FROM THE LITERATURE

by Fausto Calderazzo

Two adjacent papers contributed by the Los Alamos National Laboratory {A.J. Gaunt, *et al.,* "Structural characterization of $Pu[N(SiMe_3)_2]_3$, a synthetically useful non-aqueous plutonium(III) precursor", *Inorg. Chem.*, 2008, **47,** 26; idem, *et al.,* "Experimental and theoretical comparison of actinide and lanthanide bonding in $M[N(EPR_2)_2]_3$ complexes (M = U, Pu, La, Ce; E= S, Se, Te; R = Ph, ^{i}Pr, H)", *Inorg. Chem.*, 2008, **47,** 29} report the crystallographic data for some of the title compounds. The point of specific interest is the comparison of the ionic radii of lanthanide (n=4) and actinide (n=5) elements having the same nf^n electronic configuration. In $Pu[N(SiMe_3)_2]_3$, the Pu-N distance is 2.315(10) Å. The appropriate comparison with the cation of the same outer electronic configuration, namely the Sm(III) derivative, is not possible at the present time since the structural parameters of $Sm[N(SiMe_3)_2]_3$ are not available. In this connection, an X-ray structural study (J.H. Matonic *et al., Inorg. Chem.*, 2001, **40,** 2638) has appeared of the triflate $[Pu(H_2O)_9][CF_3SO_3]_3$, a compound containing Pu(III) in a tricapped trigonal prismatic arrangement, the Pu-O prismatic bond distance of 2.476(2) Å being 0.058 Å longer than in the corresponding 4*f* derivative of the "isoelectronic" Sm(III). A similar study carried out in France (L. Karmazin *et al., Inorg. Chem.*, 2004, **43,** 5147) compares bond distances between Nd(III) and U(III) for some iodo-complexes of a nitrogen-containing ligand. The U(III)-I bond distances of 3.1695(10) and 3.1432(11) Å are 0.018 and 0.021 Å longer than the corresponding distances in the Nd(III) derivatives.

A review-article (G. Erker *et al., Organometallics*, 2008, **27,** 27) has pointed out the importance of alkali-metal cyclopentadienides (Cp) bearing organic functional groups, as intermediates for the preparation of functionalized Cp-derivatives of transition metals. The functionalisation of Cp derivatives goes back to the early work by M.D. Rausch in USA, M.I. Bruce in Australia, H. Schumann in Germany and others. The group at the University of Bologna headed by L. Busetto and M.C. Cassani has been active in this area of organometallic chemistry and in one of the more recent papers in collaboration with the University of Perugia (D. Zuccaccia *et al., Organometallics*, 2006, **25,** 2201) the PGSE-NMR data have been reported for a number of Cp-substituted derivatives of Rh(I). The catalytic activity in the hydroformylation reaction had been established earlier in a joint paper between the Universities of Bologna and Firenze (L. Busetto, M.C. Cassani, P. Frediani *et al., J. Organometal. Chem.*, 2004, **689,** 2216). With early transition elements in a high oxidation state, oxygen-functionalized Cp-ligands bind through the oxygen atoms. Thus, for example, in a contribution by some research institutions of Pisa and Aachen (L. Calucci, U. Englert, G. Pampaloni *et al., J. Organometal. Chem.*, 2005, **690,** 4844), VCl_3 and the potassium derivative of the deprotonated pentacarbomethoxy-cyclopentadiene are reported to react giving the corresponding vanadium(III) complex containing the hexacoordinated oxygen-bonded central metal atom. The mixed cycloheptatrienyl-cyclopentadienyl derivative of tantalum, of formula $Ta(\pi\text{-}C_5H_5)(\pi\text{-}C_7H_7)$, has been reported by G.S. Girolami (W. Noh *et al.*, *Inorg. Chem.*, 2008, **47,** 535). This is a long-standing interesting subject, the first mixed derivative of this type, namely $V(p\text{-}C_5H_5)(p\text{-}C_7H_7)$, having appeared in 1959 (R.B. King, F.G.A. Stone, *J. Am. Chem. Soc.*, 1959, **81,** 5263). Further information on this subject can be found in a review-article by M.L.H. Green and D.K.P. Ng (*Chem. Rev.*, 1995, **95,** 439).

The entire October 2007 issue of *Chem. Rev.*, coordinated by Wolfgang Lubitz and Bill Tumas, is dedicated to several aspects of the production and future uses of di-hydrogen. The scientific interest for this field of research is certainly very high, and essential to the development of probably small-scale future applications.

The production of small-size particles of transition metals, as such or supported on a metal oxide such as Al_2O_3, silica or others, is an area of intense research activity. H. Bönnemann and his coworkers in a review-article appeared in the year 2005 (*Eur. J. Inorg. Chem.*, 2005, 3625) describe, *inter alia*, the formation of platinum particles as obtained through the reduction of $Pt(acac)_2$ with $AlMe_3$ in toluene as medium. The metal particles are proposed to be protected from collapsing and thus forming aggregates of a greater size, by the presence of both aluminium-bonded acetylacetonato- and methyl groups, the latter allowing the further reaction with bifunctional phenolic derivatives. A 1996 article (H. Bönnemann *et al.*, *J. Organometal. Chem.*, 1996, **520,** 143) describes the catalytic activity of systems of this type in the hydrogenation of crotonic acid or butyronitrile, using heterogeneous catalysts based on platinum or rhodium or several of their combinations.

Eight subsequent review-articles in the March 19th 2007 issue of *Inorganic Chemistry*, covering the first 82 pages, discuss several aspects of palladium-catalyzed reactions. One of the articles by D. Astruc ("Palladium nanoparticles as efficient green homogeneous and heterogeneous carbon-carbon coupling precatalysts: a unifying view", *Inorg. Chem.*, 2007, **46,** 1884) suggests that some of the reactions are in fact catalyzed by palladium nanoparticles. This is actually a rather interesting suggestion supported by experimental results dating back to the beginning of this century (D.M. de Jesus *et al.*, *Langmuir*, 2000, **16,** 4896; A. Biffis *et al.*, *J. Molec. Catal. A: Chemical*, 2001, **173,** 249; V. Calò *et al.*, *Organometallics*, 2003, **22,** 4193; idem *et al.*, *J. Org. Chem.*, 2003, **68,** 2929). Organic syntheses in the presence of palladium compounds as catalytic precursors has a long-standing tradition in this country. The problem of the palladium-catalyzed organic syntheses has been discussed in Chapter 5 of the recently appeared book entitled "Metal catalysis in industrial organic processes", G.P.

Chiusoli and P.M. Maitlis, Eds., RSC Publishing, 2006, p. 181, whereby mention is made of the observation that palladium-containing molecular precursors may be a source of highly active nano-particles, possibly modified on the surface by the ligands or by one of the reagents, which may be responsible for the catalytic activity. Along the lines of metal-assisted organic reactions, a recent paper (E. Motti *et al.*, *Adv. Synth. Catal.*, 2008, **350,** 503) has shown the possibility for palladium of catalytically dehydrogenating *o*-alkylated or *o*-alkoxylated iodo-arenes. Palladium-catalyzed reactions have been reported by R. Rossi and his co-workers: in one of their recent papers F. Bellina *et al.*, *J. Org. Chem.*, 2005, **70,** 3997), the palladium-catalyzed arylation of 1-aryl-1H-imidazoles to 1,5-diaryl-1H-imidazoles was found to give the best results in the presence of $AsPh_3$. Less satisfactory results were obtained with PAr_3, probably in agreement with the possibility for $AsPh_3$ to form weaker bonds to palladium than the lighter homologue of phosphorous. However, good conversions were also obtained with the $Pd(OAc)_2/P(2\text{-furyl})_3$ combination, thus avoiding the presence of the toxic arsenic derivative, as shown in a forthcoming review-article [F. Bellina *et al.*, *Curr. Org. Chem.*, 2008, **12,**..., accepted for publication].
Catalysis by transition metals in aqueous solution led M. Peruzzini and his co-workers (M. Erlandsson *et al.*, *Inorg. Chem.*, 2008, **47,** 8) to synthesize a diastereoselective analogue of a phosphorous-based ligand, supported by the crystal structures of both a single diastereoisomer of the ligand, and its Ir(III) complex. The determination of the relative configuration in organic compounds by NMR and by computational methods has been reviewed by a group of scientists operating at the University of Salerno (G. Bifulco *et al.*, *Chem. Rev.*, 2007, **107,** 3744).
The Fischer-Tropsch (F.-T.) reaction is a subject of a worldwide renewed interest due to the incoming shortage of oil. The process, discovered by the chemists Franz Fischer and Hans Tropsch, working at the Kaiser-Wilhelm-Institut für Kohlenforschung in Mülheim-Ruhr, was first disclosed in 1925 (German Patent 484,337, 1925; idem, *Chem. Ber.*, 1926, **59,** 830. For a detailed account of the initial developments of the reaction, see: H.H. Storch, *Adv. Catal.*, 1948, **1,** 115; H. Pichler, *ibidem*, 1952, **4,** 271). A joint paper from the Politecnico of Milano and Eni laboratories by C.G. Visconti *et al.* (*Appl. Catal. A: General*, 2007, **330,** 49) points out the effect of sulfur poisoning on the cobalt-catalyzed F.-T. reaction with Al_2O_3 as support. The presence of sulfur decreases the catalytic activity and promotes the formation of lighter products. The F.-T. reaction produces water and is strongly exothermic, one of the problems being consequently related to the removal of heat. Moreover, the product distribution depends on the H_2/CO ratio and by the local distribution of the gaseous reagents in the liquid phase. As the temperature is lowered, the production of heavier hydrocarbons increases; however, cooling the reactor is a challenging problem. For metals supported on alumina, the activity in the F.-T. process is Ru>Fe>Co. Iron is preferred for both its activity and low cost. I. Wender and his co-workers have discussed, at the CFFS Annual Meeting, Roanoke, WV, Aug. 1-4, 2004, several technological aspects of the F.-T. reaction concluding that cobalt, in spite of its higher price with respect to iron, can be used in smaller amounts and can be regenerated by oxidation/reduction, thus allowing its use over a long time. It has also been pointed out that the addition of acetylene causes the F.-T. reaction, as catalyzed by iron and cobalt, to initiate at a temperature about 100 °C lower than in the absence of the triply-bonded hydrocarbon.
The solution of the energy problem is probably related to the simultaneous use of several sources, the ultimate goal being that of controlling the emissions of CO_2. Alternative, new energy sources are to be recognized, while those already identified should be reduced to practice. In a recent review-article by V. Balzani and his co-workers ("Photochemical conversion of solar energy", *ChemSusChem*, 2008, **1,** 26) it has been pointed out that energy must be saved, but also finding clean energy sources is a stringent requirement, solar irradiation being one of the most convenient ones. Earth receives an enormous amount of energy through solar irradiation and it would be of great interest to exploit more of it than we do presently. More information about this problem can be found visiting the site of I. E. A, namely www.iea.org/Textbase/nppdf/free/2007/key_stats_2007.pdf.
V. Balzani has co-authored an article on a similar subject with N. Armaroli ("The future of energy supply: challenges and opportunities", *Angew. Chem., Int. Ed.*, 2007, **46,** 52). The formation of carbon-carbon bonds through photocatalysis has been reviewed by A. Albini and co-workers of the University of Pavia (M. Fagnoni *et al.*, *Chem. Rev.*, 2007, **107,** 2725), the authors pointing out that photochemical reactions occur under mild conditions and are generally characterized by high yields and high selectivities.
On the track (Politecnico di Milano → Università di Napoli → Università di Salerno) of a long-standing tradition in the stereo-regular polymerization of olefins, G. Guerra and his co-workers have recently published (C. Daniel *et al.*, *Chem. Mater.*, 2008, **20,** 577) the results of sorption experiments on syndiotactic polystyrene aerogels. Experiments of dinitrogen adsorption carried out at 77 K confirm that the polymer contains crystalline nanocavities in addition to an amorphous porosity.

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