

The combination of mononuclear metallocene and phenoxyimine complexes to give trinuclear catalysts for the polymerization of ethylene

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Abstract

Trinuclear complexes were synthesized by combination of metallocene and phenoxyimine zirconium complexes. After activation with methylalumoxane (MAO), these catalysts polymerize ethylene with moderate and good activities. Due to the presence of different catalytic centers, polyethylenes with broad or bimodal molecular weight distributions were obtained.
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1. Introduction

In the past 20 years, a huge number of transition metal complexes useful for the polymerization of ethylene and other α -olefins was developed. Especially metallocene complexes proved to be very active candidates [1–7]. New generations of catalyst precursors were presented by Brookhart et al. [8–12] and Gibson et al. [13–15] employing catalysts with late transition metals. In 1998, the group of Fujita presented bis(phenoxyimine)zirconium and titanium complexes [16–29] as “single site” catalysts for monomodal polyethylenes. In contrast to numerous mononuclear complexes, only a few papers dealing with multinuclear complexes containing different active sites were published up to now [30–38]. Multinuclear complexes should be able to produce polyethylenes with bimodal or broad molecular weight distributions. Since mixtures of different mononuclear catalyst precursors often lead to polyethylenes with averaged molecular weights, the synthesis of multinuclear complexes containing combined ligand frameworks seemed

to be attractive to produce polyethylenes with bimodal or broad molecular weight distributions. In these complexes the differently surrounded metal centers should be kept separated from each other by the ligand frameworks. In contrast to the results of Pronko [37], the combination of bis(arylimino)pyridine iron complexes and metallocene complexes failed [39]. Therefore, it was decided to combine metallocene complex fragments and phenoxyimine moieties applying only zirconium as metal center which is then coordinated in different ligand spheres. Combinations of different ligand precursors were performed employing palladium catalyzed Sonogashira coupling reactions.

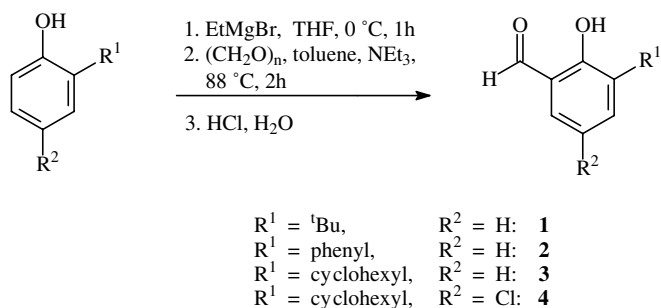
2. Results and discussion

2.1. Synthesis of 3-substituted salicylaldehydes

Deprotonation of *ortho* substituted phenol derivatives with Grignard reagents and subsequent reaction with para-formaldehyde furnished 3-substituted salicylaldehydes [19] (see Scheme 1).

The introduction of iodo substituents into aniline [42] or phenol [43] derivatives can be easily accomplished at room

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Scheme 1. Synthesis of 3-substituted salicylaldehydes (see [40,41]).

temperature using benzyltrimethylammonium dichloroiodate. Therefore, 3-*tert*-butyl salicylaldehyde (**1**) was reacted with benzyltrimethylammonium dichloroiodate to give 3-*tert*-butyl-5-iodosalicylaldehyde (**5**) (Scheme 2).

2.2. Preparation of phenoxyimine compounds

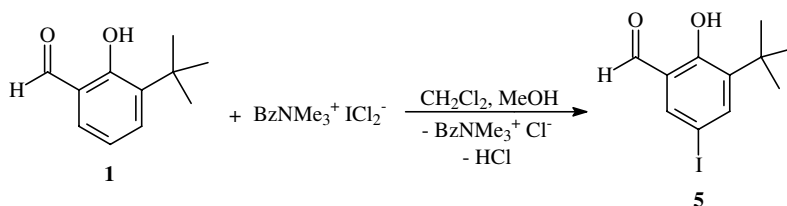
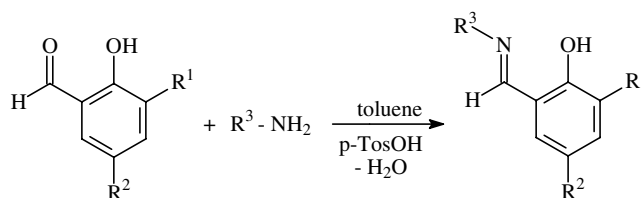
Condensation reactions of substituted salicylaldehydes with aniline derivatives yielded the phenoxyimine compounds **6–15** (see Scheme 3 and Table 1).

Due to its lower boiling point, condensation reactions using propargylamine as amine component were performed at room temperature using molecular sieves (3 Å) as water absorbing agent [45]. While toluene was applied as a solvent for reactions with propargylamine, ethanol had to be used for the reaction of 4-ethynylaniline with 3-*tert*-butyl salicylaldehyde due to the insolubility of the aniline in toluene. Due to steric reasons, phenoxyimine compounds containing halogen substituents at the *para* positions of the iminophenyl rings seemed to be most suitable for further Sonogashira coupling reactions.

2.3. Synthesis of unbridged indenyl and fluorenyl derivatives

Deprotonation of indene with *n*-butyllithium and subsequent alkylation furnished the substituted indene compounds **16–18** (see Scheme 4).

While the bromo compound **17** did not undergo the palladium catalyzed coupling reaction with trimethylsilylacetylene, the reaction of **18** proceeded smoothly at room temperature. Removal of the trimethylsilyl group yielded 1-(4-ethynylbenzyl)indene (**20**) (see Scheme 5).

Scheme 2. Synthesis of 3-*tert*-butyl-5-iodosalicylaldehyde (**5**) (see [44]).

Scheme 3. Synthesis of phenoxyimine compounds.

2-Iodofluorene was reacted with 2-methylbut-3-yn-2-ol under Sonogashira conditions. Deprotection using potassium hydroxide furnished 2-ethynylfluorene (Scheme 6).

2.4. Synthesis of bridged indenyl and fluorenyl derivatives

For the synthesis of alkynyl substituted bridged metallocene type ligand precursors 5-hexyn-2-one (**23**) was prepared. Reaction with freshly distilled cyclopentadiene or indene in a mixture of pyrrolidine and methanol yielded the alkynyl fulvenes **24** and **25** (see Scheme 7).

The reaction of indenyllithium or fluorenyllithium with the fulvenes **24** or **25** and the subsequent hydrolysis gave three C₁ bridged ligand precursors (Schemes 8 and 9).

2.5. Sonogashira coupling reactions of phenoxyimine compounds with indene or fluorene derivatives

A Sonogashira coupling reaction of 2-ethynylfluorene (**22**) and the phenoxyimine derivative **6** furnished compound **29** (see Scheme 10).

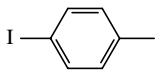
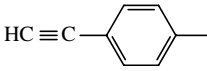
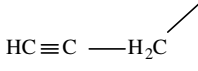
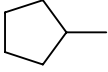
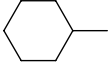
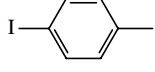
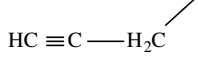
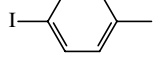
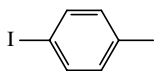
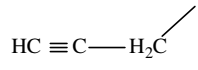
According to Scheme 10, Sonogashira reactions of phenoxyimine compounds with unbridged indene derivatives were performed leading to the coupling products **30–33** (see Table 2). Partial isomerization at the indenyl rings occurred during the Sonogashira reactions caused by the triphenylphosphine ligands of the palladium complex [50]. The coupling products mostly exhibited 3-substitution at the five-membered ring.

In the same manner, bridged metallocene type ligand precursors were reacted with iodo substituted phenoxyimine compounds applying Sonogashira conditions.

A total of eight combined phenoxyimine/metallocene type ligand precursors were prepared according to Scheme 11 (see also Table 3).

The ¹³C NMR spectra of compounds **29** and **36** are shown in Schemes 12 and 13. In the ¹³C NMR spectrum of **29**, the imino carbon atom appears at $\delta = 163.4$ ppm.

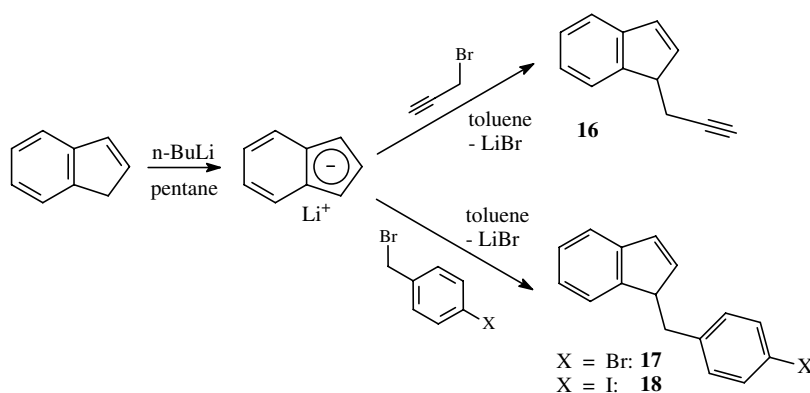
Table 1
Synthesized phenoxyimine compounds

Compound	R ¹	R ²	R ³
6	^t Bu	H	
7 [45]	^t Bu	H	
8 [45]	^t Bu	H	
9	^t Bu	I	
10	^t Bu	I	
11	Phenyl	H	
12	Phenyl	H	
13	Cyclohexyl	H	
14	Cyclohexyl	Cl	
15	Cyclohexyl	Cl	

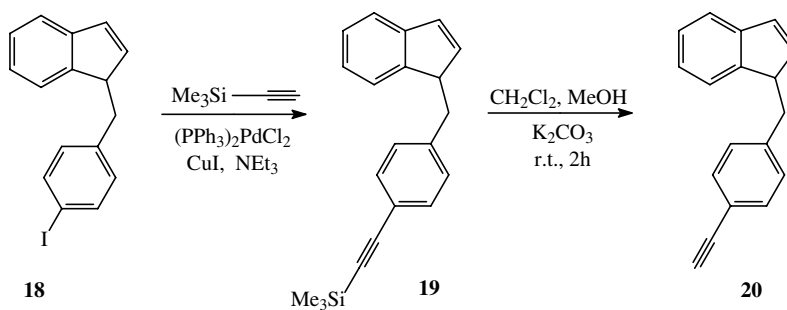
The quaternary carbon atoms of the aromatic ring systems give ten signals at $\delta = 160.6, 147.8, 143.5, 143.2, 141.9, 141.0, 137.7, 121.9, 121.2$ and 119.0 ppm, while the aromatic CH groups yield twelve resonance signals at $\delta = 132.7, 130.8$ (2 signals), $130.5, 128.1, 127.2, 126.9, 125.1, 121.3, 120.2, 119.8$ and 118.5 ppm. The signals at $\delta = 132.7$ and $\delta = 121.3$ ppm with doubled intensity can be assigned to the equivalent carbon atoms of the iminophenyl ring (11/12). The quaternary alkynyl carbon atoms (14/15) appear at $\delta = 91.2$ and $\delta = 89.2$ ppm. The methylene group of the fluorenyl moiety produces the signal at $\delta = 36.2$ ppm, while the residual signals at $\delta = 34.9$ ppm (C_q) and $\delta = 29.4$ ppm (CH₃) can be assigned to the *tert*-butyl substituent.

The chiral compounds **34–41** were obtained as racemic mixtures. Due to this fact, the assignment of the NMR signals is more complicated.

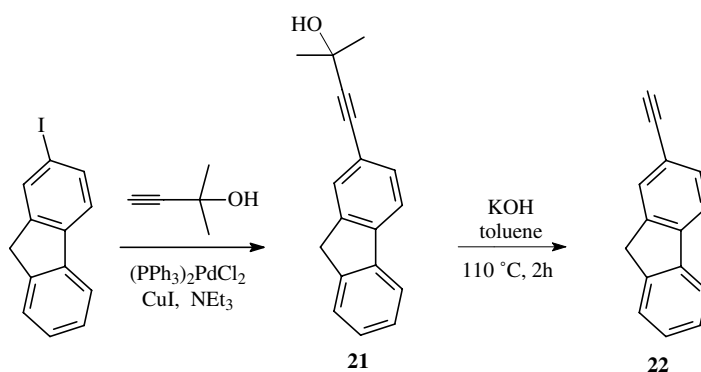
The ¹³C NMR spectrum of **36** (see Scheme 13) shows the imine carbon atom at $\delta = 162.6$ ppm. The quaternary carbon atoms of the aromatic ring systems appear at $\delta = 160.6, 151.7, 144.9, 144.7, 142.5, 141.9, 137.7, 118.3$ and 113.0 ppm, while the signals at $\delta = 134.9, 132.9, 132.7, 132.5, 128.0, 127.3, 127.1, 126.9, 126.2, 126.1, 126.0, 119.7$ and 119.2 ppm can be assigned to the aromatic CH groups. The quaternary alkynyl carbon atoms produce the signals at $\delta = 88.3$ and $\delta = 80.6$ ppm. The carbon atom C¹ of the cyclopentyl ring (10) yields the resonance signal at $\delta = 69.9$ ppm, the carbon atom C⁹ of the fluorenyl moiety (32) appears at $\delta = 56.1$ ppm. The less intensive signal at $\delta = 58.3$ ppm can be assigned to C¹ of the allylic substituted cyclopentadienyl ring (19), while the methylene group of the vinylic isomer produces the signal at $\delta = 46.3$ ppm. The quaternary carbon atom of the *tert*-butyl substituent appears at $\delta = 35.0$ ppm, the methylene groups of the hexynyl moiety give the signals at $\delta = 41.1$ and $\delta = 15.4$ ppm. The quaternary bridging atom (17) furnishes the signal at $\delta = 43.1$ ppm. The CH₂ groups of the cyclopentyl ring appear as two signals with doubled intensity at $\delta = 34.8$ and $\delta = 24.5$ ppm. The methyl groups of the *tert*-butyl function generate the intensive signal at $\delta = 29.4$ ppm,



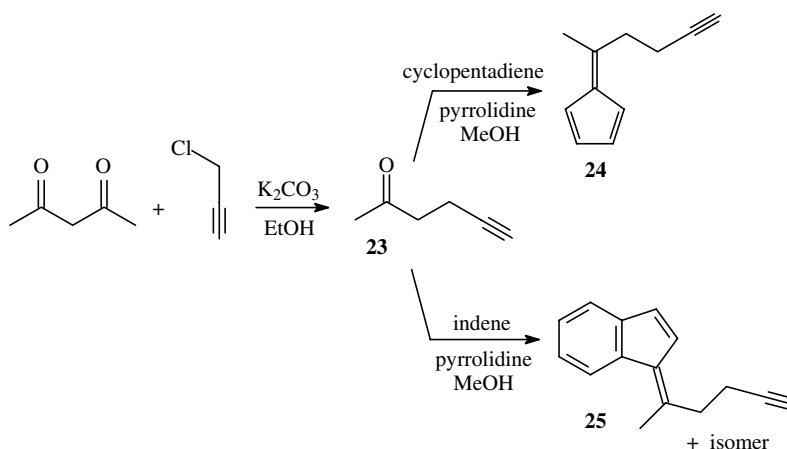
Scheme 4. Synthesis of 1-substituted indenenes (see [46]).



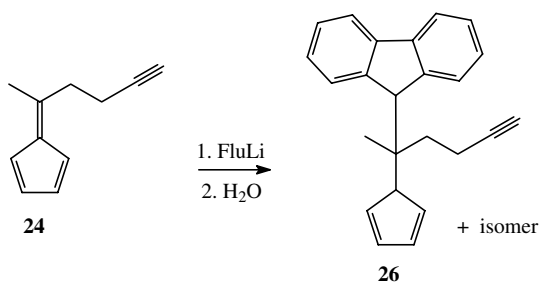
Scheme 5. Synthesis of 1-(4-ethynylbenzyl)indene (20).



Scheme 6. Synthesis of 2-ethynylfluorene (22) (see [47]).



Scheme 7. See [48,49].



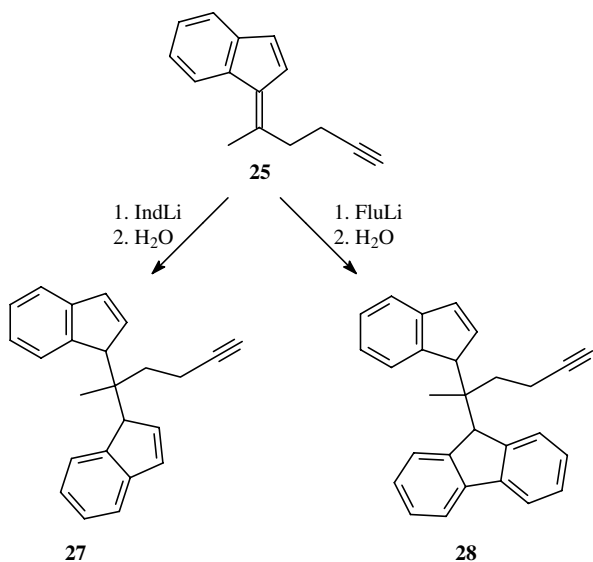
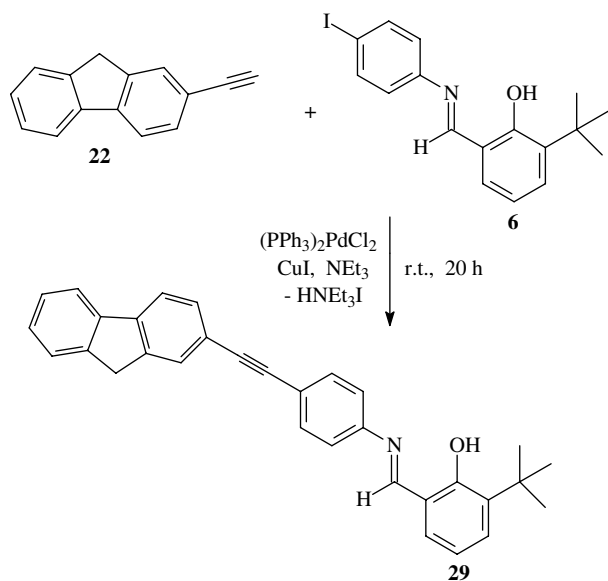
Scheme 8. See [49].

while the terminal methyl group of the hexynyl moiety (18) produces the signal at $\delta = 17.4$ ppm.

The mass spectrum of 36 shows the molecular ion at $m/z = 553$. Loss of the fluorenyl moiety yields the base peak at $m/z = 388$. Partial degradation of the hexynyl function including the Cp ring leads to $m/z = 282$ (see Scheme 14).

2.6. Synthesis of mononuclear zirconium complexes

Deprotonation of the phenolic hydroxy group of the phenoxyimine compounds 6–15 and 29–33 with 1 equiv.

Scheme 9. Synthesis of C₁ bridged ligand precursors from fulvene 25.

Scheme 10.

of potassium hydride and subsequent reaction with *half an* equivalent of zirconium tetrachloride resulted in the formation of the mononuclear bis(phenoxyimine)zirconium dichloride complexes **42–56** (see [Scheme 15](#) and [Tables 4 and 9](#)). In the complexes, the metal center is octahedrally coordinated by two chelating phenoxyimine ligands and two chloro ligands. The complexes **42–51** obtained from the ligand precursors **6–15** were already described in a previous paper [51].

The *cis* configuration of the chloro ligands is necessary for a high activity of the catalyst after activation with MAO and can be found in the three isomers with the lowest energy (five isomers are possible) [21].

Attempts to prepare trinuclear zirconium complexes starting with compounds **29–33** failed. Deprotonation of

these compounds with 2 equiv. of potassium hydride and subsequent reactions with zirconium tetrachloride only produced polymeric products. Therefore, 1.5 equiv. of the half sandwich complex cyclopentadienylzirconium trichloride were used instead of zirconium tetrachloride, but defined complexes could not be obtained.

2.7. Synthesis of trinuclear zirconium complexes

The reaction of the combined metallocene/phenoxyimine ligand precursors **34–41** with 3 equiv. of potassium hydride and 1.5 equiv. of zirconium tetrachloride furnished the trinuclear zirconium complexes **57–64**, wherein the zirconium centers are differently coordinated. The central bis(phenoxyimine) moiety contains octahedrally coordinated zirconium, while the metallocene fragments show tetrahedral coordination for the metal centers (see [Scheme 16](#)).

The prepared trinuclear complexes are listed in [Table 5](#).

All of the synthesized bis(phenoxyimine)zirconium complexes were characterized by mass spectrometry and elemental analysis. Due to the presence of at least three isomers of the phenoxyimine moieties in solutions and their poor solubilities in deuterated solvents, the characterization of the trinuclear complexes by NMR spectroscopy was quite difficult. Despite of the broad signals found in all ¹H NMR spectra, assignments of the signal groups were still possible. As can be seen from the MS data, the formation of indenyl and fluorenyl cations is highly favored over all other cleavage reactions since the positive charge can be delocalized easily. Therefore, the molecular ions are not visible for most of the complexes. However, the elemental analysis data agree very well with the theoretical predictions. The MS, ¹H NMR and elemental analysis data of the trinuclear complexes are collected in [Table 10](#).

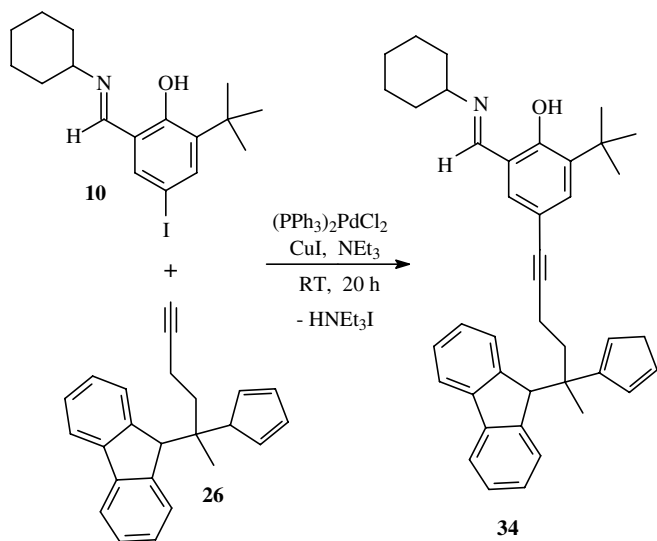
2.8. Results of ethylene polymerization

The zirconium complexes **42–64** were used as catalyst precursors for the homogeneous polymerization of ethylene. The complexes were activated with methylalumoxane (MAO) applying a ratio Zr:Al = 1:500. The polymerization runs were routinely performed at a temperature of 35 °C over 1 h employing an ethylene pressure of 10 bar. As a solvent *n*-pentane was used. The polymerization results are given in [Table 6](#). The values for the activities of the trinuclear complexes **57–64** are always related to 1 mol of the catalyst precursor.

The phenoxyimine ligands of complexes **42**, **47**, **49** and **50** were prepared from 4-iodoaniline and differently substituted salicylaldehydes. Therefore, the substituents at the salicylaldehyde rings are exclusively responsible for differences in polymerization activities and polymer properties (see [Scheme 17](#)). The highest activity (8320 kg PE/mol Zr h) was obtained for complex **42** containing a *tert*-butyl substituent at position 3 of the aldehyde ring. Exchange of the *tert*-butyl group against a cyclohexyl rest (**49**) slightly

Table 2
Coupling products of phenoxyimines and unbridged indenyl compounds

R-I	R'C≡CH	Product	R-I	R'C≡CH	Product
6	16		18	7	
18	8		10	20	



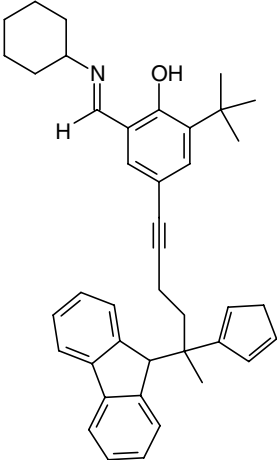
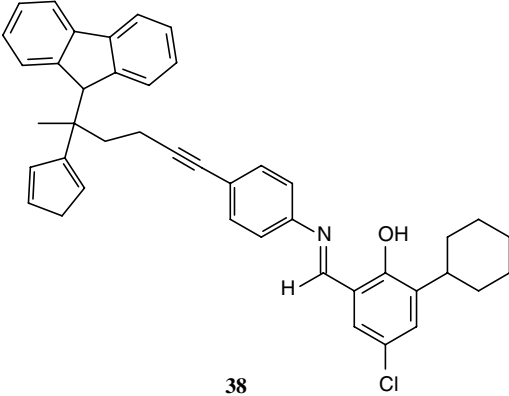
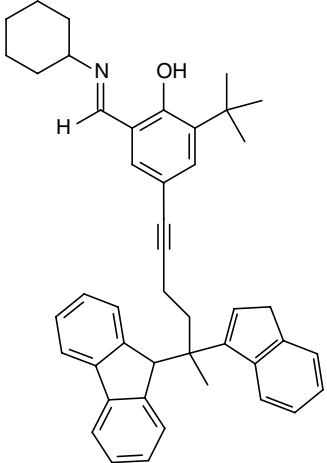
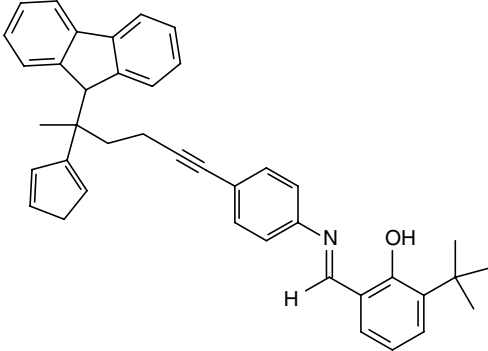
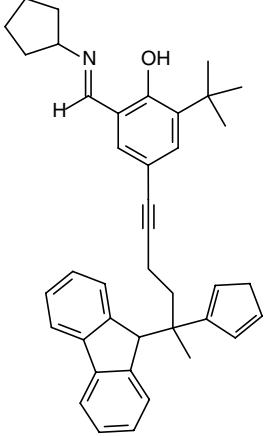
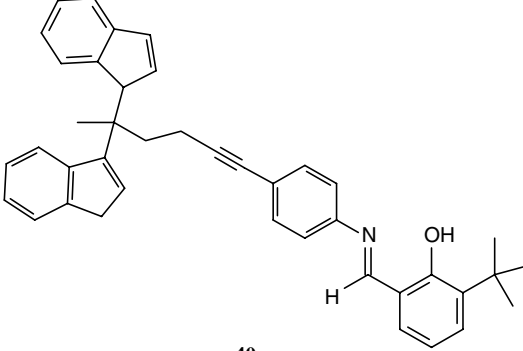
(50) leads to a further decrease of the activity due to its electron withdrawing effect. Exchange of alkyl or cycloalkyl groups at position 3 of the aldehyde ring against a more electron withdrawing phenyl substituent (47) destabilizes the cationic active center resulting in a reduced activity of 1760 kg PE/mol Zr h.

While the polymerization activity decreases with increasing electronegativity of the substituents at the aldehyde ring, the molecular weights of the polyethylenes increase in the same order. Finally, the polyethylene produced with 47/MAO could not be dissolved in 1,2,4-trichlorobenzene (for GPC analysis) due to its high molecular weight.

The complexes 43, 44, 48 and 51 are the first ones containing terminal alkynyl groups, that are active in the polymerization of ethylene [51]. Therefore, the affinity of the cationic zirconium centers towards ethylene is high enough to produce polyethylene instead of polyacetylene derivatives. As expected, complexes 43 and 44 containing 3-*tert*-butyl substituted aldehyde rings showed higher activities than 48 and 51 bearing electron withdrawing substituents at the aldehyde rings. The very high molecular weights M_w of the resulting polyethylenes are noticeable compared

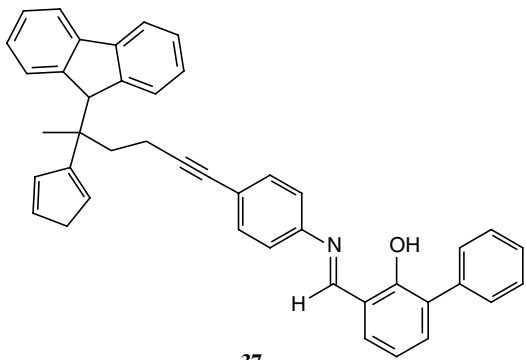
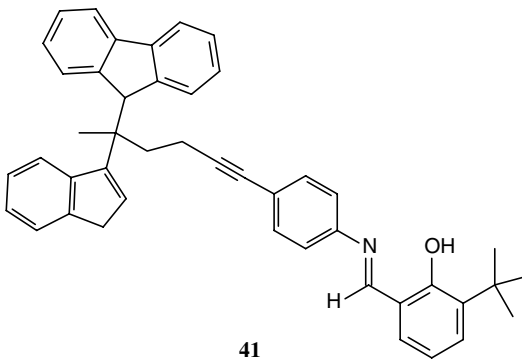
decreases the polymerization activity, since the steric bulk at the α -carbon atom bonded to the aldehyde ring is lowered. An additional chloro substituent at the para position

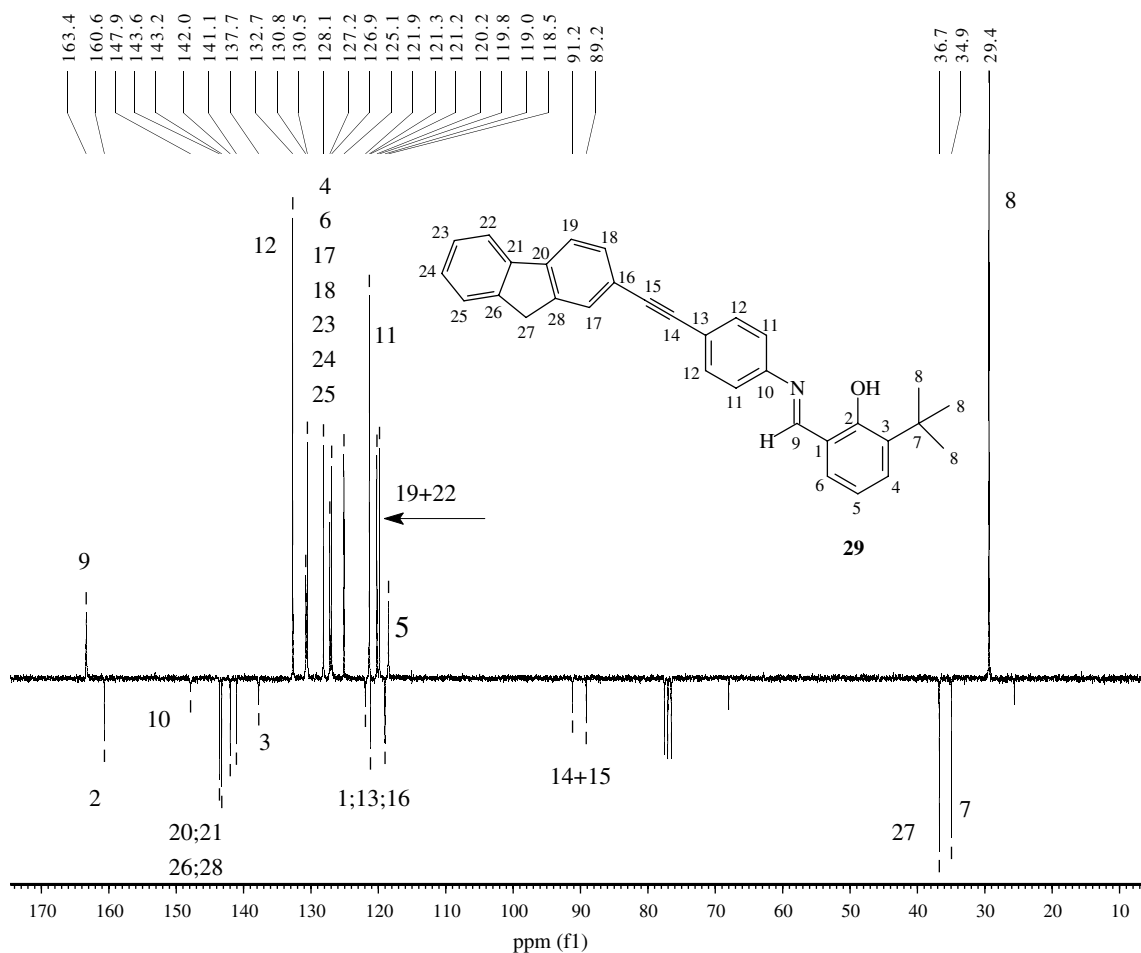
Table 3
Synthesized ligand precursors for trinuclear complexes

R-I	R'C≡CH	Product	R-I	R'C≡CH	Product
10	26		14	26	
10	28		6	26	
9	26		6	27	

(continued on next page)

Table 3 (continued)

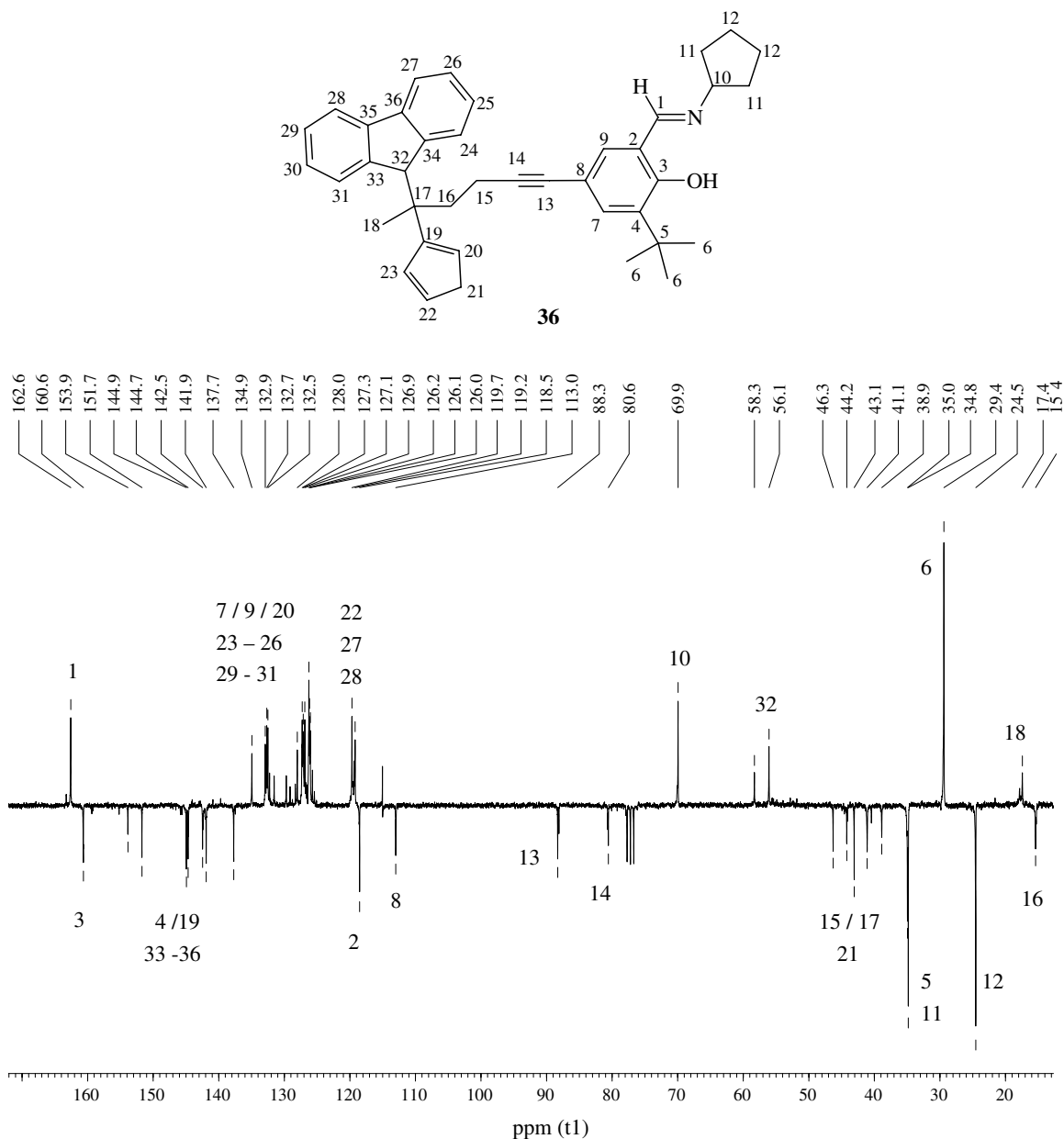
R-I	R'C≡CH	Product	R-I	R'C≡CH	Product
11	26		6	28	
		37			41

Scheme 12. ^{13}C NMR spectrum of **29**.

to the very low ones obtained with **45** and **46** having cycloalkyl groups at the imino moieties. The complexes **43**, **44** and **48** produced polyethylenes with very broad molecular weight distributions (PD = 44.0/55.4/21.4). As expected, complex **48** containing phenyl substituted phenoxyimine

ligands yielded the highest molecular weight polyethylene in this series.

Due to the stronger electron withdrawing effect of the alkyne groups, the mononuclear bis(phenoxyimine)zirconium dichloride complexes **52–57** containing indenylalky-



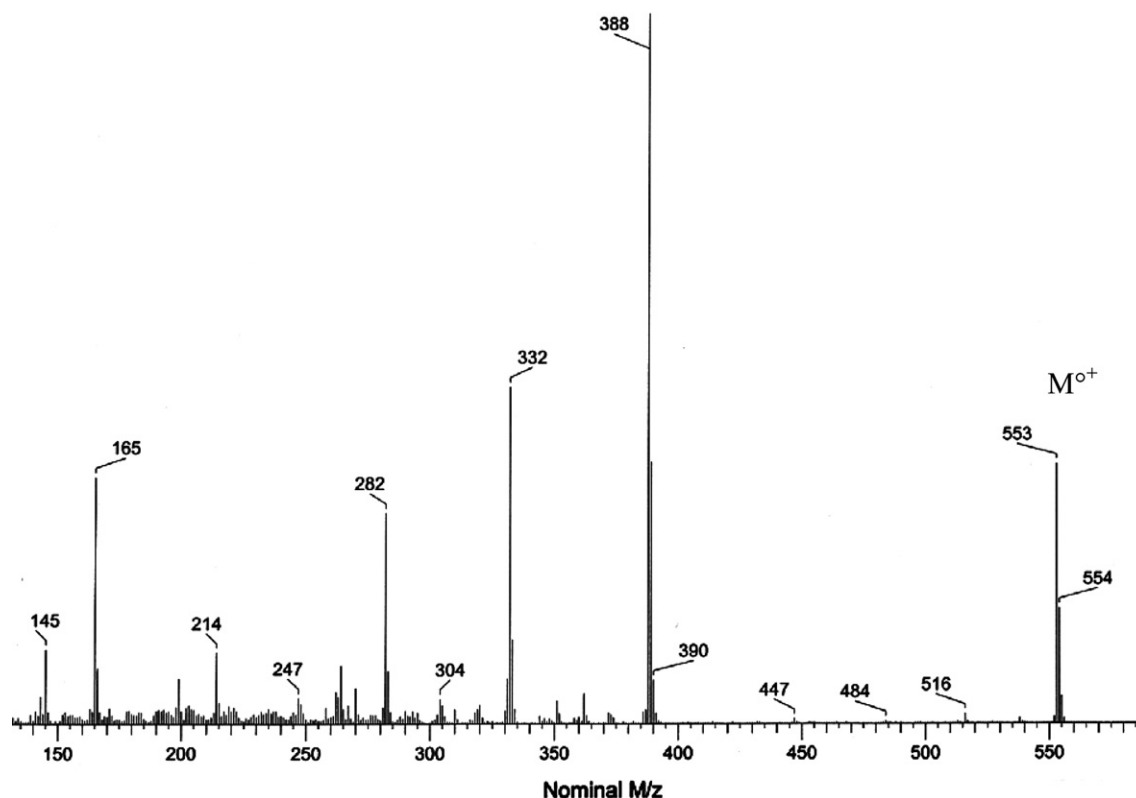
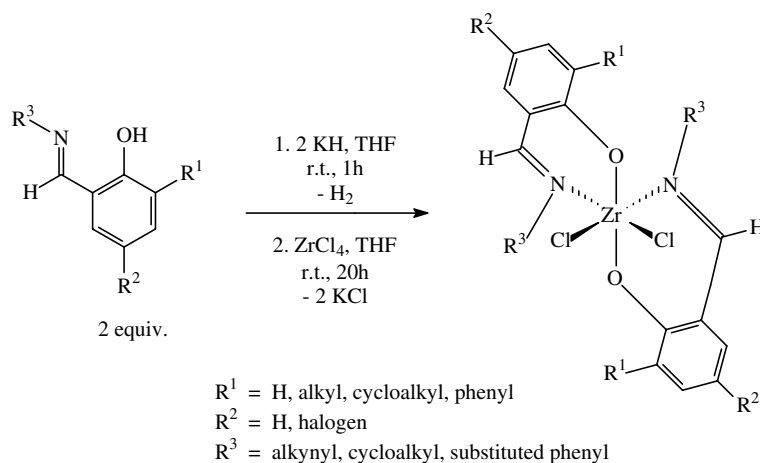
nyl or fluorenylalkynyl substituents on their ligand frameworks consistently showed lower polymerization activities compared to their iodo substituted “precursor” complexes (see Scheme 18).

However, comparison of the activities of **43** (2080 kg PE/mol Zr h) containing a terminal ethynyl function and **52–54** displays similar values. Since the steric bulk caused by the indenyl substituents in complex **55** is significantly higher than that of the propynyl groups of complex **44**, it is more difficult for the ethylene molecules to reach the active metal center leading to a reduced activity. In contrast to this result, the activity is less influenced, if the alkynyl substituent is introduced at position 5 of the aldehyde ring. The properties of the polyethylene produced with

56/MAO are nearly identical to that obtained from **46/MAO**.

In most cases, the polymerization activities of the trinuclear complexes **57–64** are lower compared to the summarized activities of their mononuclear “precursor” complexes (see Scheme 20). Since zirconocene complexes containing terminal alkynyl groups are inactive in ethylene polymerization [52], the analogously structured *ω*-alkenyl substituted complexes **A** [4] (activity: 3950 [kg PE/mol Zr h]) and **B** [53] (activity: 2200 [kg PE/mol Zr h]) are used for comparison purposes (see Scheme 19).

While the system **57/MAO** displayed an activity similar to the summarized activities of the mononuclear complexes, the analogous complexes **58** and **59** were inactive

Scheme 14. Mass spectrum of **36** (ions with $m/z < 150$ were omitted).

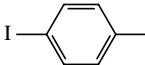
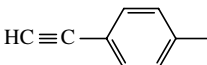
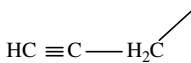
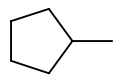
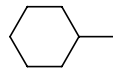
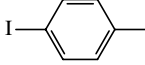
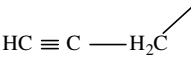
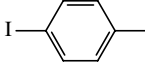
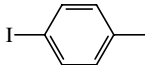
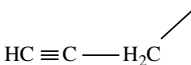
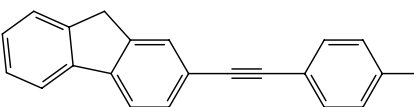
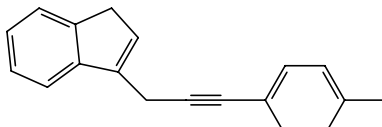
Scheme 15. Synthesis of mononuclear bis(phenoxyimine)zirconium dichloride complexes.

or less active compared to the summarized activities of the single-site compounds (see Scheme 20). The decrease in activity of the complexes **60–62** may be explained by the electron withdrawing effect of the introduced alkynyl groups. On the other hand, the steric hindrance, also caused by the MAO cages, around the central phenoxyimine moiety is dramatically increased resulting in lower activities. Considering the ethynyl substituted complex **43** as phenoxyimine “precursor”, the activity values obtained for **62/MAO** and **64/MAO** are comparable with the summarized values of the mononuclear compounds.

Analogously to mononuclear phenoxyimine zirconium complexes, polymerization activity decreases when electron withdrawing substituents (R^1 and R^2) are introduced into the aldehyde rings (see Table 7).

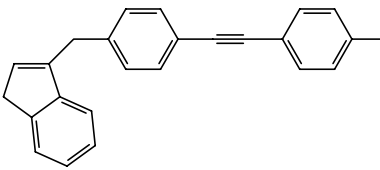
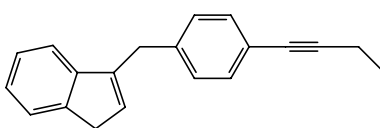
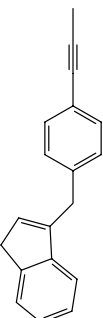
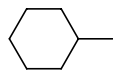
While the polymerization activities of the trinuclear complexes are somewhat lower than expected, the resulting polyethylenes displayed the desired broad or bimodal molecular weight distributions. The PD values varied between 15 and 40. The GPC spectra of polyethylenes produced with the trinuclear complexes are compared to those of the “single-site precursors”. The molecular weights of

Table 4
Synthesized mononuclear bis(phenoxyimine)zirconium complexes **42–56**

Complex	R ¹	R ²	R ³
42	^t Bu	H	
43	^t Bu	H	
44	^t Bu	H	
45	^t Bu	I	
46	^t Bu	I	
47	Phenyl	H	
48	Phenyl	H	
49	Cyclohexyl	H	
50	Cyclohexyl	Cl	
51	Cyclohexyl	Cl	
52	^t Bu	H	
53	^t Bu	H	

(continued on next page)

Table 4 (continued)

Complex	R ¹	R ²	R ³
54	^t Bu	H	
55	^t Bu	H	
56	^t Bu		

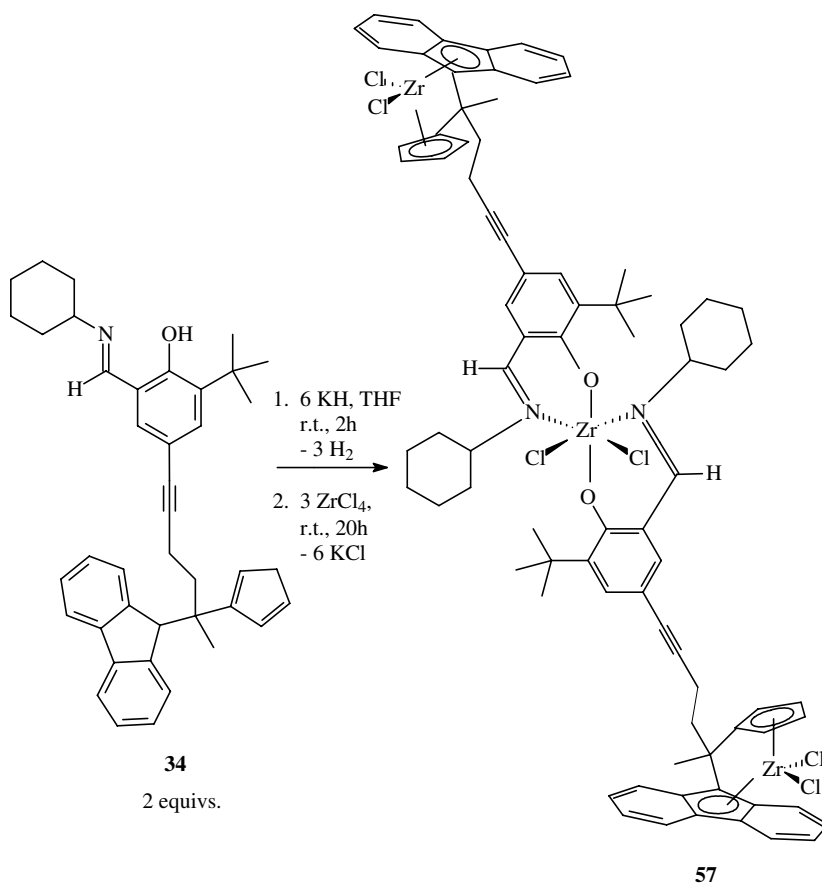
Scheme 16. Synthesis of the trinuclear zirconium complex **57**.

Table 5
Synthesized trinuclear complexes

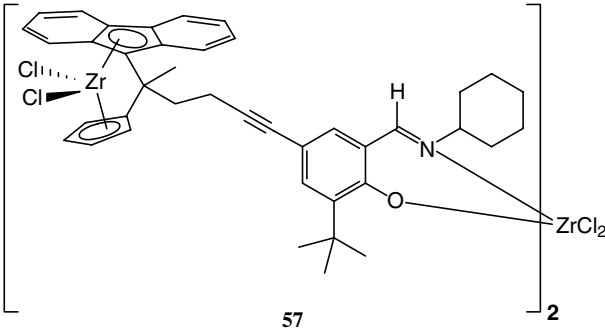
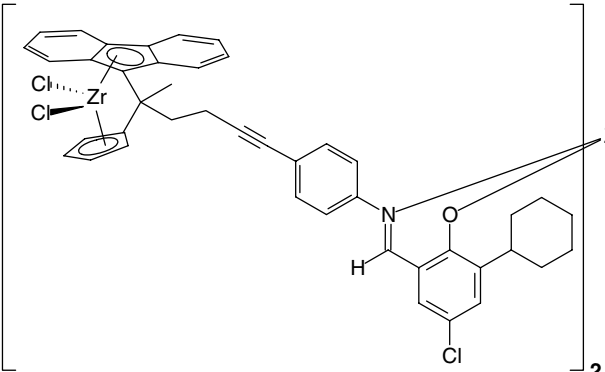
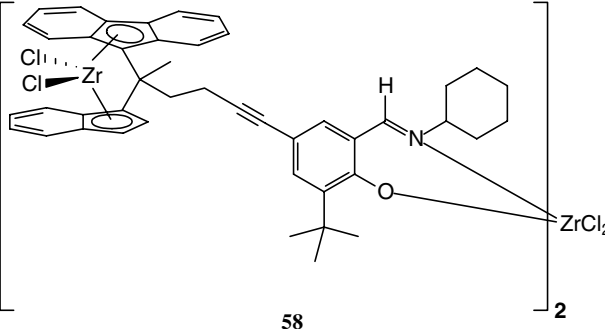
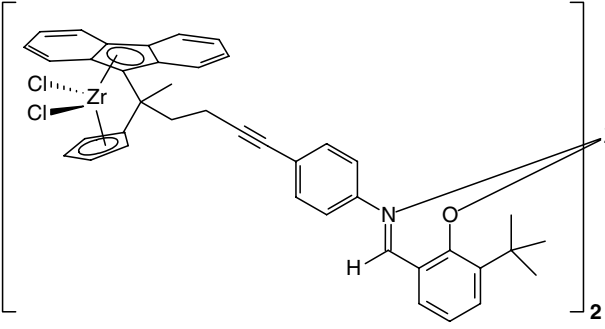
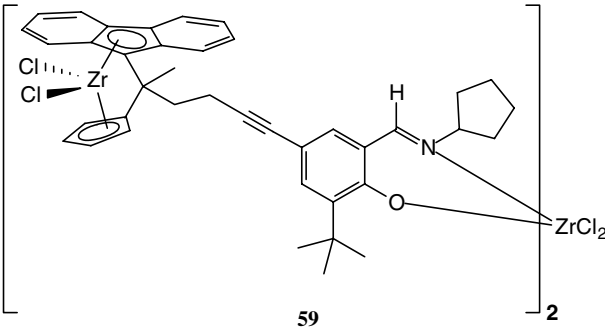
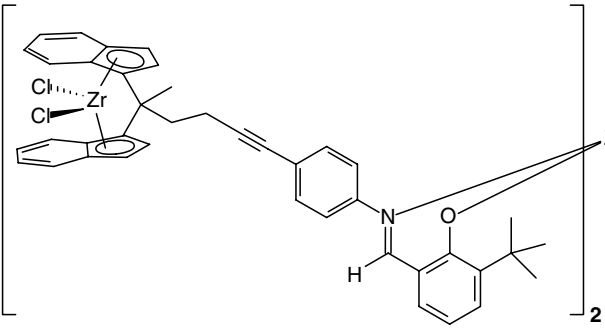
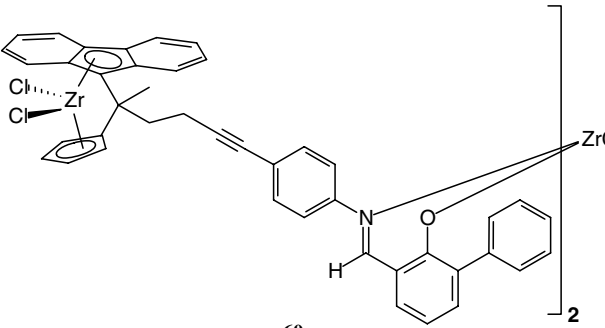
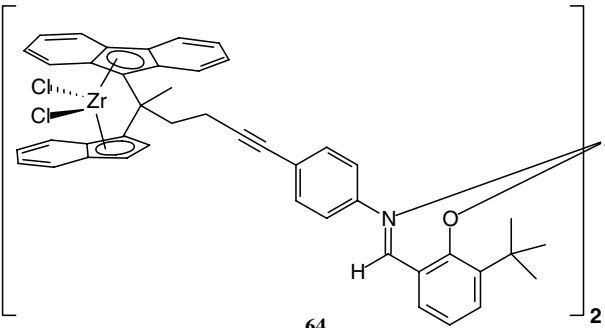
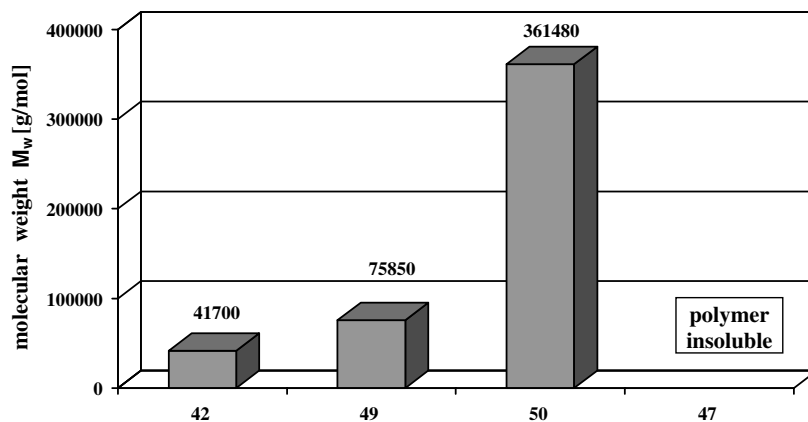
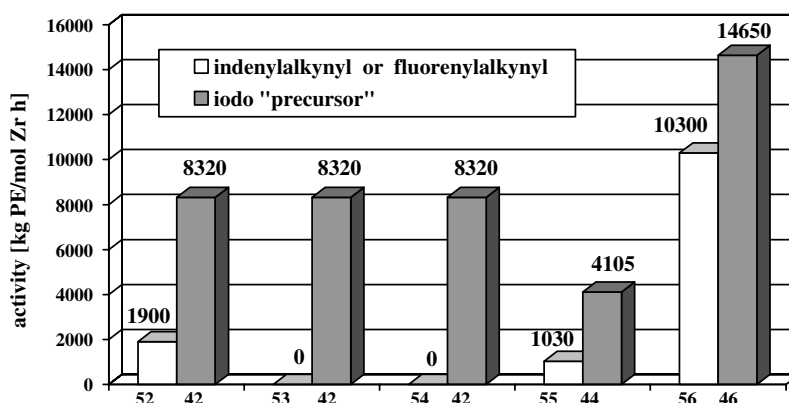
Complex	Complex
 <p>57</p>	 <p>61</p>
 <p>58</p>	 <p>62</p>
 <p>59</p>	 <p>63</p>
 <p>60</p>	 <p>64</p>

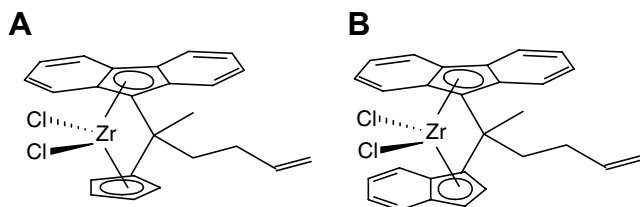
Table 6

Results of the ethylene polymerization with bis(phenoxyimine)zirconium dichloride complexes (polymerization conditions: 250 ml *n*-pentane, 35 °C, 10 bar ethylene, 1 h, *Zr:Al 1:500*)

Complex	Activity (kg PE/mol Zr h)	M_n (g/mol)	M_w (g/mol)	PD
42	8320	7260	41 700	5.74
43	2080	5830	256 700	44.0
44	4105	4280	237 000	55.4
45	15 600	3370	9500	2.83
46	14 650	10 700	32 150	3.00
47	1760	Polymer insoluble in 1,2,4-trichlorobenzene		
48	168	24 700	527 900	21.4
49	7780	5420	75 850	14.0
50	5100	8770	361 480	41.2
51	–	–	–	–
52	1900	Polymer insoluble in 1,2,4-trichlorobenzene		
53	–	–	–	–
54	–	–	–	–
55	1030	7380	86 200	11.7
56	10 300	10 350	30 700	2.97
57	24 500	7800	134 750	17.3
58	–	–	–	–
59	2840	2915	125 600	43.1
60	710	6620	292 900	44.3
61	2580	10 810	418 500	38.7
62	7770	7270	255 400	35.1
63	1060	5000	173 500	34.6
64	5630	9640	702 550	72.9

Scheme 17. Increase of M_w at decreasing electron density in the aldehyde ring.

Scheme 18. Comparison of the polymerization activities of the complexes 52–56 with their iodo substituted “precursor” complexes.

Scheme 19. ω -Alkenyl substituted zirconocene complexes [4,53].

the polyethylenes resulting from **A**/MAO and **B**/MAO are 140 000 g/mol and 210 000 g/mol, respectively [4,53]. Therefore, it could be estimated which zirconium center of the trinuclear complexes produced the higher molecular weight fraction.

The GPC spectrum of the polyethylene produced with **42**/MAO exhibits a quite narrow molecular weight distribution with PD = 5.74 (see Scheme 21). Contrary to this behaviour, the trinuclear complex **62** yields a polyethylene with a broad molecular weight distribution (PD = 35.1). While M_n remains nearly constant (**42**: 7240 g/mol; **62**: 7270 g/mol), M_w increases from 40 200 g/mol (**42**) to 255 400 g/mol (**62**). The curve maximum (M_{peak}) is shifted from 12 070 g/mol to 50 170 g/mol. Therefore, in this case the phenoxyimine moiety produced the lower molecular weight fraction, while the metallocene fragments yielded the higher molecular weight component.

The differences of the molecular weight distributions are more obvious when the GPC spectra of the polyethylenes produced with **42**/MAO and **64**/MAO are compared. In case of **64**/MAO, the introduction of indenyl rings instead of cyclopentadienyl rings lead to the production of higher molecular weight polyethylene by the metallocene moieties (see Schemes 21 and 22). The molecular weights M_{peak} and M_w are shifted up to 81 700 g/mol and 702 550 g/mol, respectively.

Table 7

Influence of the substituents R^1 and R^2 on the polymerization activities of analogously structured trinuclear complexes

Complex	R^1	R^2	Activity (kg PE/mol Zr h)
62	<i>tert</i> -Butyl	H	7770
61	Cyclohexyl	Cl	2580
60	Phenyl	H	710

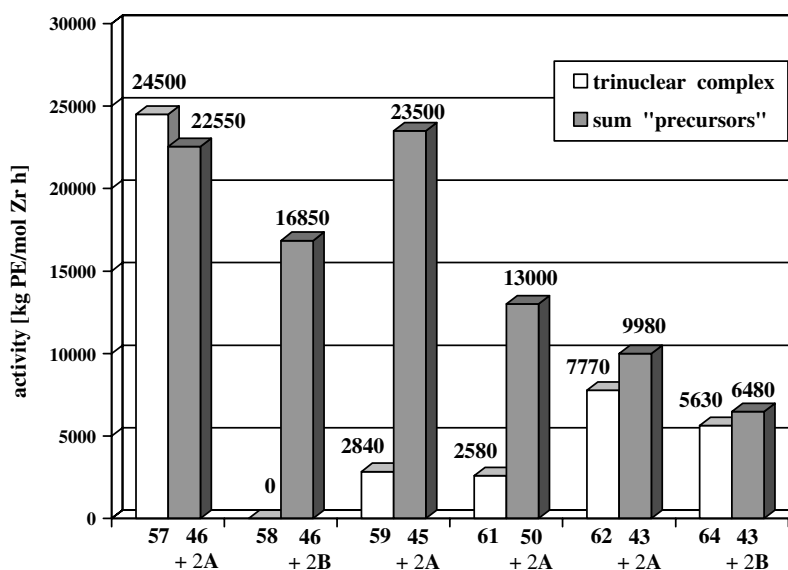
Considering complex **43** containing terminal ethynyl groups as the “single-site precursor” for the trinuclear complexes **62** and **64**, the GPC spectra are better comparable (see Scheme 23).

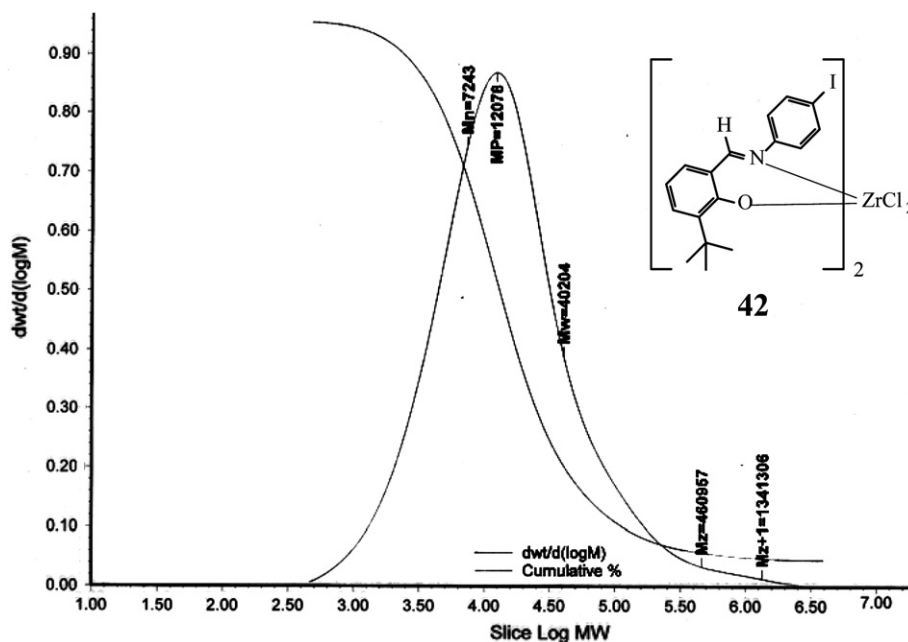
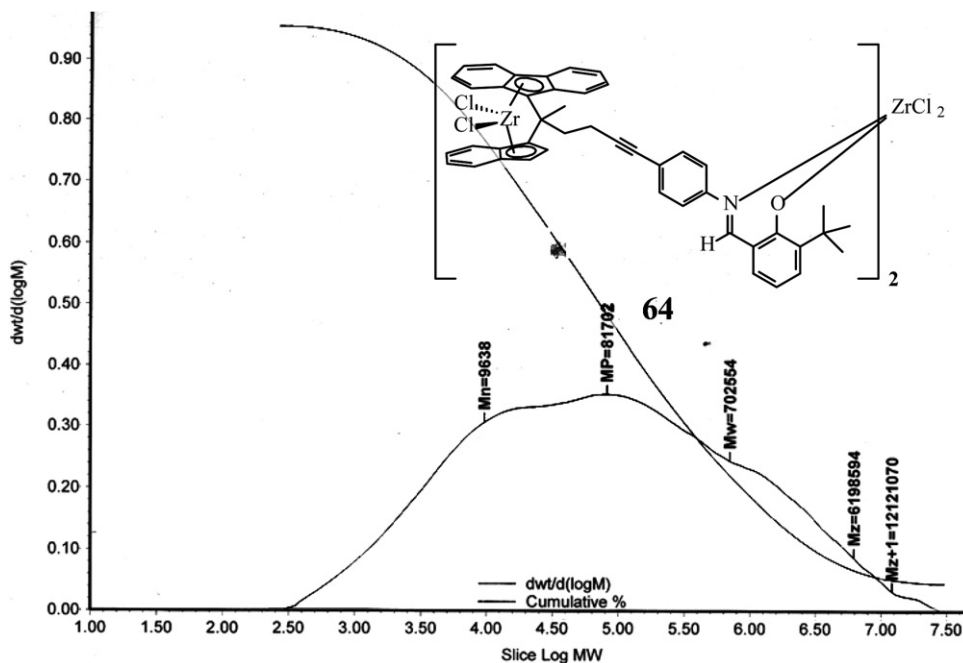
The values for M_{peak} (51 100 g/mol) and M_w (237 000 g/mol) of the polyethylene obtained with **43**/MAO are comparable to those for **62**/MAO (M_{peak} = 50 170 g/mol, M_w = 255 400 g/mol), but are significantly lower than those of the polyethylene produced with **64**/MAO.

While the mononuclear complex **47** produced very high molecular weight polyethylene that could not be dissolved in 1,2,4-trichlorobenzene, the trinuclear complex **60** yielded a polyethylene with an almost bimodal molecular weight distribution (see Scheme 24).

Since the metallocene moieties produce a polyethylene with M_w = 140 000 g/mol [4], the solubility in 1,2,4-trichlorobenzene is increased, and GPC spectroscopy can be performed.

The influence of alkynyl substituents at position 5 of the former aldehyde rings on the molecular weight M_w is significantly lower. The M_n and M_w values of the polyethylenes obtained with **46**/MAO and **56**/MAO agree very well with each other (see Table 6). Therefore, comparisons of the polyethylenes obtained from the iodo containing “precursor” complexes **45** and **46** to those obtained from the trinuclear complexes **59** and **57** are useful. The iodo substituted complexes **45** and **46** produced polyethylenes with narrow molecular weight distributions (**45**:

Scheme 20. Comparison of the polymerization activities of the trinuclear complexes **57**–**64** and their “precursor” complexes.

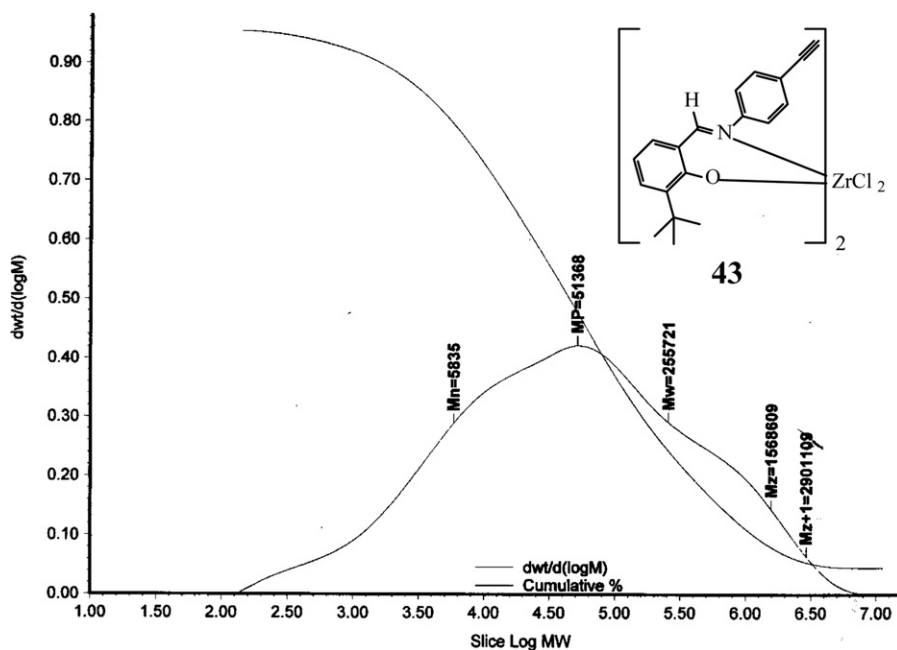
Scheme 21. GPC spectrum of the polyethylene produced with **42**/MAO.Scheme 22. GPC spectrum of the polyethylene obtained with **64**/MAO.

$M_w = 9500$ g/mol; **46**: $M_w = 32150$ g/mol; PD's < 3). By introduction of the metallocene moieties into the ligand frameworks (complexes **59** and **57**), these metal centers produce a higher molecular weight polyethylene resulting in broad or bimodal molecular weight distributions. This effect is clearly visible in the GPC spectra (see Schemes 25 and 26).

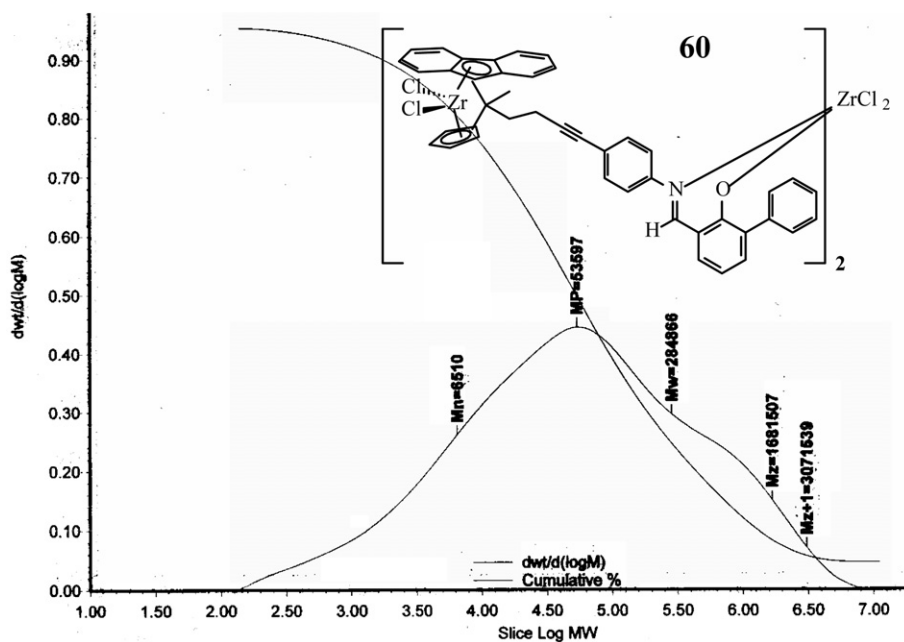
The polyethylene produced with **59**/MAO still contains a low molecular weight fraction. Additionally, a shoulder is

visible in the spectrum corresponding to the metallocene catalyzed part. M_w increases from 9500 g/mol (**45**) to 125600 g/mol (**59**), the polydispersity index PD also increases from 2.83 (**45**) to 43.1 (**59**).

A better separation of the peaks in the GPC spectra may be accomplished using metallocene moieties containing 4,5-disubstituted fluorenyl fragments. Such zirconocene complexes are known to produce very high molecular weight polyethylenes [54].



Scheme 23. GPC spectrum of the polyethylene produced with 43/MAO.



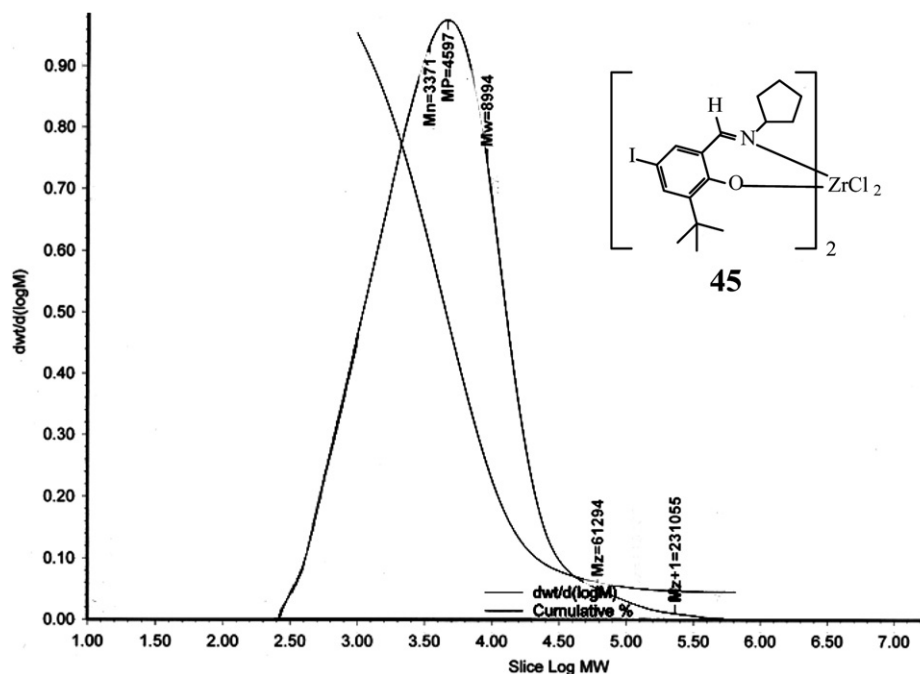
Scheme 24. GPC spectrum of the polyethylene resulting from 60/MAO.

3. Experimental

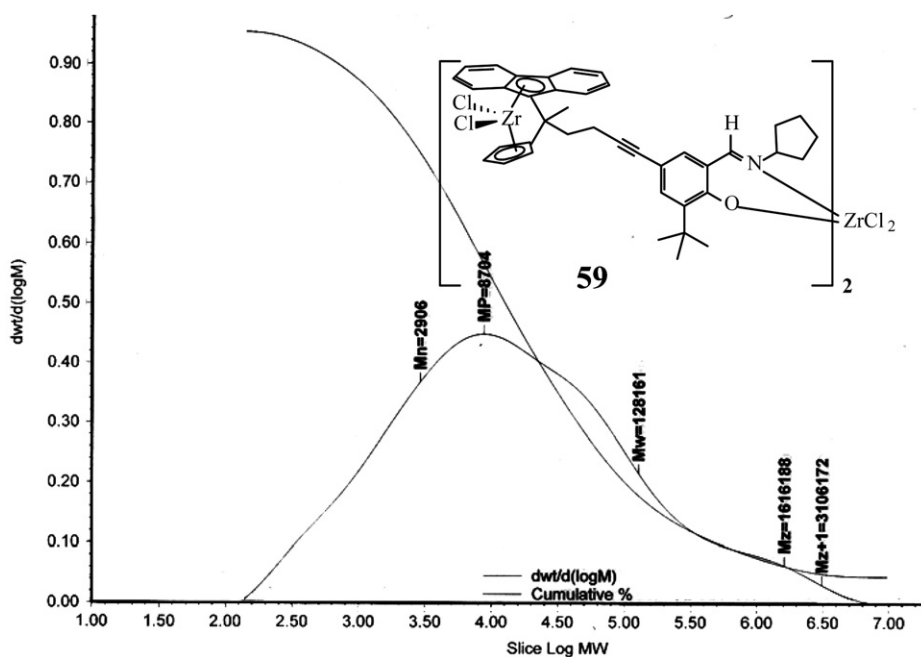
All experimental work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. *n*-Pentane, diethyl ether, toluene and tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether was additionally distilled over lithium aluminum hydride. Methylene chloride was dried with phosphorus pentoxide and calcium hydride. Methanol and ethanol

were dried over molecular sieves. Deuterated solvents (CDCl_3 , CDCl_2) for NMR spectroscopy were stored over molecular sieves (3 Å).

Methylalumoxane (30% in toluene) was purchased from Crompton (Bergkamen) and Albemarle (Baton Rouge, USA/Louvain – La Neuve, Belgium). Ethylene (3.0) and argon (4.8/5.0) were supplied by Rießner Company (Lichtenfels). All other starting materials were commercially available and were used without further purification.



Scheme 25. GPC spectrum of the polyethylene produced with 45/MAO.



Scheme 26. GPC spectrum of the polyethylene produced with 59/MAO.

3.1. NMR spectroscopy

The spectrometer Bruker ARX 250 was available for the recording of the NMR spectra. The samples were prepared under inert atmosphere (argon) and routinely recorded at 25 °C. The chemical shifts in the ^1H NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for CDCl_3 , $\delta = 5.32$ ppm for CD_2Cl_2) and in ^{13}C NMR spectra to the

solvent signal ($\delta = 77.0$ ppm for CDCl_3 , $\delta = 53.5$ ppm for CD_2Cl_2).

3.2. Mass spectrometry

Mass spectra were routinely recorded at the Zentrale Analytik of the University of Bayreuth with a VARIAN MAT CH-7 instrument (direct inlet, EI, $E = 70$ eV) and a VARIAN MAT 8500 spectrometer.

Table 8
NMR and MS data for compounds 1–41

Compound	¹ H NMR	¹³ C NMR	MS [<i>m/z</i>]
1	11.84 s (1H, OH), 9.72 s (1H, O=C–H), 7.43–7.47 m (1H, Ar–H), 7.25–7.29 m (1H, Ar–H), 6.86 t (1H, Ar–H), 1.38 s (9H, ^t Bu–CH ₃)	197.2 (O=C–H), 161.1, 138.0, 120.7 (C _q), 134.1, 132.0, 119.3 (Ar–CH), 34.8 (C _q), 29.2 (^t Bu–CH ₃)	178 M ^{o+} (26) 163 M–Me (100) 135 M–C ₃ H ₇ (39)
2	11.53 s (1H, OH), 9.94 s (1H, O=C–H), 7.36–7.62 m (7H, Ar–H), 7.09 t (1H, Ar–H)	196.8 (O=C–H), 158.9, 136.3, 130.5, 120.9 (C _q), 137.8, 133.2, 128.3, 127.7, 119.9 (Ar–CH)	198 M ^{o+} (100) 197 M–H (53) 169 M–H–C=O (21)
3	11.38 s (1H, OH), 9.83 s (1H, O=C–H), 7.41–7.45 m (1H, Ar–H), 7.34–7.37 m (1H, Ar–H), 6.95 t (1H, Ar–H), 2.96–3.02 m (1H, CH), 1.80–1.89 m (4H, CH ₂), 1.33–1.42 m (6H, CH ₂)	196.9 (O=C–H), 159.2, 136.3, 120.1 (C _q), 134.1, 131.2, 119.6 (Ar–CH), 36.2 (CH), 32.8, 26.9, 26.4 (CH ₂)	204 M ^{o+} (100) 186 M–H ₂ O (69) 135 M–C ₃ H ₉ (96)
4	11.26 s (1H, OH), 9.79 s (1H, O=C–H), 7.35 d (1H, Ar–H), 7.31 d (1H, Ar–H), 2.91–3.00 m (1H, CH), 1.82–1.86 m (4H, CH ₂), 1.19–1.50 m (6H, CH ₂)	195.9 (O=C–H), 157.8, 138.9, 124.5, 120.6 (C _q), 134.2, 129.7 (Ar–CH), 36.2 (CH), 32.6, 26.7, 26.1 (CH ₂)	238 M ^{o+} (100) 220 M–H ₂ O (36) 203 M–Cl (98) 169 M–C ₃ H ₉ (70)
5	11.71 s (1H, OH), 9.75 s (1H, O=C–H), 7.67 d (1H, Ar–H), 7.66 d (1H, Ar–H), 1.36 s (9H, ^t Bu–CH ₃)	195.9 (O=C–H), 160.8, 141.2, 122.4 (C _q), 142.5, 139.9 (Ar–CH), 80.7 (C _q , C–I), 35.0 (C _q), 29.0 (^t Bu–CH ₃)	304 M ^{o+} (58) 289 M–Me (100) 261 M–C ₃ H ₇ (30)
6	13.67 s (br, 1H, OH), 8.58 s (1H, N=C–H), 7.70–7.73 m (2H, Ar–H), 7.39 dd (1H, Ar–H), 7.23 dd (1H, Ar–H), 7.01–7.04 m (2H, Ar–H), 6.87 t (1H, Ar–H), 1.45 s (9H, ^t Bu–CH ₃)	163.7 (N=C–H), 160.5, 148.1, 137.7, 118.9, 91.3 (C _q), 138.4, 130.8, 130.7, 123.2, 118.5 (Ar–CH), 34.9 (C _q), 29.3 (^t Bu–CH ₃)	379 M ^{o+} (66) 364 M–Me (100) 336 M–C ₃ H ₇ (79)
7	13.71 s (br, 1H, OH), 8.60 s (1H, N=C–H), 7.21–7.55 m (6H, Ar–H), 6.87 t (1H, Ar–H), 3.13 s (1H, ≡CH), 1.46 s (9H, ^t Bu–CH ₃)	163.8 (N=C–H), 160.6, 148.6, 137.7, 120.3, 118.9 (C _q), 133.3, 130.8, 130.7, 121.2, 118.5 (Ar–CH) 83.3 (C _q , C≡C), 77.9 (≡CH), 34.9 (C _q), 29.3 (^t Bu–CH ₃)	277 M ^{o+} (74) 262 M–Me (100) 234 M–C ₃ H ₇ (84)
8	13.56 s (br, 1H, OH), 8.67 s (1H, N=C–H), 7.36 dd (1H, Ar–H), 7.19 dd (1H, Ar–H), 6.85 t (1H, Ar–H), 4.52 t (2H, CH ₂), 2.56 t (1H, ≡CH), 1.47 s (9H, ^t Bu–CH ₃)	166.5 (N=C–H), 160.0, 137.4, 118.6 (C _q), 130.1, 129.8, 118.1 (Ar–CH), 76.7 (C _q , C≡C), 76.2 (≡CH), 45.2 (CH ₂), 34.9 (C _q), 29.3 (^t Bu–CH ₃)	215 M ^{o+} (54) 200 M–Me (100) 172 M–C ₃ H ₇ (66)
9	14.22 s (br, 1H, OH), 8.21 s (1H, N=C–H), 7.48 d (1H, Ar–H), 7.36 d (1H, Ar–H), 3.71–3.76 m (1H, N–CH), 1.67–1.95 m (8H, CH ₂), 1.38 s (9H, ^t Bu–CH ₃)	161.6 (N=C–H), 160.4, 140.4, 120.8, 79.1 (C _q), 137.6, 137.5 (Ar–CH), 69.9 (N–CH), 34.9 (C _q), 34.7, 24.4 (CH ₂), 29.1 (^t Bu–CH ₃)	371 M ^{o+} (100) 356 M–Me (81) 328 M–C ₃ H ₇ (87) 244 M–I (6)
10	14.36 s (br, 1H, OH), 8.24 s (1H, N=C–H), 7.48 d (1H, Ar–H), 7.37 d (1H, Ar–H), 3.17–3.21 m (1H, N–CH), 1.24–1.82 m (10H, CH ₂), 1.39 s (9H, ^t Bu–CH ₃)	161.6 (N=C–H), 160.7, 140.5, 120.8, 78.9 (C _q), 137.7, 137.6 (Ar–CH), 67.4 (N–CH), 34.9 (C _q), 34.2, 24.4, 22.7 (CH ₂), 29.1 (^t Bu–CH ₃)	385 M ^{o+} (100) 370 M–Me (64) 342 M–C ₃ H ₇ (73)
11	13.73 s (br, 1H, OH), 8.64 s (1H, N=C–H), 7.64–7.74 m (4H, Ar–H), 7.36–7.50 m (5H, Ar–H), 7.00–7.04 m (3H, Ar–H)	163.0 (N=C–H), 158.5, 147.7, 137.4, 130.1, 119.1, 91.7 (C _q) 138.5, 134.4, 131.9, 129.3, 128.2, 127.3, 123.1, 119.2 (Ar–CH)	399 M ^{o+} (100) 398 M–H (42) 272 M–I (18)
12	13.57 s (br, 1H, OH), 8.73 s (1H, N=C–H), 7.64–7.68 m (2H, Ar–H), 7.32–7.49 m (5H, Ar–H), 6.99 t (1H, Ar–H), 4.52 d (2H, CH ₂), 2.57 t (1H, ≡CH)	166.0 (N=C–H), 158.0, 137.7, 129.8, 118.9 (C _q), 133.6, 131.2, 129.8, 128.3, 127.1, 118.8 (Ar–CH), 77.4 (C _q , C≡C), 76.6 (≡CH), 45.3 (CH ₂)	235 M ^{o+} (100) 196 M–propynyl (23)
13	13.42 s (br, 1H, OH), 8.57 s (1H, N=C–H), 7.69–7.73 m (2H, Ar–H), 7.31 dd (1H, Ar–H), 7.21 dd (1H, Ar–H), 6.99–7.03 m (2H, Ar–H), 6.90 t (1H, Ar–H), 3.01–3.06 m (1H, CH), 1.74–1.93 m (4H, CH ₂), 1.24–1.50 m (6H, CH ₂)	163.4 (N=C–H), 158.6, 148.1, 135.8, 118.3, 91.3 (C _q), 138.4, 130.7, 129.9, 123.1, 118.9 (Ar–CH), 36.6 (CH), 32.9, 27.0, 26.4 (CH ₂)	405 M ^{o+} (100) 404 M–H (39) 350 M–C ₄ H ₇ (24) 278 M–I (3)
14	13.39 s (br, 1H, OH), 8.45 s (1H, N=C–H), 7.68–7.73 m (2H, Ar–H), 7.23 d (1H, Ar–H), 7.16 d (1H, Ar–H), 6.97–7.01 m (2H, Ar–H), 2.97–3.03 m (1H, CH), 1.74–1.90 m (4H, CH ₂), 1.24–1.43 m (6H, CH ₂)	162.0 (N=C–H), 157.2, 147.5, 138.1, 123.7, 119.0, 91.6 (C _q), 138.5, 130.6, 128.6, 123.8 (Ar–CH) 36.6 (CH), 32.7, 26.9, 26.3 (CH ₂)	439 M ^{o+} (100) 404 M–Cl (24) 384 M–C ₄ H ₇ (40) 312 M–I (6)
15	13.20 s (br, 1H, OH), 8.58 s (1H, N=C–H), 7.17 d (1H, Ar–H), 7.12 d (1H, Ar–H), 4.51 d (2H, CH ₂), 2.93–3.02 m (1H, N–CH), 2.55 t (1H, ≡CH), 1.79–1.87 m (4H, CH ₂), 1.20–1.40 m (6H, CH ₂)	165.0 (N=C–H), 156.7, 137.7, 123.2, 118.8 (C _q), 129.7, 128.1 (Ar–CH), 77.1 (C _q , C≡C), 76.8 (≡CH), 36.6 (CH), 45.3, 32.7, 26.8, 26.3 (CH ₂)	275 M ^{o+} (81) 240 M–Cl (29) 236 M–propynyl (100)
16	7.68–7.71 m (1H, Ar–H), 7.36–7.50 m (3H, Ar–H), 6.98–7.01 m (1H, Ar–H), 6.72–6.75 m (1H, Ar–H), 3.76 dt (1H, Ind-H ¹), 2.73–2.82 m (1H, CH ₂), 2.43–2.54 m (1H, CH ₂), 2.19 t (1H, ≡CH)	146.3, 144.4 (C _q), 138.4, 131.9, 127.3, 125.2, 123.2, 121.4 (Ar–CH), 82.8 (C _q , C≡C), 69.5 (≡CH), 48.9 (CH, Ind-C ¹), 21.2 (CH ₂)	154 M ^{o+} (69) 115 M–propynyl (100)

(continued on next page)

Table 8 (continued)

Compound	¹ H NMR	¹³ C NMR	MS [<i>m/z</i>]
17	7.11–7.48 m (8H, Ar–H), 6.84 dd (1H, Ar–H), 6.45 dd (1H, Ar–H), 3.68–3.76 m (1H, Ind–H ¹), 3.09 dd (1H, CH ₂), 2.75 dd (1H, CH ₂)	146.7, 144.3, 139.2, 120.1 (C _q), 138.5, 131.4, 126.9, 124.8, 123.2, 121.3 (Ar–CH), 131.4, 130.9 (je 2 Ar–CH), 51.5 (CH, Ind–C ¹), 37.3 (CH ₂)	284/286 M ^{o+} (58) 169/171 M-indenyl (100)
18	7.61–7.65 m (2H, Ar–H), 7.19–7.35 m (4H, Ar–H), 6.97–7.00 m (2H, Ar–H), 6.79–6.81 m (1H, Ar–H), 6.39–6.42 m (1H, Ar–H), 3.66–3.72 m (1H, Ind–H ¹), 3.02–3.10 dd (1H, CH ₂), 2.66–2.74 dd (1H, CH ₂)	146.7, 144.3, 139.8 (C _q), 138.4, 131.3, 126.8, 124.8, 123.1, 121.3 (Ar–CH), 137.3, 131.2 (je 2 Ar–CH), 91.5 (C _q , C–I), 51.4 (CH, Ind–C ¹), 37.4 (CH ₂)	332 M ^{o+} (48) 217 M-indenyl (100)
19	(¹ H NMR data for the vinylic, 3-substituted isomer) 7.19–7.47 m (8H, Ar–H), 6.10–6.12 m (1H, Ind–H ²), 3.88 d (2H, CH ₂ , Ind–H ¹), 3.35 d (2H, CH ₂), 0.25 s (9H, SiMe ₃)	(¹³ C NMR data for the vinylic, 3-substituted isomer) 144.8, 144.5, 142.9, 140.0, 120.8 (C _q), 132.0, 128.8 (je 2 Ar–CH), 130.3, 126.0, 124.7, 123.8, 119.3 (Ar–CH), 105.2, 93.6 (C _q , C=C), 37.7, 34.4 (CH ₂), 0.0 (SiMe ₃)	n. d.
20	7.16–7.48 m (8H, Ar–H), 6.14 m (1H, Ind–H ²), 3.90 d (2H, CH ₂ , Ind–H ¹), 3.35 d (2H, CH ₂), 3.04 s (1H, ≡CH)	144.8, 144.5, 142.8, 140.3, 119.8 (C _q), 132.2, 128.9 (je 2 Ar–CH), 130.3, 126.0, 124.7, 123.8, 119.3 (Ar–CH), 84.3 (C _q , C=C), 76.8 (≡CH), 37.7, 34.4 (CH ₂)	230 M ^{o+} (51) 115 M-indenyl (100)
21	7.30–7.72 m (7H, Ar–H), 3.82 s (2H, CH ₂), 2.43 s (br, 1H, OH), 1.67 s (6H, CH ₃)	143.5, 143.1, 141.8, 141.0, 120.7, 65.7 (C _q), 130.5, 128.2, 127.1, 126.9, 125.1, 120.2, 119.7 (Ar–CH), 93.8, 82.8 (C _q , C=C), 36.7 (CH ₂), 31.6 (CH ₃)	248 M ^{o+} (72) 233 M–Me (100)
22	7.35–7.78 m (7H, Ar–H), 3.87 s (2H, CH ₂), 3.11 s (1H, ≡CH)	143.6, 143.1, 142.3, 140.9, 120.0 (C _q), 131.0, 128.7, 127.3, 126.9, 125.1, 120.2, 119.7 (Ar–CH), 84.4 (C _q , C=C), 76.9 (≡CH), 36.7 (CH ₂)	190 M ^{o+} (100) 189 M–H (98)
23	2.65 t (2H, CH ₂), 2.36–2.43 m (2H, CH ₂), 2.13 s (3H, CH ₃), 1.91 t (1H, ≡CH)	206.3 (C _q), 82.8 (C _q , C=C), 68.7 (≡CH), 42.1, 12.9 (CH ₂), 29.8 (CH ₃)	96 M ^{o+} (7) 95 M–H (60) 81 M–H–Me (67)
24	6.53–6.56 m (4H, Cp), 2.79 t (2H, CH ₂), 2.43–2.50 m (2H, CH ₂), 2.26 s (3H, CH ₃), 2.04 t (1H, ≡CH)	150.2, 143.6 (C _q), 131.5, 131.2, 120.8, 120.4 (Cp–CH), 83.1 (C _q , C=C), 69.7 (≡CH), 35.5, 18.5 (CH ₂), 20.9 (CH ₃)	144 M ^{o+} (11) 143 M–H (18) 129 M–Me (100)
25	7.72–7.75 m (1H, Ar–H), 7.25–7.38 m (3H, Ar–H), 6.83–6.89 m (2H, Ar–H), 3.05/2.85 t (2H, CH ₂), 2.51–2.63 m (2H, CH ₂), 2.46/2.33 s (3H, CH ₃), 2.14/2.07 t (1H, ≡CH) (signals for the isomers 1:1)	144.8/144.2, 144.1/143.8, 138.0/137.5, 135.8/134.9 (C _q), 129.5/129.3, 127.8/127.2, 126.5/126.4, 125.2/124.9, 123.9/123.3, 121.3/121.2 (Ar–CH), 84.9/83.5 (C _q , C=C), 69.4/69.2 (≡CH), 23.0/21.0 (CH ₃), 37.2/34.8, 18.5/17.3 (CH ₂) (signals for the isomers 1:1)	194 M ^{o+} (65) 179 M–Me (98) 155 M-propynyl (100)
26	7.63–7.84 m (3H, Ar–H), 7.36–7.50 m (3H, Ar–H), 7.17–7.20 m (1H, Ar–H), 6.83–7.00 m (1H, Ar–H), 6.57–6.73 m (2H, Cp), 6.22–5.99 m (1H, Cp), 4.19/4.13 s (1H), 3.14 m (2H, Cp), 2.30–2.39 m (2H, CH ₂), 2.07–2.10 m (3H, CH ₂ /≡CH), 0.68 s (3H, CH ₃)	153.8/151.6, 144.9/144.6, 144.5, 142.5/142.4, 141.9 (C _q), 135.1, 132.8, 132.3, 131.6, 129.8, 128.1, 127.4, 127.3, 127.3, 127.2, 126.9, 126.4, 126.3, 126.2, 126.1, 126.1, 125.7, 119.8, 119.4, 119.3 (Ar–CH) 85.3/85.1 (C _q , C=C), 68.6/68.5 (≡CH), 58.2/56.0 (CH), 43.0, 41.1, 41.0, 40.3, 38.7, 14.5/14.4 (CH ₂ /C _q /Brücke), 17.8/17.3 (CH ₃)	310 M ^{o+} (100) 295 M–Me (21) 165 Fluorenyl (42) (vinylic isomer)
27	6.79–7.88 m (8H, Ar–H), 6.08–6.63 m (4H, Ar–H), 4.19–4.23 m (1H), 3.41–3.54 m (1H), 2.77–3.02 m (2H, CH ₂), 1.90–2.17 m (3H, CH ₂ /≡CH), 0.71/0.80/0.86/0.88 s (3H, CH ₃)	153.0, 146.1, 146.0, 145.9, 145.9, 145.8, 145.8, 145.0, 145.0, 144.3, 144.2, 143.7, 143.5, 143.5, 143.4, 143.2 (C _q), 143.3, 138.2, 137.1, 134.2, 132.7, 132.0, 131.9, 131.6, 131.2, 126.8, 126.7, 126.5, 126.5, 126.5, 126.4, 126.2, 126.0, 125.4, 125.4, 125.3, 125.0, 124.9, 124.6, 124.5, 124.4, 124.3, 124.2, 124.1, 123.9, 123.7, 123.6, 123.4, 122.3, 122.2, 122.2, 122.1, 122.0, 122.0, 121.8, 121.7, 121.7, 121.6, 121.4, 121.3, 121.2, 121.0, 120.8, 120.5 (Ar–CH), 84.9/84.7 (C _q , C=C), 68.6/68.5 (≡CH), 58.3, 57.9, 57.3, 56.8, 55.7, 55.4, 55.2, 54.8 (CH), 43.4, 43.0, 39.3, 39.2, 38.9, 37.5, 29.0, 22.5 (CH ₂ /C _q /Brücke), 20.4/19.5/19.3/19.0 (CH ₃), 15.0/14.8/14.6/14.5 (CH ₂)	310 M ^{o+} (46) 295 M–Me (36) 195 M-fluorenyl (100)
28	7.55–7.96 m (4H, Ar–H), 7.19–7.43 m (6H, Ar–H), 6.92–7.03 m (1H, Ar–H), 6.22–6.35 m (1H, Ar–H), 4.70–4.76 m (1H), 3.38–3.52 m (1H), 2.28–3.18 m (2H, CH ₂), 1.88–2.17 m (3H, CH ₂ /≡CH) 0.66/0.60 s (3H, CH ₃)	153.1, 150.3, 148.6, 148.1, 146.4, 145.4, 144.9, 144.6, 143.3, 142.6, 142.5, 141.9 (C _q), 143.9, 143.8, 131.8, 131.4, 128.5, 127.3, 127.0, 126.8, 126.7, 126.7, 126.7, 126.4, 126.3, 126.3, 126.1, 126.0, 125.8, 125.6, 125.4, 125.3, 125.0, 124.9, 124.7, 124.6, 123.5, 122.3, 121.8, 121.7 (Ar–CH), 85.0/84.9 (C _q , C=C), 68.4/68.2 (≡CH), 54.9/54.8, 54.1/54.0 (CH), 52.8, 44.1, 42.7, 39.7, 37.3, 28.8 (CH ₂ /C _q /Brücke), 19.7 (CH ₃), 14.9/14.4 (CH ₂)	360 M ^{o+} (30) 195 M-fluorenyl (100) 165 Fluorenyl (78)

Table 8 (continued)

Compound	¹ H NMR	¹³ C NMR	MS [m/z]
29	13.80 s (br, 1H, OH), 8.62 s (1H, N=C–H), 7.71–7.79 m (3H, Ar–H), 7.53–7.61 m (4H, Ar–H), 7.22–7.43 m (6H, Ar–H), 6.88 t (1H, Ar–H), 3.90 s (2H, CH ₂), 1.49 s (9H, ^t Bu–CH ₃)	163.4 (N=C–H), 160.6, 147.8, 143.5, 143.2, 141.9, 141.0, 137.7, 121.9, 121.2, 119.0 (C _q), 132.7, 130.8, 130.8, 130.5, 128.1, 127.2, 126.9, 125.1, 121.3, 120.2, 119.8, 118.5 (Ar–CH), 91.2, 89.2 (C _q , C≡C), 36.2 (CH ₂), 34.9 (C _q), 29.4 (^t Bu–CH ₃)	441 M ^{o+} (32) 426 M–Me (10) 400 M–C ₃ H ₅ (9) 280 Flu–C≡C–Ph–NH (100)
30	13.88 s (br, 1H, OH), 8.62 s (1H, N=C–H), 7.24–7.55 m (10H, Ar–H), 6.91 t (1H, Ar–H), 6.48–6.63 m (1H, =CH), 3.75 m (2H, Ind–CH ₂), 3.53–3.61 m (1H, CH ₂), 3.48–3.52 m (1H, CH ₂), 1.53 s (9H, ^t Bu–CH ₃)	163.4 (N=C–H), 160.6, 147.7, 144.5, 144.2, 139.1, 137.7, 122.2, 119.0 (C _q), 132.8 (2C), 130.8, 130.6, 129.9, 126.2, 125.0, 123.9, 121.2 (2C), 118.9, 118.5 (Ar–CH), 87.5, 82.0 (C _q , C≡C), 37.7, 19.2 (CH ₂), 35.0 (C _q), 29.4 (^t Bu–CH ₃)	405 M ^{o+} (26) 390 M–Me (22) 362 M–C ₃ H ₇ (26) 290 M–indenyl (25) 115 Indenyl (100)
31	13.65 s (br, 1H, OH), 8.61 s (1H, N=C–H), 6.98–7.38 m (10H, Ar–H), 6.85 t (1H, Ar–H), 6.10–6.16 m (1H, =CH), 4.51 t (2H, CH ₂), 3.79–3.83 m (2H, CH ₂), 3.75 m (2H, Ind–CH ₂), 1.47 s (9H, ^t Bu–CH ₃)	163.1 (N=C–H), 160.6, 147.8, 145.0, 141.6, 138.0, 136.2, 122.2, 118.5 (C _q), 133.0 (2C), 130.4, 130.3, 128.7 (2C), 126.1, 125.7, 124.3, 123.6, 121.3, 119.4 (Ar–CH), 89.5, 83.5 (C _q , C≡C), 48.3, 38.3, 33.8 (CH ₂), 34.9 (C _q), 29.7 (^t Bu–CH ₃)	419 M ^{o+} (88) 404 M–Me (28) 376 M–C ₃ H ₇ (25) 128 Ind=CH ₂ (100)
32	13.81 s (br, 1H, OH), 8.63 s (1H, N=C–H), 7.25–7.58 m (14H, Ar–H), 6.88 t (1H, Ar–H), 6.13–6.16 m (1H, =CH), 3.91 m (2H, CH ₂), 3.36 m (2H, CH ₂), 1.47 s (9H, ^t Bu–CH ₃)	163.4 (N=C–H), 160.6, 147.9, 144.9, 144.5, 142.9, 139.9, 137.7, 121.8, 120.9, 119.0 (C _q), 132.7 (2C), 131.7 (2C), 131.0, 130.8, 130.6, 130.3, 129.0 (2C), 126.1, 124.7, 123.8, 121.3 (2C), 119.3, 118.5 (Ar–CH), 90.4, 88.7 (C _q , C≡C), 37.8, 34.4 (CH ₂), 34.9 (C _q), 29.3 (^t Bu–CH ₃)	481 M ^{o+} (100) 466 M–Me (52) 438 M–C ₃ H ₇ (52)
33	14.69 s (br, 1H, OH), 8.30 s (1H, N=C–H), 7.23–7.52 m (10H, Ar–H), 6.13–6.17 m (1H, =CH), 3.91 m (2H, CH ₂), 3.37 m (2H, CH ₂), 3.18–3.28 m (1H, N–CH), 1.81–1.85 m (4H, CH ₂), 1.26–1.69 m (6H, CH ₂), 1.46 s (9H, ^t Bu–CH ₃)	162.4 (N=C–H), 161.8, 144.9, 144.5, 143.0, 139.3, 138.1, 121.4, 118.5, 112.0 (C _q), 132.9, 132.5, 131.5 (2C), 130.3, 129.0 (2C), 126.1, 124.7, 123.8, 119.4 (Ar–CH), 89.5, 87.3 (C _q , C≡C), 67.2 (N–CH), 34.4 (C _q), 37.8, 35.0, 34.3 (2C) 25.5, 24.5 (2C) (CH ₂), 29.3 (CH ₃)	487 M ^{o+} (100) 472 M–Me (22) 436 M–C ₃ H ₅ (25) 404 M–cyclohexyl (13)
34	14.50 s (br, 1H, OH), 8.26 s (1H, N=C–H), 7.66–7.73 m (4H, Ar–H), 7.22–7.44 m (4H, Ar–H), 6.92–7.14 m (2H, Ar–H), 6.46–6.77 m (3H, Ar–H), 4.17 s (1H, Flu–H ⁹), 3.17–3.26 m (1H, N–CH), 3.05–3.13 m (2H, Cp–CH ₂), 2.12–2.38 m (4H, CH ₂), 1.78–1.84 m (4H, CH ₂), 1.22–1.70 m (6H, CH ₂), 1.40 s (9H, ^t Bu–CH ₃), 0.59 s (3H, CH ₃)	162.4 (N=C–H), 160.9, 151.6, 144.9, 144.6, 142.4, 141.8, 137.7, 118.4, 112.6 (C _q), 134.9, 132.8, 132.6, 132.4, 128.0, 127.1, 127.0, 126.8, 126.1, 126.0, 125.9, 119.6, 119.1 (Ar–CH), 88.2, 80.4 (C _q , C≡C), 67.3 (N–CH), 56.0 (Flu–CH) 43.0, 34.8 (C _q), 46.0, 41.0, 34.3 (2C), 25.5, 24.4 (2C), 15.3 (CH ₂), 29.2, 17.2 (CH ₃)	567 M ^{o+} (34) 402 M–Flu (89) 346 M–Flu–C ₄ H ₈ (43) 165 Flu (100)
35	14.48 s (br, 1H, OH), 8.24 s (1H, N=C–H), 7.45–7.84 m (5H, Ar–H), 7.27–7.40 m (4H, Ar–H), 6.89–7.21 m (5H, Ar–H), 6.26 m (1H, =CH), 4.18 s (1H, Flu–H ⁹), 3.87–3.94 m (1H, N–CH), 3.05–3.24 m (2H, Ind–CH ₂), 2.60–2.91 m (2H, CH ₂), 2.05–2.17 m (2H, CH ₂), 1.77–1.85 m (4H, CH ₂), 1.16–1.70 m (6H, CH ₂), 1.39 s (9H, ^t Bu–CH ₃), 0.56 s (3H, CH ₃)	162.6 (N=C–H), 160.6, 151.8, 144.9, 144.7, 144.5, 143.9, 142.1, 141.5, 137.7, 118.9, 104.9 (C _q), 132.4, 131.4, 128.5, 127.0, 126.8, 126.7, 126.3, 126.1, 125.5, 125.4, 125.3, 124.5, 122.2, 119.3, 118.7 (Ar–CH), 87.8, 80.6 (C _q , C≡C), 67.3 (N–CH), 54.9 (Flu–CH), 44.1, 34.8 (C _q), 44.0, 39.7, 34.3 (2C), 25.5, 24.4 (2C), 15.9 (CH ₂), 29.2, 14.9 (CH ₃)	617 M ^{o+} (16) 452 M–Flu (59) 296 M–Flu–Me–C(Ind)–CH ₂ (18) 165 Flu (100)
36	14.46 s (br, 1H, OH), 8.26 s (1H, N=C–H), 7.64–7.88 m (4H, Ar–H), 7.28–7.50 m (5H, Ar–H), 6.52–7.17 m (4H, Ar–H), 4.22 s (1H, Flu–H ⁹), 3.77 m (1H, N–CH), 3.13–3.20 m (2H, Cp–CH ₂), 2.57–2.73 m (2H, CH ₂), 2.18–2.51 m (2H, CH ₂), 1.65–2.13 m (8H, CH ₂), 1.51 s (9H, ^t Bu–CH ₃), 0.69 s (3H, CH ₃)	162.6 (N=C–H), 160.6, 151.7, 144.9, 144.7, 142.5, 141.9, 137.7, 118.3, 113.0 (C _q), 134.9, 132.9, 132.7, 132.5, 128.0, 127.3, 127.1, 126.9, 126.2, 126.1, 126.0, 119.7, 119.2 (Ar–CH), 88.3, 80.6 (C _q , C≡C), 69.9 (N–CH), 56.1 (Flu–CH) 43.1, 35.0 (C _q), 46.3, 41.1, 34.8 (2C), 24.5 (2C), 15.4 (CH ₂), 29.4, 17.4 (CH ₃)	553 M ^{o+} (37) 388 M–Flu (100) 332 M–Flu–C ₄ H ₈ (48) 282 M–Flu–Me–C(Cp)–CH ₂ (30)
37	13.91 s (br, 1H, OH), 8.66 s (1H, N=C–H), 7.59–7.79 m (6H, Ar–H), 7.18–7.53 m (12H, Ar–H), 6.91–7.14 m (3H, Ar–H), 6.50–6.82 m (2H, Ar–H), 4.20 s (1H, Flu–H ⁹), 3.13–3.22 m (2H, Cp–CH ₂), 2.18–2.37 m (4H, CH ₂), 0.65 s (3H, CH ₃)	162.5 (N=C–H), 158.5, 151.6, 147.0, 144.8, 144.6, 142.4, 141.9, 137.6, 130.1, 122.9, 119.3 (C _q), 135.0, 134.3, 132.8, 132.7, 131.8, 129.4 (2C), 128.2 (2C), 128.1, 127.3, 127.2, 127.2, 127.1, 126.8, 126.2, 126.1, 126.0, 121.2 (2C), 119.7, 119.2 (2C) (Ar–CH), 91.8, 80.2 (C _q , C≡C), 56.0 (Flu–CH), 38.6 (C _q), 43.0, 41.1, 15.3 (CH ₂) 17.3 (CH ₃)	581 M ^{o+} (19) 416 M–Flu (71) 310 M–Flu–Me–C(Cp)–CH ₂ (18) 165 Flu (100)
38	13.62 s (br, 1H, OH), 8.46 s (1H, N=C–H), 7.53–7.80 m (4H, Ar–H), 6.50–7.46 m (13H, Ar–H), 4.18 s (1H, Flu–H ⁹), 2.89–3.18 m (3H, CH/Cp–CH ₂), 2.13–2.45 m (4H, CH ₂), 1.78–1.98 m (4H, CH ₂), 1.18–1.57 m (6H, CH ₂), 0.65 s (3H, CH ₃)	161.5 (N=C–H), 157.3, 151.6, 146.8, 144.8, 144.6, 142.4, 141.9, 138.0, 123.6, 123.1, 119.2 (C _q), 135.0, 132.8, 132.7 (2C), 130.4, 128.6, 127.3, 127.2, 127.1, 126.8, 126.2, 126.1, 126.0, 126.2, 126.1, 126.0, 121.2 (2C), 119.7, 119.2 (2C) (Ar–CH), 92.2, 80.1 (C _q , C≡C), 56.0 (Flu–CH), 38.6 (C _q), 43.0, 41.0, 32.8 (2C), 26.9 (2C), 26.4, 15.4 (CH ₂), 36.7 (CH), 17.3 (CH ₃)	621 M ^{o+} (20) 456 M–Flu (39) 165 Flu (100)

(continued on next page)

Table 8 (continued)

Compound	¹ H NMR	¹³ C NMR	MS [<i>m/z</i>]
39	13.93 s (br, 1H, OH), 8.60 s (1H, N=C–H), 7.59–7.82 m (4H, Ar–H), 7.28–7.53 m (8H, Ar–H), 7.09–7.22 m (2H, Ar–H), 6.54–7.01 m (4H, Ar–H), 4.21 s (1H, Flu–H ⁹), 3.07–3.21 m (2H, Cp–CH ₂), 2.18–2.46 m (4H, CH ₂), 1.56 s (9H, ^t Bu–CH ₃), 0.69 s (3H, CH ₃)	163.2 (N=C–H), 160.6, 151.6, 147.4, 144.9, 144.6, 142.5, 141.9, 137.7, 122.6, 119.1 (C _q), 135.0, 132.9, 132.7 (2C), 130.8, 127.3, 127.2, 127.1, 126.8, 126.6, 126.3, 126.1, 126.0, 121.5, 121.2 (2C), 119.7, 118.5 (Ar–CH), 91.9, 80.3 (C _q , C≡C), 56.1 (Flu–CH), 38.7, 35.0 (C _q), 43.1, 41.1, 15.5 (CH ₂), 29.5, 17.4 (CH ₃)	561 M ^{o+} (24) 396 M–Flu (100) 290 M–Flu–Me–C(Cp)–CH ₂ (14) 165 Flu (30)
40	13.73 s (br, 1H, OH), 8.58 s (1H, N=C–H), 7.67–7.82 m (2H, Ar–H), 6.70–7.54 m (14H, Ar–H), 6.45 t (1H, Ar–H), 4.55–4.70 m (2H, Cp–CH ₂), 3.39–3.56 m (2H, Cp–CH ₂), 2.66–3.01 m (2H, CH ₂), 2.09–2.41 m (2H, CH ₂), 1.46 s (9H, ^t Bu–CH ₃), 1.25 s (3H, CH ₃)	163.7 (N=C–H), 160.5, 153.0, 150.1, 148.1, 146.1, 145.0, 143.3, 137.7, 118.9, 105.1 (C _q), 143.3, 138.4 (2C), 132.6, 131.9, 131.6, 130.8, 126.8, 126.7, 126.1, 125.2, 123.9, 123.6, 123.1 (2C), 122.0, 121.2, 118.5 (Ar–CH), 91.3, 80.5 (C _q , C≡C), 57.8 (Ind–CH), 38.8, 34.9 (C _q), 51.9, 39.3, 26.9 (CH ₂), 29.3, 20.3 (CH ₃)	561 M ^{o+} (18) 546 M–Me (4) 446 M–Ind (26) 290 M–Me–C(Ind) ₂ –CH ₂ (27) 115 Ind (37)
41	13.84 s (br, 1H, OH), 8.60 s (1H, N=C–H), 7.90–8.10 m (1H, Ar–H), 7.52–7.79 m (4H, Ar–H), 7.06–7.48 m (13H, Ar–H), 6.89 t (1H, Ar–H), 6.07–6.14 m (1H, =CH), 4.21 s (1H, Flu–H ⁹), 2.60–3.50 m (4H, CH ₂), 2.06–2.37 m (2H, CH ₂), 1.50 s (9H, ^t Bu–CH ₃), 0.72 s (3H, CH ₃)	163.2 (N=C–H), 160.6, 153.1, 148.2, 145.5, 144.7, 143.6, 142.5, 141.9, 137.7, 122.5, 119.0, 105.0 (C _q), 132.8, 132.6 (2C), 131.9, 130.7, 130.6, 127.3, 127.0, 126.7, 126.4, 126.3, 126.1, 125.9, 124.9, 124.6, 121.9, 121.2, 121.1 (2C), 119.8, 119.1, 118.5 (Ar–CH), 91.7, 80.2 (C _q , C≡C), 54.2 (Flu–CH), 44.1, 34.9 (C _q), 39.7, 37.3, 15.5 (CH ₂), 29.4, 14.2 (CH ₃)	611 M ^{o+} (7) 446 M–Flu (31) 431 M–Flu–Me (15) 290 M–Flu–Me–C(Ind)–CH ₂ (26) 165 Flu (100)

3.3. GC/MS

GC/MS spectra were recorded with a HP 5890 gas chromatograph in combination with a HP 5971A mass detector. A 12 m J&W Scientific fused silica column (DB1, diameter 0.25 mm, film 0.33 μm, flow 1 ml/min) respectively 25 m J&W Scientific fused silica column (DB5ms, diameter 0.25 mm, film 0.33 μm, flow 1 ml/min) were used, helium (4.6) was applied as carrier gas. Using a 12 m column the routinely performed temperature program started at 70 °C (2 min). After a heating phase of 11 min (20 K/min, final temperature 290 °C) the end temperature was held for a variable time (plateau phase).

At the Zentrale Analytik of the University of Bayreuth, GC/MS spectra were routinely recorded with a HP5890 gas chromatograph in combination with a MAT 95 mass detector.

3.4. Gas chromatography

For the analysis of organic compounds, especially oligomer mixtures, a PERKIN ELMER Auto System gas chromatograph (column: HP1, 28 m, diameter 0.32 mm/carrier gas helium, flow 5.7 ml/min, split 3.5 ml/min) was used. The standard temperature program contained a starting phase at 50 °C (3 min), a heating phase of 50 min (heating rate 4 K/min, final temperature 250 °C) and a plateau phase at 250 °C (37 min).

3.5. Gel permeation chromatography (GPC)

GPC measurements were routinely performed by SABIC Company (Riyadh, Saudi Arabia).

3.6. Elemental analysis

Some of the analyses were performed by the Mikroanalytisches Labor Pascher at Remagen.

The residual analyses were performed with a VarioEl III CHN instrument. For this purpose 4–6 mg of the complex were weight into a standard tin pan. The tin pan was carefully closed and introduced into the auto sampler of the instrument.

The raw values of the carbon, hydrogen, and nitrogen contents were multiplied with calibration factors (calibration compound: acetamide).

3.7. Synthesis of the substituted salicylaldehydes 1–4

To 50 mmol of the appropriate phenol derivative in 40 ml of tetrahydrofuran was added dropwise a 3-molar methylmagnesium bromide solution (18.5 ml; 55.5 mmol) in diethyl ether. After 2 h of stirring at room temperature, gas evolution ceased. About 90% of the solvent were removed in vacuo and toluene (100 ml), triethylamine (10 ml), and paraformaldehyde (3.75 g; 125 mmol) were added. The mixture was heated to 88 °C and held at this temperature for 2 h. After cooling to room temperature, the yellow solution was poured into cold hydrochloric acid (1 M, 250 ml). The organic phase was separated and dried over sodium sulfate. After removal of the solvent in vacuo, 3-*tert*-butyl salicylaldehyde (**1**) and 3-cyclohexyl salicylaldehyde (**3**) were purified by high vacuum distillation. 3-Phenyl salicylaldehyde (**2**) and 3-cyclo-hexyl-5-chlorosalicylaldehyde (**4**) were recrystallized from ethanol or *n*-pentane at –20 °C. Yields: 59–88%.

3.8. Synthesis of 3-*tert*-butyl-5-iodosalicylaldehyde (**5**)

3-*tert*-Butyl salicylaldehyde (8.4 mmol) was dissolved in 100 ml of a mixture of methanol and methylene chloride (3:7). Benzyltrimethylammonium dichloroiodate (3.23 g; 9.2 mmol) and water free calcium carbonate (1.1 g; 11 mmol) were added. After 2 h, the excess calcium carbonate was filtered off. After removal of about 80% of the solvent, 20 ml of a sodium hydrogensulfite solution (5%) was added decolourizing the mixture. Extraction with diethyl ether, drying over sodium sulfate and removal of the solvent yielded the aldehyde as raw product. Purification by recrystallization from *n*-pentane furnished 3-*tert*-butyl-5-iodosalicylaldehyde in a 48% yield as yellow crystals which are slightly light sensitive and should be stored in the dark.

3.9. Synthesis of the alkyl or halogen substituted phenoxyimine compounds

An amount of 15 mmol of the appropriate aldehyde derivative was dissolved in 150 ml of toluene. After addition of a substituted amine or aniline (1.2 equiv.) and a few crystals of *para*-toluenesulfonic acid, the reaction mixture was stirred under reflux for 3 h applying a Dean-Stark-trap. After cooling to room temperature, sodium hydrogencarbonate (150 ml) was added. The organic phase was separated and filtered over sodium sulfate and silica. Removing the solvent and recrystallization from ethanol at -20°C yielded the phenoxyimine compounds. Yields: 70–98%.

3.10. Synthesis of the alkynyl functionalized phenoxyimine compounds

The substituted salicylaldehyde (15 mmol), propargylamine (17 mol), and molecular sieves (3 Å, 15 g) were dissolved in 100 ml of toluene and stirred at room temperature for 3 days. After filtration over sodium sulfate and removal of the solvent, the residue was extracted several times with *n*-pentane. The solution was filtered again over sodium sulfate, and the solvent was removed. The phenoxyimine compounds were obtained as yellow or brownish powders. Yields: 24–40%. If 4-ethynylaniline was used as amine component, ethanol was applied as a solvent. Yield: 65%.

3.11. Synthesis of the indene derivatives **16–18**

Indenyllithium (50 mmol) was suspended in 200 ml of toluene. The appropriate alkylation reagent (50 mmol) was added, and the reaction mixture was stirred at room temperature over night. Filtration over sodium sulfate and removal of the solvent in vacuo yielded the title compounds as bright yellow viscous oils (90–95%). Compound **18** was obtained as a white powder and purified by recrystallization from *n*-pentane. Yield: 89%.

3.12. Synthesis of 1-(4-ethynylbenzyl)indene (**20**) and 2-ethynylfluorene (**22**)

1-(4-Iodobenzyl)indene (6 mmol) or 2-iodofluorene (6 mmol) were dissolved in 30 ml of triethylamine. Bis(triphenylphosphino)palladium dichloride (83 mg, 0.12 mmol), copper(I) iodide (45 mg, 0.24 mmol), and trimethylsilylacetylene (7 mmol) or 2-methylbut-3-yn-2-ol (1 ml, 7 mmol) were added, and the reaction mixture was stirred for 20 h at room temperature. After removal of the solvent, water (50 ml) and *n*-pentane (50 ml) were added. The organic phase was separated, and the aqueous phase was extracted with *n*-pentane. The combined organic phases were dried over sodium sulfate. Removal of the solvent in vacuo and recrystallization from *n*-pentane furnished 1-(4-trimethylsilylethynylbenzyl)indene (**19**), respectively, 4-(2-fluorenyl)-2-methylbut-3-yn-2-ol (**21**). Yields: 85–90%.

The protected compounds **19** or **21** (5 mmol) were dissolved in 100 ml of a mixture of methanol and methylene chloride (4:1). Anhydrous potassium carbonate (7.5 mmol) was added. After 2 h of stirring at room temperature, the mixture was filtered over sodium sulfate, and the solvent was removed in vacuo. The raw products were purified by column chromatography (ethyl acetate/*n*-pentane 3:7). Yields: 80–85%.

3.13. Synthesis of 5-hexyn-2-one (**23**)

2,4-Pentanedione (100 g, 103 ml, 1 mol), anhydrous potassium carbonate (152 g, 1.1 mol), and propargylchloride (71 g, 69 ml, 0.95 mol) were dissolved in 500 ml of ethanol. The reaction mixture was stirred under reflux for 24 h. After cooling to room temperature, 300 ml of water were added. The mixture was then extracted with diethyl ether, and the organic phase was washed with brine and dried over sodium sulfate. Removal of the solvent and subsequent vacuum distillation yielded 5-hexyn-2-one as colourless liquid in 48% yield.

3.14. Synthesis of the alkynyl fulvenes **24** and **25**

Cyclopentadiene (125 mmol) or indene was dissolved in 50 ml of methanol. 5-Hexyn-2-one (50 mmol) and pyrrolidine (75 mmol) were added. The mixture was stirred for 24 h at 40°C . Glacial acetic acid (100 mmol), water (150 ml) and *n*-pentane (150 ml) were introduced into the reaction mixture. The organic phase was separated and dried over sodium sulfate. Vacuum distillation yielded the desired compounds as yellow oils (47–75%).

3.15. Synthesis of the C_1 -bridged ligand precursors **26–28**

Indene or fluorene (30 mmol) was dissolved in 100 ml of diethyl ether and reacted with *n*-butyllithium (1.6 M, 18.75 ml, 30 mmol). After 8 h, the desired fulvene derivative (30 mmol) was added, and the mixture was stirred for 2 h at room temperature. Hydrolysis was performed

Table 9
MS and elemental analysis data of the zirconium complexes **42–56**

Complex	MS (<i>m/z</i>)	C _{exp} (%)	C _{theor} (%)	H _{exp} (%)	H _{theor} (%)	N _{exp} (%)	N _{theor} (%)
42	918 M ^{o+} (67), 881 M–Cl (99), 866 M–Cl–Me (29)	44.3	44.5	3.79	3.73	3.00	3.05
43	714 M ^{o+} (54), 677 M–Cl (11), 661 M–Cl–H–Me (100)	64.0	63.8	5.07	5.08	3.83	3.92
44	590 M ^{o+} (66), 553 M–Cl (42) 537 M–(<i>N</i> -propynyl)/M–Cl–H–Me (100)	56.3	56.9	5.54	5.46	4.87	4.74
45	902/904 M ^{o+} (5), 865 M–Cl (6), 777 M–I (11), 742 M–I–Cl (12)	42.2	42.6	4.78	4.69	3.07	3.10
46	930 M ^{o+} (43), 895 M–Cl (13), 879 M–Cl–H–Me (14) 545 M-ligand (20)	43.2	43.9	4.94	4.98	2.92	3.01
47	958 M ^{o+} (60), 921 M–Cl (97), 832 M–I (68), 795 M–I–Cl (100)	47.8	47.6	2.81	2.73	2.89	2.92
48	630 M ^{o+} (2), 595 M–Cl (2), 553 M-phenyl (3)	60.1	60.9	3.93	3.84	4.38	4.44
49	970 M ^{o+} (88), 933 M–Cl (59), 566 M-ligand (33)	47.8	47.0	3.90	3.95	2.77	2.89
50	1038 M ^{o+} (100), 1003 M–Cl (50), 912 M–I (13), 600 M-ligand (69)	43.5	43.9	3.40	3.49	2.63	2.69
51	710 M ^{o+} (100), 675 M–Cl (43), 637 M–2Cl–H (25), 436 M-ligand (44)	54.6	54.0	4.69	4.82	3.94	3.94
52	1042 M ^{o+} (1), 1027 M–Me (1), 951 M–Cl–C ₄ H ₈ (2), 601 M–1 ligand–H (100)	72.8	73.7	5.16	5.02	2.79	2.68
53	970 M ^{o+} (2), 955 M–Me (5), 935 M–Cl (2), 115 indenyl (100)	n.b.	71.7	n.b.	5.40	n.b.	2.88
54	1122 M ^{o+} (5), 957 M–2 indenyl–Cl (6), 641 M–1 ligand–H (8)	73.9	74.8	5.45	5.38	2.56	2.49
55	998 M ^{o+} (1), 883 M-indenyl (2), 735 M–2 indenyl–Cl (2)	71.5	72.1	5.74	5.65	2.74	2.80
56	1134 M ^{o+} (1), 1078 M–C ₄ H ₈ (2), 630 M-ligand–Me (2), 487 ligand (19)	73.3	74.0	6.52	6.39	2.48	2.47

Table 10
MS, ¹H NMR, and elemental analysis data of the zirconium complexes 57–64

Complex	¹ H NMR (ppm)	MS (<i>m/z</i>)	C _{exp} (%)	C _{theor} (%)	H _{exp} (%)	H _{theor} (%)	N _{exp} (%)	N _{theor} (%)
57	8.30, 8.28, 8.26 s (2H, N=C–H), 7.68–8.01 m (4H, Ar–H), 7.43–7.51 m (4H, Ar–H), 7.31–7.08 m (3H, Ar–H), 6.48–6.81 m (2H, Ar–H), 5.75–6.03 m (4H, Cp), 5.27–5.59 m (4H, Cp), 3.64–3.78 m (2H, N–CH), 2.94–3.23 m (6H, CH ₂), 2.60–2.77 m (2H, CH ₂), 2.19 s (br, 6H, CH ₃), 1.80–1.93 m (8H, CH ₂), 1.48–1.74 m (12H, CH ₂), 1.40, 1.38, 1.36, 1.29, 1.24 s (18H, ^t Bu–CH ₃)	1616 M ^{o+} (0), 1451 M–Flu (2), 1403 M–Zr–3 Cl–Me (2), 1286 M–2 Flu (2), 1049 M–ligand (3), 165 Flu (100)	61.2	60.9	5.31	5.24	1.68	1.73
58	8.27 s (br, 2H, N=C–H), 7.87–8.14 m (4H, Ar–H), 7.51–7.76 m (8H, Ar–H), 6.97–7.48 m (12H, Ar–H), 6.42–6.61 m (4H, Ar–H), 5.63–5.89 m (4H, Cp), 5.17–5.48 m (4H, Cp), 3.54–3.81 m (2H, N–CH), 2.62–3.06 m (8H, CH ₂), 2.13 s (br, 6H, CH ₃), 1.76–2.11 m (16H, CH ₂), 1.40, 1.24, 1.21 s (br, 18H, ^t Bu–CH ₃)	1718 M ^{o+} (0), 1198 M–2 Zr–4 Cl–Flu (2), 1004 M–ligand–cyclohexyl–Me (3), 967 M–Cl–ligand–cyclohexyl–Me (4), 165 Flu (100)	62.5	63.0	5.12	5.17	1.53	1.63
59	8.24 s (br, 2H, N=C–H), 7.51–8.07 m (4H, Ar–H), 7.14–7.43 m (10H, Ar–H), 6.91–7.06 m (4H, Ar–H), 6.46–6.72 m (2H, Ar–H), 5.92–6.19 m (4H, Cp), 5.47–5.64 m (4H, Cp), 3.72 m (2H, N–CH), 2.87–3.10 m (4H, CH ₂), 2.48–2.69 m (4H, CH ₂), 1.61–2.37 m (8H, CH ₂), 2.19 s (br, 6H, CH ₃), 1.38, 1.24 s (br, 18H, ^t Bu–CH ₃)	1588 M ^{o+} (0), 1431 M–Flu (2), 1264 M–2 Zr–4 Cl (2), 1035 M–ligand (2), 870 M–ligand–ZrCl ₂ (3), 165 Flu (100)	61.0	60.4	5.40	5.32	1.85	1.76
60	8.73, 8.71, 8.67 s (2H, N=C–H), 7.54–7.93 m (12H, Ar–H), 7.18–7.49 m (18H, Ar–H), 6.79–7.08 m (8H, Ar–H), 6.50–6.78 m (2H, Ar–H), 5.69–6.03 m (4H, Cp), 5.21–5.52 m (4H, Cp), 2.61–3.07 m (4H, CH ₂), 2.18–2.39 m (4H, CH ₂), 2.15 s (br, 6H, CH ₃)	1642 M ^{o+} (0), 1318 M–2 Zr–4 Cl (2), 1291 M–Zr–3 Cl–2 phenyl (2), 1248 M–2 Zr–6 Cl (2), 1167 M–3 Cl–Zr–(Me)C(Flu)(Cp)CH ₂ (5)	62.9	62.8	4.05	3.92	1.61	1.70
61	8.55, 8.52 s (2H, N=C–H), 7.60–7.98 m (8H, Ar–H), 7.12–7.43 m (18H, Ar–H), 6.52–7.09 m (2H, Ar–H), 5.93–6.27 m (4H, Cp), 5.28–5.33 m (4H, Cp), 2.89–3.10 m (4H, CH), 2.48–2.83 m (4H, CH ₂), 2.15, 2.22, 2.30 s (6H, CH ₃), 1.74–1.88 m (8H, CH ₂), 1.21–1.48 m (12H, CH ₂)	1726 M ^{o+} (0), 1448 M–Zr–3Cl–C ₆ H ₉ (2), 1412 M–Zr–4Cl–C ₆ H ₁₀ (2), 165 Flu (100)	59.6	59.9	4.41	4.32	1.59	1.62
62	8.61, 8.59 s (br, 2H, N=C–H), 7.85–8.17 m (2H, Ar–H), 7.53–7.83 m (6H, Ar–H), 7.22–7.29 m (12H, Ar–H), 6.78–7.15 m (8H, Ar–H), 6.43–6.72 m (2H, Ar–H), 5.85–6.14 m (4H, Cp), 5.44–5.57 m (4H, Cp), 3.08–3.24 m (4H, CH ₂), 2.49–3.06 m (4H, CH ₂), 2.23, 2.21, 2.18 s (br, 6H, CH ₃), 1.46, 1.44, 1.43, 1.42, 1.39, 1.30, 1.28, 1.25, 1.23 s (18H, ^t Bu–CH ₃)	1602 M ^{o+} (0), 1587 M–Me (2), 816 M–ZrCl ₂ –ligand–C ₄ H ₈ (2), 803 M–Zr–4 Cl–ligand (3), 734 M–Zr–4 Cl–ligand–C ₄ H ₈ (2), 165 Flu (100)	62.0	61.4	4.66	4.53	1.64	1.75
63	8.56 s (br, 2H, N=C–H), 7.63–7.74 m (4H, Ar–H), 7.09–7.54 m (16H, Ar–H), 6.69–7.03 m (10H, Ar–H), 6.29–6.51 m (4H, Ar–H), 5.91–6.17 m (2H, Ar–H), 2.97–3.22 m (6H, CH ₂), 2.26–2.51 m (2H, CH ₂), 2.13 s (6H, CH ₃), 1.46, 1.42, 1.39, 1.38, 1.36, 1.33, 1.26, 1.23, 1.22 s (18H, ^t Bu–CH ₃)	1600 M ^{o+} (1), 1585 M–Me (2), 720 M–2 Zr–4 Cl–ligand (2)	62.1	61.4	4.61	4.53	1.66	1.75
64	8.35, 8.33, 8.19 s (2H, N=C–H), 7.76–7.79 m (2H, Ar–H), 7.52–7.74 m (8H, Ar–H), 7.06–7.36 m (22H, Ar–H), 6.61–7.02 m (6H, Ar–H), 6.38–6.53 m (2H, Ar–H), 6.16–6.28 m (2H, =CH), 2.41–3.45 m (6H, CH ₂), 2.03–2.29 m (2H, CH ₂), 2.11 s (6H, CH ₃), 1.53, 1.50, 1.46, 1.45, 1.43, 1.40, 1.32, 1.26, 1.22 s (18H, ^t Bu–CH ₃)	1706 M ^{o+} (0), 1117 M–Zr–3 Cl–Flu–2 Ind (2), 1050 M–2 Zr–4 Cl–2 Flu (3) 165 Flu (100)	62.8	63.4	4.58	4.50	1.57	1.64

If there are more signals for the same group of protons in the ¹H NMR spectra due to the presence of isomers, the sum of the corresponding integral values is given.

adding 50 ml of water. Separation of the organic phase and removal of the solvent yielded raw products which were recrystallized from *n*-pentane at -20°C . Yields: 32–73%.

3.16. General procedure for the Sonogashira coupling reactions of phenoxyimine compounds with indene and fluorene derivatives

In 15 ml of triethylamine, an amount of 1.0 mmol of the phenoxyimine compound, 1.0 mmol of a substituted indene or fluorene derivative, bis(triphenylphosphino)-palladium dichloride (0.01 mmol) and copper(I) iodide (0.02 mmol) were dissolved. The mixture was stirred for 20 h at room temperature. After removal of the solvent, water (50 ml) and *n*-pentane (50 ml) were added. The organic phase was separated, and the aqueous phase was extracted several times with *n*-pentane. The combined organic phases were dried over sodium sulfate. Removal of the solvent in vacuo, purification by column chromatography, and recrystallization from *n*-pentane gave the coupling products as yellowish or orange brown powders (yields: 68–95%).

3.17. Synthesis of the mononuclear zirconium complexes 42–56

An amount of 1.2 mmol of the desired phenoxyimine compound was dissolved in 30 ml of tetrahydrofuran. Potassium hydride (48 mg; 1.2 mmol; 1 equiv.), suspended in 10 ml of tetrahydrofuran, was added, and the mixture was stirred at room temperature for 1 h till the hydrogen evolution had ceased. Zirconium tetrachloride (140 mg; 0.6 mmol; 0.5 equiv.) was added and stirring was continued for 20 h. After the solvent was removed in vacuo, methylene chloride (30 ml) was added, and the solution was filtered over sodium sulfate. Removal of about 25 ml of the solvent in vacuo and subsequent addition of 50 ml of *n*-pentane resulted in the precipitation of the zirconium complexes. Decantation of the mother liquor, washing with *n*-pentane (3×15 ml), and drying in vacuo furnished the complexes as yellow or brownish powders. Yields: 57–92% (Table 8).

3.18. Synthesis of the trinuclear zirconium complexes 57–64

An amount of 0.4 mmol of the appropriate ligand precursor 34–41 was dissolved in 30 ml of tetrahydrofuran. Potassium hydride (48 mg; 1.2 mmol; 3 equiv.), suspended in 10 ml of tetrahydrofuran, was added, and the mixture was stirred at room temperature for 1 h till the hydrogen evolution had ceased. Zirconium tetrachloride (140 mg; 0.6 mmol; 1.5 equiv.) was added and stirring was continued for 20 h. After the solvent was removed in vacuo, methylene chloride (30 ml) was added, and the solution was filtered over sodium sulfate. Removal of about 25 ml of the solvent in vacuo and subsequent addition of 50 ml of *n*-pentane resulted in the precipitation of the zirconium complexes. The overstanding solution was decanted. The

complexes were washed with *n*-pentane (3×15 ml) and dried in vacuo furnishing yellow or brownish powders. Yields: 30–92%. MS and elemental analysis data of the complexes 42–64 are given in Table 9.

3.19. Polymerization of ethylene in the 1l Büchi autoclave

The desired zirconium complex (1–5 mg) was suspended in 5 ml of toluene. The mixture was transferred to a 1l Schlenk flask filled with 250 ml *n*-pentane. This mixture was transferred to a 1l Büchi laboratory autoclave under inert atmosphere. An ethylene pressure of 1 bar was applied for 5 min. Methylalumoxane (30% in toluene, Zr:Al = 1:500) was added via a cannula, and the autoclave was thermostated to 35°C applying an ethylene pressure of 10 bar over 1 h. The resulting polymer was filtered off over a glass frit, washed with diluted hydrochloric acid, water, and acetone, and finally dried in vacuo.

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