

## 09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.3-24 THE CRYSTAL STRUCTURE OF DEACARBONYL(BIS = (DIPHENYLPHOSPHINO)ETHYLAMINE)TRIRUTHENIUM By L. Subramony, D.W. Engel and K.G. Moodley, Departments of Physics and Chemistry, University of Durban-Westville, Private Bag X54001, Durban, 4000, South Africa.

$[\text{Ru}_3(\text{CO})_{10}\{(\text{C}_6\text{H}_5)_2\text{PN}(\text{C}_2\text{H}_5)_2\}(\text{C}_6\text{H}_5)_2]$  was prepared by dissolving  $\text{Ru}_3(\text{CO})_{12}$  and the specially prepared ligand in cyclohexane and irradiating with UV light. The product was isolated on a silica gel column and recrystallized from a dichloromethane-hexane mixture.

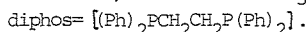
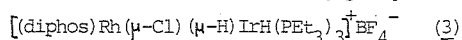
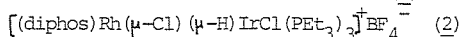
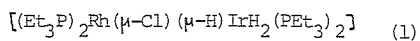
The unit cell of the complex is triclinic, space group  $P\bar{1}$  with dimensions  $a=14.732$ ,  $b=12.386$ ,  $c=10.982$  Å,  $\alpha=104.52$ ,  $\beta=100.64$  and  $\gamma=94.89^\circ$ , and  $Z=2$ .

5169 independent reflections were measured using MoK $\alpha$  radiation on a Philips PW 1100 diffractometer. The structure was solved by Patterson and Fourier methods and refined by blocked full-matrix least squares to a residual of 0.054 for 300 parameters and 3537 reflections with  $I>5\sigma(I)$ .

The effect of the ligand is to shorten the bridged Ru-Ru bond from 2.854 to 2.798 Å. The two trans axial phenyl groups on the phosphorus atoms cause the two neighbouring axial carbonyl ligands to tilt away from them and the pair of axial carbonyl ligands on the third Ru atom to rotate considerably from the normal to the Ru plane in order to maintain acceptable non-bonded distances.

09.3-25 COMPARATIVE STRUCTURAL STUDIES OF BINUCLEAR RHODIUM IRIIDIUM COMPLEXES WITH ( $\mu\text{Cl}$ ) AND ( $\mu\text{H}$ ) LIGANDS. By A. Albinati, H. Lehner and L.M. Venanzi, Institute of Pharmaceutical Chemistry, University of Milano, Italy, and Laboratorium für Anorganische Chemie, ETH Zürich, Switzerland.

The crystal structures of the following series of related Rh(I)-Ir(III) compounds have been determined:



The coordination geometry around the Rh atom is square planar; that around the Iridium is distorted octahedral with two phosphine ligands in axial positions and the third  $\text{PET}_3$  group trans to the  $\mu\text{-H}$  ligand in 2 and 3. The Rh-Ir distances show systematic differences (2.899(1) Å in 1, 2.903(1) Å in 2, 2.969(1) Å in 3) reflecting a change in the M-M interactions as a function of the electron densities at the metal centers, which, in turn, are influenced by the nature of the coordinated ligands. Systematic variations in the values of the Rh-Cl-Ir bond angles and Ir-P bond lengths will also be discussed.

The asymmetry in the Ir-Rh-P angles (145.11(6)° and 116.99° (8) in 1, 152.64(2)° and 122.36(6)° in 2, 155.09(3)° and 122.04(9)° in 3) suggests the presence of asymmetric  $\mu\text{-H}$  bridges. This assumption is supported, in compound 2, by the experimental localization of the H atom and its lsq refinement.

09.3-26 NEUTRON DIFFRACTION STUDIES OF  $\text{Fe}(\text{CO})_3[\eta^3\text{-}(\text{C}_6\text{H}_5)_2\text{C-C-O}]$  AND  $\text{Fe}_2(\text{CO})_6[\text{CH}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)]$ : CHARACTERIZATION OF AN UNUSUAL  $\pi\text{-ALLYL}$ ,  $\sigma\text{-ARYL}$ ,  $\pi\text{-OLEFIN}$  SYSTEM.\* By I. Bkouche-Waksman,† J.S. Ricci, Jr.,‡ T.F. Koetzle, Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973 USA; J. Weichmann and W.A. Herrmann, Institut für Anorganische Chemie, Johann Wolfgang Goethe Universität, D-6000 Frankfurt-am-Main 50 BRD.

Single-crystal neutron diffraction studies of the title compounds have confirmed that  $\text{Fe}(\text{CO})_3[\eta^3\text{-}(\text{C}_6\text{H}_5)_2\text{C-C-O}]$  (I), formed by photolysis of diphenylketene in the presence of iron pentacarbonyl, is transformed upon irreversible thermal decarbonylation into the  $\pi\text{-allyl}$ ,  $\sigma\text{-aryl}$ ,  $\pi\text{-olefin}$  complex  $\text{Fe}_2(\text{CO})_6[\text{CH}(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)]$  (II). The unusual bridging organic ligand in (II) is related formally to diphenyl carbene by transfer of a phenyl ring proton to the carbene carbon atom. Crystal Data. Compound (I): space group  $P\bar{1}$ ,  $Z=4$ ,  $a=8.852(2)$ ,  $b=11.571(4)$ ,  $c=14.558(6)$  Å,  $\alpha=106.94(2)$ ,  $\beta=89.76(2)$ ,  $\gamma=91.94(2)^\circ$  at  $T=15$  K.  $R(F^2)=0.08$  for 5206 independent reflections with  $(\sin\theta)/\lambda < 0.69$  Å $^{-1}$ , and 578 variable parameters. Compound (II): space group  $P2_1/n$ ,  $Z=4$ ,  $a=8.298(3)$ ,  $b=12.463(6)$ ,  $c=17.380(3)$  Å,  $\beta=97.95(1)^\circ$  at  $T=230$  K.  $R(F^2)=0.11$  for 2622 independent reflections with  $(\sin\theta)/\lambda < 0.69$  Å $^{-1}$ , and 335 variable parameters.

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09.3-27 THE CHARACTERIZATION OF THE  $\mu\text{-CYCLO-PROPYLIDENE}$  AND METHYL CYCLOPROPYLIDENE DIIRON COMPLEXES  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CCH}_2\text{CH}_2)$  AND  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CCH}(\text{CH}_3)\text{CH}_2)$ . MODEL INTERMEDIATES FOR HYDROCARBATION AND FISCHER-TROPSCH MECHANISMS. By Gerald B. Ansell and Susan Leta, Analytical Division, and Edwin L. Hoel, Corporate Research Science Laboratories, Exxon Research and Engineering Company, Clinton Township, NJ 08801.

The structures of the first reported cyclopropylidene complexes, the stable diiron complexes  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CCH}_2\text{CH}_2)$  (A), and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CCH}(\text{CH}_3)\text{CH}_2)$  (B), will be described. They were synthesized as model compounds during the investigation of hydrocarbation and Fischer-Tropsch synthesis mechanisms. (A), crystallized from ether, is orthorhombic,  $Pnma$   $a = 13.008(77)$ ,  $b = 14.126(71)$ ,  $c = 7.836(27)$  Å,  $Z = 4$ ,  $R = 0.032$ ,  $R_w = 0.037$ . (B), crystallized from hexane, is monoclinic,  $P2_1/n$   $a = 8.884(3)$ ,  $b = 11.601(3)$ ,  $c = 15.021(4)$  Å,  $\beta = 102.84(10)^\circ$ ,  $Z = 4$ ,  $R = 0.070$ ,  $R_2 = 0.076$ . Both clusters possess an  $\text{Fe}_2$  backbone with Fe-Fe distances of 2.504 Å ( $\pm 2$ ) bridged by a  $\mu\text{-carbonyl}$  and one carbon atom of a cyclopropylidene ring. In both compounds each iron is also bonded to a linear carbonyl and a cyclopentadienyl ring, which are in cis configuration with respect to the plane of the bridging ligands. Corresponding bond lengths within the materials are similar and will be compared. The major differences in the geometries of the cluster relate to the mirror plane found in (A) and the lack of such symmetry resulting from the methyl substitution on the cyclopropylidene ring in (B).