

PROGRAMMA MINI-SYMPOSIUM
International Research Training Group
 "Generation of Supramolecular Functional Cavities -
 Container Molecules, Macrocycles and Related Compounds"
 HRSMC-WWU Münster

26 November 2008

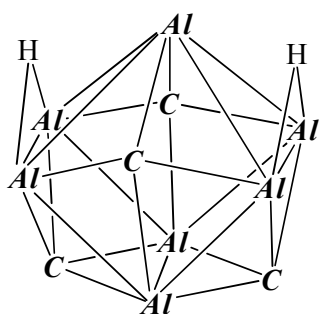
ROOM C2.03		
13.30	Prof. Uhl	NEW ASPECTS OF HYDROALUMINATION AND HYDROGALLATION REACTIONS – CARBAALANE CLUSTERS, CHELATING LEWIS-ACIDS AND CARBOCATIONS
14.15	Henrik Bock (Group Uhl)	REACTIONS OF DIGALLAN WITH FUNCTIONALISED CARBOXYLIC ACIDS
14.35	Johannes Dömer (Group Hahn)	NEW POLYDENTATE HETERODONOR LIGANDS AND THEIR USE IN SUPRAMOLECULAR CHEMISTRY
14.55	TEA	TEA
15.15	Sandra Fibikar (Group DeCola)	ZEOLITE L NANOCONTAINERS. A STRUCTURAL MODIFICATION AND DYE INSERTION.
15.35	Nina Wichner (Group Koller)	SINTER-RESISTENT METAL NANOPARTICLES CATALYSTS IN SOL-GEL CONTAINERS
15.55	Dr Jan Weigand	PHOSPHORUS LIKES IT POSITIVE: CATIONIC PHOSPHORUS CENTERS AS BUILDING BLOCKS FOR SMALL MOLECULE, RING, AND CLUSTER SYSTEMS
16.25	TEA	TEA
Room E.020 17.00 uur	Thesis Defense Oliver Kaufhold	'SYNTHESIS OF COMPLEXES WITH MACROCYCLIC LIGANDS INCORPORATING A MIXED DONOR SET OF N-HETEROCYCLIC CARBENES AND PHOSPHINES'
RTTR 18.00	RECEPTION RTTR	RECEPTION RTTR

NEW ASPECTS OF HYDROALUMINATION AND HYDROGALLATION REACTIONS – CARBAALANE CLUSTERS, CHELATING LEWIS-ACIDS AND CARBOCATIONS

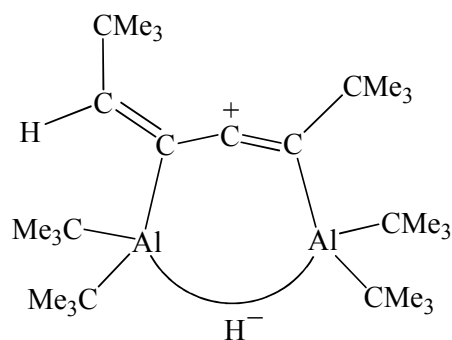
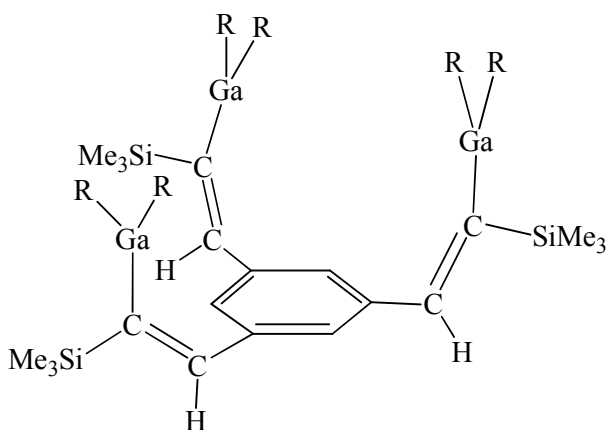
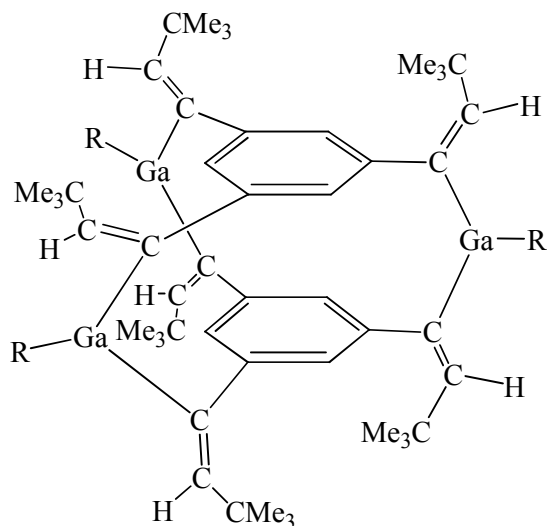
Werner Uhl

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The addition of Al-H bonds to the C≡C triple bonds of alkynes (hydroalumination) is a very effective method for the reduction of unsaturated hydrocarbons and is described in many textbooks of Organic or Inorganic Chemistry. However, in most cases the organoaluminum intermediates were not isolated and characterized, but destroyed by hydrolysis. Accordingly, the knowledge of the true constitution of these organoaluminum compounds is rather limited and many misleading statements are found in the literature. This lecture presents some recent results obtained in our group with respect to the courses of hydroalumination and hydrogallation reactions. Secondary processes are observed in many cases which by the elimination of the corresponding trialkylelement compounds gave carbaalane clusters or cyclophane-type molecules. *cis/trans*-Isomerisation is important for the application of oligonuclear addition products as chelating Lewis-acids. Persistent carbocations are formed which are stabilized by hyperconjugation and the effective coordination of the hydride counterion by two aluminum atoms.



(Al = AlMe; C = CCH₂CH₃)



REACTIONS OF DIGALLAN WITH FUNCTIONALISED CARBOXYLIC ACIDS

Werner Uhl , Matthias Voß and Henrik Bock

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Treatment of the digallan derivate $R_2Ga-GaR_2$ [$R = CH(SiMe_3)_2$] with dicarboxylic acid yield macrocyclic compounds by retention of the Ga-Ga single bonds and release of 2 equiv. of bis(trimethylsilyl)methan per formula unit of $R_2Ga-GaR_2$.¹ Those macrocycles can vary in size and form depending on the dicarboxylic acid and the reaction pattern.² In the course of our investigation the question arose, whether or not we can use carboxylic acid carrying functional groups. Those products could lead to a new and exciting chemistry concerning organoelement compounds based on Ga-Ga single bonds.

Reaction of the tetraalkyldigallium compound with functionalized monocarboxylic acids resulted in compounds that can be seen as building-blocks for organometallic macrocycles.

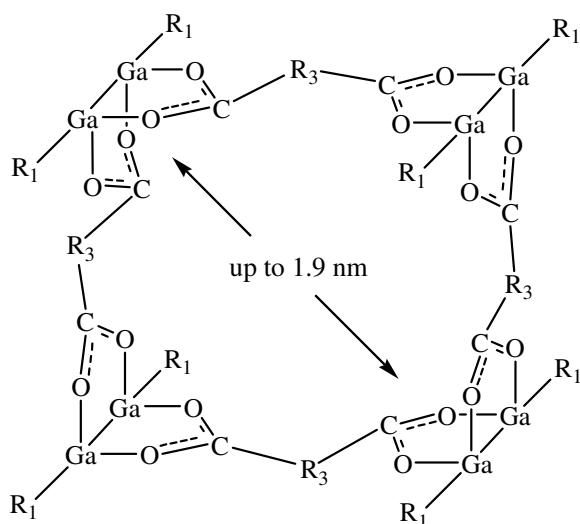


fig. 1

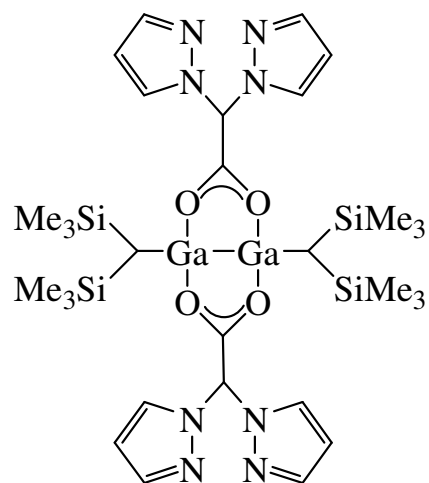


fig. 2

[1] W. Uhl, L. Cuyper, M. Prött, K. Harms, *Polyhedron*, **2002**, 21, 511-518

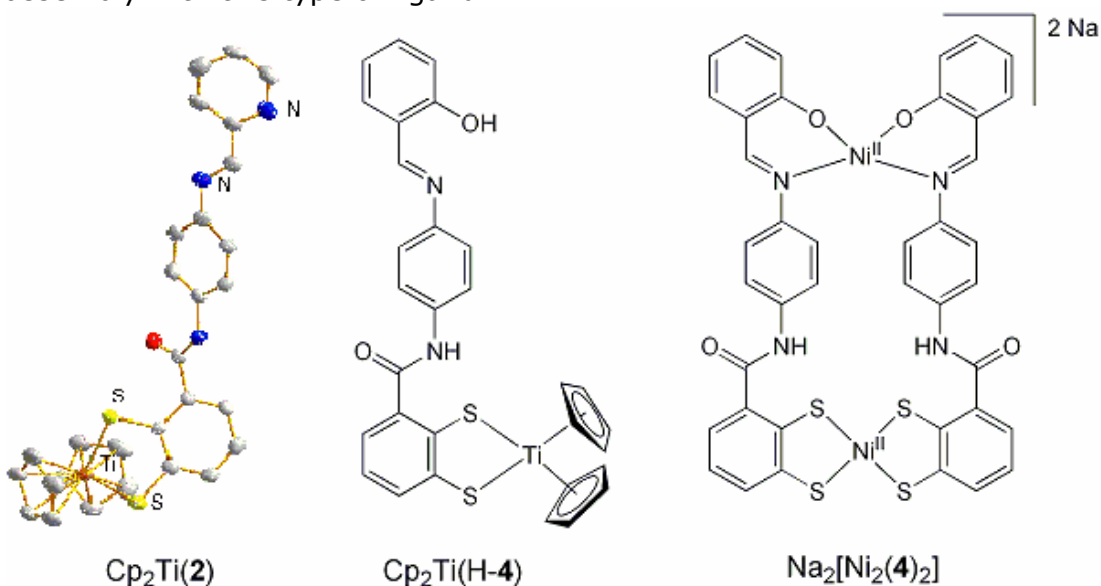
[2] W. Uhl, E. Er, *Organometallics*, **2006**, 25, 5832-5834

NEW POLYDENTATE HETERODONOR LIGANDS AND THEIR USE IN SUPRAMOLECULAR CHEMISTRY

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Metallosupramolecular chemistry allows for the generation of unique and large molecular structures using non-covalent, metal-ligand interactions. Many publications involving the formation of impressive metallosupramolecular compounds, such as helicates^[1] or cages^[2], have appeared during the last few years. Although the use of directional heterodonor ligands should allow for the formation of even more sophisticated supramolecular structures, only a few complexes with heterodonor ligands were reported.^[3] The main problem in the syntheses of suitable ligands is the incorporation of different metal binding sites that are specific for different metal ions. We show the synthesis of new directional heterodonor ligands containing benzene-*o*-dithiolato (S-S) and ether pyridylimine (N-N) or salicylimine (N-O) donor groups. Reaction of these ligands with titanocenedichloride proves the selective metalation of the sulfur donor site (Cp₂Ti(**2**) and Cp₂Ti(H-**4**)). Furthermore we report the synthesis of the dinuclear double-stranded complex Na₂[Ni₂(**4**)₂] as first supramolecular assembly with this type of ligand.



[1] Albrecht, *Chem. Rev.* **2001**, *101*, 3457-3497. [2] Raymond et al., *J. Am. Chem. Soc.* **2001**, *123*, 8923-8938. [3] Hahn et al., *Chem. Commun.* **2007**, 1111-1120.

ZEOLITE L NANOCONTAINERS. A STRUCTURAL MODIFICATION AND DYE INSERTION.

Sandra Fibikar, Luisa De Cola

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Zeolite L is an aluminosilicate [$K^+_9(Al_9Si_{27}O_{72}) \cdot xH_2O$] with a framework that provides a unique unidimensional channel system with an opening of 7.1 Å. This structure and the presence of cations and solvent molecules inside the channels offer the possibility to create a host-guest system. Molecules with an appropriate size can be inserted into the cavities of the crystals by ion exchange from solution, or by molecule insertion from the gas phase (see Figure 1). Along with its transparency in the visible spectral range, the crystal permits the study of the photophysical properties of ordered organic dye molecules.[1+2]

The aim of my work is the replacement of the Al^{3+} sites by Fe^{3+} in the framework while porosity and crystallinity are maintained. Fe^{3+} is best suitable despite being difficult to introduce into a basic gel because it is a nontoxic and paramagnetic cation, with a similar size than the Al^{3+} cation. Because of the paramagnetic modification of the zeolite L framework, and insertion of organic fluorescent dyes, this system can be applied for biomedicine, imaging and targeted delivering.

In this talk I will introduce my work on the structural modification of zeolite L crystals towards magnetic properties.

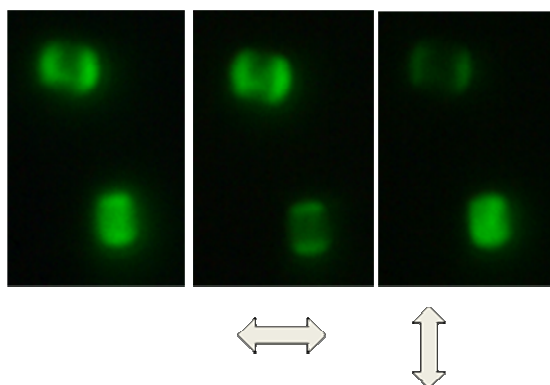


Figure 1: Effect of the polarization of emission of pyronine dye in the zeolite L crystals. Fluorescence Microscope Image (100fold magnification).

[1] G. Calzaferri, S. Huber, H. Maas, C. Minkowski, *Angew. Chem.Int. Ed.* **2003**, 42, 3732.

[2] M. Busby, Christian Blum, Marc Tibben, Sandra Fibikar, Gion Calzaferri, Vinod Subramaniam, Luisa De Cola, *J. Am. Soc.* **2008**, 130, 10970.

SINTER-RESISTENT METAL NANOPARTICLES CATALYSTS IN SOL-GEL CONTAINERS

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The target of this project is generating dispersed, catalytically active metal nanoclusters in sol-gel silica cages with well-defined container sizes. For catalytic activity of these metal nanoclusters their particle size is very important. To this end, gold or silver nanoclusters surrounded by a stabilizing shell are incorporated in a sol-gel process of alkoxysilanes. The stabilizing shells have aromatic groups at the surface. The particle size of the gold nanoclusters are around 2-3 nm.¹ These nanoclusters are combined with the silica precursor phenyltriethoxysilane (PhTS) allowing the formation of π - π interactions with the cluster surface. PhTS is cross-linked with a silica backbone in a sol-gel process by co-condensation with tetramethoxysilane (TMOS). In literature the incorporation of metal nanoclusters in silica gels is already known² but the encapsulation of metal clusters with aromatic stabilizing shell by phenyl-phenyl interactions in a sol-gel process is new. After calcination, the bare metal nanoclusters remain dispersed in the silica gel. The accessibility of the containers with the metal clusters, e.g. for catalytic applications, critically depends on the matrix porosity. The goal is to generate channels interconnecting the containers which are too small for the metal nanoclusters to agglomerate, but sufficiently large for diffusion of molecules. The porosity of the silica matrix depends on the synthesis pH in the sol-gel process. The porosity is investigated by N₂ adsorption measurements. The size of the metal clusters is determined by TEM and XRD. TEM images of mesoporous silica show that metal nanoparticles grow during the calcination at 600 °C which is also well-known in literature.² It is remarkable that gold particles of 3-4 nm are still in the microporous silica after 600 °C, so they survive the sol-gel process and calcination.

References

1. S.Chen and R.W. Murray, *Langmuir*, 1999, **15**, 682.
2. M.G. Garnica-Romo, J.M. Yanez-Limon, M. Villicana, J.F. Perez-Robles, R. Zamorano-Ulloa and J. Gonzalez-Hernandez, *J. of Physics and Chemistry of Solids*, 2004, **65**, 1045.

PHOSPHORUS LIKES IT POSITIVE: CATIONIC PHOSPHORUS CENTERS AS BUILDING BLOCKS FOR SMALL MOLECULE, RING, AND CLUSTER SYSTEMS

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The emerging importance of the pnictogen elements of the main group (E = N, P, As, Sb, Bi) in homogeneous catalysis, effective new inorganic polymeric materials, energy storage, functional molecules (i.e. sensors, molecular magnets, OLEDs, ionic liquids), single-source precursors for new materials, and pharmaceuticals requires an understanding of the fundamental chemistry of these elements which has not yet been developed. We are investigating efficient and effective synthetic routes to new, fundamentally important poly-onio substituted elements of group 15, predominantly phosphorus, in which the central atom exhibits an unusual local structure, is engaged in a new connectivity, or provides materials with new, spectroscopic, physical, or, reactive properties. Poly-onio substituted phosphorus centers, coordinated to an appropriate ligand, are used as building blocks for small molecule, ring, and cluster systems, boding well for the development of rich and highly diverse chemistry.