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Isolation and characterization of the first bis(2-pyridyl)carbyltitanium(IV) complex derived from the C–O bond cleavage of the alkoxide ligand in Cp*TiMe$_2$(OCMePy$_2$). X-Ray crystal structure of [Cp*Ti(μ-O)(CMePy$_2$)]$_2$ (Cp* = C$_5$Me$_5$) †

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The reaction of Cp*TiMe$_2$(OCMePy$_2$) with one equivalent of xylylisocyanide (xylyl = 2,6-dimethylphenyl) affords the first bis(2-pyridyl)carbyl titanium(IV) as final complex in which the ligand acts as chelate and it is directly bonded to the titanium atom through both nitrogen atoms.

In recent years, there has been considerable effort focused on the development of new ancillary ligands with the aim of tailoring the chemical reactivity and properties of transition metal complexes.[1–3] In a previous work,[4] we reported on the synthesis of a new family of bis(2-pyridyl) and tris(2-pyridyl)alkoxide complexes of titanium, zirconium and tantalum in order to explore the coordination behaviour of this type of ligands. The reaction of Cp*TiMe$_2$(OCMePy$_2$)[4] with xylylisocyanide takes place through a C–O bond cleavage[5] of the coordinated bis(2-pyridyl)alkoxide ligand to yield a bis(2-pyridyl)ethyl containing titanium complex. Herein we describe the first example of a bis(2-pyridyl)carbyl titanium(IV) complex. In fact, the reaction between Cp*TiMe$_2$(OCMePy$_2$) **1** and xylylisocyanide (xylyl = 2,6-dimethylphenyl) in a 1 : 1 molar ratio in toluene results in the formation of a deep green crystalline complex after appropriate work-up, which has been characterized as complex [Cp*Ti(μ-O)(CMePy$_2$)] **2** by ^{1}H NMR, ^{13}C NMR spectra, elemental analysis and single crystal X-ray diffraction. ‡ It is sparsely soluble in pentane and somewhat more soluble in toluene. The first outstanding feature the ^{1}H NMR and ^{13}C NMR spectra show is that there are no signals assignable to the xylyl moiety. The ^{1}H NMR spectrum displays two singlet signals at δ 1.53 and 2.14 corresponding to the Cp* ligand and to the methyl group of the ethanide moiety, respectively, and three multiplet signals at δ 6.20, 6.97 and 9.47 which are tentatively assigned to the protons of equivalent pyridyl fragments. A single crystal X-ray diffraction study of **2** confirmed the structural predictions based on analytical and spectroscopic data, namely the absence of the xylyl group as well as the presence of the ethanide ligand formed by the activation of the C–O bond of the alkoxide ligand. Fig. 1 shows an ORTEP[13] view of centrosymmetric dimer **2** along with some important bond distances and angles. The molecular structure is not of high quality because of the relatively poor quality of the crystals obtained, therefore caution must be taken in reading too much into actual bond lengths and angles.

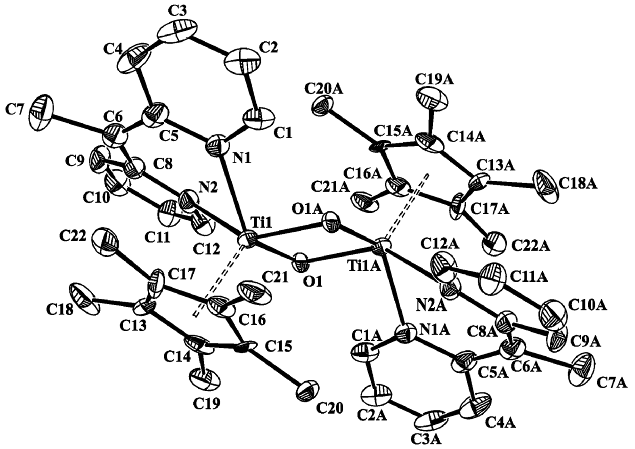

Fig. 1 Molecular structure of [Cp*Ti(μ-O)(CMePy$_2$)]$_2$ **2** with thermal ellipsoids representing 30% probability; hydrogen atoms omitted for clarity. Selected distances: Ti(1)–O(1) 1.845(7), Ti(1)–N(1) 2.165(9), Ti(1)–N(2) 2.199(9), Ti–Ti 2.863(4) Å; angles: C(8)–C(6)–C(5) 128.7(13), C(8)–C(6)–C(7) 115.2(13), C(5)–C(6)–C(7) 116.0(13), Ti(1)–O(1)–Ti(1A) 101.0(4), O(1)–Ti(1)–O(1A) 79.0(4)°.

The titanium–O bond distances [Ti(1)–O(1), 1.845(7) and Ti(1)–O(1A) 1.860(7) Å] and the Ti–O–Ti bond angles are within the range expected for di-μ-oxo-dititanium bridging systems.[6] The Ti–Ti distance [2.863(4) Å] is short enough to propose a M–M bond. However, the presence of a Ti–Ti bond in the complex can be ruled out since we are dealing formally with Ti(IV), d^0. This situation has been observed previously[7] and it strengthens the difficulties in determining whether or not there is a M–M bond in these multi-bridged systems. The Ti(1)–N(1) and Ti(1)–N(2) bond distances [2.165(9) and 2.199(9) Å respectively] compare well with those found in other titanium tris(pyrazolyl)borate complexes.[8] The bonding of the bis(2-pyridyl)ethyl ligand to the titanium centre can be described by three mesomeric resonance forms[9] (see Scheme 1). According to the structural parameters at the central carbon C(6) atom [the sum of C(8)–C(6)–C(5), C(8)–C(6)–C(7) and C(5)–C(6)–C(7) bond angles is 359.9°] a sp^2 hybridization must be assigned to this carbon atom and so we can conclude that only forms **a**

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† Electronic supplementary information (ESI) available: experimental details and tables of crystallographic data. See http://www.rsc.org/suppdata/dt/b1/b106481a/

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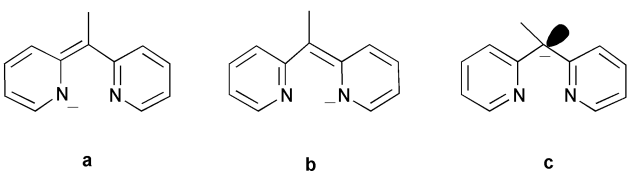

Scheme 1

and **b** contribute to describing the bonding. Presumably, the formation of **2** arises *via* a pathway involving initial insertion of xylylisocyanide into one Ti–Me bond to form the corresponding mono(η^2-iminoacyl) complex. A second methyl migration would then occur, forming an η^2-imine complex. Finally, elimination of the imine moiety would result in the formation of a Ti(II) complex which throughout an O–C bond activation would evolve to yield complex **2** (see Scheme 2).

An analogous mechanism has been found[10] for the reaction of t-BuNC with $Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(CH_2Ph)_2$. It involves formation of an aza-titanacyclopropane complex from which elimination of the imine fragment, induced by the coordination of a pyridine ligand, results on the reduction of the metallic centre. In order to gain insight into the mechanism through which formation of complex **2** would occur, the reaction of complex **1** with xylylisocyanide in 1 : 1 molar ratio was monitored by means of NMR experiments. At room temperature, in C_6D_6 as solvent, **1** reacts immediately to afford an aza-titanacyclopropane complex [Cp*Ti{η^2-(CN)-C(Me)$_2$NXylyl}-(OCMePy$_2$)] **3** as the main product (*ca.* 80%). The proposed η^2-acyl-containing intermediate **A**, which would result from the initial insertion of xylylisocyanide into one Ti–Me bond, was not observed, probably because it has a short existence on the NMR time scale. In their NMR spectra there are signals both for the diastereotopic methyl groups of the imine moiety and non-equivalent pyridyl groups of the alkoxide ligand. A noteworthy feature of the ^{13}C NMR spectrum of **3** is the presence of a singlet at δ 71.9, assigned to the aza-titanacyclopropane carbon atom. The high field shift of this resonance points to an η^2-coordination mode of the imine group.[11] Complex **3** was isolated on a preparative scale as a brown solid by reaction of **2** with xylylisocyanide in toluene over 10 min after appropriate work-up. When the NMR spectra were subsequently recorded (*ca.* 1 h), the appropriate signals corresponding to both complex **2** and the free imine, $Me_2C{=}Nxylyl$, were observed. On the other hand, no signals for the proposed dimeric intermediate **B** of Ti(II) (see Scheme 2) were observed, and an explanation for this fact analogous to that commented above for **A** could be considered. It has also been found that, in accordance with NMR data, the formation rate of **2** from **3** depends on the sample concentration and it was faster for concentrated samples than for diluted ones. This behaviour suggests, as was proposed in Scheme 2, intermediate **B**, that the formation of **2** from **3** occurs *via* an intermolecular process. In summary, the results reported here clearly reveal that the bis(2-pyridyl)-alkoxide ligand in a titanium species reacts through a C–O bond activation to yield the first bis(2-pyridyl)carbyl titanium(IV) complex. We are working now on the possible extension of this reaction to other titanium and zirconium compounds.

Acknowledgements

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Notes and references

‡ Crystallographic data for **2**: $C_{44}H_{52}N_4O_2Ti_2$, MW = 764.7, crystal dimensions, 0.3 × 0.2 × 0.2 mm, monoclinic, space group $P2_1/n$, a = 11.034(2), b = 10.346(3), c = 16.992(7) Å, β = 103.960(10)°, V = 1882.5(10) Å^3, Z = 4, D_c = 1.349 g cm^{-3}, μ(Mo-Kα) = 4.68 cm^{-1}, $F(000) = 808$, T = 200 K, λ = 0.71070 Å, ω–2θ scan, $2 < \theta < 22$ ($0 \le h \le 11$, $0 \le k \le 10$, $-17 \le l \le 17$). From 2288 independent reflections, 1050 were considered with $I > 2\sigma I$. Final R indices, $R_1 = 0.0971$, $wR_2 = 0.2134$ (for $I > 2\sigma I$). Maximum and minimum residual electron densities, 0.431 and −0.447 e Å^{-3}. Nonius-Mach 3 diffractometer; programs used: SHELXL-97.[12] CCDC reference number 173685. See http://www.rsc.org/suppdata/dt/b1/b106481a/ for crystallographic data in CIF or other electronic format.

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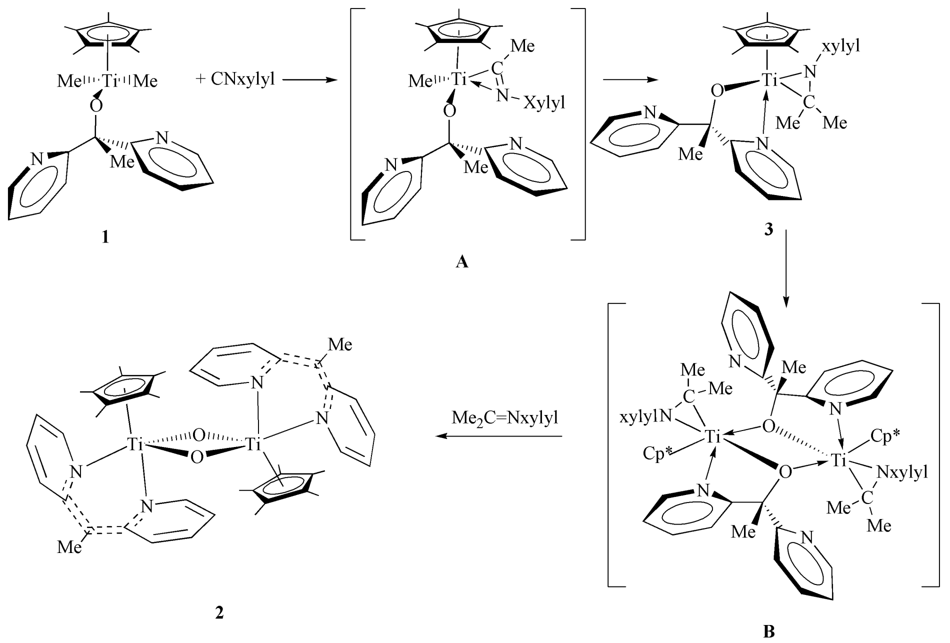

Scheme 2 Proposed mechanism for the formation of complex **2**.

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