FROM THE LITERATURE by Fausto Calderazzo - Università di Pisa

◆ A contribution from some research institutions located at the Università di Perugia in collaboration with the RWTH Aachen [B. Blümich *et al.*, *Acc. Chem. Res.*, 2010, **43**, 357; Publication Date (Web): March 26, 2010] has reported the application of a permanent magnet to the study of art objects. Relaxation ¹H measurements are carried out, penetration of a few millimetres becoming possible for small–size devices. This technique was applied to: (a) wall paintings, (b) wood and paper, (c) old paintings, (d) mummies. The article is dedicated to the memory of Dr. Annalaura Segre, who promoted the use of the NMR–MOUSE methodology applied to objects of the cultural heritage.

♦ A review-article contributed by the Università di Pisa [F. Bellina *et al.*, *Chem. Rev.*, 2010, **110**, 1082] has appeared concerning the transition-metal-catalyzed direct arylation, with aryl halides or pseudo-halides, of compounds containing activated *sp*³-hydribized C-H bonds and some relevant synthetic equivalents. This is a convenient method for the formation of carbon-carbon bonds in the α-position with respect to electron-withdrawing functional groups. ♦ In this connection, the palladium-catalyzed arylation of 3-unsubstituted 4-chromanones [F. Bellina *et al.*, *Eur. J. Org. Chem.*, **2010**, 1339] was reported to give racemic isoflavanones in satisfactory to good yields.

The Scuola Normale Superiore di Pisa and NEST CNR–INFM [V. Tozzini, Acc. Chem. Res., 2010, 43, 220] have contributed with a paper concerning the multiscale modeling of the green fluorescent protein and the proteins involved in the human immunodeficiency virus (HIV) replication. ◆ A contribution from the Università di Pisa and the Scuola Normale Superiore di Pisa, in collaboration with some European Institutions and with the University of Toronto [A. Klamt et al., Acc. Chem. Res., 2009, 42, 489] summarizes the application of continuum solvation methods to non–aqueous media. ◆ The application of two–dimensional vibrational spectroscopy to rotaxane–based molecular machines is the subject of a contribution from the Università di Trieste in collaboration with the University of Amsterdam and the University of Edinburgh [P. Bodis et al., Acc. Chem. Res., 2009, 42, 1462]: bond distances and angles within the macrocycle can be determined by using the parameters obtained from the 2D–IR spectra.

◆ The subject of transition-metal complexes containing catenanes and rotaxanes in the perspective of their function as molecular machines was also the subject of an earlier contribution from the Université Louis Pasteur de Strasbourg [J.-P. Sauvage, *Chem. Commun.*, **2005**, 1507]. ◆ Fundamental contributions on this subject have been published by the group of Vincenzo Balzani of the Università di Bologna: details can be found in a recent book [V. Balzani, *et al.*, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2003]. ◆ The Università di Firenze [C. Andreini *et al.*, *Acc. Chem. Res.*, 2009, **42**, 1471] has contributed with a review-article dealing with an informatic approach to the study of metallo-proteoms. Specific attention was for zinc- and copper proteins, the former proteins being particularly important in higher organisms.

◆ The reaction of LiR, R=(2-CH₂NEt₂)C₆H₄, with BiCl₃ produced BiR₃ and BiCl₂R, in relative amounts depending on the molar ratios of the reagents, according to a contribution from the Università di Cagliari, in collaboration with the Rumanian Babes-Bolyal University and the Universität Bremen [A. Soran et al., J. Organometal. Chem., 2010, 695, 850]. The ligand exchange reaction between BiCl₃ and BiR₃ was also reported. The molecular structures of BiR₃, BiCl₂R, and BilR₂ have been solved by X-ray crystallography. ♦ The diphenyl derivative of bismuth(II) of formula Bi₂Ph₄ has been reported some time ago [F. Calderazzo et al., Inorg. Chem., 1988, 27, 3730; F. Calderazzo, Coord. Chem. Rev., 1992, 120, 209] and the mixed product BiPh₂SePh was crystallographically established, the synthesis consisting in the redistribution reaction between Bi₂Ph₄ and Se₂Ph₂. ♦ Three bismuth-containing carboxylato derivatives were synthesized and characterized by X-ray diffraction methods [O. Anjaneyulu et al., Dalton Trans., 2010, 39, 1935]: the synthesis consists of the treatment of Bi(NO₃)₃ with the appropriate carboxylic acid (picolinic, dipicolinic, or guinaldic), according to a contribution from the Indian University of Hydarabad.

♦ Researchers of Jilin University, PRC, report some aryloxo-cyclopentadienyl complexes of titanium(IV), whose crystal and molecular structures were solved by X-ray diffraction. Some of the new complexes were used [Q. Wu et al., Dalton Trans., 2010, 39, 2525] as catalyst precursors for the propylene polymerization and the propylene/1-hexene copolymerization, in the presence of Al/Bu₃ and $[CPh_3][B(C_6F_5)_4]$. \blacklozenge Intense and pioneering activity in this and related areas has been reported by some Italian research groups, both in industrial and academic research institutions [L. Resconi et al., J. Am. Chem. Soc., 1992, 114, 1253; G. Guerra et al., J. Am. Chem. Soc., 1997, 119, 4394; L. Resconi et al., Chem. Rev., 2000, 100, 1253; C. De Rosa et al., Cryst. Growth & Design, 2009, 9, 165; C. De Rosa et al., Angew. Chem., Int. Ed. Engl., 2010, 48, 9871]. Moreover, amorphous polyolefins have been synthesized in the EniChem Laboratories of Novara [F. Masi et al., US Patent 5,070,051, Dec. 3, 1991], the catalyst being based on alcoholates of titanium or zirconium: with these catalysts, amorphous, high MW polyolefins, possessing elastomeric properties, were obtained.

◆ Researchers of the Chinese Laboratory of Nanjing [H. Pang *et al.*, *Chem. Commun.*, 2010, **46**, 2010–2] have reported the glucose–assisted formation of copper microstructures to be used in non–enzymatic glucose sensors. ◆ A paper from the Università di Pisa has appeared [D. Preti *et al.*, *Angew. Chem.*, *Int. Ed. Engl.*, 2009, **48**, 4763] reporting the formation of highly reactive copper by reduction of CuO with alkaline formaldehyde, formate and fuel–cell grade H₂ resulting from this reaction, selectively and quantitatively. ◆ Incorporation of

CO₂/H₂ into NEt₃ produced HCOOH/ NEt₃ adducts (1.33 molar ratio) in the presence of an appropriate catalyst [D. Preti *et al.*, *Angew. Chem.*, *Int. Ed.*, 2010, **49**, 2581].

♦ A contribution from the Jiao Tang University in Shangai and from Jilin University [X–X. Zou *et al.*, *Chem. Commun.*, 2010, **46**, 2112] reports the UV light–induced formation of amorphous TiO₂ starting from titanium gly-colate Ti(OCH₂CH₂O)₂. The product thus formed performed a negligible hysteresis upon dinitrogen adsorption, suggesting a regular porous structure and a small pore diameter. ♦ The stepwise hydrolysis of the *N*,*N*–diethylcarbamato derivative of titanium(IV) Ti(O₂CNEt₂)₄ in DME has been shown in a contribution from the Università di Pisa [D. Belli Dell'Amico *et al.*, *J. Mol. Struct.*, 2008, **890**, 295] to yield a cyclic, crystal-lographically established, μ–oxo compound of formula Ti₈O₈(O₂CNEt₂)₁₆ possessing sequestering properties for NH₂Et₂[O₂CNEt₂].

The octanuclear portion of the system hosts the diethylammonium cation.

♦ A contribution resulting from the collaboration of the Università di Milano with three Indian institutions [K. Dhara *et al.*, *Chem. Commun.*, 2010, **46**, 1754] has reported that the copper(II) derivative [Cu₂(OH)(H₂O)(H₂L)](ClO₄)₂ in aqueous solution acts as a selective fluorescence sensor for the azido anion N₃⁻ [H₃L=2,6-bis-(2,2'-dimethyl)-hydroxymethyliminomethyl-4-methylpheno]].

• On the track of a long-standing tradition on the coordination properties of tetraphosphorous, researchers of the Università di Firenze and of the adjacent ICCOM-CNR Laboratory [M. Di Vaira *et al., J. Organometal. Chem.*, 2010, **695**, 816] have reported the reaction of $Fe(\eta^5-C_5H_5)Cl(dppe)$, dppe=diphenylphosphinoethane, with P_4 and P_4S_3 giving, respectively, the cyclopentadienyl derivatives $[Fe(\eta^5-C_5H_5)(dppe)(\eta^1-P_4)]PF_6$ and $[Fe(\eta^5-C_5H_5)(dppe)(\eta^1-P_4S_3)](OTf)$. • A contribution from the Università di Milano-Bicocca in collaboration with the Chinese Universities of Nanchang and Jingangshan [Z. Xiao *et al., J. Organometal. Chem.*, 2010, **695**, 721] has reported that the reaction of 2–(1 (pyridin–2–yl)ethyl)propane–1,3–dithiol with Fe₃(CO)₁₂ resulted in the formation of the di–iron–pentacarbonyl complex of formula $[Fe_2L(CO)_5]$, containing the doubly deprotonated and partially hydrogenated ligand. The resulting compound was characterized by X-ray diffraction and by conventional spectroscopic methods.

♦ A contribution from the Università di Padova and the Università di Pisa [A. Biffis *et al., J. Organanometal. Chem.*, 2010, **695**, 792] has reported that $[Rh_2(MeCN)_2(NaPhth)_4](BF_4)_4$, NaPhth=µ–1,8–naphthyridine, is a catalyst for the silylformylation of internal and functionalized alkynes. Preliminary experiments suggest that the precursor is reduced under catalytic conditions to a dinuclear rhodium(I) species.

• η^6 -Arene derivatives of ruthenium(II) have been reported as a contribution from the Università di Camerino [F. Marchetti *et al., Inorg. Chem.,* 2009, **48**, 6096]. The new compounds contain the Ru(η^6 -arene) moiety and the HL or the L⁻ ligand, HL being bis(pyrazol-1-yl)acetic acid or

bis(3,5-dimethylpyrazol-1-yl)acetic acid.

Sub-nanometric palladium particles have been formed inside a commercially available polymeric matrix, namely poly(4-ethylstyreneco-divinylbenzene) or poly(divinylbenzene-co-4-vinylpyridine). The supports were subjected to impregnation with a Pd(OAc)₂ solution followed by reduction in a H₂ atmosphere at 120 °C. The products were characterized by UV-VIS, FT-IR, and XAS spectroscopies, and by TEM microscopy. This is a contribution from the Università di Torino [E. Groppo et al., Chem. Mater., 2010, 22, 2297]. As mentioned in an earlier report of this series, work carried out at the Università di Pisa in collaboration with Alta SpA, Pisa [L. Romeo et al., 43rd Joint Propulsion Conference, July 2007, Cincinnati; 5th Int. Spacecraft Propulsion Conference, May 5-8 2008, Heraclion, Crete, Greece; 44th Joint Propulsion Conference and Exhibit, Hartford, Conn., USA, July 2008] has shown the possibility of preparing catalytic beds based on transition metals, including platinum, by using silica or γ -Al₂O₃ as the support. • A review-article describes the transformation of inexpensive graphitic precursors into graphenes (both single- and multiple layers) by using ultrasonics [G. Cravotto et al., Chem. Eur. J., 2010, in press], as a contribution from the Università di Torino and the Departamento de Química Inorgánica of the Universidad de Extremadura. Graphene is a two-dimensional material consisting of a monolayer of sp²-hybridized carbon atoms arranged in six-membered rings. • In a contribution from the New Jersey Institute of Technology [Y. Chen, Chem. Commun., 2010, 46, 1652] the hybrid system (platinum particles)/(multi-walled carbon nanotubes, MWNT) has been obtained by microwave irradiation of platinum(II) chloride, preferentially in the presence of EtOH.

♦ A contribution resulting from the collaboration of the Università di Catania with the Università di Firenze [M.E. Fragalà *et al.*, *Chem. Mater.*, 2009, **21**, 2062] describes the preparation of the hexa-fluoacetylacetonato derivative of magnesium(II) of formula Mg(htf)₂•2 H₂O•diglyme. The single–crystal X–ray diffractometry of the compound shows the hexacoordinated central metal atom to be surrounded by four oxygen atoms of the bidentate ligand and by two oxygen atoms of the water ligands. The product has been used for the chemical vapour deposition (CVD) of MgF₂ films on a glass or a quartz surface under the pressure of 2 torr and in the 350–650 °C temperature range. No magnesium oxide or carbon were detected.

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