FROM THE LITERATURE

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Among the recent results of general interest, two papers can be mentioned. One of them (K.F. Hirsekom *et al., J. Am. Chem. Soc.,* 2008, **130**, 1183) reports a number of metal complexes of Group 5 of formula [M(OSi^{t}Bu)$_3$(olefin)] with M = Nb, or Ta: the rate of olefin dissociation was found to be much faster for the niobium derivatives than for the corresponding tantalum complexes, thus confirming the general trend to a more pronounced lability of the 4d derivatives with respect to their 5d homologues. A contribution, somewhat related to the previous one in terms of periodic trends of metal–ligand bond properties, deals with the gas–phase enthalpies of formation of a number of organometallic derivatives whose central metal atom belongs to a Group from 12 to 16 (J. Jover *et al., J. Organometal. Chem.,* 2008, **693**, 1261): of considerable interest is the series of the tetramethyl derivatives of Group 14 having experimental ΔH^0_f (kJ x mol^{-1}) in the sequence: Ge (–107.5), Sn (–10.1), Pb (+118.8). This is the general trend one would have expected in a series of *typical* Main Group elements within a given vertical sequence.

The July 2007 issue of *Acc. Chem. Res.* is dedicated to the problem of dioxygen activation by metallo-enzymes and their models, a problem of great interest since several decades. Mention should also be made of the December 2007 issue of *Acc. Chem. Res.* which is totally dedicated to hydrogenation and transfer hydrogenation phenomena.

Metal–catalyzed oxidations and epoxidations of unsaturated hydrocarbons continue to be under careful scrutiny by researchers for their implications in obtaining functionalized organic molecules. The research group of the University of Venezia headed by G. Strukul (M. Colladon *et al., J. Am. Chem. Soc.,* 2007 , **129**, 7680) has reported the highly active and complete substrate selectivity in the epoxidation of terminal alkenes performed by a catalyst precursor consisting of a cationic platinum complex, whose coordination positions are occupied by two phosphorous atoms of a bidentate ligand, a pentafluorophenyl group, and a water group, with CF$_3$SO$_3^-$ as counteranion. A somewhat related paper (C.N. Cornell *et al., Inorg. Chem.,* 2007, **46**, 1903) has paid particular attention to the role of copper in the palladium–catalyzed oxidation of olefins to carbonyl products. In this context, reference should be made to the original paper by J. Smidt and coworkers (*Angew. Chem.,* 1959, **71**, 176), through which the primary data on the Wacker process (*alias* the Hoechst–Wacker process) had been reported in the open literature. Selectivity in catalysis has been discussed by A. Zecchina *et al.* in a review–article (*Chem. Eur. J.,* 2007, **13**, 2440), especially covering the specific cases of hydrogenation and polymerization of alkenes.

The photogeneration of dihydrogen from water on TiO$_2$ in the presence of di–imine–dithiolatoplatinum(II) complexes has been communicated (J. Zhang *et al., J. Am. Chem. Soc.,* 2007, **129**, 7726): particularly efficient sensitizers are two square–planar complexes of platinum(II) with a set of N$_2$S$_2$ donor atoms, *i.e.* substituted 2,2'–dipyridyl and dithiolato ligands. On a related subject, a paper by researchers of the University of Perugia, in collaboration with the University of Princeton and the Lausanne Federal Institute of Technology (F. De Angelis *et al., J. Am. Chem. Soc.,* 2007, **129**, 14156) confirms an injection mechanism for ruthenium(II) dyes on TiO$_2$.

Still on problems of periodicity, a recent paper by K.N. Raymond and his co–workers from the University of California (M. Seitz *et al., J. Am. Chem. Soc.,* 2007, **129**, 11153) has reported crystallographic data on a series of heptacoordinated lanthanide complexes: six of the seven oxygen donor atoms originate from a hexadentate ligand, the coordination sphere being completed by a water group. Some earlier papers from the University of Pisa had reported crystallographic and metric data for a series of heptacoordinated mononuclear lanthanide complexes with bidentate oxygen donor ligands (U. Baisch *et al., Eur. J. Chem.,* 2004, 1219). The trend of the metric data along the series of elements was confirmed for lanthanide complexes containing monodentate anionic ligands of formula [LnCl$_3$(DME)$_2$]$_n$, n=1 or 2, DME=2,2'–dimethoxyethane (U. Baisch *et al., Inorg. Chim. Acta,* 2004, **357**, 1538): for this series covering a range of 12 atomic numbers, the plot of the individual metal–ligand bond distances *vs.* the 4d^n electronic configuration is best described by an expression of the following type: d(Ln-Cl) = A$_0$ – A$_1$n + A$_2$n^2. An earlier communication from the University of Pisa (E.A. Quadrelli, *Inorg. Chem.,* 2002, **41**, 167) on the isotypical cationic aquo–complexes [Ln(OH$_2$)$_9$][EtOSO$_3$]$_3$ has pointed out that the Ln–O bond distances fit the above quadratic decay across this series of compounds covering the whole sequence of lanthanide elements (with the sole exception of the Pm derivative, whose structural data are not yet available).

An award article (W.J. Evans, *Inorg. Chem.,* 2007, **46**, 3435) represents a most interesting overview of the organometallic chemistry of 4f and 5f elements carried out in the Author's laboratory.

One of the most prominent recent results in organometallic chemistry has been obtained by a group of researchers of the University of Sevilla under the supervision of Ernesto Carmona (I. Resa *et al., Science,* 2004, **305**, 1136). In the October 15th issue of that year the compound Zn$_2$(η^5–C$_5$Me$_5$)$_2$ of Zn(I) has been reported, the molecular structure by X–ray diffraction methods at low temperature being included. A more recent paper by the same group (A. Grirrane *et al., J. Am. Chem. Soc.,* 2007, **129**, 693) describes the crystal and molecular structure of the above product and of its homologue Zn$_2$(η^5–C$_5$Me$_4$Et)$_2$, whose preparative procedure can be found in a subsequent description (*J. Am. Chem. Soc.,* 2007, **129**, 14100). Also, aryl molecular compounds of Zn(I), Cd(I), and Hg(I) have been synthesized by the group of P.P. Power at the University of California–Davis (Z. Zhu *et al., J. Am. Chem. Soc.,*

2007, **129**, 10847): these compounds have the formula Ar'M–MAr', Ar' = C_6H_3–2,6–$(C_6H_3$-2,6–$^iPr_2)_2$. The metal-metal bond distance in the zinc derivative is 2.3591(9) Å, to be compared with the value of 2.305(3) Å in $Zn_2(\eta^5–C_5Me_5)_2$. Recently, also the molecular structure has been reported of a compound containing a Zn(I)–Zn(I) bond in a coordination environment including a doubly reduced α–di–imine ligand (X.-J. Yang *et al., Chem. Commun.,* 2007, 2363): in this case the Zn–Zn separation has been reported to be 2.399(1) Å.

K.G. Caulton and his co–workers (R. Dale Rimmer *et al., J. Am. Chem. Soc.,* 2007, **129**, 15430) have carried out flash photolysis experiments on a cobalt(I) derivative containing a tridentate phosphorous–nitrogen-phosphorous set of donor atoms, of formula Co(PNP)(CO). The transient produced by photodissociation of CO oxidatively adds across the C–H bond of an internal ^tBu group. It is of interest that ligand–stabilized organometallic derivatives of cobalt(I) have a long–standing tradition in inorganic chemistry. Equilibria involving di–hydrogen and di–nitrogen were reported as early as 1967 (A. Sacco, M. Rossi, *Chem. Commun.,* 1967, 316; M. Rossi, A. Sacco, *ibidem,* 1969, 471) for cobalt(I) with phosphorous–based supporting ligands. The propensity to bind "small" molecules, including H_2, is well established nowadays for several PR_3–substituted metal centres including molybdenum(0) and tungsten(0), of nd^6 electronic configuration, as shown by G.J. Kubas and his co–workers [e.g., see: *J. Am. Chem. Soc.,* 1984, **106**, 451; idem, *ibidem,* 1986, **108**, 7000; G.J. Kubas, "Metal Dihydrogen and σ–Bond Complexes", Kluwer Academic/Plenum Publishers, New York, 2001). It is of interest to note that M. Aresta, P. Giannoccaro, M. Rossi, and A. Sacco (*Inorg. Chim. Acta,* 1971, **5**, 115) had reported the synthesis and properties of iron complexes of formula FeH_4L_3, L=$PEtPh_2$, $PBuPh_2$, and carefully noted that they display a broad unusual IR band at 2380÷2400 cm^{-1}. Only through a neutron diffraction study on the $PEtPh_2$ derivative carried out by G.J. Kubas, K.G. Caulton and their co–workers (L.S. Van Der Sluys *et al., J. Am. Chem. Soc.,* 1990, **112**, 4831) was it possible to conclude that the compound reported 19 years earlier actually contained a dihydrogen ligand and therefore had to be formulated as a dihydrido–dihydrogen derivative of iron(II), namely $Fe(H_2)(H)_2(PEtPh_2)_3$ in an octahedral *cis, mer* coordination around the central metal atom. The H–H separation within the dihydrogen ligand is 0.821(10) Å. The authors also pointed out that an X–ray diffraction experiment turned out to be unsuccessful in solving the molecular structure. A review–article on the coordination chemistry of di–hydrogen has also appeared (D.M. Heinekey *et al., Chem. Rev.,* 1993, **93**, 913).

Metallocene chemistry is still an area of intense research activity in relation to olefin polymerization. In a joint paper from the Universities of Perugia and East Anglia (C. Alonso–Moreno *et al., J. Am. Chem. Soc.,* 2007, **129**, 9282), NMR data evidence the formation of mixed–ion aggregates in the interaction of a trityl activator with the neutral zirconium(IV) precursor to give [*rac*–$Me_2Si(1$-indenyl$)_2Zr$– CH_2 $SiMe_3^+$…$B(C_6F_5)_4^-$] or [$Me_2C(C_5H_4)(9$–fluorenyl$)^+$…$B(C_6F_5)_4^-$]. The catalytic activity in olefin polymerization depends on the molar ratio between the metallocene derivative and [CPh_3][$B(C_6F_5)_4$]. Aggregation of ion pairs favours the catalytic activity.

Trinuclear complexes were prepared (C. Görl, H.G. Alt, *J. Organometal. Chem.,* 2007, **692**, 5727) by combining zirconocene derivatives with a phenoxy–imine of zirconium, and used as catalytic precursors in the polymerization of ethylene, after activation with methylalumoxane. Due to the presence of zirconium centres of a different nature in the precursor, broad or bimodal molecular weight distributions of the polymer were obtained.

A paper contributed by some academic and industrial groups coordinated by S. Aime of the University of Torino (D. Dalli Castelli *et al., Inorg. Chem.,* 2008, **47**, 2928) has reported that lanthanide-loaded paramagnetic liposomes undergo orientation in a static magnetic field depending on the sign of their magnetic susceptibility anisotropy ΔX, whose properties (magnitude and sign) depend on the nature of the lanthanide ion (Gd, Dy, or Tm).

A contribution by the Universität Duisburg-Essen and McMaster University (K. Koppe *et al., Inorg. Chem.,* 2008, **47**, 3205) has reported new derivatives of the [$Xe(C_6F_5)$]$^+$ cation with weakly coordinating anions [BY_4]$^-$, Y=CN, CF_3, C_6F_5. The X–ray structures of [$Xe(C_6F_5)$][$B(CF_3)_4$], [$Xe(C_6F_5)(MeCN)$][$B(CF_3)_4$], [$Xe(C_6F_5)(MeCN)$][$B(C_6F_5)_4$], and [$Xe(C_6F_5)$][$B(CN)_4$] have been reported. The Xe–C bond distances are, respectively (Å): 2.104(5), 2.100(6), 2.100(10), and 2.081(3). The distance of 2.104 Å in the [$Xe(C_6F_5)$]$^+$ cation may be compared with the distance of 2.077 Å separating C and I in the isoelectronic neutral molecule C_6F_5–I.

A paper contributed by four Italian institutions of the National Research Council (CNR), in collaboration with the French Laboratoire de Physique et de Chimie de Nano–objets (INSA, Toulouse) has described the one–pot two–step preparation (A. Figuerola *et al., J. Am. Chem. Soc.,* 2008, **130**, 1477) of bimagnetic hybrid nanocrystals (HNC) based on domains formed by the size–tunable face–centred cubic structure of FePt and by inverse spinel cubic iron oxide. The FePt nanocrystals, which were obtained by using an earlier methodology (M. Chen *et al., J. Am. Chem. Soc.,* 2006, **128**, 7132) based on Fe(CO)$_5$ and bis–acetylacetonatoplatinum(II), Pt(acac)$_2$, as molecular precursors, were thermally treated to give the final products.

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