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Palladium-Catalyzed Pathways to Aryl-Substituted Indenes: Efficient Synthesis of Ligands and the Respective *ansa*-Zirconocenes

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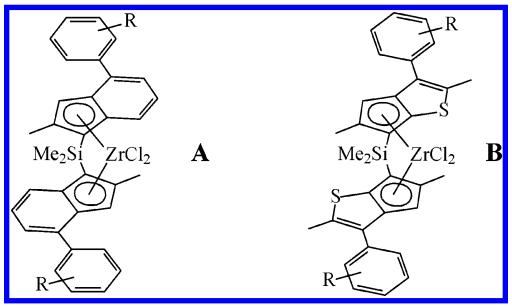
Substituted 4-/7-halo-1*H*-indenes and 5-methyl-3-bromo-4-/6*H*-cyclopenta[*b*]thiophenes were shown to be convenient starting materials for Suzuki−Miyaura, Negishi, and Murahashi protocols to give the corresponding aryl-subsituted indenes and cyclopenta[*b*]thiophenes of importance for further synthesis of *ansa*-metallocenes. Alternatively, (2-methyl-1*H*-inden-4-yl)boronic acid and (1-methoxy-2-methyl-2,3-dihydro-1*H*-inden-4-yl)boronic acid as well as the respective organozinc and -magnesium reagents can be used for synthesizing aryl-subsituted indenes via the Pd-catalyzed reactions with aryl halides. These synthetic methods were shown to have a very broad scope to afford libraries of aryl-substituted indenes. Finally, synthesis and structure characterization of several representative chiral *ansa*-zirconocenes, potentially useful as components of highly active and stereoselective olefin polymerization catalysts, have been performed.

Introduction

The last 15−20 years have witnessed major advances in α-olefin polymerization catalyst chemistry: in particular, the stereochemical control of polypropylene synthesis using metallocene-based catalysts. A very important contribution came from Brintzinger et al., who were the first to obtain C_2-symmetrical *ansa*-metallocenes.[1a] These chiral stereorigid complexes were soon investigated by Ewen[1b] and Kaminsky and Brintzinger et al.[1c] as precatalysts in propylene polymerization. The respective zirconium complexes in the presence of a suitable activator, such as MAO,[2] $B(C_6F_5)_3$, $[CPh_3]^+[B(C_6F_5)_4]^-$,[2b,3] etc. were found to give new homogeneous, highly stereoselective catalysts for polymerization of α-olefins.[4] Extensive studies of the relationship between *ansa*-metallocene structure and activity/stereoselectivity of the respective propylene polymerization catalysts showed that, in the general case, the best results are observed for so-called advanced *ansa*-zirconocenes of structure **A** involving a dimethylsilanediyl−bis(indenyl) chelating ligand



bearing methyl in position 2 and aryl in position 4 of the indenyl fragments.[5] The slightly different geometries of analogous *ansa*-heterocenes involving cyclopenta[*b*]thiophene fragments seems to exert a dramatic effect on the stereoselectivity of the respective catalysts in propylene polymerization. Thus, an additional methyl in a position ortho to sulfur is apparently required to obtain the best results (structure **B**).[6]

Though many complexes of this type have been studied so far at major research centers all over the world, several possibilities for changing the coordination environment of zirconium to enhance activity and/or stereoselectivity of the respective catalysts remain largely unexplored. First of all, the introduction of various aryls in position 4 of the indenyl or heteroindenyl fragments of zirconocenes is of interest. Of analogous importance would be the study of a similar structural change for zirconocenes involving, for example, methyls in position 5 or 6 of the indenyls in structure **A** or without methyl in a position ortho to sulfur in a metallocene of type **B**, etc. Another important problem is the investigation of such metallocene families for development of polymerization catalysts targeted mostly at the design of new highly specific catalytic systems for the preparation of novel brands of special polyolefins with controlled sets of properties, including morphology, uniform particle size distribution, physicomechanical parameters, etc., due to highly stereoselective and stereochemically stable catalysts.

It should be noted that theoretical investigations involving quantum-chemical calculations on the relationship between catalyst structure and catalytic activity have recently been performed for a number of catalytic systems, though satisfactory results were obtained in only a few cases.[7] It is obvious that reasonable theoretical models for catalytic systems involving

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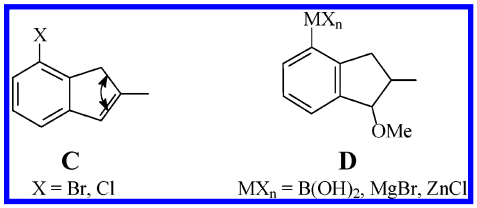
transition metals are still too complex to allow computations at high levels of theory. Therefore, currently and for at least the near future, there is no alternative to experimental testing of various catalysts, conditions, additives, etc.

Until recently, in olefin polymerization catalyst studies, high-throughput methods of research were not applied. The first reports on such approaches appeared around 5 years ago.[8] There is yet another important incentive for the development of catalyst screening. Indeed, currently, the major industrial processes are (i) gas-phase polymerization of ethene and propene, (ii) suspension polymerization of ethene, and (iii) propene polymerization in liquid monomer solution. In all of these processes, highly effective catalysts (e.g., Ziegler-type catalysts) are used. Technological and economic reasons command the application of heterogeneous (supported) catalysts, which, however, suffer from considerable inhomogeneity of active center distribution and modest net activity. Supported catalysts of the new generation are expected to overcome these significant drawbacks. The new generation of supported metallocene catalysts features active centers of rigorously defined structure uniformly distributed over the surface. Such catalysts based on metallocenes will allow design of fully automated polymerization processes. On the other hand, any quantitative theoretical reasoning for supported catalysts is a much more sophisticated procedure than for homogeneous catalysts, well beyond the current level of theoretical calculations. Thus, empirical high-throughput screening is apparently the only way to new generation catalysts and processes. The sources of potential catalysts should be manifold: in addition to screening of available samples and conventional synthesis, high-output procedures for parallel concurrent synthesis of tens and hundreds of new compounds employing fast and highly reliable transformations of organometallic compounds. From this point of view, various metal-catalyzed cross-coupling procedures using, for example, readily available arylboronic acids and parental halo-substituted metallocenes would be desirable. Unfortunately, similar procedures have not been realized so far for several reasons: in particular, instability of the coordination environment of zirconium under the conditions for cross-coupling. Moreover, the chiral *ansa*-zirconocenes are known to epimerize readily in the presence of various additives[9] or on irradiation with light.[10] Alternatively, high-throughput catalytic cross-coupling reactions of the respective haloindenes and related substrates can be used (see also ref 11) to synthesize libraries of arylindenes and then *ansa*-zirconocenes of types **A** and **B**, of interest for olefin polymerization. It is desirable to develop in this way such conditions for Pd-catalyzed cross-coupling under which a possible side intermolecular Heck reaction with the olefinic fragment of indenes is suppressed.[12]

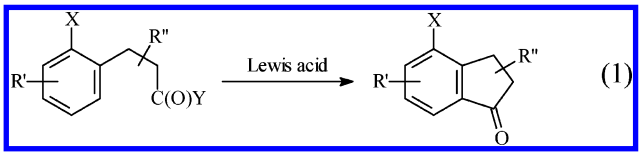
Thus, this work is aimed at the development of convenient and high-yield Pd-catalyzed cross-coupling procedures for 4-/7-halo-1*H*-indenes and related substrates to obtain the respective 4-/7-aryl-1*H*-indenes and analogues, including aryl-substituted heteroindenes, currently available only via multistage procedures.[6] First, we analyze general synthetic methods to obtain starting haloindenes and show how these methods work for the selected substrates. Next, Pd-catalyzed synthesis of various arylindenes from haloindenes is described in detail; in particular the Suzuki−Miyaura, Negishi, and Murahashi protocols for the key substrates **C** and **D** are compared. Finally, the synthesis of



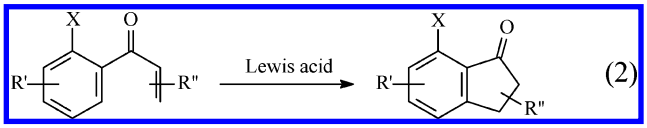
the selected bis(indenyl)dimethylsilanes and the respective *ansa*-zirconocenes has been performed to illustrate the approach for the development of potential olefin polymerization catalysts.

Results and Discussion

Synthesis of 4-/7-Halo-2-methyl-1*H*-indenes and Analogues. Two general selective methods can be used to synthesize 4-/7-halo-2-methylindan-1-ones and analogous compounds starting from the readily available substrates, i.e. (1) intramolecular acylation of 3-(2-halophenyl)-2-methylpropanoyl chloride and related compounds under Friedel−Crafts conditions (eq 1; X



= Cl, Br, I; Y = Cl, OH, etc.) to afford 4-/7-bromoindan-1-ones[11a,13]) and (2) Lewis-acid-catalyzed Nazarov cyclization of 1-(2-halophenyl)-2-methyl-2-propen-1-one and related compounds (eq 2; X = Cl, Br, I).[13j,14]



Next, 4-/7-halo-2-methyl-1*H*-indenes can be obtained via the reduction of the respective 4-/7-halo-2-methylindan-1-ones followed by dehydration of the substituted indan-1-oles formed.

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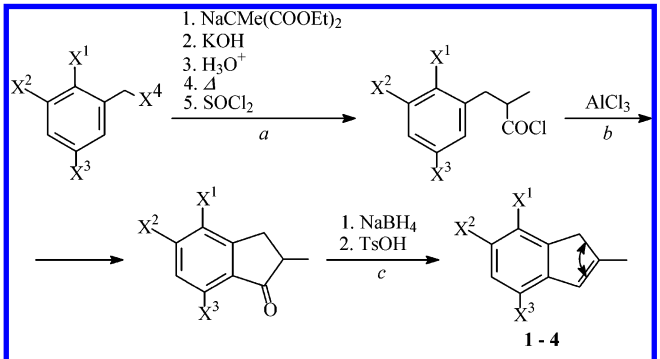
Alternatively, 4-/7-halo-2-methyl-1*H*-indenes can be obtained via ortho lithiation of the respective indan-1-oles[15] followed by lithium−halogen exchange with subsequent dehydration. Several alternative procedures to obtain the desired 4-/7-haloindan-1-ones or the respective haloindenes can be applied for this purpose also, though their scope is very narrow.[16] At the same time, other reported methods were found to result in undesirable mixtures of products or include multistage transformations of low synthetic interest.[14d,17] The only example to be mentioned separately is direct electrophilic halogenation of indan-1-ones (containing no substituents in position 7) and related substrates in the presence of Lewis acids.[18] This method is very useful for the preparative synthesis of some 4-/7-halo-1*H*-indenes[19] (see below).

Here, to synthesize 4-/7-bromo-2-methyl-1*H*-indenes **1**−**4**, we used the first method mentioned above: i.e., the Lewis acid catalyzed cyclization of the respective 3-(2-halophenyl)-2-methylpropanoyl chlorides as shown in eq 3. The starting 3-(2-

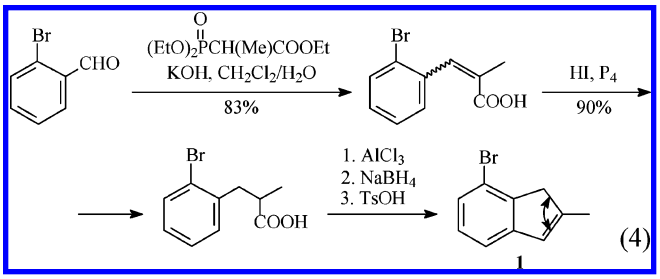


compound	X^1	X^2	X^3	X^4	yield, % *a*	*b*	*c*
1	Br	H	H	Br	79	95	93
2	Cl	H	H	Cl	86	91	75
3	Br	Me	H	Br	94	90	85
4	H	Br	Br	Br	91	94	92

(3)

halophenyl)-2-methylpropanoyl chlorides were obtained via the standard malonate method, which is based on the reaction of the respective benzyl halide with sodium diethylmethylmalonate followed by saponification of ester and then decarboxylation of the dibasic acid. 3-Aryl-2-methylpropanoic acids formed were converted into the respective acid chlorides, giving 2-methylindan-1-ones via Lewis acid catalyzed cyclization. The reduction of 2-methylindan-1-ones with $NaBH_4$ followed by acid-catalyzed dehydration gave the desired indenes **1**−**5** as mixtures of isomers. It should be noted that *p*-toluenesulfonic acid is a softer and more selective acidic catalyst than, for example, P_4O_{10} for dehydration of the alcohol. In some cases, the use of P_4O_{10} leads to partial oligomerization of indene formed and, therefore, a decreased yield of product. The malonate method has been applied to synthesize many different aryl-/alkyl-substituted indenes[5] and 4-bromo-1*H*-indene.[11a] The most important problems in this case are (1) availability of the desired benzyl halide and (2) selectivity of the Lewis acid-catalyzed cyclization reaction (stage *b*, eq 3) if X^1 is hydrogen and $X^2 \neq X^3$. For the synthesis of **1**−**4**, the selectivity is apparently not an issue. Indene **1** was obtained as a colorless oil consisting of two isomers, i.e., 7-bromo-2-methyl-1*H*-indene (71% by HPLC) and a minor isomer, 4-bromo-2-methyl-1*H*-indene (29%). The major isomer crystallizes slowly at room temperature and, thus, was isolated in an analytically pure form. The analogous Cl-substituted indene **2** was obtained as a ca. 1:9 (HPLC) mixture of 4- and 7-chloro-2-methyl-1*H*-indenes. The isomeric compositions of **3** and **4** were found to be ca. 7.7:1 and 10:1 (NMR) in favor of 7-bromo-2,6-dimethyl-1*H*-indene and 5,7-dibromo-2-methyl-1*H*-indene, respectively.

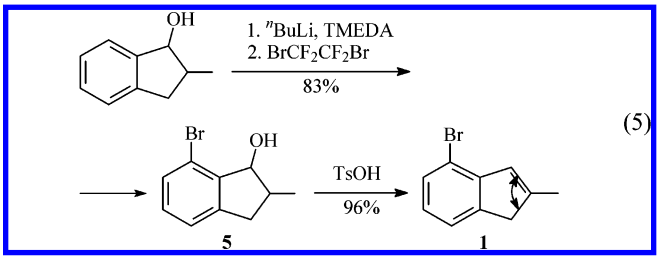
Alternatively, 3-(2-bromophenyl)-2-methylpropanoic acid was synthesized via the reaction of *o*-bromobenzaldehyde with triethyl 2-phosphonopropionate[20] followed by reduction of the substituted cinnamic acid formed (eq 4). This procedure gave



(4)

the desired saturated acid in 75% total yield. The reduction was carried out using red phosphorus in aqueous HI at reflux.[21] Then, the substituted propanoic acid was converted into 4-bromo-2-methylindan-1-one and indene **1** as shown in eq 4.

A very promising synthetic procedure for 4-/7-halo-1*H*-indenes is based on the ortho lithiation[22] of readily available 1-indanoles. For instance, the reaction of 2-methyl-1-indanole with ^{n}BuLi/TMEDA in pentane for 10 h at reflux followed by treatment with 1,2-dibromoperfluoroethane[23] gave 7-bromo-2-methyl-1-indanol (**5**) in 83% yield at 93% conversion (HPLC) of the starting material (eq 5). It should be noted that this



(5)

procedure was optimized to achieve a better yield. Further, 4-bromo-2-methyl-1*H*-indene was obtained from **5** in almost quantitative yields as shown below.

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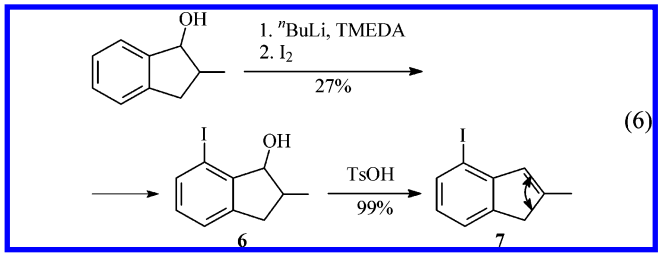
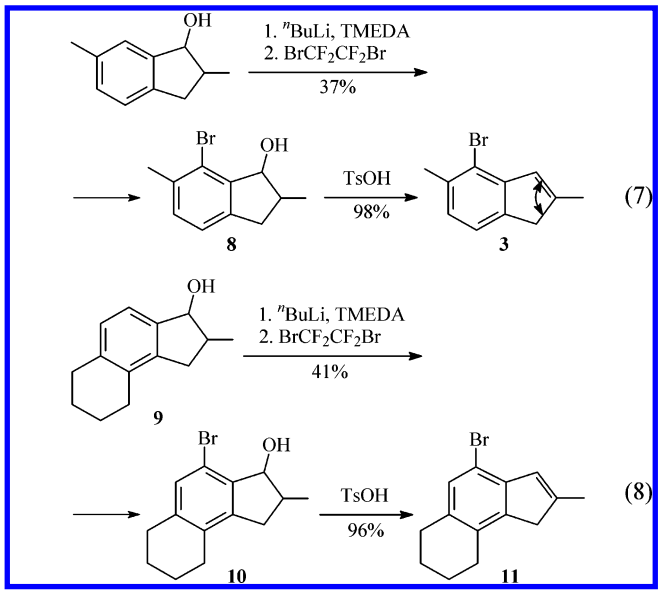
The treatment of the ortho-lithiated product with iodine in an ether/*n*-pentane mixture resulted in 7-iodo-2-methyl-1-indanol (**6**), isolated in as low as 27% yield (eq 6). Side oxidation of



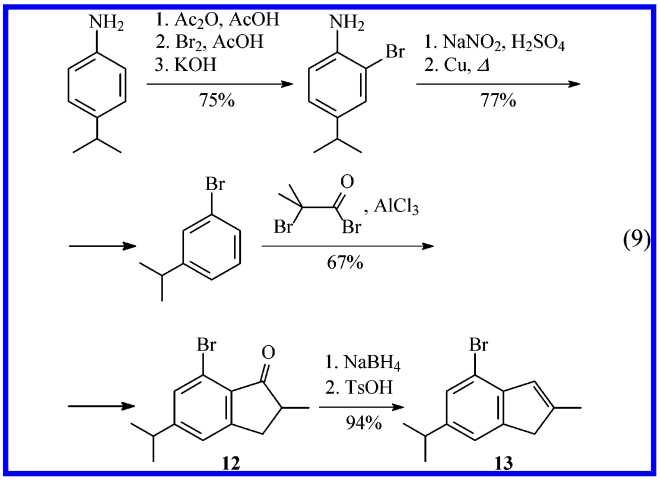
the starting lithium salt with iodine to form some radical coupling products seems to explain this relatively low yield observed. 7-Iodo-2-methyl-1*H*-indene (including ca. 3% of another isomer) was further synthesized from **7** in almost quantitative yield, as shown in eq 6.

This straightforward and practical method was shown to work well for other 1-indanoles studied. Though conditions of these reactions were not optimized, 7-bromo-2,6-dimethyl-1-indanol (**8**) and 4-bromo-2-methyl-2,3,6,7,8,9-hexahydro-1*H*-cyclopenta[*a*]naphthalen-3-ol (**10**) were synthesized in this way by starting from 2,6-dimethyl-1-indanol (eq 7) and 2-methyl-2,3,6,7,8,9-



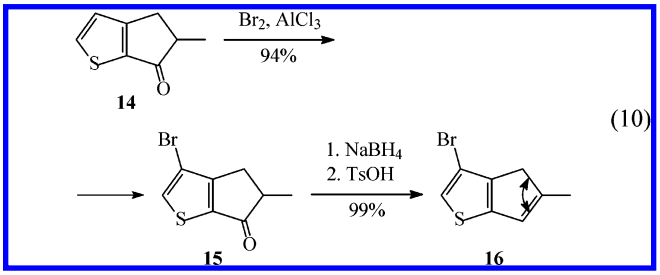
hexahydro-1*H*-cyclopenta[*a*]naphthalen-3-ol (**9**) (eq 8) in 37 and 41% yields at 57 and 59% conversions (HPLC) of the starting materials, respectively. Thus, the corresponding bromoindenes **3** and **11** were isolated in 36 and 39% overall yields, respectively.

The other synthetic method used by us is the one-pot acylation of arene by 2-bromoisobutyryl bromide followed by Nazarov cyclization.[24,25] Thus, 4-bromo-6-isopropyl-2-methyl-1-indanone (**12**) and indene **13** were obtained from 4-isopropylaniline as shown in eq 9. In this way, bromination of *N*-(4-isopropylphenyl)acetamide followed by deamination of the deprotected aniline gave 1-bromo-3-isopropylbenzene in 53% total yield. One-pot acylation−cyclization of this substrate with a mixture



of 2-bromoisobutyryl bromide and $AlCl_3$ in dichloromethane resulted in 7-bromo-5-isopropyl-2-methyl-1-indanone in 67% yield. This reaction is very sensitive to the conditions used; thus, the yield is shown for the optimized procedure. Finally, the reduction of the obtained indanone by $NaBH_4$ followed by dehydration resulted in indene **7** as a pure 4-bromo-substituted isomer.

Next, 3-bromo-5-methyl-4*H*-cyclopenta[*b*]thiophene (**16**) was obtained via the reactions shown in eq 10. The key stage of



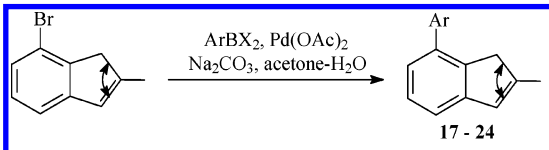
this synthesis is the regioselective bromination of 5-methyl-5,6-dihydro-4*H*-cyclopenta[*b*]thiophen-4-one (**14**), giving bromoindanone **15** in 94% yield. The observed high regioselectivity of this reaction seems to result from the concerted directing effect of the substituents (2-acyl and 3-alkyl) in the thiophene ring. Though the synthesis of an analogous dibromide, 2,3-dibromo-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one, via electrophilic dibromination of 4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one was described,[25c] monobromination has never been used. In contrast, 2,5-dimethyl-3-bromo-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one, a half-product of interest for synthesizing promising olefin polymerization catalysts, was obtained via multistage transformations as described by Ewen et al.[25d,e] It should be noted that the starting ketone **14** can be obtained from thiophene and methacrylic acid via a published procedure.[25f,g] Thus, the bromination of this ketone followed by its reduction and then acid-catalyzed dehydration gave thioindene **16** including ca. 5% of the other isomer, 3-bromo-5-methyl-6*H*-cyclopenta[*b*]thiophene.

(23) (a) Wang, W.; Snieckus, V. *J. Org. Chem.* **1992**, *57*, 424. (b) Paquette, L. A.; Ross, R. J.; Shi, Y.-J. *J. Org. Chem.* **1990**, *55*, 1589. (c) Paquette, L. A.; DeRussy, D. T.; Gallucci, J. C. *J. Org. Chem.* **1989**, *54*, 2278.

(24) (a) Kizhner, N. *Zh. Russ. Fiz.-Khim. O-va.* **1914**, 1411. (b) Fabrycy, A.; Bal, S.; Majewski, E.; Soroka, J. *Polish J. Chem.* **1978**, *52*, 2059. (c) Stehling, U.; Diebold, J.; Kirsten, R.; Röll, W.; Brintzinger, H.-H. *Organometallics* **1994**, *13*, 964.

(25) (a) Schneider, N.; Huttenloch, M. E.; Stehling, U.; Kirsten, R.; Schaper, F.; Brintzinger, H.-H. *Organometallics* **1997**, *16*, 3413. (b) Foster, P.; Raush, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1998**, *571*, 171. (c) Garreau, R.; Roncali, J.; Garnier, F.; Lemaire, M. *J. Chim. Phys., Phys. Chim. Biol.* **1989**, *86*, 93. (d) 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. (e) Ewen, J. A.; Jones, R. L.; Elder, M. J.; Rheingold, A. L.; Liable-Sands, L. M. *J. Am. Chem. Soc.* **1998**, *120*, 10786. (f) Ryabov, A. N.; Gribkov, D. V.; Izmer, V. V.; Voskoboynikov, A. Z. *Organometallics* **2002**, *21*, 2842. (g) Meth-Cohn, O.; Gronowitz, S. *Acta Chim. Scand.* **1966**, *20*, 1577.

Synthesis of Arylindenes from Haloindenes and Their Derivatives via Cross-Coupling Reactions. The palladium-catalyzed Suzuki−Miyaura coupling reaction has been used for decades as a powerful tool for synthesizing biaryls.[26−29] For simple aryl bromides, this reaction is known to be carried out using $Pd(OAc)_2$ as a catalyst and Na_2CO_3 as a base in acetone or an acetone−H_2O mixture (3/1 v/v). We applied these conditions to synthesize 4-/7-aryl-2-methyl-1*H*-indenes from 4-/7-bromo-2-methyl-1*H*-indene (1 equiv) and the respective arylboron derivatives (1 mol for $RB(OH)_2$ and 0.25 mol for $NaBPh_4$) using 2 mol % of $Pd(OAc)_2$ as a catalyst and 3 equiv of Na_2CO_3 (eq 11). This reaction works well for a wide range

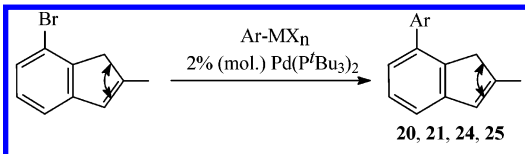


(11)

compound	Ar	Ar source	yield, %
17	Ph	$NaBPh_4$	92
18	4-^{t}BuC$_6$H$_4$	4-^{t}BuC$_6$H$_4$B(OH)$_2$	90
19	2-MeC$_6$H$_4$	2-MeC$_6$H$_4$B(OH)$_2$	89
20	1-naphthyl	(1-naphthyl)B(OH)$_2$	94
21	2,4,6-Me$_3$C$_6$H$_2$	2,4,6-Me$_3$C$_6$H$_2$B(OH)$_2$	<1
22	2-MeOC$_6$H$_4$	2-MeOC$_6$H$_4$B(OH)$_2$	71
23	3-O$_2$NC$_6$H$_4$	3-O$_2$NC$_6$H$_4$B(OH)$_2$	92
24	2-thienyl	(2-thienyl)B(OH)$_2$	32

of arylboron substrates and gives, for example, the respective products involving ortho-substituted aryls (**19**, **22**) and naphthyl (**20**) in high yield after 6 h at reflux. However, sterically hindered mesitylboronic acid failed to react under these conditions. 2-Thienylboronic acid gave a low yield of the respective (2-thienyl)indene with this protocol.

As soon as we began to seek a protocol working reliably for as wide a scope of coupling partners as possible that was suitable for combinatorial applications, our attention turned to a new generation of catalysts recently introduced into Pd-catalyzed cross-coupling.[27,29] One of the most convenient catalysts of this type is $Pd(P^tBu_3)_2$, now commercially available.[30] Here, we performed a comparative study of the Suzuki−Miyaura,[26−29] Murahashi,[27−29,31] and Negishi[27−29,31,32] cross-coupling protocols using 4-/7-bromo-2-methyl-1*H*-indene and the representative series of substrates involving *p*-tolyl, 1-naphthyl, mesityl, and 2-thienyl fragments (eq 12). It should be noted that conversion



(12)

MX_n	Ar: 4-MeC$_6$H$_4$	Ar: 1-naphthyl	Ar: 2,4,6-Me$_3$C$_6$H$_2$	Ar: 2-thienyl
	25	**20**	**21**	**24**
	yield, %[a]			
B(OH)$_2$[b]	99(96[e,f])	99	95	71
MgBr[c]	86(0.8[e,g])	51	15[h]	52
ZnCl[d]	99(1.4[e,g])	45[k]	16[k]	87

[a] at almost quantitative conversion of **1**; [b] for 8.5 h in toluene at 110°C with K_3PO_4 as a base; [c] for 24 h in THF at 65°C; [d] for 7 h in THF at 65°C; [e] for **2** at 2% conversion; [f] for 14 h; [g] for 26.5 h; [h] at 44% conversion of **1**; [k] at 46% conversion of **1**.

of **1** in all cases was almost quantitative even if the desired product was obtained in low yield. The studied boronic acids in Suzuki−Miyaura coupling were found to give 4-/7-aryl-2-methyl-1*H*-indenes in high yields. Interestingly, $Pd(P^tBu_3)_2$ catalyzes well the Suzuki−Miyaura coupling of bulky mesitylboronic acid but not the Murahashi and Negishi reactions applying mesitylmagnesium and mesitylzinc reagents, respectively. However, both Suzuki−Miyaura coupling and the Murahashi and Negishi reactions gave isomeric 4-/7-*p*-tolyl-2-methyl-1*H*-indenes from 4-/7-bromo-2-methyl-1*H*-indene in high yield. On the other hand, 4-/7-chloro-2-methyl-1*H*-indene failed to react with *p*-tolylmagnesium and -zinc reagents (a ca. 1% yield of target material at a ca. 5% conversion of **2**) in THF at 65 °C but reacted readily with *p*-tolylboronic acid in toluene at 110 °C. An analogous but less dramatic effect was found in the case of the synthesis of **20**, bearing a 1-naphthyl fragment. Lower yields were observed for **24**, involving the nonbulky 2-thienyl fragment. Probably, thienyl derivatives (products or byproducts) poison the Pd catalyst, causing these lower yields of **24** compared with, for example, the yields of **25**.

Ligandless Suzuki−Miyaura coupling with $NaBPh_4$ was also used for bromoindene **3** bearing a substituent in a position ortho

(26) (a) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749. (b) Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419. (c) Martin, A. R.; Yang, Y. *Acta Chem. Scand.* **1993**, *47*, 221. (d) Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213. (e) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (f) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263. (g) Miyaura, N. In *Advances in Metal-organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Amsterdam, 1998; Vol. 6, pp 187−243. (h) Suzuki, A. In *Metal-catalyzed Cross-coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 49−89. (i) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147. (j) Suzuki, A. In *Organoboranes for Synthesis*; ACS Symposium Series 783; Ramachandran, P. V., Brown, H. C., Eds.; American Chemical Society: Washington, DC, 2001; pp 80−93. (k) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633 and references therein.

(27) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359 and references therein.

(28) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-I., Ed.; Wiley-VCH: Weinheim, Germany, 2002, and references therein.

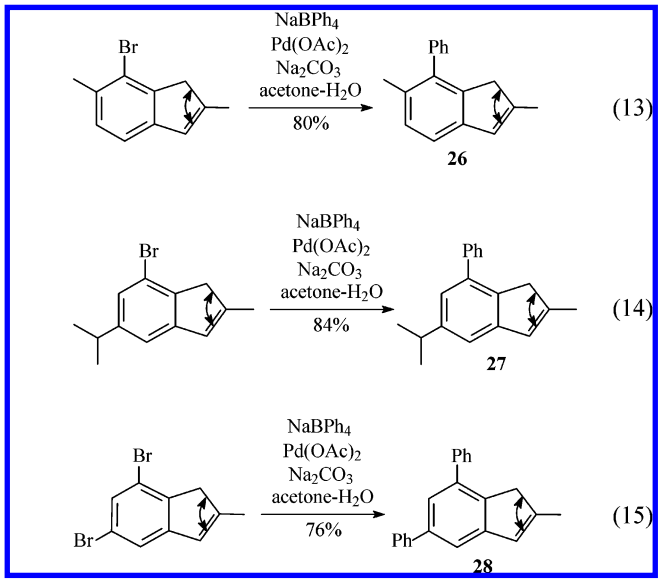
(29) For applications of other bulky, electron-rich phosphines, see: (a) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348. (b) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609. (c) Zhao, S. H.; Miller, A. K.; Berger, J.; Flippin, L. A. *Tetrahedron Lett.* **1996**, *37*, 4463. (d) Reddy, N. P.; Tanaka, M. *Tetrahedron Lett.* **1997**, *38*, 4807. (e) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 7369. (f) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2413. (g) Alt, M. H.; Buchwald, S. L. *J. Org. Chem.* **2001**, *66*, 2560. (h) Yin, J.; Rainka, M. P.; Zhang, X.-X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162. (i) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1871. For applications of carbene ligands, see: (j) Huang, J.; Grasa, G.; Nolan, S. P. *Org. Lett.* **1999**, *1*, 1307. (k) Stauffer, S. R.; Lee, S.; Stambuli, J. P.; Hauck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2*, 1423. (l) Caddick, S.; Cloke, F. G. N.; Clentsmith, G. K. B.; Hitchcock, P. B.; McKerrecher, D.; Titcomb, L. R.; Williams, M. R. V. *J. Organomet. Chem.* **2001**, *617−618*, 635. (m) Gstöttmayr, C. W. K.; Böhm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1363.

(30) Applications of P^tBu_3 are as follows. (a) Negishi reaction: Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 2719. (b) Gauthier, D. R., Jr.; Szumigala, R. H., Jr.; Dormer, P. G.; Armstrong, J. D., III; Volante, R. P.; Reider, P. J. *Org. Lett.* **2002**, *4*, 375. (c) Kumada reaction: Walla, P.; Kappe, C. O. *Chem. Commun.* **2004**, *5*, 564. (d) Buchwald−Hartwig amination: Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 617. (e) Yamamoto, T.; Nishiyama, M.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 2367. (f) Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*, 5575. (g) Lee, S.; Jørgensen, M.; Hartwig, J. F. *Org. Lett.* **2001**, *3*, 2729. (h) Lebedev, A. Y.; Izmer, V. V.; Kazyul'kin, D. N.; Beletskaya, I. P.; Voskoboynikov, A. Z. *Org. Lett.* **2002**, *4*, 623.

(31) Negishi, E.; Liu, F. In *Metal-catalyzed Cross-coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 1−47.

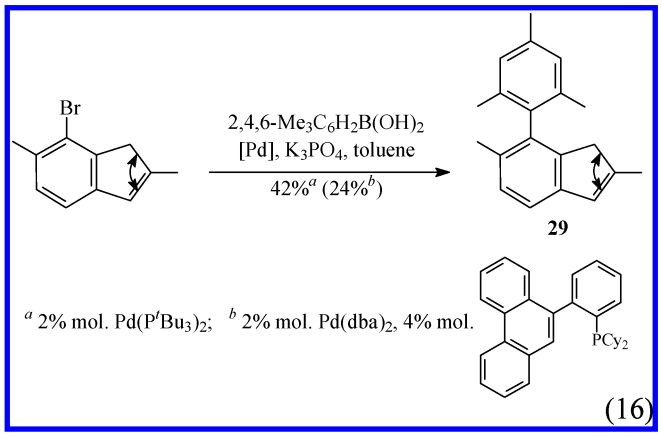
(32) Negishi, E. In *Organozinc reagents. A Practical Approach*; Knochel, P., Jones, P., Eds.; Oxford University Press: London, 1999; pp 213−243, and references therein.

to bromine (eq 13), as well as for bromoindene **13** (eq 14) and dibromoindene **4** (eq 15). In all cases studied, the respective



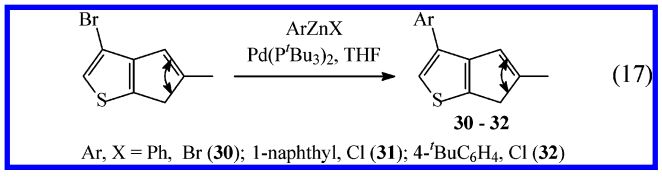
Ph-substituted indenes and diphenylindene **28** were isolated in high yields and unambiguously characterized.

However, an attempt to obtain the sterically crowded arylindene **29** involving four ortho substituents in the biphenyl fragment from bromoindene **3** and mesitylboronic acid using the phosphine-free Pd catalysis failed. Indene **29** was synthesized in moderate yield (42%) using $Pd(P^tBu_3)_2$ as a catalyst and an excess of anhydrous K_3PO_4 as a base in toluene at 110 °C (eq 16). It is of interest that a mixture of $Pd(dba)_2$ and dicyclohexyl-



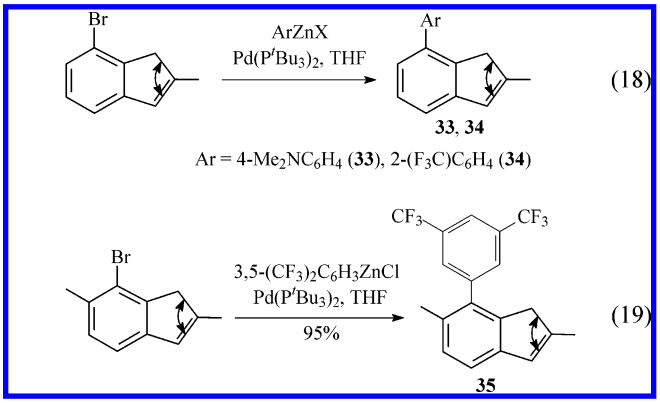
[2-(9-phenanthryl)phenyl]phosphine ligand especially designed to catalyze Suzuki−Miyaura coupling of bulky substrates[29h] gave **29** in only 24% yield.

Further, the Negishi reaction using 3-bromo-5-methyl-4*H*-cyclopenta[*b*]thiophene (**16**) was successfully carried out (eq 17). In this way, a mixture of 5-methyl-3-phenyl-6*H*-cyclopenta-

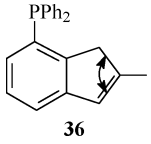


[*b*]thiophene and 5-methyl-3-phenyl-4*H*-cyclopenta[*b*]thiophene (**30**) in a ca. 1/4 ratio was obtained in almost quantitative yield by starting from **16** and phenylzinc bromide in the presence of 2 mol % of $Pd(P^tBu_3)_2$ in THF for 10 h at 70 °C. The same reactions using 1-naphthylzinc chloride gave a ca. 1/2 mixture of 5-methyl-3-(1-naphthyl)-6(4)*H*-cyclopenta[*b*]thiophenes (**31**) in almost quantitative yields. However, the reaction with 4-*tert*-butylphenylzinc chloride gave 5-methyl-3-(4-*tert*-butylphenyl)-6(4)*H*-cyclopenta[*b*]thiophenes (**32**) as the only isomeric product.

Analogously, hetero-substituted arylindenes **33**−**35** were obtained in almost quantitative yields using the Negishi protocol starting from bromoindenes **1** and **3**, respectively, in the presence of $Pd(P^tBu_3)_2$ in THF for 5 h at reflux (eqs 18 and 19).



The other Pd-catalyzed cross-coupling method involved in this study is the Stille reaction with aryltin reagents.[27−29,33] This versatile cross-coupling method is known to be tolerant of a wide range of substituents in aryls. Moreover, while arylboron, -magnesium, and -zinc reagents involving basic heterocyclic fragments, e.g. pyridinyl, are either unstable or difficult to prepare, heteroarylstannanes of this type are readily available stable reagents. Nevertheless, our attempts to apply this reaction to obtain 2-thienyl- and 2-pyridyl-substituted indenes from **1** and the respective heteroarylstannanes failed. The reaction of **1** with (2-thienyl)Sn^nBu_3 in the presence of 2 mol % of $Pd(PPh_3)_4$ in toluene at 120 °C gave the Ph_2P-substituted indene **36**[34] in 6% yield as a result of transfer of the PPh_2 group from

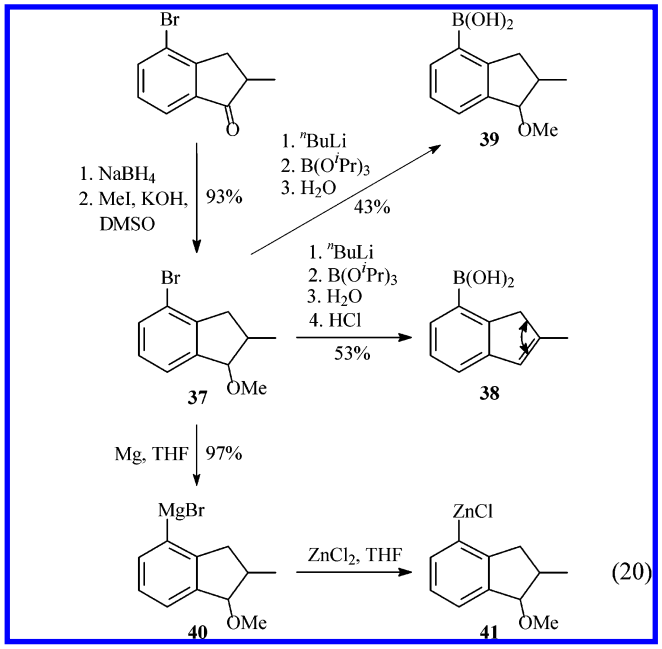


PPh_3 but did not give the desired product **24**. Analogously, 2-(2-methylinden-4-yl)pyridine was not obtained in the Pd-catalyzed reaction of **1** with 2-pyridyltin reagent in toluene at reflux. The only product of this reaction was 2,2′-bipyridine, which was isolated in 10% yield.

To access the 2-pyridyl-substituted and analogous indenes, as well as to develop more practical combinatorial procedures for synthesizing libraries of aryl-substituted indenes, we turned our attention to a different strategy and attempted to use the organometallic derivatives of indane as a nucleophilic coupling partner. We aimed, first, to synthesize such reagents and, then, to study the scope of their Pd-catalyzed reactions. An isomeric mixture of indenylboronic acids **38** was obtained in moderate yield from 4-bromo-1-methoxy-2-methylindane (**37**)[35] (eq 20).

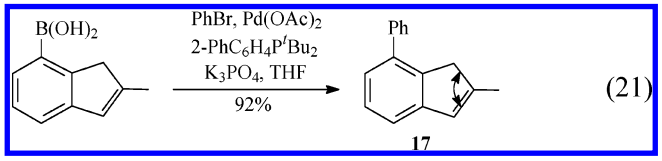
The alternative substrate, 1-methoxy-2-methyl-2,3-dihydroinden-4-ylboronic acids (**39**), was prepared as a mixture of

(33) (a) Farina, V.; Krishnamurthy, V.; Scott, W. J. *The Stille Reaction*; Wiley-VCH: Weinheim, Germany, 1998. (b) Mitchell, T. N. In *Metal-catalyzed Cross-coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 167−197, and references therein.



diastereomers in a similar manner, omitting the postreaction acidification by HCl to avoid the elimination of MeOH. Both **38** and **39** can be used as substrates in Suzuki cross-coupling with various aryl bromides (and chlorides). If this reaction is carried out with the MeO derivative **39**, treatment by HCl or TsOH is required to eliminate MeOH and obtain the desired indenes. Boronic acid **38** was obtained after workup of the reaction mixture as a pure 7-isomer. The boron-substituted methoxyindane **39** was isolated in 43% yield as an equimolar mixture of the respective diastereomers, though the individual diastereomers could be separated by fractional crystallization from ethyl acetate. One of them—the trans isomer—was obtained in analytically pure form and characterized by X-ray crystal structure analysis. The molecular structure of *trans*-**39** is shown in Figure 1. The structure consists of molecules bound together by strong hydrogen bonds (B−O−H···O; see the Supporting Information for details).

Boronic acid **38** was found to react readily with bromobenzene in the presence of $Pd(OAc)_2$/2-(di-*tert*-butylphosphino)-1,1′-biphenyl[29a] as a catalyst and K_3PO_4 as a base to give **17** in high yield (eq 21).



Next, we performed the comparative study of the $Pd(P^tBu_3)_2$-catalyzed Suzuki−Miyaura coupling of boronic acid **39**, as well

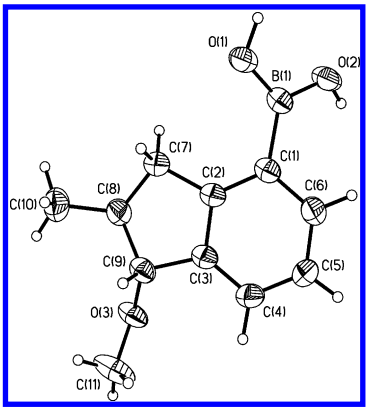
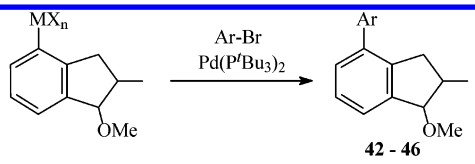


Figure 1. Molecular structure of *trans*-**39** with the non-hydrogen atom labeling scheme. The thermal ellipsoids are drawn at the 50% probability level.

as the Murahashi and Negishi reactions of Grignard and arylzinc reagents **27** and **41** (prepared from **37**), as shown in eq 22. The



MXn	Ar				
	4-MeC_6H_4	1-naphthyl	2,4,6-$Me_3C_6H_2$	2-thienyl	2-pyridyl
	42	**43**	**44**	**45**	**46**
			yield, %[a]		
$B(OH)_2$ (**39**)[b]	97	82 (51[c])	99	69	26
MgBr (**40**)[d]	99	93	60	55	70
ZnCl (**41**)[d]	85	28	54	50	20

[a] at almost quantitative conversion of the starting aryl halide; [b] for 21 h in toluene at 110°C with K_3PO_4 as a base; [c] for 1-chloronaphthalene for 24 h; [d] for 19 h in THF at 75°C.

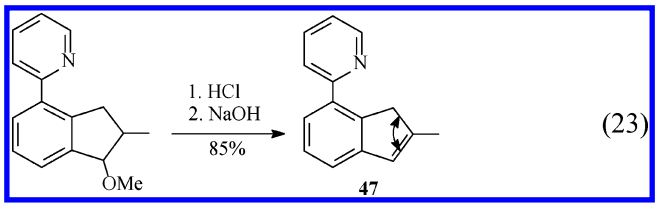
concentration of Grignard reagent **40** in THF solution was established by the standard titration procedure.[36] The concentration of organozinc reagent **41** was estimated by assuming the quantitative conversion of **40** into **41**, ensured by a 2-fold excess of $ZnCl_2$ used to obtain the organozinc reagent. A representative series of various aryl halides was used to study the scope of the cross-coupling reactions (eq 22). In some cases, the methoxyindanes initially formed were not isolated but transformed in situ into indenes by acidification with HCl. Like the Suzuki−Miyaura reaction using 4-/7-bromo-2-methyl-1*H*-indene (eq 12) discussed above, an alternative version of this reaction using boronic acid **39** (eq 22) has been found to give cross-coupling products with *p*-tolyl, 1-naphthyl, mesityl, and 2-thienyl fragments in high yields. However, the latter protocol is advantageous from the combinatorial point of view. Boronic acids are less readily available than aryl halides; therefore, a method that cross-couples a single boronic acid to a series of aryl/heteroaryl indenes is more convenient and productive than the cross-coupling of a simple halide to a series of boronic acids. Similar considerations are relevant for the Murahashi and Negishi reactions of arylmagnesium **40** and -zinc reagents **41** with readily available aryl halides. In all cases, the Murahashi protocol using **40** gave indenes **20**,

(34) **Mixture of (2-methyl-1*H*-inden-4-yl)diphenylphosphine and (2-methyl-1*H*-inden-7-yl)diphenylphosphine (36).** This compound was isolated as a ca. 1/6.5 mixture of 4- and 7-substituted indenes. Anal. Calcd for $C_{22}H_{19}P$: C, 84.06; H, 6.09. Found: C, 83.90; H, 6.14. (2-Methyl-1*H*-inden-7-yl)diphenylphosphine: ^{1}H NMR ($CDCl_3$) δ 7.29−7.33 (m, 10H, PPh_2), 7.23 (m, 1H, 4-H in indenyl), 7.14 (m, 1H, 5-H), 6.64 (ddd, J = 7.6 Hz, J = 5.2 Hz, $^3J_{PH}$ = 1.1 Hz, 1H, 6-H), 5.47 (m, 1H, 3-H in indenyl), 3.20 (m, 2H, CH_2), 2.08 (m, 3H, Me); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 148.0, 147.8, 146.6 (d, J_{PC} = 1.5 Hz), 145.6 (d, J_{PC} = 6.6 Hz), 136.1 (d, J_{PC} = 9.9 Hz), 133.8 (d, J_{PC} = 19.8 Hz), 128.6 (d, J_{PC} = 17.6 Hz), 128.4, 127.5 (d, J_{PC} = 1.8 Hz), 126.8 (d, J_{PC} = 1.8 Hz), 126.7 (d, J_{PC} = 1.5 Hz), 120.3, 42.8 (d, J_{PC} = 10.7 Hz), 16.7; ^{31}P{^{1}H} NMR ($CDCl_3$) δ −14.2. The 4-Ph_2P-substituted indene **36** has been also prepared via an independent route by starting from Grignard reagent **40** and 1 equiv of Ph_2PCl followed by treatment of the reaction mixture with aqueous HCl. In this way, indene **36** has been obtained in 87% yield.

(35) Successful synthesis and application of an analogous substrate—4-bromo-1-(trimethylsiloxy)-2-methylindane—has recently been described in a U.S. patent.[11b]

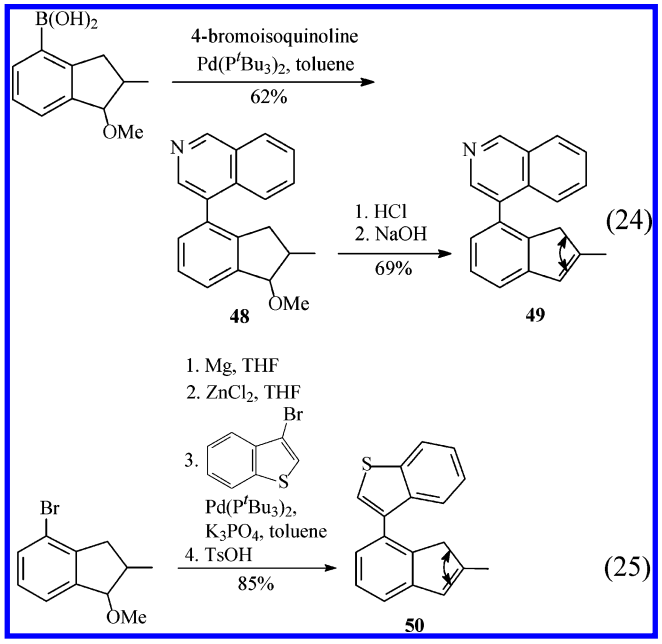
(36) Ioffe, S. T.; Nesmeyanov, A. S. *Methods of Elementoorganic Chemistry: Magnesium, Beryllium, Calcium, Strontium, Barium*; Acad. Sci. USSR Publ.: Moscow, 1963.

21, **24**, and **25** in better yields than the alternative method using **1** as the starting material (eq 12). The lower yields of the products in the latter case are likely to be accounted for by metalation of 4-/7-bromo-2-methyl-1*H*-indene by Grignard reagents. The Murahashi reaction using (1-methoxy-2-methyl-2,3-dihydroinden-4-yl)magnesium bromide was shown to serve better for the cross-coupling with 2-bromopyridine. The respective Suzuki−Miyaura and Negishi cross-coupling reactions gave lower yields of **46**, probably because of complexation of organoboron and -zinc reagents with the pyridine substrate. Thus, the Murahashi protocol gave pyridyl−methoxyindane **46** from **40** in 70% yield. Further, a ca. 1:1.5 mixture of 7- and 4-(2-pyridyl)indenes was obtained after acidification of **46** with 12 M HCl and methanol at reflux followed by treatment of the reaction mixture with aqueous NaOH, as shown in eq 23.



(23)

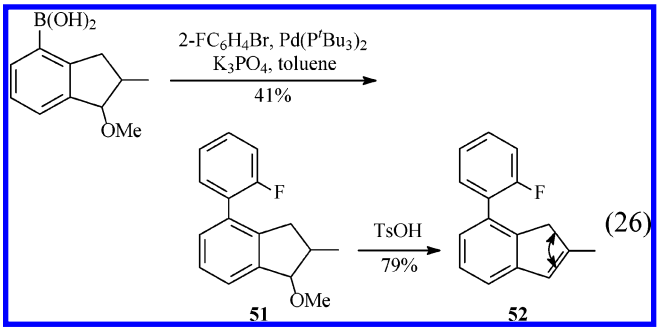
Boronic acid **39** was also used to synthesize various heteroaryl-substituted indenes, such as **49** and **50**, bearing 4-isoquinolyl and 3-benzothienyl fragments, respectively (eqs 24 and 25). Under the conditions studied, 2-bromoisoquinoline gave



(24)
(25)

4-(1-methoxy-2-methyl-2,3-dihydroinden-4-yl)isoquinoline (**48**) in 62% yield and then indene **49** in 43% total yield. Whereas the Suzuki−Miyaura cross-coupling of 4-/7-bromo-2-methyl-1*H*-indene and 1-benzothien-3-ylboronic acid in the presence of 2 mol % of Pd(P^{t}Bu$_3$)$_2$ and an excess of K$_3$PO$_4$ gave **50** in 2−3% yield after 15 h in toluene at reflux, the cross-coupling of the respective organozinc derivative with **41** resulted in **50** in 85% yield.

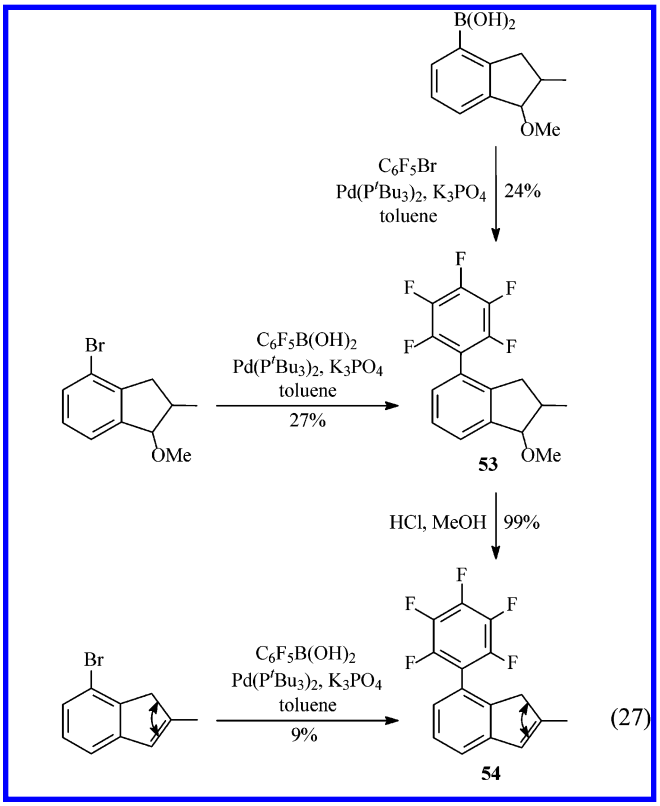
Next, we studied the synthesis of indenes bearing electron-withdrawing fluoroaryl fragments in position 4/7. Boronic acid **39** was found to give 4-(2-fluorophenyl)-1-methoxy-2-methylindane (**51**) and then indene **52**, bearing the electron-withdrawing 2-fluorophenyl fragment (eq 26). Thus, treatment



(26)

of **39** by TsOH gave **52** in 32% yield as a ca. 25/1 mixture of 7- and 4-substituted indenes after 1 h at reflux.

It is of interest that the Pd-catalyzed reaction of **39** with C$_6$F$_5$-Br gave the respective coupling product bearing a C$_6$F$_5$ fragment in low yield (eq 27). Probably, this can be accounted for by the



(27)

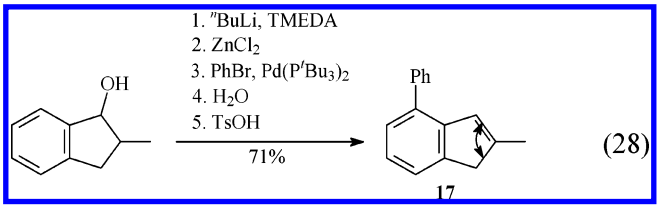
low reactivity of the intermediate C$_6$F$_5$Pd^{II}Br (formed via the oxidative addition of C$_6$F$_5$Br to Pd^0) under the conditions studied.[37] However, the alternative approach using **37** and perfluorophenylboronic acid (to exclude the formation of this unreactive intermediate) also gave the desired coupling product in low yield. Since **53** was found to give indene **54** (as a ca. 9.5/1 mixture of 7- and 4-isomers) readily after 5 h at reflux in an aqueous HCl−methanol mixture, the described two-stage pathways using either **37** or **39** seem to be more useful for obtaining the target indene **54** than the procedure using the Pd-catalyzed reaction of **1** with C$_6$F$_5$B(OH)$_2$, giving **54** in as low as 9% yield.

Thus, either bromo-substituted indene **1** (or its derivative **37**) or boronic acid **39** (as well as the respective Mg and Zn reagents **40** and **41** or indenylboronic acid **37**) can be effectively used as a starting material, depending on the structure of 4-/7-aryl-

(37) Quite recently C$_6$F$_5$Br has been successfully used as a substrate in Pd-catalyzed Heck reactions: Albeniz, A. C.; Espinet, P.; Martin-Ruiz, B.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 11504.

2-methyl-1*H*-indene to be synthesized. Obviously, the methods described can be successfully applied to synthesize other aryl-substituted indene ligands.

Finally, an alternative synthesis of aryl-substituted indenes can be achieved via direct ortho lithiation of 2-methyl-1-indanol or its analogues (see above) followed by Pd-catalyzed coupling of the respective arylzinc reagent with aryl halide. This multistage transformation for 2-methyl-1-indanol was carried out without purification of half-products and found to give **17** in 71% yield (eq 28). In this way, the only time-consuming



(28)

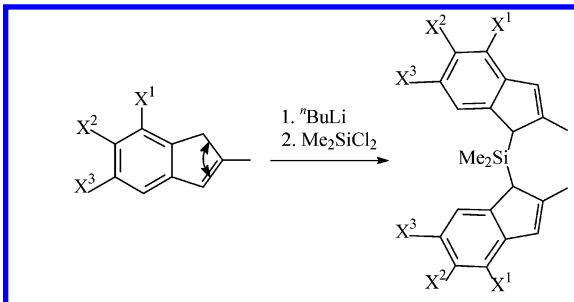
stage is the ortho-lithiation reaction followed by evaporation of the reaction mixture to replace the hydrocarbon solvent by THF and remove excess TMEDA.

Regarding NMR data for the compounds under investigation, the only interesting issue to be discussed is the AB splitting pattern observed in ^{1}H NMR spectra of indenes **20** and **49** for 1,1′-protons of the indenyl system involving unsymmetrical bulky aryls in position 4/7. This inequivalence of CH_2 protons is likely to be explained by hindered rotation of such ortho-substituted aryls around the indenyl−aryl bond. A similar phenomenon was observed for methoxyindane **37**. Similarly to methoxyindanes **37**, **39**, **42**, **45**, **46**, **51**, and **53**, the compounds **43** and **48** each consist of a mixture of two diastereomers. On the other hand, in the ^{1}H NMR spectrum of methoxyindane **44**, bearing a bulky C_2-symmetrical mesityl fragment in position 4, the AB splitting, as expected, is not developed.

Me_2Si-Bridged Ligands and *ansa*-Zirconocenes. Further, to synthesize the respective bis(indenyl)dimethylsilanes using a well-known protocol,[1d] several of the substituted indenes thus prepared were deprotonated with ^{n}BuLi and then treated with 0.5 equiv of Me_2SiCl_2, as shown in eq 29. Ligands **56**−**60** and **64**−**66** were isolated as 1/1 mixtures of *rac* and *meso* diastereomers using flash chromatography. Ligands **55**, **61**, and **63** were obtained by low-temperature crystallization as pure racemates, while ligand **62** was obtained in this way as a ca. 1/1 mixture of *rac* and *meso* isomers.

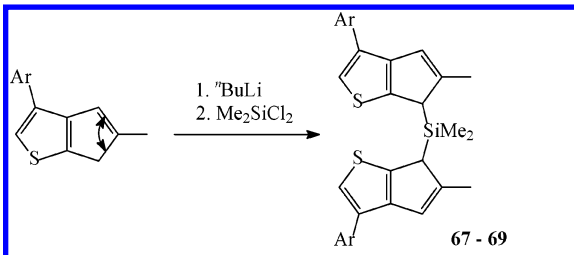
Analogously, the bridging ligands **67** (Ar = Ph), **68** (Ar = 1-naphthyl), and **69** (Ar = 4-^{t}BuC$_6$H$_4$) were obtained using MeLi instead of ^{n}BuLi to metalate the starting cyclopenta[*b*]-thiophene **31** (eq 30). *rac*-**67** and *rac*-**68** were isolated in analytically pure form in 46 and 31% yields, respectively, by crystallization from hexanes. A mixture of *rac*- and *meso*-**69** was isolated in 57% yield by flash chromatography on silica gel.

The bridging ligands **57**−**62** and **64**−**66** were deprotonated with 2 equiv of ^{n}BuLi, and the resulting dilithium bis(indenyls) were treated with $ZrCl_4$ in toluene[5] to give the respective zirconocene dichlorides **70**−**78** (eq 31; yields of analytically pure isomers are shown here and below). Fractional crystallization from toluene at −30 °C gave pure *rac* isomer and a ca. 1/1 mixture of *rac* and *meso* isomers of **74** in 21 and 9% yields, respectively. The analogous procedure for **70**−**72** and **78** gave pure *rac* materials and, in the case of **78**, several crystals of *meso*-zirconocene, which was characterized by an X-ray crystal structure analysis (see below). On the other hand, only *meso*-**75** was isolated as an analytically pure material by low-



(29)

compound	X^1	X^2	X^3	yield, %
55	2-MeC_6H_4	H	H	55
56	2-$MeOC_6H_4$	H	H	58
57	2-$CF_3C_6H_4$	H	H	71
58	4-MeC_6H_4	H	H	65
59	4-^{t}BuC$_6$H$_4$	H	H	60
60	4-$Me_2NC_6H_4$	H	H	49
61	2-thienyl	H	H	37
62	1-benzothien-3-yl	H	H	47
63	Ph	Me	H	54
64	3,5-$(CF_3)_2C_6H_3$	Me	H	72
65	Ph	H	^{i}Pr	55
66	Ph	H	Ph	61



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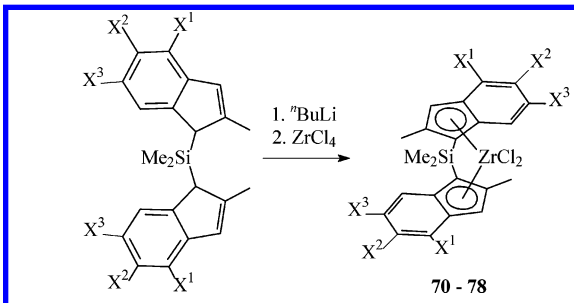


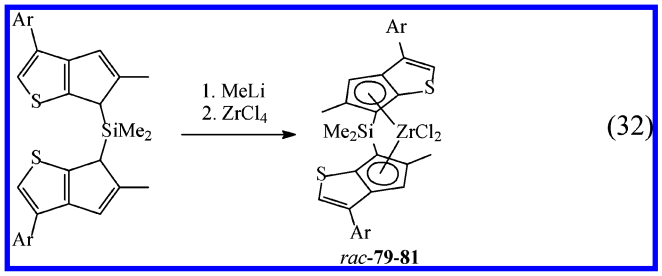
(31)

compound	X^1	X^2	X^3	yield, % *rac-*	yield, % *meso-*
70	2-$CF_3C_6H_4$	H	H	28	
71	4-MeC_6H_4	H	H	35	
72	4-^{t}BuC$_6$H$_4$	H	H	18	
73	4-$Me_2NC_6H_4$	H	H	30	
74	2-thienyl	H	H	21	
75	1-benzothien-3-yl	H	H		15
76	3,5-$(CF_3)_2C_6H_3$	Me	H	19	
77	Ph	H	^{i}Pr	14	
78	Ph	H	Ph	29	

temperature crystallization from toluene. Additionally, this synthesis gave a ca. 4:1 mixture of *rac*- and *meso*-**75** in 20% yield. The complexes *rac*-**73**, *rac*-**76**, and *rac*-**77** were obtained

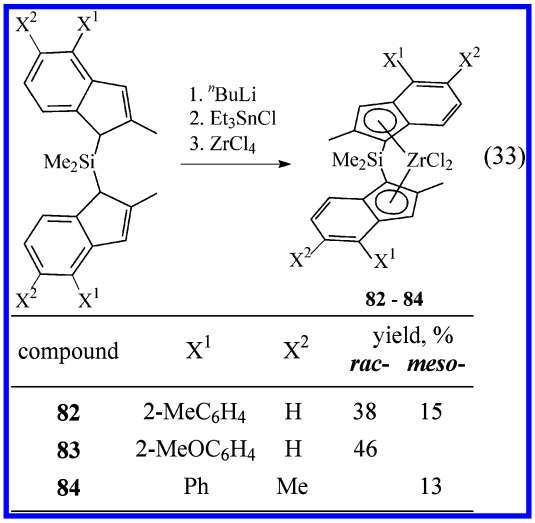
by washing the crude products with dichloromethane. *rac*-**77** was additionally recrystallized from toluene to obtain an analytically pure material.

Next, the deprotonation of **67**−**69** involving cyclopenta[*b*]-thienyl fragments by 2 equiv of MeLi followed by reaction with $ZrCl_4(THF)_2$ in ether gave pure *rac*-**79** (Ar = Ph; eq 32), *rac*-



80 (Ar = 1-naphthyl), and *rac*-**81** (Ar = 4-^{t}BuC$_6$H$_4$). The racemates were isolated in analytically pure form in 37, 41, and 24% yields, respectively, by crystallization from dichloromethane (for **79** and **80**) or toluene (for **81**).

Alternatively, transmetalation using milder organotin reagents[38] was applied to synthesize *ansa*-zirconocenes **82**−**84** (eq 33). In this way, the bridging ligands **55**, **56**, and **63** were



compound	X^1	X^2	yield, % *rac-*	yield, % *meso-*
82	2-MeC$_6$H$_4$	H	38	15
83	2-MeOC$_6$H$_4$	H	46	
84	Ph	Me		13

first deprotonated with 2 equiv of ^{n}BuLi followed by the treatment with 2 equiv of Et_3SnCl to obtain the respective tin-substituted bis(indenyl)silanes. Finally, these organotin reagents and $ZrCl_4$ in toluene gave the desired zirconium complexes. In this case, both *rac* and *meso* isomers of **82** could be obtained by fractional crystallization from toluene. Analogously, analytically pure *meso*-**84** and a ca. 3:1 mixture of *rac* and *meso* isomers were obtained in 13 and 17% yields, respectively. *rac*-**83** contaminated with ca. 8% *meso* complex was obtained from toluene solution at −30 °C.

Next, the solid-state structures of *rac*-**74**, *meso*-**78**, and *rac*-**81** were investigated by X-ray crystallography. The molecular

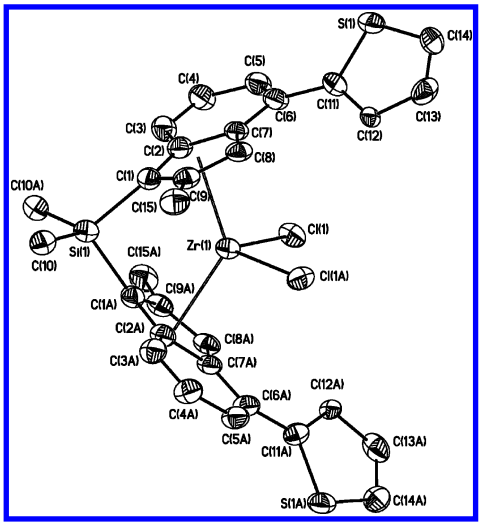


Figure 2. Molecular structure of *rac*-**74** with the non-hydrogen atom labeling scheme. The minor disordered part of the thophene cycle is omitted. Thermal ellipsoids correspond to 50% probability.

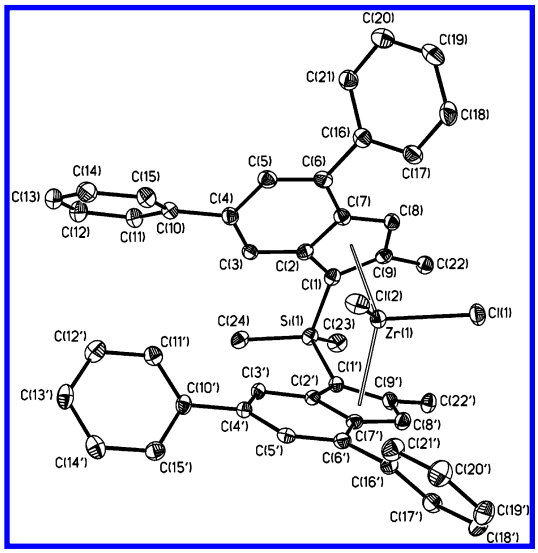


Figure 3. Molecular structure of *meso*-**78** with the non-hydrogen atom labeling scheme. Thermal ellipsoids correspond to 50% probability.

structures of the complexes are illustrated in Figures 2−4, respectively, and selected bond distances and angles are given in Table 1.

The geometry and bonding of these complexes are quite similar to those of other analogous *ansa*-zirconocenes reported in the literature.[5,24c,25a,39] In all three complexes the Zr atom adopts a distorted-pseudotetrahedral coordination. The Zr−Cl and Zr−Cp(c) distances, as well as the Cp(c)−Zr−Cp(c) and Cl−Zr−Cl angles, are comparable to those observed for the

(38) (a) Huttenhofer, M.; Prosenc, M.-H.; Rief, U.; Schaper, F.; Brintzinger, H.-H. *Organometallics* **1996**, *15*, 4816. (b) Nifant'ev, I. E.; Ivchenko, P. V. *Organometallics* **1997**, *16*, 713. (c) Voskoboynikov, A. Z.; Agarkov, A. Y.; Chernishev, E. A.; Beletskaya, I. P.; Churakov, A. V.; Kuz'mina, L. G. *J. Organomet. Chem.* **1997**, *530*, 75. (d) Agarkov, A. Y.; Izmer, V. V.; Riabov, A. N.; Kuz'mina, L. G.; Howard, J. A. K.; Beletskaya, I. P.; Voskoboynikov, A. Z. *J. Organomet. Chem.* **2001**, *619*, 280. (e) Izmer, V. V.; Agarkov, A. Y.; Nosova, V. M.; Kuz'mina, L. G.; Howard, J. A. K.; Beletskaya, I. P.; Voskoboynikov, A. Z. *Dalton Trans.* **2001**, 1131.

(39) (a) Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Spaleck, W.; Winter, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1511. (b) Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1347. (c) Luttikhedde, H. J. G.; Leino, R. P.; Nasman, J. H.; Ahlgren, M.; Pakkanen, T. *J. Organomet. Chem.* **1995**, *486*, 193. (d) Kaminsky, W.; Rabe, O.; Schauwienold, A.-M.; Schupfner, G. U.; Hanss, J.; Kopf, J. *J. Organomet. Chem.* **1995**, *497*, 181. (e) Barsties, E.; Schaible, S.; Prosenc, M.-H.; Rief, U.; Roll, W.; Weyand, O.; Dorer, B.; Brintzinger, H.-H. *J. Organomet. Chem.* **1996**, *520*, 63. (f) Krut'ko, D. P.; Borzov, M. V.; Churakov, A. V.; Lemenovckii, D. A.; Reutov, O. A. *Russ. Chem. Bull.* **1998**, 2351. (g) Maciejewski Petoff, J. L.; Agoston, T.; Lal, T. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 11316. (h) Yoon, S. C.; Park, J.-W.; Jung, H. S.; Song, H.; Park, J. T.; Woo, S. I. *J. Organomet. Chem.* **1998**, *559*, 149.

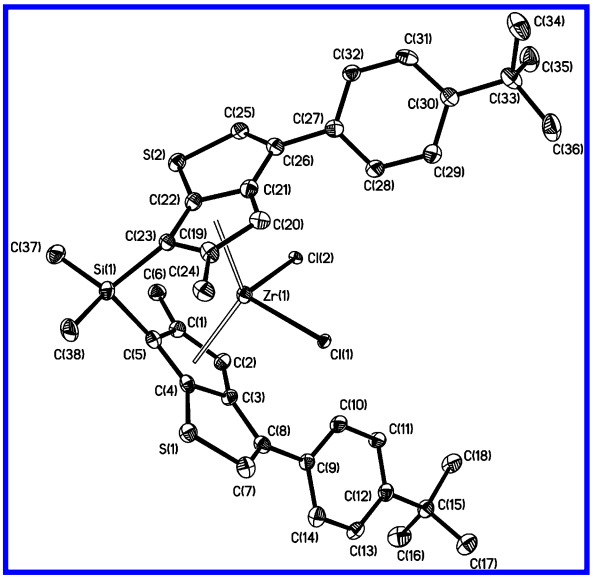


Figure 4. Molecular structure of *rac*-**81** with the non-hydrogen atom labeling scheme. Thermal ellipsoids correspond to 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for *rac*-74, *meso*-78, and *rac*-81

	meso-**78**	*rac*-**81**	*rac*-**74**[a]
Zr(1)−Cl(1)	2.4275(12)	2.4737(17)	2.4282(9)
Zr(1)−Cl(2)	2.4069(12)	2.4753(16)	
Zr(1)−Cp(c)[b]	2.246	2.218	2.241
Zr(1)−Cp(c)′	2.243	2.223	
Si(1)−C_b[c]	1.880(4)	1.869(7)	1.877(3)
Si(1)−C_b′	1.887(4)	1.876(7)	
Cl(1)−Zr(1)-Cl(2)	100.07(4)	98.55(6)	97.44(5)
C_b−Si(1)−C_b′	95.01(17)	94.7(3)	94.8(2)
Cl(1)−Zr(1)−Cp(c)	105.8	132.8	107.7
Cl(1)−Zr(1)−Cp(c)′	104.9	106.2	
Cl(2)−Zr(1)−Cp(c)	105.8	88.6	105.7
Cl(2)−Zr(1)−Cp(c)′	108.2	107.3	
Cp(c)−Zr(1)−Cp(c)′	128.5	128.4	128.4

[a] *C*2/*c* space group. [b] Cp(c) denotes the centroid of the cyclopentadienyl ring of the indenyl or cyclopenta[*b*]thienyl ligand. [c] C_b corresponds to the bridgehead carbon.

previously studied dimethylsilyl-bridged zirconocene derivatives.[40] Interestingly, the value of the Cp(c)−Zr−Cp(c) angle in dimethylsilyl-bridged zirconocene complexes practically does not depend on the bulk of the substituents at Cp ligands (the range of values is 124.3−128.5° [41]). The bending of the Si−C bonds out of the mean planes of the adjacent C_5 rings is 16.3 and 17.5° for *meso*-**78**, 17.6 and 18.1° for *rac*-**81**, and 8.6° for *rac*-**74**, which has a local 2-fold symmetry. The dihedral angle between the two C_5 fragments is 59.5° for *rac*-**74**, 62.4° for *meso*-**78**, and 59.1° for *rac*-**81**. The angles between indenyl and phenyl rings are 34.2, 56.9, 43.3, and 40.4° for *meso*-**78**, and those between the respective phenyl and thiophenyl rings are 29.3 and 46.9°, respectively, for the major and minor disordered thiophenyl cycles of *rac*-**74** and 40.2 and 44.4° for *rac*-**81**. The phenyl substituents of the opposite indenyl ligands in *meso*-**78** in identical positions are almost perpendicular to each other (the angles between the respective phenyl planes are 108.4°). The disposition of the remaining phenyl substituents in *meso*-**78** is defined by the stacked packing of molecules in the crystal. The *meso*-**78** complex is similar to the other known *meso* isomers in that the two chloride ligands and, hence, the two coordination sites are nonequivalent (see Zr−Cl distances, Table 1), one of them being sterically hindered by the benzo units from both top and bottom, whereas the other is essentially unencumbered.

(40) Cambridge Crystallographic Database, Release 2003, Cambridge.
(41) (a) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121. (b) Ukai, T.; Kawazawa, H.; Ishii, Y.; Bonnett, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

Conclusion

In this work, we have developed convenient strategies for the combinatorial synthesis of 4-/7-aryl-substituted indenes, cyclopenta[*b*]thiophenes, and related ligands of importance to obtain libraries of metallocenes. To realize this approach, we synthesized 4-/7-bromo-substituted indenes using both well-known and novel (e.g., via ortho lithiation of 1-indanols) methods and further studied in detail Pd-catalyzed cross-coupling of these substrates with arylboron, -zinc, and -magnesium reagents. In parallel, a different strategy using organometallic derivatives of indane as nucleophilic coupling partners has been developed. In this way, 4-boron, -zinc, and -magnesium derivatives of 1-methoxy-2-methylindane, as well as the respective indenylboronic acid, were synthesized and unambiguously characterized. These substrates were tested in Pd-catalyzed cross-coupling reactions and shown to have wider scope to access well-designed and not readily available products, such as 4-heteroaryl- and 4-fluoroaryl-substituted 2-methyl-1*H*-indenes. Moreover, the latter protocol is advantageous from the combinatorial point of view. The organometallic derivatives of 1-methoxy-2-methylindane are less readily available than aryl halides; therefore, a method that cross-couples a single organometallic reagent to a series of aryl/heteroaryl halides is more convenient and productive than the cross-coupling of a simple halide to a series of organometallic substrates. Finally, to illustrate the synthetic utility of these protocols, we have reported the synthesis of selected bis(indenyl)dimethylsilanes and the respective *ansa*-zirconocenes of importance for single-site olefin polymerization catalysis.

Experimental Section[42]

General Procedure. All manipulations with compounds which are sensitive to both moisture and air were performed either under an atmosphere of thoroughly purified argon using a standard Schlenk technique or in a controlled-atmosphere glovebox (VAC). Analytical and semipreparative liquid chromatography was performed using a Waters Delta 600 HPLC system including a 996 photodiode array detector, Symmetry C18 (Waters, 60 Å, 5 μm, 4.6 × 250 mm) or Chromolith RP-18 (Merck, 4.6 × 100 mm) columns, and a Nova-Pack C18 column (Waters, 60 Å, 6 μm, 3.9 and 19 × 300 mm), respectively, in a methanol−water mobile phase. For analytical runs, calculations of yields of the products were performed under the assumption that extinction coefficients of isomeric indenes and diastereomeric methoxyindanes are equal. ^{1}H and ^{13}C spectra were recorded with Bruker DPX-300 and Avance-400 spectrometers for 1−10% solutions in deuterated solvents. Chemical shifts for ^{1}H and ^{13}C were measured relative to TMS. In ^{1}H NMR spectra, the assignment was made on the evidence of double-resonance, NOE, and NOEdif experiments. C and H microanalyses were done using a Carlo Erba 1106 analyzer.

Typical Procedure for Suzuki−Miyaura Reaction (Method A). A mixture of 1 mmol of aryl bromide, 1 mmol of arylboronic acid, 3 mmol of K_3PO_4, 10.2 mg (0.02 mmol) of Pd(P^tBu_3)$_2$, and 2 mL of toluene was placed together with a magnetic stirrer bar in an 8 mL vial under the nitrogen atmosphere of a glovebox. The reaction was carried out with vigorous stirring at a preset temperature. Then, this mixture was cooled to ambient temperature and evaporated to dryness. Then, 5 mL of methyl *tert*-butyl ether was

(42) All experimental details can be found in the Supporting Information.

added to the residue. The resulting mixture was passed through a short column with silica gel 60 (40−63 μm, diameter 20 mm, length 30 mm). Additionally, this column was washed with 40 mL of methyl *tert*-butyl ether. The combined eluate was evaporated to dryness. The residue was dissolved in 4 mL of acetonitrile; then, the product was isolated by preparative HPLC.

Typical Procedure for Kumada Reaction (Method B). A mixture of 1 mmol of aryl bromide, 8 mL of a 0.25 M solution of Grignard reagent in THF, 10.2 mg (0.02 mmol) of $Pd(P^tBu_3)_2$, and 3 mL of THF was placed together with a magnetic stirrer bar in a 24 mL vial under the nitrogen atmosphere of a glovebox. The reaction was carried out with vigorous stirring at a preset temperature. Then, this mixture was cooled to ambient temperature and passed through a short column with silica gel 60 (40−63 μm, diameter 20 mm, length 30 mm). Additionally, this column was washed with 30 mL of methyl *tert*-butyl ether. The combined eluate was evaporated to dryness. The residue was dissolved in 4 mL of acetonitrile; then, the product was isolated by preparative HPLC.

Typical Procedure for Negishi Reaction (Method C). A mixture of 1 mmol of aryl bromide, 8 mL of a 0.25 M solution of Grignard reagent in THF, 7 mL of a 0.5 M solution of $ZnCl_2$ in THF, 10.2 mg (0.02 mmol) of $Pd(P^tBu_3)_2$, and 3 mL of THF was placed together with a magnetic stirrer bar in a 24 mL vial under the nitrogen atmosphere of a glovebox. The reaction was carried out with vigorous stirring at a preset temperature. Then, this mixture was cooled to ambient temperature and passed through a short column with silica gel 60 (40−63 μm, diameter 20 mm, length 30 mm). Additionally, this column was washed with 30 mL of methyl *tert*-butyl ether. The combined eluate was evaporated to dryness. The residue was dissolved in 4 mL of acetonitrile; then, the product was isolated by preparative HPLC.

Mixture of 2-(2-Methyl-1*H*-inden-4-yl)thiophene and 2-(2-Methyl-1*H*-inden-7-yl)thiophene (24). To a mixture of 1.74 g (3.40 mmol) of $Pd(P^tBu_3)_2$, 22.0 g (0.17 mol) of 2-thienylboronic acid, and 108 g (0.51 mol) of K_3PO_4 was added a solution of 35.8 g (0.17 mol) of **1** in 500 mL of toluene. This mixture was stirred for 6 h at reflux and then washed with 300 mL of water. The aqueous layer was separated and washed with 400 mL of methyl *tert*-butyl ether. The combined extract was dried over $CaCl_2$ and evaporated to dryness. Fractional distillation gave a yellow oil, bp 144−147 °C/1 mmHg. Yield: 25.9 g (71%). Anal. Calcd for $C_{14}H_{12}S$: C, 79.20; H, 5.70. Found: C, 79.09; H, 5.74. ^{1}H NMR ($CDCl_3$): 2-(2-methyl-1*H*-inden-4-yl)thiophene, δ 7.47 (dd, J = 7.5 Hz, J = 1.1 Hz, 1H, 5-H in indenyl), 7.44 (dd, J = 3.6 Hz, J = 1.1 Hz, 1H, 3-H in thienyl), 7.39 (dd, J = 5.1 Hz, J = 1.1 Hz, 1H, 5-H in thienyl), 7.35 (t, J = 7.5 Hz, 1H, 6-H in indenyl), 7.29 (dd, J = 7.5 Hz, J = 1.1 Hz, 1H, 7-H in indenyl), 7.19 (dd, J = 5.1 Hz, J = 3.6 Hz, 1H, 4-H in thienyl), 6.59 (m, 1H, 3-H in indenyl), 3.57 (m, 2H, CH_2), 2.25 (s, 3H, Me); 2-(2-methyl-1*H*-inden-7-yl)thiophene, δ 7.47 (d, J = 7.5 Hz, 1H, 6-H in indenyl), 7.38 (dd, J = 5.2 Hz, J = 1.3 Hz, 1H, 5-H in thienyl), 7.35 (t, J = 7.5 Hz, 1H, 5-H in indenyl), 7.32 (dd, J = 3.6 Hz, J = 1.3 Hz, 1H, 3-H in thienyl), 7.22 (d, J = 7.6 Hz, 1H, 4-H in indenyl), 7.19 (dd, J = 5.2 Hz, J = 3.6 Hz, 1H, 4-H in thienyl), 7.02 (m, 1H, 3-H in indenyl), 3.40 (m, 2H, CH_2), 2.25 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): 2-(2-methyl-1*H*-inden-4-yl)thiophene, δ 146.8, 146.1, 143.4, 139.4, 129.6, 127.3, 127.04, 126.99, 124.52, 124.49, 123.0, 119.1, 43.8, 16.6; 2-(2-methyl-1*H*-inden-7-yl)thiophene, δ 147.0, 146.1, 145.5, 144.2, 143.1, 127.4, 126.5, 126.3, 125.0, 124.6, 123.8, 122.5, 42.9, 16.8.

Dimethylbis[2-methyl-4-(2-thienyl)inden-1-yl]silane (61). To a solution of 21.0 g (99 mmol) of **24** in a mixture of 260 mL of toluene and 20 mL of THF was added 39.5 mL of 2.5 M (99 mmol) ^{n}BuLi in hexanes dropwise with vigorous stirring at −45 °C. Then 6.0 mL (6.38 g, 49.5 mmol) of dichlorodimethylsilane was added in one portion. The resulting mixture was stirred overnight at room temperature, and 200 mL of cold water was added. The organic layer was separated, dried over $CaCl_2$, and evaporated to dryness. The residue was recrystallized from hexanes−methyl *tert*-butyl ether (1/1 v/v). Yield: 8.67 g (37%) of white solid of ca. 1/1 mixture of *rac* and *meso* isomers. Anal. Calcd for $C_{30}H_{28}S_2Si$: C, 74.95; H, 5.87. Found: C, 75.11; H, 5.98. ^{1}H NMR ($CDCl_3$): δ 7.41 (d, J = 7.5 Hz, 1H, 7-H in indenyl of *rac* compound), 7.37 (d, J = 7.5 Hz, 1H, 7-H in indenyl of *meso* compound), 7.32 (dd, J = 5.1 Hz, J = 1.2 Hz, 2H, 3-H in thienyl of *rac* and *meso* compounds), 7.31 (m, 2H, 5-H in indenyl of *rac* and *meso* compounds), 7.27 (dd, J = 3.5 Hz, J = 1.2 Hz, 1H, 5-H in thienyl of *meso* compound), 7.26 (dd, J = 3.5 Hz, J = 1.2 Hz, 1H, 5-H in thienyl of *rac* compound), 7.12 (t, J = 7.5 Hz, 1H, 6-H in indenyl of *rac* compound), 7.11 (dd, J = 5.1 Hz, J = 3.5 Hz, 2H, 4-H of thienyl in *rac* and *meso* compounds), 7.10 (t, J = 7.5 Hz, 1H, 6-H in indenyl of *meso* compound), 7.07 (s, 3-H in indenyl of *meso* compound), 7.01 (s, 3-H in indenyl of *rac* compound), 3.76 (s, 1-H in indenyl of *meso* compound), 3.73 (s, 1-H in indenyl of *rac* compound), 2.25 (m, 3H, 2-Me in indenyl of *meso* compound), 2.15 (m, 3H, 2-Me in indenyl of *rac* compound), −0.17 (s, 6H, $SiMe_2$ in *rac* compound), −0.19 (s, 3H, Si*Me*Me′ in *meso* compound), −0.24 (s, 3H, SiMe*Me*′ in *meso* compound). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.3, 148.1, 145.8, 143.6, 142.6, 142.4, 127.5, 126.6, 126.2, 126.1, 125.54, 125.51, 125.1, 124.7, 123.0, 122.43, 122.38, 47.8, 47.6, 18.1, 17.9, −5.35, −5.45, −5.51.

Complexes *rac*- and *meso*-74. To a solution of 8.67 g (18 mmol) of **61** in 180 mL of toluene was added 14.4 mL of 2.5 M (36 mmol) ^{n}BuLi in hexanes dropwise at −50 °C. This mixture was stirred overnight at room temperature, and then 4.40 g (19 mmol) of $ZrCl_4$ was added. The resulting mixture was refluxed for 5 h. The precipitate was separated and washed with 4 × 70 mL of hot (90 °C) toluene using a funnel with a glass frit (G4). The combined toluene filtrate was evaporated to dryness. The residue was recrystallized from 200 mL of toluene at −30 °C. Crystals that precipitated at this temperature were collected, washed with 2 × 10 mL of cold toluene, and dried under vacuum. Yield: 2.42 g (21%) of pure *rac*-**74**. Anal. Calcd for $C_{30}H_{26}Cl_2S_2SiZr$: C, 56.22; H, 4.09. Found: C, 56.01; H, 4.16. The mother liquid was evaporated to ca. 50 mL. Crystals precipitating at −30 °C from this solution were collected, washed with 2 × 10 mL of cold toluene, and dried under vacuum. This procedure gave 1.04 g (9%) of a ca. 1:1 mixture of *rac*- and *meso*-**74**. Found: C, 56.13; H, 4.00. ^{1}H NMR (CD_2Cl_2): *rac*-**74**, δ 7.64 (dd, J = 8.7 Hz, J = 0.9 Hz, 2H, 7,7′-H in indenyl), 7.45 (dd, J = 7.1 Hz, J = 0.8 Hz, 2H, 5,5′-H in indenyl), 7.36 (dd, J = 3.6 Hz, J = 1.2 Hz, 2H, 3,3′-H in thienyl), 7.32 (dd, J = 5.1 Hz, 1.2 Hz, 2H, 5,5′-H in thienyl), 7.09 (m, 2H, 3,3′-H in indenyl), 7.08 (dd, J = 5.1 Hz, J = 3.6 Hz, 2H, 4,4′-H in thienyl), 7.05 (dd, J = 8.7 Hz, J = 7.1 Hz, 2H, 6,6′-H in indenyl), 2.22 (d, J = 0.5 Hz, 6H, 2,2′-Me in indenyl), 1.31 (s, 6H, $SiMe_2$); *meso*-**74**, δ 7.62 (dt, J = 8.7 Hz, J = 0.8 Hz, 7,7′-H in indenyl), 7.30 (dd, J = 5.1 Hz, J = 1.2 Hz, 2H, 5,5′-H in thienyl), 7.28 (dd, J = 3.6 Hz, J = 1.2 Hz, 3,3′-H in thienyl), 7.20 (dd, J = 7.1 Hz, J = 0.8 Hz, 2H, 5,5′-H in indenyl), 7.07 (dd, J = 3.6 Hz, J = 5.1 Hz, 2H, 4,4′-H in thienyl), 6.98 (m, 2H, 3,3′-H in indenyl), 6.79 (dd, J = 8.7 Hz, J = 7.1 Hz, 2H, 6,6′-H in indenyl), 2.45 (d, J = 0.5 Hz, 6H, 2,2′-Me in indenyl), 1.44 (s, 3H, Si*Me*Me′), 1.24 (s, 3H, SiMe*Me*′).

Crystal Structure Determinations. Data were collected on a Siemens P3/PC four-circle automated diffractometer (λ(Mo Kα) radiation, graphite monochromator, $\theta/2\theta$ scan mode) for *trans*-**39** and on a Bruker SMART 1000 CCD diffractometer (λ(Mo Kα) radiation, graphite monochromator, ω and φ scan modes) for *rac*-**74**, *meso*-**78**, and *rac*-**81** and corrected for Lorentz and polarization effects (for *trans*-**39**, *rac*-**74**, *meso*-**78**, and *rac*-**81**) and for absorption (for *rac*-**74**, *meso*-**78**, and *rac*-**81**).[43] For details, see Table 2.

(43) Sheldrick G. M. SADABS, V2.01, Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS, Madison, WI, 1998.

Table 2. Crystallographic Data for *trans*-39, *rac*-74, *meso*-78, and *rac*-81

	trans-**39**	*rac*-**74**	*meso*-**78**·0.5C_7H_8	*rac*-**81**·C_7H_8
empirical formula	$C_{11}H_{15}BO_3$	$C_{30}H_{26}Cl_2S_2SiZr$	$C_{49.5}H_{42}Cl_2SiZr$	$C_{45}H_{50}Cl_2S_2SiZr$
fw	206.04	640.84	827.04	845.18
temp (K)	293(2)	120(2)	110(2)	112(2)
cryst size (mm)	0.30 × 0.20 × 0.20	0.40 × 0.20 × 0.20	0.30 × 0.30 × 0.10	0.35 × 0.30 × 0.25
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_1/n$
a, Å	7.777(2)	13.299(3)	9.961(3)	10.373(2)
b, Å	8.536(2)	14.064(3)	13.732(4)	22.669(5)
c, (Å)	8.748(2)	14.392(3)	16.317(4)	17.646(4)
α (deg)	80.84(3)	90.0	66.730(4)	90.0
β (deg)	72.12(3)	98.414(5)	82.080(5)	97.91(3)
γ (deg)	78.97(3)	90.0	74.276(4)	90.0
V (Å^3)	539.3(2)	2663(1)	1972.3(9)	4110(1)
Z	2	4	2	4
d_{calcd} (Mg m^{-3})	1.269	1.598	1.393	1.366
F(000)	220	1304	854	1760
μ (mm^{-1})	0.089	0.835	0.480	0.559
θ range (deg)	2.45−26.06	2.12−28.05	2.48−26.37	1.47−27.03
index range	$0 \le h \le 9$	$-17 \le h \le 12$	$-11 \le h \le 12$	$-8 \le h \le 13$
	$-10 \le k \le 10$	$-12 \le k \le 18$	$-16 \le k \le 17$	$-14 \le k \le 28$
	$-10 \le l \le 10$	$-18 \le l \le 19$	$-20 \le l \le 20$	$-22 \le l \le 22$
no. of rflns collected	2302	7756	10 629	19 361
no. of unique rflns	2133	3207	7432	8908
no. of rflns with $I > 2\sigma(I)$	1607	2196	5133	3902
R1; wR2 ($I > 2\sigma(I)$)	0.0431; 0.1197	0.0452; 0.0917	0.0565; 0.1336	0.0733; 0.1493
R1; wR2 (all data)	0.0649; 0.1253	0.0712; 0.1008	0.0833; 0.1506	0.1253; 0.1934
no. of data/restraints/params	2133/0/196	3207/6/183	7432/2/657	8908/0/460
GOF on F^2	1.045	1.023	0.979	0.888
largest diff peak/hole (e Å^{-3})	0.248/−0.215	0.978/−0.385	1.583/−0.656	1.209/−0.748
abs cor T_{max}; T_{min}		0.851; 0.813	0.970; 0.850	0.928; 0.884

The structures were solved by direct methods and refined by full-matrix least squares against F^2 in anisotropic (for non-hydrogen atoms) approximation. All the H(C) atom positions were calculated and refined in isotropic approximation in a riding model with the U_{iso}(H) parameters equal to 1.2[U_{eq}(Ci)] and for methyl groups equal to 1.5[U_{eq}(Cii)], where U(Ci) and U(Cii) are respectively the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded. The solvate toluene molecule in the structure *meso*-**78** is disordered over two positions related by an inversion center. The thiophenyl cycle of the molecule *rac*-**74** is disordered over two positions related by a 43° rotation around the C(6)−C(11) bond with the site occupancy factors being equal to 0.8 and 0.2. All calculations were carried out with the SHELXTL (PC version 5.10) program package.[44] Crystallographic data for *trans*-**39**, *rac*-**74**, *meso*-**78**, and *rac*-**81** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 294827−294830. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk; web, www.ccdc.cam.ac.uk).

(44) Sheldrick, G. M. SHELXTL, V5.10; Bruker AXS Inc., Madison, WI, 1997.

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Supporting Information Available: Text giving all experimental procedures and tables and CIF files giving crystal structure data for *trans*-**39**, *rac*-**74**, *meso*-**78**, and *rac*-**81**. This material is available free of charge via the Internet at http://pubs.acs.org.

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