

[1] G.W. Coates, *Chem. Rev.* **2000**, *100*, 1223-1252; (b) S.K. Spitzmesser and V.E. Gibson, *Chem. Rev.* **2003**, *103*, 283-315. [2] S.J. McLain, R.R. Schrock, P.R. Sharp, M.R. Churchill and W.J. Youngs, *J. Am. Chem. Soc.* **1979**, *101*, 263-265. [3] D. Copolovici, V.R. Bojan, C.I. Rat, A. Silvestru, H.J. Breunig and C. Silvestru, *Dalton Trans.*, **2010**, *39*, 6410-6418.

Keywords: tantalum, chlorido, aryl, cyclopentadienyl complexes

MS61.P16

Acta Cryst. (2011) **A67**, C610

Isocyanide insertion processes into the oxonitrido [$\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-O})\}_3(\mu_3\text{-N})$]

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The synthesis of the new oxonitrido complex [$\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-O})\}_3(\mu_3\text{-N})$] (**1**) through ammonia bonds activation by the oxoalkylidyne complexes [$\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-O})\}_3(\mu_3\text{-CR})$] (R = H, Me) has been discovered very recently.^[1] Nowadays we are exploring the reactivity of this interesting compound both in coordination and insertion processes. The ability of **1** to act as a neutral monodentate or tridentate ligand has been pointed out by the incorporation of some inorganic fragments such as $[\text{AlEt}_3]$ or $[\text{Mo}(\text{CO})_3]$, while the apical nitrido group can play an active role when the starting compound reacts with several group 6 hexacarbonyl derivatives.^[2] Here we report the reactions of complex **1** with some organic isocyanides.

Although they seem similar, tertbutyl and 2,6-dimethylphenyl isocyanides behave in a very different way when they interact with **1**. Thus, as it can be seen in figure 1, the reaction of **1** with tertbutyl isocyanide in a 1:2 ratio leads to formation of NCN*t*Bu moieties linked to the Ti(3) titanium atom as a result of an insertion process into the Ti-N bonds of **1**; simultaneously an intermolecular coupling of two *t*Bu groups takes place allowing to establish two bridging CN units between the two $[\text{Ti}_3\text{O}_3]$ rings.

On the other hand, reaction of **1** with 2,6-dimethylphenyl isocyanide in a 1:3 ratio also leads to formation of a NCNAr (Ar = 2,6- $\text{C}_6\text{H}_3\text{Me}_2$) unit linked to a titanium atom. Interestingly, the other two titanium atoms of the $[\text{Ti}_3\text{O}_3]$ ring are now bridged by a ArNCCNAr moiety, product of the intramolecular coupling of two isocyanide fragments. This compound is stable at room temperature but evolves at 150°C to give a terminal cyanide group linked to a titanium atom, a ArNCNAr bridging fragment between the other two metal centers and a free 1,3-xylene molecule.

Further studies on this insertion processes are being undertaken to clarify the possible reaction mechanisms.

Acknowledgements: Financial support for this work was provided by the Dirección General de Investigación (CTQ2008-00061/BQU) and Factoría de Cristalización (CONSOLIDER-INGENIO 2010).

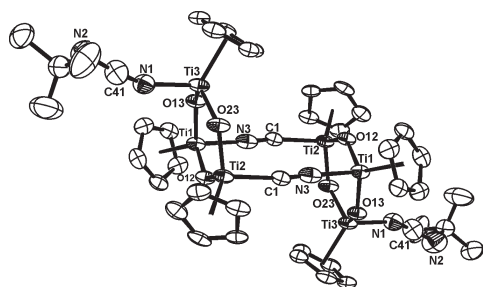


Figure 1. Methyl groups of the pentamethylcyclopentadienyl rings have been omitted for clarity.

[1] S. Aguado-Ullate, J.J. Carbó, O. González-del Moral, A. Martín, M. Mena, J.-M. Poblet, C. Santamaría, submitted to publish. [2] S. Aguado-Ullate, J.J. Carbó, O. González-del Moral, M. Gómez-Pantoja, A. Hernán-Gómez, A. Martín, M. Mena, J.-M. Poblet, C. Santamaría, submitted to publish.

Keywords: nitride, oxide, titanium

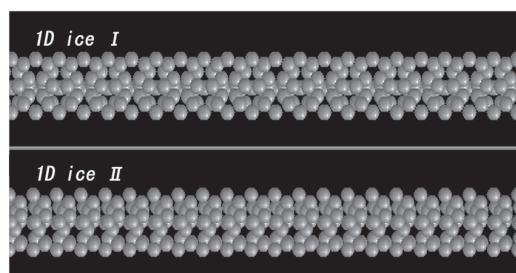
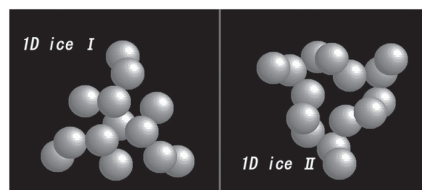
MS61.P17

Acta Cryst. (2011) **A67**, C610

The structure of 1D ice, water nanowire, in crystal host

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Two kinds of novel one-dimensional ices (1D ice I & II) are prepared in the single crystal by mixing tryptophan and pyridoxal-5-phosphate in $\text{H}_2\text{O}/\text{D}_2\text{O}$ solution. The structure of 1D ice I (from H_2O , diameter=1.642nm) is best similar to hexagonal ice (Ih). Inner part of this nanowire is almost completely the same as ice Ih, where three boat-type hydrogen-bonded six-membered rings are formed around a 3-fold symmetry axis. Outer side of this nanowire is alternatively arrayed by five- and seven-membered rings parallel to the 3-fold axis. The structure of 1D ice I is constructed in such a way that 26 water molecules form a water cluster unit and these units are then piled up by six or seven hydrogen bonds to form an infinite water nanowire along to the needle direction of the crystal. The structure of 1D ice II (from D_2O , diameter=1.649nm) consists of a hollow-wire type nanowire that is constructed by piling up the cluster unit consisting of 15 D_2O around a 3-fold axis. There are seven kinds of hydrogen bonds in ice II structure, and two of these are very strong (0.246 and 0.247nm). In both ices I & II, the overall structures may be described as infinite three-square column-like nanowires constructed by hydrogen-bonded water molecules, and the outermost three-cornered portions of these nanowires form infinite *trans* zig-zag water chains. It is worthy to note that very long needle crystals (up to 26mm) are obtained in both cases, and the linearity of both nanowires is completely perfect because of wire-structure formation around the 3-fold axis, where the longest nanowire exhibits *aspect ratio* (length-to-width ratio) $> 1.5 \times 10^7$. Therefore, it would be reasonable to consider that the present structures provide the structural scaffold for a bridge between the nano world (nm) and the real world (mm) in the water/ice structure.



Keywords: 1D ice, water nanowire, three-square column