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Group 4 metal alkoxide complexes as catalysts for olefin polymerization

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The complexation of 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde **I** with titanium or zirconium tetrachloride yielded two classes of complexes containing either one or two didentate alkoxide ligands. The structures of three monomeric, six-co-ordinate complexes, *cis*-dichlorobis(3-*tert*-butyl-5-methyl-2-oxobenzoyl)titanium(IV) **1**, *cis*-dichlorobis(3-*tert*-butyl-5-methyl-2-oxobenzoyl)zirconium(IV) **2** and *mer*-trichloro(3-*tert*-butyl-5-methyl-2-oxobenzoyl)(tetrahydrofuran)zirconium(IV) **3** were characterized by single-crystal X-ray diffraction. Compounds **I** and **3** crystallize in the monoclinic space group $P2_1$ with $Z = 2$, compound **1** in Cc with $Z = 4$ and compound **2** in orthorhombic space group $Pbca$ with $Z = 8$. In the presence of methylaluminooxane complexes **1**–**3** give homogeneous catalysts, which for the polymerization of ethylene produced high molecular weight polyethylene with a broad molecular weight distribution.

The Lewis acidity of early transition metals in high oxidation states together with the co-ordinative and electronic unsaturation of complexes are important characteristics of many catalytically active complexes.[1-4] These characteristics are the key features to obtaining any metal-centered reactivity. The 'sites' of co-ordinative unsaturation (two reducible ligands or vacant co-ordination sites) must be *cis* to one another around the metal ion to obtain the insertion step which is required in many transition-metal catalysed reactions.[3,5]

Mononuclear complexes are proposed to be the active species in homogeneous catalytic systems[6] and can be obtained using sterically-hindered ligands.[7,8] Very bulky ligands, however, can lower the activity of the catalyst as complexation of the substrates is sterically hindered,[3,9] but on the other hand, can protect the metal against deactivating side reactions.[3]

The chirality and structural rigidity of complexes can affect the selectivity of catalysts which are used in stereospecific olefin polymerization processes.[10] This is illustrated by many stereospecific catalysts of Group 4 metallocene derivatives, especially those employed in the polymerization of propene.[3,10,11] The use of chiral ligands provides a challenge to obtain optically pure products in the asymmetric hydrogenation of prochiral olefins.[12] Chiral transition-metal complexes also play a key role in asymmetric epoxidation reactions.[4]

Our aim is to combine the above properties and generate new early transition-metal alkoxide complexes for catalytic purposes. Here, we report the complexation studies of the salicylaldehyde derivative, 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde, with titanium and zirconium tetrachloride. Earlier[13,14] we published the synthesis and molecular structure of a titanium complex with a monodentate alkoxide ligand, trichloro(2,6-di-*tert*-butylphenoxo)titanium(IV), together with studies of its reactivity in ethylene–styrene copolymerization. Polymerization studies with ethylene and propylene and some copolymerization studies have shown that the new complexes $[TiCl_2L_2]$ **1**, $[ZrCl_2L_2]$ **2** and $[ZrCl_3(L)(thf)]\cdot CH_2Cl_2$ **3** catalyse olefin polymerization reactions.

Experimental

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. *n*-Butyllithium (1.6 mol dm^{-3} solution in hexane, Merck) and metallic Na (pro analysis grade, Merck) were used as received; pentane (analytical grade, Lab-Scan), tetrahydrofuran (thf) (HPLC grade, Rathburn) and toluene (pro analysis grade, R. P. Normapur) were dried and purified by refluxing over $LiAlH_4$; dichloromethane (pro analysis grade, Merck) was dried and purified by refluxing over phosphorus pentoxide and $TiCl_4$ and $ZrCl_4$ (Aldrich) were 99.9% pure.

Syntheses

3-*tert*-Butyl-2-hydroxy-5-methylbenzaldehyde I. The compound was prepared by the method of Casiraghi *et al.*[15] The crude product was purified by distillation under reduced pressure (104–105 °C, 8 mmHg, ≈1066.576 Pa). Part of this (2 g) was recrystallized from diethyl ether (100 cm^3) to give lemon yellow crystals (80%) suitable for X-ray diffraction.

Metallation of compound I. The hydroxyl unit of compound **I** was deprotonated *in situ* by general methods with *n*-butyllithium (*a*) or metallic sodium (*b*). (*a*) *n*-Butyllithium was added to a stirred solution of compound I in thf at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The solvent medium was evaporated and a crystalline light yellow solid was obtained. (*b*) Compound **I** was added in solid form to a stirred mixture of metallic sodium and thf at room temperature. The reaction mixture was refluxed for several hours until no metallic sodium could be seen in the mixture. The solvent was evaporated and a yellow solid was obtained.

Dichlorobis(3-*tert*-butyl-5-methyl-2-oxobenzoyl)titanium(IV) 1. Compound **I** (4 g, 0.0208 mol) was metallated with sodium (0.48 g, 0.0208 mol) as described above. The resulting yellow solid was dissolved in CH_2Cl_2 (100 cm^3) and cooled to −78 °C. It was then added dropwise to a stirred, cooled (−78 °C) solution of $TiCl_4$ (1.2 cm^3, 0.0104 mol) in CH_2Cl_2 (100 cm^3). The deep red mixture was allowed to warm slowly to room temperature and was stirred overnight. The reaction mixture was filtered through Celite to remove NaCl. The dichloromethane was evaporated and the deep red crude product was dissolved in toluene (100 cm^3) and filtered again. Part of the product was crystallized by the diffusion[16] of pentane and the rest by adding pentane to the toluene solution of the product (1:6). The resulting deep red solid was recrystallized twice from pentane–toluene solution. Yield of crystalline compound **1** 3.5 g (68%).

Dichlorobis(3-*tert*-butyl-5-methyl-2-oxobenzoyl)zirconium(IV) 2. Compound **I** (3 g, 0.016 mol) was metallated with *n*-

Table 1 Summary of crystal data and structure refinement of compounds **I** and **1**–**3**

Formula	$C_{12}H_{16}O_2$	$C_{24}H_{30}Cl_2O_4Ti$	$C_{24}H_{30}Cl_2O_4Zr$	$C_{17}H_{25}Cl_5O_3Zr$
M	192.25	501.28	544.60	545.84
Colour, habit	Light yellow, plate	Red, prism	Yellowish, prism	Yellowish, prism
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1$	Cc	$Pbca$	$P2_1$
a/Å	8.419(3)	8.984(4)	19.049(4)	11.076(4)
b/Å	6.706(1)	24.396(5)	28.872(5)	8.619(4)
c/Å	9.788(2)	11.758(6)	9.170(4)	12.255(4)
β/°	96.53(2)	98.30(4)		93.49(3)
U/Å^3	549.0(2)	2550(2)	5043(2)	1167.7(8)
Z	2	4	8	2
D_c/g cm^{-3}	1.163	1.306	1.434	1.552
$F(000)$	208	1048	2240	552
μ/mm^{-1}	0.078	0.571	0.674	1.057
Crystal size/mm	0.40 × 0.30 × 0.20	0.30 × 0.15 × 0.10	0.30 × 0.20 × 0.10	0.20 × 0.15 × 0.10
2θ Range/°	4–53	5–53	5–50	5–53
Reflections refined (n)	1242	2610	3488	2437
No. of variables (p)	130	165	280	234
R	0.047	0.095	0.057	0.063
wR_2	0.113	0.139	0.091	0.090
Goodness-of-fit (on F^2)	0.892	1.045	0.818	1.068
Maximum peak, hole/e Å^{-3}	0.157, −0.198	0.343, −0.418	0.505, −0.439	0.491, −0.619

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F > 4\sigma(F)$, function minimized is $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$; $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{\frac{1}{2}}$.

butyllithium (10 cm^3, 0.016 mol) as described above. The resulting pale yellow solid was dissolved in dichloromethane (100 cm^3) and cooled to −20 °C. This solution was added to a stirred, cooled (−20 °C) suspension of $ZrCl_4$ (1.9 g, 0.008 mol) in dichloromethane (100 cm^3). The reaction mixture was allowed to warm to room temperature and was stirred overnight. It was then filtered through Celite to remove LiCl and the solvent evaporated. The crude product was dissolved in toluene (100 cm^3) and filtered again. The volume of toluene was reduced to one third and the product precipitated as pale yellow crystals at −20 °C. The product was recrystallized once from toluene–dichloromethane (6:1). Yield: 3.1 g (70%).

Trichloro(3-*tert*-butyl-5-methyl-2-oxobenzoyl)(tetrahydrofuran)zirconium(IV)–dichloromethane (1/1) 3. Compound **I** (5.0 g, 0.026 mol) was metallated with sodium (0.6 g, 0.026 mol). The resulting yellow solid was dissolved in dichloromethane (100 cm^3) and cooled to −78 °C. Zirconium tetrachloride (6.0 g, 0.027 mol) was added to the solution in solid form. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The solution was filtered through Celite, and its volume reduced to one third. The product crystallized at −20 °C. Yield: 11.1 g (75%).

Crystal data collection and structure determinations

The crystal data and structure refinement of the four compounds is summarized in Table 1. The manipulation of the air-sensitive crystals were made as described by Hope.[17] Unit cell parameters were calculated from least-squares fitting of the 2θ angles for 15, 13, 20 and 24 reflections found by the zigzag-mode search of the diffractometer for compounds **I**, **1**, **2** and **3**, respectively. Intensities were collected by ω–2θ scan mode for **I** and **3**, and by ω mode for **1** and **2** on a Rigaku AFC7S diffractometer using Mo-Kα radiation (λ = 0.710 73 Å) at 193 K. During data collection the intensities of three check reflections were monitored after every 200 reflections, and only statistical fluctuations were detected. The raw data were corrected for Lorentz and polarization effects, and an empirical correction for absorption was performed in each case (ψ scan).[18] The structures were solved using direct methods (SHELXTL-PC) and subsequent Fourier syntheses.[19] Final least-squares refinements were calculated using SHELXL.[20] Neutral atomic scattering and dispersion factors were those included in the program packages. The function minimized was $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

Table 2 Final atomic coordinates (× 10^{-4}) for compound **I**

Atom	x	y	z
O(1)	−3252(2)	4967(12)	5665(2)
O(2)	−841(2)	4976(13)	7581(2)
C(1)	−2272(3)	4995(15)	4829(3)
C(2)	−556(2)	4950(13)	5184(2)
C(3)	120(2)	4989(12)	6561(2)
C(4)	1792(2)	4992(13)	6900(2)
C(5)	2695(2)	5016(13)	5806(2)
C(6)	2072(3)	4947(14)	4423(2)
C(7)	430(3)	4997(16)	4130(2)
C(8)	2555(3)	5008(16)	8407(2)
C(9)	4381(3)	5045(9)	8507(3)
C(10)	2043(3)	6758(8)	9130(7)
C(11)	2050(6)	3008(9)	9120(8)
C(12)	3171(3)	4866(18)	3307(3)

The structure of compound **I** could be solved in two monoclinic space groups, in the centric space group $P2_1/m$ and non-centric $P2_1$. The refinement in $P2_1$ gave $R(F)$ 0.047 and $wR_2(F^2)$ 0.113 compared to $R(F)$ 0.063 and $wR_2(F^2)$ 0.208 in $P2_1/m$. In the centric space group the entire molecule, with the exception of one methyl group, must be exactly on the crystallographic mirror plane, giving higher final residual electron densities (0.44 and −0.27 e Å^{-3}) than in $P2_1$ (0.157 and −0.198 e Å^{-3}). Therefore the non-centric space group $P2_1$ was chosen. Non-hydrogen atoms were anisotropically refined and H atoms were picked from the Fourier-difference map. The hydrogen atoms were isotropically refined as a rigid group, except for one phenolic hydrogen which was fixed at an O–H distance of 0.85 Å, but otherwise left to refine (riding model). The displacement parameters of the H atoms were 1.5 times those of the host atom. The final atomic coordinates are given in Table 2.

In the structure of complex **1**, non-hydrogen atoms with the exception of the carbon atoms, were anisotropically refined. Hydrogen atoms were isotropically refined at calculated positions with displacement parameters 1.5 times those of the host atom (riding model). Space group Cc was confirmed through absent reflections and structure analysis. The final atomic coordinates are given in Table 3.

In the structures of compounds **2** and **3**, all non-hydrogen atoms were anisotropically refined and H atoms isotropically refined at calculated positions with displacement parameters 1.5 times those of the host atom (riding model). Space group

Table 3 Final atomic coordinates ($\times 10^{-4}$) for compound **1**

Atom	*x*	*y*	*z*
Ti	4 633(3)	1 943(1)	2 949(3)
Cl(1)	4 203(4)	2 852(2)	3 422(4)
Cl(2)	2 692(5)	1 885(2)	1 506(4)
O(1)	6 182(11)	2 300(4)	1 995(9)
O(2)	5 608(10)	1 292(4)	2 594(8)
O(3)	6 502(10)	2 003(4)	4 309(9)
O(4)	3 705(10)	1 639(4)	4 097(9)
C(1)	7 193(15)	2 086(6)	1 539(12)
C(2)	7 594(16)	1 528(6)	1 559(13)
C(3)	6 701(16)	1 148(6)	2 047(12)
C(4)	7 056(17)	592(6)	1 975(13)
C(5)	8 307(18)	440(7)	1 437(14)
C(6)	9 125(18)	823(7)	945(14)
C(7)	8 763(17)	1 373(6)	997(12)
C(8)	6 172(19)	127(7)	2 564(15)
C(9)	6 767(19)	−442(8)	2 413(17)
C(10)	4 549(19)	144(8)	1 961(15)
C(11)	6 227(18)	249(7)	3 845(13)
C(12)	10 452(13)	643(6)	311(11)
C(13)	6 446(13)	1 942(6)	5 332(11)
C(14)	5 174(17)	1 813(6)	5 866(13)
C(15)	3 804(15)	1 627(5)	5 219(12)
C(16)	2 550(15)	1 472(6)	5 727(12)
C(17)	2 818(17)	1 485(6)	6 960(13)
C(18)	4 139(17)	1 663(7)	7 617(14)
C(19)	5 312(16)	1 820(6)	7 057(12)
C(20)	1 074(18)	1 295(7)	5 011(14)
C(21)	−51(19)	1 075(7)	5 825(14)
C(22)	373(18)	1 793(6)	4 375(14)
C(23)	1 341(19)	824(8)	4 202(16)
C(24)	4 254(19)	1 664(8)	8 919(15)

Table 4 Final atomic coordinates ($\times 10^{-4}$) for compound **2**

Atom	*x*	*y*	*z*
Zr	1948(1)	1684(1)	170(1)
Cl(1)	882(1)	1946(1)	−1038(3)
Cl(2)	2429(1)	1322(1)	−1966(2)
O(1)	2318(3)	2393(2)	−50(6)
O(2)	2854(2)	1669(2)	1292(5)
O(3)	1514(3)	2023(2)	2139(6)
O(4)	1581(3)	1142(2)	1230(6)
C(1)	2777(4)	2608(3)	630(9)
C(2)	3268(4)	2434(3)	1646(9)
C(3)	3311(4)	1952(3)	1916(9)
C(4)	3849(4)	1778(3)	2858(8)
C(5)	4267(4)	2112(3)	3499(8)
C(6)	4233(4)	2590(3)	3307(9)
C(7)	3727(4)	2740(3)	2343(8)
C(8)	3923(5)	1254(3)	3145(10)
C(9)	4526(4)	1162(3)	4216(10)
C(10)	4092(5)	1015(3)	1686(10)
C(11)	3257(4)	1065(2)	3824(9)
C(12)	4715(4)	2910(3)	4080(9)
C(13)	1334(4)	1842(3)	3332(10)
C(14)	1268(4)	1362(3)	3637(9)
C(15)	1409(4)	1014(3)	2606(9)
C(16)	1349(4)	548(3)	3011(8)
C(17)	1150(4)	450(3)	4451(9)
C(18)	1022(5)	784(3)	5487(9)
C(19)	1090(4)	1247(3)	5094(9)
C(20)	1477(5)	155(3)	1895(10)
C(21)	1389(5)	−328(2)	2582(9)
C(22)	941(4)	184(3)	671(9)
C(23)	2230(4)	180(3)	1315(10)
C(24)	818(5)	651(3)	7024(9)

Table 5 Final atomic coordinates ($\times 10^{4}$) for compound **3**

Atom	*x*	*y*	*z*
Zr	3 471(1)	0	2 642(1)
Cl(1)	1 533(2)	−1 360(4)	2 650(2)
Cl(2)	2 894(2)	1 466(4)	1 029(2)
Cl(3)	5 575(2)	846(4)	2 723(2)
Cl(4)	869(4)	4 633(5)	10 156(3)
Cl(5)	1 603(4)	6 413(6)	8 350(3)
O(1)	3 937(6)	−1 373(8)	4 122(5)
O(2)	2 977(6)	1 442(7)	3 760(5)
O(3)	4 099(6)	−2 098(8)	1 814(5)
C(1)	3 576(9)	−1 182(12)	5 062(7)
C(2)	2 886(7)	104(15)	5 441(6)
C(3)	2 623(9)	1 428(11)	4 791(7)
C(4)	2 037(8)	2 707(11)	5 228(7)
C(5)	1 698(8)	2 588(12)	6 290(7)
C(6)	1 896(8)	1 286(12)	6 948(7)
C(7)	2 491(7)	60(16)	6 521(6)
C(8)	1 806(9)	4 186(11)	4 537(8)
C(9)	1 184(10)	5 459(13)	5 155(9)
C(10)	3 011(9)	4 836(15)	4 157(8)
C(11)	956(9)	3 798(14)	3 506(8)
C(12)	1 483(9)	1 232(14)	8 095(7)
C(13)	3 425(11)	−2 868(16)	907(9)
C(14)	4 189(10)	−4 117(17)	502(10)
C(15)	5 076(11)	−4 450(15)	1 457(9)
C(16)	5 205(9)	−2 970(13)	2 089(10)
C(17)	439(10)	5 988(17)	9 184(13)

*P*2$_1$ for **3** was verified by systematic absences and structure analysis. Final atomic coordinates for compounds **2** and **3** are given in Tables 4 and 5, respectively.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Polymerization

The polymerizations were performed in a 2 dm^3 autoclave reactor (Büchi). The evacuated autoclave was charged with pentane under a nitrogen atmosphere at room temperature. A toluene solution of the catalyst and the cocatalyst (methylaluminooxane, mao) was mixed in a catalyst cylinder and then introduced into the reactor. The temperature was raised to 80 °C and the ethylene (and comonomer) feed was started. The process was stopped by cooling and degassing the reactor. Polymerization conditions: partial pressure of ethylene 10 bar (10^6 Pa), temperature 80 °C, pentane solvent.

Results and Discussion

Synthetic studies

A straightforward route to easily isolable Group 4 metal alkoxide halide complexes is halide displacement from metal chlorides by alkoxide ligands using an alkali metallated alkoxide complex.[21] The compound 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde was first metallated using metallic sodium or organolithium compounds (*e.g.* *n*-butyllithium). The metallated ligand was introduced to MCl_4 in ratios of 1 : 2 and 1 : 1, see Scheme 1. The reaction route used led to a relatively good yield of Group 4 metal complexes of **I**. To the best of our knowledge co-ordination of this chelating alkoxide ligand with Group 4 metals and the structures of resulting complexes has not previously been studied. The Cambridge Structural Database revealed that very few structures of mononuclear Group 4 metal alkoxo complexes with didentate alkoxo ligands have been structurally characterized. However, many reports exist on acetyl acetonate complexes.[22]

Attempts to displace one chloro ligand from titanium tetrachloride by introducing one equivalent of metallated ligand failed. Only complexes with two didentate alkoxide ligands were observed in our studies. With $ZrCl_4$, however, a complex with one alkoxide ligand and three chlorides could be synthesized by this route.

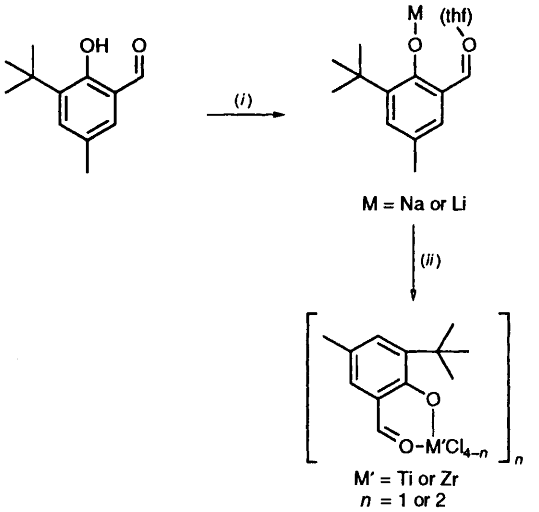
The relatively air-sensitive complexes were crystallized several ways to obtain good quality crystals for X-ray diffraction studies. The most successful method was found to be that described by Friedman and Ford.[16] The complex was first dissolved in toluene in an open sample holder. The holder was then placed in a bottle containing pentane, the bottle was closed and the slow diffusion of pentane into the sample solution caused the formation of good quality crystals.

The titanium complex **1** was dark red while the zirconium complexes **2** and **3** were yellowish. The complexes were relatively air-sensitive, however, the observable decomposition of complex **1** did not begin for several hours in air. The complexes decomposed immediately in moist solvents. The complexes were readily soluble in chlorinated solvents and diethyl ether, soluble in aromatic solvents, but insoluble in alkanes. All complexes were crystalline solids at room temperature.

Structural studies

The structures of the compounds were determined by X-ray diffraction analyses. The molecular structures and atom numbering of compounds **I**, **1**, **2** and **3** are presented in Figs. 1, 2, 3 and 4, respectively. Selected interatomic distances and angles for compound **I**, including hydrogen bond data, are given in Table 6. The bond distances and angles are typical for this sort of organic molecule. There is a hydrogen bond between the phenolic hydrogen and the aldehyde oxygen. Conjugation between the aromatic ring and the double bond of the aldehyde oxygen shortens the bond between C(1) and C(2) from the normal single C–C bond length (1.54 Å) to 1.447(3) Å. The usual conjugated C–C bond length is 1.46 Å.[23] The compound is otherwise planar except for the methyls of the *tert*-butyl group which are out of the plane. The planarity of the molecule is retained upon co-ordination.

Selected bond lengths and angles for complexes **1** and **2** are given in Tables 7 and 8, respectively. The overall co-ordination



Scheme 1 Derivation of titanium and zirconium complexes from compound **I**. (*i*) Na or LiBu^n. (*ii*) 0.5 or 1.0 equivalent M'Cl$_4$ (M' = Ti or Zr)

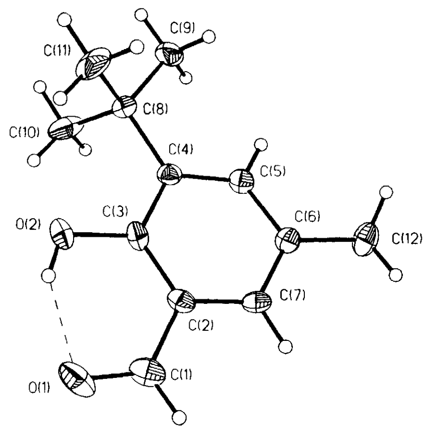


Fig. 1 Molecular structure and atom numbering scheme of compound **I**

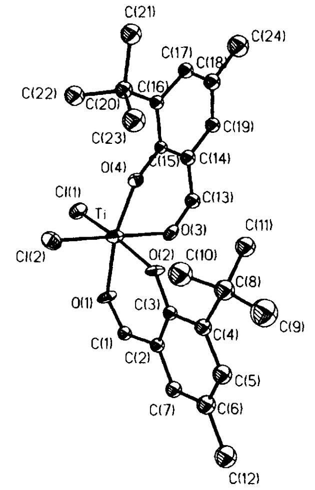


Fig. 2 Molecular structure and atom numbering scheme of complex **1**

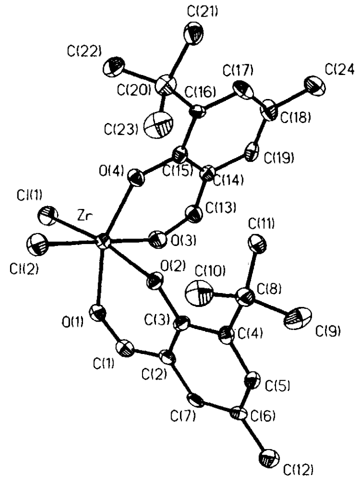


Fig. 3 Molecular structure and atom numbering scheme of complex **2**

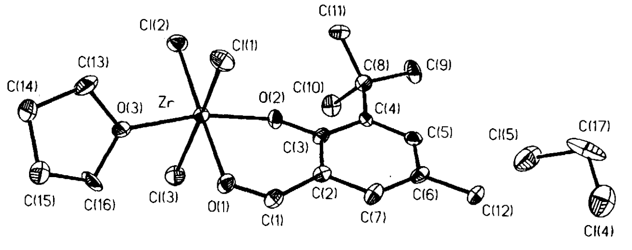


Fig. 4 Molecular structure and atom numbering scheme of complex **3**

Table 6 Selected interatomic distances (Å) and angles (°) for compound **I**

O(1)–C(1)	1.227(3)	O(2)–H(2A)	0.850(2)
O(2)–C(3)	1.356(3)	C(1)–C(2)	1.447(3)
O(1)–O(2)	2.602(3)	C(2)–C(3)	1.402(3)
O(1)···H(2A)	1.848(2)		
O(1)–C(1)–C(2)	124.7(3)	O(2)–H(2A)···O(1)	147.0(7)
C(3)–C(2)–C(1)	121.0(2)	C(1)–O(1)···H(2A)	97.3(6)
O(2)–C(3)–C(2)	119.8(2)		

Table 7 Selected bond lengths (Å) and angles (°) for complex **1**

Ti–O(4)	1.842(10)	O(2)–C(3)	1.30(2)
Ti–O(2)	1.889(10)	O(3)–C(13)	1.22(2)
Ti–O(1)	2.098(9)	O(4)–C(15)	1.31(2)
Ti–O(3)	2.151(10)	C(1)–C(2)	1.41(2)
Ti–Cl(2)	2.254(5)	C(2)–C(3)	1.40(2)
Ti–Cl(1)	2.332(5)	C(13)–C(14)	1.42(2)
O(1)–C(1)	1.236(14)	C(14)–C(15)	1.42(2)
O(4)–Ti–O(2)	95.6(4)	O(3)–Ti–Cl(1)	84.0(3)
O(4)–Ti–O(1)	164.6(5)	Cl(2)–Ti–Cl(1)	95.9(2)
O(2)–Ti–O(1)	82.3(4)	C(1)–O(1)–Ti	130.0(9)
O(4)–Ti–O(3)	82.5(4)	C(3)–O(2)–Ti	138.2(9)
O(2)–Ti–O(3)	83.4(4)	C(13)–O(3)–Ti	125.9(9)
O(1)–Ti–O(3)	82.0(4)	C(15)–O(4)–Ti	140.8(9)
O(4)–Ti–Cl(2)	98.3(3)	O(1)–C(1)–C(2)	127.1(14)
O(2)–Ti–Cl(2)	96.6(3)	C(3)–C(2)–C(1)	119.1(13)
O(1)–Ti–Cl(2)	97.1(3)	O(2)–C(3)–C(2)	122.9(13)
O(3)–Ti–Cl(2)	179.2(4)	O(3)–C(13)–C(14)	127.9(13)
O(4)–Ti–Cl(1)	95.7(3)	C(13)–C(14)–C(15)	121.6(13)
O(2)–Ti–Cl(1)	161.8(3)	O(4)–C(15)–C(14)	117.3(12)
O(1)–Ti–Cl(1)	83.0(3)		

Table 8 Selected bond lengths (Å) and angles (°) for complex **2**

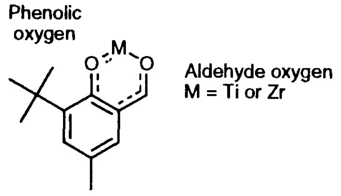
Zr–O(4)	1.971(5)	O(2)–C(3)	1.324(8)
Zr–O(2)	2.011(5)	O(3)–C(13)	1.260(9)
Zr–O(1)	2.173(5)	O(4)–C(15)	1.355(8)
Zr–O(3)	2.214(6)	C(1)–C(2)	1.411(10)
Zr–Cl(2)	2.403(2)	C(2)–C(3)	1.415(10)
Zr–Cl(1)	2.432(2)	C(13)–C(14)	1.418(10)
O(1)–C(1)	1.241(8)	C(14)–C(15)	1.406(10)
O(4)–Zr–O(2)	92.0(2)	O(3)–Zr–Cl(1)	85.6(2)
O(4)–Zr–O(1)	155.3(2)	Cl(2)–Zr–Cl(1)	94.70(9)
O(2)–Zr–O(1)	77.8(2)	C(1)–O(1)–Zr	130.8(5)
O(4)–Zr–O(3)	79.5(2)	C(3)–O(2)–Zr	140.6(5)
O(2)–Zr–O(3)	85.0(2)	C(13)–O(3)–Zr	128.7(5)
O(1)–Zr–O(3)	77.3(2)	C(15)–O(4)–Zr	139.5(5)
O(4)–Zr–Cl(2)	101.0(2)	O(1)–C(1)–C(2)	128.3(7)
O(2)–Zr–Cl(2)	94.6(2)	C(1)–C(2)–C(3)	120.2(7)
O(1)–Zr–Cl(2)	102.1(2)	O(2)–C(3)–C(2)	119.5(7)
O(3)–Zr–Cl(2)	179.4(2)	O(3)–C(13)–C(14)	126.9(8)
O(4)–Zr–Cl(1)	100.1(2)	C(15)–C(14)–C(13)	123.3(8)
O(2)–Zr–Cl(1)	163.0(2)	O(4)–C(15)–C(14)	118.6(7)
O(1)–Zr–Cl(1)	86.35(14)		

sphere of metal ions in complexes **1** and **2** is octahedral. The small angles (O′–M–O) between the oxygen atoms of the chelating ligands causes some distortion from the ideal octahedron. The shortening of the bond between the carbonyl carbon atoms and α-carbon atoms of the alkoxide ligands, with respect to the usual conjugated C–C bond length, indicates that the charge is delocalized over the aromatic ring and that a metallocycle is formed upon co-ordination. In complex **1** the distances between the phenolic oxygen atoms and the central metal are shorter, 1.886(10) Å (average), than the calculated single covalent bond length for Ti–O (2.01 Å),[24] which indicates that there is some double bond nature between Ti and the phenolic oxygen atoms. Also in complex **2** the short Zr–O bonds [1.991(5) Å (average)] between the metal and the phenolic oxygen can be taken as an indication of the double bond character. According to the literature the short distance between Group 4 metal and alkoxide oxygen together with the almost linear M–O–C angle caused by the dp–pp interaction is a feature often observed in monodentate complexes, which indicates the strong p-donation ability of oxygen.[1,25] In our case the complexes cannot achieve the linear M–O–C angle because of chelation.

Selected bond lengths and angles for complex **3** are given in Table 9. The zirconium atom has a distorted octahedral co-ordination sphere, which consists of three chlorides and three oxygen atoms. The oxygen atoms originate from molecule **I** and a thf molecule. A dichloromethane molecule has also been incorporated into the structure. The short Zr–O(2) distance indicates that there is p interaction between the phenolic oxygen atom of the chelating ligand and zirconium also in this complex. Interestingly, in this complex the bond distance between C(1) and C(2) does not shorten on co-ordination, the bond distances of the co-ordinated ligand remaining almost unchanged in comparison with the free molecule.

Table 9 Selected bond lengths (Å) and angles (°) for complex **3**

Zr–O(2)	1.953(6)	Cl(4)–C(17)	1.71(2)
Zr–O(1)	2.200(7)	Cl(5)–C(17)	1.73(2)
Zr–O(3)	2.207(6)	O(1)–C(1)	1.253(10)
Zr–Cl(2)	2.400(3)	O(2)–C(3)	1.345(10)
Zr–Cl(3)	2.438(3)	C(1)–C(2)	1.439(14)
Zr–Cl(1)	2.446(3)	C(2)–C(3)	1.412(14)
O(2)–Zr–O(1)	79.9(2)	O(2)–Zr–Cl(1)	91.1(2)
O(2)–Zr–O(3)	162.5(2)	O(1)–Zr–Cl(1)	84.3(2)
O(1)–Zr–O(3)	82.7(2)	O(3)–Zr–Cl(1)	84.9(2)
O(2)–Zr–Cl(2)	99.9(2)	Cl(2)–Zr–Cl(1)	93.79(10)
O(1)–Zr–Cl(2)	178.1(2)	Cl(3)–Zr–Cl(1)	168.50(11)
O(3)–Zr–Cl(2)	97.4(2)	C(1)–O(1)–Zr	128.0(7)
O(2)–Zr–Cl(3)	95.1(2)	C(3)–O(2)–Zr	139.8(6)
O(1)–Zr–Cl(3)	87.2(2)	O(1)–C(1)–C(2)	127.1(9)
O(3)–Zr–Cl(3)	86.4(2)	C(3)–C(2)–C(1)	122.4(8)
Cl(2)–Zr–Cl(3)	94.71(10)	O(2)–C(3)–C(2)	118.3(8)



The M–Cl distances of all three complexes are normal, the Ti–Cl distance of complex **1** being 2.293(5) Å (average) and the Zr–Cl distances are 2.400(3)–2.446(3) Å. There is a tendency in these complexes for the distance between the carbonyl carbon and the aldehyde oxygen to increase upon ligand co-ordination.

Although compound **I** is a highly planar molecule, maintaining its planar mode upon chelation, the six-membered chelate ring is almost planar only in one chelating ligand in complex **1**, where the titanium atom deviates by 0.075(17) Å from the mean O(1)–C(1)–C(2)–C(3)–O(2) plane. Corresponding deviations in the other metallocyclic plane of complex **1** and also in complexes **2** and **3** range from 0.347(9)–0.434(11) Å, which indicates that the central atom is bent away from the O–C–C–C–O part of the metallocycle. However, this bending does not significantly affect the geometric parameters of chelation, *viz.* the chelate angle O–M–O or the bond lengths of the phenolic and aldehydic oxygen atoms.

Polymerization studies

Polymerization of ethylene. Table 10 summarizes the ethylene polymerization data. Methylaluminooxane (mao) was used as cocatalyst with Al:M 1000:1 (M = Ti or Zr). The titanium complex **1** was clearly more active than the zirconium complexes **2** and **3**.

Polyethylene molecular weights were determined by gel permeation chromatography (GPC). The polyethylenes produced have high molecular weights, that produced by complex **3**, containing one didentate alkoxide ligand, having a higher molecular weight than polymers produced by species containing two alkoxide ligands (**1** and **2**). Molecular-weight distributions of the polymers are broad, the amount of alkoxide

Table 10 Ethylene polymerization data

			Molecular weight		
Catalyst	Yield/g	Activity/kg polyethylene per g M per h	$10^{-3} M_w$	$10^{-3} M_n$	M_w/M_n
1[a]	40	80.0	700	45	16.0
2[b]	6.5	15.3	633	37	17.1
3[a]	8.0	8.1	906	54	16.7

Catalyst amount 5 mg. [a] Run time 1 h. [b] Run time 30 min.

Table 11 Ethylene–hex-1-ene polymerization data

Catalyst	**1**
Yield/g	25
Activity/kg polyolefin per g Ti per h	52.2
M_n	57 300
M_w	1 650 000
M_w/M_n	28.8
Comonomer content (%)	3

Cocatalyst mao; Al : Ti ratio 1000 : 1; hex-1-ene content in polymerization 60 cm^3; run time 1 h; catalyst amount 5 mg.

ligands and metal having no effect on the polydispersity values. This resembles the results of the studies by Schaverien and co-workers[26] on soluble catalyst components with didentate alkoxide ligands. Broad polydispersity values indicate that the complexes have more than one active site which is surprising since the central metal atoms are quite heavily sterically crowded. One explanation for this could be that at the polymerization temperature used (80 °C) the alkoxide ligands rearrange. The rearrangement of didentate alkoxide ligands by the torsional twist is typical for β-diketonate complexes.[27]

Copolymerization of ethylene and hex-1-ene with complex 1. Copolymerization data is presented in Table 11. The rate of copolymerization is slightly slower than that for ethylene homopolymerization. The copolymer produced has a very high molecular weight. The molecular weight distribution is very broad, however, there may be some inaccuracy in the values owing to solubility problems of the high molecular weight polymer sample. The comonomer content of the polymer was measured by IR methods.

Conclusion

Characteristics for Group 4 metal complexes with chelating alkoxide ligands which are required for the development of new catalytic processes are (*a*) high metal oxidation state, (*b*) two reducible ligands *cis* to one another, (*c*) co-ordinative and electronic unsaturation, (*d*) mononuclearity and (*e*) structural rigidity around the metal. The series of complexes synthesized in this work fulfills these requirements. Titanium and zirconium metals are in their highest oxidation state, 4. The two reducible chloride ligands are *cis* to one another and the reducibility of these ligands provides the vacant co-ordination sites for incoming substrates. The halogen ligand can also be exchanged for another, *e.g.* alkyl ligand. The stronger π-donating ability of alkoxide oxygen compared to chloride, together with chelate effect, makes the displacement of chloride markedly favoured over the loss of alkoxide ligand.[1,25] If the oxo group is taken as a two-electron donor, all complexes are unsaturated 16-electron compounds. If the π-donation capability of the oxo unit is proposed to be considerable, the complexes can be thought to obey the 18-electron rule. This would explain the relative stability of complex **1** in air. The chelation of alkoxide ligands provides the structural rigidity for the complexes.

The delocalization of the electronic charge over the aromatic ring and the metallocycle formed in complexation provide an interesting challenge for the ligand. It may accept electron density from the metal and act as an 'electron store', or it can donate electron density to the metal.

The new complexes **1**–**3**, begin a new class of soluble catalysts for olefin polymerization. The salicylaldehyde ligand can easily be altered using various substituents. Complexes **1**–**3** have been shown to be active in the ethylene polymerization process with mao as cocatalyst. The polyethylenes produced have high molecular weights with broad molecular weight distributions. Complex **1** is also an active catalyst for ethylene–hex-1-ene copolymerization, producing extremely high molecular weight copolymers.

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