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Synthesis and characterisation of $[M(\eta^5\text{-}NC_4Me_4)(CH_2Ph)_3]$ (M = Ti, Zr, Hf) and $[Ti(\eta^5\text{-}NC_4Me_4)(Me)Cl_2]$. Structural determination and bonding of $[Ti(\eta^5\text{-}NC_4Me_4)(Me)Cl_2]$ depicting an agostic interaction

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On the occasion of Professor Alberto R. Dias 60th birthday.

Abstract

The complex $[Ti(\eta^5\text{-}NC_4Me_4)(Me)Cl_2]$ (**1**) has been synthesised and characterised. Based upon the X-ray structure and ab initio theoretical calculations performed on the model complex $[Ti(\eta^5\text{-}NC_4H_4)(Me)Cl_2]$ an agostic interaction has been postulated. The synthesis and characterisation of $[M(\eta^5\text{-}NC_4Me_4)(CH_2Ph)_3]$ (M = Ti, **2**; Zr, **3**; Hf, **4**) complexes are also described as well as the possibility of similar agostic interactions, which are discussed from the NMR data and the comparison with analogue carbocyclic compounds.

Keywords: Group IV transition metals; Pyrrolyl; Agostic interaction; X-ray diffraction; Ab initio calculations

1. Introduction

Organometallic complexes with η^5-cyclopentadienyl (Cp) ligands constitute a very broad area within transition metal chemistry [1], performing some important roles, namely as homogeneous catalysts in polymerisation reactions [2] and anticarcinogenic agents [3,4]. However, the isoelectronic pyrrolyl ligands are considerably less prone to undergo η^5-co-ordination to transition metals, the instability of the correspondent compounds often being attributed to the lower ionisation potential of the non-bonding electron pair of the nitrogen atom when compared to that of the π-electrons [5–7].

In the sequence of the prior synthesis of $[Ti(\eta^5\text{-}NC_4Me_4)Cl_3]$ and some derivatives $\{[Ti(\eta^5\text{-}NC_4Me_4)_2Cl_2]$, $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}NC_4Me_4)Cl_2]$, $[Ti(\eta^5\text{-}NC_4Me_4)(SPh)_n]$ $(n = 1, 3)\}$ [8], we continued the reactivity studies on $[Ti(\eta^5\text{-}NC_4Me_4)Cl_3]$ by testing the substitution of the chlorides with alkyl ligands, in an attempt to reproduce the behaviour of the Cp and Cp* ($\eta^5\text{-}C_5Me_5$) analogues [9,10]. In fact, the complex $[Ti(\eta^5\text{-}NC_4Me_4)(Me)Cl_2]$ was obtained as indicated above, but it was not possible to achieve selective substitution of two or three chloride ligands by the same synthetic route. Therefore, following the good results in the preparation of Ti [11], Zr [12] and Hf [12] amide complexes by adding 2,3,4,5-tetramethylpyrrole to an appropriate amide starting material, we used an identical strategy to produce the compounds $[M(\eta^5\text{-}NC_4Me_4)(CH_2Ph)_3]$ (M = Ti, Zr, Hf).

Bearing in mind the general tendency of Group IV d^0 metal atoms to establish agostic interactions to σ-hydrocarbyl fragments [13–17] and the particular evidences in the $[Ti(\eta^5\text{-}C_5Me_5)(CH_2Ph)_3]$ analogue [13], the possible agostic interactions in complexes **1**–**4** were investigated.

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2. Results and discussion

2.1. Chemical studies

Following the traditional chemical path used for the synthesis of alkyl–Cp–Ti complexes [9,13,18], the compound $[Ti(\eta^5\text{-}NC_4Me_4)(Me)Cl_2]$ (**1**) has been prepared by reaction of $[Ti(\eta^5\text{-}NC_4Me_4)Cl_3]$ with one molar equivalent of MeLi (Eq. (1)).

$$[Ti(\eta^5\text{-}NC_4Me_4)Cl_3] + LiMe \xrightarrow[-80°C]{\text{toluene}} [Ti(\eta^5\text{-}NC_4Me_4)(Me)Cl_2] + LiCl \quad (1)$$

The orange crystals of **1** are sensitive to oxygen and moisture and present an elemental analysis compatible with the formulation $[Ti(NC_4Me_4)(Me)Cl_2]$, corresponding to the substitution of a chloride for a methyl ligand.

The ^{1}H-NMR spectrum reveals three singlets (δ 1.45, 1.75, 2.10) with relative areas 2:1:2 resulting from the three types of methyl groups in the molecule; the minor area of the peak at 1.75 ppm makes it readily assignable to the σ-hydrocarbyl ligand, while the other two signals correspond to the two types of pyrrolyl methyl groups.

In the ^{13}C-NMR spectrum, the three quartets ($^1J_{CH} \approx 130$ Hz) arise from the three types of methyl groups indicated above: 11.02 and 16.24 ppm for the pyrrolyl substituents and 84.24 ppm for the alkyl ligand. The quaternary carbons of the heterocyclic ring originate the two singlets at 147.40 and 136.44 ppm, considerably deshielded relative to those of the pro-ligand HNC_4Me_4 (δ 120.20 and 113.80). This significant deshielding of the ring carbons suggests an active donation of electron density to the metal, making reasonable the postulation of an η^5-co-ordination of the pyrrolyl, which was confirmed a posteriori by the X-ray structure. Additionally, the deshielding values are similar to those reported for the compounds $[Ti(\eta^5\text{-}NC_4Me_4)Cl_3]$ [8] and $[Ti(\eta^5\text{-}NC_4H_2Bu^t_2\text{-}2,5)Cl_3]$ [19] where the heterocyclic ring is η^5-co-ordinated to titanium.

Following the successful synthesis of $[Ti(\eta^5\text{-}NC_4Me_4)(Me)Cl_2]$ (**1**), the substitution reactions of two and three chlorides for an equivalent number of methyl groups were tested using the complex $[Ti(\eta^5\text{-}NC_4Me_4)Cl_3]$ as starting material. However, a lack of selectivity was verified when trying to reproduce the reaction depicted in Eq. (1) with two and three molar equivalents of the alkylating agent. In fact, the ^{1}H-NMR data from the dark green mixture obtained by reaction of $[Ti(\eta^5\text{-}NC_4Me_4)Cl_3]$ and LiMe in the proportion 1:2 strongly suggest that the substitution of all the chloride ligands has occurred. Apart from 2,3,4,5-tetramethylpyrrole signals and other impurities, we observe three singlets (δ 1.27, 1.48, 2.07) with relative areas 3:2:2 in the methyl protons range. The chemical shifts of the peaks with the same area (δ 1.48, 2.07) are very similar to those of the pyrrolyl methyl groups in compound **1** and the singlet at 1.27 ppm may certainly result from three methyl ligands bonded to Ti.

On the other hand, the reaction of the trichloride complex $[Ti(\eta^5\text{-}NC_4Me_4)Cl_3]$ with three molar equivalents of MeLi yields an unidentified black oily solid, proving that the chloride substitution becomes less and less selective as we increase the molar amount of the alkylating agent.

After verifying the difficulty in the selective preparation of the tri-methylated compound $[Ti(NC_4Me_4)Me_3]$ by the synthetic route indicated above and considering the successful path for the synthesis of Ti [11], Zr [12] and Hf [12] amide complexes by using an appropriate amide compound as starting material, we followed a similar strategy to obtain the set of complexes $[M(\eta^5\text{-}NC_4Me_4)(CH_2Ph)_3]$ (M = Ti, **2**; Zr, **3**; Hf, **4**). In fact, the reaction of the tetrabenzyl compounds of the three group IV transition metals with an equimolar amount of 2,3,4,5-tetramethylpyrrole led to the substitution of one benzyl ligand for the heterocyclic ring, as depicted in Eq. (2).

$$[M(CH_2Ph_4)] + HNC_4Me_4 \xrightarrow{\text{toluene}} [M(\eta^5\text{-}NC_4Me_4)(CH_2Ph)_3] + CH_2Ph$$

2 (M = Ti); **3** (M = Zr); **4** (M = Hf) (2)

The $[M(\eta^5\text{-}NC_4Me_4)(CH_2Ph)_3]$ compounds are very sensitive to oxygen and moisture, preventing reliable elemental analyses or IR data. On the other hand, none of the several attempts to obtain crystals suitable for X-ray diffraction was successful and therefore the characterisation of **2**–**4** was made exclusively from the NMR data, as well as the investigation of the presumable agostic interactions.

The ^{1}H-NMR spectra of compounds **2**–**4** exhibit in each case two singlets with equivalent areas and chemical shifts in the range 1.32–1.82 ppm, assigned to the two types of pyrrolylic methyl protons; the remaining singlet (1.90–2.94 ppm) arises from the CH_2 groups of the benzyl ligands and the equivalency of its area to that of each pyrrolyl signal is consistent with the stoichiometry $[M(NC_4Me_4)(CH_2Ph)_3]$. Near the deuteriated solvent broad band lie the peaks resulting from the aromatic protons of the benzyl rings. In the Ti compound **2** it was not possible to distinguish between the several types of protons, which appear as multiplets in the δ range 6.99–7.17, with a 8 Hz coupling constant which is typical of H–H interactions in six-membered aromatic rings [20]. It is worth referring that the chemical shifts exhibited by complex **2** (δ 2.94 and 6.99–7.17) are comparable to those reported for the parent carbocyclic compound $[Ti(\eta^5\text{-}C_5Me_5)(CH_2Ph)_3]$ (δ 2.73 and 6.84–7.36) [18].

For the Zr and Hf compounds, **3** and **4**, it is possible to differentiate the three types of aromatic protons: the

doublet with $J = 7$ Hz (δ 6.68 for **3** and 6.85 for **4**) with the same area of the methylenic singlet results from the resonance of the six *ortho* protons; the triplets at 6.99 (complex **3**) and 6.92 ppm (compound **4**) are assigned to the three *para* protons because of its area (half of the area of the CH_2 peaks); finally the more deshielded triplets (δ 7.09 for **3** and 7.16 for **4**), although partially covered by the solvent band, show a similar area relative to the *ortho* protons signal, being compatible with the presence of the six *meta* protons from the benzyl rings.

The ^{13}C-NMR data of complexes **2**–**4** include (for each one) two quartets with $^1J_{CH} = 128–129$ Hz and chemical shifts between 10 and 15 ppm, which are assigned to the two types of pyrrolylic methyl substituents. On the other hand, in the range 70–100 ppm lie the triplets of triplets ($^1J_{CH} = 124–125$ Hz; $^3J_{CH} = 4$ Hz) arising from the methylenic groups. Concerning the tertiary carbons of the benzyl rings, it was possible to make the individual assignments, mainly by analysing the multiplicity of the signals and using the approximate area of the peaks as a clue. Therefore, the more shielded doublets of triplets (≈ 123 ppm) were attributed to the *para* carbons, while the doublets of doublets (128–129 ppm) correspond to the *ortho* carbons and the doublets of triplets between 127 and 129 ppm are assigned to the *meta* carbons. Finally, the singlets in the range 130–150 ppm result from the resonance of the three types of quaternary carbons whose individual assignments were accomplished by analogy with the similar Ti–Cp*–tri-benzyl complex [13,18] and using the area of the peaks as an indicative factor.

Similarly to the characterisation of **1**, the deshieldings of the pyrrolyl quaternary carbons allowed us to postulate an η^5-co-ordination of the heterocyclic ring in compounds **2**–**4**, reproducing the structural tendency of the Cp and Cp* analogues. In fact, the deshielding of the ring carbons relative to the free pro-ligand (δ 24.2 and 16.5 for **2**; 17.6 and 15.5 for **3**; 19.1 and 16.0 for **4**), although inferior to those of other η^5-pyrrolyl compounds [8], are considerably superior to Zr and Hf complexes with an average η^3-co-ordination of the pyrrolyl rings [12].

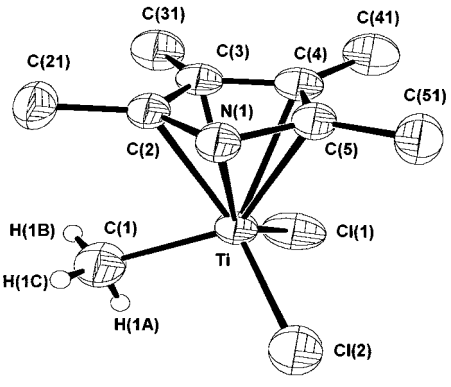

Fig. 1. X-ray structure of [Ti(η^5-NC_4H_4)(Me)Cl_2] (**1**) with 40% ellipsoids.

Taking into consideration the well known tendency of the d^0 Group IV transition metals to establish intramolecular agostic interactions with alkyl ligands (which was in fact elucidated for compound **1**), we tried to demonstrate this possibility in the set of complexes [M(η^5-NC_4Me_4)(CH_2Ph)$_3$] (M = Ti, Zr, Hf).

As a possible way to investigate the existence of agostic interactions, the ^{1}H-NMR spectra of the Ti and Zr complexes were recorded in d_8-toluene between room temperature and -80°C but no significant changes were detected. This result does not exclude the existence of agostic interactions, meaning that the methylenic protons exhibit a fluxional behaviour in the NMR experimental conditions. In fact, the same result arises from the similar [Ti(η^5-C_5Me_5)(CH_2Ph)$_3$] for which a double agostic interaction has been proved [13]. Another consequence of the fluxionality are the normal values for the $^1J_{CH}$ coupling constants of the benzyl carbons (≈ 124 Hz); this fact is also verified for [Ti(η^5-C_5Me_5)(CH_2Ph)$_3$] [18], in contrast to the abnormally low values of 105 and 113 Hz for [Ti(η^5-C_5Me_5)(CH_2SiMe_3)$_2$Cl] [18].

Despite the inconclusive results stated above, agostic interactions in **2**–**4** can be postulated by the analysis of the pyrrolyl ring carbons deshielding values. The presumed donation of at least one C–H benzylic bond to the metal would make the heterocyclic ring donation slightly weak, i.e. the deshielding would be lower than for complexes without that type of interactions. This hypothesis is confirmed by compound **1**, showing deshieldings of 27.2 and 22.6 ppm, considerably smaller to those reported for [Ti(η^5-NC_4Me_4)Cl_3] [8]. Following this trend, the values of 24.2 and 16.5 ppm for compound **2** strongly suggest the presence of at least one agostic interaction. On the other hand, the parent Cp* compound [Ti(η^5-C_5Me_5)(CH_2Ph)$_3$] behaviour [13,18], as well as the reduction of pyrrolyl deshielding when compared to 1 may suggest a double C–H_2···Ti interaction, helped by the lower donating power of the pyrrolyl relative to Cp*.

For compounds **3** and **4** the postulated double agostic interaction would be even more favourable due to the better overlap of the C–H bonds to the expanded Zr and Hf orbitals.

2.2. Structural studies

Confirming the η^5-co-ordination of the heterocyclic ligand pointed out by the ^{13}C-NMR data, compound **1** reveals a piano-stool configuration as we can observe in the X-ray structure presented in Fig. 1, depicting a ring slippage of the heteroatom towards the metal centre.

Table 1
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for complex **1**

Bond lengths			
Ti–N	2.1882(2)	Ti–Cl (average)	2.239
Ti–C(1)	2.0771(1)	C–Me (average)	1.494
Ti–C(2)	2.3105(1)	Ti–centroid	2.008
Ti–C(3)	2.4375(1)	Ti–H(1A)	2.28
Ti–C(4)	2.4362(1)	Ti–H(1B)	2.61
Ti–C(5)	2.2778(2)	Ti–H(1C)	2.56
Bond angles			
Cl(1)–Ti–Cl(2)	105.57(6)	Cl(1)–Ti–Me	100.2(2)
Centroid–Ti–Me	110	Cl(2)–Ti–Me	100.8(2)
Cl(1)–Ti–centroid	113	N–centroid–Ti	82
Cl(2)–Ti–centroid	124		
Torsion angles			
N–centroid–Ti–Cl(1)	195	Ti–C(1)–H(1A)	93
N–centroid–Ti–Cl(2)	325	Ti–C(1)–H(1B)	117
N–centroid–Ti–Me	84	Ti–C(1)–H(1C)	113

As reported previously [8] for similar complexes, this structural trend can be quantified by the N–centroid–Ti angle of 82°, Table 1, which is comparable to those obtained for the similar compounds [Ti(η^5-NC_4Me_4)L_3] (L = Cl, SPh) [8] (82–80°, respectively).

The projection of the four ligands in a plane perpendicular to the Ti–centroid axis shows the five-membered ring in an approximately staggered conformation relative to the triangle formed by the two chlorides and the methyl, characterised by the torsion angles N–centroid–Ti–X (X = Cl, Me) of 84, 195 and 325°.

Apart from the bond and torsion angles, Table 1 also presents the bond lengths for complex **1** and we can conclude that the average Ti–Cl distance of 2.239 Å compares well with the indenyl analogue [21a] also depicting a slightly longer Ti–Me bond length of 2.115 [21a] against 2.077 Å. Although the hydrogen positions derived from X-ray diffraction data are not entirely reliable, an agostic interaction can be postulated by the shorter distance Ti–H1A of 2.28 Å against 2.61 and 2.56 Å of the other two hydrogens. The geometry of the methyl group can also be compared with the original work of Green et al. [21b] where neutron diffraction data confirmed a similar agostic Ti–methyl bond with d(Ti–C) = 2.122 Å, d(Ti–$H_{agostic}$) = 2.45 Å, d(Ti–H) = 2.80 and 2.74 Å, Ti–C–$H_{agostic}$ = 93.5°, Ti–C–H = 118.4 and 112.9°.

Theoretical calculations were also used in the present work to investigate further the postulated agostic interaction.

2.3. Calculations

Using as a starting model the X-ray crystal structure with pyrrolylic methyls replaced by hydrogens ab initio calculations at HF and DFT levels using, respectively, LANL2MB and B3LYP basis set were carried out with GAUSSIAN-94/DFT [22]. Both methods predict the experimental structures with good accuracy (the experimental value lying between the values given by each method), namely the N–centroid–Ti slippage angle (80.3 and 81.3°), average Ti–Cl (2.319 and 2.195 Å), Ti–Me (2.053 and 2.096 Å) and Ti–N (2.177 and 2.192 Å). The Ti–H bonds predicted by both ab initio methods are slightly longer then the experimental values with the HF method predicting the closest results to the X-ray values. The hydrogen *trans* opposite to the centroid shows a shorter distance to the metal centre (2.47 against 2.70 Å of the other two hydrogens) and a bending of the Ti–C–H (99° HF, 93° X-ray) when compared to the near tetrahedral values of the other two hydrogens (115° average in both HF and X-ray). An Extended Hückel calculation performed in the optimised geometry has shown a positive overlap population between the 1s hydrogen orbital and the d_{xz} (xz being the centroid–Ti–C–H plane) on the metal centre, confirming the agostic interaction.

3. Experimental

3.1. Synthesis

All reactions and manipulations were carried out under an atmosphere of argon, using standard Schlenk-tube techniques. The NMR samples were prepared in a Mbraun glove-box as well as the mounting of the crystals, carried out in Lindemann glass capillaries. All the solvents were dried with sodium and distilled over Na/benzophenone, under nitrogen. Deuteriated benzene and toluene were dried with molecular sieves and deoxygenated by several freeze–pump–thaw cycles.

[Ti(η^5-NC_4Me_4)Cl_3] [8], [Ti(CH_2Ph)$_4$] [23], HNC_4Me_4 [24] [Zr(CH_2Ph)$_4$] [25] and [Hf(CH_2Ph)$_4$] [25] were prepared as described. Methyllithium was obtained from Aldrich and used without further purification.

3.2. Analytical procedures

Microanalysis was performed by Laboratório de Análises of Instituto Superior Técnico on a Fisons Instruments 1108 spectrometer. Proton and carbon NMR spectra were recorded in deuteriated benzene or toluene-d_8 on a Varian 300 MHz spectrometer and referenced internally to the residual solvent resonance.

3.2.1. Preparation of [Ti(η^5-NC_4Me_4)(Me)Cl_2] (**1**)

A 1.51 mol dm^{-3} solution of methyllithium (0.77 cm^3, 1.16 mmol) in diethyl ether was added to a stirred and cooled solution (−80°C) of [Ti(η^5-NC_4Me_4)Cl_3] (0.32 g, 1.17 mmol) in toluene (ca. 50 cm^3). The mixture was left stirring overnight and it was noticeable the

changing of the initial orange colour to dark yellow. After filtering, the solution was evaporated to dryness, to give a yellowish–brown oil which was extracted with *n*-hexane. The resulting yellow–orange solution was cooled to −80°C and orange crystals ($0.4 \times 0.3 \times 0.3$ mm^3) were obtained after filtration and drying under vacuum (yield 0.12 g, 42%). Anal. Found: C, 40.97; H, 5.78; N, 5.25. Calc. for $C_9H_{15}Cl_2NTi$: C, 42.22; H, 5.91; N, 5.47%.

^{1}H-NMR spectrum (benzene-d_6, r.t.), δ (ppm): 1.45 (s, 6H, pyrrolyl CH_3); 1.75 (s, 3H, CH_3 bonded to Ti); 2.10 (s, 6H, pyrrolyl CH_3). ^{13}C-NMR spectrum (benzene-d_6, r.t.), δ (ppm): 11.02 (q, [$^1J(^{13}C-^1H) = 129$], pyrrolyl *C*H$_3$); 16.24 (q, [$^1J(^{13}C-^1H) = 129$], pyrrolyl *C*H$_3$); 84.24 (q, [$^1J(^{13}C-^1H) = 130$], *C*H$_3$ bonded to Ti); 136.44 (s, pyrrolyl ring *C*); 147.40 (s, pyrrolyl ring *C*).

3.2.2. Preparation of [Ti(η^5-NC$_4$Me$_4$)(CH$_2$Ph)$_3$] (2)

A solution of 2,3,4,5-tetramethylpyrrole (0.15 g, 1.24 mmol) in toluene (ca. 30 cm^3) was added to a stirred and cooled solution (−70°C) of tetrabenzyltitanium (0.51 g, 1.24 mmol) in the same solvent (ca. 30 cm^3). The mixture was left stirring for 3.5 days and was then evaporated to dryness, to give a dark red oil which was extracted with *n*-hexane. The resulting red solution was slightly concentrated and then cooled to −80°C. Dark red crystals unsuitable for X-ray diffraction analysis were obtained after filtration and drying under vacuum (yield 0.15 g, 27%). Anal. Found: C, 69.08; H, 6.02; N, 2.89. Calc. for $C_{29}H_{33}NTi$: C, 78.54; H, 7.50; N, 3.16%.

^{1}H-NMR spectrum (benzene-d_6, r.t.), δ (ppm): 1.32 (s, 6H, pyrrolyl CH_3); 1.82 (s, 6H, pyrrolyl CH_3); 2.94 (s, 6H, benzyl CH_2); 6.99–7.17 (m, 15H, [$^1J(^1H-^1H) = 8$], benzyl aromatic *H*). ^{13}C-NMR spectrum (benzene-d_6, r.t.), δ (ppm): 10.35 (q, [$^1J(^{13}C-^1H) = 128$], pyrrolyl *C*H$_3$); 14.79 (q, [$^1J(^{13}C-^1H) = 128$], pyrrolyl *C*H$_3$); 97.48 (tt, [$^1J(^{13}C-^1H) = 124$; $^3J(^{13}C-^1H) = 4$], benzyl CH_2); 123.16 (dt, [$^1J(^{13}C-^1H) = 162$; $^2J(^{13}C-^1H) = 7$], benzyl *para*-*C*); 127.60 (dt, [$^1J(^{13}C-^1H) = 157$; $^2J(^{13}C-^1H) = 6$], benzyl *meta*-*C*); 128.51 (dd, [$^2J(^{13}C-^1H) = 7$], benzyl *ortho*-*C*); 130.29 (s, pyrrolyl ring *C*); 144.45 (s, pyrrolyl ring *C*); 148.96 (s, benzyl quaternary *C*). There were also performed ^{1}H-NMR spectra between r.t. and −80°C (in toluene-d_8) but there were no noticeable changes in the compound signals.

3.2.3. Preparation of [Zr(η^5-NC$_4$Me$_4$)(CH$_2$Ph)$_3$] (3)

A solution of 2,3,4,5-tetramethylpyrrole (0.18 g, 1.46 mmol) in toluene (ca. 20 cm^3) was added to a stirred and cooled solution (−40°C) of tetrabenzylzirconium (0.67 g, 1.47 mmol) in the same solvent (ca. 20 cm^3). The mixture was left stirring overnight and was then evaporated to dryness, to give a yellow–orange oily solid, which was extracted with *n*-hexane. The resulting orange solution was cooled to −80°C but it was not possible to obtain any crystals.

^{1}H-NMR spectrum (benzene-d_6, r.t.), δ (ppm): 1.50 (s, 6H, pyrrolyl CH_3); 1.63 (s, 6H, pyrrolyl CH_3); 1.97 (s, 6H, benzyl CH_2); 6.68 (d, 6H, [$^1J(^1H-^1H) = 7$], benzyl *ortho*-*H*); 6.99 (t, 3H, [$^1J(^1H-^1H) = 8$], benzyl *para*-*H*); 7.09 (t, 6H, [$^1J(^1H-^1H) = 7$], benzyl *meta*-*H*). ^{13}C-NMR spectrum (benzene-d_6, r.t.), δ (ppm): 10.63 (q, [$^1J(^{13}C-^1H) = 129$], pyrrolyl *C*H$_3$); 14.72 (q, [$^1J(^{13}C-^1H) = 129$], pyrrolyl *C*H$_3$); 70.15 (t, [$^1J(^{13}C-^1H) = 125$], benzyl CH_2); 123.75 (dt, [$^1J(^{13}C-^1H) = 160$; $^2J(^{13}C-^1H) = 8$], benzyl *para*-*C*); 128.76 (dt, [$^2J(^{13}C-^1H) = 6$], benzyl *meta*-*C*); 129.30 (s, pyrrolyl ring *C*); 129.68 (dd, [$^1J(^{13}C-^1H) = 158$; $^2J(^{13}C-^1H) = 7$], benzyl *ortho*-*C*); 137.80 (s, pyrrolyl ring *C*); 143.09 (s, benzyl quaternary *C*). There were also performed ^{1}H-NMR spectra between r.t. and −80°C (in toluene-d_8) and a slight broadening of one of the pyrrolyl signals was observed.

3.2.4. Preparation of [Hf(η^5-NC$_4$Me$_4$)(CH$_2$Ph)$_3$] (4)

A solution of 2,3,4,5-tetramethylpyrrole (0.14 g, 1.10 mmol) in toluene (ca. 20 cm^3) was added to a stirred and cooled solution (−60°C) of tetrabenzylhafnium (0.59 g, 1.09 mmol) in the same solvent (ca. 15 cm^3). The mixture was left stirring overnight and was then evaporated to dryness, to give a yellow–orange oil which was extracted with *n*-hexane. The resulting orange solution was cooled to −80°C but it was not possible to obtain any solid.

^{1}H-NMR spectrum (benzene-d_6, r.t.), δ (ppm): 1.42 (s, 6H, pyrrolyl CH_3); 1.76 (s, 6H, pyrrolyl CH_3); 1.90 (s, 6H, benzyl CH_2); 6.85 (d, 6H, [$^1J(^1H-^1H) = 7$], benzyl *ortho*-*H*); 6.92 (t, 3H, [$^1J(^1H-^1H) = 7$], benzyl *para*-*H*); 7.16 (t, 6H, [$^1J(^1H-^1H) = 8$], benzyl *meta*-*H*). ^{13}C-NMR spectrum (benzene-d_6, r.t.), δ (ppm): 10.05 (q, [$^1J(^{13}C-^1H) = 128$], pyrrolyl *C*H$_3$); 14.02 (q, [$^1J(^{13}C-^1H) = 128$], pyrrolyl *C*H$_3$); 83.38 (tt, [$^1J(^{13}C-^1H) = 124$; $^3J(^{13}C-^1H) = 4$], benzyl CH_2); 123.18 (dt, [$^1J(^{13}C-^1H) = 163$; $^2J(^{13}C-^1H) = 8$], benzyl *para*-*C*); 128.44 (dm, [$^2J(^{13}C-^1H) = 9$], benzyl *meta*-*C*); 128.82 (dd, $^2J(^{13}C-^1H) = 7$], benzyl *ortho*-*C*); 129.81 (s, pyrrolyl ring *C*); 139.32 (s, pyrrolyl ring *C*); 144.38 (s, benzyl quaternary *C*).

3.3. Crystallography

Complex **1** crystallises in the tetragonal system, space group $I4_1/a$, with $a = b = 26.910(2)$ and $c = 6.7597(5)$ Å, $V = 4895.0(6)$ Å^3, $Z = 16$, $D_{calc} = 1.39$ g cm^{-3} and $\mu(Mo-K_\alpha) = 10.2$ cm^{-1}. 8571 reflections $1.5 < \theta < 25°$ were collected by the ω–2θ scan mode, in an Enraf-Nonius MACH3 diffractometer using graphite monochromated radiation. Two standard reflections were monitored during data collection with no instrumental instability detected. Data were corrected for linear decay (average correction 1.07) and using the CAD4 software for Lorentz and polarisation effects and em-

pirically for absorption (minimum transmission factor 92.3%, average transmission factor 96.5%). 2154 unique reflections with $F^2 \geq 0$ ($R_{int} = 0.04$) were used in structure solution and refinement of 130 parameters. The position of the Ti atom was obtained by a tridimensional Patterson synthesis and all the other non-hydrogen atoms were located in subsequent difference Fourier maps and refined with anisotropic thermal motion parameters. With exception of the co-ordinated methyl group the hydrogen atoms were inserted in calculated positions and refined isotropically with fixed distances to the parent carbon atom. The co-ordinated methyl hydrogens were allowed to refine isotropically without restrains. Final refinement converged at $R_1 = 0.04$ and $wR_2 = 0.11$. The largest peak in the final difference Fourier synthesis was 0.35 e $Å^{-3}$. The molecular structure of complex **1** is shown in Fig. 1 and lists of observed and calculated structure factors, tables of anisotropic thermal parameters, atomic co-ordinates, bond lengths and angles and inter and intra molecular contact distances are available as supplementary material. The structure solution and refinement were performed with SHELX-86 [27] and SHELXL-93 [28], respectively, and the illustrations were drawn with ORTEP-III [26]. The atomic scattering factors and anomalous scattering terms were taken from International Tables [29].

3.4. Calculations

GAUSSIAN-94/DFT [22] was used in all ab initio HF and DFT calculations using respectively LANL2MB and B3LYP basis set. An η^5-NC_4H_4 co-ordinated ring was used as a model to our more complex tetramethyl–pyrrolyl ligand. The starting geometry was built from X-ray structural data and fully optimised without any symmetry restraints. All calculations were performed on a 3400 Alfa Station running under OpenVMS.

4. Conclusions

The structural features of the complexes studied are similar to those observed in other pyrrolyl η^5-derivatives, namely the slippage of the heterocyclic ring towards the metal centre. This particular behaviour increases the reactivity of this type of compounds relative to Cp and Cp* analogues, making it comparable to that of indenyl complexes.

The X-ray structure of **1** has shown an agostic interaction between an α C–H bond and the titanium atom, corroborated by ab initio calculations. The comparison of the carbon atoms deshielding relative to the free pro-ligand in complexes **2**–**4** with previously reported data in carbocyclic analogues strongly indicates the establishment of at least one of that type of interaction. In fact, agostic interactions between a Group IV unsaturated transition metal and a C–H bond are well known as a means to minimise the metal centre unsaturation acting simultaneously as powerful tool for C–H activation.

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