FROM THE LITERATURE

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F.A. Cotton and his colleagues (F.A. Cotton *et al., J. Am. Chem. Soc.,* 2007, **129,** 12666) have reported the X–ray crystal structure, as obtained at variable temperature, of the N,N–diphenylformamidinato (DPhF) derivative of mixed–valent ruthenium of formula $[Ru_2(OAc)(DPhF)_3(H_2O)][CF_3SO_3] \cdot {}^1/_2CH_2Cl_2$. The crystals contain two independent molecules with ruthenium–ruthenium distances, at 30 K, of 2.3637(6) Å for Ru(1)–Ru(2) and 2.3950(6) Å for Ru(3)–Ru(4). At room temperature, the corresponding distances are 2.3255(5) and 2.3064(5) Å.

In the preceding report of this series mention had been made of the contribution by the group of Prof. T.J. Marks at Northwestern University (N. Guo *et al., J. Am. Chem. Soc.,* 2008, **130,** 2246) describing the homo–polymerization of styrene and the ethylene/styrene (E/S) co–polymerization in the presence of titanium– or zirconium–based bimetallic catalysts, with $B(C_6F_5)_3$ as activator. A paper from the research laboratories of Dow Chemical Company (D.J. Arriola *et al., J. Am. Chem. Soc.,* 2007, **129,** 7065) shows that E/S co–polymerization can be catalyzed by mononuclear titanium derivatives containing substituted cyclopentadienyl groups [with $B(C_6F_5)_3$ as activator], the best results in terms of styrene content being obtained by using a catalytic precursor of titanium containing a cyclopentadienyl group with a biphenyl substitution condensed to it, of formula $C_{17}H_{11}^-$. In this connection, relevant is an article by the Università di Salerno (C. Pellecchia, L. Oliva, *Rubber Chem. Technol.,* 1999, **72,** 553, and refs. therein) reviewing the studies on E/S polymerization, carried out at that University under the supervision of Prof. A. Zambelli: E–S co–polymers containing up to 35 mol% of styrene were obtained by using the $Ti(Cp)Cl_3$/methylalumoxane (MAO) catalytic system. The mechanism of stereocontrol in the polymerization of 1–alkenes promoted by traditional Ziegler–Natta catalysts has been discussed by P. Corradini, G. Guerra, L. Cavallo (*Acc. Chem. Res.,* 2004, **37,** 231). The co–polymerization of olefins with unsaturated monomers bearing a polar function is an interesting area of research: C. Carlini *et al.* (*Macromol. Chem. Phys.,* 2002, **203,** 1606) have reported the co–polymerization of ethylene with methyl methacrylate by using a catalytic system consisting of MAO and some sterically hindered Schiff base complexes of nickel.

The mechanism of formation of branched polyethylene in a catalytic system consisting of a metallocene and MAO has been studied at the Università di Salerno by both theoretical and experimental methods (L. Caporaso *et al., Organometallics,* 2008, **27,** 1367). Branch formation has been suggested to involve two diastereotopic sites.

New azolato ligands have been prepared through the equimolar condensation of 3,5–diamino–1,2,4–triazole with salicylaldehyde, the resulting deprotonated ligand H_2L forming the corresponding copper complex of formula $[Cu(H_2L)(MeCN)]_2$. The latter was found (G.A. Ardizzoia *et al., J. Organometal. Chem.,* 2008, **693,** 1870) to be a highly diastereoselective catalyst for olefin cyclopropanation in the presence of ethyl diazoacetate.

Organic nitriles are generally regarded as weak ligands (J.A. Davies, F.R. Harthley, *Chem. Rev.,* 1981, **81,** 79). Information about the CO/EtCN competition for platinum(II) can be found in a recent article (D. Belli Dell' Amico *et al., Inorg. Chim. Acta.,* 2007, **360,** 3765). The displacement of acetonitrile by CO in (*cis* + *trans*)–$PtCl_2(CO)(NCEt)$ to give *cis*–$PtCl_2(CO)_2$ is characterized by the following thermodynamic parameters: $K_{eq} = 48\pm6$ at 23.4 °C; $\Delta G^0 = -9.5\pm0.3$ kJ mol^{-1}.

A paper co–authored by A. Credi (M. Amelia *et al., Chimia.,* 2008, **62,** 204) of the Dipartimento di Chimica, Università di Bologna, has reviewed the problem of artificial molecular machines based on rotaxane–type structures.

The collaboration between the Università di Verona and two USA research institutions (T.K. Ahn *et al., Science,* 2008, **320,** 794) has produced a paper describing the charge transfer between the coupled molecules of chlorophyll and zeaxanthin in the light–harvesting antenna of Photosystem II (PSII).

Related to the recent discoveries by E. Carmona *et al.,* see a preceding Report of the present series, on the methyl–substituted cyclopentadienyl derivatives of Zn(I) containing a Zn–Zn bond, is a contribution from the Laboratory of Theoretical and Computational Chemistry of the University of Jilin, PRC (N. He *et al., Organometallics,* 2007, **26,** 6839): the stability of complexes of the type CpM–M'Cp (M=Li, Na, K; M'=B, Al, Ga, In, Tl), with the elements of Group 13 in their +I oxidation state has been discussed. In this connection it has to be noted that a *feature article* (A.H. Cowley, *Chem. Commun.,* 2004, 2369) had previously summarized the experimental and theoretical results obtained in the author's laboratory and in other research institutions on the donor–acceptor bond involving elements of Group 13 in their +I oxidation state, showing that the HOMO of the univalent $M(\mu^5–C_5Me_5)$ system has a lone–pair character. The list of references therein is a useful repertory of the theoretical and experimental work carried out in that area.

Imido–amido complexes of tantalum on the silica surface or on MCM–41 (MCM is the acronym for Mobile Crystalline Material, an ordered silicate mesoporous material) have been obtained by reacting the supported hydrido complexes $[(=SiO)_2TaH]$ or $[(=SiO)_2TaH_3]$ with NH_3 at room temperature (P. Avenier *et al., J. Am. Chem. Soc.,* 2007, **129,** 176). This paper was contributed by three European research institutions including the Laboratoire de Chimie Organométallique de Surface headed by J.–M. Basset. Thus, the surface complex $[(=SiO)_2Ta(NH)(NH_2)]$ was obtained and characterized by solid–state NMR, IR and EXAFS data.

A contribution from different laboratories in Grenoble, Firenze and Modena coordinated by D. Gatteschi of the Università di Firenze (A.–L. Barra *et al., J. Am. Chem. Soc.,* 2007, **129,** 10754) has reported single–crystal high–frequency EPR spectroscopy on a single–molecule–magnet of formula $[Mn_{12}O_{12}({}^tBuCH_2CO_2)_{16}(MeOH)_4] \cdot MeOH$, a mixed–valence derivative of Mn(III)/IV).

A paper from the Università di Firenze (C. Bazzicalupi *et al., J. Am. Chem. Soc.,* 2008, **130,** 2440) has reported the first crystal structure of an adduct between thymidine–5´–triphosphate and a synthetic receptor constituted by two terpyridine moieties bridged by two diamine residues. The interaction is mainly carried out by hydrogen bonds between the polyphosphate chain of the nucleotide and the protonated nitrogen atoms of the receptor, further supported by other weak interactions.

A paper contributed by the Università della Calabria, the Università di Firenze and the Universidad de Valencia (D. Armentano *et al., Inorg. Chem.,* 2008, **47,** 3772) has presented some oxalato–bridged anionic complexes of iron(III) of formula $\{[Fe_2O(C_2O_4)_2Cl_2]^{2-}\}_n$. The compound $[EtNH_3][Fe_2(OH)(C_2O_4)_2Cl_2] \cdot 2\ H_2O$ undergoes a solid–state transformation to the new species $[(EtNH_3)(H_3O)][Fe_2(O)(C_2O_4)_2Cl_2] \cdot H_2O$, both compounds being characterized by X–ray crystallography.

A contribution from the Università di Milano in collaboration with the Universidad de Granada (E. Barca *et al., Dalton Trans.,* 2008, 1825) reports the preparation of a two–dimensional organometallic/coordination system by reacting the dinuclear anion $[Re_2(\mu\text{–}1,2,4\text{–triazolato})_2(\mu\text{–}OH)(CO)_6]^-$ with Ag^+. The resulting product of formula $Ag[Re_2(\mu\text{–}1,2,4\text{–triazolato})_2(\mu\text{–}OH)(CO)_6] \cdot 4n\ MeOH$ undergoes reversible structural changes upon desorption/absorption of guest molecules (e.g. N_2, CO), with a moderate gas storage capacity.

In a paper in collaboration (Laboratoire de Chimie de Coordination of Toulouse, the Universidad de Almeria and the CNR Istituto di Chimica dei Composti Organometallici of Firenze) two new series of phosphorous–containing dendrimers (from the ancient Greek word δενδρον, meaning tree) capped by bis(diphenylphosphinomethyl)amino groups linked to tyramine or L–tyrosine methyl ester have been reported (P. Servin *et al., Organometallics,* 2008, **27,** 2066). The corresponding palladium complexes were used in some catalytic reactions for three types of C–C coupling reactions.

In a paper (C. Giansante *et al., Angew. Chem.,* 2008, **47,** in press) in collaboration between the Dipartimento di Chimica of the Università di Bologna, and the Kekulé–Institut für Organische Chemie und Biochemie, Universität Bonn, the effect has been studied of adding $Nd(CF_3SO_3)_3$ to a $MeCN/CH_2Cl_2$ solution of a dendrimer containing ether groups and a central cavity with four tertiary amine functions, in combination with $Ru(bipy)_2(CN)_2$. The luminescence of the ruthenium(II) complex was quenched, while that of Nd(III) was sensitized.

A contribution from three research institutions (Università di Padova, Università di Trieste, Princeton University) has reported the isolation of a γ–decatungstosilicate supporting a tetra–ruthenium(IV)–oxo core which acts as a water oxidation catalyst (A. Sartorel *et al., J. Am. Chem. Soc.,* 2008, **130,** 5006). The resulting product, of formula $Cs_{10}[Ru_4(\mu\text{–}O)_4(\mu\text{–}OH)_2(H_2O)_4(\gamma\text{–}SiW_{10}O_{16})_2]$, was obtained by reacting the $[\gamma\text{–}SiW_{10}O_{36}]^{8-}$ anion with $[Ru_2OCl_{10}]^{4-}$ in aqueous solution. The corresponding lithium derivative was reacted with an excess of cerium(IV) and the catalytic activity towards water oxidation was evaluated.

A group operating at the Università di Sassari has reported some new cyclometalated hydrido complexes of platinum(II) containing additional nitrogen–based donor atoms of general formula Pt(N–N–C)H, where N–N–CH is a 6–R–2,2’–bipyridyl (A. Zucca *et al., Organometallics,* 2007, **26,** 5621).

A paper contributed by the University of Wisconsin–Madison (E.G. Mednikov, M.C. Jewell, L.F. Dahl*, J. Am. Chem. Soc.,* 2007, **129,** 11619) describes the synthesis (yield <10%) and the molecular and crystal structure of a nanosized palladium/platinum compound of formula $(\mu_{12}\text{–}Pt)Pd_{164-x}Pt_x(CO)_{72}(PPh_3)_{20}$, $x \approx 7$, that was claimed to be the largest crystallographically determined discrete transition metal cluster with direct metal–metal bonds. The product was synthesized from $Pd_{10}(CO)_{12}(PPh_3)_6$ and $Pt(CO)_2(PPh_3)_2$, the Pd/Pt molar ratio being about 10. Related to this new finding are the data by I.I. Moiseev and his coworkers (M.N. Vargaftik *et al., J. Chem. Soc., Chem. Commun.,* 1985, 937; *Faraday Discuss.,* 1991, **92,** 13; T.A. Stromnova, I.I. Moiseev, *Russ. Chem. Rev.,* 1998, **67,** 485) who synthesized the so–called “palladium–561 cluster”, as obtained by reducing $Pd(OAc)_2$ with H_2 in the presence of 1,10–phenanthroline or 2,2’–dipyridyl. The cluster (no single crystal appropriate for a X–ray data collection could apparently be obtained) was characterized by electron microscopy and EXAFS. The diameter of the particles was evaluated to be 26±3.5 Å, consistent with the specified nuclearity.

Conductive nanowires have recently been prepared starting from anionic platinum–carbonyl clusters of formula $[Pt_{3n}(CO)_{6n})]^{2-}$, $n = 4 \div 6$, as reported through a collaboration within three different research institutions located in Bologna (P. Greco *et al., J. Am. Chem. Soc.,* 2008, **130,** 1177). The precursor particularly used was the $[Pt_{15}(CO)_{30}]^{2-}$ anion, whose tetrabutylammonium derivative was crystallographically established in 1974 (J.C. Calabrase, L.F. Dahl, P. Chini, G. Longoni, S. Martinengo, *J. Am. Chem. Soc.,* 1974, **96,** 2614; G. Longoni, P. Chini, *J. Am. Chem. Soc.,* 1976, **98,** 7225).

Gold nanoparticles stabilized by a palladium(II) thiolato–acetylide function have been reported (F. Vitale *et al., J. Organometal. Chem.,* 2008, **693,** 1043). They were characterized by XRD, TEM and XPS analyses, and shown to possess a homogeneous size distribution.

A contribution from the Dipartimento di Chimica, Università della Calabria (M. Leopoldini *et al., J. Am. Chem. Soc.,* 2007, **129,** 7776) has studied, at the DF/B3LYP level of theory, the catalytic hydrolysis of a methionyl–peptide substrate by a methionine aminopeptidase active site model, both in the gas phase and in the protein environment, the rate–determining step of the process being the nucleophilic addition of hydroxide.

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