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. Darguenaue, Y. Darguenaue and B. Canelle, Laboratoire de Chimie de Coordination du CNRS associé a 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 Co3PMe3(CH3CN)2, which is paramagnetic, reacts with ethylene in acetonitrile to form a diamagnetic five-coordinate compound (Co(PMe3)2(CH3CN)(Ethylene))BPh4,CH3CN. 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(CH3CN)(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)(OPMe3)2]BPh4, in which the metal is divalent and the phosphine has been oxidized to the oxide.


The complex [Ru(C2CP)3(PMe3)2]PF6 was synthesized by addition, at room temperature, of a molar equivalent of Ph3CCCH to the red solution formed by mixing [RuH(Cod)2(PMe3)2]PF6 in acetic acid in an equilibrated reaction. The crystal structure was determined by X-ray diffraction. The crystal data are: space group P21/n, a = 16.042, 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 (2.17 Å compared with 2.343, 2.393 and 2.415 Å).


As part of our program concerned with the structural chemistry of complexes of the fairly rigid bidentate ligand 2,11-bis(diphenylphosphinomethyl)benzene[4]phenanthrene, the X-ray analysis of the ruthenium (II) complex [RuCl3(NO)(PPh3-CH2-CH=CH2)]PF6 was undertaken. Its crystal data are: a = 13.185(3), b = 10.106(3), c = 31.067(13) Å, v = 4131.4(13) Å3, Z = 4, space group P21/n2, dcalc = 1.52 g cm−1. 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 (NORSBORNAIDIENE)RHODIUM PERCHLORATE. By J. D. Oliver and C. Strickland, Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio 45247.

The title compound, C39H4204ClP2Rh, 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 = 105.67° (4)° and Z = 4.

The crystal structure was determined by X-ray diffraction. The crystal data are: space group P21/a, a = 18.832, b = 9.599, c = 20.869 Å, β = 105.67°. 2738 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 Rh is distorted square planar. 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 Rh to the apical P is much shorter than the other Ru−P bonds (2.17 Å compared with 2.343, 2.393 and 2.415 Å).