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Synthesis and crystal structure of E.O. Fischer's "red crystalline modification of tris-cyclopentadienylbismuth, $(^1h\text{-}C_5H_5)_3Bi$" ☆

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Abstract

E.O. Fischer's red crystalline modification of tris-cyclopentadienylbismuth, $Bi(C_5H_5)_3$, was obtained by acid-base reaction of tris(dialkylamino)bismuth compounds with monomeric cyclopentadiene in THF. Crystallisation from ether gave transparent deep red crystals in 70% yield; as a by-product of this reaction, a polymeric, monovalent bismuth compound, cyclopentadienylbismuth (I), $(BiC_5H_5)_\infty$, was also isolated. The crystal structure of "red $Bi(C_5H_5)_3$" has been determined at −70°C by single crystal X-ray diffraction methods: monoclinic crystals, space group $P2_1/c$, $a = 8.898(4)$ $b = 8.684(3)$, $c = 17.945(7)$ Å, $\beta = 110.10(4)°$ and $Z = 4$. On exposure to light a colour change is observed from transparent red to opaque red which is maintained at 15°C. Warming to 20°C the material rapidly turns black. This colour change phenomenon is probably a result of the interaction of the bismuth atom of one molecule with one cyclopentadienyl ligand of a neighbouring molecule of $Bi(C_5H_5)_3$.

Keywords: Bismuth; Tris-cyclopentadienyl bismuth; Red modification; X-ray diffraction; Group 15; Cyclopentadienyl

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1. Introduction

In 1960, E.O. Fischer et al. were the first to report on the synthesis of $Bi(C_5H_5)_3$ [1] by the reaction of bismuth chloride with cyclopentadienylsodium in a 1 : 3 ratio in ether. They investigated $Bi(C_5H_5)_3$ again in 1970 [2] and concluded that the compound exists as two crystalline forms of different colours: a "red $Bi(C_5H_5)_3$" occurring only at lower temperatures, up to about 15°C, which then changes rapidly to a black form above this temperature, the process being fully reversible. These different colours of $Bi(C_5H_5)_3$ could not be satisfactorily explained on the basis of the scarce structural information at that time on $Bi(C_5H_5)_3$ [3].

We synthesized $Bi(C_5H_5)_3$ differently by reacting tris(dialkylamino)bismuth compounds $Bi(NR_2)_3$ with monomeric cyclopentadiene, an acid-base reaction of the weak acid cyclopentadiene with the strong base tris(dialkylamino)bismuth, and determined the crystal structure of the resulting "red crystalline form of $Bi(C_5H_5)_3$".

2. Results and discussion

$Bi(C_5H_5)_3$ was prepared by the reaction of tris(dialkylamino)bismuth compounds with an excess of monomeric cyclopentadiene in THF at room temperature in a yield > 70% according to Eq. (1a,b):

$$Bi(NR^1R^2)_3 + 3\ H\text{–}C_5H_5 \rightarrow Bi(C_5H_5)_3 + 3\ HNR^1R^2 \qquad (1)$$

a) $R^1 = R^2 = CH_3$ and $Si(CH_3)_3$;

b) $R^1 = CH_3$, $R^2 = Si(CH_3)_3$.

Pure $Bi(C_5H_5)_3$ was obtained as transparent, deep red crystals by recrystallisation, in the absence of light, from a mixed solvent of THF/n-hexane (in a 3 : 1 ratio). $Bi(C_5H_5)_3$ is light-sensitive and becomes opaque, under the impact of daylight, within a few minutes. The colour change from transparent red to opaque red is irreversible — we hypothesise that under the influence of light, bismuth metal is formed, which gives the

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☆ Dedicated to Prof. E.O. Fischer on the occasion of his 75th birthday.

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$Bi(C_5H_5)_3$ crystals a non-transparent appearance (recrystallisation of $Bi(C_5H_5)_3$ in daylight from ether does not result in formation of the transparent red form). The red form of $Bi(C_5H_5)_3$ converts rapidly to a black form on warming to about 15°C. This process is reversible, but the reversion process is rather slow, more so at lower temperatures: four weeks at -30°C is required for complete reversal. Moreover, we have always observed the formation of traces of bismuth metal after this change had occurred.

During our synthesis of $Bi(C_5H_5)_3$ a byproduct with the overall formula "BiC_5H_5" was also obtained, probably by a reductive elimination reaction or a ligand coupling reaction, a reaction type which is often reported in the literature [5–7] and proceeds according to Eq. (2):

$$Bi(C_5H_5)_3 \xrightarrow{\substack{\text{①}h\nu \\ \text{②}\Delta T}} 1/x(BiC_5H_5)_x + (C_5H_5)_2 \qquad (2)$$

In contrast to $Bi(C_5H_5)_3$, polymeric $(BiC_5H_5)_x$ is a thermostable compound characterised by elemental analyses and EI mass spectra. Until now we have not found a suitable solvent which dissolves $(BiC_5H_5)_x$ without decomposition; we therefore suggest that the compound may have a polymeric structure, analogous to the zig-zag polymers $(TlC_5H_5)_x$ or $In(C_5H_5)_x$.

2.1. Crystal structure of the "red modification of $Bi(C_5H_5)_3$"

The crystal structure of E.O. Fischer's "red crystalline modification of $Bi(C_5H_5)_3$" was determined by a single crystal X-ray diffraction study. The experimental data are collected in Table 1. The structure was solved by Patterson and difference Fourier methods and refined against F_o data (SHELX76) [19]. The H atoms were included on calculated positions using a common isotropic temperature factor. The other atoms could all be refined with anisotropic temperature factors, resulting in a final conventional $R = 0.060$ and a $wR = 0.043$. Fig. 1 illustrates the molecular structure of $Bi(C_5H_5)_3$ in the crystal; selected bond lengths and bond angles are given in Table 2.

Viewing a single molecule of $Bi(C_5H_5)_3$, the bismuth atom displays a distorted pyramidal coordination geometry; the metal is directly bonded to the three carbon atoms of the cyclopentadienyl ligands in a "monohapto" fashion with σ-bonds from the metal to the ring carbon atoms, thus allowing for interpretation as "$(^1h\text{-}C_5H_5)_3Bi$", with an average Bi–C bond length of 2.37 Å and a small average bond angle (CBiC) at bismuth of 94.5°. The Bi–C distance in $Bi(C_5H_5)_3$ is the largest bond length, and the sum of the bond angles at the bismuth atom of 283.5° is one of the smallest among the values of previously reported bis-

Table 1
Crystallographic data of $Bi(C_5H_5)_3$

Formula	$C_{15}H_{15}Bi$
Molecular mass (g mol^{-1})	404.25
Crystal size (mm × mm × mm)	~ 0.2 × 0.1 × 0.1
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.898(4)
b (Å)	8.684(3)
c (Å)	17.945(7)
β (°)	110.10(4)
Z	4
D (calculated) (Mg m^{-3})	2.062
μ (Mo Kα) (mm^{-1})	13.00, empirical corr., Ψ-scans
Diffractometer	Enraf-Nonius, CAD4
Radiation	Mo Kα, graphite monochromator
Measuring temperature (K)	203
Scan type	ω-scan
Independent reflections	1456
Reflections with $F_o > 3\sigma$	1333
Structure refinement	full matrix least squares on F_o
R	0.060
wR	0.043 [$w = 1/\sigma^2[F_o]$]

Supplementary material to the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76433 Eggenstein-Leopoldshafen, Germany, under specification of deposit no. CSD-58214, names of the authors and the journal reference.

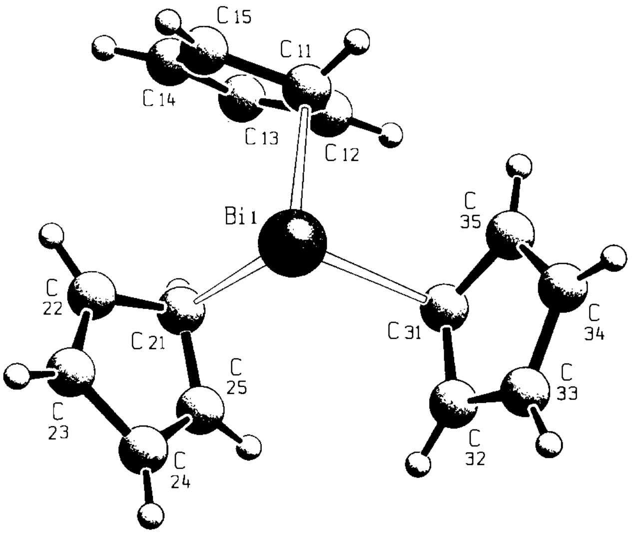


Fig. 1. Molecular structure of $Bi(C_5H_5)_3$ (SCHAKAL92 [18]).

Table 2
Selected bond lengths (Å) and bond angles (°) at bismuth (with standard deviations in parentheses)

Bi–C11	2.37(2)	Bi–C21	2.34(2)
Bi–C31	2.41(2)		
Bi′–C31	3.25(2)	Bi′–C32	3.24(2)
Bi′–C33	3.44(2)	Bi′–C34	3.57(2)
Bi′–C35	3.43(2)		
C11–Bi–C21	94.3(7)	C11–Bi–C31	91.7(7)
C21–Bi–C31	98.0(6)		
Ring1–C11–Bi	113(1)	Ring2–C21–Bi	93(1)
Ring3–C31–Bi	105(1)		

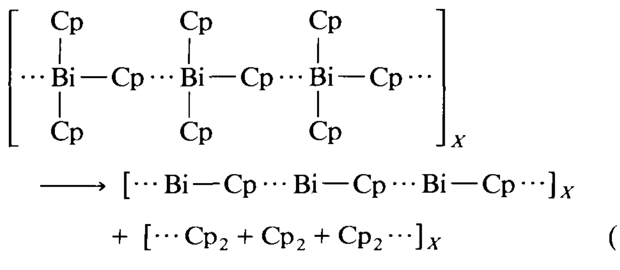
muth compounds: $Bi(C_6H_5)_3$ (2.24 Å and 282°) [8], $Bi_2(C_6H_5)_4$ (2.28 Å) [9], $\{[C_6H_2(CH_3)_3]_2Bi\}_2O$ (2.27–2.28 Å and 295°) [10], $Bi[C_6H_2(CH_3)_3]_3$ (2.24–2.32 Å and 308°) [11], $Bi[C_6H_2(C_6H_5)_3]_3$ (2.34–2.38 Å and 317°) [10], $Bi[C_6H_2(CF_3)_3]_3$ (2.36–2.38 Å and 318°) [12] and $[C_6H_2(CF_3)_3]_2BiCl$ (2.34–2.36 Å and 294°) [12].

This suggests that bonds between bismuth centres and carbon atoms of the cyclopentadienyl ligands are much weaker than those between bismuth and carbon atoms of e.g. phenyl ligands. In fact, we found some Bi–C distances in substituted cyclopentadienyl bismuth compounds which are even longer than those described in the presented structure of $Bi(C_5H_5)_3$: $CpBiCl_2$ (2.38–2.64 Å) [13], Cp_2^*BiCl (2.43–2.45 Å) [4] and Cp^*BiCp_2 (2.59–2.94 Å) [4].

Focussing now on the molecular packing in the crystal structure of $Bi(C_5H_5)_3$, we observe that the bismuth atom of one molecule of $Bi(C_5H_5)_3$ in the zig-zag arrangement is weakly bonded to the cyclopentadienyl ring (C31–C35) of a neighbouring molecule of $Bi(C_5H_5)_3$, with a bismuth–Cp–ring (centroid) distance of 3.17 Å or Bi–C distances from 3.24 to 3.57 Å — much shorter distances than the sum of the van der Waals radii of bismuth and carbon atoms of 4.04 Å according to Bondi [15]. By these contacts, chains of 2_1-symmetry are formed along the *b*-axis (Fig. 2a,b).

As in the analogous structure of $Sb(C_5H_5)_3$ [13], two of the cyclopentadienyl rings are bent "up" and one of them is bent "down" when viewing the top of the pyramid of our reported $Bi(C_5H_5)_3$ (Fig. 1). The angles between the best planes of the cyclopentadienyl rings and the corresponding Bi–C–σ-bonds show a wide variation: Bi–C/ring 1 = 113°; Bi–C/ring 2 = 93°, Bi–C/ring 3 = 105°, these differences are probably due to packing effects.

This kind of interaction at the bismuth atom with an organic ligand was also reported by Frank in a description of the structure of $CpBiCl_2$ [14]. From the chain structure of $Bi(C_5H_5)_3$ we can now easily explain the reductive elimination reaction of $Bi(C_5H_5)_3$, yielding "BiC_5H_5" and bis-cyclopentadiene $C_{10}H_{10}$, according to Eq. (3):



$$\left[\begin{array}{ccc} \mathrm{Cp} & \mathrm{Cp} & \mathrm{Cp} \\ | & | & | \\ \cdots\mathrm{Bi}-\mathrm{Cp}\cdots & \mathrm{Bi}-\mathrm{Cp}\cdots & \mathrm{Bi}-\mathrm{Cp}\cdots \\ | & | & | \\ \mathrm{Cp} & \mathrm{Cp} & \mathrm{Cp} \end{array}\right]_X \longrightarrow [\cdots\mathrm{Bi}-\mathrm{Cp}\cdots\mathrm{Bi}-\mathrm{Cp}\cdots\mathrm{Bi}-\mathrm{Cp}\cdots]_X + [\cdots\mathrm{Cp}_2+\mathrm{Cp}_2+\mathrm{Cp}_2\cdots]_X \quad (3)$$

From investigations of compounds like R_4Bi_2 it was deduced that the bismuth–bismuth interaction between molecules of R_4Bi_2 may be the reason for their typical colour change phenomenon [16,17]. Indeed, those compounds of R_4Bi_2 containing bulky organic ligands, e.g. R = phenyl or i-propyl, in general, do not exhibit such phenomena. The bulky ligands protect the metal centre efficiently, and the elusive Bi–Bi interaction becomes impossible. In $Bi(C_5H_5)_3$, three cyclopentadienyl ligands protect the metal centre sufficiently, and there is no chance for a metal–metal interaction. We assume that the interaction of the lone s-orbital electrons at the bismuth atom in one molecule of $Bi(C_5H_5)_3$ with the π-electrons of a cyclopentadienyl ring of a neighbouring molecule is a possible explanation for the intense red colour of crystalline $Bi(C_5H_5)_3$. At higher temperatures, however, the chain structure resulting from these weak interactions of bismuth atoms and cyclopentadienyl rings is easily broken, and a molecular rearrangement may take place,

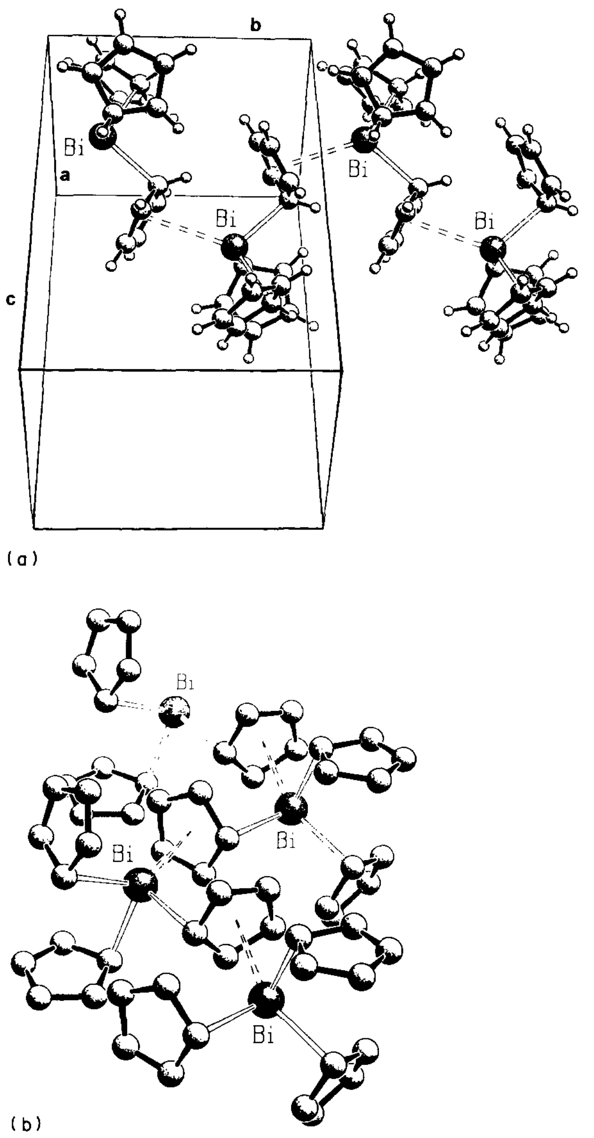


Fig. 2. Zig-zag-chain structure of $Bi(C_5H_5)_3$: (a) View on the plane defined by the Bi atoms of one chain. A second parallel chain in the lower front part of the cell is generated by the inversion centre at 1/2 1/2 1/2; (b) b-axis horizontal.

consistent with the observed colour change. Approaching room temperature, Bi–C bond rupture and C–C bond formation (either concerted or sequential) becomes the dominating process, leading to thermodynamically favourable polymeric $(BiC_5H_5)_x$ and the cyclopentadienyl dimer, $C_{10}H_{10}$, a situation already described by us for the synthesis of $(Cp^*Sb)_4$ and bis(pentamethylcyclopentadiene), commonly known as "decamethylfulvalene" $C_{20}H_{30}$ [4].

3. Experimental section

All manipulations were carried out under an argon atmosphere. Solvents were dried by standard methods and freshly distilled prior to use. $Bi[N(SiMe_3)_2]_3$, $Bi[N(CH_3)SiMe_3]_3$, and $Bi(NMe_2)_3$ were prepared according to the literature [4]. Monomeric cyclopentadiene was freshly prepared by crack distillation. CH analyses were performed on a CHN-Rapid automat (Heraeus); NMR spectra were recorded on a Bruker AMX-500 (500 MHz) spectrometer.

3.1. Typical preparation

Monomeric cyclopentadiene (10 g, 150.0 mmol) was added to a stirred solution of $Bi(NMe_2)_3$ (9.00 g, 26.39 mmol) in absolute THF (60 ml) at −70°C. All manipulations have to be done in the dark! After 2 h, the mixture was allowed to reach room temperature and stirred for an additional 2 h. The mixture developed a deep purple to red colour, and a dark brown precipitate was formed. The solution was filtered through a Celite column, the red coloured filtrate was concentrated to about 6 ml, cooled to −30°C, 6 ml n-hexane was added. $Bi(C_5H_5)_3$ was obtained as deep red, transparent crystals, after drying at 0°C in vacuo: yield 7.40 g (73.2%). The filtered brown solid was dried in vacuo and $(BiC_5H_5)_x$ obtained as a brown, insoluble powder. Found: C, 42.09; H, 3.68; Bi. 51.66. $C_{15}H_{15}Bi$ calc.: C, 44.56; H, 3.74; Bi, 51.69%. ^1H NMR (C_6D_6, 283 K): δ (ppm), 5.67, s, 15H, C_5H_5. ^{13}C NMR: 118.49, C_5H_5. Found: C, 22.59; H, 2.21. C_5H_5Bi calc.: C, 21.90; H, 1.83%. EI mass spectrum (70 eV): *m/e*, ion, intensity: 274, BiCp, 2.0; 209, Bi, 8.4%.

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