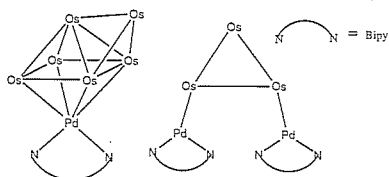


**PS07.03.12 THE CHEMISTRY OF PALLADIUM-OSMIUM MIXED-METAL CARBONYL CLUSTERS.** Wing-Tak Wong  
Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.

The heterometallic cluster  $\text{Os}_6\text{Pd}(\text{CO})_{18}(\text{bipy})$  has been isolated in moderate yield from the reaction of  $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$  and  $(\text{bipy})\text{Pd}(\text{CO}_2\text{Me})_2$ , and has been shown by a single crystal X-ray structure analysis to contain a monocapped octahedral metal core with the palladium occupying one vertex of the octahedron. Reaction of  $(\text{bipy})\text{Pd}(\text{CO}_2\text{Me})_2$  with  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  affords  $\text{Os}_3(\text{CO})_{12}(\text{Pd}(\text{bipy}))_2$  which exhibits an A-frame metal core. The unsaturated cluster  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  also react with *trans*-[ $\text{py}_2\text{PdCl}_2$ ] to give a range of mixed-metal clusters of palladium and osmium. All new clusters have been fully characterized by spectroscopic methods and crystallography. Some structural formula of these mixed-metal clusters are shown in the following figure:



**PS07.03.13 MOLECULAR DESIGN FOR NOVEL SULFUR-COORDINATED TRANSITION METAL CLUSTERS.** X.-T. Wu, Q. Huang, Q.-M. Wang, T.-L. Sheng, J.-X. Lu, State Key Laboratory of Structural Chemistry, Fujian Institute of Research or Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China

Molecular design for some novel molybdenum(tungsten)-copper(silver)-sulfur clusters is reported. The following clusters have been synthesized and characterized (1) Two novel octanuclear clusters  $[\text{Et}_4\text{N}]_4[\text{M}_4\text{Cu}_4\text{S}_2\text{O}_4]$  ( $\text{M}=\text{Mo}, \text{W}$ )

(2) Two novel dodecanuclear clusters  $[\text{M}_4\text{Cu}_4\text{S}_2\text{O}_4(\text{CuTMEN})_4]$  ( $\text{M}=\text{Mo}, \text{W}$  and  $\text{TMEN}=\text{N}, \text{N}, \text{N}', \text{N}'$ -Tetramethylethylenediamin).

(3) The novel double-chain cluster  $[\text{S}_2\text{W}_2\text{Ag}(\text{NH}_3\text{C}(\text{CHOH})_3(\text{H}_2\text{O}))_n]$ .

### Exotic Molecules-Organometallic

**PS07.04.01 NOVEL LANTHANIDE PYRAZOLYL BORATE COMPLEXES WITH FAST DATA ACQUISITION AT LOW TEMPERATURE.** Mark R.J. Elsegood,<sup>a</sup> Andrea Sella,<sup>b</sup> Graham H. Maunder<sup>b</sup> and Sung-Ying Liu<sup>b</sup>, <sup>a</sup>Dept. of Chemistry, Bedson Building, The University of Newcastle-upon-Tyne, Newcastle-upon-Tyne, NE1 7RU, UK., <sup>b</sup>Dept. of Chemistry, University College London, 20 Gordon St., London, WC1H 0AJ, UK.

We present the structures of several lanthanide complexes containing sterically demanding polypyrazolylborate ligands. Such compounds show considerable potential in organic synthesis. Structural data are therefore vital in the understanding of structure-reactivity relationships.

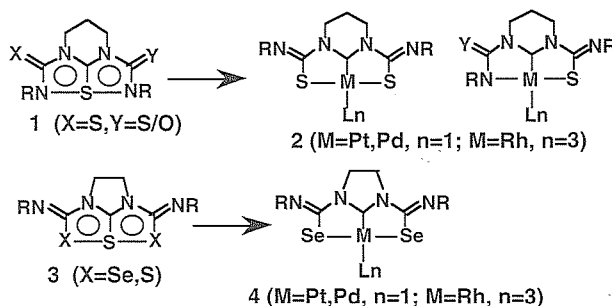
Data were collected either on a state-of-the-art Siemens SMART area detector diffractometer, or on a Stoe-Siemens 4-circle instrument. Data sets are typically collected overnight on the SMART, aided by the excellent sensitivity of the CCD detector, rapid data read-out times, and high data redundancy.

Since many of the compounds are air and moisture sensitive, and frequently crystallise with solvent molecules included in their lattices, data are routinely collected at low temperature using a Siemens LT2 low temperature device (SMART), or a Cryostream Cooler (Stoe-Siemens). Previous attempts at collecting data at ambient temperatures were unsuccessful.

We present our latest results, including complexes of La, Sm, and Yb. The structure of  $[\text{Sm}(\text{bis-pyrazolylborate})-\text{O}-\text{C}-\text{Mo}(\text{CO})_2(\text{MeCp})].1.5\text{C}_7\text{H}_8$ , for example, illustrates the great benefits of rapid data collection at low temperature.

**PS07.04.02 STRUCTURES OF NOVEL METAL-CARBENE COMPLEXES DERIVED FROM HYPERVALENT DIAZADISELENATHIAPENTALENES.** F. Iwasaki, H. Nishiyama, N. Manabe, M. Yasui, N. Matsumura<sup>†</sup>, Dept. of Applied Phys. and Chem., The Univ. of Electro-Comm., Chofu, Tokyo 182, Japan, <sup>†</sup>Dept. of Applied Chem., College of Eng., Univ. of Osaka Prefecture, Sakai, Osaka 591, Japan

Novel metal-carbene complexes (2) with a metallapentalene framework were obtained from 6a-thiatetraazapentalenes (1) which contain a hypervalent N-S-N bond by treating with  $\text{Pt}(\text{PPh}_3)_4$ ,  $\text{Pd}(\text{PPh}_3)_4$  and  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  [Matsumura, et al. (1995) J. Am. Chem. Soc. 117, 3623]. X-Ray investigations revealed that the central sulfur atom in 1 was substituted by a metal atom and that thioamide groups on one or both sides were rotated to form metal-sulfur bonds in the resultant metallapentalene framework. From the MO calculations on Frontier electron densities of the tetraazathiapentalenes, 1, and the results of the structures of carbene complexes, we proposed the mechanism of the formation of these metal-carbene complexes. This mechanism suggests that starting compounds could be S-S-S or Se-S-Se hypervalent systems instead of N-S-N hypervalent systems. In fact, recently we obtained metal complexes from diselenathiapentalenes, 3. X-ray structure analyses revealed that these complexes were also novel metal-carbene complexes 4 coordinated by Se atoms. In this presentation, the structural features of diaza-tri-thia/selena-pentalenes (3) and metal-carbene complexes (4), as well as those of 2 and the reaction mechanism will be reported.



**PS07.04.03 TOPOCHEMICAL AND HEAT-PHYSICAL PROPERTIES OF  $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2$  COMPLEX AND ITS CRYSTALLOSOLVATES.** L. K. Kim, Kh. T. Sharipov, V. P. Bruskov, Institute of Chemistry, Tashkent, Uzbekistan

This study is devoted to the investigation of physical and chemical properties of  $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2$  complex and its crystallosolvates. The quantitative estimation of the energy of solvent molecules tearing off complex molecule depending on structure of crystallosolvate and solvent nature is given. Dominant mechanism of crystallosolvates thermodissociation kinetics in a 0.5-50% range of conversion amount has been determined.  $\lg A = aE + b$  compensation effect relationship is established to be specific to the isostructural or similarly constructed coordinative compounds.

In 270-320K temperature range with constant pressure in adiabatic regime the heat capacity of  $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2$  complex and its crystallosolvates have been measured. The polynomials of the heat capacity equations have been calculated for the substances under study. The crystallosolvates thermodynamic parameters calculated have been compared with the kinetic ones of their topochemical dissociation and correlated with their packing types. On adsorption parameters of polar solvent (n-butanol and acetone) from unpolar medium (benzene) the comparative adsorptive characteristics of the  $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2$  and  $\text{WO}_2(\text{C}_6\text{H}_5\text{CONHO})_2$  complexes are given. These substances are recommended as synthetic sorbents for unpolar solvents cleaning from minute quantities of polar ones.