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COBALT COMPLEXES OF 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE

II. REACTIONS WITH MOLECULAR HYDROGEN AND CONJUGATED DIENES IN THE PRESENCE OF TERTIARY PHOSPHINES

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SUMMARY

$[CoChel(PR_3)_2]^+$ intermediates (Chel = 2,2'-bipyridine or 1,10-phenanthroline) undergo reversible addition of molecular hydrogen, to yield stable dihydridic derivatives. The reductive elimination step is light-accelerated. Dihydridic derivatives catalyze the hydrogenation of butadiene to butenes. They react also with alkyl halides (RX) giving $[CoChel(PR_3)_2PX]^+$. Polarography confirms that Bipy or Phen are more useful than phosphines for stabilizing σ-Co–C bonds in octahedral species of Co in low valence states.

INTRODUCTION

Conjugated chelating ligands such as 2,2'-bipyridine (Bipy) and 1,10-phenanthroline (Phen) seem to be more useful than tertiary phosphines for stabilizing the σ-metal–carbon bond in complexes of d^6, d^7 and d^8 configurations[1], while phosphines appear to be more useful for stabilizing the metal–hydrogen bond[2].

Previously[1b] we reported the synthesis of stable dimetalorganic derivatives of the type *cis*-$[Co^{III}(Chel)_2R_2]X$ (Chel = Bipy or Phen), now we examine the possibility of stabilizing both Co–C and Co–H bonds in mixed complexes with ligands having phosphorus or nitrogen as donor atoms. Some of the results have already been reported in a preliminary communication[3].

RESULTS AND DISCUSSION

Co^I derivatives of the type $[Co(Chel)_3]^+$ undergo oxidative and coordinative addition reactions with molecular hydrogen, carbon monoxide and conjugated diolefins in the presence of tertiary phosphines at room temperature and atmospheric pressure.

(*a*). *Reactions with molecular hydrogen*

Under the above conditions, compounds of formula $[CoChel(PR_3)_2H_2]X$

TABLE 1 ANALYTICAL DATA FOR THE ISOLATED COMPLEXES

Number	*Complex*	*Colour*	*Analyses found (calcd.) (%)*		
			C	*H*	*N*
(Ia)	$[CoBipy(PBu_3)_2H_2]ClO_4$	Orange	56.8	8.74	3.93
			(56.63)	(8.94)	(3.88)
(Ib)	$[CoBipy(PBu_3)_2H_2]PF_6$	Orange	52.1	8.25	3.60
			(53.26)	(8.41)	(3.65)
(Ic)	$[CoPhen(PBu_3)_2H_2]ClO_4$	Orange-red	59.1	8.71	3.69
			(58.02)	(8.66)	(3.76)
(Id)	$[CoBipy(PPr_3)_2H_2]ClO_4$	Orange-red	52.7	8.39	4.38
			(52.79)	(8.23)	(4.40)
(Ie)	$[CoPhen(PPr_3)_2H_2]ClO_4$	Orange-red	55.2	8.17	4.25
			(54.50)	(7.93)	(4.24)
(If)	$[CoBipy(PEt_3)_2H_2]ClO_4$	Red	47.3	7.32	5.06
			(47.79)	(7.29)	(5.06)
(Ig)	$[CoBipy(PEt_2Ph)_2H_2]ClO_4$	Yellow	55.9	6.23	4.60
			(55.52)	(6.21)	(4.32)
(Ih)	$[CoPhen(PEt_2Ph)_2H_2]ClO_4$	Yellow-orange	56.2	5.90	4.36
			(57.11)	(5.99)	(4.16)
(IIIa)	$[Co(CO)_3(PEt_3)_2]ClO_4$	White	37.9	6.44	
			(37.64)	(6.32)	
(IIIb)	$[Co(CO)_3(PPr_3)_2]ClO_4$	White	44.4	7.42	
			(44.81)	(7.52)	
(IIIc)	$[Co(CO)_3(PBu_3)_2]ClO_4$	White	50.0	8.55	
			(50.12)	(8.41)	
(IVa)	$[CoBipy(PBu_3)C_4H_6]ClO_4$	Red	53.7	7.41	4.85
			(54.69)	(7.24)	(4.91)
(IVb)	$[CoPhen(PBu_3)C_4H_6]ClO_4$	Red	56.8	7.07	4.68
			(56.52)	(6.95)	(4.71)
(IVc)	$[CoBipy(PPr_3)C_4H_6]ClO_4$	Red	51.7	6.98	5.03
			(52.23)	(6.67)	(5.30)
(IVd)	$[CoPhen(PPr_3)C_4H_6]ClO_4$	Red	55.8	6.57	4.98
			(54.31)	(6.38)	(5.07)
(IVe)	$[CoBipy(PEt_3)C_4H_6]ClO_4$	Red	47.8	6.45	5.36
			(49.35)	(6.00)	(5.75)
(IVf)	$[CoPhen(PEt_3)C_4H_6]ClO_4$	Red	52.0	5.63	5.61
			(51.72)	(5.72)	(5.48)
(IVg)	$[CoBipy(PEt_2Ph)C_4H_6]ClO_4$	Red	53.7	5.46	5.32
			(53.89)	(5.46)	(5.24)
(IVh)	$[CoPhen(PEt_2Ph)C_4H_6]ClO_4$	Red	56.3	5.21	5.42
			(55.88)	(5.23)	(5.02)
(IVi)	$[CoBipy(PBu_3)C_5H_8]ClO_4$	Red	55.0	7.57	4.79
			(55.44)	(7.41)	(4.79)
(IVj)	$[CoBipy(PPr_3)C_5H_8]ClO_4$	Red	51.2	7.41	4.82
			(53.10)	(6.87)	(5.16)
(IVk)	$[CoPhen(PPr_3)C_5H_8]ClO_4$	Red	55.8	6.57	5.09
			(55.08)	(6.58)	(4.94)
(IVl)	$[CoBipy(PEt_3)C_5H_8]ClO_4$	Red	48.9	6.54	5.57
			(50.36)	(6.24)	(5.59)
(IVm)	$[CoPhen(PEt_3)C_5H_8]ClO_4$	Red	50.9	5.94	5.45
			(52.63)	(5.95)	(5.34)
(IVn)	$[CoBipy(PEt_2Ph)C_5H_8]ClO_4$	Red	55.2	5.70	5.24
			(54.71)	(5.69)	(5.10)
(Va)	$[CoBipy(PBu_3)_2EtI]PF_6$	Red	45.9	7.33	3.35
			(46.96)	(7.34)	(3.04)
(Vb)	$[CoPhen(PEt_3)_2MeI]PF_6$	Red	39.8	5.41	3.90
			(39.40)	(5.42)	(3.67)

(I) can be isolated in low yield from the reaction with molecular hydrogen. The same complexes can also be obtained in high yield by reducing with $NaBH_4$ methanolic solutions containing $CoCl_2$, Chel and PR_3 in a 1/1/2 ratio in the presence of the appropriate anion. Analytical data for the isolated compounds are listed in Table 1. The PBu_3 derivative is a diamagnetic complex, and is a 1/1 electrolyte in 1,2-dichloroethane (DCE); it has a molecular weight (DCE) lower than that expected for the monomeric form. The other complexes, though less stable, give similar results.

IR spectra show the characteristic bands of the chelating systems, coordinated phosphines and ionic anions. In the hydridic region (2000–1800 cm^{-1}) there are rather complex patterns in the solid state (see Fig. 1), these do not change significantly in CH_2Cl_2 solutions. They disappear if the complexes are synthesized in a deuterated medium.

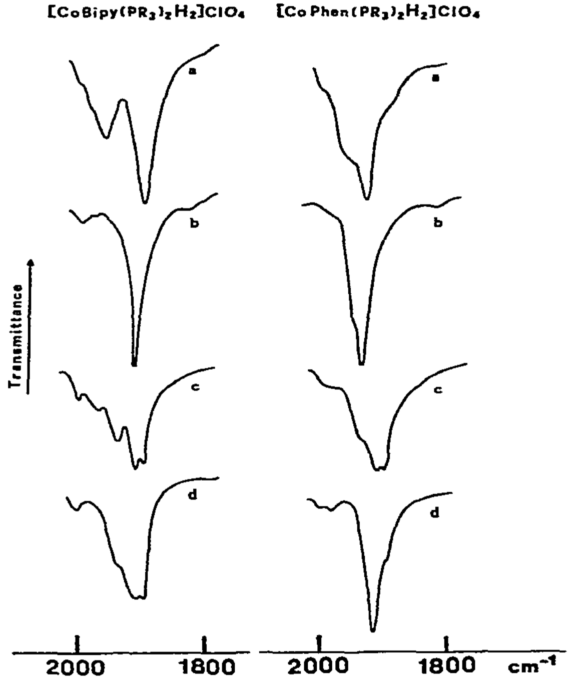
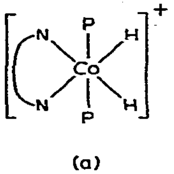
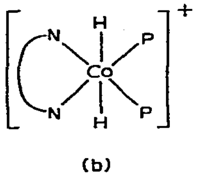


Fig. 1. IR spectra of $[CoChel(PR_3)_2H_2]ClO_4$ complexes (Nujol mulls). PR_3 = (a) PEt_3; (b) PEt_2Ph; (c) PPr_3; (d) PBu_3.

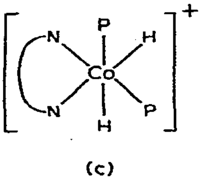
Three stereoisomeric configurations, (a)–(c), are possible for the complexes (I). Structure (c) can be ruled out on the basis of the PMR spectra of the $[CoBipy(PBu_3)_2H_2]ClO_4$ and $[CoBipy(PR_3)_2H_2]ClO_4$ derivatives, which show a 1/2/1



(a)



(b)



(c)

triplet due to magnetically equivalent hydridic protons coupled with ^{31}P and an equivalence, two by two, of the bipyridine protons, implying the presence of a plane of symmetry perpendicular to that of the coordinate chelate. The high hydridic shifts ($\tau \sim 32$), which can be explained by assuming that a nitrogen atom is *trans* to hydrogen*, indicate (a) as the probable structure. In agreement with this, PMR spectra of $[CoBipy(PEt_3)_2H_2]ClO_4$ and $[CoBipy(PEt_2Ph)_2H_2]ClO_4$ compounds show a 1/4/6/4/1 quintet centered at about τ 9.3 and τ 9.0 respectively, characteristic of methyl resonances in complexes with *trans* P–Et groups[5], so that configuration (b) can also be excluded.

Dihydridic compounds react slowly with an excess of chelate in the dark at room temperature, to give $[Co(Chel)_3]^+$ complexes with hydrogen evolution, suggesting that reaction (1) is reversible. The existence of equilibrium (1) explains the low

$$[CoChel(PR_3)_2H_2]^+ + Chel \rightleftarrows [Co(Chel)_3]^+ + 2\ PR_3 + H_2 \qquad (1)$$

yield obtained in the synthesis of dihydridic derivatives by oxidative addition of molecular hydrogen to $[Co(Chel)_3]^+$ complex in the presence of phosphine. This equilibrium is rapidly established in the presence of light. $[CoChel(PR_3)_2H_2]^+$ undergoes photolysis in methanol under vacuum, with darkening of the solution. On restoring atmospheric pressure in the reaction vessel with molecular hydrogen, the original yellow-orange colour reappears, suggesting the existence of equilibrium (2). In agreement with this, exposure to light under hydrogen does not cause any spectral change, confirming that the product is stable under these conditions. Furthermore, photolysis of $[CoBipy(PR_3)_2D_2]ClO_4$ in methanol under hydrogen permits isolation of the corresponding dihydridic complex, showing that there can be exchange between molecular and coordinated hydrogen. On this basis we suggest sequence (3) for the formation of the dihydridic derivatives. Intermediate (II) undergoes an oxidative addition of molecular hydrogen, and complex (I) a reductive elimination reaction which is the light-promoted step.

$$[CoChel(PR_3)_2H_2]^+ \overset{h\nu}{\rightleftarrows} \underset{(II)}{[CoChel(PR_3)_2]^+} + H_2 \qquad (2)$$

$$[Co(Chel)_3]^+ + 2\ PR_3 \rightleftarrows \underset{(II)}{[CoChel(PR_3)_2]^+} \overset{H_2}{\rightleftarrows} \underset{(I)}{[CoChel(PR_3)_2H_2]^+} \qquad (3)$$

(b). Reactions with carbon monoxide and conjugated diolefins

$[Co^I(Chel)_3]^+$ derivatives react with carbon monoxide in the presence of tertiary phosphines, to give, after addition of ClO_4^- ions, crystalline compounds, which on the basis of analyses (Table 1) and IR spectra appear to be the known[6] compounds $[Co(CO)_3(PR_3)_2]ClO_4$ (III). If butadiene or isoprene is used in place

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* Chatt and coworkers[4] have pointed out that in octahedral transition metal complexes a hydride ligand in a *trans* position to tertiary phosphine or carbon monoxide ligands has chemical shifts within the range τ 18–22. This is true even for AsR_3, CN^-, H^- [2a], while larger shifts are shown when the hydride is *trans* to a chloride ligand. The effect of Bipy must be not very different from that of chloride ligand.

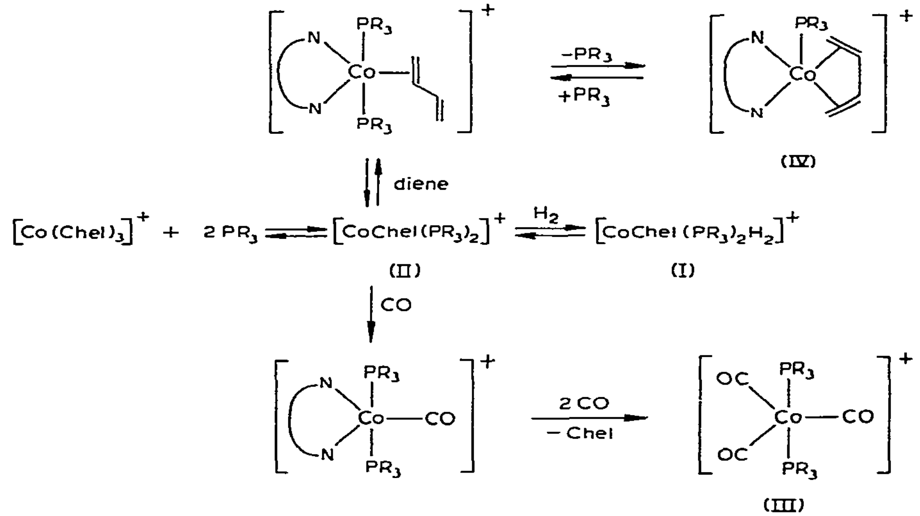
of carbon monoxide, crystalline complexes of formula $[CoChel(PR_3)diene]ClO_4$ (IV) (Table 1) can be isolated. Gas chromatography of their thermal decomposition products reveals the presence of the diene as a main component, confirming that there is π-coordination of the olefin.

Complexes (IV), like the dihydric derivatives, react with an excess of chelate to give the corresponding $[Co(Chel)_3]^+$ and the free diolefin. Reaction (4) is thus also reversible.

$$[Co(Chel)_3]^+ + PR_3 + diene \rightleftarrows \underset{(IV)}{[CoChel(PR_3)diene]^+} + 2\ Chel \qquad (4)$$

Complexes (IV) react further with carbon monoxide and molecular hydrogen in the presence of phosphine, giving the compounds $[Co(CO)_3(PR_3)_2]^+$ and $[Co(Chel)(PR_3)_2H_2]^+$, respectively. All these reactions can be interpreted on the basis of a common intermediate (II) as in Scheme 1:

SCHEME 1



According to this scheme, dihydridic derivatives react with carbon monoxide to give complexes (III) with hydrogen evolution. This reaction also is accelerated by light.

Complexes (I) react with butadiene giving complexes (IV). Among the gaseous products of the reaction are considerable amounts of butenes, but very little hydrogen (see Table 2), so that the reaction proceeds by a path different from that depicted in Scheme 1. If the reaction is carried out in hydrogen, the yield of butenes increases, suggesting that these dihydridic derivatives can act as catalyst for the hydrogenation of butadiene. If Scheme 2 is correct, use of an excess of phosphine and a high H_2/C_4H_6 ratio might increase the rate of the reaction.

SCHEME 2

$$\begin{tikzcd}
{[CoChel(PR_3)_2H_2]^+ + C_4H_6} \arrow[r, "-\text{butenes}"] & {[CoChel(PR_3)_2]^+} \arrow[l, bend left, "H_2"] \arrow[r, shift left, "C_4H_6"] & {[CoChel(PR_3)C_4H_6]^+ + PR_3} \arrow[l, shift left]
\end{tikzcd}$$

TABLE 2

REACTIVITY OF $[CoBipy(PBu_3)_2H_2]ClO_4$ WITH BUTADIENE AND RX

Conditions	*Reagent*	*Products in the gas phase (hydrocarbon ratio)*
MeOH, 48 h, in the dark, under N_2	Butadiene[a]	(H_2), 1-butene, *trans*-2-butene, *cis*-2-butene (9/10/1)
MeOH, 48 h, in the dark, under H_2[b]	Butadiene	1-Butene, *trans*-2-butene, *cis*-2-butene (40/2/1)
MeOH, 2 h, by light, under N_2	Butadiene	(H_2), 1-butene, *trans*-2-butene, *cis*-2-butene (20/4/1)
MeOH, 2 h, by light, under H_2[b]	Butadiene	1-butene, *trans*-2-butene, *cis*-2-butene (46/2.5/1)
MeOH, 48 h, in the dark, under N_2	MeI	H_2+CH_4
MeOH, 48 h, in the dark, under N_2	EtI	$H_2+C_2H_6$, C_2H_4 (20/1)
MeOH, 48 h, in the dark, under N_2	PrBr	$H_2+C_3H_8$, C_3H_6 (1/1), CH_3Br[c]
MeOH, 48 h, in the dark, under N_2	i-PrI	$H_2+C_3H_8$, C_3H_6 ($\geq 1/1$)

[a] Contrary to the behaviour with pentacyanocobaltate complexes[7], the use of MeOH as solvent does not promote greatly the formation of *cis*-2-butene. [b] Yield much higher than under nitrogen. [c] Formed from the collateral reaction between HX and the solvent. Very small amounts of CH_3I are present when X is iodine.

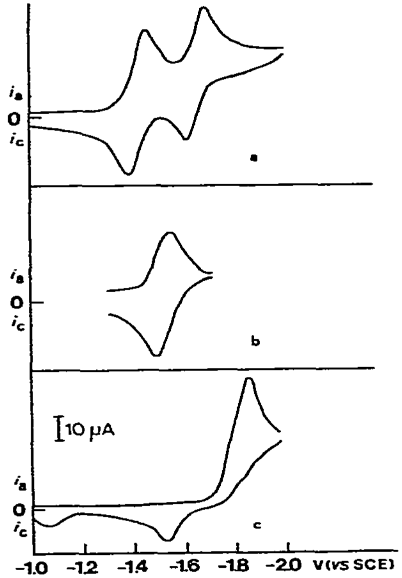
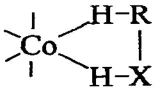


Fig. 2. Voltammograms ($\sim 10^{-3}$ *M* in DMF with 0.2 *M* $LiClO_4$ as base electrolyte, 0°, in the dark) of (a) $[Co(Bipy)_2(CH_3)_2]ClO_4$ (voltage sweep rate 1.5 V/s); (b) $[CoBipy(PBu_3)_2H_2]ClO_4$ (voltage sweep rate 1.5 V/s); (c) $[Co(DPE)_2H_2]ClO_4$ (voltage sweep rate 1 V/s).

Complexes (I) also react with an excess of an alkyl halide to give hydrocarbons as reduction products of the halides (see Table 2), and $[CoBipy(PR_3)_2RX]^+$ complexes as final products. These reactions also are accelerated by light.

A plausible mechanism for the hydrogenation reaction involves, as the first step, the transfer of a hydrogen atom from the complex to butadiene or the halide of the organic halide, giving hydridic derivatives of Co^{II} and radicals. These radicals can then either react with the solvent, or bond with the metal to give the saturated hydrocarbon by reductive elimination, or displace the olefin to regenerate the dihydride. The absence of dimers R–R can be attributed to cage effects. Intermediates of the type



can be ruled out, as they could give only alkanes.

From the above results we can see that, unlike $[Co(Bipy)_2]^+$ but like $[Co(DPE)_2]^+$ complexes [DPE = 1,2-bis(diphenylphosphino)ethane], $[CoChel(PR_3)_2]^+$ derivatives undergo oxidative addition of hydrogen; this is associated with their increased soft character. As expected, stable dihydridic and organometallic derivatives of Co^{III} can be made from them. These show the properties of both $Co(N_4)^+$ and $Co(P_4)^+$ systems.

Polarographic reduction and cyclic voltammetry (see Fig. 2) of complexes $[Co(Bipy)_2(CH_3)_2]^+$, $[CoBipy(PBu_3)_2H_2]^+$ and $[Co(DPE)_2H_2]^+$ confirm that Bipy is more useful than phosphines in stabilizing dimetalorganic and dihydric octahedral complexes of Co in low valence states. $[Co^{III}(Bipy)_2(CH_3)_2]^+$ shows two monoelectronic reversible waves, which correspond to the formation of octahedral organometallic complexes of Co^{II} and Co^{I}, respectively*, whose stability is confirmed by cyclic voltammetry; $[CoBipy(PBu_3)_2H_2]^+$ shows a monoelectronic reversible wave, giving a stable Co^{II} complex**; $[Co(DPE)_2H_2]^+$ shows also a monoelectronic reversible wave, but the reduction product is thermodynamically unstable, as can be seen from cyclic voltammetry.

The stability of the Co–C bond seems not to change very much throughout the $[Co(Bipy)_2R_2]^{+,0,-}$ series. This is probably, as suggested recently[8] for a series of $[Cr(Bipy)_3]^{n+}$ derivatives ($n=3, 2, 1, 0$), due to compensation of σ- and π-bonding electronic effects, which maintain a similar electron density around Co atom even when its oxidation state changes. In accord with this point of view, mixed complexes involving only one mole of Bipy show a reduced stabilizing power, and this is even lower in DPE derivatives.

EXPERIMENTAL

$[CoChel(PR_3)_2H_2]X$ [*(Ia)*–*(Ih)*] ($PR_3 = PEt_3$, PPr_3, PBu_3, PEt_2Ph; $X = ClO_4^-$, PF_6^-)

These complexes were obtained by two methods:

(*a*). An ethanolic solution (25 ml) of 0.6 g (2.5 mmoles) of $CoCl_2 \cdot 6\,H_2O$ was added dropwise to an ethanolic solution (50 ml) of 0.78 g (5 mmoles) of Bipy. The resulting yellow-orange solution was reduced under nitrogen with a stoichiometric amount of $NaBH_4$, to give the blue colour characteristic of $[Co^{I}(Bipy)_2]^+$. This then turned to brown after addition of an excess (1 ml) of PR_3 and saturation with molecular hydrogen. Addition of $NaClO_4$ caused the precipitation of a brown solid which was filtered off. Concentration of the filtered yellow-orange solution gave the dihydridic derivatives in low yield.

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* $[Co(Bipy)_2(CH_3)_2]^-$ is the first example of an organometallic complex of Co^{I}.

** $[CoBipy(PBu_3)_2H_2]^0$ is the first example of a dihydridic derivative of Co^{II}.

(*b*). 5 mmoles of the appropriate phosphine were added under nitrogen to a methanolic solution (50 ml) of 0.6 g (2.5 mmoles) of $CoCl_2 \cdot 6\,H_2O$ and 0.39 g of Bipy or 0.49 g Phen (2.5 mmoles). A green colour developed immediately, and turned to red-violet on addition of $NaBH_4$ and then to yellow-orange when the solution was added to an aqueous $NaClO_4$ or NH_4PF_6 solution after a reaction time of $\frac{1}{2}$ h. The crystalline solids obtained on evaporation were washed with water and petroleum ether and recrystallized from acetone/water. PF_6 derivatives were characterized by their IR spectra, which were in excellent agreement with those of the perchlorates.

The deuterated $[CoBipy(PPr_3)_2D_2]ClO_4$ was obtained by method (b) using deuterated solvents and $NaBD_4$.

$[CoChel(PR_3)diene]ClO_4$ [(IVa)–(IVn)] (PR_3 = PEt_3, PPr_3, PBu_3, PEt_2Ph; diene = butadiene, isoprene)

These complexes were obtained by two methods:

(*a*). A deaerated methanolic solution of $[Co(Chel)_3]^+$ was saturated with butadiene (or treated with isoprene) and a slight excess of PR_3 was added. From the red solution crystalline solids were obtained by adding an aqueous $NaClO_4$ solution and evaporating the solvent. The precipitate was washed with water and petroleum ether and recrystallized from methanol/acetone plus water.

(*b*). A deaerated methanolic solution (50 ml) of 0.5 g of $[CoChel(PR_3)_2H_2]$-ClO_4 was saturated with butadiene (or 1 ml isoprene was added). After 12 h reaction, the complexes were isolated as above from the red solution.

Reactions of $[CoChel(PR_3)H_2]ClO_4$ and $[CoChel(PR_3)diene]ClO_4$ with excess of Chel

1 mmole of complex in ethanol was treated under nitrogen with an excess of Chel, and set aside overnight. A blue colour of $[Co(Bipy)_3]ClO_4$ appeared for Bipy derivatives, while from Phen derivatives large dark brown crystals of the known $[Co(Phen)_3]ClO_4$ were precipitated, and were identified by analysis. Butadiene was identified in the gas phase by GLC.

Reactions of $[CoChel(PR_3)diene]ClO_4$ with PR_3 and H_2

A deaerated solution of 1 mmole of the complex was saturated with H_2 in the presence of a slight excess of the corresponding phosphine. After 12 h, addition of water and evaporation of the solvent gave crystalline solids, whose IR spectra were identical with those of $[CoChel(PR_3)_2H_2]ClO_4$.

$[Co(CO)_3(PR_3)_2]ClO_4$ [(IIIa)–(IIIc)] (PR_3 = PEt_3, PPr_3, PBu_3)

These complexes were obtained by three methods:

(*a*). Saturating a $[Co(Chel)_3]^+$ solution with CO in the presence of an excess of PBu_3, filtering off the separated dark precipitate and adding $NaClO_4$ to the clear, stable colourless solution.

(*b*). Saturating with CO a methanolic solution of $[CoChel(PR_3)_2H_2]ClO_4$, crystalline compounds of the above formula were obtained from the light yellow solution after 12 h by adding water and evaporating the solvent.

(*c*). Starting from $[CoChel(PR_3)diene]ClO_4$, and carrying out a procedure similar to (b) but in the presence of phosphine.

Reactions of $[CoChel(PR_3)_2H_2]^+$ *with organic halides*

The experimental conditions and gaseous products are summarized in Table 2. During the reaction, free halide ions are formed and the methanolic solution becomes acid. By addition of water and evaporation of the solvent, crystalline $[CoChel(PR_3)_2RX]^+$ were obtained. Examples of the analyses of some of them are listed in Table 1 [(Va)–(Vb)].

Techniques

IR spectra were recorded on Nujol mulls with a Perkin–Elmer 225 spectrophotometer. NMR spectra were recorded at 0° in CD_3COCD_3 or at $-20°$ in $CDCl_3$ with a JEOL JNM-C-60-HL spectrometer. Gas analyses were performed with a C. Erba GT gas chromatograph, with 2 m columns of Molecular Sieve 5A for hydrogen detection and alumina or silica gel for light hydrocarbon determinations. Butene separation was effected by combining the alumina column (which separates *cis*-2-butene from butadiene and *trans*-2-butene + 1-butene) with a Vaseline 10 m column (which separates *cis*-2-butene from *trans*-2-butene and 1-butene + butadiene).

Polarographic measurements were performed with an Amel three electrodes controlled potential polarograph Model 462 and the cyclic voltammetry was carried out using an Amel operational amplifier-based three electrode polarograph Model 448.

Photolyses were carried out under an Osram HQA 400 W mtX lamp.

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