

09.5-7 THERMAL REACTION OF $H_3Re_3(CO)_{12}$ WITH $P(C_6H_5)_3$ AND $P(OC_6H_5)_3$. By L.K. Liu, Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan 115; S.C. Lin and C.P. Cheng, Department of Chemistry, National Tsing Hua University, Hsin-Chu, Taiwan 300, Republic of China.

The thermal reaction of $H_3Re_3(CO)_{12}$ with excess $P(C_6H_5)_3$, results in trisphenylphosphine substituted rhenium cluster, $H_3Re_3(CO)_9(P(C_6H_5)_3)_3$, as the major product with a 71% yield. An x-ray structure analysis of $H_3Re_3(CO)_9(P(C_6H_5)_3)_3$, has been performed with the following results: M_r 1597.57, monoclinic $P2_1/n$, $a=15.598(1)$, $b=9.530(2)$, $c=41.685(3)\text{\AA}$, $\beta=80.60(1)^\circ$, $V=6113.1(1)\text{\AA}^3$, $Z=4$, $CuK\alpha$ radiation, room temperature data, $R=0.049$ for 7361 reflections with $I \geq 2.5\sigma(I)$. The $H_3Re_3(CO)_9(P(C_6H_5)_3)_3$ molecule has a triangular Re_3 core coordinated propeller-wise by 3 $P(C_6H_5)_3$ ligands in the molecular plane with a virtual C_{3h} symmetry, not counting the orientation of phenyl groups. The bulky $P(C_6H_5)_3$ introduces crowding such that all of the *cis*-CO ligands are tilted away from it. The mono-substituted $H_3Re_3(CO)_{11}(P(C_6H_5)_3)$ exists in two interconvertible isomeric forms with $P(C_6H_5)_3$ axial or equatorial (C.Y. Wei et. al, *J. Organomet. Chem.*, 1981, 213, 63-78). Nonetheless, the tris-substituted $H_3Re_3(CO)_9(P(C_6H_5)_3)_3$ has a structure consistent with a minimal steric interaction. The thermal reaction of $H_3Re_3(CO)_{12}$ with excess $P(OC_6H_5)_3$, similarly results in trisphenylphosphite substituted $H_3Re_3(CO)_9(P(OC_6H_5)_3)_3$, as a major product but with only a 37.5% yield because of further ligand substitutions.

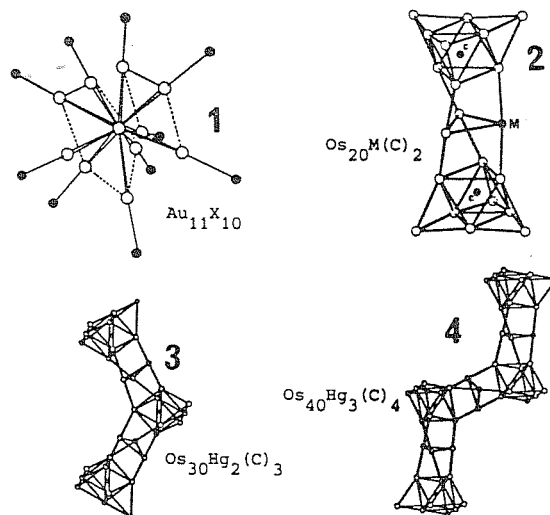
09.5-8 THE CRYSTAL AND MOLECULAR STRUCTURE OF A NOVEL GOLD-SULPHIDO CLUSTER COMPOUND
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The three-dimensional structure of a novel cluster compound of gold has been determined by the X-ray method. The complex $[Au_{13}S_8(Ph_2PCH_2CH_2PPh_2)_6]H_2O$ crystallises from chloroform solution in the monoclinic system, space group $P2_1/n$, with $a = 17.746(11)$, $b = 34.544(3)$, $c = 29.272(6)\text{\AA}$, $\beta = 92.12(3)$, $U = 17932\text{\AA}^3$, $Z = 4$. A total of 17365 data were collected with $MoK\alpha$ radiation ($\mu(Mo-K\alpha) = 153.8\text{ cm}^{-1}$) on a CAD4 diffractometer using the $\omega/2\theta$ scan technique. A crystal of size $0.03 \times 0.012 \times 0.004\text{ cm}$ was employed in the data collection. The structure was solved by a combination of direct methods, Patterson and Fourier techniques and refined by a large-block least-squares process to a final R of 0.066 on the 5113 unique data for which $F^2 > 3\sigma(F^2)$.

In the cluster two structurally distinct types of gold atom can be identified. Type I gold is bound to two sulphide groups to form an inner core of six gold and two sulphur atoms; type II gold forms an outer ring of metal atoms where the donors are one sulphur and one phosphorus atom. Each bidentate phosphine ligand spans two adjacent gold atoms around the outside of the cluster. The inner cube is distinguished by the approximately octahedral geometry of its six metal atoms with the two sulphurs occupying *trans* coordination sites. The remaining sites involve $Au \dots Au$ interactions. The binding geometry of the type II gold atoms is less well defined although in each instance a *trans* arrangement of sulphur and phosphorus donors is observed. Further $Au \dots Au$ interactions are noted with at least one of these being with a type I metal.

09.5-9 STRUCTURES OF HIGH NUCLEARITY CLUSTERS; FACT AND FICTION. By Mary McPartlin, School of Chemistry The Polytechnic of North London, U.K.

Much frontier work in high nuclearity cluster chemistry depends, like protein crystallography, on an ability to extract an extraordinary amount of information from very limited X-ray data. Metal core geometry alone, judiciously combined with spectroscopic and analytical data, often proves to be the only means of assigning a correct molecular formula to a new cluster. For example the first high nuclearity cluster ever reported was shown from poor data to have a highly improbable metal centred $Au_{11}X_{10}$ ($X = P$ or S) core (1)



and allowed correct formulation as $Au_{11}(PPh_3)_7(SCN)_3$ (M. McPartlin, K. Mason and L. Malatesta, *Chem. Commun.* 1969, 334; F. Cariati and L. Naldini, *Inorg. Chim. Acta*, 1971, 172). This undreamt of Au_{11} framework has proved to be an arachno version of the Au_{13} unit which now dominates gold cluster work and which is thought to be the building block of 'super clusters' $[(Au_{13})_n]_n$ (G. Smith and N. Klein, *Angew. Chem.*, 1986, 98, 843.

Recent partial structure analyses of new large heterometallic osmium clusters established the unexpected metal framework (2) and this, together with the evidence of their quantitative decomposition to $[Os_{10}C(CO)_{24}]^{2-}$, allows them to be formulated unambiguously as $[Os_{20}M(C)_2(CO)_{48}]^{2-}$ ($M = Au$ or Hg) (S.R. Drake, K. Henrick, B.F.G. Johnson, J. Lewis, M. McPartlin and J. Morris, *J. Chem. Soc., Chem. Commun.*, 1986, 928). These structure analyses, and attempts to apply 'protein methods' to location of missing carbonyl ligands, will be reported.

Two key structural features established are (i) the mode of cluster build-up is *via* tetrahedral Os_4 cap opening and (ii) the total framework is a small fragment of a c.c.p. array of metal atoms with a translational dislocation at the central Os_2M triangle. These principles allow computer simulation (without X-ray data, another protein technique!) of probable frameworks for the new giant clusters $[Os_{30}Hg_2(C)_3(CO)_{72}]^{2-}$ (3) and $[Os_{40}Hg_3(C)_4(CO)_{96}]^{2-}$ (4) clusters, formulated on the basis of L.M.M.S. (S.R. Drake, B.F.G. Johnson, D. Kelland, J. Lewis and M. McPartlin and E.R. Wallach, *J. Chem. Soc., Chem. Commun.*, in press *Comm. No. 1810*).

Encouraged by the gold story, it is interesting to speculate that repetition of the building principles underlying the stepwise formation of the known $[(Os_{10}C)(M)_{n-1}((CO)_{24})_n]^{2-}$ clusters could lead to network structures, reminiscent of zeolites, possibly providing 'super clusters' for the next millenium.