## FROM THE LITERATURE by Fausto Calderazzo - Università di Pisa

♦ A review-article from the Philipps-Universität Marburg has pointed out that gold has a future in biology, according to R.A. Sperling et al. (Chem. Soc. Rev., 2008, 37, 1896). The authors describe the extensive use (labelling, delivering, heating and sensing) of gold nanoparticles. Within the area of gold chemistry, D. Zuccaccia et al. (J. Am. Chem. Soc., 2009, 131, 3170) of the Università di Perugia have reported results related to the cation/anion orientation in the two compounds  $[Au(PPh_{2})(4-methylstyrene)]BF_{4}$  and  $[Au(NHC)(4-methylstyrene)]BF_{4}$ , NHC denoting a N-heterocyclic carbene. The compounds were investigated by <sup>1</sup>H- and <sup>2</sup>H multinuclear NMR spectra. It has been shown that, contrary to expectations, the counterion is located in the periphery of the cation. ♦ Gold nanorods (GNR) have been used for surface functionalization and entrapment into polyethyleneglycol, a potential method for drug delivery in vivo, as for a paper contributed by the Università di Bologna, in collaboration with the Università di Modena e Reggio Emilia (D. Gentili et al., Chem. Commun., 2009, 5874). ♦ In the preceding literature survey of this series, mention was made of gold nanoparticles coated with a carbonic anhydrase inhibitor with anticancerogenic properties (M. Stiti et al., J. Am. Chem. Soc., 2008, 130, 16130) as a contribution from the Università di Firenze, in collaboration with the Université de Guelma, Algeria, and the Université de Montpellier II. In a closely related area, it has now been reported (J. Nam et al., J. Am. Chem. Soc., 2009, 131, 13639) that gold nanoparticles were found to aggregate as a function of pH, the proposal being made that this system may be used in photochemical cancer therapy, as for a paper from the Pohang University of Science and Technology, South Korea.

◆ A review-article (P. Bodis et al., Acc. Chem. Res., 2009, 42, 1462) describes the use of two-dimensional vibrational spectroscopy in rotaxane-based molecular compounds: this paper is a contribution from the Università di Trieste in collaboration with the Universities of Amsterdam and Edinburgh, the spectroscopic methodology there described being capable of detecting structural changes with subpicosecond time resolution. A review-article (C. Bianchini et al., Chem. Rev., 2009, 109, 4183) reports on electrocatalysis in the presence of nanoparticles of palladium or palladium alloy for alcohol oxidation in half cells and in direct alcohol cells: this is a contribution from the ICCOM-CNR Institute located in Sesto Fiorentino, near Firenze, with the collaboration of the Sun-Yat-Sen University in the P.R. of China. ♦ A Feature Article appeared in Chem. Commun., 2009, 2809, by M. Cametti et al. (a contribution from the Università di Roma "La Sapienza" and the Finnish University of Jyväskylä) reports on the recognition and sensing of the fluoride ion in water, with special attention to fluoride binding in protic solvents and water. • A contribution from the Consiglio Nazionale delle Ricerche, i.e. the CNR-ISOF institution of Bologna, in collaboration with the Università di Trieste and the Université de Namur describes acetylenic derivatives which consist of two compounds containing a central substituted aromatic ring connected through ethynyl bridges to two diacetylamino substituents, each attached to a pyridine residue (K. Yoosaf *et al.*, *Chem.Commun.*, **2009**, 2830). These systems are believed to be important in electronic or biological applications.

• P. Halder *et al.* (*Dalton Trans.*, **2009**, 5386) in a paper from the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science in Kolkata, India, in collaboration with the Università di Trieste, have reported on the supramolecular self–assembly of one tetranuclear silver(I) complex, and three coordination polymers of silver(I), as characterized by conventional spectroscopic methods and by X–ray diffraction analysis. Bidentate Schiff bases with a symmetric or asymmetric spacer between the binding domains were prepared together with the corresponding products resulting from reduction and *N*–alkylation.

• Crystals of the component compounds  $[PtMe_3(OH) \cdot PtMe_2(OH)_2]_2$  and  $[PtMe_2(CO_3)(dpe)]$ , dpe=diphenylphosphane, have been isolated and structurally characterized (M.S. Safa *et al.*, *Chem. Commun.*, **2009**, 1487).  $[PtMe_2(CO_3)(dpe)]$  was claimed to be the first structurally characterized carbonato complex of platinum(IV).

♦ Clusters of platinum were synthesized and structurally characterized (C. Cavazza *et al.*, *Inorg. Chem.*, 2009, **48**, 1385), as for a contribution from the Università di Pisa in collaboration with the Università di Siena. For example, the compound  $Pt_3(\mu-P^tBu_2)_3(CO)_2CI$  contains a  $Pt_3$  core forming a triangle with two short [2.853(1) Å] and one long [3.152(1) Å] Pt–Pt bond distances.

• A paper contributed by the Università di Torino (L. Salassa *et al.*, *J. Am. Chem. Soc.*, 2009, **130**, 9590) deals with the mechanism of ligand dissociation in the ruthenium(II) cationic complexes  $[Ru(bpy)_2L_2]^{2+}$ , bpy=2,2'-bipyridine, L=4-aminopyridine, pyridine, *n*-butylamine,  $\gamma$ -aminobutyric acid, *i.e.* a monodentate nitrogen-based ligand. DFT calculations have been performed to describe the photodissociation of one monodentate ligand.

◆ Ruthenium complexes containing variably substituted 2,2'-bipyridyl ligands (A. Grabulosa *et al.*, *Dalton Trans.*, **2009**, 63) have been reported in a contribution from the Università di Ferrara in collaboration with the Université de Nancy and the Université P. Verlaine, Metz. The complexes, containing the extended conjugated ligand pyrrole–styryl-bipyridine, were shown to exhibit an outstanding harvesting behaviour in the visible region.

• As a contribution from the Università di Sassari (U. Azzena *et al.*, *J. Organometal. Chem.*, 2009, **694**, 3619), the direct metalation of arylmethyl methoxymethyl ethers has been reported to generate a series of  $\alpha$ -methoxymethoxy-substituted arylmethyl lithium derivatives. Through this methodology, the use of organotin derivatives for the same purpose is consequently unnecessary.

◆ A paper contributed by three Chinese institutions (J. Hao *et al.*, *Chem. Commun.*, **2009**, 3460) describes the oxidation of cyclohexane

to cyclohexanol and cyclohexanone catalyzed by a product of composition  $Ti_{70}Zr_{10}Co_{20}$ : this was reported to contain a quasi-crystalline phase and to operate in solvent-free cyclohexane with  $O_2$ . The highest conversion was reported to be 7% with a selectivity to cyclohexanol and cyclohexanone better than 90%.  $\blacklozenge$  As mentioned in a preceding report of this series, extensive work in the general area of oxidation processes has been carried out in the Laboratories of Ente Nazionale Idrocarburi (ENI), and an account of this activity can be found in a 2006 review-article in English (M.G. Clerici *et al.*, *Enciclopedia degli Idrocarburi*, Istituto della Enciclopedia Italiana, Vol. 2, pp. 661–685) dealing with oxidation processes with hydrogen peroxide and hydroperoxides, catalyzed by titanium silicalite. This titanium-based catalyst first appeared in the patent literature in the early Eighties of last century (M. Taramasso *et al.*, US Patent 4,410,501 to SnamProgetti).

◆ A paper from the Università di Milano, in collaboration with the Universitat de Barcelona and the Universidad de Granada, has reported on enhanced ferromagnetic interactions in metal complexes of Cu(II) and Ag(I) with bridging *m*-phenylenediamidato ligands, which were characterized by single-crystal X-ray diffraction (M.A. Palacios *et al.*, *Dalton Trans.*, **2009**, 8538). The copper(II) derivative shows the strongest ferromagnetic exchange coupling.

◆ The Università di Perugia in collaboration with the Universidad de Valencia and the Swiss ETH in Lausanne (H.J. Bolink *et al.*, *Chem. Commun.*, **2009**, 4672) has reported that (acetylacetonato)bis-(1-methyl-2-phenylimidazole) exhibits photo- and electroluminescence in the range 440÷800 nm.

• *Highlights in Chemical Science* (2009, **6**, C59) has outlined out the results obtained by a research group operating at the Università di Torino (G. Di Nardo *et al.*, *Dalton Trans.*, **2009**, 6507), in collaboration with researchers at Imperial College London: a biocatalyst was used to convert catechol into *cis–cis–*muconate, an important intermediate in the production of adipic acid and nylon. Catechol 1,2–dioxygenase from *Acinetobacter radioresistens S13* was immobilized on  $\beta$ -cyclodextrin cross–linked with carbonato groups.

*Highlights in Chemical Technology* (2009, 6, T60) summarize the results obtained by a team operating at the Università dell'Insubria, Como (A. Andreoni *et al., Photochem. Photobiol. Sci.*, 2009, 8, 1202) on the use of fluorescent nucleotides aimed at identifying single polymorphism in a group of genes associated with the development of type-1 diabetes. ◆ A preceding contribution from the same research group, in collaboration with the National Laboratory for Ultrafast and Ultraintense Optical Science in Como (L. Nardo *et al., Photochem. Photobiol.*, 2008, 84, 101), describes a method for detecting the type of ligand–DNA binding mode, distinguishing between minor groove binding and intercalation.

• A contribution from four different institutions of the Università di Milano (G. Prencipe *et al., Chem. Commun.*, **2009**, 6017) describes a synthetic method for the immobilization of peptide nucleic acids on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> super-

paramagnetic nanoparticles. The sequestering ability for DNA was established by measuring the NMR relaxation response in aqueous solution.

♦ Aerobic copper-mediated oxidation of formaldehyde CH<sub>2</sub>O to formate, accompanied by H<sub>2</sub> evolution, *i.e.* 1/2CuO + CH<sub>2</sub>O + OH<sup>-</sup> → HCO<sub>2</sub><sup>-</sup> + 1/2H<sub>2</sub> + 1/2H<sub>2</sub>O, has been reported in a paper from the Università di Pisa (D. Preti *et al.*, *Angew. Chem.*, 2009, **48**, 4763). In the area of the catalytic hydrogenation of carbon dioxide, a paper has appeared (R. Tanaka *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 14168) describing the formation of potassium formate at 200 °C by hydrogenation of CO<sub>2</sub> in aqueous KOH. The reaction was reported to be catalyzed by a series of pincer complexes of iridium(III).

◆ A Feature Article resulting from the collaboration of Columbia University with the Science Department of the J. Jay College of Criminal Justice and with the Università di Pisa (N. Berova *et al.*, *Chem. Commun.*, **2009**, 5958) deals with the use of dinuclear achiral metal-lo-porphyrins combining with a chiral non-racemic guest. The circular dichroism response is in the spectral region of the porphyrin and is related to the absolute configuration of the guest.

◆ A paper from the Università di Parma (G. Maestri *et al.*, *Chem. Commun.*, **2009**, 4892) reports the synthesis of selectively substituted biaryl derivatives, by coupling *ortho*-substituted aryl iodides with ketones in the presence of norbornene, with palladium as catalyst.

◆ The collaboration between the Università di Milano–Bicocca with Northwestern University, with the Friedrich–Alexander–Universität in Erlanger, and with the Universidad Autónoma de Madrid (F. Silvestri *et al., Chem. Commun.*, **2009**, 4500) reports the preparation of an ensemble constituted by bis(phthalocyaninato)ruthenium(II) and a substituted squaraine. The supramolecular system covers a large portion of the solar spectrum from 850 to 250 nm.

◆ A paper from a laboratory of CNR in Roma in collaboration with the Institute INFM–CNR of Trieste, the University College London, and Oxford University (R. Coates *et al.*, *Dalton Trans.*, **2009**, 5943) reports the studies carried out on the electronic states of the [CeCp<sub>3</sub>]<sup>+</sup> cation, a 4f<sup>0</sup> system, both experimentally by variable photon energy photoelectron spectroscopy, and by computational methods. The starting observations were collected on CeCp<sub>3</sub>, a 4f<sup>1</sup> system.

• Researchers of the Università di Torino (E. Gianolio *et al.*, *Chem. Commun.*, **2009**, 6044) describe a NMR methodology (by proton relaxation enhancement) to assess the binding affinity of a gadolini-um-containing complex functionalized with an adamantane derivative in the supramolecular adduct obtained from the combination of a <sup>19</sup>F-containing molecule with a poly- $\beta$ -cyclodextrine.

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