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Synthesis, characterisation, crystal structure, reactivity and bonding in titanium complexes containing 2,3,4,5-tetramethylpyrrolyl†

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The complex [Ti(η^5-NC_4Me_4)Cl_3] **1** has been synthesized, characterised and used as a precursor for the preparation of the bis(pyrrolyl) complex [Ti(η^5-NC_4Me_4)$_2$$Cl_2$] **2** and the thiolate complexes [Ti(η^5-NC_4Me_4)(SPh)$_3$] **3** and [Ti(η^5-NC_4Me_4)(SPh)Cl_2] **4**. The η^5 co-ordination of the heterocyclic ring was predicted by the ^{13}C NMR data and confirmed by the structure determination of complexes **1** and **3**, which present a piano-stool conformation and a slippage of the pyrrolyl towards the titanium. The mixed-ring complex [Ti(η^5-C_5H_5)(η^5-NC_4Me_4)Cl_2] **5** has also been synthesized and its structure determined, revealing a distorted pseudo-tetrahedral geometry and slippage of the heterocyclic ring.

Organometallic compounds with cyclopentadienyl ligands are very common in organotransition metal chemistry[1] and have some important applications, namely as homogeneous catalysts in polymerisation reactions[2] and as anticarcinogenic agents.[3,4] However, although the pyrrolyl ligand is isoelectronic with cyclopentadienyl, the complexes with an η^5-pyrrolyl are much less common. The instability of the π-bound pyrrolyl complexes is often attributed to the lower ionisation potential of the non-bonding electron pair of the nitrogen atom relative to that of the π electrons.[5–7] Therefore, there are several compounds where pyrroles and pyrrolyls are σ-bound to a transition-metal atom,[5,7–16] as in biological systems, while π co-ordination is rarer.

Our aim is the synthesis and characterisation of mono- and bis-η^5-pyrrolyl complexes with transition metals and the comparison with the corresponding cyclopentadienyl complexes in terms of stability, structural features and catalytic properties. We started our studies with titanium given the well known catalytic activity of its complexes.[2] The 2,3,4,5-tetramethylpyrrolyl ligand was chosen because substitution of the pyrrolyl ring with electrodonating groups, like alkyl groups, promotes the η^5 co-ordination[5,6,12,17] and there are already some examples of η^5-2,3,4,5-tetramethylpyrrolyl complexes: [Mn(η^5-NC_4Me_4)(CO)$_3$],[18] [Fe(η^5-NC_4Me_4)$_2$]·2NHC_4Me_4,[14,19] [Ru(η^5-C_5Me_5)(η^5-NC_4Me_4)] and [Ru(η^5-NC_4Me_4)$_2$].[20]

Although there are some literature references concerning the complex [Ti(NC_4Me_4)Cl_3],[21,22] mass spectrometry was the only technique used for its characterisation. Therefore, we synthesized this complex by an alternative route, fully characterised it and used it as a precursor for the preparation of other titanium complexes, in an attempt to reproduce the titanium mono- and bis-cyclopentadienyl chemistry.[23]

Experimental

General procedures

All reactions and manipulations were carried out under an argon atmosphere, using standard Schlenk-tube techniques and some of the NMR samples were prepared in a Mbraun glove-box. All the solvents were dried with sodium and distilled over sodium–benzophenone, under nitrogen. Deuteriated benzene was dried with molecular sieves and deoxygenated by several freeze–pump–thaw cycles. 2,3,4,5-Tetramethylpyrrole[24] and sodium benzenethiolate[25] were prepared as described. Titanium tetrachloride and butyllithium were obtained from Aldrich and used without further purification. The NMR spectra were recorded in deuteriated benzene on a Varian 300 MHz spectrometer and referenced internally to the residual benzene resonance, IR spectra (in Fluorolube mulls) on a FTIR Nicolet DX spectrometer. Elemental analyses were performed by Laboratório de Análises do Instituto Superior Técnico on a Fisons Instruments 1108 spectrometer. Mass spectra were recorded at Instituto de Tecnologia Nuclear on a Finnigan FTMS 2001 instrument.

Syntheses

Li[NC_4Me_4]. To a stirred and cooled suspension (0 °C) of 2,3,4,5-tetramethylpyrrole (1.3 g, 10.55 mmol) in tetrahydrofuran (*ca.* 40 cm^3) was added 1.7 mol dm^{-3} butyllithium (6.5 cm^3, 11.05 mmol). The reaction mixture was left stirring overnight and then the white solid was filtered off, washed with tetrahydrofuran and dried under vacuum (yield 1.22 g, 90%).

[Ti(η^5-NC_4Me_4)Cl_3] 1. To a stirred and cooled suspension (−60 °C) of 2,3,4,5-tetramethylpyrrolyl lithium (1.56 g, 12.08 mmol) in toluene (*ca.* 50 cm^3) was added $TiCl_4$ (1.33 cm^3, 12.10 mmol). The mixture was left stirring overnight and then the volatile components were removed under vacuum. The yellow-brownish residue was extracted with pentane and the resulting yellow-orange solution evaporated, yielding an orange-reddish *solid* (*ca.* 1.00 g, 30%) (Found: C, 33.8; H, 4.6; N, 4.7. $C_8H_{12}Cl_3NTi$ requires C, 34.75; H, 4.4; N, 5.05%); $\tilde{\nu}_{max}$/cm^{-1} 2916s and 2853w (CH_3), 1652w and 1574w (aromatic C=C) and 1468w and 1378w (C–CH_3) (Fluorolube); δ_H(300 MHz, C_6D_6) 1.53 (6 H, s) and 2.28 (6 H, s); δ_C(300 MHz, C_6D_6) 11.30 (s, CH_3), 17.32 (s, CH_3), 141.95 (s, ring C) and 153.65 (s, ring C); *m/z* 277 (M^+, 2.2%), 239 ($M^+ - $HCl), 203 ($M^+ - 2$ HCl), 155 ($TiCl_3^+$) and 122 ($NC_4Me_4^+$). Crystals suitable for X-ray diffraction analysis were obtained from a solution of the residue in pentane at −30 °C. The selected crystal was mounted in a glove-box, in a Lindemann glass capillary.

[Ti(η^5-NC_4Me_4)$_2$$Cl_2$] 2. To a stirred and cooled solution (−60 °C) of [Ti(η^5-NC_4Me_4)Cl_3] (0.20 g, 0.72 mmol) in toluene (*ca.* 30 cm^3) was added 2,3,4,5-tetramethylpyrrolyl lithium (0.1 g, 0.77 mmol). The mixture was left stirring overnight and then the volatile compounds were removed under vacuum. A red *solid* was obtained (*ca.* 0.029 g, 13%); δ_H(300 MHz, C_6D_6) 1.86 (6 H, s), 1.90 (6 H, s), 2.00 (6 H, s) and 2.25 (6 H, s); δ_C(300 MHz, C_6D_6) 9.58 (s, CH_3), 11.05 (s, CH_3), 12.16 (s, CH_3), 17.04 (s, CH_3), 113.48 (s, ring C), 119.86 (s, ring C), 140.09 (s, ring C) and 147.71 (s, ring C); *m/z* 362 (M^-, 100.00%), 362 (M^+, 0.26%) and

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† *Non-SI unit employed*: eV ≈ 1.60 × 10^{-19} J.

122 ($NC_4Me_4^+$). The red solid was extracted with pentane, the solution was cooled to −30 °C and the precipitation of red *crystals* occurred. Several crystals were mounted in Lindemann glass capillaries in an attempt to determine the molecular structure.

[Ti(η^5-NC_4Me_4)(SPh)$_3$] 3. To a stirred solution of [Ti(η^5-NC_4Me_4)Cl_3] (0.28 g, 1.01 mmol) in toluene (*ca.* 30 cm^3), at room temperature, was added sodium benzenethiolate (0.40 g, 3.03 mmol). The mixture immediately turned from orange to dark red. It was left stirring overnight and then filtered, evaporated under vacuum and the residue extracted with diethyl ether. The resulting dark red solution was cooled to −30 °C giving dark red *crystals* suitable for X-ray diffraction analysis (*ca.* 0.095 g, 19%); δ_H(300 MHz, C_6D_6) 1.83 (6 H, s, CH_3 of the pyrrolyl), 2.38 (6 H, s, CH_3 of the pyrrolyl), 6.93 (9 H, m, *m*- and *p*-H of the thiolates) and 7.57 [6 H, d, *J*(HH) 7.2 Hz, *o*-H of the thiolates]; δ_C(300 MHz, C_6D_6) 11.29 (s, CH_3), 17.36 (s, CH_3), 126.33 (s), 130.58 (s), 132.16 (s), 133.35 (s), 134.98 (s, quaternary C of the thiolates), 142.31 (s, quaternary C of the pyrrolyl) and 148.28 (s, quaternary C of the pyrrolyl). The crystal selected for X-ray diffraction analysis was mounted in a Lindemann glass capillary, under an argon flow.

[Ti(η^5-NC_4Me_4)(SPh)Cl_2] 4. To a stirred solution of [Ti(η^5-NC_4Me_4)Cl_3] (0.20 g, 0.72 mmol) in toluene (*ca.* 50 cm^3), at room temperature, was added sodium benzenethiolate (0.10 g, 0.76 mmol). The mixture immediately changed from orange to dark red. It was left stirring overnight, then evaporated *in vacuo* and the red residue extracted with pentane. The resulting red solution was cooled to −30 °C and dark red *crystals* were obtained (*ca.* 0.025 g, 11%); δ_H(300 MHz, C_6D_6) 1.70 (6 H, s, CH_3 of the pyrrolyl), 2.33 (6 H, s, CH_3 of the pyrrolyl), 6.89 (3 H, m, *m*- and *p*-H of the thiolate) and 7.78 [2 H, d, *J*(HH) 7.2 Hz, *o*-H of the thiolate]; δ_C(300 MHz, C_6D_6) 11.76 (s, CH_3 of the pyrrolyl), 17.19 (s, CH_3 of the pyrrolyl), 129.46 (s), 132.66 (s), 138.96 (s, quaternary C of the thiolate), 143.25 (s, quaternary C of the pyrrolyl) and 150.77 (s, quaternary C of the pyrrolyl).

[Ti(η^5-C_5H_5)(η^5-NC_4Me_4)Cl_2] 5. To a stirred solution of [Ti(η^5-C_5H_5)Cl_3] (0.27 g, 1.23 mmol) in toluene (*ca.* 50 cm^3) was added 2,3,4,5-tetramethylpyrrolyl lithium (0.16 g, 1.24 mmol). After a few minutes the mixture turned from yellow to orange and finally became red. The reaction mixture was left stirring overnight, then filtered, evaporated *in vacuo* and the residue extracted with diethyl ether. The red solution obtained was cooled to −30 °C giving red *crystals* suitable for X-ray diffraction analysis (*ca.* 0.020 g, 5%); δ_H(300 MHz, C_6D_6) 1.82 (s, 6 H, CH_3), 1.84 (s, 6 H, CH_3) and 6.24 (s, 5 H, C_5H_5). The crystal selected for X-ray diffraction analysis was mounted in a glovebox, in a Lindemann glass capillary.

Crystallography

Data in the range $1.5 < \theta < 25°$ were collected by the ω–2θ scan mode on an Enraf-Nonius TURBO CAD4 diffractometer equipped with a rotating anode, using graphite-monochromated radiation ($\lambda = 0.710\,69$ Å), at room temperature. The unit cells and orientation matrices were obtained by least-squares refinement of 25 centred reflections.

For each crystal two standard reflections were monitored during data collection. For complex **1** no decay or instrumental instability was detected (the loss of intensity is less than 0.07% h^{-1}), but for compounds **3** and **5** the data were corrected for a decay of 0.24 and 0.18% h^{-1}, respectively. Using the CAD4 software, the data for the three complexes were corrected for Lorentz-polarisation effects and empirically for absorption (minimum transmission factors: 90.0, 68.4 and 91.3%, for complexes **1**, **3** and **5**, respectively; average transmission factors 94.7, 83.1 and 96.6%). The following weighting schemes were used for the structure solutions: $w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 0.76P]$ for **1**, $w = 1/[\sigma^2(F_o^2) + (0.0675P)^2 + 3.55P]$ for **3** and $w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 1.86P]$ for **5** $[P = (F_o^2 + 2F_c^2)/3]$. The positions of the Ti atoms were obtained by three-dimensional Patterson syntheses. All the other non-hydrogen atoms were located in subsequent Fourier-difference maps and refined with anisotropic thermal motion parameters. The hydrogen atoms were inserted in calculated positions and refined isotropically with fixed distances to the parent carbon atom: 0.96 Å for **1** and for H−C (Me) in **3** and **5**, 0.93 Å for H−C (Ph) in **3** and H−C (C_5H_5) in **5**. The isotropic thermal parameters of the hydrogen atoms in complex **3** were made equal to 1.2 [H−C (Ph)] and 1.5 [H−C (Me)] times the corresponding U_{eq} of the parent carbon atom and in **5** the isotropic thermal parameter was considered as 1.2 times the corresponding U_{eq} of the parent carbon atom.

Table 1 summarises the crystallographic data. The structure solution and refinement for all the structures (based on F^2) were performed with SHELX 82[26] and SHELXL 93[27] and the illustrations were drawn with ORTEP II.[28] The atomic scattering factors and anomalous scattering terms were taken from ref. 29.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/330.

Results and Discussion

[Ti(η^5-NC_4Me_4)Cl_3] 1

Although the synthesis of [Ti(η^5-NC_4Me_4)Cl_3] by direct reaction of $TiCl_4$ and 2,3,4,5-tetramethylpyrrole has already been reported in a patent,[21] the mass spectrum was the only evidence given for its formation. We synthesized this complex by an alternative route, using the lithium salt of 2,3,4,5-tetramethylpyrrole [equation (1)]. The orange-reddish solid **1**,

$$TiCl_4 + Li[NC_4Me_4] \xrightarrow[-60\,°C]{\text{toluene}} \underset{\mathbf{1}}{[Ti(\eta^5\text{-}NC_4Me_4)Cl_3]} + LiCl \qquad (1)$$

obtained in a moderate yield, is very sensitive to moisture, leading easily to decomposition with formation of the protonated pro-ligand, which is confirmed by the ^1H NMR spectrum. The infrared spectrum in Fluorolube mulls shows the expected vibrations for CH_3 (2916 and 2853 cm^{-1}), aromatic C=C (1652 and 1574 cm^{-1}) and C−CH_3 (1468 and 1378 cm^{-1}) bonds. The peak of highest *m*/*z* value in the mass spectrum (277) is consistent with the molecular ion [Ti(NC_4Me_4)Cl_3]$^+$. There are other peaks that can be assigned to the following cations: [Ti(NC_4Me_4)Cl_3]$^+$−HCl (*m*/*z* = 239), [Ti(NC_4Me_4)Cl_3]$^+$−2HCl (*m*/*z* = 203), $TiCl_3^+$ (*m*/*z* = 155) and $NC_4Me_4^+$ (*m*/*z* = 122).

The ^1H NMR spectrum is consistent with the formulation [Ti(NC_4Me_4)Cl_3], showing two singlets (δ 1.53 and 2.28) with relative areas 1 : 1, corresponding to the protons of the 3,4- and 2,5-methyl groups. The ^{13}C-{^1H} NMR spectrum suggests an η^5 co-ordination of the heterocyclic ligand, since the ring carbons (δ 153.65 and 141.95) are considerably deshielded when compared to those of the free pro-ligand (δ 120.20 and 113.80). In fact this deshielding relative to the pro-ligand is very similar to that reported for the compound [Ti(η^5-$NC_4H_2Bu^t_2$-2,5)Cl_3][22] and indicates the donation of electron density from the carbons to the metal, *i.e.* η^5 co-ordination. The carbons of the two types of methyl groups give two singlets at δ 11.30 and 17.32.

The η^5 co-ordination of the heterocyclic ligand was also confirmed by the crystal structure, which reveals a piano-stool configuration (Fig. 1). The five-membered ring was found to be planar with an average deviation of its atoms of 0.017 Å and the titanium atom lies 1.985 Å away from this plane. The C(1A) and C(4A) carbon atoms deviate 0.2 Å from that plane away from

Table 1 Crystal data, data collection and structure refinement for complexes **1**, **3** and **5**

	1	**3**	**5**
Empirical formula	$C_8H_{12}Cl_3NTi$	$C_{26}H_{27}NS_3Ti$	$C_{13}H_{17}Cl_2NTi$
M	276.44	497.57	306.08
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	6.734(2)	12.648(3)	6.987(2)
b/Å	7.314(3)	12.643(3)	24.132(4)
c/Å	12.760(6)	15.780(3)	8.682(4)
α/°	92.93(3)	—	—
β/°	96.63(2)	102.78(1)	107.34(2)
γ/°	107.25(2)	—	—
U/Å^3	593.7(4)	2460.8(9)	1397.3(8)
Z	2	4	4
D_c/g cm^{-3}	1.546	1.343	1.455
μ/cm^{-1}	13.52	6.16	9.72
Reflections collected	2279	4481	2661
Observed independent reflections ($F^2 \geqslant 0$)	1780	3181	1943
Parameters	134	280	154
Goodness of fit on F^2	1.08	1.07	1.07
Final $R1$, $wR2$ indices	0.07, 0.14	0.12, 0.24	0.088, 0.16
Largest difference peak/e Å^{-3}	0.38	0.4	0.37

Table 2 Selected bond lengths (Å) and angles (°) for $[Ti(\eta^5\text{-}NC_4Me_4)Cl_3]$ **1**, $[Ti(\eta^5\text{-}NC_4Me_4)(SPh)_3]$ **3** and $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}NC_4Me_4)Cl_2]$ **5**. Optimised *ab initio* structures for η^1 (**1a**) and η^5 (**1b**) $[Ti(NC_4H_4)Cl_3]$ complexes

	1	**3**	**5**	**1a**	**1b**
Ti–N	2.181(6)	2.168(10)	2.254(9)	1.777	2.164
Ti–C(1)	2.299(7)	2.299(14)	2.297(12)	2.907	2.275
Ti–C(2)	2.423(7)	2.46(2)	2.549(12)	3.991	2.462
Ti–C(3)	2.426(6)	2.460(14)	2.528(12)	3.991	2.462
Ti–C(4)	2.278(7)	2.317(14)	2.365(12)	2.907	2.275
Ti–Cl (average)	2.205	—	2.330	2.314	2.340
Ti–S (average)	—	2.301	—	—	—
C–C(A) (average)	1.487	1.48	1.51	—	—
Ti–C(5)	—	—	2.33(2)	—	—
Ti–C(6)	—	—	2.40(2)	—	—
Ti–C(7)	—	—	2.356(14)	—	—
Ti–C(8)	—	—	2.33(2)	—	—
Ti–C(9)	—	—	2.36(2)	—	—
Ti–XX	2.00	2.03	2.10	—	2.00
XX–Ti–Cl(1)/S(1)	116	124	—	102	109
XX–Ti–Cl(2)/S(2)	119	105	—	108	115
XX–Ti–Cl(3)/S(3)	111	108	—	108	115
N–XX–Ti	82	80	81	3	81
Ti–S(1)–C(11)	—	111.4(5)	—	—	—
Ti–S(2)–C(21)	—	102.5(5)	—	—	—
Ti–S(3)–C(31)	—	112.9(5)	—	—	—
N–XX–Ti–Cl(3)/S(1)	172	21	—	297	297
N–XX–Ti–Cl(2)/S(2)	54	132	—	63	63
N–XX–Ti–Cl(1)/S(3)	288	251	—	180	180
XX–Ti–S(1)–C(11)	—	311	—	—	—
XX–Ti–S(2)–C(21)	—	178	—	—	—
XX–Ti–S(3)–C(31)	—	187	—	—	—
Ti–S(1)–C(11)–C(12)	—	129	—	—	—
Ti–S(2)–C(21)–C(22)	—	91	—	—	—
Ti–S(3)–C(31)–C(32)	—	132	—	—	—

XX is the centroid of the heterocyclic ring.

the metal atom, probably due to steric hindrance, caused by the slippage of the ring (defined by the Ti–XX–N angle δ, represented in Fig. 5). The heterocyclic ring and the three chloride ligands are in an approximately staggered conformation, where the Ti–N and Ti–Cl(3) bonds projected into the plane perpendicular to the Ti–XX axis which contains the Ti atom point in opposite directions [from Table 2, N–XX–Ti–Cl(3) 172°].

$[Ti(\eta^5\text{-}NC_4Me_4)_2Cl_2]$ 2

In an attempt to obtain an analogous compound to $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$, we tested the reaction between $TiCl_4$ and 2 equivalents of 2,3,4,5-tetramethylpyrrolyl lithium, but the product obtained was the monosubstituted complex **1**. Using an alternative route, when a second equivalent of the lithium salt was added to **1** (although Kuhn *et al.*[22] were not successful using this process) a red solid was obtained, the mass spectrum ($m/z = 362$) of which is consistent with the compound $[Ti(NC_4Me_4)_2Cl_2]$, equation (2). The solid was recrystallised with pentane, yielding red crystals, with high sensitivity to moisture and oxygen.

$$[Ti(\eta^5\text{-}NC_4Me_4)Cl_3] + Li[NC_4Me_4] \xrightarrow[-60\,^{\circ}C]{\text{toluene}} \underset{\mathbf{2}}{[Ti(\eta^5\text{-}NC_4Me_4)_2Cl_2]} + LiCl \quad (2)$$

Although the mass spectrum is consistent with the formulation $[Ti(NC_4Me_4)_2Cl_2]$, the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra are

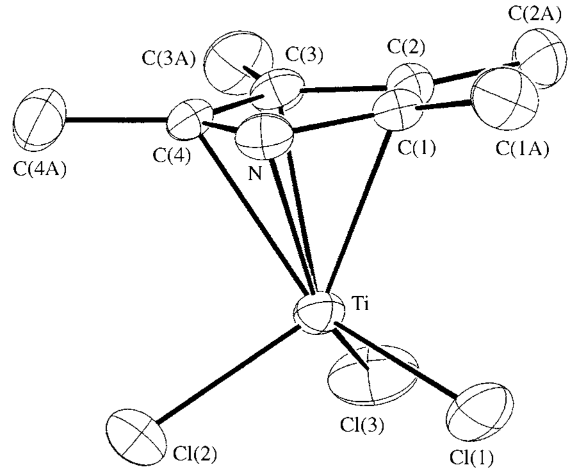

Fig. 1 Crystal structure of [Ti(η^5-NC_4Me_4)Cl_3] **1**

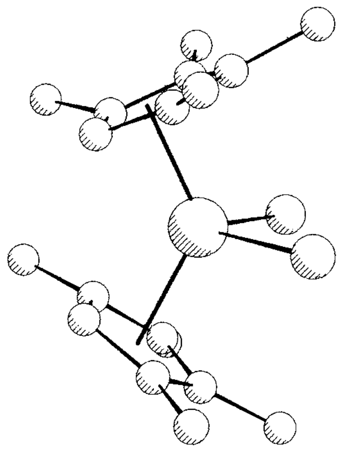

Fig. 2 Crystal structure of [Ti(η^5-NC_4Me_4)$_2Cl_2$] **2**

insufficient to determine the type of co-ordination of the heterocyclic rings. The ^{1}H spectrum shows four singlets with equivalent areas, corresponding to four types of methyl groups (δ 1.86, 1.90, 2.00 and 2.25). The peaks at δ 1.90 and 2.00 may be assigned to the presence of free 2,3,4,5-tetramethylpyrrole, which also presents two singlets at δ 1.90 and 2.00, or to an η^1-co-ordinated heterocyclic ring. From the ^{13}C-{^{1}H} NMR spectrum we can conclude that one of the heterocyclic ligands is η^5 co-ordinated, since the corresponding quaternary carbons are considerably deshielded (δ 140.09 and 147.71) relative to the free pro-ligand. The methyl carbons of this η^5-pyrrolyl give two singlets at δ 12.16 and 17.04 and the protons resonate at δ 1.86 and 2.25. Therefore, the structural possibilities for complex **2** are: two pyrrolyl rings η^5 co-ordinated (and the remaining signals in the NMR spectra are due to the presence of 2,3,4,5-tetramethylpyrrole as an impurity) or one pyrrolyl ring η^5 co-ordinated and another with η^1 co-ordination to the titanium.

Despite the extreme sensitivity of complex **2** to moisture and oxygen, several attempts were made to determine its crystal structure, but none yielded results with sufficient quality for publication. However, the set of crystallographic data clearly reveals that both pyrrolyl rings are η^5 co-ordinated (Fig. 2),‡

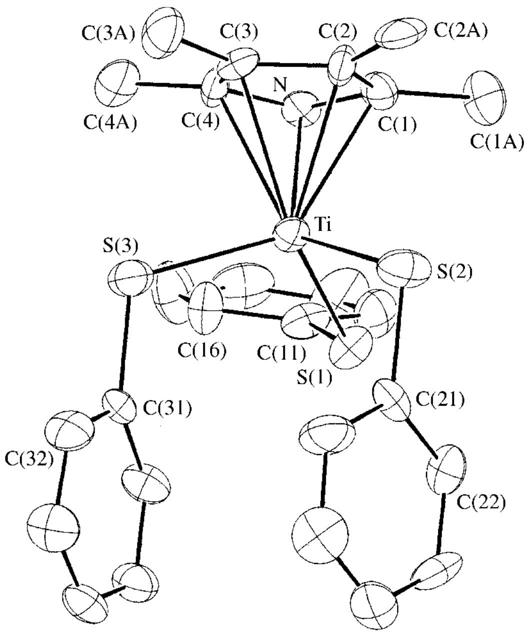

Fig. 3 Crystal structure of [Ti(η^5-NC_4Me_4)$(SPh)_3$] **3**

which means that the doubtful peaks in the NMR spectra are due to the presence of free pro-ligand.

[Ti(η^5-NC_4Me_4)$(SPh)_3$] 3

In an attempt to reproduce the chemistry of the monocyclopentadienyl complexes of titanium, we tested the substitution of the chlorides in complex **1** for thiolate groups. The reaction of **1** with 3 equivalents of sodium benzenethiolate at room temperature (r.t.) led to the expected product **3**, corresponding to substitution of the three chloride ligands, equation (3). The

$$[\mathrm{Ti}(\eta^5\text{-}\mathrm{NC_4Me_4})\mathrm{Cl_3}] + 3\ \mathrm{NaSPh} \xrightarrow[\text{r.t.}]{\text{toluene}} \underset{\mathbf{3}}{[\mathrm{Ti}(\eta^5\text{-}\mathrm{NC_4Me_4})(\mathrm{SPh})_3]} + 3\ \mathrm{NaCl} \quad (3)$$

recrystallisation with diethyl ether led to the formation of dark red crystals, very sensitive to moisture.

The ^{1}H NMR spectrum reveals two signals due to the two types of pyrrolyl ligand methyl protons (δ 1.83 and 2.38) and two peaks that can be assigned to the thiolates, a multiplet at δ 6.93 from the *m*- and *p*-protons of the rings and a doublet (δ 7.57) corresponding to the *o*-protons. The integration of the peaks is consistent with the number of protons of each type. The ^{13}C-{^{1}H} NMR spectrum shows two singlets corresponding to the methyl carbons (δ 11.29 and 17.36), three signals assigned to quaternary carbons (δ 134.98 for the thiolate quaternary carbons, 142.31 and 148.28 corresponding to the quaternary carbons of the pyrrolyl) and four non-quaternary and non-methyl carbons (δ 126.33, 130.58, 132.16 and 133.35), three of them corresponding to the remaining carbon atoms of the thiolates.

The piano-stool structure (Fig. 3) confirms the η^5 co-ordination of the heterocyclic ligand. The pyrrolyl ring was found to be planar with an average deviation of its atoms of 0.020 Å and the titanium atom lies 2.005 Å away from this plane. The methyl carbon atoms deviate between 0.08 and 0.21 Å from that plane away from the titanium, probably because of steric hindrance, caused either by slippage of the ring or by the bulkiness of the thiolate groups. The heterocyclic ring and the three sulfur atoms are in an approximate eclipsed conformation, where the Ti–N and Ti–S(1) bonds projected in the plane perpendicular to the Ti–XX axis which contains the Ti atom point approximately in the same direction [from Table 2, N–XX–Ti–S(1) = 21°].

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‡ M_r = 544.8, monoclinic, space group *C*2/*c*, a = 24.58(1), b = 16.02(1), c = 15.28(1) Å, β = 115.1(1)°, U = 5453 Å^3, Z = 8, D_c = 1.33 g cm^{-3}, μ(Mo-Kα) = 7.0 cm^{-1}. 2733 Unique reflections with $F^2 \geqslant 0$ were used in structure solution and refinement of 114 parameters. Using a three-dimensional Patterson synthesis, two different Ti atoms were found in the crystal structure, one located at the special position 2. All the other non-hydrogen atoms were located in subsequent Fourier-difference maps. The chloride and titanium atoms were refined with anisotropic thermal motion parameters. Final refinement converged at R = 0.135, computed for 591 reflections with $I > 3\sigma(I)$.

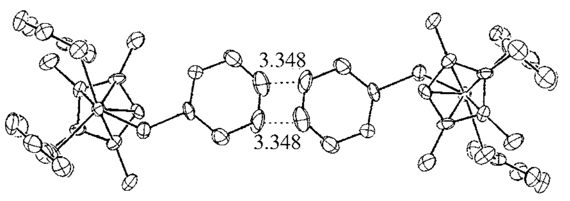

Fig. 4 Partial packing diagram showing the interaction between one molecule of complex **3** and its centrosymmetrically related one

The molecular structure depicted in Fig. 3 also shows that two of the thiolate rings point in the same direction as the pseudo-C_3 axis of the piano-stool conformation [from Table 2, XX–Ti–S–C 178 and 187°, for S(2) and S(3), respectively], while the third ligand has its ring almost orthogonal to this direction [from Table 2, XX–Ti–S(1)–C(11) = 311°]. The packing diagram in Fig. 4 shows that this feature is caused by an intermolecular interaction with a centrosymmetrically related molecule. As a consequence of this interaction, the XX–Ti–S(1) angle increases from 105/108 [S(2)/S(3)] to 124° (Table 2). The relative conformation of the phenyl ring and the Ti–S–C plane can be defined by the dihedral angle Ti–S–C–C [Table 2, 129, 91 and 132° for S(1), S(2) and S(3), respectively].

[Ti(η^5-NC$_4$Me$_4$)(SPh)Cl$_2$] 4.

After synthesizing complex **3**, using 3 equivalents of sodium benzenethiolate, we tried the reaction with only 1 equivalent of the thiolate in order to investigate whether control of stoichiometry in chloride substitution was possible. In fact, the NMR spectra (^{1}H and ^{13}C-{^{1}H}) demonstrated that the complex [Ti(η^5-NC$_4$Me$_4$)(SPh)Cl$_2$] was obtained.

[Ti(η^5-C$_5$H$_5$)(η^5-NC$_4$Me$_4$)Cl$_2$] 5

In order to prepare a mixed-ring complex, containing the pyrrolyl ligand and one cyclopentadienyl ring, we started to test the reaction between **1** and sodium cyclopentadienyl. However, this reaction led to unidentified products, apparently without the heterocyclic ring. Therefore, cyclopentadienyltitanium trichloride was treated with the lithium salt of 2,3,4,5-tetramethylpyrrole, equation (4). The red crystals of **5** are extremely sensitive to oxygen and moisture, leading to a yellow solid which prevented satisfactory elemental analyses of C, H and N and even measurement of the ^{13}C-{^{1}H} NMR spectrum. The ^{1}H NMR spectrum shows the expected two singlets corresponding to the two types of methyl groups (δ 1.82 and 1.84), while the signal corresponding to the five protons of the cyclopentadienyl ring appears at δ 6.24.

$$[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl_3}] + \mathrm{Li}[\mathrm{NC_4Me_4}] \xrightarrow[\text{r.t.}]{\text{toluene}} \underset{\mathbf{5}}{[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{NC_4Me_4})\mathrm{Cl_2}]} + \mathrm{LiCl} \quad (4)$$

The distorted pseudo-tetrahedral structure (Fig. 5) shows the η^5 co-ordination of both rings. The pyrrolyl and cyclopentadienyl rings were found to be planar with average deviations of the atoms of 0.022 and 0.016 Å, respectively. The metal atom lies 2.076 and 2.056 Å from those planes, respectively, with an angle between the ring normals of 122.4°. A similar mixed-ring complex, [Ti(η^5-C$_5$H$_5$)(η^5-NC$_4$H$_4$)Cl$_2$] was prepared by an analogous method,[30,31] but no real evidence of the η^5 co-ordination is presented in this case (neither ^{13}C-{^{1}H} NMR data nor the crystal structure).

Comparing the ^{13}C-{^{1}H} NMR data of complexes **1**–**4** there is, for all of them, a large deshielding of the pyrrolyl quaternary carbons (from δ 26.29 to 33.46) relative to the ring carbons of the free protonated pro-ligand. This had been reported for the complex [Ti(η^5-NC$_4$H$_2$Bu$^t_2$-2,5)Cl$_3$][22] and is a direct consequence of the η^5 co-ordination of the heterocyclic ring. The donation from the ring carbon atoms to the metal centre decreases the electron density on those atoms, causing the deshielding revealed by the ^{13}C-{^{1}H} spectra. In the corresponding ^{1}H NMR spectra there is an interesting feature that, as far as we know, has never been reported for analogous compounds. For all the complexes we observe a deshielding for one type of methyl protons of the heterocyclic ligand (as expected from the ^{13}C-{^{1}H} data), but we verify a shielding of the other type of methyl protons which may be attributed to slippage of the heterocyclic ring. For instance, for [Ti(η^5-NC$_4$H$_2$Bu$^t_2$-2,5)Cl$_3$],[22] similar to **1** apart from the substitutents on the heterocyclic ligand, the spectrum reveals the deshielding of both types of methyl protons.

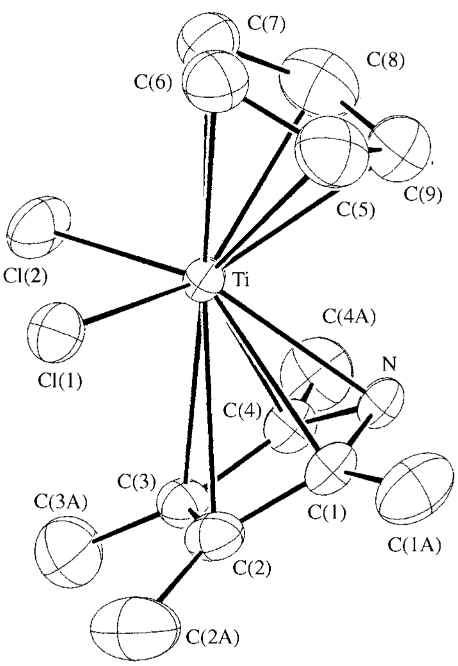

Fig. 5 Crystal structure of [Ti(η^5-C$_5$H$_5$)(η^5-NC$_4$Me$_4$)Cl$_2$] **5**

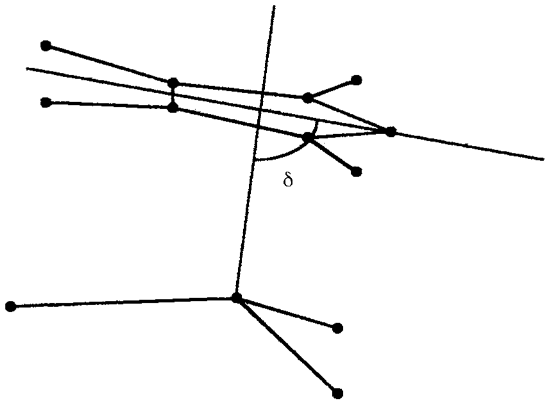

Fig. 6 Tilt angle δ characterising the slippage of the pyrrolyl ring

For the mixed-ring complex **5** the ^{1}H NMR spectrum shows the shielding of both types of methyl protons, similar to that with the analogous compound [Ru(η^5-C$_5$Me$_5$)(η^5-NC$_4$Me$_4$)].[20] Among all the complexes studied, this effect only appears for **5**, which suggests that it is caused by the presence of the non-heterocyclic C$_5$H$_5$ ring.

The stuctures of compounds **1** and **3** show a distorted piano-stool co-ordination geometry while **5** has a distorted psuedo-tetrahedral arrangement of the ligands around the titanium atom. In these three compounds the NC$_4$Me$_4^-$ ligand is η^5-co-ordinated, showing a ring slippage of the heteroatom towards the metal centre, which can be inferred from Table 2 by the

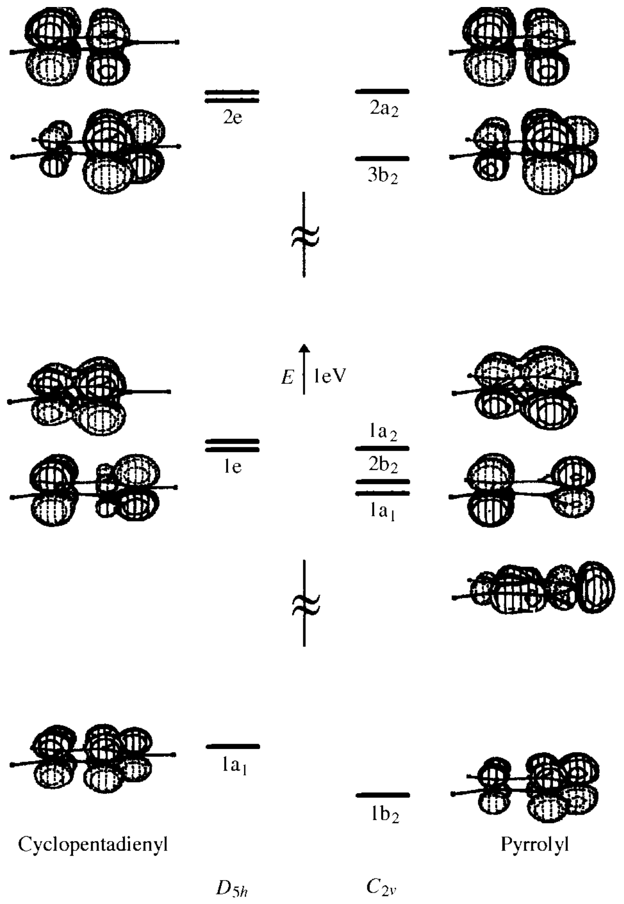

Fig. 7 Cyclopentadienyl *vs.* pyrrolyl comparative MO diagram

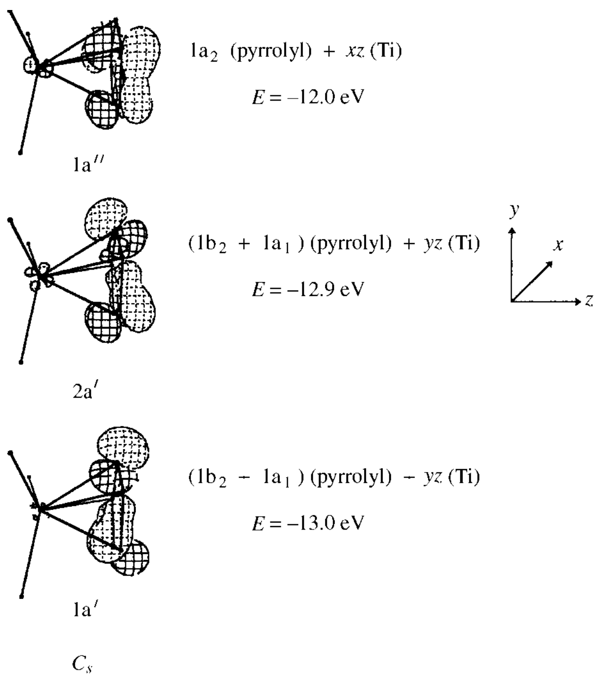

Fig. 8 Occupied frontier orbitals of [Ti(η^5-NC_4H_4)Cl_3]

bond lengths between the titanium and the ring atoms of the heterocycle, as well as by the tilting angle N–XX–Ti of 82 (**1**), 80 (**3**) and 81° (**5**) (Fig. 6). The slippage of the ring can also be computed in terms of the Δ parameter, defined by Mingos *et al.*[32] as the distance between the projection of the metal atom in the five-membered ring plane and the centre of the ring. For our compounds, Δ takes the values 0.25 (**1**), 0.29 (**3**) and 0.33 Å (**5**).

The ring slippage was also predicted by *ab initio* molecular orbital (MO) calculations in the model complex [Ti(NC_4H_4)Cl_3] at the second-order Møller-Plesset perturbation (MP2) level using a LANL1MB basis set. For complex **5**, containing C_5H_5 and $NC_4Me_4^-$ η^5 ligands, Table 2 shows that the C_5H_5 ligand has, within experimental error, all the five carbon atoms at equal distances to the metal, while the heterocyclic ring slips towards the metal centre. Extended-Hückel MO calculations, performed on the model complex [Ti(NC_4H_4)Cl_3], were used to understand the tendency to slippage.

As can be seen in Fig. 7, the main difference between cyclopentadienyl and pyrrolyl ligands, aside from the presence of a non-bonding orbital 1a$_1$, is the splitting of each e degenerate pair of C_5H_5 orbitals into two new orbitals of a$_2$ and b$_2$ symmetry, the latter lowered in energy when compared with the C_5H_5 analogue. Upon co-ordination the 1a$_1$ lone-pair orbital is allowed to mix with the 2b$_2$, giving rise to two new orbitals, 1a′ and 2a′, depicted in Fig. 8, with different directionality. Therefore, to improve the overlap population in the interaction of the new π orbital with the appropriate metal orbital the ring must slip towards the titanium atom. The reduced overlap population between the fragments $TiCl_3$ and NC_4H_4 is 0.04 and 0.05 electron for the non-slipped and the slipped conformations, respectively. Slippage of a heteroatom towards the metal centre has been reported for other pyrrolyl complexes, such as [Mn(η^5-NC_4H_4)$(CO)_3$],[33] [Mn(η^5-$NC_4H_2Me_2$-3,4)$(CO)_3$] and [Mn(η^5-$NC_4H_2Me_2$-2,5)$(CO)_3$].[34] It is considered to be the cause for the faster carbonyl substitution in those complexes, relative to their cyclopentadienyl analogues. This result can be easily explained, since the carbonyl substitution reactions occur by an associative mechanism, with formation of an intermediate having η^3 co-ordination; therefore, the slippage η^5 to η^3 of the heterocyclic ring maintains the 18-electron configuration, avoiding the unfavourable 20-electron transition state.[33,34]

Appendix

All the extended-Hückel[35] calculations were made with CACAO[36] with modified H_{ij} values.[37] The basis set for the metal atom consisted of *n*s, *n*p, ($n - 1$)d orbitals. The s and p orbitals were described by single Slater-type wavefunctions and d orbitals were taken as contracted linear combinations of two Slater-type wavefunctions. The five-membered rings were taken as regular 140 pm side pentagons. All the C–H distances were assumed to be 108 pm. A non-slipped ring model was used with distances titanium–pyrrolyl 190, Ti–C 224 and Ti–Cl 220 pm.

The *ab initio* calculations were made with the GAUSSIAN 94[38] program and the LANL1MB basis set. The geometries were optimised at the Hartree–Fock (HF) level with the five-membered rings kept as regular pentagons. An MP2 post HF calculation was performed for the optimised geometry. All the computational calculations were done on a DEC Alpha PC 150 computer.

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