metal-organic compounds

Chlorobis(dimethylamido)(η^5-2,5-dimethylpyrrolyl)titanium(IV), [Ti(NMe$_2$)$_2$(DMP)Cl]

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The structure of the title compound, [Ti(C$_2$H$_6$N)$_2$(C$_6$H$_8$N)Cl], displays a η^5-coordination mode for the pyrrolyl ring, confirmed by the values of the slip parameter [0.073 (9) Å] and the fold angle [4.6 (6)°]. This coordination is confirmed by NMR data, which point to the involvement of the complex in a fluxional process in solution above 285 K, passing through an intermediate involving simultaneously a metal–azaallyl and a metal–olefin bond.

Comment

Organometalic complexes with η^5-pyrrolyl (pyr*) ligands have been attracting considerable attention in recent years (Tanski & Parkin, 2002; Llop et al., 2002), including that of our own group (Dias et al., 1997, 1998, 2001, 2003; Ascenso et al., 2003). A relevant feature of these complexes is the possibility of inducing changes in the pyrrolyl hapticity by means of changing the other ligands in the coordination sphere. The series [Ti(pyr*)(NMe$_2$)$_{4-n}$Cl$_n$] is very useful for this kind of study because the progressive substitution of the amide ligands by chloride forces a change towards a more η^5-coordination of the pyrrolyl ligand. This change can also be followed by ^{13}C NMR studies on the ring C atoms, allowing a comparison between the deshielding effect felt by these atoms and the coordination mode.
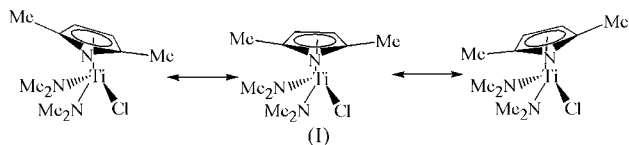

The title complex, [Ti(DMP)(NMe$_2$)$_2$Cl] (DMP is 2,5-dimethylpyrrolyl), (I), is unusual because its solid-state structure contains a η^5-pyrrolyl ring, while the deshielding effect felt by the ring C atoms is very low, roughly 10 p.p.m. relative to the free proligand. These facts may indicate that this kind of hapticity is more common than anticipated (based on ^{13}C NMR data).

Complex (I) crystallizes in the monoclinic system in space group $P2_1/c$. The molecular structure is depicted in Fig. 1. The coordination geometry can be best described as a piano-stool arrangement, a pseudo-tetrahedral geometry being confirmed by the angles around the metal centre (see Table 1) as well as by the X—Ti—Cp(centroid) angles [Cl1—Ti1—Cp(centroid) = 115.5 (8)°, N—Ti—Cp(centroid) = 119.9 (8)° and N—Ti—Cp(centroid) = 112.7 (8)°]. Although these angles all have values around 109° (ideal tetrahedral geometry), the angles involving the Cp centroid are considerably larger than those involving any two of the other ligands.

The attribution of a η^5 hapticity to the ligand ring is based on the Ti1—Cn (n = 1–4) and Ti1—N1 bond lengths (Table 1). Table 2 gives the Ti—N and Ti—C (maximum) bond lengths for similar compounds (Galvão, 1999; Kuhn et al., 1992), where η^5 hapticity was proposed on the basis of the X-ray structures. The difference between these two bond lengths in the present structure [0.184 (4) Å] is smaller than the differences found for several of these compounds. This discrepancy results in part from the fact that the Ti—N bond in (I) is longer than in the related compounds included in Table 2. Other important parameters considered in the attribution of this hapticity are the slip parameter and the fold angle. The slip parameter (Δ) is defined as the difference between the average bond lengths from the metal to the C atoms opposite the N atom, and the average bond lengths from the metal to the C atoms adjacent to the N atom, while the fold angle (FA) is defined as the angle between the C1/N1/C4 and C1–C4 planes (Cadierno et al., 1999). The values obtained [Δ = 0.073 (9) Å and FA = 4.6 (6)°] are well within the values accepted for η^5-Cp compounds. The N1—Cp(centroid)—Ti1 angle is also close to 90° [84.5 (7)°], as expected for a η^5 ring; this angle is larger than that for other compounds, such as [Ti(η^5-TMP)(NMe$_2$)Cl$_2$] [75.3 (7)°], to which a η^5 coordination has been unequivocally attributed (Galvão, 1999). Despite the η^5 coordination, the relative Ti1—Cn (n = 1–4) bond lengths are indicative that the ring exhibits a slippage, with one side of the ring (C3—C4) above the other.

The ^{1}H and ^{13}C room-temperature NMR spectra of (I) supply information that is, in part, contradictory to the X-ray structure. The spectra show the β H atoms and the two α C
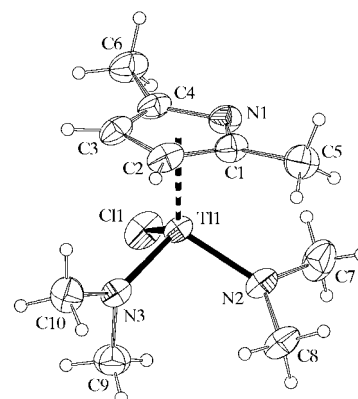
Figure 1
A view of (I) (30% probability displacement ellipsoids) with the atomic labelling scheme.

atoms originating two peaks, which is in good agreement with the loss of the symmetry plane usually formed by atoms N1 and Ti1 and the Cp centroid caused by the slippage of the ring. However, the deshielding values observed for the ring C atoms (6.64 p.p.m. for atoms C2 and C5, and 12.49 p.p.m. for atoms C3 and C4) are the lowest ever reported for a η^5-pyrrolyl, indicating the possibility of a coordination intermediate between N-σ (where no deshielding for atoms C3 and C4 should be detected) and η^5, as proposed for Ti(2,3,4,5-tetra-methylpyrrolyl)(NMe$_2$)$_2$Cl (Galvão, 1999).

The variation of the splitting between the ^{13}C peaks of atoms C3 and C4 with temperature was analysed, and a merging temperature of 285 K was determined; this result indicates the existence of a fluxional process above this temperature, passing through an intermediate involving simultaneously a metal–azaallyl and a metal–olefin bond (see scheme); this mechanism would explain the low values of deshielding observed.

The value of the Gibbs free energy for this process (ΔG_c = 71.61 kJ mol^{-1}) was calculated using the Eyring equation ($\Delta \mu$ = 3.9 Hz, k_c = 17.33 s^{-1} and T_c = 285.15 K).

Experimental

Ti(NMe$_2$)$_3$Cl (0.5 g, 2.3 mmol) was dissolved in toluene (30 ml) and HDMP (2.5 mmol) was added slowly. The mixture was refluxed for 2 h, after which time the solvent was removed *in vacuo*, resulting in the formation of a red oil. This oil was extracted with *n*-hexane, producing a red extract that was cooled to 193.15 K. From the cooled solution, red crystals were obtained and characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis (*ca* 0.33 g, 53% yield). Analysis found: C 44.8, H 7.8, N 14.6%; C$_{10}$H$_{20}$ClN$_3$Ti requires: C 45.2, H 7.6, N 15.8%. ^{1}H NMR (300 MHz, C$_6$D$_6$): 2.28 (6H, *s*), 3.01 (12H, *s*), 5.93 (2H, *s*); ^{13}C NMR (300 MHz, C$_6$D$_6$): 16.5 (CH$_3$), 47.0 [Ti—N(CH$_3$)$_2$], 112.9 (ring C), 138.0 (ring C).

Crystal data

[Ti(C$_2$H$_6$N)$_2$(C$_6$H$_8$N)Cl]	D_x = 1.301 Mg m^{-3}
M_r = 265.64	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
a = 8.421 (2) Å	reflections
b = 11.915 (2) Å	θ = 18–22°
c = 13.932 (2) Å	μ = 6.95 mm^{-1}
β = 104.04 (2)°	T = 298 (2) K
V = 1356.1 (5) Å^3	Plate, red
Z = 4	0.40 × 0.25 × 0.09 mm

Data collection

Enraf–Nonius CAD-4	θ_{max} = 66.9°
diffractometer	h = −10 → 1
$\omega/2\theta$ scans	k = −1 → 14
3232 measured reflections	l = −16 → 16
2406 independent reflections	3 standard reflections
1813 reflections with $I > 2\sigma(I)$	every 500 reflections
R_{int} = 0.111	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.049	$+ 0.5834P]$
$wR(F^2)$ = 0.142	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max}$ = 0.031
2406 reflections	$\Delta\rho_{max}$ = 0.52 e Å^{-3}
143 parameters	$\Delta\rho_{min}$ = −0.45 e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.0028 (5)

Table 1
Selected geometric parameters (Å, °).

Ti1—N3	1.880 (3)	Ti1—C3	2.465 (4)
Ti1—N2	1.886 (3)	N1—C1	1.382 (5)
Ti1—N1	2.283 (3)	N1—C4	1.384 (5)
Ti1—Cl1	2.3211 (12)	C1—C2	1.384 (6)
Ti1—C1	2.328 (4)	C2—C3	1.408 (5)
Ti1—C4	2.398 (4)	C3—C4	1.392 (6)
Ti1—C2	2.407 (4)		
N3—Ti1—N2	101.36 (14)	N2—Ti1—Cl1	101.72 (11)
N3—Ti1—Cl1	103.51 (11)		

Table 2
Comparative geometrical parameters (Å) for selected complexes.

	Ti—N	Ti—Cβ
Ti(η^5-DMP)(NMe$_2$)$_2$Cl	2.283 (3)	2.465 (4)
Ti(η^5-TMP)(NMe$_2$)Cl$_2$	2.149 (7)	2.580 (9)
Ti(η^5-TMP)Cl$_2$	2.181 (6)	2.426 (6)
Ti(η^5-Cp)(η^5-TMP)Cl$_2$	2.254 (9)	2.549 (12)
Ti(η^5-TMP)(SPh)$_3$	2.168 (10)	2.460 (14)
Ti(η^5-TMP)(CH$_3$)Cl$_2$	2.188 (2)	2.437 (1)
Ti(η^5-di-*tert*-butylpyrrolyl)Cl$_3$	2.249 (11)	2.344 (14)

Crystals of (I) were recovered from toluene and crystallized in the monoclinic space group $P2_1/c$. Methyl H atoms were positioned using an idealized methyl geometry, with the torsion angle taken from the electron density [C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C)]; in addition, Cp H atoms were placed in idealized aromatic positions [C—H = 0.93 Å and U_{iso}(H) = 1.3U_{eq}(C)]. Refinement was carried out based on F^2 against all reflections. The weighted R factor, wR, and goodness-of-fit, S, were based on F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ was used only for calculating R factors and is not relevant to the choice of reflections for refinement. No absorption correction was performed, because of the instability to air, moisture and temperature of the compound and its low diffracting power.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR99* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PLATON* and *enCIFer* (Allen *et al.*, 2004).

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