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The *ansa*-bridged cyclopentadienyl titanium complex [{η^5-$C_5Me_4CH_2$-C(NMe$_2$)=N}$TiCl_2$]

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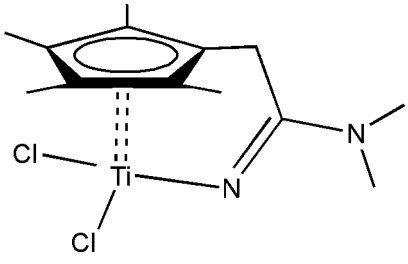
Key indicators: single-crystal X-ray study; T = 213 K; mean σ(C–C) = 0.005 Å; R factor = 0.056; wR factor = 0.117; data-to-parameter ratio = 15.8.

The title complex, dichlorido[*N*,*N*-dimethyl-2-(η^5-tetramethylcyclopentadienyl)acetamidinido-$\kappa N'$]titanium(IV), [$Ti(C_{13}H_{20}N_2)Cl_2$], exhibits an unusual *ansa*-bridged conformation. The cyclopentadienyl ring and the mean plane of the Ti—N=C—C—C fragment form a dihedral angle of 88.08 (11)°.

Related literature

For related crystal structures, see: Hughes *et al.* (1993); Zhang *et al.* (2004). For general background, see: Chen & Marks (1997); Mahanthappa *et al.* (2004).



Experimental

Crystal data

$[Ti(C_{13}H_{20}N_2)Cl_2]$
M_r = 323.11
Orthorhombic, *Pbca*
a = 12.600 (5) Å
b = 15.498 (6) Å
c = 15.574 (5) Å
V = 3041.1 (19) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.90 mm^{-1}
T = 213 K
0.30 × 0.20 × 0.20 mm

Data collection

Siemens SMART diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
T_{min} = 0.774, T_{max} = 0.841
11691 measured reflections
2677 independent reflections
2554 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.117
S = 1.27
2677 reflections
169 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2554).

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supporting information

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The *ansa*-bridged cyclopentadienyl titanium complex [{η^5-$C_5Me_4CH_2$-C(NMe_2)&z-dbnd;N}$TiCl_2$]

Donglong Guo, Hong-Bo Tong and Meisu Zhou

S1. Comment

The homogeneous coordination polymerization catalysts, especially group IV metallocene catalysts, have created new opportunities for the production of ethylene *α*-olefin copolymers and received extensive attention in recent years (Mahanthappa *et al.*, 2004). The constrained geometry catalysts with a pendant nitrogen or oxygen donor on the cyclopentadienyl ligand, such as Me_2Si-(η^5-Me_4C_5)(*t*-BuN)$TiCl_2$ (Hughes *et al.*, 1993) and 2-tetramethylcyclopentadienyl-4-methylphenoxytitaniumdibenzyl (Zhang *et al.*, 2004) have been developed due to their structural features and good catalytic activities (Chen *et al.*, 1997). Here we present the synthesis and crystal structure of a new ansa-bridged cyclopentadienyl titanium complex (**I**)

In (**I**) (Fig. 1), the distance from the central metal atom Ti to the centroid of Cp* is 2.024 (2) Å. The bond lengths Ti—N1, Ti—Cl1 and Ti—Cl2 are 1.823 (3), 2.3104 (12) and 2.3036 (12) Å, respectively. The bond angle Cl1—Ti—Cl2 is 105.40 (5) °. Atoms C1, C6, C7, N1 and Ti are exactly co-planar with a highest deviation of 0.0191 Å. The two planes - Cp* and C1/C6/C7/N1/Ti are almost perpendicular making a dihedral angle of 88.08 (11)°. The bond angles C1—C6—C7, C6—C7—N1 and C7—N1—Ti are 106.7 (3),116.7 (3) and 129.5 (2) °, respectively.

S2. Experimental

$(CH_3)_2NCN$ (0.36 ml, 4.52 mmol) was added to a solution of $PhN(Li)SiMe_3$(0.386 g, 2.26 mmol) in THF (30 cm^3) at -78 °C. The resulting mixture was warmed to *ca*.25°C and stirred for overnight. $CpTiCl_3$ (0.99 g, 4.52 mmol) was added at -78°C. The resulting mixture was warmed to *ca*.25°C and stirred for 24 h. The volatiles were removed in *vacuo*, and there residue was extracted with dichloromethane and filtered. The filtrate was concentrated to give red crystals of **(I)**(0.14 g, 13%).

Anal. calcd. for $C_{13}H_{20}Cl_2N_2Ti$(%): C, 48.33; H, 6.24; N, 8.67. Found: C, 48.25; H, 6.25; N, 8.73. A l l manipulations were performed under argonusing standard Schlenk and vacuum line techniques. THF was dried and distilled over Na underargon prior to use. Elemental analysis and NMR spectra are completely in agreement with the structure of (**I**). Spectroscopic analysis, ^{1}HNMR ($CDCl_3$): d 2.11~2.18 (d, 12 H, Cp—CH_3), d 2.80, 3.10 (d, 6 H, N(CH_3)$_2$), d 4.09 (s, 2 H, CH_2). ^{13}CNMR ($CDCl_3$): d 10.0, 10.8 (Cp-*C*H_3), d 28.9 (*C*H_2), d 33.3, 35.9 (N(*C*H_3)$_2$), d 118.5, 123.2, 127.4,128.6, 129.0 (Cp), 171.6 (CH_2-*C*(NMe_2)-N).

S3. Refinement

The H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93-0.97 Å, and U_{iso} = 1.2-1.5 U_{eq}(parent atom).

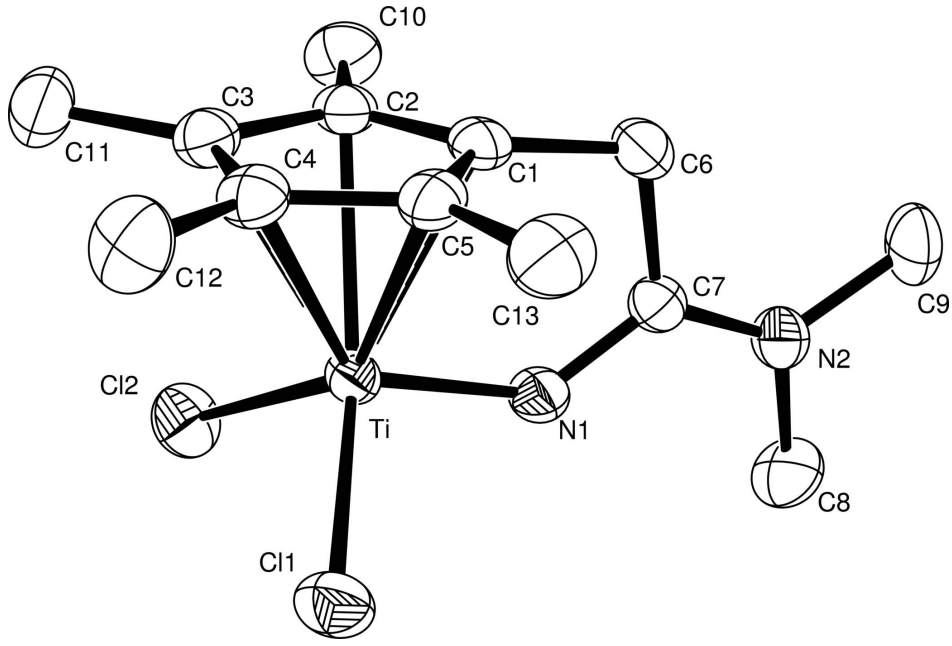

Figure 1

The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

dichlorido[*N*,*N*-dimethyl-2-(η^5- tetramethylcyclopentadienyl)acetamidinido-$\kappa N'$]titanium(IV)

Crystal data

$[Ti(C_{13}H_{20}N_2)Cl_2]$
$M_r = 323.11$
Orthorhombic, *Pbca*
$a = 12.600\ (5)$ Å
$b = 15.498\ (6)$ Å
$c = 15.574\ (5)$ Å
$V = 3041.1\ (19)$ Å^3
$Z = 8$
$F(000) = 1344$
$D_x = 1.411$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4409 reflections
$\theta = 2.5$–$27.0°$
$\mu = 0.90$ mm^{-1}
$T = 213$ K
Block, orange
0.30 × 0.20 × 0.20 mm

Data collection

Siemens SMART diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.774$, $T_{max} = 0.841$
11691 measured reflections
2677 independent reflections
2554 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.5°$
$h = -14 \rightarrow 14$
$k = -18 \rightarrow 12$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.117$
$S = 1.27$
2677 reflections
169 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map	$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 4.3005P]$ where $P = (F_o^2 + 2F_c^2)/3$
Hydrogen site location: inferred from neighbouring sites	$(\Delta/\sigma)_{max} = 0.001$
H-atom parameters constrained	$\Delta\rho_{max} = 0.38$ e Å^{-3}
	$\Delta\rho_{min} = -0.30$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ti	0.21528 (5)	0.56734 (4)	0.10562 (4)	0.02449 (19)
Cl1	0.10277 (7)	0.66810 (6)	0.04506 (6)	0.0396 (3)
Cl2	0.11570 (8)	0.49802 (7)	0.20873 (6)	0.0416 (3)
N1	0.3122 (2)	0.63161 (19)	0.16445 (18)	0.0302 (7)
N2	0.4755 (2)	0.69295 (19)	0.19627 (19)	0.0326 (7)
C1	0.3752 (3)	0.5272 (2)	0.0479 (2)	0.0289 (8)
C2	0.3304 (3)	0.4522 (2)	0.0835 (2)	0.0285 (8)
C3	0.2387 (3)	0.4307 (2)	0.0348 (2)	0.0314 (8)
C4	0.2270 (3)	0.4933 (2)	−0.0298 (2)	0.0313 (8)
C5	0.3117 (3)	0.5534 (2)	−0.0221 (2)	0.0299 (8)
C6	0.4650 (3)	0.5788 (2)	0.0867 (2)	0.0347 (9)
H6A	0.5014	0.6123	0.0423	0.042*
H6B	0.5166	0.5403	0.1141	0.042*
C7	0.4158 (3)	0.6384 (2)	0.1528 (2)	0.0282 (8)
C8	0.4285 (3)	0.7477 (3)	0.2621 (3)	0.0458 (10)
H8A	0.3529	0.7362	0.2658	0.069*
H8B	0.4396	0.8078	0.2473	0.069*
H8C	0.4615	0.7356	0.3171	0.069*
C9	0.5892 (3)	0.7047 (3)	0.1806 (3)	0.0447 (10)
H9A	0.6176	0.6536	0.1531	0.067*
H9B	0.6253	0.7141	0.2348	0.067*
H9C	0.5999	0.7544	0.1437	0.067*
C10	0.3711 (3)	0.4014 (3)	0.1590 (2)	0.0421 (10)
H10A	0.4040	0.3486	0.1387	0.063*
H10B	0.3125	0.3872	0.1968	0.063*
H10C	0.4229	0.4355	0.1900	0.063*
C11	0.1708 (3)	0.3522 (2)	0.0475 (3)	0.0442 (10)
H11A	0.0967	0.3678	0.0412	0.066*
H11B	0.1826	0.3290	0.1046	0.066*
H11C	0.1892	0.3090	0.0050	0.066*

C12	0.1436 (3)	0.4946 (3)	−0.0985 (3)	0.0448 (10)
H12A	0.1733	0.4725	−0.1516	0.067*
H12B	0.1194	0.5534	−0.1073	0.067*
H12C	0.0842	0.4588	−0.0812	0.067*
C13	0.3304 (3)	0.6293 (3)	−0.0800 (2)	0.0438 (10)
H13A	0.3836	0.6667	−0.0547	0.066*
H13B	0.2647	0.6611	−0.0872	0.066*
H13C	0.3550	0.6091	−0.1355	0.066*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti	0.0217 (3)	0.0269 (3)	0.0249 (3)	0.0006 (3)	0.0008 (2)	−0.0016 (3)
Cl1	0.0328 (5)	0.0388 (5)	0.0471 (6)	0.0091 (4)	−0.0028 (4)	0.0043 (4)
Cl2	0.0404 (5)	0.0474 (6)	0.0370 (5)	−0.0053 (5)	0.0098 (4)	0.0072 (4)
N1	0.0284 (16)	0.0325 (16)	0.0296 (15)	0.0011 (13)	0.0017 (13)	−0.0100 (13)
N2	0.0275 (16)	0.0341 (17)	0.0362 (17)	−0.0027 (13)	−0.0056 (13)	−0.0058 (14)
C1	0.0254 (18)	0.0333 (19)	0.0281 (18)	0.0029 (15)	0.0048 (14)	−0.0097 (16)
C2	0.0273 (18)	0.0292 (18)	0.0292 (18)	0.0055 (15)	0.0010 (15)	−0.0057 (15)
C3	0.0316 (19)	0.0304 (19)	0.0322 (19)	0.0039 (16)	−0.0029 (16)	−0.0050 (16)
C4	0.034 (2)	0.0330 (19)	0.0270 (18)	0.0037 (16)	−0.0009 (15)	−0.0057 (16)
C5	0.0337 (19)	0.0284 (18)	0.0275 (18)	0.0008 (16)	0.0073 (15)	−0.0039 (15)
C6	0.0242 (18)	0.040 (2)	0.040 (2)	−0.0016 (16)	0.0036 (16)	−0.0100 (17)
C7	0.0259 (18)	0.0284 (18)	0.0302 (19)	0.0013 (15)	−0.0026 (15)	−0.0004 (15)
C8	0.049 (2)	0.041 (2)	0.047 (2)	−0.002 (2)	−0.010 (2)	−0.018 (2)
C9	0.035 (2)	0.045 (2)	0.054 (3)	−0.0144 (19)	−0.0090 (19)	0.000 (2)
C10	0.044 (2)	0.041 (2)	0.041 (2)	0.0107 (19)	−0.0116 (19)	0.0001 (19)
C11	0.045 (2)	0.034 (2)	0.054 (3)	−0.0069 (19)	−0.009 (2)	−0.0018 (19)
C12	0.052 (3)	0.049 (2)	0.034 (2)	−0.003 (2)	−0.0164 (19)	−0.0002 (19)
C13	0.053 (3)	0.042 (2)	0.036 (2)	−0.001 (2)	0.0120 (19)	0.0009 (18)

Geometric parameters (Å, º)

Ti—N1	1.823 (3)	C6—C7	1.515 (5)
Ti—C1	2.292 (3)	C6—H6A	0.9800
Ti—Cl2	2.3036 (12)	C6—H6B	0.9800
Ti—Cl1	2.3104 (12)	C8—H8A	0.9700
Ti—C2	2.325 (3)	C8—H8B	0.9700
Ti—C5	2.341 (3)	C8—H8C	0.9700
Ti—C4	2.405 (3)	C9—H9A	0.9700
Ti—C3	2.406 (4)	C9—H9B	0.9700
N1—C7	1.322 (4)	C9—H9C	0.9700
N2—C7	1.319 (4)	C10—H10A	0.9700
N2—C8	1.457 (5)	C10—H10B	0.9700
N2—C9	1.464 (5)	C10—H10C	0.9700
C1—C2	1.406 (5)	C11—H11A	0.9700
C1—C5	1.412 (5)	C11—H11B	0.9700
C1—C6	1.512 (5)	C11—H11C	0.9700

C2—C3	1.422 (5)	C12—H12A	0.9700
C2—C10	1.504 (5)	C12—H12B	0.9700
C3—C4	1.405 (5)	C12—H12C	0.9700
C3—C11	1.500 (5)	C13—H13A	0.9700
C4—C5	1.422 (5)	C13—H13B	0.9700
C4—C12	1.500 (5)	C13—H13C	0.9700
C5—C13	1.500 (5)		

N1—Ti—C1	75.92 (13)	C5—C4—Ti	70.10 (19)
N1—Ti—Cl2	105.63 (10)	C12—C4—Ti	125.2 (3)
C1—Ti—Cl2	128.71 (10)	C1—C5—C4	107.5 (3)
N1—Ti—Cl1	104.29 (10)	C1—C5—C13	126.9 (3)
C1—Ti—Cl1	124.25 (10)	C4—C5—C13	125.5 (3)
Cl2—Ti—Cl1	105.40 (5)	C1—C5—Ti	70.40 (19)
N1—Ti—C2	94.34 (13)	C4—C5—Ti	75.1 (2)
C1—Ti—C2	35.44 (13)	C13—C5—Ti	121.3 (2)
Cl2—Ti—C2	94.88 (10)	C1—C6—C7	106.7 (3)
Cl1—Ti—C2	147.26 (9)	C1—C6—H6A	110.4
N1—Ti—C5	97.46 (13)	C7—C6—H6A	110.4
C1—Ti—C5	35.48 (12)	C1—C6—H6B	110.4
Cl2—Ti—C5	146.31 (9)	C7—C6—H6B	110.4
Cl1—Ti—C5	91.94 (10)	H6A—C6—H6B	108.6
C2—Ti—C5	58.66 (12)	N2—C7—N1	122.9 (3)
N1—Ti—C4	131.33 (13)	N2—C7—C6	120.4 (3)
C1—Ti—C4	58.19 (12)	N1—C7—C6	116.7 (3)
Cl2—Ti—C4	114.96 (10)	N2—C8—H8A	109.5
Cl1—Ti—C4	90.13 (9)	N2—C8—H8B	109.5
C2—Ti—C4	57.72 (12)	H8A—C8—H8B	109.5
C5—Ti—C4	34.83 (12)	N2—C8—H8C	109.5
N1—Ti—C3	128.99 (13)	H8A—C8—H8C	109.5
C1—Ti—C3	58.23 (12)	H8B—C8—H8C	109.5
Cl2—Ti—C3	88.61 (10)	N2—C9—H9A	109.5
Cl1—Ti—C3	118.89 (9)	N2—C9—H9B	109.5
C2—Ti—C3	34.93 (12)	H9A—C9—H9B	109.5
C5—Ti—C3	57.70 (12)	N2—C9—H9C	109.5
C4—Ti—C3	33.97 (12)	H9A—C9—H9C	109.5
C7—N1—Ti	129.5 (2)	H9B—C9—H9C	109.5
C7—N2—C8	120.2 (3)	C2—C10—H10A	109.5
C7—N2—C9	123.5 (3)	C2—C10—H10B	109.5
C8—N2—C9	116.3 (3)	H10A—C10—H10B	109.5
C2—C1—C5	108.4 (3)	C2—C10—H10C	109.5
C2—C1—C6	125.4 (3)	H10A—C10—H10C	109.5
C5—C1—C6	125.5 (3)	H10B—C10—H10C	109.5
C2—C1—Ti	73.55 (19)	C3—C11—H11A	109.5
C5—C1—Ti	74.12 (19)	C3—C11—H11B	109.5
C6—C1—Ti	110.9 (2)	H11A—C11—H11B	109.5
C1—C2—C3	108.0 (3)	C3—C11—H11C	109.5
C1—C2—C10	127.2 (3)	H11A—C11—H11C	109.5

C3—C2—C10	124.8 (3)	H11B—C11—H11C	109.5
C1—C2—Ti	71.01 (19)	C4—C12—H12A	109.5
C3—C2—Ti	75.7 (2)	C4—C12—H12B	109.5
C10—C2—Ti	119.9 (2)	H12A—C12—H12B	109.5
C4—C3—C2	107.8 (3)	C4—C12—H12C	109.5
C4—C3—C11	126.4 (3)	H12A—C12—H12C	109.5
C2—C3—C11	125.7 (3)	H12B—C12—H12C	109.5
C4—C3—Ti	73.0 (2)	C5—C13—H13A	109.5
C2—C3—Ti	69.41 (19)	C5—C13—H13B	109.5
C11—C3—Ti	125.7 (3)	H13A—C13—H13B	109.5
C3—C4—C5	108.3 (3)	C5—C13—H13C	109.5
C3—C4—C12	126.4 (3)	H13A—C13—H13C	109.5
C5—C4—C12	125.2 (3)	H13B—C13—H13C	109.5
C3—C4—Ti	73.1 (2)		