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[η^5,σ-3,3-Dimethyl-1-(2,3,4,5-tetramethylcyclopentadienyl)but-1-en-2-amino](η^5-pentamethylcyclopentadienyl)titanium

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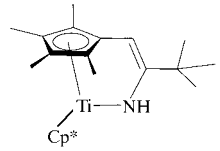
The titanocene complex [Ti($C_{10}H_{15}$)($C_{15}H_{23}N$)] features a pentamethylcyclopentadienyl ligand and a substituted cyclopentadienyl ligand Me_4C_5R, where R is an amino functional group which is subsequently attached to the titanium metal centre. The structure has been determined to ascertain the conformational properties of the side chain with regard to extended conjugation between the π systems and the nature of the amino interaction with the metal centre.

Comment

Pentamethylcyclopentadienyl ligands (η^5-C_5Me_5 or Cp*) are generally preferred to their cyclopentadiene analogues due to their electron richness, steric bulk and relative inertness. In turn, one or more of the methyl substituents can be deprotonated to produce functionalized pendant arms which may react with or induce other reactions at the metal, or additionally be bonded to form extended units.



(I)

The bent sandwich geometry of the title complex, (I), shown in Fig. 1, is a titanocene complex featuring a pendant amino-substituted pentamethylcyclopentadienyl group. The Cp* and substituted cyclopentadienyl ligands form a staggered conformation about the Ti1 atom (viewed from above the functionalized Cp* plane), with an acute angle between the ligands of 28.5 (5)°. The molecule possesses near crystallographic mirror symmetry through the N atom, the metal atom and Cp* ligands. The substituted Cp* ring is unsymmetrical; there is a shorter Ti1—C1 distance of 2.312 (4) Å compared with the remaining C atoms in either Cp* ligands attached to titanium [2.335 (4)–2.423 (4) Å for the functionalized Cp* and 2.380 (4)–2.407 (4) Å for Cp*]. A further measure of the ligand asymmetry is the ring slippage of the Ti atom relative to two Cp* ligands; 0.13 (2) Å for the substituted ring and 0.02 (2) Å for the unsubstituted Cp*.

There is a distorted planar geometry around the titanium metal centre as shown by the angles between the centroids of the ring, and the Ti and N atoms: *Cg*1—Ti1—*Cg*2 = 147.0 (5), *Cg*1—Ti1—N1 = 103.8 (5) and *Cg*2—Ti1—N1 = 109.1 (5)° (where *Cg*1 is the ring centroid of the C1–C5 ring and *Cg*2 the centroid of the C16–C20 ring). These angles are in the range observed for other $\mathrm{Cp}^*_2\mathrm{Ti}L_n$ systems.

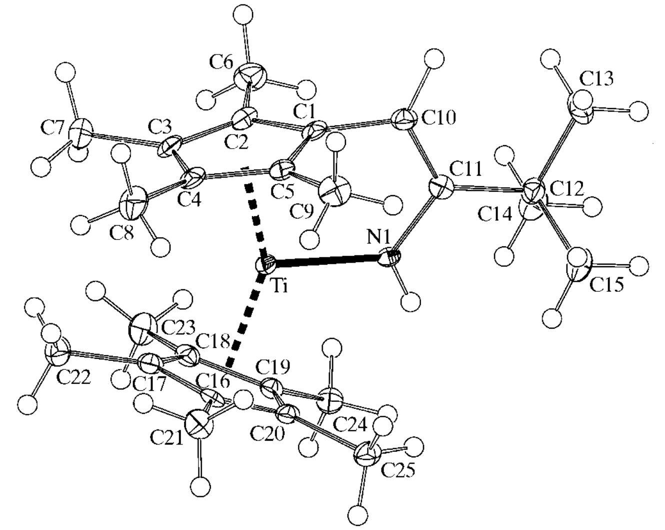


Figure 1
Displacement ellipsoid plot (50% probability) of (I) with the atom labels.

There is no Ti1···H1*A* interaction [2.47 (2) Å] since the distance exceeds the covalent radii of the relevant atoms; $r_{\rm cov}$(Ti) = 1.47 and $r_{\rm cov}$(H) = 0.35 Å. There are no suitable N—H hydrogen-bond acceptor atoms in the molecule.

The other interesting feature concerns the planar nature of the substituent at C1 of the tetramethylcyclopentadienyl ring. The H10 atom on on C10 and the *tert*-butyl group at C11 are arranged in a *cis* configuration. The C1—C10 distance of 1.462 (5) Å has single-bond characteristics, whereas the inner C10—C11 distance of 1.339 (6) Å is in accordance with a double bond. The N atom is nearly planar (Σangles = 358.8°) and connects to C11 *via* an intermediate bond length [N1—C11 = 1.393 (5) Å]. This suggests small or little delocalization of the ligand. The three atoms in the side chain, C10, C11 and N1, are all sp^2 hybridized, as shown by their bond angles (close to the expected 120°) and near-zero torsion angles (Table 1). In this case, the planarity of the pendant arm produces a more rigid group compared with those in previous studies of titanocene compounds (Beckhaus *et al.*, 1997; Sinnema *et al.*, 1997). The Ti1—N1 distance of 2.000 (3) Å is longer than those observed in simple titanocene–amido complexes (Brady *et al.*, 1995; Lukens *et al.*, 1996), but is in the normal range for a Ti—N σ bond.

Experimental

The complex was prepared by the addition of *tert*-C≡N (0.072 g, 0.87 mmol) to a pentane solution of $[(\eta^5\text{-}C_5Me_5)(Me_4C_5CH_2)Ti]$ (0.276 g, 0.87 mmol) at 193 K. The reaction mixture turned dark red and was warmed to room temperature. After 4 h, the volatiles were removed and the residue extracted and cooled slowly to 243 K to give dark-red crystals in 84% yield (Pattiasina, 1988).

Crystal data

$[Ti(C_{10}H_{15})(C_{15}H_{23}N)]$
$M_r = 400.46$
Monoclinic, $C2/c$
$a = 14.518\ (9)$ Å
$b = 13.701\ (7)$ Å
$c = 23.924\ (4)$ Å
$\beta = 106.59\ (4)^\circ$
$V = 4561\ (4)$ Å^3
$Z = 8$
$D_x = 1.166$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9 reflections
$\theta = 11.4\text{–}13.8^\circ$
$\mu = 0.384$ mm^{-1}
$T = 100\ (2)$ K
Block, brown
0.38 × 0.30 × 0.25 mm

Data collection

Enraf–Nonius CAD-4*F* diffractometer
$\omega/2\theta$ scans
4951 measured reflections
4006 independent reflections
2813 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.060$
$\theta_{\text{max}} = 25^\circ$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 16$
$l = -28 \rightarrow 6$
3 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.162$
$S = 1.066$
4006 reflections
262 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 21.1265]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.47$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.55$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

*Cg*1 is the centroid of the C1–C5 ring and *Cg*2 the centroid of the C16–C20 ring.

Ti1—N1	2.000 (3)	Ti1—C17	2.407 (4)
Ti1—C1	2.312 (4)	Ti1—C3	2.419 (4)
Ti1—C5	2.336 (4)	Ti1—C4	2.423 (4)
Ti1—C2	2.336 (4)	N1—C11	1.393 (5)
Ti1—C20	2.374 (4)	N1—H1*A*	0.83 (5)
Ti1—C19	2.375 (4)	C11—C10	1.339 (6)
Ti1—C18	2.381 (4)	C1—C10	1.462 (6)
Ti1—C16	2.386 (4)	C10—H10	1.06 (4)
C11—N1—Ti1	125.8 (3)	*Cg*1—Ti1—*Cg*2	147.0
C10—C11—N1	115.3 (4)	*Cg*1—Ti1—N1	103.8
C10—C11—C12	125.5 (4)	*Cg*2—Ti1—N1	109.1
N1—C11—C12	119.2 (4)		
Ti1—N1—C11—C10	−0.4 (5)	N1—C11—C10—C1	0.0 (6)

All H atoms, with the exception of those on C10 and N1, were constrained and allowed to ride on their methyl C atoms with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. H10 and H1*A* were located from a difference Fourier map and their coordinates allowed to refine with their isotropic displacement parameters constrained to $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$; the dimensions refined to C10—H10 = 1.06 (4) Å and N1—H1*A* = 0.83 (5) Å.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *DIRDIF*97 (Beurskens *et al.*, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1577). Services for accessing these data are described at the back of the journal.

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