Salicylidene-imine–Zirconium(IV) Complexes in Combination with Methylalumoxane as Catalysts for the Conversion of Hexa-1,5-diene: Adjusting of the Catalytic Activity

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Dedicated to Professor Egon Uhlig on the Occasion of his 70th Birthday

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Abstract. A variety of substituted Schiff base complexes of the composition ("salen")$ZrCl_2$(thf) (**1**–**21**) were synthesized, with methylalumoxane ("MAO") activated and used for a systematic study of their catalytic activity towards hexa-1,5-diene ("salen": substituted salicylidene–ethylene-iminato ligands). Main product of the catalytic cycle is methylenecyclopentane. Dimers are only formed in minor amounts. The catalytic activity and selectivity of the Ziegler–Natta systems strongly depend on the nature and the position of the peripheric substituents in the Schiff base ligands. Electron-withdrawing substituents in *para*-position to the phenolato oxygen (5-position) decrease the catalytic activity. Improved activity and selectivity were obtained with electron-donating substituents in 5-position. Altering the ethylene bridge causes a lowering of the activity or inactivation. According to the X-ray analysis the metal center in the related complex (L)$ZrCl_2$ (**22**) (L: *N′*,*N′*-bis(ethylene)-*N′*-methyl-*N*,*N″*-bis(benzoylacetonatoimine) has a pentagonal-bipyramidal environment. The pentadentate Schiff base ligand lies in the plane, and both chloro groups occupy the axial positions. In contrast to the catalytically active salene complexes **22** can not rearrange to form a species in which the both chlorides are *cis* to each other. Consequently **22** is catalytically inactive.

Over the last decade enormous efforts and progress have been made in the investigation of metallocene-type catalysts of group IV: The discovery that methylalumoxanes (MAO) promote the formation of highly active cationic species, the design of "single site" catalysts for the polymerization of 1-olefines, the isolation of cationic species involving $[Cp_2M\text{-}R]^+$ cations, which are responsible for the catalytic reactivity, the tuning of the catalytic reactivity by adjusting the ligands, and the development of industrial processes are some examples for this rapidly growing field [1–5].

Most recently group IV metal complexes that contain inorganic donor sets have been to focus attention as potential catalysts [2, 6–34]. However, the coordination chemistry and organometallic chemistry of these compounds is more complicated and much less developed than the metallocene chemistry. Especially, the understanding of the controlling effects of ligands containing an inorganic donor set in group IV metal catalysts is not well understood. This might be the most important problem in the development of new highly active and selective group IV catalysts containing anionic ancillary ligands having for example *N* or *O* donor atoms.

In this paper we report on the catalytic conversion of hexa-1,5-diene by a number of MAO-activated (salicylidene-ethylene-imine)Zr(IV)(thf) complexes in which a N_2–O_2 donor set is coordinated as four-dentate chelate ligand opening the possibility to study the electronic and steric influence of peripheric groups on the catalytic reactivity.

Our aim was to get a deeper insight into the possibility to control the catalytic reactivity of the metal center depending on the coordinative environment. Since the catalytic conversion of hexa-1,5-diene was a slow reaction it was also possible to indicate the starting steps of the catalysis.

Catalytic Reactions of (Salen)$ZrCl_2$(thf)/MAO with Hexa-1,5-diene

For the preparation of the Zr(IV) complexes **1**–**21** the quadridentate Schiff base *N*,*N′*-ethylene-bis(salicylideneimine) ("salen") ligands were treated with two equivalents *n*-butyl-lithium to form the lithium salts. Reaction with $ZrCl_4(thf)_2$ at ambient temperature resulted in the formation of the Zr(IV) complexes which could be isolated in excellent yields from THF.

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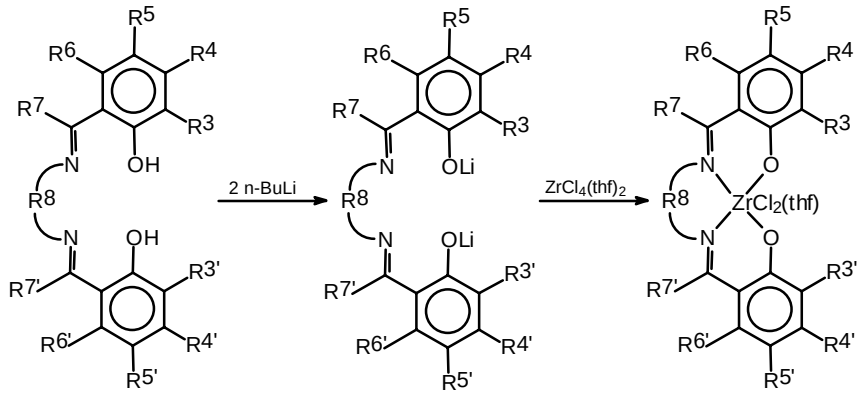
Scheme 1 shows the general structure and the variation of the complexes used as precursors in the catalytic reaction.

The structures of a small number of Ti(IV) and Zr(IV)-complexes with quadridentate Schiff base ligands were determined by X-ray structural analysis. Whereas titanium complexes have a distorted octahedral structure in the compounds (acen)$TiCl_2$ and (salen)TiX_2 [28, 29, 35–38, 41], the structures of the Zr and Hf analogues are variable: Adducts with THF show a pentagonal-bipyramidal structure with both chloro ligands in axial positions and THF together with the N_2–O_2 donor set of the chelate ligand in the equatorial plane; in the octahedral THF- free complexes, however, the chlorides are *cis* to each other [27, 39, 40]. In a complex of the type (acen)ZrR_2 (L: quadridentate Schiff base with diamino-biphenyl bridge) the metal center has a trigonal-prismatic environment with an C–Zr–C angle of 130° [26]. The *cis*-arrangement of the chloro or alkyl ligands may be one prerequisite for the catalytic activity of these complexes. This arrangement can be achieved either by thermal removal of THF or by treating with Lewis acids (R_3Al or MAO in Ziegler–Natta systems).

We have prepared the complexes **22** and **23**, in which Schiff bases with a N_3–O_2 donor set are coordinated, in order to proof this assumption. According to the X-ray structural analyses the donor atoms of the pentadentate chelate ligands occupy the equatorial plane and the chlorides are *trans* to each other. Figure 1 shows the bis(chloro) zirconium complex **22** with the dianion of



1-21

Complex	R^8	$R^7/R^{7'}$	$R^6/R^{6'}$	$R^5/R^{5'}$	$R^4/R^{4'}$	$R^3/R^{3'}$
1	1,2-ethandiyl	H	H	H	H	H
2	methylen	H	H	H	H	H
3	1,3-propandiyl	H	H	H	H	H
4	1,2-phenyl	H	H	H	H	H
5	1-methyl-1,2-ethandiyl	H	H	H	H	H
6	1,1-dimethyl-1,2-ethandiyl	H	H	H	H	H
7	*cis*-1,2-cyclohexyl	H	H	H	H	H
8	*trans*-(1*R*,2*R*)-(-)-cyclohexyl	H	H	H	H	H
9	1,2-ethandiyl	Me	H	H	H	H
10	1,2-ethandiyl	Ph	H	H	H	H
11	1,2-ethandiyl	H	phenyl	H	H	
12	1,2-ethandiyl	H	H	NO_2	H	H
13	1,2-ethandiyl	H	H	Br	H	H
14	1,2-ethandiyl	H	H	*t*-Bu	H	H
15	1,2-ethandiyl	H	MeO	H	H	H
16	1,2-ethandiyl	H	H	MeO	H	H
17	1,2-ethandiyl	H	H	H	MeO	H
18	1,2-ethandiyl	H	H	H	H	MeO
19	1,2-ethandiyl	H	H	Me_2N	H	H
20	1,2-ethandiyl	H	H	H	Et_2N	H
21	1-methyl-1,2-ethandiyl	H	H	MeO	H	H
22	pentadentate ligand (see text)					
23	pentadentate ligand (see text)					

Scheme 1 Composition of the complexes **1**–**23**, used as cocatalysts for the conversion of hexa-1.5-diene in the systems complex/MAO

N',*N'*-bis(ethylene)-*N'*-methyl-*N*,*N''*-bis(benzoylacetonato-imine*)*. The Cl–Zr–Cl bond angle is 172°, other relevant bond distances, and angles are listed in Figure 1.

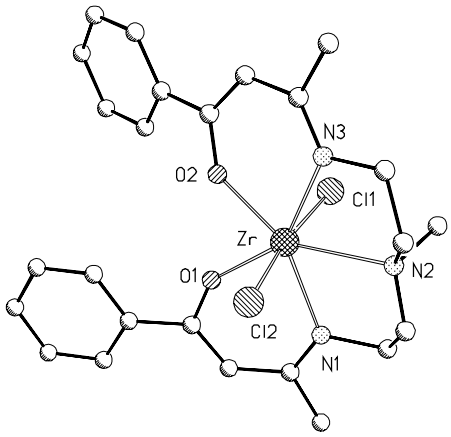


Fig. 1 Molecular structures of **22** with selected bond distances (Å) and bond angles (°) without the disorder: Zr–Cl1 2.477(2), Zr–Cl2 2.474(1), Zr–O1 2.053(3), Zr–O2 2.044(3), Zr–N1 2.401(3), Zr–N2 2.425(4), Zr–N3 2.397(3), Cl1–Zr–Cl2 172.38(5), Cl1–Zr–O1 99.3(1), Cl1–Zr–O2 86.8(1), Cl1–Zr–N1 85.9(1), Cl1–Zr–N2 87.1(1), Cl1–Zr–N3 90.4(1), Cl2–Zr–O1 87.2(1), Cl2–Zr–O2 98.9(1), Cl2–Zr–N1 92.0(1), Cl2–Zr–N2 85.3(1), Cl2–Zr–N3 86.5(1), O1–Zr–O2 73.9(1), O1–Zr–N1 74.0(1), O1–Zr–N2 142.6(1), O1–Zr–N3 146.0(1), O2–Zr–N1 145.5(1), O2–Zr–N2 143.5, O2–Zr–N3 74.2(1), N1–Zr–N2 69.7(1), N1–Zr–N3 69.7(1), N2–Zr–N3 69.9(1).

22 shows a similar structure as found in the abovementioned thf adducts. However in contrast to these THF complexes the additional ligand group can not be removed and therefore a *cis*-arrangement of the chloro ligands can not be achieved. This explains the difference in the catalytic activity of **22**/MAO towards 1-olefines compared with those of the system **1**/MAO (and other salen complexes): **22**/MAO is catalytically inactive whereas the most salen-type complexes are catalytically active in Ziegler–Natta systems (Table 1).

The structure of the dimeric Zirconium complex **23** complex with a very similar pentadentate Schiff base ligand (bearing *t*-butyl groups instead of the phenyl substituents at the C–O-groups) is displayed in Figure 2. It is yielded by hydrolytic splitting of the (L)$ZrCl_2$ complex by traces of water. The complex consists of two pentagonale pyramides which are connected by a bridging oxo group.

The chloro ligands occupy axial positions in complex **23**. A rearrangement of these ligands to form a species containing *cis*-positioned ligands similar to **22** is not possible. Consequently, this compound is catalytically inactive when treated with MAO. The chemistry of analogous Ti complexes with salen-type ligands has been described recently [42].

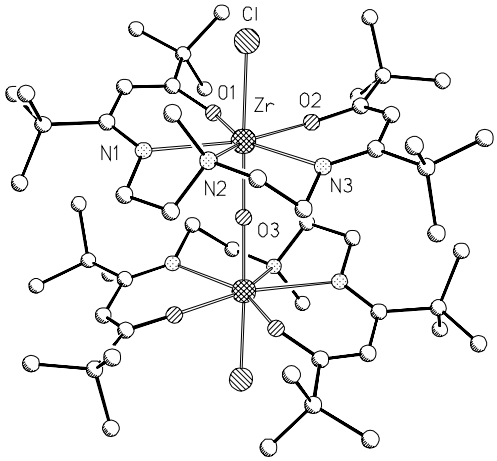


Fig. 2 Molecular structure of complex **23** with selected bond distances (Å) and bond angles (°): Zr–Cl 2.532(1), Zr–O1 2.088(2), Zr–O2 2.091(2), Zr–O3 1.9675(3), Zr–N1 2.444(3), Zr–N2 2.477(3), Zr–N3 2.398(3), Cl–Zr–O1 88.86(8), Cl–Zr–O2 86.68(8), Cl–Zr–O3 175.64(3), Cl–Zr–N1 95.31(8), Cl–Zr–N2 82.00(8), Cl–Zr–N3 90.62(8), O1–Zr–O2 76.54(9), O1–Zr–O3 95.50(7), O1–Zr–N1 74.7(1), O1–Zr–N2 137.8(1), O1–Zr–N3 150.8(1), O2–Zr–O3 94.06(7), O2–Zr–N1 150.6(1), O2–Zr–N2 143.1(1), O2–Zr–N3 74.3(1), O3–Zr–N1 86.17(7), O3–Zr–N2 94.90(8), O3–Zr–N3 85.45(8), N1–Zr–N2 65.9(1), N1–Zr–N3 134.9(1), N2–Zr–N3 70.8(1), Zr–O3–ZrA 180.0. Symmetry transformations used to generated equivalent atoms: A -x, -y, -z.

We treated the Ziegler–Natta system **6**/MAO (1/100) at 25 °C in toluene with different 1-olefines to get a general idea of the catalytic capability of our series of complexes and found that ethylene as well as propylene were polymerized only with low turnover numbers (200 and 8, respectively) to form products of low molecular weights. In other words, in contrast to the metallocene-type catalysts in the salen complexes the β-hydride elimination is much faster than the insertion reaction and therefore salen Zr complexes are poor catalysts for polymerization reactions.

Related studies with amidinato- or silanolato complexes of Zr(IV) also showed poor to moderate polymerization activity of these compounds in combination with MAO [22, 26, 43].

While the zirconocene/MAO system typically catalyzes the polymerization of hexa-1,5-diene and only a few fine-tuned systems yield dimers or oligomers [44], the reaction of (salen)$ZrCl_2$/MAO catalysts with hexa-1,5-diene typically results in a almost selective cyclization to form methylenecyclopentane as main product. Since this catalysis is a slow reaction it was possible not only to keep this reaction in the monomeric regime, but also to investigate key products arising from initial steps.

Table 1 Product distribution in the reaction of hexa-1,5-diene in systems complex/methylalumoxane 1/100 (ton after 3d) (conditions: 0.1 mmol/complex, 10 mmol methylalumoxane in 10 ml toluene, 8.43 mmol hexa-1,5-diene)

run	complex	*T* (°C)	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**
1	**1**	25	2.5	0.9	18	1.5	–	–	1.0	–
2	**1**	0	3.0	0.5	30	1.7	–	–	1.5	–
3	**6**	25	0.9	–	2	–	1.1	–	0.7	–
4	**13**	25	1.1	0.2	7	0.4	-	–	0.4	–
5	**14**	25	2.3	–	5	0.4	0.6	–	0.7	–
6	**15**	25	0.6	–	2	–	0.4	–	0.2	–
7	**16**	25	1.4	0.2	20	1.5	–	–	0.5	–
8	**17**	25	3.3	0.5	14	0.4	4.0	0.6	2.5	0.2
9	**19**	25	1.1	0.2	12	1.1	0.4	–	–	–
10	**19**	0	1.0	0,2	30	2.5	0.4	–	–	–
11	**20**	25	–	–	–	–	3.6	0.6	–	–
12	**21**	25	0.8	0.1	12	0.7	–	–	–	–
13	**22**	0	< 0.1	0	0	0	0	0	0	0
14	**23**	0	< 0.1	0	0	0	0	0	0	0

Table 1 displays that in the reaction of complex /MAO systems with hexa-1,5-diene the organic products **A**–**H** were formed, when the reaction mixture was hydrolyzed by dilute HCl after 72 h.

The formation of the methylated organic products **A**, **B**, **E** and **F** (Scheme 2) is the direct evidence that the starting step of the catalysis consists in the methylation of the zirconium complexes by MAO. Subsequent insertion of hexa-1,5-diene to yield an alkenyl compound followed by cyclization to form the organometallic species **III** are the next steps (Scheme 2). From **III** three reactions can start:

(i) a fast β-hydride elimination to form both 3-methylmethylenecyclopentane (**A**) and the Zr–H species **V**,

(ii) the next insertion step to give the organometallic product **IV**.

(iii) hydrolytic splitting at the end of the reaction or chain transfer to aluminum followed by hydrolysis leading to the saturated cyclization product 1,3-dimethylcyclopentane (**E**).

The β-hydride elimination of the organometallic species **IV** yields the methylated unsaturated dimer **B** as well as the Zr–H species **V**, which can insert hexa-1,5-diene to form **VI**. This intermediate is able to react in similar reactions as described for species **III** (Scheme 2): Methylenecyclopentane C as result of the β-hydride elimination is the main product closing the catalytic cycle. Additionally the insertion of a further molecule hexa-1,5-diene into **VI** leads to the organometallic species **VII**, which reacts to the unsaturated dimer **D** by β-hydride elimination.

As expected from Scheme 2 the sum of the molar amounts of the methylated products **A**, **B**, **E** and **F** lies almost in the range of the amount of the used (salen) $ZrCl_2$(thf) complexes. Therefore, we can conclude that the possible competitive carboalumination reaction is a minor reaction.

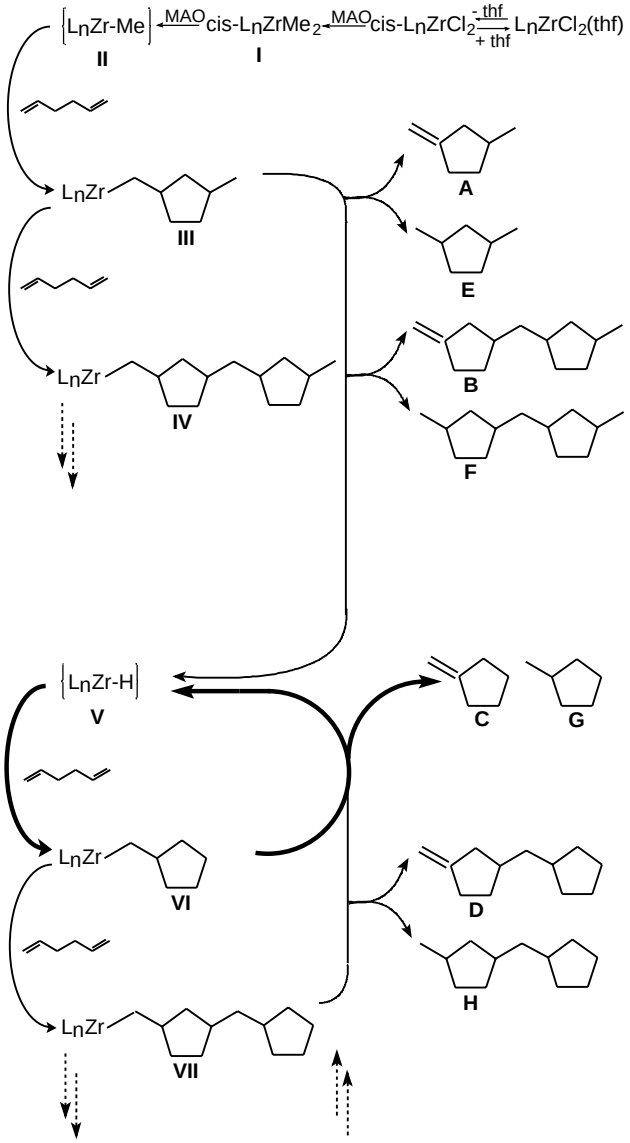
The temperature dependence of the catalytically formed products **C** and **D** were investigated with the system **1**/MAO (Table 2). We found the optimum of the selectivity for the formation of methylenecyclopentane to be in the range of 0 °C. At higher temperatures the yield of methylene cyclopentane decreases, because the catalytic systems becomes less active.

Table 3 shows that the catalysts behave very sensitive to variations in the ligand framework with respect to their activity and selectivity. Starting with the basic system **1**/MAO we discovered that the catalytic system is inactivated by altering the alkylene bridge (complexes **2**–**8**).

Introduction of substituents in the peripheric 7-positions of the imino carbons (Table 3) decreases the catalytic reactivity too.

Table 2 Temperature dependence of hexa-1,5-diene cyclization with **1**/MAO (ton); (conditions: 0.1 mmol 10 mmol methylalumozane in 10 ml toluene, 8.43 mmol hexa-1,5-diene)

run	*T* (°C)	time (d)	**C**	**D**
1	–20	3	2	0
2		7	8	traces
3	0	1	25	1.3
4		3	30	1.7
5		6	34	2.1
6		12	44	2.9
7		20	50	3.5
8		27	54	3.8
9	25	3	18	1.5
10		10	20	1.6
11	60	3h	2	0
12		8h	2	0



Scheme 2 Pathways of the formation of the products **A**–**H** in the conversion reaction of hexa-1,5-diene with the zirconium complexes **1**–**21**, activated by MAO

The complexes **15**–**18** containing the MeO substituent in different positions show very different catalytic activities. An improved activity – compared with **1** – is found for compound **16**, where this substituent is situated in the 5- position. The same substituent in 3-position effects inactivation possibly due to the steric hindrance in this position (complex **18**, Table 3).

In case of a series of further substituents in 5-position, like Br in **13**, *t*-Bu in **14** and Me_2N- in **19**, the catalytic activity of the complexes depends on the ability of the substituents to transfer electron density through the aromatic ring system of the ligand. The stronger this ability the higher is the catalytic activity. This result can be compared with the influence of electronic factors on metallocene-based catalysts [45].

Table 3 Cyclization of hexa-1,5-diene with systems complex/MAO (ton); (conditions: 0.1 mmol complex, 10 mmol methylalumoxane in 10 ml toluene, 8.43 mmol hexa-1,5-diene)

run	complex	*T* (°C)	**C**	**D**
1	**1**	25	18	1,5
2	**5**	25	14	1,0
3	**6**	25	2	0
4	**7**	25	2	0
5	**8**	25	0	0
6	**9**	25	2	0
7	**10**	25	3	0
8	**13**	25	7	0,4
9	**14**	25	5	0
10	**15**	25	2	0
11	**16**	25	20	1,5
4	**16**	0	15	1,4
5	**16**	0	50	3,5
6	**16**	0	54	4,9
12	**17**	25	14	0
13	**18**	25	0	0
14	**19**	25	12	1,1
7	**19**	0	30	0,4
8	**19**	0	57	0,9
9	**19**	0	60	1,0
15	**21**	25	12	0,7

Furthermore, the comparison of the complex pairs **1**/**5** with **16**/**21** (Table 3) clearly demonstrates that especially the substitution at the ethylene bridge is important for the catalytic activity. It shows that steric hindrance at this bridge is a limiting factor for this type of catalysts in general.

The catalytic systems are distinctly more stable and reach substantial higher turnover numbers when the catalyses were carried out at 0 °C. With the most active complexes **1**, **16** and **19** the turnover numbers are in the range of 50–60 (Table 2 and 3).

All catalytically active systems give methylenecyclopentane as main product, however the selectivity of this cyclization reaction is different and reached a maximum in the most active complex **19**, when the reaction was carried out at 0 °C.

A general result from our investigations is the following: Most Zr(IV) complexes containing inorganic donor sets do β-hydride elimination much faster than zirconocene-based catalysts. That is why the formation of low molecular organic products is observed.

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Experimental

All reactions and analytical investigations were conducted under an atmosphere of dry argon using standard Schlenk tech-

niques. Prior to use, tetrahydofuran, diethylether and carbon hydrogens were dried over potassium hydroxide and distilled from sodium benzophenone ketyl. Deuterated compounds were dried over molecular sieve 4A for 24 h. Methylalumoxanes ("MAO") was purchased from Witko GmbH, Bergkamen (Germany) as solution (30%) in toluene. – NMR spectra were recorded on Bruker AC 200 F and DRX 400 spectrometers. For NMR data, the following abbreviations are used: s: singlet; d: doublet; t: triplet; m: multiplet. – Mass spectra were recorded on Finnigan MAT SSQ 710 spectrometer. Elemental analyses were performed with Leco CHNS-932. For recording infrared spectra a Perkin Elmer 2000 FT-IR was used (nujol mull between KBr plates). For GC-IR measurements a Perkin-Elmer Autosystem XL was used.

Ligand Synthesis (General Procedure)

A solution of the aldehyde or the ketone, respectively, in ethanol was treated with an ethanolic solution of the corresponding diamine in a 2:1 ratio. In most cases the product precipitates. If necessary the reaction mixture was filtered off, washed with a small amount of ethanol and dried *in vacuo*. After stirring of the reaction mixture for 1 hour at 60 °C a part of the solvent was removed. The products were obtained as crystalline materials at 0 °C, filtered off, washed with a small amount of ethanol and dried *in vacuo*. Yields were in the range of 70–95%. The following ligands were prepared by this procedure with analytical data in accordance to literature data: *N,N'*-ethylene-bis(acetylacetoneimine), *N,N'*-ethylene-bis (benzoylacetoneimine) [46], *N,N'*-1,3-propylene-bis(salicylideneimine) [47], *N,N'*-1,2-phenylene-bis(salicylideneimine) [48], *N,N'-cis*-1,2-cyclohexylene-bis(salicylideneimine) and *N,N'*-trans-(1*R*,2*R*)-cyclohexylene-bis(salicylideneimine) [49], *N,N'*-ethylene-bis(2-hydroxy-acetophenoneimine) [50], *N,N'*-ethylene-bis(2-hydroxy-benzophenoneimine) [51], *N,N'*-ethylene-bis(2-hydroxy-1-naphthylideneimine) [52], *N,N'*-ethylene-bis(5,5'-dinitro-salicylideneimine) [53]. Since a number of further ligands with incomplete analytical data are described, in the following we report here these data.

rac-N,N'-Methyl-ethylene-bis(salicylideneimine) [54]

Solidified oil; *m.p*. 105–110 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.25 (m, 3H, CH_3); 3.60 (m, 3H, CH_2 and CH); 6.72–7.24 (m, 8H, aryl-H); 8.17 (s, 1H, 7-CH=N); 8.22 (s, 1H, 7'-CH=N); 13.20 (broad s, 2H, OH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 20.1 (CH_3); 64.7 (CH); 65.5 (CH_2); 116.8; 118.5; 131.4; 132.2; 160.9; 164.4 (aryl-C); 166.3 (CH=N). – IR: ν/cm^{-1} = 3480, 1631, 1582, 1326, 1279, 1151, 1045, 1026, 980, 945, 904, 888, 843, 780, 755, 738, 656, 634.

N,N'-Methyl-ethylene-bis-salicylideneimine [55]

Yellow powder; *m.p*. 80–82 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.39 (s, 6H, CH_3); 3.69 (s, 4H, CH_2); 6.80–7.31 (m, 8H, aryl-H); 8.33 (s, 1H, 7-CH=N); 8.39 (s, 1H, 7'-CH=N); 13.38 and 13.76 (two broad S, 2H, OH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 25.3 (CH_3), 60.2 ($\underline{C}Me_2$); 70.5 (CH_2); 116.9 (C3); 117.0 (C3'); 118.4 (C5); 118.6 (C5'); 118.6 (C1); 118.8 (C1'); 131.5 (C6); 131.6 (C6'); 132.2 (C4); 132.4 (C4'); 161.1 (C2); 161.3 (C2'); 161.5 (7-CH=N); 166.5 (7'-CH=N). – IR: ν/cm^{-1} = 3440, 1639, 1623, 1579, 1279, 1175, 1145, 1059, 1030, 979, 923, 870, 854, 782, 761, 651, 564.

N,N'-Ethylene-bis-(5,5'-di-t-butyl-salicylideneimine) [56]

Yellow powder; *m.p*. 168–170 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.26 (s, 18H, *t*-Bu); 3.91 (s, 4H, CH_2); 6.84–7.34 (m, 6H, aryl-H); 8.33 (s, 2H, CH=N); 13.60 (broad s, 2H, OH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 31.4 ($C\underline{Me}_3$); 33.9 ($\underline{C}Me_3$); 59.9 (CH_2); 116.4; 117.9; 127.9; 129.7; 141.3; 158.6 (aryl-C); 166.8 (CH=N). – IR: ν/cm^{-1} = 3380, 1635, 1586, 1483, 1397, 1376, 1362, 1338, 1289, 1261, 1251, 1187, 1137, 1111, 1080, 1053, 978, 909, 891, 830, 782, 746, 711, 653, 623.

N,N'-Ethylene-bis(6,6'-dimethoxy-salicylideneimine)

Yellow crystals; *m.p*. 134–136 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 3.74 (s, 6H, MeO); 3.84 (s, 4H, CH_2); 6.20–7.32 (m, 6H, aryl-H); 8.77 (s, 2H, CH=N); 14.17 (broad s, 2H, OH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 55.5 (MeO); 59.5 (CH_2); 99.7; 108.0; 110.1; 133.4; 159.6; 163.7 (aryl-C); 162.5 (CH=N). – IR: ν/cm^{-1} = 3388, 1626, 1584, 1296, 1250, 1209, 1179, 1100, 1035, 838, 781, 723, 639, 529.

N,N'-Ethylene-bis(4,4'-dimethoxy-salicylideneimine)

Pale yellow crystals; *m.p*. 178 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 3.77 (s, 6H, CH_3O); 3.81 (s, 4H, CH_2); 6.32–7.08 (m, 6H, aryl-H); 8.17 (s, 2H, CH=N); 13.65 (broad s, 2H, OH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 55.3 (CH_3O); 58.8 (CH_2); 101.1; 106.4; 112.3; 132.7; 163.5; 164.6 (aryl-C); 166.4 (CH=N). – IR: ν/cm^{-1} = 3471, 1620, 1578, 1286, 1211, 1174, 1114, 1025, 965, 854, 800, 582.

N,N'-Ethylene-bis(3,3'-dimethoxy-salicylidenimine) [57]

Bright yellow crystals; *m.p*. 172–174 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 3.85 (s, 6H, CH_3O); 3.91 (s, 4H, CH_2); 6.70–6.89 (m, 6H, aryl-H); 8.29 (s, 2H, CH=N); 13.58 (broad s, 2H, OH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 56.0 (CH_3O); 59.4 (CH_2); 114.2; 118.0; 118.4; 123.1; 148.3; 151.4 (aryl-C); 166.6 (CH=N). – IR: ν/cm^{-1} = 3400, 1633, 1250, 1082, 1056, 963, 837, 792, 741, 731, 622.

N,N'-Ethylene-bis(5,5'-bis-dimethylamino-salicylideneimine)

Dark yellow powder; *m.p*. 192–195 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.80 (s, 12H, Me_2N); 3.90 (s, 4H, CH_2); 6.60–6.85 (m, 6H, aryl-H); 8.28 (s, 2H, CH=N); 12.50 (broad s, 2H, OH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 42.0 (Me_2N); 60.0 (CH_2); 116.1; 117.2; 118.4; 119.6; 144.6; 153.4 (aryl-C); 166.8 (CH=N). – IR: ν/cm^{-1} = 3408, 1632, 1584, 1341, 1273, 1202, 1154, 1129, 1061, 1046, 970, 967, 909, 851, 819, 776, 746, 666, 603. – MS (*m/e*): 354 (M^+), 205, 190, 177, 164, 149.

N,N'-Ethylene-bis(4,4'-bis-diethylamino-salicylideneimine)

Ochre powder (62%); *m.p*. 138–142 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.14 (t, 6H, CH_3); 3.34 (q, 4H, NCH_2); 3.72 (s, 4H, CH_2); 6.06–6.96 (m, 6H, aryl-H); 7.99 (s, 2H, CH=N); 13.60 (very broad s, 2H, OH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 12.7 (CH_3); 44.4 (NCH_2); 58.3 (CH_2); 98.1; 103.0; 108.3; 132.9; 151.5; 165.6 (aryl-C); 164.3 (CH=N). – IR: ν/cm^{-1} = 3457, 1615, 1561, 1519, 1349, 1304, 1288, 1241, 1222, 1197, 1130, 1077, 1037, 823, 788, 704. MS (CI, m$^+$/e): 411 (M^++1), 218, 205.

N,N'-8-Methyl-ethylene-bis(5,5'-dimethoxy-salicylideneimine)

Yellow powder; *m.p*. 104–106 °C. – ^{1}H NMR ($CDCl_3$):

δ/ppm = 1.37 (d, 3H, CH_3); 3.72 (m, 9H, CH_3O, CH_2 and CH); 6.69–6.92 (m, 6H, aryl-H); 8.23 (s, 1H, 7-CH=N); 8.27 (s, 1H, 7'-CH=N); 12.72 (s, 2H, OH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 20.4 (CH_3); 55.9 (CH_3O); 65.1 (CH); 65.9 (CH_2); 114.9; 117.6; 118.2; 119.5; 152.0; 155.1 (aryl-C); 164.2 (7-CH=N); 166.1 (7'-CH=N). – IR: ν/cm^{-1} = 3420, 1633, 1613, 1586, 1330, 1271, 1195, 1160,1129, 1035, 983, 854, 830, 786, 662.

N,N'-Methylene-bis(salicylideneimine) [58]

A solution of 5,0 g (42 mmol) diaminomethane-dihydrochloride in 20 ml water was treated with a solution of 1,7g (42 mmol) NaOH in 15ml water at 0 °C. Addition of a cooled solution of 10,4 g (85 mmol) salicyclaldehyde in 35 ml ethanol under stirring and allowing the solution to reach 25 °C results in formation of an oil in neutral solution. After removal of ethanol, the aqueous residue was extracted several times with diethylether. The combined extracts were washed with brine and dried over Na_2SO_4. Chromatography at silica gel 100 with diethylether as eluent leads to an oily product, which was crystallized from diethylether/hexane at 0 °C. Yellow crystals 2.4 g (22%); *m.p.* 126–130 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 5.40 (s, 2H, CH_2); 6.85–7.36 (m, 8H, aryl-H); 8.48 (s, 2H, CH=N); 12.94 (s, 2H, OH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 77.6 (CH_2); 117.1; 118.5; 118.9; 132.0; 132.9; 161.0 (aryl-C); 165,7 (CH=N). – IR: ν/cm^{-1} = 3400, 1623, 1576, 1500, 1344, 1280, 1215, 1153, 1124, 1047, 1038, 1010, 977, 857, 780, 760, 652, 564. – MS (*m*/*e*): 254 (M^+), 134, 107.

N',N'-bis(ethylene)-N'-methyl-N,N''-bis(benzoylacetonatoimine)

was prepared from 10 g (61.6 mmol) benzoylacetone and 5.8 g (49.9 mmol) bis(2-aminoethyl)-methylamine, dissolved in 20 ml ethanol at 60 °C. Upon distillation of the solvent the yellow-brown oil was dried i.V. and as crude product used for the synthesis of the complexes. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.96, 2.03 (s, 9H, CH_3), 2.58, 3.32 (t,q , 8H, CH_2), 5.57 (s, 2H, CH), 7.35 (m, 10H, aromat.), 11.37 (s, 2H, NH). – ^{13}C NMR ($CDCl_3$): δ/ppm = 19.4, 42.6 (CH_3); 41.5, 57.2 (CH_2), 92.0 (CH), 126.7, 128.0, 130.2, 140.5 (CH, aromat.), 164.8 (CN), 187.2 (CO). – IR: ν/cm^{-1} = 1603 (ν_{CO}), 1544 ($\nu_{C=N}$).

Complex Synthesis (General Procedure)

A solution of 5 mmol ligand in 40 ml tetrahydrofuran was treated with 6.25 ml (10mmol) of a 1.6 molar solution of *n*-butyl-lithium in hexane at –40 °C. This mixture was then added slowly to a solution of 1.89 g (5mmol) $ZrCl_4(thf)_2$ in 30 ml THF. After stirring for 2 hours at 25 °C the solvent was removed, the residue suspended in 20 ml CH_2Cl_2, and the suspension was filtered. From the filtrate the solvent was distilled off and the complexes were dried *in vacuo*. *N,N'*-Ethylene-bis(salicylideneiminato)-zirconium(IV)-dichlorid(thf) **1** and *N,N'*-1,2-phenylene-bis-(salicylideneiminato)-zirconium (IV)-dichlorid-(thf) **4** are in accordance with literature data [39].

N,N'-Methylene-bis(salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**2**)

1.3g (52%) yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.85 (m, 4H, thf); 3.88 (m, 4H, thf); 6.03 (s, 2H, CH_2); 6.83–7.38 (m, 8H, aryl-H); 8.26 (s, 2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 26.0 (thf); 69.0 (thf); 78.0 (CH_2); 118.8; 121.0; 123.1; 134.4; 137.0; 162.5 (aryl-C); 169.2 (CH=N). – IR: ν/cm^{-1} = 1632, 1600, 1543, 1315, 1301, 1150, 1123, 1011, 911, 858, 762, 604.

$C_{19}H_{20}Cl_2N_2O_3Zr$ (486.48)

Calcd.:	C 46.90	H 4.14	N 5.76	Cl 14.57
Found:	C 47.57	H 4.34	N 5.59	Cl 14.70.

N,N'-1,3-Propylene-bis(salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**3**)

1.75g (68%) yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.82 (m, 6H, CH_2 and thf); 3.69(m, 8H, NCH_2 and thf); 6.50–7.50 (m, 8H, aryl-H); 8.21 (s, 2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 26.0 (thf); 30.5 (CH_2); 64.2 (NCH_2); 70.9 (thf); 118.8; 123.1; 125.7; 134.0; 134.8; 163.0 (aryl-C); 166.5 (CH=N). – IR: ν/cm^{-1} = 1654, 1618, 1554, 1299, 1211, 1151, 1124, 1099, 1055, 1032, 906, 852, 814, 757, 736, 614.

$C_{21}H_{24}Cl_2N_2O_3Zr$ (514.5)

Calcd.:	C 49.02	H 4.70	N 5.44	Cl 13.78
Found:	C 49.14	H 4.93	N 5.22	Cl 14.08.

N,N'-8-Methyl-ethylene-bis(salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**5**)

1.80 g (70%) slight yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1,44 (m, 3H, CH_3); 1.88 (m, 4H, thf); 3.85 (m, 4H, thf); 4.23 (m, 2H, CH_2); 4.62 (m, 1H, CH); 6.85–7.51 (m, 8H, aryl-H); 8.40 (s, 1H, 7-CH=N); 8.45 (s, 1H, 7'-CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm =19.3 and 20.8 (CH_3); 26.0 (thf); 64.7 (CH); 67.6 (CH_2); 69.1 (thf); 119.4; 122.2; 135.0; 136.7; 162.0; 166.5 (aryl-C); 167.5 (CH=N). – IR: ν/cm^{-1} = 1621, 1542, 1302, 1281, 1149, 1029, 905, 880, 755, 602.

$C_{21}H_{24}Cl_2N_2O_3Zr$ (514.54)

Calcd.:	C 49.02	H 4.70	N 5.44	Cl 13.78
Found:	C 49.19	H 5.02	N 5.23	Cl 13.95.

N,N'-8,8-Dimethyl-ethylene-bis(salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**6**)

1.80 g (68%) slight yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.51 (broad s, 6H, CH_3); 1.83 (m, 4H, thf); 3.62 (s, 4H, CH_2); 3.75 (m, 4H, thf); 6.86–7.50 (m, 8H, aryl-H); 8.36 (s, 1H, 7-CH=N); 8.45 (s, 1H, 7'-CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 26.2 (Me and thf); 62.4 ($\underline{C}Me_2$); 68.6 (thf); 74.8 (CH_2); broad signals at 116.0; 120,8; 121.8; 134.0; 136.4; 161.4 (aryl-C) and 164.4 (7-CH=N); 165.7 (7'-CH=N). – IR: ν/cm^{-1} = 1615, 1598, 1553, 1304, 1277, 1244, 1150, 1124, 1065, 892, 816, 758, 617.

$C_{22}H_{26}Cl_2N_2O_3Zr$ (528.5)

Calcd.:	C 50.00	H 4.96	N 5.30	Cl 13.41
Found:	C 50.46	H 5.17	N 5.02	Cl 13.89.

N,N'-cis-1,2-Cyclohexylene-bis(salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**7**)

2.35 g (85 %) slight yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.23–2.00 (m, 12H, CH_2 and thf); 3.71–3.78 (m, 6H, CH and thf); 6.45–7.35 (m, 8H, aryl-H); 8.07 (2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 23.9 (10-CH_2); 26.2 (thf); 30.8 (9-CH_2); 66.4 (CH); 68.4 (thf); 116.6; 118.5; 119.4; 129.6; 133.8; 164.1 (aryl-C); 163.1 (CH=N). – IR: ν/cm^{-1} = 1617, 1596, 1552, 1280, 1151, 1124, 916, 890, 825, 757, 724, 604.

$C_{24}H_{28}Cl_2N_2O_3Zr$ (554.5)
Calcd.: C 51.98 H 5.09 N 5.05 Cl 12.79
Found: C 51.55 H 5.15 N 4.78 Cl 13.22.

N,N'-trans-(1R,2R)-Cyclohexylene-bis(salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**8**)

2.40 g (87%) yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.16–1.80 (m, 8H, CH_2); 1.85 (m, 4H, thf); 3.46 (m, 2H, CH); 3.70 (m, 4H, thf); 6.60–7.33 (m, 8H, aryl-H); 8.22 (2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 25.4 (10-CH_2); 26.0 (thf); 32.0 (9-CH_2); 67.6 (CH); 68.3 (thf); 116.4; 118.4; 119.2; 129.5; 133.8; 163.0 (aryl-C); 159.2 (CH=N). – IR: ν/cm^{-1} = 1622, 1598, 1552, 1323, 1296, 1225, 1203, 1150, 1121, 1030, 911, 879, 822, 756, 738, 724, 611, 577.
$C_{24}H_{28}Cl_2N_2O_3Zr$ (554.50)
Calcd.: C 51.98 H 5.09 N 5.05 Cl 12.79
Found: C 52.54 H 5.66 N 5.21 Cl 13.00.

N,N'-Ethylene-bis(2-hydroxy-acetophenoneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**9**)

1.05 g (40%) yellow powder. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.82 (m, 4H, thf); 2.38 (s, 6H, Me); 3.72 (m, 4H, thf); 4.38 (s, 4H, CH_2); 6.72–7.55 (m, 8H, aryl-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 25.6 (thf); (CH_2); 67.9 (thf); (aryl-C); (CH=N). – IR: ν/cm^{-1} = 1599, 1544, 1321, 1298, 1257, 1245, 1157, 1134, 1099, 865, 754, 730, 587.
$C_{22}H_{26}Cl_2N_2O_3Zr$ (528.5)
Calcd.: C 49.99 H 4.96 N 5.30 Cl 13.41
Found: C 49.85 H 6.01 N 5.12 Cl 13.66.

N,N'-Ethylene-bis(2-hydroxy-benzophenoneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**10**)

2.67 g (82%) yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.85 (m, 4H, thf); 3.70 (m, 4H, thf); 4.00 (s, 4H, CH_2); 6.22–7.80 (m, 18H, aryl-H). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 26.0 (thf); (thf); 115.6; 120.0; 124.0; 127.6; 129.1; 129.7; 132.9; 133.9; 138.5; 163.6 (aryl-C); 180.4 (C=N). – IR: ν/cm^{-1} = 1595, 1578, 1540, 1327, 1261, 1250, 1224, 1147, 1026, 859, 750, 703, 600.
$C_{32}H_{30}Cl_2N_2O_3Zr$ (652.7)
Calcd.: C 58.88 H 4.63 N 4.29 Cl 10.86
Found: C 59.41 H 4.81 N 4.54 Cl 9.75.

N,N'-Ethylene-bis(2-hydroxy-1-naphthylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**11**)

In difference to the general procedure, the suspension of the poor soluble ligand in 40 ml THF was treated with a solution of *n*-butyl-lithium in hexane at –40 °C under *vigorous* stirring. On warming up to 25 °C in a yellow clear solution result, which was used as described. 2.73 g (91%) ochre powder. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.83 (m, 4H, thf); 3.76 (m, 4H, thf); 4.58 (s, 4H, CH_2); 6.30–7.72 (m, 12H, aryl-H); 9.17 (broad s, 2H, CH=N). – ^{13}C NMR ($CDCl_3$): δ/ppm = 25.5 (thf); 62.9 (CH_2); 67.9 (thf); 118.5; 120.8; 121.5; 123.0; 126.6; 128.6; 133.9; 156.9 (aryl-C); 164.6 (CH=N). – IR: ν/cm^{-1} = 1621, 1593, 1548, 1506, 1343, 1304, 1275, 1245, 1186, 983, 943, 820, 742, 647, 549, 477.
$C_{28}H_{26}Cl_2N_2O_3Zr$ (600.6)
Calcd.: C 55.99 H 4.36 N 4.66 Cl 11.80
Found: C 56.28 H 4.45 N 4.23 Cl 12.09.

N,N'-Ethylene-bis(5,5'-dinitro-salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**12**)

In difference to the general procedure, the suspension of the poor soluble ligand in 40 ml THF was treated with a solution of *n*-butyl-lithium in hexane at –50 °C under *vigorous* stirring. Slow warming up to 25 °C a red solution result. This mixture was then added slowly to a solution of $ZrCl_4(thf)_2$ in 30 ml thf. After stirring for 2 hours at 25 °C the solvent was removed, and the rough product was extracted in a Soxhlet apparatus several hours with 50 ml CH_2Cl_2. From the extract the solvent was distilled off, and the complex was dried in vacuum to yield 0.94 g (32%) bright yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.76 (m, 4H, thf); 3.58 (m, 4H, thf); 4.22 (s, 4H, CH_2); 6.91–8.48 (m, 6H, aryl-H); 8.75 (s, 2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 26.27 (thf); 62.98 (CH_2); 68.17 (thf); 120.26; 120.98; 130.69; 131.05; 140.80; 163.08 (aryl-C); 166.62 (CH=N). – IR: ν/cm^{-1} = 1635, 1605, 1561, 1505, 1341, 1319, 1247, 1203, 1132, 1101, 1076, 1048, 953, 870, 844, 812, 757, 731, 705, 653.
$C_{20}H_{20}Cl_2N_4O_7Zr$ (590.5)
Calcd.: C 40.68 H 3.41 N 9.49 Cl 12.01
Found: C 40.71 H 3.44 N 10.18 Cl 11.88.

N,N'-Ethylene-bis(5,5'-dibromo-salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**13**)

2.3 g (70%) yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.83 (m, 4H, thf); 3.60 (m, 4H, thf); 3.73 (s, 4H, CH_2); 6.30–7.55 (m, 6H, aryl-H); 8.35 (s, 2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 26.0 (thf); 62.4 (CH_2); 71.0 (thf); 107.3; 121.5; 122.8; 135.2; 136.8; 161.3 (aryl-C); 166.0 (CH=N). – IR: ν/cm^{-1} = 1625, 1588, 1542, 1285, 1274, 1188, 1133, 1100, 823, 695, 648.
$C_{20}H_{20}Br_2Cl_2N_2O_3Zr$ (658.3)
Calcd.: C 36.49 H 3.06 N 4.25
Found: C 36.62 H 3.34 N 4.02.

N,N'-Ethylene-bis(5,5'-di-t-butyl-salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**14**)

2.6 g (85%) yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.33 (s, 18H, *t*-Bu); 1.87 (m, 4H, thf); 3.85 (m, 4H, thf); 4.14 (s, 4H, CH_2); 6.77–7.62 (m, 6H, aryl-H); 8.43 (s, 2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 26.0 (thf); 31.5 (C$\underline{Me}_3$); 34.3 ($\underline{C}Me_3$); 62.3 (CH_2); 70.9 (thf); 119.5; 120.0; 129.6; 131.6; 138.0; 148.0 (aryl-C); 162.2 (CH=N). – IR: ν/cm^{-1} = 1623, 1551, 1311, 1269, 1188, 1147, 840, 545.
$C_{28}H_{38}Cl_2N_2O_3Zr$ (612.7)
Calcd.: C 54.88 H 6.25 N 4.57 Cl 11.57
Found: C 55.12 H 6.77 N 4.13 Cl 11.86.

N,N'-Ethylene-bis(6,6'-dimethoxy-salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**15**)

2.3 g (82%) yellow powder. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.85 (m, 4H, thf); 3.76–3.87 (m, 14H, CH_2, MeO and thf); 6.27–7.37 (m, 6H, aryl-H); 8.95 (s, 2H, CH=N). – ^{13}C NMR ($CDCl_3$): δ/ppm = 25.5 (thf); 55.7 (MeO); 61.6 (CH_2); 68.5 (thf); 100.4; 111.1; 112.7; 136.2; 156.2; 164.5 (aryl-C); 162.9 (CH=N). – IR: ν/cm^{-1} = 1615, 1595, 1558, 1310, 1250, 1184, 1112, 1075, 969, 860, 786, 759, 726, 611, 587.
$C_{22}H_{26}Cl_2N_2O_5Zr$ (560.6)

Calcd.: C 47.13 H 4.67 N 5.00 Cl 12.65
Found: C 47.45 H 4.80 N 4.75 Cl 12.97.

N,N'-Ethylene-bis(5,5'-dimethoxy-salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**16**)

2.5 g (89%) yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.93 (m, 4H, thf); 3.75 (m, 4H, thf); 3.79 (s, 6H, MeO); 4.30 (s, 4H, CH_2); 6.75–7.16 (m, 6H, aryl-H); 8.37 (s, 2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 26.0 (thf); 56.3 (MeO); 61.2 (CH_2); 70.1 (thf); 116.6; 119.8; 121.9; 124.5; 152.7; 157.1 (aryl-C); 166.3 (CH=N). – IR: ν/cm^{-1} = 1630, 1607, 1557, 1290, 1268, 1224, 1163, 1037, 822, 785, 734, 568, 539.
$C_{22}H_{26}Cl_2N_2O_5Zr$ (560.6)
Calcd.: C 47.13 H 4.67 N 5.00 Cl 12.65
Found: C 47.43 H 4.91 N 4.76 Cl 12.88.

N,N'-Ethylene-bis(4,4'-dimethoxy-salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**17**)

2.2 g (78%) slight yellow powder. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.83 (m, 4H, thf); 3.61–3.83 (m, 10H, MeO and thf); 4.23 (s, 4H, CH_2); 6.24–7.23 (m, 6H, aryl-H); 8.07 (s, 2H, CH=N). – ^{13}C NMR ($CDCl_3$): δ/ppm = 25.5 (thf); 55.3 (MeO); 62.2 (CH_2); 68.5 (thf); 102.6; 103.7; 115.4; 133.7; 160.6; 164.3 (aryl-C); 165.5 (CH=N). – IR: ν/cm^{-1} = 1607, 1543, 1491, 1311, 1256, 1230, 1208, 1165, 1123, 1029, 976, 840, 757, 636, 579.
$C_{22}H_{26}Cl_2N_2O_5Zr$ (560.6)
Calcd.: C 47.13 H 4.67 N 5.00 Cl 12.65
Found: C 47.50 H 5.00 N 4.51 Cl 12.95.

N,N'-Ethylene-bis(3,3'-dimethoxy-salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**18**)

1.5 g (54%) slight yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.80 (m, 4H, thf); 3.62 (s, 6H, MeO); 3.75 (m, 4H, thf); 4.49 (s, 4H, CH_2); 6.52–6.95 (m, 6H, aryl-H); 8.15 (s, 2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 25.5 (thf); 56.1 (MeO); 62.0 (CH_2); 67.9 (thf); 114.5; 115.2; 121.3; 124.5; 150.4; 155.1 (aryl-C); 161.3 (CH=N). – IR: ν/cm^{-1} = 1631, 1597, 1562, 1312, 1246, 1133, 1080, 1039, 973, 866, 738, 632.
$C_{22}H_{26}Cl_2N_2O_5Zr$ (560.6)
Calcd.: C 47.13 H 4.67 N 5.00 Cl 12.65
Found: C 47.54 H 4.97 N 4.72 Cl 13.00.

N,N'-Ethylene-bis(5,5'-bis-dimethylamino-salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**19**)

2.15 g (73%) yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.88 (m, 4H, thf); 2.89 (s, 12H, Me_2N); 3.92 (m, 4H, thf); 4.13 (s, 4H, CH_2); 6.80–7.10 (m, 6H, aryl-H); 8.37 (s, 2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 26.0 (thf); 42.0 (Me_2N); 611 (CH_2); 69.4 (thf); 117.7; 119.3; 122.2; 123.8; 145.0; 155.2 (aryl-C); 166.9 (CH=N). – IR: ν/cm^{-1} = 1628, 1605, 1552, 1296, 1256, 1188, 1053, 915, 814, 754, 553.
$C_{24}H_{32}Cl_2N_4O_3Zr$ (586.6)
Calcd.: C 49.13 H 5.50 N 9.55 Cl 12.08
Found: C 48.39 H 6.10 N 8.32 Cl 12.44.

N,N'-Ethylene-bis(4,4'-bis-diethylamino-salicylideneiminato)-zirconium(IV)-dichlorid-0.25-tetrahydrofuran (**20**)

2.3 g (71%) yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.15 (m, 12H, Me); 1.81 (m, 1H, thf); 3.33 (m, 8H, NCH_2); 3.73 (m, 1H, thf); 3.94 (s, 4H, CH_2); 6.03–7.35 (m, 6H, aryl-H); 8.00 (s, 2H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 14.0 (Me); 26.0 (thf); 45.0 (NCH_2); 61.0 (CH_2); 71.0 (thf); 100.0; 104.1; 112.0; 136.5; 154.8; 165.7 (aryl-C); 164.3 (CH=N). – IR: ν/cm^{-1} = 1599, 1513, 1354, 1249, 1140, 1077, 832, 784, 712, 634.
$C_{28}H_{40}Cl_2N_4O_3Zr$ (642.8)
Calcd.: C 52.32 H 6.27 N 8.72 Cl 11.03
Found: C 51.39 H 6.52 N 8.22 Cl 11.45.

N,N'-8-Methyl-ethylene-bis(5,5'-dimethoxy-salicylideneiminato)-zirconium(IV)-dichlorid-tetrahydrofuran (**21**)

2.45 g (85%) yellow powder. – ^{1}H NMR (CD_2Cl_2): δ/ppm = 1.42 (s, 3H, Me); 1.85 (m, 4H, thf); 3.66 (m, 4H, thf); 3.80 (m, 9H, MeO, CH_2 and CH); 6.57–7.00 (m, 6H, aryl-H); 8.34 (s, 1H, 7-CH=N); 8.39 (s, 1H, 7'-CH=N). – ^{13}C NMR (CD_2Cl_2): δ/ppm = 19.3 (Me); 26.0 (thf); 56.3 (MeO); 64.7 (CH); 65.3 (CH_2); 70.3 (thf); 116.2; 120.4; 121.9; 124.7; 150.2; 152.6 (aryl-C); 166.2 (7-CH=N); 167.2 (7'-CH=N). – IR: ν/cm^{-1} = 1629, 1604, 1554, 1296, 1269, 1198, 1163, 940, 824, 783, 733.
$C_{23}H_{28}Cl_2N_2O_5Zr$ (574.6)
Calcd.: C 48.07 H 4.91 N 4.87 Cl 12.34
Found: C 48.12 H 5.09 N 4.48 Cl 12.66.

N',N'-Bis(ethylene)-N'-methyl-N,N''-bis(benzoylacetonato-iminato)-zirconium-dichloride (**22**)

4.83 g (12 mmol) of the Schiff base ligand in 30 ml THF were treated with 14.9 ml (24 mmol) *n*-butyllithium (1.6M solution in *n*-hexane) at –78 °C. At –30 °C the orange reaction mixture was slowly added to 4.49 g $ZrCl_4(thf)_2$ in 30 ml thf under stirring. The yellow suspension was allowed to react 3 h at ambient temperature. Removal of the solvents under vacuum resulted in a yellow crude product, which was recrystallized from dichloromethane to yield single crystals of **22**. Yield of the crude product: 85%. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.27, 2.70 (s, 9H, CH_3), 3.61, 4.02 (m , 8H, CH_2), 6.19 (s, 2H, CH), 7.43 (m, 10H, aromat.). – ^{13}C NMR ($CDCl_3$): δ/ppm = 24.7, 46.8 (CH_3); 50.8, 59.6 (CH_2), 102.9 (CH), 127.6, 128.5, 130.4, 137.5 (CH, aromat.), 169.7 (CN), 173.6 (CO). – IR: ν/cm^{-1} = 1593 (ν_{CO}), 1573 (ν_{CN}).
$C_{25}H_{29}Cl_2N_3O_2Zr$ (565.6)
Calcd.: C 53.08 H 5.17 N 7.43 Cl 12.53
Found: C 53.10 H 5.37 N 6.91 Cl 12.47.

Compound **23**, obtained by an analogous reaction to form the Schiff base complex followed by hydrolysis with 0.5 equivalents of water, crystallized upon storage of the reaction mixture at –30 °C as colourless crystals.

Catalytic Reactions

Reaction with Ethylene or Propylene

In a 200 ml stainless autoclave 0.1mmol complex was treated with 10 mmol MAO in 50 ml toluene solution at 10 bar ethylene or propylene pressure and 25 °C under stirring. After 24 h the excess of gas was removed, and the reaction mixture was hydrolyzed with dilute hydrochloric acid at 0 °C. The solid product was filtered off, washed with toluene and ethanol, and dried *in vacuo*. The nearly colourless polyethylene, insoluble inTHF, was not further investigated. Turnover numbers for polymers were calculated as mmol consumed educt/mmol catalyst.

In the filtrates only very small amounts of oligomers were detectable in the case of propylene as substrate. When complex **1** in the reaction with propylene was used, oily distillation residues (30–40 mg) were investigated by NMR, showing a mixture of higher atactic oligomers with methylene end groups. – ^{1}H NMR ($CDCl_3$): δ/ppm = 0.78–0.88 (m, 70H, Me); 0.96 (m, 8H, Me); 1.19–1.41 (m, 50H, CH_2); 1.50–1.60 (m, 22H, CH); 1.65 (s, 2.7H, Me–C=); 4.65 (m, 2H, $=CH_2$). – ^{13}C NMR ($CDCl_3$): δ/ppm = 11.07; 14.02; 14.33; 20.0–20.5 (broad); 23.05; 23.36; 23.76; 27.87; 29.11; 29.65; 41.99; 45.5–46.8 (broad); 65.32; 111.22; 144.84. From the spectra an average molar mass in the range of 1000 g/mol (25 monomer units) was calculated by comparing the integral units of methylene groups and of other groups.

Reaction with Hexa-1.5-diene

To 0.1 mmol of the complex and 10 mmol MAO in 10 ml toluene 1ml (0.692 g = 8.43 mmol) Hexa-1.5-diene was added after 1 minute, and the mixture was stirred or shaked. During the reaction proceeded, probes were taken from the mixture, which were hydrolyzed under cooling with dilute hydrochloric acid. The organic layer was treated with sodium carbonate and investigated by GC-MS and GC-IR. Methylenecyclopentane was further identified by NMR measurements. Quantitative determination was carried out under the assumption, that GC-correction factors of all products are very similar. The ratio of peak areas therefore correlate with the ratio of the masses of the appropriate products. Turnover numbers for cyclization products were calculated as mmol product/mmol catalyst stated turnover. Thus the turnover number (mmol product/mmol catalyst) of a product is defined as: ton = mass(hexa-1.5-diene) × peak area(product)/Σ peak areas × molar mass(product) × molar amount(catalyst). If Cp_2ZrCl_2 as catalyst is used under same conditions, all educt was consumed after 3 h. The product mixture contained 33% monomeric cyclization products (including 19% methylenecyclopentane), further dimers (37%), trimers (23%), tetramers (7%) and traces of pentamers.

Product Analyses

3-Methyl-methylenecyclopentane (**A**)

GC-MS *(m/e*, intens.): 96 (M^+, 30), 81 (100), 79 (20), 70 (27), 67 (24), 55 (38), 39 (62). – GC-IR: ν/cm^{-1} = 3074 (=CH); 2958 and 2888 (CH_2/CH_3); 1656 (C=C); δ/cm^{-1} = 1449 (CH_2); 1366 (CH_3); 879 ($=CH_2$).

3-(3-Methyl-cyclopentylemethyl)-methylenecyclopentane (**B**)

GC-MS (*m/e*, intens.): 178 (M^+, 4), 163 (4), 149 (3), 135 (2), 122 (3), 107 (9), 95 (12), 81(100), 67 (21), 55 (28), 41 (24). – GC-IR: ν/cm^{-1} = 3079 (=CH); 2954 and 2875 (CH_2/CH_3); 1657 (C=C); δ/cm^{-1} = 1446 (CH_2); 880 ($=CH_2$).

Methylenecyclopentane (**C**)

GC-MS (*m/e*, intens.): 82 (M^+, 38), 67 (100), 54 (22), 42 (20), 39 (32). – GC-IR: ν/cm^{-1} = 3071(=CH); 2965 and 2892 (CH_2); 1660 (C=C); δ/cm^{-1} = 1445 (CH_2); 880 ($=CH_2$). – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.64 (m, 4H, 3- and 4-CH_2), 2.25 (m, 4H, 2- and 5-CH_2), 4.82 (m, 2H, $=CH_2$). – ^{13}C NMR ($CDCl_3$): δ/ppm = 26.29 (3- and 4-CH_2); 32.97 (2- and 5-CH_2); 104.46 ($=CH_2$), 153.33 (=C).

3-(Cyclopentyemethyl)-methylenecyclopentane (**D**)

GC-MS (*m/e*): 164 (M^+, 6), 149 (5), 135 (6), 121 (5), 108 (9), 95 (18), 93 (18), 82 (29), 81(100), 67 (40), 55 (22), 41 (43). – GC-IR: ν/cm^{-1} = 3078 (=CH); 2955 and 2873 (CH_2); 1662 (C=C); δ/cm^{-1} = 1479 and 1442 (CH_2); 880 ($=CH_2$).

1,3-Dimethyl-cyclopentane (cis/trans mixture) (**E**)

GC-MS (*m/e*, intens.): 98 (M^+, 18), 83 (22), 70 (100), 56 (95), 55 (80), 41 (75). – GC-IR: ν/cm^{-1} = 2957 and 2879 (CH_2/CH_3); δ/cm^{-1} = 1463 (CH_2); 1378 (CH_3).

3-(3-Methyl-cyclopentyemethyl)-methylcyclopentane (**F**)

GC-MS (*m/e*): 180 (M^+, 5), 165 (3), 151 (2), 137 (2), 123 (5), 110 (8), 109 (8), 97 (24), 96 (24), 83 (40), 81(100), 67 (40), 55 (78), 41 (41). – GC-IR: ν/cm^{-1} = 2955 and 2875 (CH_2/CH_3), δ/cm^{-1} = 1458 (CH_2).

Methylcyclopentane (**G**)

GC-MS (*m/e*, intens.): 84 (M^+, 18), 69 (42), 56 (100), 41 (55). – GC-IR: ν/cm^{-1} = 2961 and 2881(CH_2/CH_3); δ/cm^{-1} = 1466 (CH_2); 1366 (CH_3).

3-(Cyclopentymethyl)-methylcyclopentane (**H**)

GC-MS (*m/e*, intens.): 166 (M^+, 4), 151 (7), 109 (23), 96 (24), 97 (24), 83 (32), 82 (48), 81(100), 69 (35), 67 (57), 55 (81), 41 (67). – GC-IR: ν/cm^{-1} = 2956 and 2877 (CH_2/CH_3), δ/cm^{-1} = 1455 (CH_2).

Crystal Structure Determination

The intensity data for the compound **22** were collected on a Nonius CAD4 diffractometer and for the compound **23** on a Nonius Kappa CCD diffractometer, by using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption [59, 60].

The structures were solved by direct methods (SHELXS [61]) and refined by full-matrix least squares techniques against Fo2 (SHELXL-97 [62]). The hydrogen atoms of the both structures were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically [62]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for **22** [63]

$C_{25}H_{29}Cl_2N_3O_2Zr \cdot 2CH_2Cl_2$, Mr = 735.48 g mol^{-1}, colourless prism, size 0.40 × 0.38 × 0.30 mm^3, monoclinic, space group $P2_{1/c}$, a = 15.011(3), b = 14.970(3), c = 15.127(3) Å, (β = 109.84(3)°, V = 3197(1) Å^3 , T = –90 °C, Z = 4, $\rho_{calcd.}$ = 1.528 gcm^{-3}, μ (Mo-K_α = 8.75 cm^{-1}, F(000) = 1496, 5368 reflections in h(–17/0), k(–17/0), l(–17/17), measured in the range 2.72° ≤ θ ≥ 25.70°, 5162 independent reflections, R_{int} = 0.017, 4060 reflections with Fo > 4σ(Fo), 421 parameters, $R1_{obs}$ = 0.044, $wR2_{obs}$ = 0.099, $R1_{all}$ = 0.065, $wR2_{all}$ = 0.118, GOOF = 1.049, largest difference peak and hole: 0.594 /–0.614 e Å^{-3}.

Crystal Data for **23** [63]

$C_{60}H_{110}Cl_2N_6O_5Zr_2$, Mr = 1248.88 g mol^{-1}, colourless prism, size 0.35 × 0.30 × 0.26 mm^3, triclinic, space group P-1, a = 10.8087(4), b = 12.5393(5), c = 12.8926(5) Å, (α = 69.664(2), (β = 83.955(2), χ = 73.264(2) °, V = 1569.0(1) Å^3, T = –90 °C, Z = 1, (calcd. = 1.322 gcm^{-3}, μ (Mo-K_α = 4.67 cm^{-1},

F(000) = 666, measured in the range 3.18°, 23.29°, completeness (max = 95%, 16597 reflections in h(−12/0), k(−**13**/**12**), l(−**14**/**14**, 4258 independent reflections, R_{int} = 0.055, 4008 reflections with Fo > 4σ(Fo), 340 parameters, 3 restraints, R1obs = 0.043, wR2obs = 0.131, R1all = 0.045, wR2all = 0.134, GOOF = 1.055, largest difference peak and hole: 1.164 /−1.358 e Å^{-3}.

References

[1] H.-H. Brintzinger, D. Fischer, R. Mühlhaupt, B. Rieger, R. Waymouth, Angew. Chem. **1995**, *107*,1255
[2] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, Angew. Chem. **1999**, *111*, 448 and references therein
[3] P. C. Möhring, N. J. Coville, J. Organomet. Chem. **1994**, *479*, 1
[4] M. Bochmann, J. Chem. Soc., Dalton Trans. **1996**, 255
[5] W. Kaminsky, Macromol. Chem. Phys. **1996**, *197*, 3907
[6] Y. Tajima, E. Kunioka, J. Polym. Sci., Polym. Chem. Ed. **1968**, *6*, 241
[7] J. A. Canich, H. W. Turner (Exxon), PCT Int. Appl. WO 92/ 12162, (23.07.1992); Chem. Abstr. **1993**, *118*, 81615j
[8] V. C. Vernon, B. S. Kimberley, A. J. P. White, D. J. Williams, P. Howard, J. Chem. Soc., Chem. Comm. **1998**, 313
[9] S. A. A. Shah, H. Dorn, A. Voigt, H. W. Roesky, E. Parasini, H.-G. Schmidt, M. Noltemeyer, Organometallics **1996**, *15*, 3176
[10] F. Jäger, H. W. Roesky, H. Dorn, S. Shah, M. Noltemeyer, H.-G. Schmidt, Chem. Ber./Recueil **1997**, *130*, 399
[11] A. D. Horton, J. de With, A. J. van der Linden, H. van de Weg, Organometallics **1996**, *15*, 2672
[12] A. D. Horton, J. de With, J. Chem. Soc., Chem. Comm. **1996**, 1375
[13] H. Mack, M. S. Eisen, J. Organomet. Chem. **1996**, *525*, 81
[14] S. Tinkler, R. J. Deeth, D. J. Duncalf, A. Mccamley, J. Chem. Soc., Chem. Comm. **1996**, 2623
[15] T. H. Warren, R. R. Schrock, W. M. Davis, Organometallics **1996**, *15*, 562
[16] R. Baumann, W. M. Davis, R. R. Schrock, J. Am. Chem. **Soc**. 1997, *119*, 3830
[17] J. D. Scollard, D. H. Mcconville, J. Am. Chem. Soc. **1996**, *118*, 10008
[18] L. Scoles, R. Minhas, R. Duchateau, J. Jubb, S. Gambarotta, Organometallics **1994**, *13*, 4978
[19] J. C. Flores, J. W. Chien, M. D. Rausch, Organometallics **1995**, *14*, 1827
[20] J. C. Flores, J. W. Chien, M. D. Rausch, Organometallics **1995**, *14*, 2106
[21] D. Heroskovics-Korine, M. S. Eisen, J. Organomet. Chem. **1995**, *503*, 307
[22] D. Walther, R. Fischer, H. Görls, J. Koch, B. Schweder, J. Organomet. Chem. **1996**, *508*, 13
[23] C. Janiak, T. G. Scharmann, K. C. H. Lange, Macromol. Rapid. Comm. **1994**, *15*, 655
[24] L. Matilainen, I. Mutikainen, M. Leskela, Acta Chem. Scand. **1996**, *50*, 755
[25] P. Sobota, J. Utko, S. Szafert, K. Szczegot, J. Chem. Soc., Dalton Trans. **1997**, 679
[26] a) E. B. Tjaden, D. C. Swenson, R. F. Jordan, Organometallics **1995**, *14*, 371; b) E. B. Tjaden, R. F. Jordan, Macromol. Symp. **1995**, *89*, 231
[27] T. Repo, M. Klinga, P. Pietkäinen, M. Leskelä, A.-M. Uusitalo, T. Pakkanen, K.Hakala, P. Aaltonen, B. Löfgren, Macromolecules **1997**, *30*, 171
[28] C. Floriani, E. Solari, F. Corazza, A. Chiesi-Villa, C. Guastini, Angew. Chem. **1989**, *101*, 91; Angew. Chem. Int. Ed. Engl. **1989**, *281*, 64
[29] V. I. Taranov, D. E. Hibbs, M. B. Hursthouse, N. S. Ikonnikov, K. M. A. Malik, M. North, C. Orizu, Y. N. Belokon, J. Chem. Soc., Chem. Comm. **1998**, 387
[30] D. G. Black, D. C. Swensson, R. F. Jordan, R. D. Rogers, Organometallics **1995**, *14*, 3539
[31] a) T. Tsukahara, D. C. Swenson, R. F. Jordan, Organometallics **1997**, *16*, 3303; b) J. Kim, Y. Nishihara, R. F. Jordan, R. D. Rogers, A. L. Rheingold, G. P. A. Yap, Organometallics **1997**, *16*, 3314
[32] P. G. Cozzi, E. Gallo, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics **1995**, *14*, 4994
[33] K. Soga, E. Kaji, T. Uozumi, J. Polymer Sci. Part A – Polymer Chemistry **1997**, *35*, 823
[34] E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, J. Chem. Soc., Dalton Trans. **1992**, 367
[35] G. Dell'Amico, F. Marchetti, C. Floriani, J. Chem. Soc., Dalton Trans. **1982**, 2197
[36] M. Mazzanti, J. M. Rosset, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Chem. Soc., Dalton Trans. **1989**, 953
[37] C. Floriani, Polyhedron **1989**, *8*, 1717
[38] G. Gilli, D. W. J. Cruickshank, R. L. Beddoes, O. S. Mills, Acta Cryst. 1972, B28, 1889
[39] F. Corazza, E. Solari, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Chem. Soc., Dalton Trans. **1990**, 1335
[40] P. Woodman, P. B. Hitchcock, P. Scott, J. Chem. Soc., Chem. Comm. **1996**, 2735
[41] J. P. Corden, W. Errington, P. Moore, M. G. H. Wallbridge, J. Chem. Soc., Chem. Comm. **1999**, 323
[42] F. Franceschi, E. Gallo, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, A. Sgamellotti, Chem. Eur. J. **1996**, *2*, 1466
[43] B. Schweder, H. Görls, D. Walther, Inorg. Chim. Acta **1999**, *286*, 14
[44] a) G. W. Coates, R. M. Waymouth, J. Am. Chem. Soc. **1993**, *115*, 91; b) S. Thiele, G. Erker, Chem. Ber. **1997**, *130*, 201
[45] C. Janiak, U. Versteeg, K. C. H. Lange, R. Weimann, E. Hahn, J. Organomet. Chem. **1995**, *501*, 219
[46] K. Kasuga, T. Nakahara, A. Tsuge, K. Sogabe, Y. Yamamoto, Bull. Chem. Soc. Jpn., **1983**, *56*, 95
[47] G. Bandoli, M. Nicilini, U. Mazzi, F. Refosco, J. Chem. Soc., Dalton Trans. **1984**, 2505
[48] N. Platzer, N. Goasdoue, R. Bonnaire, J. Organomet. Chem. **1978**, *160*, 455
[49] a) M. Gulotti, A. Pasini, P. Fantucci, R. Ugo, R. D. Gillard, Gazz. Chim. Ital. **1972**, *102*, 855; b) M. L. Ilingsworth, B. P. Cleary, A. J. Jensen, L. S. Schwartz, A. L. Rheingold, Inorg. Chim. Acta **1993**, *207*, 147
[50] J. P. Tandon, Monatsh. Chem. **1976**, *107*, 1379
[51] a) B. N. Ghose, Acta Chim. Hung. **1985**, *118*, 191; b) A. Scullane, J. Coord. Chem. **1979**, *9*, 151
[52] M. Caivin, N. C. Melchior, J. Am. Chem. Soc. **1948**, *70*, 3273
[53] C. S. Marvel, N., Tarköy, J. Am. Chem. Soc. **1958**, *80*, 832
[54] E. Profft, M. Pannach, Ber. Dtsch. Pharm. Ges. **1966**, *299*, 633
[55] K. S. Patel, J. C. Bailar (jun.), J. lnorg. Nucl. Chem. **1971**, *33*, 1399
[56] J. M. Kerr, C. J. Suckling, P. Bamfield, J. Chem. Soc., Perkin Trans. **1990**, 887
[57] K. Terenjew, Zh. Obshch. Khim. **1966**, *36*, 1590
[58] S. R. Salman, J. M. A. Al-Rawi, Org. Magn. Reson. **1984**, *22*, 535
[59] MOLEN, An Interactive Structure Solution Procedure, **En**raf-Nonius, Delft, The Netherlands 1990

[60] Z. Otwinowski & W. Minor, „Processing of X-Ray Diffraction Data Collected in Oscillation Mode“, in Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A, (C.W. Carter, R.M. Sweet , Eds.) Academic Press, pp. 307–326
[61] G. M. Sheldrick, Acta Crystallogr. Sect. A **1990**, *46*, 467
[62] G. M. Sheidrick, University of Göttingen, Germany 1993
[63] Further details of the crystal structure investigations are available on requests from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD118854 (22) and CSD118855 (23), the names of the authors, and the journal citation.

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