

A review-article has appeared concerning the systems based on trinuclear metallacycles (E. Zangrando *et al.*, *Chem. Rev.*, 2008, **108**, 4979) as a contribution from the Dipartimento di Scienze Chimiche of the Università di Trieste. This is a comprehensive and critical survey of the trinuclear metallacycles known until now. These compounds are frequently obtained by combining metal fragments with some labile ligands and ditopic linkers. In general, metal-metal interactions in the systems considered in this review are weak, as a distinction with respect to metal clusters containing metal-metal bonds. Among the products obtained with monodentate binding units, mention was made of a trinuclear organo-gold molecule, reported as early as 1970 (L.G. Vaughan, *J. Am. Chem. Soc.*, 1970, **92**, 730), containing bridging 2-pyridyl linkers and linear gold(I) edges. The trinuclear cyano-bridged complex of rhenium(I) of formula $\text{Re}_3(\mu\text{-CN})_3(\text{CO})_{12}$, mentioned in this review-article, is a by-product of the synthesis of $\text{Re}_2(\text{CO})_{10}$ by carbonylation of $[\text{NH}_4][\text{ReO}_4]$ at high temperature and pressure (F. Calderazzo *et al.*, *Gazz. Chim. Ital.*, 1989, **119**, 241). The trinuclear product contains bridging cyano groups C- and N-bonded to the rhenium(I) centres.

A paper from the University of Toronto (C.S. Yeung *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 7826) has reported the nickel- and palladium catalyzed organozinc coupling with carbon dioxide. By using the well-known complex of formula $\text{Ni}(\eta^2\text{-CO}_2)(\text{PCy}_3)_2$, published as early as 1975 (M. Aresta *et al.*, *J. Chem. Soc., Chem. Commun.*, 1975, 636), the authors report that a catalytic amount of the Aresta's compound promote the carboxylation of $\text{Zn}(\text{C}_6\text{H}_5)(\text{PCy}_3)_2$ in tetrahydrofuran. Thus, through an intermediate carboxylato derivative, a number of functionalized aryl-ZrBr derivatives are converted to the appropriate acid under mild conditions (0 °C, atmospheric pressure of carbon dioxide).

A contribution from the Universities of Venezia and Roma "Tor Vergata" (B. Crociani *et al.*, *J. Organometal. Chem.*, 2008, **693**, 3932) has described some neutral and cationic palladium complexes with 8-(di-tert-butylphosphino-oxy)quinoline. The compound $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{N},\text{O})]^+\text{BF}_4^-$ contains the tetracoordinated palladium(II) centre in a distorted square-planar coordination, the donors being the carbon atom of the allyl group and the P,N atoms of the substituted quinoline.

High yields of a structurally characterized octanuclear cyclic μ -oxo diethylcarbamato derivative of titanium(IV) have been obtained through a hydrolytic process on $\text{Ti}(\text{O}_2\text{CNET}_2)_4$ (D. Belli Dell'Amico *et al.*, *J. Mol. Struct.*, 2008, **890**, 295). The compound, of formula $\text{Ti}_8\text{O}_8(\text{O}_2\text{CNET}_2)_{16}$, consists of an eight-membered ring of octa-coordinated titanium centres with a Ti...Ti average distance of 3.356 Å. The eight $\text{TiO}_{2/2}(\text{O}_2\text{CNET}_2)_{4/2}$ units of the cyclic frame exhibit sequestering properties for $[\text{NH}_2\text{Et}_2][\text{O}_2\text{CNET}_2]$. It is interesting

to note that a redox-active cage has been reported, which has been proposed as an electrochemical sensor for anions (V. Amendola *et al.*, *Inorg. Chem.*, 2008, **47**, 4808), according to a contribution from the Università di Pavia. Specifically, three arms from imidazolium fragments, each linked to a 2,2'-bipyridine subunit, were connected to a 1,3,5-triethylbenzene platform, and the corresponding cobalt(II) derivative has been synthesized: this system provides a suitable cavity for solvent- or anion inclusion.

The cationic tris(ethylene)-gold(I) complex of formula $[\text{Au}(\text{C}_2\text{H}_4)_3][\text{SbF}_6]$ was synthesized by reacting AuCl with AgSbF₆ in the presence of excess ethylene (H.V.R. Dias *et al.*, *Angew. Int. Ed.*, 2008, **47**, 556), as a contribution from the University of Texas at Arlington, the University of North Texas and Bruker AXS Inc. The structural investigation by X-ray diffraction has shown the gold atom to coordinate the three ethylene groups in a trigonal planar arrangement, the ethylene ligands lying in the trigonal plane: this form has been calculated to be more stable than that with the ethylene groups in the upright position.

Palladium(II) and palladium(0) complexes of 2-pyridyldiphenylphosphine (py) have been prepared (A. Scrivanti *et al.*, *J. Organometal. Chem.*, 2009, **694**, 131), as a contribution from the Università di Venezia and the Istituto di Scienza e Tecnologia dei Materiali (ISTM), Consiglio Nazionale delle Ricerche (CNR), Padova. Among the products reported is the palladium(I) derivative with two py ligands and one fumaronitrile.

Researchers of the Laboratoire de Chimie de Coordination, Toulouse, France, and of the Istituto dei Composti di Coordinazione ed Organometallici (ICCOM-CNR), Firenze (M. Ciclosi *et al.*, *Organometallics*, 2008, **27**, 2281) have studied the oxidation of benzothiophene and two other thiophene derivatives by H_2O_2 to the corresponding sulfoxides and sulfones using $\text{M}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{O}_5$, M=Mo, W, as catalytic precursor. The tungsten derivative is about 100 times more efficient than the molybdenum analogue, a trend which is quite common in reactions involving a change of the oxidation state.

A contribution from the Ecole Supérieure de Paris and from the Dipartimento di Chimica Organica e Industriale, Università di Parma (C. Amatore *et al.*, *Organometallics*, 2008, **27**, 4549) has reported the oxidative addition of $\text{C}_6\text{H}_5\text{CH}_2\text{X}$, X=Br and Cl, to a palladium(II) metallacycle yielding the corresponding palladium(IV) derivatives. The order of reactivity is Br>Cl, with almost three orders of magnitude of the rate constant favouring the heavier halide.

A series has been reported of heterobimetallic chromium(0) derivatives containing a η^6 -ferrocenylindene ligand for the $\text{Cr}(\text{CO})_3$ moiety (S. Santi *et al.*, *J. Organometal. Chem.*, 2008, **693**, 3797), as a contribution from two institutions located in Padova (Università and CNR-Istituto di Chimica Inorganica e delle

Superfici). Three of the compounds have been studied by X-ray crystallography. The corresponding mono- and dications were generated by chemical and electrochemical oxidations.

A contribution from the Politecnico di Bari in collaboration with the RWTH, Aachen (M.M. Dell'Anna *et al.*, *Dalton Trans.*, 2008, 6005) has described the reactivity of $M(1,5\text{-cyclooctadiene})Cl_2$, $M = Pd$ and Pt , with (ferrocenylmethyl)phosphane (Fc) to give the dinuclear complexes of formula $(cod)CIM(\mu\text{-}PHCH_2Fc)M(PH_2CH_2Fc)Cl_2$, $cod = 1,5\text{-cyclooctadiene}$. One of the trimetallic palladium complexes reported in this paper, of formula $[Pd((\mu\text{-}PHCH_2Fc)(PPh_3)Cl)_3]$, has been studied by X-ray diffractometry.

A communication (L. Rocchigiani *et al.*, *Chem. Eur. J.*, 2008, **14**, 6589) from the Università di Perugia has reported, on the basis of the self-aggregation tendency of zirconocenium ion pairs, that the presence of an aliphatic chain of variable length, mimicking the growth of a polymer chain, does not modify the tendency of the zirconocenium ion pair to self-aggregate; this is due to the fact that the position of the anion is not affected by the length of the chain. This study was based on pulsed-field-gradient-spin-echo (PGSE) NMR measurements. A contribution by the same group in collaboration with the Università di Napoli, the Dow Chemical Company and the University of Florida (C. Zuccaccia *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 10354) has investigated the mechanism of olefin polymerization by some arylcyclometallated hafnium pyridyl-amido pre-catalysts, and their activation by $B(C_6F_5)_3$, $[CPh_3][B(C_6F_5)_4]$ and $[NHR_3][B(C_6F_5)_4]$.

A contribution (A. Abbotto *et al.*, *Chem. Commun.*, 2008, 5318) from research institutions located at the Università di Milano-Bicocca, Università di Torino, Università di Perugia, and the Swiss Federal Institute of Technology of Lausanne has reported a new heteroleptic ruthenium complex containing a heteroaromatic-4,4'- π -conjugated 2,2'-bipyridine, which was used in dye-sensitized solar cells. A photovoltaic efficiency of 9.1% was obtained. The *trans*-metalation reaction between some palladium(II) butadienyl complexes, $PdCl(ZC=CZ)_2Me(L-L')$, $L-L'$ being a bidentate ligand, and $SnBu_3$ (phenylethynyl) was studied in the presence of some stabilising olefins (L. Canovese *et al.*, *J. Organometal. Chem.*, 2008, **693**, 3324). The most active olefins for the reaction were found to be maleic anhydride and fumaronitrile.

A contribution from the Università di Salerno (F. Grisi *et al.*, *Organometallics*, 2008, **27**, 4649) has reported the synthesis of some ruthenium-based catalysts containing *N*-heterocyclic carbene ligands of C_2 or C_1 symmetry. Through variable-temperature NMR studies, the interconversion of atropisomers in solution was evaluated. The NMR data and DFT calculations suggest that the interconversion between atropisomers is due to rotation of the benzyldiene group around the $Ru=C$ bond. The activity and ste-

reoselectivity of some of the complexes were studied in ring-closing metathesis, asymmetric ring-closing metathesis, cross-metathesis and ring-opening metathesis polymerization. The complexes of C_1 symmetry showed the highest activity in all reactions.

A contribution from the ETH Zürich, the Università di Milano and the Centro de Química Estrutural of the Instituto Superior Técnico, Lisboa (S. Filipuzzi *et al.*, *Organometallics*, 2008, **27**, 4580) reports NMR, X-ray and DFT studies on some $RhCl(diene)(phosphoramidite)$ complexes. The X-ray study on one of the complexes shows that the carbon-carbon bond *trans* to the chloride ligand is elongated.

A paper in collaboration between the University of Illinois at Urbana-Champaign and the Università di Milano-Bicocca (A.K. Justice *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 5293) has reported on the oxidation of the electron-rich ethanediolato complex of iron $Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$, $dppv = cis\text{-}Ph_2PCH=CHPPh_2$, leading to $[Fe_2(S_2C_2H_4)(\mu\text{-}CO)(CO)_2(dppv)_2]^+$, a model for the comparable transformation in $[FeFe]$ -hydrogenases. The crystallographic characterization of the thermodynamically favoured symmetrical isomer confirmed the structure of C_2 symmetry with a 2.7012(14) Å long Fe-Fe bond.

A feature article from the Università di Camerino has appeared (R. Ballini *et al.*, *Chem. Commun.* 2008, 2975) describing the use of nitroalkanes as acyclic building blocks to synthesize polyfunctionalized benzene derivatives.

An article released by the Università del Piemonte Orientale in Alessandria (F. Carniato *et al.*, *Dalton Trans.*, 2008, 36) has reported a facile synthetic procedure leading to satisfactory yields of bifunctional polyhedral oligomeric silsesquioxanes.

Some hexacyanoferrates have been studied by X-ray absorption spectroscopy as for a contribution (M. Giorgetti *et al.*, *Inorg. Chem.*, 2008, **47**, 6001) from two research institutions located in Bologna, namely Università and Istituto Nazionale di Scienza e Tecnologia dei Materiali. The CN bond length has been determined with a statistical error of a few thousandths of an angstrom.

A contribution from the Universidad Complutense in Madrid, the Università "Tor Vergata" in Roma, and the Universitat de Valencia (E.M. Pérez *et al.*, *Chem. Commun.*, 2008, 4567) has described the relevance of several intermolecular forces on the stability of complexes formed between structurally related receptors and [60]-fullerene: a concave-convex complementarity has been evidenced to be of importance for this process.

Authors are cordially invited to submit recent or forthcoming accepted publications for consideration in this section of the journal, by using the following e-mail address: facal@dccl.unipi.it