ligand PPh_2^-, via intra- or intermolecular acid elimination, has been previously reported.[9]

It should be noted that with other secondary phosphines, such as $HP(C_2H_5)_2$, $HP(CH_3)C_6H_5$, or $HP(C_2H_5)C_6H_5$, the $CoY_2 \cdot 6H_2O$ salts give the low-spin five-coordinate complexes $[Co(HPR_2)_5]Y_2$ in alcoholic solutions.[10] If the reaction between $HPPh_2$ and CoY_2 is carried out in acetone, instead of alcohols, no formation of the phosphido derivative is observed, and from the red solutions only red tenacious oils are recovered. However, the visible spectra of these products in acetone show a spectral pattern, which is effectively consistent with the presence of a $[Co(HPPh_2)_5]^{2+}$ chromophore.

The $[Co(PPh_2)(HPPh_2)_3]Y$ complexes, if kept under an atmosphere of H_2, slowly afford the dihydrido derivatives *cis*-$[CoH_2(HPPh_2)_4]Y$. Quite similarly, on treating alcoholic suspensions of $[Co(PPh_2)(HPPh_2)_3]Y$ with a slight excess of HX (X = halogen or pseudohalogen), another class of hydrido complexes of cobalt(III) of the type $[CoHX(HPPh_2)_4]Y$ can be obtained. The presence of the hydrido group was inferred from a CCl_4 test and from IR spectra, which exhibit one very weak band, attributable to the Co–H stretch, in the 1950–2050 cm^{-1} region. The Co–H stretching frequency is sensitive to the anionic ligand X and decreases in the sequence Br (2045 cm^{-1}) > I (2030 cm^{-1}) > NCS (2020 cm^{-1}) > CN (1980 cm^{-1}), thus suggesting a trans octahedral structure for the cation.[11]

The low solubility and the low stability in solution of the $[CoHX(HPPh_2)_4]Y$ complexes have prevented a general NMR investigation. Only in the case of $[CoHBr(HPPh_2)_4]ClO_4$ and for freshly prepared $CDCl_3$ solutions was one hydrido resonance observed, at room temperature as a symmetrical quintet at 30.8 ppm (J_{PH} = 51 Hz), thus confirming the trans stereochemistry.

The preparation of *trans*-$[CoHX(HPPh_2)_4]Y$ with X = Br, I, NCS can be simply made by gently warming alcoholic solutions containing equimolar amounts of CoY_2 and CoX_2 in the presence of an excess of phosphine. The green mixtures initially formed slowly turn color and deposit the yellow hydrido complexes. If the reaction is carried out at low temperature (0 °C), no formation of the hydrido complexes occurs, and the green products can be isolated. In the case of X = Br, it was possible to characterize the green complex as the low-spin five-coordinate $[CoBr(HPPh_2)_4]Y$ (see Table I). It is noteworthy that, under the same conditions, other secondary phosphines react with the alcohol solutions of "CoBrY" to yield $[CoBr(HPR_2)_4]Y$ (HPR_2 = $HP(C_2H_5)_2$, $HP(CH_3)Ph$, and $HP(C_2H_5)Ph$).[10] In this case no evidence of hydrido derivatives has been observed even after prolonged warming.

Finally, $CoBr_2$ has been reported[2] to react in hot methanol with $HPPh_2$ to give the well-known $CoBr_2(HPPh_2)_3$ as the major product. From the mother liquor was also obtained a yellow complex to which binuclear structure $[CoBr(HPPh_2)_4]_2Br_2$ was attributed. We find that the IR spectra of this product show a weak band in the ν_{CoH} region and this fact, together with the observed diamagnetism, indicates that the complex actually must be the cobalt(III) hydrido derivative *trans*-$[CoHBr(HPPh_2)_4]Br$.

The mechanism of the formation of the cations *trans*-$[CoHX(HPPh_2)_4]^+$ and *cis*-$[CoH_2(HPPh_2)_4]^+$ from cobalt(II) is difficult to understand. Doubtless the peculiar reducing properties of diphenylphosphine play a determining role in these reactions, which do not occur even with the homologous phosphines HPRPh (R = CH_3, C_2H_5).

Finally, it must be noted that the route which leads to these hydrido derivatives apparently becomes unfavorable in the presence of coordinating anions, which are able to stabilize the initially formed cobalt(II) adduct.

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Registry No. $[CoHBr(HPPh_2)_4]ClO_4$, 65338-74-1; $[CoHBr(HPPh_2)_4]BF_4$, 65293-50-7; $[CoHI(HPPh_2)_4]ClO_4$, 65293-48-3; $[CoHI(HPPh_2)_4]BF_4$, 65293-47-2; $[CoH(NCS)(HPPh_2)_4]ClO_4$, 65293-45-0; $[CoH(NCS)(HPPh_2)_4]BF_4$, 65293-44-9; $[CoH(CN)(HPPh_2)_4]BF_4$, 65293-42-7; $[Co(PPh_2)(HPPh_2)_3]ClO_4$, 65293-40-5; $[Co(PPh_2)(HPPh_2)_3]BF_4$, 65293-61-0; $[CoBr(HPPh_2)_4]BF_4$, 65293-60-9; *cis*-$[CoH_2(HPPh_2)_4]ClO_4$, 56648-28-3.

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Wall Reactions and Thermodynamics in the Decomposition of Low-Pressure VCl_4 in an Electrical Discharge

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Recently Fisa, Revol, and Marchessault[1] (FRM) published results indicating that the reaction

$$2VCl_4(g) \rightarrow 2VCl_3(s) + Cl_2(g)$$

takes place very rapidly in their electrical discharge at an optimum total pressure of 0.1–1 mmHg with the formation of crystals of much smaller size and hence greater catalytic activity than those of other reaction procedures.

Using one set of older[2] thermodynamic data, $K = 0.52$ and 0.25 for the above reaction at 160 and 180 °C, respectively, FRM concluded that "the ease of decomposition in the discharge appears surprising in the light of known thermodynamic data" and suggested that excited species may interact with the reactor wall by collision and subsequent absorption.

We suggest that mean free path considerations make such a simple mechanstic interpretation unlikely; for conditions ranging from 250 to 5000 °C and 0.1 to 1.0 mmHg the mean free path varies between 10^{-4} and 10^{-2} cm, with their experiments performed in a discharge tube of ca. 2.8-cm inside diameter.

Critically reviewed thermodynamic data[3,4] and reasonable estimates[5] of C_p for $VCl_4(g)$, the last a relatively minor ingredient in determining the temperature dependence of K, have been used to determine for the above reaction

$$\ln K = -47.89 + 1.31 \times 10^{-3}T + 2.694 \ln T + 1.423 \times 10^4/T - 3.4 \times 10^3/T^2$$

by fitting the C_p data[5] to the empirical form[4] $C_p = A + BT$

Table I. Calculated Equilibrium Percent Decomposition (P_{tot} = 1 mmHg[a]) for $VCl_4(g) \rightarrow VCl_3(s) + {}^1/_2Cl_2(g)$

Temp, °C	This work	FRM[1]
120	23	
140	6	
160	2	0.1
180	0.5	0.07
200	0.1	

[a] If P_{tot} = 0.1 mmHg, the middle column entries become 3, 0.7, 0.2, 0.05, and 0.01%, respectively.

$+ C/T^2$. The results of these calculations are summarized in Table I.

It is seen that the correct thermodynamic data are much more conducive to a traditional interpretation of the reaction in terms of thermodynamics. The older data[2] are immediately suspect as they lead to a ΔH of −14 kcal for the reaction rather than our value of −25 or −26 kcal.[3]

Presumably the virtue of carrying out this or other reactions in an electrical discharge is that chemical bonds are broken, and hence activation energies are readily supplied, by a nonthermal process in an extremely complex system with a number of nonequilibrated degrees of freedom; yet with the great number of collisions occurring as the reactive species move toward the wall one expects rather rapid thermalization to take place at these pressures.

We have checked whether or not other possible reaction products, for which good thermodynamic data are available, might be present at equilibrium in more than trivial amounts by means of the computer programs of Gordon and McBride.[6-9] The other compounds considered were V(s), $VCl_2(s)$, $VCl_4(l)$, V(g), and Cl(g). At complete heterogeneous phase and chemical equilibria at these temperatures and pressures, the three condensed-phase substances had mole fractions identically zero while V(g) and Cl(g) had completely negligible mole fraction.

It would have been appealing to examine the equilibrium concentrations of VCl(s), VCl(g), $VCl_2(g)$, and $VCl_3(g)$ except that the appropriate thermodynamic data could not be located in the literature, in contrast to results for the corresponding chlorides of Ti[8,10] and Cr.[10]

We rationalize this omission as follows. Since these compounds are unstable enough to thus far avoid having their thermodynamic properties determined, they should have chemical potentials at least as high as those of other related compounds whose properties have been determined and which themselves turn out to be present at vanishingly small concentrations.

Acknowledgment. We are grateful to G. R. Eaton for bringing the work of FRM to our attention.

Registry No. VCl_4, 7632-51-1.

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Carbonyl Ligand Mobility in the C_s Isomer of $Cp_3Rh_3(CO)_3$

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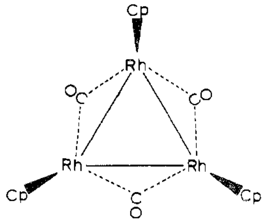
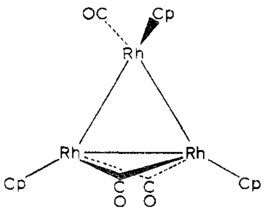
Two crystalline compounds, isolated after extended photolysis of $CpRh(CO)_2$ ($Cp = \eta^5$-C_5H_5), were characterized by x-ray diffraction as isomeric forms (**1** and **2**) of $Cp_3Rh_3(CO)_3$.[1-3] We[4] recently reported ^{13}C NMR spectra showing that the C_{3v} structure of **1** is maintained in solution and that the carbonyl ligands scramble over the Rh_3 triangle. We predicted that the carbonyls in C_s structure **2** also would scramble, without interconversion of **2** with **1**. At that time, a sample of isomer **2** was not available, but we have since developed a good procedure for preparing **2** and therefore have attempted to determine its solution structure and carbonyl ligand mobility.



1



2

Experimental Section

C_{3v}-$Cp_3Rh_3(CO)_3$ was prepared as previously described.[4] About 50% ^{13}CO-enriched $CpRh(CO)_2$ was used to prepare samples for ^{13}C NMR. Infrared spectra were recorded on a Perkin-Elmer 467 or Beckman IR-12 spectrophotometer and calibrated with polystyrene. ^1H NMR spectra were recorded on a Varian HA-100 instrument (100 MHz). ^{13}C NMR spectra were obtained on a Varian XL-100 (25.16 MHz) spectrometer with solutions containing ~0.015 M $Cr(acac)_3$. The solvents used were CD_2Cl_2/CH_2Cl_2, $CD_2Cl_2/CHFCl_2$, or $C_2H_3Cl/CHFCl_2$ (external ^{19}F lock), depending on the temperature range. Chemical shifts were measured relative to CH_2Cl_2 = 54.6 ppm downfield from Me_4Si. Field-desorption mass spectra were obtained on a Varian 731 mass spectrometer by Mr. J. C. Cook, Jr. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences. A medium-pressure 450-W mercury lamp (Hanovia) and a quartz apparatus (Ace Glass) were used for photolysis.

Preparation of C_s-$Cp_3Rh_3(CO)_3 \cdot {}^1/_2C_6H_{12}$. A solution of C_{3v}-$Cp_3Rh_3(CO)_3 \cdot {}^1/_2CH_2Cl_2$ (93 mg, 0.15 mmol) in 300 mL of benzene was deoxygenated by bubbling through a stream of N_2 for 15 min and then photolyzed for 4 h under a continuous N_2 flush. The solvent was removed on a rotary evaporator and the residue extracted with cyclohexane until the extracts were no longer green. The cyclohexane-insoluble residue was largely the C_{3v} isomer. The cyclohexane solution was taken to dryness, keeping the temperature below 40 °C. The residue was washed with pentane (3 × 5 mL) and vacuum dried. Yield: 70 mg, 0.11 mmol, 75%. Anal. Calcd for $C_{21}H_{21}O_3Rh_3$: C, 40.02; H, 3.36. Found: C, 40.19; H, 3.44. Mass spectrum (field desorption): *m/e* 588, M^+. ^1H NMR ($CDCl_3$; +25 and −50 °C): τ 4.48 (s, br), η^5-C_5H_5. IR(ν_{CO}) (cm^{-1}): 1973 (s), 1967 (s), 1851 (w), 1797 (m), 1748 (s) in KBr (lit.[2] 1973 (vs), 1827 (m), 1794 (m), 1744 (vs)); 1975 (m), 1827 (w), 1778 (m) in C_6H_{12}; 1961 (s), 1809 (w), 1761 (s) in CH_3CN; similar three-band spectra in CH_2Cl_2 and THF.

Results

Direct UV photolysis of a deoxygenated benzene solution of C_{3v}-$Cp_3Rh_3(CO)_3$ (**1**) provides C_s-$Cp_3Rh_3(CO)_3$ (**2**) in high yield. The usual chromatographic methods cannot be used to isolate **2**, since it decomposes on polar supports, largely into **1**. However, **2** is soluble in cyclohexane (whereas **1** is not)

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