Chinese Chemical Letters Vol. 11, No. 5, pp. 459–462, 2000

X-ray Crystal Structure and Molecular Mechanics Calculations of (2,6-iso-dipropyl-phenylamide) Dimethyl (tetra-methylcyclopenta-dienyl) Silane Titanium Dichloride

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Abstract: Crystal and molecular structure of (2,6-dipropylphenylamide) dimethyl (tetra-methyl cyclopentadienyl) silane titanium dichloride (I) was fully characterized by X-ray diffraction. The crystal is obtained from a mixture of ether/hexane as orthorhombic, with a = 12.658 (3) Å, b = 16.62 (3) Å, c = 11.760 (2) Å, V = 2474.2 (9) Å^3, Z = 4, space group Pnma, R = 0.0399. Componud I compose of the π-bounded ring with its dimethylsilyl-dipropyl phenyl amido group and the two terminal chloride atoms coordinated to central metal to form a so-called constrained geometry catalyst (CGC) structure. The result of molecular mechanics (MM) calculations on compound I shows that bond lengths and bond angles from the MM calculation are comparable to the data obtained from the X-ray diffraction study. The relation of the structure of CGCs and their catalytic activity by MM calculations is also discussed.

Keywords: Crystal structure, constrained geometry catalyst, metallocene, molecular mechanics calculation.

Experimental

Synthesis of **I**: To 1.5g (4mmol.) $TiCl_3$ • THF in 25 mL THF was added 1.5g (4 mmol.) dilithium (2,6-propylphenylamide) dimethyl (tetra-methyl cyclopentadienyl) silane and the mixture was allowed to stir for 1 hour, then 0.63g AgCl (4 mmol.) was added. After 4 hours stirring, the solvent was moved and the residue was extracted with diethyl ether. The ether extract was filtered and evaporated to dryness to give 0.40g yellow crystalline solid, yield 41%. ^{1}H-NMR(C_6D_6): 0.48(6H), 1.12(6H), 1.49(6H), 1.98(6H), 2.18(6H), and 3.04(2H).

A suitable single crystal was obtained from a mixture of diethyl ether/hexane (2:1) solution by slowly cooling to 253K. The structure was refined by full-matrix least-squares techniques, using SHELXL93 (Sheldrick, 1993). All non-H atoms were assigned anisotropic displacement parameters in the refinement.

The molecular model of individual catalyst was built on Silicon Graphics O_2 work station using the program Cerius^2 version 3.8 developed by Molecular Simulations Incorporated (MSI). Molecular mechanics was used with the Universal 1.02 force field[1-3].

In the calculations, all the geometrical parameters were optimized without any constraint. The charge equilibration (QEq) [4] was selected for charge distribution, which allows the charges to respond to changes in the geometry of molecular structure, and can be applied to any material (polymer, ceramic, semiconductor, biological, metallic). The obtained QEq charges are in reasonable agreement with both experiment and *ab initio* theory [4].

Results and Discussion

Constrained geometry catalyst (CGC) developed by DOW company is known to produce homogenous random olefin copolymers with very narrow molecular weight distribution (MWD) with commoner, or short chain branching distributions (SCBD) which together improve physical properties. Up to now, molecular structure of several titanium based constrained geometry catalysts have been determined, which are $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NPh)Cl_2$[5,6], $Ti\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N(MePh)\}Cl_2$[5,6], $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N(CH_2Ph)(CH_2Ph)_2$[7], $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)\{(\eta^2\text{-}(C{=}N^tBu)\ Et)\ Cl$[8], $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$[9], $(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2N\ ^tBu)\ Ti$ (Prone-2,4-hexadiene)[10]. We report here the molecular structure of (2,6-dipropylphenylamide) dimethyl (tetra-methyl cyclopentadienyl) silane titanium dichloride. **Table 1** gives the selected bond distances and angles from X-ray diffraction and MM calculation. A perspective view of the molecules including the atom-numbering scheme is presented in **Figure 1**.

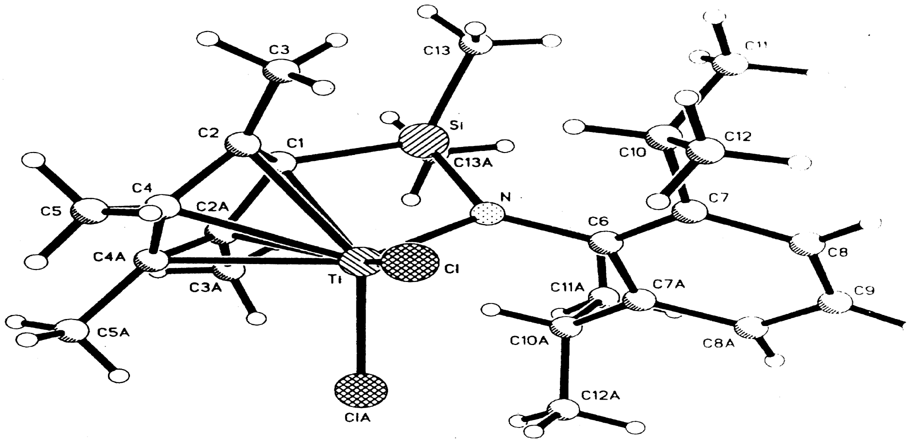
Table 1 Selected bond lengths and angles from X-ray diffraction and MM calculation method for compound I

	Bond lengths(Å)	
	X-ray diffraction	MM Calculation
Ti-C(1)	2.281(4)	2.191
Ti-C(2)	2.330(3)	2.320
Ti-C(2)#1	2.330(3)	2.316
Ti-C(4)	2.413(3)	2.427
Ti-C(4)#1	2.413(3)	2.339
Ti-N	1.930(3)	2.065
Ti-Cl	2.260(1)	2.335
Ti-Cl#1	2.260(1)	2.337
$Ti\text{-}Cent_{Cp}$	2.020	2.007
	Bond angles°	
C(1)-Ti-N	74.3(1)	74.2
C(1)-Si-N	90.1(2)	90.9
Si-C(1)-Ti	89.4(2)	93.9
Cl-Ti-Cl#1	102.6(1)	106.2
N-Ti-Cl#1	102.6(1)	106.5
Ti-N-Si	106.3(2)	107.5
$N\text{-}Ti\text{-}Cent_{Cp}$	106.6	106.5

Symmetry code: (1) x, -y+3/2, z.

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 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 data. The Ti-C_{Cp} distances associated with the η^5-cyclopentadienyl ring are in a wider range 2.281(4)~2.413(3) Å and comparable to other published data[5-10]. The angle of Cp_{cent}-Ti-N is 106.6°, which is a little larger than that of Ti (η^5:η^1-$C_5Me_4SiMe_2NPh)Cl_2$ (106.1°)[5,6] and Ti{η^5:η^1-$C_5Me_4SiMe_2N(MePh)\}Cl_2$ (105.7°)[5,6], probably due to the large substitutions of the *iso*-propyl in the benzene ring. The angle of Cl-Ti-Cp_{cent} is 115.2° , and the inner angles of 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.

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



Since there are great relations between the catalytic property of metallocene and their structures, in the last fifteen years, numerous investigations have been conducted to elucidate the relation of the structure and catalytic activity of the metallocene catalyst. Usually, ligands of metallocene with electron donating groups enhances catalytic activity, steric effects play a minor role, provided access to the metal by reagent is possible. However, a steric threshold exists in these systems and if large α-olefins or a small metal ion (Ti, versus Zr) are used then catalyst activity will be dominated by steric effects[11].

Although density functional theory (DFT) methods have been introduced to predict the reactivity of metallocene, few data were published to study on the structure-catalytic activity relations of metallocene by use of MM calculations[12-15]. From **Table 1**, we can see that the results of the bond lengths and angles from the MM calculation are well fit to those from X-ray diffraction method. We used this method to calculate Ti $\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NPh(^iPr)_2\}Cl_2$, and Ti $\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NPh\}Cl_2$, the partial charge on the central metal titanium is 0.8157 and 0.8510, respectively. This mean the ligand of compound **I** has stronger electron donating ability than that of Ti $\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NPh\}Cl_2$, and Ti $\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NPh(^iPr)_2\}Cl_2$ should have high activity to polymerize monomers, and this result get support from that Ti $\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NPh(^iPr)_2\}Cl_2$ has high activity than that of Ti $\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NPh\}Cl_2$ in the ethylene/styrene copolymerization[5,6]. Further study on the relation of the structure of the CGCs and their catalytic activities of ethylene and styrene polymerization is in process.

Acknowledgment

This work was supported by the National Natural Science Foundation, SINOPEC under grant No. 29734141, and the Foundation of Director of Chemistry Institute, Chinese Academy of Sciences.

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16. Crystal structure data of Ti $\{\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NPh(^iPr)_2\}Cl_2$ (I) : Orthorhombic, Pnma, a = 12.658 (3) Å, b = 16.62(3) Å, c = 11.760 (2) Å, Z=4, V=2474.2 (9) Å ^{3}. Measurement temperature 293 K, $Mo_{k\alpha}$ = 0.71073 Å , R = 0.0399. wR = 0.0905. Structure was solved by use of program SHELXL 93. Crystallographic parameters have been deposited in the editorial office of CCL.

Received 19 October 1999
Revised 14 January 2000