FROM THE LITERATURE by Fausto Calderazzo - Università di Pisa

♦ A Perspective Article published in Dalton Trans., 2010, 1673, by G. Süss-Fink of the Université de Neuchâtel has reviewed the chemistry of ruthenium-arene complexes and their use as anticancer agents. The Author points out that the rates of ligand exchange in aqueous solution are similar for platinum(II) and ruthenium(II), the latter, of 4d⁶ electronic configuration, being therefore a good candidate in this kind of therapy, in view of its low toxicity. • In this connection, it should be noted that some years ago the preparation and properties, including the crystallographic data, of the fac-[Ru(CO)₃(H₂O)₃]+2 cation, isolated as the tetrafluoborato derivative, were reported. The latter was crystallographically characterized and shown to be stable only in the solid state and in strongly acidic solution, as reported in a contribution from the Università di Pisa [T. Funaioli et al., Inorg. Chem., 1999, 38, 3361]. ♦ S.L. Binkley et al. [Chem. Commun., 2010, 46, 1203], in a contribution from the University of Akron, the College of the Holy Cross, and Colgate University located in Hamilton, NY, have reported that the reaction of the aquo-complex of rhenium(I), a 5d⁶ system, of formula [Re(CO)₃(H₂O)₃]+, with the hen egg lysozyme in an aqueous medium yields an adduct where the metal cation is bonded to the His15 site. The biological action of these complexes is probably to be related to the rather inert character of the metal centre, allowing the active chemical to be released at the appropriate site before under-atives of ruthenium(II) containing p-methyl-iso-propylbenzene as supporting ligand have been reported [D. Belli Dell'Amico et al., J. Organometal. Chem., 2002, 651, 52], as a contribution from the Università di Pisa.

◆ A publication from two research Institutions of the Università della Calabria [A.M. Talarico *et al.*, *Dalton Trans.*, 2010, **39**, 1709] located in Arcavacata di Rende deals with the highly luminescent feature of a bis-cyclometalated cationic complex of iridium(III) containing ethylenediamine and two deprotonated groups derived from 2-phenylpyridine. The solid-state properties of this system characterized by a distorted octahedral geometry of the metal centre have been studied: two polymorphs of this compound have been isolated, studied crystallographically and for their photophysical properties.

◆ A contribution from the Università di Bologna [N. Sändig *et al.*, *Chem. Commun.*, 2010, **46**, 667] has reported on a semi–empirical computational model able to describe the behaviour of molecules adsorbed on a gold surface, particularly as far as mobility and reactivity are concerned.

♦ The collaboration between the Università di Padova, the Université de Versailles and the Universität Stuttgart has resulted in the elucidation of the interaction products of the oxo–cluster $Zr_6O_4(OH)_4(OMe)_{12}$ with some dicarboxylic acids (*trans, trans*–muconic acid, terephthalic acid). Porous dicarboxylato compounds were obtained under mild conditions with a controlled particle size distribution [V. Guillerm *et al.*,

Chem. Commun., 2010, 46, 767].

◆ An *in situ* X-ray diffraction study of the cobalt-catalyzed Fischer-Tropsch reaction has been reported as for a joint contribution from the Université de Lille, Total Petrochemicals, and the Swiss-Norwegian Beamlines located in Grenoble [H. Karaca *et al.*, *Chem. Commun.*, 2010, **46**, 788]. Catalyst (cobalt on alumina) deactivation coincides with sintering followed by carbide formation.

♦ A contribution from the Institutes ICCOM-CNR and INSTM of Trieste, in collaboration with the Università di Venezia and the University of Pennsylvania [M. Cargnello et al., Dalton Trans., 2010, 46, 2122] has reported the preparation of Pd/CeO₂ catalysts, as obtained by co-precipitation of palladium nanoparticles in the presence of ceria. The resulting catalytic systems were used in the water-gas-shift (WGS) reaction: good stability was exhibited by the catalyst prepared according to a microemulsion technique. • A paper by D. Gianolio et al. of the Università di Torino [Chem. Commun., 2010, 46, 976] reports that chromium(II) grafted on silica undergoes adsorption of carbon monoxide at 100 K, as evidenced by in situ temperature-dependent XAFS measurements. Upon CO adsorption, chromium is extracted from the surface, the process occurring in two separate steps: (a) displacement of weakly bonded siloxane groups; (b) bonding of CO and relaxation to the classical Cr-CO bonding situation.

◆ Researchers of the Università di Sassari [G.L. Petretto *et al., J. Organometal. Chem.*, 2010, **695**, 256] have reported the palladium-catalyzed synthesis of 2-(pyridin-2-yl)-6-*R*-nicotinic acid and ester by carbonylation of 6-alkyl-substituted 2,2'-bipyridines.

♦ The interaction of the carbonyl–hydrido derivative of $4d^4$ molybdenum(II) of formula Mo(η^5 –C₅Me₅)H(CO)(PMe₃)₂ with Brønsted– and Lewis acids has been reported, as for a contribution from the Russian Academy of Sciences in Moscow and the Université de Toulouse [P.A. Pub *et al.*, *Dalton Trans.*, 2010, **39**, 2008]. The carbonyl groups were found to be the predominant site of attack by weak acids, while stronger proton donors [(CF₃)₃C–OH and CF₃COOH] prefer to form hydrogen–bonds to the hydride ligand.

• The Università di Milano and the Indian Jadavpur University have collaborated [P. Roy *et al.*, *Dalton Trans.*, 2010, **39**, 1539] in the preparation of new tetranuclear phenolato copper(II) complexes of formula $Cu_4(O)(L)_2(CH_3COO)_4$, LH being the starting reagent containing the phenolic function.

◆ The collaboration of the Université de Namur with some other European Universities (Trieste, Padova and Antwerp) [J.–F. Colomer *et al., Chem. Mater.*, 2009, **21**, 4747] deals with the microwave–assisted bromination of double–walled nanotubes (DWCNT). A 5–8% of functionalization was obtained through a repeated bromination procedure.

• Imine complexes of ruthenium and osmium have been prepared

according to a contribution from the Università di Venezia [G. Albertin *et al.*, *J. Organometal. Chem.*, 2010, **695**, 574] by reacting the precursors $MCl_2(\eta^6-p-cymene)(PR_3)$ with benzylazide in the presence of NaBH₄. The molecular structure of the complex of formula $\{RuCl((\eta^6-p-cymene)(\eta^6-NH=CH-p-tolyl)[PPh(OEt)]_2\}^+$ as its tetraphenyl borato derivative has been described.

• New di-organo derivatives of tin(IV) with L-arginine, *Na-t*-Boc-L-arginine and L-alanyl-L-arginine have been studied for their structural and citotoxic properties, according to a contribution from the Università di Palermo [M.A. Girasolo *et al., J. Organometal. Chem.*, 2010, **695**, 609].

◆ Metallacyclic dithiocarbamato complexes of palladium(II) of formula PdCl(L)(PR₃), L being a dithiocarbamato group, were prepared and characterized by conventional methodologies. Two of the complexes, characterized by X-ray crystallography, were shown to display a slightly distorted square-planar geometry around the central metal atom. Some of the complexes were found to be active against some fungi. This is a contribution from the Università di Alessandria in collaboration with other Universities [F. Shaheen *et al., J. Organometal. Chem.*, 2010, **695**, 335].

♦ Visible- and UV light trigger the formation of gold nanoparticles with a size distribution comprised between 3 and 30 nm: different methodologies were used to obtain the required size of the particles, as for a contribution from several European research Institutions [C. Raimondo et al., Chem. Commun., 2010, 46, 1147]. The smaller particles were obtained by reducing tetrachloroauric acid with NaBH₄ in the presence of octadecylamine; the medium-size particles resulted from the reduction of the gold-containing product with citrate, while the bigger particles were formed upon reaction with NaBH₄ in the presence of hexylamine. A contribution by D. Gianolio et al., of the Università di Torino [Chem. Commun., 2010, 976] describes the adsorption of chromium(II) on a SiO₂ surface, the mobility and extraction of the adsorbed cation in the presence of carbon monoxide at 100 K being investigated by XANES and EXAFS spectroscopies. • Formation of silica-supported gold nanoparticles has been reported as a contribution from some Italian research institutions [L. Abis et al., J. Chem. Soc., Dalton Trans., 2001, 2704] starting from AuCI(CO) as a precursor. The resulting violet gold-containing silica was characterized by XPS, TEM, XRD, and UV spectra. Based on XRD experiments, the average particle size was found to be 11 nm.

• A paper resulting from the collaboration of the Università dell'Insubria in Como with the Universidad de Murcia [J. Vicente *et al.*, *Chem. Commun.*, 2010, **46**, 2704] has reported the self-assembly of looped triple-stranded helicates obtained by reacting organo-gold derivatives of formula [(AuC=CbpyI)₂(μ -Ph₂PCH₂CH₂CH₂CH₂PPh₂)], bpyI=2,2'-bipyridine-5-yl, with iron(II)- and zinc(II) perchlorate.

A contribution from the Università di Palermo in collaboration with

other Italian Universities [G. Ruisi *et al., J. Organometal. Chem.*, 2010, **695**, 546] has described some trialkyl– and triaryl derivatives of tin(IV) containing the conjugate base of 7–amino–2–(methylthio)[1,2,4]triazolo[1,5–a]pyrimidine–6–carboxylic acid. The compounds were characterized by spectroscopic methods and by X–ray crystallography for two of them.

• A paper has described the preparation of chiral and non-chiral complexes of osmium(II) of $5d^{6}$ electronic configuration, as a contribution from the Università di Udine [W. Baratta *et al.*, *Chem. Eur. J.*, 2010, **16**, 3201]. The complexes, of formula OsX₂(diphosphane)-(diamine), X=CI, OR, have an unprecedented activity in the hydrogenation of ketones and aldehydes with turn-over frequencies up to $3x10^{5}h^{-1}$, and molar substrate/catalyst ratioes as high as $2x10^{5}$. The osmium-ligated diphosphane is 1,1'-bis(diphenylphosphino)-ferrocene, while the diamine is $H_2N(CH_2)_nNH_2$, n=2, 3.

♦ A contribution from Cornell University [M.C. Orilall *et al.*, *J. Am. Chem. Soc.*, 2009, **131**, 9389] reports the incorporation of platinum nanoparticles in a composite constituted by niobium oxide and carbon. Loading of Carbon Vulcan with several metals including platinum has been reported. ♦ Work carried out at the Università di Pisa in a collaboration with Alta SpA, Pisa [L. Romeo *et al.*, 43rd Joint Propulsion Conference, July 2007, Cincinnati; 5th Int. Spacecraft 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 support, utilized in hydrogen peroxide decomposition.

• Silica was loaded with palladium or platinum by using the halo-carbonyl complexes of formula $M_2(\mu-Cl)_2Cl_2(CO)_2$, M=Pd, Pt. These precursors contain the correct amount of coordinated CO required to carry out the reduction of the central metal atom to its zerovalent state. This is a contribution from the Università di Pisa, in collaboration with the Università di Padova, and the Istituto "G. Donegani" of Novara [L. Armelao *et al.*, *Dalton Trans.*, **2009**, 5559]. • A publication resulting from studies carried out at the Università di Brescia [I. Alessandri *et al.*, *Chem. Commun.*, **2009**, 2359] describes the formation of citrate-stabilized gold nanoparticles and their utilization in the crystallization of titanium dioxide by plasmon heating through irradiation with a low-power continuous-wave He-Ne laser.

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