



DAYS

Synthetic Chemistry

Venerdì 30 Maggio 2014, ore 14, aula D1

14:00-14:15 La sintesi dal lato della simulazione
Roberto Dovesi (10 min di discussione)

14:25-14:40 Gold Catalysis in Organic Synthesis: New Opportunities for C-C Bond Formation.
Cristina Prandi

14:40-14:55 Utilizzo di acidi protici forti quali catalizzatori in sintesi organica
Stefano Dughera

14:55-15:10 Reactivity of alpha-beta-unsaturated compounds in the presence of organometallic derivatives.
Annamaria Deagostino

15:10-15:30 *Discussione*

15:30-15:40 Commissione Spokes

15:40-16:10 Coffee Break (networking)

16:10-16:25 Synthesis of organometallic compounds for catalysis
Carlo Nervi (10 min discussione)

16:35-16:50 Catalytic conversion of ethylene and propylene: from polyolefins to linear- α -olefins through a rational design of the catalyst
Elena Groppo (10 min discussione)

17:00-17:15 Bridging the gap between homogeneous and heterogeneous catalysis: a contribution to the sustainability of fine chemistry processes
Gianmario Martra (10 min discussione)

17:25-17:40.
Metodi Di Diffrazione Dei Raggi X Non Convenzionali Per L'analisi Di Mof E Di Composti Organometallici.
Domenica Marabello (10 min discussione)

17.50 chiusura

La "sintesi" dal lato della simulazione

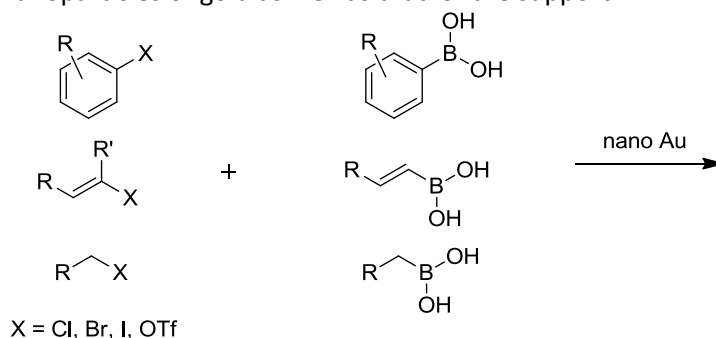
Roberto Dovesi

In molte circostanze l'approccio teorico e quello sperimentale partono da punti di vista diversi, usano variabili diverse, devono sottostare a vincoli (diciamo in generale di fattibilità) diversi. Questo si verifica, ovviamente, anche nel caso della "sintesi", cioè nel caso in cui ci si propone di preparare un determinato composto e di verificarne le proprietà. Potrebbe essere utile mettere in evidenza con qualche semplice esempio come questa diversa prospettiva (che spesso rende difficile, o addirittura pericoloso, confrontare misura e calcolo) possa rendere la simulazione e la sintesi (o più in generale l'esperimento) estremamente sinergici.

Gold Catalysis in Organic Synthesis: New Opportunities for C-C Bond Formation

Cristina Prandi, Annamaria Deagostino, Paolo Venturello

Gold in organic chemistry has been considered for a long time as a catalytically inactive element or in some cases active but inferior to other late transition metals. More recently, starting from 1970 onwards the ability of gold to catalyze different type of reactions with unique selectivity has been revealed both in heterogeneous catalysis,^[1] and in the following years in homogeneous catalysis too.^[2] The ongoing research is focused on the ability of gold to catalyze cyclization or cross-coupling reactions under either heterogeneous or homogeneous conditions.^[3] The aim of our ongoing researches are to expand the scope of the cross-couplings to aliphatic substrates and chloro compounds which are usually quite unreactive in transition metal catalyzed reactions. A further appealing feature of gold catalysis is the possibility to operate in water as solvent and without the need of excluding oxygen from the reaction vessel, thus permitting an easier working system. As part of this project, and thanks to collaborations within the Department of Chemistry, the surface of the solid catalyst will be extensively studied before and after the reaction in order to point out the effective role of the nanoparticles of gold as well as that of the support.



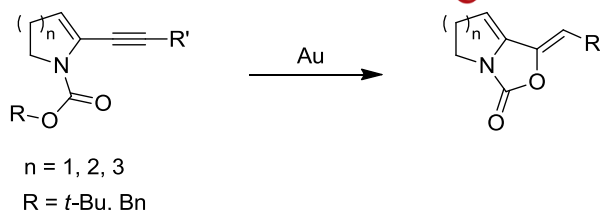
Considering homogeneous catalysis, gold reactivity is tested for different type of reactions. One of this involves the intramolecular cyclization of oxygen nucleophiles on alkynes.^[4] Once confirmed the expected reactivity of gold on this kind of substrates, the successive step will be the *in situ* functionalization of the vinyl gold intermediate *specie*. The gold intermediate can be in fact trapped with boron or silicon or other similar organometallic compounds by means of a transmetalation process, followed by a reductive elimination to give the resulting coupled products. The idea is to exploit the cycle Au^I/Au^{III} with the help of strong oxidants to realize feasible oxidative couplings.

¹ A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.*, **2006**, 45, 7896-7936

² A. S. K. Hashmi, *Chem. Rev.*, **2007**, 107, 3180-3211

³ M. N. Hopkinson, A. D. Gee, V. Gouverneur, *Chem. Eur. J.*, **2011**, 17, 8248-8262

⁴ A. Corma, A. Leyva-Pérez, M. J. Sabater, *Chem Rev.*, **2011**, 111, 1657-1712



Utilizzo di acidi protici forti quali catalizzatori in sintesi organica

Margherita Barbero, Silvano Cadamuro e Stefano Dughera

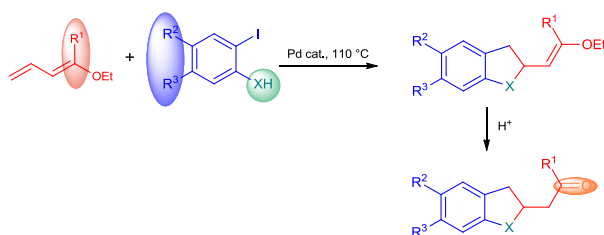
L'organocatalisi con acidi di Brønsted è diventato negli anni uno dei settori più dinamici in sintesi organica. In questo ambito, si collocano le nostre ricerche che vertono sull'utilizzo dell'*o*-benzendisolfonimmide (OBS), quale catalizzatore acido di Brønsted non volatile, non corrosivo, facilmente maneggiabile e conservabile a lungo. Le applicazioni finora studiate sono numerose e competitive con i diversi altri metodi riportati in letteratura. Modifiche strutturali dell'OBS ci hanno consentito di ottenere alcuni suoi derivati chirali che sono stati impiegati con risultati incoraggianti come catalizzatori in sintesi asimmetrica. Anche l'anione dell'OBS è notevolmente interessante: estremamente stabile ma per nulla basico o nucleofilo, è stato recentemente utilizzato nella preparazione di cationi diarilmetilici, per la prima volta isolati e caratterizzati allo stato solido. Attualmente allo studio è la reattività di questa classe di composti carbocationici, intermedi alchilanti altamente reattivi, di solito formati in situ e direttamente fatti reagire con nucleofili vari.

Reactivity of alpha-beta-unsaturated compounds in the presence of organometallic derivatives.

A. Deagostino, C. Prandi, P. Venturello

Unsaturated compounds are very interesting substrates due to their high reactivity and versatility which permit several new compounds to be obtained.

In last years our group paid attention to the reactivity of alkoxy dienes in the presence of Pd(0) species. 1,2-Dienes and 1,3-dienes are interesting substrates because of their high reactivity, moreover the presence of the alkoxydic moiety, an acid sensitive functionality allow the synthesis of biologically interesting structures such as dihydrobenzofuranes, indolidines and indolines in a domino fashion.



Another topic concerns the reactivity of unsaturated derivatives in the presence of mixture of Butyllithium and Potassium *tert*-butoxide, the so-called Schlosser bases, using nitrones as weak electrophiles. Imines are obtained in good yields thank to a domino process which involves an elimination process followed by the nitrones attack and an E1cb reaction.

Synthesis of Organometallic Compounds for Catalysis

Roberto Gobetto, Carlo Nervi

In several catalytic processes the organometallic complexes play crucial roles. Some strategies for the synthesis of transition metal organometallic complexes are outlined. Furthermore, we developed an electrochemical technique to chemically bond our intact organometallic compounds to carbon surface, and show that in some cases their electrocatalytic activity is retained, thus bringing more near the world of heterogeneous and homogeneous catalysis.



Catalytic conversion of ethylene and propylene: from polyolefins to linear- α -olefins through a rational design of the catalyst

Elena Groppo

Ethylene and propylene are the building blocks of a large variety of synthetic chemicals, ranging from polyolefins to linear- α -olefins (LAOs). Polyolefins are ubiquitous in nowadays life: being cheap, non toxic, easy to recycle, and with many diversified industrial applications, they meet the demands of sustainable development. On the other hand, C_4 - C_{20} linear α -olefins are increasingly requested as co-monomers with ethylene to afford LLDPE (C_4 - C_8), for the synthesis of lubricants (C_{10}), and for the production of plasticizers (C_6 - C_{10}) and surfactants (C_{12} - C_{20}).

Olefin conversion to polyolefins/LAOs is achieved through polymerization/oligomerization catalysts. The catalyst has a primary influence on the properties of the produced polyolefins (in terms of molecular weight, branching and stereoregular architecture) and on the length distribution of LAOs. Even small changes in the catalyst formulation may cause important changes in catalyst activity and/or selectivity. For this reason, catalytic olefin polymerization and (selective) oligomerization reactions are topics of considerable interest in industry.

Opposite to the case of homogeneous catalysts (which can be modified through a molecular design that acts directly on the ancillary ligands), the industrial heterogeneous catalysts for olefin polymerization/oligomerization are still evolving mainly through a trial-and-error procedure. In order to get over the current trial-and-error approach, and to rationally design the right catalyst for the desired product, a detailed understanding of the structure of the active catalytic sites at a molecular level must be achieved. This should be possible in an academic laboratory equipped with advanced and highly sensitive characterization techniques. Some trials in this direction are currently attempting in the Department, in strict connection with industrial realities.

Bridging the gap between homogeneous and heterogeneous catalysis: a contribution to the sustainability of fine chemistry processes

Giuseppina Cerrato, Maela Manzoli, Gianmario Martra

This contribution is aimed at presenting how in-situ spectroscopic studies can provide results of interest for a virtuous interplay with Chemists interested in fine chemistry, targeting the disclosure of optimized synthetic strategies, with the design of sustainable chemical processes as final objective.

The achievements in studying surface species involved in the following heterogeneously catalyzed reactions will be presented:

- furfural esterification to methylfuroate
- furfural hydroxymethylation
- Sonogashira coupling and/or Suzuki reactions
- activation of H_2O_2 in the oxidation of alkenes to 1,2-diols
- direct synthesis of amides (peptides) from amines and unactivated carboxylic acids (unactivated aminoacids)

Metodi Di Diffrazione Dei Raggi X Non Convenzionali Per L'analisi Di Mof E Di Composti Organometallici

Domenica Marabello

Il diffrattometro Gemini R-Ultra, che si trova nel Dipartimento di Chimica, è stato concepito come una macchina versatile che permette di effettuare diverse tipologie di misure nell'ambito della diffrazione dei raggi X. In particolare la presenza della doppia sorgente permette di ottimizzare gli esperimenti al momento del montaggio del campione e questo risulta particolarmente utile nel campo dei composti organometallici ad uso farmacologico. Infine la sorgente al rame molto intensa permette di effettuare esperimenti di diffrazione di polveri non eseguibili con i diffrattometri tradizionali, che risultano molto utili nello studio del meccanismo di formazione dei MOF.