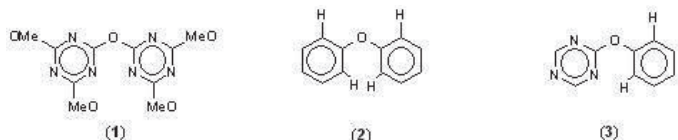


P08.09.71*Acta Cryst.* (2008). A64, C440**Asymmetric reactivity of a symmetric di-s-triazinyl ether**Marek L Glowka¹, Michal P Blaszczyk¹, Andrzej Olczak¹, Janina E Kaminska²¹Technical University of Lodz, Chemistry - 117, ul. Zeromskiego 116, Lodz, 90-924, Poland, ²Technical University of Lodz, Institute of General Food Chemistry, ul. Wolczanska 171/173, 90-924 Lodz, Poland, E-mail : marekglo@p.lodz.pl

While studying acylation of less reactive nucleophiles by 2-acyloxy-4,6-dimethoxy-1,3,5-triazine, a crystalline byproduct **1** was isolated and its X-ray structure determined. The study showed significant molecular asymmetry of **1**. Comparison of its geometry with those of diaromatic ethers (CSD) revealed several regularities, concerning conjugation: - maximal conjugation of both rings requires their coplanarity, which is hindered by spatial repulsions; - in mixed ethers **3** the triazine shows always better conjugation; - in asymmetric diphenyl ethers **2** substituents influence conjugation; - in symmetric ethers **2** packing influence conjugation through AGIBA effect. The observed asymmetry of **1** enable us to use it as a gentle alkylation (by a triazine residue) agent.



Keywords: symmetric ethers, s-triazine ethers, AGIBA effect in aromatic ethers

P08.09.72*Acta Cryst.* (2008). A64, C440**Mononuclear Rh(II) PNP-type complexes. Structure and reactivity**Yael M. Diskin-Posner, Moran Feller, Eyal Ben-Ari, Tarkeshwar Gupta, Linda J.W. Shimon, Gregory Leitun, Lev Weiner, David Milstein
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While Rh(I) and Rh(III) complexes are ubiquitous, and have found many uses, Rh(II) complexes are less common. In particular, mononuclear Rh(II) complexes are relatively rare. Herein, we report on the synthesis of (PNPtBu)Rh(II) complexes (PNPtBu = 2,6-bis-(di-tert-butyl phosphino methyl)pyridine), their characterization and reactivity. The Rh(II) mononuclear complexes [(PNPtBu)RhCl][BF₄] (**2**), [(PNPtBu)Rh(OC(O)CF₃)] [OC(O)CF₃] (**4**) and [(PNPtBu)Rh(acetone)][BF₄]₂ (**6**) were synthesized by oxidation of the corresponding Rh(I) analogs with silver salts. On the other hand, treatment of (PNPtBu)RhCl with AgOC(O)CF₃ led only to chloride abstraction, with no oxidation. Complexes **2** and **6** were characterized by X-ray diffraction, EPR, cyclic voltammetry and dipole moment measurements. Although the paramagnetic complexes are relatively stable, they exhibit interesting reactivity. The mono- and di-cationic Rh(II) complexes [(PNPtBu)RhCl][BF₄] (**2**) and [(PNPtBu)Rh(acetone)][BF₄]₂ (**6**) exhibit different reactivity patterns. While complex **6** is reduced to Rh(I) in the presence of isonitriles or CO, complex **2** disproportionates in the presence of

acetonitrile, isonitriles or CO. Complexes **2** and **6** are reduced in the presence of phosphines and water to Rh(I) complexes. In case of complex **2** and triphenylphosphine, the reduced Rh(I) complex undergoes protonation to give a Rh(III) complex with a coordinated BF₄ [(PNPtBu)Rh(Cl)(H)(BF₄)].

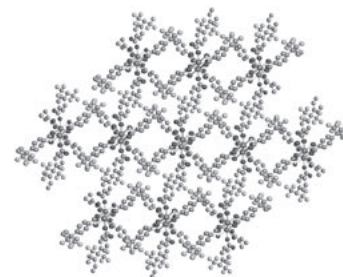
Keywords: rhodium compounds, catalysts, organometallic Complexes

P08.09.73*Acta Cryst.* (2008). A64, C440**Design of new MOFs based on alkaline earth metals with promising catalytic applications**Ana E. Platero-Prats¹, Victor A. De la Peña-O'Shea², Felipe Gándara¹, Natalia Snejko¹, Ángeles Monge¹, Enrique Gutiérrez-Puebla¹¹Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Sintesis y Estructura de Oxidos, Sor Juana Ines de la Cruz, 3, Cantoblanco, Madrid, Madrid, 28049, Spain, ²Instituto Madrileño de Estudios Avanzados en Energia (IMDEA ENERGIA), Tulipán s/n, Móstoles, Madrid, 28933, Spain, E-mail : aplatero@icmm.csic.es

The design of new porous 3D polymeric structures is becoming increasingly important, due to their applications as catalysts and molecular sieves. Our group has great experience in the design of 3D metal-organic frameworks (MOFs) involving the use of long flexible linker ligands (eg. 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H₂hfpbb)). Thus, new unexpected structures have been synthesised with Zn, In and rare-earth elements [1-3]. This work deals with the design of new MOFs based on alkaline earth metals and H₂hfpbb. The use of these elements has been less explored in this field, despite their interesting sorption (e. g. CO₂ fixation) and catalytic properties (e. g. Lewis acid catalysts). Thus, a new porous polymeric calcium structure with an unusual topology has been described. DFT calculates were performed in order to study the stability, as well as to understand the behaviour of the active site of these materials. Moreover, studies have been done to evaluate the catalytic and sorption properties of new MOFs based on Mg, Sr, Ba.

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Keywords: organic inorganic hybrid materials, microporous materials, catalysis

**P08.09.74***Acta Cryst.* (2008). A64, C440-441**Change in the molecular structure of muconic esters during photoisomerization in the solid state**

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