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Nitrogen Fixation. I. Hydrido- and Nitrogen-Complexes of Cobalt

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The preparation and properties are described of hydrido-complexes of cobalt(III), CoH_3L_3 ($L = P(C_6H_5)_3$, $P(C_6D_5)_3$, $PEtPh_2$, PEt_2Ph). These compounds react with nitrogen at room temperature and atmospheric pressure giving stable hydrido nitrogen-complexes of cobalt(I), $CoHN_2L_3$. The chemical evidence concerning the presence of a Co—H bond in these later compounds is reported.

Introduction

Although a number of hydrido-complexes of rhodium(III) and iridium(III), of general formula $[MH_nX_{3-n}(PR_3)_3]$, are known,[1] analogous complexes of cobalt have not been described.

As we reported in a previous note,[2] the trihydrido-complexes of cobalt(III), of formula $CoH_3(PR_3)_3$, are of particular interest because they provide the first example of well characterized compounds capable of reacting with molecular nitrogen to give stable nitrogen-complexes of formula $CoHN_2(PR_3)_3$.

Molecular nitrogen compounds of cobalt have recently been reported by two other research groups[3,4] and the formula of the complex, obtained by reaction of cobalt(III) acetylacetonate with a trialkylaluminium in presence of triphenylphosphine and nitrogen gas, is claimed to be $CoN_2(PPh_3)_3$. However, recent structural data[5] on the nitrogen-complex prepared by the method of Yamamoto *et al.* provide evidence that this compound contains one hydridic hydrogen atom bound to the metal and that it should, therefore, be formulated as $CoHN_2(PPh_3)_3$.

In this paper we report the detailed preparation and the properties of the trihydrido- and hydrido-nitrogen-complexes of cobalt. Because the infrared spectra of the nitrogen-complexes do not show any band ascribable to Co—H stretching, we also report chemical evidence which strongly supports our formulation.

Experimental Section

Unless otherwise specified, the hydrido-complexes were prepared and manipulated in an atmosphere of dry argon, and the nitrogen-complexes were prepared in an atmosphere of dry nitrogen by standard vacuum-line techniques.

Samples for m.p. determination were contained in evacuated tubes. Infrared spectra were measured using a Perkin-Elmer 337 spectrometer. Gaschromatographic determinations were carried out using a Carlo Erba Fractovap Mod. B.

*Trihydrido*tris(*triphenylphosphine*)*cobalt*(*III*). $CoH_3[P(C_6H_5)_3]_3$. Cobalt(II) chloride hexahydrate (0.85 g, 3.57 mmols) was dissolved in 20 ml of warm ethanol and added to a solution of triphenylphosphine (3.0 g, 11.5 mmols) in 40 ml of hot ethanol. After cooling to room temperature, this solution was added slowly, in a countercurrent of argon and under vigorous stirring, to a flask connected to a manifold, and containing sodium borohydride (0.90 g, 23.7 mmols) partially dissolved in 30 ml of ethanol. After the addition was complete (about 15 minutes), stirring was continued until the initial, red precipitate became yellow (about 20 minutes). After filtration, the precipitate was washed twice with ethanol, four times with deoxygenated water, and six times with ethanol, using 15 ml of solvent each time. After drying in vacuo, 2.8 g of product, d.p. 80°C, was obtained (90% yield).

Anal. Calcd. for $C_{54}H_{48}P_3Co$: C, 76.4; H, 5.7; P, 11.0; Co, 7.0. Found: C, 76.0; H, 6.0; P, 11.0; Co, 6.9%.

Other preparations, carried out in an atmosphere of hydrogen, gave the same results.

The compound, recrystallized from benzene by adding ethanol or petroleum ether, gave pale yellow needles.

*Trihydrido*tris(*tri-pentadeuterophenyl-phosphine*)-*cobalt*(*III*). $CoH_3[P(C_6D_5)_3]_3$. This compound was similarly prepared from cobalt(III) chloride, fully deuterated triphenylphosphine, and sodium borohydride.

Anal. Calcd. for $C_{54}H_3D_{45}P_3Co$: P, 10.4; Co, 6.6. Found: P, 10.3; Co, 6.5%.

*Trideuterido*tris(*triphenyl phosphine*)*cobalt*(*III*). $CoD_3[P(C_5H_5)_3]_3$. The powdered trihydrido-complex was kept in a deuterium atmosphere at room tem-

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(1) (a) L. Vaska and J. V. Di Luzio, *J. Am. Chem. Soc.*, 83, 756 (1961); L. Malatesta, ''Advances in the Chemistry of the Coordination Compounds'', Kirschner, Ed., McMillan, New York, N. Y., p. 475 (1961); J. Lewis, R. S. Nyholm, and G. . N. Reddy, *Chem. and Ind.*, 1386 (1960); (b) J. Chatt, R. S. Coffer, and B. L. Sham, *J. Chem. Soc.*, 7391 (1965).

(2) (a) A. Sacco and M. Rossi, *Chem. Comm.*, 316 (1967); (b) A. Sacco and M. Rossi, ''Proceeding of the tenth International Conference on Co-ordination Chemistry, The Chemical Society of Japan, Tokyo, p. 125 (1967).

(3) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Comm.*, 79 (1965).

(4) A. Misono, Y. Uchida, and T. Saito, *Chem. Comm.*, 419 (1967); *Bull. Chem. Soc. Japan*, *40*, 700 (1967).

(5) J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, *Chem. Comm.*, 2, 96 (1968).

perature and atmospheric pressure for 24 hours. From time to time the vessel was evacuated and refilled with deuterium. The I.R. spectrum of the product, run in Nujol mull, showed the formation of the deuterido-compound (see Table V and Figure 1), while the bands of the hydrido-complex had disappeared.

*Trideuterido*tris(*tri-pentadeuterophenyl-phosphine*)-*cobalt(III)*. $CoD_3[P(C_6D_5)_3]_3$. This compound was prepared from the corresponding trihydrido-complex in a similar way.

*Trihydrido*tris(*ethyldiphenylphosphine*)*cobalt*(*III*). $CoH_3(PEtPh_2)_3$. A solution of cobalt(II) chloride hexahydrate (1.1 g, 4.3 mmols) and ethyldiphenylphosphine (2.85 g, 13.3 mmols) in 70 ml of ethanol was cooled to 0°C and treated, in an argon atmosphere and with stirring, with an ethanolic solution of sodium borohydride (1.0 g, 26.2 mmols). The reaction mixture was stirred until an orange solution was obtained. The compound, identified by means of its I.R. spectrum, was obtained by addition of deoxygenated water as an untractable oil, soluble in all organic solvents.

Anal. Calcd. for $C_{42}H_{48}P_3Co$: P, 13.2; Co, 8.36. Found: P, 13.0; Co, 7.9%.

The corresponding deuterid-complex, identified by means of its I.R. spectrum, was obtained by exchange with deuterium at room temperature and atmospheric pressure.

The *trihydrido*tris(*diethylphenylphosphine*)*cobalt*-(*III*), $CoH_3(PEt_2Ph)_3$, was similarly prepared from cobalt(II) chloride, diethylphenylphosphine and sodium borohydride.

Hydridonitrogen tris(*triphenylphosphine*)*cobalt*(*I*). $CoHN_2[P(C_6H_5)_3]_3$. (a) A benzene solution of $CoH_3(PPh_3)_3$ was stirred under a nitrogen atmosphere for a few minutes at room temperature and atmospheric pressure where upon the exchange the initially yellow solution rapidly became red-orange. On addition of light petroleum ether, red-orange crystals, d.p. 80°C, were obtained. The compound is soluble in benzene, toluene, tetrahydrofuran, or diethyl ether.

Anal. Calcd. for $C_{54}H_{46}N_2P_3Co \cdot C_6H_6$: C, 75.6; H, 5.5; N, 2.94; P, 9.76; Co, 6.2. Found: C, 74.5; H, 5.5; N, 3.0; P, 9.8; Co, 6.3%.

(b) The powdered trihydrido-complex was kept in a nitrogen atmosphere at room temperature and atmospheric pressure for 24 hours. From time to time the vessel was evacuated and refilled with nitrogen. The I.R. spectrum, run in Nujol mull, of the resulting red-orange compound showed a very strong absorption band at 2096 cm^{-1}, but it did not show any band assignable to a Co–H stretching.

Anal. Calcd. for $C_{54}H_{46}N_2P_3Co$: C, 74.2; H, 5.3; N, 3.2; P, 10.6; Co, 6.7. Found: C, 73.9; H, 5.5; N, 3.1; P, 10.4; Co, 6.8%.

*Deuteridonitrogen*tris(*triphenylphosphine*)*cobalt*(*I*), $CoDN_2[P(C_6H_5)_3]_3$, *hydridonitrogen* tris(*tri-pentadeuterophenylphosphine*)*cobalt*(*I*), $CoHN_2[P(C_6D_5)_3]_3$ and *deuteridonitrogen* tris(*tri-pentadeuterophenylphosphine*)*cobalt*(*I*), $CoDN_2[P(C_6D_5)_3]_3$, were similarly obtained as red-orange crystals from $CoD_3[P(C_6H_5)_3]_3$, $CoH_3[P(C_6D_5)_3]_3$, and $CoD_3[P(C_6D_5)_3]_3$, respectively. The hydridonitrogen-complexes with ethyldiphenylphosphine and diethylphenylphosphine were similarly obtained, as deep red oils, from the corresponding trihydrido-complexes.

Thermal Decomposition. The samples (about 30 mg) were decomposed in a closed apparatus, in vacuo or in an atmosphere of nitrogen or carbon monoxide, by heating at 100-150°C. The gas evolved was analysed by gaschromatography on a 4 m column, int. diam. 6 mm, filled with molecular sieves (5 A). Temperature of the column: 100°C. Carrier gas: argon, 1.5 l/h. The results are summarized in Table I.

A sample of non-recrystallized trihydrido*tris*(triphenylphosphine)cobalt(III) (450 mg) was decomposed in vacuo in a closed apparatus connected to a trap cooled with liquid nitrogen. The liquid collected in the trap was identified as benzene by means of its I.R. spectrum.

A sample of hydridonitrogen*tris*(triphenylphosphine)-cobalt(I), obtained by reaction of nitrogen with the solid, non-recrystallized trihydrido-complex, was treated in the same way and gave the same result. The black residue from the decomposition was treated with concentrated hydrochloric acid until it was completely decolorised. Water was added and the solution was extracted with diethyl ether. In addition to triphenylphosphine, diphenylphosphine

Table I. Products of the thermal decomposition of $CoH_3[P(C_6H_5)_3]_3$, $CoHN_2[P(C_6H_5)_3]_3$, and $CoHN_2[P(C_6D_5)_3]_3$

Compound	μmols	T(C°)	Atm.	Gas evolved		H₂/Co	N₂/Co
				H_2 (μmols)	N_2 (μmols)		
$CoH_3[P(C_6H_5)_3]_3$	20.3	100	vacuo	25,3	—	1.25	—
»	36.1	120	»	43.7	—	1.21	—
»	31.2	150	»	40.7	—	1.30	—
$CoHN_2[P(C_6H_5)_3]_3$	26.3	110	»	8.4	26.6	0.32	1.01
»	24.2	125	»	5.1	24.0	0.21	0.99
»	29.6	150	»	11.6	29.5	0.39	1.0
»	32.0	140	N_2	15.4	—	0.48	—
»	27.5	150	»	11.2	—	0.41	—
»	34.2	140	CO	13.7	34.1	0.40	1.0
»	31.6	140	»	14.2	31.4	0.45	0.99
$CoHN_2[P(C_6D_5)_3]_3$	28.3	140	vacuo	9.0	28.0	0.32	0.99
»	21.2	140	»	4.6	20.8	0.22	0.98
»	26.4	150	»	9.3	26.3	0.35	1.0

was identified in the ethereal extract by means of its I.R. spectrum.

The decomposition, carried out in the same conditions, of a sample of hydridonitrogen*tris*(tri-pentadeuterophenyl-phosphine)cobalt(I) which had been recrystallized four times from benzene by adding petroleum ether, gave a mixture of benzene and deuterated benzene, identified by means of their I.R. spectra.

Reaction with Hydrochloric Acid and with Iodine. The hydrido*tris*(triphenylphosphine)cobalt(I) was treated, in current of argon, with an excess of hydrochloric acid in ethanol, or with variable amounts of iodine in benzene, in an apparatus connected to the gas-chromatographic apparatus. Table II shows the results.

Table II. Products of the reaction of $CoHN_2(PPh_3)_3$ with HCl and with I_2

Sample µmols	T (°C)	HCl	I_2 µmols	H_2 µmols	N_2 µmols	H_2/Co	N_2/Co	H_2/N_2
34.5	10	excess	—	35.1	34.1	1.02	0.99	1.03
29.7	10	»	—	31.0	29.6	1.04	1.00	1.04
30.3	25	»	—	35.4	29.7	1.17	0.98	1.20
31.8	30	»	—	38.6	31.3	1.21	0.98	1.24
26.6	20	—	4.1	4.0	8.1	—	—	0.49
30.9	20	—	10.0	9.6	19.8	—	—	0.48
28.4	20	—	14.0	13.2	27.5	—	—	0.48
33.2	20	—	17.0	15.8	33.0	0.48	0.99	0.48
29.6	20	—	40.0	13.9	29.4	0.47	0.99	0.47
31.9	20	—	excess	15.3	31.8	0.48	1.00	0.48

Reaction with Oxygen and with Nitric Oxide. A small flask (3 ml) containing weighed amounts of hydridonitrogen*tris*(triphenyl-phosphine)cobalt(I) under argon was cooled to about −30°C, evacuated, filled with dry oxygen, and connected to the gaschromatographic apparatus. On raising the temperature of the sample to about 0°C, a vigorous reaction took place.

The reaction with nitric oxide, carried out in a similar way, occured more slowly at room temperature. The residue of this reaction was identified as $Co(NO)(PPh_3)_3$[6] by means of its I.R. spectrum.

The gaschromatographic analyses of the reactions gaseous products are summarized in the following table.

Table III. Products of the reaction of $CoHN_2(PPh_3)_3$ with O_2 and NO

Sample (µmols)	Reagent	Gas evolved (µmols) H_2	N_2	H_2/Co	N_2/Co
38.2	O_2	9.9	37.5	0.26	0.98
35.3	O_2	10.8	35.0	0.31	0.99
37.6	NO	16.5	36.8	0.44	0.98

Reaction with Carbon Tetrachloride. The hydrido-nitrogen-complexes with triphenylphosphine, and with fully deuterated triphenylphosphine (0.3 g), were treated with carbon tetrachloride (0.4 ml) under argon. After a few minutes, the solvent was distilled off under reduced pressure, being collected in a dry ice trap.

Its I.R. spectrum was recorded, using carbon tetrachloride as reference. The presence of chloroform in the solvent was proved by the band at 1217 cm^{-1}, and that of tetrachloroethylene by the band at 910 cm^{-1}. The blue-green residue of the reaction, repeatedly washed with petroleum ether and dried, was identified as $CoCl_2(PPh_3)_2$.

Anal. Calcd. for $C_{36}H_{30}Cl_2P_2Co$: Cl, 10.8; P, 9.5; Co, 9.0. Found: Cl, 11.0; P, 9.3; Co, 8.8%.

A sample of chloro*tris*(triphenylphosphine)cobalt(I), treated under the same conditions with carbon tetrachloride, gave tetrachloroethylene, identified by means of its I.R. spectrum, and $CoCl_2(PPh_3)_2$.

Reaction with 1,2-bis(diphenylphosphine)ethane. A solution of $CoHN_2(PPh_3)_3$ (0.5 g) in benzene was treated with a benzene solution of the chelating diphosphine (1.0 g) under argon. The originally orange solution rapidly became red, gas being evolved. On adding ethanol, orange crystals of hydridodi-(1,2-bisdiphenylphosphinoethane)cobalt(I), identified by means of its I.R. spectrum, were obtained.

On treating $CoDN_2(PPh_3)_3$ in the same way, a mixture of $CoH(dp)_2$ and $CoD(dp)_2$, identified by means of its I.R. spectrum (bands at 1884 cm^{-1} and 1335 cm^{-1}), was obtained. The same result was obtained on treating $CoH[P(C_6D_5)_3]$ with the chelating diphosphine. A sample of pure $CoD(dp)_2$ did not show any appreciable exchange between deuterium and hydrogen after recrystallization under argon from benzene-ethanol.

$CoHN_2(PPh_3)_3$ (0.1696 g) was treated, in an evacuated apparatus, with a solution of the chelating diphosphine (0.25 g) in benzene (2 ml), and nitrogen (4.70 ml at 22°C and 754 mm) was evolved. The molar ratio nitrogen/cobalt was 0.992.

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(6) W. Hieber and K. Heinike, *Zeit anorg. allgem. Chem.*, *316*, 305 (1962); A. Sacco, M. Rossi, F. C. Nobile, and L. Uva, *La Chim e l'Ind.*, *48*, 986 (1966).

Variable amounts of the chelating diphosphine were added to a solution of $CoHN_2(PPh_3)_3$ in benzene; after each addition, the residual amount of the hydrido-nitrogen-complex was determined spectrophotometrically by means of the $N \equiv N$ stretching frequency at 2090 cm^{-1}. Table IV shows the results.

Table IV. Spectrophotometric titration of $CoHN_2(PPh_3)_3$ with $C_2H_4(PPh_2)_2$

Molar ratio of added diphosphine to $CoHN_2(PPh_3)_3$	Mole fraction of the residual $CoHN_2(PPh_3)_3$	Molar ratio of diphosphine to reacted $CoHN_2(PPh_3)_3$
0.38	0.79	1.81
0.85	0.57	1.98
1.21	0.38	1.95
1.98	0.0	1.98

Results and Discussion

Trihydrido-complexes. Trihydridotris(triphenylphosphine)cobalt(III) is a pale yellow crystalline compound, unstable to air, soluble in non-polar solvents such as benzene, toluene, or tetrahydrofuran, insoluble in methanol, ethanol, or petroleum ether. The corresponding complexes with ethyldiphenylphosphine are very soluble in all these organic solvents and were obtained only as oils. All attempts to obtain them in a crystalline form were unsuccessful.

Their I.R. spectra show two sharp absorption bands assignable to Co–H stretching (Table V): one of medium intensity at 1933-1958 cm^{-1}, and a stronger one at 1720-1745 cm^{-1}. By comparison with the Ir–H stretching values reported for the *trans*-trihydrido-*tris*(tertiaryphosphine)iridium(III) compounds,[1b] we assign to these cobalt hydrido-complexes an octahedral configuration with two hydrogen atoms in *trans*-position.

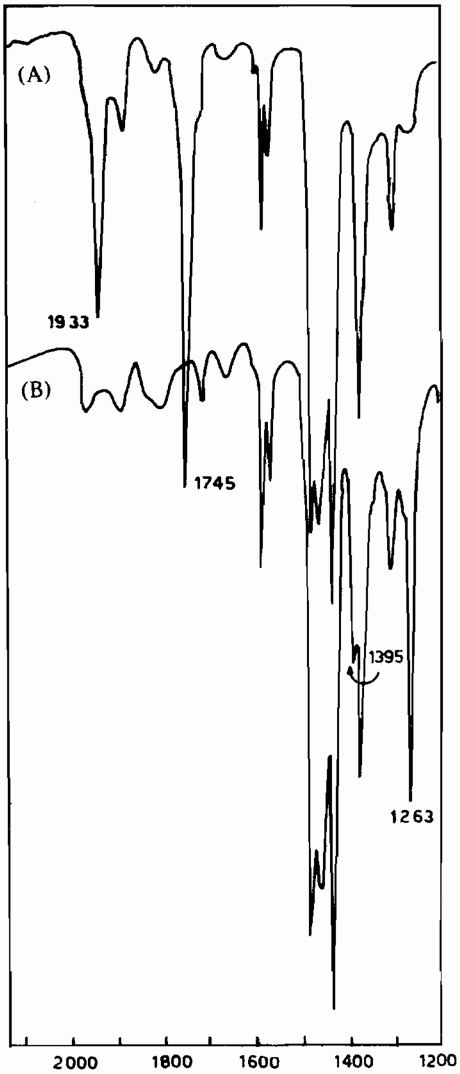

Figure 1. Infrared Spectra of: (A) $CoH_3(PPh_3)_3$, (B) $CoD_3(PPh_3)_3$, mulled in Nujol.

Table V. Infrared Absorption Bands (cm^{-1})

L	Solvent	CoH_3L_3 ν_{Co-H}	CoD_3L_3 ν_{Co-D}	$CoHN_2L_3$ $\nu_{N\equiv N}$	$CoDN_2L_3$ $\nu_{N\equiv N}$
$P(C_6H_5)_3$	Nujol	1933 m, 1745 s	1395 m, 1263 s	2096 vs [a]	2096 vs [a]
	»			2102 vs, 2087 vs [b]	2102 vs, 2087 vs [b]
	C_6H_6	1947 w, 1760 m	—	2090 vs	2090 vs
$P(C_6D_5)_3$	Nujol	1933 m, 1745 s	1395 m, 1263 s	2096 vs [a]	2096 vs [a]
	C_6H_6	—	—	2090 vs	2090 vs
$PEtPh_2$	—	1958 m, 1736 s	1260 m	2075 vs	—
PEt_2Ph	—	1940 m, 1720 s	—	2060 vs	—

[a] Compound recrystallized from benzene. [b] Compound recrystallized from tetrahydrofuran.

Trideuterido-complexes. On treating the trihydrido-complexes with deuterium, both in solution and in the solid state, a rapid exchange takes place. As shown in Figure 1 for the triphenylphosphine derivative, the bands at 1933 and 1745 cm^{-1} disappear and are replaced by two new bands at 1395 and 1263 cm^{-1} (ratio $\nu_{Co-H}/\nu_{Co-D} = 1.39$).

Hydridonitrogen-complexes. The trihydrido-complexes readily react with nitrogen at room temperature and atmospheric pressure, both in solution and in the solid state, according to equilibrium (1).

$$CoH_3L_3 + N_2 \rightleftharpoons CoHN_2L_3 + H_2 \qquad (1)$$

The equilibrium is quantitatively displaced to the right in a nitrogen atmosphere and to the left in a hydrogen atmosphere.

Hydridonitrogen*tris*(triphenylphosphine)cobalt(I) is an orange-red crystalline compound, moderatetly stable to air, soluble in non-polar solvents such as benzene, toluene, diethylether, or tetrahydrofuran, insoluble in methanol, ethanol, or petroleum ether.

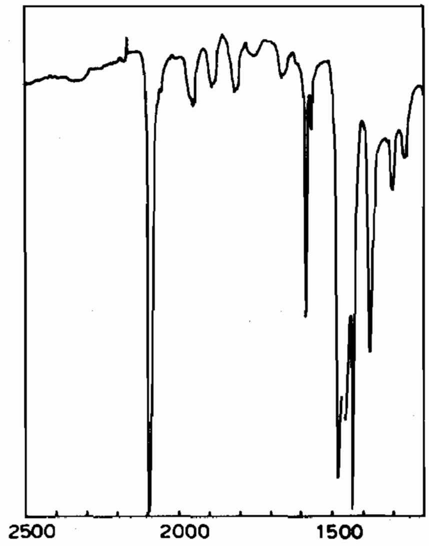

Figure 2. Infrared Spectra of $CoHN_2(PPh_3)_3$, mulled in Nujol.

The I.R. Spectrum (Table V and Figure 2) of the crude material, or of the product recrystallized from benzene, shows a very strong absorption band at 2096 cm^{-1} (Nujol mull) assignable to the N–N stretch of coordinated nitrogen. The I.R. spectrum of the product recrystallized from tetrahydrofuran shows two very strong absorption bands, of equal intensity, at 2102 and at 2087 cm^{-1}. This splitting seems to be due to a crystalline effect, and none of these bands is assignable to the Co–H stretch because the same bands are shown by $CoDN_2(PPh_3)_3$, obtained from the trideutero-complex and recrystallized from the same solvent. Moreover, all these compounds show in solution only one very strong absorption band at 2090 cm^{-1}.

The samples obtained from the solid trihydrido-complex by reaction with nitrogen are solvent-free, whereas those recrystallized from benzene, diethylether and tetrahydrofuran usually contain molecules of solvent.

The corresponding complexes with ethyldiphenylphosphine and with diethylphenylphosphine are very soluble in all the organic solvents and were obtained as oils.

The I.R. spectra of the hydridonitrogen-complexes do not show any band assignable to Co–H stretching; however, examples of hydrido-complexes that do not show any detectable metal-hydrogen stretching frequency are known.[7]

Thermal Decomposition. The trihydrido- and hydridonitrogen-complexes decompose in vacuo at about 80°C. The crude trihydrido*tris*(triphenylphosphine)cobalt(III), not recrystallized from benzene but free from boron-compounds, gave by thermal decomposition at 100-150°C in a evacuated apparatus 1.2-1.3 mol of hydrogen per cobalt atom, besides undetermined amounts of benzene, identified by its I.R. spectrum, and decomposition products. The decomposition of the nitrogen-complex, obtained from the solid trihydrido-complex kept under N_2 until completely free from the metal-hydrogen absorption bands, gave 1 mol of nitrogen and 0.2-0.4 mol of hydrogen per cobalt atom, besides undetermined amounts of benzene. When treated with hydrochloric acid, the residue of the decomposition gave some diphenylphosphine, identified by means of its I.R. spectrum. The thermal decomposition of the hydridonitrogen-complex containing the fully deuterated triphenylphosphine, and recrystallized several time in a nitrogen atmosphere from benzene plus petroleum ether, gave 1 mol of nitrogen and 0.2-0.35 mol of hydrogen per cobalt atom, together with undetermined amounts of benzene and deuterated benzene.

Thermal decomposition of the hydridonitrogen*tris*(triphenylphosphine)cobalt(I) in a nitrogen atmosphere gave 0.40-0.48 mol of hydrogen per cobalt atom, and thermal decomposition of the same compound in a carbon monoxide atmosphere* gave 1 mol of nitrogen and 0.40-0.45 mol of hydrogen per cobalt atom.

These data suggest that the thermal decomposition of the hydridonitrogen-complexes occurs by two different paths:

$$\text{(a)}\quad CoHN_2(PPh_3)_3 \rightarrow N_2 + 0.5H_2 + [Co(PPh_3)_3] \qquad (2)$$

$$\text{(b)}\quad CoHN_2(PPh_3)_3 \rightarrow N_2 + PhH + [CoPPh_2(PPh_3)_2] \qquad (3)$$

$$[CoPPh_2(PPh_3)_2] \xrightarrow{HCl} PHPh_2 + CoCl_2 + PPh_3 \qquad (4)$$

When the thermal decomposition is carried out under nitrogen or carbon monoxide, the reaction (b) seems almost completely suppressed.

Reaction with Hydrochloric Acid. Hydridonitrogen*tris*(triphenylphosphine)cobalt(I) reacts with hydrochloric acid giving off 1 mol of nitrogen and 1-1.2 mols of hydrogen per cobalt atom (reaction (5)).

When the reaction is carried out at about 10°C, the resulting green solid residue consists of chloro*tris*(triphenylphosphine)cobalt(I), identified by means of its electronic spectrum.[2b] At higher temperatures this later compound reacts further with hydrochloric acid, giving off hydrogen (reaction (6)).

$$\text{(a)}\quad CoHN_2(PPh_3)_3 + HCl = N_2 + H_2 + CoCl(PPh_3)_3 \qquad (5)$$

$$\text{(b)}\quad CoCl(PPh_3)_3 + HCl = CoCl_2 + 3PPh_3 + 0.5H_2 \qquad (6)$$

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[7] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 5507 (1961).

(*) Although the complex reacts very quickly with CO in solution, it is fairly stable in a CO atmosphere in the solid state at room temperature.

Reaction with Iodine. Hydridonitrogen*tris*(triphenylphosphine)cobalt(I) reacts very smoothly at room temperature with iodine in benzene solution giving off 1 mol of nitrogen and 0.45-0.50 mol of hydrogen per cobalt atom. The evolution of the gas stops after the addition of one iodine atom per cobalt atom. When the reaction is carried out with a stoicheiometric amount of iodine, iodi*tris*(triphenylphosphine)cobalt(I), identified by means of its electronic spectrum,[2b] is quantitatively formed according to equation (7).

$$\mathrm{CoHN_2(PPh_3)_3 + 0.5I_2 = N_2 + 0.5H_2 + CoI(PPh_3)_3} \qquad (7)$$

Reaction with Oxygen and with Nitric Oxide. Hydridonitrogen*tris*(triphenylphosphine)cobalt(I) reacts in the solid state, with oxygen, at room temperature giving off 1 mol of nitrogen and about 0.3 mol of hydrogen per cobalt atom. With nitric oxide, in the same conditions, it reacts according to equation (8).

$$\mathrm{CoHN_2(PPh_3)_3 + NO = N_2 + 0.5H_2 + Co(NO)(PPh_3)_3} \qquad (8)$$

Reaction with Carbon Tetrachloride. On treating both hydridonitrogen*tris*-(triphenylphosphine)cobalt-(I), and the corresponding complex containing the fully deuterated triphenylphosphine, with carbon tetrachloride at room temperature, a vigorous reaction takes place and chloroform and tetrachloroethylene, identified by means of their I.R. spectra, are formed. The reaction occurs according to equation (9).

$$\mathrm{CoHN_2(PPh_3)_3 + CCl_4 = CHCl_3 + N_2 + CoCl(PPh_3)_3} \qquad (9)$$

The tetrachloroethylene comes from the reaction of the excess of carbon tetrachloride with the chloro*tris*(triphenylphosphine)cobalt(I). In fact, pure samples of this later compound, treated in the same conditions with carbon tetrachloride, give $\mathrm{C_2Cl_4}$ in addition to $\mathrm{CoCl_2(PPh_3)_2}$.

Reaction with 1,2-bis(diphenylphosphino)ethane. On treating the hydridonitrogen*tris*(triphenylphosphine)cobalt(I) with an excess of the chelating diphosphine in benzene solution, one mol of nitrogen per mol of complex is evolved, and the well known hydrido-di-(1,2-bisdiphenylphosphinoethane)cobalt(I) [8] is formed. On treating the deuteridonitrogen*tris*(triphenylphosphine)cobalt(I) in the same way a mixture of hydrido- and deuterido-di-(1,2-bisdiphenylphosphinoethane)cobalt(I) is obtained. Because this later compound does not exchange its deuterium atom with hydrogen when recrystallized from benzene-ethanol, the above-mentioned result suggests that a exchange occurs in the hydridonitrogen*tris*(triphenylphosphine)-cobalt(I) between the hydrogen bound to the metal and the hydrogen of the phenyl group. This has been confirmed by treating the hydridonitrogen-complex of the fully deuterated triphenylphosphine with the chelating diphosphine. Further, a mixture of hydrido- and deuterido-di-(1,2-bisdiphenylphosphinoethane)-cobalt(I) has also been obtained in this case.

The infrared spectrophotometric titration of the hydrido-nitrogen-complex with the diphosphine shows that the reaction proceeds according to equation (10).

$$\begin{aligned}&\mathrm{CoHN(PPh_3)_2 + 2C_2H_4(PPh_2)_2 =}\\&\mathrm{N_2 + CoH\{C_2H_4(PPh_2)_2\}_2 + 3PPh_3}\end{aligned} \qquad (10)$$

Conclusion

All the above-mentioned data furnish unambiguous evidence concerning the presence of a Co–H bond in the nitrogen-complex. Further evidence is furnished by the diamagnetism of the compound, consistent with a previously suggested[2] and recently confirmed[5] trigonal bipyramidal coordination about the cobalt atom.

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