APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 758–765
Published online 1 September 2006 in Wiley InterScience
(www.interscience.wiley.com) DOI:10.1002/aoc.1124

Synthesis of novel zirconium complexes bearing mono-Cp and tridentate Schiff base [ONO] ligands and their catalytic activities for olefin polymerization

Qihui Chen and Jiling Huang*

Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, PO Box 310, Shanghai 200237, People's Republic of China

Received 13 March 2006; Accepted 13 May 2006

A series of novel zirconium complexes {$R^2Cp[2\text{-}R^1\text{-}6\text{-}(2\text{-}CH_3OC_6H_4N{=}CH)C_6H_3O]ZrCl_2$ (1, $R^1 = H$, $R^2 = H$, 2: $R^1 = CH_3$, $R^2 = H$; 3, $R^1 = {}^tBu$, $R^2 = H$; 4, $R^1 = H$, $R^2 = CH_3$; 5, $R^1 = H$, $R^2 = n\text{-Bu}$)} bearing mono-Cp and tridentate Schiff base [ONO] ligands are prepared by the reaction of corresponding lithium salt of Schiff base ligands with $R^2CpZrCl_3{\cdot}DME$. All complexes were well characterized by ^1H NMR, MS, IR and elemental analysis. The molecular structure of complex 1 was further confirmed by X-ray diffraction study, where the bond angle of Cl–Zr–Cl is extremely wide [151.71(3)°]. A nine-membered zirconoxacycle complex $Cp(O{-}2{-}C_6H_4N{=}CHC_6H_4\text{-}2{-}O)ZrCl_2$ (6) can be obtained by an intramolecular elimination of CH_3Cl from complex 1 or by the reaction of $CpZrCl_3{\cdot}DME$ with dilithium salt of ligand. When activated by excess methylaluminoxane (MAO), complexes 1–6 exhibit high catalytic activities for ethylene polymerization. The influence of polymerization temperature on the activities of ethylene polymerization is investigated, and these complexes show high thermal stability. Complex 6 is also active for the copolymerization of ethylene and 1-hexene with low 1-hexene incorporation ability (1.10%). Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: zirconium; Schiff base; tridentate ligand; olefin polymerization

INTRODUCTION

The discovery of Ziegler–Natta catalysts and their use as homogeneous catalysts for the polymerization of ethylene greatly promoted the development of organometallic chemistry. The quest for the metallocene catalysts that can produce polymers with novel properties is one of the major goals of transition metal coordination chemistry over the last decade.[1,2] To date, many organometallic complexes have been synthesized, especially group 4 metal complexes supported by the ubiquitous cyclopentadienyl (Cp) ligand because of the motivation arising from academic research and ever-increasing support from industry.[3–7] At the same time, another branch of non-Cp complexes has also been extensively studied.[8,9] The non-Cp complexes may be supported by many kinds of ancillary ligands. McConville *et al.* found that propylene-bridged arylsubstituted diamido group 4 complexes promote the living polymerization of α-olefins.[10] More recently, Fujita and co-workers discovered that group 4 complexes bearing the bidentate salicylaldimine chelate ligands show extremely high activities for ethylene polymerization.[11,12]

Among the numerous group 4 complexes, mixed ligands titanium complexes of the type $Cp'Ti(L)X_2$ containing cyclopentadienyl ligand and non-Cp ligand have attracted considerable attention, because this type of catalyst has been expected to exhibit unique characteristics as olefin polymerization catalyst that would combine the merits of metallocene and non-Cp catalyst type.[13–19] A number of groups have explored the use of catalysts with one cyclopentadienyl and a second, tridentate, bidentate or monoanionic ligand. Amongst the first examples are the cyclopentadienyl benzamidinate complexes.[20] More recently Nomura has reported the nonbridged half-metallocene

---

*Correspondence to: Jiling Huang, Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, P.O. Box 310, Shanghai 200237, People's Republic of China.
E-mail: kahncph@yahoo.com.cn
Contract/grant sponsor: National Basic Research Program of China; Contract/grant number: 2005CB623801.
Contract/grant sponsor: National Natural Science Foundation of China; Contract/grant number: 20372022.

Copyright © 2006 John Wiley & Sons, Ltd.

type group 4 transition metal complexes $CpTi(OAr)X_2$, $CpTiCl_2[N(R)(Ar)]$ or $CpTiCl_2(N = C^tBu_2)$ that are active for the ethylene or styrene polymerization and copolymerization of ethylene/α-olefin.[21–23] The mixed ligands group 4 complexes are mainly focused on titanium metal, and there have been only a few reports on the use of mixed ligands zirconium complexes for the olefin polymerization.[24,25]

Schiff base ligands represent one of the most widely utilized classes of ligand in metal coordination chemistry. Their complexes have shown many important catalytic applications, ranging from asymmetric epoxidation[26,27] and Lewis acid-assisted organic transformations,[28] to various types of polymerization.[29,30] The attractive features are that the electron and bulkiness of Schiff base ligands are easily controlled. Recently we reported mono-Cp and Schiff base ligands titanium complexes and their application for α-olefin polymerization.[31] A mechanism involving a four-membered transition state is proposed for the formation of titanoxacycle. We further investigate the analogous zirconium complex and confirm our proposed mechanism by the obtained intermediate in our previous communication.[32] Therefore, we wish to present the full details concerning the synthesis and structure of zirconium complexes bearing mono-Cp and tridentate Schiff base [ONO] ligands and their catalytic activities for ethylene polymerization and copolymerization of ethylene/1-hexene.

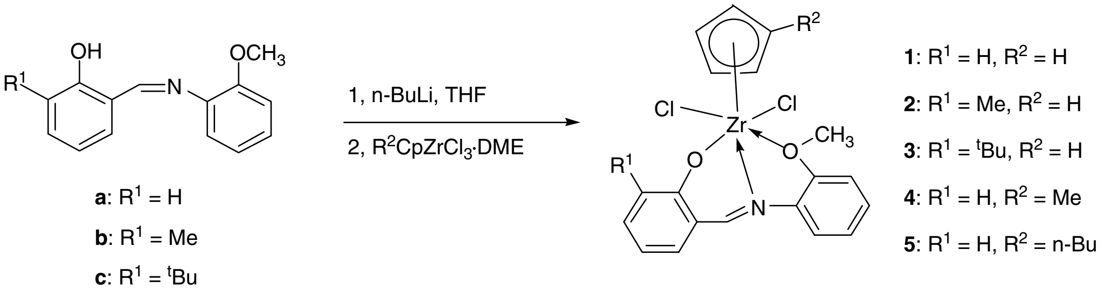
RESULTS AND DISCUSSION

Synthesis and characterization of complexes

The reaction of corresponding lithium salt of ligands with $R^2CpZrCl_3 \cdot DME$ (DME = 1,2-dimethoxyethane) in THF gives mixed ligands zirconium complexes **1–5** (Scheme 1). The complexes were separated from the LiCl by the extraction with dichloromethane. Analytical pure samples were obtained by recrystallization from dichloromethane or layering concentrated dichloromethane solutions with light petroleum and cooling. The zirconium compounds **1–5** were obtained as the yellow crystalline solids in 60–80% yields. Complexes **1–5** are extremely soluble in chlorinated solvents (chloroform and dichloromethane) and dissolve with difficulty in aromatic solvents (benzene, toluene). Integration of the ^1H NMR spectra of complexes **1–5** confirms a 1 : 1 proportion of cyclopentadienyl ligand to Schiff base ligand, and complexes **1, 2** and **4** contain dichloromethane solvent. The result of elemental analysis is consistent with the containing CH_2Cl_2 solvent. The ^1H NMR spectra of complexes **1–5** show that the protons of OCH_3 group are shifted to the downfield approximately 0.57 ppm relative to the free ligand. For the ^{13}C NMR spectrum of complex **1**, the OCH_3 group is shifted to the downfield 10.9 ppm relative to free ligand, which indicates that the OCH_3 group is coordinated to the central metal. The chemical shift difference in the ^1H NMR spectra for the CH=N proton in complexes **1–5** and the free ligand is only 0.13 ppm. From ^1H NMR spectra of complex **1–5**, we cannot confirm whether the N atom is coordinated to the central metal.

The single crystal X-ray diffraction result confirms the structure that the N and O atoms are both coordinated to zirconium atom, and the Schiff base ligand acts as a chelating tridentate ligand (Fig. 1). Crystallographic data together with the collection parameters and the refinement parameters are summarized in Table 1. The selected bond lengths and angles are listed in Table 2. If the centroid of the cyclopentadienyl ring is considered as a single coordination site, the geometry around the zirconium center can be described as octahedral with *trans*–O and *trans*–Cl arrangement. The two *trans* components Cl–Zr–Cl and O–Zr–O with big bond angle values of 151.71(3) and 148.25(8)°, respectively, are bent away from the Cp plane. The wide angles appear to be governed by steric repulsion between the Cp ligand and tridentate Schiff base ligand. The plane of the Schiff base ligand is nearly perpendicular to the Cp ligand plane. The sum of the angles around N atom is approximately 360°, indicating sp^2 hybridization at the nitrogen atom. The Zr–N(1) bond [2.341(3) Å] is slightly shorter than that of FI zirconium complexes (2.355–2.382 Å),[33] which indicates significantly coordination of imino nitrogen atom to metal center in the solid state. As expected for the coordinated methoxy group, the Zr–O(1) bond distance [2.354(2) Å] is much longer than the Zr–O(2) bond [1.993(2) Å]. The Zr–O(2) bond length [1.993(2) Å] is in the range of the structurally related mono-Cp zirconium complexes (1.954–2.040 Å).[24,25]

Complexes **1–5** that are coordinated with the methoxy group are synthesized. According to our previous study



Scheme 1.

Copyright © 2006 John Wiley & Sons, Ltd.

DOI: 10.1002/aoc

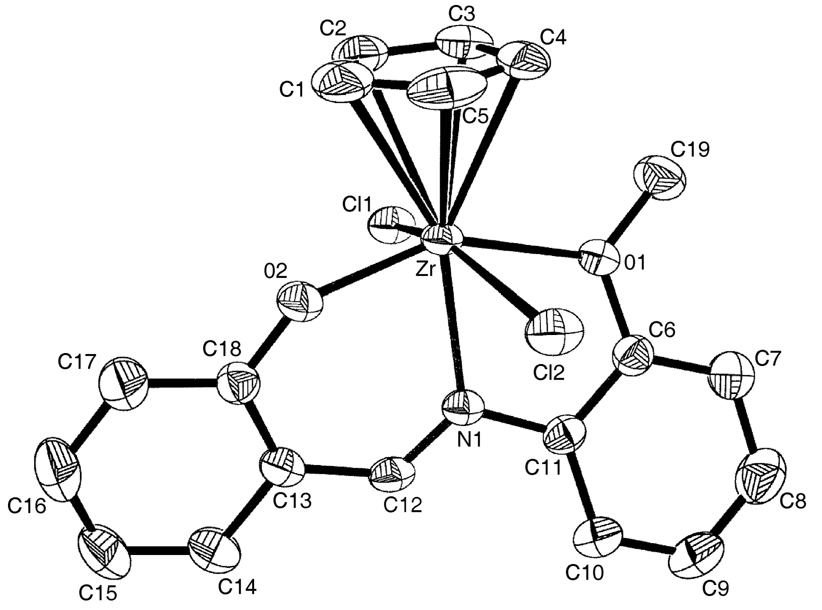
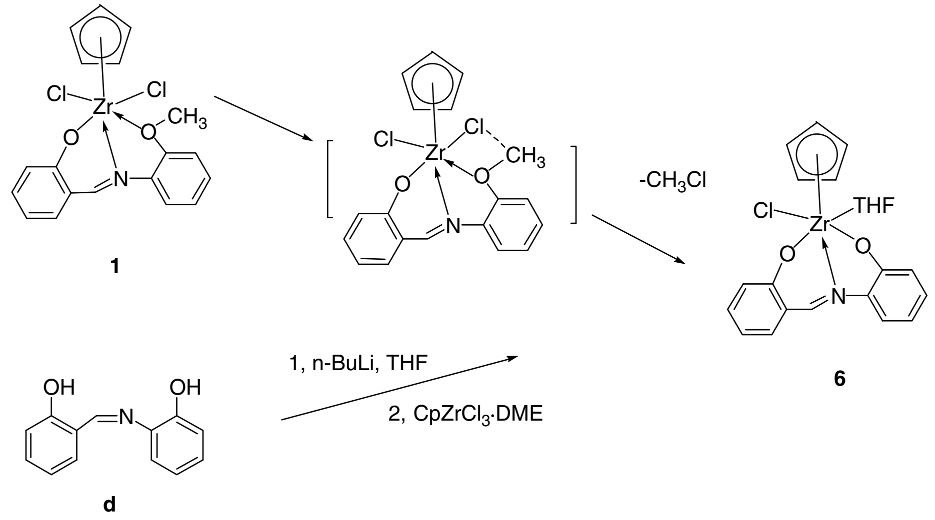


Figure 1. The ORTEP diagram of complex **1** (50% probability ellipsoids). CH_2Cl_2 solvent molecule present in the unit cell and all hydrogen atoms are omitted for clarity.



Scheme 2.

for titanium complex, the coordinated methoxy group will eliminate CH_3Cl through a transition state and form a titanoxacycle complex in some conditions, so complex **1** is selected as an example to confirm an intramolecular elimination reaction. The solution of complex **1** in THF was refluxed for 4 h, and the orange crystals were obtained by recrystallization from dichloromethane. In the ^1H NMR spectrum of the complex, the strong singlet peak of OCH_3 at 4.44 has disappeared in complex **1** and 3.87 ppm in the free ligand **a** cannot be found, which indicates that the methyl has been eliminated from complex **1**. The zirconoxacycle complex **6** can be also be synthesized from dilithium salt of ligand **d** and $CpZrCl_3 \cdot DME$ (Scheme 2). Complex **6** retains one equivalent of THF from either synthetic route and even after recrystallization from dichloromethane. The chemical shift difference for the CH=N group in complex **6** and free ligand **d** is only 0.04 ppm. According to the crystal structure of complex **1**, we assume that the N atom is also coordinated to the zirconium center. The EI mass spectra generally does not contain the peaks of the molecular ion $[M]^+$; however, the particularly intense ion peaks $[M-CH_3-Cl]^+$ can be observed in all mass spectra of complexes **1–5**, which indicates again that the coordinated methoxy group would be eliminated in some conditions.

Copyright © 2006 John Wiley & Sons, Ltd.

Table 1. Crystal data and structure refinement details for complex **1**

Empirical formula	$C_{19}H_{17}Cl_2NO_2Zr \cdot CH_2Cl_2$
Formula weight	538.38
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Apace group	$P2_1/c$
a (Å)	12.4841(16)
b (Å)	10.6215(14)
c (Å)	17.674(2)
α (deg)	90
β (deg)	107.167(2)
γ (deg)	90
Volume (Å^3)	2239.2(5)
Z	4
Calculated density (mg/m^3)	1.597
Absorption coefficient (mm^{-1})	0.984
F(000)	1080
Crystal size (mm)	0.506 × 0.232 × 0.117
Theta range for data collection (deg)	1.71–27.00
Limiting indices	$-15 \leq h \leq 15, -13 \leq k \leq 13, -22 \leq l \leq 19$
Reflections collected/unique	12848/4832 [R(int) = 0.1010]
Completeness to $\theta = 27.00$	98.9%
Absorption correction	Empirical
Maximum and minimum transmission	1.00000 and 0.58673
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4832/6/310
Goodness-of-fit on F^2	0.967
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0449, wR_2 = 0.1022$
R indices (all data)	$R_1 = 0.0616, wR_2 = 0.1092$
Largest difference peak and hole (e. Å^{-3})	0.594 and −0.469

Table 2. Selected bond distances (Å) and bond angles (deg) for complex **1**

Zr–O(2)	1.993(2)	Zr–C(1)	2.552(4)
Zr–O(1)	2.354(2)	Zr–C(2)	2.534(4)
Zr–Cl(1)	2.5064(9)	Zr–C(3)	2.536(4)
Zr–Cl(2)	2.5090(10)	Zr–C(4)	2.520(4)
Zr–N(1)	2.341(3)	Zr–C(5)	2.520(4)
Cl(1)–Zr–Cl(2)	151.71(3)	O(2)–Zr–O(1)	148.25(8)
O(2)–Zr–N(1)	79.29(9)	C(18)–O(2)–Zr	139.1(2)
N(1)–Zr–O(1)	69.16(8)	O(2)–Zr–Cl(1)	91.29(8)
N(1)–Zr–Cl(1)	78.34(6)	O(1)–Zr–Cl(1)	79.28(6)
O(2)–Zr–Cl(2)	95.91(8)	N(1)–Zr–Cl(2)	76.21(6)
O(1)–Zr–Cl(2)	80.30(6)	O(2)–Zr–C(5)	96.43(17)
C(12)–N(1)–C(11)	118.3(3)	C(19)–O(1)–Zr	125.9(2)
C(11)–N(1)–Zr	116.0(2)	C(12)–N(1)–Zr	125.6(2)

Table 3. Ethylene polymerizarion with complexes **1**–**6**/MAO[a]

Entry	Complex	Temperature/(°C)	Activity[b]	M_η[c]	M_w[d]	M_w/M_n[d]
1	**1**	30	0.59	19.6		
2	**1**	50	2.31	14.2		
3	**1**	70	5.86	10.6	20.6	2.10
4	**1**	80	7.69	10.4		
5	**2**	80	3.20	11.2		
6	**3**	80	2.32	12.5		
7	**4**	80	5.65	10.9		
8	**5**	80	2.23	12.1		
9	**6**	30	0.10	26.9		
10	**6**	50	0.35	19.5		
11	**6**	70	1.20	9.43	21.0	2.10
12	**6**	80	2.72	6.34		
13	Cp_2ZrCl_2	80	8.75	9.54		

[a] Conditions: solvent, toluene 50 ml; pressure, 1 atm; time, 0.5 h; Zr, 5 μmol.
[b] 10^5 g PE/(mol Zr h).
[c] Molecular weights determined by intrinsic viscosity.
[d] M_w and M_w/M_n were determined by GPC.

Ethylene polymerization and ethylene/1-hexene copolymerization

Complexes **1**–**6** were tested as catalyst precursors for ethylene polymerization in the presence of excess methylaluminoxane (Al:Zr = 2000 : 1). The results are summarized in Table 3. Complexes **1**–**6** exhibit high catalytic activities and high thermal stability. Compared with the Cp_2ZrCl_2–MAO catalytic system, complexes **1**–**5**–MAO catalytic systems show slightly low catalytic activities, which is attributed to the *trans*–Cl disposition. The wide bond angle of Cl–Zr–Cl of zirconium complex is the result of tridentate ligand, and there are examples with wide bond angles for ethylene polymerization.[34]

The activity depends strongly on the substituent attached to the Cp ligand or Schiff base ligand. The catalytic activity increased in the order **5** < **3** < **6** < **2** < **4** < **1** under the same conditions. Complex **1** demonstrates the highest catalytic activity (7.69 × 10^5 g PE/mol Zr h) among the rest of the catalysts by 2- to 3-fold at 80 °C. Increasing the bulkiness on the R^1 substitutents on the phenoxide or on the R^2 substitutents on the Cp ligand decreases the catalytic activity, which can be attributed to increased steric hindrance around the active site. The steric bulkiness on the phenoxide or on the Cp ligand rather than the electronic effect thus plays an essential role in the catalytic activity. In any case, it is found that the activity of complex **1** is much higher than that of complex **6**, which can be attributed to complex **6** bearing only one chloro ligand. We assume that cocatalyst MAO reacts under the Zr–O bond cleavage, presumably by reaction

Copyright © 2006 John Wiley & Sons, Ltd.

with the $AlMe_3$ component of MAO, to generate an active cationic zirconium alkyl species in a Ziegler–Natta olefin polymerization model.[35] There are some examples of the use of monochloro complexes for ethylene polymerization.[25,36]

The polymerization was run at different temperatures (30–80 °C) to probe the catalyst's thermal stability. The polymerization temperature has a remarkable effect on the catalytic behavior, as demonstrated in Table 3. When the polymerization temperature is elevated from 30 to 80 °C, the activity of complex **1** rises from 0.59 to 7.69×10^5 g PE/(mol Zr h). This is due to faster generation of the active species and the increase of the propagation rate with temperature. At the high temperature a decrease in the activity is a common behavior for the metallocene system, and the optimal polymerization temperature for each system depends on the balance between the propagation rate and the thermal stability.[37,38] Table 3 indicates that this type complexes are high thermal stability catalysts and the Schiff base ligand seems to play an important role in stablizing the active species. A high catalytic activity at high polymerization temperature should be important, especially from the aspect of industrial applications, because performing a solution polymerization at high temperature improves the viscosity of the reaction mixture, leading to better mass transportation and temperature control.[39]

The molecular weight of the resulting polymers with M_η values is in the range of $63.4–269 \times 10^3$ g/mol. Changing the bulkiness for complexes **1**–**5** does not significantly influence the molecular weights of polymer. The molecular weight of obtained polymers significantly decreases with increasing polymerization temperature, which could be attributed to the chain transfer rate being faster than the chain propagation. The molecular weight of the polymer obtained complex **6**–MAO catalytic system is more sensitive to polymerization temperature than that of the complex **1**–MAO system. The ^{13}C NMR spectrum of the PE obtained with the complex **1**–MAO system at 70 °C indicates that the resultant polymer is linear (entry 3). Narrow molecular weight distributions ($M_w/M_n = 2.10$, entries 3 and 11) are observed for polymers produced by complexes **1** and **6**, which is characteristic of single site catalysts, indicating that these precursors produced polyethylene with unimodal molecular weight distribution at the polymerization temperature 70 °C.

In preliminary copolymerization experiments, complexes **1** and **6** were tested as catalysts for ethylene–1-hexene copolymerization upon activation with MAO (Al:Zr = 2000, 0.5 h, 5 μmol of Zr, 2 ml of 1-hexene, 50 ml of toluene, $T = 70$ °C, $P_{\text{ethylene}} = /1$bar). To our disappointment, complex **1** does not exhibit 1-hexene incorporation ability from the analysis of ^{13}C NMR spectrum of resultant polymer. Complex **6** exhibits the high catalytic activity (2.56×10^5 g/mol Zr h) and low 1-hexene incorporation ability (1.10%). 1-Hexene incorporation level were significantly lower than our cyclopentadienyl bis(phenoxy-imine) titanium complex[31] and much lower than Nomura's cyclopentadienyl phenoxide titanium complexes.[40] Obviously the introduction of tridentate ligand to zirconium complex has reduced the coordination space around the metal center, which is less open for 1-hexene coordination.

CONCLUSIONS

Six zirconium complexes with mono-Cp and tridentate Schiff base ligands were synthesized, and they were well characterized by ^1H NMR, MS, IR and elemental analysis. A suitable crystal of complex **1** was obtained and determined by X-ray diffraction. In the presence of MAO, the zirconium complexes can serve as efficient catalyst precursors for ethylene polymerization with high thermal stability. Among them, the complex **1**–MAO system exhibits the highest activity for ethylene polymerization. The complex **6**–MAO system shows high catalytic activity for ethylene–1-hexene copolymerization with 1-hexene incorporation ability (1.10%). The activity depends strongly on the substituent attached to the Cp ligand or Schiff base ligand, and increasing the bulkiness on the R^1 substitutents on the phenoxide or on the R^2 substitutents on the Cp ligand decreases the catalytic activity. The obtained polyethylenes have high molecular weights and narrow molecular weight distributions.

EXPERIMENTAL

All operations were carried out under a dry argon atmosphere using standard Schlenk techniques. Toluene, diethyl ether, tetrahydrofuran (THF) and hexane were refluxed over sodium/benzophenone ketyl and dichloromethane (CH_2Cl_2) was refluxed over CaH_2, from which they were distilled prior to use. Polymerization-grade ethylene was purified before use. 1-Hexene was distilled over sodium under argon and stored in the presence of activated 4 Å molecular sieves. The cocatalyst 10% methylaluminoxane (MAO) in toluene was purchased from Witco. $CpZrCl_3 \cdot DME$, $MeCpZrCl_3 \cdot DME$ and n-$BuCpZrCl_3 \cdot DME$ were prepared by the modified literature procedures.[41–43]

IR spectra were recorded on a Nicolet Magna-IR 550, Nicolet 5SXC spectrometer as KBr disks. Elemental analysis was carried out on an EA-1106 type analyzer. ^1H NMR spectra were recorded on a Bruker Avance-500 MHz spectrometer with TMS as internal standard. ^{13}C NMR spectra were recorded on a Bruker Avance-300 MHz spectrometer. EI mass spectra were recorded on an HP 5989A instrument.

Synthesis of Schiff base ligand a

The salicylaldehyde (12.2 g, 100 mmol) and 70 ml of ethanol in a 250 ml three-neck flask was heated to reflux, then a solution of 2-methoxyaniline (12.3 g, 100 mmol) in 20 ml ethanol was added dropwise. The reaction mixture was refluxed for 2 h

Copyright © 2006 John Wiley & Sons, Ltd.

and then cooled to room temperature. A precipitate was formed, which was recrystallized from ethanol to afford yellow crystals in 89% (20.2 g) yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 13.81 (s, 1H, OH), 8.65 (s, 1H, CH=N), 7.50–6.92 (m, 8H, ArH), 3.87 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 162.0, 161.7, 152.9, 136.5, 133.3, 132.2, 121.0, 119.9, 119.6, 119.3, 118.9, 117.5, 111.9, 55.9 (OCH_3).

Synthesis of Schiff base ligand b

Lgand **b** was prepared using the similar procedure for ligand **a**. 3-Methylsalicylaldehyde (1.36 g, 10.0 mmol) and 2-methoxyaniline (1.23 g, 10.0 mmol) were used to give 2.07 g (yield, 86%) of yellow needle crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.69 (s, 1H, CH=N), 7.24–7.20 (m, 4H, ArH), 7.01–6.98 (m, 2H, ArH), 6.83 (t, $J = 7.5$ Hz, 1H, ArH), 3.90 (s, 3H, OCH_3), 2.33 (s, 3H, CH_3).

Synthesis of Schiff base ligand c

Lgand **c** was prepared using the similar procedure for ligand **a**. 3-*tert*-Butylsalicylaldehyde (1.78 g, 10.0 mmol) and 2-methoxyaniline (1.23 g, 10.0 mmol) were used to give 2.09 g (yield, 74%) of yellow crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.70 (s, 1H, CH=N), 7.39 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, 1H, ArH), 7.24–7.22 (m, 2H, ArH), 7.19 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, 1H, ArH), 7.02–6.98 (m, 2H, ArH), 6.86 (t, $J = 7.5$ Hz, 1H, ArH), 3.93 (s, 3H, OCH_3), 1.48 (s, 9H, ^{t}Bu). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 163.4, 161.0, 152.9, 137.7, 137.4, 130.6, 128.1, 127.7, 121.0, 120.2, 118.1, 116.6, 111.8, 55.9 (OCH_3), 35.0, 29.5.

Synthesis of Schiff base ligand d

Lgand **d** was prepared using the similar procedure for ligand **a**. Salicylaldehyde (1.22 g, 10.0 mmol) and 2-aminophenol (1.09 g, 10.0 mmol) were used to give 1.90 g (yield, 89%) of red needle crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.27 (s, 1H, OH), 8.69 (s, 1H, CH=N), 7.44–6.98 (m, 8H, ArH), 5.80 (s, 1H, OH).

Synthesis of complex 1

A solution of *n*-BuLi (2.78 ml, 5.00 mmol) in *n*-hexane was added dropwise to 30 ml of THF solution of ligand a (1.14 g, 5.00 mmol) at −78 °C during 30 min, a cloudy yellow precipitate was formed. The above mixture was cooled to −78 °C and $CpZrCl_3 \cdot DME$ (1.76 g, 5.00 mmol) was added. Then it was stirred over 4 h at room temperature. The solvent was removed under vacuum and the residue was recrystallized from CH_2Cl_2 giving a yellow crystal of complex **1** (1.94 g, 72%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.52 (s, 1H, CH=N), 7.48 (m, 1H, ArH), 7.41 (d, $J = 8.3$ Hz, 2H, ArH), 7.31 (t, $J = 7.8$ Hz, 1H, ArH), 7.19 (t, $J = 7.8$ Hz, 1H, ArH), 7.14 (d, $J = 8.3$ Hz, 1H, ArH), 6.93 (t, $J = 7.8$ Hz, 1H, ArH), 6.80 (d, $J = 8.3$ Hz, 1H, ArH), 6.73 (s, 5H, Cp), 5.29 (s, 2H, CH_2Cl_2), 4.44 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 161.5, 160.1, 153.3, 137.4, 136.9, 135.6, 129.3, 125.8, 122.3, 120.7, 119.4, 118.8, 117.8, 115.5, 66.8 (OCH_3), 53.5 (CH_2Cl_2). IR (KBr, cm^{-1}) ν: 3087m, 3020m, 2965w, 2923w, 1609vs, 1585s, 1551s, 1496s, 1474vs, 1442s, 1396s, 1395s, 1303vs, 1283vs, 1264s, 1231m, 1222s, 1187m, 1174w, 1150s, 1122s, 1110m, 1053w, 1022s, 976s, 925m, 862m, 847s, 820vs, 808s, 791m, 778m, 762s, 749s, 732s. MS (70 eV) *m/z* (%): 401 (46, $[M-CH_3-Cl]^+$), 366 (9, $[M-CH_3\text{-}2Cl]^+$), 336 (100, $[M-CH_3-Cl-Cp]^+$), 225 (50, $[M-OC_6H_4CH{=}NC_6H_4OCH_3]^+$). Anal. calcd for $C_{19}H_{17}NO_2Cl_2Zr \cdot (CH_2Cl_2)$: C, 44.62; H, 3.56; N, 2.60; Found: C, 44.69; H, 3.61; N, 2.59%.

Synthesis of complex 2

Complex **2** was prepared using the similar procedure for complex **1**. *n*-BuLi (2.78 ml, 5.00 mmol), ligand **b** (1.21 g, 5.00 mmol) and $CpZrCl_3 \cdot DME$ (1.76 g, 5.00 mmol) were used to give 1.84 g (yield, 72%) of yellow needle crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.52 (s, 1H, CH=N), 7.41–7.27 (m, 4H, ArH), 7.20 (t, $J = 7.5$ Hz, 1H, ArH), 7.14 (d, $J = 8.3$ Hz, 1H, ArH), 6.85 (t, $J = 7.5$ Hz, 1H, ArH), 6.76 (s, 5H, Cp), 5.29 (s, 1H, CH_2Cl_2), 4.44 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3). IR (KBr, cm^{-1}) ν: 3038w, 2952w, 2916w, 1611s, 1592s, 1551s, 1560vs, 1497s, 1449m, 1426w, 1396s, 1301m, 1280s, 1225s, 1196m, 1164w, 1110m, 1085w, 1047w, 1022m, 981s, 880m, 852w, 808vs, 763m, 744s. MS (70 eV) *m/z* (%): 415 (24, $[M-CH_3-Cl]^+$), 400 (6, $[M-Cp]^+$), 350 (100, $[M-CH_3-Cl-Cp]^+$). Anal. calcd for $C_{20}H_{19}Cl_2NO_2Zr \cdot (CH_2Cl_2)_{0.5}$: C, 48.28; H, 3.95; N, 2.75; found: C, 48.63; H, 4.07; N, 2.58%.

Synthesis of complex 3

Complex **3** was prepared using the similar procedure for complex **1**. *n*-BuLi (2.78 ml, 5.00 mmol), ligand **c** (1.42 g, 5.00 mmol) and $CpZrCl_3 \cdot DME$ (1.76 g, 5.00 mmol) were used to give 1.71g (yield, 67%) of yellow needle crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.53 (s, 1H, CH=N), 7.55 (d, $J = 8.2$ Hz, 1H, ArH), 7.37–7.30 (m, 3H, ArH), 7.20 (t, $J = 7.7$ Hz, 1H, ArH), 7.15 (d, $J = 8.2$ Hz, 1H, ArH), 6.92 (t, $J = 7.7$ Hz, 1H, ArH), 6.82 (s, 5H, C_5H_5), 4.49 (s, 3H, OCH_3), 1.49(s, 9H, ^{t}Bu). IR (KBr, cm^{-1}) ν: 3017w, 2989w, 2953w, 2859w, 1611s, 1584s, 1551vs, 1495s, 1452m, 1423m, 1395vs, 1353w, 1316m, 1278m, 1261m, 1225s, 1206w, 1187m, 1143w, 1111m, 1089w, 1022m, 979s, 933w, 876s, 857w, 821s, 796vs, 778m, 748vs, 692m, 642m. MS (70 eV) *m/z* (%): 457 (49, $[M-CH_3-Cl]^+$), 442 (4, $[M-Cp]^+$), 406 (100, $[M-Cl-Cp]^+$), 392 (51, $[M-CH_3-Cl-Cp]^+$). Anal. calcd for $C_{23}H_{25}Cl_2NO_2Zr$: C, 54.21; H, 4.94; N, 2.75; found: C, 54.07; H, 4.96; N, 2.49%.

Synthesis of complex 4

Complex **4** was prepared using the similar procedure for complex **1**. *n*-BuLi (2.78 ml, 5.00 mmol), ligand **a** (1.14 g, 5.00 mmol) and $MeCpZrCl_3 \cdot DME$ (1.83 g, 5.00 mmol) were used to give 1.98 g (yield, 74%) of yellow needle crystals. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.53 (s, 1H, CH=N), 7.50–7.40 (m, 3H, Ar-H), 7.31(t, $J = 8.3$ Hz, 1H, Ar-H), 7.20 (t, $J = 8.0$ Hz, 1H, ArH), 7.13 (d, $J = 8.3$ Hz, 1H, ArH), 6.93 (t, $J = 8.0$ Hz, 1H, ArH), 6.80 (d, $J = 8.3$ Hz, 1H, ArH), 6.56 (t, $J = 2.7$ Hz, 2H, Cp), 6.48 (t, $J = 2.7$ Hz, 2H, Cp), 5.29 (s, 1.6H, CH_2Cl_2), 4.45 (s, 3H, OCH_3), 2.44 (s, 3H, CH_3). IR (KBr, cm^{-1}) ν: 3057w, 2952w, 2921w, 1613vs, 1586s, 1548vs, 1495s, 1472s, 1444s,

Copyright © 2006 John Wiley & Sons, Ltd.

DOI: 10.1002/aoc

1396s, 1302vs, 1252w, 1220s, 1188m, 1151m, 1122m, 1110m, 1038w, 979s, 924m, 862s, 817s, 763vs, 623s, 593w. MS (70 eV) *m/z* (%): 415 (22, $[M-CH_3-Cl]^+$), 379 (11, $[M-CH_3\text{-}2Cl]^+$), 336 (100, $[M-CH_3-Cl-MeCp]^+$), 300 (4, $[M-CH_3\text{-}2Cl-MeCp]^+$) Anal. calcd for $C_{20}H_{19}Cl_2NO_2Zr \cdot (CH_2Cl_2)_{0.8}$: C, 46.66; H, 3.88; N, 2.62; Found: C, 46.87; H, 4.13; N, 2.58%.

Synthesis of complex 5

Complex **5** was prepared using the similar procedure for complex **1**. *n*-BuLi (2.22 ml, 4.00 mmol), ligand **a** (0.912 g, 4.00 mmol) and *n*-$BuCpZrCl_3 \cdot DME$ (1.63 g, 4.00 mmol) were used to give 1.76g (yield, 69%) of yellow needle crystals. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.52 (s, 1H, CH=N), 7.49–7.39 (m, 3H, ArH), 7.30 (t, $J = 8.5$ Hz, 1H, ArH), 7.18 (t, $J = 8.5$ Hz, 1H, ArH), 7.12 (d, $J = 8.3$ Hz, 1H, ArH), 6.92 (t, $J = 8.3$ Hz, 1H, ArH), 6.77 (d, $J = 8.3$ Hz, 1H, ArH), 6.56 (t, $J = 2.7$ Hz, 2H, Cp), 6.51 (t, $J = 2.7$ Hz, 2H, Cp), 4.45 (s, 3H, OCH_3), 2.84 (t, $J = 7.4$ Hz, 2H, CH_2), 1.68 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 0.96 (t, $J = 7.4$ Hz, 3H, CH_3). IR (KBr, cm^{-1}) ν: 3062m, 2949s, 2925m, 2866w, 1613vs, 1591vs, 1548vs, 1495vs, 1397s, 1301s, 1222s, 1186m, 1149w, 1052w, 1036m, 975vs, 924m, 861m, 815s, 751vs, 924m, 861s, 815vs, 750vs, 674w, 623s. MS (70 eV) *m/z* (%): 457 (27, $[M-CH_3-Cl]^+$), 421 (27, $[M-CH_3\text{-}2Cl]^+$), 336 (100, $[M-CH_3-Cl-nBuCp]^+$), 281 (1, $[M-OC_6H_4CH{=}NC_6H_4OCH_3]^+$). Anal. calcd for $C_{23}H_{25}Cl_2NO_2Zr$: C, 54.21; H, 4.94; N, 2.75; found: C, 54.05; H, 4.98; N, 2.53%.

Synthesis of complex 6

Method a

A solution of *n*-BuLi (2.78 ml, 5.00 mmol) in n-hexane was added dropwise to 30 ml THF solution of ligand **a** (1.14 g, 5.00 mmol) at −70 °C during 30 min; a cloudy yellow precipitate was formed immediately. The above mixture was cooled to −70 °C and $CpZrCl_3 \cdot DME$ (1.76 g, 5.00 mmol) was added. The temperature was allowed to rise to room temperature, and the mixture was refluxed for 4 h. The solvent was removed under vacuum and the residue was extracted with CH_2Cl_2. The solution was concentrated and afforded an orange crystal of complex **6** (1.09 g, 46%).

Method b

Using the same procedure as for complex **1**, 1.06 g (5.00 mmol) of ligand **d**, 5.56 ml (10.0 mmol) of *n*-BuLi and 1.76 g (5.00 mmol) of $CpZrCl_3 \cdot DME$ were used to give an orange crystal of complex **6** (1.85 g, 79%). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.65 (s, 1H, CH=N), 7.44 (d, $J = 7.4$ Hz, 3H, ArH), 7.26 (d, $J = 7.4$ Hz, 1H, ArH), 6.89–6.78 (m, 4H, ArH), 6.32 (s, 5H, Cp), 3.76 (m, 4H, THF), 1.76 (m, 4H, THF). IR (KBr, cm^{-1}) ν: 3087m, 3065m, 3027m 2973w, 2905w, 1609vs, 1585s, 1550s, 1481vs, 1455m, 1442m, 1396s, 1302vs, 1261vs, 1226m, 1173w, 1151m, 1121w, 1040w, 1011m, 980w, 925m, 848vs, 814m, 789vs, 753s, 739s. MS (70 eV) *m/z* (%): 401 (7, M^+), 366 (5, $[M-Cl]^+$), 336 (17, $[M-Cp]^+$). Anal. calcd for $C_{18}H_{14}NO_2ClZr \cdot (THF)$: C, 55.58; H, 4.67; N, 2.95; found: C, 55.11; H, 4.67; N, 2.68%.

X-ray crystallography of the complex 1

The yellow crystal of 1 was sealed in capillary under argon atmosphere. All measurements were made on a Bruker AXSD8 diffractometer with graphite monochromatic Mo Kα (= 0.71073 Å) radiation. All data were collected at 20 °C using the scan techniques. All structures were solved by direct methods and refined using Fourier techniques. An absorption correction based on SADABS was applied.[44] All non-hydrogen atoms were refined by full-matrix least-squares on F^2. Hydrogen atoms were located and refined by the geometry method. The cell refinement, data collection, and reduction were done by Bruker SAINT.[45] The structure solution and refinement were performed by SHELXS-97[46] and SHELXL-97,[47] respectively. For further crystal data and details of measurements see Table 1.

Polymerization procedure and polymer analysis

A 150 ml flask equipped with an ethylene inlet, magnetic stirrer and vacuum line. Toluene, the comonomer (1-hexene, in the case of copolymerization) and MAO were sequentially added, then the flask was placed in a bath at the desired polymerization temperature for 10 min. The polymerization reaction was started by adding a solution of the catalyst precursor with a syringe. The polymerization was carried out for 0.5 h and then quenched with 3% HCl in ethanol. The precipitated polymer was filtered and then dried overnight in a vacuum oven at 80 °C to constant weight. The intrinsic viscosity $[\eta]$ of polyethylenes (PE) in decahydronaphathrene was measured with an Ubbelohde viscometer at 135 °C. The viscosity average molecular weight (M_η) was calculated as follows: $[\eta] = 6.77 \times 10^{-4}\, M_\eta^{0.67}$. The gel permeation chromatography (GPC) performed on a Waters 150 ALC/GPC system in a 1,2,4-trichlorobenzene solution at 135 °C, was used to determine the weight-average molecular weights (M_w) and the molecular weight distributions (M_w/M_n) of the polymers. The ^{13}C NMR spectrum was recorded on a Varian GEMINI-300 spectrometer in 1,2-dichlorobenzene-d_4 at 130 °C.

Acknowledgements

This work is subsidized by the National Basic Research Program of China (2005CB623801) and the National Natural Science Foundation of China (20372022).

REFERENCES

1. Gibson VC, Spitzmesser SK. *Chem. Rev.* 2003; **103**: 283.
2. Qian Y, Huang J, Bala MD, Lian B, Zhang H, Zhang H. *Chem. Rev.* 2003; **103**: 2633.
3. Stevens JC, Timmers FJ, Wilson DR, Schmidt GF, Nickias PN, Rosen RK, Knight GW, Lai S. Eur. Patent Applic. EP 416 815-A2, 1991; (Dow Chemical Co.).
4. Canich JM. Eur. Patent Appl. EP 420 436-A1, 1991; (Exxon Chemical Co.).
5. Brintzinger HH, Fischer D, Mülhaupt R, Rieger B, Waymouth RM. *Angew. Chem., Int. Edn* 1995; **34**: 1143.
6. Möhring PC, Coville NJ. *J. Organomet. Chem.* 1994; **479**: 1.

Copyright © 2006 John Wiley & Sons, Ltd.

7. Halterman RL. *Chem. Rev.* 1992; **92**: 965.
8. Britovsek GJP, Gibson VC, Wass DF. *Angew. Chem., Int. Edn* 1999; **38**: 428.
9. Huang J, Lian B, Yong L, Qian Y. *Inorg. Chem. Commun.* 2001; **4**: 392.
10. Scollard JD, McConville DH. *J. Am. Chem. Soc.* 1996; **118**: 10008.
11. Matsui S, Tohi Y, Mitani M, Saito J, Makio H, Tanaka H, Nitabaru M, Nakano T, Fujita T. *Chem. Lett.* 1999; 1065.
12. Saito J, Mitani M, Mohri J, Yoshida Y, Matsui S, Ishii S, Kojoh S, Kashiwa N, Fujita T. *Angew. Chem., Int. Edn* 2001; **40**: 2918.
13. Nomura K, Okumura H, Komatsu T, Naga N. *Macromolecules* 2002; **35**: 5388.
14. Nomura K, Fujii K. *Organometallics* 2002; **21**: 3042.
15. Nomura K, Hatanaka Y, Okumura H, Fujiki M, Hasegawa K. *Macromolecules* 2004; **37**: 1693.
16. Kim Y, Han Y, Do Y. *J. Organomet. Chem.* 2001; **634**: 19.
17. Kim Y, Han Y, Hwang J, Kim MW, Do Y. *Organometallics* 2002; **21**: 1127.
18. Keaton RJ, Jayaratne KC, Henningsen DA, Koterwas LA, Sita LR. *J. Am. Chem. Soc.* 2001; **123**: 6197.
19. Mahanthappa MK, Cole AP, Waymouth RW. *Organometallics* 2004; **23**: 836.
20. Gómez R, Duchateau R, Chernega AN, Teuben JH, Edelmann FT, Green MLH. *J. Organomet. Chem.* 1995; **491**: 153.
21. Zhang H, Nomura K. *J. Am. Chem. Soc.* 2005; **127**: 9364.
22. Nomura K, Komatsu T, Imanishi Y. *Macromolecules* 2000; **33**: 8122.
23. Nomura K, Itagaki K, Fujiki M. *Macromolecules* 2005; **38**: 2053.
24. Doherty S, Errington RJ, Jarvis AP, Collins S, Clegg W, Elsegood MRJ. *Organometallics* 1998; **17**: 3408.
25. Sanz M, Cuenca T, Galakhov M, Grassi A, Bott KJ, Hughes DL, Schormann M, Lancaster SJ, Bochmann M. *Organometallics* 2004; **23**: 5324.
26. Noda K, Ito Y, Matsumoto N, Katsuki T. *Tetrahedron Lett.* 1990; **31**: 7345.
27. Sigman MS, Jacobsen EN. *J. Am. Chem. Soc.* 1998; **120**: 4901.
28. Atwood DA, Jegier JA, Rutherford D. *J. Am. Chem. Soc.* 1995; **117**: 6779.
29. Younkin TR, Connor EF, Henderson JI, Friedrich SK, Grubbs RH, Bansleben DA. *Science* 2000; **287**: 460.
30. Nimitsiriwat N, Marshall EL, Gibson VC, Elsegood MRJ, Dale SH. *J. Am. Chem. Soc.* 2004; **126**: 13598.
31. Huang J, Lian B, Qian Y, Zhou W, Chen W, Zheng G. *Macromolecules* 2002; **35**: 4871.
32. Chen Q, Huang J, Yu J. *Inorg. Chem. Commun.* 2005; **8**: 444.
33. Matsui S, Mitani M, Saito J, Tohi Y, Makio H, Matsukawa N, Takagi Y, Tsuru K, Nitabaru M, Nakano T, Tanaka H, Kashiwa N, Fujita T. *J. Am. Chem. Soc.* 2001; **123**: 6847.
34. Kettunen M, Vedder C, Schaper F, Leskela M, Mutikainen I, Brintzinger HH. *Organometallics* 2004; **23**: 3800.
35. Firth AV, Stewart JC, Hoskin AJ, Stephan DW. *J. Organomet. Chem.* 1999; **591**: 185.
36. Sudhakar P, Amburose CV, Sundararajan G, Nethaji M. *Organometallics* 2004; **23**: 4462.
37. Junior PAC, Nele M, Coutinho FMB. *Eur. Polym. J.* 2002; **38**: 1471.
38. Antiñolo A, Carrillo-Hermosilla F, Corrochano A, Fernández-Baeza J, Lara-Sanchez AR, Ribeiro M, Lanfranchi M, Otero A, Pellinghelli MA, Portela MF, Santos JV. *Organometallics* 2000; **19**: 2837.
39. Wang W, Fujiki M, Nomura K. *Macromol. Rapid Commun.* 2004; **25**: 504.
40. Nomura K, Oya K, Imanishi Y. *J. Mol. Catal. A: Chem.* 2001; **174**: 127.
41. Charles SK, Losee ML. *J. Am. Chem. Soc.* 1968; **90**: 4701.
42. Frita HP, Kreiter CG. *J. Organomet. Chem.* 1965; **4**: 313.
43. Lund EC, Livinghouse T. *Organometallics* 1990; **9**: 2426.
44. *SADABS, Bruker Nonius Area Detector Scaling and Absorption Correction-V2.05.* Bruker AXS: Madison, WI, 1996.
45. *SAINT, Version 6.02.* Bruker AXS: Madison, WI, 1999.
46. Sheldrick GM. SHELXS-97 Program for the Solution of Crystal Structures. University of Gottingen: Gottingen, 1990.
47. Sheldrick GM. SHELXL-97 Program for the Refinement of Crystal Structures. University of Gottingen: Gottingen, 1997.

Copyright © 2006 John Wiley & Sons, Ltd.

DOI: 10.1002/aoc