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Synthesis and crystal structure of highly soluble ansa-titano- and zirconocene dichloride complexes $[Me_2Si(\eta^5\text{-}C_5H_2(SiMe_3)_2]_2MCl_2$ (M = Ti, Zr)

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Abstract

The synthesis and X-ray characterization of ansa-metallocene dichloride titanium and zirconium complexes of the type $[Me_2Si(\eta^5\text{-}C_5H_2(SiMe_3)_2)_2]MCl_2$ (M = Zr (**1**), Ti (**2**)) are reported. The complexes have been tested for ethylene polymerization.

Keywords: ansa-Metallocene; Zirconium; Titanium; Structure determination; Electrochemistry

1. Introduction

The synthesis of Group **4** metallocene dichloride complexes has received considerable attention in recent years in particular since the 1980s and the discovery that C_2-symmetry ansa-metallocenes can form an effective catalyst for the stereoregular polymerization of propene [1]. The selectivity being possible by the use of a ligand that alters the geometry of monomer insertion into a single configuration. The structure of the bridge between the two cyclopentadienyl rings greatly influences the polymerization behavior of these catalysts, the use of a silylene group leading to higher activities for ethylene polymerization [2] and reducing the syndiotacticity of the polypropylene which is generate [3].

Our group has already reported on some zirconium chemistry on substituted trimethylsilyl cyclopentadienyl ligands [4–6] and we were interested in the synthesis of ansa (Me_2Si) metallocene derivatives (Ti, Zr) of this type of complexes. We have recently reported on the cyclic voltammetry (CV) of some trimethylsilyl-substituted zirconocene dichlorides including the ansa complex $[Me_2Si(\eta^5\text{-}C_5H_2(SiMe_3)_2)_2]ZrCl_2$ (**1**) [7].

In this paper, we report on the synthesis of **1** as well as the synthesis of the ansa-titanocene analogue with the ansa prochiral bridged tetrasubstituted bis-cyclopentadienyl ligand $[Me_2Si(\eta^5\text{-}C_5H_2(SiMe_3)_2)_2]$, L, together with their X-ray crystal structure determination.

2. Results and discussion

The reaction of Me_2SiCl_2 with two equivalents of $C_5H_3(SiMe_3)_2Li$ (formed by lithiation of $C_5H_4(SiMe_3)_2$ with one equivalent of BuLi) leads to the ligand precursor $[Me_2Si(C_5H_3(SiMe_3)_2)_2]$, LH_2, after purification by distillation under reduced pressure. Addition of two equivalents of $KOCMe_3$ to LH_2 in THF at −78 °C gives $[Me_2Si(C_5H_2(SiMe_3)_2)_2]$, LK_2, with 98% yield (Scheme 1).

The synthesis of the metallocene dichloride complexes is carried out using a standard method, which consists of reacting the disalt of the bis-Cp ligand LK_2 with zirconium tetrachloride, or titanium tetrachloride bis-THF adduct, in toluene under reflux. Complexes $LZrCl_2$ (**1**) and $LTiCl_2$ (**2**) are obtained with a 45 and 34% yield, respectively, after several recrystallizations from pentane solutions at −50 or −80 °C. Both **1** and **2** are remarkably soluble in pentane which reduces their isolated yield after purification (Scheme 2).

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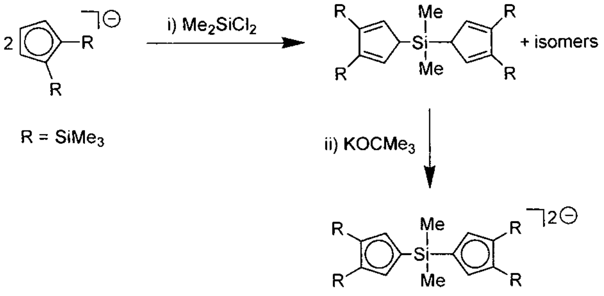
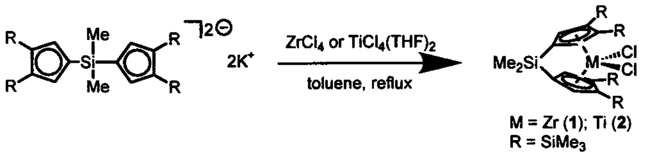
The nature of compounds **1**–**2** has been confirmed by X-ray analysis (Figs. 1 and 2). Table 1 contains the most relevant bonding and geometrical parameters for the two compounds. In both complexes the metal atom is pseudotetrahedrally co-ordinated by the two Cp groups of the ansa ligand and the two-chloro ligands. Figs. 3 and 4 show another view of **1** and **2** when both cyclopentadienyl rings with the TMS ligands are superimposed showing the distorted geometry of both molecules. For molecule **1**, the centroid of one Cp ring is contained in the plane defined by Si(**1**), C(**5**), and C(**6**) atoms (the distances of the centroids of Cp(**1**) and Cp(**2**) (Cp(**1**)=(C(**1**)–C(**5**), Cp(**2**)=C(**6**)–C(**10**)) to the plane are nearly 0.07 and 0.10 Å, respectively) and the Zr atom is out of this plane by nearly 0.50 Å. For molecule **2**, the Si(**1**)C(**5**)C(**6**) plane contains both centroids of the Cp rings (Cp(**1**) and Cp(**2**) distances to the plane are nearly 0.05 and 0.04 Å) and the Ti atom is out of this plane from nearly 0.42 Å. The dihedral angle between the Si(**1**)C(**5**)C(**6**) plane and the Cp(**1**)MCp(**2**) plane is nearly the same (23.0 and 24.8° for **1** and **2**, respectively). Another geometrical feature of the molecules is the plane ZrCl(**1**)Cl(**2**) that contains the Si(**1**) atom of the Me_2Si bridge. This bridge (C(**5**)–Si(**1**)–C(**6**) nearly 90°) constrains the bent metallocene geometry in such a way that the distances from the metal to the carbons of the cyclopentadienyl rings are different (d(Zr–C) range: 2.466–2.621 Å; d(Ti–C) range: 2.355–2.511 Å) and force the η^5-coordination mode of the ligands towards η^3-coordination. So the Cp(**1**)–M–Cp(**2**) angle θ ($M = Zr$, Ti) and the dihedral angle ϕ between the cyclopentadienyl planes are $\theta =$ 124.72 and 129.61°, $\phi = 58.74$ and 62.85° for **1** and **2**, respectively.



Scheme 1. Synthesis of LH_2 and LK_2.



Scheme 2. Synthesis of $LMCl_2$ complexes **1**–**2**.

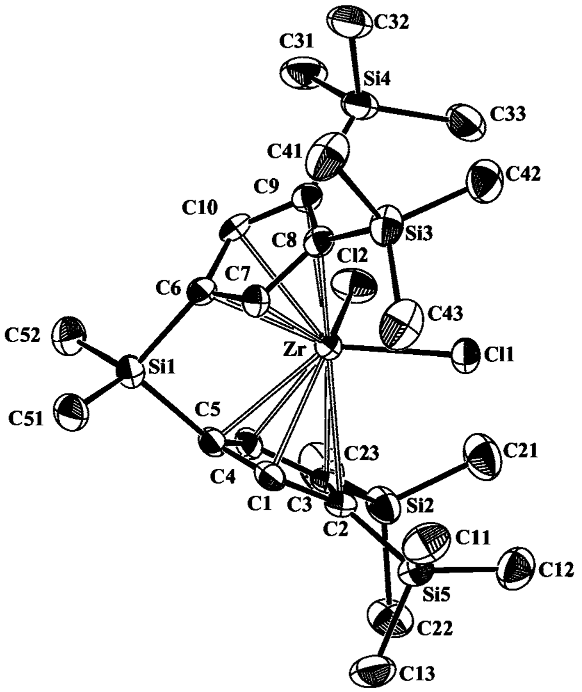


Fig. 1. ORTEP view of **1**.

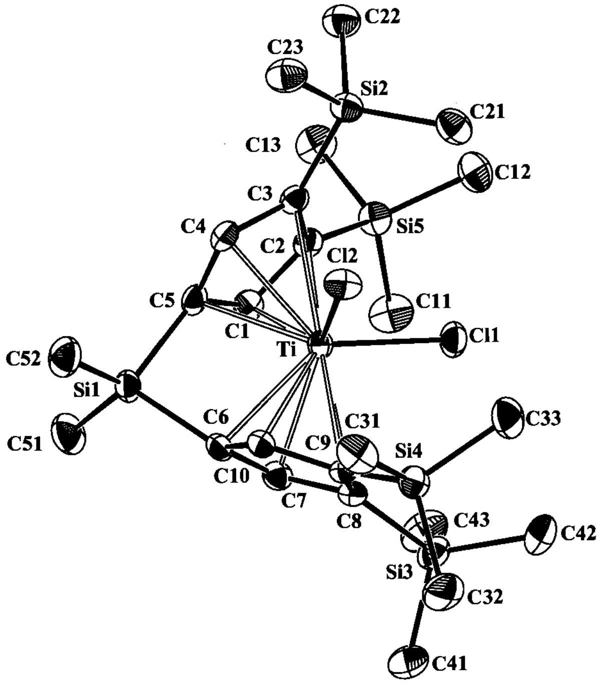


Fig. 2. ORTEP view of **2**.

Although the distortion of molecules **1** and **2** can be observed in the solid state, the ^{1}H-NMR VTP from − 80 to + 80 °C of **1** and **2** display one set of resonances corresponding to the different signals of C_5H_2, $SiMe_2$ and equivalent $SiMe_3$. Cyclovoltammogram of complex **1** was recently studied ($E° = -2.215$ V) [7]

Table 1
Selected bond distances (Å), bond angles and relevant geometrical parameters (°)

	1 (M = Zr)	**2** (M = Ti)
Bond distances		
M–Cl(1)	2.422(2)	2.3220(8)
M–Cl(2)	2.442(3)	2.3524(7)
M–C(1)	2.466(8)	2.360(2)
M–C(2)	2.621(8)	2.511(2)
M–C(3)	2.601(7)	2.492(2)
M–C(4)	2.505(7)	2.378(2)
M–C(5)	2.499(8)	2.355(2)
M–C(6)	2.493(9)	2.367(2)
M–C(7)	2.481(8)	2.358(2)
M–C(8)	2.610(8)	2.490(2)
M–C(9)	2.588(8)	2.478(2)
M–C(10)	2.502(7)	2.383(2)
M–Cp(1)	2.219	2.100
M–Cp(2)	2.242	2.009
Bond angles		
Cl(1)–M–Cl(2)	98.32(11)	97.40(3)
C(5)–Si–(1)C(6)	93.73(35)	90.76(10)
Cp(1)–M–Cl(1)	110.08	107.54
Cp(1)–M–Cl(2)	105.07	104.22
Cp(2)–M–Cl(1)	110.02	108.87
Cp(2)–M–Cl(2)	105.02	104.33
Cp(1)–M–Cp(2)	124.72	129.61

Cp(1) and Cp(2) are the centroids of the cyclopentadienyl rings C(1)–C(5), C(6)–C(10).

and the electronic effect of the $SiMe_3$ groups was established regarding their steric effect in comparison with the redox standard potential of $Me_2Si(C_5H_4)_2ZrCl_2$ ($E° = -2.068$ V), keeping in mind that both complexes have nearly similar structural geometry. Cyclovoltammogram of complex **2** was studied in THF with tetrabutylammonium tetrafluoroborate as a supporting electrolyte, in the presence or absence of Cp_2Fe as reference and shows two reversible peaks at $E° = -1.406$ and -2.333 V ($E_c - E_a = 110$ mV). In comparison, compounds $Me_2Si(C_5H_4)_2TiCl_2$ and $Me_2Si(C_5Me_4)_2TiCl_2$ give potentials of the first and second waves at -1.295, -2.519 and -1.641, -2.599 V, respectively. According to Mach and coll. [8] and in relation to the ϕ angle of **2** (62.8°) which is more or less similar to that of $Me_2Si(C_5Me_4)_2TiCl_2$ (59.3°), it seems that steric effects play a minor role in the shifts of the electron potentials observed in the ansa-titanocene series as already observed for the ansa-zirconocene series [7].

Complexes **1** and **2**, after being activated with methylalumoxane (MAO; in a ratio MAO/catalyst = 500, 1 atm C_2H_4, room temperature) are highly active catalysts for ethylene polymerization, with activities of 2.2×10^5 and 1.5×10^5 g P.E. (mol of M)$^{-1}$ h^{-1} (P.E.: polyethylene), respectively, (T_f(°C): (**1**), 130.3; (**2**), 130.5). Lower activity of **2** versus **1** might be due to smaller ionic radii of titanocenes versus zirconocenes. Further studies are still needed to improve this polymerization behavior and preparation of the dimethyl zirconocene species, the building block for obtaining the cationic species [9], is underway.

3. Experimental

3.1. General

All experiments were performed under an inert atmosphere of argon using standard Schlenk and glove-box

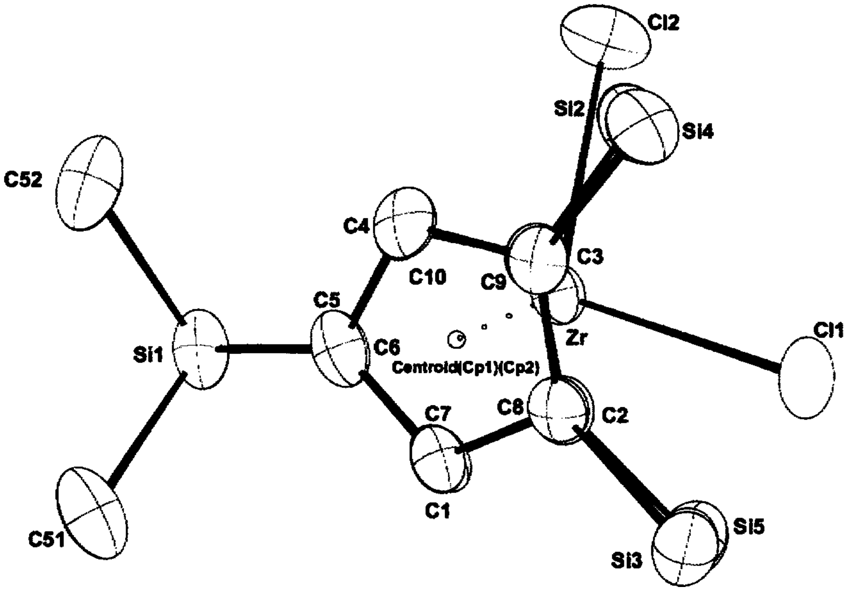


Fig. 3. Projection of **1** on the $ZrCl_2$ plane showing the distorted environment around the metal atom.

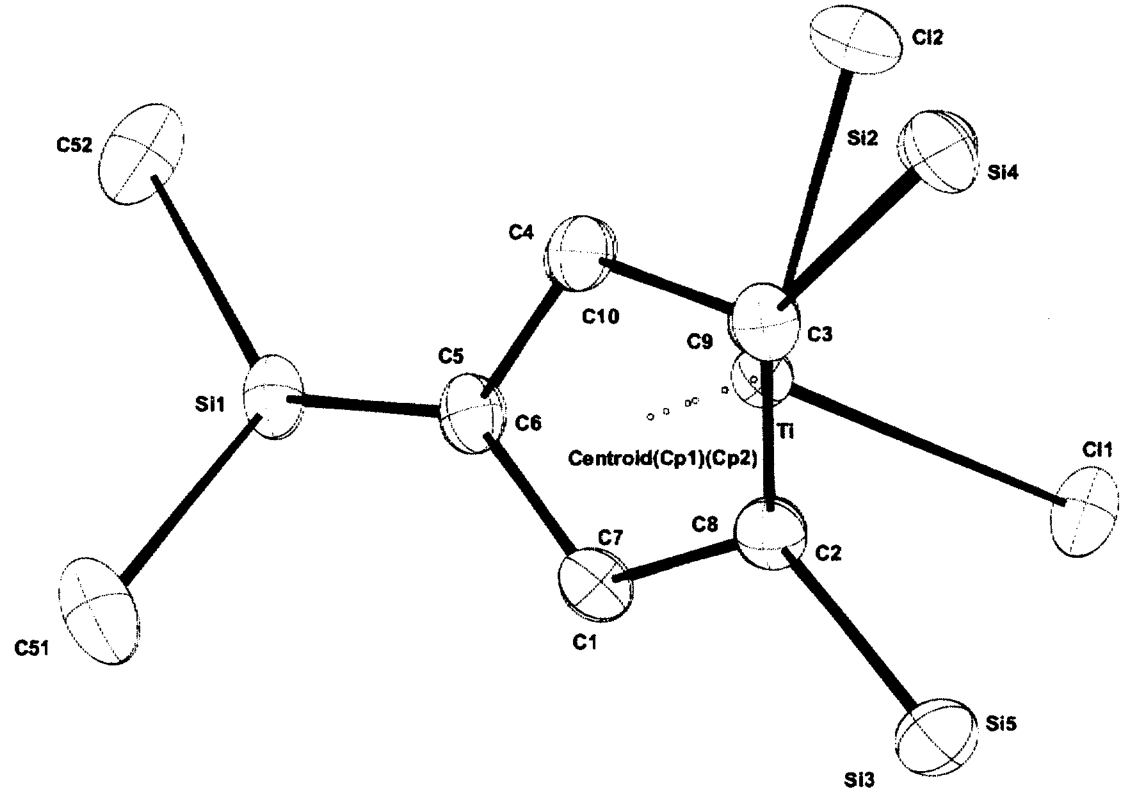


Fig. 4. Projection of **2** on the $TiCl_2$ plane showing the distorted environment around the metal atom.

techniques. Solvents were dried and distilled over Na–K alloy (pentane, toluene) or Na-benzophenone ketyl (THF, diethyl ether) under argon before use. $C_5H_5(SiMe_3)$, $C_5H_4(SiMe_3)_2$, and $TiCl_4(THF)_2$ were synthesized following known procedures [10,11]. NMR spectra were run on Brücker AC200, AM250 or DPX300 spectrometers. Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France) (C, H) or by the Service Central de Microanalyses du CNRS at Vernaison (France). A ‘homemade microcomputer-controlled instrument’ with ohmic resistance compensation was used for CV studies. A platinum auxiliary electrode and an SCE reference electrode as a working electrode were used in conjunction with a platinum-disk electrode as working electrode. NBu_4BF_4 was used as a supporting electrolyte for CV studies. It was melted under vacuum before use to ensure efficient dehydratation. Melting transition temperatures of the polyethylenes were determined by DSC (Model 204 Netzsch) at a heating rate of 5 °C per min^{-1}.

3.2. Synthesis of LH_2, [$Me_2Si(C_5H_3(SiMe_3)_2$-1,3]

From a solution of [$C_5H_4(SiMe_3)_2$] (17 g, 81.0 mmol) in THF (100 ml) cooled at 0 °C, 33 ml LiBu (2.5 M in hexane, 82.5 mmol) was added under stirring. After 2 h, the mixture was allowed to warm to room temperature (r.t.) and Me_2SiCl_2 (5.28 g, 41 mmol) was added. After 1 day stirring, a saturated solution of NH_4Cl (2 × 50 ml) and 50 ml H_2O were added and the organic layer was extracted with diethylether (3 × 100 ml) and dried on $MgSO_4$. Evaporation of the solvents with a water-pump followed by a distillation of the liquid (100 °C per 10^{-3} mmHg) gives LH_2 as a colorless liquid (10.8 g, 30%). Anal. Calc. for $C_{24}H_{48}Si_5$: C, 60.44; H, 10.07. Found: C, 60.10; H, 10.15%.

3.3. Synthesis of LK_2

About 2.62 g (23.62 mmol) of $KOCMe_3$ dissolved in THF was added to a solution of 5.56 g (11.67 mmol) of LH_2 in 20 ml of THF at −80 °C under stirring. The solution was left to reach r.t. under stirring, and the volatiles were later removed under vacuum. The brown solid residue was extracted with diethylether, and dried again. In order to remove traces of THF, the light brown solid was dissolved in pentane with a minimum amount of ether and stirred for 4 h. Removal of the volatiles yielded 6.37 g of a light brown solid (98%). Elemental analysis: Calc. for $C_{24}H_{46}K_2Si_5$: C, 52.17; H, 8.33. Found: C, 52.10; H, 8.61%.

3.4. Synthesis of $LZrCl_2$ (**1**)

Hundred milliliter of toluene was added to a mixture of 3.81 g of LK_2 and 1.60 g of $ZrCl_4$. The resulting suspension was refluxed for 12 h, and filtered through a bed of celite. The clear filtrate was evaporated to dryness. The brown residue was recrystallized from cold pentane (−50 °C) to give **1** as a light brownish microcrystalline solid (1.96 g, 45%). Crystals suitable for X-ray experiments were obtained from a cold pentane solution. Elemental analysis: Calc. for $C_{24}H_{46}Cl_2Si_5Zr$: C, 45.26; H, 7.23. Found: C, 44.53; H, 7.08%. ^{1}H-NMR ($CDCl_3$) δ 6.3 (s, 4H, C_5H_2), 0.7 (s, 6H, Me_2Si), 0.3 (s, 36H, $SiMe_3$). $^{13}C\{^1H\}$ (CD_2Cl_2) 144.09(CSiMe$_3$), 127.53 (C_5H_2), 112.04 (CSiMe$_2$), 0.75 (Si(CH$_3$)$_3$); −4.56 (Si(CH$_3$)$_2$).

Table 2
Summary of crystal data, data collection, and structure refinement parameters

	Crystal data	
	1	**2**
Empirical formula	$C_{24}H_{46}Cl_2Si_5Cl_2Zr$	$C_{24}H_{46}Cl_2Si_5Cl_2Ti\cdot 1/4C_7H_8$
Formula weight	637.18	617.89
Temperature (K)	273	160
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	13.1664(17)	10.405(2)
b (Å)	12.7984(16)	18.656(3)
c (Å)	20.3723(21)	18.241(2)
β (°)	90.256(10)	92.34(2)
V(Å^3)	3432.9(7)	3537.9(8)
Z	4	4
F(000)	1336	1314
D_{calc} (g cm^{-3})	1.233	1.158
Absorption coefficient (mm^{-1})	0.662	0.576
Crystal description	colorless needle	red parallelepiped
Crystal size (mm)	0.87 × 0.12 × 0.12	0.4 × 0.2 × 0.1
Data collection		
Collection method	φ rotation	φ rotation
2θ range for data collection (°)	3.76–46.52	3.3–52.1
Reflections collected/unique	19827/4699 [$R_{int} = 0.1928$]	20350/5050 [$R_{int} = 0.044$]
Completeness to 2θ	90.3%	99.1%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	4699/0/303	5050/51/351
Goodness-of-fit on F^2	0.934	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0683$, $wR_2 = 0.1439$	$R_1 = 0.0320$, $wR_2 = 0.0806$
R indices (all data)	$R_1 = 0.1282$, $wR_2 = 0.1708$	$R_1 = 0.041$, $wR_2 = 0.0842$
Largest difference peak and hole(e Å^{-3})	0.715 and −0.714	0.727 and −0.251

3.5. Synthesis of $LTiCl_2$ (**2**)

Ten milliliter of toluene was added to a mixture of 810 mg (1.471 mmol) of LK_2 and 500 mg (1.471 mM) of $TiCl_4(THF)_2$. The resulting suspension was refluxed for 20 h. The volatiles were removed under vacuum and the residue was extracted with 2 × 5 ml of pentane and filtered through celite. The clear filtrate was evaporated to dryness to give a sticky red solid (650 mg) which was recrystallized from cold pentane (−80 °C; 300 mg, yield: 34%). Crystals suitable for X-ray experiments were obtained from a cold toluene–pentane solution. Elemental analysis: Calc. for $C_{24}H_{46}Cl_2Si_5Ti$: C, 48.54; H, 7.81. Found: C, 48.87; H, 7.30%.^{1}H-NMR (C_6D_6) δ 6.32 (s, 4H, C_5H_2), 0.50 (s, 6H, Me_2Si), 0.22 (s, 36H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 152.52 (CSiMe$_3$), 130.26 (C_5H_2), 108.99 (CSiMe$_2$), 0.82 (Si(CH$_3$)$_3$); −4.88 (Si(CH$_3$)$_2$).

3.6. Typical ethylene polymerization tests

The catalyst precursor (about 5 μmol) and 500 equivalents of MAO (10% in toluene) were premixed for 5 min in 5 ml of toluene. Ethylene (1 atm) was introduced under stirring at r.t. After 15–20 min, the polymerization was quenched with acidified methanol. The polyethylenes were filtered, washed with methanol and then acetone, and dried under vacuum at 80 °C for 24 h.

3.7. Crystallographic data for **1–2**

For structures **1** and **2** (Table 2), data collection was done using a Stoe Imaging Plate Diffraction System (IPDS). The final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections, and crystal decay was monitored by measuring 200 reflections by image. Any fluctuations of the intensity were observed over the course of the data collection. The numerical correction absorptions [12] were applied to the data, by using a set of symmetry equivalent reflections selected with the criterion [$I > 3\sigma(I)$] such that all directions of reciprocal space are equally represented. All structures have been solved by direct methods using SIR92 [13], and refined by least-squares procedures on a F^2 with the aid of SHELXL97 [14]. The atomic scattering factors were taken from international tables for X-ray crystallography [15]. All hydrogen atoms were located on difference Fourier maps, and refined with a riding model and all the remaining non-hydrogen atoms were anisotropically refined. In the last refinement cycles a weighting scheme was used for each structure where weights were calculated from the following formula: $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Drawing of the molecules was performed using the program ZORTEP [16] with 50% probability displacement ellipsoids for non-hydrogen atoms.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary information, CCDC no 159 325 for compound **1** and CCDC no 159 326 for compound **2**. Copies of the data can be obtained free of charge on application from The Director, CCDC, 12 Union Road, Cambridge CB2 lEZ, UK (fax: +44-1223-336033; e-mail: deposit @ccdc.cam.ac.uk, htpp://www.ccdc.cam.ac.uk.).

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