FROM THE LITERATURE

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A review–article has appeared (D.D. Jacquemin *et al.*, *Acc. Chem. Res.*, 2009, **42**, 326) on the simulation of optical properties in dyes. These substances, which are based on molecules absorbing in the UV–VIS region of the electromagnetic spectrum, have a wide range of applications in the fields of colouring, energy production and pharmaceutical products. Important contributions in this area come from the work of Balzani and his coworkers at the Università di Bologna (*e.g.*, A. Juris *et al.*, *Chem. Rev.*, 1996, **96**, 759).

Polymerization catalysts characterized by a bimetallic constrained geometry have been reported in a paper resulting from the collaboration of Northwestern University with the Università di Catania and with the Istituto di Scienza e Tecnologia dei Materiali located in the same institution (A. Motta *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 3974). The proximity effects on the ethylene polymerization mediated by a dinuclear zirconium(IV) catalytic precursor have been studied, together with the ion–pair formation in the presence of the binuclear fluorinated bis(borane) co–catalyst $C_6F_4[B(C_6F_5)_2]_2$. The data thus obtained are compared with those collected with the corresponding mononuclear co–catalyst. The possibility has been taken into consideration of agostic interactions between the Zr–bonded α–alkene and the second zirconium centre. On the other hand, a theoretical paper from the same institutions (Università di Catania and Northwestern University) discusses the catalytic properties of $ZrMe_2Cp_2$ as a pre–catalyst chemisorbed on dehydroxylated γ–Al_2O_3, by using a density functional approach (A. Motta *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 16533). It was found that the interaction of the $[ZrCp_2Me]^+$ cation with the μ_2–O sites of Al_2O_3 is far stronger than that with the μ_3–O sites; moreover, a Cossee–type enchainment mechanism was regarded to be operating *via* a preliminary π–complex formation of the olefin with the zirconium centre. In a related subject, intra– and intermolecular interactions have been studied (C. Zuccaccia *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 10354) *via* NMR measurements. In this case, a pyridyl–amido arylcyclometallated hafnium pre–catalyst of C_1 symmetry has been taken into consideration, as activated by $B(C_6F_5)$, $CPh_3[B(C_6F_5)_4]$ or $NHR_3[B(C_6F_5)_4]$. This paper, contributed by the Universities of Perugia and Napoli, the Dow Chemical Company and the University of Florida, reports that a particularly stable outer–sphere ion–pair is formed when the naphthyl substituent is present around the hafnium central metal atom. Fluorenyl–based metallocenes of C_1 and C_s symmetries have been discussed for their ability to produce high–molecular–weight polymers in the course of the ethylene/propylene co–polymerization (T. Wondimagegn *et al.*, *Organometallics*, 2009, **28**, 1383). A contribution from the Universities of Napoli and Manitoba (G. Talarico *et al.*, *Organometallics*, 2008, **27**, 4098) describes computational studies on a variety of polymerization catalysts. Two mechanisms are considered, namely a metal–hydrido–bis(olefin) complex and the direct transfer of an alkyl β–hydrogen to a metal–coordinated olefin with no metal–H interaction. Zirconium, at variance to titanium and hafnium, appears to prefer the metal–hydrido–bis(olefin) intermediate.

A paper contributed by the University of Southampton (A.L. Hector *et al.*, *Chem. Mater.*, 2008, **20** 5100) has reported the preparation of selenolato– and tellurato complexes of Group 4 metals (Ti, Zr, Hf) in the oxidation state IV, of formula $MCp_2(ER)_2$, E=Se, Te. These compounds have been shown to be suitable precursors for the generation of the corresponding metal chalcogenide through a low–pressure and aerosol–assisted Low–Pressure Chemical Vapour Deposition (LPCVD) process. The crystal structures of some of the representative compounds are reported, in addition to that of the μ–oxo derivative $[Zr_2Cp_4(SeMe)_2](\mu\text{–}O)$ resulting from a hydrolytic process involving the precursor. It is interesting to note that manganese chalcogenido–bridged complexes are well established as obtained, for example, through the reaction of $Mn(Cp\text{–}Me)(CO)_3$ with E_2R_2 (A. Belforte *et al.*, *Gazz. Chim. Ital.*, 1985, **115**, 125).

Some considerations have appeared on the mechanism of the Wacker process converting ethylene to acetaldehyde in the presence of $PdCl_2$ and $CuCl_2$ in hydrochloric acid solution (J.A. Keith *et al., Organometallics*, 2009, **28**, 1618): under the conditions of low concentrations of both Cl^- and $CuCl_2$, it is confirmed that the reaction proceeds *via* a mechanism of *syn* nucleophilic attack.

The nickel(II) complex of 2,5–dihydroxyterephthalic acid (dhtp) of formula $Ni(dhtp)(H_2O)_2 \cdot 8\ H_2O$ maintains its crystallinity and porosity after removal of water (F. Bonino *et al.*, *Chem. Mater.*, 2008, **20**, 4957), as communicated in a joint paper contributed by the Università di Torino, in collaboration with two research institutions located in Norway. The resulting nickel(II) product coordinates nitrogen oxide NO quite efficiently.

Benzene displacement by MeCN has been reported for the $[Fe(\eta^5\text{–}C_6H_7)(C_6H_6)]^+$ cation (P. Zanello *et al.*, *J. Organometal. Chem.*, 2009, **694**, 1161). A similar substitution pattern has been observed with ^{t}BuNC, $P(OMe)_3$ and $P(OEt)_3$.

A paper resulting from the collaboration of the Università di Roma with the University of Minnesota and the Institute of Organo–Element Compounds located in Moscow has reported metal–free and tetraferrocenyl–porphyrins of transition metals, namely zinc, nickel, cobalt and copper (V.N. Nemykin *et al.*, *Dalton Trans.*, **2008**, 4233). The compounds were characterized by several spectroscopic techniques, and the deviation from planarity of the system was found to decrease in the following sequence: Ni>Co>Cu>Zn.

Coating of TiO_2 particles with silica has been reported (A.F. Demirörs *et al.*, *Chem. Mater.*, 2009, **21**, 979) through a process controlling the access of silica by applying different experimental conditions. When the TiO_2 particles are treated with silica before drying, TiO_2/SiO_2 composites were obtained, the two materials being uniformly distributed.

The combined efforts of the Universities of Calabria and Basilicata in collaboration with the ISOF–CNR of Bologna have produced a paper (M. Ghedini *et al.*, *Dalton Trans.*, **2008**, 4303) describing the photochemical and electrochemical properties and the computational study on a series of cyclometallated palladium(II)– and platinum(II) complexes. This study has shown that the electronegativity of the ancillary ligand has an effect on the frontier orbitals of the complexes, as particularly evidenced in the case of the platinum(II) derivatives.

A contribution from two research institutions located in Roma, in collaboration with the Università de L’Aquila (C. Zazza *et al.*, *Chem. Comun.*, **2008**, 3399) describes the application of a perturbed matrix method (PMM) to the characterization of a system consisting of a succinimide site separated by a C_{12} alkyl spacer from a 3,6–di–*tert*–butyl–1,8–naphthalimide site, as a potential molecular machine.

Two research institutions located in Milano (Politecnico and the CNR Istituto per lo Studio delle Macromolecole) have reported (P. Arosio *et al.*, *Chem. Mater.*, 2009, **21**, 78) the synthesis, structural characterization and crystallization behaviour of a highly regular head–to–tail poly(3–*n*–butylthiophene). A crystal polymorph was identified and found to be best described as a limit–ordered orthorhombic model in the space group $C222_1$ with refined lattice parameters a=7.64(1), b=7.75(1), c=24.97(8) Å, and a calculated density of 1.24 gxcm^{-3}, in good agreement with the experimental values.

A contribution due to the collaboration of the Istituto Italiano di Tecnologia located in Genova with the Scuola Normale Superiore of Pisa, the Dipartimento di Scienze Farmaceutiche of Bologna and the Department of Chemistry and Applied Biosciences of ETH Zürich (A. Berteotti *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 244) has reported on the kinase large–scale conformations. This computational study has simulated the energetics and dynamics of the open–to–close movements of the cyclin–dependent kinase 5.

Optically active α–amino phosphonic acid derivatives have been reported to be obtained through phase–transfer catalysis, according to a contribution from the Università di Bologna (F. Fini *et al.*, *Chem. Commun.*, **2008**, 4345). α–Amido sulfones react with phosphite esters leading to the required products.

A contribution resulting from the collaboration of the Universities of Bologna with those of Edinburgh and Amsterdam (P. Altoè *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 104) describes the study of both fumaramide and solvated nitrogen–substituted fumaramides, carried out by computational methods and time–resolved spectroscopic techniques. Singlet photochemistry appears to follow a pattern where non–equilibrium dynamic factors control the photochemical process.

Photochromic fluorescent proteins have been investigated by researchers operating at Scuola Normale Superiore of Pisa (S. Luin *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 96). The molecules behave as reversibile switchable fluorophores, repeatadly undergoing fluorescent → non–fluorescent state upon irradiation, as shown through pre–resonant Raman spectroscopy and model calculations.

The combined efforts of researchers operating in several European research institutions including the Università di Ferrara and the CNR Institute ISOF located in Bologna have produced a contribution (J.M. Mativetsky *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 9192) reporting that azobenzenes act as light–controlled molecular electronic devices in metal/molecule/metal junctions produced by contacting a gold–supported self–assembled monolayer with a metal–coated atomic force microscope tip.

Exchange equilibria have been reported (L. Canovese *et al.*, *J. Organometal. Chem.*, 2009, **694**, 411) for the palladium complex Pd(neocup)(nq), neocup=2,9–dimethylphenanthroline; nq=naphthoquinone, *vs*. several alkenes and alkynes. Moreover, a kinetic study was carried out of the reaction between the alkene $(MeOOC)_2C=C(COOMe)_2$ and the palladium complexes Pd(η^2–dmfu)(L–L’), dmfu being dimethylfumarate and L–L’ denoting a bidentate *N*–containing ligand. The crystal and molecular structures of two of the palladium complexes were reported

A paper resulting from the collaboration between the Università di Firenze and the Institut L. Pasteur of Paris (C. Caillet–Saguy *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 1736) has reported NMR spectrometric studies of the interaction between the heme acquisition system (HAS–A) and its outer membrane receptor (HAS–R).

The recombination kinetics of the primary light–induced charge–separated state and the thermal stability of the photosynthetic reaction centre of *Rhodobacter sphaeroides* were studied in trehalose–H_2O and in sucrose–H_2O media (F. Francia *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 10240), as for a contribution from the Universities of Bologna, Palermo and Bari. The data show that in sucrose–water the system undergoes a nanophase separation for water/sugar mole fractions lower than the threshold value of 0.8. The results suggest that the hydrogen–bond network anchoring the reaction centre to the surrounding is present for trehalose and is absent for sucrose.

A research group operating at the Università di Padova in collaboration with the Université de Genève (M. Mba *et al.*, *Inorg. Chem.*, 2008, **47**, 8616) has characterized a vanadium(V) tetraphenolato complex capable of catalyzing the H_2O_2–promoted oxidation of sulfides to the corresponding sulfoxides, in quantitative yields and high selectivities.

A joint paper from the Russian “G.A. Razuvaev” Institute of Organometallic Chemistry and the CNR–ICCOM of Firenze (D.M. Lyubov *et al.*, *Organometallics*, 2009, **28**, 1227) reports that some dialkyl complexes of yttrium(III), containing the additional ligand 6–aryl–amido–pyridinato, undergo selective intramolecular sp^2 and sp^3 C–H bond activation. Metathetical reactions with $SiPhH_3$ produce the appropriate dinuclear aryl–hydrido and benzyl–hydrido metal complexes; the crystallographic analysis was carried out for two of the complexes isolated in the course of this study.

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