

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

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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**

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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.

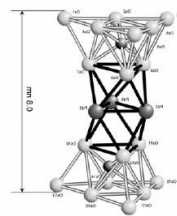
Keywords: 2,2'-diphenyldicarboxylic acid, barium complexes, crystal structure

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

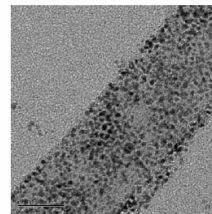
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Metal nanoparticles have aroused considerable attention in the

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**

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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**

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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

different electronic and structural effects when compared with the analogues. Very little has been done on poly(pyrazolyl)borate systems bearing electron withdrawing substituents. The electron withdrawing groups in polyfluorinated ligands commonly improve the volatility, oxidation resistance, thermal stability, and solubility of metal complexes. To our knowledge, no poly(azolyl)borates containing a -NO₂ function have been prepared, presumably due to difficulties in the synthesis of ligands having both a hydride and a nitro group. However, a poly(azolyl)borate containing a -NO₂ substituent could be of interest due to its high coordinative flexibility from κ⁴- to μ⁴-N₂O₂ coordination ability.

We report here on the syntheses and structural investigations of main-group metal elements Ca, Ba and Sr with the hydrotris(3-methylpyrazolyl)borate, the hydrotris(1,2,4-triazolyl)borate and the new hydrotris(3-nitro-1,2,4-triazolyl)borate, an emerging category of electron withdrawing substituted scorpionate ligands.

Keywords: metalloorganic chemistry, pyrazolyl, crystal structures

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Synthesis and Crystal Structure of [Co(HL)L]·CH₃OH (H₂L = Pyridoxal S-methylisothiosemicarbazone)

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Brown single crystals of the title compound, C₂₁H₂₉CoN₈O₅S₂, were prepared by the reaction of MeOH solutions of Co(Oac)₂·4H₂O and H₂L·H₂O in mole ratio 1 : 1. The complex has a *mer*-octahedral configuration with two non-equivalent tridentate ligands with O,N,N donors: one of the ligands having deprotonated isothiosemicarbazido fragment, whereas for the other additional deprotonation involves the pyridine nitrogen. The compound crystallizes in the P 2₁/c space group with a = 11.375(3) Å, b = 14.263(5) Å, c = 15.854(6) Å, β = 99.63(2)°, V = 2535.9(15) Å³. X-ray diffraction data were recorded on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Anisotropic refinement of all non-hydrogen atoms converged to R = 0.0567 for 4966 independent reflections and 356 parameters.

Keywords: cobalt(III) complex, pyridoxal S-methylisothiosemicarbazone, mer-octahedral configuration

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Novel Five-membered B-N-C Heterocycles

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Stable N-heterocyclic carbenes [1] have found a multitude of applications as catalyst components due to their remarkable ligand properties [2]. Their growing significance prompted us to investigate the stability of carbenes with inorganic backbones, as well as influence of the inorganic backbone on the ligand properties of the carbon ligand. To date, only one N-heterocyclic carbene with an inorganic backbone (:C(NR)₂PR') has been reported [3].

The tremendous importance of cyclopentadienyl (Cp) as a ligand in organometallic chemistry has prompted the design and synthesis of numerous five-membered, anionic heterocyclic analogs involving besides C also B, N, P, O and S. To our knowledge not more than three carbon atoms have been replaced by heteroatoms in heterocyclic analogs of Cp. We decided to investigate the synthesis, stability and coordination chemistry of Cp analogs derived from 1,2-diaza-3,5-diborolidine, where two C₂ fragments have been replaced with (B,N) pairs. The structures of novel five-membered B-N-C heterocycles will be presented.

[1] Arduengo III A. J., Harlow R. L., Kline M., *J. Am. Chem. Soc.*, 1991, **113**, 361. [2] Perry M. C., Burgess K., *Tetrahedron: Asymmetry*, 2003, **14**, 951. [3]

Despagnet-Ayoub E., Grubbs R. H., *J. Am. Chem. Soc.*, 2004, **126**, 10198.

Keywords: coordination complexes, heterocycles, catalysts

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A new Trinuclear Europium(III) Complex [Eu₃(C₁₀H₉N₃O₂)₄(C₁₀H₉N₃O)(CF₃CO₂)₆](C₆H₆)·2H₂O

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The new trinuclear Europium complex consists of composite ligands which include four di-2-pyridylamine N,N' dioxide, one di-2-pyridylamine N-oxide and six trifluoroacetate groups. All europium atoms are nine-coordinate: the coordination sphere of the Eu₂ and Eu₃ ions is completed by the amine N atom and two O atoms of each di-2-pyridylamine N,N' dioxide, and the carboxylate O atoms of three trifluoroacetate groups. The middle Eu₁ ion, which has no contact with trifluoroacetate groups, is coordinated by di-2-pyridylamine N,N' dioxide molecules and a di-2-pyridylamine N-oxide molecule. There are triple bridge bonds through the O atoms of the di-2-pyridylamine N,N' dioxide between all adjacent Eu ions, thus forming a discrete trinuclear complex. The Eu₁...Eu₂ and Eu₁...Eu₃ distances are 3.831 and 3.783 Å, respectively.

The benzene molecule and two water molecules should be included in this structure, because the complex single crystal has been prepared by solvothermally synthesized method.

Crystal Data: monoclinic; P2(1)/c; a=22.084(4) Å, b=16.973(3) Å, c=21.398(4) Å; β= 97.14(3)°; V=7959(3) Å³; Z= 4; Final R indices [I>2σ(I)]: R1 = 0.0570, wR2 = 0.1430; Goodness-of-fit on F²: 1.022.

Keywords: crystalline structure, rare-earth materials, pyridine complexes



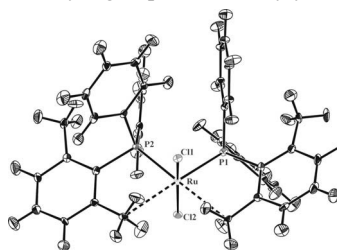
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Non Classical vs. Classical Metal...H₃C-C Interactions: A Neutron Diffraction Study of a 14-Electron Ruthenium(II) System

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A neutron diffraction study establishes the precise nature of the δ agostic interactions in the complex RuCl₂[PPh₂(2,6-Me₂C₆H₃)]₂ (1). By contrast to the classical agostic bonding, it is shown that two ortho-methyl groups of the xylyl substituents interact with the



unsaturated metal centre through two C-H bonds each. The result is also substantiated by the NMR data in solution. [1], [2] Re-examination of all the X-ray structures with β, γ, δ and ε M...H₃C-C moieties as well as DFT calculations on models of 1 allow to conclude that the agostic interactions span the range between the classical (M...η²-HC) and the non-classical (M...η³-H₂C) types, depending on the number of atoms between the metal and the methyl group.

[1] Baratta W., Mealli C., Herdtweck E., Ienco A., Mason S. A., Rigo P., *J. Am. Chem. Soc.*, 2004, **126**, 5549. [2] Baratta W., Herdtweck E., Rigo P., *Angew. Chem. Int. Ed.*, 1999, **38**, 1629.

Keywords: neutron structure determination, hydrogen bonding of coordination compounds, databases