

Chlorido(η^5 -cyclopentadienyl)bis- (dimethylamido)titanium, [TiCl(η^5 -C₅H₅)(NMe₂)₂]

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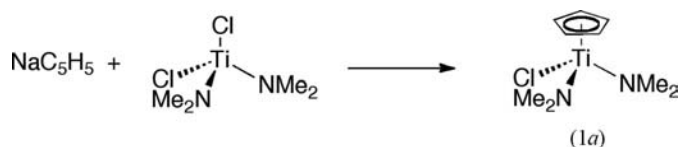
The title complex, [Ti(C₅H₅)(C₂H₆N)₂Cl], exhibits two nearly planar dimethylamide groups oriented approximately perpendicular to each other. The Ti→cyclopentadienyl centroid vector lies nearly in the plane of one of the dimethylamide groups. Long-range contacts between Ti—Cl and cyclopentadienyl H—C groups give rise to geometric ordering in the extended solid.

Comment

Titanium complexes are used extensively for catalytic transformations (Ramón & Yus, 2006). Careful control of the ligand environment allows for subsequent control of the reactivity of the resulting complex. We required a titanium complex containing a cyclopentadienyl group and a bidentate amino alcohol ligand for use in asymmetric hydroamination reactions. The starting material for our synthesis was TiCl(η^5 -C₅H₅)(NMe₂)₂. While there are a number of examples of cyclopentadienyl (Cp) titanium complexes with a three-legged piano-stool geometry that have different 'legs', we were surprised to find that this starting material had not been structurally characterized. The complex contains two dimethylamide groups suitable for reaction with protic reagents, and a single chloride ligand that can react with alkylating reagents or other anionic nucleophiles through a salt-elimination metathesis reaction. The divergent and orthogonal reactivity of halides and dimethylamides has been used to prepare chiral titanium complexes (Johnson *et al.*, 1996).

The title complex, (1a), was prepared from TiCl₂(NMe₂)₂ (Benzing & Kornicker, 1961) and dark-red block-like crystals suitable for X-ray diffraction were obtained by recrystallization from diethyl ether at 238 K. The complex crystallizes in the space group *P*2₁/*n* (Fig. 1). The two nearly planar

dimethylamide groups are oriented approximately perpendicular to each other in order to maximize π -*d* donation into two orthogonal orbitals from the strongly π -basic groups; the sum of angles about each N atom is >358°. The Ti—Cp centroid vector lies approximately in the plane of one of the dimethylamide groups, allowing for good overlap between the nitrogen lone pair and a $d_{xy}/d_{x^2-y^2}$ type orbital. The second dimethylamide group lies approximately in the *xy* plane, allowing for the lone pair to overlap with a d_{xz}/d_{yz} type orbital.



There are significant long-range contacts that give rise to geometric ordering in the solid-state structure of (1a). There are Ti—Cl⋯H—C interactions with Cl⋯H distances of 2.71 and 2.82 Å between each Cl atom and two H atoms on the Cp groups of adjacent molecules; these contacts give rise to a zigzag layer of molecules oriented approximately perpendicular to the *bc* plane. In addition, there are NCH₃⋯Cp_{centroid} contacts with H⋯Cp_{centroid} distances of 2.91 Å oriented approximately along the *c* axis that link sets of parallel zigzag layers.

Analysis of the Cambridge Structural Database (CSD; Version 5.31, release 2010; Allen, 2002) reveals a modest number of structurally characterized CpTiCl_x(NR₂)_{3-x} complexes. CpTiCl₃ (Engelhardt *et al.*, 1984) and CpTiCl₂(NⁱPr₂) (Pupi *et al.*, 1995) are known [Fig. 2, complexes (2) and (3), respectively], but there are no structurally characterized examples of CpTiCl(NR₂)₂ or CpTi(NR₂)₃ with monodentate amides. Relaxing the search to allow for using a mono-substituted cyclopentadienyl ring (Cp') leads to six structurally characterized examples with the connectivity Cp'TiCl(NR₂)₂, though all but one are either constrained-geometry complexes with at least one of the groups attached to the Cp ring, or complexes containing amides linked together with an organic group. The remaining complex [Fig. 2, complex (1b); R =

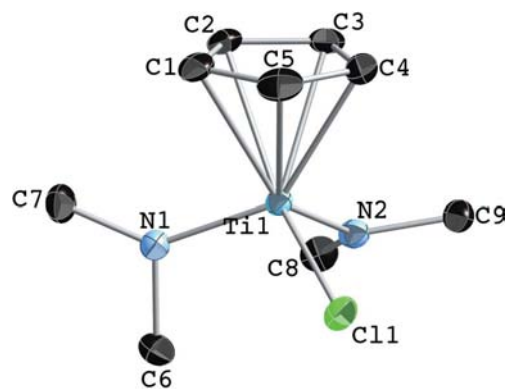
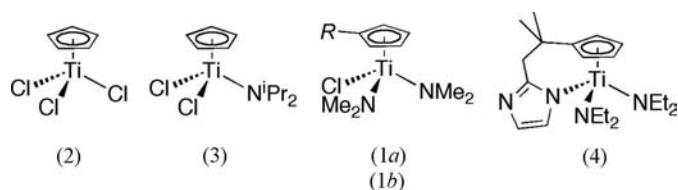


Figure 1

The molecular structure of (1a), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.


Figure 2

Structurally characterized $\text{CpTiCl}_x(\text{NR}_2)_{3-x}$ complexes. For (1a), $R = \text{H}$, and for (1b), $R = \text{CH}_2(\eta^5\text{-indenyl})\text{TiCl}(\text{NMe}_2)_2$.

indenyl] is a unique dimeric complex with a C_5H_4 group linked to an indenyl group (Cho *et al.*, 2004), and is a good structural comparison with (1a), as the monosubstituted Cp ring is coordinated in an η^5 fashion to a $\text{TiCl}(\text{NMe}_2)_2$ group. Further analysis of the CSD gives five structurally characterized examples of $\text{Cp}^*\text{Ti}(\text{NR}_2)_3$, but all have a constrained geometry, with one amide group linked directly to the Cp ring by a one- or two-carbon linker. The best comparative example of $\text{Cp}^*\text{Ti}(\text{NR}_2)_3$ is a tethered complex with a two-carbon linker (Wang *et al.*, 2009); its geometry is therefore much less distorted than other similar compounds [Fig. 2, complex (4)]. Although $\text{Cp}^*\text{Ti}(\text{NMe}_2)_3$ is known ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; Martin *et al.*, 1994), the Ti–C bond distances in Cp^* complexes are significantly longer (mean Ti–C = 2.441 Å, longer by 0.064 Å than in Cp complexes), and it is thus not directly comparable with the bond distances reported here.

Considering the $\text{CpTiCl}_x(\text{NR}_2)_{3-x}$ series of complexes in Fig. 2, there is a general lengthening of the mean Ti–C and Ti–N bond lengths as the number of chloride ligands decreases (Table 1) [the Ti–N(imidazolyl) bond length in complex (4) of 2.0551 (14) Å is significantly longer than in the corresponding diethylamides of 1.8945 (14) and 1.8984 (14) Å]. The Ti–Cl bond distances also generally increase as the number of chloride ligands decreases, with a minimum distance of 2.223 (7) Å observed for the average Ti–Cl bond length in CpTiCl_3 [complex (2)]. The Cl–Ti–N bond angles (where present) for all complexes are larger than the corresponding Cl–Ti–Cl or N–Ti–N angles, but all angles relating Ti and the three coordinating atoms in the basal plane are within a 6° range, indicating that the gross structural differences between Cl and NR_2 in these complexes are minimal. The general increase in bond length in the series of complexes shown in Fig. 2 can be rationalized by both a steric and an electronic argument. Replacement of the relatively weak π -donor chloride ligand with the much stronger π -donor dialkylamide will reduce the ionic character of the bonding. Additionally, the dialkyl amide ligands are larger and a slight increase in bond length would relax the steric pressure at the metal center.

Complex (3) has a single essentially planar amide group; the sum of the angles about the N atom is 360° and the Ti–Cp centroid vector lies approximately in the plane defined by the N atom and the two tertiary C atoms. The lowest-energy conformation of an amide in this family of complexes would be expected to be in this ‘vertical’ orientation, in order to maximize π -bonding in the xy plane and minimize competition for π -bonding to the Cp ring. The mean planes defined by the

Cp ring and the three coordinating atoms of the three basal ligands are almost parallel.

The structural features of the title complex, (1a), are very similar to those of the dimeric complex (1b). Comparing the molecule of (1a) with the half of the molecule of (1b) attached to the Cp group, the mean Ti–N and Ti–C bond lengths are almost identical in both compounds, while the Ti–Cl bonds are quite different (Table 1). The N–Ti–N and Cl–Ti–N bond angles are very similar. Finally, both complexes have their amide groups oriented at approximately 90° with respect to each other. The mean planes defined by the Cp ring and the three coordinating atoms of the three basal ligands are again almost parallel in both complexes.

The tethered complex, (4), also has essentially parallel mean planes, suggesting that the geometry is not ‘constrained’, as seen for complexes with only a single-atom linker between the Cp ring and the basal ligand. The tethered amide group (an imidazolyl group) is not aligned along the Ti–centroid vector, but is tilted by approximately 45°. One of the remaining diethylamide groups is essentially vertical and the second is essentially horizontal with respect to that vector. The π -bonding in (4) is set up to maximize overlap between the more strongly basic dialkylamides; the imidazolyl group has very little π -overlap with the Ti atom. The structural features of the complex are related to those for $\text{Cp}^*\text{Ti}(\text{NMe}_2)_3$, aside from the longer Ti–C bond lengths (Martin *et al.*, 1994). The Cp^* complex has two of the planar amide groups roughly perpendicular and one roughly parallel to the Ti–centroid vector. The calculated structure of $\text{CpTi}(\text{NMe}_2)_3$, on the other hand, has a pseudo- C_3 geometry of the three amide groups (Haaland *et al.*, 2001).

Experimental

Solvents were purified by passage through a column of activated alumina (Innovative Technology PS-400-5-MD) and stored under nitrogen. In a nitrogen-filled glove-box (MBraun UNILab), $\text{TiCl}_2(\text{NMe}_2)_2$ (0.438 g, 2.12 mmol) was dissolved in diethyl ether (5 ml) and NaC_5H_5 (0.186 g, 2.11 mmol) was dissolved in diethyl ether (5 ml). Both solutions were chilled to 238 K and the sodium cyclopentadienide slurry was added to the titanium solution. The reaction was stirred overnight, filtered through glass fibers and evaporated to dryness. The desired complex, (1a), was recrystallized from diethyl ether and obtained as a dark-red solid (yield 0.175 g, 0.740 mmol, 35%; m.p. 336–341 K). ^1H NMR (400 MHz, CDCl_3): δ 5.903 (5H, C_5H_5), 2.990 [12H, $\text{N}(\text{CH}_3)_2$]; ^{13}C NMR (100 MHz, CDCl_3): δ 113.488 (C_5H_5), 48.435 [$\text{N}(\text{CH}_3)_2$]; CHN analysis calculated for $\text{C}_9\text{H}_{17}\text{ClN}_2\text{Ti}$: C 45.69, H 7.24, N 11.84%; found: C 45.82, H 7.11, N 11.40%. Dark-red X-ray quality crystals of (1a) were obtained from a solution in diethyl ether at 238 K over a period of several months.

Crystal data

$[\text{Ti}(\text{C}_5\text{H}_5)(\text{C}_2\text{H}_6\text{N})_2\text{Cl}]$	$V = 1163.37 (19) \text{ \AA}^3$
$M_r = 236.60$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.3621 (9) \text{ \AA}$	$\mu = 0.93 \text{ mm}^{-1}$
$b = 11.0618 (10) \text{ \AA}$	$T = 100 \text{ K}$
$c = 11.5907 (11) \text{ \AA}$	$0.20 \times 0.20 \times 0.20 \text{ mm}$
$\beta = 104.259 (1)^\circ$	

Table 1Mean structural parameters (\AA , $^\circ$) for $\text{CpTiCl}_x(\text{NR}_2)_{3-x}$ complexes.

	(2)	(3)	(1a)	(1b)	(4)
Ti–C	2.31 (4)	2.345 (5)	2.374 (4)	2.378 (15)	2.377 (3)
Ti–N		1.865 (2)	1.896 (2)	1.899 (8)	1.897 (2)/ 2.0551 (14)
Ti–Cl	2.223 (7)	2.298 (1)	2.348 (5)	2.308 (2)	
Cl–Ti–Cl	102.9 (4)	103.38 (4)			
Cl–Ti–N		106.2	104.89 (6)	104.2 (3)	
N–Ti–N			100.48 (6)	99.5 (3)	102.57 (12)

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.837$, $T_{\max} = 0.837$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.064$
 $S = 1.08$
2133 reflections

14937 measured reflections
2133 independent reflections
1960 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

122 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$

All H atoms were placed in geometrically idealized positions and allowed to ride on their respective parent atoms, with C–H = 0.98–1.00 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups and $1.2U_{\text{eq}}(\text{C})$ otherwise.

Data collection: SMART (Bruker, 2003); cell refinement: SMART; data reduction: SAINT (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics:

CrystalMaker (Palmer, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3132). Services for accessing these data are described at the back of the journal.

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