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The First Organobismuth Compound with Differently Substituted, π-bonded Cyclopentadienylring, η^5-$C_5(CH_3)_5Bi(\eta^5$-$C_5H_5)_2$

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서로 다른 씨클로펜타디엔 유도체가 결합된 최초의 비스무스 화합물, η^5-$C_5(CH_3)_5Bi(\eta^5$-$C_5H_5)_2$의 합성과 결정구조

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요 약

서로 다른 씨클로펜타디엔 유도체가 π-결합된 최초의 비스무스 화합물인 η^5-$C_5(CH_3)_5Bi(\eta^5$-$C_5H_5)_2$이 디펜타메틸씨클로펜타디에닐 비스무스디메틸아미드 $Cp^*_2BiNMe_2$[Cp^*=$C_5(CH_3)_5$]와 씨클로펜타디에닐 모노머와의 반응으로 합성되었다. 반응조건은 에테르 용매하에 −78℃ 반응온도 조건하에서 얻어졌다. 합성된 반응물을 노르말 헥산 용매에서 재결정시킨 결과, 검은색 결정이 60% 수율로 얻어졌다. 그리고 재결정시킨 반응물을 190K에서 X-선 단결정 구조 분석 방법에 의해 그 구조를 밝혔다. 그 결과 결정계의 격자계는 I2/a, a=1756.00 picometer, b=906.00 picometer, c=2211.00 picometer, β=104.04, Z=8로 확인되었다. 여기서 a, b, c는 결정격자 상수이고, β는 결정격자 상수인 b와 c간의 각도이며, Z는 단위 결정 격자당 분자의 갯수이다.

I. Introduction

Since triscyclopentadienylbismuth was synthesized by E. O. Fischer et al. $Bi(C_6H_5)_3$, $Bi[C_6H_2(CH_3)_3]_3$, $Bi[C_6H_2(C_6H_5)_3]_3$ and $Bi[C_6H_2(CF_3)_3]_3$ were reported as trisphenylbismuth compounds and the molecular structures of these compounds were determined by several research groups[1~4]. The bonding types between the bismuth atom and carbon atoms of phenyl ligands are "monohapto" fashion with σ-bonds.

Only a few π-bonded substituted cyclopentadienylbismuth compounds were reported : since bis-pentamethylcyclopentadienylbismuthchloride was synthesized and single crystal structure was reported as a first π-bonded cyclopentadienylbismuth compound by Lorberth et al[5], we

have obtained a new π-bonded substituted cyclopentadienylbismuth compound, Cp*BiCp$_2$ from the reaction of Cp*$_2$BiNMe$_2$ with monomeric cyclopentadiene, an acid-base reaction of weak acid cyclopentadiene with base bispentamethylcyclopenta-dienylbismuthdimethyl amide, and determined the single crystal structure by X-ray diffraction method.

Ⅱ. Experiment

All solvents were dried using $LiAlH_4$ and freshly distilled before use. The elementary analysis was performed with CHN-Rapid automat (Heraeus) ; NMR spectra were taken by Bruker AMX-500 (500MHz) spectrometer.

1. Preparation of Cp*BiNMe$_2$

To the suspension of 2.50g (7.46mmol) Bi $(NMe_2)_3$ in absol. ether, 3.00g (22.39mmol) of pentamethylcyclopentadiene was added at RT. The reaction of mixture was stirred for a max. 4min. at this temperature and quenched at −78℃. After condensation of 30% of total reaction mixture volume, the reaction of mixture was kept at −78℃. After 20 hrs at −78℃, the reaction of mixture was filtered using a G3-glass filter and black crystals were obtained. The crystals were dried in a high vacuum.

Elementary Analysis : found C : 48.26%, H : 6.36%, N : 2.38%, theory C : 50.5%, H : 6.88%, N : 2.68%, ^{1}H-NMR(d_8-Toluene solution, i-TMS, 283K) : 2.40ppm for CH_3, 2.63ppm for $N(CH_3)_2$. ^{13}C-NMR(d_8-Toluene solution, i-TMS, 283K) : 9.74ppm for CH_3, 35.59ppm for $N(CH_3)_2$, 119.81 ppm for C_5H_5. EI mass spectrum(70eV) : m/e, ion, intensity : 39, NMe_2, 100% ; 66, CpH, 2.05 %, Me_5Cp, 29.86% ; 136, Me_5CpH, 45.54% ; 209, Bi, 5.35% ; 253, $BiNMe_2$, 4.62% ; 270, (Me_5CP), 23.26%.

2. Preparation of Cp*BiCp$_2$

To the solution of 4.3g(8.22mmol) Cp_2BiNMe_2 in 30mL of absol. ether, the excess of freshly distillated cyclopentadiene was added dropwise at −50℃ After stirring for 2 hrs at this temp., the reaction of mixture was evacuated to condensate ether at −40℃. 30mL of n-hexane, which was cooled to −78℃, was added to the reaction of mixture. After 20 hrs at −78℃, the reaction of mixture was filtered using a G3-glass filter and black crystals were obtained.

Yield : 2.68g(60.00% of theory), Decomposition temp. : >120℃

Elementary Analysis : found C : 49.52%, H : 5.35%, theory C : 50.66%, H : 5.27%. ^{1}H-NMR (d_8-Toluene solution, i-TMS, 283K) : 5.66 ppm for C_5H_5, 2.23ppm for CH_3. EI mass spectrum(70eV) : m/e, ion, intensity : 129, Cp_2H, 100% : 136, Me_5CpH, 40.73% : 209, Bi, 17.33% : 274, BiCp, 19.70% : 339, $BiCp_2$, 13.42%

Ⅲ. Results and discussion

From the reaction of excess monomeric cyclopentadiene and Cp*$_2$BiNMe$_2$ in ether at −50℃ to prepare Cp*$_2$BiCp, Cp*BiCp$_2$, which is the first representative of organobismuth compound with differently substituted π-bonded cyclopentadienylring, was obtained in a yield > 60% according to Eq. (1). :

$$Cp^*_2BiNMe_2 + \text{excess } H\text{-}C_5H_5 \xrightarrow[-50℃]{} Cp^*BiCp_2 + Cp^*H + HNMe_2 \quad \cdots\cdots\cdots(1)$$

The pure title compound, Cp*BiCp$_2$, was obtained as black crystals by recrystallization in n-Hexane at −78℃, and the reason why the title compound Cp*BiCp$_2$ was obtained instead of expected product Cp*$_2$BiCp, can be suggested by the following Eq. (2a), (2b) :

$$Cp^*_2BiNMe_2 + \text{excess } H-C_5H_5 \longrightarrow [Cp^*_2BiCp]^* + HNMe_2 \quad \cdots\cdots (2a)$$

$$[Cp^*_2BiCp]^* + H-C_5H_5 \longrightarrow Cp^*BiCp_2 + Cp^*H \quad \cdots\cdots (2b)$$

Probably such a ligand exchange reaction results from the steric hindrance between the two bulky pentamethylcyclopentadienyl group in Cp^*_2BiCp ; but in contrast to triscyclopentadienylbismuth, Cp_3Bi, as reported by J. Lorberth et al[6], there is not sufficient space for two bulky pentamethlycyclopentadienyl ligands to bond on the central bismuth atom in bispentamethylcyclopentadienyl-bismuthchloride[5].

The crystal structure of the title compound, Cp_2BiCp^*, was determined by the single crystal X-ray diffraction method. The experimental data are listed in Table 1. The structure was solved by Patterson and difference Fourier methods. The selected bond lengths are listed in Table 2. Fig. 1 shows the molecular structure of Cp_2BiCp^* in crystal form. In contrast to $BiCp_3$, Cp^*BiCp_2 did not show pyramidal structure clearly and influence of lone pair electron on bismuth atom. The angle between plane of Cyclopentadienylring and pentamethylcyclopentadienylring is about 90°(Fig. 1), the bond length of Bismuth and centre of Cyclopentadienyl Ring 1 and Ring 2 are 257.85pm and 289.27pm. the bond length of Bismuth atom and pentamethylcyclopentadienyl ring(centre) is 246.28pm ; these bond lengths are the longest bond lengths and longer than 240.0pm for σ-bonded species like $(\eta^1-C_5H_5)_3Bi$, and 243.3, 244.9pm for π-bonded species like $(\eta^5-C_5(CH_3)_5)_4BiCl$. From this longest distance between Bi a tom and C atom among the previously reported bismuth compounds, it can be explained by the steric effect of Cp_2BiCp^*. This suggests that the bonds strength between Bi and C atoms of cyclopentadienylrings are weaker than any other cyclopentadienyl derivatives of bismuth

Table 1. Crystallographic data of Cp^*BiCp_2

Formula Weight	474.399g/mol
Cell volume	3412.63Å
Number of Molecule per Cell(Z)	8
D(calculated)	1.748g/cm³
Crystal system	Monoclinic
Space group	I2/a
a(pm)	1745.00
b(pm)	906.00
c(pm)	2211.00
β(°)	104.04
Diffractometer	Enraf-Nonius, CAD4
Radiation :	Mo Kα(Graphate-Monochromator)
Measuring temperature(K) :	190
Number of unique reflection	1828
Number of reflections measured	2343
R	0.0490
wR	0.0388

Table 2. Important bond length(pm) and angle(°)

Ring Cp* :	
Bi-C_1 : 259.96	Bi-C_2 : 274.55
Bi-C_3 : 288.79	Bi-C_4 : 281.40
Bi-C_5 : 264.44	
Ring 1 :	
Bi-C_{11}: 289.22	Bi-C_{12}: 273.24
Bi-C_{13}: 275.31	Bi-C_{14}: 288.08
Bi-C_{15}: 293.80	
Ring 2 :	
Bi-C_{21}: 270.61	Bi-C_{22}: 269.04
Bi-C_{23}: 327.99	Bi-C_{24}: 358.05
Bi-C_{25}: 327.14	
Average values :	
C-C(Ring 1) : 139.53	C-C(Ring 2) : 140.38
C-C(Ring Cp*) : 141.44	
Bi-Ring centre(centroid 1) : 257.85	
Bi-Ring centre(Centroid 2) : 289.27	
Bi-Ring centre(centroid Cp*) : 246.28	

atom. The third cyclopentadienyl Ring plane is facing to the other cyclopentadienyl ring plane and pentamethylcyclopentadienyl ring plane and slightly at an angle to the vertical plane. Focussing now on the molecular packing in the crystal structure of Cp^*BiCp_2, any interaction between bismuth atom of one molecule, Cp^*BiCp_2, and cyclopentadienyl ring of a neighbouring molecule of Cp^*BiCp_2, which was observed in Cp_3Bi and $CpBiCl_2$ molecules[6,7], was not observed.

Ⅳ. Conclusion

η^5-$C_5(CH_3)_5Bi(\eta^5$-$C_5H_5)_2$ was synthesis by reaction of $Cp^*{}_2BiNMe_2[Cp^*{=}C_5(CH_3)_5]$ and cyclopentadiene monomer in ether at −78℃. This compound was found as a-bonded cyclop-

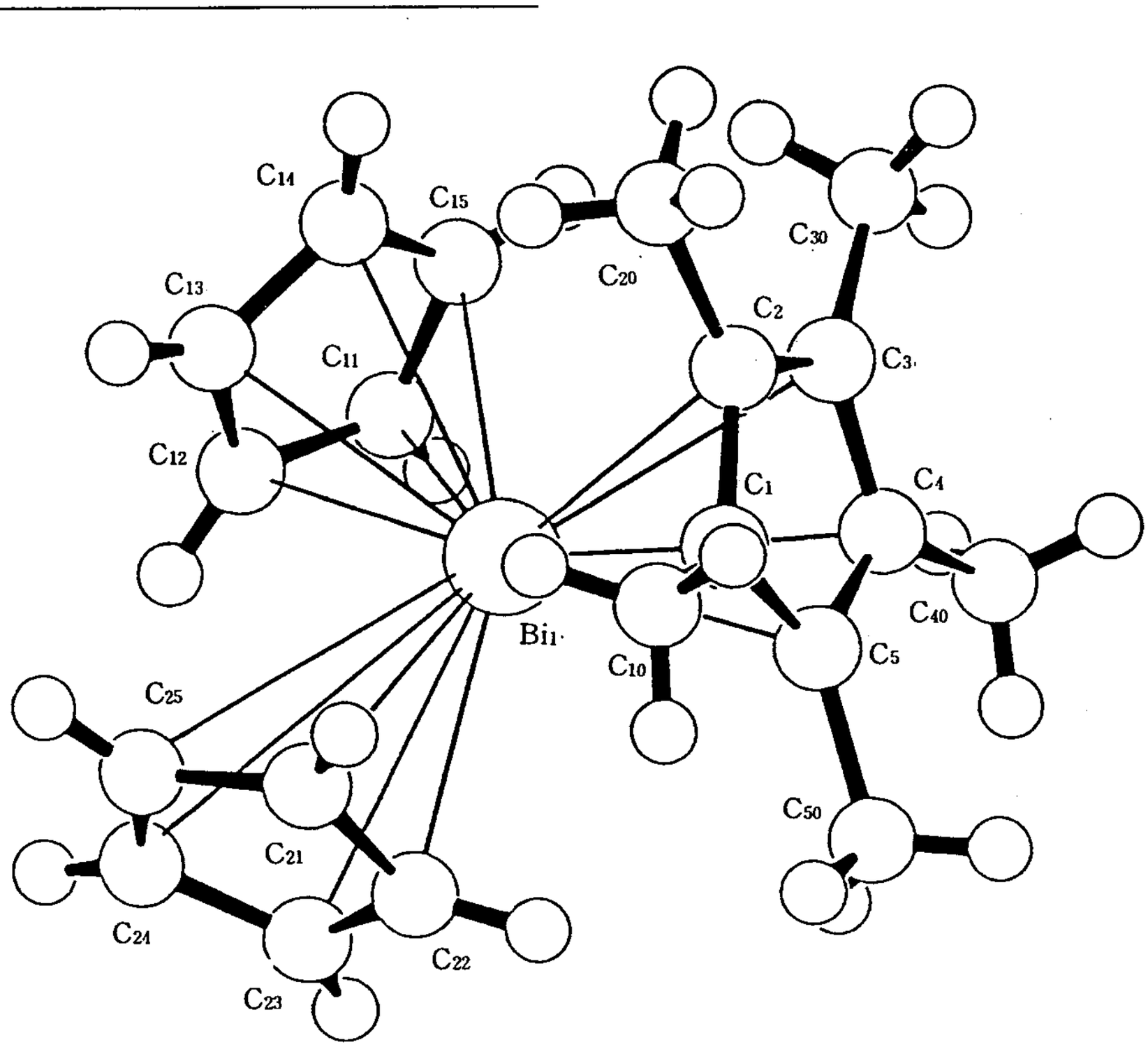

Fig. 1. Molecular structure of CP^*BiCp_2 in crystal.

entadienyl complex of bismuth by the single crystal X-ray diffraction and from the molecular packing in the crystal structure, any interaction between bisthmuth atom of one molecule(Cp^*BiCp_2) and cyclopentadienyl ring of a neighbouring molecule of Cp^*BiCp_2 was not observed.

References

1. D. M. Hawley and G. Ferguson, *J. Chem. Soc. (A)*, 2059(1968).
2. I. P. Romm, V. K. Bel'skii and E. N. Gur'yanova, *Koord. Klum.*, 6, 945(1980).
3. X. -W. Li, *Ph. D. Thesis*. University of Marburg, Germany, (1994).
4. K. H. Whitmire, D. Labahn, H. W. Roesky, M, Noltermeyer and G. M. Sheldrick, *J. Organomet. Chem.*, 402, 55(1991).
5. S.-H. Shin, Ph D Thesis, University of Marburg, Germany, (1989).
6. J. Lorberth, W. Massa, S, Wocadlo, I. Sarraie, S.-H. Shin, and X.-W. Li, *J. Organomet. Chem.*, 485, 149(1995).
7. W. Frank, *J. Organomet. Chem.*, 386, 177 (1990).