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Crystal structure of (η^5-pentamethylcyclopentadienyl)(η^5-1-(2,2-dimethylpropyl)cyclopentadienyl)(hydroxy)titaniumchloride, $C_{20}H_{31}ClOTi$

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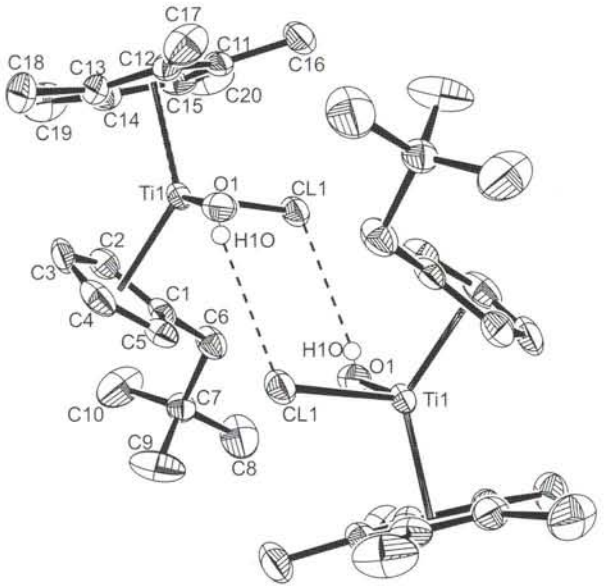

Abstract

$C_{20}H_{31}ClOTi$, monoclinic, $P12_1/c1$ (No. 14), $a = 12.8041(9)$ Å, $b = 9.2935(4)$ Å, $c = 17.348(1)$ Å, $\beta = 110.027(7)°$, $V = 1939.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.033$, $wR_{ref}(F^2) = 0.078$, $T = 193$ K.

Source of material

0.09 g (5.0 mmol) water (in 5 ml of THF) was added to a stirred solution of 1.764 g (5.0 mmol) of Cp*Ti(η^6-$C_5H_4C(H)^tBu$)Cl in 20 ml of THF at ambient temperature. The colour of the reaction mixture changed immediately from green to orange. After stirring the solution at 298 K for an additional 0.5 h the solvent was removed in vacuo and the product was recrystallized from *n*-hexane (10 ml); by fractionated crystallization suitable crystals for diffraction are obtained at 273 K, crystallization at 213 K yields 1.52 g (82%) Cp*(η^5-$C_5H_4CH_2C(CH_3)_3$)Ti(OH)Cl.

Discussion

Pentafulvene complexes of titanium are easily available through reductive complexation of fulvenes to cyclopentadienyltitanium fragments [1]. Due to the strong nucleophilic reactivity of the dianionic fulvene ligand, substituted titanocene derivatives are formed with electrophiles. In such a manner the title compound is formed from Cp*Ti(η^6-$C_5H_4C(H)^tBu$)Cl and water. The crystal structure of the reaction product shows weak intermolecular O–H···Cl interaction (d(O···Cl) = 338.1 pm). Concentration dependence of the ^{1}H-NMR chemical shift of the hydroxid proton (Ti—OH, 0.1 M: 8.72 ppm, 0.001 M: 8.46 ppm) point out that this interaction also exists in solution. Using Cp instead of Cp* ligands, the Ti–O–Ti species are formed [2,3].

Table 1. Data collection and handling.

Crystal:	orange prism, size 0.10 × 0.23 × 0.45 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.82 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 127 exposures, $\Delta\varphi = 1.5°$
$2\theta_{max}$:	52.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13957, 3766
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2584
$N(param)_{refined}$:	332
Programs:	SHELXS-97 [4], SHELXL-97 [5] ORTEP-3 [6]

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

Atom	Site	x	y	z	U_{iso}
H(1O)	4*e*	0.484(2)	0.007(3)	0.102(2)	0.012(9)
H(2)	4*e*	0.095(2)	0.070(3)	–0.077(2)	0.034(6)
H(3)	4*e*	0.153(2)	–0.043(3)	0.060(2)	0.046(8)
H(4)	4*e*	0.321(2)	–0.179(3)	0.086(2)	0.049(8)
H(5)	4*e*	0.376(2)	–0.160(3)	–0.032(2)	0.042(8)
H(6A)	4*e*	0.309(2)	–0.012(3)	–0.173(2)	0.039(7)
H(6B)	4*e*	0.205(2)	0.079(3)	–0.189(2)	0.045(8)
H(8A)	4*e*	0.260(5)	–0.106(6)	–0.309(3)	0.15(2)
H(8B)	4*e*	0.144(2)	–0.019(3)	–0.329(2)	0.041(9)
H(8C)	4*e*	0.136(3)	–0.163(4)	–0.356(2)	0.07(1)
H(9A)	4*e*	0.272(4)	–0.276(5)	–0.200(3)	0.10(2)
H(9B)	4*e*	0.159(3)	–0.338(4)	–0.249(2)	0.07(1)
H(9C)	4*e*	0.193(4)	–0.302(5)	–0.155(3)	0.11(2)
H(10A)	4*e*	0.026(4)	–0.006(5)	–0.268(3)	0.12(2)
H(10B)	4*e*	0.024(3)	–0.109(4)	–0.197(3)	0.09(1)
H(10C)	4*e*	0.002(3)	–0.173(4)	–0.284(2)	0.07(1)
H(16A)	4*e*	0.435(3)	0.493(4)	0.033(3)	0.09(1)
H(16B)	4*e*	0.520(3)	0.403(4)	0.084(2)	0.08(1)
H(16C)	4*e*	0.464(3)	0.534(5)	0.114(3)	0.11(2)
H(17A)	4*e*	0.455(4)	0.219(5)	0.277(3)	0.11(2)
H(17B)	4*e*	0.508(4)	0.336(6)	0.254(3)	0.12(2)
H(17C)	4*e*	0.513(4)	0.164(5)	0.233(3)	0.10(1)
H(18A)	4*e*	0.173(3)	0.083(4)	0.182(2)	0.07(1)
H(18B)	4*e*	0.251(3)	0.164(4)	0.253(2)	0.07(1)
H(18C)	4*e*	0.288(3)	0.031(5)	0.224(2)	0.10(1)
H(19A)	4*e*	0.044(4)	0.147(5)	0.052(3)	0.12(2)
H(19B)	4*e*	0.046(3)	0.279(4)	–0.008(3)	0.08(1)
H(19C)	4*e*	0.039(3)	0.327(4)	0.068(2)	0.08(1)
H(20A)	4*e*	0.262(3)	0.474(4)	–0.056(2)	0.08(1)
H(20B)	4*e*	0.188(3)	0.549(5)	–0.020(2)	0.09(1)
H(20C)	4*e*	0.166(3)	0.405(5)	–0.076(3)	0.10(1)

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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*	0.32809(3)	0.12030(4)	0.03714(2)	0.0249(2)	0.0238(2)	0.0200(2)	–0.0069(2)	0.0072(1)	–0.0002(2)
Cl(1)	4*e*	0.39150(5)	0.22516(6)	–0.06499(3)	0.0435(3)	0.0315(3)	0.0292(3)	–0.0126(2)	0.0166(2)	–0.0030(2)
O(1)	4*e*	0.4698(2)	0.0582(2)	0.1053(1)	0.034(1)	0.030(1)	0.043(1)	–0.0018(9)	0.0140(8)	–0.0085(9)
C(1)	4*e*	0.2378(2)	–0.0338(2)	–0.0868(1)	0.031(1)	0.026(1)	0.027(1)	–0.0128(9)	0.0060(9)	–0.0038(9)
C(2)	4*e*	0.1599(2)	0.0133(3)	–0.0512(2)	0.028(1)	0.037(1)	0.038(1)	–0.011(1)	0.007(1)	–0.009(1)
C(3)	4*e*	0.1895(2)	–0.0491(3)	0.0282(2)	0.051(2)	0.047(2)	0.039(2)	–0.032(1)	0.026(1)	–0.013(1)
C(4)	4*e*	0.2847(2)	–0.1278(3)	0.0421(2)	0.056(2)	0.030(1)	0.031(1)	–0.016(1)	0.007(1)	0.004(1)
C(5)	4*e*	0.3171(2)	–0.1172(2)	–0.0275(1)	0.038(1)	0.025(1)	0.033(1)	–0.007(1)	0.007(1)	–0.005(1)
C(6)	4*e*	0.2338(2)	–0.0104(3)	–0.1730(2)	0.043(2)	0.038(1)	0.027(1)	–0.014(1)	0.008(1)	–0.003(1)
C(7)	4*e*	0.1621(2)	–0.1209(3)	–0.2354(1)	0.031(1)	0.036(1)	0.024(1)	–0.007(1)	0.0063(9)	–0.006(1)
C(8)	4*e*	0.1838(4)	–0.0998(5)	–0.3160(2)	0.074(2)	0.087(3)	0.033(2)	–0.031(2)	0.015(2)	–0.016(2)
C(9)	4*e*	0.1969(4)	–0.2730(4)	–0.2060(3)	0.094(3)	0.041(2)	0.055(2)	0.001(2)	0.002(2)	–0.018(2)
C(10)	4*e*	0.0409(3)	–0.1049(6)	–0.2468(3)	0.035(2)	0.110(3)	0.056(2)	–0.003(2)	0.001(1)	–0.041(2)
C(11)	4*e*	0.3664(2)	0.3621(2)	0.0942(1)	0.043(1)	0.028(1)	0.024(1)	–0.011(1)	0.017(1)	–0.0090(9)
C(12)	4*e*	0.3740(2)	0.2718(2)	0.1603(1)	0.029(1)	0.034(1)	0.020(1)	–0.0033(9)	0.0081(9)	–0.0052(9)
C(13)	4*e*	0.2687(2)	0.2083(2)	0.1463(1)	0.034(1)	0.032(1)	0.029(1)	–0.0048(9)	0.017(1)	–0.003(1)
C(14)	4*e*	0.1939(2)	0.2674(3)	0.0725(2)	0.027(1)	0.040(1)	0.037(1)	–0.001(1)	0.006(1)	–0.011(1)
C(15)	4*e*	0.2542(2)	0.3604(2)	0.0394(1)	0.050(1)	0.029(1)	0.023(1)	0.006(1)	0.010(1)	0.000(1)
C(16)	4*e*	0.4583(4)	0.4556(4)	0.0877(2)	0.091(3)	0.054(2)	0.057(2)	–0.045(2)	0.050(2)	–0.027(2)
C(17)	4*e*	0.4753(2)	0.2511(4)	0.2344(2)	0.038(2)	0.072(2)	0.026(1)	0.003(2)	0.003(1)	–0.008(2)
C(18)	4*e*	0.2428(3)	0.1152(4)	0.2077(2)	0.065(2)	0.052(2)	0.046(2)	–0.014(2)	0.036(2)	–0.000(2)
C(19)	4*e*	0.0692(2)	0.2531(5)	0.0438(3)	0.029(2)	0.079(3)	0.072(3)	0.006(2)	0.003(2)	–0.024(2)
C(20)	4*e*	0.2069(4)	0.4538(4)	–0.0344(2)	0.106(3)	0.050(2)	0.036(2)	0.028(2)	0.017(2)	0.012(2)

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