

P.08.09.11*Acta Cryst.* (2005). A61, C335**Au(I)-arene Interactions**

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Gold(I) chloride complexes catalyze a wide range of reactions, in the presence of different silver(I) salts. In particular alkoxy cyclization and skeletal rearrangement of 1,6-enynes proceed at room temperature with [Au(PPh₃)Cl]/AgSbF₆.^[1] In addition, dienyne and 1,6-enynes with an aryl ring at the alkyne, give [4+2] products in a reaction catalyzed by gold(I) complexes with bulky phosphines.^[2]

In order to avoid the use of silver salts, we have synthesized new cationic complexes with bulky phosphines. The preparation of this new type of gold(I) compounds involves the reaction with AgSbF₆ in different coordinating solvents. When aromatic solvents are used, a new type of complexes are formed, which show an interaction between the arene and the electrophilic metal center. The structures of these new gold(I) complexes have been studied by X-ray diffraction.

[1] Nieto-Oberhuber C., Muñoz M. P., Buñuel E., Nevado C., Cárdenas D.J., Echavarren A.M., *Angew. Chem. Int. Ed.*, 2004, **43**, 2402-2406. [2] Nieto-Oberhuber C., López S., Echavarren A.M., *J. Am. Chem. Soc.*, 2005, **127**, ja04225t.

Keywords: gold catalysis, 1,6-enynes, π -interactions

P.08.09.12*Acta Cryst.* (2005). A61, C335**Comparative Study of Structural Aspects of Monocyclopentadienyl Niobium and Tantalum Complexes. Synthesis and Reactivity**

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Cyclopentadienyl complexes of early transition metals are well established as important types of olefin polymerization catalysts. Recently a spectacular development of a new generation "non-metallocene" catalysts have been designed and several systems capable of catalyzing the living polymerization of olefins was made. Alternatively, this kind of compounds also provided convenient routes to synthetic applications by unsaturated organic derivatives coupling reactions, via metallacyclic intermediates.

The broad success of early transition metal based organic synthesis is due in part to the unique ability of the metal to activate ligands to which it is directly bound through organometallic transformations than are often highly chemo-, regio- and stereoselective processes. In the group 5, niobium and tantalum alkynes complexes, via metallacyclic compounds, have provided good examples of that behaviour [1].

We report herein the synthesis and the structural study of monocyclopentadienyl alkyl and chloro azatantalacyclo-propane, -pentane and -pentene derivatives, their reactivity in the insertion of isocyanides and the intramolecular rearrangements processes observed in the resulting complexes. Comparative studies with the alkyl Niobium complexes will be presented.

[1] Galakhov M., Gómez M., Gómez-Sal P., Velasco P., *Organometallics*, 2005, **24**, 848.

Keywords: organometallic reactivity, group 5 metals, catalysis

P.08.09.13*Acta Cryst.* (2005). A61, C335**Synthesis of cis,cis-1,2,3,4-tetrakis(diphenylphosphino)butadiene Exploiting the "Template Effect"**

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In 1999 we reported the synthesis of cis,trans,cis-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane, which was obtained by an

intramolecular [2+2] photocycloaddition reaction.^[1] A similar template effect has been exploited in a Pd(II) complex, promoting an asymmetric [4+2] Diels-Alder reaction.^[2]

In order to synthesize cis,cis-1,2,3,4-tetrakis(diphenylphosphino)butadiene (dppbd), a bis-bidentate tetraphosphine ligand with a conjugated backbone, we designed a synthesis, which comprises three steps. The first step is the synthesis of the mixed bridged Pt(II) compound [Pt₂Cl₂(dppa)(t-dppen)] containing trans-1,2-bis(diphenylphosphino)ethene (t-dppen) and bis(diphenylphosphino)acetylene (dppa). In the second step a [2+2] photocycloaddition reaction takes place, where a phosphine substituted cyclobutene is formed, which is not stable under these reaction conditions. A conrotatory ring opening of the cyclobutene leads to the formation of [Pt₂Cl₂(dppbd)]. Finally in the third step the free ligand is obtained by a cyanolysis reaction.

[1] Oberhauser W., Bachmann C., Stampfl T., Haid R., Langes C., Kopacka H., Rieder A., Brueggeller P., *Inorg. Chim. Acta*, 1999, **290**, 167. [2] Leung P.-H., Siah S.-Y., White A.J.P., Williams D.J., *J. Chem. Soc., Dalton Trans.*, 1998, 893.

Keywords: photochemistry coordination compounds, phosphorous compounds, platinum compounds

P.08.10.1*Acta Cryst.* (2005). A61, C335**Yellow and Violet Polymorphs of (2Z)-2-(Nitromethylene)-2H-1,4-benzothiazine-3(4H)-one**

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The title compound, (2Z)-2-(nitromethylene)-2H-1,4-benzothiazine-3(4H)-one, C₉H₆N₂O₃S, was obtained in the reaction of bromonitroacrylate and o-aminothiophenol [1]. In the solid state, two crystalline polymorphic modifications of the title compound were found - monoclinic, (**I**), and triclinic, (**II**). Single-crystal structure determination of **I** and **II** revealed the closeness of molecular conformations in both polymorphs. Moreover, the molecules in **I** and **II** form centrosymmetric dimers via N-H...O hydrogen bonds. The dimers are further linked into the identical ribbons by the weak intermolecular C-H...O interactions. The distinctions in crystal structures and colours, yellow for **I** and violet for **II**, are provided by different packing of the ribbons in both polymorphs.

[1] Berestovitskaya V.M., Tafeenko V.A., Makarenko S.V., Sadikov K.D., Chernyshev I.V., *Russ. Zh. Obshchey Khimii*, 2005, submitted.

Keywords: polymorphs, polymorphic structures, organic molecular packing

P.08.10.2*Acta Cryst.* (2005). A61, C335-C336**Isostructurality of Analogues Triarylsilanol and -Methanol Inclusion Compounds**

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Developing strategies for host design require synthesis and structural comparison of enormous variety of crystalline inclusion compounds. The vast quantities of host molecules are organic while others containing inorganic elements, such as silicon, are relatively rare.

Single crystal X-ray structures of 22 inclusion compounds [1] of triphenylsilanol (**1**), triphenylmethanol (**2**), trinaphthylsilanol (**3**) and trinaphthylmethanol (**4**) hosts, respectively, with various guest molecules are compared. Half of them are newly prepared inclusion compounds. Cell similarity indices (π), isostructurality indices (I_s) and molecular isometricity indices for the host molecules (I_m) are