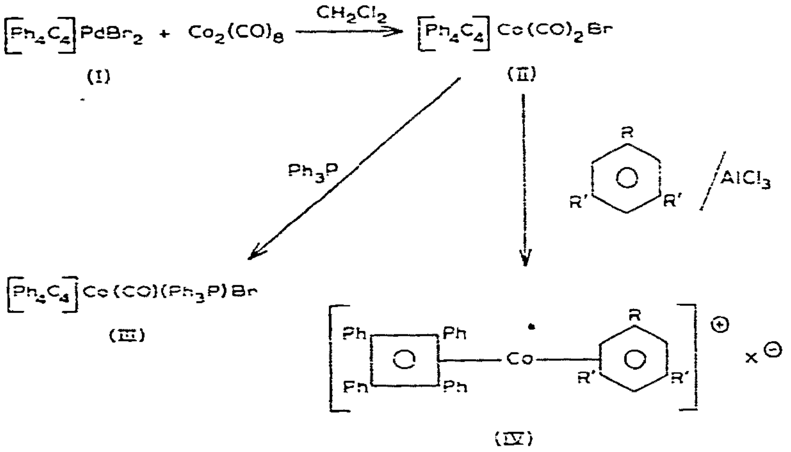
PRELIMINARY NOTES

Cyclobutadiene–metal complexes

VI*. (Tetraphenylcyclobutadiene)cobalt(I) complexes

Previous papers in this series have dealt with the transfer of a tetraphenylcyclobutadiene group from palladium onto iron, nickel, molybdenum and tungsten by reaction of (tetraphenylcyclobutadiene)palladium halides (I) with the appropriate metal carbonyl or substituted carbonyl[1]. These reactions usually give optimum yields when they are carried out under heterogeneous conditions [(I) being rather insoluble], by heating the reactants in an inert solvent, frequently an aromatic hydrocarbon. Attempts to transfer the tetraphenylcyclobutadiene group onto cobalt by reaction of (I) with dicobalt octacarbonyl under these conditions were unsuccessful, but it was found that the desired reaction occurred easily under homogeneous conditions on stirring the reactants together in dichloromethane solution for 45 hours at 25°. The product, obtained in 50–60 % yield, was (tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (II)**, a red-brown crystalline solid m.p. 255–262° (decomp.), fairly air-stable in the solid but air- and heat-sensitive in solution. It was characterized by its infra-red spectrum and by other reactions which have already been mentioned[2] and which show that the cyclobutadiene group is intact in the cobalt complex.



Rather surprisingly for a compound of cobalt(I) which obeys the effective atomic number formalism, the complex (II) is strongly paramagnetic and appears to have an anomalous temperature-dependence of its magnetic moment. Preliminary measurements suggest that at room temperature the complex has μ_{eff} of about 3.5 B.M.***, close to that obtained for some tetrahedral or distorted tetrahedral nickel(II) complexes[3] [Ni(II) and Co(I) are both d^8 ions]. Another cobalt(I) complex, the bis(hexamethylbenzene)cobalt(I) cation has recently been found by Fischer and Lindner[4] to exhibit paramagnetism corresponding to the presence of two unpaired

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* Part V: *J. Organometal. Chem.*, 4 (1965) 172.

** All new compounds described gave satisfactory analyses.

*** A detailed magnetic study of (II) and (III) is being undertaken by Dr. Stager and Mr. Goren and will be reported in due course.

electrons. In this compound, however, the effective atomic number of the cobalt is two greater than that of krypton.

On reaction of (II) with triphenylphosphine in benzene only one carbonyl group was displaced to give (tetraphenylcyclobutadiene)(triphenylphosphine)cobalt carbonyl bromide (III) (m.p. 225–230° decomp.), which was also paramagnetic.

Numerous workers have described the aluminum chloride catalyzed reaction of metal carbonyl halides with aromatic hydrocarbons to give π-arene–metal complexes[5]. (Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (II) reacted similarly with benzene, toluene or mesitylene under these conditions to give, after treatment of the product with saturated aqueous potassium bromide, the (π-arene)(π-tetraphenylcyclobutadiene)cobalt(I) bromides (IV, $X = Br$, $R = R' = H$; $R = CH_3$, $R' = H$ and $R = R' = CH_3$) in 55, 62 and 72% yields respectively. These complexes were very stable yellow crystalline solids, readily soluble in methanol, and like the well-known isoelectronic (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)cobalt, were all diamagnetic. This was shown by the sharp proton resonances which were observed for these complexes, the positions and intensities of which were in agreement with the proposed structures.

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The ultraviolet properties of some perphenylated linear and cyclic polysilanes

Subsequent to the initial work by Hague and Prince[1] on the ultraviolet properties of hexaphenyldisilane, related investigations with other linear and branched-chain polysilanes have been carried out[2,3,4,5,6]. These later investigations suggested that the ultraviolet spectral properties of polysilanes are due to the silicon–silicon bond chromophore, and allowed a number of structure-absorption rules to be formulated. We have now examined the ultraviolet properties of the perphenylated linear polysilane series, $Ph(SiPh_2)_nPh$ ($n = 2$ through 7) and of all the available cyclosilane* derivatives.

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* For a current review of the chemistry of cyclosilane derivatives, see refs. 4 and 6.

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