FROM THE LITERATURE

by Fausto Calderazzo - Università di Pisa

The September 2008 special issue of *Acc. Chem. Res.*, dedicated to *Advanced Polymer Design and Synthesis* contains a contribution from two laboratories of the Consiglio Nazionale delle Ricerche (CNR) located in Padova and Milano (G. Zotti *et al*., 2008, **41,** 1098). This Account deals with nanosized conjugated polymers formed on electrode surfaces, in combination with gold nanoparticles.

A Feature Article contributed by the Università di Pavia (V. Amendola *et al.*, *Chem. Commun.*, **2009**, 513) covers the area of anion receptors containing transition metal cations.

The November 2008 issue of *Acc. Chem. Res.*, containing the Guest Editorial by Professor S.L. Buchwald of Massachusetts Institute of Technology, is dedicated to cross–coupling reactions. Within this special issue, a review–article has appeared on catalytic sequential reactions involving palladacycle–directed aryl coupling steps, as for a contribution (M. Catellani *et al.*, *Acc. Chem. Res.*, 2008, **41**, 1512) from the Università di Parma. The methodology used by this research group consists of the cooperative action of the palladium centre and norbornene to achieve selective aryl–aryl coupling through C–halide and C–H activation. The metal–catalyzed reaction sequence is initiated by the oxidative addition of an aryl halide to palladium(0) to form a palladium(II)–aryl bond.

The December 2008 issue of *Acc. Chem. Res.*, with a Guest Editorial by T.W. Odom, Northwestern University, and M.–P. Pileni of the Université Pierre et Marie Curie of Paris, is dedicated to Nanoscience.

The January 2009 issue of *Acc. Chem. Res*. contains a contribution from the Università di Ferrara (P. Gilli *et al*., 2009, **42**, 33) on the prediction of hydrogen–bond strengths from acid–base molecular properties. The covalent and electrostatic contributions to the bond were discussed, as a function of the donor–acceptor proton affinities or acidic constants.

A Feature Article has appeared on the role of electrophilic species in the Fischer–Tropsch (FT) reaction (P.M. Maitlis, V. Zanotti, *Chem. Commun.*, **2009**, 1619): activation of CO at imperfections on the surface involves CO cleavage to generate a surface carbide, which is further hydrogenated. The suggestion was made that the polymerization reaction at a metal–oxide interface proceeds with the intermediacy of an electrophilic species such as the methylidyne $CH^+_{(ad)}$.

A review–article contributed by the Consiglio Nazionale delle Ricerche (CNR), Area di Ricerca di Firenze (P. Barbaro *et al*., *Chem. Rev.*, 2009, **109**, 515) deals with recent achievements in the field of the heterogenization of chemical catalysts on ion–exchange resins, covering the literature in the period January 2005–April 2008. This article appears in the February issue of *Chem. Rev.*, completely dedicated to *Facilitated Synthesis*, the Guest Editors being D. Bergbreiter and S. Kobayashi, of Texas A&M University and University of Tokyo, respectively. The catalytic reactions taken into consideration are: carbonylations, hydroformylations, hydrogenations, asymmetric hydrogenations, oxidations, polymerizations.

A Perspective Article has appeared on the adsorption and desorption of H_2 on metal–organic framework (MOF) materials (K.M. Thomas, *Dalton Trans.*, **2009**, 1487) in comparison with dihydrogen absorption by covalent organic frameworks (COF). The maximum isosteric enthalpies connected with the MOF process are about 13 kJ/mol at 77 K, to be compared with the ~8 kJ/mol observed for covalent organic frameworks (COF). References cited in this article include the activity carried out in this field at the Universities of Torino (see refs. 170, 219, 222, 230 and 231) and Milano (see refs. 221, 223, and 224).

A paper contributed by the Università di Firenze and the University of Massachusetts at Amherst (C.K. Kim *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 1360) has reported on the entrapment of hydrophobic drugs in nanoparticle monolayers, as a delivery system in cancer cells. For this purpose, gold nanoparticles were used, whose alkylthiol monolayer generates hydrophobic pockets, capable of partitioning organic solutes. This is a further interesting development of earlier findings by researchers of the Universities of Bologna, Trieste, Venezia and Padova (M. Lucarini *et al.*, *J. Am. Chem. Soc.*, 2005, **127**, 16384) on monolayer–protected gold clusters.

In view of the anticancer properties exhibited by ruthenium(III) complexes, some compounds containing *N*,*N*–dithiocarbamato ligands derived from methyl–ethyl– ^{t}butyl esters of sarcosine have been reported in a contribution from the Universities of Padova and Siena and from the Consiglio Nazionale delle Ricerche (CNR), Istituto di Chimica Inorganica e delle Superfici, Padova (L. Giovagnini *et al.*, *Dalton Trans*., **2008**, 6699).

The bis(triphenylphosphano)iminium cation, $(N(PPh_3)_2)^+$, abbreviated as PPN^+, has frequently been used for the isolation of organometallic complex anions. It has now been reported (V.J. Sussman *et al.*, *Chem. Commun.*, **2008**, 5642) that in an attempted isolation of tris(η-naphthalene)tantalate(–I) as the PPN^+ derivative, a product arising from the ortho–metallation of two phenyl rings, has been isolated and structurally characterized. It is of interest to note that the use of (PPN)Cl for the isolation of the anionic hexacarbonyl derivatives of Group 5 of formula $(PPN)(M(CO)_6)$, did not result in any metallation (F. Calderazzo *et al.*, *Inorg. Chem*., 1983, **22**, 1865).

A contribution from the Università di Salerno and the Università del Sannio (L. Annunziata *et al*., *Organometallics*, 2009, **28**, 688) has reported the synthesis, characterization and catalytic activity in olefin polymerization of some zirconium(IV) derivatives containing substituted (amidomethyl)pyridine ligands of general formula $(6–X–C_5H_3N)CH_2NC_6F_5$, X= CH_3, Br, H. Upon treatment with Al^iBu_2H or methylalumoxane the zirconium precursors yield active, multisite polymerization catalysts for ethylene and propylene.

A group of researchers working at the Dipartimento Chimico–Farmaceutico, Università di Bari (V. Capriati *et al.*, *J. Org. Chem.*, 2008, **73**, 9552) has reported the structure, configurational stability and stereodynamics in solution of 2–lithio–3,3–dimethyl–2–oxazolinyloxirane, abbreviated as **Li–1**, that is configurationally unstable in ethereal solvents: however, **Li–1** exhibits an unusual thermal stability as indicated by the successful deuterium incorporation even at 25 °C.

An intermolecular cross–coupling between a η^2–coordinated olefin and a η^1–allyl group has been reported by researchers of the Università di Napoli "Federico II" (M.E. Cucciolito *et al.*, *J. Organometallics*, 2008, **27**, 6360), the coordinating metal being palladium(II) or platinum(II) complexed to the tridentate "pincer" ligand 2,6–bis–diphenylphosphinomethylpyridine.

A contribution resulting from the collaboration of the Università del Piemonte Orientale located in Alessandria with the Russian A.N. Nesmeyanov Institute located in Moscow and the Department of Chemistry of the University of Montana (A.A. Koridze *et al.*, *Organometallics*, 2008, **27**, 6163) has reported on a bis(ferrocenylethynyl)–substituted digold–tetrarhenium cluster of formula $Re_4(AuPPh_3)_2(CO)_{12}(\mu_3\text{–}C{\equiv}CFc)_2$, characterized by X–ray diffractometry. The compound has a butterfly Re_4 geometry, with both Re_3 wings being capped by $AuPPh_3$ groups.

A collaboration of the Dipartimento di Chimica Inorganica, Metallorganica ed Analitica "L. Malatesta", Università di Milano, with the Laboratoire de Chimie Organique of the French CNRS in Paris has produced a report on cobalt(II) complexes of chiral bis–binaphthyl porphyrins, including their use in the asymmetric cyclopropanation of alkenes with ethyl diazoacetate, performimg an enantiomeric excess up to 90% (S. Fantauzzi *et al.*, *Organometallics*, 2008, **27**, 6143).

A paper contributed by the Università di Milano–Bicocca (A. Comotti *et al.*, *Chem. Commun.*, **2009**, 284) has described dipeptide crystals containing nanochannels of various sizes showing selective absorption of methane, carbon dioxide, or di–hydrogen. This report describes the unprecedented use of a biomolecule of permanent porosity to capture gases of potential application in the field of energy sources.

A theoretical study resulting from the collaboration of the Università di Messina with the Università di Cagliari and two research institutions located in Portugal (G. Bruno *et al.*, *Dalton Trans.*, **2009**, 495) has used DFT methods to obtain geometry optimization and spectroscopic properties of dithiolato complexes of nickel and gold at various degrees of reduction.

A paper resulting from the collaboration between the Università di Cagliari and the Università di Parma (M. Salidu *et al.*, *Dalton Trans.*, **2009**, 557) has described the synthesis, X-ray structure and magnetic properties of two chromium(III) derivatives, containing the croconato ligand $C_5O_5^{2-}$, characterized by a central core of general formula $Cr_2(\mu\text{–}C_5O_5)_2(\mu\text{–}OH)_2(OH_2)_4$. The magnetic properties of one of the products in the temperature range 5-400 K show the presence of antiferromagnetic interactions.

The collaboration between the Università di Milano-Bicocca and Northwestern University has produced a paper (F. Silvestri *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 17640) which describes the fabrication of bulk–heterojunction solar cells based on squaraine derivatives as donors and a fullerene derivative, namely (6,6)-phenyl C_{61} butyric acid methyl ester, as the acceptor.

A joint paper from the Università located in L'Aquila and the Università di Teramo (A. Arcadi *et al.*, *J. Organometal. Chem.*, 2009, **694**, 576) has reported some sequential gold–catalyzed reactions of 1–phenylprop–2–yn–1–ol with 1,3–dicarbonyl compounds, different outcomes being produced depending on the nature of the catalyst, reaction conditions and properties of the 1,3–dicarbonyl derivative.

A contribution from the Università di Trieste, the Université Louis Pasteur de Strasbourg, the Université de Namur, and the ISOF–CNR of Bologna has reported (A. Llanes–Pallas *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 509) on the engineering of supramolecular hydrogen–bonded nanopolygons, as obtained by self–assembly of molecular modules. The molecular models taken into consideration are: (a) a unit containing two 2,6–di(acylamino)pyridyl recognition sites; (b) an angular unit constituted by a peripherally functionalized 1,3,6,8–tetraethynylpyrene core. The supramolecular oligomers were studied by optical spectroscopy in solution and by scanning tunnelling microscopy (STM) at the solid (pyrolytic graphite)–liquid interface.

Ultrahigh–vacuum co–deposition of Zn–tetraphenylporphyrin and C_{70} has been shown (P. Vimercati *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 644) to induce the self–assembly of electron–rich aromatic molecules at the curved surface of C_{70}, leading to a supramolecular multilayer donor–acceptor structure, as for a contribution from some research institutions located in Trieste and from a CNR Institute located in Roma.

The mechanism of the nitrosoarene–alkyne cycloaddition has been studied as for a contribution from the Università degli Studi dell'Insubria, in collaboration with three research institutions located in China (Shanghai Jiao Tong University), and USA (University of California at Los Angeles and University of Oklahoma). This paper (A. Penoni *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 653) has shown that the thermal reaction of nitrosoarenes with alkynes produces *N*–hydroxyindoles as the major product.

Authors are cordially invited to submit recent or forthcoming accepted publications for consideration in this section of the journal, by using the following e–mail address: facal@dcci.unipi.it