Crystal structure of bis(η^5-cyclopentadienyl)-pyrrolide-titanium(III), $Ti(C_{10}H_{15})_2(C_4H_4N)$

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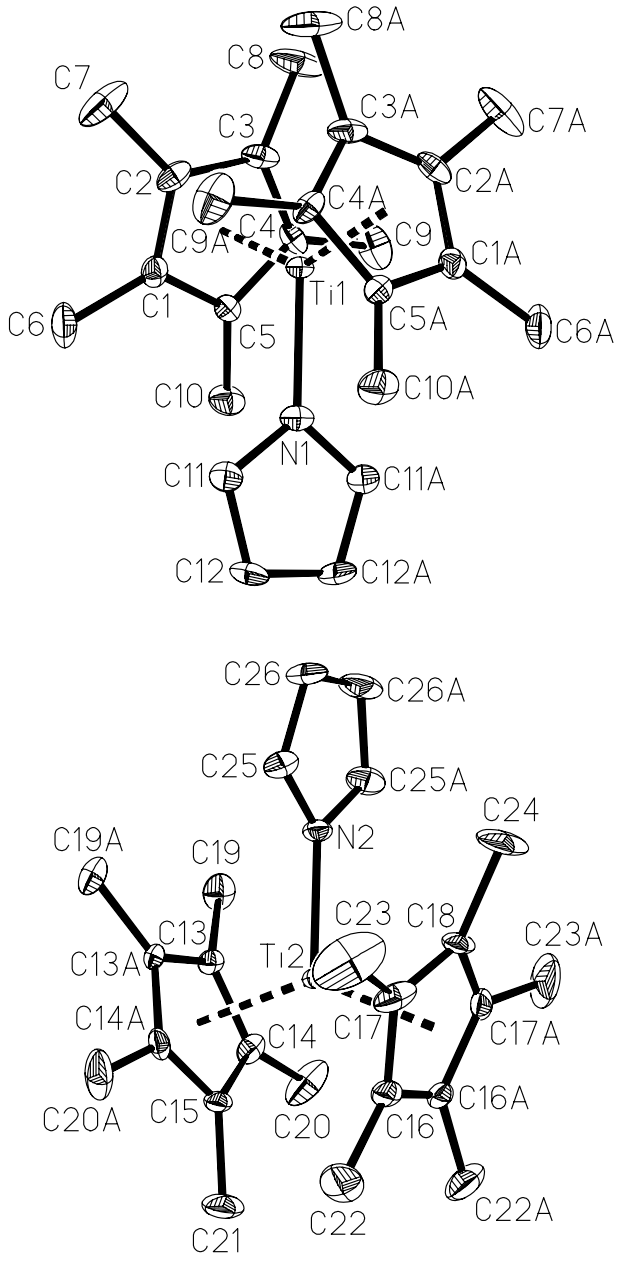

Abstract

$C_{24}H_{34}NTi$, orthorhombic, *Pbcm* (no. 57), a = 10.864(2) Å, b = 14.281(3) Å, c = 27.535(6) Å, V = 4272.0 Å^3, Z = 8, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.111, T = 200 K.

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Source of material

Pyrrole (0.9 mL, 13.0 mmol) was added to $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Cp^* = C_5Me_5, 0.256 g, 0.52 mmol). The reaction mixture was stirred at 393 K for 12 days. After cooling the solution to room temperature dark green crystals had formed which were separated from the mother liquor by decanting, washed with *n*-hexane, and dried in vacuum (yield 0.110 g, 49.6 %).

Discussion

The activation of several bonds in reactions of different titanocene and zirconocene complexes of bis(trimethylsilyl)acetylene was described in several reviews [1-4]. For example, cleavage of C—H, C—C, Si—C, N—H, N—C, N—N, N—O, C—O, C—F and C—B bonds gave complexes of potential applicability in stoichiometric and catalytic reactions. Very recently Beckhaus and coworkers published a series of examples for reactions of titanocene bis(trimethylsilyl)acetylene complexes with different N-heterocyclic compounds. After dissociation of the alkyne the titanocene "Cp'_2Ti" (Cp' = substituted cyclopentadienyl) sources dimerize and trimerize the heterocycles to exciting compounds [5]. In the activation of pyrrole a typical different reaction behavior of titanocene and zirconocene bis(trimethylsilyl)acetylene complexes is obtained giving for titanium a favored release of the alkyne with formation of Ti(III) complexes. For zirconium the formation of Zr(IV) complexes took place and the formed compound $Cp^*_2Zr(NC_4H_4)[C(SiMe_3)=CH(SiMe_3)]$ was confirmed by X-ray crystal structure analysis [6].

The molecular structure of the paramagnetic titanocene compound $Cp^*_2Ti(\eta^1\text{-}NC_4H_4)$ shows behind the two bent cyclopentadienyl rings the pyrrolide ligand coordinated in an η^1-manner to the central metal atom. Two molecules are in the asymmetric unit. The Ti—N distances are with 2.096(4) Å and 2.100(3) Å comparable with those in other complexes as the $Cp_2Ti(\eta^1\text{-}NC_4H_4)$ (d(Ti—N) = 2.090(1) Å [6]) and the Ti(IV) bispyrrolide $Cp_2Ti(\eta^1\text{-}NC_4H_4)_2$ (d(Ti—N) = 2.070(5) Å, 2.100(4) Å) [7].

Table 1. Data collection and handling.

Crystal:	dark green prism, size 0.2 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.08 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS I, φ
$2\theta_{max}$:	48.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12090, 3458
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1738
$N(param)_{refined}$:	245
Programs:	SHELXS-97 [8], SHELXL-97 [9]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(6A)	8*e*		0.3701	0.0370	0.5552	0.080
H(6B)	8*e*		0.2477	–0.0052	0.5790	0.080
H(6C)	8*e*		0.2906	0.0990	0.5921	0.080
H(7A)	8*e*		–0.0760	0.1361	0.5614	0.101
H(7B)	8*e*		0.0407	0.1479	0.5963	0.101
H(7C)	8*e*		–0.0020	0.0457	0.5795	0.101
H(8A)	8*e*		–0.1324	0.1643	0.4877	0.097
H(8B)	8*e*		–0.1030	0.1025	0.4406	0.097
H(8C)	8*e*		–0.0799	0.2132	0.4397	0.097
H(9A)	8*e*		0.2394	0.1260	0.3801	0.080
H(9B)	8*e*		0.1339	0.2038	0.3841	0.080
H(9C)	8*e*		0.0976	0.0959	0.3779	0.080
H(10A)	8*e*		0.3807	0.0655	0.4229	0.060
H(10B)	8*e*		0.3792	–0.0121	0.4648	0.060
H(10C)	8*e*		0.4411	0.0879	0.4746	0.060
H(11)	8*e*		0.4541	0.2216	0.5710	0.044
H(12)	8*e*		0.6726	0.2318	0.5450	0.060
H(19A)	8*e*		0.1855	0.5613	0.1589	0.063
H(19B)	8*e*		0.0894	0.5918	0.2000	0.063
H(19C)	8*e*		0.1455	0.4882	0.2001	0.063
H(20A)	8*e*		0.3584	0.6063	0.1347	0.094
H(20B)	8*e*		0.4915	0.5708	0.1514	0.094
H(20C)	8*e*		0.4625	0.6806	0.1490	0.094
H(21A)	8*e*	0.5	0.6263	0.6487	0.2168	0.091
H(21B)	8*e*	0.5	0.6320	0.5795	0.2625	0.091
H(21C)	8*e*	0.5	0.6229	0.6902	0.2707	0.091
H(22A)	8*e*		0.5346	0.8533	0.3418	0.087
H(22B)	8*e*		0.6181	0.9024	0.3012	0.087
H(22C)	8*e*		0.6016	0.7910	0.3014	0.087
H(23A)	8*e*		0.3626	0.8813	0.3646	0.141
H(23B)	8*e*		0.2212	0.8660	0.3504	0.141
H(23C)	8*e*		0.2794	0.9689	0.3493	0.141
H(24A)	8*e*	0.5	0.1075	0.9636	0.2835	0.163
H(24B)	8*e*	0.5	0.0780	0.9192	0.2314	0.163
H(24C)	8*e*	0.5	0.1443	1.0189	0.2351	0.163
H(25)	8*e*		0.0571	0.7557	0.3222	0.049
H(26)	8*e*		–0.1598	0.7756	0.2956	0.062

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)	8*e*	0.2120(3)	0.0891(3)	0.5244(1)	0.034(2)	0.025(2)	0.030(2)	–0.009(2)	–0.005(2)	0.003(2)
C(2)	8*e*	0.0890(3)	0.1181(3)	0.5256(1)	0.034(2)	0.024(2)	0.041(2)	–0.014(2)	0.011(2)	–0.007(2)
C(3)	8*e*	0.0527(3)	0.1417(3)	0.4778(1)	0.019(2)	0.019(2)	0.060(3)	–0.002(2)	–0.005(2)	–0.012(2)
C(4)	8*e*	0.1556(3)	0.1280(2)	0.4468(1)	0.034(2)	0.020(2)	0.026(2)	0.004(2)	–0.014(2)	–0.006(1)
C(5)	8*e*	0.2529(3)	0.0921(2)	0.4757(1)	0.026(2)	0.018(2)	0.027(2)	–0.001(2)	–0.005(2)	–0.003(2)
C(6)	8*e*	0.2867(4)	0.0517(3)	0.5664(1)	0.068(3)	0.049(3)	0.043(2)	–0.020(2)	–0.019(2)	0.025(2)
C(7)	8*e*	0.0056(4)	0.1114(3)	0.5696(2)	0.077(3)	0.043(3)	0.081(3)	–0.023(2)	0.049(3)	–0.012(2)
C(8)	8*e*	–0.0770(3)	0.1567(3)	0.4599(2)	0.024(2)	0.040(3)	0.130(4)	0.003(2)	–0.021(2)	–0.029(3)
C(9)	8*e*	0.1567(4)	0.1394(3)	0.3925(1)	0.080(3)	0.042(3)	0.037(2)	0.005(2)	–0.019(2)	–0.010(2)
C(10)	8*e*	0.3739(3)	0.0551(3)	0.4580(1)	0.036(2)	0.030(2)	0.054(2)	0.010(2)	0.003(2)	–0.007(2)
C(11)	8*e*	0.4812(3)	0.2344(3)	0.5389(1)	0.029(2)	0.041(3)	0.039(2)	–0.004(2)	–0.005(2)	0.004(2)
C(12)	8*e*	0.6024(3)	0.2400(3)	0.5248(1)	0.018(2)	0.063(3)	0.068(3)	–0.001(2)	–0.012(2)	0.015(3)
C(13)	8*e*	0.2669(3)	0.5869(2)	0.2245(1)	0.023(2)	0.017(2)	0.029(2)	–0.004(2)	–0.001(1)	–0.006(2)
C(14)	8*e*	0.3848(3)	0.6164(2)	0.2087(1)	0.036(2)	0.017(2)	0.036(2)	–0.003(2)	0.013(2)	–0.007(2)
C(15)	4*d*	0.4587(4)	0.6315(3)	¼	0.016(2)	0.017(3)	0.055(3)	0.001(2)	0	0
C(16)	8*e*	0.4496(3)	0.8603(3)	0.2752(1)	0.022(2)	0.020(2)	0.047(2)	–0.004(2)	–0.003(2)	–0.005(2)
C(17)	8*e*	0.3318(3)	0.8884(3)	0.2912(1)	0.031(2)	0.028(2)	0.063(3)	–0.012(2)	0.017(2)	–0.023(2)
C(18)	4*d*	0.2605(4)	0.9093(4)	¼	0.015(2)	0.017(3)	0.092(5)	0.004(2)	0	0
C(19)	8*e*	0.1628(3)	0.5542(3)	0.1932(1)	0.052(2)	0.032(3)	0.042(2)	–0.012(2)	–0.010(2)	–0.006(2)
C(20)	8*e*	0.4281(4)	0.6188(3)	0.1563(1)	0.085(3)	0.047(3)	0.054(3)	–0.027(2)	0.041(2)	–0.025(2)
C(21)	4*d*	0.5970(4)	0.6381(4)	¼	0.021(3)	0.033(4)	0.128(6)	0.007(3)	0	0
C(22)	8*e*	0.5607(3)	0.8509(3)	0.3077(2)	0.047(2)	0.048(3)	0.079(3)	–0.012(2)	–0.030(2)	–0.002(2)
C(23)	8*e*	0.2956(5)	0.9024(4)	0.3434(2)	0.101(4)	0.093(5)	0.088(4)	–0.036(3)	0.041(3)	–0.070(3)
C(24)	4*d*	0.1368(5)	0.9569(5)	¼	0.020(3)	0.023(4)	0.28(1)	0.010(3)	0	0
C(25)	8*e*	0.0302(3)	0.7577(3)	0.2894(1)	0.027(2)	0.049(3)	0.045(2)	–0.000(2)	0.011(2)	0.008(2)
C(26)	8*e*	–0.0902(3)	0.7690(3)	0.2750(1)	0.018(2)	0.061(3)	0.075(3)	0.002(2)	0.014(2)	0.006(2)
N(1)	4*c*	0.4048(3)	¼	½	0.021(2)	0.030(3)	0.037(2)	0	0	–0.005(2)
N(2)	4*d*	0.1055(3)	0.7500(3)	¼	0.016(2)	0.025(3)	0.045(3)	–0.002(2)	0	0
Ti(1)	4*c*	0.21184(7)	¼	½	0.0153(4)	0.0205(6)	0.0236(5)	0	0	–0.0032(4)
Ti(2)	4*d*	0.29880(6)	0.74603(6)	¼	0.0135(4)	0.0171(6)	0.0195(4)	–0.0006(4)	0	0

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