

P.07.01.14*Acta Cryst.* (2005). A61, C298**From P₄ to PH₃ Metal Complexes by Plane Hydrolysis**

Massimo Di Vaira^a, Piero Frediani^b, Stefano Seniori Costantini^a, Maurizio Peruzzini^c, Piero Stoppioni^a, ^a*Department of Chemistry, University of Florence.* ^b*Department of Organic Chemistry, University of Florence.* ^c*ICCOM-CNR, Florence, Italy.* E-mail: massimo.divaira@unifi.it

The large-scale production of PH₃, a valuable feedstock material for the synthesis of many organophosphorus derivatives, is hampered by difficult operational conditions. This makes conversion routes, possibly catalytic, of elemental phosphorus to phosphine highly desirable.

The monometal [CpRu(PPh₃)₂(η¹-P₄)]PF₆ (**1**) and the dimetal [{CpRu(PPh₃)₂}₂(μ,η^{1,1}-P₄)](PF₆)₂ (**2**) P₄ derivatives, respectively containing a monodentate and bridging P₄ molecule, surprisingly undergo hydrolysis in very mild conditions yielding the PH₃ complex [CpRu(PPh₃)₂(PH₃)]PF₆ (**3**) in stoichiometric amount. Remarkably, this behaviour had not been observed for the Cp* analog of **1** [1]. The structures of **1-3** have been determined; this should help to rationalise the observed reactivity of **1** and **2**, which appears to disclose new paths of phosphorus chemistry.

[1] de los Rios I., Hamon J.-R., Hamon P., Lapinte C., Toupet L., Romerosa A., Peruzzini M., *Angew. Chem. Int. Ed.*, 2001, **40**, 3910.

Keywords: phosphorus compounds, ruthenium compounds, hydrolysis

P.07.01.15*Acta Cryst.* (2005). A61, C298**New Polymeric Barium(II) 2,2'-diphenyldicarboxylate Complex**

Fadila Balegroune^a, S. Djehni^a, A. Guehria-Laidoudi^a, E. Wenger^b, ^a*Laboratoire de Cristallographie-Thermodynamique, Faculté de Chimie, USTHB, El-Alia, BEZ, Alger, Algérie.* ^b*LCM3B, Université de Nancy 1, Faculté des Sciences, 54506 Vandoeuvre, France.* E-mail: fadilabalegroune@yahoo.fr

A multidentate ligand such as 2,2'-diphenyldicarboxylic acid (H₂dpdc) is a good candidate for the construction of coordination polymers. In the crystal structures of transition metal complexes with H₂dpdc, the ligand exhibits several kinds of coordination modes [1-3]. Owing to the higher coordination number, the reactions of H₂dpdc with alkaline-earth metals may generate polymers with different coordination modes. To the best of our knowledge, alkaline-earth 2,2'-diphenyldicarboxylate complexes have never been reported.

A new barium(II) complex [Ba(Hdpdc)₂(H₂O)₂] has been synthesized. It crystallizes in the monoclinic space group P2₁/n. The barium atoms are nine coordinated and the coordination geometry around them can be best described as a distorted capped square antiprism. The geometry of the two monoanions is similar to those found in the pure acid [4]. The three-dimensional structure is polymeric and consists of infinite chains of face-sharing Ba polyhedra, running parallel to the [010] axis. The Ba..Ba distances across these chains are 4.139(2) Å.

[1] Rueff J. M., Pillet S., Claiser N., Bonaventure G., Souhassou M., Rabu P., *Eur. J. Inorg. Chem.*, 2002, 895. [2] Kumagai H., Inoue K., Kurmoo M., *Bull. Chem. Soc. Jpn.*, 2002, **75**, 1283. [3] Lu J. Y., Schauss V., *Inorg. Chem. Comm.*, 2003, **6**, 1332. [4] Fronczek F. R., Davis S. T., Gehrig L. M. B., Gaudour R. D., *Acta Cryst.*, 1987, **C43**, 1615.

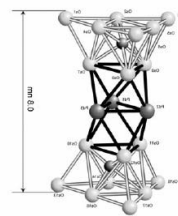
Keywords: 2,2'-diphenyldicarboxylic acid, barium complexes, crystal structure

P.07.01.16*Acta Cryst.* (2005). A61, C298**Fabrications of Carbon Nanotube Coated with Os-Pd Mixed-Metal Nanoparticles**

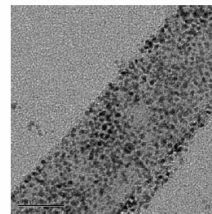
Wing-Tak Wong, Ka-Fu Yung, *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P.R. China.* E-mail: wtwong@hkucc.hku.hk

Metal nanoparticles have aroused considerable attention in the

past few years. Most of the preparations are based on the reduction of metal salt with organic stabilizers or metal vapour deposition from the corresponding metal. Both of the above methods result in particles with a range of sizes. We are interested in preparing metal particles with exact size and shape. We recently established a reliable route to Os-Pd mixed-metal nanoclusters with 21 metal atoms and precise geometry [1]. We also try to prepare larger metal nanoparticles coated on carbon nanotubes using this nanocluster as starting material. The resultant nanoparticles were found to have uniform size and same metal ratio as the nanocluster.



Metal core geometry of



TEM micrograph of metal

[1] Yung K.-F., Wong W.-T., *Angew. Chem. Int. Ed.*, 2003, **5**, 553-555.

Keywords: carbon nanotube, metal cluster, osmium

P.07.01.17*Acta Cryst.* (2005). A61, C298**Synthesis and Structural Characterization of a Series of High-Hydride Content Osmium-Rhodium Carbonyl Complexes**

Jasmine P.K. Lau, Wing-Tak Wong, *Department of Chemistry, The University of Hong Kong, Pokfulam Road, HKSAR, P. R. China.* E-mail: h9924717@hkusua.hku.hk

Hydrido-transition metal clusters have been known for years, however few are reported in which the ratio hydride : metal exceeds unity. Such high hydrogen content of the clusters is important for the transition metal complexes to serve as hydrogenation catalyst and potential hydrogen storage materials. Hydrogenation of [Os₅Rh₂(η⁶-C₆H₅CH₃)(μ-CO)(CO)₁₆] with [Os₃(μ-H)₂(CO)₁₀] in chloroform under reflux resulted in two hydrogen rich compounds [{Os₇Rh₃(μ-H)₁₁(CO)₂₃·CH₂Cl₂} **1** and [{Os₅Rh₃Cl(μ-H)₈(CO)₁₈}₂·CH₂Cl₂] **2** in moderate yield. While treatment of [Os₅Rh₂(η⁶-C₆H₅CH₃)(μ-CO)(CO)₁₆] with hydrogen in refluxing chloroform yielded another new cluster compound, [Os₅Rh(μ-H)₅(CO)₁₈] **3** in 20% yield, together with a known osmium-rhodium cluster, [Os₆Rh(μ-H)₇(μ-CO)(CO)₁₈] as the major compound. The molecular structures of the three clusters have been established by single crystal X-ray diffraction, carried out on crystals of compounds **1-3** by slow evaporation of *n*-hexane into CH₂Cl₂. The metal core of **2** consists of two tetrahedral, Os(1), Os(2), Rh(2), Rh(1) and Os(4), Os(5), Rh(3), Rh(1) units fused together to form a bitetrahedron via the Rh(1) vertex. The bitetrahedron is additionally bonded to another Os(3) by Rh(2) and Rh(3), which form a triangular face with a Cl atom tri-capping the three metal atoms in a μ³ mode. The corresponding Rh-Cl-Rh and Rh-Cl-Os bond angles fall in the range 70.1(3) to 73.0(3) °, which is comparable to that observed in a Cl face-bridged tritungsten cluster, [W₃(μ₃-Cl)(μ-Cl)₃Cl₉]³⁻.

Keywords: osmium-rhodium clusters, hydride content, single crystal X-ray diffraction

P.07.01.18*Acta Cryst.* (2005). A61, C298-C299**Scorpionate Complexes with the Main Group Elements Ca, Ba, Sr**

Riccardo Spagna², Carlo Santini¹, Maura Pellei¹, Giancarlo Gioia Lobbia¹, Massimo Pallotta¹, Simone Alidori¹, Mercedes Camalli², ¹*Dipartimento di Scienze Chimiche, Università di Camerino, Italy.* ²*IC-CNR Sezione di Monterotondo, Roma, Italy.* E-mail: riccardo.spagna@ic.cnr.it

The poly(pirazolyl)borate ligands together with various substituted forms have developed into one of the most versatile ancillary ligand in metal coordination chemistry. Particular attention is sometimes devoted to special azolyl rings, such as triazolyl, methyl- or trifluoromethyl-pyrazolyl rings. These ligands can exert quite