Reactivity of the Hydride $[CoH\{P(OEt)_2Ph\}_4]$ with RN_2^+ (R = aryl), NO^+, and H^+ Cations: Preparation and Properties of New Cobalt Complexes. Measurements of T_1 for $[CoH\{P(OEt)_2Ph\}_4]$ and $[CoH_2\{P(OEt)_2Ph\}_4]BPh_4$†

Gabriele Albertin,* Paola Amendola, Stefano Antoniutti, and Emilio Bordignon*
Dipartimento di Chimica dell'Università di Venezia, Dorsoduro 2137, 30123 Venice, Italy

The reaction of $[CoH\{P(OEt)_2Ph\}_4]$ with RN_2^+ ($R = 4\text{-}CH_3C_6H_4$) affords the paramagnetic cationic hydride $[CoH\{P(OEt)_2Ph\}_4]^+$, with NO^+ the dinitrosyl cation $[Co(NO)_2\{P(OEt)_2Ph\}_2]^+$, and with $HBF_4{\cdot}Et_2O$ the cationic dihydride $[CoH_2\{P(OEt)_2Ph\}_4]^+$. Characterization of the complexes by i.r., e.s.r., and variable-temperature ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra is described. Variable-temperature ^1H n.m.r. T_1 measurements at 80, 200, and 400 MHz for both $[CoH\{P(OEt)_2Ph\}_4]$ and $[CoH_2\{P(OEt)_2Ph\}_4]BPh_4$ are also reported. The reactivity of the cationic hydrides with CO, RNC, NO, I_2, and RN_2^+ was investigated and the new cations $[Co(CNR)_2\{P(OEt)_2Ph\}_3]^+$ ($R = 4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$, or $4\text{-}ClC_6H_4$) and $[CoH(I)\{P(OEt)_2Ph\}_4]^+$ synthesized. The unstable intermediate $[CoH(NO)\{P(OEt)_2Ph\}_4]^+$ [ν(NO) at 1 680 cm^{-1}] was also detected.

Arenediazonium cations are reported to react with transition-metal hydrides to give aryldiazene or arylhydrazido complexes[1] by insertion of RN_2^+ into the M–H bond. Aryldiazenido derivatives have also been obtained by this reaction, generally by deprotonation of the initial diazene intermediate.[1e,f,2] However, no data are yet available on the reactivity of cobalt hydrides towards arenediazonium cations.

Previous reports from our laboratory have dealt with studies on reactions of iron(II) mono-[3] and di-hydrides[4] with RN_2^+, and on the synthesis of the first aryldiazenido complexes of cobalt(I).[5] We have now extended these studies to include the reactivity of the cobalt(I) hydride $[CoH\{P(OEt)_2Ph\}_4]$ towards arenediazonium cations: instead of insertion or substitution reactions, we found oxidation of the complex to cobalt(II). The results of these studies are reported here, including those related to the properties of the cobalt(II) hydride obtained. Furthermore, the use of other electrophilic reagents, such as NO^+ and H^+, was tested on $[CoH\{P(OEt)_2Ph\}_4]$, in order to compare the results with those obtained with RN_2^+ and, in the case of H^+, to verify whether protonation leads to the formation of $\eta^2\text{-}H_2$ complexes or to oxidative addition of H^+ to give a new cobalt(III) hydride species.

Experimental

General Comments.—Unless otherwise noted all manipulations were carried out in an argon atmosphere using standard Schlenk and syringe techniques or a Vacuum Atmosphere dry-box. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Diethoxy(phenyl)phosphine was prepared by the method of Rabinowitz and Pellon;[6] triethyl and trimethyl phosphite were Ega Chemie products purified by distillation under nitrogen. Deuterium was obtained[7] from D_2O and Na; high-purity HD was prepared from $LiAlH_4$ and D_2O (99.8%) following the reported method.[8] Diazonium salts were obtained in the usual way.[9] The salt $NO^+PF_6^-$ was an Alfa Ventron product and was used as received. Substituted phenyl isocyanides were obtained by the phosgene method of Ugi *et al.*[10] Other reagents were purchased from commercial sources in the highest available purity and used as received.

Infrared spectra were recorded on a Perkin-Elmer model 683 spectrophotometer, electronic spectra on Cary 219 and Perkin-Elmer EPS-3T spectrophotometers. Solution ^1H n.m.r. spectra were obtained using Varian FT-80A, Bruker AC200, and Bruker AC400 spectrometers at temperatures varying between −85 and +34 °C unless otherwise noted, and are referred to internal tetramethylsilane. Fourier-mode, proton-noise-decoupled ^{31}P n.m.r. spectra were collected on a Varian FT-80A spectrometer operating at 32.203 MHz. All chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. Values of T_1 (±10%) were determined by the inversion recovery method between +30 and −95 °C in CD_2Cl_2 with a standard 180°–τ–90° pulse sequence. Conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in nitromethane at 25 °C were measured with a Radiometer CDM 83 instrument. Magnetic susceptibility measurements were performed on powdered samples at ambient temperature with a Cahn Instrument Faraday balance using $Hg[Co(NCS)_4]$ as standard. Solution susceptibilities were determined by the Evans method.[11] Susceptibilities were corrected for diamagnetism of the ligands by use of tables given by Figgis and Lewis.[12]

Synthesis of Complexes.—All experiments were carried out under an inert atmosphere using standard Schlenk techniques and/or a nitrogen-filled glove-box. The hydrides $[CoH\{P(OEt)_2Ph\}_4]$, $[CoH\{P(OEt)_3\}_4]$, and $[CoH\{P(OMe)_3\}_4]$ were obtained following the procedures previously described.[13] The compound $[CoD\{P(OEt)_2Ph\}_4]$ was prepared exactly as $[CoH\{P(OEt)_2Ph\}_4]$, using $NaBD_4$ in EtOD instead of $NaBH_4$ as the reducing agent.

$[CoH\{P(OEt)_2Ph\}_4]BPh_4$ (**1a**). A solution of $[CoH\{P(OEt)_2Ph\}_4]$ (2 mmol, 1.70 g) in CH_2Cl_2 (20 cm^3) was cooled to −80 °C and quickly transferred, at the same temperature, to a reaction flask containing the stoicheiometric amount of $4\text{-}CH_3C_6H_4N_2^+BF_4^-$ (2 mmol, 0.41 g). The reaction mixture was brought to room temperature in *ca.* 20 min, and shaking was continued for 30—40 min. The solvent was removed under reduced pressure to give a green oil which was triturated in ethanol (20 cm^3). The addition of $NaBPh_4$ (2 mmol, 0.69 g) afforded a yellow-green solid which was crystallized from dichloromethane (5 cm^3) and ethanol (20 cm^3); yield ⩾ 80%. The deuteriated compound [CoD-

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† *Non-S.I. unit employed:* G = 10^{-4} T.

$\{P(OEt)_2Ph\}_4]BPh_4$ was prepared in the same way, starting from $[CoD\{P(OEt)_2Ph\}_4]$ and using EtOD instead of EtOH.

$[CoH\{P(OEt)_2Ph\}_4]ClO_4$ (**1b**) This compound was prepared as the related BPh_4^- salt using $LiClO_4$ in ethanol as the precipitating agent; yield $\geqslant 70\%$.

$[Co\{P(OEt)_3\}_5]BPh_4$ (**6**). A solution of $[CoH\{P(OEt)_3\}_4]$ (2 mmol, 1.45 g) in CH_2Cl_2 (20 cm^3) was cooled to −80 °C and transferred, at the same temperature, to a reaction flask containing the diazonium salt $4\text{-}CH_3C_6H_4N_2^+BF_4^-$ (2 mmol, 0.41 g, ratio 1:1). The reaction mixture was brought to room temperature and after 30 min of shaking the solvent was removed under reduced pressure. The remaining oil was triturated with ethanol (20 cm^3) and $NaBPh_4$ (2 mmol, 0.69 g) was added to give a yellow solid which was crystallized from CH_2Cl_2 (5 cm^3) and ethanol (20 cm^3); yield $\geqslant 40\%$.

$[Co(NO)_2\{P(OEt)_2Ph\}_2]BPh_4$ (**2**). A solution of $[CoH\{P(OEt)_2Ph\}_4]$ (1 mmol, 0.85 g) in CH_2Cl_2 (10 cm^3) was cooled to −80 °C and transferred to a reaction flask containing an excess of $NO^+PF_6^-$ (3 mmol, 0.53 g). The reaction mixture was brought to room temperature and stirred for 1 h. Removal of the solvent at reduced pressure gave a brown oil which was treated with ethanol (10 cm^3). On stirring a red-brown solid *separated*, which was crystallized from ethanol; yield $\geqslant 75\%$. M.p. 84 °C, λ_M 52.6 S cm^2 mol^{-1} ($MeNO_2$)(Found: C, 63.25; H, 6.15; N, 3.40. Calc. for $C_{44}H_{50}BCoN_2O_6P_2$: C, 63.30; H, 6.05; N, 3.35%); ν(NO) 1 858vs and 1 806s cm^{-1} (CH_2Cl_2).

$[CoH_2\{P(OEt)_2Ph\}_4]BPh_4$ (**3**). A slight excess of $HBF_4\cdot Et_2O$ (54% solution, *ca.* 1.2 mmol, 0.17 cm^3) was slowly added to a suspension of $[CoH\{P(OEt)_2Ph\}_4]$ (1 mmol, 0.85 g) in ethanol (20 cm^3) cooled to −80 °C. The reaction mixture was brought to 20 °C and stirred until a colourless solution was obtained (5—10 min). Addition of $NaBPh_4$ (1.2 mmol, 0.41 g) caused the precipitation of a white product which was crystallized from CH_2Cl_2 (5 cm^3) and ethanol (20 cm^3); yield $\geqslant 65\%$. The $[CoD_2\{P(OEt)_2Ph\}_4]^+$ complex was prepared by protonation with CF_3CO_2D of the deuteride $[CoD\{P(OEt)_2Ph\}_4]$ in EtOD at −80 °C. We also attempted to prepare the isotopomer $[CoH(D)\{P(OEt)_2Ph\}_4]^+$ by HD exchange on $[CoH_2\{P(OEt)_2Ph\}_4]^+$, but the ^1H n.m.r. spectra of the compound obtained did not indicate formation of the HD complex.

$[Co(RNC)_2\{P(OEt)_2Ph\}_3]BPh_4$ (**4**) (R = $4\text{-}CH_3C_6H_4$, **a**; or $4\text{-}CH_3OC_6H_4$, **b**). An excess of the appropriate isocyanide (3.5 mmol) was added to a dichloromethane solution (20 cm^3) of $[CoH\{P(OEt)_2Ph\}_4]BPh_4$ (1 mmol, 1.17 g), cooled to −80 °C. The reaction mixture was brought to room temperature, stirred for 20 min, and the solvent then removed under reduced pressure. The red-brown oil obtained was treated with ethanol (10—15 cm^3) to give an orange solid which was crystallized by slow cooling of its saturated solution prepared at about 30—40 °C in ethanol; yield $\geqslant 80\%$.

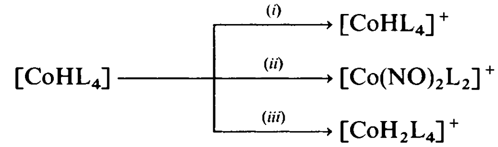
$[Co(4\text{-}ClC_6H_4NC)_2\{P(OEt)_2Ph\}_3]PF_6$ (**4c**). This compound was prepared as the related (**4a**) and (**4b**) starting from $[CoH\{P(OEt)_2Ph\}_4]ClO_4$ and using $NaPF_6$ in ethanol as the precipating agent; yield $\geqslant 70\%$.

$[Co\{2,6\text{-}(CH_3)_2C_6H_3NC\}_3\{P(OEt)_2Ph\}_2]BPh_4$ (**4d**). An excess of $2,6\text{-}(CH_3)_2C_6H_3NC$ (5 mmol, 0.66 g) in CH_2Cl_2 (5 cm^3) was added to a solution of $[CoH\{P(OEt)_2Ph\}_4]BPh_4$ (1 mmol, 1.17 g) in CH_2Cl_2 (20 cm^3) and the reaction mixture stirred for 30 min. After the solvent was removed at reduced pressure, the remaining oil was treated with ethanol (20 cm^3) to afford a yellow solid which was crystallized from CH_2Cl_2–ethanol (5 cm^3:30 cm^3); yield $\geqslant 80\%$.

$[CoH(I)\{P(OEt)_2Ph\}_4]BPh_4$ (**5**). Iodine (0.5 mmol, 0.127 g) dissolved in CH_2Cl_2 (10 cm^3) was added to a solution of $[CoH\{P(OEt)_2Ph\}_4]BPh_4$ (1 mmol, 1.17 g) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred at room temperature for 2 h and the solution was then brought to dryness. The oil obtained was triturated in ethanol (10 cm^3) yielding a red solid which was crystallized by slow cooling to −30 °C of its saturated ethanol solution prepared at room temperature; yield $\geqslant 80\%$.

Results and Discussion

The reactions of $[CoH\{P(OEt)_2Ph\}_4]$ with RN_2^+, NO^+, and H^+ are summarized in Scheme 1. At low temperature (−30 °C) in CH_2Cl_2 with a stoicheiometric amount of arenediazonium cation the derivative $[CoH\{P(OEt)_2Ph\}_4]^+$ (**1**) is obtained in an almost quantitative yield ($\geqslant 90\%$) and may be isolated as its BPh_4^- (**1a**) or ClO_4^- (**1b**) salt. Studies on this reaction showed evolution of N_2 and that the hydrocarbon RH was also present in solution at the end of the reaction. On this basis it is plausible to suppose[5,14] that RN_2^+ oxidizes the central metal to Co^{II}, giving N_2 and the unstable radical R˙[equation (1)]. Presumably by abstraction of one hydrogen atom from the solvent, the intermediate R· gives the observed hydrocarbon. When an excess of arenediazonium cation was used only decomposition products were detected. Thus the oxidation to $[CoH\{P(OEt)_2Ph\}_4]^+$ probably takes place but the latter is decomposed by the RN_2^+.



Scheme 1. L = $P(OEt)_2Ph$. (*i*) RN_2^+, 1:1; (*ii*) NO^+; (*iii*) H^+

$$[CoH\{P(OEt)_2Ph\}_4] + RN_2^+ \xrightarrow{CH_2Cl_2} [CoH\{P(OEt)_2Ph\}_4]^+ + N_2 + RH \quad (1)$$

We also studied the reaction of other cobalt(I) hydrides containing phosphite ligands such as $[CoH\{P(OEt)_3\}_4]$, $[CoH\{P(OMe)_3\}_4]$, and $[CoH\{P(OEt)Ph_2\}_4]$ with arenediazonium cations, but in every case no evidence for the formation of a cobalt(II) hydride was obtained. The complex $[Co\{P(OEt)_3\}_5]BPh_4$ (**6**) was isolated in low yield (*ca.* 40%) from $[CoH\{P(OEt)_3\}_4]$, whereas only decomposition products were observed with the other hydrides.

Nitrosonium hexafluorophosphate reacts in both stoicheiometric and excess amounts with $[CoH\{P(OEt)_2Ph\}_4]$ to afford in every case the dinitrosyl complex[15] $[Co(NO)_2\{P(OEt)_2Ph\}_2]^+$ (**2**) in high yield. Studies on the progress of the reaction by i.r. and n.m.r. spectroscopy showed neither nitrosyl intermediates beyond (**2**) nor the presence of paramagnetic species in the reaction mixture. This suggests that, in contrast to the arenediazonium cations, NO^+ does not oxidize the hydride but gives a complicated reaction, leading to a formal cobalt(−I) complex as the final product.

The hydride $[CoH\{P(OEt)_2Ph\}_4]$ can also be protonated at low temperature (−80 °C) in CH_2Cl_2 with strong acids such as $HBF_4\cdot Et_2O$ or CF_3CO_2H to give the cobalt(III) dihydride $[CoH_2\{P(OEt)_2Ph\}_4]^+$ (**3**), which can be isolated as its BPh_4^- salt and characterized.

These results show that $[CoH\{P(OEt)_2Ph\}_4]$ reacts in a different way with the three electrophilic reagents RN_2^+, NO^+, and H^+. However, an oxidation reaction takes place with both RN_2^+ and H^+, affording one-electron, $[CoH\{P(OEt)_2Ph\}_4]^+$ and two-electron, $[CoH_2\{P(OEt)_2Ph\}_4]^+$, oxidation products, respectively. In contrast, the cation NO^+, which is known to react as a moderately oxidizing agent, gives only a complicated

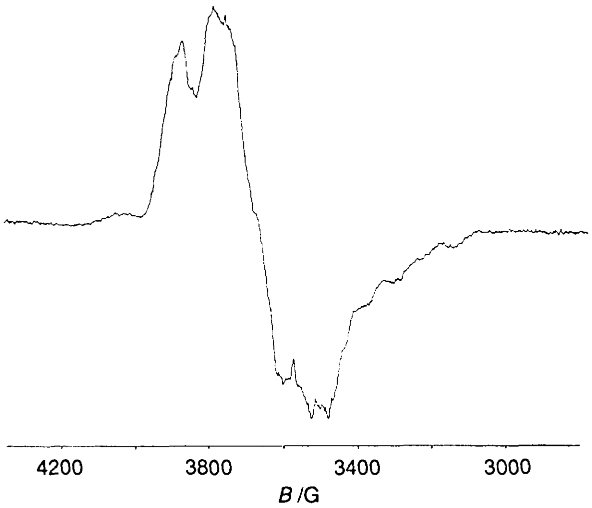


Figure 1. *X*-Band e.s.r. spectrum of $[CoH\{P(OEt)_2Ph\}_4]BPh_4$ in a CH_2Cl_2–benzene glass at 77 K

reaction, affording as final product the two-electron reduction complex $[Co(NO)_2\{P(OEt)_2Ph\}_2]^+$.

The cobalt(II) hydride $[CoH\{P(OEt)_2Ph\}_4]^+$ has been previously prepared[16] as its PF_6^- or BF_4^- salt in a different way, by reaction of $[CoH\{P(OEt)_2Ph\}_4]$ with the appropriate triphenylmethyl (trityl) salt. However, this paper reports a more complete characterization, including the preparation of the deuteride $[CoD\{P(OEt)_2Ph\}_4]^+$ and e.s.r. spectra.

The i.r. spectra (KBr pellets) of $[CoH\{P(OEt)_2Ph\}_4]^+$ derivatives show a medium-intensity band at 1 960 cm^{-1} for (**1a**) and at 1 950 cm^{-1} for (**1b**) (Table 1), attributed to ν(CoH). This absorption is not present for the deuteride $[CoD\{P(OEt)_2Ph\}_4]BPh_4$, thus confirming the proposed attribution. However, the ν(CoD) band was also not observed, probably because it is obscured by the presence of intense bands in the expected 1300—1500 cm^{-1} region. It may be observed that ν(CoH) occurs at 2 010 cm^{-1} in the spectrum of the precursor $[CoH\{P(OEt)_2Ph\}_4]$. In the solid state the magnetic moments of the complexes at room temperature are 1.95, (**1a**), and 1.98 μ_B, (**1b**), in accord with low-spin cobalt(II) complexes. However, slightly higher values (2.0—2.3 μ_B) are expected for five-co-ordinate cobalt(II) species, whereas our values also suggest a low-spin octahedral complex.[17] A distorted-octahedral geometry for the five-co-ordinate complex may be obtained by interaction of the phenyl ring of one of the $P(OEt)_2Ph$ ligands with the central atom. In CH_2Cl_2 solution at room temperature similar magnetic moment values were found [1.97 μ_B for (**1a**)], not changing significantly between +30 and −80 °C, indicating that the formation of a dimeric species with a Co–Co bond (diamagnetic) can reasonably be excluded.

The Figure shows the *X*-band e.s.r. spectrum obtained for a frozen diluted solution of complex (**1a**) at 77 K, which is typical of low-spin cobalt(II) with $g_1 = 1.97$, $g_2 = 2.13$, $g_3 = 2.28$, and $A_1 = 80$ G. The *g* values indicate that the co-ordination environment around cobalt(II) is rhombic and that the unpaired electron is in an orbital which may be loosely described as metal z^2. This is consistent with either square-pyramidal or distorted-octahedral co-ordination.[18] Unfortunately, no evidence of either phosphorus or hydrogen superhyperfine splitting was found.

The polycrystalline power spectrum recorded at 4.2 K is rather similar to the frozen-solution spectrum, with $g_1 = 2.01$, $g_2 = 2.12$, $g_3 = 2.19$, and no hyperfine splitting, as expected for narrowed exchanged spectra. The small differences in *g* values between the powder and frozen-solution spectra may be caused by crystal effects.[19]

Although suitable crystals for *X*-ray analysis were also obtained, they decomposed during data collection[20] and therefore no conclusive structural information could be obtained. However, the i.r., magnetic, and e.s.r. data strongly suggest the proposed $[CoH\{P(OEt)_2Ph\}_4]^+$ formulation.

Electronic spectra in the range 500—1000 nm for the $[CoH\{P(OEt)_2Ph\}_4]^+$ cations in CH_2Cl_2 solution show two absorptions at 758—760 and 990 nm, unaffected by the addition of an excess of free phosphite. This seems to indicate the absence of an equilibrium of the type $[CoHL_4]^+ \rightleftharpoons [CoHL_3]^+ + L$ [L = $P(OEt)_2Ph$] which had previously been observed with the five-co-ordinate $[CoClL_4]^+$ derivatives.[17b]

In the high-field region of the ^1H n.m.r. spectra the complex $[CoH_2\{P(OEt)_2Ph\}_4]BPh_4$ (**3**) at room temperature shows a broad signal at δ −12.6 (Table 2) which remains unchanged until −80 °C. The presence of a broad signal in the hydridic region may suggest the existence of a non-classical hydride[21] of the type $[Co(\eta^2-H_2)\{P(OEt)_2Ph\}_4]^+$. However, the i.r. spectra stongly indicate the classical dihydride formulation, showing a medium-intensity band at 1 980 cm^{-1} which is absent for the deuteriated compounds and is therefore attributable to ν(MH) of the $[CoH_2\{P(OEt)_2Ph\}_4]^+$ derivative.

In order to distinguish between classical and non-classical (η^2-H_2) hydrides a criterion based on T_1 measurements has been proposed by Crabtree and co-workers.[22] In this context, we have already reported[23] a number of T_1 measurements on classical hydrides and molecular-hydrogen complexes of comparable structure and found unexpectedly low values, especially for the hydride resonance. On this basis, we suggested 'care' be taken in the use of absolute T_1 values and proposed some 'terms of reference.' For example, at −60 °C, for the broad resonance at δ −12.6, complex (**3**) has a T_1 value (22 ms) which falls in the range generally attributed to η^2-H_2 complexes, but the monohydride precursor $[CoH\{P(OEt)_2Ph\}_4]$ gives a similar value (T_1 = 21 ms at −60 °C), confirming a classical formulation $[CoH_2\{P(OEt)_2Ph\}_4]^+$ for (**3**). After our communication, other papers appeared on T_1 measurements[21b,24] and the T_1 criterion,[21b] and Luo and Crabtree[25] stated that our data were not strictly comparable with those previously reported because they were measured at 80 MHz and were not adjusted on the basis that T_1 (min.) scales with the magnetic field. Luo and Crabtree[25] also reported that, if our data were adjusted to 250 MHz, the compounds would have T_1 values greater than *ca.* 150 ms. We have remeasured the T_1 values of $[CoH\{P(OEt)_2Ph\}_4]$ and $[CoH_2\{P(OEt)_2Ph\}_4]BPh_4$ at 200 and 400 MHz (in the temperature range −80 to +30 °C). The results are reported in Table 3. A T_1 (min.) of 38 ms was found for both hydrides at 200 MHz, whereas it was 70 ms for $[CoH\{P(OEt)_2Ph\}_4]$ and 72 ms for $[CoH_2\{P(OEt)_2Ph\}_4]^+$ at 400 MHz. These data show of course that T_1 changes with the magnetic field, but the values found for our classical hydrides are in any case low and therefore, as also observed by Cotton *et al.*,[24] care must be taken in the use of the T_1 value only to distinguish between classical and non-classical hydrides.

At room temperature the $^{31}P-\{^1H\}$ n.m.r. spectrum of complex (**3**) appears as a broad signal. Lowering the sample temperature results in a change in the profile, but even at −90 °C only a broad multiplet is observed. However, this suggests the existence of a *cis* geometry in solution for the complex, because only one signal would be expected for a *trans* structure.

We studied the reactivity of both paramagnetic and diamagnetic cobalt hydrides. Results are summarized in Schemes 2 and 3. The reaction of $[CoH\{P(OEt)_2Ph\}_4]^+$ with

Table 1. Physical, analytical, and selected i.r. data for the cobalt complexes

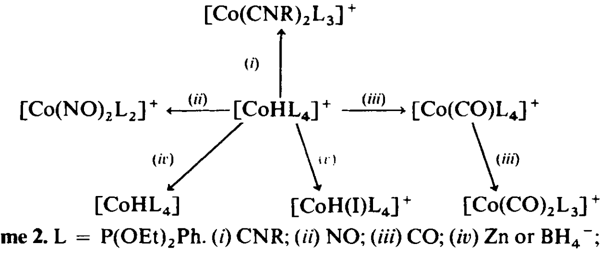
Compound[a]	M.p./ °C	Λ_M[b]/S cm^2 mol^{-1}	Analysis[c]/% C	H	N	I.r. (cm^{-1})[d]	
(1a) $[CoH\{P(OEt)_2Ph\}_4]^{+}$[e]	—	48.4	65.75 (65.60)	6.90 (6.95)	—	1 960w	ν(MH)
(1b) $[CoH\{P(OEt)_2Ph\}_4]ClO_4$[f,g]	—	93.1	50.40 (50.45)	6.40 (6.45)	—	1 950w	ν(MH)
(3) $[CoH_2\{P(OEt)_2Ph\}_4]^+$	—	53.2	65.40 (65.55)	7.10 (7.05)	—	1 980w	ν(MH)
(4a) $[Co(4\text{-}CH_3C_6H_4NC)_2\{P(OEt)_2Ph\}_3]^+$	129	53.2	69.35 (69.65)	6.55 (6.60)	2.30 (2.30)	2 104s, 2 045 (sh) [2 115s, 2 045 (sh)]	ν(CN)
(4b) $[Co(4\text{-}CH_3OC_6H_4NC)_2\{P(OEt)_2Ph\}_3]^+$	115	54.8	67.85 (67.85)	6.40 (6.45)	2.25 (2.25)	2 113s [2 118s]	ν(CN)
(4c) $[Co(4\text{-}ClC_6H_4NC)_2\{P(OEt)_2Ph\}_3]PF_6$[h]	160	84.7	49.05 (49.20)	5.10 (5.00)	2.55 (2.60)	2 098s, 2 033(sh) [2 104s, 2 035 (sh)]	ν(CN)
(4d) $[Co\{2,6\text{-}(CH_3)_2C_6H_3NC\}_3\{P(OEt)_2Ph\}_2]^+$	124	51.0	72.85 (73.00)	6.55 (6.65)	3.65 (3.60)	2 061s, 2 005 (sh) [2 050s]	ν(CN)
(5) $[CoH(I)\{P(OEt)_2Ph\}_4]^+$	110	51.9	59.25 (59.20)	6.25 (6.30)	—	1 980w	ν(MH)
(6) $[Co\{P(OEt)_3\}_5]^+$	96	53.1	53.45 (53.65)	7.80 (7.90)	—	—	—

[a] All compounds are BPh_4^- salts, except **(1b)** and **(4c)**. [b] In nitromethane solution (10^{-3} mol dm^{-3}) at 25 °C. [c] Calculated values in parentheses. [d] In CH_2Cl_2, except for those values in square brackets (KBr). [e] Visible spectra: $\lambda_{max.}(CH_2Cl_2)$ 758 (ε 112) and 990 nm (195 dm^3 mol^{-1} cm^{-1}). $\mu_{eff.}$ = 1.95 (solid state), 1.97 μ_B (CH_2Cl_2) at 25 °C. [f] Visible spectra: $\lambda_{max.}(CH_2Cl_2)$ 760 (ε 120) and 990 nm (200 dm^3 mol^{-1} cm^{-1}). $\mu_{eff.}$ = 1.98 μ_B (solid state) at 25 °C. [g] Cl, 3.90 (3.70)%. [h] Cl, 6.90 (6.60)%.

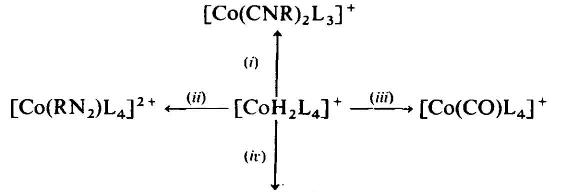
Table 2. Proton and $^{31}P\text{-}\{^1H\}$ n.m.r. data

Compound[a]	^1H N.m.r., δ[b,c] Aromatic	OCH_2CH_3	CH_3	OCH_2CH_3	Hydride	$^{31}P\text{-}\{^1H\}$ N.m.r., δ[c,d]
(3)[e]	7.37 (m), 6.96 (m)	3.66 (m)	—	1.13 (m)	−12.6 (br)	+167 (m, br)
(4a)	7.75 (m), 7.44 (m), 6.87 (m)	3.95 (m)	2.28 (s)	1.26 (t)	—	+162.1 (s)
(4b)	7.75 (m), 7.44 (m), 6.83 (m)	3.91 (m)	3.73 (s)	1.26 (t)	—	+161.7 (s)
(4c)	7.76 (m), 7.46 (m), 6.75 (m)	3.95 (m)	—	1.30 (t)	—	+161.5 (s)
(4d)	7.62 (m), 7.31 (m), 7.19 (m), 6.87 (m)	4.23 (m)	2.27 (s)	1.28 (t)	—	+163 (s, br)
(5)	7.85 (m), 7.35 (m), 6.87 (m)	3.82 (m)	—	1.21 (t)	−16.12 (qnt) (J_{PH} = 56 Hz)	+152.8 (m, br)
(6)	7.40 (m), 6.97 (m)	3.96 (m)	—	1.20 (t)	—	+131.1 (s)[b]

[a] All compounds are BPh_4^- salts, except **(4c)**. [b] At room temperature. [c] In $(CD_3)_2CO$. [d] At −80 °C. Positive shift downfield from 85% H_3PO_4. [e] In CD_2Cl_2.



Scheme 2. L = $P(OEt)_2Ph$. (*i*) CNR; (*ii*) NO; (*iii*) CO; (*iv*) Zn or BH_4^-; (*v*) I_2



Scheme 3. L = $P(OEt)_2Ph$. (*i*) CNR; (*ii*) RN_2^+; (*iii*) CO; (*iv*) L

CO (1 atm, 101 325 Pa) proceeds at room temperature with reduction of Co^{II} to Co^{I} and formation of the monocarbonyl $[Co(CO)\{P(OEt)_2Ph\}_4]^+$, which reacts further with CO to give $[Co(CO)_2\{P(OEt)_2Ph\}_3]^+$.[26]

Isocyanides quickly react at low temperature (−20 to −10 °C) with $[CoH\{P(OEt)_2Ph\}_4]^+$ (in the Co:CNR ratio of 1:3) to give $[Co(CNR)_2\{P(OEt)_2Ph\}_3]^+$ (4) complexes which can be isolated in almost quantitative yields as BPh_4^- or PF_6^- salts. When an excess of isocyanide is used in this reaction, tris(isocyanide) complexes $[Co(CNR)_3\{P(OEt)_2Ph\}_2]^+$ are also formed. A slightly different behaviour is shown by $2,6\text{-}(CH_3)_2C_6H_3NC$ which even at a low Co:CNR ratio reacts with $[CoH\{P(OEt)_2Ph\}_4]^+$ to give a mixture of bis- and tris(isocyanide)cobalt(I) complexes, and therefore only $[Co\{2,6\text{-}(CH_3)_2C_6H_3NC\}_3\{P(OEt)_2Ph)_2]^+$ can be isolated as a pure compound.

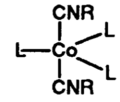
The new five-co-ordinate complexes $[Co(CNR)_2\{P(OEt)_2Ph\}_3]BPh_4$ are yellow-orange solids, diamagnetic, and 1:1 electrolytes.[27] Their i.r. spectra in the ν(CN) region (Table 1) show only one strong band, both in the solid state (at 2 104—2 118 cm^{-1}) and in CH_2Cl_2 solution (at 2 098—2 113 cm^{-1}), indicating the existence of two isocyanide ligands in mutually *trans* position. In the temperature range +30 to −80 °C the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra display only one sharp singlet (Table 2), in agreement with the presence of three magnetically equivalent phosphorus atoms. It is therefore reasonable to hypothesize the existence in solution of a trigonal-bipyramidal geometry of type (I) with the two CNR ligands in the apical positions.

The mixed-ligand isocyanidephosphinecobalt(I) complexes previously reported[28] generally contained three CNR ligands, $[Co(CNR)_3L_2]^+$. Only with P-P-P and As-P-As tridentate ligands[29] or with $4\text{-}NO_2C_6H_4NC$ isocyanide[30] were bis-

Table 3. Measurements[a] of T_1 for $[CoH\{P(OEt)_2Ph\}_4]$ and $[CoH_2\{P(OEt)_2Ph\}_4]BPh_4$ in CD_2Cl_2 at 80, 200, and 400 MHz and various temperatures

$[CoH\{P(OEt)_2Ph\}_4]$		$[CoH_2\{P(OEt)_2Ph\}_4]BPh_4$	
T/°C	T_1/ms	T/°C	T_1/ms
(*a*) At 80 MHz			
+30	172	+30	154
+8	125	+4	86
−13	81	−13	66
−33	80	−28	44
−53	32	−60	22
−60	21	−64	17
−72	18		
(*b*) At 200 MHz[b]			
+24	188	+19	138
+4	127	+4	96
−16	79	−16	64
−36	51	−39	40
−56	41	−56	38
−71	45	−71	56
−86	111	−86	117
(*c*) At 400 MHz[c]			
+27	165	+25	184
+7	150	+5	132
−13	114	−15	99
−33	87	−35	80
−53	72	−55	81
−73	81	−71	102
−97	194	−86	132

[a] For hydride resonance. [b] T_1(min.) = 38 (−61) and 38 ms (−51 °C) respectively for the two complexes. [c] T_1 (min.) = 70 (−55) and 72 ms (−43 °C), respectively.



(I)

(I) L = $P(OEt)_2Ph$

(isocyanide) complexes $[Co(CNR)_2L_3]^+$ obtained, whose geometry in solution is that of a *cis* CNR derivative. The use of $[CoH\{P(OEt)_2Ph\}_4]^+$ as starting material allows easy synthesis of new *trans* bis(isocyanide) compounds.

Nitric oxide reacts under mild conditions (20 °C, 1 atm) with $[CoH\{P(OEt)_2Ph\}_4]^+$ in CH_2Cl_2 to yield the dinitrosyl complex $[Co(NO)_2\{P(OEt)_2Ph\}_2]BPh_4$ as final product. Following the progress of the reaction by i.r. spectra, it was observed that the addition of NO to complex (**1**) first results in the appearance of a ν(NO) band at 1 680 cm^{-1} which, as the reaction proceeds, slowly decreases, while two new absorptions appear at 1 858 and 1 806 cm^{-1}, due to the $[Co(NO)_2\{P(OEt)_2Ph\}_2]^+$ cation. No other ν(NO) bands were observed and at the end of the reaction only the absorptions at 1 858—1 806 cm^{-1} were observed. In an attempt to isolate the intermediate with the ν(NO) band at 1 680 cm^{-1} we carried out the reaction with a $[CoH\{P(OEt)_2Ph\}_4]^+$: NO ratio of 1 : 1. The solution obtained revealed the band at 1 680 cm^{-1}, but this disappeared on evaporation of the solvent and the isolated solid contained only $[Co(NO)_2\{P(OEt)_2Ph\}_2]^+$. On the basis of these data, and taking into account previous results on cobalt nitrosyls,[15,31] we hypothesize that the reaction of $[CoH\{P(OEt)_2Ph\}_4]^+$ with NO proceeds with the formation of the intermediate mononitrosyl $[CoH(NO)\{P(OEt)_2Ph\}_4]^+$ which, by further reaction with NO, gives $[Co(NO)_2\{P(OEt)_2Ph\}_2]^+$ as final product. In such a $[CoH(NO)\{P(OEt)_2Ph\}_4]^+$ derivative the low value of ν(NO) (1 680 cm^{-1}) suggests the existence of a bent MNO group, as previously observed in octahedral compounds[31b] $[CoXL_2(NO)]^+$ (X = halogen, L = diarsine). A five-co-ordinate mononitrosyl of the type $[CoH(NO)\{P(OEt)_2Ph\}_3]^+$, analogous to the known derivatives[15,31c] where X replaces H (X = Cl, Br, I, or SCN), may also be proposed as an intermediate, but in this case a higher ν(NO) value (1 780—1 800 cm^{-1}) should be expected.

The $[CoH\{P(OEt)_2Ph\}_4]^+$ derivative reacts in CH_2Cl_2 with the equivalent amount of I_2 to afford the one-electron oxidation product $[CoH(I)\{P(OEt)_2Ph\}_4]^+$ (**5**), which can be isolated as the BPh_4^- salt in almost quantitative yield. In the ^1H n.m.r. spectrum the hydride resonance appears as a quintet at δ −16.12 and a *trans* geometry had therefore previously been assigned[32] to the compound. However, the $^{31}P-\{^1H\}$ n.m.r. spectrum is temperature-dependent and while only one broad signal is present at room temperature a multiplet appears at −80 °C. Although even at this temperature the signal is still too broad to allow any simulation, the multiplet seems to indicate the presence of a *cis* geometry because only one singlet should be expected for a *trans* structure.

The hydride $[CoH\{P(OEt)_2Ph\}_4]^+$ cannot be protonated with acids such as $HBF_4 \cdot Et_2O$ to give a molecular hydrogen complex, and the starting compound can be recovered unchanged even after prolonged reactions with excess of acid. Reduction of $[CoH\{P(OEt)_2Ph\}_4]^+$ with zinc dust or $NaBH_4$ is easy and affords the cobalt(I) precursor $[CoH\{P(OEt)_2Ph\}_4]$.

We also studied some properties of the diamagnetic cobalt(III) hydride $[CoH_2\{P(OEt)_2Ph\}_4]^+$ and observed that the reaction with π-acceptor ligands such as CO, phosphite, and CNR proceeds to give five-co-ordinate cobalt(I) complexes and hydrogen. These reactions, involving reductive elimination of H_2, are similar to those previously observed for the related $P(OR)_3$ complexes.[33] With carbon monoxide the reaction of $[CoH_2\{P(OEt)_2Ph\}_4]^+$ gives $[Co(CO)\{P(OEt)_2Ph\}_4]^+$, whereas with isocyanides the complexes $[Co(CNR)_2\{P(OEt)_2Ph\}_3]^+$ can be obtained. Furthermore, the easy elimination of H_2 in complex (**3**) also allows the aryldiazenido[5] $[Co(RN_2)\{P(OEt)_2Ph\}_4]^{2+}$ to be prepared by a new method involving the reaction of a cobalt(III) dihydride with arenediazonium cations.

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