FROM THE LITERATURE

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One of the most recent review–articles on the Fischer–Tropsch synthesis has been compiled by Mark E. Dry of the University of Capetown (*Encyclopedia of Catalysis*, Vol. 3, István T. Horváth, Ed., Wiley–Interscience, 2003). The plants operating in South Africa at Sasolburg and at Secunda use iron–based catalysts, while the Malaysian plant operated by Shell uses a cobalt–containing catalyst.

G.J. Kubas, the discoverer of the first recognized di–hydrogen complex of a transition metal has reviewed (*J. Organometal. Chem.*, 2001, **635**, 37) the subject. The important question has been addressed as to whether catalytic hydrogenation is preceded by the formation of the metal complex to an elongated H_2 ligand. In some instances, there is evidence that this is actually the case (see, for example: A.M. Joshi *et al.*, *J. Organometal. Chem.*, 1995, **488**, 161). The formation of the di–hydrogen complex is presumably mediated by the so–called *agostic* interaction between the transition metal and an aliphatic C–H bond of a tertiary phosphine ligand, whenever this is present.

Stabilization through an *agostic* interaction in the nickel–catalyzed polymerization of ethylene (with iminophosphonamido– or amidinato as supporting ligand) has been calculated to be an important step in the process (S. Collins, T. Ziegler, *Organometallics*, 2007, **26,** 6612). The corresponding ethylene–hydrido complex $Ni(C_2H_4)H$ is weakly bonded and therefore is suggested to play a relatively minor role.

A joint paper between the University of Padova and one of the CNR (Consiglio Nazionale delle Ricerche) Institutes of Milano (G. Zotti *et al.*, *Chem. Mater.*, 2008, **20**, 397) has described the formation of gold particles linked by pyrrole– and thiophene–based thiols. The latter form monolayers on gold with a high surface coverage.

The group of Prof. T.J. Marks at Northwestern University (N. Guo *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 2246) has described the homo–polymerization of styrene and the ethylene/styrene co–polymerization in the presence of titanium– or zirconium–based bimetallic catalysts. Thus, for example, a bimetallic titanium catalyst precursor has a 65 times higher activity than that of a monometallic control system. The same bimetallic system enchains 15.4% more styrene than a monometallic derivative. Interestingly, the corresponding zirconium analogues only give mixtures of polyethylene and polystyrene, no co–polymer being formed. A model compound of titanium(IV) of formula $(\mu\text{–}CH_2CH_2\text{–}3,3')\{(\eta^5\text{–indenyl})[1\text{–}Me_2Si({}^tBuN)][Ti(CH_2Ph)_2]\}_2$ was structurally characterized.

A contribution from the University of North Carolina (A.B. Jackson *et al.*, *J. Am. Chem. Soc.*, 2007, **129**, 10628) describes the adducts of bis(acetylacetonato)(CO)tungsten(II), a 14–e system, with 2,6–dichlorobenzonitrile or *N*–benzylideneaniline, PhN=CHPh, the corresponding X–ray crystal structures being reported. In this connection, it is interesting to note that carbonyl groups are frequently appropriate ancillary ligands for β–diketonato complexes. Examples of this type of ligand combinations can be found, for example, as the 18–e species bis(acetylacetonato)$(CO)_3$tungsten(II), $W(acac)_2(CO)_3$ (A.B. Jackson *et al.*, *Inorg. Chem.*, 2006, **45**, 6205). The first β–diketonato carbonyl derivative of a metal in a +II oxidation state, $Ru(acac)_2(CO)_2$, an 18–e species, was reported as early as 1969 (F. Calderazzo *et al.*, *J. Chem. Soc.* (A), 1969, 1378), prepared by reacting $Ru_3(CO)_{12}$ with acetylacetone, or by treating $Ru(acac)_3$ with CO/H_2. Several examples of β–diketonato carbonyl derivatives of a metal in a +I oxidation state (F. Bonati, G. Wilkinson, *J. Chem. Soc.*, 1964, 3156; F.A. Hartman *et al.*, *Inorg. Chem.*, 1967, **6**, 34; F. Bonati, R. Ugo, *J. Organometal. Chem.*, 1968, **11**, 341) are known.

A paper contributed by four research institutions (J.E. McDonough *et al.*, *Inorg. Chem.*, 2008, **47**, 2133) has estimated bond energies for complexes of the type $Mo(E)(N^tBuAr)_3$, E=S, Se, Te, the metal–chalcogen bond becoming slightly weaker as the chalcogen donor atom becomes heavier. This is interesting because opposite trends had been found previously in the addition of pentachlorotantalum(V) to EMe_2 (R. Good, A.E. Merbach, *J. C. S. Chem. Commun.*, 1974, 163), and in the carbonyl substitution by EMe_2 on $VCp(CO)_4$ (A. Belforte *et al.*, *Gazz. Chim. Ital.*, 1985, **115**, 71), showing a slightly preferred coordination of the heavier chalcogen to the central metal atom: this paper reports the crystal and molecular structures of the isostructural $M(\eta^5\text{–}C_5H_5)(CO)_3(SMe_2)$ derivatives, M=V (red, CUDNIY in the Cambridge Crystallographic Data Centre, CCDC), Nb (black, CUDNOE in CCDC), both crystallizing in the $P2_1/n$ space group, the M–S bond length being 2.465(2) Å and 2.578(1) Å, respectively. The thermodynamic aspects of oxo/sulfido exchange reactions have been discussed recently (J.P. Donahue, *Chem. Rev.*, 2006, **106**, 4747). This is certainly an aspect of coordination chemistry which deserves further attention.

In a paper contributed by the Institute of Chemical Research of Cataluña, West Virginia University, the German company KemKom and the Università di Salerno, some platinum(II) complexes containing *N*–heterocyclic carbene (NHC) have been described (S. Fantasia *et al.*, *Organometallics*, 2007, **26**, 5880), three of them being characterized crystallographically. Computational analysis suggests a small degree of metal–to–ligand π–back–donation. This result is consistent with the general behaviour of platinum(II) in its combinations with carbon–based ligands. An earlier paper (S. Fantasia *et al.*, *Organometallics*, 2007, **26**, 3286) had reported the insertion of a NHC in between a platinum–olefin bond: this paper has been highlighted, in the Spring 2008 issue of *Excellence*, the supplement to ACS publications, as one of the most cited ones.

The hexanuclear cationic platinum cluster $[Pt_6(\mu\text{–}P^tBu_2)_4(CO)_6]^{2+}$, with $[CF_3SO_3]^-$ as counteranion, contains a central tetrahedron of platinum atoms further bonded to two additional platinum atoms. Reaction of this compound with one eq of $[NBu_4]Cl$ or with an excess of halide gives the cationic mono–chloride $[Pt_6(\mu\text{–}{}^tBu_2)_4(CO)_5Cl]^+$, or the neutral dihalide $Pt_6(\mu\text{–}P^tBu_2)_4(CO)_4X_2$, X=Cl, Br, I, respectively (C. Bonaccorsi *et al.*, *Chem. Eur. J.*, 2008, **14**, 847). The reaction of $Pt_6(\mu\text{–}P^tBu_2)_4(CO)_4Cl_2$ with

$NaBH_4$ gave the dihydrido derivative $Pt_6(\mu\text{–}P^tBu_2)_4(CO)_4(H)_2$.

The water–soluble ethylene complex of platinum(II) of formula *cis*–$PtCl_2(TPPTS)(C_2H_4)$, TPPTS = $P(m\text{–}C_6H_4SO_3Na)_3$ has been reported (R.S. Pryadun, J.D. Atwood, *Organometallics*, 2007, **26**, 4830) and shown to undergo reaction with diethylamine yielding the zwitterionic adduct *cis*–$PtCl_2(TPPTS)(CH_2CH_2NHEt_2)$, characterized by NMR.

L. von Szentpály (*J. Am. Chem. Soc.*, 2008, **130**, 5962) has discussed the possibility of referencing the thermodynamic state functions to free atoms rather than to the elements in their standard state.

A density functional study of the stereocontrol in the syndiotactic polymerization of propylene catalyzed by *ansa*–zirconocenes of C_2 symmetry has appeared (S. Tomasi *et al.*, *Organometallics*, 2007, **26**, 2024). Enantiomeric mis–insertion is primarily induced by the structure of the ligand, while the nature of the counteranion and the type of solvent have a less important effect.

A relatively strong binding of dihydrogen forming a η^2–adduct with copper in a ZSM–5 zeolite has been reported in a paper contributed by four different research institutions including the University of Milano (P.A. Georgiev, A. Albinati *et al.*, *J. Am. Chem. Soc.*, 2007, **129**, 8086). Inelastic neutron scattering experiments at 4 K carried out at the Institut Laue–Langevin of Grenoble have allowed the authors to conclude that dihydrogen is more tightly bonded to copper than to iron in the cation–doped ZSM–5 zeolite.

A review–article contributed by a group of the Università di Ferrara (P.G. Baraldi *et al.*, *Chem. Rev.*, 2008, **108**, 238) deals with medicinal chemistry and specifically with adenosine receptor antagonists.

A paper contributed by three European research institutions including the Istituto per la Sintesi Organica e la Fotoreattività of the CNR (A. Liscio *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 780) has discussed the advantages connected with the use of *organic* solar cells consisting of a blend of an electron–acceptor (A) and –donor (D). The blend was obtained by co–deposition of both poly(3–hexylthiophene) and the acceptor [*N*,*N*'–bis(1–ethylpropyl)–3,4:9,10–perylenebis(dicarboximide). Photovoltaic activity was demonstrated for this system.

An Italian–Swiss–Dutch paper (L. Belpassi *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 1048) has treated the nature of the chemical bond between gold(I) and the noble gases (Ng) Ar, Kr, Xe in (Ng)AuF and in $[(Ng)Au]^+$. The Ar–Au bond dissociation energy was found to be essentially unchanged in the neutral and cationic species and the Ng–Au bond was regarded to be essentially covalent.

It has been shown that bis(pentafluorophenyl)borinic acid, $(C_6F_5)_2B\text{–}OH$ in dichloromethane solution exists as an equilibrium mixture of the monomer and the trimer. At 183 K, the addition of 0.33 eq of tetrahydrofuran (THF) caused the instantaneous formation of the 1:1 adduct with the trimer, *i.e.* $[(C_6F_5)_2B\text{–}OH]_3$◊THF (T. Beringhelli *et al.*, *Organometallics*, 2007, **26**, 2088).

The dicationic palladium(II) and platinum(II) derivatives of formula $[M(PNP)(olefin)]^{2+}$ react with aromatic compounds activated by methoxy substituents, PNP=2,6–bis(diphenylphosphinomethyl)pyridine, according to recent results obtained at the Università di Napoli (M.E. Cucciolito *et al.*, *Organometallics*, 2007, **26**, 5216). The crystal and molecular structure of the σ–alkyl derivative $[Pt(PNP)(CH_2CH_2\text{–}C_6H_2(OMe)_3][BF_4]$, as prepared by reacting the cationic ethene complex $[Pt(PNP)(CH_2CH_2)]^{2+}$ with 1,3,5–trimethoxybenzene, has been determined.

Tetra–isocyanide complexes of titanium(II) of formula $Ti(\eta^5\text{–}C_5H_5)(CN\text{–}2,6\text{–}Me_2C_6H_3)_4X$, X=I, $SnPh_3$, $SnMe_3$, have been synthesized in the group of Prof. J.E. Ellis of the University of Minnesota (J.M. Allen *et al.*, *J. Organometal. Chem.*, 2008, **693**, 1536). The molecular structure of the compound with X=I shows the central metal atom to be approximately octahedrally surrounded by the four carbon–containing ligands in the equatorial positions, the other two positions being occupied by the Cp and the I ligands. The possibility for titanium(III) and titanium(IV) to coordinate alkyl– and aryl–isocyanides –two *per* metal atom– had been disclosed by C. Floriani and coworkers (*e.g.*, see: C. Floriani, G. Fachinetti, *J. Chem. Soc., Dalton Trans.*, **1973**, 1954; T. Carofiglio *et al.*, *Organometallics*, 1993, **12**, 2726).

A contribution from the Università di Roma "La Sapienza" (B. Chiavarino *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 3208) deals with the mechanism of oxidative de–alkylation of amines by heme enzymes. The question has been addressed whether the oxidation sequence is initiated by a hydrogen atom transfer (HAT) event or by an electron transfer (ET) process. The gas–phase reaction was studied by ESI–FT–ICR mass spectrometry. In no case, an initial HAT process has been observed, while the reaction of the majority of the amines appears to be initiated by an ET mechanism.

The complexation of lanthanide(III) cations with tris(2–aminoethylamine), tren, and with tetraethylenepentamine, tetren, has been studied (P. Di Bernardo *et al.*, *Inorg. Chem.*, 2008, **47**, 1155) in DMSO as solvent by potentiometric and calorimetric methods, as reported in a contribution in collaboration between Italian and USA research institutions.

A joint paper from two institutions of the Università di Bologna (S. Bordoni *et al.*, *Organometallics*, 2008, **27**, 945) has reported the diastereoselective synthesis of some rhodium–based cyclopentadienyl derivatives carrying three $CH(CH_2)_3CHOH$ substituents in the 1,2,4 positions of the five–membered ring.

New amino–carbonyl complexes of palladium(II) or nickel(II) have been prepared and used as intermediates to cyclic carbamates, as reported by researchers of the Università di Bari (P. Giannoccaro *et al.*, *Organometallics*, 2008, **27**, 967).

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