

## X-선 회절 분석법에 의한 고리화펜타디에닐 고리가 $\pi$ -결합된 최초의 유기비스무트화합물의 구조결정

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## $(\eta^5\text{-C}_5\text{Me}_5)_2\text{BiCl}$ , The First Organobismuth Compound with $\pi$ -bonded Cyclopentadienyl Ring Analyzed by X-ray Diffractometry

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**요 약:** 고리화펜타디에닐  $\pi$ -결합된 최초의 비스무트 화합물( $\eta^5\text{-C}_5\text{Me}_5)_2\text{BiCl}$ 이 에테르 용매하에서 칼륨펜타메틸고리화펜타다이엔과 삼염화비스무트의 반응결과 짙은 보라색의 결정이 30%의 수율로 얻어졌다. 이 화합물의 분해 생성물로서 pentamethylcyclopentadienylbismuth chloride(PCpBiCl<sub>2</sub>)가 얻어졌으며( $\eta^5\text{-C}_5\text{Me}_5)_2\text{BiCl}$ 은 칼륨펜타메틸고리화펜타다이엔과  $-78^\circ\text{C}$ 에서 반응하지 않음을 확인하였다. ( $\eta^5\text{-C}_5\text{Me}_5)_2\text{BiCl}$ 의 구조가 192 K에서 X선 단결정 구조분석 방법에 의해 밝혀졌다: triclinic crystal, space group p1, Z=2. C<sub>20</sub>H<sub>30</sub>의 이탈반응이 확인되었으며 고리화펜타다이엔의 두 고리가 C-C  $\sigma$ -단일 결합으로 이루어져 있다는 것이 X선 단결정 구조분석 방법에 의해 밝혀졌다.

**Abstract:** The reaction of ( $\eta^5\text{-C}_5\text{Me}_5$ )K with BiCl<sub>3</sub> yielded ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>BiCl[I], the first organobismuth compound with  $\pi$ -bonded cyclopentadienyl ring. The compound I which was the violet crystal (yield, 30%) was decomposed to PCpBiCl<sub>2</sub>. The Structure of ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>BiCl was identified as single crystal by X-ray diffraction method. The eliminated product C<sub>20</sub>H<sub>30</sub>, triclinic crystal of space group p1(Z=2) which was attached with C-C  $\sigma$ -bond of two cyclopentadienyl was defined by the structural analysis.

**Key words:** bis (pentamethylcyclopentadienyl) bismuth, single crystal X-ray crystallography, organobismuth compound.

### 1. INTRODUCTION

The pentamethylcyclopentadiene anion is an effective ligand for stabilizing complexes of transition and main group elements in low oxidation state. The newest example of cyclopentadienyl derivatives of the main group elements is Sb<sup>I</sup>-compound.<sup>1</sup> Many

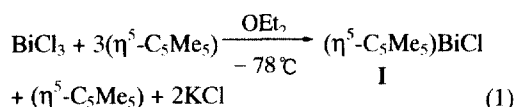
other  $\pi$ -complexes of the main group elements have been prepared recently and these compounds were characterized by several physical methods.<sup>2</sup> However, a few representatives of these kind of compounds for 15 group element were found and most of these compounds are cationic  $\pi$ -bonded cyclopentadienyl complex of phosphorus, arsenic and

antimony. On the other hand, the representative of the heaviest element bismuth complexes has still not been found. Only tris (cyclopentadienyl) bismuth and mono- and dicyclopentadienylbismuth chloride are known as a cyclopentadienyl compound of bismuth; the tris (cyclopentadienyl) bismuth which was prepared by O. Fischer *et al*<sup>3</sup> shows coordination number 4 of the bismuth atom and  $\eta^1$ -bonded cyclopentadienyl ring.<sup>4</sup> This compound is analogous essentially to the antimony compound.<sup>5</sup> We synthesized bis (pentamethylcyclopentadienyl) bismuthchloride, (PCp)<sub>2</sub>BiCl, by reacting of potassium cyclopentadiene, KPCp, with bismuth trichloride, BiCl<sub>3</sub>, and determined the crystal structure of the resulting compound bis (pentamethylcyclopentadienyl) chloride, (PCp)<sub>2</sub>BiCl.

The dimer of pentamethylcyclopentadiene, C<sub>20</sub>H<sub>30</sub>, was observed from the reaction of tin tetrachloride with lithium pentamethylcyclopentadiene *et al*<sup>6</sup>; through the nucleophilic decomposition of bis (pentamethylcyclopentadienyl) stannousdihalide (PCp)<sub>2</sub>SnX<sub>2</sub> in the presence of pyridine by reductive elimination of C<sub>20</sub>H<sub>30</sub>. Recently several research groups have tried to synthesize the cyclopentadiene derivatives of heavy main group elements of high oxidation numbers and their reports have shown that the reductive elimination of C<sub>20</sub>H<sub>30</sub> in the heavy main group elements after 5 period is the general reaction principle; this principle was applied to the heavy elements of 10-15 group.<sup>1,6,7,8,9,10,11,12</sup>

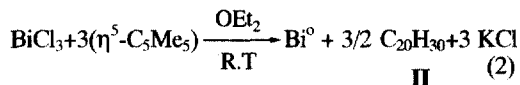
## 2. RESULTS AND DISCUSSION

From the reaction of BiCl<sub>3</sub> with KMe<sub>5</sub>C<sub>5</sub> in ether at -78°C to prepare "(PCp)<sub>3</sub>Bi" [PCp=C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>], we obtained the representative of a  $\pi$ -bonded cyclopentadienyl complex of bismuth which is the title compound in 30% yield and the form of deep violet crystal with F.p 74°C (decomp.).

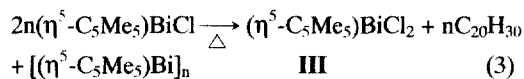


Also in the synthesis for "(PCp)<sub>3</sub>Bi" in the stoichiometric reaction (1BiCl<sub>3</sub>:3KPCp) at -78°C, "(PCp)<sub>3</sub>

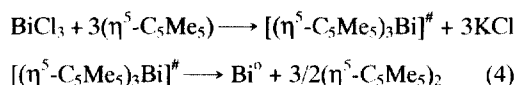
Bi" was not obtained and "(PCp)<sub>2</sub>BiCl" was isolated as a final product. When the reaction (1) is run at room temperature, however, the bismuth metal is coated, mirror-like, on the surface of the flask and C<sub>20</sub>H<sub>30</sub> is formed as a colourless crystal which melted at 46-48°C, and this reaction may be carried by a reductive elimination reaction according to equation (2).



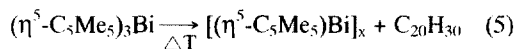
When the ethereal solution of I is allowed to warm up to -30°C, (PCp)BiCl<sub>2</sub> is obtained as a decomposed product, probably by a reductive elimination of bis (pentamethylcyclopentadienyl).



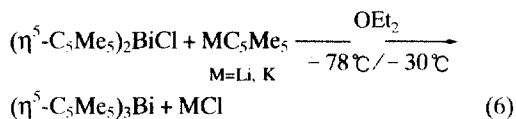
The compound of III was identified by C/H analysis and unfortunately no suitable solvent to dissolve was found. The above result suggest that (PCp)<sub>3</sub>Bi is formed as Equation (4). But it decomposes due to its low stability.



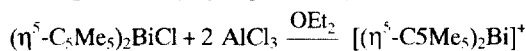
(PCpBi)<sub>x</sub> could be also postulated as a decomposition product of (PCp)<sub>3</sub>Bi as Eq. (5).<sup>13,14</sup>

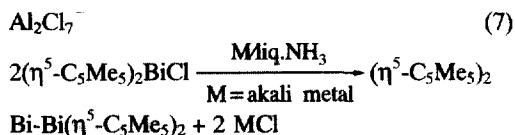


Unfortunately no evidence for the formation of (PCpBi)<sub>x</sub> was obtained and no further reaction of compound I with LiCp\* or KCp\* was observed from -70°C to -30°C:



The title compound I seems to be a starting material for synthesis of cyclopentadienyl bismuth-cation and tetrakis (pentamethylcyclopentadienyl) dibismuthan:





### 2.1. Crystal Structure of I

The crystal structure of  $(\text{PCp})_2\text{BiCl}$  was determined by single crystal X-ray diffraction methods. The experimental data are shown in Table 1. The structure was solved by Patterson methods. The H atoms were included in calculated positions using a common isotropic temperature factor. The other atoms could be refined with anisotropic temperature factors resulting in a final conventional  $R=0.025$  and  $wR=0.026$ . The detailed bond lengths and bond angles are given in Table 2.

The cyclopentadienyl rings are in the eclipsed sandwich structure (Fig. 1). The bond distance of Bi to the centre of the cyclopentadienyl ring are 243.3(3) pm and 244.9(3) pm. These Bi-C bond length are almost comparable with the bond length 240.0 pm of  $\sigma$ -bonded species like  $(\eta^1\text{-C}_5\text{H}_5)_3\text{Bi}^4$ ,  $\text{CpBiCl}_2^5$  (238-264 pm),  $\text{PCpBiCp}_2^{15}$  (259-294 pm) or 226-228 pm in  $\text{Bi}_2\text{Ph}_4^{16}$ , 234-238 pm in  $\text{Bi}[\text{C}_6\text{H}_2(\text{C}_6\text{H}_5)_3]_3^{17}$ . As the value of the "Ring-Slippage" (distance bet-

Table 1. Crystallographic data of  $(\text{PCp})_2\text{BiCl}$

Crystal system	triclinic
Space group	P1
a (pm)	863.4(6)
b (pm)	1002.8(4)
c (pm)	1347.3(4)
$\alpha$ (°)	74.25(3)
$\beta$ (°)	71.73(4)
$\gamma$ (°)	64.99(6)
Cell Volume	990.7 Å <sup>3</sup>
Z	2
D (calculated), (g/cm <sup>3</sup> )	1.726
Measuring temperature(K)	193
Number of unique Reflections	2650
Number of reflections measured	3285
Absorptions coefficient	$\mu=86.8 \text{ cm}^{-1}$
R	0.025
wR	0.026
Radiation	MoK $\alpha$ (graphite monochromator)
Diffractometer	Enraf-Nonius, CAD4

Table 2. Important bond length [pm] and angle[°]

Bi-Cl: 269.5(2)	
Ring 1: Bi-C1: 260.8(7)	Bi-C2: 274.1(6)
Bi-C3: 286.2(7)	Bi-C4: 283.1(7)
Bi-C5: 269.0(6)	
Ring 2: Bi-C1A: 261.4(7)	Bi-C2A: 270.0(7)
Bi-C3A: 282.7(6)	Bi-C4A: 279.0(6)
Bi-C5A: 268.0(6)	
Average: C-C (ring)	141.6 pm
C-C-C (ring)	111°
Bi-Ring 1, centre: 245.0(3)	
Bi-Ring 2, centre: 243.0(2)	
Ring 1, centre-Bi-Ring 2, centre:	144°

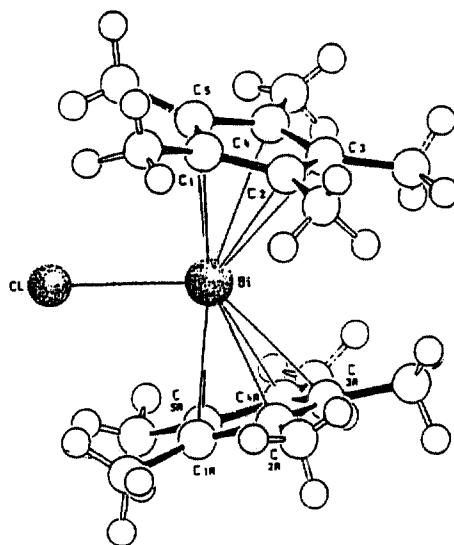


Fig. 1. The molecular structure of  $\text{C}_{20}\text{H}_{30}\text{BiCl}$  in crystal form.

ween the vertical projection of central atom onto ring plane) was shown as a small value of 24.8 pm for ring 1 and 29.5 pm for ring 2 (Fig. 2), the bond length from metal atom to the C-atom of each cyclopentadienyl ring was almost the same (261-286 pm).

The bond length from bismuth to chlorine is 269.6(6) pm. The continuous contact length of the metal atom to another groups was not confirmed. The plane of the two cyclopentadienyl rings are tilted at an angle of 144° to each other; the localized lone electron pair on the bismuth atom affects the tilted bonding axis of Bi-Cl at an angle of 5.0°. The main reason for this tilting of bonding axis of Bi-Cl is to

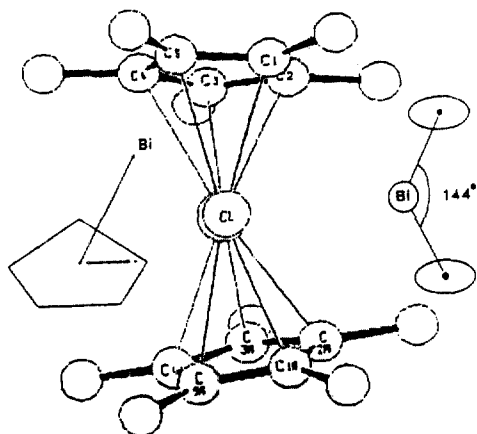


Fig. 2. The molecular structure of  $C_{20}H_{30}BiCl$ (Ring-Slippage) in crystal form.

satisfy the space demand of cyclopentadienyl rings to rotate and to provide space for the Cl-ligand.

## 2.2. Crystal Structure of II

The structure of bis (pentamethylcyclopentadienyl) in the gas phase was studied by R. Blom *et al*<sup>10</sup> and the molecular structure of II in the gas phase was determined by the gas phase electron diffraction method (GED). The C-C  $\sigma$ -bond between two cyclopentadienyl rings was observed. The crystal struc-

Table 3. Crystallographic data of  $C_{20}H_{30}$

Crystal system	triclin
Space group	P-1
a (pm)	1098.68(6)
b (pm)	1223.06(8)
c (pm)	1329.90(6)
$\alpha$ ( $^\circ$ )	78.138(4)
$\beta$ ( $^\circ$ )	78.740(4)
$\gamma$ ( $^\circ$ )	84.250(6)
Cell volume	1711.88 $\text{\AA}^3$
Z	2
Number of Molecule per Cell(Z)	4
D (calculated)	0.525 g/cm <sup>3</sup>
Measuring temperature(K)	168
Number of unique Reflection	5870
Number of reflections measured	6920
R	0.048
wR	0.054
Radiation	Cu K $\alpha$ (Graphate-Monochromator)
Diffractometer	Enraf-Nonius, CAD4

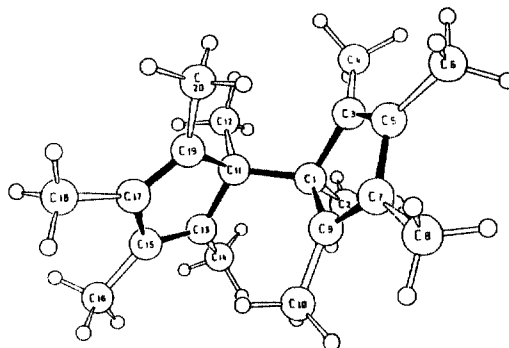


Fig. 3. Molecular structure of  $C_{20}H_{30}$  in crystal.

Table 4. The important bond length (pm) and angle ( $^\circ$ )

Ring 1: C5-C7, 146.7(2)	C3-C1, 153.5(2)
C9-C1, 152.7(2)	C5-C3, 134.6(2)
C7-C9, 134.8(2)	
Ring 2: C17-C15, 146.8(2)	C11-C19, 152.5(2)
C11-C13, 153.1(2)	C19-C17, 134.6(2)
C13-C15, 134.3(2)	
Inter plane angle: 65.7(1) for Molecular I	
58.2(1) for Molecular II	
Torsion angle: (3, 1, 11, 19) 67.8 (9, 1, 11, 13) 67.5	
(9, 1, 11, 19) 47.4 (3, 1, 11, 13) 177.0	

ture of  $C_{20}H_{30}$  has been determined by single crystal X-ray diffraction methods: triclinic crystals, space group p-1,  $a=1098.68(6)$ ,  $b=1223.06(8)$ ,  $c=1329.90(6)$  pm,  $\alpha=78.138(4)^\circ$ ,  $\beta=78.740(4)^\circ$ ,  $\gamma=84.250(6)^\circ$  and  $Z=2$ . The experimental data are collected in Table 3. The final conventional  $R=0.048$  and  $wR=0.054$ . Fig. 3 illustrates the molecular structure of  $C_{20}H_{30}$  in crystal form. Viewing a single molecule of  $C_{20}H_{30}$ , each carbon atom between two cyclopentadienyl rings is bonded with  $\sigma$ -bond, the bond distance is 153.9(2) pm. The important bond length and angles are given in Table 4.

## 3. EXPERIMENTAL

All solvents were dried by standard methods and were freshly distilled before use. CHN-analysis was performed with CHN-Rapid automat (Heraeus); NMR spectra were taken by a Bruker AMX-500 (500 MHz) spectrometer.

The solution of  $BiCl_3$ , 1.55 g (4.90 mmol) in 15

ml of ether is added dropwise to a suspension of  $\text{KC}_5\text{Me}_5$ , 2.56 g (14.7 mmol) in 40 ml  $\text{Et}_2\text{O}$  at  $-78^\circ\text{C}$  within 30 min. After addition of  $\text{BiCl}_3$  ether solution, the colour of the reaction mixture changes to deep violet. After additional stirring at  $-78^\circ\text{C}$  for 3 hrs., the reaction mixture is filtered through a G4-glass filter under argon atmosphere. After the filtered solution was kept at  $-78^\circ\text{C}$  for 24 hrs, the black-violet, transparent crystal is collected from the filtrate by filtration.

Yield: 0.9 g, 30% of theory. Fp.  $74^\circ\text{C}$  (Decomp.). The elementary analysis for  $\text{C}_{20}\text{H}_{30}\text{BiCl}$ ; found C:45.70%, H:6.14%, Bi:42.26%, Cl:5.00% theory C:46.68%, H:5.83%, Bi:40.61%, Cl:6.89%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , at 223 K, i-TMS): 2.58 ppm for  $-\text{CH}_3$ , singlet,  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , at 223 K, i-TMS): 122.91 ppm for  $\text{C}_5\text{H}_5$ , 9.72 ppm for  $\text{CH}_3$ .

After the filtrate is warmed up to  $-30^\circ\text{C}$  slowly for 4-5 hrs, the orange coloured precipitation is filtered and dried in high vacuum.

The elementary analysis for  $\text{C}_{10}\text{H}_{15}\text{BiCl}_2$ ; found C: 24.35%, H:3.16%, Bi:57.32%, Cl:10.04% theory C: 28.94%, H:3.61%, Bi:50.36%, Cl:17.07. The NMR-Spectrum was not taken due to poor solubility of product.

After evaporation of the filtrate, colourless crystals were obtained. This crystal is recrystallized in ether/n-hexane solution and filtered, dried in high vacuum. mp  $46-48^\circ\text{C}$ . The elementary analysis for  $\text{C}_{20}\text{H}_{30}$ ; found C:86.91%, H:11.48% theory C:88.89%, H:11.10%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , i-TMS); 1.00 ppm, 1.56 ppm, 1.59 ppm, all singlet,  $^{13}\text{C-NMR}$

( $\text{CDCl}_3$ , i-TMS); 10.87 ppm, 12.51 ppm, 19.32 ppm, 59.81 ppm, 133.18 ppm, 141.75 ppm.

## REFERENCES

1. T. F. Berlitz, H. Sinning, J. Lorberth and U. Mueller, *Z. Naturforsch.*, **43b**, 744(1988).
2. P. Jutzi, *Adv. Organometal. Chem.*, **26**, 217(1986).
3. E. O. Fischer and S. Schreiner, *Chem. Ber.*, **93**, 1417(1960).
4. J. Lorberth, W. Massa, S. Wocadlo, I. Sarraje and S. H. Shin, *J. Organomet. Chem.*, **485**, 449(1995).
5. M. Bierkhahn, P. Krommes, W. Massa and J. Lorberth, *J. Organomet. Chem.*, **208**, 161(1981).
6. P. Jutzi and F. Kohl, *J. Organomet. Chem.*, **164**, 141(1979).
7. E. O. Fischer and H. Schuster-Woldan, *Chem. Ber.*, **100**, 705(1967).
8. N. M. Boag, *Organometallics*, 4462(1988).
9. C. Zybilla and G. Mueller, *Organometallics*, 2489(1987).
10. R. Blom, *Acta Chem. Scand.*, **A42**, 445(1988).
11. J. Lorberth, T. F. Berlitz and W. Massa, *Angew. Chem.*, **101**, 623(1988).
12. T. F. Berlitz, Dissertation, Marburg (1988).
13. P. Krommes and J. Lorberth, *J. Organomet. Chem.*, **131**, 415(1977). P. Krommes, Ph D. Thesis, University of Marburg, Germany (1975).
14. E. Hedaya, *Accounts Chem. Res.*, **2**, 367(1969).
15. S. H. Shin, Ph D. Thesis, University of Marburg, Germany (1989).
16. F. Calderazzo, A. Morvillo, G. Pelizzi and R. Poli, *J. Chem. Soc., Chem. Commun.*, 507(1983).
17. I. P. Romm, V. K. Bel'skii and E. N. Gur'yanova, *Koord. Klum.*, **6**, 945(1980).