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Neutral Dimethylzirconocene Complexes as Initiators for the Ring-Opening Polymerization of ε-Caprolactone

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The synthesis, structures, and ring-opening polymerization (ROP) activity of new dimethyl-*ansa*- and -non-*ansa*-zirconocene complexes are reported. The substituted indene precursors 1-C_9H_7R [R = CH_3 (**1**), CH_2Ph (**2**) and $C_2H_4(C_4H_7O_2)$ (**3**)] were synthesised by treating RBr [R = CH_2Ph and $C_2H_4(C_4H_7O_2)$] or MeI with indenyllithium. Likewise, bridged indenyl/cyclopentadiene compounds [$Me_2Si(3\text{-}C_9H_6R)(C_5Me_4H)$] [R = H (**4**), CH_3 (**5**), CH_2Ph (**6**) and $C_2H_4(C_4H_7O_2)$ (**7**)] were obtained by treating the lithium salt of the appropriately substituted indene with $ClSiMe_2$-(C_5Me_4H). *ansa*-Indenyl–cyclopentadienylmetallocenes [$Zr\{Me_2Si(3\text{-}\eta^5\text{-}C_9H_5R)(\eta^5\text{-}C_5Me_4)\}Cl_2$] [R = H (**8**), CH_3 (**9**), CH_2Ph (**10**), $C_2H_4(C_4H_7O_2)$ (**11**)] were subsequently obtained by treating the dilithium salts of the corresponding ligands with $ZrCl_4$ in toluene. The dimethyl derivatives [$Zr\{Me_2Si(3\text{-}\eta^5\text{-}C_9H_5R)(\eta^5\text{-}C_5Me_4)\}Me_2$] [R = H (**12**), CH_3 (**13**), CH_2Ph (**14**), $C_2H_4(C_4H_7O_2)$ (**15**)] were prepared by treating the corresponding *ansa*-zirconocene dichloride complex with MgMeBr. Dialkyl derivative [$Zr\{Me_2Si\{3\text{-}\eta^5\text{-}C_9H_5(CH_2Ph)\}$-$(\eta^5\text{-}C_5Me_4)\}(CH_2SiMe_3)_2$] (**16**) was prepared by adding 2 equiv. of $LiCH_2SiMe_3$ to complex **10**. Mixed indenyl/cyclopentadienylzirconocene complexes [$Zr(\eta^5\text{-}C_9H_6R)(\eta^5\text{-}C_5H_5)$-$Cl_2$] [R = H (**17**), $C_2H_4(C_4H_7O_2)$ (**18**)] were prepared by treating the lithium salt of the appropriately substituted indene with [$Zr(\eta^5\text{-}C_5H_5)Cl_3$]. Likewise, dimethyl derivatives [$Zr(\eta^5$-$C_9H_6R)(\eta^5\text{-}C_5H_5)Me_2$] [R = H (**19**), $C_2H_4(C_4H_7O_2)$ (**20**)] were prepared by treating the corresponding mixed indenyl/cyclopentadienyl dichloride complex with 2 equiv. of MgMeBr. The X-ray crystal structures of **7**, **12**, and **13** were also established. Finally, comparative catalytic studies of zirconium complexes **12**–**16**, **19** and **20** in ROP reactions of ε-caprolactone are described.

Introduction

Since the discovery of metallocene/MAO catalytic systems for the polymerization of olefins by Sinn and Kaminsky,[1] rapid progress has been made in this field at both the academic and industrial levels.[2] Indeed, it is well known that the structural conformation of the metallocene complex directly influences its catalytic activity and selectivity in polymerization processes.[2c]

The use of *ansa*-cyclopentadienyl and related ligands has received wide attention in the chemistry of group IV metals,[3] mainly due to their ability to impart a selective degree of catalytic activity to their complexes.[4] In this respect, several studies have demonstrated that the incorporation of an *ansa* bridge may have a profound influence on the behaviour of metallocene systems.[5] Furthermore, the use of substituted *ansa* ligands in the stereoselective synthesis of group IV metal complexes, and their importance in catalysis, has received special attention.[5] However, – although various examples of asymmetric *ansa*-zirconocene complexes containing indenyl or fluorenyl systems[6] have been described – there are currently few examples of *ansa*-indenyl–cyclopentadienylzirconocene complexes. We have previously described the synthesis and catalytic activity of *ansa*-indenyl–cyclopentadienylzirconocene complexes bearing bulky ligands.[7] The application of these complexes in stereospecific olefin coordination, together with the stereoregularity of the polymers obtained by using these metallocene catalysts, has also been a focus of past efforts.[7] Although many examples of isospecific unbridged bis-(indenyl)- or bis(cyclopentadienyl)zirconocene catalysts have been described,[8] unbridged mixed indenyl/cyclopentadienylzirconocene systems have received much less attention than their symmetric counterparts.[9]

The ring-opening polymerization (ROP) of heterocyclic monomers invoking the coordination/anionic (also termed coordination/insertion) mechanism[10] is one of the leading

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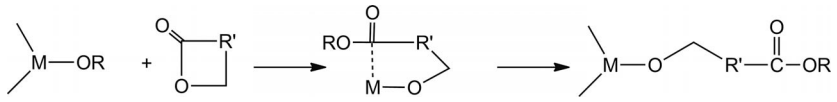


Scheme 1.

polymerization techniques for producing high-molecular-weight (M_W) polymers typical of a chain-growth mechanism (Scheme 1). Several metal complexes have been investigated as catalysts/initiators for ROP of heterocyclic monomers, particularly cyclic esters (lactides such as L-LA and *rac*-LA; lactones such as ε-CL; LA = lactide, CL = caprolactone),[11] largely due to the biodegradation and biocompatibility characteristics of the resulting lactide and lactone polymers.[12] group IV non-metallocenes (non-Cp complexes) and metallocenes, typically in their cationic forms,[13] are best known for their remarkable success in the production of revolutionary polyolefin materials. On the other hand, coordination/anionic ROP of lactones by using group IV *non-metallocene* complexes is well known thanks to extensive studies in this area. These catalysts/initiators are typical of group IV metal *alkoxides* (as initiating groups) as supported by bis(β-ketoamidate),[14] bis(phenoxy)amine,[15] pyrrolylamine,[16] tris(alkoxy or aryloxy)amine,[17] chalcogen-bridged chelating bis(aryloxy),[18] and methylene-bridged bis(phenoxy)[19] ligands. In addition to alkoxides, bis(amido)titanium complexes characterized by chelating diaryloxy ligands have also been used for the ROP of ε-CL[20] together with other catalysts such as homoleptic group IV alkoxide[21] and acetylacetonate[22] complexes, as well as the titanium-organic framework derived from $Ti(OiPr)_4$ and 1,4-butanediol.[23] Fewer reports have described the polymerization of ε-CL by using group IV *metallocene* complexes. Titanocene– and zirconocene–alkyne complexes,[24] as well as their dimetallic congeners formed from iBu_2AlH,[25] are active for the polymerization of ε-CL. Likewise, titanocene alkoxide species derived from the Cp_2TiCl-catalyzed radical ROP of epoxides can initiate the controlled polymerization of ε-CL.[26] Recently, neutral metallocene ester enolate and non-metallocene alkoxy complexes of zirconium[10c] have been found to be active for the polymerization of ε-CL. Additionally, half-sandwich (half-metallocene) dichlorotitanium alkoxides have been utilized to mediate controlled polymerization of ε-CL;[27] replacement of the Cp ligand in half-titanocenes by the indenyl ligand resulted in a significant (> 10-fold) enhancement in the rate of ε-CL polymerization.[28] Cationic zirconocene complexes such as $[Cp_2ZrMe]^+[B(C_6F_5)_4]^-$ and $Cp_2ZrMe^+MeB(C_6F_5)_3^-$, which are formed upon activation of the dimethyl precursor with $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$, respectively, promote the living polymerization of ε-CL, although this occurs through a noncoordination, *cationic* mechanism.[29]

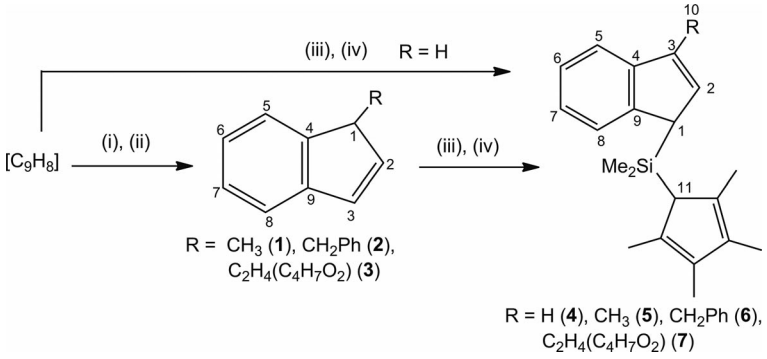
To the best of our knowledge, there have been no reports to date regarding lactone polymerization by using neutral dimethylzirconocene complexes. As part of our ongoing studies into the design of new zirconocene polymerization catalysts,[30] we report here the synthesis, and characterization of new chiral *ansa*-zirconocene complexes, new unbridged, mixed indenyl/cyclopentadienylzirconocene systems, and the first efficient lactone polymerization system based on neutral dimethylzirconocene complexes.

Results and Discussion

Synthesis and Structural Characterization

Substituted indene precursors 1-C_9H_7R [R = CH_3 (**1**), CH_2Ph (**2**) and $C_2H_4(C_4H_7O_2)$ (**3**)] were prepared by treating RBr [R = CH_2Ph and $C_2H_4(C_4H_7O_2)$] or MeI with indenyllithium (Scheme 2). ^1H NMR spectroscopy showed isolated products **1**–**3** to be almost exclusively the 1-isomers. The 1-H signal for compounds **1**–**3** was observed at δ = 3–4 ppm as a multiplet corresponding to one proton. Protons 2-H and 3-H appeared as two multiplets in the region δ = 6–7 ppm, each corresponding to two protons.

Bridged indenyl/cyclopentadiene compounds [Me_2Si(3-C_9H_6R)(C_5Me_4H)] [R = H (**4**), CH_3 (**5**), CH_2Ph (**6**) and $C_2H_4(C_4H_7O_2)$ (**7**)] were obtained by treating the lithium salt of the appropriately substituted indene with $ClSiMe_2(C_5Me_4H)$ (Scheme 2). ^1H NMR spectroscopy showed that isolated products **4**–**7** were predominantly isomers



Scheme 2. (i) *n*BuLi, (ii) RBr [R = CH_2Ph, $C_2H_4(C_4H_7O_2)$], (iii) *n*BuLi, (iv) $ClSiMe_2(C_5Me_4H)$.

bearing the $SiMe_2$ bridge at the 1-position of both the indenyl and cyclopentadienyl moieties. The presence of an asymmetric center at C-1 leads to the formation of a racemic mixture of enantiomers for compounds **4**–**7**. As a result, ^{1}H NMR of **6** revealed two diastereotopic protons for the methylene group, thus affording an AA′B spin system with 2-H upon coupling.

Compound **7** crystallized upon cooling of a toluene solution to –30 °C, and its molecular structure was solved by X-ray diffraction (Figure 1). This compound was found to crystallize in the orthorhombic system, space group *Pbca*; selected bond lengths and angles are presented in Table 1. The silicon atom showd a distorted tetrahedral coordination, with a C25–Si–C26 bond angle of 109.8(2)° and a C1–Si–C10 bond angle of 110.7(2)°. The Si–C bond lengths were found to be between 1.858(3) and 1.899(4) Å, which is normal for such compounds. The heterocyclic group exhibited a chair conformation with H21 in the axial position.

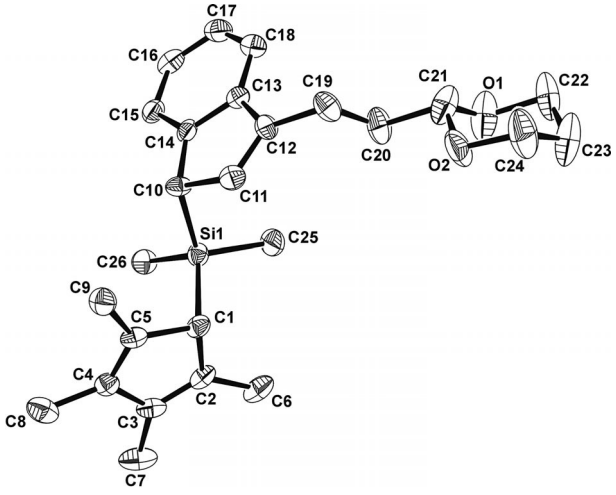
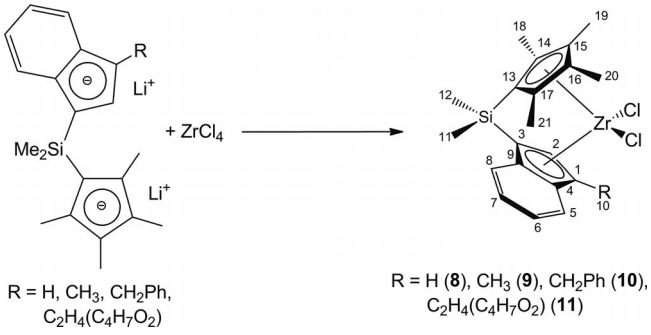


Figure 1. ORTEP drawing of complex **7**. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are shown at 30% probability.

Table 1. Selected bond lengths [Å] and angles [°] for **7**.

Si1–C1	1.899(4)	C1–Si1–C10	110.7(2)
Si1–C10	1.883(4)	C1–Si1–C25	110.8(2)
Si1–C25	1.873(3)	C10–Si1–C25	106.5(2)
Si1–C26	1.858(3)	C10–Si1–C26	110.9(2)
O1–C21	1.308(5)	C25–Si1–C26	109.8(2)
O2–C21	1.411(5)	Si1–C1–C2	108.2(3)
C10-C11	1.504(4)	Si1–C10–C11	107.5(3)
C10-C14	1.501(5)	Si1–C10–C14	111.5(3)
C11-C12	1.342(4)	O1–C21–O2	108.6(5)
C12-C13	1.441(5)	O1–C21–C20	108.0(5)
C13-C14	1.404(5)	O2–C21–C20	104.6(5)

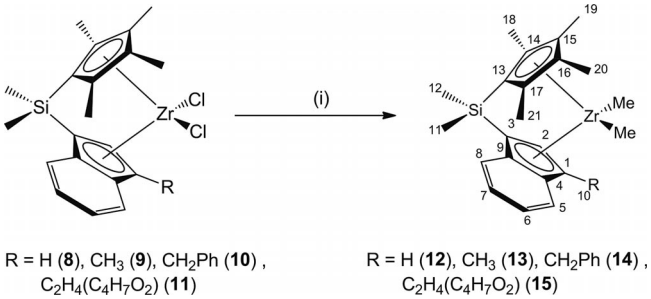
ansa-Indenyl–cyclopentadienylmetallocenes [Zr{Me_2Si-(3-η^5-C_9H_5R)(η^5-C_5Me_4)}Cl_2] [R = H (**8**), CH_3 (**9**), CH_2Ph (**10**), $C_2H_4(C_4H_7O_2)$ (**11**)] were obtained as yellow solids by treating the dilithium salts of the corresponding ligands with $ZrCl_4$ in toluene (Scheme 3). The ^{1}H NMR spectra of complexes **8**–**11** show a lack of symmetry of these chiral complexes, with four signals being assigned to the cyclopentadienyl methyl groups, a singlet to the 2-H proton of the indenyl group, and four multiplets to the protons on the C_6 ring of the indenyl moiety.



Scheme 3.

The conformational chirality of these compounds means that the methylene protons in compounds **10** and **11** are not equivalent and show diastereotopic behaviour. Thus, four signals corresponding to an AB spin system, with a J_{AB} value of 16 Hz, were observed at δ = 4.28 ppm in the NMR spectra of complex **10**. Compound **11** and its X-ray structure have been discussed in a previous report.[28]

Dimethyl derivatives [Zr{Me_2Si(3-η^5-C_9H_5R)(η^5-C_5Me_4)}Me_2] [R = H (**12**), CH_3 (**13**), CH_2Ph (**14**), $C_2H_4(C_4H_7O_2)$ (**15**)] were prepared by treating the corresponding *ansa*-zirconocene dichloride complex with 2 equiv. of MgMeBr (Scheme 4). Compounds **12**–**15** were characterized by spectroscopic methods, and complexes **12** and **13** were amenable to X-ray diffraction studies. We have previously demonstrated that alkylation of silicon-bridged *ansa*-zirconocenes is controlled by steric interactions between the alkyl ligand and the substituent on the cyclopentadienyl or similar group.[31] The ^{1}H NMR spectra of these complexes show two unique signals at high field (between δ = –0.2 and –1.7 ppm) corresponding to the metal-bonded methyl groups, thereby confirming dialkylation of the *ansa*-metallocene complexes. The ^{13}C{^{1}H} NMR spectra also confirmed the dialkylation process. The conformational chirality of these compounds means that the methylene protons in compounds **14** and **15** are again inequivalent and show diastereotopic behaviour. Thus, four signals corresponding to an AB spin system, with a J_{AB} value of 16 Hz, were observed at δ = 4.24 ppm in the ^{1}H NMR spectra of complex **14**.



Scheme 4. (i) MeMgBr.

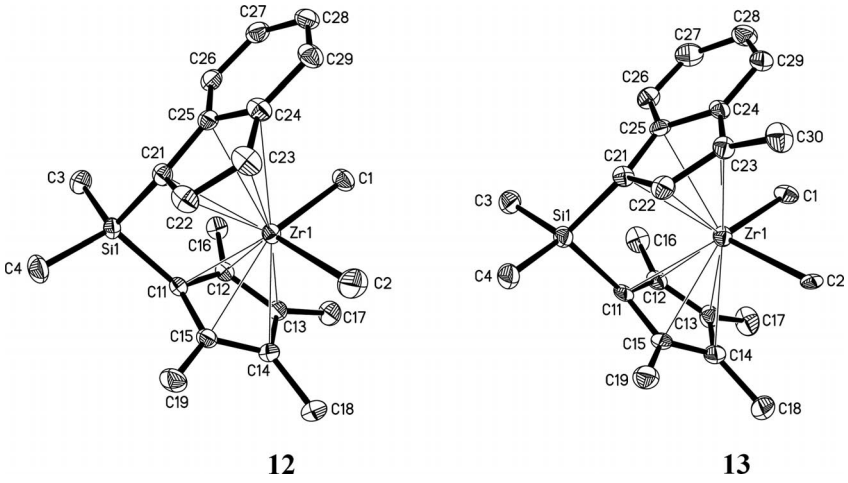


Figure 2. ORTEP drawing of complexes **12** and **13**. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are shown at 30% probability.

Table 2. Selected bond lengths [Å] and angles [°] for **12** and **13**.

	12	**13**
Zr1–C1	2.267(2)	2.299(4)
Zr1–C2	2.271(2)	2.344(3)
Zr1–C21	2.485(2)	2.485(4)
Zr1–C22	2.500(2)	2.511(4)
Zr1–C23	2.600(2)	2.654(4)
Zr1–C24	2.670(2)	2.685(4)
Zr1–C25	2.580(1)	2.572(4)
Si1–C3	1.860(2)	1.851(4)
Si1–C4	1.866(2)	1.858(4)
Si–C11	1.880(1)	1.870(4)
Si–C21	1.867(2)	1.858(4)
Zr1-Cent1	2.222	2.229
Zr1-Cent2	2.264	2.278
av Zr1–C(Cent1)*[a]	2.531	2.535
av Zr1–C(Cent2)*	2.567	2.581
C1–Zr1–C2	96.41(8)	94.8 (1)
C3–Si1–C4	107.35(9)	106.9(2)
C11–Si1–C21	97.09(7)	96.8(2)
Cent1–C11–Si1	160.6	161.8
Cent2–C21–Si1	161.5	162.4
Cent1–Zr1–Cent2	128.1	128.7
C1–Zr1-Cent1	105.8	106.5
C2–Zr1-Cent1	108.0	107.4
C1–Zr1-Cent2	107.4	107.8
C2–Zr1-Cent2	106.6	106.5

[a] *Refers to the average bond length between Zr1 and the carbon atoms of the C_5 ring of the corresponding cyclopentadienyl moiety. Cent1 and Cent2 are the centroids of C11–C15 and C21–C25 respectively.

Compounds **12** and **13** crystallized from toluene solution upon cooling to –30 °C and their molecular structures established by X-ray diffraction. The molecular structures and atomic numbering schemes are shown in Figure 2. Selected bond lengths and angles are presented in Table 2.

The structures of **12** and **13** show the typical bent *ansa*-metallocene conformation observed in their asymmetric zirconocene dichloride precursors.[30] Thus, the *ansa* ligand chelates the zirconium atom, and both C_5 rings are bound to the metal atom in an η^5-mode. The pseudo-tetrahedral environment of the zirconium atom is completed by the two carbon atoms of the methyl groups. The centroids of the cyclopentadienyl rings form an angle of 128.7° and 128.1° with the zirconium atom in **12** and **13**, respectively, which is typical for *ansa*-zirconocene complexes. The Zr1–C1 and Zr1–C2 bond lengths are 2.267(2) and 2.271(2) Å for **12** and 2.299(4) and 2.344(3) Å for **13**, respectively. The Zr1-Cent1 and Zr1–Cent2 bond lengths are 2.227 and 2.279 Å for **12** and 2.222 and 2.264 Å for **13**, respectively. The substituent is oriented in the lateral sector in the direction opposite to indenyl six-membered ring.

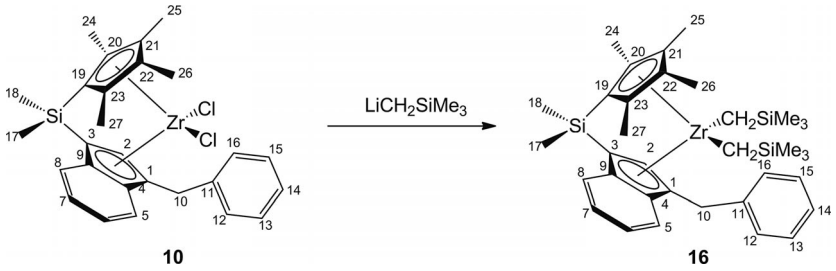
A comparison of **12** and **13** with related *ansa*-zirconocene complexes is given in Table 3 and shows that the molecular structures of all these complexes are essentially the same.

Dialkyl derivative [Zr{Me_2Si\{3-η^5-$C_9H_5(CH_2Ph)$\}(η^5-C_5Me_4)}$(CH_2SiMe_3)_2$] (**16**) was prepared by adding 2 equiv. of $LiCH_2SiMe_3$ to complex **10** (Scheme 5). The ^{1}H NMR

Table 3. Selected structural data of some zirconocene complexes.

Complex	Zr–Cp[a]	Zr–Me	Cp–Zr–Cp	Me–Zr–Me	$C_{(Cp)}$–Si–$C_{(Cp)}$	Ref.
[Zr(Me)(CH_2SiMe_3)($\{\eta^5$-$C_9H_5\}_2SiMe_2$)]	2.26	2.34	127.4	100.0	97.1	[32]
[Zr$(CH_2Ph)_2$($\{\eta^5$-$C_{13}H_7$(Me)\}$\{\eta^5$-$C_5H_4\}SiMe_2$)]	2.21 Cp*, 2.26 Cp	2.31	125.8	97.4	95.4	[33]
[Zr$(Me)_2$\{(η^5-C_5H_3)(*t*Bu)\}$_2$($SiMe_2$)]	2.24	2.27	126.9	99.6	96.6	[34]
[ZrMe_2($\{\eta^5$-$C_9H_6\}\{\eta^5$-$C_5Me_4\}SiMe_2$)] (**12**)	2.222 Cp*, 2.264 Cp	2.267(2), 2.271(2)	128.1	96.41(8)	93.3(7)	this work
[ZrMe_2($\{\eta^5$-$C_9H_5(CH_3)\}\{\eta^5$-$C_5Me_4\}SiMe_2$)] (**13**)	2.227 Cp*, 2.279 Cp	2.294(5), 2.347(4)	128.7	97.09(7)	96.7(2)	this work

[a] Cp refers to the cyclopentadienyl moiety; Cp* refers to the C_5Me_4 moiety.

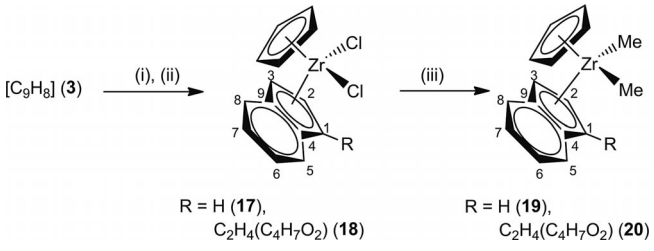


Scheme 5.

spectra of this complex shows two unique doublets (geminal coupling constant of 12 Hz) for the methylene group of the metal-bonded alkyl ligands at high field (δ = –0.57 and –3.04 ppm), thus confirming the dialkylation of the *ansa*-metallocene complex. The ^{1}H NMR spectra for this complex also show its lack of symmetry, with four signals being assigned to the cyclopentadienyl methyl groups, a singlet to the 2-H proton of the indenyl group, and four multiplets to the protons on the C_6 ring of the indenyl moiety. The $^{13}C\{^1H\}$ NMR spectra also confirm the dialkylation process.

Mixed indenyl/cyclopentadienylzirconocene complexes [Zr(η^5-C_9H_6R)(η^5-C_5H_5)Cl_2] {R = H (**17**), $C_2H_4(C_4H_7O_2)$ (**18**)} were prepared by treating the lithium salt of the appropriately substituted indene with [Zr(η^5-C_5H_5)Cl_3]. Complexes **17** and **18** were isolated as yellow solids and characterized spectroscopically. The ^{1}H NMR spectra of these complexes show four multiplets in the range δ = 6.0–8.0 ppm due to the indenyl ligand protons. In addition, one singlet at $\delta \approx$ 6.0 ppm was assigned to the unsubstituted cyclopentadienyl rings. The $^{13}C\{^1H\}$ NMR spectra of **17** and **18** show one signal at $\delta \approx$ 116 ppm corresponding to unsubstituted cyclopentadienyl rings. The signals for the different indenyl substituents are similar to those described for the previous compounds.

Dimethyl derivatives [Zr(η^5-C_9H_6R)(η^5-C_5H_5)Me_2] [R = H (**19**), $C_2H_4(C_4H_7O_2)$ (**20**)] were prepared by treating the corresponding mixed indenyl/cyclopentadienyl dichloride complex with 2 equiv. of MgMeBr. Complexes **19** and **20** were isolated as yellow solids and characterized spectroscopically. The ^{1}H NMR spectra of **19** show a unique signal at δ = –0.47 ppm corresponding to the two metal-bonded methyl groups, whereas spectra for complex **20** show two signals at high field (δ = –0.64 and –0.3 ppm), also corresponding to the metal-bonded methyl groups, thereby confirming the dialkylation of the *ansa*-metallocene complexes.



Scheme 6. (i) *n*BuLi, (ii) $ZrCl_4$, (iii) MeMgBr.

The $^{13}C\{^1H\}$ NMR spectra also confirm the dialkylation process (Scheme 6).

Polymerization Studies

A good initiator for ROP of cyclic esters requires a redox-inactive metal during the polymerization process, an inorganic template LnM that is inert with respect to undesirable reactions, and a labile ligand that is able to undergo an insertion reaction with C–X multiple bonds. In this context, many alkoxide and alkyl complexes, in combination with a co-catalyst such as BnOH or *i*PrOH, have displayed good catalytic activity for the ROP of cyclic esters. However, to the best of our knowledge, very few zirconocene complexes are successful initiators for ROP polymerization without a co-catalyst.[10c,10d] In addition, the only alkylzirconocene initiators[29] used for this type of polymerization are cationic complexes generated by the ionization of dimethylzirconocene with the abstracting reagents $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$. These cationic zirconocene complexes are of particular interest due to the enhanced Lewis acidity of the zirconium centre, a characteristic that is often associated with higher ROP activity. Herein we report the first efficient lactone polymerization system catalyzed by neutral alkylzirconocene complexes. Polymerization of lactides did not result in appreciable levels of products clearly warranting studies into the design of cationic complexes derived from chiral neutral precursors. Such efforts will be necessary in order to find active catalysts that allow stereocontrol in polylactide syntheses under solution-based ROP conditions.

Dialkyl complexes **12**–**16**, **19** and **20** were assessed in ROP of polar monomer ε-caprolactone (CL). Dimethyl initiators **12**–**15** acted as efficient single-component catalysts for the polymerization of ε-CL, in hexane at room temperature, to give medium to high molecular weight polymers. Complex **16** exhibited no ε-CL polymerization activity under these conditions, and only traces of polymer were formed at 60 °C. This very slow initiation rate can probably be attributed to steric hindrance of the TMS groups that prevent sufficient interactions between the zirconium centre and the lactone. Dimethyl initiators **19** and **20** also acted as efficient catalysts for the polymerization of ε-CL; such reactions required toluene due to the poor solubility of **19** and **20** in hexane. These catalysts showed lower monomer conversion rates than their bridged counterparts, probably

Table 4. Polymerization of ε-caprolactone catalyzed by alkyl complexes **12**–**16**, **19** and **20**.[a]

Entry	Initiator	Temp. [°C]	Solvent	$[CL]_0/[Zr]$	Time [h]	Conv. [%][b]	M_n(theor) [Da][c]	M_n(exptl) [Da][d]	M_w/M_n
1	**12**	25	hexane	500	1	100	41291	55316	1,39
2	**13**	25	hexane	500	1	98	48219	56422	1,36
3	**14**	25	hexane	500	1	86	56714	83121	1,63
4	**15**	25	hexane	500	1	71	33411	36920	1,45
5	**16**	25	hexane	500	1	trace	n.d.[e]	n.d.[e]	n.d.[e]
6	**12**	60	hexane	500	0.083	84	43412	62181	1,98
7	**12**	25	THF	500	1	64	20315	25555	1,22
8	**12**	25	toluene	500	1	90	49315	61141	1,42
9	**12**	25	hexane	1000	1	95	106410	128314	1,33
10	**16**	60	hexane	500	1	trace	n.d.[e]	n.d.[e]	n.d.[e]
11	**19**	25	toluene	500	2	58	45972	48836	1,24
12	**20**	25	toluene	500	2	22	39745	37412	1,11

[a] Polymerization conditions: 90 μmol of initiator, 20 mL of solvent. [b] Percentage conversion of monomer: (weight of polymer recovered/weight of monomer) × 100. [c] Theoretical M_n = (monomer/initiator) × (% conversion) × (M_W of ε-CL). [d] Determined by GPC relative to polystyrene standards in THF. The experimental M_n was calculated by using Mark–Houwink's corrections for M_n {M_n(exp) = 0.56[M_n(GPC)]}. [e] n.d. = not determined.

due to their instability in solution. The results of these experiments are summarized in Table 4. In all cases, a decrease in the yield of monomer conversion can be observed with an increase in substituent volume for the indenyl ligand.

We first studied the catalytic performance, namely the activity and the degree of control, for this polymerization process. The activities were evaluated by comparing the kinetic parameters, which were obtained by monitoring the polymerization of ε-CL over time and manual sampling followed by ^{1}H NMR analysis to determine the degree of monomer conversion. The polymerization kinetics were studied for complexes **12**–**15** with $[\varepsilon\text{-CL}]_0/[Zr]$ = 500 and $[Zr] = 6 \times 10^{-3}$ M at 25 °C by using toluene as solvent and with no co-catalyst or activator. We did not use hexane as polymers precipitate in this solvent, thus preventing the degree of conversion from being determined by ^{1}H NMR analysis. A semi-logarithmic plot of $\ln([\varepsilon\text{-CL}]_0/[\varepsilon\text{-CL}]_t)$ vs. reaction time is shown in Figure 3, where $[\varepsilon\text{-CL}]_0$ is the initial lactone monomer concentration and $[\varepsilon\text{-CL}]_t$ the lactone concentration at a given reaction time t. In all cases, the linearity of the plot shows that propagation was first-order with respect to lactone monomer when polymerized at 25 °C in toluene. Furthermore, an induction period, which probably occurs due to the use of a Zr–alkyl group as initiator, was observed in all cases. Such complexes are known to be less nucleophilic than alkoxides, thus leading to a delay in the formation of active species. The linearity of the plot also shows that no termination reactions occurred during the polymerization. The fastest ε-CL polymerization reaction was observed for unsubstituted derivative **12**. The polymerization rate decreases weakly with the volume of the substituent located at C-1 of the indenyl ring, although the K_{app} values found for all complexes were of the same order of magnitude.

For complex **12**, plots of both ε-CL M_n and polydispersity vs. monomer conversion (Figure 4) gave a linear relationship (R^2 = 0.998) that is indicative of a living polymerization process. This means that the polymer chain grows proportionally with the presence of monomer, thereby suggesting that termination or chain-transfer reactions do not occur during the polymerization.

A variety of polymerization conditions were explored for compound **12**, which initiates very rapid polymerization of ε-CL in hexane at 25 °C (Table 4, Entry 1), giving 100% conversion of 500 equiv. of ε-CL in just 1 h. This polymeri-

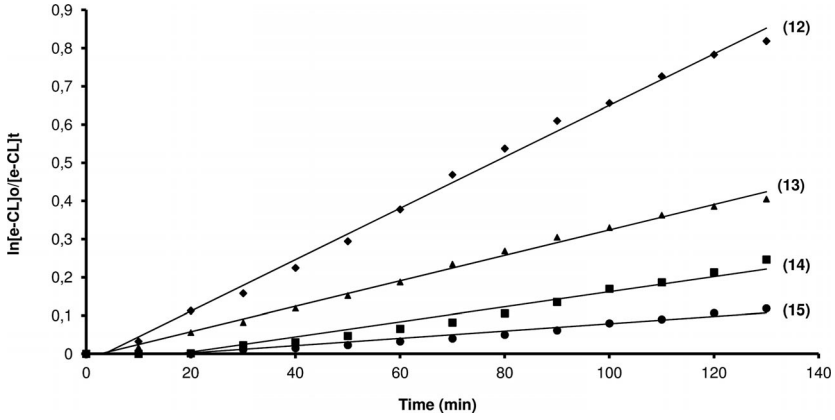


Figure 3. First-order kinetic plots for CL polymerizations in toluene at 25 °C with [CL]/[Zr] = 500 and $[Zr] = 6 \times 10^{-3}$ M: **12**, $k_{aap} = 5.1 \times 10^{-3}$; **13**, $k_{aap} = 4.3 \times 10^{-3}$; **14**, $k_{aap} = 3.8 \times 10^{-3}$; **15**, $k_{aap} = 2.0 \times 10^{-3}$.

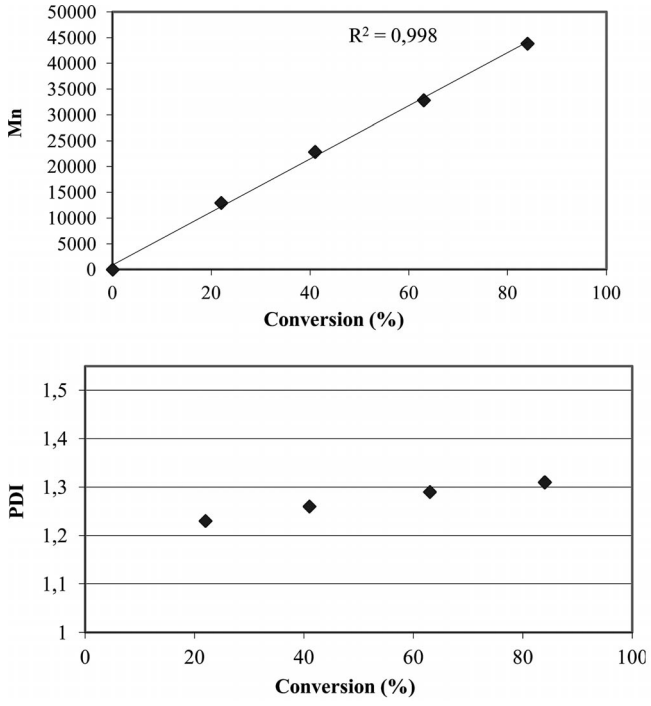
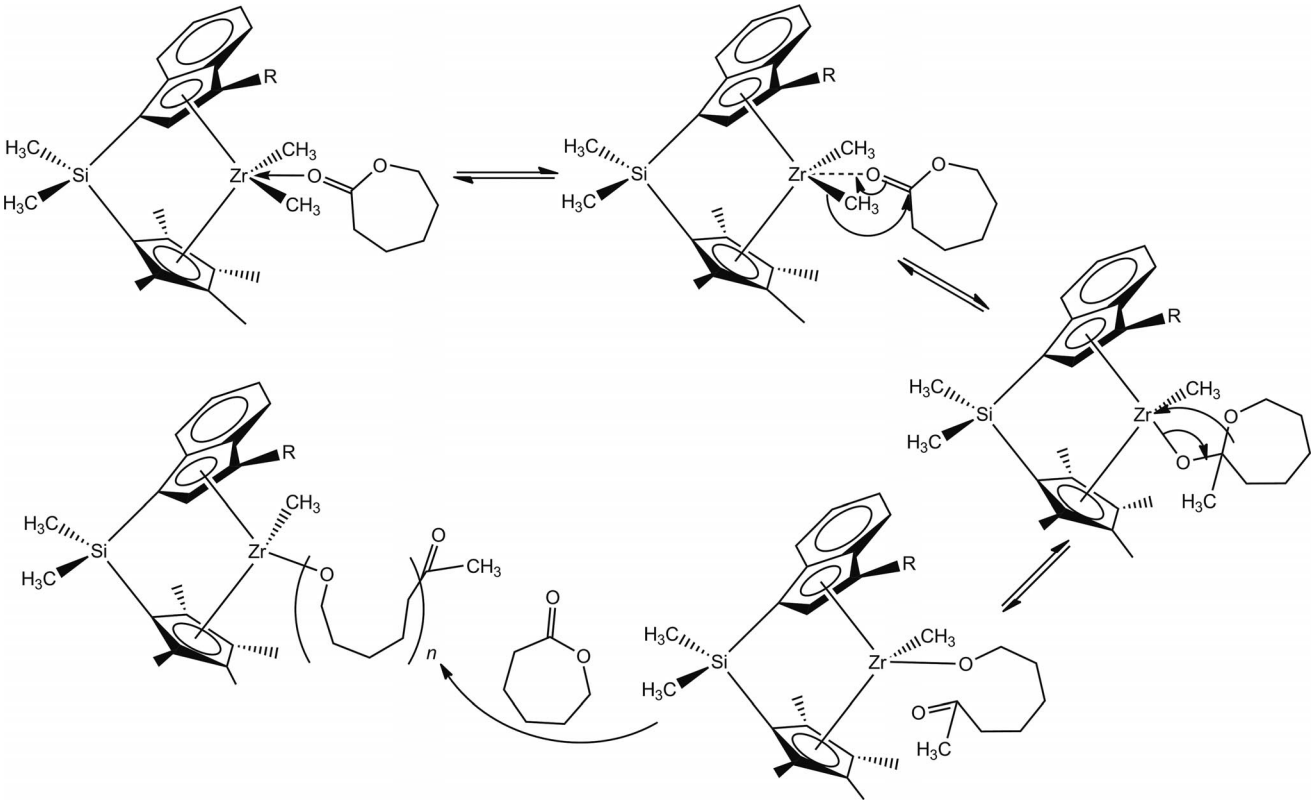


Figure 4. Plot of M_n and PDI by **12** vs. monomer conversion. Conditions: [CL]/[Zr] = 500, toluene, 25 °C.

zation reaction resulted in a medium–high molecular weight polymer with a medium–broad polydispersity (M_n = 55316, M_w/M_n = 1.39). As expected, a temperature increase to 60 °C led to 84% monomer conversion in 0.083 h with a higher polydispersity index (M_w/M_n = 1.98) (Table 4, Entry 6), thus indicating reduced control. Also as expected, changing the reaction solvent to THF resulted in a monomer conversion of only 64% in 1 h and a lower molecular weight (M_n = 25555) (Table 4, Entry 7). These changes are due to coordination of THF to the metal centre, a process that competes with monomer binding during the polymerization process. Changing the reaction solvent to toluene resulted in no significant change. The polymers in these tests were obtained by using a monomer/initiator ratio of 500:1. A 2-fold increase in this ratio gave a polymer with a significantly higher molecular weight but similar molecular weight distribution (Table 4, Entry 9), thereby again indicating a living polymerization process. The relatively broad polydispersities obtained with complexes **12**–**15** can be explained by the presence of a Zr–alkyl complex, which is known to be less nucleophilic than alkoxide, as initiator, thus slowing the initiation process.[35] The M_n values measured by gel-permeation chromatography (GPC) were substantially higher than those predicted on the basis of conversions and on the assumption that each zirconium centre is catalytically active. This deviation could be consistent with poor rates of initiation and ε-CL insertion into the Zr–Me bond compared to propagation, which is a well-established feature of metal–alkyl initiators.[36] Catalyst decomposition may also have had an effect on these results.

The NMR spectra of the polymers obtained show the corresponding signals for chain terminal groups (a triplet



Scheme 7.

at δ = 3.64 ppm due to the terminal CH_2OH group and a singlet at δ = 2.17 ppm due to the terminal $COCH_3$ group). Likewise, the $^{13}C\{^1H\}$ NMR spectra show signals at δ = 173.29 and 62.71 ppm corresponding to the carbonyl ($COCH_3$) and terminal methyl groups ($COCH_3$), respectively. These spectra confirm the existence of a coordination/insertion mechanism involving an alkoxide complex as the active species (Scheme 7).

Conclusions

We have reported the synthesis of a new family of substituted bridged indenyl/cyclopentadiene compounds and new *ansa*- and non-*ansa*-zirconocene dichloride derivatives. Subsequent treatment of these complexes with MeMgBr leads to the corresponding dimethyl compounds. NMR spectroscopic and X-ray single-crystal studies allowed the ligands and zirconocene complexes to be characterized structurally. A detailed study of ROP processes involving these dialkyl complexes was performed. ε-Caprolactone was polymerized to give medium molecular weight polymers with moderate to broad polydispersities. The broader polydispersities are due to the lower rates of initiation compared to propagation, which is a well-established feature of metal–alkyl initiators. Polymerization of lactides did not result in appreciable levels of polymer. Consequently, further studies of cationic or unsaturated complexes derived from these chiral neutral derivatives will be required to obtain active catalysts capable of providing stereochemical control in ROP-mediated polylactide syntheses.

Experimental Section

General: All reactions were performed by using standard Schlenk techniques under dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Deuterated solvents were stored over activated molecular sieves (4 Å) and degassed by several freeze-pump-thaw cycles. ^1H and ^{13}C NMR spectra were recorded with a Varian Inova FT-500 (^1H: 500 MHz; ^{13}C: 125 MHz) spectrometer and referenced to the residual deuterated solvent. The different peaks were assigned by means of 2D COSY, NOESY and g-GHSQC experiments, using standard VARIAN-FT software, and processed using an IPC-Sun computer. Gel permeation chromatography (GPC) measurements were performed with a Polymer Laboratories PL-GPC-220 instrument equipped with a TSK-GEL G3000H column and an ELSD-LTII light-scattering detector. The GPC column was eluted with THF at 45 °C at 1 mL/min and calibrated by using eight monodisperse polystyrene standards in the range 580–483000 Da. C and H microanalyses were carried out by using a Perkin–Elmer 2400 microanalyzer. $ZrCl_4$, neat indene, $BrC_2H_4(C_4H_7O_2)$, $BrCH_2Ph$, MeI, $ClSiMe_2(C_5Me_4H)$, $LiCH_2SiMe_3$ and MeMgBr were purchased from Aldrich and used directly. ε-Caprolactone (ε-CL) was purchased from Aldrich Chemical Co., degassed and dried with CaH_2 overnight, followed by vacuum distillation. The purified monomer was stored over activated molecular sieves (4 Å).

Synthesis of 1-Methylindene (1): *n*BuLi (1.60 M in hexane, 23.57 mL, 37.72 mmol) was added to a cooled (–78 °C) solution of C_9H_8 (4.00 mL, 34.29 mmol) in Et_2O (60 mL) over 15 min. At the end of the addition, the solution was allowed to reach room temp. and stirred for 4 h, cooled again to –78 °C, and MeI (2.13 mL, 34.29 mmol) was added. The reaction mixture was allowed to reach room temp. and stirred for 4 h. The solvent was removed in vacuo and the product extracted with hexane (2× 50 mL). The solvent was removed from the filtrate under reduced pressure to yield the title compound as a yellow solid. Yield 3.75 g (84%). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.34 (d, 3 H, CH_3), 3.56 (m, 1 H, 1-H), 6.39 (dd, 1 H, 2-H), 6.85 (d, 1 H, 3-H), 7.24 and 7.37 (2t, J = 7.3 Hz, 1 H, each, 6-H, 7-H), 7.33 and 7.43 (2d, J = 6.9 Hz, 1 H, each, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.43 (CH_3), 44.85 (C-1), 122.43 (C-5), 123.96 (C-8), 124.72 (C-6), 126.35 (C-7), 130.11, 135.50 (C-2, C-3), 141.21 (C-4), 146.20 (C-9) ppm. $C_{10}H_{10}$ (130): calcd. C 92.31, H 7.69; found C 92.36, H 7.58.

Synthesis of 1-Benzylidene (2): Compound **2** was synthesized in a manner identical to that for **1** from *n*BuLi (1.60 M in hexane, 23.57 mL, 37.72 mmol), C_9H_8 (4.00 mL, 34.29 mmol) and benzyl bromide (5.86 mL, 34.29 mmol). Yield 6.83 g (96%). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.69 (dd, ^2J = 13.5, ^3J = 9 Hz, 1 H, CH_2Ph), 3.04 (dd, ^2J = 13.4, ^3J = 7 Hz, 1 H, CH_2Ph), 3.73 (t, ^3J = 8 Hz, 1 H, 1-H), 6.44 (dd, ^3J = 1.8, 5.5 Hz, 1 H 2-H), 6.79 (d, ^4J = 1.5 Hz, 1 H, ^3J = 5.43 Hz 3-H), 7.14–7.36 (m, 9 H, 5-H/8-H, CH_2Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.44 (CH_2Ph) 42.55 (C-1), 132.35, 135.36 (C-2, C-3), 122.84–129.53 (C-5/C-8, C-12/C-16), 138.76 (C-11)140.28 (C-4), 144.18 (C-9) ppm. $C_{16}H_{15}$ (207): calcd. C 92.75, H 7.25; found C 92.80, H 7.29.

Synthesis of 2-[2-(1*H*-Inden-1-yl)ethyl]-1,3-dioxane (3): Compound **3** was synthesized in a manner identical to that for **1** from *n*BuLi (1.60 M in hexane, 24.64 mL, 39.43 mmol), C_9H_8 (4.00 mL, 34.29 mmol) and 2-(2-bromoethyl)-1,3-dioxane (4.67 mL, 34.29 mmol). Yield 7.62 g (96%). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.33 (m, 1 H, 14-H_{eq}), 1.66 (m, 3 H, 10-H, 11-H, 11′-H), 2.06 (m, 2 H, 10′-H, 14-H_{ax}), 3.49 (m, 1 H, 1-H), 3.72 (m, 2 H, 13-H_{ax}, 15-H_{ax}), 4.09 (m, 2 H, 13-H_{eq}, 15-H_{eq}), 4.49 (t, J = 4.8 Hz, 1 H, 12-H), 6.52 (m, 1 H, 2-H), 6.81 (m, 1 H, 3-H), 7.18 and 7.24 (2t, J = 7 Hz, 1 H, each, 6-H, 7-H), 7.33 and 7.43 (2d, J = 7 Hz, 1 H, each, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.87 (C-11), 26.15 (C-14), 32.98 (C-10), 50.13 (C-1), 67.09 (C-13, C-15), 102.36 (C-12), 121.09 (C-5), 123.01 (C-8), 124.79 (C-6), 126.54 (C-7), 131, 24, 138.94 (C-2, C-3), 144.38 (C-4), 144.70 (C-9) ppm. $C_{15}H_{17}O_2$ (229): calcd. C 78.60, H 7.42; found C 78.54, H 7.48.

Synthesis of $(C_9H_7)(C_5HMe_4)SiMe_2$ (4): *n*BuLi (1.60 M in hexane, 21.12 mL, 33.79 mmol) was added to a cooled (–78 °C) solution of C_9H_8 (4.00 mL, 34.29 mmol) in Et_2O (60 mL) over 15 min. At the end of the addition, the solution was allowed to reach room temp. and stirred for 4 h, cooled again to –78 °C, and $(C_5HMe_4)SiMe_2Cl$ (7.41 mL, 34.78 mmol) in Et_2O (30 mL) was added. The reaction mixture was warmed up to room temp. and stirred for 16 h. The solvent was removed in vacuo and the product extracted with hexane (2× 50 mL). The solvent was removed from the filtrate under reduced pressure to yield the title compound as a pale-yellow oil. Yield 7.12 g (75%). ^1H NMR (500 MHz, $CDCl_3$): δ = –0.43, –0.18 [2 s, H each, $Si(CH_3)_2$], 1.83, 1.98, 2.05, 2.26 [4 s, 3 H each, $C_5(CH_3)_4$], 3.41 (s, 1 H, 1-H), 4.08 (m, 1 H, 10-H), 6.30 (m, 1 H, 2-H) 6.41, (m, 1 H, 3-H), 7.16 (m, 1 H, 6-H), 7.32 (m, 1 H, 7-H), 7.45 (m, 2 H, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.71, –5.22 [$Si(CH_3)_2$], 11.29, 11.32, 14.75, 14.82 [$C_5(CH_3)_4$], 42.60 (C-10), 54.01 (C-1), 119.02 (C-5), 122.94 (C-8), 123.85 (C-6), 124.98 (C-7), 131.01 (C-2), 122.12 (C-3), 145.87 (C-4), 145.99 (C-9), 121.34, 132.45, 137.24, 138.31 [$C_5(CH_3)_4$] ppm.

Synthesis of [(C$_9$H$_6$)CH$_3$](C$_5$HMe$_4$)SiMe$_2$ (5): Compound **5** was synthesized in a manner identical to that for **4** from *n*BuLi (1.60 M in hexane, 21.12 mL, 33.79 mmol), **1** (4.00 g, 30.72 mmol) and (C$_5$HMe$_4$)SiMe$_2$Cl (6.78 mL, 30.72 mmol). Yield 6.52 g (65%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = –0.41, –0.17 [2 s, H each, Si(C*H*$_3$)$_2$], 1.88, 2.02, 2.03, 2.24 [4 s, 3 H each, C$_5$(C*H*$_3$)$_4$], 3.07 (s, 1 H, C*H*$_3$) 3.54 (s, 1 H, 1-H), 4.01 (m, 1 H, 11-H), 6.26 (m, 1 H, 2-H), 7.20 (m, 1 H, 6-H), 7.30 (m, 1 H, 7-H), 7.42 (m, 2 H, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = –5.73, –5.18 [Si(*C*H$_3$)$_2$], 12.94 (*C*H$_3$), 11.25, 11.31, 14.70, 14.80 [C$_5$(*C*H$_3$)$_4$], 42.57 (C-11), 54.65 (C-1), 118.90 (C-5), 120.98 (C-3), 122.89 (C-8), 123.61 (C-6), 124.70 (C-7), 130.56 (C-2), 145.50 (C-4), 145.86 (C-9), 120.98, 131.55, 136.35, 137.35 [*C*$_5$(CH$_3$)$_4$] ppm.

Synthesis of [(C$_9$H$_6$)CH$_2$(C$_6$H$_5$)](C$_5$HMe$_4$)SiMe$_2$ (6): Compound **6** was synthesized in a manner identical to that for **4** from *n*BuLi (1.60 M in hexane, 13.33 mL, 21.33 mmol), **2** (4.00 g, 19.39 mmol) and (C$_5$HMe$_4$)SiMe$_2$Cl (4.20 mL, 19.39 mmol). Yield 5.99 g (80%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = –0.46, –0.09 [2 s, H each, Si(C*H*$_3$)$_2$], 1.77, 1.84, 1.91, 2.01 [4 s, 3 H each, C$_5$(C*H*$_3$)$_4$], 2.99 (s, 1 H, 1-H), 3.48 (s, 1 H, 17-H), 3.93 (s, 2 H, C*H*$_2$Ph) 6.06 (m, 1 H, 2-H), 7.13–7.43 (m, 9 H, 5-H/8-H, CH$_2$*Ph*) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = –5.58, –4.23 [Si(*C*H$_3$)$_2$], 11.21, 11.25, 14.68, 14.78 [C$_5$(*C*H$_3$)$_4$], 34.44 (*C*H$_2$Ph), 37.67 (C-17), 42.55 (C-1), 119.01 (C-3), 119.31 (C-5), 123.01 (C-8), 123.72 (C-6), 124.68 (C-7), 125.98–128.89 ([*C*$_5$(CH$_3$)$_4$], CH$_2$*Ph*), 129.26 (C-2), 144.50 (C-4), 146.32 (C-9) ppm.

Synthesis of [(C$_9$H$_6$)CH$_2$CH$_2$(C$_4$H$_7$O$_2$)](C$_5$HMe$_4$)SiMe$_2$ (7): Compound **7** was synthesized in a manner identical to that for **4** from *n*BuLi (1.60 M in hexane, 11.88 mL, 19.08 mmol), **3** (4.00 g, 17.36 mmol) and (C$_5$HMe$_4$)SiMe$_2$Cl (3.84 mL, 17.36 mmol). Yield 6.52 g (91%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = –0.48, –0.21 [2 s, H each, Si(C*H*$_3$)$_2$], 1.31 (m, 1 H, 14-H$_{eq}$), 1.79, 1.83, 1.96, 1.98 [4 s, 3 H each, C$_5$(C*H*$_3$)$_4$], 2.08 (m, 3 H, 14-H$_{ax}$, 11-H, 11′-H), 2.68 (m, 2 H, 10-H, 10′-H), 3.01 (s, 1 H, 1-H), 3.49 (s, 1 H, 16-H), 3.74 (m, 2 H, 13-H$_{ax}$, 15-H$_{ax}$), 4.10 (m, 2 H, 13-H$_{eq}$, 15-H$_{eq}$), 4.59 (m, 1 H, 12-H), 6.21 (m, 1 H, 2-H), 7.14 (m, 1 H, 6-H), 7.22 (m, 1 H, 7-H), 7.38 (m, 2 H, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = –5.62, –4.72 [Si(*C*H$_3$)$_2$], 11.27, 11.31, 14.72, 14.80 [C$_5$(*C*H$_3$)$_4$], 25.66 (C-11), 26.31 (C-14), 31.52 (C-10), 42.69 (C-1), 54.06 (C-16), 67.82 (C-13), 67.91 (C-15), 104.61 (C-12), 121.31 (C-5), 123.31 (C-8), 125.03 (C-6), 126.86 (C-7), 127.90 (C-2), 119.01 (C-3), 120.12 (C-4), 122.05 (C-9), 124.09, 124.98, 126.02, 129.63 [*C*$_5$(CH$_3$)$_4$] ppm.

Synthesis of [ZrCl$_2${(η^5-C$_9$H$_6$)(η^5-C$_5$Me$_4$)SiMe$_2$}] (8): A cooled (–78 °C) slurry of ZrCl$_4$ (5.40 g, 23.20 mmol) in toluene (50 mL) was rapidly added to a cooled (–78 °C) solution of Li$_2$[(C$_9$H$_7$)(C$_5$Me$_4$)SiMe$_2$] in Et$_2$O (50 mL) obtained by treating **4** (7.83 g, 23.20 mmol) with *n*BuLi (31.95 mL, 46.50 mmol). The reaction mixture was stirred at –20 °C for 30 min and then warmed to room temp.; the solvent was removed in vacuo and toluene (75 mL) added. The yellow suspension was filtered through a G4 frit with Celite. The filtrate was concentrated to dryness under reduced pressure to yield a yellowish product, which was washed with hexane (2× 20 mL) and dried to give a yellow solid. Yield 9.86 g (93%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.49, 0.67 [2 s, 3 H each, Si(C*H*$_3$)$_2$], 1.71, 1.74, 1.87, 1.93 [4 s, 3 H each, C$_5$(C*H*$_3$)$_4$], 5.66 (s, 1 H, 2-H), 5.98 (s, 1 H, 1-H), 6.85 (t, *J* = 7.6 Hz, 1 H, 6-H), 7.25 (t, *J* = 7.6 Hz, 1 H, 7-H), 7.29 (d, *J* = 7.6 Hz, 1 H, 5-H), 7.51 (d, *J* = 7.6 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 0.98, 1.23 [Si(*C*H$_3$)$_2$], 12.13, 12.35, 14.85, 15.26 [C$_5$(*C*H$_3$)$_4$], 86.30 (3-C), 96.83 (12-C), 117.11 (2-C), 120.22 (1-C), 124.90 (5-C), 126.12 (8-C), 126.34, 126.55 (6-C, 7-C), 128.11, 133.18, 135.39, 135.83 (14-C, 15-C, 16-C, 17-C), 144.31, 144.50 (4-C, 9-C) ppm. C$_{20}$H$_{24}$Cl$_2$SiZr (454.22): calcd. C 52.84, H 5.28; found C 53.01, H 5.21.

Synthesis of [ZrCl$_2$({η^5-C$_9$H$_5$(CH$_3$)}{η^5-C$_5$Me$_4$}SiMe$_2$)] (9): Compound **9** was synthesized in a manner identical to that for **8** from ZrCl$_4$ (2.51 g, 10.80 mmol), **5** (3.34 g, 10.80 mmol) and *n*BuLi (14.86 mL, 23.78 mmol). Yield 4.650 g (91%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.93, 1.18 [2 s, 3 H each, Si(C*H*$_3$)$_2$], 1.90, 1.95, 1.96, 2.02 [4 s, 3 H each, C$_5$(C*H*$_3$)$_4$], 2.51 (s, 3 H, 10-H), 5.54 (s, 1 H, 2-H), 7.06 (t, *J* = 7.6 Hz, 1 H, 6-H), 7.35 (t, *J* = 7.6 Hz, 1 H, 7-H), 7.47 (d, *J* = 7.6 Hz, 1 H, 5-H), 7.56 (d, *J* = 7.6 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 1.14, 1.39 [Si(*C*H$_3$)$_2$], 12.18, 12.48, 13.70, 15.29 [C$_5$(*C*H$_3$)$_4$], 13.71 (10-C), 85.21 (3-C), 95.46 (13-C), 117.33 (2-C), 124.11 (1-C), 124.19 (5-C), 125.38 (8-C), 126.19, 126.41 (6-C, 7-C), 128.29, 133.06, 134.99, 135.16 (14-C, 15-C, 16-C, 17-C), 145.32, 145.45 (4-C, 9-C) ppm. C$_{21}$H$_{26}$Cl$_2$SiZr (468.22): calcd. C 53.82, H 5.55; found C 53.81, H 5.52.

Synthesis of [ZrCl$_2${(η^5-C$_9$H$_5${CH$_2$(C$_6$H$_5$)})(η^5-C$_5$Me$_4$)SiMe$_2$}] (10): Compound **10** was synthesized in a manner identical to that for **8** from ZrCl$_4$ (3.35 g, 14.39 mmol), **6** (5.53 g, 14.39 mmol) and *n*BuLi (19.78 mL, 31.65 mmol). Yield 6.07 g (77%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.01, 1.28 [2 s, 3 H each, Si(C*H*$_3$)$_2$], 1.99, 2.05, 2.07, 2.14 [4 s, 3 H each, C$_5$(C*H*$_3$)$_4$], 4.38 (dd, J_{AB} = 16 Hz, 2 H, C*H*$_2$Ph), 5.71 (s, 1 H, 2-H), 7.15, (t, *J* = 7.6 Hz, 1 H, 6-H), 7.26 (d, *J* = 7.6 Hz, 1 H, 7-H), 7.33, 7.42 (m and t respectively, *J* = 6.7, 7.6 Hz, respectively, 5 H, 12-H, 13-H, 14-H, 15-H, 16-H), 7.57 (d, *J* = 8.6 Hz, 1 H, 5-H), 7.57 (d, *J* = 8.6 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 1.25, 1.56 [Si(*C*H$_3$)$_2$], 12.34, 12.67, 14.83, 15.48 [C$_5$(*C*H$_3$)$_4$], 34.88 (10-C), 85.31 (3-C), 95.90 (19-C), 117.49 (2-C), 124.38 (1-C), 124.47, 125.62 (5-C, 8-C), 126.45, 126.65 (6-C, 7-C), 126.24–128.86 (1-C, 13-C, 14-C, 15-C, 16-C), 128.70–135.27 (20-C, 21-C, 22-C, 23-C), 132.74 (11-C), 135.62, 140.53 (4-C, 9-C) ppm. C$_{27}$H$_{30}$Cl$_2$SiZr (544.22): calcd. C 59.53, H 5.51; found C 59.59, H 5.45.

Synthesis of [ZrCl$_2${(η^5-C$_9$H$_5${C$_2$H$_4$(C$_4$H$_7$O$_2$)})(η^5-C$_5$Me$_4$)SiMe$_2$}] (11): Compound **11** was synthesized in a manner identical to that for **8** from ZrCl$_4$ (1.753 g, 7.525 mmol), **7** (3.07 g, 7.52 mmol) and *n*BuLi (10.34 mL, 16.54 mmol). Yield 3.474 g (81%). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ = 0.93, 1.34 [2 s, 3 H each, Si(C*H*$_3$)$_2$], 1.34 (d, *J* = 13.7 Hz, 1 H, 14-H$_{eq}$), 1.90, 1.90, 1.95, 2.01 [4 s, 3 H each, C$_5$(C*H*$_3$)$_4$], 2.09 (m, 1 H, 14-H$_{ax}$), 2.11 (m, 2 H, 11-H, 11′-H), 3.04 (m, 2 H, 10-H, 10′-H), 3.74 (m, 2 H, 13-H$_{ax}$, 15-H$_{ax}$), 4.11 (m, 2 H, 13-H$_{eq}$, 15-H$_{eq}$), 4.51 (t, *J* = 5.1 Hz, 1 H, 12-H), 5.60 (s, 1 H, 2-H), 7.06 (dd, *J* = 8.1, 4.1 Hz, 1 H, 6-H), 7.34 (dd, *J* = 8.1, 4.1 Hz, 1 H, 7-H), 7.46 (d, *J* = 8.1 Hz, 1 H, 5-H), 7.60 (d, *J* = 8.1 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 1.09, 1.40 [Si(*C*H$_3$)$_2$], 12.15, 12.48, 14.67, 15.29 [C$_5$(*C*H$_3$)$_4$], 23.19 (10-C), 25.81 (14-C), 35.27 (11-C), 66.86, 66.88 (13-C, 15-C), 84.61 (3-C), 95.74 (18-C), 101.70 (12-C), 116.30 (2-C), 124.03 (1-C), 124.40 (5-C), 125.42 (8-C), 126.18, 126.30 (6-C, 7-C), 127.86 (6-C), 126.30 (7-C), 127.86–13.80 (19-C, 20-C, 21-C, 22-C), 134.92, 135.34 (4-C, 9-C) ppm. C$_{26}$H$_{34}$Cl$_2$O$_2$SiZr (568.22): calcd. C 54.90, H 5.98; found C 54.87, H 6.15.

Synthesis of [ZrMe$_2${(η^5-C$_9$H$_6$)(η^5-C$_5$Me$_4$)SiMe$_2$}] (12): MeMgBr (3 M in Et$_2$O, 4.08 mL, 12.25 mmol) was added to a cooled (–78 °C) solution of **8** (2.536 g, 5.57 mmol) in THF (60 mL) over 15 min. At the end of the addition, the solution was allowed to reach room temp. and stirred protected from light for 4 h. The solvent was removed in vacuo and the product extracted with toluene (2× 50 mL). The solvent was removed from the filtrate under reduced pressure and the remaining solid washed with hexane (2× 25 mL) to yield the title compound as a pale-yellow solid. Yield 1.78 g (77%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = –1.33, –0.18 [2 s, 3 H each, Zr(C*H*$_3$)$_2$], 0.49, 0.67 [2 s, 3 H each, Si(C*H*$_3$)$_2$], 1.64, 1.72, 1.83, 1.85 [4 s, 3 H each, C$_5$(C*H*$_3$)$_4$], 5.57 (s, 1 H, 2-H), 5.99 (s, 1

H, 1-H), 6.90 (t, J = 7.6 Hz, 1 H, 6-H), 7.29 (t, J = 7.6 Hz, 1 H, 7-H), 7.32 (d, J = 7.6 Hz, 1 H, 5-H), 7.63 (d, J = 7.6 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.96, 1.35 [Si(CH_3)$_2$], 11.56, 11.64, 14.14, 14.83 [C_5(CH_3)$_4$], 32.27, 37.35 [Zr(CH_3)$_2$], 83.58 (3-C), 91.21 (12-C), 113.02 (2-C), 118.01 (1-C), 121.39–124.59 (14-C, 15-C, 16-C, 17-C), 124.10 (5-C), 126.34 (8-C), 124.24, 124.28 (6-C, 7-C), 126.74 (1-C), 128.73, 130.35 (4-C, 9-C) ppm. $C_{23}H_{32}SiZr$ (427.22): calcd. C 64.60, H 7.49; found C 64.98, H 7.00. $C_{22}H_{30}SiZr$ (413.22): calcd. C 61.22, H 7.26; found C 61.34, H 7.12.

Synthesis of [ZrMe$_2$({η^5-C$_9$H$_5$(CH$_3$)}{η^5-C$_5$Me$_4$}SiMe$_2$)] (13): Compound **13** was synthesized in a manner identical to that for **12** from MeMgBr (3 M in Et_2O, 6.55 mL, 19.65 mmol) and **9** (3.84 g, 8.19 mmol). Yield 2.28 g (65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = –1.41, –0.39 [2 s, 3 H each, Zr(CH_3)$_2$], 0.51, 0.71 [2 s, 3 H each, Si(CH_3)$_2$], 1.59, 1.78, 1.86, 1.87 [4 s, 3 H each, C_5(CH_3)$_4$], 2.38 (s, 3 H, 10-H), 5.27 (s, 1 H, 2-H), 6.90 (t, J = 7.6 Hz, 1 H, 6-H), 7.18 (t, J = 7.6 Hz, 1 H, 7-H), 7.30 (d, J = 7.6 Hz, 1 H, 5-H), 7.48 (d, J = 7.6 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.17, 1.64 [Si(CH_3)$_2$], 11.67, 11.78, 14.09, 15.02 [C_5(CH_3)$_4$], 12.98 (10-C), 36.24, 37.14 [Zr(CH_3)$_2$], 80.20 (3-C), 90.24 (13-C), 118.30 (2-C), 120.34–124.59 (14-C, 15-C, 16-C, 17-C), 124.10 (5-C), 126.34 (8-C), 124.24, 124.28 (6-C, 7-C), 126.74 (1-C), 128.73, 130.35 (4-C, 9-C) ppm. $C_{23}H_{32}SiZr$ (427.22): calcd. C 64.60, H 7.49; found C 64.98, H 7.00.

Synthesis of [ZrMe$_2${(η^5-C$_9$H$_5$CH$_2$(C$_6$H$_5$)})(η^5-C$_5$Me$_4$)SiMe$_2$}] (14): Compound **14** was synthesized in a manner identical to that for **12** from MeMgBr (3 M in Et_2O, 6.63 mL, 19.89 mmol) and **10** (4.52 g, 8.29 mmol). Yield 3.49 g (83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = –1.37, –0.24 [2 s, 3 H each, Zr(CH_3)$_2$], 0.44, 0.70 [2 s, 3 H each, Si(CH_3)$_2$], 1.59, 1.77, 1.88, 1.89 [4 s, 3 H each, C_5(CH_3)$_4$], 4.27 (dd, J_{AB} = 16 Hz, 2 H, CH_2Ph), 5.43 (s, 1 H, 2-H), 6.94, (t, J = 7.3 Hz, 1 H, 6-H), 7.01 (d, J = 7.3 Hz, 1 H, 7-H), 7.09, 7.18 (2m, 5 H, 12-H, 13-H, 14-H, 15-H, 16-H), 7.29 (d, J = 8.4 Hz, 1 H, 5-H), 7.56 (d, J = 8.6 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.43, 1.53 [Si(CH_3)$_2$], 11.67, 11.81, 14.12, 15.02 [C_5(CH_3)$_4$], 33.02 (10-C), 34.69, 36.93 [Zr(CH_3)$_2$], 81.49 (3-C), 90.52 (19-C), 118.52 (2-C), 123.02, 124.27 (5-C, 8-C), 124.66, 124.76 (6-C, 7-C), 126.32–128.70 (1-C, 13-C, 14-C, 15-C, 16-C), 129.21–132.04 (20-C, 21-C, 22-C, 23-C), 134.74 (11-C), 136.62, 141.59 (4-C, 9-C) ppm. $C_{29}H_{36}SiZr$ (483.22): calcd. C 72.02, H 7.45; found C 72.20, H 7.31.

Synthesis of [ZrMe$_2${(η^5-C$_9$H$_5$C$_2$H$_4$(C$_4$H$_7$O$_2$)})(η^5-C$_5$Me$_4$)SiMe$_2$}] (15): Compound **15** was synthesized in a manner identical to that for **12** from MeMgBr (3 M in Et_2O, 4.88 mL, 14.66 mmol) and **11** (3.85 g, 6.11 mmol). Yield 2.65 g (82%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = –1.44, –0.36 [2 s, 3 H each, Zr(CH_3)$_2$], 0.50, 0.71 [2 s, 3 H each, Si(CH_3)$_2$], 1.34 (m, 1 H, 14-H$_{eq}$), 1.57, 1.77, 1.83, 1.85 [4 s, 3 H each, C_5(CH_3)$_4$], 2.17 (m, 1 H, 14-H$_{ax}$), 2.25 (m, 2 H, 11-H, 11′-H), 3.04 (m, 2 H, 10-H, 10′-H), 3.34 (m, 2 H, 13-H$_{ax}$, 15-H$_{ax}$), 3.85 (m, 2 H, 13-H$_{eq}$, 15-H$_{eq}$), 4.50 (t, J = 5.1 Hz, 1 H, 12-H), 5.42 (s, 1 H, 2-H), 6.89 (dd, J = 8.5, 4.1 Hz, 1 H, 6-H), 7.12 (dd, J = 8.1, 4.1 Hz, 1 H, 7-H), 7.30 (d, J = 8.5 Hz, 1 H, 5-H), 7.60 (d, J = 8.1 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.15, 1.62 [Si(CH_3)$_2$], 11.62, 11.71, 14.07, 14.99 [C_5(CH_3)$_4$], 23.04 (10-C), 26.12 (14-C), 36.73, 36.82 [Zr(CH_3)$_2$], 36.78 (11-C), 66.72, 66.74 (13-C, 15-C), 80.78 (3-C), 90.39 (18-C), 101.92 (12-C), 117.41 (2-C), 121.03 (1-C), 124.26 (5-C), 125.65 (8-C), 126.32 (6-C), 126.65 (7-C), 128.31–128.86 (19-C, 20-C, 21-C, 22-C), 135.11, 136.03 (4-C, 9-C) ppm. $C_{28}H_{40}O_2SiZr$ (527.22): calcd. C 63.73, H 7.59; found C 63.78, H 7.58.

Synthesis of [Zr(CH$_2$SiMe$_3$)$_2${(η^5-C$_9$H$_5$CH$_2$(C$_6$H$_5$)})(η^5-C$_5$Me$_4$)-SiMe$_2$}] (16): Me_3SiCH_2Li (1 M in pentane, 1.21 mL, 1.21 mmol) was added to a cooled (–78 °C) solution of **10** (0.330 g, 0.60 mmol) in Et_2O/toluene (20:40, 60 mL) over 15 min. At the end of the addition, the solution was allowed to reach room temp. and stirred protected from light for 4 h. The solvent was removed in vacuo and the product extracted with toluene (2× 50 mL). The solvent was removed from the filtrate under reduced pressure and the remaining solid washed with hexane (2× 25 mL) to yield the title compound as a yellow solid. Yield 0.325 g (83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = –3.04, –0.57 [2 d, J = 8 Hz, 2 H each, Zr(CH_2-SiMe$_3$)$_2$], 0.11, 0.36 [2 s, 9 H each, Zr(CH$_2$SiMe_3)$_2$], 0.45, 0.67 [2 s, 3 H each, Si(CH_3)$_2$], 1.71, 1.86, 1.89, 2.00 [4 s, 3 H each, C_5-(CH_3)$_4$], 4.58 (dd, J_{AB} = 16 Hz, 2 H, CH_2Ph), 5.94 (s, 1 H, 2-H), 6.79, (t, J = 7.3 Hz, 1 H, 6-H), 7.00 (d, J = 7.3 Hz, 1 H, 7-H), 6.98, 7.20 (2m, 5 H, 12-H, 13-H, 14-H, 15-H, 16-H), 7.59 (d, J = 8.4 Hz, 1 H, 5-H), 7.61 (d, J = 8.6 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.82, 1.22 [Si(CH_3)$_2$], 3.01, 5.46 [Zr(CH$_2$SiMe_3)$_2$], 12.58, 12.99, 14.97, 15.66 [C_5(CH_3)$_4$], 35.14 [Zr(CH_2SiMe$_3$)$_2$], 41.00 (10-C), 83.50 (3-C), 92.16 (19-C), 1186.91 (2-C), 122.03, 122.94 (5-C, 8-C), 123.19, 124.03 (6-C, 7-C), 124.18–128.88 (1-C, 13-C, 14-C, 15-C, 16-C, 20-C, 21-C, 22-C, 23-C), 128.88 (11-C), 132.63, 141.55 (4-C, 9-C) ppm. $C_{35}H_{52}Si_3Zr$ (647.22): calcd. C 64.89, H 8.03; found C 64.82, H 8.14.

Synthesis of [ZrCl$_2$(η^5-C$_9$H$_7$)(η^5-C$_5$H$_5$)] (17): nBuLi (1.60 M in hexane, 3.92 mL, 6.28 mmol) was added to a cooled (–78 °C) solution of C_9H_8 (0.6 mL, 5.71 mmol) in Et_2O (20 mL) over 5 min. At the end of the addition, the solution was allowed to reach room temp. and stirred for 4 h, cooled again to –78 °C and a solution of $CpZrCl_3$ (1.49 g, 5.71 mmol) in toluene (25 mL) added. The reaction mixture was allowed to reach room temp. and stirred for 4 h. The solvent was then removed in vacuo and the product washed with hexane (2× 15 mL) to yield the title compound as a yellow solid. Yield 1.59 g (81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.71 (s, 5 H, C_5H_5), 6.02 (d, ^3J = 3.4 Hz, 2 H, 1-H, 3-H), 6.43 (t, ^3J = 3.4 Hz, 1 H, 2-H), 6.86 (dd, J = 6.6, 3.2 Hz, 2 H, 6-H, 7-H), 7.30 (dd, J = 6.5, 3.1 Hz, 2 H, 6-H, 7-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 102.94 (1-C, 3-C), 114.91 (2 C), 116.28 (C_5H_5), 125.61 (6-C, 7-C), 126.07 (5-C, 8-C), 132.44 (4-C), 134.12 (9-C) ppm. $C_{14}H_{12}Cl_2Zr$ (342.22): calcd. C 49.11, H 3.53; found C 49.25, H 3.48.

Synthesis of [ZrCl$_2$(η^5-C$_9$H$_6${C$_2$H$_4$(C$_4$H$_7$O$_2$)})(η^5-C$_5$H$_5$)] (18): Compound **18** was synthesized in a manner identical to that for **17** from nBuLi (1.60 M in hexane, 5.34 mL, 8.54 mmol), **3** (1.79 g, 7.77 mmol) and $CpZrCl_3$ (2.04 g, 7.77 mmol). Yield 3.10 g (87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21–1.40 (m, 1 H, 14-H$_{eq}$), 1.93 (m, 2 H, 11-H, 11′-H), 2.09 (m, 1 H, 14-H$_{ax}$), 2.99, 3.13 (2 m, 2 H, 10-H, 10′-H), 3.73 (m, 2 H, 13-H$_{ax}$, 15-H$_{ax}$), 4.11 (dd, J = 11.5, 4.9 Hz, 2 H, 13-H$_{eq}$, 15-H$_{eq}$), 4.50 (t, ^3J = 5 Hz, 1 H, 12-H), 6.14 (s, 5 H, C_5H_5), 6.45 (d, ^3J = 3.2 Hz, 1 H, 3-H), 6.67 (d, ^3J = 3.2 Hz, 1 H, 2-H), 7.28 (m, 2 H, 6-H, 7-H), 7.64 (m, 2 H, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.54 (10-C), 25.92 (14-C), 35.56 (11-C), 66.99, 67.03 (13-C, 15-C), 98.15 (3-C), 101.52 (12-C),116.37 (C_5H_5), 121.35 (1-C), 124.19 (2-C), 124.07, 125.58, 125.69, 126.10 (5-C/8-C), 127.93, 126.56 (4-C, 9-C) ppm. $C_{20}H_{22}Cl_2O_2Zr$ (456.26): calcd. C 52.62, H 4.86; found C 52.73, H 4.81.

Synthesis of [ZrMe$_2$(η^5-C$_9$H$_7$)(η^5-C$_5$H$_5$)] (19): MeMgBr (3 M in Et_2O, 0.65 mL, 1.96 mmol) was added to a cooled (–78 °C) solution of **17** (0.31 g, 0.89 mmol) in toluene (25 mL) over 15 min. At the end of the addition, the solution was allowed to reach room temp. and stirred protected from light for 4 h. The suspension was filtered and the solvent removed from the filtrate in vacuo. The product was then washed with hexane (2× 15 mL) to yield the title compound as a yellow solid. Yield 0.19 g (71%). ^{1}H NMR (500 MHz,

Table 5. Crystal data and structure refinement for complexes **7**, **12** and **13**.

	7	**12**	**13**
Empirical formula	$C_{26}H_{36}O_2Si$	$C_{22}H_{30}SiZr$	$C_{23}H_{32}SiZr$
Formula mass	408.64	413.77	427.80
T [K]	260 (2)	260(2)	260(2)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	$P2_1/n$	$P2_1/n$
a [Å]	10.402(6)	9.0584(2)	9.015(1)
b [Å]	11.264(6)	16.0232(4)	25.162(2)
c [Å]	41.397(9)	13.7879(3)	9.709(1)
α [°]	90	90	90
β [°]	90	94.336(1)	109.762(1)
γ [°]	90	90	90
V [Å^3]	4850(4)	1995.51(8)	2072.7(3)
Z	8	4	4
$\rho_{calcd.}$ [g/cm^3]	1.119	1.377	1.371
μ [mm^{-1}]	0.115	0.612	0.591
F(000)	1776	864	896
Crystal size [mm]	0.24 × 0.32 × 0.41	0.14 × 0.27 × 0.41	0.48 × 0.54 × 0.63
Index ranges	$-12 \le h \le 12$	$-11 \le h \le 12$	$-10 \le h \le 10$
	$-13 \le k \le 11$	$-22 \le k \le 22$	$-29 \le k \le 29$
	$-48 \le l \le 48$	$-19 \le l \le 19$	$-9 \le l \le 11$
Reflections collected	23072	24542	11978
Independent reflections	4191 [R(int) = 0.1578]	6129 [R(int) = 0.0289]	3538 [R(int) = 0.0509]
Observed reflections	1594	5082	2623
No. of data/restraints/parameters	4191/0/268	6129/0/225	3538/0/235
Goodness-of-fit on F^2	0.877	1.050	0.922
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0496	$P1$ = 0.0284	$R1$ = 0.0443
	$wR2$ = 0.0863	$wR2$ = 0.0713	$wR2$ = 0.0999
Largest difference peak/hole [e Å^{-3}]	0.152/–0.146	0.361/–0.381	0.623/–0.538

C_6D_6): δ = –0.47 [s, 6 H, Zr(CH_3)$_2$], 5.61 (s, 5 H, C_5H_5), 5.81 (t, ^3J = 3.3 Hz, 1 H, 2-H), 5.91 (d, ^3J = 3.2 Hz, 2 H, 1-H, 3-H), 6.94 (dd, ^3J = 6.5, 3.1 Hz, 2 H, 6-H, 7-H), 7.28 (dd, ^3J = 6.3, 3.2 Hz, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 33.07 [Zr(*C*H$_3$)$_2$], 99.12 (1-C, 3-C), 110.63 (C_5H_5), 113.08 (2-C), 124.36, 124.98 (5-C, 8-C) ppm. $C_{16}H_{18}Zr$ (301.22): calcd. C 63.73, H 6.02; found C 63.68, H 6.07.

Synthesis of [ZrMe$_2$(η^5-C$_9$H$_6${C$_2$H$_4$(C$_4$H$_7$O$_2$)})(η^5-C$_5$H$_5$)] (20): Compound **20** was synthesized in a manner identical to that for **19** from MeMgBr (3 M in Et_2O, 0.38 mL, 1.15 mmol) and **19** (0.48 g, 1.05 mmol). Yield 0.34 g (78%). ^{1}H NMR (500 MHz, C_6D_6): δ = –0.64, –0.3 [2 s, 6 H, Zr(CH_3)$_2$], 0.65 (m, 1 H, 14-H$_{eq}$), 1.84 (m, 2 H,11-H, 11′-H), 2.09 (m, 1 H, 14-H$_{ax}$), 2.82 (m, 1 H, 10-H), 3.13 (m, 1 H, 10′-H), 3.25–3.39 (m, 2 H, 13-H$_{ax}$, 15-H$_{ax}$), 3.76–3.89 (m, 2 H, 13-H$_{eq}$), 4.42 (t, ^3J = 5.1 Hz, 12-H), 5.61 (s, 5 H, C_5H_5), 5.73 (d, ^3J = 3.4 Hz, 3-H), 5.80 (d, ^3J = 3.2 Hz, 2-H), 6.92 (m, 2 H, 6-H, 7-H), 7.15, 7.45 (2m, 2 H, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 25.57 (10-C), 26.14 (14-C), 33.75, 34.58 [Zr(*C*H$_3$)$_2$], 36.89 (11-C), 66.72, 66.75 (13-C,15-C), 95.25 (3-C), 101.73 (12-C), 110.82 (C_5H_5), 114.30 (2-C), 115.78 (1-C), 123.18, 123.67, 123.77 (5-C/8-C), 124.14, 125.47 (4-C, 9-C) ppm. $C_{22}H_{28}O_2Zr$ (415.22): calcd. C 63.57, H 6.79; found C 63.51, H 6.82.

General Procedure for the Solution Polymerization of ε-Caprolactone: ε-Caprolactone (CL) was polymerized in a flame-dried round-bottomed flask, attached to a Schlenk line, equipped with a magnetic stirrer. In a typical procedure, the initiator was dissolved in the appropriate amount of solvent and, for Entry 6 of Table 4, temperature equilibration was ensured by stirring the solution in a temperature-controlled bath for 15 min. ε-CL was injected, and polymerization times were measured from that point. Polymerizations were terminated by the addition of acetic acid (5 vol-%) in methanol. Polymers were precipitated from methanol, filtered, dissolved in THF, reprecipitated from methanol, and then dried in vacuo to constant weight.

X-ray Crystallographic Structure Determination: Crystals of **7**, **12** and **13** were obtained by cooling toluene solutions. Crystals of complexes were mounted at low temperature in inert oil on a glass fiber. Data were collected with a Bruker X8 APEX II CCD area detector diffractometer at 260 K by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were integrated by using SAINT,[37] and absorption correction was performed with the program SADABS.[38] The structures were solved by direct methods using SHELXTL[39] and refined by full-matrix least-squares methods based on F^2. Non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions and refined with an overall isotropic temperature factor by using a riding model. Crystallographic data are summarized in Table 5. CCDC-892880 (for **7**), -892881 (**12**), and -892882 (for **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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