Reactions of Nitrogen-Co-ordinated- and Hydrido-Complexes of Cobalt with Carbon Monoxide, Aldehydes, and Carbon Dioxide

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WE have reported the preparation of nitrogen-co-ordinated- and hydrido-complexes of cobalt[1] by the reduction of cobalt(III) acetylacetonate with tri-isobutylaluminium in the presence of triphenylphosphine under nitrogen and hydrogen, respectively. Although these two complexes were previously determined to be a mixture of $CoN_2(PPh_3)_3$ and $CoHN_2(PPh_3)_3$, and $CoH_2(PPh_3)_3$, respectively, recent structural data on the nitrogen complex[2] and n.m.r. and i.r. spectra of both complexes[3] indicate that these are correctly formulated as $CoHN_2(PPh_3)_3$ and $CoH_3(PPh_3)_3$. We report the reactions of these complexes with carbon monoxide, aldehydes, and carbon dioxide, which clearly indicate the presence of a hydride hydrogen in the nitrogen complex of cobalt.

When carbon monoxide was bubbled through a solution of the nitrogen complex, $CoHN_2(PPh_3)_3$, in benzene at room temperature, the original red colour changed rapidly to yellow-brown and after several hours a brown complex precipitated. The complex is insoluble in the usual organic solvents and stable to air. The elemental analysis and the i.r. spectrum of the complex indicate that it is bis[tricarbonyl(triphenylphosphine)cobalt], $[Co(CO)_3(PPh_3)]_2$. This complex is prepared by the reaction of $Co_2(CO)_8$ with triphenylphosphine.[4] On the other hand, two crystalline complexes, hydridocarbonyltris(triphenylphosphine)cobalt(I), $CoH(CO)(PPh_3)_3$, and hydridodicarbonylbis(triphenylphosphine)cobalt(I), $CoH(CO)_2(PPh_3)_2$, were obtained by the addition of light petroleum to the residual yellow-brown solution.† $CoH(CO)(PPh_3)_3$ is an orange crystalline solid, fairly stable to air, ν(CO) 1910s and ν(Co-H) 1960w cm.$^{-1}$, τ (benzene) 22 (q, *J* 48 c./sec.) with intensity ratios of the four equally spaced bands 1 : 3 : 3 : 1, which indicates an interaction with ^{31}P nuclei (spin $\frac{1}{2}$) and equivalence of the three co-ordinated phosphines. Accordingly a trigonal bipyramidal structure similar to that of $CoHN_2(PPh_3)_3$[2] is implied. $CoH(CO)_2(PPh_3)_2$ is a yellow crystalline solid, ν_{max} 1920br and 1990br cm.$^{-1}$, characteristic of terminal carbonyl groups; τ 20 (t, *J* 41 c./sec.) with intensity ratios of the three equally spaced bands 1 : 2 : 1. This complex is synthesized by the reduction of halogenodicarbonylbis(triphenylphosphine)cobalt(I) with alkali metal amalgam.[5] These carbonyl complexes of cobalt were also prepared by using the hydrido- instead of the nitrogen-complex of cobalt.

Reactions of the hydrido-complex, $CoH_3(PPh_3)_3$, with aldehydes under hydrogen at room temperature yield hydrogenated and decarbonylated products of the aldehydes. Thus, the reaction of $CoH_3(PPh_3)_3$ (1 mmole) with n-heptanal (3·0 mmoles) gave heptyl alcohol (2 mmoles) and n-hexane (0·3 mmole). The decarbonylation reaction also occurs with the nitrogen complex. Hydridocarbonyltris(triphenylphosphine)cobalt(I) was isolated from the reaction solution of formaldehyde and the nitrogen complex.

When carbon dioxide was bubbled through a toluene solution of the nitrogen complex at 0° for several hours, the original red colour of the solution changed to dark yellow and a yellow-brown air-sensitive complex precipitated from the solution, ν_{max} 1585br and 1360br cm.$^{-1}$, characteristic of carboxylate group, and sharp bands characteristic of triphenylphosphine. The complex decomposes *in vacuo* above *ca.* 190° evolving a gas consisting of carbon dioxide, hydrogen, carbon monoxide, water, benzene, and a trace of oxygen. The reaction of the complex with methyl iodide gives methyl formate. From these results, it may be concluded that the complex is a cobalt formate co-ordinated with triphenylphosphine. On the other hand, an orange-yellow crystalline complex $Co(CO)(PPh_3)_3$, was isolated from the residual dark yellow solution, ν_{max} 1870s cm.$^{-1}$, characteristic of a bridged carbonyl group.

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† All compounds prepared gave satisfactory elemental analysis.

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