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Pentaphosphine-complexes of Cobalt(II) and Hydridopentaphosphine-complexes of Cobalt(III) with Secondary Phosphines

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The secondary phosphines $HP(C_2H_5)_2$, $HP(CH_3)Ph$ *and* $HP(C_2H_5)Ph$ *react with* $Co(BF_4)_2\cdot 6H_2O$ *to yield cationic pentaphosphine derivatives, which have been obtained in the solid state in two forms of different color. The red* $[Co(HPR_2)_5](BF_4)_2$ *are truly five-coordinate (low-spin) complexes. whereas the green* $[Co(HPR_2)_5]^{2+}$ *moieties, which have* C_{4v} *symmetry, are probably weakly coordinated in the sixth position with a water molecule or a tetrafluoroborate ion. In common organic solvents the green forms convert immediately into the red. Some chemical properties of the* $[Co(HPR_2)_5]^{2+}$ *cations have been investigated and the preparation of a few hydrido-derivatives of cobalt(III) of the type* $[CoH(HPR_2)_5](BF_4)_2$ *is reported.*

Introduction

A number of five-coordinate low-spin complexes of cobalt(II) have been obtained from the reactions of cobalt(II) salts with monodentate phosphines [1–11]. These complexes are generally of the type $[CoX_2(P)_3]$ (X = halogen or pseudohalogen, P = phosphine), and only with "small" secondary phosphines have five-coordinate $[CoX(HPR_2)_4]^+$ complexes ($R_2 = (C_2H_5)_2, (C_2H_5)Ph, (CH_3)Ph$), containing four phosphine ligands been obtained [3]. More recently the hydride $[CoH(P(CH_3)_3)_4]^+$ has been obtained via protonation of the cobalt(0) derivative $[Co(P(CH_3)_3)_4]$ [10].

Extending our earlier studies on the low-spin cobalt(II) complexes, we have now found that cobalt (II) salts containing poorly coordinating anions react with "small" secondary phosphines to give pentaphosphine adducts. The $[Co(HPR_2)_5]^{2+}$ complexes have been obtained in the solid state as tetrafluoroborate salts in two forms: red crystals and olive-green hydrated powders. Two logical possibilities could be proposed to account for the different color of the crystalline compounds: a stereochemical change in geometries from a trigonal bipyramid (D_{3h}) to a square pyramid (C_{4v}), or, if they possess the latter geometry, some type of weak axial interaction in the sixth coordination site with a solvent molecule or BF_4^- ions. Apparently there could be some analogies with the yellow or green forms of the $[Co(CN)_5]^{3-}$ and $[Co(CNPh)_5]^{2+}$ ions, which have occasioned a good deal of interest lately [12–18]. Only recently the determination of the crystalline structures of the yellow $[N(C_2H_5)_2(i\text{-}C_3H_7)_2]_3[Co(CN)_5]$ [19] and of the green $[Co(CNPh)_5](ClO_4)_2\cdot 0.5C_2H_4Cl_2$ [20] has clarified the situation. The yellow forms are truly five-coordinate square-pyramidal complexes, whereas in the green forms there is a solvent molecule (or perchlorate ion) weakly coordinated in the sixth axial position.

In addition to the preparation and characterization of the $[Co(HPR_2)_5](BF_4)_2$ complexes, this paper describes the synthesis of some hydridopentaphosphine derivatives of cobalt(III) of composition $[CoH(HPR_2)_5](BF_4)_2$.

Experimental

Reactions and handling of the compounds were carried out in an inert atmosphere. Previously reported procedures were used to prepare diethyl-, ethylphenyl- and methylphenylphosphines. $Co(BF_4)_2\cdot 6H_2O$ was prepared starting from cobalt carbonate and aqueous HBF_4. Microanalyses were made by Mr. L. Turiaco, Istituto di Chimica Analitica, University of Padua.

Infrared spectra were recorded on a Perkin Elmer 547 instrument; visible spectra were determined on an Optica CF4RNI spectrophotometer; conductance data were obtained using a LKB conductance bridge; magnetic susceptibilities were measured by a standard Gouy method. ^1H n.m.r. spectra were recorded on a Bruker WP-60 instrument. E.s.r. spectra were recorded with a JEOL PE-3X spectrometer; the g factors were measured with reference to the signal of a sample of Mn(II) in MgO.

I.r. spectra of the reported complexes show broad absorptions in the 2300–2400 cm^{-1} region, attributable to P–H stretching of the coordinated phosphines.

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$[Co(HP(C_2H_5)Ph)_5](H_2O)(BF_4)_2$

Ethylphenylphosphine (0.7 ml, 5 mmol) dissolved in 2-propanol (10 ml) was slowly added to 0.34 g of $Co(BF_4)_2 \cdot 6H_2O$ (1 mmol) in 2-propanol (10 ml). On shaking, the resulting red solution gave within 10 min green microcrystals of the complex, which was purified by recrystallisation from dichloromethane–2-propanol, in the presence of small amounts of free phosphine (yield 60%). By recrystallisation from acetone–2-propanol a red complex, probably $[Co(HP(C_2H_5)Ph)_5](BF_4)_2$, was obtained, but contaminated by the hydrido-derivative $[CoH(HP(C_2H_5)Ph)_5](BF_4)_2$.

$[Co(HPR_2)_5](H_2O)(BF_4)_2$ and $[Co(HPR_2)_5](BF_4)_2$ $(R_2 = (CH_3)Ph)$

Methylphenylphosphine (0.6 ml, 5 mmol) in 2-propanol (10 ml) was added dropwise to a solution of $Co(BF_4)_2 \cdot 6H_2O$ (0.34 g, 1 mmol) in 2-propanol (10 ml). On shaking, the resulting red solution gave within 10 min green crystals of $[Co(HP(CH_3)Ph)_5](H_2O)(BF_4)_2$ (yield 80%). The compound was not further purified. In fact, by recrystallisation from acetone–2-propanol, red crystals of $[Co(HP(CH_3)Ph)_5](BF_4)_2$ were obtained in pure form (yield 50%). It should be noted that when the phosphine was rapidly added to the solution of $Co(BF_4)_2 \cdot 6H_2O$, a red viscous oil separated, which produced a crystalline solid only after prolonged stirring. The resulting crude product, however, was often a mixture of the green and the red forms, from which only the red $[Co(HP(C_2H_5)Ph)_5](BF_4)_2$ complex can be obtained in pure form.

$[Co(HP(C_2H_5)_2)_5](BF_4)_2$

Diethylphosphine (0.6 ml, 5 mmol) was added to a solution of 0.34 g of $Co(BF_4)_2 \cdot 6H_2O$ (1 mmol) in 10 ml of 2-propanol. Red crystals immediately separated, which were purified by recrystallisation from dichloromethane–2-propanol, in the presence of small amounts of free phosphine (80% yield).

$[CoH(HP(C_2H_5)Ph)_5](BF_4)_2$

This was prepared as in the manner described above for $[Co(HP(C_2H_5)Ph)_5](H_2O)(BF_4)_2$, except that the reaction mixture was shaken for a much longer time at room temperature. The reaction was complete within 48 hr (yield 60%). The white complex was slightly soluble in common organic solvents and was not further purified.

$[CoH(HP(C_2H_5)_2)_5](BF_4)_2$

$[Co(HP(C_2H_5)_2)_5](BF_4)_2$ (1.4 g, 2 mmol), suspended in tetrahydrofuran (40 ml), was stirred with sodium amalgam (47 mg of metallic sodium in 2 ml of mercury). The resulting red solution was filtered and treated with 0.3 ml of a 50% aq. solution of HBF_4 (2.4 mmol) diluted in diethyl ether (20 ml). The color of the solution slowly discharged and white crystals precipitated. The compound was recrystallised from dichloromethane–2-propanol (yield 60%).

Reactions of $[Co(HPR_2)_5](BF_4)_2$ with CO

The reactions between CO and the $[Co(HPR_2)_5](BF_4)_2$ complexes were carried out in a standard gas-buret apparatus. Isopropyl alcohol (10 ml) was saturated with carbon monoxide at 25 °C and then a known weight of complex was added with stirring. The uptake of carbon monoxide was measured at constant pressure with allowance for the vapour pressure of the solvent. The i.r. spectrum (1900–2000 cm^{-1} region) of the solutions was taken at the end of CO absorption. Removal of the solvent under vacuum gave yellow oils whose i.r. spectra show at 1150–1200 cm^{-1} a band attributable to P=O stretching of the phosphine oxide.

Reactions of $[Co(HP(C_2H_5)_2)_5](BF_4)_2$ with C_2H_5I or I_2

To 0.78 g of $[Co(HP(C_2H_5)_2)_5](BF_4)_2$ (1.1 mmol), suspended in tetrahydrofuran (50 ml), ethyl iodide was added dropwise (0.19 g, 1.2 mmol). The reaction is complete in *ca.* 5 hr. From the green solution dark green crystals of $[CoI(HP(C_2H_5)_2)_4]BF_4$ separated by evaporating the solvent. The compound was washed with benzene and dried *in vacuo* (yield 70%). The same product was obtained when the $[Co(HP(C_2H_5)_2)_5](BF_4)_2$ complex was reacted with a stoichiometric amount of iodine.

When the same complex was treated in tetrahydrofuran with excess (1:3) of C_2H_5I (or I_2) a red solution was slowly formed. By concentration *in vacuo* orange-red crystals were obtained. This material (probably $[CoI_2(HP(C_2H_5)_2)_3]$) was impure and even after recrystallisation no acceptable analysis could be obtained.

Results and Discussion

Preparation and Characterization

Addition of secondary phosphines HPR_2 to 2-propanol solutions of $Co(BF_4)_2 \cdot 6H_2O$ gives deep red solutions, which rapidly deposit red ($HPR_2 = HP(C_2H_5)_2$) or olive-green ($HPR_2 = HP(C_2H_5)Ph$, $HP(CH_3)Ph$) crystals [21]. Recrystallisation of the $HP(CH_3)Ph$ green adduct from acetone–2-propanol gives a red product. A similar green-red transformation is also observed in the recrystallisation of the $HP(C_2H_5)Ph$ derivative, but the final product appears to contain some amount of a hydrido-complex.

Analytical data for all these complexes (red or green) indicate the presence of five molecules of secondary phosphines *per* cobalt atom, in agreement with a formulation $Co(HPR_2)_5(BF_4)_2$. Con-

TABLE I. Analytical Data and Physical Constants.

Compound	Color	Mp[a]	μ_{eff}[b]	Λ_M[c]	Anal., %			
					C		H	
					Calcd	Found	Calcd	Found
$[Co(HP(C_2H_5)_2)_5](BF_4)_2$	red	175	2.30	175	35.17	34.55	8.12	8.13
$[Co(HP(C_2H_5)C_6H_5)_5](H_2O(BF_4)_2$	green	129	2.45	171	50.76	50.80	6.07	6.05
$[Co(HP(CH_3)C_6H_5)_5](BF_4)_2$	red	140	2.11	141	49.29	50.30	5.31	5.44
$[Co(HP(CH_3)C_6H_5)_5](H_2O)(BF_4)_2$	green	184	2.45	185	48.27	49.05	5.44	5.41
$[CoH(HP(C_2H_5)_2)_5](BF_4)_2$	white	200	diam.	150	35.11	34.35	8.25	8.38
$[CoH(HP(C_2H_5)C_6H_5)_5](BF_4)_2$	white	158	diam.	...[d]	51.70	49.68[e]	6.07	6.32
$[CoI(HP(C_2H_5)_2)_4]BF_4$	green	154	2.11	96	30.35	30.29	7.10	7.40

[a] °C, in sealed tube under vacuum. [b] B.M., at 20 °C. [c] S cm^2 mol^{-1} for 10^{-3} solutions in nitromethane at 20 °C. [d] Decomposes. [e] This complex could not be purified.

ductance measurements on 10^{-3} *M* solution in nitromethane give values in the range expected for 2:1 electrolytes (Table I).

The red $[Co(HPR_2)_5](BF_4)_2$ (R_2 = $(C_2H_5)_2$, $(CH_3)Ph$) complexes have μ_{eff} around 2.2 B.M., corresponding to the values previously reported for five-coordinate low spin complexes of cobalt(II). Solid state spectra resemble each other and show a single band at 21,000 cm^{-1}. Solution spectra are complicated by the occurrence of the dissociative process (1):

$$[Co(HPR_2)_5]^{2+} \rightleftarrows [Co(HPR_2)_4]^{2+} + HPR_2 \qquad (1)$$

but in the presence of excess phosphine, the dissociation is reduced and the final spectra appear very similar to those in the solid state. Under these conditions the complexes appear to maintain also in solution a discrete five-coordinate structure. In the absence of X-ray structural data [22], it is difficult to predict if the red $[Co(HPR_2)_5](BF_4)_2$ complexes will have trigonal bipyramidal or square pyramidal geometry. Electronic spectra alone are not sufficient [23] to assign unambiguously the geometries of the five-coordinate low-spin cobalt(II) complexes. It can be noticed, however, that the known square-pyramidal $[Co(CN)_5]^{3-}$ and $[Co(CNR)_5]^{2+}$ ions are yellow [12, 13, 17] and have no distinct absorption peaks in the visible region whereas the electronic spectra of the red $[Co(HPR_2)_5]^{2+}$ cations appear to be related to those of the $[Co(CN)_2(PR_3)_3]$ complexes (one band around 21,000 cm^{-1}, for which an intermediate geometry has been suggested [2, 3].

The green $Co(HPR_2)_5(BF_4)_2$ (R_2 = $(CH_3)Ph$, $(C_2H_5)Ph$) complexes give red solutions in all common organic solvents. Solid state and solution spectra, the latter in the presence of excess phosphine, are very different. The solid state spectra (Fig. 1) exhibit two bands around 18,000 cm^{-1} and 25,000 cm^{-1}, whereas the solution spectra are identical with those of the red $[Co(HPR_2)_5]^{2+}$ cations (a single peak at about 21,000 cm^{-1}, (Table II). These data indicate that the structures of the green and red forms, which are different in the solid, become identical in solution.

TABLE II. Electronic (Visible) Spectra.

Compound	Absorption max. 10^3 cm^{-1} (ϵ_M)*
$[Co(HP(C_2H_5)_2)_5](BF_4)_2$	*a*: 20.4 *b*: 22.2
$[Co(HP(C_2H_5)C_6H_5)_5](H_2O)(BF_4)_2$	*a*: 17.9, 26.3 *b*: 20.4
$[Co(HP(CH_3)C_6H_5)_5](BF_4)_2$	*a*: 20.8(sh) *b*: 21.8(sh)
$[Co(HP(CH_3)C_6H_5)_5](H_2O)(BF_4)_2$	*a*: 18.5, 24.1 *b*: 21.8(sh)
$[CoI(HP(C_2H_5)_2)_4]BF_4$	*c*: 16.7(700), 24.1(2300), 26.3(2300)

*Key: *a*, Nujol mull; *b*, acetone solutions at 25 °C, in the presence of excess (*ca.* 100-fold) phosphine (in these conditions the dissociation is not yet completely repressed and ϵ_M values are not reported); *c*, acetone solution at 25 °C.

Also, the green complexes are paramagnetic (μ_{eff} around 2.4 B.M.) and this fact rules out the possibility that the red-green interconversion arises from a dimerization reaction, with formation of diamagnetic dimers $[Co_2(HPR_2)_{10}]^{4+}$ containing a cobalt–cobalt bond. Dimeric products Co_2L_{10} have been obtained from solutions containing the five-coordinate $[Co(CN)_5]^{3-}$ and $[Co(CNCH_3)_5]^{2+}$ complexes [24].

The e.s.r. spectra of polycrystalline samples of the green $Co(HPR_2)_5(BF_4)_2$ consist, both at room temperature and at 77 K, of an asymmetric line, lacking hyperfine structure, with $g_\perp > g_\parallel$. The g values obtained are, in the case of the methylphenylphosphine derivative, $g_\perp$ = 2.144 and $g_\parallel$ = 2.018 (Fig. 2), and in the case of the ethylphenylphosphino derivative, $g_\perp$ = 2.140 and $g_\parallel$ = 1.922 [25].

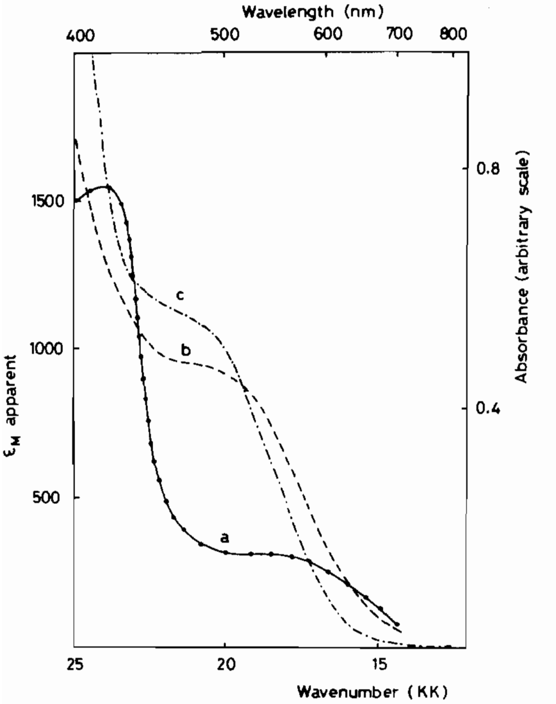

Fig. 1. Electronic absorption spectra: (a) –•–•–, $[Co(HP(CH_3)Ph)_5](H_2O)(BF_4)_2$ (green form) in Nujol mull; (b) – – –, $[Co(HP(CH_3)Ph)_5](BF_4)_2$ (red form) in Nujol mull; (c) – · – · –, $[Co(HP(CH_3)Ph)_5](BF_4)_2$, 2.32×10^{-3} *M* in acetone containing 1.6 *M* methylphenylphosphine.

These results are consistent with a C_{4v} symmetry [16]. However, on the basis of the following observations, a true square pyramidal structure seems unlikely, it being most probable that in the green solids the $[Co(HPR_2)_5]^{2+}$ moieties have some type of weak axial interaction. The i.r. spectra of the green $Co(HP(CH_3)Ph)_5(BF_4)_2$ exhibit, along with the phosphine and the anion modes, peaks at 3640, 3560 and 1620 cm^{-1}, which suggest the presence of water molecules. In the case of the green $Co(HP(C_2H_5)Ph)_5(BF_4)_2$ broad absorptions were observed in the 3500–3600 cm^{-1} region and at 1620 cm^{-1}. The above bands are still present after prolonged drying *in vacuo* and do not appear in the i.r. spectra of the corresponding red forms. Moreover, when the green $Co(HP(CH_3)Ph)_5(BF_4)_2$ is treated with a stoichiometric amount of sodium amalgam in tetrahydrofuran suspension, gas evolution is observed with immediate formation of the red $[Co(HP(CH_3)Ph)_5](BF_4)_2$ complex. The green ethylphenylphosphine derivative behaves similarly, but the red compound was not isolated in pure form.

It seems possible that the green $Co(HPR_2)_5(BF_4)_2$ products have a weakly coordinated water molecule in the sixth position. However, when water is added to the red acetone solutions of the $[Co(HPR_2)_5]^{2+}$ cations, there are no appreciable changes in the visible spectrum. These observations could suggest that the water molecule is maintained into the sixth position of the coordination sphere of cobalt, only as a result of restriction imposed by crystal lattice.

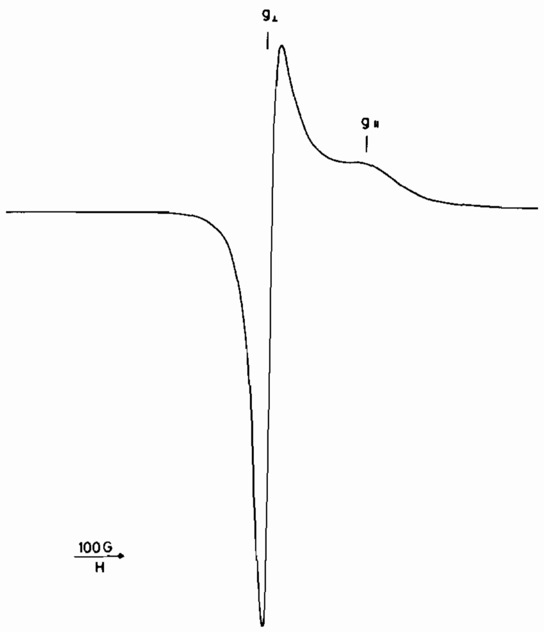

Fig. 2. Electron spin resonance spectrum for $[Co(HP(CH_3)Ph)_5](H_2O)(BF_4)_2$ (green form) as polycrystalline sample, 110 K.

A structure with a water molecule simply trapped in the crystal lattice is also possible, the sixth coordination site being occupied by a tetrafluoroborate ion, as found in the $[Co(CNPh)_5](ClO_4)_2 \cdot 0.5C_2H_4Cl_2$, which has a weakly coordinated perchlorate ion in the sixth position [20]. I.r. data do not allow to unambiguously establish whether or not a BF_4^- ion interacts with cobalt, because the regions where bands of the coordinated ion are expected [26] are partially obscured by absorptions of the phosphine ligands [21]. Nevertheless, i.r. spectra in the $\nu_3(BF_4^-)$ region (950–1150 cm^{-1}) appear to be much more complicated for the green forms than for the red ones. This fact could arise from an interaction of BF_4^- ions with the metal atom, but also from hydrogen bond formation between the anion and water molecules and/or PH of the secondary phosphines.

Attempts to obtain $[Co(P)_5]^{2+}$ complexes with other secondary ($HPPh_2$, $HP(C_6H_{11})_2$, $HP(C_6H_{11})Ph$) or tertiary phosphines ($P(CH_3)_3$, $PRPh_2$, PR_2Ph) have been unsuccessful, although with diphenyl-, trimethyl- and dimethylphenylphosphine there was evidence of the presence of pentakisphosphino adducts in solution at low temperature. This suggests that the formation of these five-coordinate complexes is primarily dependent on the size, rather than on the electronic character of the ligands.

Chemical Behavior

The chemistry of $[Co(HPR_2)_5]^{2+}$ complexes has been studied in some detail to permit a comparison with the isoelectronic $[Co(CN)_5]^{3-}$ and $[Co(CNR)_5]^{2+}$ ions.

The reaction between $Co(BF_4)_2 \cdot 6H_2O$ and $HP(C_2H_5)Ph$ in 2-propanol leads to the immediate formation of the pentaphosphine adduct. However, if the reaction mixture is allowed to stir for some days, the initial product slowly transforms into a hydrido-derivative of cobalt(III), $[CoH(HP(C_2H_5)Ph)_5](BF_4)_2$. Also in the case of the methylphenylphosphine complex a partial transformation is observed, but the reaction is hardly reproducible. The formation of these $[CoH(HPR_2)_5](BF_4)_2$ complexes bears some resemblance to the "aging" process of $[Co(CN)_5]^{3-}$, which, in aqueous solution, slowly gives $[CoH(CN)_5]^{3-}$ [27].

By contrast, the complex $[Co(HP(C_2H_5)_2)_5](BF_4)_2$ was recovered unchanged from the reaction mixture even after 4 days' stirring. However, $[CoH(HP(C_2H_5)_2)_5](BF_4)_2$ can be prepared by an alternative route, by protonation with fluoroboric acid of the $[Co(HP(C_2H_5)_2)_5]^+$ species generated *in situ* by treatment of the corresponding cobalt(II) adduct with sodium amalgam in tetrahydrofuran. All the white $[CoH(HPR_2)_5](BF_4)_2$ derivatives show in the i.r. spectra one band around 1950 cm^{-1}, due to the Co–H stretch.

High field nmr spectra of $[CoH(HP(C_2H_5)_2)_5](BF_4)_2$ in CH_2Cl_2 show a doublet of quintets centered at 24.79τ, which is assigned to H bound to cobalt, coupled to one *trans* P (J_{PH} = 77 Hz) and to four equivalent *cis* P nuclei (J_{PH} = 50 Hz).

The methylphenyl- and ethylphenylphosphine derivatives are slightly soluble in the common organic solvents. When suspended in a CH_2Cl_2–C_2H_5OH mixture they slowly give red solutions, which probably contain a cobalt(I) species, produced *via* the reductive elimination reaction (2):

$$[CoH(HPR_2)_5]^{2+} \rightleftarrows [Co(HPR_2)_5]^+ + H^+ \qquad (2)$$

On addition of slight excess of HBF_4 to these red solutions, the white $[CoH(HPR_2)_5]^{2+}$ cations are re-formed.

It must be noted that the hydrido-derivative with the more basic diethylphosphine appears to be rather stable under the above conditions and can be deprotonated only in the presence of strong bases.

This class of compounds provides the first example of hydrido-derivatives of cobalt(III) of the type $[CoH(P)_5]^{2+}$, those previously reported being of the type $[CoH_3(P)_3]$ [28] or $[CoH_2(P)_4]^+$ [29]. Also in the case of the isoelectronic iridium(III), a similar $[IrH(P)_5]^{2+}$ cation [30] was obtained with the "small" phosphine $HP(C_2H_5)_2$.

Attempts were made to obtain other cobalt(III) derivatives by the reaction of the $[Co(HPR_2)_5]^{2+}$ cations with halogens or alkyl halides.

By treating the red $[Co(HP(C_2H_5)_2)_5](BF_4)_2$ complex with a stoichiometric amount of iodine in tetrahydrofuran, a dark green solution is formed, from which the five-coordinate cobalt(II) derivative $[CoI(HP(C_2H_5)_2)_4]BF_4$ could be precipitated. If further iodine is added, the green solution turns red and the visible spectra show absorption bands at 15,900 and 21,300 cm^{-1}, suggesting the formation of a five-coordinate $[CoI_2(HP(C_2H_5)_2)_3]$ chromophore [3].

The same cobalt(II) complexes are obtained when $[Co(HP(C_2H_5)_2)_5](BF_4)_2$ is allowed to react with alkyl iodides, whereas no evidence of the formation of organometallic derivatives of cobalt(III) is found. It is noteworthy that $[Co(CN)_5]^{3-}$ is rapidly oxidized by iodine to the corresponding halo-pentacyanocobaltate(III) and by alkyl iodides to mixtures of iodo- and alkyl-pentacyanocobaltates(III) [31]. In the case of the pentaphosphine cations, described above, iodine or alkyl iodides clearly first react with the free phosphine (from eq. 1) generating iodide ions which in a second step coordinate to the cobalt (II).

Finally we find that the $[Co(HPR_2)_5]^{2+}$ complexes (both green and red forms) react with carbon monoxide in 2-propanol suspension at ambient conditions to give carbonyl derivatives of cobalt(I). From the reaction mixtures, however, no crystalline products have been recovered and therefore the reaction was investigated in 2-propanol, by measuring the amount of absorbed CO and the i.r. spectra of the final solutions. In all cases, more than one mol of CO per mol of cobalt was absorbed and i.r. spectra exhibited carbonyl bands at 1925 cm^{-1}, which can be attributed to $[Co(CO)(HPR_2)_4]^+$ derivatives and also at 1960 and 2000 cm^{-1}, attributed to $[Co(CO)_2(HPR_2)_3]^+$ cations [32]. The reduction of the $[Co(HPR_2)_5]^{2+}$ complexes is always accompanied by formation of oxidation products of the phosphines.

Once again the reaction with carbon monoxide proceeds differently in the cases of the isoelectronic $[Co(CN)_5]^{3-}$ and $[Co(CNCH_3)_5]^{2-}$ ions. In fact, whereas $[Co(CN)_5]^{3-}$ readily undergoes disproportionation in the presence of CO [33], to yield equimolar amounts of $[Co(CO)_2(CN)_3]^{2-}$ and $[Co(CN)_6]^{3-}$, in the case of the blue $[Co(CNCH_3)_5]^{2+}$ cation, no evidence of reaction has been observed [18].

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