

A Novel Rhodium(I) Dimer having Dibenzoyldi-imide as Bridging Ligand

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Summary Reaction of *mer*-RhCl₃(PMe₂Ph)₃ with dibenzoylhydrazine in refluxing ethanol in presence of a base gives a novel carbonylphosphinerhodium(I) dimer with dibenzoyldi-imide as bridging ligand.

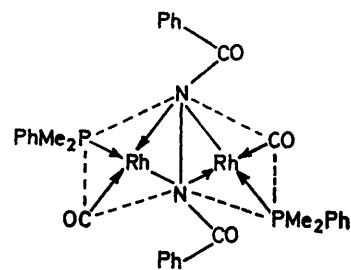
RECENTLY, reports of complexes which contain ligands co-ordinated to a transition metal solely by an azo-group have appeared.^{1,2} In these complexes the azo-group is bonded to the metal either *via* a nitrogen lone pair^{1,3} or by the formal donation of electrons from the azo-double bond, analogous to that known in metal-olefin complexes.⁴ In addition azobenzene is known to form 2-(phenylazo)phenyl-metal complexes which contain a σ -bond between the metal and the *ortho*-carbon atom of one phenyl ring together with the co-ordinate bond arising from donation of the nitrogen lone pair.⁵

We report the preparation of a novel rhodium(I) dimer having dibenzoyldi-imide as bridging ligand. *mer*-RhCl₃(PMe₂Ph)₃ reacts with dibenzoylhydrazine (dbh) in refluxing ethanol in presence of a base (NaHCO₃) to give [(PMe₂Ph)(CO)Rh·N(COPh)-]₂.[‡] The compound is air and moisture stable and crystallizes as yellow needles. The i.r. spectrum (Nujol) shows the following bands: 1976 (vs), 1926 (vw) [ν_{CO} (rhodium carbonyl)], and 1530 (vs) [ν_{CO} (benzoyl)].

The reaction probably proceeds through reductive carbonylation of the Rh^{III} chloro-compound to give the

intermediate (PMe₂Ph)₂(CO)RhCl; 2 molecules of the latter react with 1 molecule of dbh eliminating 2 molecules of HCl and one molecule of phosphine per rhodium atom to give the rhodium(I) dimer. A similar compound [(Ph₃P)(CO)Rh·N(COPh)-]₂[‡] is obtained when (Ph₃P)₂(CO)RhCl is treated with dbh under similar conditions.

A possible structure of the compound which agrees with the square-planar configuration of rhodium(I) is shown in the Figure; dibenzoyldi-imide is acting as a tetradentate



FIGURE

ligand. This structure is related to that of [Rh(CO)₂Cl]₂.⁶

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‡ Correct elemental analyses (C,H,N,P) and molecular weight determination (osmometrically in benzene) were obtained for this compound.

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