

SYNTHESIS, CHARACTERIZATION AND THEORETICAL EVALUATION OF [Ti(NC₄Me₄)(NMe₂)₃] – A COMPLEX WITH *N*-BONDED 2,3,4,5-TETRAMETHYLPYRROLYL LIGAND

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The complex [Ti(NC₄Me₄)(NMe₂)₃] has been synthesized, characterized by mass spectrometry, ¹H and ¹³C NMR and theoretically studied by *ab initio* molecular orbital calculations. The *N*-σ-coordination mode of the heterocyclic ring was predicted by the ¹³C NMR data and confirmed by the optimized geometry of the model complex [Ti(NC₄H₄)(NMe₂)₃]. The different bonding modes of the 2,3,4,5-tetramethylpyrrolyl ligand are discussed.

Key words: Organometallics; Titanium; 2,3,4,5-Tetramethylpyrrolyl ligand; *Ab initio* methods.

η⁵-Cyclopentadienyl complexes are very common in transition metal chemistry¹ and are important homogeneous catalysts in polymerization reactions², being also known as anticarcinogenic agents^{3,4}. However, although pyrrolyl is isoelectronic with cyclopentadienyl, complexes with an η⁵-pyrrolyl are much less common because of the lower ionization potential of the nonbonding electron pair of the nitrogen atom relative to that of the π electrons⁵⁻⁷.

Our aim was to synthesize and characterize mono- and bis-η⁵-pyrrolyl complexes of titanium and zirconium and to compare them with the cyclopentadienyl analogues in terms of stability, structural features and catalytic activity. Therefore, we used 2,3,4,5-tetramethylpyrrolyl as a ligand, because the electrodonating ability of the methyl groups as well as the steric hindrance acting around the nitrogen atom would discourage the *N*-σ-bonding, promoting the η⁵-coordination of the heterocyclic ring^{5,6,8,9}. In fact, we have successfully prepared some titanium complexes with η⁵-2,3,4,5-tetramethylpyrrolyl, showing, however, a ring "slippage" towards the metal centre: [Ti(η⁵-NC₄Me₄)Cl₃], [Ti(η⁵-NC₄Me₄)₂Cl₂], [Ti(η⁵-NC₄Me₄)(SPh)₃], [Ti(η⁵-NC₄Me₄)(SPh)Cl₂] and [Ti(η⁵-C₅H₅)(η⁵-NC₄Me₄)Cl₂] (ref.¹⁰). These results confirmed the η⁵-coordination mode of the pyrrolyl ligand, already stated by several other authors¹¹⁻¹⁵. In the present work we synthesized, as far as we are aware, the first *N*-bonded 2,3,4,5-tetramethylpyrrolyl complex, [Ti(NC₄Me₄)(NMe₂)₃], and used MO calculations to rationalize this apparently anomalous bonding mode of the heterocyclic ligand.

EXPERIMENTAL

General Procedures

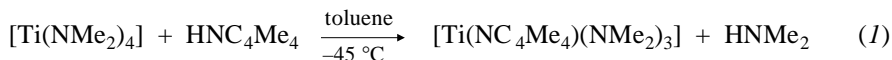
All reactions and manipulations were carried out under argon, using standard Schlenk-tube techniques and the NMR samples were prepared in Mbraun glove-box. Toluene was dried with sodium and distilled over sodium/benzophenone under nitrogen. Deuteriated toluene was dried with activated molecular sieves and deoxygenated by several freeze-pump-thaw cycles. 2,3,4,5-Tetramethylpyrrole¹⁶ and tetrakis(dimethylamido)titanium¹⁷ were prepared as described. The NMR spectra were recorded in deuteriated toluene on a Varian 300 MHz spectrometer and referenced internally to the residual toluene resonance (δ in ppm, J in Hz). Mass spectrometry data were obtained at Instituto de Tecnologia Nuclear on a Finnigan FTMS 2001 instrument.

Synthesis of [Ti(NC₄Me₄)(NMe₂)₃]

To a stirred and cooled solution ($-45\text{ }^{\circ}\text{C}$) of tetrakis(dimethylamido)titanium (0.99 g, 4.4 mmol) in toluene (*ca* 30 cm³) was added a solution of 2,3,4,5-tetramethylpyrrole (0.55 g, 4.5 mmol) in the same solvent (*ca* 20 cm³). The yellow solution obtained was left stirring overnight, yielding an orange solution, which was evaporated to dryness under vacuum. The residue was an orange liquid, solidifying after 2 days to a low-melting orange solid; ¹H NMR spectrum (toluene-*d*₈): 2.07 s, 6 H (pyrrolyl CH₃); 2.24 s, 6 H (pyrrolyl CH₃); 3.00 s, 18 H (N-CH₃); ¹³C NMR spectrum (toluene-*d*₈): 10.35 q, ¹*J*(CH) = 124 (pyrrolyl CH₃); 13.25 q, ¹*J*(CH) = 124 (pyrrolyl CH₃); 44.13 qq, ¹*J*(CH) = 134, ³*J*(CH) = 6 (N-CH₃); 113.70 s (pyrrolyl 3,4-C) and 128.40 s (pyrrolyl 2,5-C). Mass spectrum, *m/z*: 302.2005 (M⁺, 100%) and 257 (M⁺ - HNMe₂); C₁₄H₃₀N₄Ti⁺ requires 302.1944.

RESULTS AND DISCUSSION

In order to obtain a titanium complex with 2,3,4,5-tetramethylpyrrolyl and amido groups, we reacted [Ti(η^5 -NC₄Me₄)Cl₃] (ref.¹⁰) with 3 equivalents of lithium dimethylamide. However, the substitution of the chlorides by amide ligands was not successful and we tried to synthesize the desired complex by an alternative route involving the reaction of tetrakis(dimethylamido)titanium and 2,3,4,5-tetramethylpyrrole (Eq. (I)).



The evaporation to dryness of the reaction mixture led to an orange liquid that turned into a low-melting solid, whose mass spectrum is consistent with the formula above. In fact, the peak of higher *m/z* value (302.2005) corresponds to the molecular ion [Ti(NC₄Me₄)(NMe₂)₃]⁺ and we can also observe the fragment [Ti(NC₄Me₄)(NMe₂)₃]⁺ - HNMe₂ (*m/z* = 257). The sensitivity of [Ti(NC₄Me₄)(NMe₂)₃] to moisture leads to decomposition with formation of the free pro-ligand, preventing satisfactory IR spectrum and elemental analysis.

The ¹H NMR spectrum showed two singlets with relative areas 1 : 1 (2.07 and 2.24 ppm) corresponding to the two types of methyl groups of the pyrrolyl ligand and another

singlet (3.00 ppm) with a three-fold area relative to each of the other singlets, assigned to the three dimethylamido groups. In addition, we observed the characteristic peak of $[\text{Ti}(\text{NMe}_2)_4]$, which was present in a small molar amount of 2.6%. The lowering of the temperature down to $-80\text{ }^\circ\text{C}$ does not change the ^1H NMR spectrum, indicating the fluxionality of the amido and pyrrolyl methyl groups. The $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum suggests an $N\text{-}\sigma$ -coordination of the heterocyclic ligand, since one type of ring carbons has a chemical shift (113.70 ppm) very similar to that of the free ligand (113.80 ppm) and the other quaternary carbons (δ 128.40 ppm) are only slightly deshielded when compared to those of the free ligand (δ 120.20 ppm). In fact, in the similar η^5 -complexes reported in the literature – $[\text{Ti}(\eta^5\text{-NC}_4\text{Me}_4)\text{Cl}_3]$, $[\text{Ti}(\eta^5\text{-NC}_4\text{Me}_4)_2\text{Cl}_2]$, $[\text{Ti}(\eta^5\text{-NC}_4\text{Me}_4)(\text{SPh})_3]$, $[\text{Ti}(\eta^5\text{-NC}_4\text{Me}_4)(\text{SPh})\text{Cl}_2]$ (ref.¹⁰) and $[\text{Ti}(\eta^5\text{-NC}_4\text{H}_2\text{Bu}'_2\text{-2,5})\text{Cl}_3]$ (ref.¹⁸) – the deshielding of the ring carbons relative to the free ligand is considerably higher (between 22 and 33 ppm), indicating the donation of electron density from the carbons to the metal.

The chemical shift of 113.70 ppm can be easily assigned to the 3,4-quaternary carbons of $[\text{Ti}(\text{NC}_4\text{Me}_4)(\text{NMe}_2)_3]$ because the coordination by the nitrogen atom is not significantly reflected in those carbons and therefore the δ value remains identical to that of the free ligand. The carbons in positions 2 and 5 of the ring, being closer to the donor nitrogen atom, are slightly affected by the $N\text{-}\sigma$ -coordination and deshield 8 ppm from the value of the free ligand.

The versatility of the pyrrolyl ligand to adopt these different coordination modes was studied by Hartree–Fock *ab initio* MO calculations. The η^5 -coordination was previously addressed by the authors¹⁰ for complexes of general formula $[\text{Ti}(\eta^5\text{-NC}_4\text{Me}_4)\text{L}_3]$, with $\text{L} = \text{Cl}$, SPh , and compared with its cyclopentadienyl analogues. In these compounds, a ring slippage, attributed to the mixing of the pyrrolyl lone pair with a π orbital of appropriate symmetry was observed, producing an elongation of the metal–3,4-carbons bond lengths. A further slippage of the ring will bring the carbons 3 and 4 sufficiently far away from the metal to classify the pyrrolyl ligand as η^3 -coordinated.

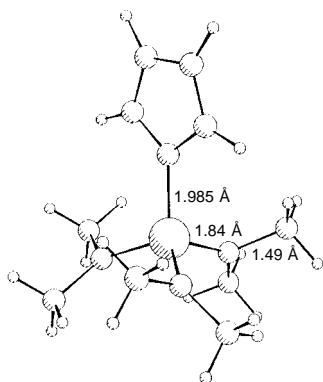


Fig. 1
Optimized Hartree–Fock *ab initio* structure of the model complex $[\text{Ti}(\text{NC}_4\text{H}_4)(\text{NMe}_2)_3]$

This will allow, for instance, addition of a fifth ligand in substitution reactions by an associative mechanism without passing through an unfavourable 18-electron transition state. On the other hand, we could also obtain an η^3 -coordination by replacing the studied one-electron donor atoms of our model complexes by three-electron donor groups, such as NMe_2^- keeping the overall formal 16-electron counting at the metal centre. In such a model complex, an alternative N - σ -bonding could be conceived with a formal π -donation of the heteroatom electron pair perpendicular to the ring plane. *Ab initio* MO calculations carried out in the model complex $[\text{Ti}(\text{NC}_4\text{H}_4)(\text{NMe}_2)_3]$ showed that the latter mode of coordination would be the most favourable (Fig. 1) in good agreement with the ^{13}C - $\{^1\text{H}\}$ NMR data. The calculations also predicted a pseudo-tetrahedral arrangement of the four ligands with the N–Ti–N bond angle in the range 107–110°.

APPENDIX

The *ab initio* calculations were made with GAUSSIAN94 program¹⁹ with LANL2MB basis set. The geometries were optimized at Hartree–Fock level with the five-membered rings kept as regular pentagons. All the computational calculations were done on a DEC3000 computer.

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