Group 4 Metallocenes Bearing η^5-2-(*N*-Azolyl)indenyl Ligands: Synthesis, Structure Characterization, and Olefin Polymerization Catalysis

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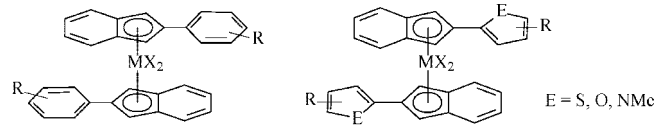
The Pd-catalyzed cross-coupling reactions of readily available 2-bromo-1*H*-indene with 1*H*-pyrrole, 1*H*-indole, 9*H*-carbazole, and their derivatives were shown to be convenient methods to obtain novel ligands containing azole fragments bonded with cyclopentadienyl via nitrogen. An alternative protocol using enol triflates of 1-indanone or 2-indanone is also useful, particularly for synthesizing indenes bearing the *N*-azolyl fragment in position 1. On the other hand, the synthesis of 2-(1*H*-benzimidazol-1-yl)-1*H*-indene can be achieved via the Cu-catalyzed reactions only. The substituted indenes with the *N*-azolyl fragment in position 2 were further used for obtaining several semisandwich complexes of zirconium, [η^5-2-(*N*-azolyl)indenyl]zirconium tribromides, as well as symmetrical and unsymmetrical Waymouth-type zirconium and hafnium complexes containing indenyl ligands bearing planar *N*-azolyl or aryl fragments in position 2. These metallocenes were unambiguously characterized, including by X-ray crystal structure analysis, and a study of the fluxional behavior of several Waymouth-type complexes in solution was carried out by NMR spectroscopy. Finally, novel Waymouth-type complexes, after being activated by MAO, were found to form active catalysts of ethylene homopolymerization and ethylene/1-octene copolymerization.

Introduction

Since the 1950s, a tremendous advance in the stereoselective polymerization of prochiral olefins, particularly propylene, using homogeneous and supported catalysts based on the group 4 metallocenes[1] has been made. Such catalysts can be used to produce an unprecedented variety of polyolefin materials. The most successful efforts in stereoselective olefin polymerization were directed toward synthesis of isotactic polypropylenes (iPP) having many industrial applications.[2] Another promising polypropylene material is a highly stretchable atactic−isotactic stereoblock polymer having elastomeric properties: i.e., the so-called elastomeric polypropylene (ePP). This polymer was first described by Natta et al. as early as 1957,[3] with the most remarkable contribution made by Waymouth et al., who developed an effective process leading to ePP using a metallocene catalyst involving an unbridged complex of type **A** (M = Zr, Hf; X = halogen, hydrocarbyl) activated by MAO.[4a−c] In the latter case, the detailed analysis of the ePP structure performed by Busico et al.[4d] using high-field ^{13}C NMR spectroscopy gave some insight into the polymerization mechanism and reveled a particular role of the conformationally "locked" *rac*-like species. Thus, the bulkiness of the aryl substituents, propene concentration, reaction temperature, solvent polarity, and nature of the cocatalyst (the counterion effect) were found to play a crucial roles in the polymer stereoblock structure.



Since the publication of the first work of Waymouth et al., researchers have obtained a large number of complexes of type **A**, including compounds bearing bulky a aryl group in position 2 of the indenyl ligands. An interesting variation, namely the replacement of aryl by heteroaryl substituents in metallocenes of type **B**, was reported by Erker et al.[4e,f] 5-Methylthien-2-yl-substituted complexes activated by MAO were used to carry out propylene polymerization, giving ePP with slightly improved mechanical properties. However, the respective 1-methylpyrrol-2-yl-substituted catalyst system was found to behave substantially differently, leading only to the formation of an atactic propene oligomer, even at −20 °C. Taking into account these

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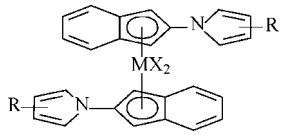
data, one can assume that a catalyst bearing the electron donor pyrrol-1-yl fragment in position 2 of the indenyl ligands can show a better performance in ePP synthesis. However, until recently, it was not clear how to obtain 2-(*N*-azolyl)indenes for synthesizing the respective group 4 metal complexes.

In this work, we aimed to study the unbridged metallocenes of type **C** (M = Zr, Hf; X = Cl, Br) bearing 2-(*N*-azolyl)indenyl ligands instead of the geometrically similar 2-arylindenyls as in the traditional Waymouth-type metallocenes (type **A**) or Erker's heterosubstituted complexes (type **B**). The difference

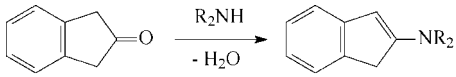


C

of electronic effects and geometry of *N*-azolyl and similarly substituted aryl fragments is apparently a major factor influencing the activity and stereochemistry of the respective catalysts. However, it should be noted that a detailed study of olefin polymerization is outside the scope of this paper. Herein, we describe the synthesis of metallocenes of type **C** and their analogues, as well as a structural study of these complexes in the solid state and solution. Additionally, different approaches to the desired *N*-azolyl-substituted indenes, particularly palladium-catalyzed protocols, are considered in detail.

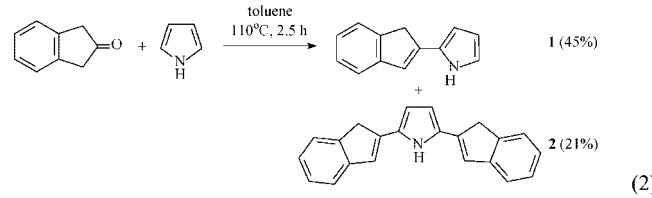
Results and Discussion

Synthesis of 2-(1*H*-Pyrrol-1-yl)-, 2-(1*H*-Indol-1-yl)-, and 2-(9*H*-Carbazol-9-yl)-1*H*-indenes via the Pd-Catalyzed Amination of 2-Bromo-1*H*-indene. 2-Indanone is known to react readily with the nucleophilic secondary amines to form 2-R_2N-substituted indenes (eq 1).[5] This approach has been recently applied for synthesizing metallocene ligands.[6] However, similar condensation with 1 equiv of the less nucleophilic 1*H*-pyrrole gave on reflux in toluene a mixture of 2-(1*H*-inden-2-yl)-1*H*-pyrrole (**1**) and 2,5-bis(1*H*-inden-2-yl)-1*H*-pyrrole (**2**) (eq 2), but not the desired 1-(1*H*-inden-2-yl)-1*H*-pyrrole. This result



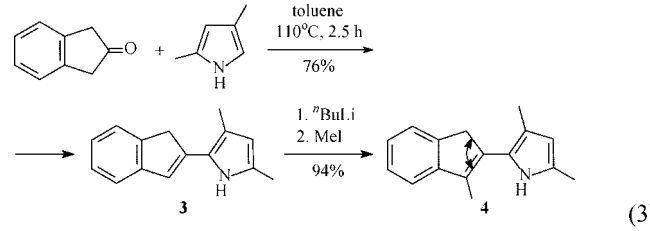
(1)

is unremarkable, as the condensation of pyrrole with aldehydes and ketones is well-known to give C−C bonds, instead of C−N bonds. For instance, pyrrole and substituted pyrroles with at least one unsubstituted α-position react with ketones to form



(2)

2,2′-bis(1*H*-pyrrol-2-yl)propanes.[7] Other products, including indolizine, indoles,[8] and pyrroles substituted with α,β-unsaturated fragments,[9] can be formed in such reactions. Next, 2,5-dimethyl-1*H*-pyrrole, as its lithium salt or 1-Me_3Sn derivative, was found not to react with 2-indanone. However, 2,4-dimethyl-1*H*-pyrrole with one free α-site reacts with 2-indanone to form 2-(1*H*-inden-2-yl)-3,5-dimethyl-1*H*-pyrrole (**3**) in almost quantitative yield (eq 3). In order to use this product for further metallocene synthesis, the acidic NH site needed to be methylated. However, methylation of the lithiated derivative lead instead to a mixture of isomeric 1(3)-Me-substituted indenes (**4**) rather than the desired 2-(1*H*-inden-2-yl)-1,3,5-trimethyl-1*H*-pyrrole, probably because the acidities of NH and CH sites in this compound are comparable while the nucleophilicity of the carbanion is undoubtedly much higher than that of the pyrrolyl anion. The well-known pathways to *N*-vinylazoles, such



(3)

as addition of azoles to acetylenes[10] and the Trofimov reaction,[11] cannot be used to obtain 2-(*N*-azolyl)-1*H*-indenes, since the

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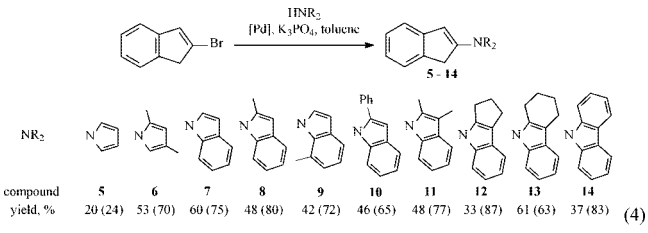
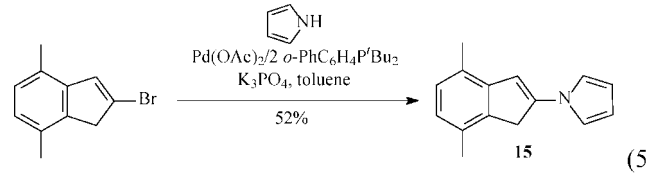
respective acetylenes do not exist. An alternative approach, the acid-catalyzed dehydration of 2-(*N*-azolyl)indan-1-ols, can hardly be expected to be useful. In fact, a few examples of such elimination were described in the literature[12] because vinylazoles are apparently not stable under acidic conditions of elimination. Therefore, the catalytic amination of 2-bromo-1*H*-indene seems to be the only appropriate alternative for synthesizing the desired ligands from azoles. Recently, we have shown that lithium salts of azoles are the best substrates for Pd-catalyzed vinylation of azoles.[13−15] For instance, indolylpotassium or -sodium and *trans*-β-bromostyrene gave 1-[(*E*)-2-phenylethenyl]-1*H*-indole in very low yield, while indolyllithium gave an almost quantitative yield of this product. However, we have found that a similar reaction of 1*H*-indole with 2-bromo-1*H*-indene in the presence of Pd(dba)$_2$/2 *o*-PhC$_6$H$_4$P^{t}Bu$_2$ cannot be performed using indolyllithium as a source of the indolyl fragment, probably because of transmetalation with 2-bromo-1*H*-indene. Alternative coupling reactions between 2-bromo-1*H*-indene and 1-(trimethylsilyl)-1*H*-pyrrole (5 mol % Pd(PPh$_3$)$_4$, toluene, 10 h, 20 °C) or 1-(trimethylstannyl)-1*H*-indole (4 mol % of Pd(dba)$_2$/2 *o*-PhC$_6$H$_4$P^{t}Bu$_2$, toluene, 10 h, 50 °C) were altogether unsuccessful. Finally, we found that the desired indenylindole can be obtained under less basic conditions, i.e. using K$_3$PO$_4$ as base, and nonmetalated azoles such as pyrrole, indole, carbazole, and their derivatives (eq 4; the isolated yields or HPLC yields are given in parentheses).



(4)

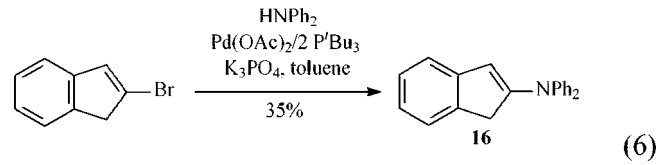
An optimization of this procedure for 1*H*-pyrrole showed that 2 mol % of Pd(OAc)$_2$/2 *o*-PhC$_6$H$_4$P^{t}Bu$_2$ is the best catalyst, giving 1-(1*H*-inden-2-yl)-1*H*-pyrrole (**5**) in 24% yield (HPLC) after 46 h in toluene at room temperature, and this compound was isolated in 20% yield. Alternatively, a catalyst such as Pd(OAc)$_2$/2 P^{t}Bu$_3$ (2 mol %) gave **5** in as low as 7% yield after 24 h at ambient temperature. No product was formed if these reactions were performed in toluene at elevated temperatures (70−110 °C), though 2-bromo-1*H*-indene was recovered in high yield. Surprisingly, a similar reaction with 2-bromo-4,7-dimethyl-1*H*-indene in the presence of 1 mol % of Pd(dba)$_2$/2 *o*-PhC$_6$H$_4$P^{t}Bu$_2$ proceeded readily at 75 °C and gave the substituted indene **15** in as high as 52% yield for 24 h (eq 5).



(5)

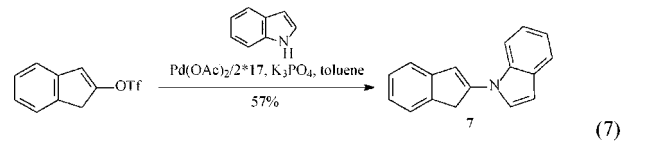
Further on, using 2 mol % of Pd(OAc)$_2$/2 P^{t}Bu$_3$ as a catalyst, other substituted indenes **6**−**14** bearing substituted pyrrole fragments were synthesized in moderate yields in toluene at 80 °C (eq 4). 2,5-Dimethyl-1*H*-pyrrole failed to react with 2-bromo-1*H*-indene under the conditions employed, probably because of steric reasons. It is of interest that the Pd-catalyzed vinylation of this azole with *trans*-β-bromostyrene was shown to proceed readily at elevated temperatures,[13] though 2,5-dimethyl-1*H*-pyrrole failed to react with more sterically crowded substrates, such as *cis*-β-bromostyrene, 2-bromopropene, and obviously 2-bromo-1*H*-indene.

Additionally, the only weakly nucleophilic amine studied by us was diphenylamine, which reacted with 2-bromo-1*H*-indene in the presence of 4 mol % of Pd(OAc)$_2$/2 P^{t}Bu$_3$ in toluene to form *N*-(1*H*-inden-2-yl)-*N*,*N*-diphenylamine (**16**) in 35% yield after 9 h at 70 °C (eq 6).



(6)

Actually, the synthesis of the indenes bearing an azole substituent on the cyclopentadienyl ring can be achieved in an alternative manner: i.e., via the Pd-catalyzed coupling of the triflate of 2-indanone enol in the presence of K$_3$PO$_4$ as a base.[14a,c,n,p] On the evidence of HPLC, this reaction with 1*H*-indole gave indene **7** in 57% yield in the presence of 4 mol % of Pd(dba)$_2$ and 8 mol % of 2-dimethylamino-2′-(di-*tert*-butylphosphino)biphenyl (**17**) after 9 h at 85 °C (eq 7).



(7)

Synthesis of 3-(1*H*-Pyrrol-1-yl)- and 3-(1*H*-Indol-1-yl)-1*H*-indenes. The scope of this protocol is wider than that of the protocol using vinyl halides as the starting substrates, since many different vinyl triflates obtained from cyclopentenones and indanones are potentially available. For instance, 1*H*-inden-3-yl triflate (**18**) can be readily obtained from 1-indanone,[16] while the respective 3-halo-1*H*-indenes are known to be less thermally

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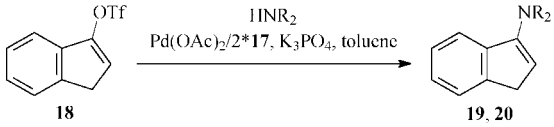
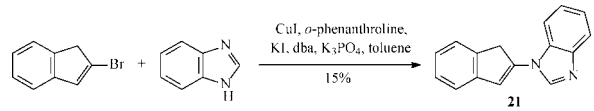
stable and, therefore, less useful.[17] Vinyl triflate **18** was found to react readily with 1*H*-pyrrole and 1*H*-indole, forming the 3-substituted indenes **19** (NR_2 = 1*H*-pyrrol-1-yl) and **20** (1*H*-indol-1-yl) in 31 and 45% yields, respectively, after 24 h in toluene at reflux (eq 8). Alternatively, several attempts to obtain **20** from 3-halo-1*H*-indene failed, probably because of a low thermal stability of the latter substrate.



(8)

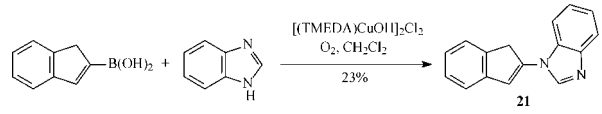
Synthesis of 2-(1*H*-Benzimidazol-1-yl)-1*H*-indene. In order to obtain zirconium complexes bearing 1*H*-benzimidazol-1-yl-substituted indenyl ligands, we first aimed to synthesize the respective substituted indenes. The unactivated aryl halides are known to react with 1*H*-benzimidazole to form 1-aryl-1*H*-benzimidazoles in the presence of copper catalysts.[18] The only described example of the Cu-catalyzed vinylation of 1*H*-benzimidazole required an ionic liquid as a solvent[19] or use of a polydentate iminopyridine ligand.[15] An attempt to apply this protocol developed for the copper-catalyzed arylation/vinylation of other N−H substrates with aryl/vinyl halides[20] failed. Thus, the reaction between 2-bromo-1*H*-indene and 1*H*-benzimidazole gave 1-(1*H*-inden-2-yl)-1*H*-benzimidazole (**21**) and a byproduct of the halogen exchange,[21] i.e. 2-iodo-1*H*-indene, in 3 and 5% yields, respectively, in the presence of 10 mol % of CuI, 40 mol % of $MeNHCH_2CH_2NHMe$, 1 equiv of KI, and 3 equiv of K_2CO_3 in toluene for 48 h at reflux. In the presence of 20 mol % of CuI, 1 equiv of KI, 1 equiv of phenanthroline, 40 mol % of dibenzylideneacetone (dba), and 2 equiv of Cs_2CO_3 (eq 9) the yield of indene **21** was higher but still did not exceed a meager 15%.

Alternatively, the vinylation can be achieved by the use of respective boronic acids in the oxidative cross-coupling reaction.



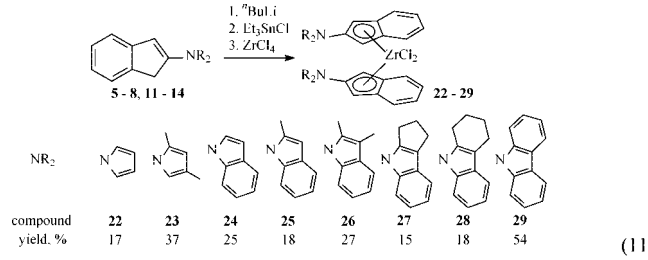
(9)

This approach was recently applied for the arylation of azoles,[22] as well as for the vinylation of 1*H*-benzimidazole.[22d] In this manner, 2 equiv of (1*H*-inden-2-yl)boronic acid have been found to react in air with 1 equiv of 1*H*-benzimidazole to form **21** in a moderate yield in the presence of 30 mol % of $[(TMEDA)CuOH]_2Cl_2$ in dichloromethane for 15 h at room temperature (eq 10). Indene **21** was isolated by flash chromatography on silica gel and unambiguously characterized by NMR spectroscopy and other means.



(10)

Synthesis of Bis[η^5-2-(*N*-azolyl)indenyl]zirconium and -hafnium Dichlorides. Transmetalation reactions using organotin reagents[23] were applied for synthesizing Waymouth-type zirconocenes from the 2-N-substituted indenes described above. In this way, the ligands **5**−**8** and **11**−**14** were deprotonated by ^{n}BuLi (eq 11) and then treated with Et_3SnCl to obtain the respective tin-substituted indenes. Finally, a reaction of the toluene solution of the organotin reagent with 0.5 equiv of $ZrCl_4$ gave **22**−**29**, which were isolated in analytically pure form by crystallization from toluene. The metallocenes **22**, **26**, and **28** were characterized by X-ray crystal structure analyses (see below).



(11)

These complexes can be also obtained via direct transmetalation using the lithium salt of the respective ligand and 0.5 equiv of $ZrCl_4$.[1] For instance, in this way, complex **29** was obtained in as high as 66% yield. Analogously, zirconium

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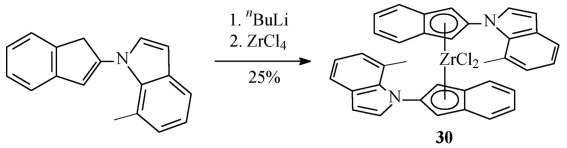
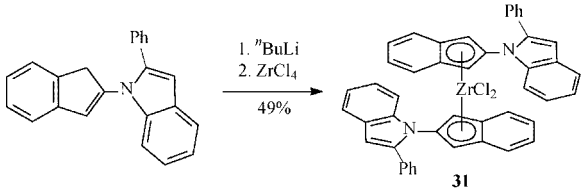
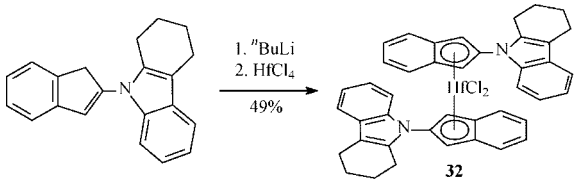
complexes **30** and **31**, including 7-methylindol-1-yl and 2-phenylindol-1-yl fragments, respectively, as well as the hafnium complex **32**, bearing N-substituted tetrahydrocarbazole fragments, and Zr and Hf complexes **33** and **34**, involving pyrrole-substituted 4,7-dimethylindenyl ligands, were successfully obtained using direct transmetalation from the lithium salts of indenes **9** (eq 12), **10** (eq 13), **13** (eq 14), and **15** (eq 15). Thus, the complexes **30**−**34** were isolated in analytically pure form in 25, 49, 49, 37, and 45% yields, respectively.



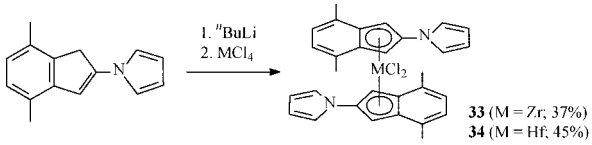
(12)



(13)

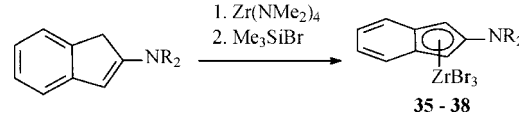


(14)



(15)

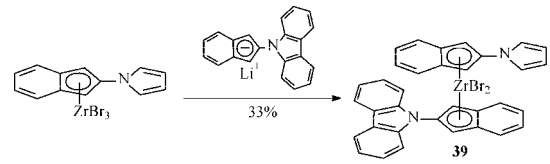
Synthesis of [η^5-2-(*N*-Azolyl)indenyl]zirconium Tribromides. The second aim of this work was to develop synthetic pathways to unsymmetrical Waymouth-type zirconocenes bearing two different 2-(*N*-azolyl)indenyl ligands or 2-arylindenyl and 2-(*N*-azolyl)indenyl ligands. In order to obtain the former compounds, first, the synthesis of [2-(*N*-azolyl)indenyl]zirconium tribromides ($Cp'ZrBr_3$) was developed. In this way, indenes **5**, **7**, **9**, and **14** reacted with $Zr(NMe_2)_4$, forming the respective tris(dimethylamido)[2-(*N*-azolyl)indenyl]zirconium complexes in ether at room temperature.[24] The following treatment of the crude tris-amide complexes thus formed with 4 equiv of Me_3SiBr resulted in the target complexes **35** (NR_2 = 1*H*-pyrrol-1-yl), **36** (1*H*-indol-1-yl), **37** (7-methyl-1*H*-indol-1-yl), and **38** (9*H*-carbazol-1-yl) and Me_3SiNMe_2 in toluene at room temperature (eq 16).[24b,c,e,f,i] Analytically pure **35**−**38** were



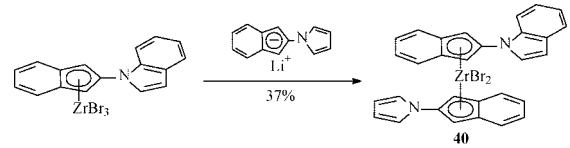
(16)

isolated in 37, 63, 76, and 53% yields, respectively, by crystallization of the crude products from toluene. Complex **36**, as characterized by an X-ray crystal structure analysis (for a full description of the structure, see below), has a dimeric structure with two bridging Br ligands: i.e., $[Cp'ZrBr_2]_2(\mu\text{-}Br)_2$. Also, as confirmed by crystal structure analysis, NMR spectroscopy, and element analysis, the "semi-sandwich" complexes include one solvate molecule of toluene per two Zr units. As the only singlet attributed to the 1,3-protons of indenyl was observed in the ^1H NMR spectrum of **35** (as well as **36**−**38**) in C_6D_6, the symmetrical structure of the dimers is retained in hydrocarbon solutions. The dissociation of a bridged complex involving the $Zr(\mu\text{-}Br)_2Zr$ fragment into monomeric species cannot be realized under the conditions studied. An attempt to obtain **35** using as little as 3 equiv of Me_3SiBr at the last stage failed, since an incomplete substitution of NMe_2 with bromide ligands in the Zr coordination sphere was observed. On the evidence of NMR spectroscopy, a ca. 1:1 mixture of **35** and a new compound was formed. The latter complex includes one NMe_2 per one indenyl ligand and seems to have a symmetrical dimeric structure: e.g., $[Cp'ZrBr_2]_2(\mu\text{-}NMe_2)_2$ or most likely $[Cp'ZrBr(NMe_2)]_2(\mu\text{-}Br)_2$.

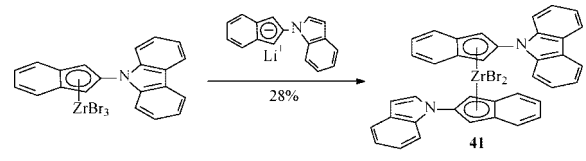
Synthesis of Unsymmetrical Complexes Bearing η^5-2-(*N*-Azolyl)indenyl Ligands. The four unsymmetrical zirconocenes **39**−**42**, bearing 1*H*-pyrrol-1-yl and 9H-carbazol-9-yl, 1*H*-pyrrol-1-yl and 1*H*-indol-1-yl, 1*H*-indol-yl and 9*H*-carbazol-9-yl, and 7-methyl-1*H*-indol-yl and 9*H*-carbazol-9-yl fragments, respectively, were synthesized from "semi-sandwich" complexes **35**−**38** and the lithium salts of the respective indenes[24i] as shown in eqs 17−20, respectively. Complex **39** was isolated in analytically pure form after crystallization of the crude product from a mixture of toluene and hexanes (1:1, vol.), while **40**−**42** were crystallized from toluene.



(17)



(18)



(19)

Furthermore, unsymmetrical complexes **44**−**46** and **48**−**50**, bearing 2-phenylndenyl and 2-mesitylindenyl as well as 2-(N-azolyl)indenyl ligands, were obtained from the respective (2-

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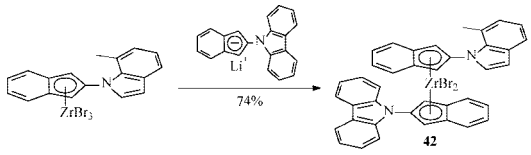
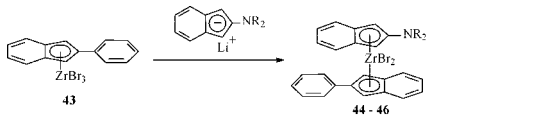


(20)

arylindenyl)zirconium tribromides **43** and **47** and lithium salts of indenes **5**, **7**, and **14** (eqs 21 and 22). Complex **49** was isolated in 58% yield by crystallization of the crude product from a mixture of hexanes and toluene (7:4 v:v), while other complexes were isolated in 22−43% yields after crystallization of the crude products from toluene. the unsymmetrical metallocenes **44**−**46** and **48**−**50** were unambiguously characterized by NMR spectroscopy. Additionally, the structure of **50** was studied by X-ray crystallography (see below for the crystallographic details).



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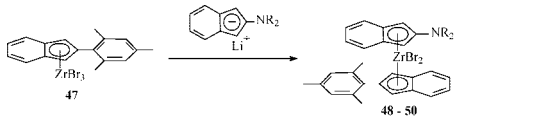
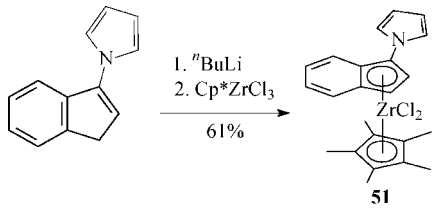
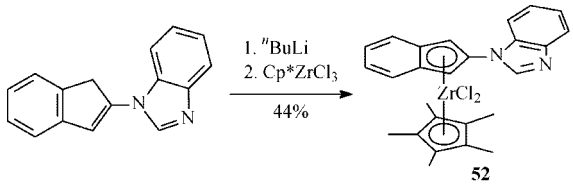


(22)

Finally, in order to illustrate a possible application of the aforementioned indenes **19** and **21** for metallocene synthesis, the unsymmetrical complexes **51** and **52** bearing C_5Me_5 ligands as well as 1-(1*H*-pyrrol-1-yl)- and 2-(1*H*-benzimidazol-1-yl)indenyl ligands were synthesized from Cp*$ZrCl_3$ and lithium salts **19** and **21**, as shown in eqs 23 and 24. These complexes were isolated in analytically pure form in 61 and 46% yields, respectively. It should be noted that, in the reaction of $ZrCl_4(THF)_2$ with 2 equiv of the lithium salt of **21** in THF at ambient temperature, the corresponding symmetrical Waymouth-type complex was not formed. This is probably due to an undesirable coordination of the imidazole fragment with the Zr atom of $ZrCl_4(THF)_2$ or, more likely, the respective monoindenylzirconium intermediate giving some oligomeric or polymeric complexes.



(23)



(24)

Temperature-Dependent Dynamic ^{1}H NMR Spectra of 25, 26, and 50. Complex **25** shows temperature-dependent dynamic ^{1}H NMR spectra. At high temperature (303 K in CD_2Cl_2, 400 MHz), this complex exhibits a spectrum featuring 1-H and 3-H indenyl protons at δ 5.96 ppm as a broad resonance. Stepwise lowering of the temperature from 303 to 203 K by 10 K increments reveals the dynamic process on a 400 MHz ^{1}H NMR time scale. At 203 K, 1-H (3-H) indenyl protons appear as two narrow singlets at δ 6.77 and 4.82 ppm in the ratio 7:4. By analogy with the previously studied conformation behavior of *bis*[2-(2-furyl)indenyl]zirconium derivatives,[4e] we can suggest that these signals belong to two diastereomeric rotamers of **25**. They arise as a result of "freezing" of the hindered rotation around the indenyl C2−N vector on the NMR time scale. The Gibbs activation energy of this process evaluated according to the described procedure[25] is 50 kJ/mol. A similar picture is observed in the case of metallocene **26**. At 203 K (in CD_2Cl_2), 1-H (3-H) indenyl protons appear as two narrow singlets at δ 5.00 and 6.84 ppm. The ratio of isomers at 203 K is ca. 53:47. Warming results in the broadening and further coalescence of these signals (T_{coal} = 275 K). Rotation barriers for **26** have been evaluated to be similar to those for **25**. It should be noted that for **22** (in CD_2Cl_2) the discussed temperature dependence of the ^{1}H NMR spectra was not observed at temperatures between 303 and 173 K.

The only unsymmetrical zirconocene studied by ^{1}H NMR at different temperatures between 303 and 203 K was complex **50**, bearing mesityl and 9*H*-carbazol-9-yl fragments. In this case, the resonances attributed to 1,3-H of both indenyl fragments are broadened at room temperature (Figure 1). The resonance attributed to 4-Me of mesityl fragment appears as a narrow singlet at low temperatures. However, cooling results in the broadening of the resonance attributed to 2,6-Me_2 of mesityl. The observed dynamic behavior is likely to originate from the hindered rotation around indenyl-aryl bond rather than around indenyl-Zr bond.[4e]

Study of the Solid-State Structures of 22, 26, 32, 38, and 50. The solid-state structures of **22**, **26**, **32**, **38**, and **50** were determined by X-ray diffraction analysis. The resulting crystallographic data for **22**, **26**, **32**, and **50** are summarized in Table 1. The structures are depicted in Figures 2−5, and schematic views of **22**, **26**, **32**, and **50** are shown in Figure 6. Complex **22** adopts a racemic-like metallocene conformation with a crystallographically imposed C_2-axial symmetry. The zirconium atom has a typical pseudotetrahedral coordination with two substituted η^5-indenyl and two σ-Cl ligands (see Table 1 for the corresponding angles). The two pyrrolyl residues are arranged toward the forward upper right and lower left quadrants (relative to each other) at the front side of the bent metallocene wedge. The angle between the indenyl planes of opposite ligands is 44.33(11)°. To characterize the orientation of the indenyl ligands, we chose the torsion angle C(2)−Cp(c)−Cp(c′)−C(2′) (Cp(c) stands for Cp centroid), presented in Table 1. These ligands occupy the respective positions almost above and below the Zr−Cl vectors. Consequently, the annelated phenylene rings are found oriented toward the respective opposite positions at the bent metallocene sectors (Figure 6). The bonding of the indenyl five-membered ring to zirconium is rather unsymmetric: the Zr(1)−C(1)/C(3) distances are somewhat shorter than the Zr(1)−C(8)/C(9) distances. It should be also noted that Zr(1)−C(1) is significantly shorter than Zr(1)−C(3). The C(2) carbon atom bearing the pyrrolyl substituent is placed markedly outside the plane of the other atoms of the indenyl moiety (0.180 Å). The pyrrolyl substituent shows a flat conformation with a trigonal-planar nitrogen atom (the sum of angles at N(1) is 359.3°). The N(1)−C(1) bond length is less than the standard X-ray value for the unconjugated C−N bond (1.426 Å).[26] The

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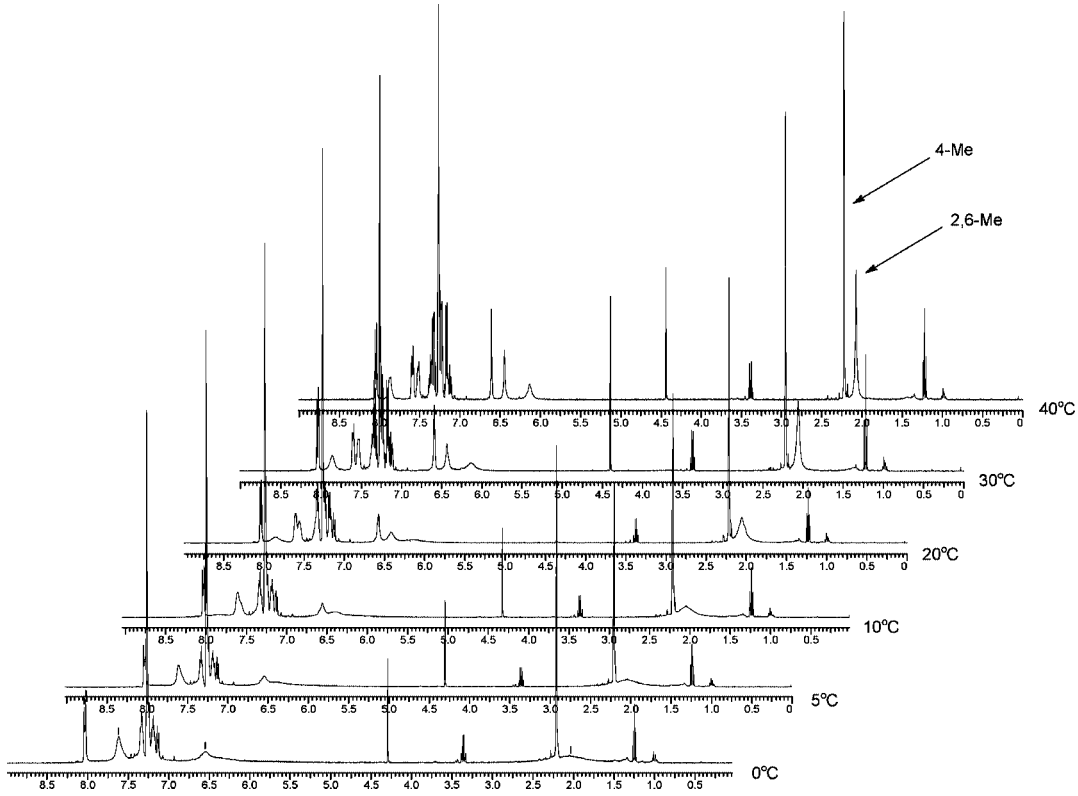

Figure 1. Dynamic ^{1}H NMR spectra (400 MHz) of **50** in CD_2Cl_2.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 22, 26, 32, and 50

bond or angle	**22** (M = Zr, Hal = Cl)	**26** (M = Zr, Hal = Cl)	**32** (M = Hf, Hal = Cl)	**50** (M = Zr, Hal = Br)
M−Hal(1)	2.4852(14)	2.4116(9)	2.3956(13)	2.5842(11)
M−Hal(1′)				2.5837(10)
M−C(1)	2.490(6)	2.476(3)	2.508(5)	2.483(6)
M−C(2)	2.594(6)	2.590(3)	2.556(4)	2.550(6)
M−C(3)	2.521(6)	2.556(3)	2.486(4)	2.579(5)
M−C(9)	2.535(6)	2.577(3)	2.563(5)	2.578(5)
M−C(8)	2.552(6)	2.579(3)	2.554(5)	2.586(6)
M−C(1′)				2.478(5)
M−C(2′)				2.576(5)
M−C(3′)				2.527(5)
M−C(9′)				2.581(5)
M−C(8′)				2.586(6)
M−Cp(c)	2.227(6)	2.252(3)	2.227(5)	2.252(5)
M−Cp(c′)				2.242(5)
N(1)−C(2)	1.374(8)	1.410(4)	1.407(6)	1.394(7)
C(22)−C(2′)				1.490(8)
Hal(1)−M−Hal(1′)	96.77(7)	95.80(5)	95.78(6)	93.72(4)
Hal(1)−M−Cp(c)	105.8(2)	105.42(8)	107.81(12)	110.11(13)
Hal(1)−M−Cp(c′)	105.7(2)	108.19(8)	105.26(12)	106.04(13)
Hal(1′)−M−Cp(c)				103.98(13)
Hal(1′)−M−Cp(c′)				108.27(13)
Cp(c)−M−Cp(c′)	131.9(2)	129.04(12)	129.72(17)	129.14(19)
C(2)−Cp(c)−Cp(c′)−C(2′)	130.2(7)	79.0(3)	73.5(6)	72.4(6)
angle between mean planes of indenyl and indenyl′ ligands	44.33(11)	55.61(7)	55.36(12)	58.20(14)
angle between mean planes of indenyl and its substituent, θ	16.1(5)	32.75(18)	36.91(16)	37.21(17)
θ'				37.09(16)

angle between the mean planes of the indenyl ligand and its substituent is 16.1° (Table 1). This might imply weak conjugation between those π-systems.

The Zr−C distances as well as Cp(centroid)−Zr−Cp(centroid) and Cl−Zr−Cl angles in **22** are comparable with those observed in the previously investigated 2-substituted bis(indenyl)zirco-

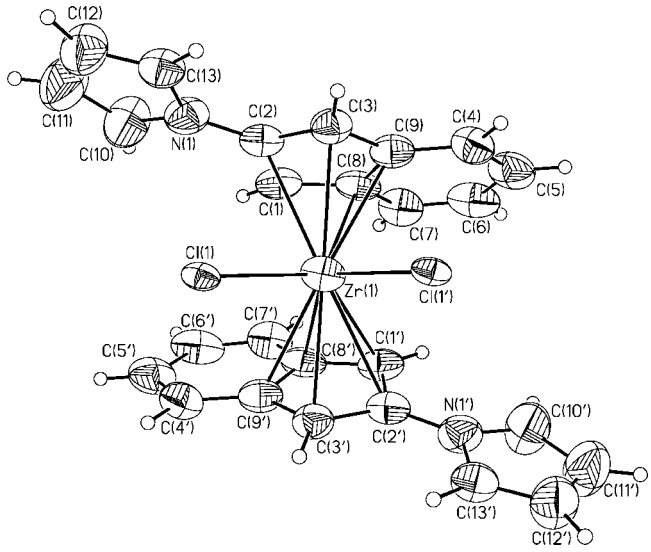

Figure 2. ORTEP view (50% probability) of **22**.

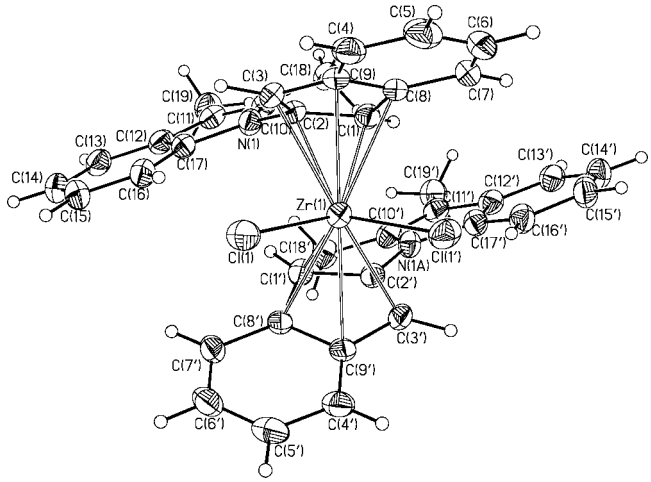

Figure 3. ORTEP view (50% probability) of **26**.

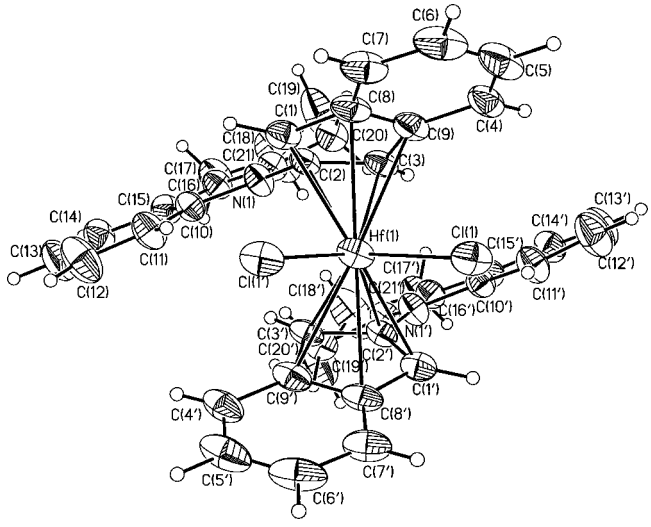

Figure 4. ORTEP view (50% probability) of **32**.

nium dichloride complexes, while the Zr−Cl bonds are substantially longer.[4b,e,f,6f,i,27] However, the analysis of the data from the Cambridge Structural Database[28] has revealed that Zr−Cl bonds vary in the wide range 2.405−2.465 Å.

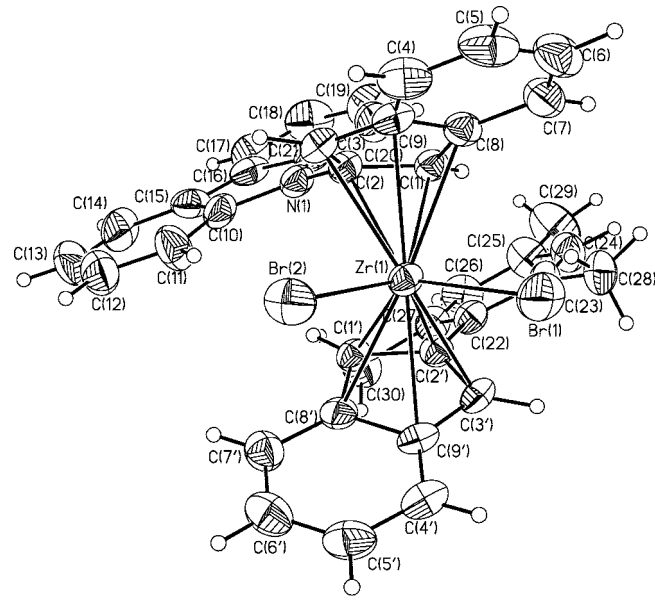

Figure 5. ORTEP view (50% probability) of **50**.

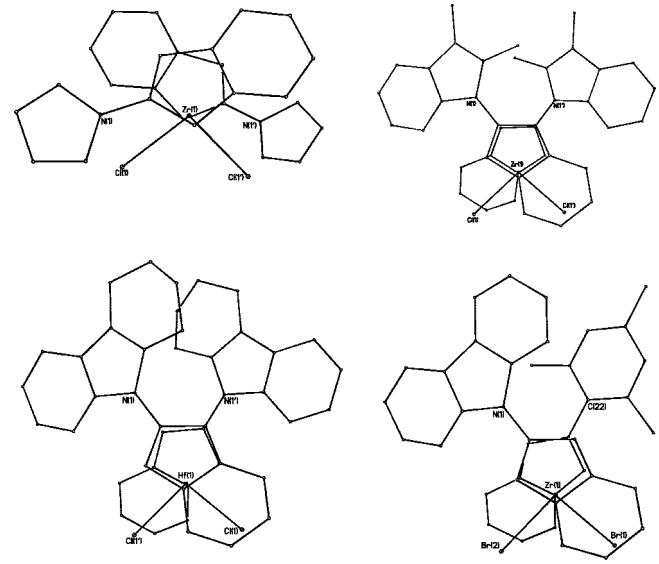

Figure 6. Overhead views of the metallocene conformations of complexes **22** (left top), **26** (right top), **32** (left bottom), and **50** (right bottom).

The X-ray diffraction study of **26** shows that this metallocene complex has a conformational arrangement different from that of **22**, in spite of the fact that it also represents the *rac* conformer with a crystallographically imposed C_2-axial symmetry (Figures 2, 3, and 6). In the crystal, complex **26** favors an arrangement in which both the annelated phenylene groups point toward the Zr−Cl vectors while both the indolyl substituents are oriented on opposite sides of the metallocene framework. The zirconium atom in **26** has also pseudotetrahedral coordination with two substituted η^5-indenyl and two

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σ-Cl ligands (Table 1). However, the distribution of the Zr−C(Cp) bonds in **26** is somewhat different from that in **22**, featuring one short Zr(1)−C(1) bond in comparison with the other Zr−C distances. However, the Zr(1)−C(3) bond length is shorter than the Zr(1)−C(8)/C(9) lengths. As for **22**, the C(2) carbon atom bearing the indolyl substituent is placed markedly outside the plane of the rest of the atoms of the indenyl moiety (0.149 Å). The indolyl substituent shows a flat conformation with a trigonal-planar nitrogen atom (sum of angles at N(1) 359.9°). The C(1)−N(1) bond length is longer than in **22** and the interplanar angle is also larger, apparently due to the sterics, thereby implying no conjugation between the indenyl ligand and its substituents.

Zirconium and hafnium are similar group 4 metals separated by only one row on the periodic table of the elements. Complexes of zirconium and hafnium with the same ligand environments are closely isostructural and possess similar chemical properties.[29] In fact, the solid-state structures of zirconium and hafnium metallocenes derived from analogous 2-substituted indene ligands are nearly identical. Comparison of the crystal structures of the zirconium and hafnium complexes **26** and **32** reveals close structural similarity (Table 1 and Figures 3, 4, and 6). As for **26**, complex **32** adopts the racemic-like metallocene conformation. The geometry around the hafnium atom in **32** is pseudotetrahedral with a crystallographically imposed C_2-axial symmetry. The bond lengths of the corresponding metal−cyclopentadienyl bonds in **26** and **32** are not the same (Table 1); the difference between M−C(1)/C(3) and M−C(8)/C(9) pairs is more pronounced in the case of **32**. The C(2) atom also deviates from the plane of the indenyl ligand (0.160 Å). The mutual orientation of the ligands as well as of the ligands and their substituents in **32** is similar to that in **26** (Table 1).

In complex **50** the two opposite indenyl ligands have different substituents and cannot be described as having any symmetry. Complex **50** is characterized by a racemic-like metallocene conformation. The zirconium atom adopts pseudotetrahedral coordination, with two substituted η^5-indenyl and two σ-Br ligands (see Table 1 for the corresponding angles). The mutual orientation of the ligands as well as the interplanar angles of the ligands and their substituents (θ, θ') are nearly identical with those of complexes **26** and **32**. The distribution of Zr−C bonds is different for two ligands. For the unprimed indenyl, it is similar to the case of complex **26**, while the bonding pattern of the Zr atom to the carbons of the primed ligand is similar to the case of complex **22**. Deviations of the C(2) and C(2′) atoms from the mean plane of the indenyl ligands are also significant, being 0.199 and 0.185 Å, respectively.

The structure of the dimeric complex **38** is depicted in Figure 7. Both Zr atoms adopt a four-legged piano-stool conformation being coordinated by η^5-indenyl ligand, two terminal, and two bridged Cl atoms. Selected characteristics of the geometry are presented in Table 2.

The distribution of the Zr−C bond lengths in **38** is similar to that for previously described complexes. The Zr−C(1,1′)/C(3,3′) distances are shorter in comparison to Zr−C(8,8′)/C(9,9′), and Zr−C(2,2′) are the longest bonds because of significant deviation of the C(2) and C(2′) atoms from the plane of the corresponding indenyl ligand (0.178 and 0.193 Å). As expected, the distances

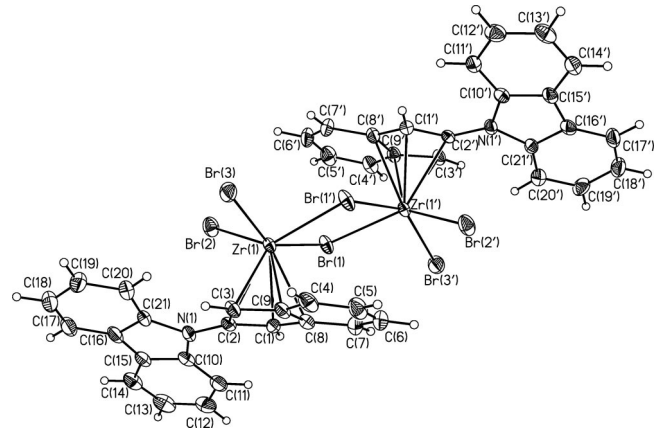

Figure 7. ORTEP view (50% probability) of **38**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 38

Zr(1)−C(1)	2.456(4)	Zr(1′)−C(1′)	2.460(4)
Zr(1)−C(2)	2.584(4)	Zr(1′)−C(2′)	2.570(3)
Zr(1)−C(3)	2.462(4)	Zr(1′)−C(3′)	2.450(4)
Zr(1)−C(9)	2.485(4)	Zr(1′)−C(9′)	2.481(4)
Zr(1)−C(8)	2.501(4)	Zr(1′)−C(8′)	2.512(4)
Zr(1)−Br(1)	2.7561(5)	Zr(1′)−Br(1′)	2.7535(6)
Zr(1)−Br(1′)	2.7152(5)	Zr(1′)−Br(1)	2.7354(5)
Zr(1)−Br2)	2.5446(6)	Zr(1′)−Br(2′)	2.5461(6)
Zr(1)−Br(3)	2.5698(6)	Zr(1′)−Br(3′)	2.5663(6)
N(1)−C(2)	1.387(5)	N(1′)−C(2′)	1.395(5)
angle between mean planes of indenyl and its substituent, θ			22.41(13)
angle between mean planes of indenyl and its substituent, θ'			19.30(14)

from the Zr atom to bridged bromines are significantly longer. The lengths of N(1,1′)−C(2,2′) bonds are slightly shorter than the standard X-ray value for the unconjugated C−N bond, and the angles (θ, θ') between mean planes of the substituents at C(2,2′) atoms and indenyl ligands are ∼20° (Table 2). This might imply weak conjugation between those π-systems.

Olefin Polymerization Catalyzed by 22, 23, and 33 Activated by MAO. A preliminary study of zirconocenes bearing 2-(*N*-azolyl)indenyl ligands showed that **22**, **23**, and **33**/MAO are active catalysts of ethylene (PE) and propylene (PP) polymerization as well as ethylene/1-octene (EO) and ethylene/propylene (EP) copolymerization (Table 3). Under the conditions of ethylene polymerization (PE) studied, the insertion of methyls in the indenyl fragment resulted in a ca. 2.3-fold increase of the catalytic activity (cf. entries 1 and 3), though the substitution of pyrrol-1-yl with 2,4-dimethylpyrrol-1-yl gave a less active catalyst (cf. entries 1 and 2). On the other hand, polyethylene with a higher molecular weight was formed in the case of the Me-substituted complexes **23** and **33**. Interestingly, both Me-substituted complexes activated by MAO gave a molecular weight distribution (PDI) of the polymer narrower than that obtained for **22**/MAO. Next, surprisingly, **22**/MAO showed close activity in ethylene polymerization and ethylene/1-octene copolymerization (entries 1 and 4). This was also the case of the catalyst based on the 4,7-dimethylindenyl complex **23**. In contrast, **33**/MAO showed a considerably lower activity in the copolymerization reaction (cf. entries 3 and 6). Additionally, each catalyst studied gave ethylene/1-octene copolymer with a lower molecular weight than the respective ethylene homopolymer. Interestingly, as in the ethylene homopolymerization, both catalysts based on the Me-substituted zirconocenes gave copolymer with a narrower molecular weight distribution (cf. entries 4 and 5/6). The catalysts based on the more sterically crowded metallocenes **23** and **33** showed a lower level of the

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Table 3. Results of Ethylene (PE) and Propylene (PP) Polymerization and Ethylene/1-Octene (EO) and Ethylene/Propylene (EP) Copolymerization Catalyzed by 22, 23, and 33 Activated by MAO

entry	complex	run type	activity, kg of P (mol of Zr)$^{-1}$ h^{-1}	M_w, kDa	PDI	comonomer content, wt %
1	**22**	PE[a]	5370	790	2.3	
2	**23**	PE[a]	1870	1560	1.6	
3	**33**	PE[a]	12200	2020	1.6	
4	**22**	EO[b]	5150	403	2.6	6.8
5	**23**	EO[b]	1700	1310	1.6	3.3
6	**33**	EO[b]	6940	330	2.0	4.6
7	**22**	EP[c]	5530	26.2	2.9	27.3
8	**23**	EP[c]	650	160	3.1	32.6
9	**33**	EP[c]	1420	6.3	1.8	30.3
10	**22**	PP[d]	890	10.0	1.9	
11	**33**	PP[d]	600	3.0	1.3	

[a] Conditions: 0.02 μmol of the zirconium complex, 10 μmol of MAO ([Zr]/[Al] = 1/500), 75 psig of ethylene, 3.80 mL of toluene, 80 °C. [b] Conditions: 0.02 μmol of the zirconium complex, 10 μmol of MAO ([Zr]/[Al] = 1/500), 75 psig of ethylene, 0.64 mL of 1-octene, 3.80 mL of toluene, 80 °C. [c] Conditions: 0.08 μmol of the zirconium complex, 40 μmol of MAO ([Zr]/[Al] = 1/500), 10 psig of ethylene, 1.066 mL of propylene, 3.77 mL of hexane, 70 °C. [d] Conditions: 0.08 μmol of the zirconium complex, 40 μmol of MAO ([Zr]/[Al] = 1/500), 1.066 mL of propylene, 0.40 mL of toluene, 3.73 mL of hexane, 70 °C.

comonomer insertion, i.e. 3.3 and 4.6 wt % of 1-octene, respectively, compared with 6.8 wt % of the comonomer obtained for **22**/MAO.

In ethylene/propylene copolymerization the activity of **22**/MAO was very close to the activity of this system for ethylene homopolymerization (cf. entries 1 and 7). This was not the case for **23**/MAO and **33**/MAO, where the activities for the copolymerization were considerably lower than for the ethylene homopolymerization (cf. entries 2 and 8 as well as 3 and 9, respectively). However, in all cases studied, ethylene−propylene copolymer had a considerably lower molecular weight than the respective ethylene homopolymer. The dramatic effect was particularly observed for **33**/MAO, which gave ethylene homopolymer and ethylene/1-octene copolymer with M_w values equal to 2020 and 330 kDa, respectively, though ethylene/propylene copolymer had a M_w value as low as 6.3 kDa. Surprisingly, in contrast to the ethylene/1-octene copolymerization, in the case of the ethylene/propylene copolymerization, the level of comonomer insertion was slightly higher for the catalysts involving more sterically crowded complexes **23** and **33** (cf. entries 8/9 and 7). Interestingly, both **22**/MAO and **33**/MAO formed low-molecular-weight propylene homopolymer, as shown in Table 3 (entries 10 and 11). Additionally, these catalysts were found to have considerably lower activities in propylene polymerization compared with ethylene homopolymerization, which is known to be a common phenomenon for the Waymouth-type catalysts.[4c] Taking into account the polymerization conditions used, one can conclude that the substitution of phenyl with pyrrol-1-yl in position 2 of the indenyls of the Waymouth-type zirconocene results in increasing catalytic activity of the respective catalyst in propylene polymerization.[4c] Detailed results of the propylene homopolymerization catalyzed by the zirconium complexes bearing 2-(*N*-azolyl)indenyl ligands activated by MAO will be published and discussed elsewhere.

Conclusion

The Pd-catalyzed cross-coupling reactions of readily available 2-bromo-1*H*-indene and triflate of 2-indanone with azoles, such as pyrrole and its analogues, were shown to be convenient and useful methods to obtain novel ligands containing azole fragments bonded with cyclopentadienyl via nitrogen. The respective Waymouth-type zirconium and hafnium complexes involving two indenyl ligands bearing planar N-azolyl fragments in position 2 were obtained and, after being activated by MAO, form active catalysts for ethylene homopolymerization and ethylene/1-octene copolymerization. The activity in propylene polymerization is, however, rather modest. Catalytic properties will be considered in detail elsewhere.

Experimental Section

General Procedure. All manipulations with air- and moisture-sensitive compounds were performed either under an atmosphere of thoroughly purified argon using standard Schlenk techniques or in a controlled-atmosphere glovebox (VAC). Tetrahydrofuran, dimethoxyethane (DME), and ether for synthesis were purified by distillation over $LiAlH_4$ and kept over sodium benzophenone ketyl. Hydrocarbon solvents (including benzene-d_8 for NMR measurements) were distilled and stored over CaH_2 or Na/K alloy. Methylene chloride (and CD_2Cl_2 for NMR measurements) was distilled and stored over CaH_2. Chloroform-*d* was distilled over P_4O_{10} and stored over molecular sieves (3 Å). 2-Bromo-1*H*-indene,[27b,30] 1*H*-inden-2-yl trifluoromethanesulfonate (**18**),[31] 2-bromo-4,7-dimethyl-1*H*-indene,[27b,32] 2-phenyl-1*H*-indene,[33] (μ-bromo)dibromo[η^5-2-phenylindenyl]zirconium dimer (**43**),[24i] 1,2,3,4-tetrahydrocyclopenta[*b*]indole,[34] $Pd(dba)_2$,[35] $[(TMEDA)Cu(OH)]_2Cl_2$,[22c] $ZrCl_4(THF)_2$,[36] and Cp^*ZrCl_3[37] were prepared according to the published methods. 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 or 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, NOEdif, APT, and DEPT experiments. C, H microanalyses were done using a Carlo Erba 1106 analyzer.

1-(1*H*-Inden-2-yl)-1*H*-pyrrole (5). In a three-necked round-bottom flask (1 L), equipped with an Allihn condenser and magnetic stirrer bar, under an argon atmosphere 4.59 g (15.4 mmol) of 2-(di-*tert*-butylphosphino)-1,1′-biphenyl and 1.73 g (7.70 mmol) of $Pd(OAc)_2$ were added to a mixture of 49.0 g (231 mmol) of anhydrous K_3PO_4, 30.0 g (154 mmol) of 2-bromo-1*H*-indene, and 11.5 mL (11.1 g, 165 mmol) of pyrrole in 500 mL of toluene and 50 mL of DME, at ambient temperature. This mixture was stirred at room temperature for 72 h. The reaction mixture was filtered through a layer (d = 100 mm, l = 40 mm) of silica gel 60 (40−63 μm) on a fritted-glass funnel. The silica gel layer was additionally washed with 200 mL of methyl *tert*-butyl ether (MTBE). The combined extract was evaporated to dryness. The crude product was purified using flash chromatography (silica gel 60, 40−63 μm,

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(37) Ryabov, A. N.; Gribkov, D. V.; Izmer, V. V.; Voskoboynikov, A. Z. *Organometallics* **2002**, *21*, 2842.

d = 40 mm, l = 500 mm; eluent 10/1 hexanes/MTBE). This procedure gave 5.62 g (20%) of white crystalline product. Anal. Calcd for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.24; H, 6.19; N, 7.55. ^{1}H NMR ($CDCl_3$): δ 8.08 (m, 1H, 7-H of indenyl), 7.92−8.01 (m, 3H, 3,4,6-H of indenyl), 7.83 (dt, J = 7.2 Hz, J = 1.5 Hz, 1H, 5-H of indenyl), 7.77 (t, J = 7.4 Hz, 2H, 2,5-H of *N*-pyrrolyl), 7.00 (t, J = 2.19 Hz, 2H, 3,4-H of *N*-pyrrolyl), 4.51 (s, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.7, 144.1, 138.0, 126.9, 123.8, 123.4, 120.2, 118.7, 111.2, 110.6, 37.4.

1-(1*H*-Inden-2-yl)-2,4-dimethyl-1*H*-pyrrole (6). The reaction was carried out similarly to the preparation of compound **5**, starting from 7.40 mL (6.84 g, 72 mmol) of 2,4-dimethylpyrrole, 13.7 g (70 mmol) of 2-bromoindene, 44.5 g (210 mmol) of K_3PO_4, 1.13 g (13.0 mL of 0.2 M solution in toluene, 5.60 mmol) of ^{t}Bu$_3$P, 1.61 g (2.80 mmol) of Pd(dba)$_2$, 170 mL of toluene, and 35 mL of DME. The reaction mixture was stirred at 80 °C for 14 h. Yield: 7.81 g (53%) of **6**. Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.99; H, 7.27; N, 6.62. ^{1}H NMR ($CDCl_3$): δ 7.43 (m, 1H, 7-H of indenyl), 7.28−7.37 (m, 3H, 3,4,6-H of indenyl), 7.19 (dt, J = 7.3 Hz, J = 1.6 Hz, 1H, 5-H of indenyl), 6.71 (s, 1H, 5-H of *N*-pyrrolyl), 6.56 (s, 1H, 3-H of indenyl), 5.94 (s, 1H, 3-H of *N*-pyrrolyl), 3.82 (s, 2H, CH_2), 2.47 (s, 3H, 2-Me of *N*-pyrrolyl), 2.15 (s, 3H, 4-Me of *N*-pyrrolyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.6, 144.4, 138.3, 129.5, 126.8, 123.9, 123.2, 120.3, 119.5, 117.6, 114.8, 112.1, 39.6, 14.8, 11.7.

1-(1*H*-Inden-2-yl)-1*H*-indole (7). Method A. The reaction was carried out similarly to the preparation of compound **5**, starting from 4.80 g (41 mmol) of indole, 8.00 g (41 mmol) of 2-bromoindene, 52.2 g (246 mmol) of K_3PO_4, 0.331 g (3.80 mL of 0.2 M solution in toluene, 1.64 mmol) of ^{t}Bu$_3$P, 0.184 g (0.82 mmol) of Pd(OAc)$_2$, 110 mL of toluene, and 20 mL of DME. The reaction mixture was stirred at 70 °C for 8.5 h. Yield: 5.64 g (60%) of **7**. Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.10; H, 5.60; N, 6.19. ^{1}H NMR ($CDCl_3$): δ 7.79 (m, 1H, 7-H of *N*-indolyl), 7.63 (m, 1H, 4-H of *N*-indolyl), 7.36 (m, 1H, 7-H of indenyl), 7.09−7.33 (m, 6H, 4,5,6-H of indenyl and 2,5,6-H of *N*-indolyl), 6.79 (s, 1H, 3-H of indenyl), 6.61 (dd, J = 3.4 Hz, J = 0.8 Hz, 1H, 3-H of *N*-indolyl), 3.84 (s, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.3, 143.9, 137.7, 135.4, 130.0, 127.0, 126.3, 123.9, 123.3, 123.0, 121.3, 121.0, 120.3, 113.9, 112.2, 104.8, 39.2.

Method B. A mixture of 100 mg (0.38 mmol) of 1*H*-inden-2-yl trifluoromethanesulfonate, 44.5 mg (0.38 mmol) of 1*H*-indole, 11.5 mg (0.02 mmol) of Pd(dba)$_2$, 13.7 mg (0.04 mmol) of **17**, and 212 mg (1.0 mmol) of K_3PO_4 in 3 mL of toluene was stirred for 9 h at 85 °C. The product was isolated by semipreparative HPLC. Yield: 50 mg (57%). Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.43; H, 5.79; N, 5.85.

1-(1*H*-Inden-2-yl)-2-methyl-1*H*-indole (8). The reaction was carried out similarly to the preparation of compound **5**, starting from 4.45 g (34 mmol) of 2-methylindole, 6.63 g (34 mmol) of 2-bromoindene, 21.6 g (102 mmol) of K_3PO_4, 0.404 g (4.65 mL of 0.2 M solution in toluene, 2.00 mmol) of ^{t}Bu$_3$P, 0.224 g (1.00 mmol) of Pd(OAc)$_2$, 80 mL of toluene, and 15 mL of DME. The reaction mixture was stirred at 75 °C for 9 h. Yield: 4.00 g (48%) of **8**. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.22; H, 6.09; N, 5.84. ^{1}H NMR ($CDCl_3$): δ 7.06−7.54 (m, 8H, 4,5,6,7-H of indenyl and 4,5,6,7-H of *N*-indolyl), 6.83 (s, 1H, 3-H of indenyl), 6.36 (s, 1H, 3-H of *N*-indolyl), 3.75 (s, 2H, CH_2), 2.41 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.0, 142.5, 140.6, 137.8, 136.8, 128.5, 127.0, 126.8, 125.1, 123.7, 121.3*, 120.2, 119.6, 110.5, 102.3, 40.0, 13.9 (the asteisk denotes two chemically nonequivalent carbon nuclei).

1-(1*H*-Inden-2-yl)-7-methyl-1*H*-indole (9). A mixture of 11.7 g (60 mmol) of 2-bromo-1*H*-indene, 7.86 g (60 mmol) of 7-methyl-1*H*-indole, 38.2 g (180 mmol) of anhydrous K_3PO_4, and 817 mg (1.6 mmol) of Pd(P^{t}Bu$_3$)$_2$ in a mixture of 180 mL of toluene and 30 mL of DME was stirred for 20 h at 95 °C. The resulting mixture was filtered through a glass frit (G3). The precipitate was additionally washed with 3 × 75 mL of dichloromethane. The combined extract was evaporated to dryness. The product was isolated by passing through a short column with silica gel 60 (40−63 um, d = 100 mm, l = 100 mm; eluent 100/1 hexanes/Et$_2$O). This procedure gave 6.18 g (42%) of **9**. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.09; H, 6.19; N, 5.75. ^{1}H NMR (DMSO-d_6): δ 7.53 (d, J = 3.2 Hz, 1H, 2-H in indol-1-yl), 7.44−7.51 (m, 3H, 4-H in indol-1-yl and 4,7-H in inden-2-yl), 7.32 (m 1H, 6-H in inden-2-yl), 7.24 (m, 1H, 5-H in inden-2-yl), 7.03 (m, 1H, 5-H in indol-1-yl), 6.96 (m, 1H, 6-H in indol-1-yl), 6.81 (s, 1H, 3-H in inden-2-yl), 6.64 (d, J = 3.2 Hz, 1H, 2-H in indol-1-yl), 3.92 (s, 2H, CH_2), 2.32 (s, 3H, Me). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 145.1, 142.8, 140.3, 135.1, 130.2, 129.3, 126.7, 125.7, 124.92, 124.90, 123.8, 121.4, 121.3, 120.4, 118.7, 103.4, 41.3, 19.5.

1-(1*H*-Inden-2-yl)-2-phenyl-1*H*-indole (10). A mixture of 7.80 g (40 mmol) of 2-bromo-1*H*-indene, 7.73 g (40 mmol) of 2-phenyl-1*H*-indole, 25.47 g (120 mmol) of anhydrous K_3PO_4, and 817 mg (1.6 mmol) of Pd(P^{t}Bu$_3$)$_2$ in a mixture of 120 mL of toluene and 20 mL of DME was stirred for 20 h at 95 °C. The resulting mixture was filtered through a glass frit (G3). The precipitate was additionally washed with 3 × 75 mL of dichloromethane. The combined extract was evaporated to dryness. The product was isolated by passing through short column with silica gel 60 (40−63 um, d = 100 mm, l = 100 mm; eluent 100/1 hexanes/Et$_2$O). This procedure gave 5.63 g (46%) of **10**. Anal. Calcd for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56. Found: C, 89.81; H, 5.61; N, 4.45. ^{1}H NMR ($CDCl_3$): δ 7.70 (m, 1H, 7-H in indenyl), 7.55−7.61 (m, 3H, 4-H in indolyl and 2,6-H in Ph), 7.50 (m, 1H, 4-H in indenyl), 7.19−7.41 (m, 8H, 5,6,7-H in indolyl, 5,6-H in indenyl and 3,4,5-H in Ph), 7.07 (s, 1H, 3-H in indolyl), 6.79 (s, 1H, 3-H in indenyl), 3.32 (s, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.7, 146.5, 143.5, 143.0, 140.7, 138.4, 132.8, 128.6, 128.5, 127.8, 126.7, 126.1, 124.9, 123.6, 122.6, 121.3, 121.0, 120.6, 111.1, 104.4, 40.4.

1-(1*H*-Inden-2-yl)-2,3-dimethyl-1*H*-indole (11). The reaction was carried out similarly to the preparation of compound **5**, starting from 7.41 g (51 mmol) of 2,3-dimethylindole, 9.95 g (51 mmol) of 2-bromoindene, 32.4 g (153 mmol) of K_3PO_4, 1.03 g (11.9 mL of 0.2 M solution in toluene, 5.10 mmol) of ^{t}Bu$_3$P, 0.572 g (2.55 mmol) of Pd(OAc)$_2$, 140 mL of toluene, and 30 mL of DME. The reaction mixture was stirred at 85 °C for 11 h. Yield: 6.37 g (48%) of **11**. Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 88.13; H, 6.68; N, 5.58. ^{1}H NMR ($CDCl_3$): δ 7.09−7.53 (m, 8H, 4,5,6,7-H of indenyl and 4,5,6,7-H of *N*-indolyl), 6.82 (s, 1H, 3-H of indenyl), 3.76 (s, 2H, CH_2), 2.35 (s, 3H, 2-Me of *N*-indolyl), 2.28 (s, 3H, 3-Me of *N*-indolyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.2, 143.0, 140.6, 136.9, 132.6, 129.2, 126.8, 126.5, 125.0, 123.7, 121.4, 121.2, 119.7, 117.9, 110.2, 108.9, 40.2, 11.4, 8.8.

4-(1*H*-Inden-2-yl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole (12). The reaction was carried out similarly to the preparation of compound **5**, starting from 6.28 g (40 mmol) of 1,2,3,4-tetrahydrocyclopenta[*b*]indole, 7.80 g (40 mmol) of 2-bromoindene, 25.4 g (120 mmol) of K_3PO_4, 0.808 g (9.30 mL of 0.2 M solution in toluene, 4.00 mmol) of ^{t}Bu$_3$P, 0.449 g (2.00 mmol) of Pd(OAc)$_2$, 120 mL of toluene, and 20 mL of DME. The reaction mixture was stirred at 85 °C for 11 h. Yield: 3.53 g (33%) of **12**. Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.60; H, 6.34; N, 5.33. ^{1}H NMR ($CDCl_3$): δ 7.68 (m, 1H, 7-H of indenyl), 7.07−7.46 (m, 7H, 4,5,6-H of indenyl and 4,5,6,7-H of *N*-azolyl), 6.72 (s, 1H, 3-H of indenyl), 3.81 (s, 2H, CH_2 of indenyl), 2.97 (m, 2H, 2-CH_2 of *N*-azolyl), 2.80 (m, 2H, 4-CH_2 of *N*-azolyl), 2.49 (m, 2H, 3-CH_2 of *N*-azolyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.6, 144.1, 143.8, 140.6, 138.3, 126.8, 125.7, 123.8, 123.2, 122.0, 121.5, 120.6, 120.2, 118.7, 115.5, 112.4, 39.5, 28.1, 28.0, 24.0.

9-(1*H*-Inden-2-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (13). The reaction was carried out similarly to the preparation of compound **5**, starting from 8.73 g (51 mmol) of 2,3,4,9-tetrahydro-1*H*-

carbazole, 10.0 g (51 mmol) of 2-bromoindene, 32.4 g (153 mmol) of K_3PO_4, 1.01 g (11.6 mL of 0.2 M solution in toluene, 5.00 mmol) of ^{t}Bu$_3$P, 0.561 g (2.50 mmol) of $Pd(OAc)_2$, 150 mL of toluene, and 30 mL of DME. The reaction mixture was stirred at 80 °C for 8.5 h. Yield: 8.92 g (61%) of **13**. Anal. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 88.29; H, 6.80; N, 4.94. ^{1}H NMR ($CDCl_3$): δ 6.96−7.38 (m, 8H, 4,5,6,7-H of indenyl and 6,7,8,9-H of *N*-azolyl), 6.65 (m, 1H, 3-H of indenyl), 3.68 (s, 2H, CH_2 of indenyl), 2.62 (m, 4H, 3-CH_2 and 4-CH_2 of *N*-azolyl), 1.75 (m, 4H, 2-CH_2 and 5-CH_2 of *N*-azolyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.4, 142.7, 140.1, 136.8, 135.5, 128.2, 126.8, 124.6, 123.7, 123.5, 121.6, 120.9, 119.9, 117.8, 112.1, 110.7, 40.0, 24.0, 23.5, 22.8, 21.1.

9-(1*H*-Inden-2-yl)-9*H*-carbazole (14). The reaction was carried out similarly to the preparation of compound **5**, starting from 6.69 g (40 mmol) of carbazole, 7.80 g (40 mmol) of 2-bromoindene, 25.5 g (120 mmol) of K_3PO_4, 817 mg (1.6 mmol) of $Pd(^tBu_3P)_2$, 120 mL of toluene, and 20 mL of DME. The reaction mixture was stirred at 95 °C for 20 h. Yield: 9.80 g (87%) of **14**. Anal. Calcd for $C_{21}H_{15}N$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.71; H, 5.31; N, 5.11. ^{1}H NMR ($CDCl_3$): δ 8.08 (d, J = 7.8 Hz, 2H, 4,5-H of *N*-carbazolyl), 7.57 (d, J = 8.0 Hz, 2H, 1,8-H of *N*-carbazolyl), 7.20−7.48 (m, 8H, 4,5,6,7-H of indenyl and 2,3,6,7-H of *N*-carbazolyl), 7.02 (s, 1H, 3-H of indenyl), 3.92 (s, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.2, 142.2, 140.6, 140.2, 126.9, 126.1, 125.7, 125.1, 123.7*, 121.2, 120.2*, 110.5, 39.0 (asterisks denote two chemically nonequivalent carbon nuclei).

1-(4,7-Dimethyl-1*H*-inden-2-yl)-1*H*-pyrrole (15). In a round-bottom flask (0.1 L) in the glovebox, a mixture of 6.69 g (30 mmol) of 2-bromo-4,7-dimethyl-1*H*-indene, 2.80 mL (2.68 g, 40.0 mmol) of pyrrole, 19.1 g (90 mmol) of anhydrous K_3PO_4, 575 mg (1.0 mmol) of $Pd(dba)_2$, and 596 mg (2.0 mmol) of 2-(di-*tert*-butylphosphino)-1,1′-biphenyl in 100 mL of toluene was stirred for 24 h at 75 °C. The resulting mixture was filtered through a glass frit (G3). The precipitate was additionally washed with 3 × 50 mL of methyl *tert*-butyl ether. The combined extract was evaporated to dryness. The product was isolated by flash chromatography (silica gel 60, 40−63 μm, d = 50 mm, l = 500 mm; eluent 50/1 hexanes/MTBE). This procedure gave 3.25 g (52%) of a white solid. Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.31; H, 7.04; N, 6.90. ^{1}H NMR ($CDCl_3$): δ 7.07 (t, J = 2.1 Hz, 2H, 2,5-H of pyrrolyl), 6.98 (d, J = 7.7 Hz, 1H, 5-H of indenyl), 6.85 (d, J = 7.7 Hz, 1H, 6-H of indenyl), 6.59 (t, J = 1.2 Hz, 1H, 3-H of indenyl), 6.29 (t, J = 2.1 Hz, 2H, 3,4-H of pyrrolyl), 3.62 (br.s, 2H, CH_2), 2.36 (s, 3H, 4-Me of indenyl), 2.29 (s, 3H, 7-Me of indenyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.1, 142.5, 136.4, 129.8, 128.3, 126.9, 125.4, 118.8, 110.4, 109.9, 36.7, 18.3, 18.2.

***N*-(1*H*-Inden-2-yl)-*N*,*N*-diphenylamine (16).** A mixture of 177 mg (1.05 mmol) of diphenylamine, 195 mg (1.00 mmol) of 2-bromo-1*H*-indene, 640 mg of K_3PO_4, 4.5 mg (0.02 mmol) of $Pd(OAc)_2$, and 2.0 mL of 0.02 M (0.04 mmol) of P^{t}Bu$_3$ in toluene was stirred for 9 h at 70 °C. The resulting mixture was passed through a short column with silica gel 60 (40−63 μm, l = 30 mm, d = 50 mm). The product was isolated from the eluate using semipreparative HPLC. Yield: 99 mg (35%). Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 89.19; H, 6.10; N, 5.01. ^{1}H NMR ($CDCl_3$): δ 7.31−7.24 (m, 4H), 7.21−7.16 (m, 4H), 7.15−7.10 (m, 2H), 7.10−7.06 (m, 2H), 7.04 (d, J = 7.3 Hz, 1H), 6.95 (dt, J = 1.0 Hz, J = 7.3 Hz, 1H), 6.04 (s, 1H), 3.45 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.9, 146.9, 145.7, 137.8, 129.2, 126.6, 125.5, 124.1, 122.9, 122.1, 118.5, 110.5, 39.1.

1-(1*H*-Inden-3-yl)-1*H*-pyrrole (19). In a round-bottom flask (0.1 L) in the glovebox, a mixture of 9.10 g (35 mmol) of 1*H*-inden-3-yl trifluoromethanesulfonate, 2.45 mL (2.35 g, 35 mmol) of pyrrole, 21.2 g (100 mmol) of anhydrous K_3PO_4, 805 mg (1.4 mmol) of $Pd(dba)_2$, and 821 mg (2.8 mmol) of 2-(di-*tert*-butylphosphino)biphenyl in 100 mL of toluene was stirred for 24 h at 120 °C. The resulting mixture was filtered through a glass frit (G3). The precipitate was additionally washed with 3 × 50 mL of methyl *tert*-butyl ether. The combined extract was evaporated to dryness. The product was isolated by flash chromatography (silica gel 60, 40−63 μm, d = 50 mm, l = 500 mm; eluent 20/1 hexanes/MTBE). This procedure gave 0.96 g (15%) of the title product. Anal. Calcd for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.34; H, 6.21; N, 7.86. ^{1}H NMR ($CDCl_3$): δ 7.58 (m, 1H, 7-H of indenyl), 7.45 (m, 1H, 4-H of indenyl), 7.21−7.34 (m, 2H, 5,6-H of indenyl), 7.08 (t, J = 2.1 Hz, 2H, 2,5-H of pyrrolyl), 6.33 (t, J = 2.1 Hz, 2H, 3,4-H of pyrrolyl), 6.23 (t, J = 2.3 Hz, 1H, 2-H of indenyl), 3.41 (d, J = 2.3 Hz, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.8, 142.2, 139.8, 126.4, 125.7, 124.3, 120.2, 119.7, 119.5, 109.4, 35.8.

1-(1*H*-Inden-3-yl)-1*H*-indole (20). In a 100 mL pressure glass vessel, a mixture of 10.0 g (38 mmol) of 1*H*-inden-3-yl trifluoromethanesulfonate, 4.45 g (38 mmol) of 1*H*-indole, 21 g of K_3PO_4, 862 mg (1.5 mmol) of $Pd(dba)_2$, 869 mg (3.0 mmol) of (biphenyl-2-yl)di-*tert*-butylphosphine, and 100 mL of toluene was stirred for 15 h at 120 °C. The resulting mixture was filtered through a short layer of silica gel 60 (40−63 μm), and this layer was additionally washed by 200 mL of methyl *tert*-butyl ether. The product was isolated from the combined elute using flash chromatography on silica gel 60 (40−63 μm, d = 40 mm, l = 500 mm, 10/1 hexanes/methyl *tert*-butyl ether). Yield: 3.95 g (45%) of dark red oil. Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.40; H, 5.70; N, 6.31. ^{1}H{^{13}C} NMR ($CDCl_3$): δ 7.72−7.67 (m, 1H), 7.58−7.53 (m, 1H), 7.52−7.47 (m, 1H), 7.42 (d, 3.12 Hz, 1H), 7.41−7.35 (m, 1H), 7.34−7.26 (m, 2H), 7.25−7.14 (m, 2H), 6.69 (dt, J = 0.6 Hz, J = 3.1 Hz, 1H), 6.55 (t, J = 2.2 Hz, 1H), 3.61 (d, J = 2.2 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.5, 140.9, 140.7, 136.2, 128.9, 127.5, 126.4, 125.8, 124.4, 123.9, 122.1, 120.9, 120.3, 119.8, 111.4, 103.2, 36.4.

1-(1*H*-Inden-2-yl)-1*H*-benzimidazole (21). In a 100 mL Erlenmeyer flask, a mixture of 3.20 g (20.0 mmol) of 1*H*-inden-2-ylboronic acid, 1.18 g (10.0 mmol) of benzimidazole, 0.93 g (2.00 mmol) of $[(TMEDA)CuOH]_2Cl_2$, and 40 mL of dichloromethane was stirred for 20 h (in air). The resulted mixture was passed through a short column with silica gel 60 (40−63 μm, d = 40 mm, l = 20 mm). This column was additionally washed with 500 mL of dichloromethane. The combined eluate was evaporated to dryness. The crude product was purified using medium-pressure chromatography on silica gel 60 (40−63 μm, d = 40 mm, l = 350 mm; eluent 1/1 v/v hexanes/dichloromethane). Yield: 530 mg (23%) of white solid. Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.65; H, 5.20; N, 11.81. ^{1}H{^{13}C} NMR ($CDCl_3$): δ 8.19 (br s, 1H, 2-H in 1*H*-benzimidazol-1-yl), 7.87 (m, 1H, 7-H in 1*H*-benzimidazol-1-yl), 7.80 (m, 1H, 4-H in 1*H*-benzimidazol-1-yl), 7.30−7.50 (m, 7H, 4,5,7-H in indenyl and 4,5,6,7-H in 1*H*-benzimidazol-1-yl), 7.23 (dt, J = 7.5 Hz, J = 1.3 Hz, 1H, 6-H in indenyl), 7.00 (m, 1H, 3-H in indenyl), 3.99 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 144.5 (br), 143.1, 141.3 (br), 140.3, 137.9, 127.3, 125.1, 124.2, 123.6 (br), 123.2, 121.1, 120.9, 117.0, 111.9, 38.7.

Bis[η^5-2-(1*H*-pyrrol-1-yl)indenyl]zirconium dichloride (22). In a round-bottom flask (0.1 L) in the glovebox, to a solution of 4.22 g (23.3 mmol) of **5** in a mixture of 60 mL of toluene and 6 mL of ether was added 9.6 mL of a 2.5 M solution of ^{n}BuLi (24 mmol) in hexanes at room temperature. This mixture was stirred overnight. Then, 4.19 mL (6.04 g, 25 mmol) of Et_3SnCl was added dropwise, and the reaction mixture was stirred for 3 h at room temperature and then was filtered through Celite 503 (on a fritted-glass funnel). The Celite layer was additionally washed with 50 mL of toluene. The combined extract was evaporated under vacuum to ca. two-thirds of its former volume. To the resulting mixture was added 2.70 g (11.6 mmol) of $ZrCl_4$ at room temperature. This mixture was stirred for 2 days and then filtered through a glass frit (G4). The crystals that precipitated at −30 °C from the filtrate were

separated, washed with 5 mL of cold toluene, and dried under vacuum. Yield: 1.03 g (17%) of yellowish crystals of **22**. Anal. Calcd for $C_{26}H_{20}Cl_2N_2Zr$: C, 59.76; H, 3.86; N, 5.36. Found: C, 59.52; H, 3.77; N, 5.34. ^{1}H NMR (CD_2Cl_2): δ 7.56 (m, 4H, 4,4′,7,7′-H in indenyl), 7.27 (m, 4H, 5,5′,6,6′-H in indenyl), 6.87 (t, J = 2.3 Hz, 4H, 2,2′,5,5′-H in *N*-pyrrolyl), 6.25 (t, J = 2.3 Hz, 4H, 3,3′,4,4′-H in *N*-pyrrolyl), 5.83 (s, 4H, 1,1′,3,3′-H of indenyl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 142.2, 141.9, 127.6, 127.0, 120.9, 112.9, 93.9.

Bis[η^5-2-(2,4-dimethyl-1*H*-pyrrol-1-yl)indenyl]zirconium Dichloride (23). The reaction was carried out similarly to the preparation of compound **22**, starting from 5.90 g (28.2 mmol) of **6** in a mixture of 85 mL of toluene and 17 mL of ether, 11.8 mL of a 2.5 M solution of ^{n}BuLi (29.6 mmol) in hexanes, 5.03 mL (7.24 g, 30 mmol) of Et_3SnCl, and 3.26 g (14.0 mmol) of $ZrCl_4$. Yield: 3.01 g (37%) of yellowish crystals of **23**. Anal. Calcd for $C_{30}H_{28}Cl_2N_2Zr$: C, 62.27; H, 4.88; N, 4.84. Found: C, 62.06; H, 4.70; N, 5.17. ^{1}H NMR (CD_2Cl_2): δ 7.51 (m, 4H, 4,4′,7,7′-H of indenyl), 7.25 (m, 4H, 5,5′,6,6′-H of indenyl), 6.53 (s, 2H, 5,5′-H of *N*-pyrrolyl), 5.84 (s, 2H, 3,3′-H of *N*-pyrrolyl), 5.77 (s, 4H, 1,1′,3,3′-H of indenyl), 2.25 (s, 6H, 2,2′-Me of *N*-pyrrolyl), 2.05 (s, 6H, 4,4′-Me of *N*-pyrrolyl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 142.7, 131.7, 127.6, 127.0, 125.0, 122.2, 119.5, 115.0, 95.8, 16.6, 13.1.

Bis[η^5-2-(1*H*-indol-1-yl)indenyl]zirconium Dichloride (24). The reaction was carried out similarly to the preparation of compound **22**, starting from 5.59 g (24.2 mmol) of **7** in a mixture of 50 mL of toluene and 10 mL of ether, 10.0 mL of a 2.5 M solution of ^{n}BuLi (25 mmol) in hexanes, 5.02 mL (7.23 g, 30 mmol) of Et_3SnCl, and 2.82 g (12.1 mmol) of $ZrCl_4$. Yield: 1.89 g (25%) of yellowish crystals of **24**. Anal. Calcd for $C_{34}H_{24}Cl_2N_2Zr$: C, 65.58; H, 3.88; N, 4.50. Found: C, 65.77; H, 3.98; N, 4.39. ^{1}H NMR (CD_2Cl_2): δ 7.17−7.63 (m, 16H, 4,4′,5,5′,6,6′,7,7′-H of indenyl and 4,4′,5,5′,6,6′,7,7′-H of *N*-indolyl), 7.13 (d, J = 3.6 Hz, 2H, 2,2′-H of *N*-indolyl), 6.64 (m, 2H, 3,3′-H of *N*-indolyl), 5.98 (s, 4H, 1,1′,3,3′-H of indenyl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 143.2, 136.7, 131.8, 128.7, 127.6, 127.3, 124.9, 123.1, 123.0, 114.0, 107.6, 107.3, 95.1.

Bis[η^5-2-(2-methyl-1*H*-indol-1-yl)indenyl]zirconium Dichloride (25). The reaction was carried out similarly to the preparation of compound **22**, starting from 4.07 g (16.6 mmol) of **8** in a mixture of 70 mL of toluene and 15 mL of ether, 7.2 mL of a 2.5 M solution of ^{n}BuLi (18 mmol) in hexanes, 3.19 mL (4.59 g, 19 mmol) of Et_3SnCl, and 1.93 g (8.3 mmol) of $ZrCl_4$. Yield: 0.98 g (18%) of yellowish crystals of **25**. Anal. Calcd for $C_{36}H_{28}Cl_2N_2Zr$: C, 66.44; H, 4.34; N, 4.30. Found: C, 66.65; H, 4.47; N, 4.50. ^{1}H NMR (CD_2Cl_2): δ 7.61 (m, 2H, 4,4′-H of *N*-indolyl), 7.82 (m, 2H, 7,7′-H of *N*-indolyl), 7.23−7.36 (m, 12H, 4,4′,5,5′,6,6′,7,7′-H of indenyl and 5,5′,6,6′-H of *N*-indolyl), 6.48 (s, 2H, 3,3′-H of *N*-indolyl), 5.96 (br s, 4H, 1,1′,3,3′-H of indenyl), 2.10 (s, 6H, 2,2′-Me of indolyl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 135.7, 135.6, 130.9, 128.6, 126.9, 126.1, 124.2, 123.5, 121.9, 114.3, 112.1 (br.), 107.7, 99.3 (br), 17.2.

Bis[η^5-2-(2,3-dimethyl-1*H*-indol-1-yl)indenyl]zirconium Dichloride (26). The reaction was carried out similarly to the preparation of compound **22**, starting from 6.30 g (24.3 mmol) of **11** in a mixture of 105 mL of toluene and 10 mL of ether, 10.0 mL of 2.5 M solution of ^{n}BuLi (25 mmol) in hexanes, 5.03 mL (7.24 g, 30.0 mmol) of Et_3SnCl, and 2.82 g (12.1 mmol) of $ZrCl_4$. Yield: 2.18 g (27%) of yellowish crystals of **26**. Anal. Calcd for $C_{38}H_{32}Cl_2N_2Zr$: C, 67.24; H, 4.75; N, 4.13. Found: C, 67.11; H, 4.73; N, 3.99. ^{1}H NMR (CD_2Cl_2): δ 7.78 (m, 2H, 4,4′-H of *N*-indolyl), 7.61 (m, 2H, 7,7′-H of *N*-indolyl), 7.20−7.37 (m, 12H, 4,4′,5,5′,6,6′,7,7′-H of indenyl and 5,5′,6,6′-H of *N*-indolyl), 5.90 (br s, 4H, 1,1′,3,3′-H of indenyl), 2.29 (s, 6H, 2,2′-Me of *N*-indolyl), 1.94 (s, 6H, 3,3′-Me of *N*-indolyl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 139.7, 135.5, 135.0, 131.8, 128.5, 126.8, 126.2 (br), 124.4, 123.1, 120.3, 120.1, 114.1, 113.8, 99.1 (br), 14.1, 13.9, 10.4, 10.2.

Bis[η^5-2-(2,3-dihydrocyclopenta[*b*]indol-4(1*H*)-yl)indenyl]zirconium Dichloride (27). The reaction was carried out similarly to the preparation of compound **22**, starting from 3.52 g (13.0 mmol) of **12** in a mixture of 60 mL of toluene and 6 mL of ether, 5.6 mL of a 2.5 M solution of ^{n}BuLi (14.0 mmol) in hexanes, 2.50 mL (3.60 g, 15.0 mmol) of Et_3SnCl, and 1.51 g (6.50 mmol) of $ZrCl_4$. The crude product was recrystallized from a toluene/hexanes mixture at −30 °C. Yield: 0.69 g (15%) of yellowish crystals of **27**. Anal. Calcd for $C_{40}H_{32}Cl_2N_2Zr$: C, 68.36; H, 4.59; N, 3.99. Found: C, 68.64; H, 4.73; N, 3.75. ^{1}H NMR (CD_2Cl_2): δ 7.84−7.91 (m, 2H, 5,5′-H of *N*-azolyl), 7.46−7.52 (m, 6H, 6,6′,7,7′,8,8′-H of *N*-azolyl), 7.27 (dd, J = 6.3 Hz, J = 3.1 Hz, 4H, 4,4′,7,7′-H of indenyl), 7.04 (dd, J = 6.3 Hz, J = 3.1 Hz, 4H, 5,5′,6,6′-H of indenyl), 6.36 (m, 4H, 1,1′,3,3′-H of indenyl), 3.08 (m, 4H, 4,4′-CH_2 of *N*-azolyl), 2.86 (m, 4H, 2,2′-CH_2 of *N*-azolyl), 2.54 (m, 4H, 3,3′-CH_2 of *N*-azolyl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 145.4, 144.9, 140.8, 128.0, 127.0, 126.8, 126.3, 125.2, 122.4, 121.9, 119.3, 113.9, 96.0, 29.2, 28.5, 24.2.

Bis[η^5-2-(1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)indenyl]zirconium Dichloride (28). The reaction was carried out similarly to the preparation of compound **22**, starting from 4.91 g (17.2 mmol) of **13** in a mixture of 70 mL of toluene and 7 mL of ether, 7.2 mL of 2.5 M solution of ^{n}BuLi (18 mmol) in hexanes, 3.19 mL (4.59 g, 19 mmol) of Et_3SnCl, and 2.00 g (8.6 mmol) of $ZrCl_4$. Yield: 1.15 g (18%) of yellowish crystals of **28**. Anal. Calcd for $C_{42}H_{36}Cl_2N_2Zr$: C, 69.02; H, 4.96; N, 3.83. Found: C, 68.86; H, 5.11; N, 3.92. ^{1}H NMR (CD_2Cl_2): δ 7.70 (m, 2H, 6,6′-H of *N*-azolyl), 7.55 (m, 2H, 9,9′-H of *N*-azolyl), 7.22−7.40 (m, 12H, 4,4′,5,5′,6,6′,7,7′-H of indenyl and 7,7′,8,8′-H of *N*-azolyl), 5.95 (br.s, 4H, 1,1′,3,3′-H of indenyl), 2.76, 2.28, 2.08, and 1.84 (four multiplets, 4 × 4H, 2,2′-CH_2, 3,3′-CH_2, 4,4′-CH_2, and 5,5′-CH_2 of *N*-azolyl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 137.2, 134.9, 133.7, 128.0, 125.4, 123.8, 123.1, 121.2, 120.0, 117.0, 113.2, 111.1, 95.3 (br.), 23.8, 22.1, 20.9, 19.6.

Bis[η^5-2-(9*H*-carbazol-9-yl)indenyl]zirconium Dichloride (29). Method A. The reaction was carried out similarly to the preparation of compound **22**,starting from 4.75 g (16.9 mmol) of **14** in a mixture of 50 mL of toluene and 6 mL of ether, 7.1 mL of 2.5 M solution of ^{n}BuLi (17.5 mmol) in hexanes, 3.02 mL (4.34 g, 18 mmol) of Et_3SnCl, and 1.96 g (11.6 mmol) of $ZrCl_4$. This compound was found to be practically insoluble in all common solvents. Therefore, the resulting mixture was filtered through a glass frit (G4), and the solid obtained was washed with 2 × 15 mL of hot toluene, 2 × 30 mL of hot DME, and 2 × 30 mL of dichloromethane and then dried under vacuum. Yield: 3.29 g (54%) of yellow powder of **29**. Anal. Calcd for $C_{42}H_{28}Cl_2N_2Zr$: C, 69.79; H, 3.90; N, 3.88. Found: C, 69.54; H, 3.78; N, 3.61. ^{1}H NMR (CD_2Cl_2): δ 8.11 (m, 4H, 4,4′,5,5′-H of *N*-carbazolyl), 7.56 (m, 4H, 1,1′,8,8′-H of *N*-carbazolyl), 7.80 (m, 16H, 4,4′,5,5′,6,6′,7,7′-H of indenyl and 2,2′,3,3′,6,6′,7,7′-H of *N*-carbazolyl), 6.17 (s, 4H, 1,1′,3,3′-H of indenyl).

Method B. To a solution of 5.21 g (18.5 mmol) of **22** in 400 mL of ether was added 7.40 mL (18.5 mmol) of 2.5 M ^{n}BuLi in hexanes at room temperature. This mixture was stirred overnight, and then 3.49 g (9.26 mmol) of $ZrCl_4(THF)_2$ was added at room temperature. The resulting mixture was stirred for 24 h and than evaporated to dryness. The residue was washed with 2 × 50 mL of hot toluene, 2 × 50 mL of dichloromethane, and 2 × 50 mL of THF and then dried under vacuum. Yield: 4.40 g (66%) of yellow powder of **29**. Anal. Calcd for $C_{42}H_{28}Cl_2N_2Zr$: C, 69.79; H, 3.90; N, 3.88. Found: C, 69.99; H, 4.04; N, 4.04.

Bis[η^5-2-(7-methyl-1*H*-indol-1-yl)indenyl]zirconium Dichloride (30). To a solution of 2.45 g (10.0 mmol) of **9** in 100 mL of Et_2O was added 4.00 mL (10.0 mmol) of 2.5 M ^{n}BuLi in hexanes at room temperature. This mixture was stirred overnight, and then 1.89 g (5.0 mmol) of $ZrCl_4(THF)_2$ was added at room temperature. This mixture was stirred for 1 day and then evaporated to dryness.

To the residue was added 150 mL of toluene. The mixture was heated to reflux and then filtered through Celite 503 (on a fritted-glass funnel). Crystals precipitating at −30 °C from the filtrate were separated, washed with 20 mL of cold toluene, and dried under vacuum. Yield: 0.80 g (25%) of **30**. Anal. Calcd for $C_{36}H_{28}Cl_2N_2Zr$: C, 66.44; H, 4.34; N, 4.30. Found: C, 66.48; H, 4.32; N, 4.45. ^{1}H NMR (CD_2Cl_2): δ 7.55 (m, 2H, 4-H in indolyl), 7.44 (d, J = 3.3 Hz, 2H, 3-H in indolyl), 7.88 (m, 4H, 4,7-H in indenyl), 7.24 (m, 4H, 5,6-H in indenyl), 7.17 (m, 2H, 5-H in indolyl), 6.86 (m, 2H, 5-H in indolyl), 6.84 (d, J = 3.3 Hz, 2H, 2-H in indolyl), 5.70 (s, 4H, 1,3-H in indenyl), 1.83 (s, 6H, Me).

Bis[η^5-2-(2-phenyl-1*H*-indol-1-yl)indenyl]zirconium Dichloride (31). To a solution of 5.63 g (18.3 mmol) of **10** in 200 mL of Et_2O was added 7.32 mL (18.3 mmol) of 2.5 M ^{n}BuLi in hexanes at room temperature. This mixture was stirred overnight, and then 3.46 g (9.16 mmol) of $ZrCl_4(THF)_2$ was added at room temperature. This mixture was stirred for 1 day and then evaporated to dryness. To the residue was added 150 mL of toluene. The mixture was heated to reflux and then filtered through Celite 503 (on a fritted-glass funnel). The Celite layer was washed with 300 mL of dichloromethane. The combined extract was evaporated to dryness to give 3.50 g (49%) of **31**. Anal. Calcd for $C_{46}H_{32}Cl_2N_2Zr$: C, 71.30; H, 4.16; N, 3.62. Found: C, 71.28; H, 4.17; N, 3.77. ^{1}H NMR (CD_2Cl_2): δ 7.77 (br.s, 4H), 7.65 (m, 4H), 7.80 (m, 4H), 7.25 (m, 4H), 7.10−7.22 (m, 8H), 7.01 (br.s, 4H), 6.77 (s, 4H).

Bis[η^5-2-(1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)indenyl]hafnium Dichloride (32). In a round-bottom flask (0.15 L) in the glovebox, to a solution of 2.41 g (8.44 mmol) of **13** in 100 mL of toluene was added 3.38 mL of a 2.5 M solution of ^{n}BuLi (8.44 mmol) in hexanes at room temperature. This mixture was stirred overnight. Then, 1.35 g (4.22 mmol) of $HfCl_4$ was added at room temperature. This mixture was refluxed for 10 h; then, this hot mixture was filtered through Celite 503. The Celite layer was additionally washed with 2 × 50 mL of hot toluene. The combined extract was evaporated to ca. 40 mL. Yellowish crystals precipitating at room temperature were separated, washed with 10 mL of cold toluene and 10 mL of hexanes, and dried under vacuum. Yield: 1.70 g (49%) of **32**. Anal. Calcd for $C_{42}H_{36}Cl_2N_2Hf$: C, 61.66; H, 4.44; N, 3.42. Found: C, 61.83; H, 4.52; N, 3.64. ^{1}H NMR (CD_2Cl_2): δ 7.70 (m, 2H, 6,6′-H of *N*-azolyl), 7.60 (m, 2H, 9,9′-H of *N*-azolyl), 7.22−7.43 (m, 12H, 4,4′,5,5′,6,6′,7,7′-H of indenyl and 7,7′,8,8′-H of *N*-azolyl), 5.88 (br.s, 4H, 1,1′,3,3′-H of indenyl), 2.80, 2.30, 1.87, and 1.76 (four multiplets, 4 × 4H, 2,2′-CH_2, 3,3′-CH_2, 4,4′-CH_2, and 5,5′-CH_2 of *N*-azolyl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 136.8, 135.1, 133.8, 128.0, 125.2, 123.8, 122.4 (br.), 121.2, 120.0, 116.9, 113.1, 111.2, 92.6 (br), 23.9, 22.2, 20.9, 19.7.

Bis[η^5-4,7-dimethyl-2-(1*H*-pyrrol-1-yl)indenyl]zirconium Dichloride (33). In a round-bottom flask (0.1 L) in the glovebox, to a solution of 1.25 g (6.00 mmol) of **15** in 70 mL of toluene was added 2.40 mL of 2.5 M ^{n}BuLi (6.00 mmol) in hexanes at ambient temperature. The suspension formed was additionally stirred overnight, and then 0.70 g (3.00 mmol) of $ZrCl_4$ was added. This mixture was stirred for 3 h at 110 °C and 1 day at ambient temperature. The hot mixture was filtered through Celite 503. The Celite layer was washed with 2 × 50 mL of hot toluene. The combined extract was evaporated to ca. 50 mL. The precipitate that formed was filtered off, washed with 2 × 10 mL of hexanes, and dried under vacuum. Yield: 0.65 g (37%) of yellowish crystalline solid. Anal. Calcd for $C_{30}H_{28}Cl_2N_2Zr$: C, 62.27; H, 4.88; N, 4.84. Found: C, 62.39; H, 4.78; N, 4.90. ^{1}H NMR (CD_2Cl_2): δ 7.10 (t, J = 3.1 Hz, 4H, 2,2′,5,5′-H of pyrrolyl), 6.84 (s, 4H, 5,5′,6,6′-H of indenyl), 6.41 (t, J = 3.1 Hz, 4H, 3,3′,4,4′-H of pyrrolyl), 5.92 (s, 4H, 1,1′,3,3′-H of indenyl), 2.28 (s, 12H, 4,4′,7,7′-Me of indenyl). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 138.9, 133.6, 128.2, 127.1, 121.5, 113.2, 93.5, 20.4.

Bis[η^5-4,7-dimethyl-2-(1*H*-pyrrol-1-yl)indenyl]hafnium Dichloride (34). The reaction was carried out similarly to the preparation of compound **33**, starting from 0.70 g (3.35 mmol) of **15** in 35 mL of toluene, 1.34 mL of a 2.5 M solution of ^{n}BuLi (3.35 mmol) in hexanes, and 0.54 g (1.57 mmol) of $HfCl_4$. The reaction mixture was stirred for 20 h at 110 °C, and the product was isolated as described for **33**. Yield: 0.53 g (45%) of white powder of **34**. Anal. Calcd for $C_{30}H_{28}Cl_2N_2Hf$: C, 54.11; H, 4.24; N, 4.21. Found: C, 54.19; H, 4.28; N, 4.13. ^{1}H NMR (CD_2Cl_2): δ 7.17 (t, J = 2.2 Hz, 4H), 6.88 (s, 4H), 6.49 (t, J = 2.2 Hz, 4H), 5.86 (s, 4H), 2.36 (s, 12H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 137.0, 132.3, 126.8, 120.4, 111.9, 89.9, 19.2.

(μ-Bromo)dibromo[η^5-2-(1*H*-pyrrol-1-yl)indenyl]zirconium Dimer (35). In a round-bottom flask (0.5 L) in the glovebox, to a solution of 7.74 g (29 mmol) of $Zr(NMe_2)_4$ in 400 mL of ether was added 5.43 g (30 mmol) of **5**. This mixture was stirred overnight at room temperature and then evaporated to dryness. The obtained oil was dissolved in 400 mL of toluene, and 17.8 g (116 mmol) of Me_3SiBr was added. The resulting mixture was stirred overnight, and then the obtained yellow solution was evaporated to a volume equal to ca. 100 mL. Crystals precipitating at −30 °C were separated, washed with 40 mL of cold toluene, and dried under vacuum. Yield: 13.4 g (40%) of yellow crystalline solid of **35**·C_7H_8. Anal. Calcd for $C_{33}H_{28}Br_6N_2Zr_2$: C, 35.56; H, 2.53; N, 2.51. Found: C, 35.73; H, 2.70; N, 2.68. ^{1}H NMR (CD_2Cl_2): δ 7.81−7.73 (m, 4H), 7.45−7.39 (m, 4H), 7.26 (t, J = 2.1 Hz, 4H), 7.14−7.24 (s, 5H), 6.88 (s, 4H), 6.40 (t, J = 2.1 Hz, 4H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 140.4, 133.8 (C_7H_8), 129.0 (C_7H_8), 128.3 (C_7H_8), 128.1, 126.5, 125.7, 125.0 (C_7H_8), 119.6, 112.2, 94.4, 38.3 (C_7H_8).

(μ-Bromo)dibromo[η^5-2-(1*H*-indol-1-yl)indenyl]zirconium Dimer (36). The reaction was carried out similarly to the preparation of compound **35**, starting from 1.92 g (8.3 mmol) of **7**, 2.22 g (8.3 mmol) of $Zr(NMe_2)_4$, 5.41 g (33 mmol) of Me_3SiBr, and 70 mL of ether. Yield: 3.17 g (63%) of yellow solid of **36**·C_7H_8. Anal. Calcd for $C_{41}H_{32}Br_6N_2Zr_2$: C, 40.54; H, 2.66; N, 2.31. Found: C, 40.78; H, 2.81; N, 2.49. ^{1}H NMR (CD_2Cl_2): δ 8.06 (d, J = 8.5 Hz, 2H), 7.87 (dd, J = 3.0 Hz, J = 6.3 Hz, 4H), 7.72 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 3.4 Hz, 2H), 7.49 (dd, J = 3.0 Hz, J = 6.3 Hz, 4H), 7.47−7.42 (m, 2H), 7.42−7.35 (m, 4H), 7.34−7.25 (m, 4H), 7.14−7.24 (s, 5H), 6.85 (d, J = 3.4 Hz, 2H), 2.37 (s, 3H).

(μ-Bromo)dibromo[η^5-2-(7-methyl-1*H*-indol-1-yl)indenyl]zirconium Dimer (37). To a solution of 5.30 g (21.6 mmol) of **9** in 220 mL of Et_2O was added 5.49 g (20.5 mmol) of $Zr(NMe_2)_4$ at room temperature. This mixture was stirred for 2 days and then evaporated to dryness. To a solution of the residue in 220 mL of toluene was added 10.26 g (67 mmol) of Me_3SiBr. The resulting mixture was stirred for 1 day and then evaporated to dryness. The residue was washed with 3 × 10 mL of toluene and 3 × 10 mL of hexanes and dried under vacuum. Yield: 9.00 g (76%) of **37**. Anal. Calcd for $C_{36}H_{28}Br_6N_2Zr_2$: C, 37.58; H, 2.45; N, 2.43. Found: C, 37.60; H, 2.44; N, 2.35. ^{1}H NMR (CD_2Cl_2): δ 7.87 (m, 8H, 4,7-H in indenyl), 7.55 (d, J = 3.5 Hz, 4H, 3-H in indolyl), 7.51 (m, 4H, 4-H in indolyl), 7.49 (m, 8H, 5,6-H in indenyl), 7.20 (m, 4H, 5-H in indolyl), 7.13 (m, 4H, 6-H in indolyl), 6.98 (s, 8H, 1,3-H in indenyl), 6.73 (d, J = 3.5 Hz, 4H, 2-H in indolyl), 2.38 (s, 12H, Me).

(μ-Bromo)dibromo[η^5-2-(9*H*-carbazol-1-yl)indenyl]zirconium Dimer (38). The reaction was carried out similarly to the preparation of compound **35**, starting from 2.83 g (10 mmol) of **14**, 2.67 g (10 mmol) of $Zr(NMe_2)_4$, 6.52 g (33 mmol) of Me_3SiBr, and 100 mL of ether. Yield: 2.56 g (39%) of yellow solid of **38**·C_7H_8. Anal. Calcd for $C_{49}H_{36}Br_6N_2Zr_2$: C, 44.77; H, 2.76; N, 2.13. Found: C, 44.91; H, 2.79; N, 2.22. ^{1}H NMR (CD_2Cl_2): δ 8.27 (d, J = 8.4 Hz, 4H), 8.14 (dq, J = 0.7 Hz, J = 7.7 Hz, 4H), 7.79 (dd, J = 3.0 Hz, J = 6.3 Hz, 4H), 7.79 (ddd, J = 1.3 Hz, J = 7.3 Hz, J = 8.4 Hz, 4H), 7.44−7.37 (m, 8H), 7.35 (s, 4H), 7.14−7.24 (s, 5H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 139.6, 133.2

(C_7H_8), 129.3 (C_7H_8), 128.7 (C_7H_8), 128.0, 126.8, 126.5, 125.9 (C_7H_8), 125.1, 124.4, 123.3, 121.9, 120.2, 113.1, 99.1, 38.5 (C_7H_8).

[η^5-2-(1*H*-Pyrrol-1-yl)indenyl][η^5-2-(9*H*-carbazol-1-yl)indenyl]zirconium Dibromide (39). To a solution of 562 mg (2.0 mmol) of **14** in 20 mL of ether was added 0.8 mL of 2.5 M (2.0 mmol) of ^{n}BuLi in hexanes at room temperature. This mixture was stirred overnight and then added to a solution of 1.12 g (2.0 mmol) of **35** in 20 mL of toluene at −35 °C. The resulting mixture was stirred for 0.5 h at this temperature and overnight at ambient temperature and then evaporated to a volume equal to ca. 25 mL. A mixture of this solution with 20 mL of toluene was filtered through a glass frit at 100−110 °C. The residue was additionally washed with 10 mL of hot toluene. The combined toluene extract was evaporated to a volume equal to 15 mL. Crystals precipitating from this solution at −30 °C were collected, washed with 5 mL of cold toluene, and dried under vacuum. Yield: 470 mg (33%) of yellowish solid of **39**. Anal. Calcd for $C_{34}H_{24}Br_2N_2Zr$: C, 57.39; H, 3.40; N, 3.94. Found: C, 57.47; H, 3.45; N, 4.08. ^{1}H NMR (CD_2Cl_2): δ 8.22 (d, J = 7.7 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.70−7.63 (m, 2H), 7.59 (ddd, J = 1.1 Hz, J = 7.5 Hz, J = 8.2 Hz, 2H), 7.50−7.45 (m, 2H), 7.40−7.39 (m, 2H), 7.34−7.26 (m, 4H), 7.24−7.15 (m, 2H), 6.84 (t, J = 2.2 Hz, 2H), 6.32 (t, J = 2.2 Hz, 2H), 6.30 (s, 2H), 5.86 (s, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 141.6, 139.6, 139.0, 126.8, 126.5, 126.4, 126.3, 126.1, 124.8, 123.9, 123.4, 121.9, 120.4, 119.3, 112.9, 111.5, 97.0, 92.8.

[η^5-2-(1*H*-Pyrrol-1-yl)indenyl][η^5-2-(1*H*-indol-1-yl)indenyl]zirconium Dibromide (40). The reaction was carried out similarly to the preparation of compound **39**, starting from 362 mg (2.0 mmol) of **5**, 0.8 mL of 2.5 M (2.0 mmol) ^{n}BuLi in hexanes, and 1.22 g (2.0 mmol) of **36**. Yield: 470 mg (37%) of yellow solid of **40**. Anal. Calcd for $C_{30}H_{22}Br_2N_2Zr$: C, 54.47; H, 3.35; N, 4.23. Found: C, 54.59; H, 3.40; N, 4.10. ^{1}H NMR (CD_2Cl_2): δ 7.72 (d, J = 7.8 Hz, 1H), 7.70−7.66 (m, 2H), 7.60 (d, J = 8.4 Hz, 1H), 7.57−7.50 (m, 2H), 7.41−7.37 (m, 2H), 7.36−7.33 (m, 2H), 7.32−7.27 (m, 2H), 7.25−7.19 (m, 1H), 6.92 (t, J = 2.2 Hz, 2H), 6.77 (dd, J = 0.7 Hz, J = 3.5 Hz, 1H), 6.36 (t, J = 2.2 Hz, 2H), 6.18 (s, 2H), 5.85 (s, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 140.9, 140.4, 135.2, 130.3, 127.3, 126.4, 126.3, 126.13, 126.12, 123.5, 123.21, 123.20, 121.8, 121.6, 119.4, 112.7, 111.5, 106.2, 94.2, 93.0.

[η^5-2-(1*H*-Indol-1-yl)indenyl][η^5-2-(9*H*-carbazol-1-yl)indenyl]zirconium Dibromide (41). The reaction was carried out similarly to the preparation of compound **39**, starting from 462 mg (2.0 mmol) of **7**, 0.8 mL of 2.5 M (2.0 mmol) of ^{n}BuLi in hexanes, and 1.32 g (2.0 mmol) of **38**. Yield: 213 mg (14%) of yellow solid of **41**. Anal. Calcd for $C_{38}H_{26}Br_2N_2Zr$: C, 59.92; H, 3.44; N, 3.68. Found: C, 59.97; H, 3.47; N, 3.66. ^{1}H NMR (CD_2Cl_2): δ 8.22 (dd, J = 0.6 Hz, J = 7.4 Hz, 2H), 7.72−7.67 (m, 3H), 7.60−7.55 (m, 3H), 7.52 (ddd, J = 1.3 Hz, J = 7.3 Hz, J = 8.0 Hz, 2H), 7.48−7.43 (m, 2H), 7.42−7.38 (m, 2H), 7.37−7.31 (m, 4H), 7.30−7.26 (m, 2H), 7.02 (d, J = 3.5 Hz, 1H), 6.63 (d, J = 3.5 Hz, 1H), 6.22 (s, 2H), 6.13 (s, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 141.0, 139.4, 139.2, 135.0, 130.3, 126.8, 126.7, 126.6, 126.5, 126.4, 126.1, 124.7, 124.0, 123.6, 123.5, 121.9, 121.7, 121.4, 120.3, 112.7, 112.5, 106.3, 97.1, 94.2.

[η^5-2-(7-Methyl-1*H*-indol-1-yl)indenyl][η^5-2-(9*H*-carbazol-1-yl)indenyl]zirconium Dibromide (42). To a solution of 1.97 g (6.99 mmol) of **14** in a mixture of 80 mL of Et_2O and 80 mL of toluene was added 2.80 mL (7.0 mmol) of 2.5 M ^{n}BuLi in hexanes at room temperature. This mixture was stirred overnight, and then 4.03 g (7.00 mmol) of **37** was added at −30 °C. This mixture was stirred for 1 day at room temperature and than evaporated to dryness. To the residue was added 150 mL of toluene. The resulting mixture was refluxed for 1 day and then filtered through Celite 503 (on a fritted-glass funnel). The filtrate was evaporated to dryness. The residue was washed with 3 × 20 mL of toluene and dried under vacuum. Yield: 4.03 g (74%) of **42**. Anal. Calcd for $C_{39}H_{28}Br_2N_2Zr$: C, 60.39; H, 3.64; N, 3.61. Found: C, 60.41; H, 3.61; N, 3.69. ^{1}H NMR (CD_2Cl_2): δ 8.17 (m, 2H), 7.53−7.63 (m, 5H), 7.27−7.42 (m, 7H), 7.12−7.20 (3H), 6.98 (m, 2H), 6.91 (m, 1H), 6.74 (m, 1H), 6.20 (s, 2H), 5.94 (s, 2H), 1.78 (s, 3H, Me).

[η^5-2-Phenylindenyl][η^5-2-(1*H*-pyrrol-1-yl)indenyl]zirconium Dibromide (44). To a solution of 0.36 g (2.0 mmol) of **5** in 20 mL of ether was added 0.80 mL (2.0 mmol) of 2.5 M ^{n}BuLi in hexanes at room temperature. This mixture was stirred for 1.5 h and then added to a suspension of 1.14 g (2.0 mmol) of **43**·C_7H_8 in 20 mL of toluene at −35 °C. The resulting mixture was stirred for 30 min at this temperature and 30 min at room temperature and then evaporated to dryness. The product was recrystallized from toluene. The crystals precipitating at −30 °C were collected, washed with hexanes, and dried under vacuum. Yield: 0.48 g (37%). Anal. Calcd for $C_{28}H_{21}Br_2NZr$: C, 54.02; H, 3.40; N, 2.25. Found: C, 54.35; H, 3.44; N, 2.02. ^{1}H NMR (CD_2Cl_2): δ 7.68 (m, 2H), 7.54 (m, 2H), 7.48 (m, 2H), 7.45 (m, 1H), 7.39 (m, 2H), 7.24 (m, 2H), 7.19 (m, 2H), 6.80 (m, 2H), 6.64 (m, 2H), 6.28 (m, 2H), 6.00 (m, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 141.4, 134.9, 134.3, 130.62, 130.55, 128.55, 128.53, 128.47, 127.7, 127.3, 127.1, 124.4, 120.9, 112.9, 105.5, 96.0, 94.6.

[η^5-2-Phenylindenyl][η^5-2-(1*H*-indol-1-yl)indenyl]zirconium Dibromide (45). The reaction was carried out similarly to the preparation of compound **44**, starting from 0.46 g (2.0 mmol) of **7**, 0.80 mL (2.0 mmol) of 2.5 M ^{n}BuLi in hexanes, and 1.14 g (2.0 mmol) of **43**·C_7H_8. Yield: 0.77 g (66%). Anal. Calcd for $C_{32}H_{23}Br_2NZr$: C, 57.15; H, 3.45; N, 2.08. Found: C, 57.31; H, 3.68; N, 2.19. ^{1}H NMR (CD_2Cl_2): δ 7.67 (m, 1H), 7.43−7.61 (m, 7H), 7.19−7.37 (m, 10H), 7.16 (m, 2H), 6.71 (m, 1H), 6.48 (s, 2H), 6.26 (s, 2H).

[η^5-2-Phenylindenyl][η^5-2-(9*H*-carbazol-1-yl)indenyl]zirconium Dibromide (46). The reaction was carried out similarly to the preparation of compound **44**, starting from 0.56 g (2.0 mmol) of **14**, 0.80 mL (2.0 mmol) of 2.5 M ^{n}BuLi in hexanes, and 1.14 g (2.0 mmol) of **43**·C_7H_8. Yield: 0.45 g (29%). Anal. Calcd for $C_{36}H_{25}Br_2NZr$: C, 59.84; H, 3.49; N, 1.94. Found: C, 59.71; H, 3.69; N, 2.05. ^{1}H NMR (CD_2Cl_2): δ 8.21 (m, 2H), 7.80 (m, 2H), 7.51−7.55 (m, 4H), 7.45 (m, 2H), 7.37−7.41 (m, 3H), 7.31−7.36 (m, 4H), 7.22 (m, 4H), 6.37 (m, 2H), 6.30 (s, 2H).

2-Mesityl-1*H*-indene. A mixture of mesitylmagnesium bromide (obtained from 535 mg of magnesium turnings and 3.98 g of mesityl bromide in 60 mL of THF), 3.90 g (20 mmol) of 2-bromo-1*H*-indene, 230 mg (0.4 mmol) of $Pd(dba)_2$, and 2.0 mL of 0.2 M (0.4 mmol) P^tBu_3 in toluene was stirred for 48 h at room temperature. To the resulting mixture was added 100 mL of brine, and the organic layer was separated. The aqueous layer was washed with 2 × 50 mL of ether. The combined extract was dried over Na_2SO_4 and evaporated to dryness. The product was isolated using flash chromatography on silica gel 60 (40−63 um; d = 40 mm, l = 200 mm; 10/1 v/v hexanes/methyl *tert*-butyl ether). Yield: 3.04 g (65%) of yellowish oil. ^{1}H NMR ($CDCl_3$): δ 7.56 (dq, J = 0.8 Hz, J = 7.4 Hz, 1H), 7.49 (dt, J = 1.0 Hz, J = 7.4 Hz, 2H), 7.38 (tt, J = 0.5 Hz, J = 7.5 Hz, 1H), 7.27 (dt, J = 1.1 Hz, J = 7.4 Hz, 1H), 7.00 (s, 2H), 6.72−6.70 (m, 1H), 3.63 (s, 2H), 2.39 (s, 3H), 2.25 (s, 6H).

(μ-Bromo)dibromo[η^5-2-mesitylindenyl]zirconium Dimer (47). A mixture of 5.37 g (22.9 mmol) of 2-mesityl-1*H*-indene and 5.89 g (22.0 mmol) of $Zr(NMe_2)_4$ in 300 mL of ether was stirred for 12 h at room temperature. The resulting mixture was evaporated to dryness, and 200 mL of toluene was added. To the solution obtained was added 11.4 g (74.5 mmol) of Me_3SiBr at room temperature. This mixture was stirred for 12 h and then evaporated to dryness. To the residue were added 30 mL of toluene and 50 mL of hexanes. The precipitate that formed was filtered off, washed with 3 × 50 mL of hexanes, and dried under vacuum. Yield: 8.98 g (72%) of yellowish solid of **47**. Anal. Calcd for $C_{18}H_{17}Br_3Zr$: C, 38.31; H, 3.04. Found: C, 38.57; H, 3.29. ^{1}H NMR (CD_2Cl_2): δ 7.89 (dd, J = 6.6 Hz, J = 3.1 Hz, 4H), 7.41 (dd, J = 6.6 Hz, J = 3.1 Hz, 4H),

7.15 (s, 4H), 7.00 (s, 4H), 2.51 (s, 12H), 2.33 (s, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 144.4, 140.6, 138.2, 131.9, 131.6, 130.3, 129.2, 128.1, 111.0, 25.9, 22.2.

[η^5-2-Mesitylindenyl][η^5-2-(1*H*-pyrrol-1-yl)indenyl]zirconium Dibromide (48). The reaction was carried out similarly to the preparation of compound **39**, starting from 362 mg (2.0 mmol) of **5**, 0.8 mL of 2.5 M (2.0 mmol) *n*BuLi in hexanes, and 1.12 g (2.0 mmol) of **47**. The reaction mixture was evaporated to dryness. The crude product was extracted with 2 × 20 mL of toluene. The combined extract was filtered through a PTFE membrane filter (0.45 um) and evaporated to a volume equal to ca. 10 mL. The precipitate that formed was filtered off, washed with 10 mL of toluene, and 3 × 10 mL of hexanes, and dried under vacuum. Yield: 575 mg (43%) of yellow solid of **48**. Anal. Calcd for $C_{31}H_{27}Br_2NZr$: C, 56.02; H, 4.09; N, 2.11. Found: C, 56.20; H, 4.25; N, 2.00. ^1H NMR (CD_2Cl_2): δ 7.54−7.47 (m, 2H), 7.43−7.38 (m, 2H), 7.35−7.24 (m, 2H), 7.15 (s, 2H), 6.92 (t, J = 2.5 Hz, 2H), 6.38 (t, J = 2.5 Hz, 2H), 5.96 (s, 2H), 5.94 (s, 2H), 2.45 (s, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.5, 138.4, 137.4, 136.5, 131.0, 129.5, 127.4, 126.7, 126.5, 126.4, 125.8, 123.4, 118.9, 111.7, 108.8, 93.0, 24.7, 20.7.

[η^5-2-Mesitylindenyl][η^5-2-(1*H*-indol-1-yl)indenyl]zirconium Dibromide (49). The reaction was carried out similarly to the preparation of compound **39**, starting from 462 mg (2.0 mmol) of **7**, 0.8 mL of 2.5 M (2.0 mmol) *n*BuLi in hexanes, and 1.12 g (2.0 mmol) of **47**. The reaction mixture was evaporated to dryness. The crude product was extracted with 2 × 20 mL of toluene. The combined extract was filtered through a PTFE membrane filter (0.45 um) and evaporated to a volume equal to ca. 10 mL. A mixture of this solution and 17 mL of hexanes was heated to reflux and carefully placed in the refrigerator. Crystals precipitating at −30 °C were collected, washed with 20 mL of hexanes, and dried under vacuum. Yield: 840 mg (58%) of yellow solid of **49**. Anal. Calcd for $C_{35}H_{29}Br_2NZr$: C, 58.82; H, 4.09; N, 1.96. Found: C, 58.75; H, 4.01; N, 2.12. ^1H NMR (CD_2Cl_2): δ 7.79−7.74 (m, 2H), 7.51−7.46 (m, 2H), 7.45−7.40 (m, 2H), 7.37−7.72 (m, 3H), 7.29−7.34 (m, 2H), 7.11 (d, J = 3.1 Hz), 7.10 (s, 2H), 6.76 (dd, J = 0.7 Hz, J = 3.5 Hz, 1H), 6.28 (s, 2H), 5.90 (s, 2H), 2.45 (s, 3H), 2.27 (s, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 139.1, 138.3, 137.2, 136.4, 134.8, 131.1, 130.4, 129.5, 127.3, 126.91, 126.86, 126.8, 126.3, 125.8, 123.8, 123.7, 121.9, 121.5, 112.4, 108.9, 106.1, 94.8, 24.5, 20.6.

[η^5-2-Mesitylindenyl][η^5-2-(9*H*-carbazol-9-yl)indenyl]zirconium Dibromide (50). The reaction was carried out similarly to the preparation of compound **48**, starting from 562 mg (2.0 mmol) of **14**, 0.8 mL of 2.5 M (2.0 mmol) *n*BuLi in hexanes, and 1.12 g (2.0 mmol) of **47**. Yield: 340 mg (22%) of yellow solid of **50**. Anal. Calcd for $C_{39}H_{31}Br_2NZr$: C, 61.25; H, 4.09; N, 1.83. Found: C, 61.07; H, 4.22; N, 1.70. ^1H NMR (C_6D_6, 70 °C): δ 8.05 (dq, J = 0.7 Hz, J = 7.7 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H), 7.61−7.54 (m, 2H), 7.51−7.44 (m, 2H), 7.38 (ddd, J = 1.5 Hz, J = 7.3 Hz, J = 8.1 Hz, 2H), 7.35−7.30 (m, 2H), 7.24−7.21 (m, 2H), 7.17−7.13 (m, 2H), 6.65 (s, 2H), 6.48 (s, 2H), 6.14 (s, 2H), 2.24 (s, 3H), 2.10 (s, 6H). $^{13}C\{^1H\}$ NMR (C_6D_6, 70 °C): δ 139.6, 137.3, 136.9, 136.7, 131.1, 129.9, 129.0, 128.2, 127.6, 127.2, 127.1, 126.4, 126.3, 125.9, 124.9, 124.7, 121.7, 120.1, 112.7, 97.4, 24.0, 20.37.

[η^5-Pentamethylcyclopentadienyl][η^5-1-(1*H*-pyrrol-1-yl)-1*H*-indenyl]zirconium Dichloride (51). In a round-bottom flask (0.1 L) in the glovebox, to a solution of 0.65 g (3.60 mmol) of **19** in 35 mL of toluene was added 1.44 mL of 2.5 M *n*BuLi (3.60 mmol) in hexanes with vigorous stirring at ambient temperature. This mixture was additionally stirred overnight, and then 1.20 g (3.60 mmol) of Cp^*ZrCl_3 was added. The resulting mixture was stirred for 2 days at ambient temperature and then for 10 h at 80 °C. The resulting hot mixture was filtered through Celite 503. The Celite layer was washed with 2 × 20 mL of hot toluene. The combined extract was evaporated to dryness. The residue was washed with 3 × 30 mL of hexanes and dried under vacuum. Yield: 1.05 g (61%) of yellowish solid. Anal. Calcd for $C_{23}H_{25}Cl_2NZr$: C, 57.84; H, 5.28; N, 2.93. Found: C, 58.11; H, 5.40; N, 2.76. ^1H NMR (CD_2Cl_2): δ 7.66 (m, 2H, 7-H in indenyl), 7.54 (m, 1H, 4-H in indenyl), 7.31 (ddd, J = 8.7 Hz, J = 6.7 Hz, J = 1.2 Hz, 1H, 6-H in indenyl), 7.22 (ddd, J = 8.4 Hz, J = 6.7 Hz, J = 1.3 Hz, 1H, 5-H in indenyl), 7.12 (t, J = 2.2 Hz, 2H, 2,5-H in pyrrolyl), 6.35 (d, J = 3.3 Hz, 1H, 2-H in indenyl), 6.30 (t, J = 2.2 Hz, 2H, 3,4-H in pyrrolyl), 5.79 (dd, J = 3.3 Hz, J = 0.9 Hz, 1H, 3-H in indenyl), 1.90 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 136.4, 128.2, 127.9, 127.1, 126.9, 126.4, 123.9, 123.5, 123.3, 111.4, 111.2, 95.6, 13.5.

[η^5-Pentamethylcyclopentadienyl][η^5-2-(1*H*-benzimidazol-1-yl)-1*H*-indenyl]zirconium Dichloride (52). In a round-bottom flask (0.1 L) in the glovebox, to a suspension of 0.53 g (2.30 mmol) of **21** in 10 mL of toluene was added 0.38 g (2.30 mmol) of $LiN(TMS)_2$ with vigorous stirring. This mixture was additionally stirred for 10 h at ambient temperature, and then 0.77 g (2.30 mmol) of Cp^*ZrCl_3 was added. The resulting mixture was stirred for 10 h at 95 °C and then filtered through Celite 503. The Celite layer was washed with 2 × 40 mL of hot toluene. The combined extract was evaporated to ca. 25 mL. Crystals precipitating from this solution at −30 °C were collected, washed with 5 mL of cold toluene, and dried under vacuum. Yield: 0.40 g (44%) of white solid. Anal. Calcd for $C_{26}H_{26}Cl_2N_2Zr$: C, 59.07; H, 4.96; N, 5.30. Found: C, 59.22; H, 5.05; N, 5.38. $^1H\{^{13}C\}$ NMR (CD_2Cl_2): δ 8.79 (br.s, 1H, 2-H in 1*H*-benzimidazol-1-yl), 8.29 (m, 1H, 7-H in 1*H*-benzimidazol-1-yl), 7.73 (m, 1H, 4-H in 1*H*-benzimidazol-1-yl), 6.87−7.58 (m, 6-H, 4,5,6,7-H in indenyl and 5,6-H in 1*H*-benzimidazol-1-yl), 6.25 (br.s, 2H, 1,3-H in indenyl), 2.06 (s, 15H, Cp*).

X-ray Structural Determinations of 22, 26, 32, 38, and 50. The resulting crystallographic data are summarized in the Supporting Information. For complex **50**, data were collected on a CAD4 Enraf-Nonius instrument (λ(Mo Kα) = 0.710 73 Å, graphite monochromator, $\theta-{}^5/_3\theta$ scans) at room temperature. All other X-ray experiments were carried out using a SMART 1000 CCD diffractometer (λ(Mo Kα) = 0.710 73 Å, graphite monochromator, ω scans) at 120 K. All structures were solved by direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. All the hydrogen atoms were placed in geometrically calculated positions (except for hydrogens of the water molecule in **50**, for which hydrogens were localized from the difference Fourier map) and included in the refinement using riding approximation. The complexes **22**, **26**, and **32** occupy a special position on the 2-fold axis. The crystal **22** contains a solvate toluene molecule which is disordered over two sites related by an inversion center. The details of data collection and crystal structure refinement, for which we used the SAINT Plus,[38] SADABS,[39] SHELXTL-97,[40] and PLATON[41] program packages, are summarized in the Supporting Information.

Olefin Polymerization Studies. Polymerizations were conducted in an inert-atmosphere (N_2) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal volume of reactor 23.5 mL for PE and EO runs and 22.5 mL for PP and EP runs), septum inlets, a regulated supply of nitrogen, ethylene and propylene, and disposable PEEK mechanical stirrers (800 rpm). The autoclaves were prepared by purging with dry nitrogen at 110 or 115 °C for 5 h and then at 25 °C for 5 h. Solvents and polymerization grade toluene and hexanes were supplied by ExxonMobil Chemical Co. and thoroughly dried and degassed prior to use. 1-Octene, 98% (Aldrich), was dried by stirring over Na/K

(38) SMART and SAINT, Release 5.0, Area Detector Control and Integration Software; Bruker AXS, Analytical X-Ray Instruments, Madison, WI, 1998.

(39) Sheldrick, G. M. SADABS: A Program for Exploiting the Redundancy of Area-Detector X-Ray Data; University of Göttingen, Göttingen, Germany, 1999.

(40) Sheldrick, G. M. SHELXTL-97 Program for Solution and Refinement of Crystal Structure; Bruker AXS Inc., Madison, WI, 1997.

(41) Spek, A. L. PLATON: A Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 2002.

alloy overnight followed by filtration through basic alumina (Aldrich, Brockman Basic 1). Polymerization grade ethylene was used and further purified by passing it through a series of columns: 500 cm^3 Oxyclear cylinder (Labclear, Oakland, CA) followed by a 500 cm^3 column packed with dried 3 Å molecular sieves (Aldrich), and a 500 cm^3 column packed with dried 5 Å molecular sieves (Aldrich). Polymerization grade propylene was used without further purification. MAO (methylalumoxane, 10 wt % in toluene) was purchased from Albemarle Corp. and used as a 1 or 2 wt % in toluene solution. Micromoles of MAO reported in the paper are based on the micromoles of aluminum in MAO. The formula weight of MAO is 58.0.

Ethylene Polymerization (PE) or Ethylene/1-Octene Copolymerization (EO). The reactor was prepared as described above and then purged with ethylene. Toluene (3.80 mL), 1-octene (0.64 mL) when used, and MAO (10 μmol) were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature (80 °C) and charged with ethylene to process pressure (75 psig) with stirring at 800 rpm. The transition-metal compound (0.02 μmol as 0.2 mmol/L solution in toluene) was added via syringe with the reactor at process conditions. Ethylene was allowed to enter (through the use of computer-controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure. Polymerizations were halted by addition of approximately a 50 psig of O_2/Ar (5 mol % O_2) gas mixture to the autoclaves for approximately 30 s. The polymer was isolated after the solvent was removed under vacuum.

Propylene Polymerization (PP). The reactor was prepared as described above and then heated to 40 °C and purged with propylene gas at atmospheric pressure. Hexanes (3.73 mL), MAO (40 μmol), and liquid propylene (1.066 mL) were added via syringe. The reactor was then heated to process temperature (70 °C) with stirring at 800 rpm. The transition-metal complex (0.08 μmol as a 0.6 mmol/L solution in toluene) was added via syringe with the reactor under process conditions. Polymerizations were halted by addition of an approximately 50 psig of O_2/Ar (5 mol % O_2) gas mixture to the autoclaves for approximately 30 s. The polymer was isolated after the solvent was removed under vacuum.

Ethylene/Propylene Copolymerization (EP). The reactor was prepared as described above and then purged with ethylene. The reactor was heated to 40 °C, and ethylene was then added to a target pressure of 10 psig (single addition), followed by the addition of hexanes (3.77 mL), MAO (40 μmol), and then liquid propylene (1.066 mL). All additions were made via syringe. The reactor was then heated to process temperature (70 °C) with stirring at 800 rpm. The transition-metal complex (0.08 μmol as a 0.6 mmol/L solution in toluene) was added via syringe with the reactor under process conditions. Polymerizations were halted by addition of an approximately 50 psig of O_2/Ar (5 mol % O_2) gas mixture to the autoclaves for approximately 30 s. The polymer was isolated after the solvent was removed under vacuum.

Polymer Characterization. For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB) containing 2,6-di-*tert*-butyl-4-methylphenol (BHT) at 160 °C in a shaker oven for approximately 3 h. The typical concentration of polymer in solution is between 0.4 and 0.9 mg/mL with a BHT concentration of 1.25 mg BHT/mL of TCB. Samples were cooled to 135 °C for testing. Molecular weights (M_w and M_n) and molecular weight distributions (PDI = M_w/M_n) of the polymer were measured by gel permeation chromatography using a Symyx Technology GPC equipped with evaporative light scattering detector and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: mp (peak M_w) between 5000 and 3 390 000). Samples were run in TCB (135 °C sample temperature, 160 °C oven/columns) using three Polymer Laboratories: PLgel 10 μm Mixed-B 300 × 7.5 mm columns in series. No column spreading corrections were employed. Numerical analyses were performed using Epoch software available from Symyx Technologies. Samples for infrared analysis were prepared by depositing the stabilized polymer solution onto a silanized wafer (Part number S10860, Symyx). By this method, between approximately 0.12 and 0.24 mg of polymer was deposited on the wafer cell. The samples were subsequently analyzed on a Bruker Equinox 55 FTIR spectrometer equipped with Pikes' MappIR specular reflectance sample accessory. Spectra, covering a spectral range of 5000−500 cm^{-1}, were collected at a 2 cm^{-1} resolution with 32 scans. For ethylene−1-octene copolymers, the weight percent of the comonomer was determined via measurement of the methyl deformation band at ca. 1375 cm^{-1}. The peak height of this band was normalized by the combination and overtone band at ca. 4321 cm^{-1}, which corrects for path length differences. The normalized peak height is correlated to individual calibration curves from ^{1}H NMR data to predict the weight percent of comonomer content within a concentration range of ca. 2−35 wt % for 1-octene. Typically, R^2 correlations of 0.98 or greater are achieved. For ethylene−propylene copolymers, the weight percent of ethylene is determined via measurement of the methylene rocking band (ca. 770−700 cm^{-1}). The peak area of this band is normalized by sum of the band areas of the combination and overtone bands in the 4500−4000 cm^{-1} range. The normalized band area is then correlated to a calibration curved from ^{13}C NMR data to predict the weight percent of ethylene within a concentration range of ca. 5−40 wt %. Typically, R^2 correlations of 0.98 or greater are achieved.

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Supporting Information Available: CIF files and a table giving crystallographic data and details of the data collection and crystal structure refinement for **20**, **24**, **28**, **33**, and **44** and text, figures, and tables regarding the NMR dynamic study of **25** and **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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