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Crystal structures of tribromo(η^5-3,6-di-*tert*-butyl-9,10,11-trimethyl-bicyclo(6.3.0)undeca-4-en-8,10-dienyl)titanium(IV), Ti($C_{22}H_{35}$)Br_3, and tribromo(η^5-4,5-dibromo-3,6-di-*tert*-butyl-9,10,11-trimethyl-bicyclo(6.3.0)undeca-8,10-dienyl)titanium(IV), Ti($C_{22}H_{35}Br_2$)Br_3

Anke Spannenberg*[,I], Vladimir V. Burlakov[II] and Uwe Rosenthal[I]

[I] Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany
[II] Russian Academy of Sciences, N. Nesmeyanov Institute of Organoelement Compounds, Vavilov St. 28, 117813 Moscow, Russia

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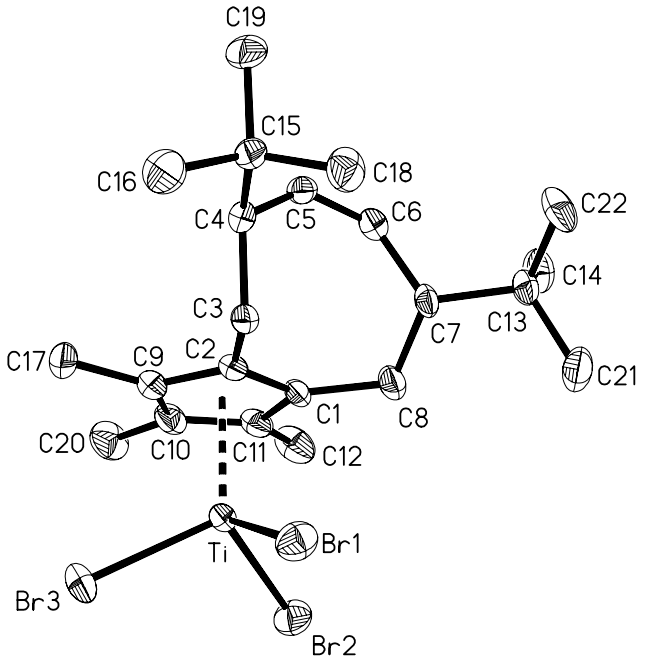

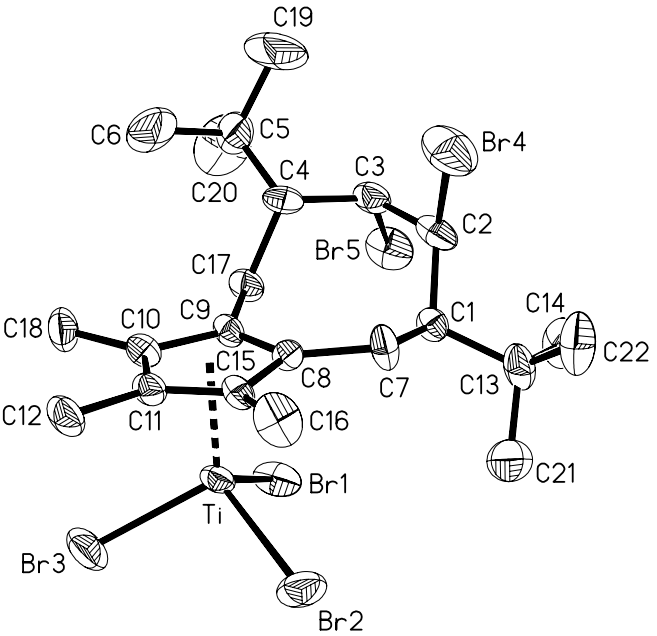

* Correspondence author (e-mail: anke.spannenberg@catalysis.de)

Abstract

$C_{22}H_{35}Br_3Ti$, triclinic, $P\bar{1}$ (no. 2), a = 9.621(2) Å, b = 11.796(2) Å, c = 12.232(2) Å, α = 102.23(3)°, β = 97.71(3)°, γ = 112.32(3)°, V = 1219.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.058, $wR_{obs}(F^2)$ = 0.134, T = 293 K.

$C_{22}H_{35}Br_5Ti$, monoclinic, $P12_1/n1$ (no. 14), a = 7.474(1) Å, b = 18.458(4) Å, c = 20.171(4) Å, β = 100.28(3)°, V = 2738.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.054, $wR_{obs}(F^2)$ = 0.119, T = 293 K.

Source of material

Dibromo-pentamethylcyclopentadienyl-trimethylcyclopentadienyl-cyclooctene-Ti(IV) [1] (**1**; 125 mg, 0.195 mmol) was dissolved in 20 ml of *n*-hexane under argon and treated with an excess (0.3 ml) of bromine. Standing at room temperature for 20 h and concentration of the orange-red solution in vacuum to 2 ml gave a mixture of red crystals of complexes Cp*$TiBr_3$, the title compounds (**2** and **3**) in a molar ratio of 35:35:30 as identified by NMR. Fractional recrystallization from *n*-hexane gave small amounts of individual complex **2** (20 mg) and complex **3** (30 mg) which were separated from the mother liquor, washed with cold *n*-hexane and dried in vacuum.

Discussion

For group 4 decamethyltitanocenes and -zirconocenes manifold C—H bond activations of methyl groups of pentamethylcyclopentadienyl ligands with coupling reactions with butadiynes $RC{\equiv}C{-}C{\equiv}CR$ have been verified for M = Ti, R = Me, Ph, *t*-Bu and M = Zr, R = *t*-Bu [2-4]. This is a facile method for functionalizing metallocenes to obtain chiral and non-chiral complexes [1,5]. One example for this is a formal Ti(II) complex with one pentamethylcyclopentadienyl and one anellated trimethylcyclopentadienylcyclooctyne ligand [1-5]. Hydrogenation of this complex yields a Ti(II) complex with one pentamethylcyclopentadienyl and one anellated trimethylcyclopentadienyl-cyclooctene ligand, which is easily oxidized by bromine to a Ti(IV) dibromide (**1**) with one pentamethylcyclopentadienyl and one anellated trimethylcyclopentadienylcyclooctene ligand [1].

In the crystal structures of the title compounds, the η^5-coordinated Cp ligand and three bromine ligands form a "piano-stool"-like coordination. As in the case of the starting complex **1** and their chloride congener the cyclooctene unit is oriented away from the metal. There is no hint for any interaction of the double bond with the metal in **2**. This was expected for the electronically saturated Ti(IV). The bromine substituents in **3** are in an *anti* conformation to each other.

1. Tribromo(η^5-3,6-di-*tert*-butyl-9,10,11-trimethyl-bicyclo(6.3.0)undeca-4-en-8,10-dienyl)titanium(IV), $Ti(C_{22}H_{35})Br_3$

Table 1. Data collection and handling.

Crystal:	red prism, size 0.3 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	52.72 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS I, φ
$2\theta_{max}$:	48.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3626, 3626
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2206
$N(param)_{refined}$:	235
Programs:	SHELXS-86 [6], SHELXL-93 [7]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3A)	2*i*	0.2923	0.3888	0.7397	0.046
H(3B)	2*i*	0.2379	0.3911	0.8552	0.046
H(4)	2*i*	–0.0112	0.2580	0.7585	0.047
H(5)	2*i*	–0.0987	0.1513	0.5717	0.045
H(6)	2*i*	0.0313	0.1081	0.4587	0.048
H(7)	2*i*	0.2958	0.3285	0.5744	0.046
H(8A)	2*i*	0.3396	0.1024	0.5434	0.065
H(8B)	2*i*	0.4581	0.2398	0.6173	0.065
H(12A)	2*i*	0.3103	–0.1296	0.7125	0.105
H(12B)	2*i*	0.4270	–0.0362	0.6594	0.105
H(12C)	2*i*	0.2513	–0.1083	0.5961	0.105
H(14A)	2*i*	0.2816	0.0575	0.3559	0.098
H(14B)	2*i*	0.2571	0.1113	0.2518	0.098
H(14C)	2*i*	0.1234	0.0628	0.3143	0.098
H(16A)	2*i*	0.1377	0.5266	0.8749	0.097
H(16B)	2*i*	–0.0364	0.4422	0.8673	0.097
H(16C)	2*i*	0.0091	0.5670	0.8280	0.097
H(17A)	2*i*	0.1250	0.2679	0.9605	0.092
H(17B)	2*i*	0.1900	0.1958	1.0324	0.092
H(17C)	2*i*	0.0281	0.1221	0.9449	0.092
H(18A)	2*i*	0.2282	0.5374	0.6898	0.089
H(18B)	2*i*	0.0965	0.5778	0.6504	0.089
H(18C)	2*i*	0.1087	0.4604	0.5711	0.089
H(19A)	2*i*	–0.2171	0.3152	0.6774	0.085
H(19B)	2*i*	–0.1612	0.3256	0.5638	0.085
H(19C)	2*i*	–0.1734	0.4430	0.6432	0.085
H(20A)	2*i*	0.1653	–0.0336	0.9644	0.105
H(20B)	2*i*	0.2975	–0.0656	0.9241	0.105
H(20C)	2*i*	0.1279	–0.1376	0.8477	0.105
H(21A)	2*i*	0.5198	0.2613	0.4532	0.101
H(21B)	2*i*	0.5083	0.3929	0.4738	0.101
H(21C)	2*i*	0.4922	0.3138	0.3487	0.101
H(22A)	2*i*	0.2566	0.3991	0.4107	0.101
H(22B)	2*i*	0.1083	0.2725	0.3481	0.101
H(22C)	2*i*	0.2420	0.3210	0.2856	0.101

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}
C(1)	2*i*	0.3020(9)	0.1513(8)	0.7023(6)	0.043(4)	0.055(5)	0.025(4)	0.029(4)	0.007(4)	0.014(4)
C(2)	2*i*	0.2471(8)	0.2214(7)	0.7824(6)	0.033(4)	0.047(5)	0.034(4)	0.017(4)	0.004(4)	0.016(4)
C(3)	2*i*	0.2197(8)	0.3386(8)	0.7775(6)	0.038(4)	0.055(5)	0.029(4)	0.025(4)	0.010(4)	0.012(4)
C(4)	2*i*	0.0549(9)	0.3017(8)	0.7123(7)	0.036(4)	0.051(5)	0.038(4)	0.020(4)	0.016(4)	0.018(4)
C(5)	2*i*	0.0070(8)	0.2028(7)	0.5964(7)	0.032(4)	0.040(5)	0.044(5)	0.016(4)	0.010(4)	0.019(4)
C(6)	2*i*	0.0887(9)	0.1765(8)	0.5240(7)	0.046(5)	0.038(5)	0.034(4)	0.015(4)	0.007(4)	0.012(4)
C(7)	2*i*	0.2585(9)	0.2388(8)	0.5298(6)	0.053(5)	0.049(5)	0.025(4)	0.029(4)	0.017(4)	0.015(4)
C(8)	2*i*	0.350(1)	0.1808(9)	0.5957(7)	0.064(6)	0.085(7)	0.034(5)	0.045(6)	0.020(4)	0.025(5)
C(9)	2*i*	0.2064(9)	0.1544(8)	0.8662(7)	0.042(5)	0.062(6)	0.039(5)	0.024(5)	0.009(4)	0.024(5)
C(10)	2*i*	0.236(1)	0.0442(8)	0.8367(7)	0.050(5)	0.048(6)	0.043(5)	0.016(5)	0.004(4)	0.022(5)
C(11)	2*i*	0.2943(9)	0.0420(8)	0.7360(7)	0.050(5)	0.051(6)	0.039(5)	0.029(5)	0.002(4)	0.013(5)
C(12)	2*i*	0.323(1)	–0.0682(9)	0.6699(8)	0.094(8)	0.066(7)	0.053(6)	0.047(7)	0.003(6)	0.006(6)
C(13)	2*i*	0.294(1)	0.2392(8)	0.4074(6)	0.055(5)	0.050(6)	0.028(4)	0.024(5)	0.016(4)	0.012(4)
C(14)	2*i*	0.233(1)	0.1053(9)	0.3247(8)	0.086(7)	0.068(7)	0.039(5)	0.029(6)	0.024(5)	0.009(5)
C(15)	2*i*	0.0168(9)	0.4179(8)	0.7078(7)	0.043(4)	0.055(6)	0.044(5)	0.031(4)	0.017(4)	0.020(4)
C(16)	2*i*	0.033(1)	0.496(1)	0.8312(8)	0.076(7)	0.070(7)	0.060(6)	0.046(6)	0.021(6)	0.010(6)
C(17)	2*i*	0.131(1)	0.188(1)	0.9594(7)	0.059(6)	0.100(8)	0.051(6)	0.045(6)	0.030(5)	0.041(6)
C(18)	2*i*	0.122(1)	0.5066(9)	0.6493(8)	0.072(6)	0.059(6)	0.067(6)	0.035(6)	0.029(5)	0.035(6)
C(19)	2*i*	–0.149(1)	0.3712(9)	0.6420(8)	0.055(5)	0.066(6)	0.072(6)	0.043(5)	0.022(5)	0.029(6)
C(20)	2*i*	0.204(1)	–0.057(1)	0.8989(9)	0.081(7)	0.064(7)	0.072(7)	0.028(6)	0.014(6)	0.040(6)
C(21)	2*i*	0.470(1)	0.308(1)	0.4222(8)	0.066(6)	0.076(7)	0.055(6)	0.017(6)	0.031(5)	0.023(6)
C(22)	2*i*	0.218(1)	0.315(1)	0.3585(8)	0.100(8)	0.070(7)	0.052(6)	0.046(7)	0.021(6)	0.037(6)
Ti	2*i*	0.4748(2)	0.2251(1)	0.8833(1)	0.0383(8)	0.051(1)	0.0299(7)	0.0217(7)	0.0079(6)	0.0145(7)
Br(1)	2*i*	0.6019(1)	0.43937(9)	0.87439(9)	0.0515(5)	0.0515(6)	0.0720(7)	0.0178(5)	0.0151(5)	0.0202(5)
Br(2)	2*i*	0.6596(1)	0.1422(1)	0.84112(9)	0.0587(6)	0.0765(7)	0.0735(7)	0.0439(6)	0.0231(5)	0.0277(6)
Br(3)	2*i*	0.4996(1)	0.2475(1)	1.08485(8)	0.0702(7)	0.1041(9)	0.0324(5)	0.0286(7)	0.0103(5)	0.0204(6)

2. Tribromo(η^5-4,5-dibromo-3,6-di-*tert*-butyl-9,10,11-trimethylbicyclo(6.3.0)undeca-8,10-dienyl)titanium(IV), $Ti(C_{22}H_{35}Br_2)Br_3$

Table 4. Data collection and handling.

Crystal:	red prism, size 0.1 × 0.1 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	76.16 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS I, φ
$2\theta_{max}$:	42.18°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5432, 2818
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1469
$N(param)_{refined}$:	253
Programs:	SHELXS-86 [6], SHELXL-93 [7]

Table 5. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	–0.1495	0.2286	0.2983	0.056
H(2)	4*e*	0.0335	0.2631	0.4080	0.083
H(3)	4*e*	0.1812	0.1546	0.4296	0.073
H(4)	4*e*	0.2414	0.1314	0.3181	0.070
H(6A)	4*e*	0.3985	0.0312	0.2996	0.196
H(6B)	4*e*	0.2254	–0.0179	0.2822	0.196
H(6C)	4*e*	0.3898	–0.0428	0.3370	0.196
H(7A)	4*e*	–0.0431	0.3053	0.2132	0.074
H(7B)	4*e*	0.1494	0.2887	0.2542	0.074
H(12A)	4*e*	0.1497	0.0729	0.0322	0.096
H(12B)	4*e*	0.2800	0.1401	0.0420	0.096
H(12C)	4*e*	0.0796	0.1486	0.0035	0.096
H(14A)	4*e*	–0.3050	0.2939	0.3828	0.144
H(14B)	4*e*	–0.2900	0.3785	0.3885	0.144
H(14C)	4*e*	–0.1262	0.3298	0.4213	0.144
H(16A)	4*e*	0.1261	0.3202	0.1328	0.118

Table 5. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(16B)	4*e*	0.0758	0.2876	0.0601	0.118
H(16C)	4*e*	0.2724	0.2774	0.1017	0.118
H(17A)	4*e*	–0.1240	0.1091	0.2882	0.068
H(17B)	4*e*	–0.0220	0.0398	0.2695	0.068
H(18A)	4*e*	0.0849	–0.0050	0.1016	0.115
H(18B)	4*e*	–0.0506	–0.0148	0.1519	0.115
H(18C)	4*e*	0.1595	–0.0125	0.1790	0.115
H(19A)	4*e*	0.4690	0.0918	0.4146	0.237
H(19B)	4*e*	0.4565	0.0153	0.4472	0.237
H(19C)	4*e*	0.3373	0.0794	0.4659	0.237
H(20A)	4*e*	0.0627	0.0073	0.4328	0.231
H(20B)	4*e*	0.1876	–0.0566	0.4175	0.231
H(20C)	4*e*	0.0232	–0.0317	0.3627	0.231
H(21A)	4*e*	–0.3898	0.3092	0.2589	0.171
H(21B)	4*e*	–0.2650	0.3552	0.2202	0.171
H(21C)	4*e*	–0.3715	0.3930	0.2710	0.171

Table 6. 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}
C(1)	4*e*	–0.053(2)	0.2651(7)	0.3069(6)	0.05(1)	0.05(1)	0.041(8)	–0.004(8)	0.013(7)	–0.004(7)
C(2)	4*e*	0.077(2)	0.2394(9)	0.3705(7)	0.05(1)	0.10(1)	0.05(1)	–0.017(9)	0.000(8)	–0.016(9)
C(3)	4*e*	0.089(2)	0.1588(8)	0.3888(6)	0.07(1)	0.08(1)	0.035(9)	0.002(9)	0.002(7)	0.002(8)
C(4)	4*e*	0.146(2)	0.1065(7)	0.3370(6)	0.06(1)	0.07(1)	0.033(9)	0.003(8)	–0.006(8)	0.019(8)
C(5)	4*e*	0.236(3)	0.037(1)	0.3720(8)	0.13(2)	0.11(2)	0.04(1)	0.04(1)	0.02(1)	0.00(1)
C(6)	4*e*	0.320(3)	–0.002(1)	0.3176(9)	0.17(2)	0.13(2)	0.09(1)	0.08(2)	0.00(1)	0.03(1)
C(7)	4*e*	0.027(2)	0.2695(7)	0.2419(6)	0.09(1)	0.05(1)	0.049(9)	–0.008(9)	0.023(8)	–0.015(8)
C(8)	4*e*	0.039(2)	0.2034(7)	0.1995(6)	0.04(1)	0.04(1)	0.035(8)	0.002(7)	0.011(6)	0.004(7)
C(9)	4*e*	0.022(2)	0.1293(8)	0.2111(6)	0.05(1)	0.06(1)	0.032(8)	–0.004(8)	0.013(6)	–0.006(8)
C(10)	4*e*	0.053(2)	0.0886(8)	0.1536(7)	0.06(1)	0.06(1)	0.034(9)	–0.001(8)	0.007(7)	0.001(9)
C(11)	4*e*	0.094(2)	0.1420(8)	0.1067(6)	0.05(1)	0.07(1)	0.031(8)	0.006(8)	0.010(7)	–0.003(9)
C(12)	4*e*	0.157(2)	0.1242(8)	0.0398(6)	0.07(1)	0.09(1)	0.034(8)	0.002(9)	0.013(7)	–0.014(8)
C(13)	4*e*	–0.149(3)	0.3371(9)	0.3186(7)	0.11(2)	0.06(1)	0.05(1)	–0.00(1)	0.03(1)	–0.015(9)
C(14)	4*e*	–0.225(3)	0.3346(9)	0.3838(7)	0.13(2)	0.11(2)	0.07(1)	0.02(1)	0.05(1)	–0.01(1)
C(15)	4*e*	0.087(2)	0.2106(8)	0.1335(6)	0.04(1)	0.05(1)	0.039(8)	–0.010(8)	0.005(7)	–0.010(8)
C(16)	4*e*	0.146(2)	0.2803(8)	0.1044(7)	0.09(1)	0.08(1)	0.07(1)	–0.03(1)	0.03(1)	0.003(9)
C(17)	4*e*	–0.011(2)	0.0916(7)	0.2770(6)	0.07(1)	0.06(1)	0.032(8)	0.003(9)	0.006(7)	0.005(7)
C(18)	4*e*	0.063(2)	0.0064(7)	0.1458(7)	0.12(2)	0.05(1)	0.06(1)	0.02(1)	0.013(9)	–0.012(8)
C(19)	4*e*	0.389(3)	0.058(1)	0.4304(9)	0.17(3)	0.19(2)	0.09(2)	0.03(2)	–0.06(2)	0.03(2)
C(20)	4*e*	0.117(3)	–0.016(1)	0.399(1)	0.21(3)	0.13(2)	0.14(2)	0.02(2)	0.09(2)	0.08(2)
C(21)	4*e*	–0.308(3)	0.350(1)	0.2620(8)	0.12(2)	0.14(2)	0.08(1)	0.05(1)	0.00(1)	–0.02(1)
C(22)	4*e*	–0.025(3)	0.4009(9)	0.3223(9)	0.16(2)	0.06(1)	0.11(2)	–0.01(1)	0.06(1)	–0.01(1)
Ti	4*e*	–0.2094(3)	0.1593(1)	0.1190(1)	0.044(2)	0.069(2)	0.028(1)	0.004(1)	0.002(1)	0.000(1)
Br(1)	4*e*	–0.4247(2)	0.1385(1)	0.19187(7)	0.047(1)	0.134(2)	0.055(1)	–0.007(1)	0.0135(8)	0.010(1)
Br(2)	4*e*	–0.3121(3)	0.2726(1)	0.06958(8)	0.097(2)	0.104(2)	0.058(1)	0.037(1)	0.0119(9)	0.029(1)
Br(3)	4*e*	–0.3079(3)	0.0753(1)	0.02995(8)	0.074(2)	0.131(2)	0.070(1)	–0.008(1)	–0.0101(9)	–0.045(1)
Br(4)	4*e*	0.3282(3)	0.2721(1)	0.3769(1)	0.083(2)	0.151(2)	0.118(2)	–0.037(1)	0.009(1)	–0.026(2)
Br(5)	4*e*	–0.1478(3)	0.1338(1)	0.41593(8)	0.095(2)	0.135(2)	0.061(1)	–0.012(1)	0.033(1)	0.010(1)

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