Novel Addition Reactions of Chlorotris(triphenylphosphine)rhodium(I)

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CHLOROTRIS(TRIPHENYLPHOSPHINE)RHODIUM(I), which has been shown to dissociate in solution to, apparently, the three-co-ordinate species $(PPh_3)_2RhCl$,[1] has been found to undergo several electrophilic addition reactions similar to those of the spin-paired, square d^8 co-ordination compounds. However, because of the vacant co-ordination position, nucleophilic attack on the rhodium atom can also occur.

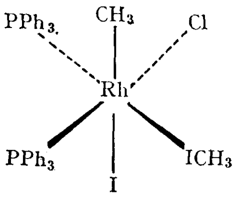
Thus, with methyl iodide we obtained a green, monomeric complex, $(PPh_3)_2RhMeClI,MeI$ which can be recrystallized unchanged from benzene. Proton n.m.r. data indicate the presence of two chemically different methyl groups, one bound directly to rhodium (split into a triplet by two equivalent ^{31}P nuclei, $J_{P-H} = 5{\cdot}1$ c./sec., and further split into a doublet by ^{103}Rh, $J_{Rh-H} = 2{\cdot}4$ c./sec.), and the other as a co-ordinated methyl iodide (a singlet with a different chemical shift from that of free methyl iodide). A possible structure is (I) or a similar isomer.[2]

Using allyl chloride, two products, both analyzing as $(PPh_3)_2RhC_3H_5Cl_2$ can be obtained. Proton n.m.r. spectra in deuterochloroform, although showing little fine structure, indicate that the allyl group is π-bonded in one compound and σ-bonded in the other.[3,4] When the latter is carbonylated, little change is observed in the n.m.r spectrum, and the expected σ-allyl complex $(PPh_3)_2Rh(CO)C_3H_5Cl_2$ can be isolated. Similar results are obtained using 2-methylallyl chloride. These are the first well-defined allyl complexes of rhodium.[3]

$(PPh_3)_3RhCl$ is a very effective decarbonylating agent for aldehydes, yielding alkanes and $(PPh_3)_2Rh(CO)Cl$.[5] Kinetic studies using n-valeraldehyde indicate that the reaction is first order in both complex and aldehyde. A possible reaction path is suggested by the analogous reactions with acyl halides, *e.g.*, benzoyl chloride in refluxing benzene, which gives the stable Rh^{III} complex $(PPh_3)_2Rh(Ph)(CO)Cl_2$ (ν_{CO} = 2072 cm.$^{-1}$), while acetyl chloride under the same conditions gives $(PPh_3)_2Rh(CO)Cl$ and methyl chloride. However, under milder conditions the Rh^{III} complex $(PPh_3)_2Rh(Me)(CO)Cl_2$ (ν_{CO} = 2051 cm.$^{-1}$) can be isolated. The intermediate in the aldehyde decarbonylation may thus involve an electrophilic attack on the rhodium by the carbonyl carbon atom, although nucleophilic attack by the oxygen atom at the vacant position cannot be discounted.

The action of HCl gas at 20°C on the red chloroform solutions of $(PPh_3)_3RhCl$ produces the yellow hydrido-species $(PPh_3)_2RhHCl_2$, which *in situ* with ethylene or acetylene at one atmosphere yields rapidly deep red solutions from which the corresponding ethyl and vinyl complexes of Rh^{III} can be isolated. These compounds are air-stable and apparently five-co-ordinate. Similar reactions occur with butadiene, propene and hept-1-ene. These reactions appear to be one of the most facile demonstrations of an alkene or alkyne insertion reaction.[6] Moreover, the action of CO at 1 atmosphere and *ca.* −10°C on a chloroform solution of the ethyl complex produces the acyl derivative. At higher temperatures, the latter rearranges and decomposes into $(PPh_3)_2Rh(CO)Cl$ and ethyl chloride.

Solutions of $(PPh_3)_3RhCl$ in dichloromethane take up 1 mole of oxygen yielding light brown crystals of $(PPh_3)_2Rh(O_2)Cl(0{\cdot}5CH_2Cl_2)$. The infrared spectrum shows a band at *ca.* 900 cm.$^{-1}$ due to co-ordinated oxygen but no band attributable to P–O stretches.[7] The oxygen can be displaced by donor ligands, *e.g.*, CO reacts to give $(PPh_3)_2Rh(CO)Cl$.



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[1] F. H. Jardine, J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Comm.*, 1965, 131.

[2] A complete crystal structure determination of this complex is in progress.

[3] M. L. H. Green and P. L. I. Nagy, *Adv. Organometallic Chem.*, 1964, **2**, 325.

[4] S. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Comm.*, 1965, 78.

[5] See also: J. Tsuji and K. Ohno, *Tetrahedron Letters*, 1965, 3969.

[6] (a) R. F. Heck and D. S. Beslow, *J. Amer. Chem. Soc.*, 1961, **83**, 4023; (b) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

[7] See also: L. Vaska, *Science*, 1963, **140**, 809.