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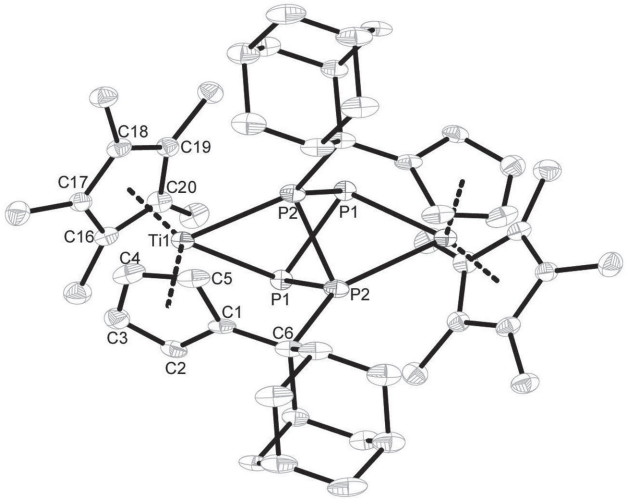
Crystal structure of a P4-bridged (η^5-pentamethylcyclopentadienyl)(η^5-adamantylcyclopentadienyl) titanium(III)complex, $C_{50}H_{66}P_4Ti_2$



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Abstract

$C_{50}H_{66}P_4Ti_2$, orthorhombic, $P2_12_12$ (no. 18), $a = 14.3799(5)$ Å, $b = 15.4444(6)$ Å, $c = 9.5555(5)$ Å, $V = 2122.17(16)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0338$, $wR_{ref}(F^2) = 0.0643$, $T = 153(2)$ K.

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The 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.

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Table 1: Data collection and handling.

Crystal:	Red blocks
Size:	$0.18 \times 0.18 \times 0.16$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.6 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, φ and ω
$2\theta_{max}$, completeness:	52.4°, >98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20384, 4200, 0.066
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3293
$N(param)_{refined}$:	254
Programs:	Stoe programs [14, 15], SHELX [16]

Source of material

All reactions were carried out under a dry nitrogen atmosphere using Schlenk-techniques. Bis[(η^5-pentamethylcyclopentadienyl)(η^5: η^1-adamantylidenepentafulvene)titanium]-μ^2, η^1, η^1-dinitrogen (**A**) (200 mg, 0.253 mmol) [1] and P_4 (31 mg, 1 mmol) were placed in a Schlenk tube and 50 mL *n*-hexane were added. After 20 minutes stirring, the solution became red and a red-brown solid precipitated. Filtration and drying in vacuo yielded the title compound (**B**) as the red-brown solid. Crystals were obtained by storing the reaction mixture at room temperature without stirring.

Experimental details

All hydrogen atoms were located by difference Fourier syntheses, and were subsequently refined using idealized geometries.

Discussion

Besides many group 15 compounds which interact as 2e-donor ligands (R_3E, $R_2E(CH_2)_nER$, E: N, P, As) owing to their free electron pair, the reactivity of E_n ligands without additional substituents is of growing interest. Generally group 15 element halides are employed for the synthesis of the desired building blocks. The direct application of elementary white phosphorus (P_4) or yellow arsene (As_4) as starting materials for the preparation of metal complexes is one of the current challenges [2–4]. In that direction the direct incorporation of P_4 into organic molecules becomes necessary, therefore prior

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ti1	0.31020(5)	0.03272(4)	0.10600(7)	0.01792(17)
P1	0.44156(8)	−0.05167(6)	−0.02460(9)	0.0185(2)
P2	0.51808(8)	−0.06977(7)	0.17245(10)	0.0200(2)
C1	0.3425(3)	−0.0858(2)	0.2775(4)	0.0211(10)
C2	0.2667(3)	−0.1076(3)	0.1885(4)	0.0236(9)
H2	0.2661	−0.1534	0.1220	0.028*
C3	0.1932(4)	−0.0505(2)	0.2151(4)	0.0293(10)
H3	0.1335	−0.0523	0.1726	0.035*
C4	0.2232(4)	0.0105(3)	0.3162(4)	0.0322(12)
H4	0.1877	0.0574	0.3522	0.039*
C5	0.3146(4)	−0.0109(2)	0.3536(3)	0.0265(10)
H5	0.3519	0.0197	0.4191	0.032*
C6	0.4336(3)	−0.1335(2)	0.2910(4)	0.0217(9)
C7	0.4229(3)	−0.2287(3)	0.2417(4)	0.0220(9)
H7	0.4010	−0.2293	0.1424	0.026*
C8	0.5158(3)	−0.2778(3)	0.2518(4)	0.0273(10)
H8A	0.5629	−0.2487	0.1927	0.033*
H8B	0.5076	−0.3376	0.2166	0.033*
C9	0.5500(4)	−0.2804(3)	0.4052(4)	0.0331(11)
H9	0.6107	−0.3117	0.4107	0.040*
C10	0.5622(4)	−0.1867(3)	0.4543(4)	0.0337(11)
H10A	0.6092	−0.1576	0.3950	0.040*
H10B	0.5852	−0.1864	0.5519	0.040*
C11	0.4698(4)	−0.1366(3)	0.4464(4)	0.0272(11)
H11	0.4793	−0.0763	0.4815	0.033*
C12	0.3974(4)	−0.1831(3)	0.5389(4)	0.0346(12)
H12A	0.3370	−0.1524	0.5335	0.041*
H12B	0.4183	−0.1828	0.6376	0.041*
C13	0.3858(4)	−0.2771(3)	0.4873(4)	0.0361(13)
H13	0.3387	−0.3070	0.5472	0.043*
C14	0.3509(4)	−0.2762(3)	0.3343(4)	0.0287(10)
H14A	0.2901	−0.2463	0.3290	0.034*
H14B	0.3425	−0.3363	0.3005	0.034*
C15	0.4777(4)	−0.3261(3)	0.4968(4)	0.0399(13)
H15A	0.4691	−0.3865	0.4644	0.048*
H15B	0.4994	−0.3276	0.5951	0.048*
C16	0.2016(3)	0.0507(2)	−0.0814(4)	0.0216(9)
C17	0.1738(3)	0.1084(2)	0.0283(4)	0.0216(9)
C18	0.2447(3)	0.1713(2)	0.0458(4)	0.0219(9)
C19	0.3149(3)	0.1557(2)	−0.0568(4)	0.0203(9)
C20	0.2879(3)	0.0811(3)	−0.1342(3)	0.0215(10)
C21	0.1441(3)	−0.0205(3)	−0.1443(4)	0.0313(11)
H21A	0.0879	−0.0290	−0.0881	0.047*
H21B	0.1266	−0.0046	−0.2401	0.047*
H21C	0.1803	−0.0742	−0.1460	0.047*
C22	0.0799(3)	0.1124(3)	0.0983(5)	0.0320(10)
H22A	0.0429	0.0620	0.0704	0.048*
H22B	0.0881	0.1123	0.2001	0.048*
H22C	0.0478	0.1655	0.0698	0.048*
C23	0.2366(4)	0.2479(3)	0.1438(4)	0.0292(11)
H23A	0.2936	0.2825	0.1389	0.044*
H23B	0.1833	0.2836	0.1161	0.044*
H23C	0.2276	0.2271	0.2397	0.044*
C24	0.3921(3)	0.2161(3)	−0.0967(4)	0.0265(9)
H24A	0.3970	0.2623	−0.0268	0.040*
H24B	0.4508	0.1840	−0.1008	0.040*
H24C	0.3789	0.2414	−0.1886	0.040*
C25	0.3343(3)	0.0477(3)	−0.2655(4)	0.0290(11)
H25A	0.3930	0.0786	−0.2803	0.043*
H25B	0.3468	−0.0144	−0.2555	0.043*
H25C	0.2932	0.0572	−0.3459	0.043*

activation by coordination to transition metals proves to be convenient [5–8]. Reacting the starting dinitrogen complex (**A**) with white phosphorus, the title compound is isolated in form of dark red crystals. The molecular structure is characterized by the formation of two P—C bonds, accompanied by the cleavage of two P—P bonds of the P_4, e. g. comparable to Co—P_4—Co [9]. The asymmetric unit of the unit cell contains two molecules. Changing the molecular nitrogen atom in between the two metal centers with phosphorus, the structural parameters of the metal fragment almost remain in the expected ranges. In comparison to the starting material (**A**), the Ti—Ct distances are slightly elongated, while the Ct—Ti—Ct angle becomes more acute. Only the C_5Me_5—Ti—C_5H_4 axes are twisted towards each other with 102.2°, while the parent compound shows a smaller torsion angle of 35.4° [1]. In contrast to the free P_4 tetrahedron, the bridging P_4 ligand distorts the tetrahedral arrangement due to the coordination between the two metal centers. While the P1—P1# (2.3201(16) Å) and P2—P2# (2.2163(16) Å) bond lengths are within range of the free P_4 molecule [10], the P1—P2# and P2—P1# distances of 2.721 Å indicate a cleavage of the phosphorus bonds. The newly formed Ti—P bond is in accordance with known metalorganic complexes [11–13].

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