Tris(triphenylphosphine)cobalt Dihydride. A Molecular-nitrogen Fixing Complex

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WE have prepared a new tris(triphenylphosphine)-cobalt dihydride complex which reacts readily with molecular nitrogen to give an N_2-containing complex.

The hydride complex, $H_2Co(PPh_3)_3$, was obtained by the reaction of cobalt(III) acetylacetonate, triphenylphosphine, and tri-isobutylaluminium in ether at 10° with hydrogen bubbled through the reaction mixture. The yellow crystalline complex was separated by filtration and washed with de-gassed ether. Yield 50% (based on Co (Found: C, 75·6; H, 5·8; Co, 6·9. Calc. for $C_{54}H_{47}P_3Co$: C, 76·5; H, 5·6; Co, 6·9%).

The complex is very air-sensitive and decomposes at 77° *in vacuo*, evolving hydrogen and benzene. When treated with iodine in a benzene solution, the complex evolves one mole of hydrogen per mole.

The high-field n.m.r. spectrum of a benzene solution (with no Me_4Si) at 60 Mc./sec. consists of four peaks with the intensity ratio of 1 : 3 : 3 : 1. The high-field chemical shifts were calibrated previously by using a 480 c./sec. side-band of tetramethylsilane in a benzene solution. The reduced τ-values of these four signals were determined as 20·6, 21·2, 21·8, and 22·4 with reference to the solvent benzene (τ 2·87). The line-width of each peak is *ca.* 9 c./sec. At 100 Mc./sec., the separation (36 c./sec.) and the normal quartet figure remain unaltered, showing that these signals are attributable to the spin–spin interaction of *trans*-dihydride protons with three ^{31}P

nuclei which are equivalent in terms of nuclear magnetic resonance. The coupling constant of 36 c./sec. indicates that the hydrogen atoms probably occupy the positions *cis* to P.[1] Although the molecular-weight determination by the cryoscopic method in benzene has not given satisfactory values so far, the dimer structure is more likely, because it is reasonable to regard the complex as diamagnetic. The infrared spectrum of the benzene solution shows three bands (at 1755, 1900, and 1935 cm.$^{-1}$) in the region 1700—2000 cm.$^{-1}$. The absorptions at 1900 and 1935 cm.$^{-1}$ are broad and much weaker than the one at 1755 cm.$^{-1}$. The structure of the complex assumed from the n.m.r. data requires only one infrared-active Co–H stretching vibration and we tentatively suggest that the absorption at 1755 cm.$^{-1}$ is due to the Co–H stretching mode, because this is the strongest and is near the reported value for a cobalt hydride complex of triphenylphosphine.[2] The assignment of the other two bands is now being investigated.

When the benzene solution of the complex is kept under nitrogen atmosphere, the colour changes instantaneously from brown to red, and on addition of petroleum, orange crystals are obtained. The infrared spectrum of the orange complex has a sharp, strong absorption at 2088 cm.$^{-1}$ instead of the bands characteristic of the hydride complex. The elemental analysis agrees well with the formula $N_2Co(PPh_3)_3$. This complex is therefore identical with the molecular-nitrogen complex reported previously.[3,4] The hydride complex provides the first example of a metal complex which takes up molecular nitrogen. In the same way, when the complex is brought into contact with carbon monoxide, the exchange of hydrogen with carbon monoxide takes place. The abstraction of carbon monoxide from aldehydes has also been observed. Ethylene is readily hydrogenated by the hydride complex at room temperature in benzene. Chloroform is formed by the reaction of the complex with carbon tetrachloride.

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