

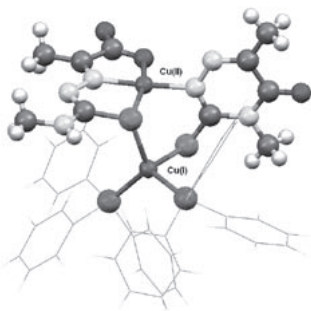
## P07.01.13

*Acta Cryst.* (2008). A64, C403**Bis(tpp)copper(I) thiosemicarbazones: Unexpected chemistry revealed by X-ray diffraction**

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Starting from bis(triphenylphosphine)copper(I) salts and from methylpyruvate thiosemicarbazone we have planned the synthesis of several complexes. The choice has fallen on these compounds for two main reasons: first, triphenylphosphines are known to stabilize copper in its lower oxidation state and, second, tertiary phosphines seem to enhance the solubility of Cu(I) thioamide complexes. The overwhelming majority of analogous compounds present the ligand that behaves as monodentate through the sulphur atom, in agreement with the soft nature of copper(I), and the remaining fourth position occupied by a halide. We have recently demonstrated that it is the presence or absence of soft ligand competitors that influence the coordination mode of thiosemicarbazones and not the protonation of the azinic nitrogen that renders them monodentate. In the course of these studies we have met with spectral and analytical anomalies that have been clarified by X-ray crystallography. A few compounds contain copper clusters, others contain ligands that have partially undergone a cyclization and in two cases linear and cyclic ligands bind two copper centres in two different oxidation states.

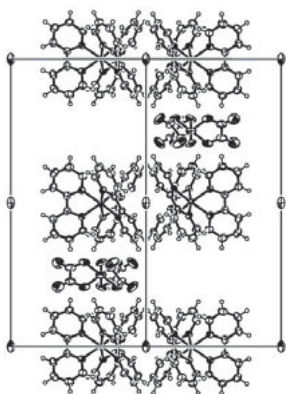


Keywords: copper coordination compounds, mixed-valence transition-metal compounds, clusters in coordination complexes

## P07.01.14

*Acta Cryst.* (2008). A64, C403**Porous structure of bis{tris(bipyridine)ruthenium(II)} tris(oxalato)cobaltate(III) chloride**Hiroshi Miyamae<sup>1</sup>, Ayumi Sato<sup>1</sup>, Satoshi Tachiyashiki<sup>2</sup>, Goro Hihara<sup>1</sup>  
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Slow mixing of water solutions of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (bpy=bipyridine) with K<sub>3</sub>[Co(ox)<sub>3</sub>] (H<sub>2</sub>ox=oxalic acid) gave red block title crystals. It crystallizes in hexagonal, space group P6<sub>3</sub>22, with *a*=13.0506(3) Å and *c*=24.1223(5) Å. The unit cell contains two metal complex sandwiches in which [Co(ox)<sub>3</sub>]<sup>3-</sup> anion is sandwiched by two [Ru(bpy)<sub>3</sub>]<sup>2+</sup> cations and two Cl<sup>-</sup> ions they are surrounded by six bpy moieties of different Ru complexes (Figure below: showing the unit cell



projection along the (110) direction). The stack forms big void which can store the volume of [Co(ox)<sub>3</sub>]<sup>3-</sup> anion.

Keywords: ruthenium compound, cobalt compound, porous structure

## P07.01.15

*Acta Cryst.* (2008). A64, C403**Structural study of hydride and dihydrogen ligands ruthenium complexes: Reversible hydrogen release**

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The widespread use of dihydrogen as an energy carrier for onboard applications is an important challenge for economical and environmental issues. Selective activation and functionalization of alkanes is also a continuing area of interest, and efficient production of dihydrogen through catalyzed dehydrogenation of abundant hydrocarbons would be very valuable. An attractive goal is to combine inorganic hydrides and organic compounds as a source of hydrogen materials. We first isolated a new bis(dihydrogen) complex RuH<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>)<sub>2</sub>(PCyp<sub>3</sub>)<sub>2</sub>, (1) characterized by NMR, single-crystal X-ray and neutron diffraction. The neutron diffraction study is the first carried out for a bis(dihydrogen) complex.[1] We present as well the X-ray structures of two new Ru complexes: the Ru(0) complex [Ru{PCyp<sub>2</sub>(h<sub>2</sub>-C<sub>5</sub>H<sub>7</sub>)<sub>2</sub>}(h<sub>2</sub>-C<sub>2</sub>H<sub>4</sub>)], and the trans dihydride [RuH<sub>2</sub>{PCyp<sub>2</sub>(η<sup>2</sup>-C<sub>5</sub>H<sub>7</sub>)<sub>2</sub>}. Both structures show the dehydrogenation of one cyclopentyl ring of each phosphine ligand. [2] The formulation of each complex has been ascertained by an X-ray structural study. Each experiment was carried out at 100 K, in order to prevent dihydrogen rotation, and to help the localisation of the hydrogen atoms around the ruthenium. We have observed an easy partial dehydrogenation of the phosphine ligands in 1, leading in a first step to equilibrium between dihydride complexes. A subsequent dehydrogenation process leads to a new Ru(0) complex. Ten hydrogen atoms have been removed from 1, which represents 1.71% of the weight of the complex. We have demonstrated that the process is fully reversible under very mild conditions. Complex 1 can serve as a model for hydrogen storage.

[1] M. Grellier et al, JACS, 2005,127, 17592 -17593.

[2] M. Grellier et al, Angew. Chem. Int. Ed., 2007, 46, 2613-2615.

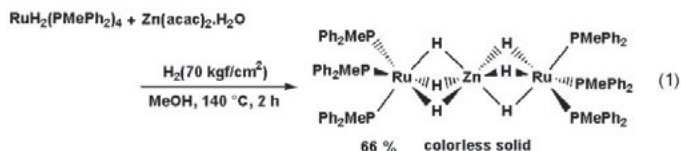
Keywords: hydride compounds, dihydrogen complexes, X-ray structure determination

## P07.01.16

*Acta Cryst.* (2008). A64, C403-404**Synthesis, structure, and reactivity of ruthenium-zinc trinuclear hydrides with phosphine ligands**Tsuneaki Yamagata<sup>1</sup>, Yukitsugu Maeda<sup>1</sup>, Hideaki Miyake<sup>1</sup>, Yasutaka Kataoka<sup>2</sup>, Kazuhide Tani<sup>3</sup><sup>1</sup>Osaka University, Department of Chemistry, Graduate School of Engineering Science, Machikaneyama 1-3, Toyonaka, Osaka, 560-8531, Japan, <sup>2</sup>Nara Women's University, Nara, 630-8506, Japan, <sup>3</sup>Higashiosaka College, Nishitutum Gakuen-chou 3-1-1, Higashiosaka, Osaka 577-8567, Japan, E-mail: qq5b5szd@coast.ocn.ne.jp

New heteropolymetallic hydride-bridged complexes, [(L)<sub>3</sub>Ru(μ-H)<sub>3</sub>]<sub>2</sub>Zn {L = 1/3 triphos (triphos = CH<sub>3</sub>C(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>) and PPh<sub>3</sub>},

were prepared in good yield from the reaction of  $\text{Ru}(\text{acac})_3$  and the corresponding phosphine under dihydrogen in the presence of excess zinc. When  $\text{MePPh}_2$  was employed as a phosphine, an analogous trinuclear complex  $[(\text{MePPh}_2)_3\text{Ru}(\mu\text{-H})_3]_2\text{Zn}$  was prepared only in 17% yield and could not be isolated in a pure state. We therefore looked for a new general procedure for the synthesis of this type of complexes and we could develop a new procedure. The reaction of  $\text{RuH}_2(\text{MePPh}_2)_4$  and an excess of  $\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$  under dihydrogen gave the  $[(\text{MePPh}_2)_3\text{Ru}(\mu\text{-H})_3]_2\text{Zn}$  in 66% isolated yield (eq. 1). We herein report the synthesis, characterization, structure, and catalytic activity of heterometallic hydride complexes,  $[(\text{L})_3\text{Ru}(\mu\text{-H})_3]_2\text{Zn}$ .



Keywords: cluster compounds, ruthenium zinc hydride compounds, catalytic hydrogenation

### P07.01.17

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#### Syntheses, characterization and DFT investigations of iridium complexes and diprotonated terpyridines

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Terpyridine complexes in the form of  $[\text{IrCl}(\text{L})(\text{terpy})](\text{PF}_6)_2$  and  $[\text{IrCl}(\text{L})(\text{tterpy})](\text{PF}_6)_2$  were prepared (L = bipyridine derivatives, terpy = 2,2':6',2''-terpyridine, tterpy = 4''-(4-tolyl)-2,2':6',2''-terpyridine). They were characterized by ESI-MS spectrometry, UV-vis spectroscopy, and cyclic voltammetry (CV). The electronic properties of some complexes were studied by using the B3LYP functional calculations and their optimized geometries were discussed in comparison with those of the experimentally observed ones. The ground and the excited triplet states were also examined by using density-functional-theory (DFT). A series of metal-free new blue emissive compounds of the type  $[\text{terpyH}_2]\text{Cl} \cdot \text{PF}_6$ ,  $[\text{tterpyH}_2]\text{Cl} \cdot \text{PF}_6$ ,  $[\text{ClterpyH}_2]\text{Cl} \cdot \text{PF}_6$ , and  $[\text{BterpyH}_2](\text{PF}_6)_2$  (Clterpy = 4'-chloro-2,2':6',2''-terpyridine and Bterpy = 4,4''-tert-butyl-2,2':6',2''-terpyridine) were also prepared and characterized by electrospray ionization mass spectrometry, UV-vis spectroscopy, and CV. The  $\pi\text{-}\pi^*$  bands in the UV region for the diprotonated ligands in acetonitrile were red-shifted relative to those of the corresponding neutral ligands. The CVs for all of the diprotonated ligands showed the first reduction wave at around -0.6 V, being more positive than those of the neutral ligands. The DFT approach was used to interpret remarkably large proton affinity of the terpy ligand.

Keywords: terpyridine, proton affinity, DFT calculation

### P07.01.18

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#### Iridium and zirconium formamidines as precursors for novel stable carbenes

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Amidines are bidentate nitrogen ligands displaying a rich coordination chemistry towards main group and transition elements. These ligands have been extensively used for the stabilization of multiple bonded transition metal moieties and as components in catalytic systems, and an extensive body of work is available on the subject. The formamidinate skeleton is also a fragment of the imidazolium precursors for the well-known N-heterocyclic carbenes, and in this case the backbone closing the heterocyclic ring has always been a main group fragment, most frequently carbon. A combination of the two fields of research for the purpose of synthesizing N-heterocyclic carbenes with transition metal backbones is an appealing target, because the transition metal backbone is expected to impart superior  $\sigma$ -donating and  $\pi$ -accepting properties to the carbene ligand. The crystal structural of the following Ir/Zr formamidines that are potential precursors to N-heterocyclic carbenes with Ir/Zr backbones will be presented: (1)  $\text{C}_{29}\text{H}_{34}\text{N}_2\text{O}_{0.25}\text{Zr}$ , FW = 505.80, triclinic, *P*-1,  $a = 8.128(1)$ ,  $b = 11.515(2)$ ,  $c = 28.177(6)$  Å,  $\alpha = 86.880(8)$ ,  $\beta = 85.367(10)$ ,  $\gamma = 72.953(11)^\circ$ ,  $V = 2511.8(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.046$ . (2)  $\text{C}_{58}\text{H}_{64}\text{BfIrN}_3\text{O}_{0.5}$ , FW = 1014.13, triclinic, *P*-1,  $a = 12.086(3)$ ,  $b = 13.590(2)$ ,  $c = 15.939(4)$  Å,  $\alpha = 85.705(13)$ ,  $\beta = 72.829(9)$ ,  $\gamma = 89.110(14)^\circ$ ,  $V = 2494.2(10)$  Å<sup>3</sup>,  $Z = 2$ ,  $R = 0.037$ . (3)  $\text{C}_{56}\text{H}_{59}\text{BfIrN}_3 \cdot 2 \text{CH}_2\text{Cl}_2$ , FW = 1146.92, triclinic, *P*-1,  $a = 12.625(3)$ ,  $b = 12.948(4)$ ,  $c = 17.065(3)$  Å,  $\alpha = 97.194(15)$ ,  $\beta = 98.857(15)$ ,  $\gamma = 110.250(11)^\circ$ ,  $V = 2537.6(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $R = 0.039$ .

Keywords: chelates, iridium compounds, zirconium compounds

### P07.01.19

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#### Synthesis and characterization of an N-heterocyclic carbene palladium-based complex

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A number of simple N-heterocyclic carbene (NHC) palladium-based complexes have recently emerged as effective catalysts for a variety of cross-coupling reactions [1]. Also some of the NHC ligands have proved to be particularly useful in olefin metathesis reactions [2]. Based on these findings and our continuing interest in developing more efficient and stable catalysts, we now report the straightforward preparation of the title type complex and its structural and spectroscopic characterization. The Pd atom lies on a center of inversion and is coordinated by two chloride anions and two C atoms from two carbene ligands and the ligands are therefore arranged in a trans-geometry. The Cl-Pd-C angles are  $91.31(7)^\circ$  and  $88.69(7)^\circ$ , and the Cl-Pd-Cl' and C-Pd-C' angles are precisely  $180^\circ$  [symmetry