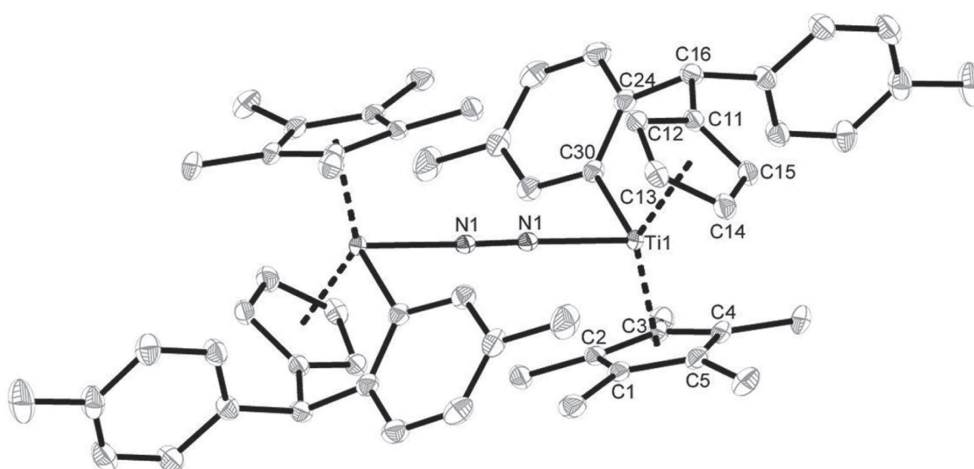


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Crystal structure of an isomeric bis[(η^5 : η^1 -6,6-di-*p*-tolylpentafulvene)(η^5 -pentamethylcyclopentadienyl)titanium(III)]- μ^2 , η^1 : η^1 -dinitrogen complex, $C_{60}H_{66}N_2Ti_2$



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Abstract

$C_{60}H_{66}N_2Ti_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.8070(3)$ Å, $b = 11.9544(5)$ Å, $c = 12.3447(5)$ Å, $\alpha = 66.7623(13)^\circ$, $\beta = 89.0505(13)^\circ$, $\gamma = 80.9952(13)^\circ$, $V = 1178.06(8)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0426$, $wR_{ref}(F^2) = 0.1046$, $T = 100(2)$ K.

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The title complex 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 $0.24 \times 0.16 \times 0.04$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	3.8 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II, φ and ω
$2\theta_{\text{max}}$, completeness:	64° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	48555, 8199, 0.043
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6433
$N(\text{param})_{\text{refined}}$:	296
Programs:	SHELX [12], Bruker programs [13]

Source of material

All reactions were carried out under a dry nitrogen atmosphere using Schlenk-technique. A solution of bis[(η^5 : η^1 -6,6-di-*p*-tolylpentafulvene)(η^5 -pentamethylcyclopentadienyl)titanium]- μ^2 , η^1 : η^1 -dinitrogen **A** [1] in *n*-hexane was stored at 60 °C. After several days, red blocks suitable for X-ray crystallography separated from the mother liquor.

Experimental details

All hydrogen atoms were located in the difference Fourier syntheses, and subsequently added using idealized geometries.

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

Atom	x	y	z	U _{iso} */U _{eq}
Ti1	0.53116(3)	0.33899(2)	0.71576(2)	0.01393(6)
N1	0.50850(12)	0.46213(10)	0.54702(9)	0.0145(2)
C1	0.26091(15)	0.35626(13)	0.67977(11)	0.0181(2)
C2	0.28058(15)	0.45221(13)	0.71683(11)	0.0168(2)
C3	0.33910(15)	0.39664(13)	0.83607(11)	0.0171(2)
C4	0.35635(16)	0.26680(13)	0.87271(11)	0.0182(2)
C5	0.30556(16)	0.24195(13)	0.77648(12)	0.0192(3)
C6	0.18615(17)	0.37304(15)	0.56464(13)	0.0244(3)
H6A	0.2246	0.4397	0.5000	0.037*
H6B	0.0743	0.3942	0.5666	0.037*
H6C	0.2107	0.2962	0.5523	0.037*
C7	0.21768(16)	0.58602(13)	0.64970(12)	0.0213(3)
H7A	0.2296	0.6317	0.6989	0.032*
H7B	0.1083	0.5952	0.6286	0.032*
H7C	0.2740	0.6187	0.5777	0.032*
C8	0.35508(17)	0.46201(14)	0.91553(12)	0.0214(3)
H8A	0.4087	0.4036	0.9900	0.032*
H8B	0.2527	0.4963	0.9314	0.032*
H8C	0.4143	0.5290	0.8773	0.032*
C9	0.39592(18)	0.17514(14)	0.99758(12)	0.0243(3)
H9A	0.4186	0.0917	0.9990	0.036*
H9B	0.3086	0.1804	1.0466	0.036*
H9C	0.4863	0.1936	1.0285	0.036*
C10	0.27447(19)	0.12026(15)	0.78139(14)	0.0271(3)
H10A	0.3015	0.1127	0.7070	0.041*
H10B	0.1651	0.1154	0.7936	0.041*
H10C	0.3365	0.0532	0.8468	0.041*
C11	0.78900(15)	0.24304(12)	0.78771(11)	0.0169(2)
C12	0.78036(15)	0.27684(13)	0.66380(11)	0.0181(2)
H12	0.8314	0.3370	0.6071	0.022*
C13	0.68253(17)	0.20540(13)	0.63917(12)	0.0206(3)
H13	0.6579	0.2081	0.5634	0.025*
C14	0.62847(17)	0.12994(13)	0.74660(13)	0.0211(3)
H14	0.5598	0.0732	0.7562	0.025*
C15	0.69434(16)	0.15311(12)	0.83849(12)	0.0188(3)
H15	0.6773	0.1144	0.9202	0.023*
C16	0.87524(15)	0.30292(13)	0.84861(12)	0.0184(2)
H16	0.9838	0.2990	0.8234	0.022*
C17	0.87884(16)	0.23641(13)	0.98252(12)	0.0197(3)
C18	0.76316(17)	0.26935(14)	1.04787(12)	0.0225(3)
H18	0.6804	0.3339	1.0085	0.027*
C19	0.76744(19)	0.20878(14)	1.17025(13)	0.0257(3)
H19	0.6865	0.2315	1.2132	0.031*
C20	0.8880(2)	0.11596(14)	1.23019(13)	0.0267(3)
C21	1.00129(19)	0.08182(15)	1.16507(14)	0.0288(3)
H21	1.0839	0.0172	1.2047	0.035*
C22	0.99647(18)	0.14033(14)	1.04293(14)	0.0250(3)
H22	1.0747	0.1143	1.0001	0.030*
C23	0.8966(3)	0.05468(18)	1.36322(15)	0.0415(5)
H23A	0.9438	0.1047	1.3956	0.062*
H23B	0.9591	-0.0276	1.3888	0.062*
H23C	0.7927	0.0471	1.3917	0.062*

Table 2 (continued)

Atom	x	y	z	U _{iso} */U _{eq}
C24	0.80193(16)	0.43806(13)	0.80495(11)	0.0183(2)
C25	0.88554(17)	0.52174(14)	0.81968(13)	0.0239(3)
H25	0.9838	0.4929	0.8601	0.029*
C26	0.82599(19)	0.64626(15)	0.77572(14)	0.0269(3)
H26	0.8827	0.7028	0.7865	0.032*
C27	0.68153(18)	0.68852(13)	0.71522(13)	0.0242(3)
C28	0.6186(2)	0.82522(15)	0.66091(17)	0.0352(4)
H28A	0.5708	0.8507	0.7216	0.053*
H28B	0.5416	0.8420	0.5977	0.053*
H28C	0.7028	0.8715	0.6283	0.053*
C29	0.59932(17)	0.60225(13)	0.70499(12)	0.0206(3)
H29	0.5005	0.6317	0.6654	0.025*
C30	0.65308(15)	0.47421(12)	0.74952(11)	0.0173(2)

Discussion

Activation and complexation of molecular nitrogen is a great field of interest in chemistry [2–5]. Besides many early transition metal complexes which are capable to activate and bind molecular nitrogen [5–9], our group reported the easy and smooth formation of dinuclear nitrogen-bridged low-valent titanium complexes [1]. These complexes appear to serve as synthons for different titanocenes, due to the weakly activated and displaceable dinitrogen. New investigations show, that the *p*-tolyl substituted complex **A** is only thermally stable until 60 °C in solution. Above this temperature, a 1,3-H-shift is observed, leading to an isomeric form **B** with a chelating σ - π -chelating ligand, characterized by the formation of a Ti–C σ -bond to the *ortho*-position of one *p*-tolyl ring, whereas the proton is now located on the exocyclic carbon atom. This bond activation process occurs twice, on both metal fragments. The isomeric compound **B** crystallizes in the triclinic space group $P\bar{1}$. Unlike the starting material **A** [1], the inversion center is located in the middle of the N₂ ligand, causing the two pentamethylcyclopentadienyl ligands to be on opposite sides. The N–N bond length of 1.151(2) Å is also slightly shorter as in **A** (1.160(3) Å), while the bond angle of Ti–N–N with 175.83(14)° is greater (171.0(2)°, 169.1(2)°). Due to the chelating properties, the newly formed Ti–C30 σ -bond is widened with 2.243(3) Å, compared with other similar complexes like the dinitrogen complex [(C₅H₅)₂Ti(*p*-CH₃C₆H₄)₂N₂] (2.216(7) Å [10]) or the titanium(IV) fulvalene complex (CpTiPh₂)₂(C₁₀H₈) (2.199(6), 2.207(4) Å [11]). Additionally, due to the 1,3-H-shift, the C11–C16 bond length with 1.5060(19) Å is now in the range of a C–C single bond, while in the case of **A** an increased double bond character (1.448(3) Å) is observed. All other bond lengths and angles are in the expected ranges.

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