PS07.03.04 STRUCTURE AND CONFORMATION OF METAL CLUSTER COMPLEXES FROM TRIPHENYLPHOSPHINE RUTHENIUM CARBONYL CARBOXYLATES.

S. Ianelli & M. Nardelli, Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Universita' di Parma, Viale delle Scienze 78, I-43100 Parma, Italy. M.Bianchi, P.Frediani, A.Salvini, C.Faggi, S. Papaleo, F. Piacenti, Dipartimento di Chimica Organica "Ugo Schiff", Universita' di Firenze, Via G. Capponi 9, I-50121 Firenze, Italy.

The behaviour of Ru(CO)2(MeCO2)2(PPh3)2 (1), Ru2(CO)4(MeCO2)2(PPh3)2 (4) and Ru4(mu-H)4(CO)8(PPh3)4 (9) with H2 under 100 atm pressure at different temperatures has been studied and the obtained products characterized. The molecular structures of Ru3(mu-H)2(CO)8(mu3-PPh) (PPh3) (5), Ru4(CO)8(mu4-PPh)2(mu-PPh2)2 (7) and Ru4(mu-H)4(CO)7(mu4-PPh) (mu-PPh2)2 (PPh3) (8), obtained from compound (4), have been determined in the solid state by single crystal X-ray diffraction. The hydride nature of compounds (5) and (8) has been shown both from the N.M.R. spectra and X-ray analysis, while no hydride hydrogen was found in compound (7). The knowledge of the structures allows to interpretate the formation reactions of the compounds obtained. The conformation of the phosphine ligands is considered in connection with the intramolecular steric hindrance and packing requirements.

PS07.03.05 STUDY ON STRUCTURES OF d^{10} METAL POLYNUCLEAR COMPLEXES.

Xianglin Jin, Kaluo Tang and Youqi Tang, Institute of Physical Chemistry, Peking University, Beijing 100871, P. R. China

More than ten d^{10} metal (Cu,Ag,Cd) cluster complexes have been synthesized by the insertion of carbon disulfide into M-S bonds and structurally characterized by x-ray diffraction. We have found that silver and copper thiolate complexes can react with CS_2 in the presence of PPh_3 to give mononuclear insertion products, which can react easily with various solvents to form unexpected polynuclear complexes, such as, $Cu_{14}(\mu_2\text{-}S)(SPh)_{12}(PPh_3)_6$(1), $Ag_{14}(\mu_6\text{-}S)(SPh)_{12}(PPh_3)_8$(2), $(Ag_5I_6)n(Ph_3PCH_2I)n$(3) and so on. We also found some cadmium thiolate complexes react with CS_2 in organic solvents, resulting polynuclear complexes $(Me_4N)_2[SCd_8(SPh)_{12}Cl_4]$(4), $[Cd(H_20)_6]$ $[SCd_8(SPh)_{12}Cl_4]$(5), $[S_4Cd_{17}(SPh)_{24}(CH_30CS_2)_2]n$(6).

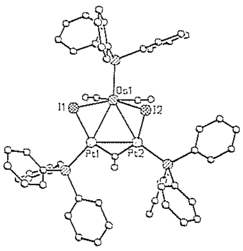
In complexes (1) or (2), there is a cage $M_{14}S_{12}$ (M=Cu,Ag) which is composed of staggered M_6, M_8 and S_{12} polyhedra. The central S atom is essential for the formation of M_{14} complexes, which might be the result of nucleophilic reaction of PhS^- and CS_2. In complex (3), the polyanion $(Ag_5I_6)n$ is composed of alternate I_6 pentagonal pyramids and Ag_5 pentagons, which connected by Ag-I bonds to form a layered "pagoda" structure. In complexes (4),(5) or (6), μ_4-S atoms which also might be from the nucleophilic reaction of PhS^- and CS_2 cement together Cd ions to form Cd_8 or Cd_{17} polynuclear complexes.

PS07.03.06 CRYSTAL STRUCTURE OF NOVEL MIXED-METAL CLUSTER COMPLEX $OsPt_2(\text{-}I)_2(\text{-}CO)(PPh_3)_3(CO)_2 0.5C_6H_{14}$.

V.P.Kirin, A.V.Virovets, V.I.Alekseev, N.V.Podberezskaya, V.A.Maksakov Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia

The title compound with unexpected asymmetry in the cluster core was prepared by the reaction (benzene, 80°C, 1.5h):
$Os_2(\text{-}I)_2(CO)_6 + Pt(PPh_3)_2(PhC_2Ph)$
$OsPt_2(\text{-}I)_2(\text{-}CO)(PPh_3)_3(CO)_2 + Os_2(\text{-}I)_2(CO)_{6\text{-}n}(PPh_3)_n$ (n=1,2).
The first product was crystallized from $Et_2O/n\text{-}C_6H_{14}$ 3:1 mixture:

Crystal data: monoclinic, a=21.073(4), b=15.533(3), c=18.753(3) Å, ß=109.86(2)°, V=5773(2) Å^3, $P2_1/c$, Z=4, D_x=2.011 gcm^{-3}, CAD4, MoK, R_F=0.0567 for 3617 F_{hkl}>4(F). Presence of two Pt atoms in this cluster corresponds with the ^{31}P and ^{195}Pt NMR data. Os and Pt atoms were distinguished taking into account their ligand environment: $2CO+2I+PPh_3$ for Os, $I+PPh_3$+CO-bridge for both Pt atoms.



Some bond distances: Os-Pt 2.796(2), 2.852(2), Pt-Pt 2.685(2), Os-I 2.769(2), 2.787(2), Pt-I 2.694(2), 2.745(2), Os-P 2.380(8), Pt-P 2.248(8), 2.250(8) Å. The most interesting feature of the complex is that the -I ligands are coordinated asymmetrically (angles between $OsPt_2$ and OsPtI planes are 42.0° and 84.5°) which affects on the Os-Pt bond lengths. The possible reason for this is the repulsion between bulky PPh_3 and I ligands.

PS07.03.07 STRUCTURAL FLEXIBILITY OF $[M_3(\mu_3\text{-}L)(\mu\text{-}dppm)_3]^{n+}$ TWIN-BOWL CLUSTERS.

Kenneth W. Muir, Ljubica Manojlovic-Muir & Mark W. Hughes. Chemistry Department, Glasgow University, Glasgow G12 8QQ, U.K.

The coordinatively unsaturated cluster complexes $[M_3(\mu_3\text{-}L)(\mu\text{-}dppm)_3]^{n+}$ (n = 0-2: M = Pd, Pt; dppm = Ph2PCH2PPh2; L = CO, Hg, $AuPh_3$, ReO_3, SnX_3 etc.) have proved useful as models for the chemistry of Pd and Pt surfaces and as homogeneous catalysts for some commercially important reactions (Puddephatt, Manojlovic-Muir & Muir, 1990).

A feature common to these complexes is the $M_3(\mu\text{-}dppm)_3$ building block in which both faces of the latitudinal M_3P_6 skeleton are encircled by an array of phenyl rings to form two bowl-shaped cavities sharing a common base. One of these cavities accommodates a μ_3-L ligand, while the other remains available for covalent binding of another ligand or for docking a small molecule or ion. Our previous crystallographic studies of the compounds obtained by addition reactions of $[M_3(\mu_3\text{-}L)(\mu\text{-}dppm)_3]^{n+}$ clusters have revealed a remarkable structural diversity, including the first examples of guest-host complexes in cluster chemistry (Manojlovic-Muir, Muir, Lloyd & Puddephatt, 1985). One of the main factors contributing to this diversity is the structural flexibility of the $M_3(\mu\text{-}dppm)_3$ core.

As part of our study of the molecular structures, bonding and guest-host recognition in these complexes and of their molecular organization in the solid state, we are investigating (i) conformational changes of the dppm ligands and (ii) their effect on the size and shape of the cavities of the $M_3(\mu\text{-}dppm)_3$ fragment in a series of twin-bowl $[M3(\mu_3\text{-}L)(\mu\text{-}dppm)_3]^{n+}$ clusters.

Manojlovic-Muir, Lj, Muir, K.W., Lloyd, & Puddephatt, R.J. (1985). *J. Chem. Soc., Chem. Commun.*, 536 - 537 and refs therein.
Puddephatt, R.J., Manojlovic-Muir, Lj., & Muir, K.W. (1990). *Polyhedron*, **9**, 2767 - 2802.