A New Route to Hydrido-palladium Complexes: Oxidative Addition Reactions of Hydrogen Chloride to Palladium(0) Complexes

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Summary Oxidative addition reactions of hydrogen chloride to palladium(0) complexes give a new route for preparation of hydrido-palladium(II) complexes.

RECENTLY oxidative addition reactions of low-valent transition-metal complexes have been investigated extensively in relation to transition-metal catalysts. Reactions of strong acids with d^{10}-metal complexes have been examined and such oxidative additions have given the hydrido-complexes of platinum[1] and nickel[2] but no hydrido-complex of palladium. Brooks *et al.* have reported[3] that neutral agents are necessary for preparation of hydrido-palladium complexes because they decompose rapidly in acidic or basic media. We have, however, succeeded in the preparation of hydrido-palladium(II) complexes by the reactions of tertiaryphosphine-palladium(0) complexes with hydrochloric acid.

$$\mathrm{Pd(CO)(PPh_3)_3} + \mathrm{HCl} \xrightarrow[\text{ether}]{} trans\text{-}\mathrm{PdHCl(PPh_3)_2}$$

When ethanolic hydrochloric acid (1 mol) was added to the ether suspension of $\mathrm{Pd(CO)(PPh_3)_3}$[4] (1 mol) at −50° under argon, the original yellow colour gradually paled and *trans*-hydridochlorobis(triphenylphosphine)palladium(II), *trans*-$\mathrm{PdHCl(PPh_3)_2}$, was obtained as a pale yellow precipitate (yield: 57%). The solid hydrido-complex is moderately stable at room temperature in an inert atmosphere but rapidly decomposes when exposed to air. The complex is slightly soluble in tetrahydrofuran or benzene but far less soluble in most organic solvents. The i.r.

spectrum (Nujol) of the complex is characterized by ν(Pd–H) at 2055, 2060(shoulder) cm^{-1} and ν(Pd–Cl) at 288, 278(shoulder) cm^{-1}. The Pd–H stretching frequency, a little higher than the 2035 cm^{-1} of *trans*-$PdHCl(PEt_3)_2$,[3] is more consistent with a *trans*-configuration rather than a *cis*. Owing to the large *trans*-effect of the phosphine ligand, the Pd–H stretching frequency of *cis*-$PdHCl(PPh_3)_2$ would be expected to fall in a region below 2000 cm^{-1}, though the *cis*-hydridohalogeno-complex of palladium is unknown. The shoulder peaks may arise from different crystalline modifications with the same empirical formula, as in the case of the platinum analogues.[5] The hydrido-complex was also obtained in a reaction using $Pd(PPh_3)_4$ instead of $Pd(CO)(PPh_3)_3$. When the reaction was carried out in a tetrahydrofuran solution of $Pd(CO)(PPh_3)_3$, it proceeded rapidly and recrystallization of the precipitate from tetrahydrofuran–hexane gave an adduct (1 : 1) of *trans*-$PdHCl(PPh_3)_2$ with tetrahydrofuran as pale yellow needles (yield: 46%). The tetrahydrofuran adduct shows ν(Pd–H) at 2045 cm^{-1} and ν(Pd–Cl) at 288, 278(shoulder) cm^{-1}. Treatment of $Pd(CO)(PPh_3)_3$ with an excess of acid led to the formation of *trans*-$PdCl_2(PPh_3)_2$.

The similar protonation of $Pd(Pcy_3)_2$,[6] where cy = cyclohexyl, prepared by the reduction of palladium(II) acetylacetonate with triethylaluminium in the presence of tricyclohexylphosphine, gave colourless *trans*-hydridochlorobis(tricyclohexylphosphine)palladium(II), *trans*-$PdHCl(Pcy_3)_2$ (yield: 40%). The i.r. spectrum (Nujol) of the

$$Pd(Pcy_3)_2 + HCl \xrightarrow[\text{ether}]{} trans\text{-}PdHCl(Pcy_3)_2$$

complex shows ν(Pd–H) at 2010 cm^{-1} and ν(Pd–Cl) at 270 cm^{-1}, also corresponding to a *trans*-configuration.

The elemental analyses of these complexes are satisfactory, and the formation of chloroform on reaction with carbon tetrachloride gives further evidence for the presence of hydridic protons.

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