09.3-09 STRUCTURE OF ORGANOMETALLIC COBALT(I) COMPLEXES CONTAINING TRIMETHYLPHOSPHINE. By A.L. Beauchamp and M.J. Olivier, Département de Chimie, Université de Montreál, Montréal, Canada, and M. Dartigenave, Y. Dartigenave and B. Canolle, 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 states have been investigated and the crystal structures of three compounds are presented. The tetrahedral trimethylphosphine compound CoBr(PMe₃)₃, which is paramagnetic, reacts with ethylene in acetonitrile to form a diamagnetic five-coordinate compound [Co(PMe₃)₃(CH₂CN)(Ethylene)]BPh₄,CH₂CN. 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 [Co(PMe₃)₃(CH₂CN)(Diphenylacetylene)]BPh₄ also assumes a trigonal bipyramidal 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 [trans-Co(CH₃CN)₃(OPMe₃)]₂(BPh₄)₂, in which the metal is divalent and the phosphine has been oxidized to the oxide.


The complex [Ru(C≡CPh)(PMe₃)₂]PF₆ was synthesized by addition, at room temperature, of a 1 mol equivalent of PF₅SCCH to the red solution formed by mixing [RuH(cod)(OPMe₃)]PF₆ in acetonitrile-1,4-diene, (T.V. Ashworth, E. Singleton, M. Leisng and L. Pope, J.C.S. Dalton, 1978, 1032) with PMe₃PF₆ (1 mol equivalent each) in methanol. This compound shows remarkable reactivity as it reacts with molecular hydrogen to give CH₃CH₂PPh 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 P2₁/n, a = 18.042, b = 14.735, c = 5.998 Å, β = 104.01°, Z = 4. 9728 Intensities were collected with MoKα 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 acetylide 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).


A 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 [RuCl₃(NO)(PMe₂CH₂CH₂PPh₂)]⁺ was undertaken. Its crystal data are the following: a = 13.185 (3), b = 10.106 (3), c = 31.067 (13) Å, β = 4131.4 (2)°, Z = 4, space group P2₁2₁2₁, Dcalc = 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-CYCLOHEXYLPHOSPHANE (NORBORNADIENE)RHODIUM PERCHLORATE. By J.D. Oliver and L.C. Strickland, Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio 45247.

The title compound, Cs₃H₂O₄Cl₃P₂Rh, shown below crystallizes in the monoclinic space group P2₁/a with a = 18.832 (9), b = 9.599 (3), c = 20.869 (10) Å, β = 105.75° (4)° 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 to 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.

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