Crystal structure of (η^5 -pentamethylcyclopentadienyl)(η^5 -1-(2,2-dimethylpropyl)cyclopentadienyl)titaniumdichloride, $C_{20}H_{30}Cl_2Ti$

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exocyclic carbon atom of the fulvene ligand [4] with HCl.

The crystal structure of the reaction product shows the metal atom residing on a crystallographic mirror plane bisecting the two staggered cyclopentadienyl rings.

Table 1. Data collection and handling.

Crystal:	red needle, size 0.10 × 0.10 × 0.70 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	6.86 cm ⁻¹
Diffractometer, scan mode:	Stoe IPDS, 136 exposures, $\Delta\varphi = 1.4^\circ$
$2\theta_{\max}$:	52.06°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	14106, 1909
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1286
$N(\text{param})_{\text{refined}}$:	175
Programs:	SHELXS-97 [5], SHELXL-97 [6] ORTEP-3 [7]

Abstract

$C_{20}H_{30}Cl_2Ti$, orthorhombic, $Pnma$ (No. 62), $a = 14.3763(8)$ Å, $b = 12.105(1)$ Å, $c = 11.6138(9)$ Å, $V = 2021.0$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.032$, $wR_{\text{ref}}(F^2) = 0.062$, $T = 193$ K.

Source of material

An excess of HCl-gas (99.9 %, Aldrich) was bubbled in a solution of 1.764 g (5.0 mmol) of $Cp^*Ti(\eta^6-C_5H_4C(H)Bu)Cl$ in 20 ml of THF at ambient temperature. The colour of the reaction mixture changed immediately from green to red. 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, the suitable crystals for diffraction are obtained at 273 K, crystallization at 213 K yields 1.654 g (85%) $Cp^*(\eta^5-C_5H_4CH_2C(CH_3)_3)TiCl_2$.

Discussion

It is well established that replacement of an η^5 -cyclopentadienyl ligand by an η^5 -pentamethylcyclopentadienyl ligand in transition metal complexes results in significant changes in reactivity, stability and other properties, owing to both steric as well as to electronic effects that accomplish replacement of the hydrogen atoms by methyl groups [1–3]. In this context use of monosubstituted η^5 -cyclopentadienyl ligands and their effects on structural properties are of high interest. Bent-metallocenes with one monosubstituted η^5 -cyclopentadienyl ligand are easily available by reaction of pentafulvene titanium complexes substituted at the

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	8d	1.015(2)	0.352(2)	0.255(2)	0.031(6)
H(2)	8d	0.910(2)	0.414(2)	0.409(2)	0.036(7)
H(4)	8d	0.780(2)	0.185(2)	0.546(2)	0.031(6)
H(6A)	8d	0.894(3)	0.422(3)	0.674(3)	0.09(1)
H(6B)	8d	0.985(3)	0.351(3)	0.626(3)	0.09(1)
H(6C)	8d	0.966(2)	0.355(2)	0.762(3)	0.068(9)
H(7A)	8d	0.759(4)	0.186(4)	0.754(4)	0.130
H(7B)	4c	0.833(5)	1/4	0.835(6)	0.130
H(11A)	8d	1.053(2)	0.189(2)	0.070(2)	0.062(9)
H(11B)	4c	1.024(3)	1/4	−0.035(4)	0.05(1)
H(12A)	8d	0.948(3)	0.472(2)	0.093(2)	0.050(9)
H(12B)	8d	0.853(2)	0.503(2)	0.117(2)	0.048(8)
H(12C)	8d	0.879(2)	0.491(2)	−0.011(3)	0.06(1)
H(13A)	8d	0.685(3)	0.445(3)	0.073(3)	0.07(1)
H(13B)	8d	0.627(3)	0.352(3)	0.062(3)	0.07(1)
H(13C)	8d	0.678(2)	0.396(2)	−0.043(3)	0.065(9)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ti(1)	4c	0.83053(4)	1/4	0.24591(4)	0.0177(3)	0.0283(3)	0.0125(2)	0	0.0013(2)	0
Cl(1)	8d	0.72965(5)	0.10689(5)	0.30347(5)	0.0351(4)	0.0427(3)	0.0258(3)	-0.0100(3)	0.0022(3)	0.0077(2)
C(1)	8d	0.9793(2)	0.3085(2)	0.3011(2)	0.022(2)	0.070(2)	0.021(1)	-0.013(1)	-0.005(1)	0.001(1)
C(2)	8d	0.9221(2)	0.3431(2)	0.3915(2)	0.033(2)	0.044(2)	0.020(1)	-0.007(1)	-0.009(1)	-0.003(1)
C(3)	4c	0.8854(3)	1/4	0.4484(2)	0.026(2)	0.045(2)	0.015(2)	0	-0.005(1)	0
C(4)	4c	0.8226(3)	1/4	0.5506(2)	0.036(3)	0.053(2)	0.017(2)	0	0.003(2)	0
C(5)	4c	0.8739(3)	1/4	0.6688(3)	0.052(3)	0.049(2)	0.018(2)	0	-0.002(2)	0
C(6)	8d	0.9341(3)	0.3521(3)	0.6821(3)	0.093(3)	0.047(2)	0.034(2)	-0.008(2)	-0.021(2)	-0.003(1)
C(7)	4c	0.7992(5)	1/4	0.7622(4)	0.090(5)	0.152(6)	0.017(2)	0	0.012(2)	0
C(8)	4c	0.9174(2)	1/4	0.0672(2)	0.020(2)	0.042(2)	0.011(1)	0	0.002(1)	0
C(9)	8d	0.8586(2)	0.3445(2)	0.0700(2)	0.025(2)	0.035(1)	0.0146(9)	-0.001(1)	0.0033(8)	0.0039(8)
C(10)	8d	0.7651(2)	0.3078(2)	0.0608(2)	0.023(2)	0.041(1)	0.0124(9)	0.002(1)	0.0028(9)	0.0025(8)
C(11)	4c	1.0193(3)	1/4	0.0429(3)	0.020(3)	0.057(3)	0.021(2)	0	0.005(1)	0
C(12)	8d	0.8879(3)	0.4627(2)	0.0669(3)	0.040(2)	0.036(2)	0.045(2)	-0.003(1)	0.006(1)	0.009(1)
C(13)	8d	0.6838(2)	0.3801(3)	0.0361(2)	0.027(2)	0.058(2)	0.030(1)	0.012(1)	0.003(1)	0.010(1)

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