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

A paper by J. Zhang et al. (Organometallics, 2009, 28, 2905) resulting from the collaboration of the National University of Singapore with the Chinese Xiamen University has reported the trimerization of ethylene to hexene-1 mainly, catalyzed by some Cr/Al intermetallic complexes. This is a subject of considerable industrial interest, for example for the use of the C<sub>6</sub>-olefin as co-monomer in the synthesis of modified polyethylene. Interesting results in this and related areas have been obtained in this country at the Laboratories of Europa-Polimeri located at Istituto "G. Donegani" of Novara. In one of these contributions (R. Santi et al., Patent WO 01/68572 A1, to EniChem SpA, published Sept. 20th 2001) hexene-1 was reported to be obtained through oligomerization of ethylene in the presence of a vanadium-based catalytic precursor of formula  $[V(n^6-arene)]X$ , X being a halide or a polyatomic anion such as [BAr<sub>4</sub>]-, [AICl<sub>4</sub>]-, carboxylato or sulfonato. A patent resulting from the collaboration of the CNR Laboratories in Firenze with researchers of Istituto "G. Donegani" (C. Bianchini et al., WO 02/34701, to Polimeri Europa srl, published May 2<sup>nd</sup> 2002) reports the selective oligomerization of ethylene to a Schultz-Flory distribution of  $\alpha$ -olefins in the presence of iron- or cobalt-based catalysts obtained from the corresponding chloride and a new family of 2,6-bis(imino)pyridyl ligands of  $C_s$ - or  $C_1$  symmetry (C. Bianchini *et al.* Eur. J. Inorg. Chem., 2003, 1620). The iron-based catalyst is the most active one with TOF as high as 7x105 mol(C2H4)x(mol of catalyst)-1xh-1. On the other hand, monocyclopentadienyl derivatives of titanium(IV) of formula  $Ti(\eta^5-C_5R_5)Cl_3$ , R=H, Me, in combination with methylalumoxane (MAO) are known to polymerize olefins, styrene and dienes and an ESR study has appeared confirming the presence of titanium(III) in the pre-catalytic system (L. Bonoldi et al., J. Mol.Catal., A: Chemical, 2004, 219, 47).

In a contribution from the Università di Pisa, the rhodium–catalyzed asymmetric addition of phenylboronic acid to cyclohexenone has been reported (A. Juliano *et al.*, *Chem. Commun.*, **2009**, 497) to occur in the presence of the 1,2–biphenylphosphite of deoxycholic acid. The reaction, carried out in a water/dioxane mixture, with a P/Rh molar ratio of 1, gave a 80% yield of the resulting product (ee=88%).

A combined study involving the Università di Bologna, the University of Basel and the Department of Chemistry of the University of Miami (S. Silvi *et al., Chem. Commun.*, **2009**, 1484) has reported the performance as a two-state luminescent switch of a system, in MeCN solution, consisting of a reversible merocyanine-type photoacid and a polypyridine complex of osmium.

Thermal treatment and extraction with supercritical carbon dioxide influences the crystal structure and morphology of syndiotactic polystyrene, as for a paper contributed by the Università di Salerno (C. Daniel *et al.*, *Chem. Mater.*, 2009, **21**, 1028l). Wide-angle X-ray diffraction and scanning electron microscopy have been used to detect the nanoporous  $\delta$ -phase and also the dense  $\gamma$ - and  $\beta$  crystalline phases. In addition, the recently discovered  $\epsilon$ -phase aerogel has been

identified to be suitable for the removal of organic pollutants.

The Politecnico di Milano (R. Spaccini *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 18018) has contributed to the description of the key role of titanium(IV) in the selective radical-radical cross-coupling. When  $\alpha$ -hydroxyl  $\alpha$ -carbonyl radicals are generated in the presence of TiCl<sub>4</sub> and 2,2'-azo-bis-isobutyronitrile (AIBN), the cross-coupling was observed to give high yields of the appropriate  $\beta$ -hydroxynitrile.

A study aimed at synthesizing hard and superhard borides of rhodium and iridium has appeared as a contribution from two research institutions (CNR and Università "La Sapienza") located in Roma (J.V. Rau *et al., Chem. Mater.*, 2009, **21**, 1407). The synthesized borides  $RhB_{1.1}$ and  $IrB_{1.35}$  were characterized by X–ray diffraction and Vickers microhardness measurements.

A contribution resulting from the collaboration of the Università di Perugia with Northwestern University (A. Marrocchi et al., Chem. Commun., 2009, 1380) has described the use of acetylenic spacers in anthracene-based conjugated semiconductors aimed at increasing the power conversion efficiency of the bulk heterojunction solar cells thus formed. On a somewhat related subject, a contribution from the Dipartimento di Chimica "G. Ciamician" of Bologna in collaboration with two Chinese research institutions (H. Qian et al., J. Am. Chem. Soc., 2008, 130, 17970) has reported the synthesis of fully conjugated tris(pervlene) bis-imides containing 19 six-membered carbon rings in the core and six amide groups at the edges, whose structural isomers were separated by HPLC. This is a promising system as a n-type functional component in optoelectronic devices. Furthermore, a paper resulting from the collaboration of the Università di Bologna with the Universitat de València (G. Tomasello et al., J. Am. Chem. Soc., 2009, 131, 5172) has reported the photoisomerization efficiency and optical properties of the retinal chromophore in Rhodopsin.

A paper resulting from a collaboration of the Università di Firenze with the Institut L. Pasteur of Paris (C. Caillet–Saguy *et al., J. Am. Chem. Soc.*, 2009, **131**, 1736) has contributed to the description of the mechanism through which heme acquisition occurs by Gram–negative pathogenic bacteria. A further contribution from the same research group of the Università di Firenze with several institutions in Finland and Germany (I. Bertini *et al., J. Am. Chem. Soc.*, 2009, **131**, 5134) reports the accurate determination of protein solution structures by using solid–state X–ray data and a set of NMR parameters, as applied to two complexes of calmodulin with target peptides.

The collaboration of the Politecnico di Milano (ICMIC "G. Natta") with the Canadian University of Alberta produced a paper (A. Lucotti *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 4239) reporting IR- and Raman spectroscopic data of adamanthyl end–capped polymers with *sp*–hybridized carbon atoms in chains of length from C<sub>4</sub> to C<sub>20</sub>. The spectral data show that these molecules are not centrosymmetric both in solution and in the solid state. These data are supported by the X-ray analysis of the C<sub>12</sub> term.

A derivative of magnesium(I) has been reported in a paper released by three Chinese research institutions (Y. Liu *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 4210). The compound, of formula [K(THF)<sub>3</sub>]<sub>2</sub>[LMg–MgL], L being the nitrogen–based bidentate ligand [2,6–/PrC<sub>6</sub>H<sub>3</sub>NCMe]<sub>2</sub><sup>2–</sup>, has been characterized by X–ray diffraction and shown to contain the singly bonded Mg(I)–Mg(I) centres at a distance of 2.9370 Å. A product containing a Mg–Mg bond has also been described as for a contribution from the Aarhus University, in collaboration with the Australian Monash University (J. Overgaard *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 4208). Pioneering work in this field was carried out at the Universidad de Sevilla by E. Carmona and coworkers: a recent article by this group (E. Carmona, A. Galindo, *Angew. Chem. Int. Ed.*, 2008, **47**, 6526) has reviewed the recent findings on  $Zn_2(\eta^5-C_5Me_5)_2$  and related organometallics of Group 12.

The crystal structure of oxalic acid  $(COOH)_2 \cdot 2H_2O$  at pressures as high as 5.3 GPa has been reported in a contribution from the Università di Milano and the University of Bern (N. Casati *et al.*, *Chem. Commun.*, **2009**, 2679). At such a pressure, proton migration to H<sub>2</sub>O was observed with formation of ionic species.

A density functional study (DFT) of a Gd(III)/Cu(II) complex of formula GdCu{[N,N'-bis(3-ethoxysalicylidene)-1,2-diamino-2-methylproprion ato][CF<sub>3</sub>COO)<sub>3</sub>]}·2EtOH has been reported in a contribution from the Università di Firenze (G. Rajaraman *et al., Dalton Trans.*, **2009**, 3153). The results show that the empty 5*d* orbitals of Gd(III) play an important role in the magnetic coupling. A further contribution from research institutions located in Firenze in collaboration with researchers of the Università di Modena e Reggio Emilia (D. Gatteschi *et al., Inorg. Chem.*, 2009, **48**, 3408) in a Forum Section of the journal has reviewed the magnetic properties of products ranging from organic radicals to single-molecule magnets, when they are organized on surfaces.

A paper contributed by the Università di Padova and the Università di Trieste (B. Longato *et al.*, *Dalton Trans.*, **2009**, 2400) has reported the preparation and properties of some cationic platinum(II) complexes containing the deprotonated 1–methylthymine (1–MeTy) and the neutral ligand 1–methylcytosine (1–MeCy), of formula [Pt(1–MeTy)(1–MeCy)L<sub>2</sub>]<sup>+</sup>, L=tertiary phosphine, as their nitrato derivative. A tautomeric transformation of the platinum–coordinated nucleobases was crystallographically established.

One-dimensional chains of hexanuclear manganese(II) complexes containing both the *iso*-phthalato- and succinato ligands have been reported, together with their crystal structures and magnetic properties (L.F. Jones *et al.*, *Chem. Commun.*, **2009**, 2023). This paper is a contribution from the University of Edinburgh and the CNR-INFM Laboratory located in Modena.

The reactions of both ReCl(CO)<sub>5</sub> and Re<sub>2</sub>(CO)<sub>10</sub> with the nucleophiles  $Me_3SiO^-$  and  $MeO^-$  have been reported in a contribution from the Dipartimento di Chimica Inorganica, Metallorganica e Analitica "L. Malatesta", Università di Milano, in collaboration with other research

institutions of Milano and Firenze (E. Lucenti *et al.*, *Organometallics.*, 2008, **28**, 3040). From the reaction with MeO-, the crystallographically characterized [Re<sub>2</sub>(CO)<sub>9</sub>(COOMe)]<sup>-</sup> anion was isolated as its tetrabutylammonium derivative.

A paper from the Californian Claremont Colleges in collaboration with the University of California (M.L. Scheuermann et al., Organometallics, 2009, 28, 1613) has described a methyl derivative of platinum(II) containing a nitrogen-based "pincer" ligand occupying three mutually cis positions. The metal-assisted alkyl-to-acyl transformation involves the cleavage of the Pt-N bond, followed by coordination of CO. A similar mechanism was first shown to operate in the case of the paradigmatic Mn(Me)(CO)<sub>5</sub> to Mn(COMe)(CO)<sub>5</sub> transformation, as studied by using <sup>13</sup>C-labelled compounds followed by IR characterization of the resulting products (K. Noack et al., J. Organometal. Chem., 1967, 10, 101). Oxidative addition reactions of organonitriles to the iridium(I) complex [Ir(PMe<sub>3</sub>)<sub>4</sub>]Cl (M.G. Crestani et al., Organometallics, 2009, 28, 2904) have been reported leading to [Ir(H)(CH<sub>2</sub>CN)(PMe<sub>3</sub>)<sub>4</sub>]Cl, as one of the described products, as for a joint contribution from the Universidad Nacional Autónoma de México and the University of Durham. The reaction of the precursor with O<sub>2</sub> gave the peroxo derivative [Ir(O<sub>2</sub>)(PMe<sub>3</sub>)<sub>4</sub>]Cl, characterized by X-ray diffraction and used as catalyst in the hydration of acetonitrile to acetamide.

Lapachol, a hydroxy–1,4–naphthoquinone derivative of natural origin forms complexes with manganese(II) (F. Caruso *et al.*, *Inorg. Chem.*, 2009, **48**, 3529), according to a paper contributed by several institutions located in Italy, Argentina and USA. Lepachol is a  $\alpha$ -hydroxyl–naphthoquinone derivative contained in the wood of *Tabebuia avellanedeae*, a plant growing in the rain forests of some South American countries. Several physico–chemical methods, including X–ray crystallography, have been used to structurally characterize the metal complex.

M. Delferro *et al.* (*Dalton Trans.*, **2009**, 544) of the Università di Parma have reported the reaction of the zwitterionic ligand  $EtNHC(S)Ph_2P=NPPh_2C(S)NEt$  with  $Ru_3(CO)_{12}$  leading to different products of carbonyl substitution. The X-ray diffraction data of three of the resulting trinuclear products have been reported.

A joint paper involving the Universidad Nacional de Rosario and the Università di Firenze (L.A. Abriata *et al., J. Am. Chem. Soc.*, 2009, **131**, 1939) have described the binuclear copper site contained in *Thermus thermophilus* Cu<sub>A</sub> in the oxidized form. The study was carried out by detecting the <sup>1</sup>H– and <sup>13</sup>C resonances from the cysteine and imidazole ligands. The presence of a hydrogen bond to a coordinated sulfur atom was detected.

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