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**Keywords:** arylsulfonamides, supramolecular architecture.

## MS61.P14

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### Double Deprotonation of functionalized aryl amines leading to new Ti (IV) imido derivatives

Lina María Aguirre, María de los Ángeles Dávila, Marta E. G. Mosquera, Pilar Gómez-Sal *Inorganic Chemistry Department, Universidad de Alcalá, Alcalá de Henares-Madrid (Spain)*. E-mail: martaeg.mosquera@uah.es

The  $\pi$ -donor imido functional group gives rise to a chemistry that is generally dominated by medium to high metal oxidation states; also showing a variety of coordination modes such as terminal metal-nitrogen multiple bond or bridging disposition. This chemistry is interesting not only because of their structural features, and their remarkable reactivity, as well, nowadays it is well recognized the importance of imido compounds in industrial processes, organic synthesis and catalysis. [1]

The most reactive of imido compounds occur within group 4. As an example, titanium imides react with many organic substrates including alkenes, allenes, alkynes, heterocumulenes, nitriles, isonitriles, isocyanates, and phosphalkynes, and in many cases these reactions result in the formation of both novel organic products and metal-containing species. [2]

Our studies are focused on species containing imido ligands which possess functionalized substituents as we are interested in analysing the effect of the additional functionality on the coordination behaviour of these derivatives and on their reactivity. As well the presence of an additional donor atom in the ligand would enhance the capacity of the species synthesized to behave as metalloligands for the construction of ordered supramolecular structures.

The treatment of the complexes  $[\text{Ti}(\text{NR}_2)_4]$ ,  $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_3]$  and  $[\text{Ti}(\text{C}_5\text{Me}_5)(\text{NR}_2)_3]$  with functionalized aromatic amines leads to the formation of new amido complexes. To achieve the double deprotonation it is necessary to introduce in the reaction an additional base such as alkyl lithium or magnesium derivatives. In these conditions it is possible to attain the formation of imido species as the one show in figure 1. This compound crystallizes as a triclinic in the space group P-1; only half of the molecule is found in the asymmetric unit, through an inversion centre is generated the titanium (IV) dinuclear species. Interestingly not many titanocenes with bridging imido arene ligands have been described. [3]

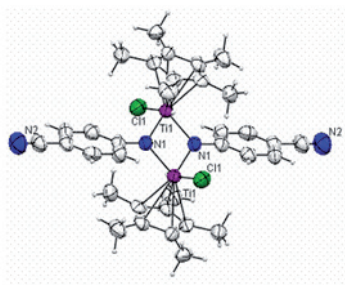


Figure 1

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**Keywords:** organometallics, titanium, imido.

## MS61.P15

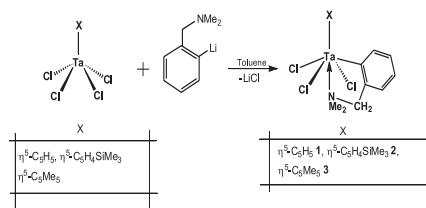
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### X-Ray Diffraction Studies of Monocyclopentadienyl Cyclometalated Aryl Tantalum(V) Compounds

Carlos García,<sup>a</sup> Agustín Galindo,<sup>b</sup> Manuel Gómez,<sup>\*a</sup> Pilar Gómez-Sal<sup>a</sup> and Andrés Parra<sup>a</sup> <sup>a</sup>Departamento de Química Inorgánica, Universidad de Alcalá de Henares, Campus Universitario, E-28871 Alcalá de Henares, Spain <sup>b</sup>Departamento de Química Inorgánica, Universidad de Sevilla, Aptdo. 1203, E-41071, Sevilla, Spain. E-mail: carlos.garciagarcia@uah.es

Mono- and bis(cyclopentadienyl) complexes of early transition metals have received an increased attention stimulated by their use in understanding the chemistry of important catalytic processes, in particular those related to olefin and ring-opening polymerization metathesis.[1] Many aryl tantalum compounds are labile and tend to decompose via  $\beta$ -H elimination reactions forming benzyne complexes, for example,  $\text{TaCp}^*\text{Me}_3\text{Ph}$ . [2] However, ancillary ligands capable of  $\pi$ -bonding have a stabilizing influence on  $\sigma$ -bonded aryl ligands in high oxidation state early transition metal chemistry. For it, a possible approach to overcome complications caused by  $\beta$ -H elimination is to prepare derivatives by employing an aryl ligand that has an ortho-substituted C,N-chelating arylamine ligands form an additional coordinative bond ( $\sigma$ -donor N) to the metal center and thereby enhance the kinetic stability of the organometallic complex formed.[3] These bidentate ligands possess a hard anionic carbon ( $\text{C}_i$ ) atom and a neutral tertiary N donor atom as ligating sites; moreover, such ligands form cyclometalated complexes which contain a five-membered chelate ring.

As part our interest in the structure-reactivity relationship analysis in Group 5 metal monocyclopentadienyl compounds, we will describe the results obtained by using the 2- $\{(\text{dimethylamino})\text{methyl}\}$ phenyl ligand in the synthesis of new tantalum(V) complexes and their structural study by spectroscopic, X-ray diffraction and DFT methods.



	1	2	3
Ta(1)-N	2.467(9)	2.524(4)	2.529(9)
Ta(1)-Cp	2.120	2.147	2.211
C(17)-N	1.482(14)	1.494(7)	1.512(14)
Cp-Ta(1)-N	175.6	176.0	174.7

<sup>a</sup>Cp is the centroid of C(1)-C(2)-C(3)-C(4)-C(5) ring.

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**Keywords:** tantalum, chlorido, aryl, cyclopentadienyl complexes

## MS61.P16

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

Avelino Martín, Octavio González-del Moral, Miguel Mena, Cristina Santamaría. *Departamento de Química Inorgánica. Universidad de Alcalá, Campus Universitario. 28871 Alcalá de Henares-Madrid (Spain)*. E-mail: avelino.martin@uah.es

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 oxoalkylidene 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.<sup>[1]</sup> 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.<sup>[2]</sup> 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 NCN*Ar* (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  $\text{ArNCCNAr}$  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  $\text{ArNCNAr}$  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.

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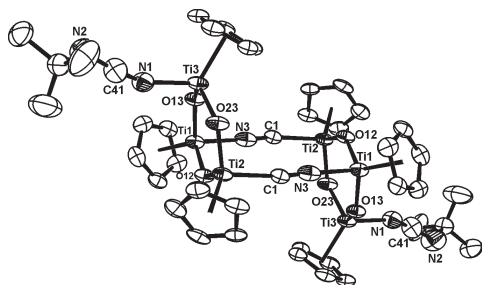


Figure 1. Methyl groups of the pentamethylcyclopentadienyl rings have been omitted for clarity.

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**Keywords:** nitride, oxide, titanium

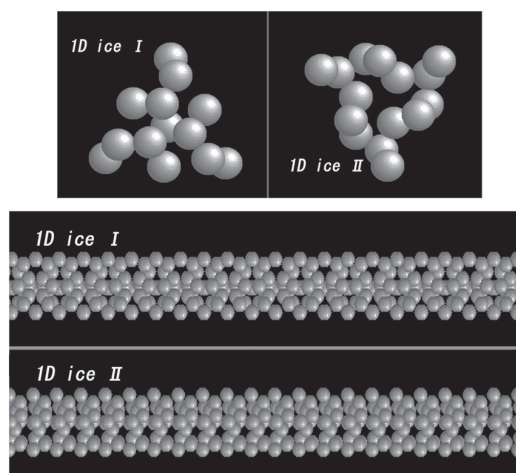
## MS61.P17

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

Akio Wakahara, Toshimasa Ishida, *Department of Physical Chemistry, Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki, Osaka, 569-1094, (Japan)*. E-mail: akio\_wakahara@k3.dion.ne.jp

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  $\text{H}_2\text{O}$ , 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  $\text{D}_2\text{O}$ , diameter=1.649nm) consists of a hollow-wire type nanowire that is constructed by piling up the cluster unit consisting of 15  $\text{D}_2\text{O}$  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