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Two 18ē Ti^{IV} η^5-Cp-tris(*sec*-amido)-type complexes derived from 1*H*-imidazol-2-yl side-chain functionalized cyclopentadienes

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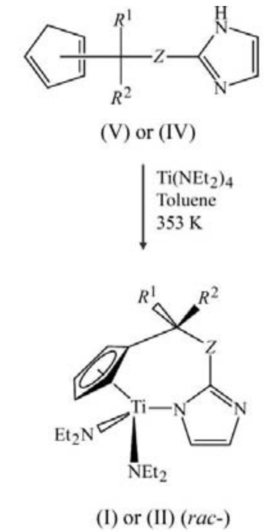
Achiral {2-[2-(η^5-cyclopentadienyl)-2-methylpropyl]-1*H*-imidazolyl-κN^1}bis(*N*,*N*-diethylamido-κN)titanium(IV), $[\text{Ti}(\text{C}_4\text{H}_{10}\text{N})_2(\text{C}_{12}\text{H}_{14}\text{N}_2)]$, (I), and closely related racemic (*SR*)-{2-[(η^5-cyclopentadienyl)(phenyl)methyl]-1*H*-imidazolyl-κN^1}-bis(*N*,*N*-diethylamido-κN)titanium(IV), $[\text{Ti}(\text{C}_4\text{H}_{10}\text{N})_2(\text{C}_{15}\text{H}_{12}\text{N}_2)]$, (II), have been prepared by direct reactions of $\text{Ti(NEt}_2)_4$ and the corresponding 1*H*-imidazol-2-yl side-chain functionalized cyclopentadienes. In compound (II), there are two crystallographically independent molecules of very similar geometries connected by a noncrystallographic pseudosymmetry operation akin to a 2_1 screw axis. All Ti-ligating N atoms in both (I) and (II) are in planar environments, which is indicative of an additional N→Ti $p\pi$–$d\pi$ donation. This fact and the 18ē nature of both (I) and (II) are additionally supported by quantum chemical single-point density functional theory (DFT) computations.

Comment

1*H*-Imidazol(in)-2-yl side-chain functionalized cyclopentadienes (Cp) were introduced as ligands into the organometallic chemistry of the Group 4 transition metals not long ago (Krut'ko *et al.*, 2006; Nie *et al.*, 2008). However, in all of the Ti (and Zr) complexes described in these papers, the imidazol(in)e part of the ligands possesses methyl groups at the N1 atoms and the *M*—N bonds are, in actual fact, coordination ones. The present contribution reports the preparation and molecular structures of the first two 'geometry-constrained' Ti^{IV} 18ē η^5-Cp-tris(*sec*-amido)-type complexes derived from 1*H*-imidazol-2-yl side-chain functionalized cyclopentadienes, namely achiral {2-[2-(η^5-cyclopentadienyl)-2-methylpropyl]-1*H*-imidazolyl}bis(*N*,*N*-diethylamido)titanium(IV), (I), and closely related racemic (*SR*)-{2-[(η^5-cyclopentadienyl)(phenyl)methyl]-1*H*-imidazolyl}bis(*N*,*N*-diethylamido)titanium(IV), (II).



(I) and (V): $Z = \text{CH}_2$, $R^1 = R^2 = \text{Me}$
(II) and (IV): Z = none, $R^1 = \text{H}$, $R^2 = \text{Ph}$

Complexes (I) and (II) have been prepared by direct reactions of $\text{Ti(NEt}_2)_4$ and the corresponding 1*H*-imidazol-2-yl side-chain functionalized cyclopentadienes (see scheme). Both (I) and (II) crystallize in centrosymmetric space groups ($P2_1/n$ and $P\overline{1}$, respectively).

In compound (II), there are two crystallographically independent molecules, denoted (II*A*) and (II*B*), of very similar geometries, connected by a noncrystallographic pseudosymmetry operation (see below). Ellipsoid plots of molecules of (I) and (II) are presented in Figs. 1 and 2, respectively.

The principal geometric parameters for (I), (II*A*) and (II*B*) are rather similar (see Table 1 and supplementary material). The coordination polyhedra of the Ti atoms in all cases are distorted tetrahedra (assuming that each Cp ring occupies one

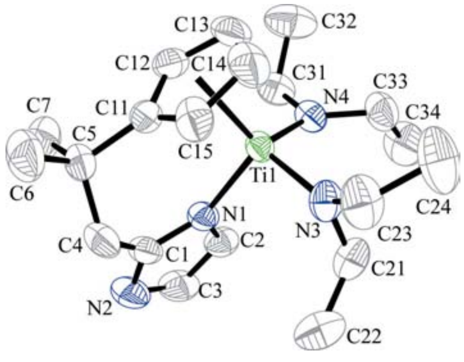


Figure 1
A view of the molecule of compound (I). Displacement ellipsoids are shown at the 50% probability level and all H atoms have been omitted for clarity.

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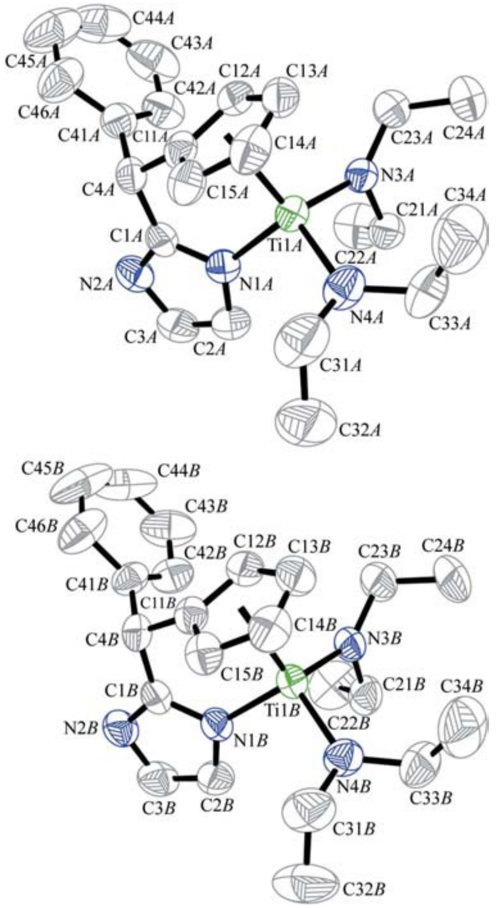

Figure 2
Views of the two crystallographically independent molecules (II*A*) (top) and (II*B*) (bottom) of compound (II) (both *S* enantiomers). Displacement ellipsoids are shown at the 50% probability level and all H atoms have been omitted for clarity. Both molecules have been oriented in a similar way to demonstrate their similarity.

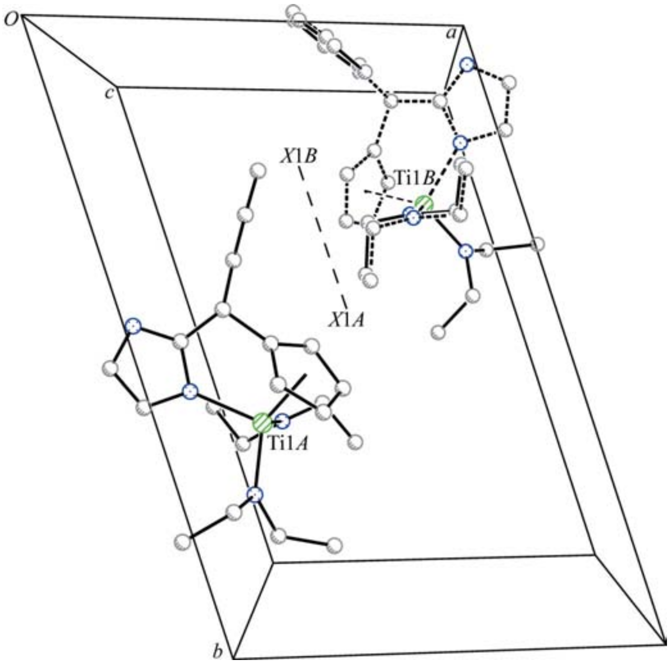

Figure 3
Perspective view of the unit cell along the direction of the *c* axis showing the noncrystallographic pseudosymmetry in (II). For clarity, non-H atoms are drawn as circles and all H atoms have been omitted. Phenyl-ring C atoms are eclipsed. Clockwise rotation of crystallographically independent molecule (II*A*) around axis *X*1*A*–*X*1*B* by 179.4°, followed by translation along vector *X*1*A*–*X*1*B*, results in a nearly complete overlap of the image (depicted with dashed lines) and molecule (II*B*). Parameters of the symmetrical transformation were optimized to minimize the sum of squared deviations of the image and molecule (II*B*) atoms (all atoms were considered; no weighting scheme was applied).

coordination site). N atoms ligating to Ti atoms are all in planar environments (see Table 2). The same is true of head-of-bridge imidazole-fragment atom C1, Cp-ring atom C11 and phenyl-ring atom C41 [in (II)] [see Table 2; here and throughout the text atoms are named as for compound (I); for atom names in molecules (II*A*) and (II*B*), the appropriate suffix *A* or *B* is appended]. Imidazole and Cp rings are all nearly planar; Ti1—PL1 distances in all moieties are approximately identical (PL1 denotes the C11–C15 Cp-ring r.m.s. plane; see Table 3). Atoms C4 and Ti1 deviate slightly from the imidazole ring planes PL2 (PL2 denotes the imidazole N1/C1/N2/C2/C3 r.m.s. plane; see Table 3). Of interest in all moieties in question, Ti1 atoms deviate considerably from the bisectrices of the outer C21—N3—C23 and C31—N4—C33 angles (see Table 1). Also noteworthy is the fact that the imidazole fragments in (I), (II*A*) and (II*B*) exhibit distinctly alternating single and double bonds (compare the C1—N1, C2—N1, C3—N2 bond lengths with the C1—N2 and C2—C3 bond lengths; see Table 1). Thus, atom N1 should be formally assigned an amido-type nature.

The presence of an additional CH$_2$ group in the hydrocarbon linkage of (I) causes certain differences in its structure compared with that of (II). Thus, while in (II) the bridging C4 atoms deviate from plane PL1 towards the same side as atom Ti1, related atom C5 in (I) is shifted to the opposite side of the ring plane from the metal centre (see Table 3). In comparison with (II), the imidazole fragment plane PL2 in (I) is less steeply inclined to plane PL1 [compare the dihedral PL1—PL2 angle of 62.58 (8)° in (I) with values of 77.52 (8) and 75.03 (8)° in (II*A*) and (II*B*), respectively]. The greater rigidity of the C$_1$ linkage in (II) than the C$_2$ linkage in (I) also results in a different positioning of the Ti1 atoms with respect to the C1—N1—C2 outer angle bisetrices (compare the C1—N1—Ti1 and C2—N1—Ti1 angles in Table 1). The same 'C$_2$-linkage effect' brings methyl atom C7 in (I) nearly into the PL1 plane [torsion angle C7—C5—C11—C12 = −3.7 (3)°].

As was mentioned above, molecules (II*A*) and (II*B*) [for convenience, the two reference molecules in the model were chosen with the same chirality (*S*)] are connected by a noncrystallographic pseudosymmetry. Thus, rotation of molecule (II*A*) around the *X*1*A*–*X*1*B* axis (passes through the middle of the Ti1*A*–Ti1*B* vector and makes angles with the *a*, *b* and *c* axes of 71.4, 1.1 and 88.4°, respectively; Fig. 3) by 179.4° followed by translation by (–0.003, −0.282, −0.004) results in a nearly complete overlap of the image with molecule (II*B*) [mean squared deviation = 0.05 (1) Å^2 (all H atoms included)].

This symmetry transformation is very close to a one-step rotation around a 2_1 screw axis nearly parallel to the *b* axis of the unit cell with a period close to a quarter of the *b*-axis length.

Analysis of the Cambridge Structural Database (CSD; Version 5.27, release February 2009; Allen, 2002) reveals 16 structurally characterized Ti complexes of a similar η^5-CpTi-tris(*sec*-amido) type (22 independent fragments) (Rhodes *et al.*, 2002; Li *et al.*, 2003; Seo *et al.*, 2001; Kunz *et al.*, 2001, 2002; Carpenetti *et al.*, 1996; Bertolasi *et al.*, 2007; Wu *et al.*, 2006; Cano *et al.*, 2005; Martin *et al.*, 1994). It is noteworthy that, except for η^5-Cp*-Ti(NMe$_2$)$_3$ (Martin *et al.*, 1994), all these complexes, as in the case of compounds (I) and (II), contain at least one amido functionality linked to the Cp ring with a flexible bridge. Bond distances and angles around the Ti centre in (I) and (II) are all within the ranges reported previously.

In all the fragments mentioned above, except for the Ti complex reported by Cano *et al.* (2005), the amido N atom environments are planar and these N atoms are usually treated as sp^2-hybridized. The question of the electron count at the Ti atom and the ability of an N-heterocyclic system to participate in an N→Ti $p\pi$–$d\pi$ donation was discussed in an earlier work (Seo *et al.*, 2001), where the structure of a close η^5-Cp-Ti-(*sec*-amido)$_3$-type counterpart of complexes (I) and (II) derived from a (pyrrol-2-yl)methyl side-chain functionalized cyclopentadiene, namely [2-[(η^5-cyclopenta-2,4-dienyl)methyl]-1*H*-pyrrolyl-κN]bis(*N*,*N*-dimethylamido-κN)titanium(IV), (III), was reported. The main features of the metal centre environment in (I), (II) and (III) are very similar, with the environments of all amido N atoms in (III) also being planar. However, since the Ti1—N1 bond in (III) is about 0.16 Å longer than other Ti—N bonds [the same is true for (I) and (II)], Seo *et al.* (2001) considered complex (III) to be formally a 16$\bar{e}$ system, suggesting that the aromatic heterocyclic moiety is exclusively a σ- but not a π-donor, only on the basis of a noticeable but noncritical Ti1—N1 bond elongation.

To investigate this further, we performed single-point density functional theory (DFT) computations for the experimentally established geometries of (I) and (II*A*) (see *Experimental* for details). The highest occupied molecular orbitals (HOMO; π-binding, two node surfaces) in both (I) and (II*A*) are fully located at the imidazole rings. The next two lower molecular orbitals in energy (HOMO-1 and HOMO-2) in both (I) and (II*A*) are evidently responsible for the $p\pi$–$d\pi$ donation from the –NEt$_2$ groups towards the metal centre. However, in the case of (I), the HOMO-3 to HOMO-6 orbitals all exhibit distinct $p\pi$–$d\pi$ overlap of the N1 and Ti1 atomic orbitals, with the node surface passing through the Ti1 and N1 atom centres being present in all of these cases. Lower energy orbitals in (I) (HOMO-7, HOMO-9, HOMO-10 and HOMO-12) provide σ-binding of all three amido-type groups to the central atom. A similar situation is observed in the case of (II*A*). Taking all this into consideration, there is no doubt about the presence of the $p\pi$–$d\pi$ donation to the Ti centre from all of the adjacent N atoms in both (I) and (II) [and, surely, in (III)], and all of these complexes should be treated as 18$\bar{e}$ systems.

In solution, compound (I) exhibits fluxional behaviour. NMR data (see *Experimental*) in both C_6D_6 and THF-d_8 (THF is tetrahydrofuran) are indicative of the pseudo-C_s symmetry of (I) at ambient temperature. This fluxional behaviour is rather typical for the class of compounds to which complex (I) belongs (see, for example, Krut'ko *et al.*, 1996*a*,*b*, 1998, 2003, 2004, 2005, 2006; Nie *et al.*, 2008) and is, actually, a degenerate interconversion of the Ti1—C11—C5—C4—C1—N1—(Ti1) six-membered pseudo-metallacycle. The 'remains' of this flexibility, of interest, are also noticeable even in the solid state, where this interconversion is 'frozen' and (I) is represented by two enantiomorphic conformers. The atomic displacement ellipsoids of C13/C14 and C12/C15 are all 'stretched' in directions close to the Cp-ring plane, with the length of the maximal principal axes of C13 and C14 being considerably greater than those of C12 and C15. This may be interpreted by assuming that in the 'geometry constrained ' (I), the Cp ring is involved in a 'slipping' movement over the Ti1 atom and may be best described as a rotational vibration of the whole Cp ring around an axis approximately normal to the Cp plane and crossing it close to atom C5.

Experimental

All operations were performed in all-sealed evacuated glass vessels with application of a high-vacuum line (the residual pressure of noncondensable gases within the range 1.5–1.0 $\times 10^{-3}$ Torr; 1 Torr = 133.322 Pa). Ti(NEt$_2$)$_4$ was prepared as described previously (Bürger & Dämmen, 1974; Bradley & Thomas, 1960). 2-{[Cyclopenta-1,3-dien-1(or 2)-yl]phenylmethyl}- and 2-{2-[cyclopenta-1,3-dien-1(or 2)-yl]-2-methylpropyl}-1*H*-imidazole, (IV) and (V), respectively, were prepared as described by Wang *et al.* (2009). Toluene and hexane were purified by distillation over an Na–K alloy. C_6D_6 was dried similarly. THF-d_8 was stored with disodium benzophenone ketyl. Both THF-d_8 and C_6D_6 were transferred into NMR sample tubes on a high-vacuum line by trapping their vapours with liquid N$_2$. NMR spectra were recorded on a Varian INOVA-400 instrument. For ^{1}H and ^{13}C{^{1}H} NMR spectra, the residual proton resonances of the *d*-solvents [δ_H = 7.15 and δ_C = 128.0 (C_6D_6); δ_H = 1.73 and δ_C = 25.3 (THF-d_8)] were used as internal reference standards.

Solutions of equimolar amounts of Ti(NEt$_2$)$_4$ and cyclopentadiene (IV) or (V) in toluene (20 ml) were mixed and heated in a water bath (353 K) for 8 h. The reaction mixture was then concentrated to dryness (by trapping the volatile components in an adjacent vessel cooled with liquid N$_2$) and extracted with hexane (6 × 40 ml). Pure (I) and (II) were obtained by recrystallization from hot hexane (50 ml). Compound (I) was prepared from Ti(NEt$_2$)$_4$ (0.984 g, 2.6 mmol) and (V) (0.496 g, 2.6 mmol). Orange crystals were obtained in a yield of 0.478 g (50%). Compound (II) was prepared from Ti(NEt$_2$)$_4$ (1.110 g, 3.3 mmol) and cyclopentadiene (IV) (0.739 g, 3.3 mmol). Well formed yellow crystals were obtained in a yield of 0.816 g (60%). Single crystals of (I) and (II) suitable for X-ray diffraction analyses were picked up directly from the isolated materials (N$_2$-filled glove-box) and mounted in Lindemann glass capillaries (diameter 0.5 mm). Details of the quantum chemical computation: the single-point DFT calculations for (I) and (II*A*) were performed using the hybrid RB3LYP functional and the valency-split 6–31+G(*d*,*p*) basis set with added diffuse and polarization functions (program package *GAUSSIAN03W*; Frisch *et al.*, 2003). Tight criteria on the self-consistent field convergence were applied. The wavefunctions were checked for stability. All additional computational materials not included in the body of the paper are available from the authors on request.

Compound (I)

Crystal data

$[Ti(C_4H_{10}N)_2(C_{12}H_{14}N_2)]$
$M_r = 378.41$
Monoclinic, $P2_1/n$
$a = 13.729$ (3) Å
$b = 14.829$ (3) Å
$c = 10.679$ (2) Å
$\beta = 92.749$ (3)°
$V = 2171.7$ (8) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.40$ mm^{-1}
$T = 293$ K
0.36 × 0.27 × 0.14 mm

Data collection

Bruker SMART APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.868$, $T_{max} = 0.946$
11087 measured reflections
4213 independent reflections
3287 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.106$
$S = 1.04$
4213 reflections
232 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Compound (II)

Crystal data

$[Ti(C_4H_{10}N)_2(C_{15}H_{12}N_2)]$
$M_r = 412.43$
Triclinic, $P\overline{1}$
$a = 9.7472$ (15) Å
$b = 14.469$ (2) Å
$c = 18.006$ (3) Å
$\alpha = 89.362$ (2)°
$\beta = 76.965$ (2)°
$\gamma = 72.161$ (2)°
$V = 2350.4$ (6) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.38$ mm^{-1}
$T = 293$ K
0.40 × 0.29 × 0.17 mm

Data collection

Bruker SMART APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.863$, $T_{max} = 0.939$
11818 measured reflections
8157 independent reflections
5573 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.116$
$S = 1.00$
8157 reflections
506 parameters
16 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

H atoms were treated as riding atoms, with distances C—H = 0.96 (CH_3), 0.97 (CH_2) or 0.93 Å (aromatic), and $U_{iso}(H) = 1.5U_{eq}(C)$, $1.2U_{eq}(C)$ and $1.2U_{eq}(C)$, respectively. The components of the anisotropic displacements of atoms C13 and C14 along the C13—C14 bond in (I), C13*A* and C14*A* along the C13*A*—C14*A* bond in (II), and N4*A* and C31*A* along the N4*A*—C31*A* bond in (II) were restrained to be the same, with standard uncertainties of 0.002, 0.01 and 0.005 Å^2, respectively. The components of the anisotropic displacements of phenyl-ring C atoms C42–C46 [both molecules (II*A*) and (II*B*)] along the 1–2 and 1–3 directions were restrained to be the same, with a standard uncertainty of 0.01 Å^2.

Table 1
Selected geometric parameters (Å, °) for (I), (II*A*) and (II*B*).

	(I)	(II*A*)	(II*B*)
Ti1—N1	2.0551 (14)	2.0655 (19)	2.0485 (18)
Ti1—N3	1.8950 (16)	1.8857 (19)	1.876 (2)
Ti1—N4	1.8988 (15)	1.905 (2)	1.906 (2)
N1—C1	1.370 (2)	1.367 (3)	1.365 (3)
N1—C2	1.385 (2)	1.377 (3)	1.375 (3)
N2—C1	1.322 (3)	1.316 (3)	1.316 (3)
N2—C3	1.372 (3)	1.377 (3)	1.374 (3)
C2—C3	1.347 (3)	1.351 (3)	1.351 (3)
N3—Ti1—N4	103.45 (7)	103.96 (8)	104.47 (9)
N3—Ti1—N1	104.48 (7)	107.24 (8)	107.31 (8)
N4—Ti1—N1	99.79 (6)	106.57 (9)	105.11 (8)
C1—N1—C2	104.17 (15)	103.30 (18)	103.65 (18)
C1—N1—Ti1	130.51 (13)	123.42 (14)	123.51 (15)
C2—N1—Ti1	124.94 (12)	132.59 (15)	132.66 (16)
C23—N3—C21	111.22 (17)	112.53 (19)	113.0 (2)
C23—N3—Ti1	137.05 (16)	139.26 (16)	138.91 (18)
C21—N3—Ti1	111.72 (12)	108.13 (15)	108.05 (15)
C33—N4—C31	114.18 (16)	113.0 (2)	113.1 (2)
C33—N4—Ti1	127.27 (14)	126.21 (19)	125.64 (18)
C31—N4—Ti1	118.07 (12)	119.10 (17)	119.78 (17)

For atom names in (II*A*) and (II*B*), suffixes *A* or *B*, respectively, should be appended.

Table 2
Sums of the valence angles (°) at atoms in planar environments for (I), (II*A*) and (II*B*).

	(I)	(II*A*)	(II*B*)
N1	359.6 (4)	359.3 (5)	359.8 (5)
N3	360.0 (5)	359.9 (5)	360.0 (5)
N4	359.5 (4)	358.3 (6)	358.5 (6)
C1	360.0 (5)	360.0 (6)	360.0 (6)
C11	360.0 (6)	359.5 (6)	359.3 (6)
C41		359.9 (8)	359.9 (8)

For atom names in (II*A*) and (II*B*), suffixes *A* or *B*, respectively, should be appended.

Table 3
R.m.s. planes and atom deviations (Å) for (I), (II*A*) and (II*B*).

	(I)	(II*A*)	(II*B*)
PL1†	0.0070 (13)	0.0111 (13)	0.008 (2)
PL2†	0.0031 (13)	0.003 (2)	0.005 (2)
Ti1—PL1	2.0555 (10)	2.0370 (10)	2.0427 (11)
Ti1—PL2	0.181 (3)	0.272 (4)	0.122 (4)
C4(or C5)—PL1	−0.061 (3)	0.200 (4)	0.220 (4)
C4—PL2	0.046 (4)	−0.058 (4)	0.013 (4)

† Maximum deviations of the r.m.s. plane-forming atoms. PL1 denotes the C11–C15 Cp-ring r.m.s. plane and PL2 the imidazole N1/C1/N2/C2/C3 r.m.s. plane. For atom names in (II*A*) and (II*B*), suffixes *A* or *B*, respectively, should be appended.

For both compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97* and *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *SHELXL97* and *OLEX2*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3099). Services for accessing these data are described at the back of the journal.

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