Crystal structure of bis(pentamethylcyclopentadienyl)difluorotitanium(IV), $Ti[C_5(CH_3)_5]_2F_2$

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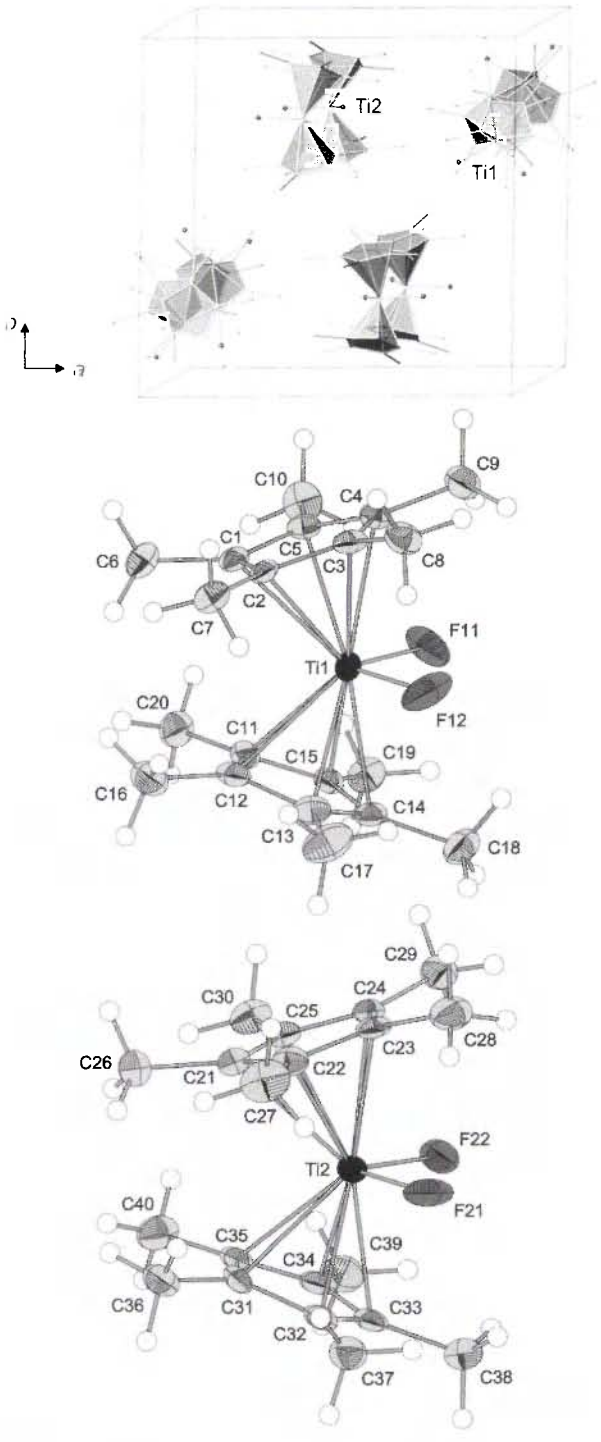

Abstract

$C_{20}H_{30}F_2Ti$, monoclinic, $P12_1/c1$ (no. 14),
a = 15.881(2) Å, b = 15.119(1) Å, c = 16.068(2) Å,
β = 109.575(3)°, V = 3635.1 Å^3, Z = 8, $R_{gt}(F)$ = 0.054,
$wR_{ref}(F^2)$ = 0.140, T = 100 K.

Source of material

Bis(pentamethylcyclopentadienyl)difluorotitanium(IV) was obtained, along the fluorination procedure described in [1], by heating the corresponding dichloro compound and a stoichiometric amount of $(CH_3)_3SnF$ in dry toluene at about 350 K for 5 h. After evaporating the solvent, the brownish residue was purified by sublimation, yielding yellow block-shaped crystals.

Discussion

Group 4 metallocene halides L_mMX_n (with L = Cp, Cp*, etc.; M = Ti, Zr, Hf and X = halide; m = 1,2; n = 1-3) exhibit various applications. They are e.g. precursors in catalytic allyltitanations [2] and act as building blocks in clusters [3] or dimetallic aggregates [4]. Furthermore, they are examined with respect to possible nonlinear optical properties [5].

Due to packing effects there are two independent molecules of the title structure within the unit cell. The angles between the centroids of the Cp* rings and Ti atoms (139.8° and 138.8°), the centroid—Ti distances (2.097 Å – 2.105 Å) and the Ti—F distances (1.85 Å – 1.88 Å) lie between the corresponding values of the dichloro compound [6] and Cp^*_2TiF [7]. The π-bonded rings exhibit a staggered configuration and are nearly planar. Two methyl groups of each ring, those which approach the CH_3 groups of the other ring due to the angular molecular structure, are bent out of the cyclopentadienyl plane at about 11°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.05 × 0.10 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.87 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, ω/φ
$2\theta_{max}$:	43°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	21424, 4183
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3343
$N(param)_{refined}$:	435
Programs:	SHELXTL [8], ATOMS [9]

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

Atom	Site	x	y	z	U_{iso}
H(6A)	4e	0.3132	0.5809	0.1257	0.044
H(6B)	4e	0.4198	0.5724	0.1585	0.044
H(6C)	4e	0.3634	0.5671	0.0553	0.044
H(7A)	4e	0.5509	0.7048	0.0506	0.044
H(7B)	4e	0.5440	0.6398	0.1267	0.044
H(7C)	4e	0.5874	0.7359	0.1517	0.044
H(8A)	4e	0.4480	0.9490	0.0294	0.048
H(8B)	4e	0.5002	0.8728	-0.0024	0.048
H(8C)	4e	0.5342	0.9038	0.0987	0.048
H(9A)	4e	0.2466	0.9150	-0.0338	0.049
H(9B)	4e	0.3149	0.9684	0.0467	0.049
H(9C)	4e	0.2314	0.9182	0.0598	0.049
H(10A)	4e	0.1868	0.7797	0.1073	0.056
H(10B)	4e	0.2058	0.6759	0.1048	0.056
H(10C)	4e	0.1690	0.7307	0.0146	0.056
H(16A)	4e	0.5989	0.6462	0.2857	0.055
H(16B)	4e	0.5191	0.5784	0.2773	0.055
H(16C)	4e	0.5881	0.6032	0.3726	0.055
H(17A)	4e	0.6577	0.8134	0.4257	0.071
H(17B)	4e	0.6178	0.8838	0.3480	0.071
H(17C)	4e	0.6474	0.7879	0.3261	0.071
H(18A)	4e	0.4376	0.9664	0.3504	0.052
H(18B)	4e	0.5254	0.9433	0.4321	0.052
H(18C)	4e	0.4287	0.9315	0.4412	0.052
H(19A)	4e	0.2494	0.7679	0.3185	0.048
H(19B)	4e	0.2883	0.8622	0.3585	0.048
H(19C)	4e	0.3005	0.7785	0.4224	0.048
H(20A)	4e	0.3382	0.6015	0.3613	0.050
H(20B)	4e	0.3815	0.5642	0.2917	0.050
H(20C)	4e	0.2934	0.6240	0.2586	0.050

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(26A)	4e	-0.0216	0.1813	0.3965	0.056
H(26B)	4e	0.0810	0.1754	0.4581	0.056
H(26C)	4e	0.0227	0.0871	0.4303	0.056
H(27A)	4e	0.2191	0.1336	0.4607	0.069
H(27B)	4e	0.2770	0.1507	0.3978	0.069
H(27C)	4e	0.2527	0.0517	0.4170	0.069
H(28A)	4e	0.2230	-0.0050	0.2232	0.063
H(28B)	4e	0.2710	0.0888	0.2508	0.063
H(28C)	4e	0.2040	0.0734	0.1523	0.063
H(29A)	4e	0.0560	0.0561	0.0708	0.058
H(29B)	4e	-0.0236	0.1245	0.0611	0.058
H(29C)	4e	-0.0327	0.0241	0.0883	0.058
H(30A)	4e	-0.1185	0.1561	0.2605	0.052
H(30B)	4e	-0.1257	0.0797	0.1896	0.052
H(30C)	4e	-0.1186	0.1809	0.1637	0.052
H(36A)	4e	0.2010	0.2899	0.4732	0.050
H(36B)	4e	0.1055	0.3169	0.4785	0.050
H(36C)	4e	0.1801	0.3911	0.4881	0.050
H(37A)	4e	0.2874	0.4501	0.3741	0.050
H(37B)	4e	0.2971	0.3855	0.2988	0.050
H(37C)	4e	0.2981	0.3458	0.3915	0.050
H(38A)	4e	0.1009	0.4245	0.0946	0.052
H(38B)	4e	0.2023	0.4047	0.1538	0.052
H(38C)	4e	0.1592	0.4994	0.1589	0.052
H(39A)	4e	-0.1003	0.3559	0.1418	0.056
H(39B)	4e	-0.0409	0.3965	0.0880	0.056
H(39C)	4e	-0.0792	0.4596	0.1469	0.056
H(40A)	4e	-0.0842	0.4009	0.3225	0.056
H(40B)	4e	-0.0353	0.3252	0.3914	0.056
H(40C)	4e	-0.0929	0.2995	0.2920	0.056

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)	4e	0.40983(6)	0.81083(6)	0.21337(6)	0.0397(6)	0.0170(5)	0.0195(5)	0.0004(4)	0.0107(4)	-0.0006(4)
F(11)	4e	0.3098(3)	0.8745(2)	0.2117(2)	0.104(3)	0.072(3)	0.029(2)	0.068(2)	0.029(2)	0.014(2)
F(12)	4e	0.4844(3)	0.9069(2)	0.2199(2)	0.146(4)	0.042(2)	0.026(2)	-0.054(2)	0.030(2)	-0.007(2)
C(1)	4e	0.3748(3)	0.6926(3)	0.1042(3)	0.025(3)	0.025(3)	0.015(3)	0.002(2)	0.007(2)	-0.005(2)
C(2)	4e	0.4511(3)	0.7389(3)	0.0983(3)	0.022(3)	0.021(3)	0.015(3)	0.000(2)	0.005(2)	-0.006(2)
C(3)	4e	0.4231(3)	0.8253(3)	0.0672(3)	0.028(3)	0.031(3)	0.015(3)	-0.004(2)	0.006(2)	-0.003(2)
C(4)	4e	0.3320(3)	0.8344(3)	0.0585(3)	0.027(3)	0.026(3)	0.017(3)	0.002(2)	0.006(2)	0.002(2)
C(5)	4e	0.3026(3)	0.7526(3)	0.0814(3)	0.024(3)	0.030(3)	0.016(3)	-0.001(2)	0.008(2)	-0.002(2)
C(6)	4e	0.3671(3)	0.5949(3)	0.1116(3)	0.033(3)	0.028(3)	0.031(3)	-0.004(2)	0.016(3)	-0.008(2)
C(7)	4e	0.5411(3)	0.7016(3)	0.1076(3)	0.029(3)	0.033(3)	0.027(3)	-0.002(3)	0.011(2)	-0.007(3)
C(8)	4e	0.4814(3)	0.8936(3)	0.0464(3)	0.033(3)	0.034(3)	0.029(3)	-0.003(3)	0.009(3)	0.007(3)
C(9)	4e	0.2764(3)	0.9161(3)	0.0304(3)	0.036(3)	0.034(3)	0.027(3)	0.006(3)	0.010(3)	0.005(3)
C(10)	4e	0.2077(3)	0.7330(4)	0.0766(4)	0.031(3)	0.041(3)	0.044(4)	0.003(3)	0.018(3)	0.001(3)
C(11)	4e	0.4069(3)	0.6959(3)	0.3188(3)	0.029(3)	0.020(3)	0.022(3)	-0.003(2)	0.004(2)	0.003(2)
C(12)	4e	0.4968(3)	0.7016(3)	0.3195(3)	0.026(3)	0.032(3)	0.015(3)	0.004(2)	0.005(2)	0.003(2)
C(13)	4e	0.5285(3)	0.7868(3)	0.3495(3)	0.024(3)	0.037(3)	0.022(3)	-0.003(3)	0.009(2)	-0.001(2)
C(14)	4e	0.4595(3)	0.8337(3)	0.3687(3)	0.031(3)	0.026(3)	0.013(3)	-0.004(2)	0.007(2)	0.000(2)
C(15)	4e	0.3851(3)	0.7767(3)	0.3504(3)	0.023(3)	0.022(3)	0.017(3)	-0.002(2)	0.004(2)	0.004(2)
C(16)	4e	0.5559(4)	0.6257(4)	0.3132(4)	0.037(3)	0.039(3)	0.031(3)	0.008(3)	0.008(3)	0.006(3)
C(17)	4e	0.6208(4)	0.8209(4)	0.3635(4)	0.038(4)	0.063(4)	0.043(4)	-0.016(3)	0.016(3)	-0.016(3)
C(18)	4e	0.4631(4)	0.9267(3)	0.4009(3)	0.045(3)	0.030(3)	0.031(3)	-0.011(3)	0.015(3)	-0.007(3)
C(19)	4e	0.2983(3)	0.7982(4)	0.3636(3)	0.032(3)	0.036(3)	0.032(3)	-0.004(3)	0.015(3)	-0.004(3)
C(20)	4e	0.3501(4)	0.6143(3)	0.3065(3)	0.043(3)	0.026(3)	0.032(3)	-0.009(3)	0.015(3)	0.001(3)
Ti(2)	4e	0.10451(6)	0.24612(6)	0.23852(6)	0.0306(6)	0.0183(5)	0.0289(6)	-0.0016(4)	0.0154(4)	-0.0028(4)
F(21)	4e	0.2224(2)	0.2428(2)	0.2381(2)	0.046(2)	0.021(2)	0.105(3)	-0.009(2)	0.049(2)	-0.015(2)
F(22)	4e	0.0492(3)	0.2546(2)	0.1164(2)	0.106(3)	0.023(2)	0.028(2)	-0.001(2)	0.027(2)	0.002(1)
C(21)	4e	0.0607(3)	0.1383(3)	0.3301(3)	0.032(3)	0.020(3)	0.029(3)	-0.004(2)	0.013(3)	0.001(2)
C(22)	4e	0.1470(3)	0.1175(3)	0.3294(3)	0.027(3)	0.021(3)	0.025(3)	0.000(2)	0.003(2)	0.002(2)
C(23)	4e	0.1394(3)	0.0902(3)	0.2422(3)	0.025(3)	0.010(3)	0.040(3)	0.001(2)	0.015(3)	0.003(2)
C(24)	4e	0.0500(3)	0.0977(3)	0.1899(3)	0.033(3)	0.016(3)	0.024(3)	-0.005(2)	0.010(3)	-0.001(2)
C(25)	4e	0.0009(3)	0.1299(3)	0.2428(3)	0.025(3)	0.016(3)	0.027(3)	-0.002(2)	0.006(2)	0.003(2)
C(26)	4e	0.0333(4)	0.1462(4)	0.4108(3)	0.051(4)	0.035(3)	0.029(3)	-0.005(3)	0.019(3)	-0.003(3)
C(27)	4e	0.2313(4)	0.1130(4)	0.4081(4)	0.038(3)	0.044(4)	0.045(4)	0.001(3)	0.000(3)	0.009(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(28)	4e	0.2160(4)	0.0592(4)	0.2147(4)	0.043(4)	0.025(3)	0.069(4)	0.004(3)	0.033(3)	0.001(3)
C(29)	4e	0.0089(4)	0.0735(4)	0.0942(3)	0.052(4)	0.034(3)	0.031(3)	−0.012(3)	0.015(3)	−0.006(3)
C(30)	4e	−0.0991(3)	0.1373(4)	0.2114(4)	0.029(3)	0.031(3)	0.044(3)	−0.002(3)	0.011(3)	0.005(3)
C(31)	4e	0.1199(3)	0.3499(3)	0.3598(3)	0.029(3)	0.021(3)	0.024(3)	−0.001(2)	0.012(3)	−0.009(2)
C(32)	4e	0.1728(3)	0.3811(3)	0.3108(3)	0.026(3)	0.019(3)	0.034(3)	−0.004(2)	0.013(3)	−0.012(2)
C(33)	4e	0.1167(3)	0.4027(3)	0.2247(3)	0.030(3)	0.012(3)	0.031(3)	0.000(2)	0.012(3)	−0.006(2)
C(34)	4e	0.0277(3)	0.3851(3)	0.2208(3)	0.033(3)	0.014(3)	0.036(3)	−0.001(2)	0.012(3)	−0.007(2)
C(35)	4e	0.0290(3)	0.3536(3)	0.3030(3)	0.028(3)	0.017(3)	0.036(3)	−0.005(2)	0.016(3)	−0.012(2)
C(36)	4e	0.1547(4)	0.3357(3)	0.4586(3)	0.041(3)	0.027(3)	0.031(3)	−0.001(3)	0.012(3)	−0.008(3)
C(37)	4e	0.2725(3)	0.3916(4)	0.3469(4)	0.033(3)	0.030(3)	0.040(3)	−0.005(3)	0.015(3)	−0.006(3)
C(38)	4e	0.1474(4)	0.4357(3)	0.1517(4)	0.040(3)	0.025(3)	0.041(3)	−0.005(3)	0.017(3)	−0.002(3)
C(39)	4e	−0.0554(3)	0.4006(4)	0.1425(4)	0.036(3)	0.035(3)	0.039(3)	0.002(3)	0.010(3)	−0.002(3)
C(40)	4e	−0.0530(3)	0.3440(4)	0.3295(4)	0.031(3)	0.029(3)	0.058(4)	0.001(3)	0.022(3)	0.002(3)

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References

1. Herzog, A.; Liu, F.-Q.; Roesky, H. W.; Demsar, A.; Keller, K.; Noltemeyer, M.; Pauer, F.: Trimethyltin Fluoride: A New Fluorinating Reagent for the Preparation of Organometallic Fluorides. Organometallics **13** (1994) 1251-1256.
2. Bareille, L.; Le Gendre, P.; Moise, C.: First catalytic allytitanation reactions. Chem. Commun. (2005) 775-777.
3. Liu, F.-Q.; Künzel, A.; Herzog, A.; Roesky, H. W.; Noltemeyer, M.; Fleischer, R.; Stalke, D.: Synthesis and structures of paramagnetic organo titanium fluoride clusters. Polyhedron **16** (1997) 61-65.
4. Liu, F.-Q.; Stalke, D.; Roesky, H. W.: $(C_5Me_5)TiF_2$ – A Versatile Building Block for Generating Large Soluble Dimetallic Aggregates. Angew. Chem., Int. Ed. Engl. **34** (1995) 1872-1874.
5. Myers, L. K.; Ho, D. M.; Thompson, M. E.; Langhoff, C.: Third Order Nonlinear Optical Properties Of Group 4 Metallocenes. Polyhedron **14** (1995) 57-67.
6. McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E.: The Crystal and Molecular Structure of Bis(pentamethylcyclopentadienyl)dichlorotitanium(IV). J. Organomet. Chem. **102** (1975) 457-466.
7. Lukens Jr., W. W.; Smith III, M. R.; Andersen, R. A.: A π-Donor Spectrochemical Series for X in $(Me_5C_5)_2TiX$, and β-Agostic Interactions in X = Et and N(Me)Ph. J. Am. Chem. Soc. **118** (1996) 1719-1728.
8. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 6.14. Bruker AXS, Madison, Wisconsin, USA 2000.
9. Dowty, E.: ATOMS. A Complete Program for Displaying Atomic Structures. Version 6.1. Shape Software, Kingsport, Tennessee, USA 2002.