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Synthesis and characterization of 1- and 2-(ω-alken-1-yl)indenes, their lithium salts and dichlorozirconium(IV) complexes☆

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Abstract

A series of new 1-, 2-, and multi-substituted indenes has been synthesized and characterized. The reaction of indenyl lithium or 4,7-dimethylindenyl lithium with alkenyl bromides yielded a mixture of 1- and 3-allylindene (**1**), 3-(3-buten-1-yl)indene (**2**), 3-(4-penten-1-yl)indene (**3**), 3-allyl-4,7-dimethylindene (**4**), 3-(3-buten-1-yl)-4,7-dimethylindene (**5**), as well as 3-(4-penten-1-yl)-4,7-dimethylindene (**6**). The 2-substituted indenes 2-allylindene (**7**), 2-(3-buten-1-yl)indene (**8**), 2-(4-penten-1-yl)indene (**9**), 2-allyl-4,7-dimethylindene (**10**), 2-(3-buten-1-yl)-4,7-dimethylindene (**11**), and 2-(4-penten-1-yl)-4,7-dimethylindene (**12**) were prepared by $PdCl_2$(DPPF) or $NiCl_2$(DPPE) catalyzed cross-coupling reactions of the appropriate Grignard reagents with 2-bromoindene or 2-bromo-4,7-dimethylindene. Alkenylation of 3-methylindenyl lithium and 2,4,7-trimethylindenyl lithium produced 1-(3-buten-1-yl)-3-methylindene (**13**) or 1-(3-buten-1-yl)-2,4,7-trimethylindene (**14**), respectively. The indene derivatives **1**–**14** react with *n*-butyl lithium in hexane yielding the corresponding lithium salts **1a**–**14a**. Zirconium tetrachloride reacts with **1a**, **2a**, **4a**–**6a** and **11a**–**14a** under formation of the corresponding bis(indenyl)zirconium dichloride complexes **1b**, **2b**, **4b**–**6b** and **11b**–**14b**. All compounds were characterized by elemental analysis, ^1H and $^{13}C\{^1H\}$-NMR spectroscopy and mass spectrometry, **5b** and **12b** also by single crystal X-ray structural analysis. **1b**, **4b**–**6b** and **11b**–**13b** are active catalysts for the polymerization of ethene and propene.

Keywords: Alkenylindenes; Alkenylindenyl lithium salts; Alkenyl indenyl zirconium complexes; Ethene polymerization; Propene polymerization

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1. Introduction

In recent years, indenyl complexes of the group 4 metals and of the lanthanides were studied very intensively due to their ability to catalyze a multitude of reactions like polymerization, hydrogenation, or epoxidation [1]. However, the potential of the lanthanidocene complexes as effective catalysts especially for the polymerization of alkenes [2] is considerably restricted by their high sensitivity to air and moisture. The use of donor substituted cyclopentadienyl or indenyl ligands was expected to reduce this sensitivity by additional coordination of the metal without considerable reduction of their catalytic capabilities. The first donor substituted ligand, an ether functionalized cyclopentadienyl ligand, was published by Qian et al. in 1986 [3] followed by the synthesis of several other donor substituted cyclopentadienyl [4] and indenyl [5] derivatives. In fact, the presence of strong donor atoms such as nitrogen [6] or oxygen [4d, 4f, 5d, 7] in the

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☆ Dedicated to Professor Dr Helmut Werner on the occasion of his 65th birthday.

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substituting groups of the soft indenyl or cyclopentadienyl ligands caused the formation of reasonably stable lanthanidocene complexes, but it pointed out that they were no longer active catalysts for the polymerization of alkenes [8]. Obviously, the additional coordination of the donor atom to the metal blocks the active site of the catalyst irreversibly.

A solution of the problem was expected from the use of ligands substituted by weaker donor systems such as alkenyl groups. In 1988, Okuda used 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadiene as a ligand in metallocenes [9]. Though the first alkenylindene, 3-allylindene, was described already in 1964 [10] followed by instructions for its improved synthesis from allylbromide and indenylmagnesium bromide or indenyllithium [11], until now, there are no systematic studies on indenyl systems substituted by alkenyl groups of varying chain length and at different sites.

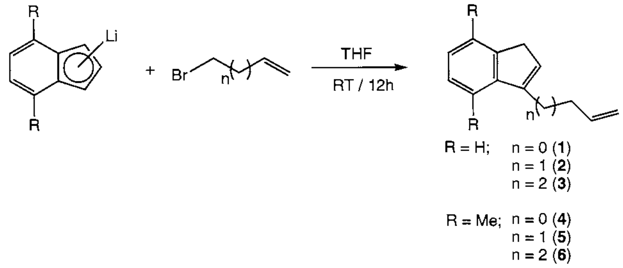
Another point of interest was to get better results in zirconocene-catalyzed polymerizations by variation of the substituents on the indenyl ring, e.g. to get complexes of higher catalytic activity, a control of the molecular weight, the molecular weight distribution, the stereochemistry and the melting points of the polymers. Examples for such successful modifications were the introduction of alkyl substituents on the 2-position of the five-membered indenyl ring which resulted in higher molecular weights and higher melting points for polypropylene [12] or the additional substitution on the 4- or 7-positions of the indene which influenced the activity of the catalyst and the regiocontrol of the polymer or the mechanism of olefin insertion [12d, 12e, 13].

Here we report a general method for the preparation of 1-, 2- and 3-alkenylindenes and of their lithium salts as well as the synthesis of some alkenylindenyl zirconium complexes and their potential for the polymerization of olefins. Corresponding lanthanide complexes will be the subject of a following paper.

2. Synthesis and properties

2.1. [1-(ω-alken-1-yl)indenyl]lithium compounds

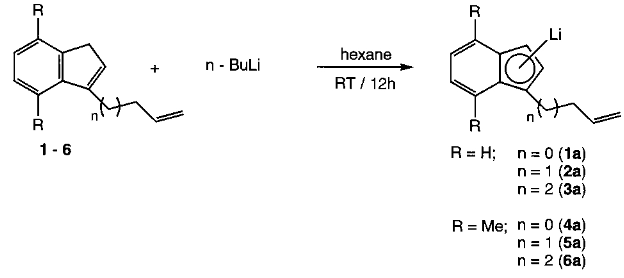
The reaction of allyl bromide, 4-bromo-1-butene or 5-bromo-1-pentene with indenyllithium or 4,7-dimethylindenyllithium in THF at 20°C yields the corresponding 3-alkenylindenes **1** to **6** (Scheme 1). If the reactions were conducted at 0°C or below 0°C, mixtures of the 1- and 3-positional isomers are formed, whereas at higher reaction temperatures the more stable 3-alkenylindenes predominate or are the lonely products. We isolated the pure alkenylindenes by fractional distillation as colorless or light yellow, distillable liquids with yields ranging from 69 to 88%.



Scheme 1.

The indenyl lithium salts **1a** to **6a** were obtained by reacting the indenes **1** to **6** with an excess of *n*-BuLi in hexane at room temperature (Scheme 2). The salts are insoluble in hexane and can be isolated by filtration and purified by washing with hexane to remove excess *n*-BuLi and unreacted indene. The colorless salts, which are very sensitive towards oxygen and moisture, are soluble readily in diethyl ether and THF.

The alkenylindenes **1** to **6** and their lithium salts **1a** to **6a** were charaterized by elemental analysis, ^{1}H-NMR, ^{13}C{^{1}H}-NMR and mass spectra. The methyl groups of the 4,7-dimethyl-1-alkenylindenyl lithium compounds **4a**, **5a**, and **6a** exhibit two clearly separated diagnostic signals in the ^{1}H and ^{13}C{^{1}H}-NMR spectra.

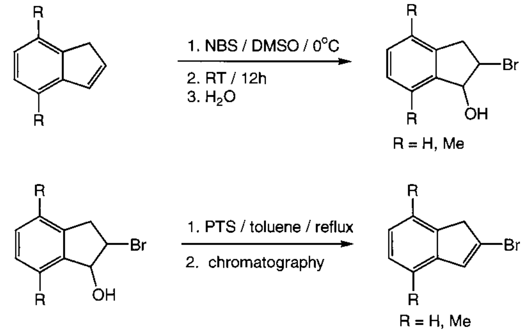


Scheme 2.

2.2. [2-(ω-alken-1-yl)indenyl]lithium compounds

2-substituted indenes can be prepared either by nucleophilic addition of organometals to 2-indanone followed by dehydration; or by nickel or palladium catalyzed coupling of Grignard reagents with 2-bromoindene [14]. Since the first pathway affords the desired products very often with only low yields due to the competing deprotonation of 2-indanone, we used the cross-coupling route. The ability of the Grignard reagents to deprotonate the bromoindene is apparently much lower than its ability to undergo the coupling reaction.

The starting compounds 2-bromoindene and 2-bromo-4,7-dimethylindene [15] are easy to obtain by bromination of indene or 4,7-dimethylindene [16] with *N*-bromosuccinimide in water–DMSO followed by acid-catalyzed dehydration of the respective 2-bromo-

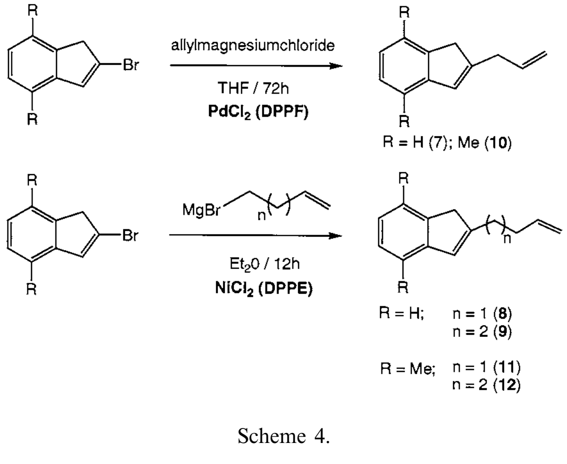


Scheme 3.

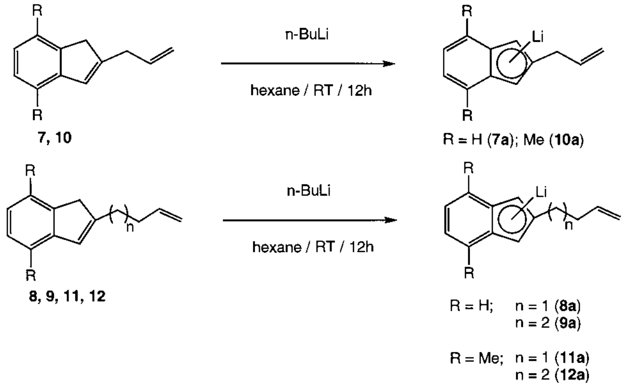
indan-1-ol derivative formed in the first step of the reaction (Scheme 3) [17]. Since the efficiency of the subsequent coupling with alkenylmagnesium halides highly depends on the purity of the 2-bromoindenes, they had to be purified by flash chromatography and fractional distillation.

Treatment of the carefully purified bromoindenes with alkenylmagnesium halides in the presence of catalysts afforded successfully the 2-alkenylindenes **7** to **12** (Scheme 4). The 2-allylindenes **7** and **10** were prepared from 2-bromoindene or 2-bromo-4,7-dimethylindene and allylmagnesium chloride in the presence of $PdCl_2$(DPPF) in THF at room temperature for 72 h. The yields varied between 25 and 35%. The reaction failed when the nickel chloride catalyst was used, probably due to the formation of unreactive allylnickel complexes [18]. The $NiCl_2$(DPPE) catalyzed coupling of 2-bromoindene or 2-bromo-4,7-dimethylindene with 3-butenyl- or 4-pentenylmagnesium bromide produced 2-(3-buten-1-yl)indene (**8**), 2-(4-penten-1-yl)indene (**9**), 2-(3-buten-1-yl)-4,7-dimethylindene (**11**), or 2-(4-penten-1-yl)-4,7-dimethylindene (**12**) with yields of 38–64%.

The 2-alkenylindenes **7** to **12** reacted with excess *n*-BuLi in hexane at room temperature with precipitation of the corresponding indenyl lithium salts **7a** to **12a** (Scheme 5).



Scheme 4.



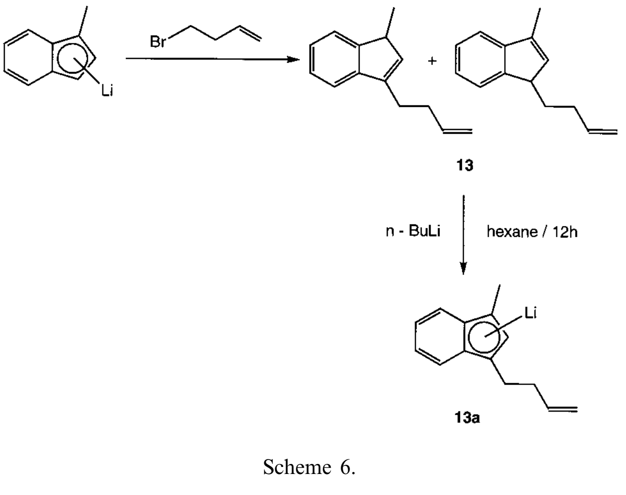
Scheme 5.

The 2-alkenylindenes as well as their lithium salts were characterized by elemental analysis, ^{1}H-NMR, ^{13}C{^{1}H}-NMR and mass spectra. The NMR spectra of the 2-alkenyl(indenyl)lithium compounds differ significantly from those of the 1-alkenyl(indenyl)lithium derivatives. The C_{2v} symmetry of the 2-substituted compounds caused the appearance of only one signal for the two hydrogen atoms on the five-membered ring of the indene and also only one signal for the 4,7-dimethyl groups in **10a**, **11a** and **12a**.

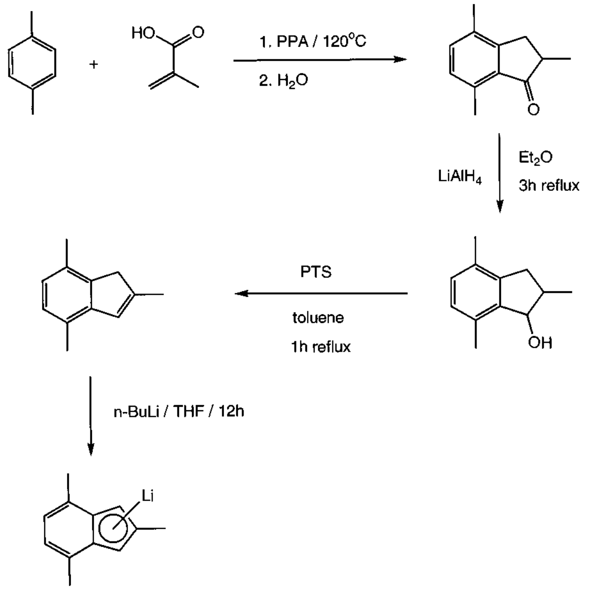
2.3. [1-(3-buten-1-yl)-3-methylindenyl]lithium and [1-(3-buten-1-yl)-2,4,7-trimethylindenyl] lithium

A mixture of 3-(3-butenyl)-1-methylindene and 1-(3-butenyl)-3-methylindene (**13**) were prepared in an almost quantitative yield by using 1-methylindenyllithium [19] and 4-bromo-1-butene in THF at 0°C. Deprotonation of the mixture with *n*-BuLi in hexane produced 40% of [1-(3-buten-1-yl)-3-methylindenyl]lithium (**13a**) (Scheme 6).

2,4,7-Trimethylindene, synthesized according to literature methods [12d], was transformed into 2,4,7-trimethylindenyllithium (Scheme 7) which reacted with



Scheme 6.

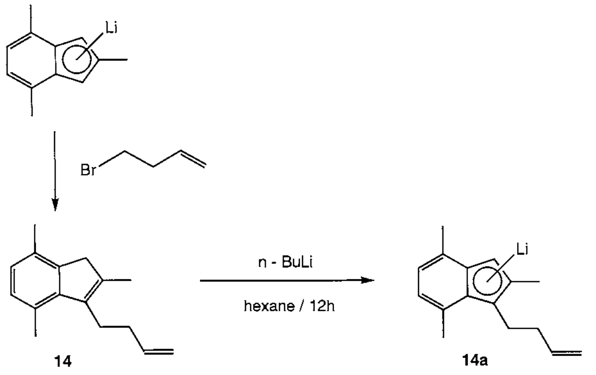


Scheme 7.

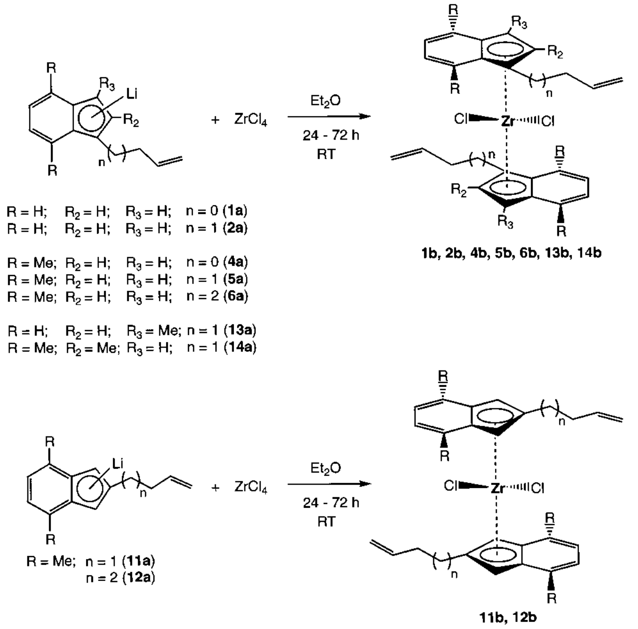
4-bromo-1-butene to give 3-(3-buten-1-yl)-2,4,7-trimethylindene (85% yield) (**14**). Treatment of **14** with *n*-BuLi afforded [1-(3-buten-1-yl)-2,4,7-trimethylindenyl]lithium (**14a**) (82% yield) (Scheme 8).

2.4. Bis(alkenylindenyl)zirconium dichloride complexes

Addition of $ZrCl_4$ to ethereal solutions of the alkenylindenyl lithium salts **1a**, **2a**, **4a** to **6a**, or **11a** to **14a** (1:2 mole ratio) at room temperature and in the dark produced the bis(alkenylindenyl)zirconium dichloride complexes **1b**, **2b**, **4b** to **6b**, or **11b** to **14b** with yields ranging from 29 to 62% (Scheme 9). The freshly prepared yellow colored complexes, among which only **5b** is appreciable stable towards air and moisture, are all soluble in polar solvents and to some extent also in hexane and pentane. The solubility in hexane is low for complexes containing indenyl ligands with short alkenyl chains in the 1-position, but increases up to 1 g/10 ml hexane for long-chain alkenyl groups in the 2-position of the indenyl ligand.



Scheme 8.



Scheme 9.

The ¹H-NMR spectra of **1b**, **2b** and **4b** to **6b** show two dd-signals for the CH groups of the five membered ring of the indenyl ligand indicating an equimolar mixture of DL/*meso* diastereomers. There are no attempts made to separate the diastereomeric mixtures by crystallization. In the low-temperature NMR spectrum of **5b**, recorded at − 70°C, the signals are only shifted, but not separated with respect to rotational isomers. The zirconocenes **11b** to **12b** do not form diastereomers and show no hindered rotation in the NMR at − 50°C. In the case of the complexes **13b** and **14b** only D,L diastereomers could be detected by NMR. The mass spectra of the complexes **1**, **2**, and **6** indicate fragmentation processes with elimination of HCl which are already known from other complexes of the group 4 and group 9 elements [20]. The mass spectroscopic results prove that the HCl elimination process is independent of the number of carbon atoms of the substituent.

3. Molecular structures of 5b and 12b

The molecular structures of bis[1-(3-buten-1-yl)-4,7-dimethylindenyl]zirconium dichloride (**5b**) and bis[2-(4-penten-1-yl)-4,7-dimethylindenyl]zirconium dichloride (**12b**) were determined by single crystal X-ray diffraction. Suitable crystals were obtained by recrystallization from hexane. The crystallographic data and refinement parameters are listed in Table 1, the molecular structures are shown in Fig. 1 (**5b**) and Fig. 2 (**12b**). In contrast to our expectations, in both complexes the double bonds of the ligand-bonded alkenyl groups do not coordinate the zirconium atom. In **12b**, the double bonds are even turned away from the metal center. The alkenyl groups do not significantly change the structural parameters of the bis(indenyl) core. For both compounds, the bond distances Zr–Cl and Zr–Cp (Cp = centroid of the 5-membered ring of the indenyl system) as well as the bond angles Cp–Zr–Cp and Cl–Zr–Cl are of the order estimated already for other bridged and unbridged zirconium complexes [1b,1k].

4. Catalytic activity

The complexes **1b**, **4b** to **6b**, and **11b** to **13b** were tested as catalytic for the polymerization of ethylene and propylene in the presence of methylaluminoxane (MAO) as a cocatalyst at 30°C. The results of these investigations are summarized in Table 2.

Table 1
Crystal data and structure refinement for **5b** and **12b**

	5b	**12b**
Empirical formula	$C_{30}H_{34}ZrCl_2(C_7H_8)$	0.5 $[C_{32}H_{38}ZrCl_2]$
Formula weight (g mol^{-1})	648.87	292.40
Crystal size (mm^3) and color	$0.36 \times 0.30 \times 0.06$; yellow	$0.54 \times 0.48 \times 0.36$; orange
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pcan$
a (Å)	10.196(2)	8.633(2)
b (Å)	25.692(9)	16.803(5)
c (Å)	13.198(2)	19.751(4)
V ($Å^3$)	3268(2)	2864.9(12)
β (°)	109.02(2)	
Z	4	8
D_{calc} (g cm^{-3})	1.319	1.356
$F(000)$	1352	1216
μ(Mo–K_α) (mm^{-1})	0.524	0.589
T (K)	193(2)	193(2)
Radiation (Mo–K_α) (Å)	0.71069	0.71069
2θ range (°)	$3 \leq 2\theta \leq 53$	$4 \leq 2\theta \leq 53$
Aperture (mm)	2.70	2.70
Scan angle (°)	$(0.80 + 0.35 \cdot \tan\alpha)$	$(0.90 + 0.35 \cdot \tan\alpha)$
Reflections collected	4962	2944
Reflections unique	4748	2944
Reflections observed, $I = 2\sigma(I)$	2233	1893
Data/Restraints/Parameter	4748/32/355	2941/0/161
R_1 observed/all data[a]	0.0813/0.1966	0.0508/0.0942
wR_2 observed/all data[b]	0.1161/0.1323	0.1184/0.1423
Goodness-of-fit[c]	1.012	1.050
Absorption correction/ min/max	difabs/0.737/1.578	
$\Delta\rho_{min/max}$	−0.825/0.554	−0.344/0.679

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|)$.
[b] $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.
[c] $GOOF = [\Sigma w(|F_o| - |F_c|)^2/(n-p)]^{1/2}$.

Table 2
Polymerization results obtained with **1b**, **4b–6b**, and **11b–13b** at 30°C, 2 bar monomer pressure, 200 ml toluene, [MAO] = 2g l^{-1}, [Zr] = 1×10^{-6} mol l^{-1} (ethylene) and 5×10^{-6} mol l^{-1} (propylene), $t_{Pol} = 60$ min[f]

Metallocene	Monomer	Activity[a]	M_n[b]	T_m[c]	ΔH_m[d]
1b	Ethylene	170 000	268 000	140	160
4b	Ethylene	16 000	591 000	143	158
5b	Ethylene	11 000	551 000	141	157
6b	Ethylene	18 000	493 000	138	154
11b	Ethylene	14 000	604 000	140	140
12b	Ethylene	27 000	742 000	138	143
13b	Ethylene	80 000	353 000	142	165
1b	Propylene	500	5100		
4b	Propylene	<10	14 000		
5b	Propylene	10	n.d.[e]		
6b	Propylene	<10	10 100		
11b	Propylene	250	17 000		
12b	Propylene	150	7200		
13b	Propylene	10	4200		

[a] In kgPol/(molZr*h).
[b] In g mol^{-1}.
[c] In °C.
[d] In J g^{-1}.
[e] n.d.: not determined.
[f] All PP products were atactic.

At least two ways are known to modify a catalytic system: changing the substituent of the indenyl rings or bridging the ligands. The positive electronic and steric effects affected by the substituent can change the nature and activity of the catalyst and, in turn, the ratio of the polymer chain propagation/termination rates [12a, 12d, 13, 22]. Concerning the influence of the metallocene substitution patterns on activity and polymer molecular weight, all new complexes observed this theory. Complex **1b** was determined to have an activity of 170 000 kg PE (mol Zr × h)$^{-1}$ and an $M_n = 268\,000$ in contrast to **12b** with an activity of 27 000 kg PE (mol Zr × h)$^{-1}$ and $M_n = 742\,000$. In the case of the propylene polymerization this theory does not fit; no systematic line is found here. The good polymerization results of the new unbridged zirconocenes are on the same order as the activities and molecular weights of known bridged zirconium complexes [1], i.e. $[Me_2Si(2,4,7\text{-}Me_3Ind)_2]ZrCl_2$, $[Me_2Si(2\text{-}Me\text{-}4,6\text{-}^iPrInd)_2]ZrCl_2$ or $[Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2]ZrCl_2$. The highest activity of the ethylene polymerization was reached with the systems **1b** and **13b** [1f, 1j, 23]. In addition it could be proposed that the methyl groups of the 4,7-substituted ligands stabilize the active center by an α-agostic interaction [1f]. These facts might give the explanation for much higher molecular weights obtained with 4,7-methyl-substituted indenyl zirconocenes. **11b** and **12b** give the highest molecular weights, because of the absence of the *meso*

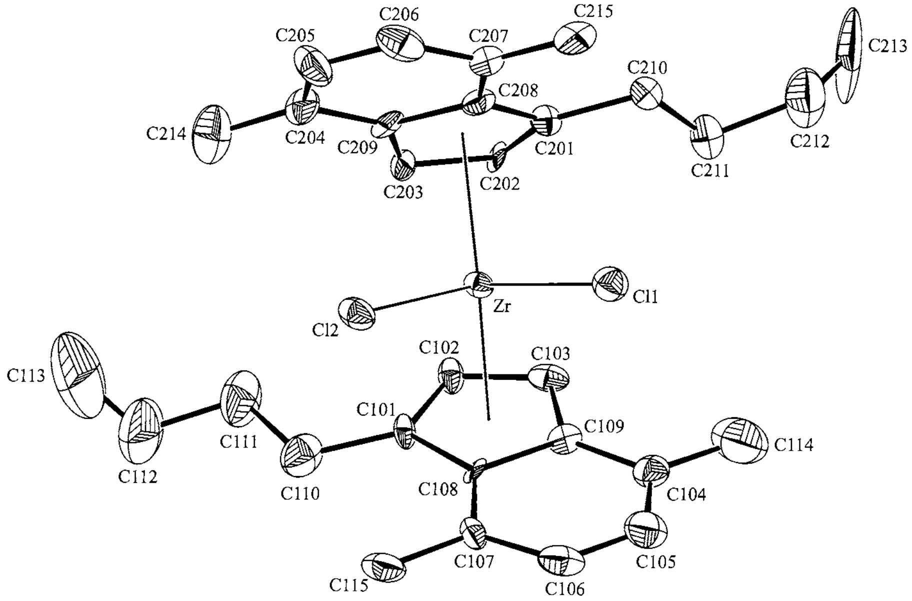


Fig. 1. ORTEP plot [21] of **5b**. Selected bond distances (Å) and angles (°), estimated standard deviations in parentheses; Cp(1) and Cp(2) define the centroids of the indenyl ring atoms C(101)–C(103), C(108), C(109) and C(201)–C(203), C(208), C(209), respectively: Zr–Cl(1) 2.439(3), Zr–Cl(2) 2.422(3), Zr–Cp(1) 2.233(5), Zr–Cp(2) 2.232(4), Cp(1)–Zr–Cp(2) 130.2(2), Cp(1)–Zr–Cl(1) 106.9(2), Cp(1)–Zr–Cl(2) 105.8(2), Cp(2)–Zr–Cl(1) 105.6(2), Cp(2)–Zr–Cl(2) 106.4(2), Cl(1)–Zr–Cl(2) 97.20(8), plane Cp(1)–plane Cp(2) 58.1(3).

isomers. The complex bis[2-(3-buten-1-yl)-4,7-dimethylindenyl]zirconium dichloride (**11b**) showed two other important effects: it yields a low M_W/M_n as well as a high propylene activity resulting in a molecular weight of 17 000. It is furthermore worth noticing that the increase in length of the alkenyl side chain from four carbons for **11b** to five carbons for **12b** causes a change of the polydispersity. While not forming a trend, this change does indicate some significant influence of the side chain on the polymerization and chain termination processes. The results reported by Waymouth [24] that 2-substituted indenyl zirconium dichlorides produce isotactic polypropylen and that they are more effective catalysts than complexes with 1-substituted indenyl ligands is confirmed for the catalytic activity of **11b** and **12b**.

5. Experimental

5.1. General comments

All operations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All the working up procedures of the hydrocarbons were carried out without protection by nitrogen. Solvents were dried over sodium/benzophenone and distilled prior to use. The NMR spectra were recorded on a Bruker ARX 200 or a Bruker ARX 400 spectrometer. Proton and carbon assignments were generally made based on COSY and HETCOR spectra. CH analyses were performed on a Perkin–Elmer 240 C elemental analyser. Mass spectra were determined on a Varian MAT 311 A spectrometer using electron impact (standard 70 eV, otherwise specified).

5.2. Substituted 1-alkenyl-indenyl compounds

5.2.1. 1-Allyl-1H-indene and 3-Allyl-1H-indene [11a] (1)

Indenyllithium (4.93 g, 40.38 mmol) was dissolved in THF (80 ml) and the colorless solution was cooled to 0°C. Allyl chloride (3.71 g, 48.46 mmol) was added slowly to the solution and the mixture was stirred for 48 h at 20°C. The solvent was removed under reduced pressure, and water (20 ml) was added. The water layer was extracted several times with Et$_2$O and the organic layer was dried over MgSO$_4$. Fractional distillation yielded **1** as a colourless liquid (4.33 g, 69%). B.p.: 54–56°C/0.2 mbar. Two double-bond isomers (3-allyl- and 1-allylindene) were evident in the NMR spectra. ^{1}H-NMR (CDCl$_3$, 400 MHz): 1-Ally-1H-indene: 7.53–7.26 (m, 4H, CH aromat.), 6.90 (dd, $J = 1.8$ Hz, 1H, =CH), 6.60 (dd, $J = 1.8$ Hz, 1H, CH=), 6.0–5.85 (m, 1H, CH=CH$_2$), 5.25–5.11 (m, 2H, CH=CH$_2$), 3.59 (dd, $J = 6.2$ Hz, 1H, CH), 2.70 (m, $J = 6.1$ Hz, 1H, CH$_2$), 2.35 (m, $J = 6.1$ Hz, 1H, CH$_2$). 3-Ally-1H-indene: 7.53–7.26 (m, 4H, CH aromat.), 6.32 (s, 1H, CH=C), 6.2–6.05 (m, 1H, CH=CH$_2$), 5.25–5.11 (m, 2H, CH=CH$_2$), 3.41 (m, 4H, CH$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 100.64 MHz): 144.40 (C), 142.43 (C), 138.93 (C), 135.56 (CH=CH$_2$), 128.85 (CH=C), 125.94 (CH aromat.),

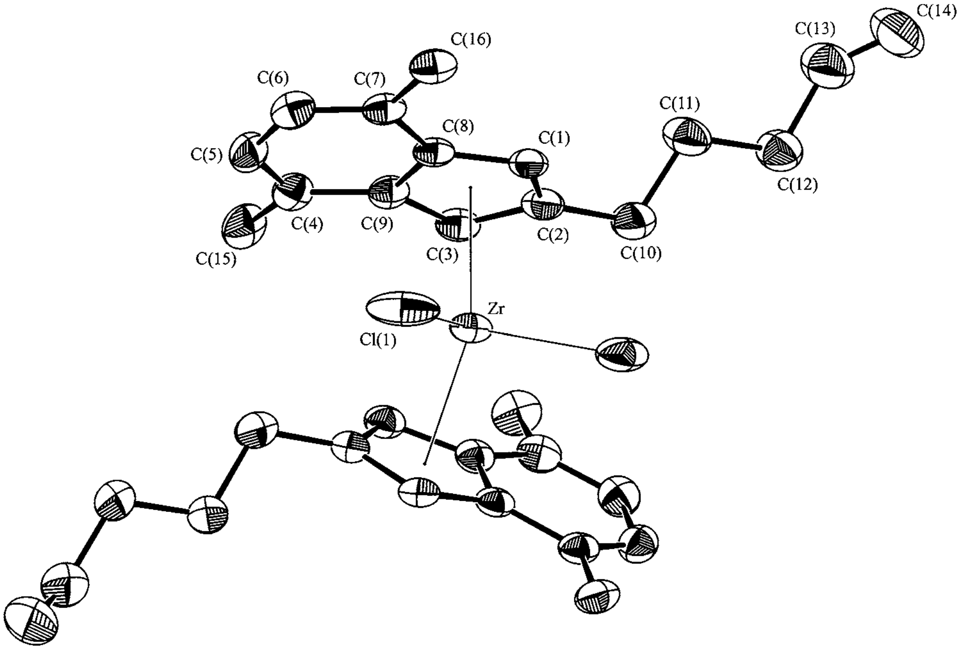


Fig. 2. ORTEP plot [21] of **12b**. Selected bond distances (Å) and angles (°) estimated standard deviations in parentheses; Cp(1) and Cp(1)′ define the centroids of the indenyl ring atoms C(1)–C(3), C(8), C(9) and C(1)′–C(3)′, C(8)′, C(9)′, respectively: Zr–Cl(1) 2.415(2), Zr–Cp(1) 2.242(2), Cp(1)–Zr–Cp(1)′ 131.76(7), Cp(1)–Zr–Cl(1) 106.83(6), Cp(1)–Zr–Cl(1)′ 105.01(6), Cl(1)–Zr–Cl(1)′ 95.69(10), Cp(1)–Cp(1)′ 52.74(11). Symmetry transformation (′): x, $-y+1$, $-z+\frac{1}{2}$.

124.70 (CH aromat.), 123.69 (CH aromat.), 119.21 (CH aromat.), 116.25 (=CH_2), 37.68 (CH_2), 32.41 (CH_2). LRMS (19°C): *m*/*z* 156 (32) $[M]^+$, 155 (16) $[C_{12}H_{11}]^+$, 141 (21) $[C_{11}H_9]^+$, 128 (25) $[C_{10}H_8]^+$, 116 (32) $[C_9H_8]^+$, 115 (100) $[C_9H_7]^+$. Anal. Found: C, 92.26; H, 7.74. $C_{12}H_{12}$ (156.23 g mol^{-1}) (**1**). Calc.: C, 91.06; H, 7.66%.

*5.2.2. 3-(3-Buten-1-yl)-1H-indene (**2**)*

Indenyllithium (4.52 g, 37.03 mmol) was dissolved in THF (50 ml). To the solution was added slowly 4-bromo-1-butene (5 g, 37.03 mmol). The reaction mixture was stirred 12 h at 20°C. The THF was removed under reduced pressure and the residue was mixed with diethyl ether (70 ml) and water (30 ml). The water phase was extracted diethyl ether (3 × 10 ml). The combined organic layers were dried over $MgSO_4$. The solvent was evaporated under reduced pressure to yield **2** as light yellow liquid (5.44 g, 86%). B.p.: 81–83°C/0.1 mbar. ^{1}H-NMR (C_6D_6, 200 MHz): 7.30 (m, 4H, CH aromat.), 5.97 (t, $J = 1.7$ Hz, 1H, =CH), 5.83 (m, 1H, $CH{=}CH_2$), 5.02 (m, 2H, $CH{=}CH_2$), 3.05 (dd, $J = 2.3$ Hz, 2H, CH_2), 2.48 (m, 2H, CH_2CH_2), 2.35 (m, 2H, CH_2CH_2). $^{13}C\{^1H\}$-NMR (C_6H_6, 50.32 MHz): 145.72 (C), 144.69 (C), 144.16 (C), 138.55 ($CH{=}CH_2$), 127.90 (CH aromat.), 126.35 (CH aromat.), 124.91 (CH aromat.), 123.98 (CH aromat.), 119.35 (CH=), 114.88 ($CH{=}CH_2$), 37.79 (CH_2CH_2), 32.42 (CH_2CH_2), 27.44 (CH_2). LRMS (24°C): *m*/*z* 170 (33) $[M]^+$, 142 (12) $[C_{11}H_{10}]^+$, 141 (16) $[C_{11}H_9]^+$, 129 (100) $[C_{10}H_9]^+$, 128 (74) $[C_{10}H_8]^+$, 116 (39) $[C_9H_8]^+$, 115 (39) $[C_9H_7]^+$. Anal. Found: C, 90.33; H, 8.20. $C_{13}H_{14}$ (170.25 g mol^{-1}) (**2**) Calc.: C, 91.71; H, 8.29%.

*5.2.3. 3-(4-Penten-1-yl)-1H-indene (**3**)*

The procedure described above for the synthesis of **2** was followed with indenyllithium (2.43 g, 19.9 mmol) and 5-bromo-1-pentene (2.97 g, 19.9 mmol) in THF (50 ml) to yield after fractional distillation **3** as a light yellow liquid (2.61 g, 71%). B.p.: 91–95°C/0.1 mbar. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.40 (m, 4H, CH aromat.), 6.28 (t, $J = 1.7$ Hz, 1H, =CH), 5.93 (m, 1H, $CH{=}CH_2$), 5.09 (m, 2H, $CH{=}CH_2$), 3.40 (d, $J = 2.0$ Hz, 2H, CH_2), 2.62 (m, 2H, CH_2CH_2), 2.24 (m, 2H, CH_2CH_2), 1.88 (m, 2H, CH_2CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 50.32 MHz): 145.47 (C), 144.49 (C), 144.28 (C), 138.68 ($CH{=}CH_2$), 127.80 (CH aromat.), 125.92 (CH aromat.), 124.42 (CH aromat.), 123.69 (CH aromat.), 118.91 (CH=), 114.72 ($CH{=}CH_2$), 37.66 (CH_2), 33.62 (CH_2CH_2), 27.17 (CH_2CH_2), 27.10 (CH_2CH_2). LRMS (24°C): *m*/*z* 184 (18) $[M]^+$, 169 (7) $[C_{13}H_{13}]^+$, 141 (12) $[C_{11}H_9]^+$, 130 (27) $[C_{10}H_{10}]^+$, 128 (25) $[C_{10}H_8]^+$, 115 (18) $[C_9H_7]^+$. Anal. Found: C, 90.97; H, 8.73. $C_{14}H_{16}$ (184.28 g mol^{-1}) (**3**). Calc.: C, 91.25; H, 8.75%.

5.2.4. *3-Allyl-4,7-dimethyl-1H-indene* (**4**)

Analogous to the preparation of **1**, 4,7-dimethylindene (6.5 g, 43.29 mmol) in THF (50 ml) and allyl chloride (4.64 g, 60.61 mmol) gave after fractional distillation **4** as a colourless liquid product (5.59 g, 70%). B.p.: 62–68°C/0.2 mbar. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.11–7.00 (m, 2H, CH aromat.), 6.97 (dd, $J = 1.9$ Hz, 1H, =CH), 6.62 (dd, $J = 1.9$ Hz, 1H, CH=), 5.79 (m, 1H, $CH=CH_2$), 5.10 (m, 2H, $CH=CH_2$), 3.65 (m, 1H, CH), 3.02 (m, 1H, CH_2), 2.47 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.25 (m, 1H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 50.32 MHz): 144.54 (C), 143.12 (C), 138.37 ($CH=CH_2$), 135.88 (CH=), 129.17 (CH aromat.), 127.95 (CH=), 126.72 (CH aromat.), 116.00 ($CH_2=CH$), 49.77 (CH), 33.72 (CH_2), 18.80 (CCH_3), 18.22 (CCH_3). LRMS (21°C): *m*/*z* 184 (41) $[M]^+$, 169 (22) $[C_{13}H_{13}]^+$, 157 (18) $[C_{12}H_{13}]^+$, 143 (100) $[C_{11}H_{11}]^+$, 128 (73) $[C_{10}H_8]^+$, 115 (51) $[C_9H_7]^+$. Anal. Found: C, 90.52; H, 8.71. $C_{14}H_{16}$ (184.28 g mol^{-1}) (**4**). Calc.: C, 91.25; H, 8.75%.

5.2.5. *3-(3-Buten-1-yl)-4,7-dimethyl-1H-indene* (**5**)

The procedure described above for the synthesis of **2** was followed with (4,7-dimethylindenyl)lithium (5.56 g, 37.03 mmol) and 4-bromo-1-butene (5.00 g, 37.03 mmol) in THF (50 ml) to yield **5** as a yellow liquid (6.45 g, 88%). B.p.: 76–78°C/0.1 mbar. ^{1}H-NMR (C_6D_6, 200 MHz): 6.97 (d, $J = 7.6$ Hz, 1H, CH aromat.), 6.89 (d, $J = 7.5$ Hz, 1H, CH aromat.), 6.01 (t, $J = 1.8$ Hz, 1H, =CH), 5.86 (m, 1H, $CH=CH_2$), 5.03 (m, 2H, $CH=CH_2$), 2.91 (dd, $J = 2.2$ Hz, 2H, CH_2), 2.70 (m, 2H, CH_2CH_2), 2.39 (s, 3H, CH_3), 2.35 (m, 2H, CH_2CH_2), 2.13 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR (C_6D_6, 50.32 MHz): 146.27 (C), 144.24 (C), 142.81 (C), 138.62 ($CH=CH_2$), 129.69 (CH aromat.), 128.30 (CH=), 126.14 (CH aromat.), 114.87 ($CH=CH_2$), 36.42 (CH_2), 33.47 (CH_2CH_2), 30.55 (CH_2CH_2), 20.00 (CH_3), 18.26 (CH_3). LRMS (24°C): *m*/*z* 198 (34) $[M]^+$, 183 (10) $[C_{14}H_{15}]^+$, 157 (100) $[C_{12}H_{13}]^+$, 142 (47) $[C_{11}H_{10}]^+$, 141 (42) $[C_{11}H_9]^+$, 129 (27) $[C_{10}H_9]^+$, 128 (26) $[C_{10}H_8]^+$, 115 (23) $[C_9H_7]^+$. Anal. Found: C, 89.94; H, 9.08. $C_{15}H_{18}$ (198.31 g mol^{-1}) (**5**) Calc.: C, 90.85; H, 9.15%.

5.2.6. *3-(4-Penten-1-yl)-4,7-dimethyl-1H-indene* (**6**)

The procedure described above for the synthesis of **2** was followed with 4,7-dimethylindene (5.04 g, 33.55 mmol) and 5-bromo-1-pentene (5 g, 33.55 mmol) in THF (50 ml) to obtain after distillation **6** as a yellow liquid (5.82 g, 82%). B.p.: 82–83°C/0.1 mbar. ^{1}H-NMR (C_6D_6, 200 MHz): 6.95 (m, 2H, CH aromat.), 6.02 (t, $J = 1.7$ Hz, 1H, =CH), 5.65 (m, 1H, $CH=CH_2$), 4.98 (m, 2H, $CH=CH_2$), 2.93 (d, $J = 2.2$ Hz, 1H, CH_2), 2.45 (m, 2H, CH_2CH_2), 2.26 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.04 (m, 2H, CH_2CH_2) 1.65 (m, 2H, CH_2CH_2). $^{13}C\{^1H\}$-NMR (C_6D_6, 50.32 MHz): 146.76 (C), 145.50 (C), 144.31 (C), 143.49 (C), 142.90 (C), 138.57 ($CH=CH_2$), 129.56 (CH aromat.), 128.24 (CH=), 126.11 (CH aromat.), 114.87 ($CH=CH_2$), 36.41 (CH_2), 33.98 (CH_2CH_2), 30.62 (CH_2CH_2), 29.02 (CH_2CH_2), 20.04 (CH_3), 18.26 (CH_3). LRMS (24°C): *m*/*z* 212 (23) $[M]^+$, 197 (15) $[C_{15}H_{17}]^+$, 183 (5) $[C_{14}H_{15}]^+$, 171 (10) $[C_{13}H_{15}]^+$, 158 (100) $[C_{12}H_{14}]^+$, 143 (77) $[C_{11}H_{11}]^+$, 141 (40) $[C_{11}H_9]^+$, 129 (39) $[C_{10}H_9]^+$, 128 (56) $[C_{10}H_8]^+$, 115 (38) $[C_9H_7]^+$. Anal. Found: C, 90.03; H, 9.42. $C_{16}H_{20}$ (212.33 g mol^{-1}) (**6**) Calc.: C, 90.51; H, 9.49%.

5.2.7. *(1-Allylindenyl)lithium* (**1a**)

A solution of 3-allylindene (4.33 g, 27.72 mmol) in hexane (100 ml) was cooled to 0°C and *n*-butyllithium (1.6 M in hexane, 24 ml, 38.81 mmol) was added slowly. The suspension was stirred 12 h at 20°C, filtered and the solid was washed with hexane (150 ml). The white solid was dried under reduced pressure to yield **1a** as a white solid (3.74 g, 83%). M.p.: 157°C. ^{1}H-NMR (C_5D_5N, 400 MHz): 8.03 (m, 2H, CH aromat.), 7.34 (t, $J = 2.6$ Hz, 1H, CH), 7.08 (m, 2H, CH aromat.), 6.82 (t, $J = 2.6$ Hz, 1H, CH), 6.55 (m, 1H, $CH=CH_2$), 5.40 (d, $J = 17.0$ Hz, 1H, $=CH_2$ *trans*), 5.03 (d, $J = 9.8$ Hz, 1H, $CH=CH_2$ *cis*), 4.24 (d, $J = 6.6$ Hz, 2H, CH_2). $^{13}C\{^1H\}$-NMR (C_5D_5N, 100.64 MHz): 143.00 (CH=), 131.40 (C), 128.85 (C), 118.97 (CH aromat.), 118.73 (CH aromat.), 116.86 (CH), 111.75 (CH aromat.), 111.10 (CH aromat.), 110.81 ($=CH_2$), 104.03 (C), 91.74 (CH), 34.90 (CH_2). LRMS (26°C): *m*/*z* 162 (0.11) $[M]^+$, 156 (45) $[C_{12}H_{12}]^+$, 141 (24) $[C_{11}H_9]^+$, 128 (100) $[C_{10}H_8]^+$, 115 (62) $[C_9H_7]^+$. Anal. Found: C, 88.61; H, 6.81. $C_{12}H_{11}Li$ (162.16 g mol^{-1}) (**1a**) Calc.: C, 88.88; H, 6.84%.

5.2.8. *[1-(3-Buten-1-yl)indenyl]lithium* (**2a**)

The deprotonation described for the preparation of **1a** using **2** (5.44 g, 31.95 mmol) and *n*-BuLi (20 ml, 31.95 mmol) in hexane (80 ml) gave **2a** as a white solid (5.06 g, 90%). M.p.: 143°C. ^{1}H-NMR (C_4D_8O, 200 MHz): 7.26 (m, 2H, CH aromat.), 6.44 (m, 2H, CH aromat.), 6.34 (d, $J = 3.2$ Hz, 1H, =CH), 6.00 (m, 1H, $CH=CH_2$), 5.68 (d, $J = 3.2$ Hz, 1H, CH=), 5.01 (m, 2H, $CH=CH_2$), 2.91 (t, $J = 8.2$ Hz, 2H, CH_2CH_2), 2.44 (q, $J = 8.2$ Hz, 2H, CH_2CH_2). $^{13}C\{^1H\}$-NMR (C_4D_8O, 50.32 MHz): 141.68 ($CH=CH_2$), 129.39 (C), 127.21 (C), 119.45 (CH aromat.), 117.36 (CH aromat.), 115.45 (CH aromat.), 113.74 (CH aromat.), 112.95/112.76 ($CH=CH_2$), 106.49 (C), 87.72 (CH=), 37.92 (CH_2CH_2), 29.17 (CH_2CH_2). LRMS (24°C): *m*/*z* 176 (0) $[M]^+$, 170 (39) $[C_{13}H_{14}]^+$, 158 (17) $[C_{12}H_{14}]^+$, 142 (27) $[C_{11}H_{10}]^+$, 141 (75) $[C_{11}H_9]^+$, 129 (100) $[C_{10}H_9]^+$, 128 (68) $[C_{10}H_8]^+$, 116 (20) $[C_9H_8]^+$, 115 (26) $[C_9H_7]^+$. Anal. Found: C, 87.99; H, 7.39. $C_{13}H_{13}Li$ (176.19 g mol^{-1}) (**2a**) Calc.: C, 88.62; H, 7.44%.

5.2.9. [1-(4-Penten-1-yl)indenyl]lithium ***(3a)***

The deprotonation described for the preparation of **1a** using **3** (2.61 g, 19.9 mmol) and *n*-BuLi (17.4 ml, 23.88 mmol, 1.6 M) in hexane (100 ml) was carried out at 20°C for 12 h. After filtration, the solid was washed with hexane (100 ml) and dried in vacuo at 0.1 mbar to yield **3a** as a white solid (3.56 g, 94%). M.p.: 120°C. ^{1}H-NMR (C_5D_5N, 200 MHz): 8.02 (m, 2H, CH aromat.), 7.32 (d, $J = 3.2$ Hz, 1H, =CH), 7.06 (m, 2H, CH aromat.), 6.79 (d, $J = 3.2$ Hz, 1H, CH=), 5.99 (m, 1H, $CH{=}CH_2$), 5.01 (m, 2H, $CH{=}CH_2$), 3.44 (t, $J = 7.3$ Hz, 2H, CH_2CH_2), 2.39 (q, $J = 7.2$ Hz, 2H, CH_2CH_2), 2.16 (q, $J = 7.3$ Hz, 2H, CH_2CH_2). $^{13}C\{^{1}H\}$-NMR (C_5D_5N, 50.32 MHz): 140.48 ($CH{=}CH_2$), 131.05 (C), 128.74 (C), 116.35 (C), 118.92 (CH aromat.), 118.28 (CH aromat.), 116.84 (CH aromat.), 113.50 ($={CH_2}$), 110.82 (CH aromat.), 110.21 (CH), 91.09 (CH), 34.55 (CH_2CH_2), 32.85 (CH_2CH_2), 29.18 (CH_2CH_2). LRMS (27°C): *m*/*z* 190 (0) $[M]^+$, 184 (26) $[C_{14}H_{16}]^+$, 169 (8) $[C_{13}H_{11}]^+$, 141 (15) $[C_{11}H_9]^+$, 130 (100) $[C_{10}H_{10}]^+$, 115 (22) $[C_9H_7]^+$. Anal. Found: C, 88.13; H, 7.93. $C_{14}H_{15}Li$ (190.21 g mol^{-1}) (**3a**) Calc.: C, 88.40; H, 7.95%.

5.2.10. [1-Allyl-4,7-dimethylindenyl]lithium ***(4a)***

The deprotonation described above for the synthesis of **1a** was carried out with **4** (5.59 g, 30.33 mmol) and *n*-BuLi (26 ml, 42.46 mmol) in hexane (100 ml) to give **4a** as a white solid (5.29 g, 92%). M.p.: 162°C. ^{1}H-NMR (C_5D_5N, 400 MHz): 7.30 (m, 1H, CH aromat.), 6.82 (m, 1H, CH aromat.), 6.80 (m, 1H, =CH), 6.75 (m, 1H, CH=), 6.61 (m, 1H, $CH{=}CH_2$), 5.30 (d, $J = 17.0$ Hz, 1H, $CH{=}CH_2$ *trans*), 5.06 (d, $J = 8.8$ Hz, 1H, $CH{=}CH_2$ *cis*), 4.37 (d, $J = 5.2$ Hz, 2H, CH_2), 3.06 (s, 3H, CH_3), 2.79 (s, 3H, CH_3). $^{13}C\{^{1}H\}$-NMR (C_5D_5N, 100.64 MHz): 144.94 (CH=), 131.54 (C), 126.64 (C), 125.19 (C), 124.28 (C), 118.47 (CH), 114.11 (CH aromat.), 112.64 (CH aromat.), 111.02 ($={CH_2}$), 106.51 (C), 90.59 (CH), 36.76 (CH_2), 22.51 (CCH_3), 20.30 (CCH_3). LRMS (22°C): *m*/*z* 190 (0.11) $[M]^+$, 184 (55) $[C_{14}H_{16}]^+$, 169 (27) $[C_{13}H_{13}]^+$, 157 (8) $[C_{12}H_{13}]^+$, 143 (100) $[C_{11}H_{11}]^+$, 128 (29) $[C_{10}H_8]^+$, 115 (9) $[C_9H_7]^+$. Anal. Found: C, 88.05; H, 7.92. $C_{14}H_{15}Li$ (190.21 g mol^{-1}) (**4a**) Calc.: C, 88.40; H, 7.95%.

5.2.11. [1-(3-Buten-1-yl)-4,7-dimethylindenyl]lithium ***(5a)***

The deprotonation described for the preparation of **1a** using **5** (6.45 g, 32.52 mmol) and *n*-BuLi (20.3 ml, 32.52 mmol) in hexane (80 ml) gave **5a** as a white solid (6.52 g, 98%). M.p.: 205°C. ^{1}H-NMR (C_5D_5N, 400 MHz): 7.23 (d, $J = 3.3$ Hz, 1H, CH aromat.), 6.73 (d, $J = 3.4$ Hz, 1H, CH aromat.), 6.71 (d, $J = 3.4$ Hz, 1H, =CH), 6.69 (d, $J = 3.4$ Hz, 1H, =CH), 6.27 (m, 1H, $CH{=}CH_2$), 5.18 (m, 1H, $={CH_2}$ *trans*), 5.01 (m, 1H, $={CH_2}$ *cis*), 3.65 (t, $J = 7.8$ Hz, 2H, CH_2CH_2), 3.03 (s, 3H, CH_3), 2.71 (q, $J = 8$ Hz, 2H, CH_2CH_2), 2.77 (s, 3H, CH_3). $^{13}C\{^{1}H\}$-NMR (C_5D_5N, 100.64 MHz): 141.29 ($CH{=}CH_2$), 131.31 (C), 126.17 (C), 124.94 (CCH_3), 124.15 (CCH_3), 117.79 (CH), 113.88 (CH aromat.), 112.82 ($={CH_2}$), 112.34 (CH aromat.), 109.24 (C), 90.30 (CH), 40.68 (CH_2CH_2), 31.78 (CH_2CH_2), 22.43 (CH_3), 20.23 (CH_3). LRMS (38°C): *m*/*z* 204 (0) $[M]^+$, 198 (33) $[C_{15}H_{18}]^+$, 183 (9) $[C_{14}H_{15}]^+$, 157 (100) $[C_{12}H_{13}]^+$, 144 (32) $[C_{11}H_{12}]^+$, 143 (14) $[C_{11}H_{11}]^+$, 142 (47) $[C_{11}H_{10}]^+$, 141 (29) $[C_{11}H_9]^+$, 129 (10) $[C_{10}H_9]^+$, 128 (12) $[C_{10}H_8]^+$, 115 (11) $[C_9H_7]^+$. Anal. Found: C, 87.51; H, 8.31. $C_{15}H_{17}Li$ (204.24 g mol^{-1}) (**5a**) Calc.: C, 88.21; H, 8.39%.

5.2.12. [1-(4-Penten-1-yl)-4,7-dimethylindenyl]lithium ***(6a)***

The deprotonation described for the preparation of **1a** using **6** (5.82 g, 27.41 mmol) and *n*-BuLi (17.1 ml, 27.41 mmol) in hexane (100 ml) gave **12** as a white solid (5.85 g, 98%). M.p.: 183°C. ^{1}H-NMR (C_4D_8O, 200 MHz): 6.15 (m, 2H, CH aromat.), 6.11 (d, $J = 3.3$ Hz, 1H, =CH), 5.95 (m, 1H, $CH{=}CH_2$), 5.57 (d, $J = 3.3$ Hz, 1H, CH=), 4.99 (m, 2H, $CH{=}CH_2$), 2.94 (t, $J = 7.5$ Hz, 2H, CH_2CH_2), 2.60 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.16 (q, $J = 7.3$ Hz, 2H, CH_2CH_2), 1.68 (q, $J = 7.3$ Hz, 2H, CH_2CH_2). $^{13}C\{^{1}H\}$-NMR (C_4D_8O, 50.32 MHz): 140.70 ($CH{=}CH_2$), 128.66 (C), 126.30 (CCH_3), 125.37 (CCH_3), 123.74 (C), 116.35 (C), 114.93 (CH aromat.), 114.74 (CH aromat.), 113.79 ($={CH_2}$), 109.00 (CH), 87.63 (CH), 34.96/34.68 (CH_2CH_2), 30.75 (CH_2CH_2), 22.16 (CH_3 aromat.), 19.86 (CH_3 aromat.). LRMS (24°C): *m*/*z* 218 (0) $[M]^+$, 197 (10) $[C_{16}H_{20}]^+$, 183 (2) $[C_{14}H_{15}]^+$, 170 (7) $[C_{13}H_{14}]^+$, 158 (100) $[C_{12}H_{14}]^+$, 143 (41) $[C_{11}H_{11}]^+$, 141 (18) $[C_{11}H_9]^+$, 128 (15) $[C_{10}H_8]^+$, 115 (8) $[C_9H_7]^+$. Anal. Found: C, 87.58; H, 8.71. $C_{16}H_{19}Li$ (218.27 g mol^{-1}) (**6a**) Calc.: C, 88.05; H, 8.77%.

5.3. Substituted 2-alkenyl indenyl compounds

5.3.1. 2-Bromo-4,7-dimethylindan-1-ol

To a stirred solution of DMSO (142 ml) and water (6.46 g, 0.36 mol) was added 4,7-dimethylindene (26.94 g, 0.187 mol) at 22°C. Afterwards *N*-bromosuccinimide (33.8 g, 0.19 mol) was added slowly. The suspension was stirred 12 h and poured into water (250 ml). The whole solution was extracted with ether (4 × 50 ml). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to give a creme-colored solid (38.5 g, 85%). M.p.: 92°C. ^{1}H-NMR ($CDCl_3$, 400 MHz): 7.02 (d, $J = 7.7$ Hz, 1H, CH aromat.), 6.97 (d, $J = 7.6$ Hz, 1H, CH aromat.), 5.41 (m, 1H, CHOH), 4.42 (q, $J = 6.4$ Hz, 1H, CHBr), 3.63 (dd, $J = 6.4$ Hz, 1H, CH_2), 3.14 (dd, $J = 3.5$ Hz, 1H, CH_2), 2.39 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.00 (d, $J = 6.8$ Hz, 1H, OH). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 100.64 MHz): 139.28 (C), 139.09 (C), 132.77 (C), 131.50 (C), 130.32 (CH aromat.), 129.11 (CH aromat.), 83.33 (CHOH), 54.24 (CHBr), 39.90 (CH_2), 18.44 (CH_3), 17.88 (CH_3). LRMS (65°C): *m*/*z* 242 (71) $[M(^{81}Br)]^+$, 240 (71) $[M(^{79}Br)]^+$, 161 (100) $[C_{11}H_{13}O^{79}Br]^+$, 144 (23) $[C_{11}H_{13}]^+$, 143 (65) $[C_{11}H_{11}]^+$, 128 (19) $[C_{10}H_8]^+$, 115 (20) $[C_9H_7]^+$. Anal. Found: C, 54.75; H, 5.42. $C_{11}H_{13}OBr$ (241.13 g mol^{-1}) Calc.: C, 54.79; H, 5.43%.

5.3.2. *2-Bromo-4,7-dimethyl-1H-indene*

The crude 2-bromo-4,7-dimethylindan-1-ol (38.5 g, 0.159 mol) was refluxed with *p*-toluenesulfonic acid (monohydrate) (1.5 g, 7.9 mmol) in toluene (200 ml) for 72 h using a Dean–Stark water trap to remove water. After cooling down, the reaction mixture was filtered. The filtrate was concentrated and purified by flash chromatography with petroleum ether. The solvent was removed and the residue further purified by fractional distillation to yield a white solid (29.6 g, 83%). M.p.: 89–90°C. ^1H-NMR ($CDCl_3$, 400 MHz): 7.02 (t, $J = 1.6$ Hz, 1H, =CH), 6.96 (d, $J = 7.6$ Hz, 1H, CH aromat.), 6.88 (d, $J = 7.6$ Hz, 1H, CH aromat.), 3.47 (s, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.27 (s, 3H, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.64 MHz): 142.51 (C), 141.15 (C), 131.65 (CH=), 129.72 (C), 128.04 (CH aromat.), 126.97 (C), 126.16 (CH aromat.), 124.00 (C), 44.73 (CH_2), 18.20 (CH_3), 18.09 (CH_3). LRMS (24°C): *m*/*z* 224 (18) $[M(^{81}Br)]^+$, 222 (18) $[M(^{79}Br)]^+$, 143 (100) $[C_{11}H_{11}]^+$, 141 (14) $[C_{11}H_9]^+$, 128 (34) $[C_{10}H_8]^+$, 115 (15) $[C_9H_7]^+$. Anal. Found: C, 59.16; H, 4.96. $C_{11}H_{11}Br$ (223.11 g mol^{-1}) Calc.: C, 59.22; H, 4.97%.

5.3.3. *2-Allyl-1H-indene (**7**)*

Allylmagnesium chloride (41.02 ml, 82.04 mmol) was dissolved in THF (50 ml). In a separate flask a suspension of 2-bromoindene (4.0 g, 9.0 mmol) and $PdCl_2$(DPPF) (0.841 g, 1.03 mmol) in THF (50 ml) was prepared and added slowly to the Grignard solution at 0°C. The reaction mixture was stirred 72 h at 20°C. The mixture was poured into 1 N HCl (100 ml) and was extracted with ether. The combined organic phases were washed with brine and dried over $MgSO_4$. The concentrated mixture was purified by flash chromatography followed by fractional distillation to give the product as a colourless liquid. Yield 0.8 g (25%). B.p.: 55–57°C/0.2 mbar. ^1H-NMR ($CDCl_3$, 400 MHz): 7.22 (m, 4H, CH aromat.), 6.55 (s, 1H, =CH), 5.85 (m, 1H, CH=CH_2), 5.03 (m, 2H, CH=CH_2), 3.35 (s, 2H, CH_2), 3.23 (d, $J = 7.2$ Hz, 2H, CH_2CH). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.64 MHz): 145.14 (C), 144.62 (C), 142.66 (C), 135.21 (CH=CH_2), 131.70 (CH aromat.), 129.59 (CH=), 128.43 (CH aromat.), 126.58 (CH aromat.), 125.86 (CH aromat.), 115.90 (CH=CH_2), 38.12 (CH_2), 34.89 (CH_2CH). LRMS (12eV, 50°C): *m*/*z* 156 (100) $[M]^+$, 141 (16) $[C_{11}H_9]^+$, 128 (32) $[C_{10}H_8]^+$, 115 (62) $[C_9H_7]^+$. Anal. Found: C, 91.46; H, 7.68. $C_{12}H_{12}$ (156.23 g mol^{-1}) (**7**). Calc.: C, 92.26; H, 7.74%.

5.3.4. *2-(3-Buten-1-yl)-1H-indene (**8**)*

To a solution of 3-butenylmagnesium bromide (5.31 g, 33.33 mmol) and 2-bromoindene (3.25 g, 16.67 mmol) in THF (80 ml) at 0°C was added dropwise $NiCl_2$(DPPE) (1.06 g, 2.0 mmol) in THF (20 ml). The reaction mixture was stirred 12 h at 20°C. The mixture was poured into 1 N HCl (100 ml). The water phase was extracted with ether and the combined organic phases were washed with brine, dried over $MgSO_4$, concentrated and purified by flash chromatography. A colourless liquid was obtained by fractional distillation. Yield 1.6 g (38%). B.p.: 65°C/0.2 mbar. ^1H-NMR ($CDCl_3$, 400 MHz): 7.24 (m, 4H, CH aromat.), 6.53 (s, 1H, =CH), 5.88 (m, 1H, CH=CH_2), 5.05 (m, 2H, CH=CH_2), 3.32 (s, 2H, CH_2), 2.56 (t, $J = 7.6$ Hz, 2H, CH_2CH_2), 2.38 (dt, $J = 7.2$, 7.2 Hz, 2H, CH_2CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.64 MHz): 145.17 (C), 143.24 (C), 141.61 (C), 136.25 (CH=CH_2), 131.05 (CH aromat.), 128.48 (CH aromat.), 126.14 (CH aromat.), 125.75 (CH aromat.), 113.70 (CH=CH_2), 108.30 (CH=), 34.76 (CH_2CH_2), 31.21 (CH_2CH_2), 28.52 (CH_2). LRMS (30°C): *m*/*z* 170 (25) $[M]^+$, 129 (100) $[C_{10}H_9]^+$, 127 (10) $[C_{10}H_7]^+$, 115 (16) $[C_9H_7]^+$. Anal. Found: C, 91.53; H, 8.27. $C_{13}H_{14}$ (170.25 g mol^{-1}) (**8**). Calc.: C, 91.71; H, 8.29%.

5.3.5. *2-(4-Penten-1-yl)-1H-indene (**9**)*

The procedure described above for the synthesis of **8** was followed using 4-pentenylmagnesium bromide (3.14 g, 18.11 mmol), 2-bromoindene (2.35 g, 12.07 mmol) and $NiCl_2$(DPPE) (0.64 g, 1.21 mmol) in THF (100 ml). **9** resulted as a light yellow liquid (Yield 1.42 g, 64%). B.p.: 90–92°C/0.2 mbar. ^1H-NMR ($CDCl_3$, 400 MHz): 6.85 (m, 4H, CH aromat.), 6.60 (s, 2H, CH), 5.90 (m, 1H, CH=CH_2), 5.09 (m, 1H, =CH_2 *trans*), 5.03 (m, 1H, =CH_2 *cis*), 3.20 (s, 2H, CH_2), 2.40 (t, $J = 7.2$ Hz, 2H, CH_2CH_2), 2.19 (dt, $J = 7.2$, 7.2 Hz, 2H, CH_2CH_2), 1.80 (tt, $J = 7.2$, 7.2 Hz, 2H, CH_2CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.64 MHz): 148.43 (C), 142.84 (C), 140.48 (C), 138.55 (CH=CH_2), 128.83 (C), 127.60 (=CH), 126.59 (C), 124.93 (CH aromat.), 122.72 (CH aromat.), 114.62 (=CH_2), 39.85 (CH_2), 32.45 (CH_2CH_2), 30.67 (CH_2CH_2), 28.22 (CH_2CH_2). LRMS (28°C, 12eV): *m*/*z* 184 (100) $[M]^+$, 169 (14) $[C_{13}H_{12}]^+$, 157 (63) $[C_{12}H_{13}]^+$, 143 (34) $[C_{11}H_{11}]^+$, 128 (25) $[C_{10}H_8]^+$. Anal. Found: C, 91.03; H, 8.70. $C_{14}H_{16}$ (184.28 g mol^{-1}) (**9**). Calc.: C, 91.25; H, 8.75%.

5.3.6. *2-Allyl-4,7-dimethyl-1H-indene (**10**)*

This compound was prepared in the same manner as **7** from 2-bromo-4,7-dimethylindene (2.0 g, 9.0 mmol), allylmagnesium chloride (9.0 ml, 18.0 mmol) in THF (50 ml) and in the separate flask $PdCl_2$(DPPF) (0.367 g, 0.45 mmol) in THF (50 ml). After all purification steps **10** was isolated as a colourless liquid. Yield 0.5 g (30%). B.p.: 72–75°C/0.2 mbar. ^1H-NMR ($CDCl_3$, 400 MHz):

7.02 (d, $J=7.2$ Hz, 1H, CH aromat.), 6.90 (d, $J=7.6$ Hz, 1H, CH aromat.), 6.69 (t, $J=1.6$ Hz, 1H, =CH), 6.40 (m, 1H, CH=CH$_2$), 5.17 (m, 2H, CH=CH$_2$), 3.31 (d, $J=7.2$ Hz, 2H, CH$_2$CH), 3.26 (s, 2H, CH$_2$), 2.43 (s, 3H, CH$_3$), 2.34 (s, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 100.64 MHz): 147.34 (C), 143.76 (C), 141.66 (C), 136.41 (CH=CH$_2$), 129.87 (C), 127.60 (CH=), 126.85 (C), 125.58 (CH aromat.), 125.12 (CH aromat.), 116.00 (CH=CH$_2$), 40.12 (CH$_2$), 35.92 (CH$_2$CH), 18.29 (CH$_3$), 18.17 (CH$_3$). LRMS (12 eV, 52°C): m/z 184 (100) [M]$^+$, 169 (20) [$C_{13}H_{13}$]$^+$, 144 (14) [$C_{11}H_{12}$]$^+$, 143 (75) [$C_{11}H_{11}$]$^+$. Anal. Found: C, 90.52; H, 8.71. $C_{14}H_{16}$ (184.28 g mol^{-1}) (**10**). Calc.: C, 91.25; H, 8.75%.

*5.3.7. 2-(3-Buten-1-yl)-4,7-dimethyl-1H-indene (**11**)*

The procedure described above for the synthesis of **8** was followed using 3-butenylmagnesium bromide (5.3 g, 33.33 mmol) in THF (80 ml) at 0°C with a suspension of NiCl$_2$(DPPE) (1.17 g, 2.22 mmol) and 2-bromo-4,7-dimethylindene (4.96 g, 22.22 mmol) in THF (30 ml). After purification via fractional distillation the product was isolated as a light yellow liquid. Yield 2.34 g (53%). B.p.: 80–88°C/0.2 mbar. ^{1}H-NMR (CDCl$_3$, 400 MHz): 7.00 (d, $J=7.6$ Hz, 1H, CH aromat.), 6.88 (d, $J=7.6$ Hz, 1H, CH aromat.), 6.65 (s, 1H, =CH), 5.93 (m, 1H, CH=CH$_2$), 5.08 (m, 2H, CH=CH$_2$), 3.25 (s, 2H, CH$_2$), 2.65 (t, $J=7.6$ Hz, 2H, CH$_2$CH$_2$), 2.45 (dt, $J=7.6$, 7.2 Hz, 2H, CH$_2$CH$_2$), 2.41 (s, 3H, CH$_3$), 2.34 (s, 3H, CH$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 100.64 MHz): 148.88 (C), 143.78 (C), 141.08 (C), 138.19 (CH=CH$_2$), 129.70 (C), 127.58 (CH=CH$_2$), 126.10 (C), 124.96 (CH aromat.), 124.92 (CH aromat.), 114.85 (CH=), 40.19 (CH$_2$CH$_2$), 33.24 (CH$_2$CH$_2$), 30.84 (CH$_2$), 18.32 (CH$_3$), 18.21 (CH$_3$). LRMS (25°C, 12 eV): m/z 198 (25) [M]$^+$, 157 (100) [$C_{12}H_{13}$]$^+$, 143 (25) [$C_{11}H_9$]$^+$. Anal. Found: C, 90.67; H, 9.13. $C_{15}H_{18}$ (198.31 g mol^{-1}) (**11**). Calc.: C, 90.85; H, 9.15%.

*5.3.8. 2-(4-Penten-1-yl)-4,7-dimethyl-1H-indene (**12**)*

Analogous to the preparation of **9** but using 4-pentenylmagnesium bromide (3.14 g, 18.11 mmol), 2-bromo-4,7-dimethylindene (2.69 g, 12.07 mmol) and NiCl$_2$(DPPE) (0.64 g, 1.21 mmol) in THF (100 ml) gave **12** as a light yellow liquid. Yield 1.54 g (60%). B.p.: 105–110°C/0.2 mbar. ^{1}H-NMR (CDCl$_3$, 400 MHz): 6.97 (d, $J=7.2$ Hz, 1H, CH aromat.), 6.85 (d, $J=7.2$ Hz, 1H, CH aromat.), 6.64 (s, 1H, CH), 5.87 (m, 1H, CC=CH$_2$), 5.06 (m, 1H, =CH$_2$ *trans*), 5.00 (m, 1H, =CH$_2$ *cis*), 3.22 (s, 2H, CH$_2$), 2.54 (t, $J=7.2$ Hz, 2H, CH$_2$CH$_2$), 2.39 (s, 3H, CH$_3$ aromat.), 2.31 (s, 3H, CH$_3$ aromat.), 2.14 (dt, $J=7.6$, 7.2 Hz, 2H, CH$_2$CH$_2$), 1.74 (tt, $J=7.6$, 7.2 Hz, 2H, CH$_2$CH$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 100.64 MHz): 149.57 (C), 143.94 (C), 141.48 (C), 138.61 (CH=CH$_2$), 129.85 (C), 127.62 (=CH), 126.65 (C), 124.93/124.85 (CH aromat.), 114.75 (=CH$_2$), 40.10 (CH$_2$), 33.45 (CH$_2$CH$_2$), 30.76 (CH$_2$CH$_2$), 28.31 (CH$_2$CH$_2$), 18.31/18.20 (CH$_3$ aromat.). LRMS (26°C, 12 eV): m/z 212 (100) [M]$^+$, 197 (12) [$C_{15}H_{17}$]$^+$, 170 (57) [$C_{13}H_{12}$]$^+$, 157 (41) [$C_{12}H_{13}$]$^+$. Anal. Found: C, 90.46; H, 9.47. $C_{16}H_{20}$ (212.33 g mol^{-1}) (**12**). Calc.: C, 90.51; H, 9.49%.

*5.3.9. 2-Allylindenyllithium (**7a**)*

n-BuLi (1.6 M in hexane, 4.8 ml, 7.68 mmol) was added slowly to a solution of **7** (0.8 g, 5.12 mmol) of in hexane (50 ml). A suspension formed during 12 h at 20°C. The mixture was filtered and the solid was washed with hexane (30 ml). The white solid was dried under reduced pressure. Yield 0.80 g (97%). ^{1}H-NMR (C$_5$D$_5$N, 400 MHz): 7.85 (m, 4H, CH aromat.), 6.74 (s, 2H, =CH), 6.35 (m, 1H, CH=CH$_2$), 5.06 (m, 2H, CH=CH$_2$), 3.58 (m, 2H, CH$_2$CH). ^{13}C{^{1}H}-NMR (C$_5$D$_5$N, 100.64 MHz): 147.24 (CH=CH$_2$), 143.24 (C), 142.55 (C), 140.21 (C), 133.61 (CH aromat.), 128.43 (CH=), 128.33 (CH aromat.), 126.58 (CH aromat.), 125.43 (CH aromat.), 113.83 (CH=CH$_2$), 34.65 (CH$_2$CH). LRMS (50°C): m/z 162 (0) [M]$^+$, 156 (56) [$C_{12}H_{12}$]$^+$, 141 (32) [$C_{11}H_9$]$^+$, 128 (44) [$C_{10}H_8$]$^+$, 115 (35) [C_9H_7]$^+$. Anal. Found: C, 88.72; H, 6.82. $C_{12}H_{11}Li$ (162.16 g mol^{-1}) (**7a**). Calc.: C, 88.88; H, 6.84%.

*5.3.10. 2-(3-Buten-1-yl)indenyllithium (**8a**)*

To a solution of 2-(3-buten-1-yl)-1H-indene (**8**) (1.6 g, 9.4 mmol) in hexane (40 ml) was added *n*-BuLi (2.46 M in hexane, 4.2 ml, 10.34 mmol) dropwise at 0°C. The resulting suspension was stirred 12 h at 20°C. The mixture was filtered and the solid was washed with hexane (30 ml). The white solid was dried under reduced pressure. Yield 1.3 g (78%) of **8a**. ^{1}H-NMR (C$_6$D$_6$, 400 MHz): 7.97 (m, 2H, CH aromat.), 7.00 (m, 2H, CH aromat.), 6.72 (s, 2H, CH), 6.30 (m, 1H, CH=CH$_2$), 5.08 (m, 2H, CH=CH$_2$), 3.39 (t, $J=8.0$ Hz, 2H, CH$_2$CH$_2$), 2.91 (dt, $J=7.2$, 8.0 Hz, 2H, CH$_2$CH$_2$). ^{13}C{^{1}H}-NMR (C$_6$D$_6$, 100.64 MHz): 141.70 (CH=CH$_2$), 134.49 (C), 131.85 (C), 121.24 (C), 128.30 (CH aromat.), 113.35 (CH=CH$_2$), 93.95 (CH=), 38.21 (CH$_2$CH$_2$), 32.78 (CH$_2$CH$_2$). LRMS (26°C): m/z 176 (0) [M]$^+$, 170 (20) [$C_{13}H_{14}$]$^+$, 129 (98) [$C_{10}H_9$]$^+$, 128 (29) [$C_{10}H_8$]$^+$, 115 (20) [C_9H_7]$^+$. Anal. Found: C, 88.50; H, 7.41. $C_{13}H_{13}Li$ (176.19 g mol^{-1}) (**8a**). Calc.: C, 88.62; H, 7.44%.

*5.3.11. 2-(4-Penten-1-yl)indenyllithium (**9a**)*

Analogous to the preparation of **8a** but using **9** (1.42 g, 7.71 mmol) and *n*-BuLi (1.6 M in hexane, 5.3 ml, 8.53 mmol) in hexane (100 ml) gave **9a** as a white solid (1.39 g, 95%). ^{1}H-NMR (C$_5$D$_5$N, 400 MHz): 6.92 (m, 4H, CH aromat.), 6.62 (s, 2H, CH), 5.97 (m, 1H, CH=CH$_2$), 5.08 (m, 1H, =CH$_2$ *trans*), 4.98 (m, 1H, =CH$_2$ *cis*), 3.31 (t, $J=7.4$ Hz, 2H, CH$_2$CH$_2$), 2.39 (m, 2H, CH$_2$CH$_2$), 2.25 (m, 2H, CH$_2$CH$_2$). ^{13}C{^{1}H}-NMR (C$_5$D$_5$N, 100.64 MHz): 141.02 (CH=CH$_2$), 131.10 (C), 130.66 (C), 114.41 (=CH_2), 112.30 (CH aromat.), 112.27 (CH aromat.), 92.88 (CH), 34.41 (CH_2CH_2), 32.65 (CH_2CH_2), 32.20 (CH_2CH_2). LRMS (26°C, 12 eV): *m/z* 190 (0) $[M]^+$, 184 (100) $[C_{14}H_{16}]^+$, 169 (19) $[C_{13}H_{12}]^+$, 157 (87) $[C_{12}H_{13}]^+$, 143 (21) $[C_{11}H_{11}]^+$, 128 (15) $[C_{10}H_8]^+$. Anal. Found: C, 88.32; H, 7.93. $C_{14}H_{15}Li$ (190.21 g mol^{-1}) (**9a**). Calc.: C, 88.40; H, 7.95%.

5.3.12. 2-Allyl-4,7-dimethylindenyllithium (*10a*)

Following the representative procedure for the synthesis of **7a** above, using **10** (0.50 g, 2.71 mmol) in hexane (60 ml) and *n*-BuLi (1.6 M in hexane, 2.54 ml, 4.07 mmol) **10a** was isolated as a white solid (0.51 g, 98%). ^{1}H-NMR (C_5D_5N, 400 MHz): 7.59 (s, 2H, CH aromat.), 6.85 (s, 2H, =CH), 6.43 (m, 1H, CH=CH_2), 5.21 (m, 2H, CH=CH_2), 3.57 (m, 2H, CH_2CH), 2.42 (s, 6H, CH_3). $^{13}C\{^1H\}$-NMR (C_5D_5N, 100.64 MHz): 146.12 (CH=CH_2), 141.76 (C), 136.39 (C), 127.25 (CH=), 126.12 (C), 125.63 (CH aromat.), 114.02 (CH=CH_2), 34.76 (CH_2CH), 18.10 (CH_3). LRMS (45°C): *m/z* 190 (0) $[M]^+$, 184 (64) $[C_{14}H_{16}]^+$, 169 (25) $[C_{13}H_{13}]^+$, 144 (28) $[C_{11}H_{12}]^+$, 143 (48) $[C_{11}H_{11}]^+$. Anal. Found: C, 88.25; H, 7.92. $C_{14}H_{15}Li$ (190.21 g mol^{-1}) (**10a**). Calc.: C, 88.40; H, 7.95%.

5.3.13. 2-(3-Buten-1-yl)-4,7-dimethylindenyllithium (*11a*)

Following the procedure for the synthesis of **8a** above but using 2-(3-buten-1-yl)-4,7-dimethylindene (2.31 g, 11.65 mmol) in hexane (80 ml) and *n*-BuLi (1.6 M in hexane, 8.7 ml, 13.98 mmol) gave compound **11a** as a white solid (2.3 g, 97%). M.p.: > 250°C. ^{1}H-NMR (C_5D_5N, 200 MHz): 6.80 (s, 2H, CH aromat.), 6.66 (s, 2H, CH), 6.33 (m, 1H, CH=CH_2), 5.22 (m, 1H, =CH_2 *trans*), 5.03 (m, 1H, =CH_2 *cis*), 3.40 (t, $J = 6.5$ Hz, 2H, CH_2CH_2), 2.93 (dt, $J = 6.5, 6.5$, Hz, 2H, CH_2CH_2), 2.84 (s, 6H, CH_3 aromat.). $^{13}C\{^1H\}$-NMR (C_5D_5N, 100.64 MHz): 141.37 (CH=CH_2), 132.30 (C), 130.68 (C), 113.00 (=CH_2), 112.44 (CH aromat.), 93.05 (CH), 38.08 (CH_2CH_2), 32.65 (CH_2CH_2), 22.48 (CH_3 aromat.), 20.40 (CH_3 aromat.). LRMS (24°C): *m/z* 204 (0) $[M]^+$, 198 (20) $[C_{15}H_{18}]^+$, 157 (53) $[C_{12}H_{13}]^+$, 143 (82) $[C_{11}H_{11}]^+$, 128 (100) $[C_{10}H_8]^+$, 115 (**11**) $[C_9H_7]^+$. Anal. Found: C, 87.98; H, 8.36. $C_{15}H_{17}Li$ (204.24 g mol^{-1}) (**11a**). Calc.: C, 88.21; H, 8.39%.

5.3.14. 2-(4-Penten-1-yl)-4,7-dimethylindenyllithium (*12a*)

Analogous to the preparation of **8a** above but using **12** (1.51 g, 7.11 mmol) in hexane (100 ml) with *n*-BuLi (1.6 M in hexane, 5.3 ml, 8.53 mmol) gave **12a** as a white solid. Yield 1.54 g (99%). M.p.: 185°C. ^{1}H-NMR (C_5D_5N, 400 MHz): 6.79 (s, 2H, CH aromat.), 6.64 (s, 2H, CH), 6.01 (m, 1H, $CHCH_2$), 5.11 (m, 1H, =CH_2 *trans*), 4.95 (m, 1H, =CH_2 *cis*), 3.30 (t, $J = 7.4$ Hz, 2H, CH_2CH_2), 2.83 (s, 6H, CH_3 aromat.), 2.40 (m, 2H, CH_2CH_2), 2.23 (m, 2H, CH_2CH_2). $^{13}C\{^1H\}$-NMR (C_5D_5N, 100.64 MHz): 140.31 (CH=CH_2), 132.70 (C), 130.66 (C), 123.56 (C), 113.61 (=CH_2), 112.30 (CH aromat.), 92.90 (CH), 34.46 (CH_2CH_2), 32.72 (CH_2CH_2), 32.32 (CH_2CH_2), 20.46 (CH_3 aromat.). LRMS (26°C): *m/z* 218 (0) $[M]^+$, 212 (48) $[C_{16}H_{20}]^+$, 197 (13) $[C_{15}H_{17}]^+$, 171 (12) $[C_{13}H_{13}]^+$, 170 (57) $[C_{13}H_{12}]^+$, 157 (100) $[C_{12}H_{13}]^+$, 143 (22) $[C_{11}H_{11}]^+$, 141 (26) $[C_{11}H_9]^+$, 128 (12) $[C_{10}H_8]^+$, 115 (10) $[C_9H_7]^+$. Anal. Found: C, 87.78; H, 8.74. $C_{16}H_{19}Li$ (218.28 g mol^{-1}) (**12a**). Calc.: C, 88.04; H, 8.77%.

5.4. Multiply substituted 1-alkenylindenyl compounds

5.4.1. 3-(3-Buten-1-yl)-1-methyl-1H-indene and 1-(3-buten-1-yl)-3-methyl-1H-indene (*13*)

To 1-methylindenyllithium (6.66 g, 48.9 mmol) [19] in THF (50 ml) at 0°C was added 4-bromo-1-butene (6.60 g, 5.0 ml, 48.9 mmol) under stirring, which was continued for 12 h. The solvent was removed under reduced pressure and the residue was quenched with water (10 ml) and extracted with diethyl ether (50 ml). The combined organic phases were dried over $MgSO_4$, and the solvent was evaporated yielding **13** as a yellow liquid. Yield 8.53 g (95%). B.p.: 67–70°C/0.2 mbar. ^{1}H-NMR ($CDCl_3$, 200 MHz): Isomer 1: 7.44–7.25 (m, 4H, CH aromat.), 6.23 (m, 1H, CH=), 5.95 (m, 1H, CH=CH_2), 5.02 (m, 2H, CH=CH_2), 3.42 (m, 1H, CH), 2.62 (m, 1H, CH_2CH_2), 2.49 (m, 1H, CH_2CH_2), 1.92 (m, 2H, CH_2CH_2), 1.32 (m, 3H, CH_3),. Isomer 2: 7.44–7.25 (m, 4H, CH aromat.), 6.22 (m, 1H, CH=), 5.95 (m, 1H, CH=CH_2), 5.02 (m, 2H, CH=CH_2), 3.42 (m, 1H, CH), 2.62 (m, 1H, CH_2CH_2), 2.49 (m, 1H, CH_2CH_2), 2.16 (m, 3H, CH_3), 1.92 (m, 2H, CH_2CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 50.32 MHz): 148.29 (C), 145.59 (C), 138.91 (C), 138.70 (CH=CH_2), 135.26 (CH), 126.15 (CH aromat.), 124.70 (CH aromat.), 122.60 (CH aromat.), 118.87 (CH aromat.), 114.66 (CH=CH_2), 48.36 ($CHCH_3$), 31.79 (CH_2), 30.99 (CH_2), 12.96 (CH_3). LRMS (24°C): *m/z* 184 (18) $[M]^+$, 169 (6) $[C_{13}H_{13}]^+$, 157 (9) $[C_{12}H_{13}]^+$, 143 (97) $[C_{11}H_{11}]^+$, 129 (55) $[C_{10}H_9]^+$, 128 (100) $[C_{10}H_8]^+$, 115 (52) $[C_9H_7]^+$, 42 (74) $[C_3H_6]^+$, 41 (44) $[C_3H_5]^+$. Anal. Found: C, 91.25; H, 8.60. $C_{14}H_{16}$ (184.28 g mol^{-1}) (**13**). Calc.: C, 90.93; H, 8.51%.

5.4.2. 1-(3-Buten-1-yl)-3-methylindenyllithium (*13a*)

To a solution of **13** (3.0 g, 16.28 mmol) in hexane (40 ml) was added *n*-BuLi (1.6 M in hexane, 10.18 ml, 16.28 mmol) at 0°C. The reaction mixture was stirred 12 h at room temperature. The phases were separated by decanting, the solid was washed with hexane (20 ml) and then dried in vacuo to give **13a** as a white solid. Yield 1.23 g (40%). M.p.: 132°C. ^{1}H-NMR (C_5D_5N, 200 MHz): 7.98–7.90 (m, 2H, CH aromat.), 7.04–7.00 (m, 2H, CH aromat.), 7.13 (s, 1H, CH), 6.32 (m, 1H, CH=), 5.23–4.96 (m, 2H, =CH_2 *cis*, *trans*), 3.53 (t, $J = 6$ Hz, 2H, CH_2CH_2), 3.02 (s, 3H, CH_3), 2.87 (m, 2H, CH_2CH_2). $^{13}C\{^1H\}$-NMR (C_5D_5N, 50.32 MHz): 141.80 (CH=), 128.58 (C), 127.89 (C), 119.17 (CCH_3), 116.66/116.53 (CH aromat.), 112.69 (=CH_2), 110.27/110.19 (CH aromat.), 104.10 (C), 98.24 (CH), 38.56 (CH_2CH_2), 29.58 (CH_2CH_2), 14.24 (CH_3). LRMS (23°C): *m*/*z* 190 (0) $[M]^+$, 184 (25) $[C_{14}H_{16}]^+$, 170 (6) $[C_{13}H_{14}]^+$, 157 (7) $[C_{12}H_{13}]^+$, 143 (100) $[C_{11}H_{11}]^+$, 128 (64) $[C_{10}H_8]^+$, 115 (15) $[C_9H_7]^+$. Anal. Found: C, 88.05; H, 7.91. $C_{14}H_{15}Li$ (190.21 g mol^{-1}) (**13a**). Calc.: C, 88.40; H, 7.95%.

5.4.3. *1-(3-Buten-1-yl)-2,4,7-trimethyl-1H-indene (**14**)*

2,4,7-Trimethylindene (2.86 g, 18.07 mmol) was dissolved in THF (50 ml) and *n*-BuLi (1.6 M in hexane, 11.3 ml, 18.07 mmol) was added dropwise at 0°C. After stirring 12 h at 20°C, the solution was cooled to 0°C and mixed with 4-bromo-1-butene (2.32 g, 17.18 mmol). After 12 h at room temperature, the solvent was removed under vacuo and the residue quenched with water (20 ml) and diethyl ether (20 ml). The product was extracted with ether (80 ml) and dried over $MgSO_4$. **14** was obtained after fractional distillation as a colorless liquid. Yield 3.10 g (85%). B.p.: 98°C/0.1 mbar. ^1H-NMR (C_6D_6, 400 MHz): 6.96 (d, $J = 7.6$ Hz, 1H, CH aromat.), 6.83 (d, $J = 7.7$ Hz, 1H, CH aromat.), 6.46 (m, 1H, CH), 5.8–5.5 (m, 1H, CH=), 4.90–4.80 (m, 2H, =CH_2), 3.14 (t, 1H, CH), 2.26 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.14 (m, 2H, CH_2), 1.83 (s, 3H, CH_3), 1.52 (m, 2H, CH_2). $^{13}C\{^1H\}$-NMR (C_6D_6, 100.64 MHz): 147.25 (C), 144.33/144.19 (C), 139.13 (=CH_2), 128.24 (C), 126.53 (C), 126.32/126.25 (CH aromat.), 114.21 (CH=), 51.81 (CH_2), 27.44 (CH_2CH_2), 26.78 (CH_2CH), 18.72 (CH_3), 18.27 (CH_3 aromat.), 14.98 (CH_3 aromat.). LRMS (24°C): *m*/*z* 212 (31) $[M]^+$, 171 (81) $[C_{13}H_{15}]^+$, 156 (67) $[C_{12}H_{12}]^+$, 141 (48) $[C_{11}H_9]^+$, 128 (28) $[C_{10}H_8]^+$, 115 (32) $[C_9H_7]^+$. Anal. Found: C, 89.90; H, 9.63. $C_{16}H_{20}$ (212.33 g mol^{-1}) (**14**). Calc.: C, 90.51; H, 9.49%.

5.4.4. *1-(3-Buten-1-yl)-2,4,7-trimethylindenyllithium (**14a**)*

To a solution of **14** (3.46 g, 16.30 mmol) in hexane (100 ml) at 0°C was added *n*-BuLi (1.6 M in hexane, 10.2 ml, 16.30 mmol). The reaction mixture was stirred at room temperature for 12 h. The phases were separated by decanting, the solid was washed with hexane (50 ml) and then dried in vacuo yielding **14a** as a white solid (2.93 g, 82%). M.p.: 175–180°C. ^1H-NMR (C_5D_5N, 400 MHz): 6.70 (s, 2H, CH aromat.), 6.53 (s, 1H, CH), 6.27 (m, 1H, CH=), 5.22 (m, 1H, =CH_2 *trans*), 5.03 (m, 1H, =CH_2 *cis*), 3.56 (t, $J = 7.8$ Hz, 2H, CH_2CH_2), 3.06 (s, 3H, CH_3), 2.83 (s, 3H, CH_3 aromat.), 2.79 (s, 3H, CH_3 aromat.), 2.71 (m, 2H, CH_2CH_2). $^{13}C\{^1H\}$-NMR (C_5D_5N, 100.64 MHz): 141.24 (CH=), 129.57 (C), 126.84 (CCH_3), 125.08 (CCH_3), 122.79 (C), 113.86 (CH aromat.), 112.73 (=CH_2), 111.78 (CH aromat.), 106.72 (C), 92.61 (CH), 40.90 (CH_2CH_2), 28.81 (CH_2CH_2), 22.33 (CH_3), 20.25 (CH_3 aromat.), 15.31 (CH_3 aromat.). LRMS (30°C): *m*/*z* 218 (0.11) $[M]^+$, 212 (53) $[C_{16}H_{20}]^+$,171 (100) $[C_{13}H_{15}]^+$, 156 (55) $[C_{12}H_{12}]^+$, 142 (24) $[C_{11}H_{10}]^+$, 128 (15) $[C_{10}H_8]^+$, 115 (13) $[C_9H_7]^+$. Anal. Found: C, 87.17; H, 8.73. $C_{16}H_{19}Li$ (218.27 g mol^{-1}) (**14a**). Calc.: C, 88.05; H, 8.77%.

5.5. *Bis-(1-alkenylindenyl)-zirconium complexes*

5.5.1. *Bis[1-allyl-indenyl]zirconium dichloride (**1b**)*

[(1-Allyl)indenyl]lithium (0.97 g, 6.00 mmol) was dissolved in diethyl ether (60 ml). Zirconium tetrachloride (0.69 g, 3 mmol) was added slowly to the solution and the suspension was stirred 50 h in a darken flask at room temperature. The reaction mixture was filtered and the solvent removed under reduced pressure. The solid residue was washed once with hexane (50 ml) and dried in vacuo to yield **1b** as a yellow solid (0.74 g, 52%). M.p.: 82–85°C. ^1H-NMR ($CDCl_3$, 400 MHz): 7.67 (m, 8H, CH aromat.), 7.35 (m, 8H, CH aromat.), 6.48 (d, $J = 3.2$ Hz, 2H, CH), 6.18 (d, $J = 2.4$ Hz, 2H, CH), 6.02 (d, $J = 2.4$ Hz, 2H, CH), 5.77 (d, $J = 3.2$ Hz, 2H, CH), 6.22 (m, 2H, CH=CH_2), 5.12 (m, 8H, =CH_2), 3.65 (m, 8H, CH_2). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.64 MHz): 135.75/135.52 (CH=), 127.42 (C), 126.34 (CH aromat.), 126.15 (C), 125.55 (CH), 123.70 (CH aromat.), 122.14 (CH aromat.), 120.63 (C), 120.49 (CH aromat.), 116.67/116.26 (=CH_2), 99.00 (CH), 32.40/32.20 (CH_2). LRMS (166°C): *m*/*z* 470 (18) $[M]^+$, 435 (16) $[C_{24}H_{22}ZrCl]^+$, 315 (100) $[C_{12}H_{11}ZrCl_2]^+$, 280 (10) $[C_{12}H_{11}ZrCl]^+$, 253 (20) $[C_{10}H_8ZrCl]^+$, 153 (11) $[C_2H_4ZrCl]^+$, 128 (14) $[C_{10}H_8]^+$, 115 (14) $[C_9H_7]^+$. Anal. Found: C, 60.76; H, 4.67. $C_{24}H_{22}ZrCl_2$ (472.57 g mol^{-1}) (**1b**). Calc.: C, 61.00; H, 4.69%.

5.5.2. *Bis[1-(3-buten-1-yl)indenyl]zirconium dichloride (**2b**)*

To a stirred solution of [1-(3-buten-1-yl)indenyl]-lithium (0.70 g, 4.0 mmol) and Et_2O (50 ml) was added zirconium tetrachloride (0.47 g, 2.0 mmol). The reaction mixture was stirred 30 h at room temperature. The suspension was filtered and the filtrate evaporated to dryness. The yellow solid was washed with pentane (20 ml) and hexane (20 ml) to obtain after drying in vacuo **2b** as a yellow solid. Yield 0.38 g (38%). M.p.: 150°C. ^1H-NMR (C_5D_5N, 200 MHz): 7.30 (m, 16H, CH aromat.), 6.69 (d, $J = 3.2$ Hz, 2H, CH), 6.32 (d, $J = 3.2$ Hz, 2H, CH), 6.27 (d, $J = 3.2$ Hz, 2H, CH), 6.00 (d, $J = 3.2$ Hz, 2H, CH), 5.84 (m, 4H, CH=CH_2), 4.99 (m, 8H, =CH_2), 3.15 (m, 8H, CH_2), 2.43 (m, 8H, CH_2). $^{13}C\{^1H\}$-NMR (C_5D_5N, 50.32 MHz): 137.81/137.75 (CH=), 126.18 (C), 126.00 (CH aromat.), 125.36 (C), 124.64 (CH), 123.70 (CH aromat.), 123.24 (CH aromat.), 122.63 (C), 120.43 (CH aromat.), 115.20/115.13 (=CH_2), 99.26/99.18 (CH), 34.05/33.90 (CH_2), 27.74/27.41 (CH_2). LRMS (25°C): *m*/*z* 498 (3) $[M(^{90}Zr, {}^{35}Cl)]^+$, 335 (31) $[C_{13}H_{13}{}^{94}Zr^{35}Cl_{37}Cl]^+$, 333 (69) $[C_{13}H_{13}{}^{94}Zr^{35}Cl_2]^+$, 331 (99.9) $[C_{13}H_{13}{}^{90}Zr^{35}Cl_{37}Cl]^+$, 329 (100) $[C_{13}H_{13}{}^{90}Zr^{35}Cl_2]^+$, 297 (9) $[C_{13}H_{12}{}^{94}Zr^{35}Cl]^+$, 295 (15) $[C_{13}H_{12}{}^{92}Zr^{35}Cl]^+$, 293 (23) $[C_{13}H_{12}{}^{90}Zr^{35}Cl]^+$, 290 (7) $[C_{10}H_8{}^{90}Zr^{35}Cl_{37}Cl]^+$, 288 (5) $[C_{10}H_8{}^{90}Zr^{35}Cl_2]^+$, 277 (13) $[C_9H_7{}^{90}Zr^{35}Cl^{37}Cl]^+$, 275 (13) $[C_9H_7{}^{90}Zr\,{}^{35}Cl_2]^+$, 205 (12) $[C_3H_5{}^{94}Zr^{35}Cl_2]^+$, 203 (20) $[C_3H_5\,{}^{90}Zr^{35}Cl^{37}Cl]^+$, 201 (22) $[C_3H_5{}^{90}Zr^{35}Cl_2]^+$, 128 (17) $[C_{10}H_8]^+$, 115 (8) $[C_9H_7]^+$. Anal. Found: C, 62.12; H, 5.20. $C_{26}H_{26}ZrCl_2$ (500.62 g mol^{-1}) (**2b**). Calc.: C, 62.38; H, 5.23%.

*5.5.3. Bis[(1-allyl)-4,7-dimethylindenyl]zirconium dichloride (**4b**)*

The procedure described for the preparation of **1b** using [(1-allyl)-4,7-dimethylindenyl]lithium (1.14 g, 6.0 mmol) and zirconium tetrachloride (0.69 g, 3 mmol) in Et_2O (60 ml) gave **4b** as a yellow solid (0.8 g, 50%). M.p.: 115–118°C. ^1H-NMR ($CDCl_3$, 400 MHz): 6.93 (m, 8H, CH aromat.), 6.37 (d, $J = 3.2$ Hz, 2H, CH), 6.14 (d, $J = 2.5$ Hz, 2H, CH), 6.12 (d, $J = 2.5$ Hz, 2H, CH), 5.62 (d, $J = 3.2$ Hz, 2H, CH), 6.02 (m, 4H, CH=CH_2), 5.10 (m, 8H, =CH_2), 3.81 (m, 8H, CH_2), 2.66 (s, 24H, CH_3), 2.40 (s, 12H, CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.64 MHz): 136.94/136.84 (CH=), 129.00 (C), 128.19 (C), 126.86 (CH aromat.), 126.14 (CH aromat.), 122.43 (C), 120.13/119.55 (CH), 116.44/116.29 (=CH_2), 97.33/96.94 (CH), 20.56 (CH_2), 18.88/18.78 (CH_3). LRMS (80°C): *m*/*z* 526 (18) $[M]^+$, 490 (9) $[C_{28}H_{30}ZrCl]^+$, 455 (11) $[C_{28}H_{29}Zr]^+$, 343 (97) $[C_{14}H_{15}ZrCl_2]^+$, 307 (28) $[C_{14}H_{14}ZrCl]^+$, 281 (20) $[C_{12}H_{12}ZrCl]^+$, 184 (21) $[C_{14}H_{16}]^+$, 153 (14) $[C_2H_4ZrCl]^+$, 128 (16) $[C_{10}H_8]^+$, 115 (9) $[C_9H_7]^+$. Anal. Found: C, 63.10; H, 5.68. $C_{28}H_{30}ZrCl_2$ (528.68 g mol^{-1}) (**4b**). Calc.: C, 63.61; H, 5.72%.

*5.5.4. Bis[1-(3-buten-1-yl)-4,7-dimethylindenyl]-zirconium dichloride (**5b**)*

[1-(3-buten-1-yl)-4,7-dimethylindenyl)lithium (0.82 g, 4.0 mmol) was dissolved in Et_2O (60 ml) and zirconium tetrachloride (0.47 g, 2.0 mmol) was added slowly. The suspension was stirred 72 h in a dark flask at room temperature. The mixture was filtered and the solvent removed under reduced pressure. The yellow–brown residue was washed with hexane (20 ml). By decantation and subsequent vacuum drying **5b** was isolated as a yellow solid (0.54 g, 49%). M.p.: 200–205°C. ^1H-NMR ($CDCl_3$, 400 MHz): 6.89 (m, 8H, CH aromat.), 6.25 (d, $J = 3.2$ Hz, 2H, =CH), 6.04 (d, $J = 3.2$ Hz, 2H, =CH), 5.98 (d, $J = 3.2$ Hz, 2H, =CH), 5.85 (m, 4H, CH=CH_2), 5.56 (d, $J = 3.2$ Hz, 2H, =CH), 5.05 (m, 8H, =CH_2), 3.3–2.9 (m, 8H, CH_2CH_2), 2.65 (s, 24H, CH_3 aromat.), 2.40–2.27 (m, 8H, CH_2CH_2). $^{13}C\{^1H\}$-NMR (C_5D_5N, 50.32 MHz): 137.82/137.74 (CH=CH_2), 133.34 (C), 133.12 (C), 132.65 (CCH_3), 132.46 (CCH_3), 126.99/126.86 (CH aromat.), 126.15/126.11 (CH aromat.), 126.04 (C), 118.83/118.36 (CH), 115.24/115.18 (=CH_2), 97.48/96.37 (CH), 35.21/35.00 (CH_2CH_2), 30.28/30.22 (CH_2CH_2), 20.52/18.55 (CH_3 aromat.). LRMS (161°C): *m*/*z* 556 (8) $[M(^{90}Zr,{}^{35}Cl,{}^{37}Cl)]^+$, 554 (8) $[M(^{90}Zr,{}^{35}Cl,{}^{35}Cl)]^+$, 359 (99) $[C_{15}H_{17}{}^{90}Zr^{35}Cl^{37}Cl]^+$, 357 (100) $[C_{15}H_{17}{}^{90}Zr^{35}Cl_2]^+$, 323 (10) $[C_{15}H_{16}\text{-}{}^{90}Zr^{37}Cl]^+$, 321 (15) $[C_{15}H_{16}{}^{90}Zr^{35}Cl]^+$, 318 (10) $[C_{12}H_{12}{}^{90}Zr^{35}Cl_3{}^{37}Cl]^+$, 316 (9) $[C_{12}H_{12}{}^{90}Zr^{35}Cl_2]^+$, 203 (7) $[C_3H_5{}^{90}Zr^{35}Cl^{37}Cl]^+$, 201 (8) $[C_3H_5{}^{90}Zr^{35}Cl_2]^+$, 128 (14) $[C_{10}H_8]^+$, 115 (9) $[C_9H_7]^+$. Anal. Found: C, 64.58; H, 6.12. $C_{30}H_{34}ZrCl_2$ (556.75 g mol^{-1}) (**5b**). Calc.: C, 64.72; H, 6.16%.

*5.5.5. Bis[1-(4-penten-1-yl)-4,7-dimethylindenyl]zirconium dichloride (**6b**)*

To a mixture of [1-(4-penten-1-yl)-4,7-dimethylindenyl]lithium (0.96 g, 4.4 mmol) and zirconium tetrachloride (0.47 g, 2.0 mmol) was added slowly Et_2O (60 ml). The suspension was stirred for 48 h. After filtration and evaporation of the solvent, the yellow solid was purified by washing with hexane (20 ml) to yield **6b** (0.70 g, 60%). M.p.: 148–151°C. ^1H-NMR (C_5D_5N, 400 MHz): 6.71 (m, 8H, CH aromat.), 6.60 (d, $J = 3.2$ Hz, 2H, =CH), 6.50 (d, $J = 3.2$ Hz, 2H, =CH), 6.40 (d, $J = 3.2$ Hz, 2H, =CH), 6.04 (d, $J = 3.2$ Hz, 2H, =CH), 5.90 (m, 4H, CH=CH_2), 5.05 (m, 8H, =CH_2), 3.32 (m, 8H, CH_2CH_2), 3.04 (s, 12H, CH_3 aromat.), 2.70 (s, 12H, CH_3 aromat.), 2.13 (m, 8H, CH_2CH_2), 1.74 (m, 8H, CH_2CH_2). $^{13}C\{^1H\}$-NMR (C_5D_5N, 100.64 MHz): 138.65/138.33 (CH=CH_2), 133.35 (C), 133.16 (C), 132.60 (CCH_3), 132.49 (CCH_3), 126.89/126.78 (CH aromat.), 125.93/125.74 (CH aromat.), 119.01 (C), 118.40/118.07 (CH), 113.80/112.22 (=CH_2), 97.62/96.56 (CH), 35.32/35.16 (CH_2CH_2), 33.56/33.24 (CH_2CH_2), 30.49/30.30 (CH_2CH_2), 20.43/19.12 (CH_3 aromat.). LRMS (183°C): *m*/*z* 584 (10) $[M(^{90}Zr,{}^{35}Cl,{}^{37}Cl)]^+$, 582 (10) $[M(^{90}Zr,{}^{35}Cl,{}^{35}Cl]^+$, 373 (80) $[C_{16}H_{19}{}^{90}Zr^{35}Cl^{37}Cl]^+$, 371 (75) $[C_{16}H_{19}{}^{90}Zr^{35}Cl_2]^+$, 337 (6) $[C_{16}H_{18}{}^{90}Zr^{37}Cl]^+$, 335 (9) $[C_{16}H_{18}{}^{90}Zr^{35}Cl]^+$, 319 (11) $[C_{12}H_{13}{}^{90}Zr^{35}Cl^{37}Cl]^+$, 317 (9) $[C_{12}H_{13}{}^{90}Zr^{35}Cl_2]^+$, 283 (9) $[C_{12}H_{12}{}^{90}Zr^{37}Cl]^+$, 281 (14) $[C_{12}H_{12}{}^{90}Zr^{35}Cl]^+$, 128 (19) $[C_{10}H_8]^+$, 115 (11) $[C_9H_7]^+$. Anal. Found: C, 65.62; H, 6.42. $C_{32}H_{38}ZrCl_2$ (584.79 g mol^{-1}) (**6b**). Calc.: C, 65.73; H, 6.55%.

*5.5.6. Bis[2-(3-buten-1-yl)-4,7-dimethylindenyl]-zirconium dichloride (**11b**)*

[2-(3-Buten-1-yl)-4,7-dimethylindenyl]lithium (0.50 g, 2.45 mmol) was dissolved in Et_2O (60 ml). Zirconium tetrachloride (0.28 g, 1.22 mmol) was added slowly to the stirring solution. The reaction mixture was stirred for 48 h at 25°C in a darkened flask. The suspension was filtered and the yellow solid washed with hexane (20 ml). Yellow crystals of **11b** were obtained from hexane (20 ml) at

-28°C. Yield 0.37 g (54%). M.p.: 58–61°C. ^{1}H-NMR (C_5D_5N, 400 MHz): 6.97 (s, 4H, CH aromat.), 6.67 (s, 4H, =CH), 5.83 (m, 2H, CH=CH$_2$), 5.03 (m, 4H, =CH$_2$), 2.70 (m, 4H, CH$_2$CH$_2$), 2.50 (s, 12H, CH$_3$ aromat.), 2.31 (m, 4H, CH$_2$CH$_2$). ^{13}C{^{1}H}-NMR (C_5D_5N, 100.64 MHz): 139.24 (CH=CH$_2$), 138.54 (C), 131.17 (C), 128.68 (C), 125.79 (CH aromat.), 115.00 (=CH$_2$), 104.12 (CH), 33.08 (CH$_2$CH$_2$), 30.85 (CH$_2$CH$_2$), 18.78 (CH$_3$ aromat.). LRMS (58°C): *m/z* 556 (100) $[M(^{90}Zr,^{35}Cl,^{37}Cl)]^+$, 554 (91) $[M(^{90}Zr,^{35}Cl,^{35}Cl)]^+$, 521 (16) $[C_{30}H_{34}{}^{90}Zr^{37}Cl]^+$, 519 (16) $[C_{30}H_{34}{}^{90}Zr^{35}Cl]^+$, 359 (45) $[C_{15}H_{17}{}^{90}Zr^{35}Cl^{37}Cl]^+$, 357 (43) $[C_{15}H_{17}{}^{90}Zr^{35}Cl_2]^+$, 323 (10) $[C_{15}H_{16}{}^{90}Zr^{37}Cl]^+$, 321 (16) $[C_{15}H_{16}{}^{90}Zr^{35}Cl]^+$, 319 (14) $[C_{12}H_{13}{}^{90}Zr^{35}Cl^{37}Cl]^+$, 317 (9) $[C_{12}H_{13}{}^{90}Zr^{35}Cl_2]^+$. Anal. Found: C, 64.60; H, 6.13. $C_{30}H_{34}ZrCl_2$ (556.75 g mol^{-1}) (**11b**). Calc.: C, 64.72; H, 6.16%.

*5.5.7. Bis[2-(4-penten-1-yl)-4,7-dimethylindenyl]-zirconium dichloride (**12b**)*

Analogously to the preparation of **11b**, [2-(4-penten-1-yl)-4,7-dimethylindenyl]lithium (0.50 g, 2.29 mmol) in Et_2O (60 ml) was treated with $ZrCl_4$ (0.27 g, 1.15 mmol). **12b** was obtained from hexane (30 ml) at -28°C as yellow crystals (0.42 g, 62%). M.p.: 88–90°C. ^{1}H-NMR (C_5D_5N, 400 MHz): 6.90 (m, 4H, CH aromat.), 6.68 (s, 4H, =CH), 5.84 (m, 2H, CH=CH$_2$), 5.04 (m, 4H, =CH$_2$), 2.63 (t, $J = 7.7$ Hz, 4H, CH$_2$CH$_2$), 2.52 (s, 12H, CH$_3$ aromat.), 2.03 (q, $J = 7.0$ Hz, 4H, CH$_2$CH$_2$), 1.65 (q, $J = 7.5$ Hz, 4H, CH$_2$CH$_2$). ^{13}C{^{1}H}-NMR (C_5D_5N, 100.64 MHz): 138.14 (CH=CH$_2$), 136.99 (C), 131.27 (C), 128.41 (C), 125.63 (CH aromat.), 114.95 (=CH$_2$), 104.09 (CH), 33.12 (CH$_2$CH$_2$), 30.75 (CH$_2$CH$_2$), 30.54 (CH$_2$CH$_2$), 19.08 (CH3 aromat.). LRMS (73°C): *m/z* 584 (3) $[M(^{90}Zr,^{35}Cl,^{37}Cl)]^+$, 582 (2) $[M(^{90}Zr,^{35}Cl,^{35}Cl)]^+$, 373 (53) $[C_{16}H_{19}{}^{90}Zr^{35}Cl^{37}Cl]^+$, 371 (53) $[C_{16}H_{19}{}^{90}Zr^{35}Cl_2]$, 337 (7) $[C_{16}H_{18}{}^{90}Zr^{37}Cl]^+$, 335 (10) $[C_{16}H_{18}{}^{90}Zr^{35}Cl]^+$, 319 (6) $[C_{12}H_{13}{}^{90}Zr^{35}Cl^{37}Cl]^+$, 317 (6) $[C_{12}H_{13}{}^{90}Zr^{35}Cl_2]^+$, 283 (4) $[C_{12}H_{12}{}^{90}Zr^{37}Cl]^+$, 281 (6) $[C_{12}H_{12}{}^{90}Zr^{35}Cl]^+$, 128 (9) $[C_{10}H_8]^+$, 115 (8) $[C_9H_7]^+$. Anal. Found: C, 65.72; H, 6.53. $C_{32}H_{38}ZrCl_2$ (584.79 g mol^{-1}) (**12b**). Calc.: C, 65.73; H, 6.55%.

*5.5.8. Bis[1-(3-buten-1-yl)-3-methylindenyl]zirconium dichloride (**13b**)*

13b was prepared from $ZrCl_4$ (0.44 g, 2.0 mmol) and [1-(3-buten-1-yl)-3-methylindenyl]lithium (0.76 g, 4.0 mmol) in THF (50 ml) by the method described for **11b**. The solution was stirred 60 h at 25°C. The solvent were removed under reduced pressure and the residue was dissolved in Et_2O (50 ml). The yellow solution was isolated by filtration and the solvent removed in vacuo. The solid was washed with hexane (15 ml) to yield **13b** as a yellow solid (0.39 g, 37%). M.p.: 142–145°C. ^{1}H-NMR ($CDCl_3$, 200 MHz): 7.34 (m, 16H, CH aromat.), 6.73 (d, $J = 3.2$ Hz, 2H, CH), 6.43 (d, $J = 3.2$ Hz, 2H, CH), 5.91 (m, 4H, CH=CH$_2$), 5.05 (m, 8H, =CH$_2$), 2.54 (m, 8H, CH$_2$), 2.23 (m, 8H, CH$_2$), 1.42 (s, 12H, CH$_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 50.32 MHz): 145.12 (CH=), 138.83 (C), 128.90 (C), 126.25 (CH aromat.), 124.85 (CH aromat.), 123.85 (CH), 121.15/120.94 (CH aromat.), 118.90 (CCH$_3$), 113.80 (=CH$_2$), 109.10 (C), 37.50 (CH$_2$CH$_2$), 29.13 (CH$_2$CH$_2$), 12.75 (CH$_3$). LRMS (190°C): *m/z* 528 (3) $[M(^{90}Zr,^{35}Cl,^{37}Cl)]^+$, 526 (3) $[M(^{90}Zr,^{35}Cl,^{35}Cl)]^+$, 345 (97) $[C_{14}H_{15}{}^{94}Zr^{35}Cl^{37}Cl]^+$, 343 (100) $[C_{14}H_{15}{}^{94}Zr^{35}Cl_2]^+$, 331 (10) $[C_{13}H_{13}{}^{90}Zr^{35}Cl^{37}Cl]^+$, 329 (11) $[C_{13}H_{13}{}^{90}Zr^{35}Cl_2]^+$, 305 (12) $[C_{11}H_{11}{}^{94}Zr^{35}Cl]^+$, 303 (12) $[C_{11}H_{11}{}^{92}Zr^{35}Cl]^+$, 203 (14) $[C_3H_5{}^{90}Zr^{35}Cl^{37}Cl]^+$, 201 (16) $[C_3H_5{}^{90}Zr^{35}Cl_2]^+$, 128 (30) $[C_{10}H_8]^+$, 115 (17) $[C_9H_7]^+$. Anal. Found: C, 60.32; H, 5.81. $C_{28}H_{30}ZrCl_2$ (528.68 g mol^{-1}) (**13b**). Calc.: C, 63.61; H, 5.72%.

*5.5.9. Bis[1-(3-buten-1-yl)-2,4,7-trimethylindenyl]-zirconium dichloride (**14b**)*

Analogous to the preparation of **11b**, $ZrCl_4$ (0.47 g, 2.0 mmol) was added slowly to a solution of [1-(3-buten-1-yl)-2,4,7-trimethylindenyl]lithium (0.87 g, 4.0 mmol) in Et_2O (50 ml). **14b** was isolated from hexane (30 ml) at -28°C as a yellow solid (0.34 g, 29%). M.p.: 128–132°C. ^{1}H-NMR (C_5D_5N, 400 MHz): 7.02 (d, $J = 7.6$ Hz, 4H, CH aromat.), 6.90 (d, $J = 7.6$ Hz, 4H, =CH aromat.), 6.34 (s, 4H, CH), 5.94 (m, 4H, CH=CH$_2$), 5.06 (m, 8H, =CH$_2$), 2.73 (m, 8H, CH$_2$CH$_2$), 2.52 (s, 12H, CH$_3$), 2.30 (m, 8H, CH$_2$CH$_2$) 2.21 (s, 12H, CH$_3$ aromat.), 1.96 (s, 12H, CH$_3$ aromat.). ^{13}C{^{1}H}-NMR (C_5D_5N, 100.64 MHz): 213.31 (CH=CH$_2$), 143.37 (C), 141.78 (C), 138.46 (CCH3), 138.21 (CCH$_3$), 129.68 (CH aromat.), 128.88 (C), 124.81 (CH aromat.), 114.57 (=CH$_2$), 110.03 (C), 97.77 (CH), 34.24 (CH$_2$CH$_2$), 26.27 (CH$_2$CH$_2$), 19.13/17.79 (CH$_3$ aromat.), 13.46 (CH$_3$). LRMS (151°C): *m/z* 584 (7) $[M(^{90}Zr,^{35}Cl,^{37}Cl)]^+$, 582 (7) $[M(^{90}Zr,^{35}Cl,^{35}Cl)]^+$, 373 (98) $[C_{16}H_{19}{}^{90}Zr^{35}Cl^{37}Cl]^+$, 371 (100) $[C_{16}H_{19}{}^{90}Zr^{35}Cl_2]^+$, 335 (15) $[C_{16}H_{18}{}^{90}Zr^{37}Cl]^+$, 333 (14) $[C_{16}H_{18}{}^{90}Zr^{35}Cl]^+$, 295 (9) $[C_{13}H_{14}{}^{90}Zr^{37}Cl]^+$, 293 (7) $[C_{13}H_{14}{}^{90}Zr^{35}Cl]^+$, 128 (6) $[C_{10}H_8]^+$, 115 (7) $[C_9H_7]^+$. Anal. Found: C, 65.58; H, 6.49. $C_{32}H_{38}ZrCl_2$ (584.79 g mol^{-1}) (**14b**). Calc.: C, 65.73; H, 6.55%.

5.6. X-ray crystallographic analyses

Suitable crystals of **5b** and **12b** were obtained from hexane. An Enraf–Nonius CAD-4 automatic diffractometer (ω-2θ scan, $\lambda = 0.71096$ Å, variable scan time 45 s) controlled by a Compaq Deskpro 386s and fitted with a liquid nitrogen low-temperature device was used for the intensity measurements. The unit cell parameters were obtained from the angles of 25 reflections in the range of $3° < 2\theta < 21°$ for **5b** and $13° < 2\theta < 34°$ for **12b**. Reflections were scanned with variable scan time, depending on intensities, with 2/3 of the time used for scanning the peak and 1/6 measuring each the left and the right background. The intensities of three check reflections monitored every 2 h showed only statistical fluctuations during the data collection. The crystal orientation was checked every 200 intensity measurements by scanning 3 reflections. A new orientation matrix was automatically calculated from a list of 25 recentered reflections in case the angular change was greater than 0.1%. The raw data were corrected for Lorentz, polarization and adsorption effects [25]. Refinements in space group $P2_1/c$ (**5b**) and *Pcan* (**12b**) were successful. The positions of the Zr atoms were determined from three-dimensional Patterson syntheses (SHELXS86) [26]. The calculated difference Fourier map (SHELXL93) [27] revealed all other missing non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The C–H hydrogen atoms were calculated in idealized positions ($\text{C–H} = 0.96$ Å, $U_{\text{iso}} = 0.08$ Å^2). Scattering factors were taken from references [28–30]. The final residual of least squares is $R = 8.13\%$ for **5b** and $R = 5.08\%$ for **12b**. Data reduction was performed using a IBM RISC System/6000, 340 [25]. All other calculations were undertaken with (SHELXL93) [27]. The geometrical aspects of the structure were analyzed by using the PLUTON program [31]. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-410454 for **5b** and CSD-410455 for **12b**.

5.7. Catalysis test

All procedures were carried out under argon using Schlenk techniques. MAO was purchased from Witco, propene from Gerling, Holz and ethene from Linde. The gases were purified by passage through columns with Cu catalyst (BASF R3-11) and molecular sieves of 10 Å. Toluene was refluxed over Na/K for several days prior to use. Polymerizations were carried out in a 1 l Büchi AG type I autoclave equipped with an additional internal cooling system. Monomer feed was maintained with a peteric 3002 pressflow controller. The reaction was monitored by a Büchi data system bds 488. For the standard experiment, the reactor was evacuated at 95°C for 1 h and charged subsequently with 200 ml toluene, 400 mg MAO and ethylene or propylene at 2 bar. Polymerization was started by addition of toluenic metallocene solution. During the reaction the total pressure was kept constant by supplying the monomer. Polymerization was quenched by injection of ethanol (5 ml) and the polymer solution stirred overnight with dilute hydrochloric acid followed by neutralization with $NaHCO_3$, washing with water, evaporation of toluene and drying. The polymer yields were determined after drying for 48 h at 60°C in vacuo.

5.8. Polymer analyses

$^{13}C\{^1H\}$-NMR spectra were recorded at 75°C on a Bruker MSL 300 spectrometer at 75 MHz. Samples were prepared in 10 mm tubes as 10 wt% solutions of the polymer in perchlorobutadiene/tetrachloroethane-d_2. Molecular weights and molecular weight distributions were determined by gel permeation chromatography on a Waters 150-C instrument (trichlorobenzene, 135°C) using a PL-EMD-960 evaporation light scattering detector. Differential scanning calorimetry was performed on a Mettler–Toledo DSC 821e instrument at a heating rate of 20°C min^{-1}. The values obtained in the second run are reported.

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