Effect of ancillary ligands in the hapticity of the pyrrolyl ligand in [Ti(pyrrolyl)(NMe$_2$)$_x$Cl$_{3-x}$] (x = 0, 1, 2, 3) complexes

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ABSTRACT

Two complete series of titanium complexes of the type [Ti(pyrrolyl)(NMe$_2$)$_x$Cl$_{3-x}$] (pyrrolyl = 2,3,4,5-tetramethylpyrrolyl (TMP), x = 3 (**1**), 2 (**2**), 1 (**3**), 0 (**4**); pyrrolyl = 2,5-dimethylpyrrolyl (DMP), x = 3 (**5**), 2 (**6**), 1 (**7**), 0 (**8**)) were prepared by reaction of equimolar amounts of either [Ti(NMe$_2$)$_x$Cl$_{4-x}$] (x = 4, 3 and 2) with the corresponding pyrrole (**1–3** and **5–7**) or TiCl$_4$ with Li(pyrrolyl) (**4** and **8**). A study on the effect on the pyrrolyl coordination mode of the number of strong π-donor amido ligands present in the Ti coordination sphere was carried out by ^{13}C NMR spectroscopy and by X-ray diffraction, when possible. For both pyrrolyl ligands, the η^5-coordination to the metal is favoured when there are two or less coordinated amido ligands. However, the presence of a third amido ligand inhibits this type of coordination, shifting the pyrrolyl ring to a σN binding mode (η^1), due to an increase of the electron density at the metal centre. For these two complete series of Ti monopyrrolyl complexes we have observed that ^{13}C NMR deshielding parameters (in relation to the parent pyrrole molecules), in the absence of detectable η^5–η^1 dynamic behaviour, could be used as an assignment criterion for the N-heterocyclic ring type of coordination in Ti pyrrolyl complexes.

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1. Introduction

The cyclopentadienyl ring (Cp = C$_5$H$_5^-$), together with its substituted derivatives, is probably the most used ligand in organometallic chemistry [1]. Not only they have an historic relevance but also Cp complexes have a wide range of applications in areas such as homogeneous catalysis [2] and cancer therapy drugs [3,4]. Although there are known complexes where the Cp coordinates to the metal in η^1, η^2 or η^3 modes [5], in the overwhelming majority of compounds this ligand displays an η^5 hapticity. Compared to the Cp ligand, the organometallic chemistry of the isoelectronic pyrrolyl ring (NC$_4$H$_4^-$) and its derivatives is little developed, because of the relative instability of the pyrrolyl metal complexes, which can be reduced by alkyl substitution at the ring carbons [6]. That instability is often attributed to the lower ionization potential of the non-bonding electron pair of the nitrogen atom when compared to that of the π-electrons [7–9] making these complexes difficult to handle, and also determining the coordination mode. Effectively, as opposed to Cp, the pyrrolyl ligand usually shows a σN-coordination mode (η^1), being this trend confirmed by data retrieved in the Cambridge Structural Database (CSD) [10]. The analysis of the results of this search also indicates that the η^5 existing complexes display some degree of slippage of the pyrrolyl ring, as the nitrogen atoms tend to get closer to the metal. This slippage effect was first detected by infrared and quadrupole resonance spectroscopy studies by Fayer and Harris in [Mn(η^5-NC$_4$H$_4$)(CO)$_3$] [11], resulting in a pattern of coordination that the authors described as a combination of a η^2 metal–olefin bond with an η^3 azo-allylic bond (Chart 1).

For Ti and Zr, the predominant coordination mode is also σN [12]. The first example of a fully structurally characterized Ti complex with an η^5-pyrrolyl ring, [Ti(η-2,5-^{t}Bu$_2$NC$_4$H$_2$)Cl$_3$], was reported by Kuhn and co-workers [13], the type of coordination being attributed to steric hindrance of the ^{t}Bu groups that prevented the σN interaction; this same author has also published the first comprehensive review on π-coordinated pyrrolyl metal complexes [6]. Examples of Zr η^5-pyrrolyl complexes were also published by our group ([Zr(η^5-TMP)(CH$_2$Ph)$_3$], TMP = 2,3,4,5-tetramethylpyrrolyl) [14] and by Tanski and Parkin [15]. The latter authors studied the choice of coordination mode of pyrrolyl in a group of Zr complexes containing 2,5-diarylpyrrolyl and ancillary amide and/or halide ligands, examining not only steric reasons but also electronic effects on the acidity of the metal centre, and using both X-ray diffraction and DFT arguments. More recently,

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[1] Prof. A.R. Dias passed away on the 15th July 2007. He was the Ph.D. supervisor of both A.C. Galvão and A.P. Ferreira. We would like to pay him a tribute for his scientific work and friendship.
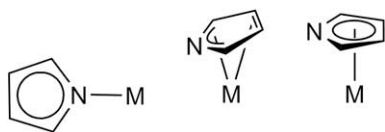
Chart 1. Pyrrolyl ring types of coordination: σN (left), $\eta^3 + \eta^2$ (centre) and η^5 (right).

Odom and co-workers prepared a series of *ansa*-dipyrrolyl bis(*N*-dimethylamido) titanium complexes, in which the two pyrrolyl rings show mixed η^5 and η^1 coordination to Ti in the solid state, and studied the experimental energy barriers involved in the η^5–η^1 interconversion in solution [16].

We have previously reported the synthesis and characterization of various group 4 η^5-pyrrolyl complexes [14,17–19] and the theoretical study of the coordination of the pyrrolyl ring in complexes of group 4 metals [20–22]. In this paper, we report the first example of two complete series of titanium-pyrrolyl compounds, [Ti(pyrrolyl)(NMe$_2$)$_x$Cl$_{3-x}$] (pyrrolyl = TMP and DMP (2,5-dimethylpyrrolyl); x = 0, 1, 2, 3), where the effect of the metal centre electron density on the type of coordination is examined by ^{13}C NMR and X-ray diffraction. This effect is interpreted on the basis of the number of ancillary π-donor amido ligands present in the titanium coordination sphere. The choice of the pyrrolyl substituents (methyl groups) was made with the purpose of not generating such large steric effects as those of *tert*-butyl and aryl groups used in previous works [6,13,15].

2. Results and discussion

2.1. Synthesis of complexes

The synthetic strategy used for the preparation of these two families of compounds was based on the studies of Bradley and Thomas [23,24] and Chandra and Lappert [25] on the reactivity of titanium, zirconium and hafnium amido compounds, [M(NR$_2$)$_4$]. The reaction of these species with more acidic substrates, such as amines, alcohols, thiols or cyclopentadiene (CpH), leads to the total or partial substitution of the amido ligands by the conjugated base of the acid, releasing amine molecules. When CpH was used, the result was the synthesis of cyclopentadienyl derivatives of group 4 metals without the involvement of organometallic intermediates [25]. Therefore, emulating these CpH reactions, pyrrolyl compounds of Ti and Zr have already been prepared using similar reactions with the pyrrole molecule as the acid substrate [14,18].

The compounds studied in this work are of the generic type [Ti(pyrrolyl)(NMe$_2$)$_x$Cl$_{3-x}$] (pyrrolyl = TMP, x = 3 (**1**), 2 (**2**), 1 (**3**), 0 (**4**); pyrrolyl = DMP, x = 3 (**5**), 2 (**6**), 1 (**7**), 0 (**8**)). The majority of them was prepared by the equimolar reaction of a pyrrole with the corresponding [Ti(NMe$_2$)$_x$Cl$_{4-x}$] complex with x = 4, 3 and 2, respectively, in toluene, at low temperatures (−50 to −80 °C), as shown in Scheme 1. In order to complete these series, the compound [Ti(η^5-DMP)Cl$_3$] (**8**) was also prepared by reacting equimolar amounts of TiCl$_4$ and LiDMP (Scheme 1). Similar synthetic procedures were previously used in the syntheses of [Ti(η^5-DMP)(NMe$_2$)Cl] (**6**) [19] and [Ti(η^5-TMP)Cl$_3$] (**4**) [17] respectively, compounds whose structural data will also be used in the present work for the discussion of the coordination modes of the pyrrolyl ligand in these two series.

These compounds were isolated as air-sensitive crystals or powders, with colours varying from orange to dark red, in yields ranging from 92% to 21%. High yields are observed for the trisamido **1** and **5** (64% and 92%, respectively), in which the pyrrolyl ring is σ-bound to the metal, whereas moderate to low yields (53–21%) are obtained for the rest of the compounds (see Section 2.2 and Section 2.3).

Spectroscopic and analytical data characterizing the compounds described in this paper are collected in Section 4.

2.2. Studies on tetramethylpyrrolyl complexes

The isolation and NMR characterization of [Ti(TMP)(NMe$_2$)$_3$] (**1**) has been previously reported [18] and a σN-coordination was predicted based on its ^{13}C NMR data. The resonances of the C$_{2,5}$ and C$_{3,4}$ ring carbons appeared at 128.40 and 113.70 ppm, respectively, resulting in a small value of deshielding (8.2 ppm) for carbons 2 and 5 and virtually no deshielding (−0.1 ppm) for carbons 3 and 4, in relation to those of tetramethylpyrrole (HTMP) (120.20 and 113.80 ppm, respectively). These observations already suggested that these ring carbons did not participate in the bonding to the metal.

A modification of the workup procedure for this compound (see Section 4.3) enabled the isolation of crystals suitable for X-ray diffraction studies, allowing the unequivocal assessment of an σN-coordination for the pyrrolyl ring. Compound **1** crystallizes in the monoclinic $P2_1/n$ space group (a = 9.344(3) Å, b = 12.185(4) Å, c = 16.507(7) Å; β = 103.95(4)°); the molecular structure of **1** is represented in Fig. 1 and selected bond distances and angles are listed in Table 1.

The structure obtained shows the complex on a pseudo-tetrahedral geometry, distorted towards a triangular-base pyramidal structure (see Table 1), with the pyrrolyl ring showing a longer Ti(1)–N(1) bond length of 2.000(3) Å in relation to the remaining Ti(1)–N$_{amido}$ distances (1.866(3)–1.877(3) Å). The distance Ti(1)–pyrrolyl centroid is 3.174 Å and the slippage angle N(1)–centroid–Ti(1) is 6.27°, clearly excluding any possibility of coordination of the pyrrolyl ring either than σN. The proximity of C(5) and N(3), nearly in an eclipsed conformation [C(5)–N(1)–Ti(1)–N(3) = 13.6(3)°], indicates that the pyrrolyl plane bisects the angle formed by the Ti atom and the two remaining amido ligands [C(5)–N(1)–Ti(1)–N(2) = 131.8(3)° and C(5)–N(1)–Ti(1)–N(4) = 105.7(3)°]. This different steric environments of the ring carbons C$_2$ and C$_5$ affect directly the angles C(2)–N(1)–Ti(1) and C(5)–N(1)–Ti(1), that should be similar (and close to 126°), displaying instead values of 120.75(19)° and 132.0(2)°, respectively. This asymmetry is also reflected in the conformation adopted by the amido groups: while that composed by N(3), C(31) and C(32) adopts an equatorial geometry in relation to the threefold N(1)–Ti(1) axis [C(31)–N(3)–Ti(1)–N(1) = 83.6(3)° and C(32)–N(3)–Ti(1)–N(1) = 253.3(3)°, close to the 90° and 270° expected for a perfect equatorial geometry], the group N(4), C(41) and C(42) is practically in an axial position [C(41)–N(4)–Ti(1)–N(1) = 3.8(3)° and C(42)–N(4)–Ti(1)–N(1) = 192.3(3)°]. In the third amido group (N(2), C(21) and C(22)) the equivalent torsion angles have intermediate values in between these two geometries [C(21)–N(2)–Ti(1)–N(1) = 48.4(3)° and C(22)–N(2)–Ti(1)–N(1) = 231.9(5)°]. These three conformations possibly reflect different degrees of amido π-donation to the metal [26].

Compound **2** was obtained in the form of red crystals which, unfortunately, presented a very quick decay rate during the X-ray data collection, and turned impossible the determination of its structure. However, the corresponding ^{1}H NMR spectrum is in good agreement with the formula [Ti(TMP)(NMe$_2$)$_2$Cl], showing three Me resonances with relative areas 1:1:2, assigned to the hydrogens of the methyl groups bound to C$_{2,5}$ and C$_{3,4}$ and to the hydrogens of both amido ligands which are magnetically equivalent. In this case, the ^{13}C NMR data can also provide information about the type of coordination of the pyrrolyl ring, since the C$_{2,5}$ and C$_{3,4}$ ring carbon resonances are deshielded by 18.15 and
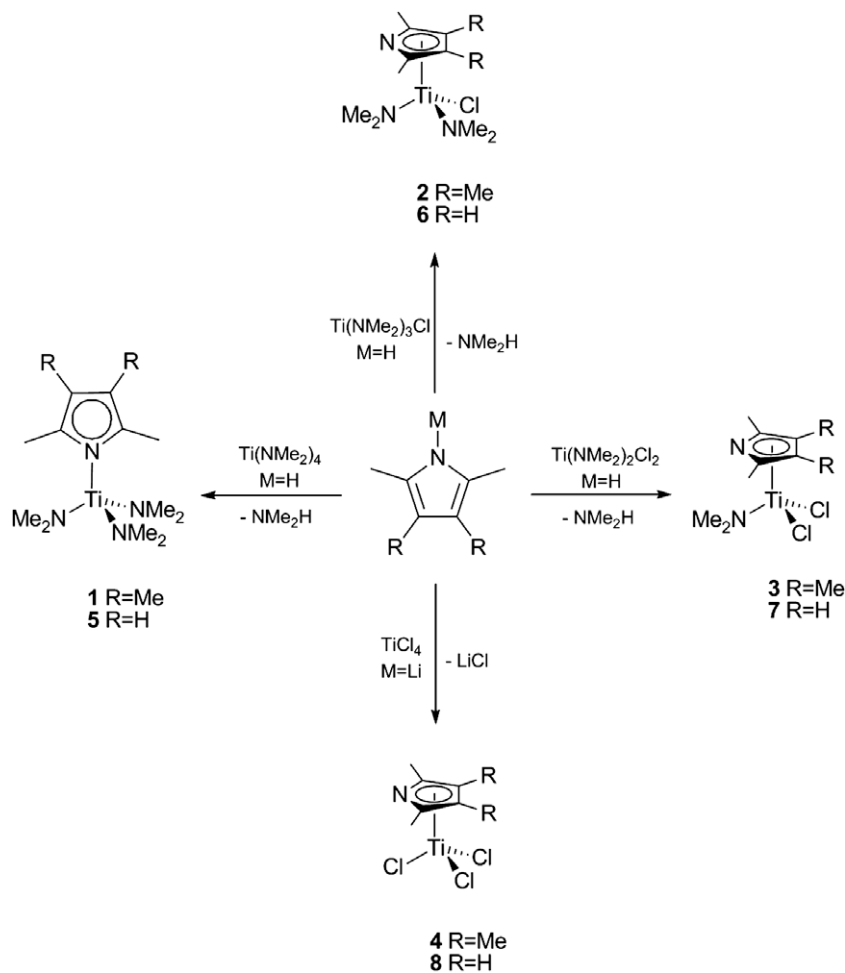
Scheme 1. Synthesis of [Ti(pyrrolyl)(NMe$_2$)$_x$Cl$_{3-x}$] (pyrrolyl = DMP, TMP; x = 1, 2, 3).

14.7 ppm, respectively. These values, although larger than those found for [Ti(σN-TMP)(NMe$_2$)$_3$] (**1**), are smaller than those observed in previously published compounds with an η^5-coordination confirmed by X-ray diffraction (see Table 2, compounds **A**, **B** and **C**), where the deshielding values for C$_{2,5}$ and C$_{3,4}$ are larger than 25 and 20 ppm, respectively. This situation indicates that in this molecule all the carbon atoms interact in some degree with the metal atom, but not enough to assume a fully orthogonal η^5-coordination. Instead, it is more reasonable to predict some degree of slippage of the pyrrolyl ring, as the nitrogen atom tends to get closer to the metal, resulting in a stronger M–N interaction.

A similar relationship between the pyrrolyl coordination type (η^5 or η^1) and the ^{13}C NMR deshielding parameters can be found in the literature in the work of Efraty et al. on azaferrocene complexes, in which we can notice C$_{2,5}$ and C$_{3,4}$ deshielding values in the range 32–38 ppm for the η^5-pyrrolyl rings of azaferrocene ([Fe(η^5-Cp)(η^5-NC$_4$H$_4$)]), while values of −8 to 0 ppm are observed for azaferrocene adducts of the type [Fe(η^5-Cp)(η^1-NC$_4$H$_4$)L$_2$] (L = CO, CNR, R$_2$NPF$_2$) [27]. Further significant examples of this trend are those of the σN-pyrrolyl compounds [Ti(η^5-C$_5$Me$_5$)(η^1-DMP)Me$_2$] **E** and [Ti(η^5-C$_5$Me$_5$)(η^1-NC$_4$H$_4$)Me$_2$] **F** (Table 2), in which low deshielding values (−3.5 to 7 ppm) are found for the ring carbons, whereas the η^5-pyrrolyl compound [Ti(η^5-C$_5$H$_5$)(η^5-DMP)Me$_2$] **D** displays considerably higher values for these parameters (21.8 and 22.2 ppm) [12b].

Compound **3** was obtained as dark red crystals. Its ^{1}H NMR spectrum displays three resonances with identical areas (six methyl hydrogens for C$_{2,5}$, six methyl hydrogens for C$_{3,4}$ and six

hydrogens of the amido ligand), in good agreement with the formula [Ti(TMP)(NMe$_2$)Cl$_2$]. In the ^{13}C NMR spectrum it is possible to identify the resonances of the two types of ring carbons, C$_{2,5}$ and C$_{3,4}$, with deshielding values of 26.04 and 23.36 ppm, respectively; these values point to a η^5-coordination of the pyrrolyl ring, confirmed by the X-ray structure of the complex (Fig. 2). Although this compound is isolated as dark red crystals, like most of the previously analyzed crystals of pyrrolyl compounds [14,19], it displays a rapid drop off in intensity at moderate to higher angles, resulting in a very weak diffraction data set (see Supplementary material) that nevertheless allows the confirmation of the coordination mode.

The most relevant structural data for the discussion of the coordination type adopted by the tetramethyl pyrrolyl ring in this series of compounds are displayed in Tables 1 and 2. The set of data in Table 1 also contains values for compound [Ti(η^5-TMP)Cl$_3$] (**4**) [17] that are necessary for this discussion. Table 2 contains ^{13}C NMR deshielding values for this series of tetramethylpyrrolyl compounds (**1–4**), together with data for other compounds reported in the literature (**A–F**). Values of the slippage angle (δ), N(1)–centroid–Ti(1), are also included for comparison.

Values reported in Table 2 clearly demonstrate that there is a direct relationship between the deshielding of the pyrrolyl ring carbons in this series and the coordination mode. In fact, the deshielding values for compounds **3** and **4** are well within the range of values observed for compounds **A–D**, previously reported in the literature as presenting a η^5-pyrrolyl coordination type, a condition confirmed by X-ray diffraction analysis. Compound **1** presents
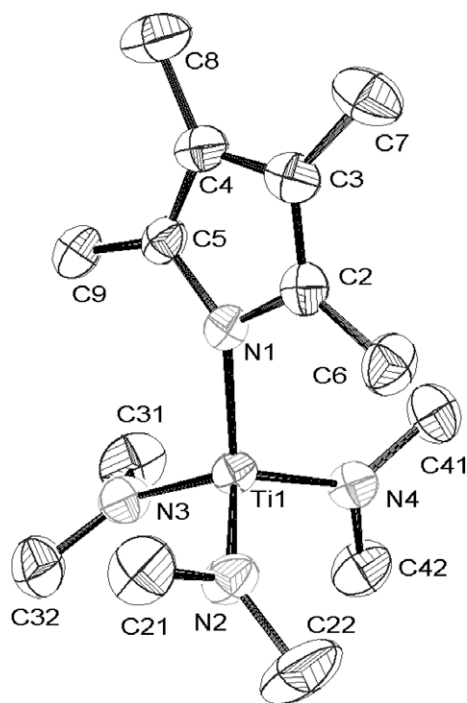
Fig. 1. ORTEP diagram showing the atomic labeling scheme for [Ti(σN-TMP)(NMe$_2$)$_3$] (**1**) (thermal ellipsoids at 30% probability level). Hydrogens were omitted for clarity.

Table 1
X-ray structural data for compounds [Ti(σN-TMP)(NMe$_2$)$_3$] (**1**) and [Ti(η^5-TMP)Cl$_3$] (**4**).

	1	**4** [18]
Bond distances (Å)		
Ti–N1	2.000(3)	2.181(6)
Ti–C2	–	2.299(7)
Ti–C3	–	2.423(7)
Ti–C4	–	2.426(6)
Ti–C5	–	2.278(7)
Ti–N2	1.866(3)	–
Ti–N3	1.887(3)	–
Ti–N4	1.879(3)	–
Bond angles (°)		
N1–Ti–N2	109.76(12)	–
N1–Ti–N3	112.59(11)	–
N1–Ti–N4	110.65(11)	–
N2–Ti–N3	106.28(14)	–
N3–Ti–N4	106.70(13)	–
N2–Ti–N4	119.75(12)	–
Ti–N2–C21	116.4(2)	–
Ti–N2–C22	131.4(3)	–
C21–N2–C22	112.2(3)	–
Ti–N3–C31	119.8(3)	–
Ti–N3–C32	127.8(3)	–
C31–N3–C32	112.6(4)	–
Ti–N4–C41	128.7(2)	–
Ti–N4–C42	119.8(3)	–
C41–Ti–C42	111.1(3)	–
δ (°)[a]	6.27	81.8
$\varDelta$ (Å)[b]	3.15	0.29
Hinge angle (°)[c]	1.16	3.93
Maximum deviation (Å)		
Ti, N2, C21, C22 plane	0.024	–
Ti, N3, C31, C32 plane	0.046	–
Ti, N4, C41, C42 plane	0.037	–

[a] Slippage angle: N1–centroid–Ti1.
[b] Distance between the centre of the ring and the projection of the metal atom in the ring plane.
[c] Angle between plane C2–N1–C5 and plane C2–C3–C4–C5.

low deshielding values that clearly indicate that the pyrrolyl carbon atoms do not interact with the metal, leaving the N atom to coordinate in a σ fashion to the metal atom, as it was confirmed above by X-ray diffraction. For compound **2**, the lack of X-ray data only allows the η^5-pyrrolyl coordination type to be predicted based on the deshielding values, which are only slightly smaller than those observed for the other η^5 compounds, indicating a considerable degree of interaction of all the ring carbons and the metal.

Opposite to what is observed for certain *ansa*-dipyrrolyl Ti compounds reported in the literature [16], variable-temperature (VT) NMR experiments in the range −80 to +80 °C show compounds **1**–**4** do not exhibit a dynamic behaviour in solution. Besides small chemical shifts variations, typical of VT experiments, no significant alterations on the ^{1}H and ^{13}C resonances shape were detected in the entire range of temperatures. Conversely, theoretical calculations for group 4 monopyrrolyl complexes determined low activation energies for a possible fluxional behaviour between η^5- and σN-coordination [21]. Therefore, our experimental results do not completely exclude the existence of such interconversion that could occur in a time scale faster than that of experimental NMR.

The effect of the relative number of amido ligands in the compounds of this series on the deshielding of the ring carbons and, therefore, in the coordination of the pyrrolyl ring, is clearly displayed in Fig. 2. In fact, while both amido and chloride ligands are inductive electronic attractors, the amido ligand is a much stronger electron donor by π interaction of the nitrogen lone pair with the metal atom. Accordingly, Martín et al. [28] has proposed a p$\pi \rightarrow$ dπ donation of NMe$_2$ in the compound [TiCp*(NMe$_2$)$_3$], not strong enough to avoid η^5-coordination of the Cp* ligand. However, it was sufficient to cause a decrease in the deshielding of the ring carbons, thus indicating a reduction in the electron density donated by the ring to the metal, in response to an increased electron donation by the other ligands. If the ring contains an electron donor heteroatom such as N, the ring slippage is then favoured (lower δ angles) leading, in the limit, to σN-coordination.

The first compound of the series, [Ti(σN-TMP)(NMe$_2$)$_3$] (**1**), with three amido ligands, is the only one where this σN-bonding of the pyrrolyl fragment was observed. In all the other three compounds (**2**–**4**) the coordination is η^5, and the ring slippage increases with the number of amido ligands present in the compound (see Table 1). An important indication of the existence of this p$\pi \rightarrow$ dπ donation is the fact that in compound **1** the amido ligands are nearly planar at the N atom, revealing an sp^2 hybridization that favours this type of interaction. The relative importance of this π contribution to the Ti–N$_{amido}$ bonds can be evaluated by their bond lengths: in compound **1** (σN-pyrrolyl) this contribution should be very significant because the bond lengths (see Table 1) are among the smallest found for Ti–NMe$_2$ bonds in the Cambridge Data Base [10].

### 2.3. Studies on dimethylpyrrolyl complexes

Unfortunately, none of the novel titanium dimethylpyrrolyl complexes (**5**, **7** and **8**) in this second series gave rise to crystals suitable for X-ray diffraction. Therefore, all the structural considerations discussed below are based on their ^{1}H and ^{13}C NMR characterization. For these compounds, as for compounds **1**–**4**, no dynamic behaviour was observed in VT experiments in the range −80 to +80 °C.

Compound **5** was obtained as a red powder, its ^{1}H NMR spectrum displaying three resonances. These correspond, respectively, to the hydrogens of the C$_{2,5}$ methyl groups, to the amido hydrogens and to the hydrogens bound to carbons C$_{3,4}$, with an integration of 3:9:1, in good agreement with the formulation [Ti(DMP)(NMe$_2$)$_3$]. Analyzing the ^{13}C NMR spectrum, it is possible to determine

Table 2
^{13}C NMR deshielding values for tetramethylpyrrolyl titanium complexes **1–4** and other monopyrrolyl titanium complexes from the literature.

Compound	Deshielding[a] $C_{2,5}$ (ppm)	Deshielding[a] $C_{3,4}$ (ppm)	δ^{b} (°)	Ref.
[Ti(σN-TMP)(NMe$_2$)$_3$] (**1**)	8.2	−0.1	6.3	This work
[Ti(η^5-TMP)(NMe$_2$)$_2$Cl] (**2**)	18.2	14.7	–	This work
[Ti(η^5-TMP)(NMe$_2$)Cl$_2$] (**3**)	26.0	23.4	$\approx 78^{c}$	This work
[Ti(η^5-TMP)Cl$_3$] (**4**)	33.4	28.2	81.8	[17]
[Ti(η^5-2,5-^{t}Bu$_2$NC$_4$H$_2$)Cl$_3$] (**A**)	33.5	22.6	86.5	[13]
[Ti(η^5-TMP)(SPh)$_3$] (**B**)	28.1	28.5	80.2	[17]
[Ti(η^5-TMP)(Me)Cl$_2$] (**C**)	27.2	22.6	81.9	[14]
[Ti(η^5-C$_5$H$_5$)(η^5-DMP)Me$_2$] (**D**)	21.8	22.2	90.8	[12b]
[Ti(η^5-C$_5$Me$_5$)(η^1-DMP)Me$_2$] (**E**)	−3.5	5.6	5.8	[12b]
[Ti(η^5-C$_5$Me$_5$)(η^1-NC$_4$H$_4$)Me$_2$] (**F**)	7.0	1.4	5.5	[12b]

[a] Measured in relation to the corresponding parent pyrrole ring carbons chemical shifts.
[b] Slippage angle: N1–centroid–Ti1.
[c] See Supplementary material.
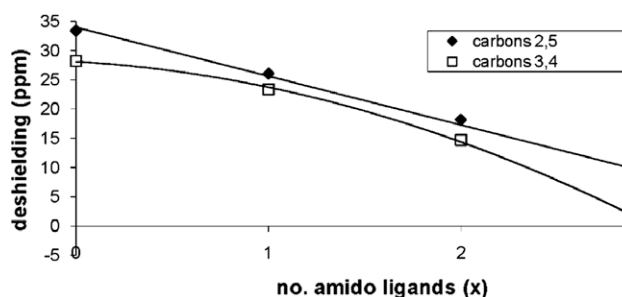
Fig. 2. Variation of the ^{13}C NMR deshielding values of the ring carbons with the number of amido ligands (*x*) bound to the metal atom in the series [Ti(TMP)(NMe$_2$)$_x$Cl$_{3-x}$] (**1–4**).

deshielding values of 8.90 and 1.02 ppm for $C_{2,5}$ and $C_{3,4}$, respectively, when compared to the chemical shifts of dimethylpyrrole (HDMP) (125.51 and 106.28 ppm, respectively). Similar to compound **1**, these values indicate a negligible participation of the ring carbon atoms in the bonding of the pyrrolyl to the metal atom, therefore corresponding to a σN type of coordination.

In the ^{1}H NMR spectrum of compound **7** it is possible to identify three ^{1}H resonances, corresponding, respectively, to the hydrogens of the methyl groups bound to $C_{2,5}$, to the hydrogens of the amido group and to the hydrogens directly connected to $C_{3,4}$, with a 3:3:1 integration, conforming to the formulation [Ti(DMP)(NMe$_2$)Cl$_2$] (**7**). The corresponding ^{13}C NMR spectrum shows deshielding values of 23.99 and 16.8 ppm, respectively, for the ring carbons $C_{2,5}$ and $C_{3,4}$, indicating that the pyrrolyl ligand is π-coordinated to the metal.

Compound [Ti(DMP)Cl$_3$] (**8**) was prepared by the same synthetic route already used for [Ti(η^5-TMP)Cl$_3$] (**4**) [17]. It was obtained as an orange solid, the ^{1}H NMR spectrum of which is in good agreement with the expected formula, showing two resonances with relative areas 1:3, assigned to the two hydrogens bonded to carbon $C_{3,4}$ and to the six methyl hydrogens of $C_{2,5}$. In the ^{13}C NMR spectrum it is possible to calculate deshielding values of 31.64 and 20.28 ppm for the two types of ring carbons, $C_{2,5}$ and $C_{3,4}$, respectively. These deshielding values are similar to those obtained for compound [Ti(η^5-TMP)Cl$_3$], indicating that the pyrrolyl ligand is also η^5-coordinated to the metal.

Within the series of complexes **5–8**, compound [Ti(DMP)(NMe$_2$)Cl$_2$] (**6**) was the only one where crystals suitable for X-ray diffraction were obtained. Its structure and other properties have already been reported [19], revealing a η^5-coordination of the pyrrolyl ring.

The deshielding data for the dimethylpyrrolyl complex series **5–8** is displayed in Table 3 and represented in Fig. 3.

Table 3
^{13}C NMR deshielding values for dimethylpyrrolyl titanium complexes **5–8**.

Compound	Deshielding $C_{2,5}$ (ppm)	Deshielding $C_{3,4}$ (ppm)	δ^{a} (°)	Ref.
[Ti(DMP)(NMe$_2$)$_3$] (**5**)	8.9	1.02	–	This work
[Ti(DMP)(NMe$_2$)$_2$Cl] (**6**)	12.39	6.63	84.5	[17]
[Ti(DMP)(NMe$_2$)Cl$_2$] (**7**)	23.99	16.8	–	This work
[Ti(DMP)Cl$_3$] (**8**)	31.64	20.28	–	This work

[a] Slippage angle: N1–centroid–Ti1.
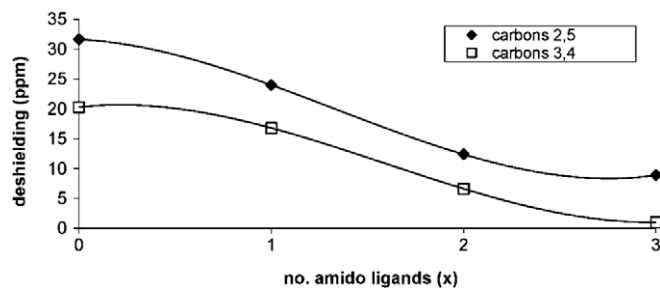
Fig. 3. Variation of the ^{13}C NMR deshielding values of the ring carbons with the number of amido ligands (*x*) bound to the metal atom in the series [Ti(DMP)(NMe$_2$)$_x$Cl$_{3-x}$] (**5–8**).

Examination of Table 3 shows that the trend already observed for the tetramethylpyrrolyl series is maintained, the deshielding diminishing with the number of amido ligands present in the complex. Again, the only compound with an unequivocal σN-coordination of the pyrrolyl ring is complex **5**, which contains three amido ligands, since the very small deshielding values indicate the absence of interaction between the ring carbons and the metal atom. On the other end of the scale is the trichloride derivative **8** that shows a deshielding pattern suitable of a η^5-coordination.

It is also possible to verify that the compounds containing the DMP ligand report lower values of deshielding than the corresponding TMP analogues. The deshielding values depend, among other factors, on the degree of interaction between the ring carbon atoms and the metal, which, in turn, depends on the electronic density of the ring. The 2,5 dimethylpyrrolyl ring is less electron-rich than the tetramethylpyrrolyl, due to the absence of two methyl electron donor groups in positions 3 and 4. The latter positions will be the more affected in terms of deshielding decrease, although this electronic effect will be extended to the entire ring, making the titanium-pyrrolyl bond weaker to some extent. The absence of the 3- and 4-methyl substituents in DMP will also reduce

the steric hindrance around these positions, allowing the ring to increase the slippage angle. This situation is better visualized if we compare the metal–ring bond lengths in compounds [Ti(η^5-TMP)Cl$_3$] (**4**) (see Table 1) and [Ti(η^5-DMP)(NMe$_2$)$_2$Cl] (**6**) [19]: the substitution of TMP by DMP causes an increase in the bond lengths between the metal atom and both the nitrogen and *ortho* carbon atoms, while for *meta* carbons the distances are in average very similar [Ti(1)–N(1) = 2.285(3) Å, Ti(1)–C(2) = 2.333(4) Å, Ti(1)–C(3) = 2.406(4) Å, Ti(1)–C(4) = 2.467(6) Å and Ti(1)–C(5) = 2.398(4) Å].

These two factors can explain both the low values of deshielding and the high value of slippage angle presented by compound **6**, [Ti(η^5-DMP)(NMe$_2$)$_2$Cl], the mixed ligand compound of this series where a η^5-coordination would be less favoured by the presence of two electron donor amido groups. If the available X-ray structural data for this compound is analyzed [19], one of the criteria used in the attribution of the pyrrolyl coordination type, the slippage angle δ, is larger ($\delta = 84.5°$) than all the angles observed for titanium η^5-tetramethylpyrrolyl compounds (see Table 2), leading to the unequivocal assignment of an η^5-coordination for compound **6**.

Although there is no X-ray diffraction data for compounds [Ti(η^5-DMP)(NMe$_2$)Cl$_2$] (**7**) and [Ti(η^5-DMP)Cl$_3$] (**8**), their larger deshielding values, associated with the less donor coordination sphere of the metal, should also point to the same η^5-coordination type.

3. Conclusions

This work aimed to study the effect of the presence of ancillary electron donor ligands in the coordination of pyrrolyl ligands in titanium complexes. The ligands compared were Cl and NMe$_2$, both inductive electron attractors, but with NMe$_2$ acting as a stronger $p\pi \rightarrow d\pi$ donor than Cl. The final results of this trial, that involved two complete series of titanium-pyrrolyl compounds, [Ti(pyrrolyl)(NMe$_2$)$_x$Cl$_{3-x}$] (pyrrolyl = 2,5-dimethylpyrrolyl and 2,3,4,5-tetramethylpyrrolyl; x = 0, 1, 2, 3), indicate that the presence of a growing number of ancillary donor amido ligands gradually increases the slippage of the pyrrolyl ring until reaching a situation where the σN-coordination is preferred. This trend can be evaluated using X-ray diffraction, by the determination of the slippage angle of the pyrrolyl ring or, when the X-ray structure is not available, by the analysis of the ^{13}C NMR deshielding values of the pyrrolyl carbons (in comparison with the corresponding parent pyrroles). It is possible to conclude that, when Cl and NMe$_2$ ligands are coordinating to Ti atoms, the supplementary $p\pi \rightarrow d\pi$ donation of the amido ligands will be strong enough to force a σN-pyrrolyl coordination only when three NMe$_2$ groups are present in the coordination sphere of Ti. In all the remaining cases a η^5-pyrrolyl coordination type will be favoured.

4. Experimental section

4.1. General procedures

All reactions and manipulations were carried out under an inert atmosphere using a dual vacuum/argon and using conventional Schlenk techniques, and the solid transfers and NMR samples preparation were performed in an MBraun glove-box. All the commercial solvents were deoxygenated and dried by refluxing over a suitable drying agent (sodium-benzophenone for toluene and tetrahydrofuran, and calcium hydride for hexane), followed by distillation under nitrogen. Deuterated benzene and toluene were dried with molecular sieves 5 Å and deoxygenated by several freeze-pump-thaw cycles. Solvents and solutions were transferred using

a positive pressure of nitrogen through stainless steel cannulae and mixtures were filtered in a similar way using modified cannulae that could be fitted with glass fibre filter disks. The NMR spectra were recorded on a Varian Unity 300 MHz spectrometer at 299.995 MHz for ^{1}H and at 75.4296 MHz for ^{13}C and referenced internally to the residual proton resonance relative to tetramethylsilane ($\delta = 0$) for both ^{1}H and ^{13}C spectra. All chemical shifts are quoted in δ (ppm) and coupling constants are given in Hz. Multiplicities are abbreviated as follows: singlet (s), quartet (q), quartet of quartets (qq). Elemental analyses were performed on a Fisons Instruments 1108 spectrometer at the IST Analysis Services (Laboratório de Análises do IST). The high resolution laser desorption/ionization mass spectra were obtained on a Finnigan FT/MS 2001-DT equipped with a three Tesla superconductor and interfaced with a Nd:YAG laser operating at the fundamental wavelength 1064 nm. Titanium tetrachloride, butyllithium and 2,5-dimethylpyrrole were obtained from Aldrich and used without further purification. Compounds 2,3,4,5-tetramethylpyrrole [29], [Ti(NMe$_2$)$_4$] [24], [Ti(NMe$_2$)$_3$Cl] [30], and [Ti(NMe$_2$)$_2$Cl$_2$] [31] were prepared as described in the literature.

4.2. Synthesis of LiDMP

To a stirred and cooled (0 °C) suspension of dimethylpyrrole (1 cm^3, 0.935 g, 9.8 mmol) in tetrahydrofuran (ca. 40 cm^3) was added a 1.7 M LiBu solution in hexane (6 cm^3, 10.2 mmol). The reaction mixture was left stirring overnight and then the white solid was filtered off, washed with tetrahydrofuran and dried under vacuum (0.84 g, 8.33 mmol, 85%).

4.3. Synthesis of [Ti(σN-TMP)(NMe$_2$)$_3$] (**1**)

This compound was prepared using the same experimental sequence reported previously [18], using [Ti(NMe$_2$)$_4$] (0.99 g, 4.4 mmol). The orange solid, obtained after filtering and evaporating the solvent, was recrystallised by dissolving it in hexane and cooling the solution to −80 °C. The solution was filtered, also at −80 °C, and the orange crystals were dried under vacuum (0.85 g, 2.8 mmol, 64%). Crystals suitable for X-ray diffraction were mounted, in a glove-box, in a Lindemann glass capillary. ^{1}H NMR (300 MHz, C$_6$D$_6$), δ (ppm): 3.00 (s, 12H, N(CH_3)$_2$), 2.24 (s, 6H, CH_3-C$_{2,5}$), 2.07 (s, 6H, CH_3-C$_{3,4}$). ^{13}C NMR (75 MHz, C$_6$D$_6$), δ (ppm): 128.40 (s, C$_{2,5}$), 113.70 (s, C$_{3,4}$), 44.13 (qq, $^1J_{CH}$ = 134 Hz, $^3J_{CH}$ = 6 Hz, N(CH$_3$)$_2$), 13.25 (q, $^1J_{CH}$ = 124 Hz, CH$_3$-C$_{2,5}$), 10.35 (q, $^1J_{CH}$ = 124 Hz, CH$_3$-C$_{3,4}$). HRMS Found (calcd for [C$_{14}$H$_{30}$N$_4$Ti]$^+$) 302.2005 (302.1950).

4.4. Synthesis of [Ti(η^5-TMP)(NMe$_2$)$_2$Cl] (**2**)

A solution of HTMP (0.30 g, 2.43 mmol) in 25 cm^3 of toluene was added dropwise into a cooled (−80 °C) and stirred [Ti(NMe$_2$)$_3$Cl] solution in toluene (0.52 g, 2.41 mmol, 25 cm^3). The mixture was allowed to warm until reaching room temperature and left stirring overnight. The volatile components of the resulting orange-red solution were removed under vacuum, leaving an oily red solid. This solid was redissolved in hexane and filtered, and the volume of the solvent was reduced to a third, in vacuum. The solution was left in a freezer at −80 °C and filtered at that same temperature. After solvent volume reduction, it was possible to obtain red crystals (0.13 g, 0.46 mmol, 21%). Anal. Calc. for C$_{12}$H$_{24}$ClN$_3$Ti: C, 49.08; H, 8.24; N, 14.31. Found: C, 49.25; H, 8.36; N, 14.42%. ^{1}H NMR (300 MHz, C$_6$D$_6$), δ (ppm): 3.17 (s, 12H, N(CH_3)$_2$), 2.15 (s, 6H, CH_3-C$_{2,5}$), 1.73 (s, 6H, CH_3-C$_{3,4}$). ^{13}C{^{1}H} (75 MHz, C$_6$D$_6$), δ (ppm): 138.35 (s, C$_{2,5}$), 128.50 (s, C$_{3,4}$), 48.04 (s, N(CH$_3$)$_2$), 14.00 (s, CH$_3$-C$_{2,5}$), 10.72 (s, CH$_3$-C$_{3,4}$).

4.5. Synthesis of [Ti(η^5-TMP)(NMe$_2$)Cl$_2$] (3)

A solution of HTMP (0.31 g, 2.52 mmol) in 25 cm^3 of toluene was added dropwise into a cooled ($-50\,°C$) and stirred solution of [Ti(NMe$_2$)$_2$Cl$_2$] (0.52 g, 2.53 mmol) in 25 cm^3 of toluene. The mixture was allowed to warm until reaching room temperature and was left stirring overnight. The volatile components of the resulting red solution were removed under vacuum, leaving a red solid. The solid was dissolved in hexane and the solution was cooled at $-30\,°C$, leading to the precipitation of dark red crystals that were separated by filtration and dried in vacuum (0.26 g, 0.91 mmol, 36%). Anal. Calc. for C$_8$H$_{14}$Cl$_2$N$_2$Ti: C, 42.14; H, 6.36; N, 9.83. Found: C, 42.20; H, 6.49; N, 9.79%. ^{1}H NMR (300 MHz, C$_6$D$_6$), δ (ppm): 3.63 (s, 6H, N(CH$_3$)$_2$), 2.09 (s, 6H, CH$_3$-C$_{2,5}$), 1.75 (s, 6H, CH$_3$-C$_{3,4}$). ^{13}C NMR (75 MHz, C$_6$D$_6$), δ (ppm): 146.24 (s, C$_{2,5}$), 137.16 (s, C$_{3,4}$), 51.17 (qq, $^1J_{CH}$ = 137 Hz, $^3J_{CH}$ = 5 Hz, N(CH$_3$)$_2$), 15.40 (q, $^1J_{CH}$ = 128 Hz, CH$_3$-C$_{2,5}$), 11.79 (q, $^1J_{CH}$ = 128 Hz, CH$_3$-C$_{3,4}$).

4.6. Synthesis of [Ti(σN-DMP)(NMe$_2$)$_3$] (5)

A toluene solution of HDMP (0.5 cm^3, 0.47 g, 4.9 mmol; 7 cm^3) was added dropwise to a stirred and cooled ($-50\,°C$) toluene yellow solution of [Ti(NMe$_2$)$_4$] (1.07 g, 4.8 mmol; 20 cm^3). During the reaction the solution turned orange. The mixture was allowed to warm to room temperature and was left stirring overnight, filtered and the volatile components were removed under vacuum, leaving a red oil. This oil was redissolved in hexane, the solvent volume was reduced and the solution was cooled to $-80\,°C$. The solution was filtered, also at $-80\,°C$, leaving a red powder, which was dried under vacuum (1.21 g, 4.4 mmol, 92%.). Anal. Calc. for C$_{12}$H$_{26}$N$_4$Ti: C, 52.56; H, 9.56; N, 20.43. Found: C, 52.87; H, 9.81; N, 20.19%. ^{1}H NMR (300 MHz, C$_6$D$_6$), δ (ppm): 6.10 (s, 2H, H$_{3,4}$), 2.95 (s, 18H, N(CH$_3$)$_2$), 2.35 (s, 6H, CH$_3$-C$_{2,5}$). ^{13}C{^{1}H} (75 MHz, C$_6$D$_6$), δ (ppm): 134.42 (s, C$_{2,5}$), 107.30 (s, C$_{3,4}$), 43.94 (s, N(CH$_3$)$_2$), 16.15 (s, CH$_3$-C$_{2,5}$).

4.7. Synthesis of [Ti(η^5-DMP)(NMe$_2$)Cl$_2$] (7)

0.25 cm^3 (0.23 g, 2.5 mmol) of HDMP were slowly added dropwise to a stirred and cooled ($-50\,°C$) solution of [Ti(NMe$_2$)$_2$Cl$_2$] (0.45 g, 2.2 mmol) in 30 cm^3 of toluene. The mixture was refluxed for 6 h and then the volatile components were removed under vacuum, leaving a red oil. This red oil was extracted with hexane and the red solution obtained was left overnight in a $-80\,°C$ freezer. The solution was filtered and the resulting red powder was dried under vacuum (0.12 g, 0.47 mmol, 21%). Anal. Calc. for C$_8$H$_{14}$Cl$_2$N$_2$Ti: C, 37.39; H, 5.49; N, 10.90. Found: C, 37.54; H, 5.62; N, 10.59%. ^{1}H NMR (300 MHz, C$_6$D$_6$), δ (ppm): 6.16 (s, 2H, H$_{3,4}$), 3.52 (s, 6H, N(CH$_3$)$_2$), 2.14 (s, 6H, CH$_3$-C$_{2,5}$). ^{13}C{^{1}H} (75 MHz, C$_6$D$_6$), δ (ppm): 149.50 (s, C$_{2,5}$), 123.10 (s, C$_{3,4}$), 52.28 (s, N(CH$_3$)$_2$), 17.40 (s, CH$_3$-C$_{2,5}$).

4.8. Synthesis of [Ti(η^5-DMP)Cl$_3$] (8)

A suspension of LiDMP (2.15 g, 21 mmol) in 60 cm^3 of toluene was cooled at $-70\,°C$ and 4 g of TiCl$_4$ (21 mmol) were dissolved in 6 cm^3 of toluene and added dropwise to the suspension. The reaction mixture turned orange and was left stirring overnight. The solution was filtered and the volatile components were removed under vacuum, leaving an orange solid. This solid was extracted with hexane and the red solution obtained was left overnight in a $-80\,°C$ freezer. The solution was filtered and the resulting orange powder was dried under vacuum (1.95 g, 7.9 mmol, 37.6%). Anal. Calc. for C$_6$H$_8$Cl$_3$NTi: C, 29.01; H, 3.25; N, 5.64. Found: C, 28.69; H, 3.60; N, 5.31%. ^{1}H NMR (300 MHz,

C$_6$D$_6$), δ (ppm): 5.87 (s, 2H, H$_{3,4}$), 2.23 (s, 6H, CH$_3$-C$_{2,5}$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$), δ (ppm): 157.15 (s, C$_{2,5}$), 126.56 (s, C$_{3,4}$), 19.14 (s, CH$_3$-C$_{2,5}$).

4.9. X-ray crystallographic analysis

X-ray crystallographic data for compound [Ti(σN-TMP)(NMe$_2$)$_3$] was collected, at room temperature, in a MACH3 (Enraf Nonius) diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation in the ω-2θ scan mode. Unit cell parameters were determined from the setting angles of 25 reflections (17 < θ < 20). Data were corrected for Lorentz polarization effects and for absorption, using ψ scans. The MOLEN software [32] was used in the data reduction. The structure was solved by direct methods using SIR2004 [33] and refined using full-matrix least-squares refinement using SHELXL-97 [34]. These last two programs are included in the WINGX package (version 1.70.01) [35]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were inserted in idealized positions, riding on the parent C atom. Drawings were made using ORTEP3 for Windows [36].

Appendix A. Supplementary material

CCDC 721863 and 721864 contain the supplementary crystallographic data for compounds **1** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.03.007.

References

[1] C. Elschenbroich, A. Salzer, Organometallics a Concise Introduction, second ed., VCH, New York, 1992. pp. 315–342.
[2] M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255–270.
[3] T.M. Klapötke, H. Köpf, I.C. Tornieporth-Oetting, P.S. White, Organometallics 13 (1994) 3628–3633.
[4] P. Köpf-Maier, in: B.K. Keppler (Ed.), Complexes in Cancer Chemotherapy, VCH, New York, 1993.
[5] J.M. O'Connor, C.P. Casey, Chem. Rev. 75 (1987) 307–318.
[6] C. Janiak, N. Kuhn, Azacyclopentadienyl-metal complexes: historical background and recent advances, in: Ch.J. Moody (Ed.), Advances in Nitrogen Heterocycles, Vol. 2, JAI Press Inc., Greenwich, Connecticut, 1996, pp. 179–210.
[7] K.H. Pannel, B.L. Kalstom, C. Pankanyi, J. Heterocyclic Chem. 15 (1978) 1057–1081.
[8] D.L. Kershner, F. Basolo, Coord. Chem. Rev. 79 (1987) 279–292.
[9] K. Yunlu, F. Basolo, A.L. Reingold, J. Organomet. Chem. 330 (1987) 221–236.
[10] F.H. Allen, Acta Crystallogr. B58 (2002) 380–388.
[11] M.D. Fayer, C.B. Harris, Inorg. Chem. 8 (1969) 2792–2796.
[12] (a) H. Lee, J.B. Bonanno, B.M. Bridgewater, D.G. Churchill, G. Parkin, Polyhedron 24 (2005) 1356–1365;
(b) I.S. Katao, K. Nomura, Organometallics 28 (2009) 111–122;
(c) R.V. Bynum, W.E. Hunter, R.D. Rogers, J.L. Atwood, Inorg. Chem. 19 (1980) 2368–2374;
(d) R.V. Bynum, H.M. Zhang, W.E. Hunter, J.L. Atwood, Can. J. Chem. 64 (1986) 1254–1257.
[13] N. Kuhn, S. Stubenrauch, R. Boese, D. Bläser, J. Organomet. Chem. 440 (1992) 289–296.
[14] A.R. Dias, A.M. Galvão, A.C. Galvão, J. Organomet. Chem. 632 (2001) 157–163.
[15] J.M. Tanski, G. Parkin, Organometallics 21 (2002) 587–589.
[16] (a) Y. Shi, C. Hall, J.T. Ciszewski, C. Cao, A.L. Odom, Chem. Commun. (2003) 586–587;
(b) D.L. Swartz II, A.L. Odom, Organometallics 25 (2006) 6125–6133;
(c) D.L. Swartz II, A.L. Odom, Dalton Trans. (2008) 4254–4258.
[17] A.R. Dias, A.M. Galvão, A.C. Galvão, M.S. Salema, J. Chem. Soc., Dalton Trans. (1997) 1055–1061.
[18] A.R. Dias, A.M. Galvão, A.C. Galvão, Collect. Czech. Chem. Commun. 63 (1998) 182–186.

[19] M.T. Duarte, A. Ferreira, A.R. Dias, M.M. Salema, J. Ferreira da Silva, Acta Cryst. C61 (2005) m104–m106.
[20] A.R. Dias, A.P. Ferreira, L.F. Veiros, Organometallics 22 (2003) 5114–5125.
[21] A.R. Dias, A.P. Ferreira, L.F. Veiros, C.R. Chimie 8 (2005) 1444–1452.
[22] A.R. Dias, L.F. Veiros, J. Organomet. Chem. 690 (2005) 1840–1844.
[23] D.C. Bradley, I.M. Thomas, Proc. Chem. Soc. (1959) 225–226.
[24] D.C. Bradley, I.M. Thomas, J. Chem. Soc. (1960) 3857–3861.
[25] G. Chandra, M.F. Lappert, J. Chem. Soc. A (1968) 1940–1945.
[26] A.M. Martins, J.R. Ascenso, C.G. de Azevedo, M.J. Calhorda, A.R. Dias, S.S. Rodrigues, L. Toupet, P. de Leonardis, L.F. Veiros, J. Chem. Soc., Dalton Trans. (2000) 4332–4338.
[27] A. Efraty, N. Jubran, A. Goldman, Inorg. Chem. 21 (1982) 868–873.
[28] A. Martín, M. Mena, C. Yélamos, R. Serrano, P.R. Raithby, J. Organomet. Chem. 467 (1994) 79–84.
[29] A.W. Johnson, R. Price, Org. Synth. Coll. V (1973) 1022.
[30] W.A. Kornicker, EP. Benzing, E. Perry, US 3,394,156 (Cl. 260-429.5), 23 July 1968.;
     W.A. Kornicker, E.P. Benzing, E. Perry, Swiss Appl. 7 March 1960–28 October 1960.
[31] E. Benzig, W. Kornicker, Chem. Ber. 94 (1961) 2263–2267.
[32] C.K. Fair, MOLEN: An Interactive Intelligent System for Crystal Structure Analysis, Enraf Nonius, Delft, 1990.
[33] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarazo, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115–119.
[34] G.M. Sheldrick, SHELXL-97, A Computer Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
[35] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.
[36] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565. (ORTEP-3 for Windows (v1.076), based on ORTEP-3 (v1.03) by: C.K. Johnson, M.N. Burnett.)