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FULL PAPER

A pyridine dialkoxide titanium dichloride complex. Synthesis and molecular structure of 2,6-bis(2,2-diphenyl-2-trimethylsilyloxyethyl)pyridine

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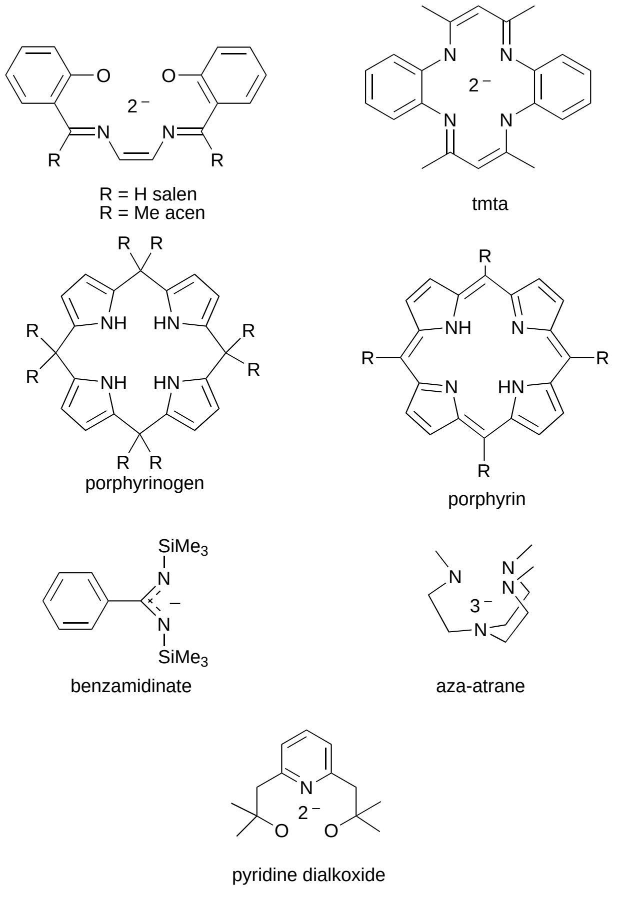
Reaction of 2,6-dimethylpyridine with 2 equivalents of LiBu^n followed by addition of 2 equivalents of benzophenone and the consecutive reaction with 2 equivalents of SiMe$_3$Cl afforded the doubly functionalised 2,6-bis(2,2-diphenyl-2-trimethylsilyloxyethyl)pyridine L. The structure of L has been determined by an X-ray diffraction study. Reaction of either a doubly lithiated intermediate or the corresponding silylated ligand L with TiCl$_4$ afforded a pyridine dialkoxide titanium dichloride complex. A cationic α-olefin polymerization catalyst was generated from this complex with an excess of methylaluminoxane (MeAlO)$_n$. A comparison of the catalytic activity with those of similar bis(alkoxide) complexes is presented.

During the last decade Group IV organometallic chemistry has made a major contribution in providing effective complexes for novel metal-assisted organic transformations.[1–9] They include stoichiometric reactions, such as hydrozirconation,[10–13] and catalytic processes, for example titanium- and zirconium-assisted olefin polymerization reactions.[14–19] The central functionality to all of these processes is the metal–carbon bond, as the active part in complexes containing the cyclopentadienyl-based spectator ancillary ligands. During this time attempts have been made to improve upon this advantageous fragment. One strategy is the use of alkoxo groups as ancillary ligands,[20–28] a second makes use of macrocyclic or related ligands (salen, acen, tmta, porphyrinogen, porphyrin, aza-atranes),[29–39] and a third uses bis(amido) and benzamidinate ligands (Scheme 1).[40–51] Recently, we and others have been interested in the use of such bis(amido) and benzamidinate Group IV complexes with these spectator ligands for the effective polymerization of α-olefins.[38,41,45–48] Early transition-metal alkoxide complexes containing the 1,1′-biphenyl or 1,1′-binaphthyl ancillary ligation have been found to be effective catalysts for the polymerization of α-olefins, whereas alike alkoxide complexes derived from the same skeleton but with the addition of a methylene bridge, in which the angle between the two alkoxide groups is larger,[27] show low or no catalytic activity toward α-olefins.[52–54] Focusing on the chemical reactivity at an alkoxide complex of an early transition-metal center upon the activated site, while effectively shielding the remaining co-ordination sphere, is the underlying motivation for the present study. The anticipated destabilization of a high-valent transition metal, by reducing the angle among the ancillary alkoxy ligands, and thus kinetically inducing a better catalytic system, prompted us to develop a bis(alkoxide) complex with a pyridine-bridged structure and to study the ligand effect as compared with other bridged alkoxide ligands in the polymerization of α-olefins.

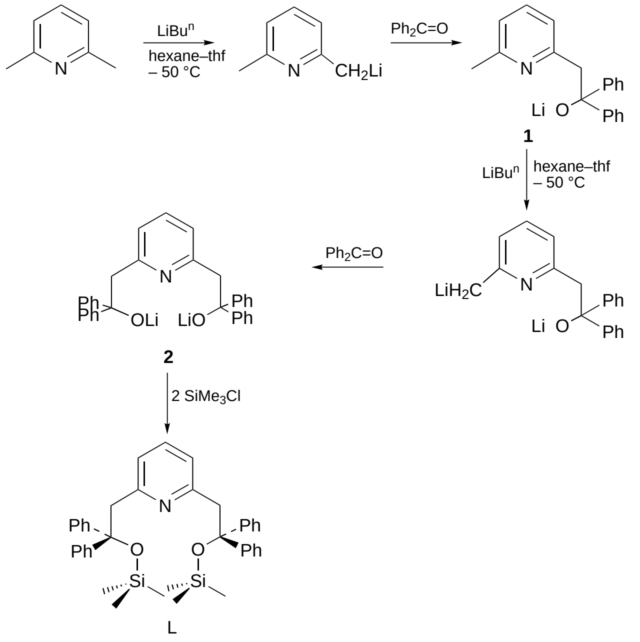


Scheme 1 Partial ancillary ligands used to replace cyclopentadienyl spectator ligands

Results and Discussion

Dialkoxide L was synthesized analogously to other members of this family (Scheme 2).[55] Reaction of 2,6-dimethylpyridine with LiBu^n in hexane–thf at −50 °C proceeded smoothly with formation of the monolithium salt.[56] The reaction of this salt with benzophenone gave, presumably, the corresponding mono-alkoxolithium complex **1** and treatment of the reaction mixture with another equivalent of LiBu^n with subsequent reaction with benzophenone gave the bis(alkoxo)lithium complex **2**. Complex **2** was not separated from the reaction mixture and was treated *in situ* with 2 equivalents of SiMe$_3$Cl to obtain the pyridine dialkoxide L in 62% yield.

The molecular structure of L was determined by X-ray diffraction methods and is illustrated in Fig. 1. Bond lengths and angles are given in Table 1. The molecule possesses an open conformation in the solid state, in which the pyridine substituents, attached to both *ortho* positions, are up and down the pyridine ring plane with a C_2 symmetry between them. Interestingly, there are no close contacts between the nitrogen and the silicon atoms as found for similar systems.[55] In solution, the



Scheme 2 Synthesis of compound L

Table 1 Bond lengths (Å) and angles (°) for compound L

Si(1)–O(1)	1.643(3)	Si(1)–C(18)	1.850(4)
Si(1)–C(20)	1.849(4)	Si(1)–C(19)	1.865(4)
O(1)–C(5)	1.429(4)	N–C(1)	1.348(4)
N–C(1A)	1.348(4)	C(1)–C(2)	1.380(5)
C(1)–C(4)	1.495(5)	C(2)–C(3)	1.373(5)
C(3)–C(2A)	1.373(5)	C(4)–C(5)	1.544(5)
C(5)–C(6)	1.527(5)	C(5)–C(12)	1.532(5)
C(6)–C(11)	1.384(5)	C(6)–C(7)	1.393(5)
C(7)–C(8)	1.377(6)	C(8)–C(9)	1.380(6)
C(9)–C(10)	1.372(6)	C(10)–C(11)	1.384(6)
C(12)–C(17)	1.373(5)	C(12)–C(13)	1.378(5)
C(13)–C(14)	1.397(6)	C(14)–C(15)	1.355(6)
C(15)–C(16)	1.369(6)	C(16)–C(17)	1.370(6)
O(1)–Si(1)–C(18)	105.6(2)	O(1)–Si(1)–C(20)	113.1(2)
C(18)–Si(1)–C(20)	112.4(2)	O(1)–Si(1)–C(19)	109.0(2)
C(18)–Si(1)–C(19)	108.0(2)	C(20)–Si(1)–C(19)	108.6(2)
C(5)–O(1)–Si(1)	137.2(2)	C(1)–N–C(1A)	118.8(4)
N–C(1)–C(2)	121.3(3)	N–C(1)–C(4)	116.5(3)
C(2)–C(1)–C(4)	122.2(3)	C(3)–C(2)–C(1)	120.2(4)
C(2)–C(3)–C(2A)	118.1(6)	C(1)–C(4)–C(5)	115.8(3)
O(1)–C(5)–C(6)	109.6(3)	O(1)–C(5)–C(12)	106.7(3)
C(6)–C(5)–C(12)	109.4(3)	O(1)–C(5)–C(4)	109.8(3)
C(6)–C(5)–C(4)	112.2(3)	C(12)–C(5)–C(4)	109.0(3)
C(11)–C(6)–C(7)	118.0(4)	C(11)–C(6)–C(5)	122.9(3)
C(7)–C(6)–C(5)	119.1(4)	C(8)–C(7)–C(6)	121.3(4)
C(7)–C(8)–C(9)	120.1(4)	C(10)–C(9)–C(8)	119.1(4)
C(9)–C(10)–C(11)	121.1(5)	C(10)–C(11)–C(6)	120.3(4)
C(17)–C(12)–C(13)	118.8(4)	C(17)–C(12)–C(5)	119.5(4)
C(13)–C(12)–C(5)	121.6(4)	C(12)–C(13)–C(14)	120.0(4)
C(15)–C(14)–C(13)	119.9(5)	C(14)–C(15)–C(16)	120.2(4)
C(17)–C(16)–C(15)	120.0(5)	C(16)–C(17)–C(12)	121.0(4)

Symmetry operation used for equivalent atoms: A $-x$, $-y$, z.

two *ortho* arms on the pyridine ring rotate freely as suggested by the ^{1}H NMR chemical shifts, showing one signal (doublet at δ 6.37) for both hydrogens of the pyridine ring and one signal for the four benzylic hydrogens (singlet at δ 3.78). Each silicon atom is four-co-ordinate and the direct co-ordination sphere is formed by three methyl ligands arranged unsymmetrically, and one alkoxo moiety [O(1)–Si(1)–C(18) 105.6(2), O(1)–Si(1)–C(19) 109.0(2), O(1)–Si(1)–C(20) 113.1(2), C(18)–Si(1)–C(20) 112.4(2), C(18)–Si(1)–C(19) 108.0(2), C(19)–Si(1)–C(20) 108.6(2)°]. The distortion at the silicon atom from the idealized tetrahedral co-ordination geometry cannot arise from the presence of a N→Si interaction due to the large distance among these two atoms (3.689 Å), but rather from steric effects. These steric effects may also account for the small differences found in Si–CH$_3$ bond lengths [Si–C(20) 1.849(4), Si–C(19) 1.865(4) Å].

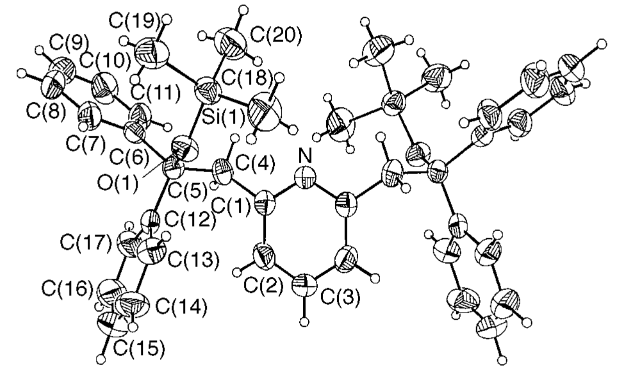
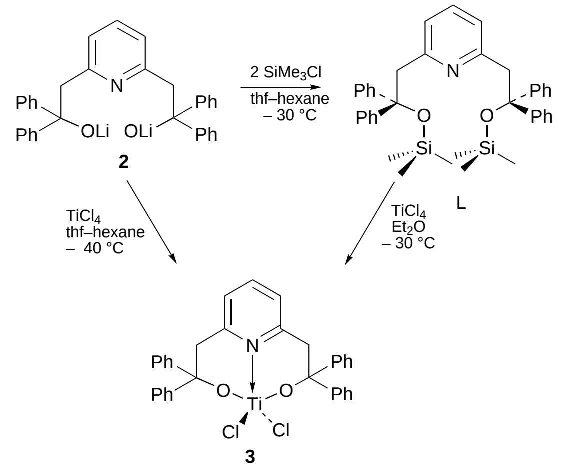
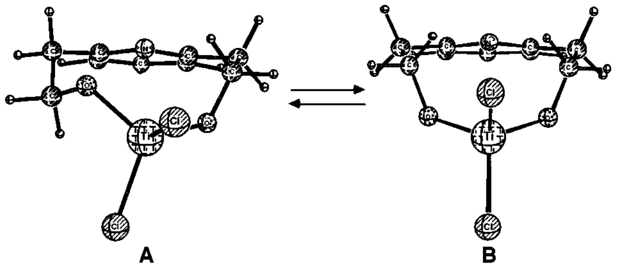


Fig. 1 An ORTEP drawing of the molecular structure of compound L. Thermal ellipsoids are shown at the 50% probability level



Scheme 3 Synthesis of complex **3**

Reaction of the ancillary ligand L or the *in situ* formed dilithium complex **2** (Scheme 2) with TiCl$_4$ led to the formation of the pyridine dialkoxide complex **3** (Scheme 3), which to the best of our knowledge is the first example of an early transition-metal dialkoxide organometallic complex with a pyridine-base skeleton.[38] The identity of complex **3** was established from analytical and spectroscopic data. At ambient temperature the ^{1}H NMR signals of the two hydrogens at the *meta* positions in the pyridine ring are equivalent (doublet, δ 6.40) as well as the four benzylic protons (singlet, δ 4.25) suggesting a symmetric co-ordination of the titanium atom in complex **3**. However upon cooling to −55 °C the signals from the *meta* position and the lutidyl methylene groups become broader, which eventually at −88 °C (CD$_2$Cl$_2$) split into two discrete not well resolved doublet of doublets for the hydrogens (δ 6.43 and 6.37) and a set of two doublets centered at δ 4.05 and 4.65 due to the geminal coupling [$^2J(H_aH_b) = 11.5$ Hz] for the two non-equivalent methylene protons of the 2,6-lutidyl fragment. This broadening can be explained by the steric hindrance in complex **3** at low temperatures, yielding a non-dynamic complex. Theoretically, two formulations of complex **3** are expected to be obtained as a function of temperature. A low temperature distorted five-co-ordinated titanium complex **A** with a weak N→Ti interaction which undergoes a flipping process, and at higher temperatures, the corresponding symmetric system **B**. The fluxional behavior expected by flipping the pyridine ring is illustrated in Scheme 4 (minimum steric energy obtained by MM2 calculations), with calculated distances between the Ti and N atoms of 3.657 and 3.667 Å, for the low- and high-



Scheme 4

temperature rotamers, respectively. In the transition state between these two rotamers the calculated distance between the five-co-ordinated titanium atom and the nitrogen atom is calculated to be 2.162 Å (Fig. 2), whereas for the isolobal pyridine diamide zirconium complex the Zr–N bond length was measured to be 2.325.[38]

The rapid flipping which theoretically may induce an interaction between the nitrogen lone pair of electrons and the titanium atom can be experimentally reinforced by analysis of the chemical shift at the *para* position of the pyridine ring. For the ancillary ligand L the hydrogen at the *para* position of the pyridine ring exhibits a triplet at δ 7.16 which is shifted to a lower field, δ 7.18, for complex **3**, suggesting an interaction between the Ti and N atoms. Complex **3** was found to be very soluble in non-polar solvents and our efforts to obtain a single crystal of it at low temperatures (−100 °C) were not successful.

The catalytic polymerization of ethylene and propylene were studied using the catalytic precursor **3**. The cationic catalyst was generated by the reaction of **3** with an excess of methylaluminoxane $(MeAlO)_n$ (MAO). The polymerizations were carried out under vigorously anaerobic/anhydrous vacuum-line conditions, and reactions were quenched after measured time intervals with methanol–HCl solutions prior to polymer collection, washing with hexane, acetone and drying. The polymer microstructure of the obtained high-density polyethylene or atactic polypropylene was characterized by ^{13}C NMR spectroscopy using standard analysis.[58] Table 2 shows the ethylene and propylene polymerization results with the complex **3**–MAO system and compared with data obtained with the zirconocene dichloride–MAO (‘Kaminsky type’), titanium tetraalkoxide–MAO, 2,2′-thiobis(6-*tert*-butyl-4-methylphenoxide) (tbp) titanium– and zirconium–MAO[59] and 2,2′-bis(6-*tert*-butyl-4-methoxyphenoxide) (obp) dibenzyl zirconium–MAO systems[53] under comparative conditions.

The polymerization activity of complex **3** toward ethylene was found to be higher than for propylene but is still low, as compared with the titanium biphenyl or the Kaminsky systems, but somewhat better compared to the alkoxo- and thioalkoxo-zirconium systems. This low reactivity toward olefins is presumably an outcome of the nitrogen–titanium interaction obtained by rapid flipping of the pyridine ring inducing a co-ordinatively saturated complex. For propylene, based on the ^{13}C NMR spectrum of the obtained polymer, the major pathway found for the termination chain mechanism is β-hydrogen elimination.

In summary, steric and electronic modifications during the catalytic polymerization of α-olefins have been found to exhibit a crucial influence on the extent of polymerization. New ancillary ligands containing a rigid backbone and larger rigid arms to avoid any co-ordination by the pyridine lone pair of electrons are under investigation.

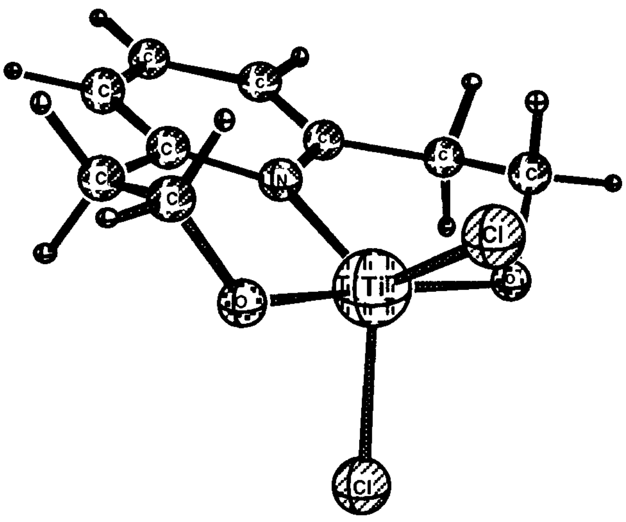


Fig. 2 Calculated transition state between complexes **A** and **B**

Table 2 Catalytic activity for the polymerization of α-olefins by complex **3** and related systems under comparable conditions

	Polymerisation activity *	
Catalyst	Ethylene	Propene
Complex **3**	58.4	11.6
$[Ti(tbp)Cl_2]$	228	186
$[Ti(tbp)(OPr^i)_2]$	188	87
$[Zr(tbp)(OPr^i)_2]$	6	0.2
$[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$	266	176
$[Zr(obp)(CH_2Ph)_2]$	2.7	0.13
$Ti(OPr^i)_4$	—	4.8

* In g of polyethylene per g of metal per s and in g of polypropylene per g of metal per h, respectively. Amount of catalyst 1.1×10^{-6} mol, of cocatalyst (MAO) 5.17 mmol; solvent (toluene) 10 cm^3; polymer pressure 1 atm; polymerization temperature 20 °C.

Experimental

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high vacuum (10^{-5} Torr, *ca.* 1.33×10^{-3} Pa) line, or in a nitrogen-filled Vacuum Atmospheres glove-box with a medium-capacity recirculator (1–2 ppm O_2). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents were distilled under argon with sodium–benzophenone. Hydrocarbon solvents ($[^2H_8]$toluene, C_6D_6, hexane) were distilled under nitrogen from Na/K alloy, $SiMe_3Cl$ was distilled under argon. All solvents for vacuum-line manipulations were stored *in vacuo* over Na/K alloy in resealable bulbs. The compounds $TiCl_4$, LiBu and 2,6-dimethylpyridine were from Aldrich and used without further purification. The NMR spectra were recorded on a Bruker AM 200 spectrometer, ^1H and ^{13}C chemical shifts being referenced to internal solvent resonances and are reported relative to tetramethylsilane. The NMR experiments were conducted on Teflon valve-sealed tubes (J-Young) after vacuum transfer of the solvent in a high-vacuum line.

Syntheses

Compound L. To a cold (−50 °C) stirred solution of 2,6-dimethylpyridine (1.07 g, 10.0 mmol) in thf (20 cm^3) was added $LiBu^n$ solution (6.3 cm^3, 10.0 mmol) in hexane (1.6 M). The mixture was allowed to warm to room temperature and then stirred for 3 h. The red mixture obtained was cooled to −50 °C and benzophenone (1.82 g, 10.0 mmol) dissolved in thf (15 cm^3), was added dropwise. The mixture was stirred for 1 h at −50 °C and then allowed to warm to room temperature. Stirring of the pale blue mixture was continued for 3 h, after which the mixture was cooled to −50 °C and a second equivalent of $LiBu^n$ (6.3

Table 3 Crystal data and data collection for compound L

Empirical formula	$C_{39}H_{45}NO_2Si_2$
M	615.94
Crystal size/mm	0.9 × 0.1 × 0.1
Crystal color and habit	Colorless needle
Crystal system	Orthorhombic
Space group	*Fdd*2
a/Å	21.003(4)
b/Å	34.958(7)
c/Å	9.574(2)
U/Å^3	7029.0(24)
Z	8
D_c/Mg m^{-3}	1.164
μ/mm^{-1}	0.134
F(000)	2640
Scan type	ω
T/K	210(2)
Index ranges	$-22 \leqslant h \leqslant 22, -37 \leqslant k \leqslant 0, -10 \leqslant l \leqslant 10$
Reflections collected	3793
Independent reflections	2226 ($R_{int} = 0.0496$)
Observed reflections	1475 [$F > 4\sigma(F)$]
Background measurement	Stationary crystal, stationary counter at beginning and end of scan, each for 25% of total scan time
Scan speed	Variable
Scan range ω/°	1.0
Weighting scheme, w^{-1}	$\sigma^2(F_o)^2 + (0.0365P)^2 + 0.000P$, where $P = (F_o^2 + 2F_c^2)/3$
Data, restraints, parameters	2226, 1, 203
Data-to-parameter ratio	11.0:1 {7.3:1 [$F > 4\sigma(F)$]}
Final $R1$, $wR2$ indices [$F > 4\sigma(F)$]	0.0376, 0.0733
(all data)	0.0913, 0.0862
Goodness of fit on F^2	0.979
Largest and mean Δ/σ	0.000
Largest difference peak, hole/e Å^{-3}	0.157, −0.190

cm^3, 10.0 mmol) was added. The brown mixture was warmed and then stirred for 3 h. After cooling to −50 °C a second portion of benzophenone (1.82 g, 10.0 mmol) was introduced. The green mixture was warmed gradually to room temperature and then stirred for 4 h to obtain compound **1** *in situ*. To the cold (−50 °C) mixture was slowly added chlorotrimethylsilane (2.53 cm^3, 20.0 mmol) in hexane (10 cm^3). The solution was warmed to room temperature and stirred for 10 h. A colorless solid was removed from the yellow solution by filtration and washed with hexane (20 cm^3). The filtrate and the washing were combined and the red solution was kept in a freezer for 1 d, which allowed formation of colorless crystals. After filtration and washing with cold hexane, 3.82 g (6.2 mmol) of crystalline compound L was obtained in 62% yield (Found: C, 76.02; H, 7.52; N, 2.15. Calc.: C, 76.06; H, 7.37; N, 2.28%). ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.29 (d, 8 H, *o*-H of phenyl), 7.16 (t, 12 H, *m*- and *p*-H of phenyl), 6.89 (t, 1 H, *p*-H of pyridine), 6.37 (d, 2 H, *m*-H of pyridine), 3.78 (s, 4 H, CH_2) and −0.12 [s, 18 H, $Si(CH_3)_3$]. ^{13}C NMR ($CDCl_3$, 20 °C): δ 156.1, 147.3, 133.6, 127.5, 127.4, 126.6, 121.8 (phenyl and pyridine), 80.8 (CH_2), 49.3 (CPh_2O) and 1.9 [$Si(CH_3)_3$]. HRMS: *m*/*z* 615.230 (calc. 615.229 for $C_{39}H_{45}NO_2Si_2$).

Complex 3. (*a*) To a cold (−30 °C) stirred solution of complex **2** (3.08 g, 5.0 mmol) in diethyl ether (100 cm^3) was added $TiCl_4$ (0.55 cm^3, 5.0 mmol) in hexane (50 cm^3). The reaction mixture was allowed to warm to room temperature and stirring was continued for 24 h, and then refluxed for 12 h. The red mixture was then cooled to room temperature, the solvents were removed *in vacuo* ($SiMe_3Cl$ was detected by ^{29}Si NMR spectroscopy) and the residue was dissolved in CH_2Cl_2. Crystallization left an orange solid (2.29 g, 3.9 mmol, 78%) of complex **3** (Found: C, 67.19; H, 4.78; Cl, 11.72; N, 2.53. Calc.: C, 67.45; H, 4.63; Cl, 11.91; N, 2.39%). ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.30 (d, 8 H, *o*-H of phenyl), 7.24 (t, 12 H, *m*- and *p*-H of phenyl), 7.18 (t, 1 H, *p*-H of pyridine), 6.40 (d, 2 H, *m*-H of pyridine) and 4.25 (s, 4 H, CH_2). ^{13}C NMR ($CDCl_3$, 20 °C): δ 158.9, 148.4, 139.1, 130.5, 129.1, 128.4, 124.1 (phenyl and pyridine), 102.9 (CPh_2O) and 53.8 (CH_2). HRMS: *m*/*z* 587.093 (calc. 587.089 for $C_{33}H_{27}Cl_2NO_2Ti$).

(*b*) A second route starts from complex **1** obtained *in situ* and $TiCl_4$. Accordingly, a solution of **1** (5.0 mmol) in hexane–thf was cooled to −30 °C and treated with $TiCl_4$ (0.55 cm^3, 5.0 mmol) in hexane (10 cm^3). The temperature was slowly raised to ambient and the solution stirred for 24 h. The precipitated LiCl was filtered off through a C4 frit and the orange filtrate kept overnight at −50 °C. Red microcrystals of **3** were isolated while cold in 78% yield (2.29 g, 3.9 mmol) and dried under vacuum.

Olefin polymerization experiments

These experiments were conducted in a flamed round-bottom reaction flask (100 cm^3) attached to a high-vacuum line. In a typical experiment, 0.65 mg (1.1 × 10^{-3} mmol) of a very freshly prepared catalyst and MAO (5.7 g, 5.17 mmol) were charged in a flask (100 cm^3) containing a magnetic stir bar. The reaction vessel was connected to a high-vacuum line, pumped-down and back-filled three times, the flask reevacuated, and a measured quantity of toluene (10 cm^3) was vacuum transferred to the reaction flask from Na/K. Next, gaseous ethylene or propylene was admitted to the vessel, after temperature equilibration, through a gas-purification column. The gas pressure was continuously maintained at 1.0 atm (101 325 Pa) with a mercury manometer. Rapid stirring of the solution was initiated and after a measured time interval the polymerization was quenched by injecting a methanol–HCl mixture. The polymeric product was filtered off, washed with acetone and hexane and dried under vacuum.

Crystallography

Owing to the sensitivity of compound L to moisture and oxygen, a suitable crystal for X-ray analysis was placed inside a glove-box in dry and degassed parathon oil (Du-Pont). Then, it was mounted on a STOE STADI IV diffractometer where it met a cold stream of nitrogen at 210 K. Data [λ(Mo-Kα) 0.710 73 Å] were collected with 25 reflections (2θ range: 5–45°)

and used for determination of the unit-cell parameters. The structure was solved by direct methods (SHELXTL[60]) and subsequent Fourier difference syntheses and refined by full-matrix least squares on F^2 (SHELXL 93).[61] The hydrogen atoms were included by use of a riding model and refined isotropically. The d(C–H) used was 0.95 Å for the aromatic and 0.98 Å for the methyl hydrogens. Preliminary data, measurement conditions and structure refinement are summarized in Table 3.

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References

1 D. J. Cardin, M. F. Lappert and C. L. Raston, in *Chemistry of Organozirconium and Hafnium Compounds*, Wiley, New York, 1986.
2 G. Erker, C. Krüger and G. Müller, *Adv. Organomet. Chem.*, 1985, **24**, 1.
3 G. Erker and R. Pfaff, *Organometallics*, 1993, **12**, 1921.
4 G. Erker, R. Pfaff, C. Krüger and S. Werner, *Organometallics*, 1993, **12**, 3559 and refs. therein.
5 E. I. Negishi, in *Comprehensive Organic Synthesis*, ed. L. A. Paquette, Pergamon, Oxford, 1991, vol. 5.
6 E. I. Negishi and T. Takahashi, *Acc. Chem. Res.*, 1994, **27**, 124 and refs. therein.
7 M. R. Reetz, *Organotitanium Reagents in Organic Synthesis*, Springer, Berlin, 1986.
8 M. T. Reetz, in *Organometallics in Synthesis*, ed. M. Schlosser, Wiley, New York, 1994, ch. 3.
9 N. E. Schore, in *Comprehensive Organic Synthesis*, ed. L. A. Paquette, Pergamon, Oxford, 1991, vol. 5.
10 E. I. Negishi and T. Takahashi, *Aldrichim. Acta*, 1985, **18**, 31.
11 J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 333.
12 R. F. Jordan, R. E, Lapointe, P. K. Bradley and N. Baenzinger, *Organometallics*, 1989, **8**, 2892 and refs. therein.
13 S. L. Buchwald, S. J. L. Maire, R. Nielsen, B. T. Watson and S. M. King, *Tetrahedron Lett.*, 1987, **28**, 3895.
14 M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255 and refs. therein.
15 T. Keii and K. Soga, in *Catalytic Olefin Polymerization*, Elsevier, Amsterdam, 1990.
16 M. A. Giardello, M. S. Eisen, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1995, **117**, 6128 and refs. therein.
17 H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143 and refs. therein.
18 W. Kaminski and H. Sinn, in *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, Springer, Berlin, Heidelberg, 1988.
19 Y.-X. Chen, C. L. Stern, S. Yang and T. J. Marks, *J. Am. Chem. Soc.*, 1996, **118**, 12 451 and refs. therein.
20 M. H. Chisholm and I. P. Rothwell, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1988, vol. 2, ch. 15.3.
21 L. R. Chamberlain, L. D. Durfee, P. E. Fau, P. E. Fanwick, L. Krobiger, S. L. Lateski, A. K. McMullen, I. P. Rothwell, K. Folting, J. C. Hauffman, W. E. Streib and R. Wang, *J. Am. Chem. Soc.*, 1987, **109**, 390 and refs. therein.
22 T. V. Lubben and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1987, **109**, 424 and refs. therein.
23 C. Floriani, F. Corazza, W. Lesueur, A. Chiesi-Villa and C. Guastini, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 66.
24 L. D. Durfee, P. E. Fanwick, I. P. Rothwell, K. Folting and J. C. Huffman, *J. Am. Chem. Soc.*, 1987, **109**, 4720.
25 C. H. Zambrano, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 1994, **13**, 1174.
26 G. Bailich, P. E. Fanwick and I. P. Rothwell, *J. Am. Chem. Soc.*, 1993, **115**, 1581 and refs. therein.
27 J. Okuda, S. Fokken, H. C. Kang and W. Massa, *Chem. Ber.*, 1995, **128**, 221 and refs. therein.
28 K. V. Gothelf, R. G. Hazell and K. A. Jørgensen, *J. Am. Chem. Soc.*, 1995, **117**, 4435.
29 L. Giannini, E. Solari, S. D. Angelis, T. R. Ward, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1995, **117**, 5801 and refs. therein.
30 E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Chem. Commun.*, 1992, 367.
31 R. Uhrhammer, D. G. Black, T. G. Gardner, J. D. Olsen and R. F. Jordan, *J. Am. Chem. Soc.*, 1993, **115**, 8493.
32 H. Brand and J. Arnold, *Angew. Chem., Int. Ed. Engl.*, 1993, **33**, 95.
33 D. Y. Dawson, H. Brand and J. Arnold, *J. Am. Chem. Soc.*, 1994, **116**, 9797.
34 Z. Duan and J. G. Verkade, *Inorg. Chem.*, 1995, **34**, 4311.
35 S. Freidrich, H. Memmler, L. H. Gade, W.-S. Li and M. McPartlin, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 676.
36 F. G. N. Cloke, P. B. Hitchcock and J. B. Love, *J. Chem. Soc., Dalton Trans.*, 1995, 25.
37 C. C. Cummins, R. R. Schrock and W. M. Davis, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 756.
38 F. Guérin, D. H. McConville and J. J. Vittal, *Organometallics*, 1996, **15**, 5586.
39 S. Friedrich, L. H. Gade, A. J. Edwards and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1993, 2861.
40 R. Gómez, M. L. H. Green and J. L. Haggitt, *J. Chem. Soc., Chem. Commun.*, 1994, 2607.
41 H. Mack and M. S. Eisen, *J. Organomet. Chem.*, 1996, **525**, 81.
42 J. R. Hagadorn and J. Arnold, *J. Am. Chem. Soc.*, 1996, **118**, 893 and refs. therein.
43 F. T. Edelmann, *Top. Curr. Chem.*, 1996, **179**, 113 and refs. therein.
44 D. Walter, R. Fischer, H. Görls, J. Koch and B. Schweder, *J. Organomet. Chem.*, 1996, **508**, 13.
45 R. Gomez, M. L. H. Green and J. L. Hagitt, *J. Chem. Soc., Dalton Trans.*, 1996, 939 and refs. therein.
46 J. C. Florez, J. C. W. Chien and M. D. Rausch, *Organometallics*, 1995, **14**, 2106.
47 D. Herskovics-Korine and M. S. Eisen, *J. Organomet. Chem.*, 1995, **503**, 307.
48 A. Chernega, R. Gómez and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1993, 1415.
49 D. G. Dick, R. Duchateau, J. J. H. Edema and S. Gambarotta, *Inorg. Chem.*, 1993, **32**, 1959.
50 H. W. Roesky, B. Meller, M. Noltemeyer, H.-G. Schmidt, U. Scholz and G. M. Sheldrick, *Chem. Ber.*, 1988, 1403.
51 R. Baumann, W. M. Davis and R. R. Schrock, *J. Am. Chem. Soc.*, 1997, **119**, 3830.
52 M. Kakugo, T. Miyatake and K. Mizunuma, *Chem. Express*, 1987, **2**, 445.
53 C. J. Schaverien, A. J. v. d. Linden and A. G. Orpen, *Am. Chem. Soc., Polym. Div., Polym. Prep.*, 1994, **35**, 672.
54 T. Miyatake, K. Mizunuma and M. Kakugo, *Makromol. Chem., Makromol. Symp.*, 1993, **66**, 203 and refs. therein.
55 J. J. H. Edema, R. Libbers, A. Ridder, R. M. Kellogg and A. L. Spek, *J. Organomet. Chem.*, 1994, **464**, 127.
56 B. Kaptein, G. Barf, R. M. Kellogg and F. v. Bolhuis, *J. Org. Chem.*, 1990, **55**, 1890.
57 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
58 J. L. Koenig, *Spectroscopy of Polymers*, American Chemical Society, Washington DC, 1992.
59 T. Miyatake, K. Mizunuma, Y. Seki and M. Kakugo, *Makromol. Chem., Rapid Commun.*, 1989, **10**, 349.
60 G. M. Sheldrick, SHELXTL, Siemens Analytical Instruments, Madison, WI, 1990.
61 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Determination, University of Göttingen, 1993.

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