Polish J. Chem., **75**, 1371–1375 (2001) **COMMUNICATION**

Molecular Structure of $[\mathrm{Ti}\{\eta^5{:}\eta^1\text{-}\mathrm{C_5Me_4SiMe_2NPh(^iPr)_2}\}\mathrm{Cl_2}]$

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(Received January 22nd, 2001; revised manuscript February 23rd, 2001)

Constrained geometry catalyst (CGC) developed by Dow company is known to produce homogeneous random olefin copolymerization with very narrow molecular weight distribution (MWD) with comonomer, or short chain branching distributions (SCBD), which together improves physical properties. Up to now, molecular structure of several titanium based constrained geometry catalysts have been determined, which are $[\eta^5{:}\eta^1\text{-}(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)](NMe_2)_2$ [1], $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NPh)Cl_2$ [2], $Ti\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N(MePh)\}Cl_2$ [2,3], $Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_3F_2\text{-}2,5)Cl_2$ [4], $Ti\{(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N(CH_2Ph)\}(CH_2Ph)_2$ [4], $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)(\eta^2\text{-}(C{=}N^tBu)Et)Cl$ [5], $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$ [6], $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2N^tBu)Ti$(prone-2,4-hexadiene) [7]. We report here the crystal and molecular structure of (2,6-dipropylphenylamide) dimethyl (tetra-methyl cyclopentadienyl) silane titanium dichloride. Table 1 and Table 2 give the crystal data and selected bond distances and angles, respectively. A perspective view of the molecules including the atom-numbering scheme is presented in Fig. 1. The molecular structure of I generally resembles the constrained geometry about the metal consisting of the π-bounded ring with its dimethylsilyl-di-propyl phenyl amido group and the two terminal chlorine atoms. The Ti–C_{Cp} distances of compound I are in a wider range 2.281(4)~2.413(3) Å, and the mean distance is 2.353(3) Å. The mean distance of Ti–C_{Cp} of compound I is a little longer than those of $Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NCHMe_2)Cl_2$ (2.346 Å) and $Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2C_6H_3F_2\text{-}2,5)Cl_2$ (2.341 Å), however, is a little shorter than that of $Ti(\eta^5{:}\eta^1\ \text{-}C_5H_4SiMe_2NCH_2C_6H_3F_2\text{-}2,5)Cl_2$ (2.375 Å). The corresponding C–C bond lengths in the cyclopentadienyl ring vary from 1.405 Å to 1.433 Å, and the distances between the carbons of benzene ring vary more than those of the cyclopentadienyl ring, which are from 1.37 Å to 1.418 Å. The Ti–Cl bond distances (mean 2.260(1) Å) are normal and comparable to other published

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data [1,4,6]. The angle of Cp_{cent}–Ti–N is 106.6°, which is little larger than those of $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NPh)Cl_2$ (106.1°) and $Ti\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N(MePh)\}Cl_2$ (105.7°), probably due to the large substitution of the iso-propyl in the benzene ring. The angle of Cl–Ti–Cp_{cent} is 115.2°, and the angles of carbons in cyclopentadienyl ring are 108.9(3), 108.2(2), 105.8(4), 108.9(3), 108.2(2), respectively. The angles of the ring formed by C(1), N, Si, and Ti, N–Ti–C(1), Ti–C(1)–Si, C(1)–Si–N, Si–N–Ti are 108.43(6), 89.4(2), 90.1(2), 106.3(2), respectively. The so called constrained geometry ring formed by centroid of the cyclopentadienyl ring, N, Si, and Ti is twisted and not in a plane. However, the atoms of Ti, C(1), Si, N is in a plane and consists of a ring.

Table 1. Crystal data and structure refinement for I.

Formula	$C_{23}H_{25}Cl_2NSiTi$
Molecular weight	471
Space group	*Pnma*
Cell length, Å	$a = 12.658(3)$
	$b = 16.62(3)$
	$c = 11.760(2)$
Cell volume, Å^3	2474(1)
Z	4
D_x/Mg.m^3	1.268
D_m	not determined
Radiation	0.71073 Å
Reflections for lattice cell parameters	23
θ range for lattice parameters	5.28–9.93
μ, mm^{-1}	0.62
T/K	293(2)
Crystal description	rhombohedron
Crystal size, mm	0.42 × 0.38 × 0.52
Crystal color	yellow
Data collection	
Diffractometer	Siemens P4
Scans	ω/2θ
h	–1~15
k	–1~19
l	–1~13
R_{int}	0.0215
θ_{max}, °	25
T_{min}	0.55211
T_{max}	0.61012
Absorption correction	Empirical *via* φ scans [8]
Measured reflections	3319

Independent reflections	2266
Standard reflections	3/100
Intensity decay	0.4%
Refinement	
Refinement on F^2	$w = 1/[\sigma^2(F_0^2) + 0.0453P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.0399$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.0905$	$\Delta\rho_{max} = 0.240$ e Å^{-3}
$S = 0.875$	$\Delta\rho_{min} = -0.206$ e Å^{-3}
2266 reflections	Extinction correction: SHELXL93 (Sheldrick, 1993)
143 parameters	Extinction coefficient: 0.00015(2)
H atoms not located	Scattering factors from International Tables for Crystallography (Vol.C)

Table 2. Selected bond lengths [Å] and angles [°].

Bond lengths [Å]			
Ti–N	1.930(3)	Ti–Cl	2.2595(10)
Ti–Cl#1	2.2595(10)	Ti–C(1)	2.281(4)
Ti–C(2)	2.330(3)	Ti–C(2)#1	2.330(3)
Ti–C(4)	2.413(3)	Ti–C(4)#1	2.413(3)
Ti–Si	2.936(2)	Si–N	1.737(3)
Si–C(13)#1	1.857(3)	Si–C(13)	1.857(3)
Si–C(1)	1.873(4)	N–C(6)	1.446(5)
C(1)–C(2)	1.433(4)	C(1)–C(2)#1	1.433(4)
C(2)–C(4)	1.410(4)	C(2)–C(3)	1.505(4)
C(4)–C(4)#1	1.405(7)	C(4)–C(5)	1.499(4)
C(6)–C(7)#1	1.418(3)	C(6)–C(7)	1.418(3)
C(7)–C(8)	1.395(4)	C(7)–C(10)	1.510(4)
C(8)–C(9)	1.371(4)	C(8)#1–C(9)	1.371(4)
C(10)–C(11)	1.522(4)	C(10)–C(12)	1.527(4)
Ti-Cp$_{cent}$	2.020		
Bond angles [°]			
N–Ti–Cl	108.43(6)	Cl–Ti–Cl#1	102.64(6)
Cl–Ti–C(1)	127.20(3)	Cl–Ti–C(2)	93.05(8)
Cl–Ti–C(4)	87.53(8)	C(1)–C(2)–C(4)	108.9(3)
C(2)–C(4)–C(4)#1	108.2(2)	C(2)–C(1)–C(2)#1	105.8(4)
C(1)–C(2)–C(3)	127.5(3)	C(3)–C(2)–C(4)	123.5(3)
C(2)–C(4)–C(5)	125.9(4)	C(5)–C(4)–C(4)#1	125.8(2)
C(1)–Si–C(13)	115.27(14)	C(13)–Si–C(13)#1	103.0(2)
Si–C(1)–C(2)	122.1(2)	N–Si–C(1)	90.1(2)

Table 2 (continuation)

N–Si–C(13)	116.88(12)	Si–C(1)–Ti	89.4(2)
Ti–N–C(6)	120.2(2)	Si–N–C(6)	133.6(3)
N–C(6)–C(7)	119.9(2)	C(6)–C(7)–C(8)	118.2(3)
C(7)–C(8)–C(9)	121.8(4)	C(8)–C(9)–C(8)#1	119.8(5)
C(6)–C(7)–C(10)	123.9(2)	C(7)–C(10)–C(11)	110.1(3)
C(11)–C(10)–C(12)	109.5(3)	Si–N–Ti	106.3(2)
Cl–N–Ti	106.3(2)	N–Ti–Cp$_{\text{cent}}$	106.6

Symmetry code: (1) x, –y + 3/2, z

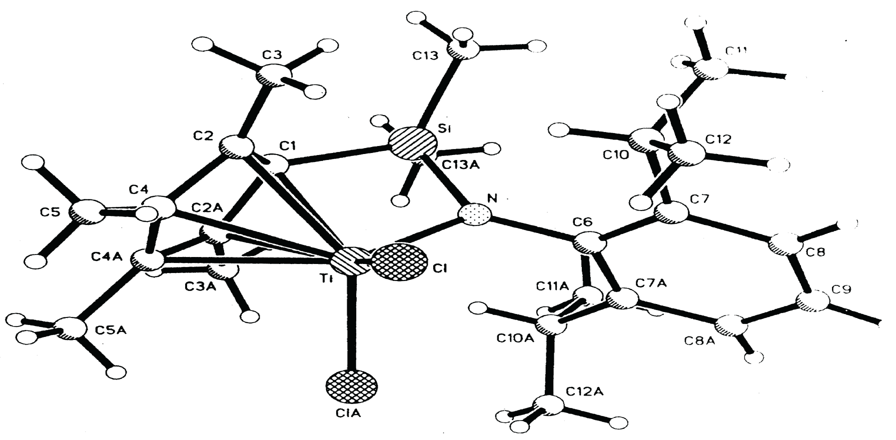

Figure 1. Perspective view of the Ti{η^5:η^1-$C_5Me_4SiMe_2NPh(^iPr)_2$}Cl_2.

Synthesis of I [2,3]: To 1.5 g (4 mmol) $TiCl_3 \cdot 3THF$ in 25 ml THF was added 1.5 g (4 mmol) dilithium (2,6-propylphenylamide) dimethyl (tetra-methyl cyclopentadienyl) silane and the mixture was allowed to stir for 1 hour, then 0.63 g AgCl (4 mmol) was added. After 4 hours stirring, the solvent was moved and the residue was extracted with diethyl ether. The ether extracted was filtered and evaporated to dryness to give 0.40 g yellow crystalline solid, yield 41%. M.p.: 267–268°C. MS(m/e): 471, 296, 177, 162.

A suitable single crystal was obtained from a mixture of diethyl ether/hexane (2:1) solution by slow cooling to 253 K. The structure was refined by full-matrix least-squares techniques, using SHELXL93 [9]. All non-H atoms were assigned anisotropic displacement parameters in the refinement. Data collection: XSCANS [10]. Cell refinement: XSCANS. Data reduction: SHELXTL-Plus [11]. Program(s) used to solve structure: SHELXS86. Program(s) used to refine structure: SHELXL93. Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXTL-Plus.

Crystallographic data are deposited with the Cambridge Crystallographic Data Centre – deposition number CCDC 164292.

Acknowledgment

This work was supported by the National Nature Science Foundation and SINOPEC under grant No. 29734141.

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