New chelating pyridyl-indenyl and quinolyl-indenyl ligands leading to C_1 symmetrical complexes of zirconium via amine elimination. X-ray structure of [3-(2-pyridylmethyl)(indenyl)]tris(dimethylamido)Zr(IV)

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Abstract

Two new chelating (1-) ligands, based on an indenyl group and either a pendant pyridylmethyl arm or a pendant quinolylmethyl arm were synthesized. The two ligands react cleanly with tetrakis(dimethylamido)zirconium by amine elimination reactions leading to complexes of C_1 symmetry. The crystal structure of the pyridyl–indenyl zirconium complex **3** was determined. Compound $C_{21}H_{30}N_4Zr$ (**3**) crystallizes in the orthorhombic space group $Pbca$ with $a = 9.588(1)$, $b = 14.858(12)$, $c = 29.932(7)$ Å, $V = 4264.1$ (Å^3), $Z = 8$. The structure refinement converged to $R1 = 0.049$ for 2363 $F_0 > 4\sigma(F_0)$ and $wR2 = 0.167$ for all 3197 unique data, $S = 1.04$. The structure shows that the indenyl is bound in a η^5 fashion blocking the top of the zirconium atom, and the pyridine is coordinated in an exceptionally long 2.536(5) Å N–Zr bond, blocking the back of the zirconium atom. © 1997 Elsevier Science S.A.

Keywords: C_1 symmetry; Amine elimination; Constrained geometry; Zr(IV); Crystal structure

1. Introduction

The development of new ligand systems for group 4 transition metals is a major direction of research in current organometallic chemistry. Since the introduction of the *ansa*-metallocene systems of Wild et al. [1], many related ligands have been introduced, which, by well defining the metal environment, aim at controlling the tacticity in α-olefin polymerization, [1] as well as being used in other catalyzed transformations. [2] Most of these ligand systems are chelating and contain either one or two cyclopentadienyl type groups. [3] Especially, chelating half metallocenes are expected to play an important role as future 'constrained geometry' type industrial catalysts for polymerization of α-olefins [20]. Most of the chelating ligands lead to either non-chiral

metal complexes or chiral complexes of C_2 symmetry. The use of C_1 complexes, on the other hand, has been much more limited [21–23]. While C_2 symmetrical complexes offer the advantage of minimizing the directions of approach of a substrate to the metal, their synthesis requires the purification of the desired *rac*-diastereoisomers from the *meso*-diastereoisomer.

Reactions between ethylene-bridged bis(indenyl) and tetrakis(dimethylamido)zirconium (amine elimination reactions) have been introduced lately, as convenient alternatives to the more conventional reactions between the ligand salts and metal chlorides. [4,5,6] In these reactions, the first indenyl group readily binds to the metal causing the elimination of a single amine group. The second indenyl group binds much less readily, and careful control of reaction conditions must be applied, in order to avoid a broad mixture of products. Here we

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[1] For some recent reviews see [2–4].
[2] For some recent reviews see [5,6].
[3] For several chelating ligands based on cyclopentadienyl-type and heteroatom groups for group 4 metals see [7–19].

[4] For *ansa*-metallocenes see [24–30].
[5] For *ansa*-cyclopentadienyl/hetero-atom see [31–33].
[6] For non-bridged metallocenes see [34].

introduce two new chelating ligands, that bind to the metal through an indenyl arm and an aromatic amine (pyridyl or quinolyl) arm. These ligands are easily prepared from readily available starting materials, and form complexes of C_1-symmetry with zirconium by amine elimination reactions with tetrakis(dimethyl-amido)zirconium. The indenyl and pyridyl or quinolyl building blocks from which these ligands are assembled are rigid, and therefore assure the 'constrained geometry' environment at the metal centre.

2. Experimental

The operations in which air-sensitive compounds were handled, were carried out under an argon atmosphere using standard Schlenk techniques, or under a nitrogen atmosphere using an Innovative Technology Labmaster 100 double station glove box equipped with a −35°C freezer. ^{1}H NMR and ^{13}C NMR were obtained on a Bruker AC-200. Proton chemical shifts are relative to internal Me_4Si or to residual protium in deuterated solvents (C_6D_6 7.15 ppm). ^{13}C NMR spectra were taken in both the H decoupled mode and DEPT-135 ^{13}C {^{1}H} mode, to determine the number of protons bound to each carbon atom. Carbon chemical shifts are relative to ^{13}C in deuterated solvents (C_6D_6 128.7 ppm). High resolution mass spectra were obtained on a VG M-250 q mass spectrometer. IR spectra were obtained on a Nicolet FT-IR 205 spectrophotometer. Melting points were measured in glass capillaries on a Büchi smp-20 and are not corrected.

All solvents were of analytical grade. Tetrahydrofuran and diethyl ether were distilled under argon from sodium benzophenone ketyl. Pentane was distilled under argon from sodium benzophenone ketyl and te-traglyme. 2-(chloromethyl)pyridine was prepared from 2-pyridylcarbinol and thionyl chloride by adapting a procedure for 2,6-bis(chloromethyl)pyridine [35]. 2-(chloromethyl)quinoline monohydrochloride was purchased from Aldrich and used as received. Indenyl lithium was prepared from indene and n-butyl lithium according to published procedures [36–38]. Tetrakis(di-methylamido)zirconium was prepared from lithium dimethylamide and zirconium tetrachloride according to a published procedure [39]. Polymerization experiments were performed as described by Kim and Jordan [30].

2.1. Synthesis of 2-(3-indenylmethyl)pyridine (1)

To a solution of 2.90 g (23.0 mmol) of 2-(chloro-methyl)pyridine in 20 ml of THF cooled to −35°C, was added dropwise a solution of 3.15 g (27.0 mmol) in-denyl lithium in 30 ml of THF. The reaction mixture turned red and was allowed to stir at room temperature overnight. 50 ml each of water and chloroform were

added and the organic layer was separated and washed with water. Drying over magnesium sulfate, and removing the solvents under reduced pressure gave a brown oily liquid, containing the desired product and indene. Flash vacuum chromatography over aluminum oxide using a mixture of ethyl acetate/hexane as the eluant, gave 3.14 g (67%) of the pure product, isolated as a colorless liquid which turns yellow in air.

^{1}H NMR (C_6D_6): δ 3.14 (s, 2H, CH_2 in indene), 4.21 (s, 2H, CH_2 in bridge), 6.12 (s, 1H, CH in indene), 7.13–7.52 (m, 7H), 8.60 (d, 1H, $J = 4.5$ Hz, CH^6 in pyridine). ^{13}C {^{1}H} NMR (C_6D_6): δ 38.6 (2 CH_2), 120.9, 121.9, 123.6, 124.7, 125.7, 127.2, 131.2, 136.7, 150.4 (vinyl and aromatic CH), 143.4, 145.4, 146.2, 160.9 (vinyl and aromatic C). Selected IR absorptions (neat, KBr, cm^{-1}): 1590 ($\nu C = N$ in pyridine). HRMS: calculated for $C_{15}H_{13}N$ 207.1048, found 207.1058.

2.2. Synthesis of 2-(3-indenylmethyl)quinoline (2)

To a suspension of 2.61 g (12.0 mmol) of 2-(chloro-methyl)quinoline hydrochloride in 20 ml of THF cooled to −35°C, was added dropwise a solution of 3.28 g (27.0 mmol) indenyl lithium in 20 ml of THF. The reaction mixture turned dark and homogeneous and was allowed to stir at room temperature overnight. Following a similar work up procedure as for 1 gave 1.81 g (58%) of the pure product, isolated as a colorless oil which turns yellow in air. The oil solidifies slowly to a waxy solid, which can be recrystallized from cold ether.

M.p. (ether) 54–56°C. ^{1}H NMR (C_6D_6): δ 3.07 (s, 2H, CH_2 in indene), 4.28 (s, 2H, CH_2 in bridge), 6.03 (s, 1H, CH in indene), 7.04–7.55 (m, 9H), 8.36 (d, 1H, $J = 8.2$ Hz). ^{13}C {^{1}H} NMR (C_6D_6): δ 38.6 (CH_2), 39.4 (CH_2), 120.9, 122.1, 124.6, 125.8, 126.7, 127.2, 130.1, 130.6, 131.4, 136.7 (vinyl and aromatic CH), 123.8, 143.2, 145.3, 146.1, 149.4, 161.1 (vinyl and aromatic C). Selected IR absorptions (nujol mull, KBr, cm^{-1}): 1600 ($\nu C = N$ in quinoline). HRMS: calculated for $C_{19}H_{15}N$ 257.1204, found 257.1200.

2.3. Synthesis of [3-(2-pyridylmethyl)(indenyl)]tris(di-methylamido)Zr(IV) (3)

To 1 (300 mg, 1.45 mmol), partially soluble in 5 ml of pentane at −35°C, was added a solution of tetrakis(dimethylamido)zirconium (427 mg, 1.60 mmol) in 5 ml of pentane. The reaction mixture turned homogeneous and was stirred at room temperature for 1 h. Removing the pentane under reduced pressure gave a yellow powder that was pure by NMR. Recrystallization from cold pentane yielded a first crop of 327 mg (0.76 mmol, 53%) of pure 3 as yellow crystals. 3 is extremely air sensitive, and hydrolyzes in seconds on exposure to air.

^{1}H NMR (C$_6$D$_6$): δ 2.86 (s, 18H, NCH_3), 3.96, 4.17 (AB system, 2H, J = 18.3 Hz, CH_2 in bridge), 6.50 (m, 2H), 6.68 (m, 2H), 6.85–7.11 (m, 4H), 7.65 (d, 1H, J = 8.5 Hz), 7.86 (d, 1H, J = 5.0 Hz). ^{13}C {^{1}H} NMR (C$_6$D$_6$): δ 35.3 (CH_2), 46.8 (NCH_3), 97.1 (CH in five membered ring of indene), 107.8 (C in five membered ring of indene), 117.9 (CH in five membered ring of indene), 121.6, 121.9, 122.8, 123.0, 123.6, 125.3, 137.1, 149.3 (CH), 164.2 (C in pyridine). IR (neat, KBr, cm^{-1}): 1601 (νC=N in coordinated pyridine).

2.4. Synthesis of [3-(2-quinolylmethyl)(indenyl)]tris(dimethylamido)Zr(IV) (4)

To 2 (300 mg, 1.17 mmol), dissolved in 5 ml of toluene and cooled to $-35°C$, was added a cold solution of tetrakis(dimethylamido)zirconium (343 mg, 1.28 mmol) in 5 ml of toluene. The reaction mixture turned brown and was stirred at room temperature for 1 h. Removing the toluene under reduced pressure gave a brown oil that was at least 95% pure 4 by NMR. Recrystallization from cold pentane yielded a first crop of 291 mg (0.61 mmol, 52%) of pure 4 as a brown crystalline solid. 4 is extremely air sensitive, and hydrolyzes in seconds on exposure to air. ^{1}H NMR (C$_6$D$_6$): δ 2.86 (s, 18H, NCH_3), 4.56, 4.72 (AB system, J = 16 Hz, CH_2 in bridge), 6.33 (d, 1H, J = 3.4 Hz, CH in five membered ring of indene), 6.54 (d, 1H, J = 3.4 Hz, CH in five membered ring of indene), 6.87–7.00 (m, 3H), 7.16–7.22 (m, 2H), 7.39–7.65 (m, 5H), 8.39 (d, 1H, J = 8.4 Hz). ^{13}C {^{1}H} NMR (C$_6$D$_6$): δ 37.9 (CH_2), 45.0 (NCH_3), 97.1 (CH in five membered ring of indene), 111.0 (C in five membered ring of indene), 118.2 (CH in five membered ring of indene), 121.7, 122.5, 123.1, 123.2, 123.7, 126.5, 128.3, 130.1, 130.3, 137.0 (CH), 125.9, 127.3, 127.6, 149.1, 162.7 (C). IR (nujol mull, KBr, cm^{-1}): 1602 (νC=N in coordinated quinoline).

2.5. Crystal and structural data for 3

Crystals of 3 were obtained by crystallization from pentane at $-35°C$. A suitable crystal was selected and sealed under an atmosphere of nitrogen in a Lindemann capillary. The X-ray diffraction measurements were carried out at ca. 295 K on an automated CAD4 diffractometer equipped with a graphite monochromator, using Mo K$_\alpha$ (λ = 0.7107 Å) radiation. Crystallographic and experimental details are summarized in Table 1.

Intensity data were collected by the ω–2θ scan mode. Possible deterioration of the analyzed crystal was tested by detecting periodically the intensities of three reference reflections from different zones of the reciprocal space. Although the analyzed crystal was enclosed in a sealed capillary to prevent decomposition, the standard intensities exhibited a uniform linear decrease of 25% over the entire experiment which required an appropriate correction of the data set. No correction for

Table 1
Crystal data and structure refinement for 3

| Empirical formula	C$_{21}$H$_{30}$N$_4$Zr
Formula weight	429.72
Temperature (K)	295
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	9.588(1)
b (Å)	14.858(12)
c (Å)	29.932(7)
Volume	4264.1 (Å^3)
Z	8
Density (calc, g cm^{-3})	1.339
$F(000)$	1792
μ(Mo K$_\alpha$)	5.3 cm^{-1}
Crystal size (mm^3)	0.15 × 0.30 × 0.40
$2\theta_{max}$ (°)	50
Scan rate (deg. min^{-1})	4
Reflections collected	3197
Observed reflections	2363 ($F_0 > 4\sigma(F_0)$)
Refinement method	Full-matrix least squares on F^2
No. of refined parameters[a]	241
Final R indices ($F_0 > 4\sigma(F_0)$)	$R1 = 0.049$
R indices (all data)	$R1 = 0.074$
	$wR2 = 0.167$.
Goodness-of-fit on F^2	1.04
Largest diff. peak and hole (e·Å^{-3})	≤ 0.63

[a]No restraints or constraints were applied.

absorption effects was found essential, as repeated calculations with data corrected for absorption did not yield any significant improvement of the results. The structure was solved by Patterson and direct methods (SHELXS-86) [40,41], and refined by full-matrix least-squares (SHELXL-93) [42]. Non-hydrogen atoms were treated anisotropically. The hydrogen atoms were introduced into the structure factor computations in calculated positions, the methyls being treated as rigid groups. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation.

3. Results

3.1. Synthesis of ligands 1 and 2

The syntheses of the two new bridging ligands 2-(3-indenylmethyl)pyridine (1) and 2-(3-indenylmethyl)quinoline (2) are shown in Scheme 1. The syntheses are based on reaction of a slight excess of indenyl lithium with the 2-(chloromethyl) derivatives of pyridine or quinoline under nitrogen, followed by hydrolysis of the excess base with water, and purification of the ligands by chromatography over aluminum oxide.
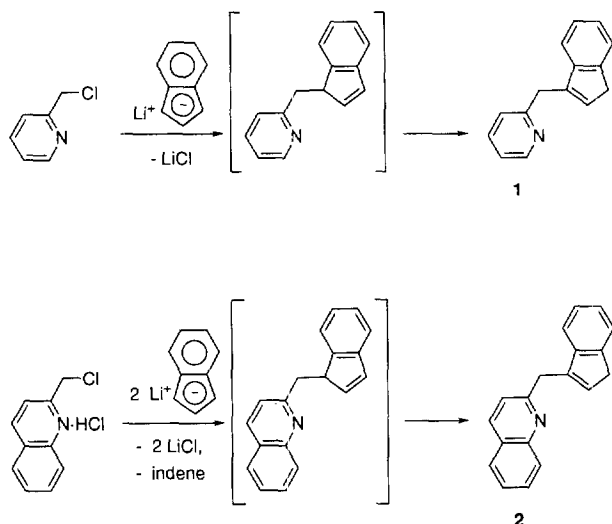
Scheme 1. Synthesis of the bridging ligands 2-(3-indenylmethyl)pyridine (1) and 2-(3-indenylmethyl)quinoline (2).

2-chloromethyl pyridine is easily obtained in high yield from the carbinol [35]. 2-chloromethyl quinoline is commercially available as the hydrochloride. We found it was more convenient not to isolate the free quinoline but instead, to form it in situ and react it further by adding two equivalents of indenyl lithium to the hydrochloride. The excess indene can be recovered at the chromatography stage.

The reactions between indenyl lithium and 2-(chloromethyl)pyridine or 2-(chloromethyl)quinoline are fast, forming the kinetic 1-indenyl derivatives at first (Scheme 1—in square brackets). These are slowly rearranging to the thermodynamically stable 3-indenyl derivatives in the presence of a slight excess of indenyl lithium [36–38]. When the reactions were worked up after two hours, mixtures of the kinetic products and the thermodynamic products were isolated. Therefore, the reactions were left to stir overnight to ensure a complete conversion to the thermodynamic products. Although the position of the double bond should not affect com-
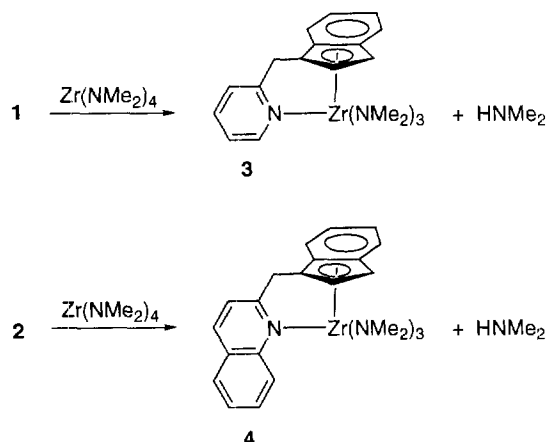
Scheme 2. Synthesis of the 'constrained geometry' zirconium complexes 3 and 4.

plexation, it is more convenient to start with a defined ligand like 1 or 2 and not from mixtures.

1 and 2 exhibit similar spectroscopic properties, consistent with their analogous structures. In the ^{1}H NMR spectra, the two characteristic peaks are: one broad singlet of an indene methylene (1: 3.14 ppm; 2: 3.07 ppm), and another broad singlet of a bridge methylene (1: 4.10 ppm; 2: 4.28 ppm). In the ^{13}C NMR spectra of both 1 and 2 these two methylene carbons are too close to distinguish: (1: 38.6 ppm; 2: 38.6, 39.4 ppm).

3.2. Synthesis of the zirconium complexes 3 and 4

The two zirconium complexes, 3 and 4, were prepared by amine elimination reactions of the neutral ligands with tetrakis(dimethylamido)zirconium (Scheme 2). Amine elimination reactions between metal amides and cyclopentadienyl groups were first reported by Chandra and Lappert [34]. The preparation of C_2-symmetrical ansa-metallocenes employing amine elimination reactions, have been introduced recently by Jordan and coworkers [24]. In these reactions, the second cyclopentadienyl type group reacts much slower than the first, and complex mixtures of products may form, due to rac–meso isomerization as well as incomplete amine elimination. In contrast, the ligands 1 and 2 react very cleanly, within a few minutes, leading to complexes of C_1 symmetry, which are purified by crystallization from pentane at −35°C. The released dimethylamine is not coordinated to the zirconium atoms in the complexes 3 and 4.

Several structural features can be deduced from the spectral data of complex 3.

(a) The deprotonation of the indene group is evident from the disappearance of the indene methylene group of 1 (^{1}H NMR: 3.14 ppm; ^{13}C NMR: 38.6 ppm) and appearance of a methine group instead in the ^{1}H NMR and ^{13}C NMR spectra; the characteristic absorptions in the ^{13}C NMR spectrum of 3 support the expected η^5 binding mode of the indenyl group [43].

(b) The coordination of the nitrogen atom of the pyridine to the zirconium atom is evident from the up field shift of the H^6 proton in the ^{1}H NMR spectrum, and the shift in the IR absorption attributed to a $\nu C=N$ (1590 to 1601 cm^{-1}) [44,45].

(c) The C_1 symmetry of 3 is evident from the appearance of an AB system pattern for the bridgehead methylene group instead of the broad singlet in the free ligand 1.

Complex 4 shows remarkable spectral similarity to 3, and is, therefore, proposed to be isostructural.

3.3. X-ray crystal structure of 3

The zirconium complex 3 crystallizes from pentane at −35°C. In order to further study the bonding in this complex, we solved its X-ray crystal structure. The molecular structure of 3 and several bond lengths and
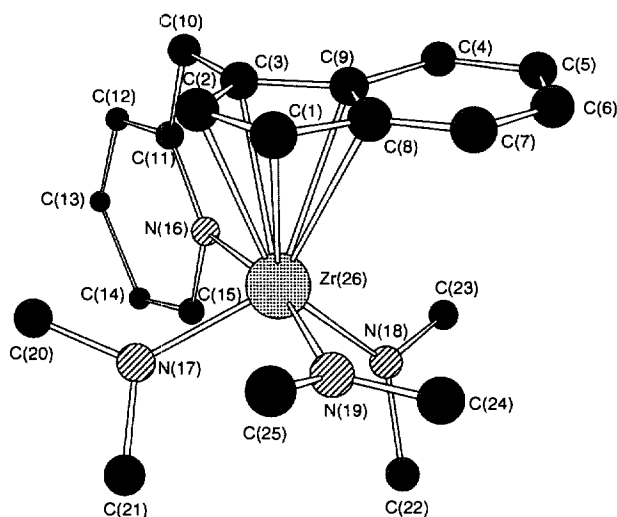
Fig. 1. Ball and stick representation of **3**. Selected bond lengths (Å) and angles (°): C(1)–Zr 2.594(8), C(2)–Zr 2.595(7), C(3)–Zr 2.655(7), C(8)–Zr 2.669(6), C(9)–Zr 2.693(5), N(16)–Zr 2.536(5), N(17)–Zr 2.054(5), N(18)–Zr 2.085(4), N(19)–Zr 2.066(5), N(16)–Zr–N(19) 162.9(2), ring centroid Zr–N(16) 90.4(2), C(11)–N(16)–C(15) 117.9(5), C(15)–N(16)–Zr 115.4(4), C(11)–N(16)–Zr 126.3(4).

angles are shown in Fig. 1, and relevant structural parameters are listed in Table 2. The geometry around the zirconium atom is best described by a trigonal

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for non hydrogen atoms of **3**

Atom	x/a	y/b	z/c	U_{eq}
C(1)	−0.1945(7)	0.3174(5)	0.1490(2)	0.0853(28)
C(2)	−0.2492(6)	0.2375(6)	0.1362(2)	0.0931(32)
C(3)	−0.2054(6)	0.2141(3)	0.0934(2)	0.0727(23)
C(4)	−0.0534(9)	0.3092(6)	0.0372(2)	0.0983(33)
C(5)	0.0169(10)	0.3883(9)	0.0339(3)	0.1281(52)
C(6)	0.0225(8)	0.4456(7)	0.0692(4)	0.1330(57)
C(7)	−0.0418(8)	0.4312(4)	0.1080(3)	0.1059(38)
C(8)	−0.1163(5)	0.3507(3)	0.1136(2)	0.0617(21)
C(9)	−0.1215(5)	0.2860(3)	0.0787(1)	0.0550(19)
C(10)	−0.2371(8)	0.1324(5)	0.0674(3)	0.1348(45)
C(11)	−0.1298(6)	0.0589(4)	0.0694(2)	0.0761(23)
C(12)	−0.1459(8)	−0.0231(5)	0.0473(2)	0.1009(35)
C(13)	−0.0503(9)	−0.0892(5)	0.0527(2)	0.1037(36)
C(14)	0.0639(8)	−0.0721(4)	0.0779(3)	0.1060(34)
C(15)	0.0771(7)	0.0088(4)	0.0984(2)	0.0875(28)
N(16)	−0.0194(4)	0.0742(3)	0.0951(1)	0.0641(17)
N(17)	−0.0199(5)	0.1073(3)	0.1929(1)	0.0696(18)
N(18)	0.2140(4)	0.1989(2)	0.1189(1)	0.0575(15)
N(19)	0.0913(5)	0.2919(3)	0.1960(1)	0.0695(18)
C(20)	−50.1285(7)	0.0394(4)	0.1914(2)	0.0974(31)
C(21)	0.0747(9)	0.0870(5)	0.2299(2)	0.1181(34)
C(22)	0.3376(6)	0.1840(5)	0.1453(2)	0.1015(34)
C(23)	0.2480(7)	0.1938(4)	0.0716(2)	0.0781(24)
C(24)	0.1906(7)	0.3643(4)	0.1898(2)	0.0954(30)
C(25)	0.0206(9)	0.3058(5)	0.2385(3)	0.1241(42)
Zr(26)	0.0153(0)	0.2073(0)	0.1469(0)	0.0461(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

bipyramide, in which the pyridine nitrogen (N(16)) and one of the amido nitrogens (N(19)) occupy the apical positions, and the remaining nitrogens and the centre of the five membered ring of the indenyl occupy the basal positions.

The crystal structure of **3** supports the spectroscopic data.

(a) The η^5 binding mode of the indenyl group is evident from the almost identical C–Zr bond lengths and the planarity of the indenyl group (The RMS deviation from the plane is 0.022 Å).

(b) The coordination of the pyridine nitrogen to the zirconium atom is clearly seen in Fig. 1. An angle sum around the pyridine nitrogen of 359.6(0.7) is consistent with a favorable geometry for coordination of the pyridine. A five membered ring centroid–Zr–N(pyridine) angle of 90.4° is also consistent with a favorable geometry for the chelating complex. However, the N(pyridine)–Zr distance of 2.536(5) Å, is an unusually long dative bond.

(c) The C_1 symmetry of **3** is well viewed in Fig. 1: the indenyl group binds to the metal from the top, and the almost perpendicular pyridine group is bound to the metal from the back.

The same structural characteristics are proposed to apply to complex **4** as well.

4. Discussion

The two chelating ligands introduced in this work are conveniently synthesized. They react readily and cleanly with tetrakis(dimethylamido)zirconium in amine elimination reactions to form the corresponding C_1-symmetrical complexes. Both ligands are made of rigid planar groups, with the only flexible point being the methylene joint. They therefore induce a constrained geometry on the metal. The X-ray structure of **3** indicates that the chelating ligand blocks the metal from the top by the indenyl group, and from the back by the perpendicular pyridyl group.

A survey of the October 1996 release of the Cambridge Structural Database [46], showed that N(pyridine)–Zr dative bond distances are in the range of 2.274–2.473 Å [47]. The N(pyridine)–Zr distance of 2.536(5) Å reported herein, is, therefore, exceptionally long. This is probably caused by steric interactions of the pyridine group with the two cis dimethylamide groups, or electronic interaction with the trans dimethylamide group, and not from constraints within the ligand, which seems to be in perfect geometry for binding to the zirconium atom.

As the relative geometries of the two binding sites in the two ligands 1 and 2 are identical, the geometry around the metal in 4 is proposed to be similar to the geometry in 3. However, since the quinolyl group ex-

tends further below the metal relative to a pyridyl group, this ligand will exhibit more pronounced steric influence on the metal.

Preliminary experiments indicate that following activation with trimethylaluminum [30] or trimethylchlorosilane [28], the zirconium complexes **3** and **4** become active catalysts for polymerization of ethylene, in the presence of methylaluminoxane. Further studies of the reactivity of these ligands and their complexes, and the synthesis of related ligands are currently under way.

References

[1] F.R.W.P. Wild, L. Zsolani, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 232 (1982) 233.

[2] H.H. Brintzinger, D. Fischer, R. Mülaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. Engl. 34 (1995) 1143.

[3] M. Bochmann, J. Chem. Soc., Dalton Trans., (1996) 255.

[4] Y. Okamoto, T. Nakano, Chem. Rev. 94 (1994) 349.

[5] R.L. Halterman, Chem. Rev. 92 (1992) 965.

[6] A.H. Hoveyda, J.P. Morken, Angew. Chem., Int. Ed. Engl. 35 (1996) 1262.

[7] P. Jutzi, U. Siemling, J. Organomet. Chem. 500 (1995) 175.

[8] J.C. Flores, J.C.W. Chien, M.D. Rausch, Organometallics 13 (1994) 4140.

[9] J.C. Flores, J.C.W. Chien, M.D. Rausch, Macromolecules 29 (1996) 8030.

[10] P. Foster, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem 527 (1997) 71.

[11] J. Okuda, F.J. Schattenmann, S. Wocadlo, W. Massa, Organometallics 14 (1995) 789.

[12] K.E. du Plooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, Organometallics 14 (1995) 3129.

[13] F. Amor, J. Okuda, J. Organomet. Chem 520 (1996) 245.

[14] J. Okuda, K.E. du Plooy, W. Massa, H.-C. Kang, U. Rose, Chem. Ber. 129 (1996) 275.

[15] D.D. Devore, F.J. Timmers, D.L. Hasha, R.K. Rosen, T.J. Marks, P.A. Deck, C.L. Stern, Organometallics 14 (1995) 3132.

[16] H.V.R. Dias, Z. Wang, S.G. Bott, J. Organomet. Chem 508 (1996) 91.

[17] S. Ciruelos, T. Cuenca, R. Gómez, P. Gómez-Sal, A. Manzanero, P. Royo, Organometallics 15 (1996) 5577.

[18] M. Enders, R. Rudolph, H. Pritzkow, Chem. Ber. 129 (1996) 459.

[19] Y. Qian, R. Guo, J. Huang, Q. Yang, Polyhedron 16 (1997) 195.

[20] J. Haggin, Chem. and Eng. News, (August 5, 1996), 26.

[21] B. Rieger, G. Jany, R. Fawzi, M. Steinman, Organometallics 13 (1994) 647.

[22] G. Jany, R. Fawzi, M. Steinman, B. Rieger, Organometallics 16 (1997) 544.

[23] J. Okuda, S. Verch, T.P. Spaniol, R. Stürmer, Chem. Ber. 129 (1996) 1429.

[24] G.M. Diamond, S. Rodewald, R.F. Jordan, Organometallics 14 (1995) 5.

[25] G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4030.

[26] J.N. Christopher, G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4038.

[27] G.M. Diamond, R.F. Jordan, J.L. Petersen, Organometallics 15 (1996) 4045.

[28] G.M. Diamond, R.F. Jordan, J.L. Petersen, J. Am. Chem. Soc. 118 (1996) 8024.

[29] A. Vogel, T. Priermeier, W.A. Herrmann, J. Organomet. Chem. 527 (1997) 297.

[30] I. Kim, R.F. Jordan, Macromolecules 29 (1996) 489.

[31] A.K. Hughes, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 1936.

[32] Y. Mu, W.E. Piers, L.R. MacGillivray, M.J. Zawortko, Polyhedron 19 (1993) 1.

[33] D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, Organometallics 15 (1996) 1572.

[34] G. Chandra, M.F. Lappert, J. Chem. Soc. A (1968) 1940.

[35] B. Rezzonico, M. Grignon-Dubois, J. Chem. Res. S (1994) 142.

[36] L. Cedheim, L. Eberson, Synthesis, (1973) 159.

[37] J.C. Winter, P.K. Gessner, D.D. Godse, J. Med. Chem. 10 (1967) 856.

[38] L. Meurling, Acta Chem. Scand. B. 28 (1974) 295.

[39] D.C. Bradley, I.M. Thomas, J. Chem. Soc., (1960) 3857.

[40] G.M. Sheldrick. SHELXL-86, in: G.M. Sheldrick, C. Kruger, R. Goddard (Eds.), Crystallographic Computing 3, Oxford Univ. Press, 1985, pp. 175-189.

[41] G.M. Sheldrick, Acta Cryst. A46 (1990) 467-473.

[42] G.M. Sheldrick, SHELXL-93, Program for the Refinement of Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1993.

[43] J.R. Ascenso, I.S. Gonçalves, E. Herdtweck, C.C. Romão, J. Organomet. Chem. 508 (1996) 169.

[44] C. Qian, J. Guo, C. Ye, J. Sun, P. Zheng, J. Chem. Soc., Dalton Trans. (1993) 3441.

[45] G. Paolucci, R.D. Fischer, F. Benetollo, R. Seraglia, G. Bombieri, J. Organomet. Chem. 412 (1991) 327.

[46] F.H. Allen, O. Kennard, Chem. Des. Autom. News 8 (1993) 31.

[47] C.H. Zambrano, A.K. McMullen, L.M. Kobriger, P.E. Fanwick, I.P. Rothwell, J. Am. Chem. Soc. 112 (1990) 6565.