Synthesis and Molecular Structure of the First Organometallic Nitride Cubane: [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_4$]

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The ammonolysis of [Ti(η^5-C_5Me_5)(NMe_2)$_3$] at 90 °C affords the nitride complex [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_4$]; the X-ray crystal structure analysis shows a Ti_4N_4 core clearly similar to the structural motif of cubic titanium nitride.

In the last few years, reactions of alkyl organometallic compounds with ammonia have been used as an elegant and efficient entry to the synthesis of polynuclear early-transition-metal nitrides.[1] In this way, tri-, penta- and hexa-nuclear complexes have been reported.[2,3] Similar reactions with the homoleptic dialkylamido compounds of formula $M(NR_2)_n$, where M is a group 4 or 5 metal in the highest oxidation state, produced oligomers which could be converted to metal nitrides at relatively low temperatures.[4]

$$\begin{array}{c} 4\ [\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})(\mathrm{NMe_2})_3] + 4\ \mathrm{NH_3} \\ \mathbf{1} \\ 90\ ^\circ\mathrm{C}\ \big\downarrow\ \text{toluene} \\ [\{\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5Me_5})\}_4(\mu_3\text{-}\mathrm{N})_4] + 12\ \mathrm{NHMe_2} \\ \mathbf{2} \end{array}$$

Scheme 1

We recently reported the synthesis and characterization of several mono-, bis- and tris-amido monopentamethylcyclopentadienyl derivatives of titanium(IV)[5] and were interested in the study of their reactivity with ammonia.

In this work we show that treatment of [Ti(η^5-C_5Me_5)(NMe_2)$_3$] **1** with an excess of ammonia in toluene at 90 °C leads to the formation of [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_4$]† **2** in good yield (Scheme 1).

The NMR data and elemental analysis‡ suggest a Ti(η^5-C_5Me_5)N stoichiometry, showing a symmetrical structure in solution. The IR spectrum shows a very strong and broad absorption at 644 cm^{-1}, assignable to the titanium–nitrogen bond.[6] The non-volatility of **2** made it impossible to obtain any information about its structure by mass spectrometry (EI, 70 eV), but fortunately suitable single crystals for X-ray diffraction were obtained by slow cooling of a hexane solution.§

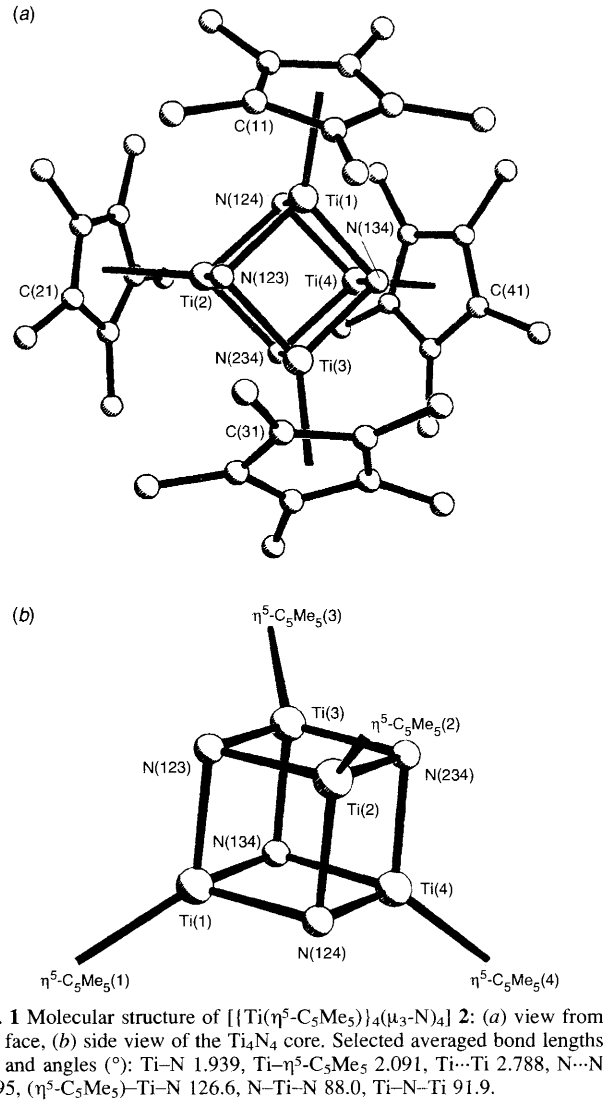

Fig. 1 Molecular structure of [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_4$] **2**: (*a*) view from one face, (*b*) side view of the Ti_4N_4 core. Selected averaged bond lengths (Å) and angles (°): Ti–N 1.939, Ti–η^5-C_5Me_5 2.091, Ti···Ti 2.788, N···N 2.695, (η^5-C_5Me_5)–Ti–N 126.6, N–Ti–N 88.0, Ti–N–Ti 91.9.

The structure of **2** (Fig. 1) consists of an almost perfect cube, where the titanium and nitrogen atoms are positioned on alternating vertices, and all Ti–N–Ti and N–Ti–N angles are *ca.* 90°. The tetrahedron formed by the four titanium atoms is slightly larger than that of the nitrogens, Ti···Ti(av.) is 0.093 Å longer than N···N(av.). The metal centres are very close to each other (av. 2.788 Å) but significant ground-state metal–metal interactions seem unlikely. The Ti–N bond lengths (av. 1.939 Å) are in the range found by Roesky *et al.* for [{Ti(η^5-C_5H_5)(μ-NH)}$_3$(μ_3-N)][2] and only slightly shorter than the theoretically calculated Ti–N single bond distance, 1.981 Å.[7]

The Ti_4N_4 core of compound **2** is similar to the Ti_4O_6 present in the oxo derivatives [{Ti_4($C_6H_{15}N_3$)$_4$(μ-O)$_6$}Br_4][8] and [{Ti(η^5-C_5Me_5)}$_4$(μ-O)$_6$].[9] In fact, the latter compound can be obtained by hydrolysis of **2** in the presence of humidity. To our knowledge, compound **2** is the first tetranuclear cubane-like organometallic nitride complex to be structurally characterized.

Interestingly, the Ti_4N_4 core of **2** manifests a clear geometrical relationship with the rock-salt structure of cubic TiN, as is illustrated in Fig. 1. Assessment of the suitability of **2** as a precursor for titanium nitride polymers and studies concerning ammonolysis of a variety of early-transition-metal derivatives are underway in our laboratory.

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Footnotes

† A solution of [Ti(η^5-C_5Me_5)(NMe_2)$_3$] (1.08 g, 3.45 mmol) in toluene (50 ml) was transferred *via* cannula into a Carius tube (capacity 120 ml). The argon atmosphere was changed to ammonia, cooled to −78 °C and the Carius tube was flame sealed. The tube was heated at 90 °C for 16 h to obtain a green solution, which afforded dark green crystals of **2** on cooling to room temp. Yield: 0.56 g (82%).

‡ *Spectroscopic data* for [{Ti(η^5-C_5Me_5)}$_4$(μ_3-N)$_4$] **2**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ): 1.99 (s, 60 H, C_5Me_5). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$,

25 °C, δ): 12.0 (C_5Me_5), 119.1 (C_5Me$_5$). IR (KBr, ν/cm^{-1}): 2910s, 1434m, 1371s, 1021w, 789vs, 644vs (br), 445vs. Analysis for $C_{40}H_{60}N_4Ti_4$. Calc.: C, 60.93; H, 7.67; N, 7.11. Found: C, 61.28; H, 7.68; N, 7.04%).

§ *Crystal data* for **2**: $C_{40}H_{60}N_4Ti_4$, M_t = 788.52, triclinic, space group $P\bar{1}$, a = 11.030(4), b = 11.115(6), c = 18.426(5) Å, α = 83.17(3), β = 83.27(2), γ = 66.47(3)°, U = 2050(1) Å^3, Z = 2, D_c = 1.277 g cm^{-3}, $F(000)$ = 832, λ = 0.71073 Å, μ(Mo-Kα) = 0.782 mm^{-1}. The data were collected on an Enraf Nonius CAD4 diffractometer. Intensity measurements were performed by ω–θ scans in the range $2 < 2\theta < 50°$ at 19 °C on a crystal of dimensions 0.43 × 0.35 × 0.32 mm. Of the 7753 measured reflections, 7208 were independent; largest minimum and maximum residual electron density in the final difference Fourier synthesis: −0.778 and 1.112 e Å^{-3}, $R1$ = 0.065 [for 5696 reflections with $F > 4\sigma(F)$] and $wR2$ = 0.251 (all data). The values of $R1$ and $wR2$ are defined by $R1 = \Sigma||F_o| - |F_c||/(\Sigma|F_o|)$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$. The structure was solved by direct methods (SHELXS-90) and refined by least squares against F^2 (SHELXL-93). The hydrogen atoms were positioned geometrically and refined by using a riding model in which the Me groups can rotate about their local axes.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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