Crystal structure of η^5-1-(tris(pentafluorophenyl)boranylmethyl)-2,3,4,5-tetramethylcyclopentadienyl-η^5,η^1-3,6-di-*tert*-butyl-9,10,11-trimethyl-bicyclo(6.3.0)undeca-3-en-8,10-dienyl)titanium(IV), $Ti(C_{50}H_{48}BF_{15})$

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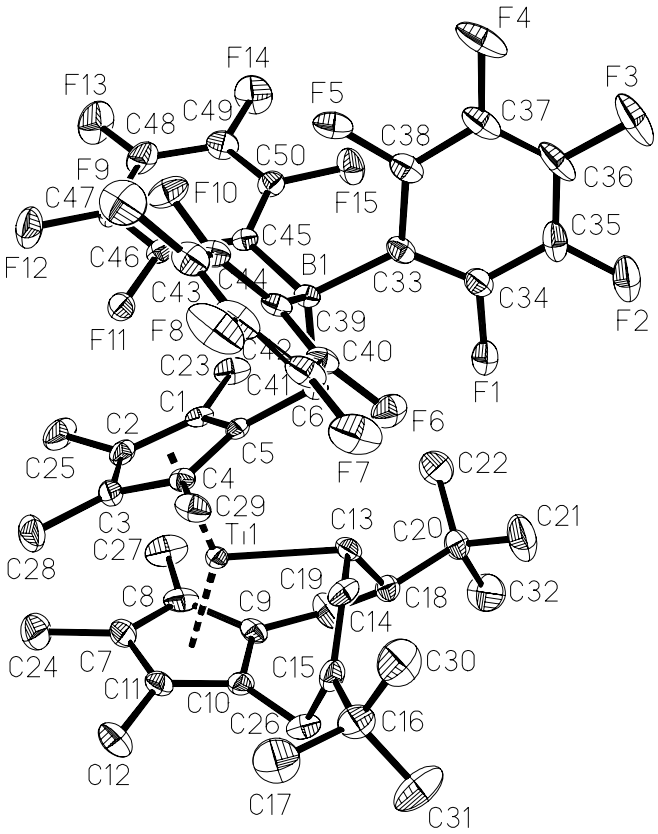
Received September 24, 2007, accepted and available on-line January 7, 2008; CCDC no. 1267/2193



Abstract

$C_{50}H_{48}BF_{15}Ti$, monoclinic, $P12_1/c1$ (no. 14), a = 12.007(2) Å, b = 19.511(4) Å, c = 20.010(4) Å, β = 98.90(3)°, V = 4631.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.052, $wR_{ref}(F^2)$ = 0.120, T = 200 K.

Source of material

An amount of $B(C_6F_5)_3$ (321 mg, 0.63 mmol) was dissolved in 10 ml of warm *n*-hexane under Ar. The obtained solution was filtered and added to a yellow-greenish filtrate of pentamethylcyclopentadienyl-trimethylcyclopentadienyl-cyclooctyne titanium(II) [1] (289 mg, 0.60 mmol) in 15 ml of warm *n*-hexane. The resulting mixture was allowed to stand in argon atmosphere at room temperature. In 3 days in the yellow solution the red-brown fine crystals were formed on the bottom and the walls of the vessel. The crystals were separated from the mother liquor by decanting, washed with *n*-hexane, and dried in vacuum to give 373 mg of the title complex. After repeated recrystallization from 20 ml of a mixture THF/*n*-hexane (1:1, *v*/*v*) a small amount of crystals well suited for X-ray structure analysis was obtained (m.p. 257-260 °C, dec. under argon).

Experimental details

The hydrogen atoms (except those attached to C13, C14 and C18) were included at calculated positions and refined by using the riding model. The remaining H atoms were refined isotropically.

Discussion

Ion pairs $[Cp'_2ZrR]^+[RB(C_6F_5)_3]^-$ which are formed by the abstraction of methyl anions from group 4 dimethyl complexes Cp'_2MMe_2 (M = Ti, Zr; Cp′ = substituted or unsubstituted η^5-cyclopentadienyl) with the strong Lewis acid $B(C_6F_5)_3$ are highly active catalysts for the polymerization of α-olefins [2]. Metallocene olefin, alkyne and butadiene complexes undergo also a similar activation for the catalytic polymerization [3].

In the title crystal structure, the titanium(IV) is coordinated by the $[Me_4C_5\text{-}CH_2\text{-}B(C_6F_5)_3]$ ligand and shows the typical environment [4]. The most interesting feature is the formed trimethylcyclopentadienylcyclooctenyl ligand interacting unsymmetrically with the metal (d(Ti1—C13) = 2.222(3) Å, d(Ti1—C14) = 2.410(3) Å). From the Ti—C and the corresponding C—C bond distances (d(C13—C14) = 1.439(5) Å and d(C14—C15) = 1.379(5) Å) one can describe the interaction of this ligand by a σ-Ti—C13 bond. The type of the structure is unprecedented. During the reaction the hydrogen is shifted to the trimethylcyclopentadienylcyclooctyne ligand giving a trimethylcyclopentadienylcyclooctenyl ligand. The remaining double bond does not coordinate to the metal.

Table 1. Data collection and handling.

Crystal:	brown prism, size 0.2 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.80 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS I, φ
$2\theta_{max}$:	52.32°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16687, 9055
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4504
$N(param)_{refined}$:	616
Programs:	SHELXS-86 [5], SHELXL-93 [6]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(6A)	4*e*	0.3472	0.1302	0.2794	0.033
H(6B)	4*e*	0.3290	0.0809	0.3404	0.033
H(12A)	4*e*	0.2943	–0.2342	0.2428	0.106
H(12B)	4*e*	0.2349	–0.2592	0.1697	0.106
H(12C)	4*e*	0.1728	–0.2052	0.2115	0.106
H(17A)	4*e*	0.2929	–0.1725	0.3702	0.124
H(17B)	4*e*	0.3706	–0.2175	0.4259	0.124
H(17C)	4*e*	0.3711	–0.2317	0.3472	0.124
H(19A)	4*e*	0.5313	–0.0080	0.1122	0.072
H(19B)	4*e*	0.6048	–0.0745	0.1372	0.072
H(21A)	4*e*	0.7248	0.0220	0.3191	0.129
H(21B)	4*e*	0.6312	0.0808	0.3154	0.129
H(21C)	4*e*	0.7537	0.0983	0.2980	0.129
H(22A)	4*e*	0.5826	0.0968	0.1362	0.106
H(22B)	4*e*	0.6673	0.1438	0.1862	0.106
H(22C)	4*e*	0.5448	0.1266	0.2038	0.106
H(23A)	4*e*	0.3118	0.1480	0.1725	0.065
H(23B)	4*e*	0.1985	0.1487	0.1185	0.065
H(23C)	4*e*	0.3005	0.0993	0.1075	0.065
H(24A)	4*e*	0.1375	–0.1213	0.0228	0.107
H(24B)	4*e*	0.0872	–0.1507	0.0866	0.107
H(24C)	4*e*	0.1628	–0.1988	0.0468	0.107
H(25A)	4*e*	0.0212	–0.0245	0.0723	0.093
H(25B)	4*e*	0.1234	0.0166	0.0484	0.093
H(25C)	4*e*	0.0234	0.0574	0.0751	0.093
H(26A)	4*e*	0.4687	–0.2050	0.2665	0.055
H(26B)	4*e*	0.5641	–0.1521	0.2517	0.055
H(27A)	4*e*	0.3938	–0.0091	0.0298	0.100
H(27B)	4*e*	0.2596	–0.0094	0.0253	0.100
H(27C)	4*e*	0.3207	–0.0687	–0.0107	0.100
H(28A)	4*e*	0.0222	–0.1063	0.2448	0.088
H(28B)	4*e*	0.0375	–0.1197	0.1678	0.088
H(28C)	4*e*	–0.0537	–0.0653	0.1850	0.088
H(29A)	4*e*	0.2030	–0.0040	0.3702	0.060
H(29B)	4*e*	0.1750	–0.0786	0.3389	0.060
H(29C)	4*e*	0.0754	–0.0248	0.3423	0.060
H(30A)	4*e*	0.3749	–0.0705	0.4278	0.118
H(30B)	4*e*	0.5082	–0.0579	0.4399	0.118
H(30C)	4*e*	0.4552	–0.1166	0.4812	0.118
H(31A)	4*e*	0.6339	–0.1438	0.3984	0.138
H(31B)	4*e*	0.5823	–0.2135	0.3646	0.138
H(31C)	4*e*	0.5809	–0.1993	0.4432	0.138
H(32A)	4*e*	0.7898	–0.0201	0.2141	0.129
H(32B)	4*e*	0.8158	0.0573	0.1948	0.129
H(32C)	4*e*	0.7348	0.0105	0.1424	0.129
H(13)	4*e*	0.455(2)	0.049(2)	0.258(1)	0.019(7)
H(14)	4*e*	0.407(3)	–0.016(2)	0.335(2)	0.05(1)
H(18)	4*e*	0.611(2)	–0.051(2)	0.241(1)	0.027(8)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	4*e*	0.30008(4)	–0.04486(3)	0.20049(3)	0.0274(3)	0.0236(3)	0.0260(3)	0.0018(3)	0.0016(2)	–0.0034(3)
B(1)	4*e*	0.2105(3)	0.1670(2)	0.3310(2)	0.030(2)	0.023(2)	0.027(2)	0.001(2)	0.007(2)	–0.001(2)
F(1)	4*e*	0.4718(2)	0.1754(1)	0.3746(1)	0.036(1)	0.055(1)	0.066(1)	–0.004(1)	–0.006(1)	–0.011(1)
F(2)	4*e*	0.5773(2)	0.2678(1)	0.4559(1)	0.065(2)	0.071(2)	0.053(1)	–0.033(1)	–0.015(1)	0.013(1)
F(3)	4*e*	0.4624(2)	0.3714(1)	0.5071(1)	0.132(2)	0.066(2)	0.045(1)	–0.052(2)	0.001(2)	–0.018(1)
F(4)	4*e*	0.2345(2)	0.3812(1)	0.4684(1)	0.131(2)	0.038(1)	0.063(2)	–0.006(1)	0.032(2)	–0.023(1)
F(5)	4*e*	0.1256(2)	0.2883(1)	0.3871(1)	0.064(2)	0.037(1)	0.057(1)	0.011(1)	0.017(1)	–0.010(1)
F(6)	4*e*	0.3009(2)	0.0856(1)	0.44942(9)	0.056(1)	0.054(1)	0.028(1)	0.013(1)	–0.002(1)	0.0030(9)
F(7)	4*e*	0.1945(2)	0.0400(1)	0.5469(1)	0.121(2)	0.054(1)	0.031(1)	0.007(1)	0.013(1)	0.011(1)
F(8)	4*e*	–0.0285(2)	0.0675(1)	0.5462(1)	0.126(2)	0.056(2)	0.050(1)	–0.031(1)	0.054(2)	–0.005(1)
F(9)	4*e*	–0.1415(2)	0.1445(1)	0.4437(1)	0.061(2)	0.077(2)	0.078(2)	–0.005(1)	0.048(1)	–0.008(1)
F(10)	4*e*	–0.0399(2)	0.1902(1)	0.3461(1)	0.040(1)	0.056(1)	0.057(1)	0.018(1)	0.023(1)	0.012(1)
F(11)	4*e*	0.0042(1)	0.11025(9)	0.24903(9)	0.031(1)	0.032(1)	0.043(1)	–0.0032(8)	0.0050(9)	0.0079(9)
F(12)	4*e*	–0.1089(2)	0.1608(1)	0.1352(1)	0.046(1)	0.073(2)	0.064(1)	–0.013(1)	–0.018(1)	0.020(1)
F(13)	4*e*	–0.0474(2)	0.2816(1)	0.0844(1)	0.076(2)	0.083(2)	0.062(2)	–0.003(1)	–0.020(1)	0.041(1)
F(14)	4*e*	0.1352(2)	0.3508(1)	0.1508(1)	0.086(2)	0.051(1)	0.063(1)	–0.015(1)	0.002(1)	0.035(1)
F(15)	4*e*	0.2517(2)	0.3012(1)	0.2619(1)	0.051(1)	0.045(1)	0.048(1)	–0.022(1)	0.001(1)	0.012(1)
C(1)	4*e*	0.2115(3)	0.0641(2)	0.1803(2)	0.033(2)	0.028(2)	0.023(2)	0.012(1)	0.007(2)	0.003(1)
C(2)	4*e*	0.1337(3)	0.0131(2)	0.1519(2)	0.033(2)	0.042(2)	0.030(2)	0.012(2)	–0.006(2)	–0.010(2)
C(3)	4*e*	0.1083(3)	–0.0293(2)	0.2053(2)	0.028(2)	0.032(2)	0.046(2)	–0.001(2)	0.002(2)	–0.009(2)
C(4)	4*e*	0.1675(2)	–0.0034(2)	0.2662(2)	0.024(2)	0.027(2)	0.032(2)	0.004(1)	0.011(2)	0.000(1)
C(5)	4*e*	0.2294(2)	0.0565(2)	0.2521(1)	0.020(2)	0.026(2)	0.023(2)	0.006(1)	0.005(1)	0.000(1)
C(6)	4*e*	0.2891(2)	0.1068(2)	0.3013(2)	0.029(2)	0.027(2)	0.027(2)	0.000(1)	0.006(2)	0.001(1)
C(7)	4*e*	0.2571(3)	–0.1284(2)	0.1087(2)	0.046(2)	0.039(2)	0.046(2)	0.003(2)	–0.002(2)	–0.021(2)
C(8)	4*e*	0.3379(3)	–0.0807(2)	0.0929(2)	0.066(3)	0.037(2)	0.025(2)	0.017(2)	0.013(2)	–0.004(2)
C(9)	4*e*	0.4360(3)	–0.0866(2)	0.1427(2)	0.038(2)	0.029(2)	0.035(2)	–0.001(2)	0.016(2)	–0.013(2)
C(10)	4*e*	0.4122(3)	–0.1374(2)	0.1891(2)	0.037(2)	0.029(2)	0.034(2)	0.007(2)	0.002(2)	–0.006(2)
C(11)	4*e*	0.3018(3)	–0.1614(2)	0.1682(2)	0.042(2)	0.027(2)	0.049(2)	0.000(2)	0.007(2)	–0.011(2)
C(12)	4*e*	0.2459(4)	–0.2203(2)	0.2010(2)	0.068(3)	0.042(3)	0.101(4)	–0.021(2)	0.008(3)	0.002(2)
C(13)	4*e*	0.4633(3)	0.0004(2)	0.2476(2)	0.032(2)	0.024(2)	0.052(2)	–0.002(2)	0.010(2)	–0.009(2)
C(14)	4*e*	0.4376(3)	–0.0422(2)	0.3018(2)	0.037(2)	0.048(2)	0.029(2)	0.015(2)	0.005(2)	0.005(2)
C(15)	4*e*	0.4566(3)	–0.1114(2)	0.3115(2)	0.035(2)	0.050(2)	0.031(2)	–0.002(2)	–0.006(2)	0.006(2)
C(16)	4*e*	0.4618(4)	–0.1445(2)	0.3815(2)	0.075(3)	0.051(3)	0.042(2)	0.000(2)	–0.004(2)	0.020(2)
C(17)	4*e*	0.3654(4)	–0.1963(3)	0.3812(2)	0.103(4)	0.084(4)	0.060(3)	–0.010(3)	0.011(3)	0.028(3)
C(18)	4*e*	0.5701(3)	–0.0140(2)	0.2168(2)	0.028(2)	0.035(2)	0.046(2)	–0.004(2)	0.005(2)	0.005(2)
C(19)	4*e*	0.5420(3)	–0.0450(2)	0.1466(2)	0.056(3)	0.057(3)	0.073(3)	–0.017(2)	0.027(2)	–0.024(2)
C(20)	4*e*	0.6548(3)	0.0461(2)	0.2217(2)	0.035(2)	0.040(2)	0.056(2)	–0.011(2)	0.005(2)	0.002(2)
C(21)	4*e*	0.6946(4)	0.0633(3)	0.2950(2)	0.081(3)	0.087(4)	0.083(3)	–0.043(3)	–0.012(3)	0.001(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(22)	4*e*	0.6084(4)	0.1088(2)	0.1837(2)	0.062(3)	0.050(3)	0.100(3)	–0.018(2)	0.011(3)	0.017(3)
C(23)	4*e*	0.2598(3)	0.1199(2)	0.1413(2)	0.062(2)	0.045(2)	0.026(2)	0.015(2)	0.015(2)	0.010(2)
C(24)	4*e*	0.1518(3)	–0.1519(2)	0.0621(2)	0.066(3)	0.069(3)	0.071(3)	0.000(2)	–0.014(3)	–0.028(3)
C(25)	4*e*	0.0698(3)	0.0159(2)	0.0807(2)	0.061(3)	0.072(3)	0.043(2)	0.025(2)	–0.021(2)	–0.017(2)
C(26)	4*e*	0.4832(3)	–0.1566(2)	0.2557(2)	0.049(2)	0.039(2)	0.051(2)	0.013(2)	0.009(2)	0.010(2)
C(27)	4*e*	0.3270(4)	–0.0382(2)	0.0286(2)	0.092(3)	0.071(3)	0.040(2)	0.027(3)	0.019(2)	0.006(2)
C(28)	4*e*	0.0210(3)	–0.0850(2)	0.2003(2)	0.030(2)	0.057(3)	0.089(3)	–0.011(2)	0.013(2)	–0.023(2)
C(29)	4*e*	0.1540(3)	–0.0301(2)	0.3355(2)	0.048(2)	0.030(2)	0.047(2)	–0.004(2)	0.025(2)	0.005(2)
C(30)	4*e*	0.4489(4)	–0.0927(3)	0.4377(2)	0.104(4)	0.094(4)	0.033(2)	–0.002(3)	–0.003(2)	0.014(2)
C(31)	4*e*	0.5744(4)	–0.1782(3)	0.3984(2)	0.085(4)	0.127(5)	0.059(3)	0.042(3)	0.000(3)	0.032(3)
C(32)	4*e*	0.7584(3)	0.0212(3)	0.1904(3)	0.045(2)	0.077(3)	0.142(5)	–0.008(2)	0.032(3)	0.003(3)
C(33)	4*e*	0.2907(3)	0.2250(2)	0.3765(2)	0.046(2)	0.027(2)	0.021(2)	–0.003(2)	0.005(2)	–0.002(1)
C(34)	4*e*	0.4062(3)	0.2247(2)	0.3964(2)	0.046(2)	0.030(2)	0.035(2)	–0.004(2)	0.003(2)	–0.001(2)
C(35)	4*e*	0.4644(3)	0.2728(2)	0.4390(2)	0.051(2)	0.050(2)	0.033(2)	–0.027(2)	–0.009(2)	0.015(2)
C(36)	4*e*	0.4059(4)	0.3248(2)	0.4641(2)	0.103(4)	0.033(2)	0.025(2)	–0.027(2)	0.008(2)	–0.008(2)
C(37)	4*e*	0.2921(4)	0.3290(2)	0.4458(2)	0.083(3)	0.030(2)	0.034(2)	–0.009(2)	0.015(2)	–0.006(2)
C(38)	4*e*	0.2386(3)	0.2802(2)	0.4032(2)	0.056(3)	0.029(2)	0.032(2)	–0.004(2)	0.010(2)	–0.001(2)
C(39)	4*e*	0.1355(3)	0.1369(2)	0.3887(2)	0.041(2)	0.020(2)	0.028(2)	0.002(2)	0.011(2)	–0.003(1)
C(40)	4*e*	0.1884(3)	0.1005(2)	0.4441(2)	0.049(2)	0.027(2)	0.026(2)	0.002(2)	0.009(2)	–0.006(2)
C(41)	4*e*	0.1364(4)	0.0766(2)	0.4962(2)	0.083(3)	0.027(2)	0.020(2)	–0.005(2)	0.007(2)	0.005(2)
C(42)	4*e*	0.0250(4)	0.0908(2)	0.4960(2)	0.081(3)	0.036(2)	0.035(2)	–0.016(2)	0.034(2)	–0.007(2)
C(43)	4*e*	–0.0321(3)	0.1280(2)	0.4442(2)	0.047(2)	0.042(2)	0.048(2)	–0.004(2)	0.026(2)	–0.006(2)
C(44)	4*e*	0.0232(3)	0.1508(2)	0.3927(2)	0.045(2)	0.028(2)	0.036(2)	0.003(2)	0.015(2)	0.002(2)
C(45)	4*e*	0.1346(2)	0.2028(2)	0.2641(1)	0.027(2)	0.024(2)	0.028(2)	0.003(1)	0.008(2)	0.003(1)
C(46)	4*e*	0.0410(3)	0.1709(2)	0.2273(2)	0.026(2)	0.030(2)	0.038(2)	0.004(2)	0.008(2)	0.009(2)
C(47)	4*e*	–0.0199(3)	0.1961(2)	0.1683(2)	0.028(2)	0.042(2)	0.042(2)	–0.004(2)	–0.006(2)	0.008(2)
C(48)	4*e*	0.0109(3)	0.2570(2)	0.1422(2)	0.048(2)	0.053(3)	0.039(2)	0.007(2)	–0.003(2)	0.022(2)
C(49)	4*e*	0.1027(3)	0.2904(2)	0.1756(2)	0.052(2)	0.033(2)	0.042(2)	–0.003(2)	0.009(2)	0.016(2)
C(50)	4*e*	0.1612(3)	0.2636(2)	0.2343(2)	0.031(2)	0.032(2)	0.036(2)	0.001(2)	0.007(2)	0.006(2)

Acknowledgments. This work was supported by the Deutsche Forschungsgemeinschaft (grant no. RO 1269/7-1) and the Russian Foundation for Basic Research (project code 05-03-32515). Funding and facilities provided by the Leibniz-Institut für Katalyse e. V. an der Universität Rostock are gratefully acknowledged.

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