2.14 g (29%) of orange crystals. Anal. Calcd for $C_{26}H_{22}Cl_2S_2SiZr$: C, 53.04; H, 3.77. Found: C, 53.20; H, 3.71. ^{1}H NMR (CD_2Cl_2): δ 7.70 (m, 2H, 5,5′-H), 7.55 (m, 2H, 8,8′-H), 7.31−7.21 (m, 4H, 6,6′,7,7′-H), 6.85 (s, 2H, 1,1′-H), 2.43 (s, 6H, 2,2′-Me), 1.19 (s, 3H, MeSi), 1.13 (s, 3H, Me′Si).

1-(1-Benzothien-2-yl)-2-methyl-2-propen-1-one (10). To a solution of 30.0 g (0.223 mol) of 1-benzothiophene in 300 mL of THF was added 160 mL (0.223 mol) of 1.40 M n-BuLi in hexanes for 30 min at −80 °C. This mixture was stirred for 30 min at room temperature, and then, 10.0 g (0.112 mol) of CuCN was added at −80 °C. The resulting mixture was stirred for an additional 30 min at room temperature, then 26.0 g (0.224 mol) of methacryloyl chloride was added for 10 min at −80 °C. The mixture was stirred for 10 h at room temperature, then 170 mL of 10% HCl was added. The organic layer was separated, and the aqueous one was extracted by 4 × 150 mL of CH_2Cl_2. The combined extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. The product was isolated using flash chromatography over silica gel with a hexanes/CH_2Cl_2 (4:1) mixture as eluent. Yield: 20.2 g (45%) of pink crystals of **10**. Anal. Calcd for $C_{12}H_{10}OS$: C, 71.25; H, 4.98. Found: C, 71.09; H, 5.04. ^{1}H NMR ($CDCl_3$): 7.88 (m, 1H, 3-H), 7.87 (m, 1H, 4-/7-H), 7.85 (m, 1H, 7-/4-H), 7.45 (m, 1H, 5-/6-H), 7.39 (m, 1H, 6-/5-H), 5.89 (m, 1H, *H*H′C═C), 5.86 (m, 1H, H*H*′C═C), 2.10 (m, 3H, Me).

2-Methyl-1,2-dihydro-3*H*-cyclopenta[*b*][1]benzothiophen-3-one (8). To 144 mL of 96% H_2SO_4 was added 20.2 g (99.8 mmol) of **10** in 20 mL of chlorobenzene. This mixture was stirred for 1 h at room temperature and then immersed in 800 cm^3 of ice. The product was extracted by 4 × 200 mL of ether. The extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. Yield: 18.9 g (94%) of a white solid. Anal. Calcd for $C_{12}H_{10}OS$: C, 71.25; H, 4.98. Found: C, 71.22; H, 5.92. ^{1}H NMR ($CDCl_3$): δ 7.84−7.90 (m, 2H, 6,7-H), 7.52−7.42 (m, 2H, 5,8-H), 3.46 (dd, J = 17.3 Hz, J = 6.7 Hz, 1H, 1-H), 3.10 (m, 1H, 2-H), 2.78 (dd, J = 17.3 Hz, J = 2.7 Hz, 1H, 1′-H), 1.41 (d, J = 7.4 Hz, 3H, 2-Me).

2,3-Dimethyl-1*H*-cyclopenta[*b*][1]benzothiophene (11). To 37.5 mL (60,8 mmol) of 1.62 M MeLi in ether was added dropwise a solution of 9.78 g (48.6 mmol) of **8** in 50 mL of THF for 30 min at −80 °C. The reaction mixture was stirred 1.5 h at room temperature, then cooled to −10 °C, and 6.08 mL of 40% HCl was added dropwise. This mixture was stirred for 40 min at 20 °C. The organic layer was separated, and the aqueous one was extracted by 2 × 40 mL of methyl-*tert*-butyl ether. The combined extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. Yield: 9.20 g (95%) of pink crystals of **11**. Anal. Calcd for $C_{13}H_{12}S$: C, 77.95; H, 6.04. Found: C, 78.06; H, 6.10. ^{1}H NMR ($CDCl_3$): δ 7.80 (m, 1H, 5-H), 7.62 (m, 1H, 8-H), 7.30 (m, 1H, 6-H), 7.15 (m, 1H, 7-H), 3.28 (m, 2H, 1-H), 2.09 (s, 3H, 3-Me), 2.06 (m, 3H, 2-Me). ^{13}C NMR ($CDCl_3$): δ 149.1, 142.4, 139.9, 137.4, 135.3, 130.1, 124.3, 123.8, 121.8, 120.1, 39.1, 14.4, 11.7.

Complex 18. To a solution of 0.88 g (4.4 mmol) of **11** in 70 mL of toluene was added 1.76 mL (4.4 mmol) of 2.5 M n-BuLi in hexanes. This mixture was stirred for 10 h at room temperature and 1 h at 100 °C, then 1.46 g (4.4 mmol) of

Cp^*ZrCl_3 was added. The resulting mixture was stirred for 24 h at room temperature and refluxed for 5 h. This hot mixture was filtered (G4); the filtrate was evaporated to ca. 2/3 of its starting volume. Hexane (100 mL) was added. The formed precipitate was filtered off (G3) and dried in vacuo. Yield: 0.79 g (36%) of yellow crystals of **18**. Anal. Calcd for $C_{23}H_{26}Cl_2SZr$: C, 55.62; H, 5.28. Found: C, 55.68; H, 5.31. ^{1}H NMR (CD_2Cl_2): δ 7.75 (m, 1H, 5-H in $C_{13}H_{11}S$), 7.66 (m, 1H, 8-H in $C_{13}H_{11}S$), 7.31−7.23 (m, 2H, 6,7-H in $C_{13}H_{11}S$), 6.12 (s, 1H, 1-H in $C_{13}H_{11}S$), 2.19 (s, 3H, 3-Me in $C_{13}H_{11}S$), 2.00 (s, 3H, 2-Me in $C_{13}H_{11}S$), 1.90 (s, 15H, C_5Me_5). ^{13}C NMR (CD_2Cl_2): δ 133.0, 129.9, 129.6, 127.2, 126.2, 125.6, 125.5, 125.3, 123.4, 122.8, 107.3, 100.1, 15.9, 14.3, 13.8.

Bis(2,3-dimethyl-1*H*-cyclopenta[*b*][1]benzothien-1-yl)-(dimethyl)silane (26). To a solution of 18.2 g (90.7 mmol) of **11** in 180 mL of a toluene/THF (10:1) mixture was added 64.8 mL of 1.4 M n-BuLi in hexanes at −80 °C. This mixture was stirred for 10 h at room temperature and 4 h at 60 °C. To this mixture was added 5.49 mL (45.3 mmol) of Me_2SiCl_2 at −40 °C. The resulting mixture was stirred for 10 h at room temperature and 1 h at 60 °C. Then, 100 mL of water was added; the organic layer was separated, dried over K_2CO_3, and evaporated to dryness. The crude product was crystallized from a hexane/pentane mixture. Yield: 4.83 g (23%) of a yellow solid of a *rac*/*meso* mixture of **26**. Anal. Calcd for $C_{28}H_{28}SSi$: C, 73.63; H, 6.18. Found: C, 73.55; H, 6.12. ^{1}H NMR ($CDCl_3$): δ 7.81 (m), 7.79 (m), 7.64 (m), 7.50 (m), 7.25−7.09 (m), 3.99 (m), 3.88 (m), 2.19 (m), 2.11 (m), 2.11 (m), 2.10 (s), −0.24 (s), −0.27 (s), −0.41 (s). ^{13}C NMR ($CDCl_3$): δ 147.2, 147.0, 142.0, 141.6, 141.5, 138.7, 138.5, 134.6, 134.5, 129.6, 129.5, 124.0, 123.6, 123.5, 123.4, 123.3, 121.4, 121.3, 121.0, 120.9, 45.9, 45.8, 15.4, 15.3, 11.5, 11.4, −4.5, −4.7, −5.5.

Mixture of *rac*- and *meso*-31. To a solution of 2.00 g (4.38 mmol) of **26** in 100 mL of toluene was added 3.50 mL (8.76 mmol) of 2.5 M n-BuLi in hexanes at −40 °C. This mixture was stirred for 10 h at room temperature, then 1.65 g (4.38 mmol) of $ZrCl_4(THF)_2$ was added at −40 °C. The resulting mixture was stirred for 12 h at room temperature and refluxed for an additional 5 h. The precipitate containing the product and LiCl was filtered off (G3), washed with 3 × 10 mL of THF to dissolve LiCl, and dried in vacuo. Yield: 0.98 g (36%) of yellow crystals of a *rac*/*meso* mixture of **31**. An exact ratio of *rac* to *meso* isomers cannot be defined because of their low solubility in all common solvents. Anal. Calcd for $C_{28}H_{26}Cl_2S_2SiZr$: C, 54.52; H, 4.25. Found: C, 54.44; H, 4.19. ^{1}H NMR (CD_2Cl_2): *meso* δ 8.12 (m, 2H, 5,5′-H in $C_{13}H_{10}S$), 7.38 (m, 2H, 8,8′-H in $C_{13}H_{10}S$), 7.09 (m, 2H, 7,7′-H in $C_{13}H_{10}S$), 7.02 (m, 2H, 6,6′-H in $C_{13}H_{10}S$), 2.24 (s, 6H, 3,3′-Me in $C_{13}H_{10}S$), 2.18 (s, 6H, 2,2′-H in $C_{13}H_{10}S$), 1.63 (s, 3H, MeSi), 1.25 (s, 3H, Me′Si).

(2*E*)-1-(1-Benzothien-2-yl)-2-methyl-2-buten-1-one (12). The respective cuprate was prepared analogously to the procedure described for the synthesis of **10** starting from 2.00 g (15.0 mmol) of 1-benzothiophene in 20 mL of THF, 12.4 mL (15.0 mmol) of 1.21 M n-BuLi in hexanes, and 0.67 g (7.5 mmol) of CuCN. To this mixture was added 1.78 g (15.0 mmol) of (2*E*)-2-methyl-2-butenoyl chloride at −80 °C. The resulting mixture was stirred for 10 h at room temperature, then 10 mL of 10% HCl was added. The organic layer was separated, and the aqueous one was extracted by 3 × 50 mL of CH_2Cl_2. The combined extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. The product was isolated using flash chromatography over silica gel with a hexane/CH_2Cl_2 (4:1) mixture as eluent. Yield: 2.47 g (76%) of beige solid. Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59. Found: C, 71.96; H, 5.50. ^{1}H NMR ($CDCl_3$): δ 7.85−7.82 (m, 2H, 4,7-H in C_8H_5S), 7.75 (m, 1H, 3-H in C_8H_5S), 7.44−7.34 (m, 2H, 5,6-H in C_8H_5S), 6.68 (m, 1H, MeC=C*H*Me), 1.99 (m, 3H, *Me*C=CHMe), 1.92 (m, 3H, MeC=CH*Me*). ^{13}C NMR ($CDCl_3$): δ 191.5, 143.3, 142.4, 139.1, 138.9, 137.7, 130.3, 127.1, 125.9, 125.0, 122.9, 14.9, 12.9.

1,2-Dimethyl-1,2-dihydro-3*H*-cyclopenta[*b*][1]benzothiophen-3-one (13). To 17 mL of 96% H_2SO_4 was added a solution of 2.47 g (11.4 mmol) of **12** in 2.5 mL of chlorobenzene with vigorous stirring. This mixture was stirred for 1 h at room temperature, then immersed in 90 cm^3 of ice. The product was extracted by 3 × 100 mL of ether. The extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. Yield: 2.39 g (97%) of beige solid as a 1:1 mixture of *cis*/*trans* isomers. Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59. Found: C, 72.05; H, 5.54. ^{1}H NMR ($CDCl_3$): δ 7.91 (m, 1H, 8-H), 7.46 (m, 1H, 5-H), 7.35−7.20 (m, 2H, 6,7-H), 3.73 (m, 0.5H, 1-H), 3.19 (m, 1H, 1,2-H), 2.61 (m, 0.5H, 2-H), 1.57 (d, J = 7.2 Hz, 1.5H, 1-/2-Me), 1.39 (d, J = 7.5 Hz, 1.5H, 2-/1-Me), 1.36 (d, J = 7.2 Hz, 1.5H, 1-/2-Me), 1.30 (d, J = 7.5 Hz, 1H, 1.5H, 2-/1-Me). ^{13}C NMR ($CDCl_3$): δ 201.1, 200.7, 168.3, 166.8, 147.0, 146.7, 139.5, 133.9, 133.8, 130.7, 129.7, 128.5, 127.8, 126.4, 124.9, 124.6, 124.2, 124.0, 55.7, 50.2, 40.6, 35.1, 19.0, 16.3, 15.4, 11.2.

Mixture of 1,2-Dimethyl-1*H*- and 1,2-Dimethyl-3*H*-cyclopenta[*b*][1]benzothiophenes (14). To a solution of 2.39 g (11.1 mmol) of **13** in 15 mL of a THF/methanol (2:1) mixture was added slowly 0.62 g (16.6 mmol) of $NaBH_4$ for 1 h at 0 °C. This mixture was stirred for 10 h at room temperature, then 20 mL of water and 10% HCl (to pH 1.0) were added. The formed cyclopentanol was extracted by 3 × 75 mL of CH_2Cl_2. The extract was washed with a saturated aqueous solution of Na_2CO_3, dried over K_2CO_3, and evaporated to dryness. Toluene (75 mL) and a catalytic quantity of *p*-toluenesulfonic acid were added to the resulting yellow oil. This mixture was refluxed for 10 min, then passed through short column with silica gel using hexanes/methyl-*tert*-butyl ether (10:1) as eluent. The combined organic extract was evaporated to dryness. Yield: 1.68 g (76%) of a beige solid of a mixture of the title isomers. Anal. Calcd for $C_{13}H_{12}S$: C, 77.95; H, 6.04. Found: C, 77.88; H, 6.11. ^{1}H NMR ($CDCl_3$): δ 7.94 (m), 7.80 (m), 7.67 (m), 7.32 (m), 7.22 (m), 7.16 (m), 7.64 (m), 3.35−3.27 (m), 2.29 (m), 2.11 (m), 2.05 (m), 1.39 (d, J = 7.7 Hz). ^{13}C NMR ($CDCl_3$): δ 145.8, 144.8, 144.7, 143.7, 143.1, 139.7, 137.9, 134.8, 133.2, 131.0, 124.2, 123.9, 123.8, 123.5, 122.8, 122.0, 121.0, 120.9, 119.8, 45.0, 40.6, 29.7, 15.1, 15.0, 13.8, 12.2.

Complex 19. To a solution of 0.78 g (3.90 mmol) of **14** in 70 mL of toluene was added 1.56 mL (3.90 mmol) of 2.5 M n-BuLi in hexanes at room temperature. This mixture was stirred for 10 h at room temperature, then 1 h at 100 °C. To this mixture was added 1.30 g (3.90 mmol) of Cp^*ZrCl_3 at −70 °C. It was stirred for 24 h at room temperature, then refluxed for 5 h. This hot reaction mixture was filtered; the filtrate was evaporated to dryness. Then, 100 mL of hexane was added. The formed precipitate was filtered off (G3), washed with 15 mL of cold hexane, and dried in vacuo. Yield: 0.68 g (35%) of a yellow solid. Anal. Calcd for $C_{23}H_{26}Cl_2SZr$: C, 55.62; H, 5.28. Found: C, 55.77; H, 5.30. ^{1}H NMR (CD_2Cl_2): δ 7.88 (m, 1H, 5-H in $C_{13}H_{11}S$), 7.62 (m, 1H, 8-H in $C_{13}H_{11}S$), 7.39 (m, 1H, 6-H in $C_{13}H_{11}S$), 7.30 (m, 1H, 7-H in $C_{13}H_{11}S$), 5.84 (s, 1H, 1-H in $C_{13}H_{11}S$), 2.42 (s, 3H, 1-Me in $C_{13}H_{11}S$), 2.00 (s, 3H, 2-Me in $C_{13}H_{11}S$), 1.95 (s, 15H, C_5Me_5). ^{13}C NMR (CD_2Cl_2): δ 139.4, 134.8, 131.7, 127.5, 126.3, 125.8, 125.5, 124.5, 121.7, 121.1, 107.3, 100.3, 15.7, 13.8, 13.6.

Bis(1,2-dimethyl-3*H*-cyclopenta[*b*][1]benzothien-3-yl)-(dimethyl)silane (27). To a solution of 20.3 g (102 mmol) of **14** in 200 mL of toluene/THF (10:1) mixture was added 73 mL (102 mmol) of 1.4 M n-BuLi in hexanes at −80 °C. This mixture was stirred for 10 h at room temperature and 4 h at 60 °C, then 6.16 mL (51 mmol) of Me_2SiCl_2 was added at −40 °C. The mixture was stirred for 10 h at room temperature and 1 h at 60 °C. To the resulting mixture was added 100 mL of water at room temperature. The organic layer was separated and evaporated to dryness. The residue was washed with 70 mL of hexane and dried in vacuo. Yield: 19.2 g (83%) of pure *meso*-**30** as a yellow solid. Anal. Calcd for $C_{28}H_{28}S_2Si$: C, 73.65;

Table 1. Crystallographic Data for Complexes 16, 17, 20, 21, 24, 28, 29, 31, and 32

	16	**17**	**20**·$(C_7H_8)_4$	**21**	**24**	**28**	**29**	**31**	**32**
formula	$C_{19}H_{24}Cl_2SZr$	$C_{19}H_{24}Cl_2SZr$	$C_{68}H_{94}Cl_{12}Li_2Zr_4$	$C_{47}H_{58}C_{l4}S_2Zr_2$	$C_{22}H_{28}S_2Si$	$C_{20}H_{22}Cl_2S_2SiZr$	$C_{20}H_{22}Cl_2S_2SiZr$	$C_{28}H_{26}Cl_2S_2SiZr$	$C_{28}H_{26}Cl_2S_2SiZr$
fw	446.56	446.56	1715.60	1011.29	384.65	516.71	516.71	616.82	616.82
color	white	white	yellowish	beige	white	yellow	yellow	yellow	yellow
cryst syst	orthorhombic	triclinic	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	*Pca*2(1)	$P\bar{1}$	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	16.763(3)	9.644(2)	23.849(4)	8.536(10)	8.7053(9)	9.18(2)	8.7712(15)	9.2891(15)	9.792(4)
b (Å)	8.9146(14)	14.207(4)	14.147(2)	8.644(8)	10.5026(10)	9.38(2)	9.1736(15)	11.8935(15)	10.288(4)
c (Å)	25.051(4)	14.786(4)	22.314(3)	17.563(16)	12.2813(12)	13.194(19)	14.473(2)	24.581(4)	13.532(6)
α (deg)	90	100.396(4)	90	86.96(3)	98.354(2)	81.74(7)	79.752(4)	97.633(4)	81.450(8)
β (deg)	90	97.017(4)	91.768(12)	79.14(3)	102.703(2)	81.43(7)	88.813(4)	94.147(3)	86.535(8)
γ (deg)	90	105.615(4)	90	61.21(3)	106.605(2)	63.39(6)	63.715(3)	110.442(3)	71.289(7)
V (Å^3)	3743.6(10)	1887.7(8)	7525.0(19)	1114.4(19)	1023.35(18)	1001(4)	1025.3(3)	2501.4(7)	1276.6(9)
Z	8	4	4	1	2	2	2	4	2
ρ_{calcd} (g cm^{-3})	1.585	1.571	1.514	1.507	1.248	1.715	1.674	1.638	1.605
μ (mm^{-1})	0.981	0.973	1.003	0.834	0.321	1.088	1.062	0.886	0.868
F(000)	1824	912	3488	520	412	524	524	1256	628
no. of reflns collected	33704	17 801	9326	9288	8503	9619	12 242	29 969	13 111
no. of ind reflns	11 837 [*R*(int) = 0.0427]	8154 [*R*(int) = 0.0295]	9117 [*R*(int) = 0.0238]	5889 [*R*(int) = 0.0510]	5847 [*R*(int) = 0.0138]	9641[a]	5927 [*R*(int) = 0.1105]	14 464 [*R*(int) = 0.0506]	6128 [*R*(int) = 0.0487]
no. of data/restraints/params	11 806/1/415	8154/0/415	9117/0/392	5839/0/272	5847/0/334	9641/176/248	5909/1/258	14464/0/821	6095/0/411
goodness-of-fit on F^2	0.980	1.155	1.050	0.948	1.100	0.861	0.745	0.881	0.855
final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0522$, $wR_2 = 0.1236$	$R_1 = 0.0785$, $wR_2 = 0.1861$	$R_1 = 0.0298$, $wR_2 = 0.0729$	$R_1 = 0.0610$, $wR_2 = 0.1450$	$R_1 = 0.0499$, $wR_2 = 0.1376$	$R_1 = 0.0838$, $wR_2 = 0.2036$	$R_1 = 0.0674$, $wR_2 = 0.1280$	$R_1 = 0.0545$, $wR_2 = 0.1164$	$R_1 = 0.0464$, $wR_2 = 0.0963$
R indices (all data)	$R_1 = 0.0654$, $wR_2 = 0.1349$	$R_1 = 0.0986$, $wR_2 = 0.1988$	$R_1 = 0.0421$, $wR_2 = 0.0765$	$R_1 = 0.0830$, $wR_2 = 0.1756$	$R_1 = 0.0574$, $wR_2 = 0.1477$	$R_1 = 0.1314$, $wR_2 = 0.2279$	$R_1 = 0.1531$, $wR_2 = 0.1708$	$R_1 = 0.0878$, $wR_2 = 0.1269$	$R_1 = 0.0858$, $wR_2 = 0.1171$
largest diff. peak and hole, e·Å^{-3}	3.227 and −1.057	2.272 and −0.757	0.828 and −0.608	1.840 and −1.407	1.277 and −0.351	1.542 and −1.043	1.006 and −0.709	2.332 and −0.801	1.489 and −0.730

[a] The refinement of **28** was carried out against twinned data (HKLF 5), and thus the R_{int} was not calculated.

H, 6.18. Found: C, 73.58; H, 6.11. ^{1}H NMR ($CDCl_3$): δ 7.99 (m, 2H, 5,5′-H), 7.80 (m, 2H, 8,8′-H), 7.36 (m, 2H, 6,6′-H), 7.24 (m, 2H, 7,7′-H), 3.83 (m, 2H, 3,3′-H), 2.40 (s, 6H, 1,1′-Me), 2.21 (s, 6H, 2,2′-Me), −0.21 (s, 3H, MeSi), −0.29 (s, 3H, Me′Si). ^{13}C NMR ($CDCl_3$): δ 144.7, 144.2, 140.7, 138.8, 133.2, 130.9, 123.9, 123.3, 122.7, 120.9, 46.3, 15.1, 12.4, −6.4, −8.2.

Mixture of *rac*- and *meso*-32. To a solution of 17.3 g (37.9 mmol) of **27** in 380 mL of toluene was added 54.1 mL (75.8 mmol) of 1.4 M n-BuLi in hexanes at −40 °C. This mixture was stirred for 10 h at room temperature, then 9.27 g (39.8 mmol) of $ZrCl_4$ was added at −40 °C. The resulting mixture was srirred for 12 h at room temperature and refluxed for an additional 5 h. The precipitate containing the product and LiCl was filtered off (G3), washed with 4 × 40 mL of THF to dissolve LiCl, and dried in vacuo. Yield: 7.62 g (33%) of yellow crystals of a *rac*/*meso* mixture of **32**. An exact ratio of *rac* to *meso* isomers cannot be defined because of their low solubility in all common solvents. Anal. Calcd for $C_{28}H_{26}Cl_2S_2SiZr$: C, 54.52; H, 4.25. Found: C, 54.69; H, 4.32. ^{1}H NMR (CD_2Cl_2): *rac* δ 7.86 (m, 2H, 5, 5′-H), 7.64 (m, 2H, 8,8′-H), 7.39 (m, 2H, 6,6′-H), 7.32 (m, 2H, 7,7′-H), 2.36 (s, 6H, 1,1′-Me), 2.13 (s, 6H, 2,2′-Me), 1.21 (s, 6H, Me_2Si); *meso* δ 7.77 (m, 2H, 5,5′-H), 7.54 (m, 2H, 8,8′-H), 7.28 (m, 2H, 6,6′-H), 7.21 (m, 2H, 7,7′-H), 2.47 (s, 6H, 1,1′-Me), 2.10 (s, 6H, 2,2′-Me), 1.22 (s, 3H, MeSi), 1.11 (s, 3H, Me′Si).

X-ray Structural Determinations of 16, 17, 20, 21, 24, 28, 29, 31, and 32. Intensities of reflections were measured with a SMART 1000 CCD diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at 110(2) K for all complexes exept **20**. Data collection for **20** was performed using a Syntex P21 diffractometer at 120(2) K. Crystallographic data for **16**, **17**, **20**, **21**, **24**, **28**, **29**, **31**, and **32** are listed in Table 1 (see also Supporting Information).

Reflection intensities were integrated using SAINT software[26] and corrected for absorption by semiempirical methods (SADABS program[27]) for all complexes exept **20**. Data reduction for **20** was performed using Siemens P3 software. The analysis of the reciprocal lattice in **28** by means of the RLAT program has revealed the twinning which was solved using GEMINI 1.0.[28] The refinement of **28** was carried out taking into consideration the possible overlap of the reflections from two components of the twin crystal. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 in the anisotropic approximation for all non-hydrogen atoms. All hydrogen atoms were placed in geometrically calculated positions and included in the refinement procedure using a riding model. The H(1M) atom in the structure **20** was refined in isotropic approximation. All calculations were performed using SHELXTL-97 software[29] on an IBM PC/AT.

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Supporting Information Available: Tables of crystal data, data collection, structure solution and refinement parameters, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **16**, **17**, **20**, **21**, **24**, **28**, **29**, **31**, and **32**. This material is available free of charge via the Internet at http://pubs.acs.org.

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