

The structure of complex cation  $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2]^{4+}$

[1] M.B. Ferrari, F. Bisceglie, G. Pelosi, P. Tarasconi, R. Albertini, P.P. Dall'Aglio, S. Pinelli, A. Bergamo, G. Sava, *J. Inorg. Biochem.* **2004**, *98* 301–312.

**Keywords:** pyridoxal, thiosemicarbazone, copper

### MS61.P12

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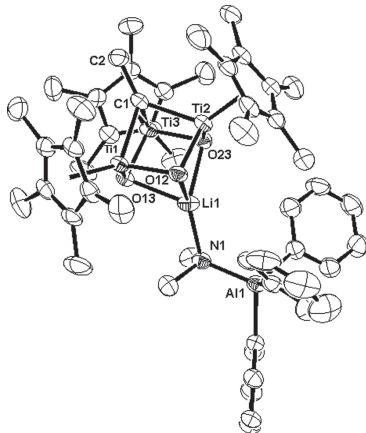
#### Incorporation of different lithium aluminates to titanium oxide organometallic ligands

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During the last years our research group has investigated the coordination of the organometallic oxides  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-O})\}_3(\mu_3\text{-CR})]$  [R = H(1), Me(2)] to different inorganic fragments of groups 1 and 13 elements. Reactions with group 1 derivatives lead to dehydrogenation processes of the alkylidyne moiety to give  $[\text{M}(\mu_3\text{-O})_3\{\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-C})\}]_2$  (M = Li, Na, K) complexes [1].

On the other hand, the novel adducts  $[\{\text{E}_3\text{M}\}(\mu_3\text{-O})(\mu\text{-O})_2\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-CR})\}]$  (R = H, Me; M = B, Al, Ga; E = alkyl, haloalkyl, halide) are obtained when group 13 derivatives react with 1 and 2 [2]. These species exhibit coordination of 1 or 2 through one of the three oxygen atoms of the  $\text{Ti}_3\text{O}_3$  ring to the metal center. Now, we are studying the chemical reactivity of this family of compounds with different alkyl, amide or alkoxyde lithium derivatives in order to isolate the theoretical possible intermediate species in the reactions between 1 and 2 with the group 1 derivatives. We will show how dimethylamide and 2,6-dimethylphenoxyde lithium derivatives coordinate to the organometallic oxides in a chelate tridentate fashion. Now, this bonding system is stabilized by the alkyl aluminum fragment, which avoids that the amide or alkoxyde fragments react with the alkylidyne moiety (see figure).

However, when the same reaction is carried out with *p*-tolyl lithium and the triphenylgallium adduct, abstraction and redistribution reactions are observed. The lithium atom is then encapsulated by two units of 1 and the new gallate species stabilizes a phenyllithium unit.



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**Keywords:** aluminate, gallium, titanium

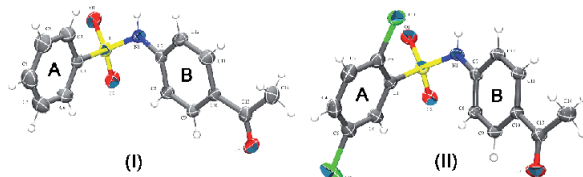
### MS61.P13

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#### Discrete role of chlorine substitutions in the conformation and supramolecular architecture of isostructural arylsulfonamides

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Compounds containing sulfonamide groups  $\text{SO}_2\text{NH}$  occur in many biologically active molecules, including antimicrobial, antithyroid, antitumor and antimalarial drugs [1,2,3,4]. In this study, two arylsulfonamide derivatives differing for two chlorine substitutions at one of their two phenyl rings were synthesised and characterized by X-ray diffraction technique in order to establish structural relationships and the chlorine role in the conformation and crystal assembly. The compounds (4-N(phenyl-sulphonyl-amide-acetophenone)) (I) and 4-N [(2, 5-dichlorophenyl)sulfonyl-amide] acetophenone (II) were obtained by the equimolar coupling between benzene sulfonyl chloride or 2,5-dichlorobenzene sulfonyl chloride and 4-amineacetophenone in dichloromethane or acetone as solvent at 343K for until six hours. The precipitate was re-crystallized in suitable solvents to obtain the single crystals. Crystallographic data for compounds (I) and (II) were collected using a Enraf Nonius diffractometer at room temperature. All crystal structures were solved by Direct Methods, and refined by full matrix least square method on  $F^2$ . The non hydrogen atoms were refined anisotropically. All C-H hydrogens were placed geometrically and refined using riding model. The hydrogen H1 bonded to nitrogen was found from the difference Fourier map and its positional parameters were refined freely. The tables, geometrical calculations, molecular packing and drawings were done with the WinGX [5,6]. program package, obtaining the following results: **(I)** Molecular Formula:  $\text{C}_{14}\text{H}_{13}\text{NO}_3\text{S}$ . Unit Cell Parameters:  $a = 13.0007(5) \text{ \AA}$ ,  $b = 8.3615(4) \text{ \AA}$ ,  $c = 12.5179(6) \text{ \AA}$ ,  $\beta = 98.118(3)^\circ$ , monoclinic, space group  $\text{P2}_1/c$ ,  $Z = 4$ ,  $V = 1347.13(1) \text{ \AA}^3$ . 5393 measured reflections with 3009 unique and 2214 observed. Final indices  $R_1 = 0.0483$  for 177 refined parameters. **(II)** Molecular formula:  $\text{C}_{14}\text{H}_{11}\text{NO}_3\text{SCl}_2$ . Structure:  $a = 13.3622(2) \text{ \AA}$ ,  $b = 8.1542(2) \text{ \AA}$ ,  $c = 15.6845(3) \text{ \AA}$ ,  $\beta = 120.180(1)^\circ$ , monoclinic, space group  $\text{P2}_1/c$ ,  $Z = 4$ ,  $1477.24(5) \text{ \AA}^3$ . 5653 measured reflections with 2972 unique and 2463 observed. Final indices  $R_1 = 0.049$  for 195 refined parameters. There are several classical and non-classical hydrogen bonds and  $\pi\text{-}\pi$  stacking interactions contributing to stabilize the crystal packing of the compounds.



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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

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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]

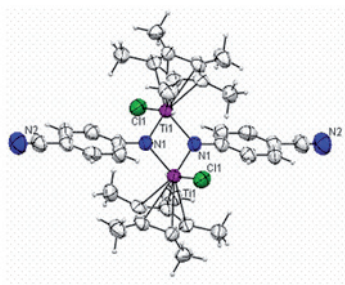


Figure 1

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

## MS61.P15

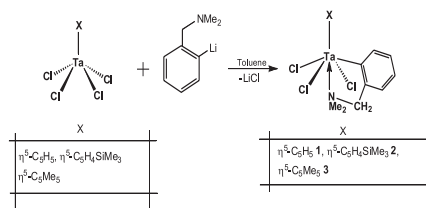
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### X-Ray Diffraction Studies of Monocyclopentadienyl Cyclometalated Aryl Tantalum(V) Compounds

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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.