



Doctoral Thesis

Some transition metal complexes of a novel diphosphine ligand

Author(s):

Johnson, David

Publication Date:

1975

Permanent Link:

<https://doi.org/10.3929/ethz-a-000093147> →

Rights / License:

[In Copyright - Non-Commercial Use Permitted](#) →

This page was generated automatically upon download from the [ETH Zurich Research Collection](#). For more information please consult the [Terms of use](#).

Diss. ETH 5538

**SOME TRANSITION METAL COMPLEXES OF A
NOVEL DIPHOSPHINE LIGAND**

A Dissertation submitted to the
SWISS FEDERAL INSTITUTE OF
TECHNOLOGY ZURICH
for the degree of
Doctor of Natural Sciences

Presented by

DAVID JOHNSON

B. Sc. Chem. University of Manchester

born February 9, 1947

from Nottingham (England)

Accepted on the recommendation of
Prof. L. M. Venanzi, Referent
Prof. W. Simon, Korreferent

Zurich 1975

Clausthal-Zellerfeld

Böneck-Druck

1975

S U M M A R Y

- - - - -

The design and synthesis are described of a novel sterically-constrained diphosphine ligand, 2,11-bis(diphenylphosphinomethyl)-benzo[c]phenanthrene (PCPH₂), and the physical and spectroscopic properties of the complexes formed between this ligand and a number of transition metal ions are discussed in terms of the stereochemistry of the complexes.

Nickel(II)halide and pseudohalide complexes (PCPH₂)NiX₂ are shown to have square planar structures in which the diphosphine spans trans-positions whilst cobalt(I) complexes [(PCPH₂)Co(CO)₃]⁺ and (PCPH₂)Co(CO)₂X (X = halide) are probably 5-coordinate. A bimetallic cobalt(III) complex involving diphosphine bridging is described and a tetrahedral environment about the cobalt atom is established for the complex (PCPH₂)CoCl₂. Depending upon the particular metal and upon the nature of X, the complexes (PCPH₂)MX (M = Cu, Ag, Au) may be either 2-coordinate ionic species or 3-coordinate covalent species and, in some cases, there is evidence for these two structures existing in equilibrium in solution. The 3-coordinate complexes (PCPH₂)MCl (M = Cu, Ag) are shown to have distorted trigonal planar structures in the solid state.

It is concluded that the steric properties of the ligand PCPH₂ show significant deviations from those predicted.