

09.3-09 STRUCTURE OF ORGANOMETALLIC COBALT(I) COMPLEXES CONTAINING TRIMETHYLPHOSPHINE. By A.L. Beauchamp and M.J. Olivier, Département de Chimie, Université de Montréal, Montréal, Canada, and M. Dartiguenave, Y. Dartiguenave and B. Capelle, Laboratoire de Chimie de Coordination du CNRS associé à l'Université P. Sabatier, Toulouse, France.

In order to develop for cobalt catalytic properties similar to those of the heavier metals Rh(I) and Ir(I), complexes of cobalt in the uncommon (+1) oxidation state have been investigated and the crystal structures of three compounds are presented. The tetrahedral trimethylphosphine compound $\text{CoBr}(\text{PMe}_3)_3$, which is paramagnetic, reacts with ethylene in acetonitrile to form a diamagnetic five-coordinate compound $[\text{Co}(\text{PMe}_3)_3(\text{CH}_3\text{CN})(\text{Ethylene})]\text{BPh}_4 \cdot \text{CH}_3\text{CN}$. The ethylene molecule is bound through its π electrons in the equatorial plane of the trigonal bipyramid, whereas acetonitrile occupies an axial position. The corresponding compound $[\text{Co}(\text{PMe}_3)_3(\text{CH}_3\text{CN})(\text{Diphenylacetylene})]\text{BPh}_4$ also assumes a trigonal bipyramid structure with the triple bond in the equatorial plane. This time, however, acetonitrile is found in an equatorial position. By reacting molecular oxygen with the starting paramagnetic material, oxidation takes place in several steps. The final product of the oxidation is an octahedral compound $[\text{trans-Co}(\text{CH}_3\text{CN})_2(\text{OPMe}_3)_4]\text{BPh}_4$, in which the metal is divalent and the phosphine has been oxidized to the oxide.

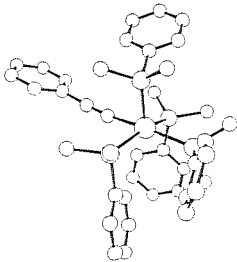
09.3-10 THE CRYSTAL STRUCTURE OF A FIVE-COORDINATE ACETYLIDO-PHOSPHINE COMPLEX OF RUTHENIUM(II). By G.J. Kruger, T.V. Ashworth, and E. Singleton, National Chemical Research Laboratory, CSIR, Pretoria, Republic of South Africa.

The complex $[\text{Ru}(\text{C}\equiv\text{CPh})(\text{PMe}_2\text{Ph})_4][\text{PF}_6]$ was synthesized by addition, at room temperature, of 1 molar equivalent of $\text{PhC}\equiv\text{CH}$ to the red solution formed by mixing $[\text{RuH}(\text{cod})-(\text{PMe}_2\text{Ph})_3][\text{PF}_6]$ (cod=cycloocta-1,5-diene), (T.V. Ashworth, E. Singleton, M. Laing and L. Pope, J.C.S. Dalton, 1978, 1032) with PMe_2Ph (1 molar equivalent each) in methanol. This compound shows remarkable reactivity as it reacts with molecular hydrogen to give $\text{CH}_2=\text{CHPh}$ under ambient conditions, a unique example of such a reaction.

The crystal structure was determined by X-ray diffraction. The crystal data are: space group $\text{P}2_1/\text{n}$, $a=18.042$, $b=14.755$, $c=15.998$ Å, $\beta=104.01^\circ$, $Z=4$. 5728 Intensities were collected with $\text{MoK}\alpha$ radiation. The structure was solved from the Patterson map and refined anisotropically to $R=0.053$.

The coordination around the Ru is distorted square pyramidal. The vacant coordination site is blocked in the crystal by a phenyl ring of one of the phosphines. The acetylido group bonds in the basal plane rather

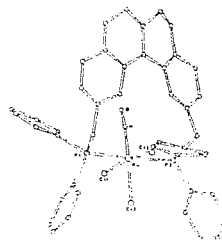
than the equally possible apical position, and is linear with a C-C triple bond of length 1.203 Å and a Ru-C distance of 2.051 Å. The bond from the Ru to the apical P is much shorter than the other Ru-P bonds (2.217 Å compared with 2.343, 2.393 and 2.415 Å).



09.3-11 CRYSTAL AND MOLECULAR STRUCTURE OF $[\text{RuCl}_3(\text{NO})(\text{Ph}_2\text{P}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{PPh}_2)]$. F. Baccetti, P. Mura, L. Zambonelli. Istituto di Strutturistica Chimica "G. Giacomello" CNR CP.10 - 00016 Monterotondo Stazione (Roma) Italy. R. Holderegger, L.M. Venanzi. Laboratorium für Anorganische Chemie Eidgenössische Technische Hochschule Universitätstrasse 6/8 CH-8006-Zürich, Switzerland.

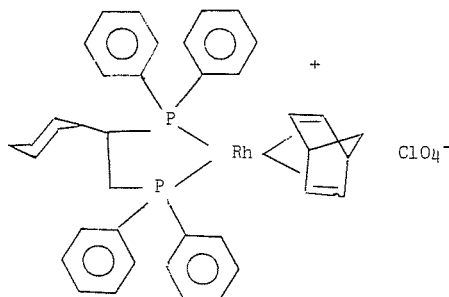
As part of our program concerned with the structural chemistry of complexes of the fairly rigid bidentate ligand 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene, the X-ray analysis of the ruthenium (II) complex $[\text{RuCl}_3(\text{NO})(\text{Ph}_2\text{P}-\text{CH}_2-\text{C}_{18}\text{H}_{10}-\text{CH}_2-\text{PPh}_2)]$ was undertaken.

Its crystal data are the following: $a = 13.185(3)$, $b = 10.106(3)$, $c = 31.067(13)$ Å, $V = 4131.4(2.3)$ Å³, $Z = 4$, space group $\text{P}2_1^2 2_1^2$, $d_{\text{calc}} = 1.52$ g.cm⁻³. The molecular structure of the complex will be presented and compared with those of related compounds.



09.3-12 A CATALYTIC CHIRAL REDUCTION PRECURSOR: 1, 2-BISDIPHENYLPHOSPHINO-1-CYCLOHEXYLETHANE (NORBORNADIENE)RHODIUM PERCHLORATE. By J. D. Oliver and L. C. Strickland, Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio 45247

The title compound, $\text{C}_{39}\text{H}_{42}\text{O}_4\text{ClP}_2\text{Rh}$, shown below crystallizes in the monoclinic space group $\text{P}2_1$ with $a = 18.832$ (9), $b = 9.599$ (3), $c = 20.869$ (10) Å, $\beta = 103.75$ (4)^o and $Z = 4$.



The structure was solved by the heavy atom method and has been refined to $R=0.12$ employing isotropic thermal parameters for the 94 non-hydrogen atoms in the asymmetric unit. The conformations of the five-atom chelate rings are similar for the two crystallographically independent molecules. The orientation of the cyclohexyl ring to the chelate ring differs greatly for the two molecules and produces significant departure from the expected edge-face arrangement of the phenyl rings. This may relate to its superior catalytic properties.¹

1. D. P. Riley and R. E. Shumate, J. Org. Chem., **45**(25), 5187 (1980).