the charge-transfer state (345 nm) are of interest in connection with recent investigations of the laser properties of rare earth 1,3-diketonates.[14,18,21] Crosby[18] has suggested that the energy transfer in the rare earth chelates occurs through the ligand triplet state. However, in Fe(HFA)$_3$ the ligand triplet state is 20 kcal lower in energy than the reactive charge-transfer state. Thus, transfer from the ligand triplet state is an unimportant process due to the photoreduction. The Fe(II) quantum yield of zero for irradiation at 450 nm indicates that this is the case. A reasonable explanation for the lack of laser emission in the transition metal 1,3-diketonates is the presence of reactive charge-transfer states at somewhat higher energies than the ligand triplet states.

The effect of water on the photochemical behavior of Fe(HFA)$_3$ is striking. The spectral data are consistent with coordinated water and a free anionic ligand molecule in 95% ethanol. However, conductance measurements show that there is not an appreciable concentration of charged species present. These facts are explained by outer-sphere complex formation, [Fe(HFA)$_2$(H$_2$O)$_2$]HFA, in the presence of sufficient quantities of water. Lister and Rivington[22] have shown that for the iron(III) aquo ion the stabilities of inner- and outer-sphere complexes are very similar for ligands which are anions of strong acids. Hexafluoroacetylacetone is a relatively strong acid. Formation of an outer-sphere complex may be expected to decrease the quantum yield of photoreduction, since it presents an efficient mechanism for the dissipation of the exciting energy into the solvent through hydrogen bonding.[14] The observed Fe(II) quantum yield for irradiation at 302 nm in 95% ethanol is 0.05 times the quantum yield in absolute ethanol.

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Reversible Addition of Carbon Monoxide to Tertiary Phosphine Complexes of Cobalt(II) and Their Reduction to Cobalt(I) Carbonyl Derivatives

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The reactions of carbon monoxide with complexes of the type Co(PR$_3$)$_2$X$_2$ (PR$_3$ = tertiary phosphine, X = mononegative ion) have been studied in C$_2$H$_4$Cl$_2$ and benzene. The reaction under ambient conditions leads to reversible formation of five-coordinate adducts Co(PR$_3$)$_2$(CO)X$_2$. The stability of the adducts is strongly influenced by the nature of R and X. The stability constants of the equilibria $\mathrm{Co(PR_3)_2X_2 + CO \rightleftarrows Co(PR_3)_2(CO)X_2}$ have been measured for several complexes in C$_2$H$_4$Cl$_2$ at 25°. Further reaction with carbon monoxide can lead to formation of the cobalt(I) derivatives Co(PR$_3$)$_2$(CO)$_2$X. The stability of the carbonyl adducts Co(PR$_3$)$_2$(CO)X$_2$ is discussed in terms of influence of the organic group R and is compared with that of the corresponding tertiary phosphine complexes Co(PR$_3$)$_3$X$_2$.

Introduction

As part of our investigations on the stability of low-spin five-coordinate complexes of cobalt(II) and nickel(II), we wish to report the results of studies on the reversible uptake of carbon monoxide by the four-coordinate complexes Co(P)$_2$X$_2$ (P = phosphorus atom of a tertiary phosphine; X = mononegative ion).[1–6]

By the reaction of carbon monoxide with benzene solutions of compounds of the type Co(PR$_3$)$_2$X$_2$ (PR$_3$ = P(C$_2$H$_5$)$_n$(C$_6$H$_5$)$_{3-n}$; X = Cl, Br, I), Booth and Chatt prepared the complexes Co(P(C$_2$H$_5$)$_3$)$_2$(CO)X$_2$. The phosphines P(C$_2$H$_5$)$_2$C$_6$H$_5$ or P(C$_6$H$_5$)$_2$C$_2$H$_5$ were reported to give rather intractable products.[7] Later, Sacco described the preparation of the compound Co(P(C$_6$H$_5$)$_3$)$_2$(CO)$_2$I by the reaction of Co(P(C$_6$H$_5$)$_3$)$_2$I$_2$ with carbon monoxide at 170 atm and 80°. He also obtained the corresponding bromide by indirect methods.[8] Finally, Hieber and Duchatsch obtained Co(P(C$_6$H$_5$)$_3$)$_2$(CO)$_2$X (X = Cl, Br, I) by mild halogenation of Na[Co(P(C$_6$H$_5$)$_3$)(CO)$_3$].[9]

Experimental Section

Starting Materials.—The complexes of the type Co(PR$_3$)$_3$X$_2$

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TABLE I

STABILITY CONSTANTS (K, M^{-1}) AT 25° FOR THE EQUILIBRIUM $Co(PR_3)_2X_2 + CO \rightleftarrows Co(PR_3)_2(CO)X_2$ IN $C_2H_4Cl_2$

X	$P(C_3H_7)_3$	$P(C_2H_5)_3$	$P(C_2H_5)_2C_6H_5$	$P(C_6H_5)_2C_2H_5$	$P(C_6H_5)_3$	$P(C_6H_{11})_3$
Cl	787 ± 31	1232 ± 63	203 ± 5	6.8 ± 0.2	<1[b]	<1[b]
Br	2317 ± 117	2476 ± 123	1020 ± 41	103 ± 2	2.9 ± 1[c]	<1[b]
NCS	*a*	*a*	*a*	503 ± 5	91 ± 2	22 ± 1

[a] Not determined. [b] Very small, not measurable. [c] Estimated error.

(X = NCS, CN) and $Co(PR_3)_2X_2$ (X = Cl, Br, I, NCS) were prepared by established methods.[1,3,7] The phosphines were prepared by standard Grignard syntheses. Compounds were handled in a drybox under argon.

$Co(P(C_6H_5)_3)_2(CO)_2I$.—The complex $Co(P(C_6H_5)_3)_2I_2$ (1.0 g) in benzene (50 ml) was shaken for 2 days under carbon monoxide at 80° (1 atm). After evaporation and filtration from a green insoluble material, the resulting yellow solution was further evaporated *in vacuo*, and enough *n*-hexane was added to start crystallization. The yellow-brown crystals which separated were collected and washed with ethyl ether. *Anal.* Calcd for $Co(P(C_6H_5)_3)_2(CO)_2I$: C, 59.55; H, 3.95; I, 16.56. Found: C, 59.2; H, 4.07; I, 16.3. The compound is diamagnetic.

Attempts to characterize the green insoluble material formed during the reaction have not been successful and only impure products with erratic composition have been obtained. The infrared spectra of these compounds showed that they did not contain carbon monoxide. *Anal.* Found: C, 47.2–50.2; H, 3.5–4.0; I, 26.6–28.6.

$Co(P(C_6H_5)_3)_2(CO)_2(CN)$.—A green solution of the complex $Co(P(C_6H_5)_3)_2Br_2$ (1.0 g) in 25 ml of methylene chloride (or benzene) was saturated with carbon monoxide and passed through a column of an anionic resin (Dowex 1-X4, 50–100 mesh) in CN^- form. The effluent was shaken with carbon monoxide at 1 atm and recycled through the same column. The operation was repeated until the effluent solution became yellow. The solution was reduced in volume, and the complex $Co(P(C_6H_5)_3)_2(CO)_2(CN)$ separated on cooling to 0° as yellow crystals which were washed with ethyl ether.

The crude product was rather impure with free phosphine and could not be recrystallized because of its low stability in solution. *Anal.* Calcd for $Co(P(C_6H_5)_3)_2(CO)_2(CN)$: C, 70.39; H, 4.54; N, 2.10. Found: C, 72.0; H, 4.79; N, 1.96. The compound is diamagnetic.

$Co(P(C_2H_5)_2C_6H_5)_2(CO)_2(CN)$.—This compound was prepared in a manner analogous to the complex $Co(P(C_6H_5)_3)_2(CO)_2(CN)$ using $Co(P(C_2H_5)_2C_6H_5)_2Br_2$ as starting material. The yellow solution was treated with *n*-hexane to yield a crude product which was rather unstable and could not be purified. *Anal.* Calcd for $Co(P(C_2H_5)_2C_6H_5)_2(CO)_2(CN)$: C, 58.35; H, 6.38; N, 2.96. Found: C, 56.3; H, 6.30; N, 3.03. The compound is diamagnetic.

Measurement of Equilibrium Constants.[10]—In a standard apparatus, a known volume (50–80 ml) of $C_2H_4Cl_2$ was saturated with carbon monoxide. Then a thin-walled glass ampoule containing a known weight of the cobalt complex (100–800 mg) was broken under stirring and the additional uptake of the gas (0.5–22 ml) was measured at constant pressure. The reaction vessel was a 100-ml flask with an outer jacket which was flattened on one side to accommodate a magnetic stirrer. The uptake of carbon monoxide was complete after about 1 min for the addition reaction

$$Co(P)_2X_2 + CO \rightleftarrows Co(P)_2(CO)X_2 \qquad (1)$$

For experimental reasons the measurements were carried out at a constant total pressure of 1 atm. Making allowance for the vapor pressure of the solvent (78 mm at 25°), the constant partial pressure of CO was 0.897 atm in the experiments in which pure carbon monoxide was introduced in the reaction vessel. In other experiments the pressure of CO was lowered by using mixtures containing an equal number of moles of CO and N_2 (the complexes do not react with nitrogen). In such experiments the partial pressure of CO was 0.449 atm before reaction with the cobalt complex.

That no side reaction occurred in the solutions under investigation during the time necessary for the equilibrium measurements was confirmed (i) by the absence in the infrared spectra of ν_{CO} absorptions other than those characteristic of the $Co(P)_2(CO)X_2$ complexes and (ii) by the fact that on changing the partial pressure of CO the mass law is not obeyed for equilibria different from (1).

The stability constants K were calculated by determining the concentrations of the two cobalt complexes from the millimoles of absorbed CO. In the experiments with pure carbon monoxide the millimoles of absorbed CO (which are equal to the millimoles of $Co(P)_3(CO)X_2$ formed) were directly obtained from the volume of absorbed gas. In the experiments in which carbon monoxide–nitrogen mixtures were used, the millimoles of reacted CO were obtained from the decrease of volume, taking into account the changes in the partial pressures of the two gases caused by the absorption of CO and the consequent changes in their solubilities.

The solubility of CO and that of N_2 in $C_2H_4Cl_2$ at 25° were measured using the Ostwald absorption coefficients, β's, determined by the method of Morrison and Billet.[11] The values found were $\beta_{CO} = 0.161$ and $\beta_{N_2} = 0.122$.

The single values of K were determined at 25° with a minimum of four runs in which the known concentration of the $Co(P)_2X_2$ complex was in the range 5×10^{-3}–5×10^{-2} M.

The values of K and their average errors are reported in Table I. An ideal behavior has been assumed for the investigated systems. This assumption is of course not strictly valid; however it can be safely used for the purpose of the discussion.

Infrared Spectra.—These were measured with a Perkin-Elmer Model 257 grating spectrometer. Positions of the infrared bands assigned to the ν_{CO} stretchings are given in Table II.

Results

Our results show that at room temperature and at 1 atm pressure, carbon monoxide reacts with the complexes $Co(PR_3)_2X_2$ ($PR_3 = P(C_2H_5)_3$, $P(C_3H_7)_3$, $P(C_2H_5)_2C_6H_5$, $P(C_6H_5)_2C_2H_5$; X = Cl, Br, I, NCS; $PR_3 = P(C_6H_5)_3$; X = Br, I, NCS; $PR_3 = P(C_6H_{11})_3$; X = NCS) in 1,2-dichloroethane solution or benzene giving first the adducts $Co(P)_2(CO)X_2$. Solutions containing the five-coordinate complexes $Co(PR_3)_3(CN)_2$ ($PR_3 = P(C_2H_5)_3$, $P(C_2H_5)_2C_6H_5$, $P(C_6H_5)_2C_2H_5$) react similarly. Under the same moderate conditions, the reaction may proceed further, with the reduction of cobalt(II) to cobalt(I) and formation of the $Co(P)_2(CO)_2X$ complexes. When this reduction reaction is sufficiently slow, the initial addition of CO to give $Co(P)_2(CO)X_2$ can be studied under equilibrium conditions.

Halogeno Complexes.—The chloro and bromo com-

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[10] The data have been deposited as Document No. NAPS-00970 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $3.00 for photocopies or $1.00 for microfiche. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

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TABLE II

THE C–O STRETCHING FREQUENCIES OF $Co(PR_3)_2(CO)X_2$ AND $Co(PR_3)_2(CO)_2X$ COMPLEXES (cm^{-1})[a]

	Cl	Br		I		NCS		CN	
PR_3	$Co(P)_2(CO)Cl_2$	$Co(P)_2(CO)Br_2$	$Co(P)_2(CO)_2Br$	$Co(P)_2(CO)I_2$	$Co(P)_2(CO)_2I$	$Co(P)_2(CO)(NCS)_2$	$Co(P)_2(CO)_2(NCS)$	$Co(P)_2(CO)(CN)_2$	$Co(P)_2(CO)_2(CN)$
$P(C_3H_7)_3$	1980	1980	1900, 1975	*d*		2000	1910, 1975 sh	*d*	
$P(C_2H_5)_3$	1985	1985	1905, 1975	1985	1905, 1975	2000	1910, 1975 sh	*d*	
$P(C_2H_5)_2C_6H_5$	1990	1990	1910, 1980[b]	1990	1910, 1975	2005	1920, 1980	2025	1925, 1980 1920, 1980, 2025 vw[c]
$P(C_6H_5)_2C_2H_5$	~1990	1990	...	1990	1910, 1975[b]	2010	1925, 1980	2030	1925, 1980[b]
$P(C_6H_5)_3$	...	~1995	...	2000	1920, 1980[b] 1915, 1980[c]	*e*	...	*d*	1935, 1985[b] 1930, 1985, 2025 vw[c]
$P(C_6H_{11})_3$	...	...	...	*d*		2005 sh	...	*d*	

[a] Spectra were recorded in $C_2H_4Cl_2$ solution, if not otherwise stated. [b] Benzene solution. [c] Nujol mull. [d] Not determined. [e] Not detected; probably covered by the ν_{CN} band.

plexes $Co(P)_2Cl_2$ or $Co(P)_2Br_2$ in $C_2H_4Cl_2$ solution at 25° react readily with carbon monoxide at 1 atm giving the addition products $Co(P)_2(CO)X_2$. The infrared spectra of the solutions show a band in the region of 1980–2000 cm^{-1} (Table II), which disappears when argon is bubbled through the solution and is assigned to the ν_{CO} stretching frequency of the complexes $Co(P)_2(CO)X_2$.[7] For the chloride complexes no further reaction could be observed within 5 hr under the same experimental conditions. However, the infrared spectra of the solutions containing the bromide complexes of $P(C_2H_5)_3$, $P(C_3H_7)_3$, and $P(C_2H_5)_2C_6H_5$ showed that the first addition of carbon monoxide was followed by another reaction, as indicated by the slow appearance of two new absorptions, a medium-intensity band in the 1975–1980-cm^{-1} region and a very strong band in the 1900–1910-cm^{-1} region. The infrared spectra of $C_2H_4Cl_2$ solutions of the complex $Co(P(C_2H_5)_3)_2Br$ after treatment with CO at 20° and 80 atm for 15 hr showed a very strong band at 1905 cm^{-1} in addition to a peak at 1985 cm^{-1} and one shoulder at 1975 cm^{-1}. The band at 1985 cm^{-1} was attributed to the ν_{CO} stretching in $Co(P(C_2H_5)_3)_2(CO)Br_2$. The two bands at 1975 and 1905 cm^{-1} were attributed to the ν_{CO} stretching in $Co(P(C_2H_5)_3)_2(CO)_2X$ by analogy with the spectra reported by Sacco[8] and Hieber[9] for the corresponding complex with $P(C_6H_5)_3$. Treatment of the complex $Co(P(C_2H_5)_2C_6H_5)_2Br_2$ with CO in benzene under the same conditions gave similar results. However, all chloride complexes were found to yield only the cobalt(II) adduct $Co(P)_2(CO)Cl_2$.

The above results show that the solutions of the complexes $Co(P)_2Br_2$ after treatment with carbon monoxide contain the compounds $Co(P)_2(CO)Br_2$ (in equilibrium with $Co(P)_2Br_2$ and CO) and $Co(P)_2(CO)_2Br$. When carbon monoxide is removed from the solutions, the first compound loses the coordinated CO molecule whereas the cobalt(I) adduct remains unaltered.

For the iodo complexes $Co(P)_2I_2$, the interaction of carbon monoxide in $C_2H_4Cl_2$ solutions readily gave the $Co(P)_2(CO)I_2$ complexes (ν_{CO} = 1985-2000 cm^{-1}). Fast reduction to complexes $Co(P)_2(CO)_2I$ followed as shown by the occurrence of two ν_{CO} absorptions in the regions of 1975–1980 and 1905–1920 cm^{-1}. In the case of the $P(C_6H_5)_3$ complex it was possible to isolate from benzene solutions the compound $Co(P(C_6H_5)_3)_2(CO)_2I$, which is one of the reaction products obtained by Sacco from $Co(P(C_6H_5)_3)_2I_2$ and CO at 80° (170 atm). The infrared spectrum in benzene of the compound shows one strong band at 1980 cm^{-1} and one very strong band at 1920 cm^{-1}. The reduction reactions are too fast to allow measurement of the equilibrium constants. However the course of the reactions may generally be followed by the steady decrease of the ν_{CO} absorption at 1985–2000 cm^{-1}, accompanied by an equivalent increase in the intensity of the ν_{CO} absorptions at 1975–1980 and 1905–1920 cm^{-1}.

Solutions of $Co(P(C_2H_5)_3)_2I_2$ in benzene or dichloroethane at 25° absorbed in less than 1 min 1 mol of carbon monoxide/mol of cobalt complex. At this stage of the reaction the ν_{CO} absorption at 1985 cm^{-1} attributed to $Co(P(C_2H_5)_3)_2(CO)I_2$ was very intense, whereas the absorptions of the two ν_{CO} bands of $Co(P(C_2H_5)_3)_2(CO)_2I$ at 1905 and 1975 cm^{-1} were very weak. No further absorption of carbon monoxide was observed, although the changes of the intensities of the ν_{CO} bands made clear that the concentration of the complex $Co(P(C_2H_5)_3)_2(CO)I_2$ steadily decreased and that of $Co(P(C_2H_5)_3)_2(CO)_2I$ increased. The changes in the infrared spectra were accompanied by a parallel change in the color of the solutions from red-brown to light green.

Experiments in which $Co(P(C_2H_5)_3)_2(CO)I_2$ replaced $Co(P(C_2H_5)_3)_2I_2$ as starting material confirmed that carbon monoxide was not absorbed during the course of the reactions which led to $Co(P(C_2H_5)_3)_2(CO)_2I$. The spectral changes of the solutions were identical with those described above. However, no reaction was observed in experiments in which carbon monoxide was replaced by nitrogen in the gas phase.

The reaction of carbon monoxide with $Co(P(C_6H_5)_3)_2I_2$ in benzene was much slower than that with $Co(P(C_2H_5)_3)_2I_2$. Under the same experimental conditions less than 0.5 mol of CO was absorbed by 1 mol of the cobalt complex in 24 hr.

Thiocyanate Complexes.—Four-coordinate complexes of the type $Co(P)_2(NCS)_2$ are known with the phosphines $P(C_6H_5)_3$, $P(C_6H_5)_2C_2H_5$, and $P(C_6H_{11})_3$.[5] The complexes with $P(C_3H_7)_3$ and $P(C_2H_5)_2C_6H_5$ are known only as the five-coordinate species $Co(P)_3(NCS)_2$, which in solution are in equilibrium with Co-

$(P)_2(NCS)_2$ and phosphine. The complexes with $P(C_2H_5)_3$ give conformational equilibria in solution.[12]

All of the thiocyanate complexes of Table II are reduced very rapidly in solution. Only for the complexes with $P(C_6H_5)_2C_2H_5$, $P(C_6H_5)_3$, and $P(C_6H_{11})_3$ the reduction rate is sufficiently slow to allow the stability constants of equilibrium 1 to be measured. The ν_{CO} stretching frequencies in the region of 2000–2010 cm^{-1} (Table II) are assigned to $Co(P)_2(CO)(NCS)_2$. The two additional bands, which appear in the regions of 1920 and 1980 cm^{-1}, can be tentatively assigned to the ν_{CO} stretching of the reduction products, possibly $Co(P)_2(CO)_2(NCS)$.

The infrared spectra in the range of 2040–2100 cm^{-1} of the $C_2H_4Cl_2$ solutions of $Co(P(C_6H_5)_2C_2H_5)_2(NCS)_2$ exhibit two absorptions at 2040 and 2060 cm^{-1} which are attributed to the asymmetric stretching (ν_{CN}) of the NCS group in the tetrahedral complex.[12] The spectra of the solutions treated with CO show a strong band at 2060 cm^{-1} but no absorption at 2040 cm^{-1}. In the 2000-cm^{-1} region one observes that the absorption at 2010 cm^{-1} (Table I) is very strong. This shows that the concentration of the compound $Co(P(C_6H_5)_2C_2H_5)_2(CO)(NCS)_2$ is relatively high. Thus, the band at 2060 cm^{-1} must be assigned to the ν_{CN} stretching in $Co(P(C_6H_5)_2C_2H_5)_2(CO)(NCS)_2$.

The spectra in the 2100-cm^{-1} region of benzene solutions of the five-coordinate complex $Co(P(C_2H_5)_2C_6H_5)_3(NCS)_2$ consist of one peak at 2040 cm^{-1} and of one sharp band at 2080 cm^{-1}. We assign the absorption band at 2040 cm^{-1} to the ν_{CN} stretching in the tetrahedral species $Co(P)_2(NCS)_2$. The band at 2080 cm^{-1} is attributed to the ν_{CN} stretching in the five-coordinate species $Co(P)_3(NCS)_2$.[3] The spectra of the solutions after treatment with CO showed two bands at 2090 and 2050 cm^{-1}. The band at 2090 cm^{-1} was assigned to the ν_{CN} stretching of $Co(P(C_2H_5)_2C_6H_5)_2(CO)_2(NCS)$. This assignment is supported by the fact that the ν_{CO} absorption at 1920 cm^{-1} (Table I) was very intense, showing that the complex was present in solution at a relatively high concentration. The intensity of the absorption at 2005 cm^{-1}, attributed to the ν_{CO} stretching of $Co(P)_2(CO)(NCS)_2$, was correspondingly weak. Addition of $P(C_2H_5)_2C_6H_5$ to the solution caused the intensity of the bands at 2005 and 2050 cm^{-1} to decrease. This behavior is consistent with an equilibrium

$$Co(P)_2(CO)(NCS)_2 + (P) \rightleftarrows Co(P)_3(NCS)_2 + CO$$

and allows one to assign the absorption at 2050 cm^{-1} to the ν_{CN} stretching in $Co(P(C_2H_5)_2C_6H_5)_2(CO)(NCS)_2$.

The infrared spectra of the thiocyanate complexes with $P(C_2H_5)_3$ or with $P(C_3H_7)_3$ after treatment with CO show two bands at 2065 and 2085 cm^{-1} which are attributed to $Co(P)_2(CO)(NCS)_2$ and $Co(P)_2(CO)_2(NCS)$, respectively.

The relatively strong intensity of the ν_{CN} absorptions in the carbonyl complexes indicates that they probably are isothiocyanates.[13] Accurate estimates of the integrated intensities were not possible owing to the strong overlapping with the bands of $Co(P)_2(NCS)_2$ or $Co(P)_3(NCS)_2$ complexes or because the concentrations of the single species were unknown. The ν_{CS} bands in the 600–850-cm^{-1} region could not be detected owing to the strong absorption of the solvents used.

Cyano Complexes.—The tendency of cobalt(II) to give the five-coordinate complexes $Co(P)_3(CN)_2$ is so strong that we could not use four-coordinate complexes $Co(P)_2(CN)_2$ as starting material. For this reason the addition of carbon monoxide was studied by using substrates $Co(P)_3(CN)_2$. The infrared spectra of the $C_2H_4Cl_2$ solutions of $Co(P(C_2H_5)_2C_6H_5)_3(CN)_2$, after treatment with CO, initially exhibit two absorptions of almost equal intensity at 2080 and 2105 cm^{-1}, which are attributed to the ν_{CN} stretching of $Co(P)_3(CN)_2$ and $Co(P)_2(CO)(CN)_2$, respectively.[4] An additional absorption at 2025 cm^{-1} can be tentatively attributed to the ν_{CO} stretching of $Co(P)_2(CO)(CN)_2$. After about 30 min at 25° two new bands begin to appear at 1980 and 1925 cm^{-1}; a third band appears as a shoulder at 2100 cm^{-1}. These absorptions are also found in the spectra of solid $Co(P(C_2H_5)_2C_6H_5)_2(CO)_2(CN)$ and $Co(P(C_6H_5)_3)_2(CO)_2CN$. The bands at 1980 and 1925 cm^{-1} are attributed to the ν_{CO} stretching and the band at 2100 cm^{-1} is attributed to ν_{CN} stretching. Similar spectral patterns were obtained by measuring the infrared spectra of benzene solutions containing $Co(P(C_6H_5)_2C_2H_5)_3(CN)_2$ and treated with carbon monoxide.

Thus, the infrared spectra indicate that the solutions treated with carbon monoxide contain compounds of the type $Co(P)_3(CN)_2$, $Co(P)_2(CO)(CN)_2$, and $Co(P)_2(CO)_2(CN)$. The ν_{CN} absorption at 2105 cm^{-1} and the ν_{CO} absorption at 2025 cm^{-1}, both characteristic of $Co(P)_2(CO)(CN)_2$, disappear when argon is bubbled through the solution or when the phosphine is added. At the same time the intensity of the ν_{CN} absorption at 2080 cm^{-1} of $Co(P)_3(CN)_2$ increases, while the intensity of the bands attributed to $Co(P)_2(CO)_2(CN)$ remains unchanged.

Discussion

On the basis of the results obtained one can draw the following conclusions. Carbon monoxide reacts with the halides or pseudohalide complexes of cobalt(II), $Co(P)_2X_2$, at room temperature and at a moderate pressure, giving first the five-coordinate complexes $Co(P)_2(CO)X_2$. The addition of CO is generally accompanied by another reaction which leads to reduction in the oxidation state of cobalt. This latter reaction appears to be favored, either in thermodynamic or in kinetic sense, by the presence in the complex of readily oxidizable anionic ligands. The results with the thiocyanato and bromide complexes indicate that the reduction reaction may also depend critically upon the nature of the organic phosphine.

A tentative interpretation of the reduction mechanism can be based on the following observations derived from

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the experiments with the iodo complexes: (i) the first product in the reactions of carbon monoxide with the complexes $Co(P)_2X_2$ is $Co(P)_2(CO)X_2$; (ii) the cobalt(I) complexes $Co(P)_2(CO)_2X$ are formed from $Co(P)_2(CO)X_2$ only in the presence of carbon monoxide, although apparently this is not absorbed during the reduction step. These observations suggest that the first step of the reduction reaction is a preequilibrium involving the addition of one CO molecule to the five-coordinate $Co(P)_2(CO)X_2$ to give the six-coordinate intermediate $Co(P)_2(CO)_2X_2$. One can speculate that the intermediate may react with $Co(P)_2(CO)X_2$ by a redox bridging mechanism yielding $Co(P)_2(CO)_2X$ and unstable carbonyl cobalt(III) complexes. One molecule of carbon monoxide must be released in the decomposition of these unstable complexes. However, more detailed investigation is necessary in order to elucidate the reduction mechanism, and this is beyond the scope of the present work.

The data in Table I show that the stability of the carbonyl adducts $Co(P)_2(CO)X_2$ is influenced also by the nature of the anionic ligand X, the order of stability being $Cl < Br < NCS$. It is interesting to note that the five-coordinate complexes $Co(P)_3X_2$ are unstable when $X = Cl$ or Br but are stable with most phosphines when $X = NCS$. With the phosphines $P(C_6H_5)_3$ or $P(C_6H_{11})_3$ the carbonyl complexes $Co(P)_2(CO)(NCS)_2$ are fairly stable, whereas the compounds $Co(P)_3(NCS)_2$ with the same phosphines are quite unstable. Thus cobalt(II) carbonyl adducts appear to be definitely more stable than the corresponding tris-phosphine adducts. Since carbon monoxide is a better π bonder than tertiary phosphines, these results show the importance of π bonding in favoring stability for five-coordination. However, consideration of the stability order, resulting from the horizontal rows of Table I, suggests that the balance of the σ and π electronic effects is more delicate than it might appear from this last conclusion.

The data of Table I show that the stability of the five-coordinate compounds decreases on replacing *n*-alkyl by phenyl or cyclohexyl groups in the phosphines. The trends in the values of K can be considered to be indicative of the actual changes in the stability of the complexes since the differences in solvation effects for the systems studied are very likely to be negligible. One might be tempted to attribute the observed trend in the horizontal rows of Table I to the increasing importance of steric factors as *n*-alkyl groups are replaced by more bulky phenyl or cyclohexyl groups. However, this factor should not be of critical importance in the present case. Thermodynamic studies in the equilibria $M(P)_3X_2 \rightleftarrows M(P)_2X_2 + (P)$ ($M = Co(II), X = NCS; M = Ni(II), X = CN$) in different solvents show that when the stability of the complexes $M(P)_3X_2$ decreases on replacing *n*-alkyl with phenyl or cyclohexyl groups in the phosphines, the decrease is due to less favorable enthalpy changes.[5,6] Such results indicate that the nature of the metal–ligand bonds, and not the bulkiness of the phosphines, is the factor that governs the stability of the five-coordinate $M(P)_3X_2$ adducts. The same explanation can best account for the trends observed in the horizontal rows of Table I, making the reasonable assumption that bulkiness of the phosphines is a factor even less important in complexes of the type $Co(P)_2(CO)X_2$ which contain only two phosphine molecules. Considering the electronegativities of the C_6H_5 and C_6H_{11} groups, the phosphine $P(C_6H_5)_3$ represents the best π bonder and the weakest σ bonder and the reverse is true for $P(C_6H_{11})_3$. However, the five-coordinate complexes are most stable with the *n*-alkyl phosphines. This comparison suggests that σ- and π-electronic effects must be properly balanced in order to give the maximum stability for five-coordination.

A final remark regards the instability of the complexes $Ni(P)_2(CO)X_2$. Booth and Chatt reported that the complexes $Ni(P)_2X_2$ do not form adducts with carbon monoxide. We find that in benzene solution even a substrate such as $Ni(P(C_2H_5)_2C_6H_5)_2(CN)_2$, which yields a stable $Ni(P)_3(CN)_2$ adduct,[6] does not show any measurable tendency to coordinate a CO molecule. By contrast, we also find that the tris-phosphine complexes $Co(P)_3(CN)_2$ react reversibly with CO in benzene solution giving the equilibrium $Co(P)_3(CN)_2 + CO \rightleftarrows Co(P)_2(CO)(CN)_2 + (P)$. We believe that the instability of the complexes $Ni(P)_2(CO)X_2$ is only a particular aspect of the known reluctance of nickel(II) to bind CO molecules.[14] Since other d^8 metals ions such as Co(I), Pd(II), or Pt(II) give stable compounds containing carbon monoxide, it is possible that this instability is due to the low energy and reduced size of the 3d orbitals in nickel(II), which causes π bonding with CO to become unfavorable.

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