Some Novel Complexes Including Very Active Hydrogenation Catalysts Formed from Rhodium Trichloride and Tertiary t-Butylphosphines

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Summary Complexes of the types *trans*-$[RhCl_2L_2]$, $[RhHCl_2L_2]$, $[RhH_2ClL_2]$, and *trans*-$[RhCl(CO)L_2]$ have been prepared from tertiary t-butylphosphines and rhodium trichloride; some of the complexes are very active hydrogenation catalysts.

WE have shown that tertiary phosphines with very bulky substituents are unusual ligands in that they induce internal transition metal–carbon bond formation in platinum[1] or palladium[2] complexes. We now find that such phosphines give unusual products with rhodium trichloride trihydrate. Thus di-t-butyl(alkyl)phosphines, PBu^t_2R, ($R = Me$, Et, or Pr^n) react rapidly with rhodium trichloride in an alcohol solvent at 20° to give rhodium(II) complexes of the type *trans*-$[RhCl_2(PBu^t_2R)_2]$ as stable purple ($R = Me$) or green ($R = Et$ or Pr^n) crystals, soluble in many organic solvents. The complexes are monomeric in benzene, and their i.r. spectra (4000—650 cm^{-1}) are virtually identical with those of palladium complexes of type *trans*-$[PdCl_2(PBu^t_2R)_2]$.[3] The complexes are paramagnetic but the magnetic moments, measured at 25°, are much lower than 'spin only' values being 1·4 (Me), 0·9 (Et), and 0·55 B.M. (Pr^n). We cannot account for these low moments; thin layer chromatography indicates that the complexes are not mixtures. Tri-*o*-tolylphosphine reacts with rhodium trichloride in ethanol at room temperature to give *trans*-$[RhCl_2\{P(o\text{-tolyl}_3\}_2]$ as a very insoluble purple or blue–green solid. It was suggested that the low solubility of this complex helped to stabilize the rhodium in the unusual valency state of two[4] but our results show that low solubility is not necessarily an important factor.

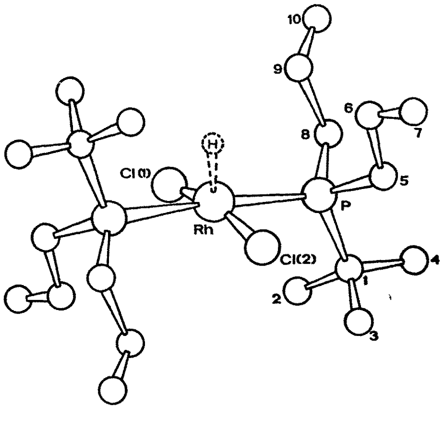
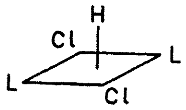


FIGURE. *Structure of* $[RhHCl_2(PBu^tPr^n_2)_2]$ *showing the probable position of the hydride ligand.*

When rhodium trichloride is heated with an excess of some t-butyl-tertiary phosphines in alcohols or methyl ethyl ketone, well defined crystals of diamagnetic five-co-ordinate rhodium(III) hydrides $[RhHCl_2L_2]$ are formed; these are red with $L = PBu^tPr^n_2$, PBu^t_2Me, or PBu^t_2Et or khaki with $L = PBu^t_2Pr^n$. They are stable and readily soluble in many organic solvents. The complex $[RhHCl_2(PBu^t_2Me)_2]$ has ν_{Rh-H} 1938s cm^{-1} and some weak bands in the range 620—570 cm^{-1}; the rest of the i.r. spectrum (over the range 4000—400 cm^{-1}) is virtually identical with that of *trans*-$[PdCl_2(PBu^t_2Me)_2]$ or *trans*-$[RhCl_2(PBu^t_2Me)_2]$ with which it is isomorphous (from their *X*-ray diffraction patterns). The hydride resonance at τ 41·4 consists of a doublet of triplets, J(Rh–H) 31·6 Hz and J(P–H) 13 Hz. The t-butyl ^1H n.m.r. pattern is a well defined triplet showing that $|J(P-P)|$ is large[5] and that the two PBu^t_2Me ligands are probably mutually *trans*.[5,6] The far-i.r. spectrum shows only one rhodium–chlorine stretching frequency (340 cm^{-1}) indicating mutually *trans*-chlorines. Similar data are found for the other complexes of type $[RhHCl_2L_2]$



(I)

suggesting they have the square–pyramidal structure (I). We have determined the structure of $[RhHCl_2(PBu^tPr^n_2)_2]$ by single-crystal *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/c$ with two molecules in the unit cell. The rhodium atom is therefore required to occupy a position of crystallographic symmetry $\bar{1}$. Refinement with anisotropic temperature factors for Rh, P, and Cl showed large vibrations normal to the co-ordination plane. This suggested that the square-pyramidal molecules with the hydrogen in the apical position were randomly arranged in two orientations so as to produce effective centro-symmetry. Refinement of such a disordered model converged satisfactorily to $R = 8·5\%$ based on 2434 reflections. The resulting structure is shown in the Figure. The Rh–P length is 2·31 Å, and Rh–Cl is 2·33 Å. The angles P–Rh–P and Cl–Rh–Cl are 174 ° and 163 °, respectively. The hydrogen atom was not located, and its postulated position is shown in the Figure.

On adding one mol of a base (*e.g.* NaOMe) per rhodium atom to $[RhHCl_2L_2]$ in ethanol or methanol the solution becomes orange and then rapidly yellow and complexes of the type *trans*-$[RhCl(CO)L_2]$ are formed in high (>80%) yield (L = a tertiary t-butylphosphine). However, in propan-2-ol plus sodium isopropoxide, abstraction of carbon monoxide from the solvent occurs only very slowly and $[RhHCl_2(PBu^tPr^n_2)_2]$ in propan-2-ol containing sodium isopropoxide (2 mol per Rh-atom) gives a very active hydrogenation catalyst for olefins or acetylenes at 1 atm and 20°. As a catalyst for the hydrogenation of hex-1-ene it is as active as $[RhCl(PPh_3)_3]$.[7] Other complexes of type $[RhHCl_2L_2]$ are also active catalysts in the presence of a base but less so than $[RhHCl_2(PBu^tPr^n_2)_2]$.

When treated with tri-t-butylphosphine, rhodium trichloride gives the five-co-ordinated dihydride $[RhH_2Cl(PBu^t_3)_2]$ as stable very dark red crystals. In the ^1H n.m.r.

spectrum the hydridic hydrogens are equivalent, τ_H 35·5 J(P–H) 14·9 Hz, J(Rh–H) 26·2 Hz and the t-butyl hydrogens form a 'virtually coupled' 1 : 2 : 1 triplet pattern. The ^{31}P n.m.r. pattern, with decoupling of the t-butyl hydrogens consists of two well defined 1 : 2 : 1 triplets J(Rh–P) 110·3 Hz. The i.r. spectrum (Nujol) has ν_{Rh-H} 2242 and 2227 cm^{-1} and ν_{Rh-Cl} 263 cm^{-1}. This dihydro-complex is a highly active hydrogenation catalyst for olefins and the presence of a base is not necessary for activity.

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