FROM THE LITERATURE

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A feature article by A. Lattanzi, Università di Salerno (*Chem. Commun.*, **2009**, 1452) deals with α,α–diarylprolinols as organic catalysts in several asymmetric reactions.

The storage of di–hydrogen keeps on attracting considerable interest. The April 2009 issue of *Chemistry World*, page 29, points out two recent articles contributed by the Chinese Shenyang National Laboratory for Materials Science (X. Kang *et al.*, *Phys. Chem. Chem. Phys.*, 2009, **11**, 2507), and by the School of Chemistry of the University of Nottingham (Y. Yan *et al.*, *Chem. Commun.*, **2009**, 1025). The former article deals with the ammonia adduct of BH_3, namely $BH_3{\cdot}NH_3$, a compound characterized by a high di-hydrogen capacity and a moderate thermal stability, both essential properties for a valuable storage material. The latter contribution was generated from the collaboration between the University of Nottingham and General Motors Corporation. The article by X. Kang *et al.* reports that the release of dihydrogen from the ammonia adduct is promoted by the mechanical milling of the starting material in the presence of magnesium hydride MgH_2. Of course, magnesium hydride is a well–established compound going back to the fifties of last century (E. Wiberg *et al.*, *Z. Naturforsch*, 1950, **5b**, 396; *Z. Naturforsch*, 1951, **6b**, 394; *Chem. Ber.*, 1952, **85**, 593) known to spontaneously decompose at 200–300 °C (G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Vol. 1, 2nd Ed, p. 905. Academic Press, New York–London, 1963). Within the area of solid state chemistry connected with dihydrogen segregation, the above mentioned article contributed by the research group of Professor Martin Schröder (Y. Yan *et al.*, *Chem. Commun.*, **2009**, 1025) has reported on an exceptionally high di–hydrogen storage by the copper(II) derivative of the hexacarboxylato ligand originated from 1,3,5–tris(3',5'–dicarboxyl[1,1'–diphenyl]–4–yl)benzene, giving rise to a polyhedral framework. Researchers of the University of South Florida, the University of California–Santa Barbara, and the University of Nevada (F. Nouar *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 2864) have reported di-hydrogen storage properties by some zeolite–like metal-containing frameworks characterized by readily exchangeable extra–framework cations.

The collaboration of researchers of the Università di Torino with institutions in Norway and France (F. Bonino *et al.*, *Chem. Mater.*, 2009, **20**, 4957) has produced a paper dealing with the nickel(II) derivative of 2,5–dihydroxyterephthalic acid behaving as a NO absorber after removal of the metal–coordinated water.

A paper has appeared (E. Doná *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 2827) contributed by the Austrian Universities of Innsbruck and Wien reporting the halogen–induced corrosion of platinum. It is well established that etching of platinum by chlorine is promoted by carbon monoxide. The previously established chemistry of chloro–carbonyl complexes of platinum(II), namely *cis*–$PtCl_2(CO)_2$ and the corresponding dimer $Pt_2Cl_4(CO)_2$ might be relevant to the present findings (D. Belli Dell'Amico *et al.*, *J. Organometal. Chem. Soc.,* 2000, **593–594**, 427). Incidentally, an important point from a historical viewpoint is that *cis*–$PtCl_2(CO)_2$ is the first metal–carbonyl derivative reported in the literature 139 years ago (P. Schützenberger, *C.R. Hebdom*, *Acad. Sci.*, 1870, **70**, 1134): its crystal structure shows an interesting solid–state stacking with a Pt···Pt interlayer distance of 3.378 Å (F. Bagnoli *et al.*, *J. Chem. Soc., Dalton Trans.*, **1996**, 4317).

A paper resulting from the collaboration between the Università di Firenze and the Australian Eskitis Institute of Brisbane (A. Maresca *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 3057) has reported the X–ray crystal structure of the adduct between the zinc metallo–enzyme carbonic anhydrase and the natural product 6–(1*S*–hydroxy–3–methylbutyl)–7–methoxy–2*H*–chromen–2–one: no interaction has been detected between the inhibitor molecule and the metal of the active site.

Through a computational approach, researchers of the Università di Salerno (A. Poater *et al.*, *Inorg. Chem.*, 2009, **48**, 2340) have considered the conversion of copper(II) derivatives to the corresponding copper(III) complexes, as carried out through the oxidative addition of a benzyl halide. Those considered in this study were copper(I) starting complexes characterized by a tetradentate nitrogen–containing ligand: the stability of the trivalent state was calculated as a function of the substituent.

Reductive coupling of six CO molecules has been reported (T. Watanabe *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 3474) with a dihydrido derivative of tantalum. The C_6O_6 fragment thus resulting undergoes encapsulation by four tantalum–containing moieties. The crystal and molecular structure of the resulting product was reported. Carbon monoxide is not new to this type of behaviour. CO can be reduced electrochemically to the squarate anion $C_4O_4^{2-}$ (G. Silvestri *et al.*, *Electrochim. Acta*, 1978, **23**, 413). A similar behaviour has been verified with an uranium(III) complex (O.T. Summerscales *et al.*, *J. Am. Chem. Soc.*, 2006, **128**, 9602), CO being reduced to the squarate anion $C_4O_4^{2-}$, while reduction by alkali metals promotes dimerization to the acetylenediolato anion (E. Weiss *et al.*, *Helv. Chim. Acta*, 1963, **46**, 1121). Moreover, neopentyl–bis(pentamethylcyclopentadienyl)thorium chloride reacts with CO (P.J. Fagan, *et al.*, *J. Am. Chem. Soc.*, 1980, **102**, 5393) yielding a CO tetramer, which remains coordinated to the central metal atom leading to a centrosymmetric dimer containing a bridging enedione diolato ligand.

The preparation of CdSe/CdS/ZnS "double–shell" nanorods has been reported (S. Deka *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 2948) as for a contribution from several research institutions located in Italy. The ZnS shell was grown epitaxially over the CdSe/CdS nanorods, leading to a fluorescence quantum yield of the final product as high as 75%.

A contribution from the Universities of Granada, Milano and Pavia, and a CNR institution of Modena has reported the potential use of Gd_2O_3 nanoparticles in magnetic resonance imaging (MRI) (P. Sánchez *et al.*, *Dalton Trans.*, **2009**, 800). The Gd–containing nanoparticles are coated by apoferritin, which prevents the oxide from aggregating. In a similar context, a study has appeared (G. Digilio *et al*., *Chem. Commun.*, **2009**, 893) on the targeting of exofacial protein thiols with complexes of Gd(III), thus leading to an efficient procedure for MRI cell labelling.

A paper has appeared reporting DFT calculations on the reaction between bis(cyclopentadienyl)titanium(II) and N_2O going through the following sequence: $TiCp_2(N_2O) \rightarrow TiCp_2(N_2O)Cp_2Ti \rightarrow [TiCp_2]_2O + N_2$ (H. Yu *et al.*, *Organometallics*, 2009, **28**, 1158). In this connection, it is interesting to note that the oxidation state +II is readily accessible by reduction of $TiCl_4(thf)_2$ with two equivalents of sodium in tetrahydrofuran leading to $TiCl_2(thf)_n$ (F. Calderazzo *et al.*, *Z. Naturforsch*, 1996, **51b**, 506). Furthermore, the bis(cyclopentadienyl) derivatives of titanium(IV), $TiCp_2X_2$, X=Cl, Br, I, undergo reduction by $CoCp_2$ (P. Biagini *et al.*, *Gazz. Chim. Ital.*, 1987, **117**, 27) to the corresponding titanium(III) complexes, isolated as their cobalticinium derivatives $CoCp_2[TiCp_2X_2]$.

A paper from the University of California, the University of Nevada–Las Vegas, the Argonne National Laboratory, and the Department of Materials and Metallurgy of the University of Cambridge (F. Poineau *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 910) has reported the preparation and the structural data of $TcBr_3$, which is isomorphous with $RuBr_3$ and $MoBr_3$. The technetium derivative is stable in air and insoluble in the common organic solvents. It has a polynuclear structure with bridging bromides in which alternating intermetallic distances are present at 3.143 and 2.828 Å. The crystal structures of $RuBr_3$ and $MoBr_3$ (S. Merlino *et al.*, *Chem. Mater.*, 2004, **16**, 3895) were studied at the Università di Pisa for samples prepared by bromination of $Ru_3(CO)_{12}$, and of finely divided molybdenum metal, respectively. The corresponding intermetallic distances were found to be: 3.203 and 2.874 Å (Mo) and 3.127 and 2.732 Å (Ru). In this contribution the crystallographic data were collected at variable temperature, thus allowing the authors to detects the effect of this experimental parameter on the solid–state data.

Sequestration of charged or neutral species by specially designed acceptors keeps on constituting a field of active research in several laboratories. Highly selective monomethylation of primary amines through host–guest sequestration has been reported, as for a contribution from the Università di Parma (R.M. Yebeutchou *et al*., *J. Am. Chem. Soc.*, 2009, **131**, 2452). The receptor is a tetraphosphonate cavitand which efficiently interacts with *N*–methylammonium derivatives.

A joint contribution from the Universities of Salerno, Girona, and Barcelona has reported the mechanism of σ^* intramolecular aromatic hydroxylation through dioxygen activation by a macrocyclic copper(I)–containing macrocycle (A. Poater *et al*., *J. Am. Chem. Soc.*, 2008, **130**, 17710). In this theoretical contribution, the initial formation of a superoxo species, evolving to a dinuclear peroxo intermediate was taken into consideration.

A group of researchers of the Università di Padova, in collaboration with the Ruhr–Universität Bochum (G. Bandoli *et al*., *Inorg. Chem.*, 2009, **48**, 82), has reported the adduct of bis(hexafluoroacetylacetonato)cobalt(II) with N,N,N',N'–tetramethylethylenediamine. The compound presents a high volatility at moderate temperatures and it can therefore be used as a chemical vapour deposition (CVD) starting material.

A collaboration of the Università di Cagliari with the Romanian Universitatea Babes-Bolyai and the German Universität Bremen has produced a paper (A. Soran *et al*., *Dalton Trans.*, **2009**, 77) reporting the synthesis and characterization, including a solid–state X–ray investigation for two of the reported derivatives, of a series of dihalo complexes of bismuth(III) containing the new pincer ligand 2,6–$[MeN(CH_2CH_2)_2NCH_2]_2C_6H_3$.

These compounds show a T–shaped $CBiX_2$ core, a feature commonly encountered in bismuth(III) chemistry.

New chelating agents have been reported containing the N_2S_2 donor set, as a contribution from the Università di Camerino, in collaboration with the Washington University School of Medicine in St. Louis (G. Papini *et al*., *Dalton Trans.*, **2009**, 177). The corresponding copper(II) derivatives containing the ^{64}Cu isotope were synthesized and evaluated in radiotherapy.

A contribution from the Università di Padova, in collaboration with the University of Kentucky Academic Medical Center (A. Dean *et al*., *Dalton Trans.*, **2009**, 1815) has reported the results of a study dealing with the application of two carboxylic acids (1,6–dimethyl–4–hydroxy– 3–pyridincarboxylic acid and 4–hydroxy–2–methyl–3–pyridinecarboxylic acid) and their iron(III) and aluminium(III) complexes, in the perspective of their use in chelation therapy.

The collaboration of researchers of the Istituto ICCOM–CNR of Firenze with the Institut für Allgemeine, Anorganische und Theoretische Chemie der Universität Innsbruck has produced a paper (M. Fessler *et al*., *Dalton Trans.*, **2009**, 1859) dealing with a novel linkage–isomeric pair of dinuclear palladium(II) complexes of a bis–bidentate tetraphos ligand. Two of the reported compounds were tested for their activity in CO/ethene copolymerization and in the CO/ethene/propene terpolymerization.

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