Crystal structure of [1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)] [hydroxytris(pentafluorophenyl)borato]titanium(III), $C_{38}H_{24}BF_{15}OTi$

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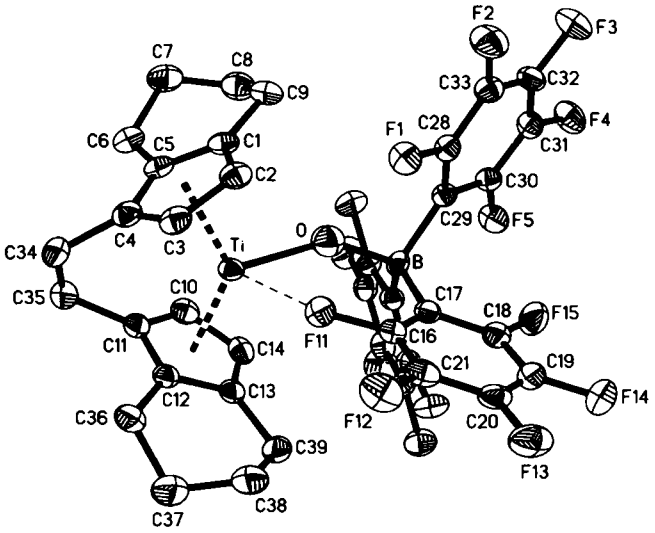

Abstract

$C_{38}H_{24}BF_{15}OTi$, monoclinic, $P12_1/c1$ (No. 14), a = 8.584(2) Å, b = 17.976(4) Å, c = 21.964(4) Å, β = 94.47(3)°, V = 3378.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.039, $wR_{all}(F^2)$ = 0.087, T = 293 K.

Source of material

An amount of 0.307 g (0.60 mmol) of $B(C_6F_5)_3$ was dissolved in 15 ml of *n*-hexane under Ar, and the obtained solution was added to a solution of 0.280 g (0.60 mmol) rac-(ebthi)Ti($Me_3SiC_2SiMe_3$) in 10 ml of *n*-hexane. The resulting yellow-brownish mixture was filtered and allowed to stand in argon atmosphere at room temperature. In two days, the yellow-greenish solution was filtered from a small amount (0.030 g) of mixture of green [rac-(ebthi)Ti]$^+$-[(η^2-$Me_3SiC_2B(C_6F_5)_3$]$^-$, blue crystals of [rac-(ebthi)Ti]$^+$-[$HOB(C_6F_5)_3$]$^-$ and blue crystals of a third compound which was assumed to be [rac-(ebthi)Ti]$^+$[$HB(C_6F_5)_3$]$^-$. The crystals were separated from the mother liquor by decanting, washed with *n*-hexane, and dried in vacuum. ESR results are included in the deposited CIF file.

Experimental details

The H-atom attached to oxygen could not be localized and is not added in a calculated position. This hydrogen is only added in the sum formula (to give a correct formula) due to the described bonding situation.

Discussion

Zwitterionic group 4 metallocene alkyl complexes [Cp_2MR]$^+$-[$RB(C_6F_5)_3$]$^-$, formed by alkyl anion abstraction starting from the Cp_2MR_2 and the Lewis acid $B(C_6F_5)_3$, are very active catalysts in polymerization of olefins [1]. Also metallocene complexes with olefins or alkynes give with tris(pentafluorphenyl)borane such active catalysts [2]. We found in reactions of metallocene complexes with silylalkynes $L_2Ti(\eta^2$-$Me_3SiC_2SiMe_3)$ for L = Cp and Cp* the formation of special zwitterionic complexes after elimination of the alkyne and a electrophilic substitution at the C—H bond with C—B-bond formation [3-5]. Here we describe the structure of the blue zwitterionic [1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)][hydroxytris(pentafluorophenyl)borato]titanium(III) [rac-(ebthi)Ti]$^+$[$HOB(C_6F_5)_3$]$^-$ isolated in the reaction of rac-(ebthi)Ti(η^2-Me_3SiC_2R), R = $SiMe_3$ [6] or *t*-Bu (prepared as in [6]), with $B(C_6F_5)_3$ with traces of water. Actually, the aqua complex H_2O-$B(C_6F_5)_3$ [7] is reacting as a Brønsted acid and always mixtures of different complexes were obtained. Starting from rac-(ebthi)Ti(η^2-$Me_3SiC_2SiMe_3$) the main product is the green complex [rac-(ebthi)Ti]$^+$[(η^2-$Me_3SiC_2B(C_6F_5)_3$]$^-$ [8] and as another byproduct the zwitterionic [1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)][hydridotris(pentafluorophenyl)borato]titanium(III) [rac-(ebthi)Ti]$^+$[$HB(C_6F_5)_3$]$^-$ is assumed.

The molecular structure of [rac-(ebthi)Ti]$^+$[$HOB(C_6F_5)_3$]$^-$ (d(Ti—O) = 2.097(3) Å, d(O—B) = 1.482(4) Å) is comparable with the titanocene complex (Cp^B)CpTi(μ-OH)Cl (Cp^B = η^5-$C_5H_4B(C_6F_5)_2$) (d(Ti—O) = 2.044(1) Å, d(O—B) = 1.532(3) Å) [9]. Therefore, its structure can be described in the same manner as the donor complex between the cationic titanium centre and the HO-$B(C_6F_5)_3$ borate anion. The B—O distance of 1.495(5) Å in the title compound is the similar to that found for [Et_3NH]$^+$[$(C_6F_5)_3BOH$]$^-$ [10]. The hydrogen atom at the oxygen in [rac-(ebthi)Ti]$^+$ [$HOB(C_6F_5)_3$]$^-$ can't be localized, but because of the described bonding situation there has to be one. Additionally the title compound is paramagnetic.

Table 1. Data collection and handling.

Crystal:	blue prism, size 0.3 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.70 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 100 exposures, $\Delta\varphi$ = 2°
$2\theta_{max}$:	48.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9996, 5356
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3082
$N(param)_{refined}$:	505
Programs:	SHELXS-86 [11], SHELXL-93 [12]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.7534(4)	0.3755(2)	0.5482(2)	0.056
H(3)	4*e*	0.8774(4)	0.3605(2)	0.4501(2)	0.057
H(6A)	4*e*	1.3000(4)	0.4891(2)	0.5649(2)	0.066
H(6B)	4*e*	1.3317(4)	0.4152(2)	0.6019(2)	0.066
H(7A)	4*e*	1.3111(4)	0.5040(2)	0.6742(2)	0.081
H(7B)	4*e*	1.1637(4)	0.5396(2)	0.6389(2)	0.081
H(8A)	4*e*	1.0979(4)	0.4721(2)	0.7244(2)	0.077
H(8B)	4*e*	1.1614(4)	0.3995(2)	0.6954(2)	0.077
H(9A)	4*e*	0.8980(4)	0.3945(2)	0.6724(1)	0.066
H(9B)	4*e*	0.8895(4)	0.4787(2)	0.6534(1)	0.066
H(10)	4*e*	1.3578(4)	0.2792(2)	0.5985(2)	0.057
H(14)	4*e*	1.2041(4)	0.1635(2)	0.6121(1)	0.057

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(34A)	4*e*	1.2522(4)	0.4451(2)	0.4475(2)	0.071
H(34B)	4*e*	1.1651(4)	0.3786(2)	0.4131(2)	0.071
H(35A)	4*e*	1.3992(4)	0.3261(2)	0.4423(2)	0.070
H(35B)	4*e*	1.4132(4)	0.3684(2)	0.5051(2)	0.070
H(36A)	4*e*	1.2067(4)	0.2307(2)	0.3856(1)	0.069
H(36B)	4*e*	1.0350(4)	0.2524(2)	0.3983(1)	0.069
H(37A)	4*e*	1.0139(5)	0.1392(2)	0.3522(2)	0.096
H(37B)	4*e*	1.1563(5)	0.1071(2)	0.3930(2)	0.096
H(38A)	4*e*	0.9202(5)	0.0614(2)	0.4226(2)	0.095
H(38B)	4*e*	0.8679(5)	0.1427(2)	0.4369(2)	0.095
H(39A)	4*e*	0.9540(4)	0.0965(2)	0.5299(2)	0.069
H(39B)	4*e*	1.1006(4)	0.0590(2)	0.5042(2)	0.069

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}
O	4*e*	0.9507(3)	0.2611(1)	0.6357(1)	0.084(2)	0.066(2)	0.073(2)	0.007(1)	0.012(1)	0.001(1)
C(1)	4*e*	0.9694(4)	0.4123(2)	0.5868(1)	0.050(2)	0.032(2)	0.051(2)	0.012(2)	–0.003(2)	–0.002(2)
C(2)	4*e*	0.8573(4)	0.3857(2)	0.5421(2)	0.042(2)	0.038(2)	0.059(2)	0.013(2)	–0.004(2)	0.002(2)
C(3)	4*e*	0.9268(4)	0.3769(2)	0.4869(2)	0.059(2)	0.038(2)	0.044(2)	0.006(2)	–0.009(2)	0.004(2)
C(4)	4*e*	1.0863(4)	0.3976(2)	0.4973(1)	0.065(2)	0.033(2)	0.042(2)	0.005(2)	0.000(2)	0.005(2)
C(5)	4*e*	1.1111(4)	0.4194(2)	0.5595(1)	0.056(2)	0.027(2)	0.049(2)	0.004(2)	–0.004(2)	–0.002(2)
C(6)	4*e*	1.2548(4)	0.4537(2)	0.5918(2)	0.062(2)	0.039(2)	0.063(2)	–0.002(2)	–0.001(2)	–0.003(2)
C(7)	4*e*	1.2153(4)	0.4928(2)	0.6496(2)	0.067(3)	0.059(3)	0.074(3)	0.001(2)	–0.008(2)	–0.020(2)
C(8)	4*e*	1.1117(4)	0.4471(2)	0.6861(2)	0.074(3)	0.065(3)	0.054(2)	0.004(2)	–0.003(2)	–0.013(2)
C(9)	4*e*	0.9519(4)	0.4338(2)	0.6523(1)	0.062(2)	0.049(2)	0.055(2)	0.013(2)	0.004(2)	–0.013(2)
C(10)	4*e*	1.2958(4)	0.2547(2)	0.5682(2)	0.037(2)	0.053(2)	0.052(2)	0.011(2)	0.001(2)	–0.004(2)
C(11)	4*e*	1.2721(4)	0.2765(2)	0.5063(1)	0.047(2)	0.041(2)	0.049(2)	0.007(2)	0.013(2)	0.000(2)
C(12)	4*e*	1.1684(4)	0.2245(2)	0.4765(1)	0.051(2)	0.038(2)	0.043(2)	0.008(2)	0.010(2)	–0.002(2)
C(13)	4*e*	1.1308(4)	0.1705(2)	0.5194(1)	0.048(2)	0.035(2)	0.050(2)	0.011(2)	0.015(2)	0.002(2)
C(14)	4*e*	1.2090(4)	0.1897(2)	0.5758(1)	0.050(2)	0.048(2)	0.047(2)	0.021(2)	0.014(2)	0.013(2)
C(16)	4*e*	0.7139(4)	0.1727(2)	0.5636(1)	0.044(2)	0.038(2)	0.044(2)	0.003(2)	0.007(2)	–0.004(2)
C(17)	4*e*	0.7491(3)	0.1583(2)	0.6243(1)	0.048(2)	0.036(2)	0.036(2)	0.004(2)	0.006(2)	–0.003(1)
C(18)	4*e*	0.6527(4)	0.1046(2)	0.6466(2)	0.061(2)	0.046(2)	0.042(2)	–0.002(2)	0.009(2)	–0.005(2)
C(19)	4*e*	0.5369(4)	0.0680(2)	0.6121(2)	0.051(2)	0.045(2)	0.081(3)	–0.007(2)	0.021(2)	–0.013(2)
C(20)	4*e*	0.5095(4)	0.0853(2)	0.5519(2)	0.034(2)	0.054(2)	0.073(3)	–0.001(2)	0.000(2)	–0.031(2)
C(21)	4*e*	0.5977(4)	0.1384(2)	0.5269(2)	0.048(2)	0.058(3)	0.044(2)	0.012(2)	–0.007(2)	–0.013(2)
C(22)	4*e*	1.0461(4)	0.0771(2)	0.6915(1)	0.052(2)	0.041(2)	0.039(2)	0.002(2)	0.005(2)	0.003(2)
C(23)	4*e*	1.1695(4)	0.0382(2)	0.7200(2)	0.060(2)	0.035(2)	0.056(2)	0.008(2)	0.016(2)	0.011(2)
C(24)	4*e*	1.2759(4)	0.0738(2)	0.7591(2)	0.041(2)	0.063(3)	0.058(2)	0.011(2)	0.003(2)	0.016(2)
C(25)	4*e*	1.2591(4)	0.1483(2)	0.7683(2)	0.041(2)	0.059(3)	0.053(2)	–0.006(2)	0.001(2)	0.003(2)
C(26)	4*e*	1.1360(4)	0.1857(2)	0.7391(1)	0.054(2)	0.036(2)	0.047(2)	0.000(2)	0.008(2)	0.000(2)
C(27)	4*e*	1.0217(4)	0.1526(2)	0.7004(1)	0.051(2)	0.039(2)	0.032(2)	0.003(2)	0.005(2)	0.001(1)
C(28)	4*e*	0.6676(3)	0.2977(2)	0.7027(1)	0.045(2)	0.041(2)	0.035(2)	–0.002(2)	–0.001(1)	0.003(2)
C(29)	4*e*	0.7768(3)	0.2440(2)	0.7205(1)	0.042(2)	0.035(2)	0.037(2)	–0.002(1)	0.000(1)	–0.002(1)
C(30)	4*e*	0.7764(4)	0.2264(2)	0.7821(1)	0.047(2)	0.039(2)	0.041(2)	0.003(2)	0.000(2)	–0.001(2)
C(31)	4*e*	0.6809(4)	0.2594(2)	0.8215(1)	0.059(2)	0.053(2)	0.031(2)	–0.006(2)	0.006(2)	–0.001(2)
C(32)	4*e*	0.5795(4)	0.3133(2)	0.8013(2)	0.050(2)	0.051(2)	0.050(2)	0.002(2)	0.012(2)	–0.015(2)
C(33)	4*e*	0.5719(4)	0.3325(2)	0.7410(2)	0.038(2)	0.042(2)	0.061(2)	0.006(2)	–0.002(2)	0.000(2)
C(34)	4*e*	1.2102(4)	0.3955(2)	0.4525(2)	0.080(3)	0.044(2)	0.055(2)	–0.007(2)	0.016(2)	0.007(2)
C(35)	4*e*	1.3414(4)	0.3426(2)	0.4760(2)	0.063(2)	0.053(3)	0.061(2)	–0.007(2)	0.017(2)	–0.005(2)
C(36)	4*e*	1.1194(4)	0.2177(2)	0.4091(1)	0.075(2)	0.055(3)	0.045(2)	0.003(2)	0.015(2)	–0.006(2)
C(37)	4*e*	1.0658(5)	0.1394(2)	0.3930(2)	0.105(3)	0.067(3)	0.068(3)	–0.011(2)	0.011(2)	–0.016(2)
C(38)	4*e*	0.9575(5)	0.1099(2)	0.4365(2)	0.094(3)	0.069(3)	0.077(3)	–0.018(2)	0.015(3)	–0.030(2)
C(39)	4*e*	1.0343(4)	0.1028(2)	0.5016(2)	0.058(2)	0.039(2)	0.078(3)	0.004(2)	0.020(2)	–0.003(2)
B	4*e*	0.8763(4)	0.2018(2)	0.6703(2)	0.052(2)	0.033(2)	0.037(2)	–0.004(2)	0.007(2)	0.008(2)
F(1)	4*e*	0.6496(2)	0.3179(1)	0.64286(8)	0.059(1)	0.062(1)	0.048(1)	0.0111(9)	–0.0022(9)	0.0113(9)
F(2)	4*e*	0.4697(2)	0.3843(1)	0.71925(9)	0.065(1)	0.074(2)	0.087(2)	0.029(1)	0.005(1)	0.007(1)
F(3)	4*e*	0.4832(2)	0.3453(1)	0.83878(9)	0.082(2)	0.091(2)	0.075(1)	0.020(1)	0.026(1)	–0.018(1)
F(4)	4*e*	0.6859(2)	0.2366(1)	0.88032(8)	0.085(2)	0.094(2)	0.042(1)	0.008(1)	0.016(1)	0.001(1)
F(5)	4*e*	0.8711(2)	0.1720(1)	0.80690(8)	0.073(1)	0.063(1)	0.046(1)	0.017(1)	0.0065(9)	0.0109(9)
F(6)	4*e*	1.1259(2)	0.2591(1)	0.75095(9)	0.068(1)	0.046(1)	0.074(1)	–0.003(1)	–0.007(1)	–0.009(1)
F(7)	4*e*	1.3632(2)	0.1840(1)	0.8072(1)	0.057(1)	0.089(2)	0.088(2)	–0.007(1)	–0.015(1)	–0.004(1)
F(8)	4*e*	1.3936(2)	0.0364(1)	0.7882(1)	0.061(1)	0.093(2)	0.111(2)	0.024(1)	–0.009(1)	0.023(1)
F(9)	4*e*	1.1852(2)	–0.0353(1)	0.70965(9)	0.080(1)	0.044(1)	0.091(2)	0.020(1)	0.008(1)	0.007(1)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(10)	4e	0.9485(2)	0.0368(1)	0.65339(8)	0.080(1)	0.041(1)	0.065(1)	0.007(1)	-0.010(1)	-0.0115(9)
F(11)	4e	0.7991(2)	0.2253(1)	0.53384(7)	0.061(1)	0.052(1)	0.041(1)	-0.0006(9)	-0.0015(9)	0.0041(9)
F(12)	4e	0.5702(2)	0.1568(1)	0.46793(9)	0.072(1)	0.099(2)	0.052(1)	0.006(1)	-0.017(1)	-0.011(1)
F(13)	4e	0.3953(2)	0.0506(1)	0.5174(1)	0.051(1)	0.085(2)	0.113(2)	-0.001(1)	-0.005(1)	-0.046(1)
F(14)	4e	0.4491(3)	0.0161(1)	0.6375(1)	0.086(2)	0.071(2)	0.116(2)	-0.031(1)	0.033(1)	-0.015(1)
F(15)	4e	0.6738(2)	0.0858(1)	0.70640(9)	0.097(2)	0.063(1)	0.059(1)	-0.020(1)	0.019(1)	0.007(1)
Ti	4e	1.03820(6)	0.28990(3)	0.55231(2)	0.0440(3)	0.0321(3)	0.0360(3)	0.0076(3)	0.0025(2)	0.0003(3)

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