

## 07-Crystallography of Organometallic and Coordination Compounds

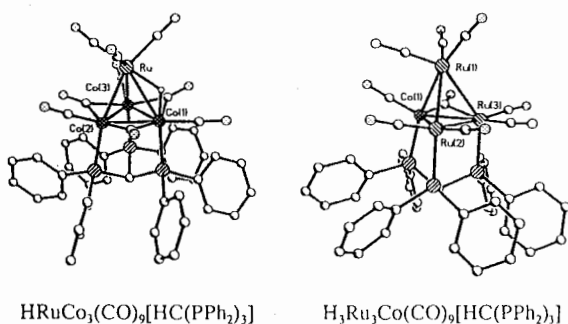
PS-07.03.20 CRYSTAL AND MOLECULAR STRUCTURES OF  $\text{HRuCo}_3(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$  AND  $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$ 

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The tetrahedral mixed metal clusters of the iron and cobalt groups form one of the most studied mixed metal system. The formula of these compounds can be generalized as  $\text{H}_x\text{M}_x\text{M}'_{4-x}(\text{CO})_{12}$ ,  $X=4-x$ , where M is Fe, Ru or Os, and M' is Co, Rh or Ir. These clusters and their derivatives are expected to possess catalytic activities in many reactions, for example in the homologation of methanol. Tridentate phosphine ligands coordinated on three different metal atoms in these compounds could provide a possibility to stabilize the metal skeleton which has been found to decompose under catalytic reaction conditions.

The reactions of  $\text{HRuCo}_3(\text{CO})_{12}$  (Hidai, M., Orisaku, M., Ue, M., Koyasu, Y., Kodama, T. and Uchida, Y. (1983). *Organometallics* 2, 292-298) and  $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_{12}$  (Gladfelter, W.L., Geoffroy, G.L. and Calabrese, J.C. (1980). *Inorg. Chem* 19, 2569-2573) with  $\text{HC}(\text{PPh}_2)_3$  in refluxing hexane produce mixtures which are separable on silica gel.  $\text{HRuCo}_3(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$  (I) and  $\text{H}_3\text{Ru}_3\text{Co}(\text{CO})_9[\text{HC}(\text{PPh}_2)_3]$  (II) were crystallized from hexane/ $\text{CH}_2\text{Cl}_2$  solution by slow evaporation. I crystallizes in the monoclinic space group  $P2_1/c$  with  $a=13.481(3)$ ,  $b=14.714(5)$ ,  $c=23.101(5)$  Å,  $\beta=97.66(2)^\circ$ ,  $V=4541(2)$  Å<sup>3</sup>,  $Z=4$ ,  $D_c=1.608$  g/cm<sup>3</sup>,  $\lambda(\text{Mo-K}\alpha)=0.71073$  Å,  $\mu=1.55$  mm<sup>-1</sup>, measurements at room temperature, final  $R=5.48\%$  for 3944 observed reflections and 485 variables. II crystallizes in triclinic space group  $P-1$ ,  $a=12.777(3)$ ,  $b=16.134(5)$ ,  $c=24.644(6)$  Å,  $\alpha=79.56(2)$ ,  $\beta=88.38(2)$ ,  $\gamma=84.15(2)^\circ$ ,  $V=4970(2)$  Å<sup>3</sup>,  $Z=4$ ,  $\lambda(\text{Mo-K}\alpha)=0.71073$  Å,  $\mu=1.37$  mm<sup>-1</sup>, measurements at room temperature, final  $R=7.9\%$  for 7063 observed reflections and 611 variables.

In the both compounds the tridentate phosphine ligand has replaced three terminal carbonyl ligands of the parent clusters. In I the arrangement of the metal atoms and bridging carbonyl ligands has been retained but the hydride ligand has moved from  $\mu_3\text{-Co}_3$  position to a Ru-Co edge bridging position due to steric requirements of the tridentate phosphine ligand, as shown in the Fig. below.



In II the tridentate phosphine ligand replaces three axial carbonyl ligands on a  $\text{CoRu}_2$  face. The rest of the cluster has remained unaltered including the positions of the hydrogen ligands except that the  $\text{CO}(4)$  carbonyl ligand forms an unsymmetrical bridge from  $\text{Co}(1)$  to  $\text{Ru}(3)$  as shown in the Fig. above.

## PS-07.03.21 HYDRIDE ATOM LOCATION AND AGOSTIC HYDRIDE INTERACTIONS IN TRIOSMIUM IMIDOYL CARBONYL CLUSTERS. By K.I. Hardcastle, Y. Yoo, S. Kabir and E. Rosenberg. Department of Chemistry, California State University, Northridge, CA 91330, USA.

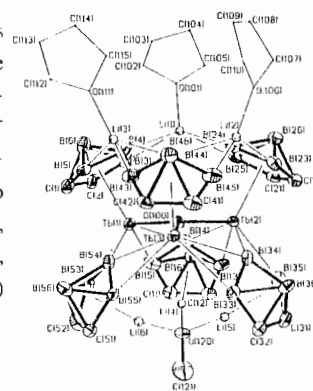
The enhanced reactivity of the cluster,

$(\text{u-H})(\text{u}_3\text{-n}^2\text{-C}=\text{NCH}_2\text{CH}_2\text{CH}_2)\text{Os}_3(\text{CO})_9$  (I), to add  $\text{HCl}$ ,  $\text{HBr}$  and  $\text{CF}_3\text{COOH}$  at room temperature to form compounds of the type,

$(\text{u-H})_2(\text{u}_3\text{-n}^2\text{-C}=\text{NCH}_2\text{CH}_2\text{CH}_2)\text{Os}_3(\text{CO})_9(\text{X})$ , where  $X = \text{Cl}$ ,  $\text{Br}$  or  $\text{CF}_3\text{COO}$ , has led to a detailed study of these compounds in order to precisely locate the hydride ligands in an attempt to understand the rather unusual chemical and nmr dynamic processes occurring in these clusters. The hydride ligand bridging the  $\text{Os1-Os3}$  edge, the same edge that the imido ligand bridges, is found to be asymmetrically located in the bridge and approximately 0.1-0.6 Å closer to the osmium to which the nitrogen atom is bound in all structures examined. In addition, the hydride bridging the  $\text{Os1-Os2}$  edge is found to be up above the triosmium plane and directed toward the axially bound chloride, bromide or trifluoroacetate ligand on  $\text{Os2}$ . The distance of this hydride to the axially bound chloride or bromide is significantly less than the sum of the van der Waals radii of the individual atoms by about 0.5 Å. These clusters also lose  $\text{HCl}$  or  $\text{HBr}$  readily and convert back to compound I.

## PS-07.03.22 STRUCTURAL STUDIES OF NOVEL METALLACARBORANE COMPLEXES OF EARLY TRANSITION METALS AND LANTHANIDES. By Hongming Zhang\*, Aderemi R. Oki, Ying Wang, Lei Jia and Narayan S. Hosmane, Department of Chemistry, Southern Methodist University, Dallas, Texas 75275, U. S. A.

There has been an increasing interest in the metallacarborane complexes of early transition metals and lanthanides, particularly in terms of their potential applications as catalysts. However, only a limited number of such complexes have been structurally characterized. The recent results in the structural studies of the species in which the carborane anion  $[\text{nido-2}-(\text{SiMe}_3)\text{-3-(R)-2,3-C}_2\text{B}_4\text{H}_4]^{2-}$  ( $R = \text{SiMe}_3, \text{Me}, \text{H}$ ) is  $\pi$ -bonded and/or bridged to  $\text{Ti(III)}$ ,  $\text{Zr(IV)}$ ,  $\text{Hf(IV)}$ ,  $\text{Y(III)}$ ,  $\text{Dy(III)}$ ,  $\text{Sm(III)}$ ,  $\text{Gd(III)}$ ,  $\text{Ho(III)}$ , and  $\text{Tb(III)}$  metals will be presented.



Trinuclear Tb(III) cluster