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Five-Coordinate Complexes of Cobalt(II) with Tertiary and Secondary Phosphines. A Dominant Role for Steric Effects

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A series of low-spin five-coordinate complexes of cobalt(II) are reported. Secondary phosphines form $[CoX_2(HPR_2)_3]$ (X = Br, $R_2 = (C_6H_5)C_6H_{11}$; X = NCS, CN, $R_2 = (C_6H_{11})_2$) and $[CoBr(HPR_2)_4]B(C_6H_5)_4$ ($R_2 = (C_2H_5)_2$, $(C_6H_5)C_2H_5$, $(C_6H_5)CH_3$). By reaction of $CoBr_2$ with the secondary phosphines HPR_2 (R = $(C_2H_5)_2$, $(C_6H_5)C_2H_5$, $(C_6H_5)CH_3$), $[CoBr_2(HPR_2)_4]$ complexes have been isolated, which probably are six-coordinate in the solid state. In solution these complexes are dissociatively unstable and give $[CoBr_2(HPR_2)_3]$ or $[CoBr(HPR_2)_4]^+$ depending on the nature of the solvents. Tertiary phosphines $P(CH_3)_n(C_6H_5)_{3-n}$ (n = 3, 2, 1) yield $[CoBr_2(PR_3)_3]$ ($R_3 = (CH_3)_3$, $(CH_3)_2C_6H_5$), $[Co(CN)_2(PR_3)_3]$ ($R_3 = (CH_3)_2C_6H_5$, $(C_6H_5)_2CH_3$), and $[CoBr_2(CO)(PR_3)_2]$. The magnetic and spectroscopic properties are discussed and related to those of other five-coordinate cobalt(II) complexes. The influence of the nature of the phosphine on the formation of five-coordinate adducts is discussed, and it is suggested that steric effects are much more important than electronic effects in determining five-coordination in low-spin cobalt(II) complexes.

Introduction

A number of low-spin five-coordinate cobalt(II) complexes have been characterized in the past years, mainly with polydentate ligands containing π-bonding donor atoms, such as phosphorus, arsenic, and selenium.[1-3]

In some cases monodentate phosphines also appear to be able to stabilize the five-coordinate state. Tris-phosphine adducts of the type $[CoX_2(P)_3]$ (X = halogen, P = monodentate phosphine) have been reported with diphenylphosphine,[4,5] with cyclic phosphines such as 2-phenylisophosphindoline[6] and some 9-alkyl-9-phosphafluorenes,[7] and with the alkylaminofluorophosphines $F_2PN(CH_3)_2$[8] and $FP(N(CH_3)_2)_2$.[9]

Systematic studies have been made in this laboratory on the tendency of the four-coordinate complexes $[CoX_2(PR_3)_2]$ (X = halogen or pseudohalogen) to add a third molecule of tertiary phosphine PR_3 to give $[CoX_2(PR_3)_3]$ complexes. It has been found that with the phosphines PR_3 (R = ethyl, n-propyl, n-butyl) or $PR_nR'_{3-n}$ (R = ethyl, R' = phenyl), the five-coordinate species are termodynamically unstable, when X = Cl, Br, or NCO, but can be formed in the presence of the anionic ligands NCS or CN. With $P(C_6H_5)_3$, $P(C_6H_{11})_3$, and $P(C_6H_{11})_2C_6H_5$ however no evidence of five-coordination is obtained, even when X = NCS or CN.[10,11]

Therefore, the stability of $[CoX_2(PR_3)_3]$ complexes appear definitely influenced by the anionic ligand, the order being halogens $\ll$ NCS $<$ CN and by the nature of the phosphine.

The role of steric and electronic effects in determining the tendency of cobalt(II) complexes to adopt four- or five-coordinate structures is not yet well established, even if some results suggest that the interligand repulsion may affect the formation of five-coordinate species.

In order to test the importance of steric hindrances in the formation of five-coordinate complexes of cobalt(II) we have investigated the reactions of $CoBr_2$ with a series of secondary and tertiary phosphines, *i.e.*, $P(CH_3)_n(C_6H_5)_{3-n}$ (n = 1, 2, 3), $HP(C_6H_5)R$ (R = CH_3, C_2H_5, C_6H_{11}), and HPR_2 (R = C_2H_5, C_6H_5, C_6H_{11}).

This paper reports the preparation and properties of five-coordinate complexes of the type $[CoBr(HPR_2)_4]^+$, $[CoBr_2(HPR_2)_3]$, $[CoBr_2(PR_3)_3]$, and $[CoBr_2(CO)(PR_3)_2]$, together with some cyano- and thiocyanate derivatives.

Experimental Section

Apparatus. Electronic spectra were obtained with an Optica CF4NI spectrophotometer. Reflection spectra were recorded using solid compounds and $MgCO_3$ as inert diluent on a Beckman DU spectrophotometer. Magnetic susceptibilities were measured by the standard Gouy method at 25° and were corrected for the diamagnetism of the ligands. Infrared spectra were obtained with a Perkin-Elmer 457 spectrophotometer.

Starting Materials. The tertiary phosphines were prepared by standard methods; diethyl- and dicyclohexylphosphines were prepared following Issleib's method.[12] The secondary phosphines $HP(C_6H_5)R$ (R = CH_3, C_2H_5, C_6H_5, C_6H_{11}) were obtained by hydrolysis of the corresponding $LiP(C_6H_5)R$.

Preparation. All solvents were degassed and all reactions carried out under dry nitrogen or argon.

$[CoBr_2(P(CH_3)_3)_3]$. $CoBr_2$ (2 mmol) and the trimethylphosphine adduct $AgI{\cdot}P(CH_3)_3$ (10 mmol) were mixed in 50 ml of methylene chloride and silver iodide was filtered off. The violet solution was evaporated to dryness and the residue was treated with ethyl ether. By adding n-hexane, dark violet crystals were obtained. The same compound is obtained by reaction of free $P(CH_3)_3$ and $CoBr_2$, always in methylene chloride.

$[CoBr_2(P)_3]$ (P = $P(CH_3)_2C_6H_5$, $HP(C_6H_5)C_6H_{11}$). $CoBr_2$ (2 mmol) was suspended in 30 ml of methylene chloride and the phosphine (8 mmol) added. After 1 hr of vigorous stirring, unreacted cobalt bromide was separated by filtration and from the solutions violet to brown crystals of the compounds were obtained by adding n-hexane.

$[CoBr_2(P)_4]$ (P = $HP(C_6H_5)C_2H_5$, $HP(C_6H_5)CH_3$). Cobalt(II) bromide (2 mmol) was suspended in 30 ml of methylene chloride and the phosphine (10 mmol) added. After 1 hr of vigorous shaking, the solutions were filtered off and green crystals precipitated by addition of n-hexane.

$[CoBr(P)_4]B(C_6H_5)_4$ (P = $HP(C_2H_5)_2$, $HP(C_6H_5)C_2H_5$, $HP(C_6H_5)CH_3$). $CoBr_2$ (2 mmol) and sodium tetraphenylborate (2 mmol) were dissolved in 30 mol of ethanol and the phosphine (10 mmol) was added. In a few minutes green crystals precipitated, which were washed with ethanol and recrystallized from methylene chloride–ethanol.

$[Co(NCS)_2(P)_3]$ (P = $HP(C_6H_{11})_2$, $HP(C_6H_{11})C_6H_5$). Anhydrous cobalt(II) thiocyanate (2 mmol) was dissolved in 30 ml of ethanol with phosphine (8 mmol) at room temperature. The solution was cooled at −70° to favor precipitation of the red compounds and then shaken several hours. The ir spectra in Nujol mull show a strong band at 2070 cm^{-1} (ν_{CN} of isothiocyanate terminal groups).

$[Co(CN)_2(P)_3]$ (P = $P(C_6H_5)_2CH_3$, $P(CH_3)_2C_6H_5$, $HP(C_6H_5)_2$, $HP(C_6H_{11})_2$). The bromo derivatives $CoBr_2(P)_2$ or $CoBr_2(P)_3$ were dissolved in a 1:1 ethanol–methylene chloride solution (10 mmol in 50 ml), to which an excess (10–20 mmol) of the corresponding phosphine was added. The solutions were passed through a column of an anionic resin (Dowex 1-X4, 50–100 mesh) in CN^- form. The resulting red solutions were evaporated to dryness and the crude products purified as follows. (a) $[Co(CN)_2(P(C_6H_5)_2CH_3)_3]$ was obtained as dark red crystals from methylene chloride–n-hexane (ν_{CN} at 2080 and 2095 (vw) cm^{-1} in Nujol mull); (b) $[Co(CN)_2(P(CH_3)_2C_6H_5)_3]$ as dark red crystals from methylene chloride–ethanol (ν_{CN} at 2080 and 2095 (vw) cm^{-1}; (c) $[Co(CN)_2(HP(C_6H_5)_2)_3]$ as light red crystals from ethanol–n-hexane (ν_{CN} at 2070 and 2080 (vw) cm^{-1}); (d) $[Co(CN)_2(HP(C_6H_{11})_2)_3]$ as red-orange prisms from methylene chloride–n-hexane (ν_{CN} at 2080 and 2090 (vw) cm^{-1}).

$[CoBr_2(CO)(P)_2]$ (P = $P(CH_3)_3$, $P(CH_3)_2C_6H_5$). The corresponding complexes $CoBr_2(P)_3$ were suspended in n-hexane under

Table I. Properties and Analytical Data of Cobalt(II) Complexes

				Anal., %					
				C		H		Other	
Compd	Color	Mp,[a] °C	μ_{eff},[b] BM	Calcd	Found	Calcd	Found	Calcd	Found
$CoBr_2[P(CH_3)_3]_3$	Dark violet	109–111	2.10	23.03	24.18	5.82	6.09	33.92	35.75 (Br)
$CoBr_2[P(CH_3)_2C_6H_5]_3$	Violet	97–99	2.05	45.07	45.53	5.27	5.25	25.20	25.24 (Br)
$CoBr_2(CO)[P(CH_3)_3]_2$	Red-brown	138–140	2.00	20.99	21.08	4.66	4.55	39.97	40.06 (Br)
$CoBr_2(CO)[P(CH_3)_2C_6H_5]_2$	Red-brown	109–111	2.10	39.42	39.00	5.42	5.23	30.34	30.55 (Br)
$CoBr_2[HP(C_6H_{11})C_6H_5]_3$	Violet	170–172	2.20	54.52	54.35	6.40	6.46	20.30	20.09 (Br)
$[CoBr(HP(C_2H_5)_2)_4]B(C_6H_5)_4$	Green	124–126	2.30	57.65	58.69	7.59	7.88	9.88	9.76 (Br)
$[CoBr(HP(C_2H_5)C_6H_5)_4]B(C_6H_5)_4$	Light green	127–130	2.20	67.09	66.28	6.35	6.35	8.28	7.87 (Br)
$[CoBr(HP(CH_3)C_6H_5)_4]B(C_6H_5)_4$	Light green	117–119	2.25	65.08	65.41	5.75	5.91	8.10	8.37 (Br)
$CoBr_2[HP(C_2H_5)C_6H_5]_4$	Light green	114–116	2.05	49.32	49.57	5.63	5.72	20.32	20.61 (Br)
$CoBr_2[HP(CH_3)C_6H_5]_4$	Light green	125–127	2.00	46.86	46.90	5.24	5.07	22.59	22.34 (Br)
$Co(NCS)_2[HP(C_6H_{11})_2]_3$	Red	83–85	2.00	58.94	59.23	8.75	9.03	3.60	3.64 (N)
$Co(NCS)_2[HP(C_6H_{11})C_6H_5]_3$	Red-brown	109–111	2.30	60.70	60.56	6.83	6.78	3.72	3.62 (N)
$Co(CN)_2[P(CH_3)_2C_6H_5]_3$	Dark red	177–179	2.00	59.47	59.43	6.48	6.33	5.23	5.33 (N)
$Co(CN)_2[P(C_6H_5)_2CH_3]_3$	Dark red	161–163	2.10	68.35	69.20	5.49	5.52	3.96	3.94 (N)
$Co(CN)_2[HP(C_6H_5)_2]_3$	Red	88–92	1.90	67.78	68.16	5.77	4.97	3.96	4.18 (N)
$Co(CN)_2[HP(C_6H_{11})_2]_3$	Red-orange	92–94	2.00	63.40	64.66	9.62	9.85	3.79	3.97 (N)

[a] Uncorrected; determined in sealed tube under nitrogen. [b] At 25°.

Table II. Molar Conductance on 1,2-$C_2H_4Cl_2$ Solutions at 25°[a]

Compd	Λ_M, cm^2 ohm^{-1} mol^{-1}	Compd	Λ_M, cm^2 ohm^{-1} mol^{-1}
$CoBr_2(HP(C_6H_{11})_2)_3$	0.5	$[CoBr(HP(CH_3)C_6H_5)_4]B(C_6H_5)_4$	22.2
$CoBr_2(HP(C_6H_5)_2)_3$	1.5	$Co(NCS)_2(HP(C_6H_{11})_2)_3$	0.5
$CoBr_2(HP(C_6H_{11})C_6H_5)_3$	2.5	$Co(NCS)_2(HP(C_6H_{11})C_6H_5)_3$	1.0
$CoBr_2(HP(C_2H_5)_2)_4$	6.5	$Co(CN)_2(HP(C_6H_5)_2)_3$	0.2
	30.0[b]	$Co(CN)_2(HP(C_6H_{11})_2)_3$	0.5
$CoBr_2(HP(C_2H_5)_2)_4 + HP(C_2H_5)_2$[c]	28.6	$CoBr_2(P(CH_3)_3)_3$	0.7
$CoBr_2(HP(C_2H_5)C_6H_5)_4$	7.5	$CoBr_2(P(CH_3)_2C_6H_5)_3$	0.5
	30.0[b]	$CoBr_2(CO)(P(CH_3)_3)_2$	0.3
		$CoBr_2(CO)(P(CH_3)_2C_6H_5)_2$	0.7
$CoBr_2(HP(CH_3)C_6H_5)_4$	6.3	$Co(CN)_2(P(CH_3)_2C_6H_5)_3$	0.7
	28.8[b]	$Co(CN)_2(P(C_6H_5)_2CH_3)_3$	0.5
$[CoBr(HP(C_2H_5)_2)_4]B(C_6H_5)_4$	25.0		
$[CoBr(HP(C_2H_5)C_6H_5)_4]B(C_6H_5)_4$	21.5		

[a] For approximately 10^{-3} *M* solutions. [b] In ethanol, for approximately 10^{-3} *M* solutions. [c] Approximately 10^{-1} *M*.

Table III. Electronic Spectral Data for the Cobalt(II) Complexes in the 29,000–12,000-cm^{-1} Region[a]

Compd	Band max, cm^{-1} ($\epsilon_{\max}$)[b]
$CoBr_2(P(CH_3)_3)_3$	23,250 sh, 19,250 (1660), 15,400 (520), 13,900 sh
$CoBr_2(P(CH_3)_2C_6H_5)_3$	19,450 (820), 16,100 (520), 13,900 sh[c]
$CoBr_2(CO)(P(CH_3)_3)_2$	19,600 (280), 15,650 sh, 14,800 (140)
$CoBr_2(CO)(P(CH_3)_2C_6H_5)_2$	18,200 (320), 15,400 (220), 14,300 sh
$Co(CN)_2(P(CH_3)_2C_6H_5)_3$	20,600 (610)
$Co(CN)_2(P(C_6H_5)_2CH_3)_3$	20,000 (400), 16,700 sh
$CoBr_2(HP(C_6H_5)_2)_3$	19,800 (990), 15,400 sh, 14,200 (740)[c]
$CoBr_2(HP(C_6H_5)C_6H_{11})_3$	19,600 (1210), 15,600 sh, 14,300 (550)[c]
$Co(NCS)_2(HP(C_6H_5)C_6H_{11})_3$	26,300, 20,400, 14,900[d]
$Co(NCS)_2(HP(C_6H_{11})_2)_3$	26,000, 19,200, 14,500[d]
$Co(CN)_2(HP(C_6H_5)_2)_3$	20,800 sh, 15,600 sh[d]
$Co(CN)_2(HP(C_6H_{11})_2)_3$	22,200, 16,400[d]
$[CoBr(HP(C_2H_5)_2)_4]B(C_6H_5)_4$	24,500 (1620), 16,500 (330), 13,900 sh
$[CoBr(HP(C_6H_5)CH_3)_4]B(C_6H_5)_4$	24,100 (1570), 15,500 (370), 14,200 sh
$[CoBr(HP(C_6H_5)C_2H_5)_4]B(C_6H_5)_4$	23,800 (1940), 15,400 (450), 13,900 sh
$CoBr_2(HP(C_2H_5)_2)_4$	23,800, 15,600, 14,800[d]
	24,100 (1220), 16,100 (170)[e]
	20,600 (880), 15,200 (400)[f]
$CoBr_2(HP(C_6H_5)CH_3)_4$	23,800 sh, 15,600 br[d]
$CoBr_2(HP(C_6H_5)C_2H_5)_4$	23,250, 15,850, 14,600[d]
	24,100 (1740), 15,400 (240), 13,900 sh[e]
	20,200 (1220), 15,400 (645), 13,900 sh[f]

[a] In 1,2-dichloroethane solution, unless otherwise stated. [b] Molar absorptivities in parentheses; sh = shoulder. [c] In the presence of excess free phosphine. [d] Solid-state spectra. [e] In ethanol solution. [f] In benzene solution.

carbon monoxide at room temperature and atmospheric pressure and throughly shaken for several hours to produce complete conversion to red-brown products, which are stable in the solid state under inert gas (νCO 1980 (vs) cm^{-1}).

Results and Discussion

The physical properties and analytical data of the cobalt(II) complexes are listed in Tables I and II. The band maxima with their extinction coefficients of the electronic spectra are listed in Table III.

Infrared spectra of all the complexes with secondary phosphines show a weak band in the 2300-cm^{-1} region, attributable to P–H group of the phosphine.

The secondary and tertiary phosphines examined in this study react with $CoBr_2$ to form a variety of complexes, the structure and stoichiometry of which are highly dependent upon the nature of phosphine employed. Crystalline compounds have been obtained, in which the cobalt atom is bonded to two, three, and four molecules of phosphine and has coordination numbers ranging from four to five and probably to six.

Dicyclohexyl-[13] and diphenylmethylphosphine react with $CoBr_2$ to give high-spin four-coordinate complexes of the type $[CoBr_2(P)_2]$. A spectrophotometric study in 1,2-$C_2H_4Cl_2$ solution indicates that these complexes do not show any measurable tendency to add a third molecule of phosphine. By contrast, the reaction of the phosphines $HP(C_6H_5)_2$, $HP(C_6H_5)C_6H_{11}$, $P(CH_3)_2C_6H_5$, and $P(CH_3)_3$ with $CoBr_2$ in CH_2Cl_2 easily yields violet to brown compounds of composition $[CoBr_2(P)_3]$.

The tris(phosphine) adducts are low spin and are nonelectrolytes in 1,2-$C_2H_4Cl_2$ (Tables I and II). Their reflectance spectra closely resemble each other (Table III), indicating that probably all four $[CoBr_2(P)_3]$ complexes should have the same distorted trigonal-bipyramidal structure found for $[CoBr_2(HP(C_6H_5)_2)_3]$.[5] In 1,2-$C_2H_4Cl_2$ solution, the complex $[CoBr_2(P(CH_3)_3)_3]$ is practically indissociate, while the tris(phosphine) adducts with $HP(C_6H_5)$, $HP(C_6H_5)C_6H_{11}$, and $P(CH_3)_2C_6H_5$ partially dissociate into the corresponding four-coordinate species and phosphine. In the presence of an excess of phosphine, the dissociation is strongly reduced and the final spectra appear to be very similar to those in the solid state.

It should be noted that Jensen, *et al.*,[14] obtained by direct reaction of CoX_2 and trimethylphosphine in ethanol green compounds of composition $[CoX_2(P(CH_3)_3)_2]$ (X = Cl, Br). With CoI_2, violet-black crystals were reported, which contain approximately 2.5 mol of trimethylphosphine *per* cobalt atom.

One molecule of phosphine in the complexes $[CoBr_2(PR_3)_3]$ (R_3 = $(CH_3)_3$, $(CH_3)_2C_6H_5$) can be easily replaced by a molecule of carbon monoxide at room temperature and 1 atm to give carbonyl derivatives of the type $[CoBr_2(CO)(PR_3)_2]$, which can be isolated in the solid state. Magnetic moments (Table I) and visible spectra (Table III) agree with a low-spin five-coordinate structure. The infrared spectra show a strong band in the 1980–1985-cm^{-1} region (ν_{CO}), as found in other analogous $[CoX_2(CO)(P)_2]$ complexes.[15]

Also the four-coordinate $[CoBr_2(P(C_6H_5)_2CH_3)]$ takes up carbon monoxide yielding the brown five-coordinate complex $[CoBr_2(CO)(P(C_6H_5)_2CH_3)_2]$. However it is much less stable than the corresponding derivatives with $P(CH_3)_3$ and $P(CH_3)_2C_6H_5$ and rapidly loses in the solid state carbon monoxide to re-form the green $[CoBr_2(P(C_6H_5)_2CH_3)_2]$ compound.

As previously found, when the anionic ligand is CN^-, the stability of the tris(phosphine) adducts increases.[11] Thus, five-coordinate $[Co(CN)_2(P)_3]$ complexes are formed either with the phosphines which give $[CoBr_2(P)_3]$ species or with $HP(C_6H_{11})_2$ and $P(C_6H_5)_2CH_3$. The cyano derivatives are prepared by passing a CH_2Cl_2–ethanol solution of the corresponding $[CoBr_2(P)_{2\text{ or }3}]$ complexes and free phosphine through a column of anionic resin in CN^- form. In the case of $P(CH_3)_3$ and $HP(C_6H_{11})C_6H_5$, only red intractable oils have been obtained.

Magnetic moments and spectral patterns—both in solid and in solution—of the red crystalline compounds are fully consistent with those of other known low-spin five-coordinate cyano derivatives of cobalt(II) of the type $[Co(CN)_2(P)_3]$ (P = $P(C_6H_5)_2C_2H_5$ and $P(C_2H_5)_2C_6H_5$).[11]

In 1,2-$C_2H_4Cl_2$ solution, the complexes are nonelectrolytes and are not dissociated, as indicated by spectrophotometric investigations. The infrared spectra, both in Nujol mull and in 1,2-$C_2H_4Cl_2$ solutions, show a strong peak at 2070–2080 cm^{-1} and another, much weaker, at 2090–2100 cm^{-1}, attributable to nonbridging CN groups. The presence of two CN stretching frequencies suggests a distorted structure, in which the two cyanides occupy structurally nonequivalent positions.

The reaction of the ligands $HP(C_2H_5)_2$, $HP(C_6H_5)C_2H_5$, and $HP(C_6H_5)CH_3$ with $CoBr_2$ in ethanol in the presence of an excess of sodium tetraphenylborate, yields green compounds which analyze as $[CoBr(P)_4]B(C_6H_5)$. The compounds have magnetic moments around 2 BM and are 1:1 electrolytes in 1,2-$C_2H_4Cl_2$ solutions (Tables I and II). Visible spectra, in the 29,000–12,000 cm^{-1} region, both in the solid state and in 1,2-$C_2H_4Cl_2$ solutions, display two definite bands (at *ca.* 24,000 and 16,000 cm^{-1}) with a shoulder around 14,000 cm^{-1} (Table III). The relative energies and shapes of the bands fit well into the qualitative pattern found for other low-spin five-coordinate complexes of cobalt(II) with a $[P_4X]$ donor set.[1,16,17]

However, electronic spectra alone, as confirmed recently by Meek, *et al.*,[1] are not sufficient to assign unambiguously square-pyramidal or trigonal-bipyramidal geometries to these complexes.

If the secondary phosphines $HP(C_2H_5)_2$, $HP(C_6H_5)C_2H_5$, and $HP(C_6H_5)CH_3$ are added to a suspension of $CoBr_2$ in CH_2Cl_2, green solutions are rapidly formed, from which green products can be precipitated of composition $[CoBr_2(P)_4]$ (μ = 2 BM). For the previously reported compound $[CoX_2(HP(C_2H_5)_2)_4]$ (X = Cl, Br) Issleib proposed a low-spin octahedral structure, both in the solid state and in solution, with the halogen atoms in cis positions, on the basis of dipole moment, molecular weight, and magnetic moment measurements.[13]

We find, instead, that in solution all three complexes $[CoBr_2(P)_4]$ are dissociatively unstable, providing a series of equilibria strongly dependent upon the nature of the solvent. In ethanol, where the compounds behave as 1:1 electrolytes, the visible spectra are different from those in the solid state but very similar to those of the corresponding $[CoBr(P)_4]B(C_6H_5)_4$ derivatives discussed above (Table III, Figure 1a), thus suggesting that the process of solution in ethanol of the $[CoBr_2(P)_4]$ complexes occurs with formation of the five-coordinate species $[CoBr(P)_4]^+$.

When the green compounds are dissolved in a less ionizing solvent, such as 1,2-$C_2H_4Cl_2$, the solutions become red-brown and the visible spectra, still different from solid-state spectra, consist in two composite bands, at 21,000–22,000 and 15,000–16,000 cm^{-1}, respectively. Moreover, the observed conductances—for 10^{-3} *M* solutions—are definitely lower than those expected for typical uni-univalent electrolytes (Λ_M = *ca.* 6–10 instead of usual values of 20–30 ohm^{-1} cm^2 mol^{-1}). On addition of phosphine, the molar conductances significatively increase and the color changes again from red-brown to green. The bands at 21,000–22,000 and 15,000–16,000 cm^{-1} disappear and are replaced by the band system typical of the ionic $[CoBr(P)_4]^+$ chromophores, discussed above (Figure 1b).

Spectroscopic and conductivity data in 1,2-$C_2H_4Cl_2$ can be simply interpreted in terms of an equilibrium involving two five-coordinate species: $[CoBr_2(P)_3] + P \rightleftharpoons [CoBr(P)_4]^+ + Br^-$.

Thus, the band system which appears in the spectra of the solutions without added phosphine is reasonably assigned to the tris(phosphine) species $[CoBr_2(P)_3]$. The assignment is also consistent with shapes and positions of the band maxima observed in the spectra of the analogous $[CoBr_2(P)_3]$ chromophores, in particular $[CoBr_2(HP(C_6H_5)_2)_3]$.

Finally, spectral patterns closely related to solid-state spectra are observed when the $[CoBr_2(P)_4]$ complexes are dissolved in benzene, in the presence of an excess of phosphine (one band around 23,500 cm^{-1} and another broader band centered at 15,000 cm^{-1}). In absence of added phosphine, the spectra show

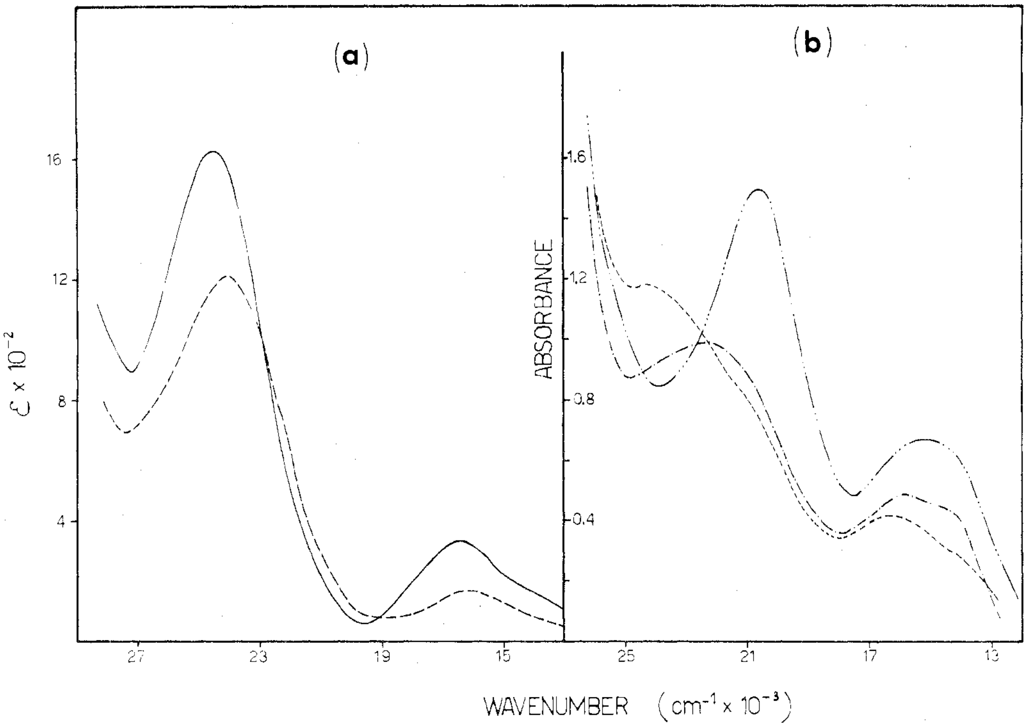

Figure 1. Electronic absorption spectra: (a) ——, $[CoBr(HP(C_2H_5)_2)_4]B(C_6H_5)_4$, 9.72 × 10^{-4} *M* in 1,2-dichloroethane; - - - -, $[CoBr_2(HP(C_2H_5)_2)_4]$, 9.47 × 10^{-4} *M* in ethanol; (b) - · - · -, $[CoBr_2(HP(C_2H_5)_2)_4]$, 1.23 × 10^{-3} *M* in 1,2-dichloroethane; - - - -, 1.23 × 10^{-3} *M* complex in 1,2-dichloroethane containing 2 × 10^{-2} *M* diethylphosphine; - ··· - ··· -, $[CoBr_2(HP(C_2H_5)_2)_4]$, 1.7 × 10^{-3} *M* in benzene.

again the characteristic band contours of the $[CoBr_2(P)_3]$ chromophores (Table III, Figure 1b), thus suggesting the existence of the equilibrium $[CoBr_2(P)_3] + P \rightleftharpoons [CoBr_2(P)_4]$.

We conclude that all the $[CoBr_2(P)_4]$ complexes are probably six-coordinate in the solid state, but extensively dissociated in solution, giving neutral or ionic five-coordinate species $[CoBr_2(P)_3]$ or $[CoBr(P)_4]^+$, respectively, depending on the nature of the solvent.

No spectral evidence has been obtained for the formation in the solvents examined of the pseudotetrahedral $[CoBr_2(P)_2]$ complexes. However it should be noted that Yoke, *et al.*, found that the solid compound $[CoCl_2(HP(C_2H_5)_2)_4]$ lost *in vacuo* half of its content of phosphine, giving the 2:1 adduct $[CoCl_2(HP(C_2H_5)_2)_2]$.[18]

Conclusions

The stability of tris(phosphine) complexes appears to be strongly dependent upon the nature of the phosphinic ligands. The influence of the organic group bound to the phosphorus atom becomes evident in the series of the complexes with the tertiary phosphines $PR_n(C_6H_5)_{3-n}$ (R = methyl, ethyl) and $P(C_2H_5)_n(C_6H_{11})_{3-n}$ (n = 0, 1, 2, 3). Whereas trimethyl- and dimethylphenylphosphine form five-coördinate $[CoBr_2(P)_3]$ complexes, with the ligands $P(C_6H_5)_2CH_3$, $P(C_2H_5)_3$, $P(C_2H_5)_2C_6H_5$, $P(C_6H_5)_2C_2H_5$, $P(C_6H_5)_3$, $P(C_6H_{11})_3$, $P(C_6H_{11})_2C_2H_5$, and $P(C_2H_5)_2C_6H_{11}$ no evidence of the formation of dibromo tris(phosphine) adducts has been obtained. However, when the anionic ligand X is CN or NCS, five-coordination in easily achieved by all the above phosphines, except $P(C_6H_5)_3$, $P(C_6H_{11})_3$, and $P(C_6H_{11})_2C_2H_5$.[10,11,20]

Thus, the tendency of the tertiary phosphines to form five-coordinate species decreases on replacing methyl groups with larger groups, such as C_2H_5, which has a comparable inductive effect, or C_6H_5, which has an opposite inductive effect. A similar stability change is observed when ethyl groups are replaced by cyclohexyl or phenyl groups.

These observations are in agreement with the fact that the secondary phosphines HPR_2 generally form five-coordinate complexes more easily than the corresponding tertiary phosphines. In fact, $[CoX_2(HPR_2)_3]$ complexes can be obtained even when X = Br, with the exception of the more bulky dicyclohexylphosphine, which gives tris(phosphine) adducts only when X = NCS or CN.

It is interesting to note that with the smallest examined phosphines $HP(C_2H_5)_2$, $HP(C_6H_5)C_2H_5$, and $HP(C_6H_5)CH_3$, cobalt(II) can attain five-coordination also by binding four molecules of phosphines to give $[CoBr(P)_4]^+$ derivatives.

The observed sequence suggests that the property, which primarily controls the formation of five-coordinate $[CoX_2(P)_3]$ complexes, is the size of phosphorus ligands, whereas the electronic effects related to the organic substituents in the phosphine do play only a secondary role.

However the fact that the four-coordinate $[CoBr_2(P(C_6H_5)_2CH_3)_2]$ can coordinate a CO molecule, while it does not form the tris(phosphine) adduct, clearly cannot be accounted for on the basis of steric arguments alone and indicates that also π-acceptor capacity of the ligands is an important factor in favoring five-coordination.

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Registry No. $CoBr_2(P(CH_3)_3)_3$, 52810-40-9; $CoBr_2(P(CH_3)_2C_6H_5)_3$, 52810-41-0; $CoBr_2(CO)(P(CH_3)_3)_2$, 52810-37-4; $CoBr_2(CO)(P(CH_3)_2C_6H_5)_2$, 52223-37-7; $Co(CN)_2(P(CH_3)_2C_6H_5)_3$, 52810-38-5; $Co(CN)_2(P(C_6H_5)_2CH_3)_3$, 52810-39-6; $CoBr_2(HP(C_6H_5)_2)_3$, 15740-84-8; $CoBr_2(HP(C_6H_5)C_6H_{11})_3$, 52810-42-1; $Co(NCS)_2(HP(C_6H_5)C_6H_{11})_3$, 52810-43-2; $Co(NCS)_2(HP(C_6H_{11})_2)_3$, 52810-44-3; $Co(CN)_2(HP(C_6H_5)_2)_3$, 52810-45-4; $Co(CN)_2(HP(C_6H_{11})_2)_3$, 52810-46-5; $[CoBr(HP(C_2H_5)_2)_4]B(C_6H_5)_4$, 52810-48-7; $[CoBr(HP(C_6H_5)CH_3)_4]B(C_6H_5)_4$, 52810-50-1; $[CoBr(HP(C_6H_5)C_2H_5)_4]B(C_6H_5)_4$, 52810-52-3; $CoBr_2(HP(C_2H_5)_2)_4$, 52810-53-4; $CoBr_2(HP(C_6H_5)CH_3)_4$, 52810-54-5; $CoBr_2(HP(C_6H_5)C_2H_5)_4$, 52810-55-6; $CoBr_2(HP(C_6H_{11})_2)_2$, 52810-56-7.

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Base Hydrolysis of Coordinated Organonitriles. Reactions of Ruthenium(III) and Rhodium(III) Complexes

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Specific rates of base hydrolysis of the pentaammineruthenium(III) complexes of acetonitrile ($2.2 \times 10^2\ M^{-1}\ \text{sec}^{-1}$) and of benzonitrile ($2.0 \times 10^3\ M^{-1}\ \text{sec}^{-1}$), $Ru(NH_3)_5(NCR)^{3+}$ (R = CH_3 or C_6H_5), are shown to be approximately 10^8 times faster than the free ligand under the same conditions and about 10^2 times faster than the analogous cobalt(III) complexes. Reaction products are the corresponding amido complexes which reversibly protonate in acidic solution to give the amide complexes. Base hydrolysis of the pentaamminerhodium(III) complex of acetonitrile ($1.0\ M^{-1}\ \text{sec}^{-1}$) occurs at a rate comparable to that of the cobalt(III) complex, while the ruthenium(II) complex is at least 10^6 times less reactive than the corresponding ruthenium(III) complex. In bicarbonate–carbonate buffer solutions the reactions of the Ru(III) complexes display general base catalysis, a result which suggests that in aqueous solution the coordinated nitriles are subject to attack by nucleophiles other than hydroxide ion.

Past efforts in these laboratories have been concerned with interpretation of ligand–metal interactions between organic ligands and metal–ammine complexes of the second transition row.[2-7] Particular emphasis has been directed toward comparisons of ligand properties and reactions between different organonitrile complexes of the type $M(NH_3)_5(RCN)^{n+}$, where M = Ru(II), Ru(III), or Rh(III) and RCN is an organonitrile such as acetonitrile or benzonitrile. In the course of these studies, it was observed[2] that ruthenium(III) complexes of benzonitrile and other substituted aromatic nitriles underwent reactions to unidentified Ru(III) products in hot water unless the solution was acidic, and speculation centered on the possible hydrolysis (hydration) of the coordinated nitrile function. In the context of some recent interest[8-10] in the hydrolysis reactions of coordinated nitriles, we decided to examine this reaction in greater detail for the acetonitrile and benzonitrile complexees of ruthenium(III), $Ru(NH_3)_5(CH_3CN)^{3+}$ and $Ru(NH_3)_5(C_6H_5CN)^{3+}$, and the analogous ruthenium(II) and rhodium(III) complexes of acetonitrile, $Ru(NH_3)_5(CH_3CN)^{2+}$ and $Rh(NH_3)_5(CH_3CN)^{3+}$. Comparisons of the reactions of these structurally analogous complexes allow evaluation of the differences in ligand reactivity resulting from changes in the nature of the central metal ion. For the present cases, rhodium(III) and ruthenium(II) complexes are isoelectronic (both low-spin $4d^6$) yet differ by one electrostatic charge. The rhodium(III) and ruthenium(III) complexes have the same charge, but differ by one d electron (Ru(III) is low-spin $4d^5$). Consequently, relative to rhodium(III), ruthenium(II) has been shown to be an electron donor to π-acceptor unsaturated organic ligands such as organonitriles,[7] while ruthenium(III) is a π acid.[11] The differences in metal–ligand interactions should show up in the reactivity patterns for base hydrolysis of organonitriles coordinated to these substitution-inert metal ions. Comparisons to recent cobalt(III) results can also be made.

Experimental Section

Equipment. Visible and ultraviolet spectra and rate studies were run on a Cary Model 14 spectrophotometer equipped with a thermostated cell compartment. Some measurements were done on a Cary Model 118. Infrared spectra were run on a Perkin-Elmer Model 225 recording spectrophotometer, using 75–100-mg KBr disks containing 1–3 mg of compound. PH measurements were made on a Sargent–Welch Model NX pH meter with a combination minielectrode.

Materials. Reagent grade ligands and chemicals were used throughout. Doubly distilled water was used for solutions. Argon used for deaerating solutions was deoxygenated by passage through Cr(II) solution in gas-scrubbing bottles. DMA (*N,N*-dimethylacetamide) was distilled and stored over molecular sieves. "Tris" refers to tris(hydroxymethyl)aminomethane. The acetonitrile and benzonitrile complexes, $[Ru(NH_3)_5(CH_3CN)](ClO_4)_3$ and $[Ru(NH_3)_5(C_6H_5CN)](ClO_4)_3$, were prepared according to the procedure of Clarke.[2] The ruthenium(III) products were recrystallized from warm (45–50°) dilute perchloric acid (pH 1–2) to minimize any production of amide complex. Purity was judged by comparison of measured extinction coefficients to those previously reported.[2] $[Rh(NH_3)_5(CH_3CN)](ClO_4)_3$ was prepared as described previously.[6]

$[Ru(NH_3)_5(CH_3CONH)](BF_4)_2$. $[Ru(NH_3)_5Cl]Cl_2$ (200 mg, 0.68 mmol) was added to a solution of silver trifluoroacetate (150 mg of Ag_2O, 0.65 mmol, in 3–4 ml of water with a minimum of concentrated HTFA) whereupon AgCl precipitated. The precipitate was digested (3–5 min) and then filtered, after cooling for several minutes. The yellow filtrate was deaerated with argon and reduced with a piece of amalgamated zinc, using a vial with a rubber serum cap as the reaction vessel, and argon was continuously passed through with syringe needles. The reduced solution was added to an open 10-ml beaker containing acetamide (0.8 g, 13.5 mmol) and a piece of Zn(Hg). The pH was adjusted to about 8 with solid tris and the solution became deep amber. After 2–3 min of stirring the Zn(Hg)