

## Gold highlights at the 10th International Conference on Heteroatom Chemistry (ICHAC-10), in Uji, Kyoto, Japan, 20–25 May 2012

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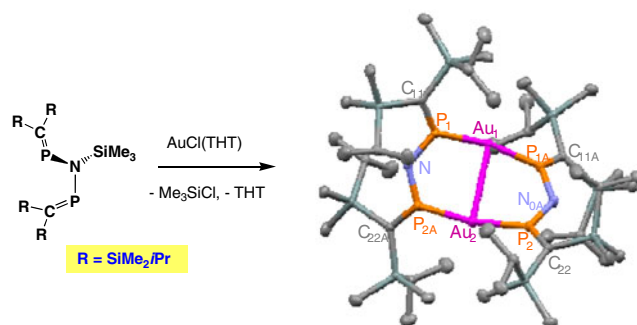
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There were over 370 participants attending this meeting, coming from diverse fields of heteroatom chemistry. Most presentations were from Japan; however, around 90 participants were from other countries (including China, Korea, Taiwan, India, Iraq, Kuwait, Saudi Arabia, Bulgaria, Poland, Italy, Germany, Netherlands, Sweden, France, UK, Spain, Portugal, USA and Canada), being the majority from universities and research institutes. Gold-related subjects had an importance presence, showing that research on gold keeps increasing all over the world. The synthesis of different gold complexes, the use of gold compounds as catalysts for heterocycle formation and gold nanoparticles or gold electrodes for several applications were referred. A brief description is indicated below.

The plenary lecture (PL3) of Wolf du Mont (Technical University of Braunschweig, Germany) dealt with “Nitrogen and oxygen-bridged bifunctional phosphalkene ligands”. N–Si bond cleavage of the *N*-silylimino-bridged bis-phosphalkene [(*i*PrMe<sub>2</sub>Si)<sub>2</sub>C=P]<sub>2</sub>NSiMe<sub>3</sub> with chlorides of Ag<sup>I</sup>, Au<sup>I</sup> and Rh<sup>I</sup> leads to complexes of the 5c-6π-heteropentadiene imidobisphosphanaalkene anion [1]. Figure 1 shows an imidobisphosphalkene gold complex.

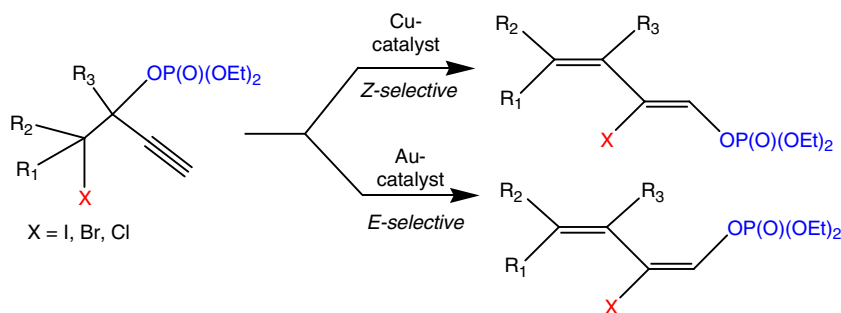
In his plenary lecture (PL5), dealing with “Transition metal-catalysed synthesis of heterocycles proceeding with migration of heteroatom groups”, Vladimir Gevorgyan (University of Illinois at Chicago, USA) spoke about novel efficient transition metal-catalysed methodologies for synthesis of multi-substituted carbo- and heterocycles by incorporation of migrating step(s) in the cyclisation cascade. It was found that in the presence of Cu, Ag and Au catalysts, a number of groups, such as X (X=I, Br, Cl), RS<sup>-</sup>, SiR<sub>3</sub>, etc., could undergo 1,2- or 1,3-migration. An example referred in a recent publication of the speaker shows an interesting example [2], as a double migratory cascade reaction of α-halogen-substituted propargylic phosphates to produce highly functionalized 1,3-dienes has been developed. This transformation features 1,3-phosphatylxy group migration followed by 1,3-shifts of bromine and chlorine as well as the



**Fig. 1** Reaction with the Au<sup>I</sup> chloro complexes leading to gold complex of the imidobis(phosphalkene) anion by N–Si cleavage—adapted from [1] and the Powerpoint slides

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**Fig. 2** E and Z-selectivity of Au and Cu catalysts, respectively, in the production of highly functionalized 1,3-dienes (adapted from [2])



unprecedented 1,3-migration of iodine. The reaction is stereodivergent: (Z)-1,3-dienes are formed in the presence of a Cu catalyst, whereas Au-catalysed reactions exhibit inverted stereoselectivity, producing the corresponding E products (Fig. 2). The Au catalysts that showed the best yields (65 and 96 %, respectively) were  $\text{Ph}_3\text{PAuCl}$  and (*p*- $\text{F}_3\text{CC}_6\text{H}_4$ ) $\text{PAuCl}$ .

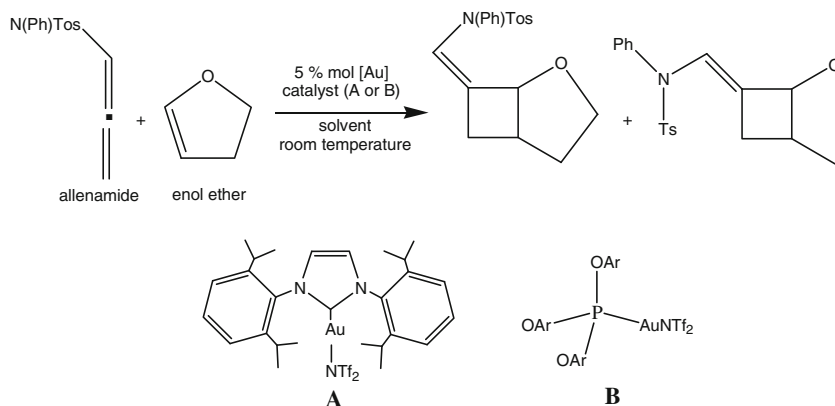
The invited lecture (IL-B3) of José Manuel González (Universidad de Oviedo, Spain) dealt with “Electrophilic activation of unsaturated systems: Applications to selective organic synthesis”. The speaker presented the recent contributions of his group to the field of electrophilic activation of unsaturated compounds using gold-catalysed transformations. One example is shown in a recent publication [3] that features the addition of catalytic amounts of a phosphite-based Au(I) catalyst efficiently triggers the intermolecular [2+2] cycloaddition of allenes and alkenes substituted by electron donor groups (Fig. 3). The reaction is fast and furnishes cyclobutane derivatives in a stereoselective manner using low catalyst loadings.

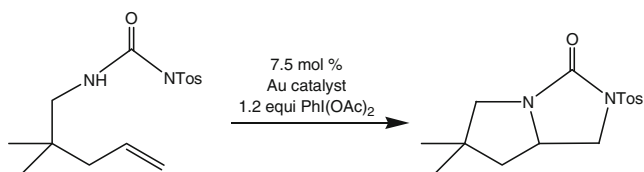
The invited lecture (IL-B4) of Kilian Muñoz (Institute of Chemical Research of Catalonia, Spain) dealt with “Oxidative

diamination of alkenes: metal catalysis and beyond”. The pioneer work carried out in recent years by his group on catalytic intramolecular deamination reactions using transition metals such as Au and Pd was presented. Diamination of alkenes by homogeneous gold catalysts was achieved [4]. Figure 4 shows an example. Under optimised conditions, the Au(I) acetate complex  $\text{AuOAcPPh}_3$  gives complete conversion and high isolated yield of product under mild reaction conditions, while a related complex with a N-heterocyclic carbene (NHC) ligand was less efficient. Less than 5 % conversion was achieved in the absence of the gold catalyst.

The oral presentation (A-08) of Mie Højer Vilhelmsen (Universität Heidelberg, Germany) dealt with “Heterocycles in gold chemistry—catalytic use, stoichiometric gain”. This talk presented the work being carried out in the group of Stephen Hashmi, one of the pioneers of homogeneous catalysis by gold. The group has been working with carbene ligands (examples are shown in Fig. 5) that proved to be versatile in several reactions, including the Au(I) catalysed syntheses of heterocycles [5].

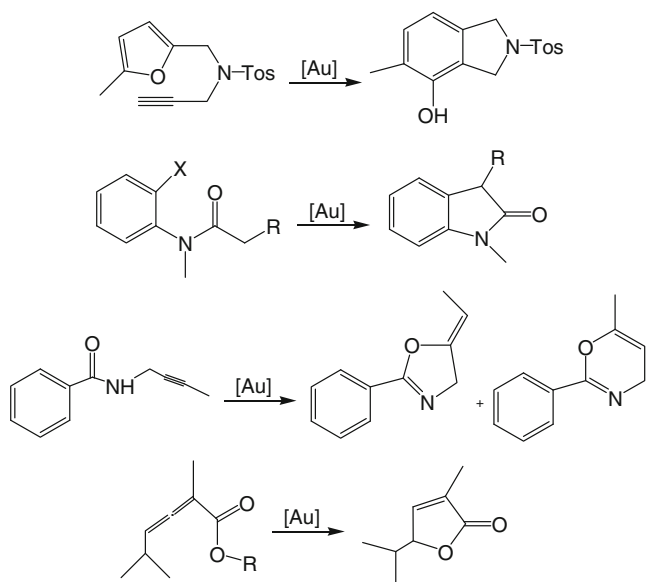
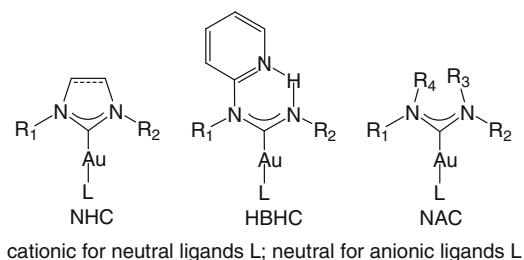
**Fig. 3** Intermolecular [2+2] cycloaddition of allenamide and enol ether catalysed by gold complexes A or B (adapted from [3]).  
Tos =  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ ;  $\text{NTf}_2$  = bis[(trifluoromethane)sulfonyl]amide; Ar = 2,4-(*t*-Bu) $_2$ - $\text{C}_6\text{H}_3$





**Fig. 4** Diamination reaction using a gold catalyst (adapted from [4])

Andreas Orthaber (Uppsala University, Sweden) presented an oral (B12) and a poster (PA-07) dealing with synthesis, structure and coordination of acetylenic phosphalkenes. Their reaction with AuCl showed selective formation of 1:1 Au(I) complexes. Reaction of these species under reactive conditions, in the presence of H<sub>2</sub>AuCl<sub>4</sub> or AuCl,



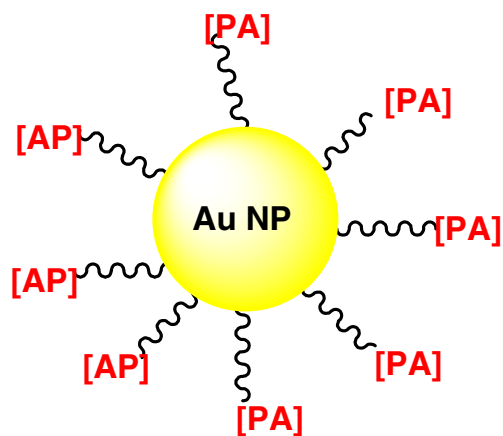
**Fig. 5** Above: Nitrogen heterocyclic carbenes (NHC), hydrogen bond-supported heterocyclic carbenes (HBHC) and nitrogen acyclic carbene (NAC) ligands (adapted from [5]). Below: Examples of four reactions of heterocycle formation catalysed by Au(I) complexes (adapted from the abstract)

yielded phosphalkene (PA) coated Au nanoparticles (NPs), schematically shown in Fig. 6. These results will soon be published.

Hayato Tsuji (University of Tokyo, Japan) spoke about “Fused furans as high performances semiconductor materials” (B15). In this work, fused furans were designed and found useful and stable as semiconducting materials. Namely, naphthodifuran derivatives served as active semiconducting materials for an organic field-effect transistor. A gold electrode was used for this purpose (Fig. 7).

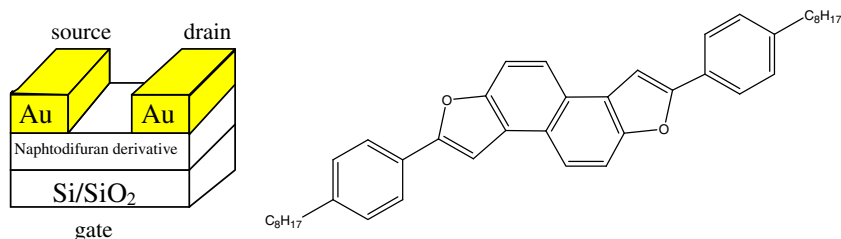
Kozo Toyota (Tohoku University, Japan) spoke about “Syntheses of 4,7-benzo[*b*]thiophenediyl derivatives and application to artificial molecular architecture” (C05). 4,7-Dibromo-benzo[*b*]thiophene was synthesised through cyclisation of 1,4-dibromo-2-tert-butylsulfanyl-3-ethynyl-benzene, catalysed by AuCl (Fig. 8). Several reactions of 4,7-dibromo-benzo[*b*]thiophene were investigated, including metallation and cross-coupling reactions [6].

Hisashi Fujihara (Kinki University, Japan) had a poster (PA33) dealing with “Functional metal nanoparticles and their polythiophene nanotube composites”. New heterosegment-junctioned hybrid nanotubes of polythiophene and heterometallic nanoparticles (Pd, Au NPs) have been synthesised. This was achieved by sequential electropolymerization of terthiophene-linked binaphthyl-bisphosphine (Fig. 9, left) modified Au and Pd NPs (Fig. 9, centre), in a nanoporous alumina template (Fig. 9, right).

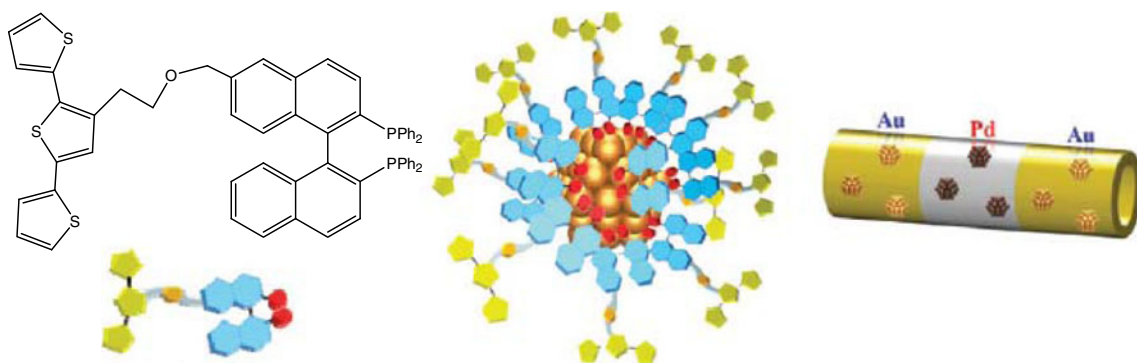
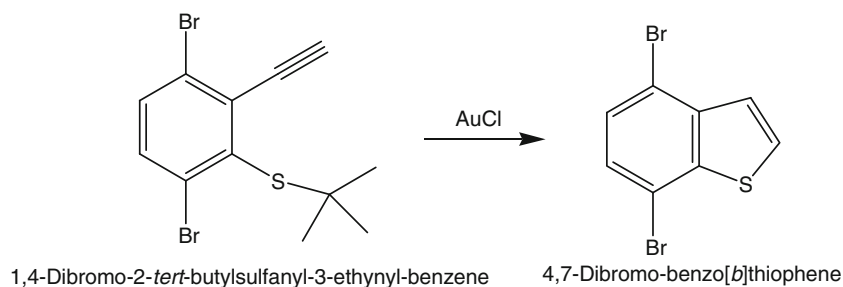


**Fig. 6** Phosphalkene (PA)-coated Au nanoparticles (NPs)—adapted from the abstract

**Fig. 7** Semiconducting material using the naphthodifuran derivative on the right, for an organic field-effect transistor, using a gold electrode (adapted from [7] and the abstract)



**Fig. 8** Synthesis catalysed by AuCl (adapted from the abstract)



**Fig. 9** Terthiophene-linked binaphthylbisphosphine ligand (*left*) and metal NPs (*centre*) and ligand Au–PT NT-deposited nanopores of the alumina membrane formed after electropolymerisation of ligand–Au NPs (adapted from [8])

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