

Polymer and colloid chemistry in Switzerland was reviewed by Christian Quellet of Givaudan Schweiz AG (*Chimia*, 2008, **62**, 773), and the contribution by Piero Pino, a former teacher at the Università di Pisa, to the development of polymer chemistry at ETH Zürich, has been highlighted.

Metal-metal quintuple bonds have been reported by chemists operating at some teaching institutions in Taiwan (C.-W. Hsu *et al.*, *Angew. Chem. Int. Ed.*, 2008, **47**, 1): the central chromium(I) atoms are separated by about 1.74 Å, with slight differences around this value as a function of the substituents.

The Met80Ala (M80A) variant of *iso*-1-cytochrome *c* from yeast, immobilized on a gold electrode, was found to undergo electron exchange and to catalyze the reduction of both O₂ and NO₂⁻, as for a contribution from the Universities of Modena and Reggio Emilia and from a CNR-INFM institution located in Modena (S. Casalini *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 15099).

The collaboration between the Universities of Palermo and Bologna has produced two papers reporting: (a), the isomerization and rearrangement of the (*E*)- and (*Z*)-phenylhydrazones of 3-benzoyl-5-phenyl-1,2,4-oxadiazole (F. D'Anna *et al.*, *J. Phys. Org. Chem.*, 2008, **21**, 306), and, (b), the structure modifications on systems consisting of a co-solvent and the tetrafluoroborate derivative of the 1-butyl-3-methylimidazolium cation (F. D'Anna *et al.*, *Tetrahedron*, 2008, **64**, 672), as studied by NMR, spectrophotometric and conductivity measurements.

A paper has appeared (K. Albahily *et al.*, *Organometallics*, 2008, **27**, 5708) concerning the chromium-catalyzed trimerization of ethylene, as for the research activity in this field carried out at the University of Ottawa and at the Eindhoven University of Technology. The catalytic precursor was reported to be the nitrogen-ligated chromium(II) derivative of formula Cr[(2,6-di-*iso*-propylphenyl)NPN(^{*i*}Bu)]₂ containing the nitrogen donor ligand (Ar)NPN(^{*i*}Bu), further treated with AlMe₃ to finally form a crystallographically established bimetallic chromium-aluminium complex. The latter, alone or with addition of methylalumoxane (MAO), was employed for the catalytic oligomerization and polymerization of ethylene. A contribution from the Università di Pisa has reported homo- and co-polymerization of ethylene to occur when bis(salicylaldiminato)copper(II) complexes are activated with MAO (A.M. Raspolli Galletti *et al.*, *J. Polym. Sci.: Part A: Polym. Chem.*, 2007, **45**, 1134). Trimerization of ethylene was the subject of a patent from the Novara Laboratories of Enichem (R. Santi *et al.*, WO 01/68572 A1, Sept. 20, 2001), the catalyst consisting of a bis(arene)vanadium(I) derivative VX(arene)₂, with X being a halide ion or an anion such as B(Ar)₄⁻, AlCl₄⁻, a carboxylato or a sulfonato group. Relevant to these findings is the paper by J.A. Olson *et al.* (*Organometallics*, 2008, **27**, 5333) reporting that some Schiff base metal complexes are active in the polymerization of ethylene. However, also the protonated Schiff base in the

absence of any copper showed an activity in the polymerization of ethylene, the suggestion being that ligand transfer from copper to aluminium could be responsible for the catalytic activity.

Metallocenium ion-pairs of the type [Me₂C(C₅H₄)(C₁₃H₈)M(CH₂SiMe₃)⁺...X⁻], M=Zr, Hf; X=MeB(C₆F₅)₃, B(C₆F₅)₄, were reported in a paper resulting from a collaboration of the University of East Anglia with the Universities of Perugia and Salerno (C. Alonso-Moreno *et al.*, *Organometallics*, 2008, **27**, 5474). While the solid-state structures of [Me₂C(C₅H₄)(C₁₃H₈)Zr(CH₂SiMe₃)₂], [Me₂C(C₅H₄)(C₁₃H₈)HfMe₂], and [Me₂C(C₅H₄)(C₁₃H₈)Zr(Me)Cl] were studied by X-ray diffraction methods, the kinetics of site epimerization of the ion pairs [Me₂C(C₅H₄)(C₁₃H₈)M(CH₂SiMe₃)₂(μ-Me)B(C₆F₅)₃], and [Me₂C(C₅H₄)(C₁₃H₈)M(CH₂SiMe₃)⁺...B(C₆F₅)₄⁻] were measured by variable-temperature NMR spectrometry. The ion-pairs containing the CH₂SiMe₃ group are significantly more stable than the M-Me analogues, probably due to an agostic interaction of the methyl group with the metal.

The regioselectivity in the rhodium-catalyzed hydroformylation of 1,1-diphenylethene, known to produce the linear aldehydes only, has been studied by computational methods as for a paper in collaboration between the Università di Pisa and a CNR Laboratory located in the same town (C. Ghio *et al.*, *Eur. J. Inorg. Chem.*, in press), density functional theory (DFT) calculations indicating a considerable higher activation energy for the pathway to the branched product. On a similar area of research, a contribution by three research institutions located in Germany (D. Selent *et al.*, *Chem. Commun.*, 2008, 6203) has reported that diastereoisomeric rhodium hydroformylation catalysts operating on 1-octene and based on binaphthol biphosphites produce 84–89% yields of *n*-nonanal, the mole fraction of the latter being as high as 0.96.

In a paper from the Dipartimento di Chimica “G. Ciamician”, Università di Bologna (M. Amelia *et al.*, *Angew. Chem., Int. Ed.*, 2008, **47**, 6240) a simple fluorophore such as 8-methoxyquinoline (8-MQ) was used to implement 2:1 multiplexer and 1:2 de-multiplexer digital functions by exploiting the proton-driven reversible modulation of two complementary absorption and fluorescence signals. The observation was carried out both in solution and in the solid state. In the latter case, films of polystyrene/8-MQ were prepared and shown to undergo conversion to MGH⁺ upon exposure to CF₃COOH, the process being reverted by further treatment with N^{*n*}Bu₃.

A convenient route to thia-bridged triarylamine heterohelicenes has been reported in a paper from the Università di Firenze in collaboration with the Università di Roma “La Sapienza” and the University of Southern California (G. Lamanna *et al.*, *Chem. Eur. J.*, 2008, **14**, 5747). The synthesis involves four consecutive electrophilic regioselective aromatic sulfur insertions: the absolute configuration of the resulting products, resolved by HPLC, was established by *ab initio* calculations and by measuring the vibrational circular dichroism

(VCD) spectra of the enantiomers. A paper by the same corresponding author (S. Menichetti), as a contribution from the Universities of Firenze and Bologna (R. Amorati *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 237) has shown that rotation about the aryl-sulfur bond in *ortho*-(alkylthio)phenols affects the bond dissociation enthalpy (BDE) and the reactivity of the OH group: specifically, in the case of weaker intramolecular hydrogen bonds, the OH group is characterized by a lower BDE and a high reactivity.

New hyperpolarized contrast agents for ^{13}C -Magnetic Resonance Imaging (MRI) have been reported (F. Reineri *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 15047), as obtained by *para*-hydrogenation of two alkyne derivatives containing one or two oxyethylene chains, namely the asymmetric 2-(2-methoxyethoxy)ethylphenylpropiolate and the symmetrical bis[2-(2-methoxyethoxy)ethyl]acetylenedicarboxylate.

A contribution from the Università di Roma "La Sapienza" and the Universitat de Barcelona (Z. El-Hachemi *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 15176) has reported on the transfer of chirality from chiral surfactants to porphyrin/surfactant aggregates, as studied by optical absorption, and by fluorescence and circular dichroism (CD) spectroscopies, three being the preferred surfactant/porphyrin ratio.

Synthetic and structural studies on lanthanide complexes continue to be constantly present in the chemical literature. The adducts of some trivalent lanthanides (Ln) and yttrium(III) with $1,4\text{-C}_6\text{H}_4(\text{CN})_2$ have been reported (C.J. Höller *et al.*, *Inorg. Chem.*, 2008, **47**, 10141), as obtained by melting the ligand in the presence of the anhydrous chloride (Ln=Sm, Gd, Tb). The derivatives of formula $\text{LnCl}_3(1,4\text{-C}_6\text{H}_4(\text{CN})_2)$ were found to be isomorphous. Similar findings over a series of lanthanide(III) complexes containing the deprotonated bis(tetrazolyl)amine (BTA) have been reported (J.-M. Lin *et al.*, *Dalton Trans.*, 2008, 6165), as a contribution from the Chinese Universities of Guangzhou and Peking. The metal complexes, of formula $\text{Ln}(\text{BTA})(\text{HCOO})(\text{H}_2\text{O})_3$, cover the range from praseodymium to ytterbium over seven members of the lanthanide series. The lanthanide contraction has been the object of studies in the Laboratories of the Università di Pisa. The isomorphous aquo complexes of formula $[\text{Ln}(\text{H}_2\text{O})_9][\text{EtOSO}_3]$ extending over the whole series from lanthanum to lutetium (with the sole exception of promethium) have been found to follow a quadratic decay of the Ln-O bond distances (E.A. Quadrelli, *Inorg. Chem.*, 2002, **41**, 167), the analysis being simplified by the presence of a single type of ligand within the central metal cation. Moreover, according to structural studies on the mononuclear dimethoxyethane complexes of formula $\text{LnCl}_3(\text{DME})_2$ over a range of 12 atomic numbers from neodymium(III) to lutetium(III) have been reported (U. Baisch *et al.*, *Inorg. Chim. Acta*, 2004, **357**, 1538), for both the Ln-O and Ln-Cl bond distances, to follow a quadratic type of decay. Finally, the iso-

typical tetranuclear di-*iso*-propylcarbamato complexes of the lanthanide series, of formula $[\text{Ln}(\text{O}_2\text{CNPr}_2)_{12}]$, over a range of twelve atomic numbers from neodymium(III) to lutetium(III) were shown to follow a similar behaviour for four different types of the Ln-O bond distances (U. Baisch *et al.*, *Eur. J. Inorg. Chem.*, 2004, 1219).

Novel carbene complexes of silver(I) have been reported as for a paper in collaboration between the Universities of Camerino and Padova (A. Biffis *et al.*, *J. Organometal. Chem.*, 2008, **693**, 3760). The silver complexes were found to catalyze the coupling of aryl iodides with terminal alkynes.

A paper from the Università di Trento, in collaboration with the Istituto Nazionale di Fisica Nucleare (INFN) of Padova and with the Università di Parma (M. Tonezzer *et al.*, *Chem. Mater.*, 2008, **20**, 6535) reports the formation of gas sensors obtained by high-vacuum evaporation, on a silicon wafer or a quartz crystal, of a tetraphosphonate or a tetrathiosphosphonate, presenting an open conformationally rigid cavity containing four P=O or P=S groups, respectively. Films of the former type exhibit active sites for the detection of ethyl alcohol.

Two hexanuclear iron clusters containing the $\text{Fe}_2\text{S}_2(\text{CO})_x$ fragments, $x=5$, or 6, have been reported (W. Zhong *et al.*, *J. Organometal. Chem.*, 2008, **693**, 3751) in a paper resulting from the collaboration of two Chinese institutions with the Università di Milano-Bicocca. The sulphur-containing ligand derives from 2-(mercaptomethyl)-2-methylpropane-1,3-dithiol. A conformational *syn/anti* equilibrium was detected, in addition to a chemical equilibrium involving a decarbonylation process.

Spherical assemblies of cobalt ferrite (CoFe_2O_4) nanoparticles with a high surface area have been reported as for a paper from the Università di Cagliari (C. Cannas *et al.*, *Chem. Mater.*, 2008, **20**, 6364). The primary CoFe_2O_4 nanoparticles assemble into spherical nanoporous aggregates with an average size of 50–60 nm, further coated with a 7–8 nm thick shell of amorphous silica. The magnetic properties of the nano-structures were investigated.

A paper resulting from the collaboration between the Università di Bari and the Università di Bologna has appeared (G. Falini *et al.*, *Chem. Commun.*, 2008, 5960) which deals with a structural synchrotron investigation on adducts of human ubiquitin (uBb), a small protein with 76 residues, with Zn(II), Cd(II) and Hg(II). Binding occurs at three different sites of the protein. This study is connected to the understanding of the mechanism of protein aggregation believed to be involved in some physiological neurodegenerative disorders.

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