
The behaviour of Ru(II)(MeCO2)2(PPh3)2 (1), Ru(II)(CO)4(MeCO2)2(PPh3)2 (2) and Ru(III)(H2)4(CO)8(PPh3)4 (9) with H2 under 100 atm pressure at different temperatures has been studied and the obtained results characterized. The molecular structures of Ru3(μ-H)2(CO)8(me3-PPh)2 (3), Ru4(μ-CO)8(me4-PPh)2(μ-PPhh) (4) and Ru4(me-H4)(CO)8(PPh3)4 (9) 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 formation of the phosphine ligands is considered in connection with the intramolecular steric hindrance and packing requirements.

PS07.03.05 STUDY ON STRUCTURES OF d10 METAL POLYNUCLEAR COMPLEXES. Xiaolin Jin, Kaifu Tang and Youji Tang. Institute of Physical Chemistry, Peking University, Beijing 100871, P.R. China.

More than ten d10 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 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 formation of the phosphine ligands is considered in connection with the intramolecular steric hindrance and packing requirements.

PS07.03.06 CRYSTAL STRUCTURE OF NOVEL MIXED-METAL CLUSTER COMPLEX OsPt2(μ-I)2 (-CO)(PPh3)2(CO)2,0.5C6H14. V.P. Kirin, A.V. Virovets, V.I. Alekseev, N.V. Podberezhkaya, 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(μ-I)(CO)x + Pt(PPh3)2Cl2 + PhCS2 + Pt(CO)(μ-I)(PPh3)2(n = 1, 2).

The first product was crystallized from Et3O/n-C6H14 3:1 mixture.

Crystal data: monoclinic, a = 21.073(4), b = 15.533(3), c = 18.753(3) Å, β = 109.86(2), β = 90°, V = 5773.2 Å³, F2, Z = 4, D = 2.011 g/cm³, CaD4, MoKα, R = 0.0576 for 3617 unique reflections.

In all the results two Pt atoms in the cluster corresponds with the 3d- and 19p- NMR data. Os and Pt atoms were distinguished using the relative gain in the Os-Pt bond lengths. The possible reason for this is the repulsion between bulky PPh3 and PPh2 ligands.

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 2.383(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 Os–Pd and Os–Pd planes are 42.0° and 84.5°) which affects the Os–Pt bond lengths. The possible reason for this is the repulsion between bulky PPh3 and PPh2 ligands.

PS07.03.07 STRUCTURAL FLEXIBILITY OF [M3(μ3-L)(μ-dppm)3]1+ TWIN-BOWL CLUSTERS. Kenneth W. Muir, Ljubica Manojlovic-Muir & Mark W. Hughes. Chemistry Department, Glasgow University, Glasgow G12 8QQ, U.K.

The coordinatively unsaturated complex clusters [M3(μ3-L)(μ-dppm)3]1+ (n = 0–2: M = Pd; dppm = Ph2PCH2PPh2; L = CO, Hg, AuPh3, ReO3, SnX3 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 M3(μ-dppm)3 building block in which both faces of the latitudinal M3P6 skeleton are encircled by an array of phenyl rings to form two bow-shaped cavities sharing a common base. One of these cavities accommodates a μ3-L ligand, which is 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 [M3(μ3-L)(μ-dppm)3]1+ 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 M3(μ-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) the conformational changes of the dppm ligands and (ii) their effect on the size and shape of the cavities of the M3(μ-dppm)3 fragment in a series of twin-bowl [M3(μ3-L)(μ-dppm)3]1+ clusters.