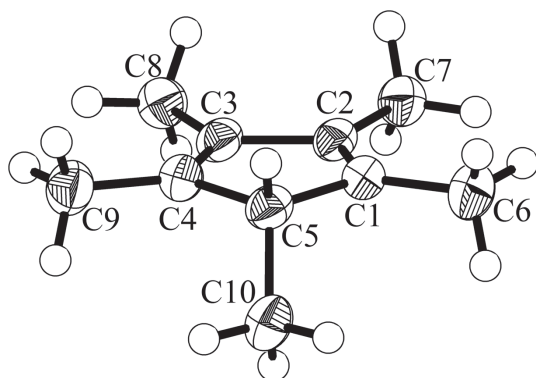


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Crystal structure of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene, C₁₀H₁₆



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Abstract

C₁₀H₁₆, orthorhombic, $P2_12_1$ (no. 19), $a = 4.4804(6)$ Å, $b = 11.7784(12)$ Å, $c = 16.761(2)$ Å, $V = 884.5(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0360$, $wR_{\text{ref}}(F^2) = 0.0596$, $T = 120$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

Zn₂(Cp*)₂ (Cp* = pentamethylcyclopentadienyl) was prepared as described in literature [5]. 40 mg Zn₂(Cp*)₂ were given into a dry Schlenk vessel and ca. 2 ml NH₃ (Westfalen AG, 99.999%, stored over elemental Na) were condensed on this. The formerly colourless complex got spontaneously black. The vessel was stored at -70 °C for five months, after this time colourless crystals of the title compound in a yield of about 20 mol% with respect to Zn₂(Cp*)₂ were found. An

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.1 × 0.1 × 0.1 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.6 cm ⁻¹
Diffractometer, scan mode:	Oxford Xcalibur 3, φ and ω
2 θ_{max} , completeness:	51°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9511, 1635, 0.098
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 718
$N(\text{param})_{\text{refined}}$:	97
Programs:	Oxford programs [1], SHELX [2, 3], DIAMOND [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.4136(7)	0.4877(2)	0.07087(17)	0.0371(8)
C2	0.2391(7)	0.5646(2)	0.10732(17)	0.0360(8)
C3	0.2210(7)	0.5342(2)	0.19327(19)	0.0375(9)
C4	0.3799(7)	0.4410(2)	0.20678(18)	0.0375(9)
C5	0.5181(7)	0.4004(2)	0.12958(15)	0.0379(8)
H5	0.7406	0.4035	0.1339	0.045*
C6	0.5042(8)	0.4825(2)	-0.01537(15)	0.0568(10)
H6A	0.4270	0.5494	-0.0434	0.085*
H6B	0.4221	0.4136	-0.0397	0.085*
H6C	0.7224	0.4812	-0.0192	0.085*
C7	0.0867(6)	0.6654(2)	0.07269(16)	0.0475(9)
H7A	0.1182	0.6668	0.0148	0.071*
H7B	0.1691	0.7347	0.0964	0.071*
H7C	-0.1276	0.6611	0.0840	0.071*
C8	0.0398(8)	0.6027(2)	0.25093(15)	0.0433(9)
H8A	0.0736	0.5747	0.3052	0.065*
H8B	-0.1724	0.5957	0.2376	0.065*
H8C	0.0997	0.6826	0.2477	0.065*
C9	0.4397(7)	0.3827(2)	0.28423(15)	0.0484(9)
H9A	0.3250	0.4197	0.3267	0.073*
H9B	0.6531	0.3873	0.2966	0.073*
H9C	0.3801	0.3028	0.2803	0.073*
C10	0.4211(7)	0.2804(2)	0.10680(14)	0.0468(10)
H10A	0.2034	0.2778	0.1016	0.070*
H10B	0.4847	0.2270	0.1483	0.070*
H10C	0.5131	0.2592	0.0559	0.070*

appropriate crystal was selected under perfluoroalkylether in a stream of cold nitrogen gas.

Experimental details

All H atoms could be located from the difference Fourier map and have subsequently been refined using a riding model with U_{iso} set to 1.2 and 1.5 $U_{\text{eq}}(\text{C})$ for the methylene and methyl H atoms, respectively. Because C₁₀H₁₆ is a weak anomalous scatterer, the Flack parameter is meaningless and has been removed from the cif.

Comment

1,2,3,4,5-Pentamethyl-1,3-cyclopentadiene was synthesized for the first time in 1960 [6], and similar to cyclopentadiene, the pentamethyl derivative easily separates one proton to form a relatively stable anion due to a 6π electron system. The striking capability of the resulting anion, $[\text{C}_5(\text{CH}_3)_5]^-$, usually abbreviated as “Cp*”, to form stable metal complexes was early discovered [7, 8], and today it is widely used as a ligand in organometallic chemistry [9]. Besides other advantageous features with respect to the non-methylated Cp ligand (i.e. $[\text{C}_5\text{H}_5]^-$), the precursor, 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (Cp*H), does not tend to dimerize and can be stored as the monomer, and it is commercially accessible. Despite these facts, and by regarding that the crystal structure of cyclopentadiene (CpH) is known since more than 50 years [10], it is a bit surprising that the crystal structure of the title compound has not been published so far.

During our studies on the reactivity of Zn(I) complexes of the type Zn_2L_2 to the bismuth polyanion $[\text{Bi}_2]^{2-}$ in liquid ammonia [11], amongst others Zn_2Cp^*_2 , the first discovered Zn(I) complex [12], was investigated. At the dissolution of Zn_2Cp^*_2 in liquid ammonia, a black residue, composed from elemental Zn, was formed in a spontaneous reaction. Besides this, colourless crystals of Cp*H have been found after a few months.

According to the crystal structure, nine C atoms of the title molecule, C1 to C9, are in plane (*cf.* the figure). Within the C₅ ring, the C1–C2 and C3–C4 double bonds are 1.343(3) Å and 1.328(4) Å, respectively, while the single bonds are in the range between 1.487(3) Å and 1.512(3) Å, the shortest one between C2 and C3 connects the double bonds. These values are very close to those in CpH [13]. The C–C bond lengths between the methyl groups and the formal butadiene moiety are in the same range with that to the exo-plane methyl group being

the longest (1.487(3) Å to 1.503(3) Å, C5–C10 1.528(3) Å). The molecules form a distorted hexagonal rod packing parallel to the crystallographic *a* axis.

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