rendering the pairwise equivalence of the methyl groups as demanded by C_2 symmetry (see Figures 2 and 3).

Experimental Section

General Procedures. $Mo_2(NMe_2)_6$ was prepared as previously described.[1] ^1H NMR spectra (100 MHz) were obtained from a Varian XL-100 spectrometer equipped with a variable-temperature probe. ^1H NMR spectra (270 MHz) were obtained with the courtesy of the Department of Chemistry, Yale University. ^1H chemical shifts are reported as ppm downfield from Me_4Si. Temperatures were calibrated with methanol or ethylene glycol.

Infrared spectra were obtained from Nujol mulls between CsI plates using a Perkin-Elmer IR 283 spectrophotometer.

Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, using drybox sampling techniques. Mass spectra were obtained on an AEI MS9 by direct insertion with probe temperatures of 100–120 °C.

All preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere or in vacuo, using standard Schlenk-type techniques. Samples were stored and handled in a Vacuum Atmospheres Dri Lab system.

Preparation of Bis(dimethylamido)tetrakis(*N*,*N*-dimethylcarbamato)dimolybdenum, $Mo_2(NMe_2)_2(O_2CNMe_2)_4$. $Mo_2(NMe_2)_6$ (1.66 mmol) was dissolved in hexane (30 mL). CO_2 (10.0 mmol, 6 equiv) was condensed into the reaction flask at liquid-nitrogen temperature. Upon warming to room temperature, a yellow solid precipitated out of solution. The reaction mixture was stirred for an additional 30 min and a yellow solid, $Mo_2(NMe_2)_2(O_2CNMe_2)_4$ (500 mg), was collected by filtration. Anal. Calcd for $Mo_2(NMe_2)_2(O_2CNMe_2)_4$: C, 30.39; H, 5.74; N, 13.29. Found: C, 30.57; H, 5.83; N, 13.01. $Mo_2(NMe_2)_2(O_2CNMe_2)_4$ is soluble in toluene; however, decomposition occurs over a period of 1–2 days.

Infrared data (Nujol mull between CsI plates): 360 (w, br), 396 (m), 449 (s), 568 (m), 610 (w), 641 (m), 645 (sh), 663 (s), 675 (m), 776 (m), 784 (m), 792 (m), 841 (w), 953 (s), 1039 (m), 1061 (vw), 1150 (vw), 1171 (vw), 1238 (s), 1262 (s), 1409 (vs), 1578 (vs) cm^{-1}.

A parent ion at *m*/*e* 632 in the mass spectrum corresponds to $Mo_2(NMe_2)_2(O_2CNMe_2)_4^+$ (based on ^{96}Mo).

Reaction of alkane solutions of $Mo_2(NMe_2)_6$ with $^{13}CO_2$ yielded the ^{13}C-labeled compound. ^1H NMR spectra identified the peaks at $\delta = 5.01$ and 3.32 ppm (relative to Me_4Si) as assignable to $MoNMe_2$ due to the absence of ^{13}C coupling; for $O_2{}^{13}CNMe_2$ ligands, $^3J_{^{13}C-H} = 3$ Hz.

Reaction of $Mo_2(NMe_2)_6$ with CO_2 in the Presence of $HN(CD_3)_2$. $Mo_2(NMe_2)_6$ (1.47 mmol) was dissolved in hexane (25 mL). CO_2 (6.0 mmol) and $HN(CD_3)_2$ (6.0 mmol) were condensed into the reaction flask at liquid-nitrogen temperature. Upon warming to room temperature, a yellow solid precipitated out of solution and was collected by filtration. IR and mass spectral data indicate the formation of the species $Mo_2(NMe_2)_2(O_2CN(CH_3)_2)_{4-x}(O_2CN(CD_3)_2)_x$. Exchange of free amine with $Mo-NMe_2$ groups was not observed.[2]

Infrared data (Nujol mull between CsI plates): 268 (m), 362 (m), 398 (m), 451 (s), 572 (m), 586 (w), 623 (m), 646 (s), 661 (s), 673 (s), 778 (s), 786 (s), 794 (s), 842 (m), 892 (w), 948 (s), 956 (s), 1040 (m), 1063 (m), 1097 (s), 1150 (m), 1163 (m), 1236 (s), 1262 (s), 1395 (m), 1408 (s), 1532 (s), 1576 (vs), 2070 (m), 2203 (m) cm^{-1}.

A parent ion pattern at *m*/*e* 640 in the mass spectrum was consistent with the formation of $Mo_2(NMe_2)_2(O_2CN(CH_3)_2)_{4-x}(O_2CN(CD_3)_2)_x$, where $x = 2$.

^1H NMR spectra (−60 °C) indicated the ratio of dimethylamido groups ($\delta = 5.01, 3.32$ ppm relative to Me_4Si) to dimethylcarbamato groups ($\delta = 2.92, 2.74, 2.46$ ppm relative to Me_4Si) was 2:2; cf. the 2:4 ratio in the protio complex.

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Registry No. I, 64728-46-7; $Mo_2(NMe_2)_2(O_2CN(CH_3)_2)_2(O_2CN(CD_3)_2)_2$, 64825-43-0; $Mo_2(NMe_2)_6$ (salt form), 33851-48-8; $Mo_2(NMe_2)_6$ (complex form), 51956-20-8; $HN(CD_3)_2$, 14802-36-9; CO_2, 124-38-9.

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Cationic Hydrido Complexes of Cobalt(III) with Diphenylphosphine

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Studies on the hydrido complexes of cobalt containing phosphorus ligands are of considerable current interest in homogeneous catalytic reactions. We have recently briefly reported[1] that hydrido derivatives of the type *cis*-$[CoH_2(P)_4]^+$ (P = tertiary or secondary phosphines) can be easily obtained by treatment at ambient conditions of alcoholic solutions of the phosphines and cobalt(II) salts of weakly coordinating anions with dihydrogen. The success of this synthetic procedure is very sensitive to changes in the phosphine ligands, and by this route we were able to prepare the *cis*-dihydrido complexes only with dimethylphenyl-, trimethyl-, and diphenylphosphine.

With the aim of elucidating the mechanism and the stoichiometry of the formation of the *cis*-$[CoH_2(P)_4]^+$ complexes, we have examined in some detail the reactions of diphenylphosphine with cobalt(II) salts of the type CoY_2 and "CoXY", where Y are weakly coordinating anions (ClO_4^-, BF_4^-) and X are halides or pseudohalides (Br^-, I^-, NCS^-, CN^-). In the course of the investigation we obtained a new series of hydrido complexes of the type *trans*-$[CoHX(HPPh_2)_4]Y$ and also the unusual cobalt(II) complexes $[Co(PPh_2)(HPPh_2)_3]Y$. Previously, it was reported[2] that diphenylphosphine reacts with methanolic solutions of cobalt bromide to give three different compounds: the five-coordinate $CoBr_2(HPPh_2)_3$, the tetrahedral $[CoBr(HPPh_2)_3]Br$, and a yellow diamagnetic $[CoBr(HPPh_2)_4]_2Br_2$. Our results show that this last compound should be reformulated as the hydrido derivative $[CoHBr(HPPh_2)_4]Br$.

This paper is part of a broad chemical study on the properties of transition-metal complexes with secondary phosphines.[3]

Experimental Section

Syntheses and handling of the complexes were carried out in the absence of air. The published procedure[4] was used to prepare diphenylphosphine. $CoY_2 \cdot H_2O$ (Y = ClO_4, BF_4) were prepared from cobalt carbonate and aqueous HY. Microanalyses were performed by Mr. L. Turiaco, Istituto di Chimica Analitica, University of Padua. IR and visible spectra were recorded on a Perkin-Elmer 457 and on an Optica CF4R instrument, respectively. IR spectra of all described complexes show weak bands in the 2300–2360-cm^{-1} region, attributable to P–H stretching of the coordinated phosphines. Conductivity data were determined using an LKB conductance bridge. Magnetic susceptibilities were measured by the standard Gouy method and NMR spectra were taken using a Bruker 90-MHz spectrometer.

***cis*-$[CoH_2(HPPh_2)_4]ClO_4$.** (a) $HPPh_2$ (1.9 g, 10 mmol) was added to a solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.7 g, 2 mmol) in isopropyl alcohol (30 mL). The mixture was stirred for 48 h under an atmosphere of

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Table I. Analytical Data and Physical Constants

Compd	Mp[a]	Λ_M[b]	% C Calcd	% C Found	% H Calcd	% H Found	% other Calcd	% other Found
$[CoHBr(HPPh_2)_4]ClO_4$	155[c]	93	58.58	58.47	4.61	4.61	8.13 (Br)	7.91 (Br)
$[CoHBr(HPPh_2)_4]BF_4$	206	102	59.32	59.31	4.63	4.51	8.22 (Br)	8.30 (Br)
$[CoHI(HPPh_2)_4]ClO_4$	162[c]	82	55.91	54.84	4.40	4.50	12.29 (I)	12.55 (I)
$[CoHI(HPPh_2)_4]BF_4$	197	80	56.61	57.78	4.45	4.63	12.46 (I)	12.76 (I)
$[CoH(NCS)(HPPh_2)_4]ClO_4$	109[c]	90	61.16	60.26	4.71	4.58	1.45 (N)	1.45 (N)
$[CoH(NCS)(HPPh_2)_4]BF_4$	143	97	61.98	60.85	4.78	4.90	1.48 (N)	1.50 (N)
$[CoH(CN)(HPPh_2)_4]BF_4$	171	107	62.83	62.34	4.95	4.76	1.50 (N)	1.40 (N)
$[Co(PPh_2)(HPPh_2)_3]ClO_4$[d]	138[c]	89	63.91	63.48	4.81	4.86	6.53 (Co)	6.7 (Co)
$[Co(PPh_2)(HPPh_2)_3]BF_4$[e]	119	92[f]	64.31	63.91	4.87	4.96	6.61 (Co)	6.5 (Co)
$[CoBr(HPPh_2)_4]BF_4$[g]	113	c	59.38	58.50	4.46	4.45	8.23 (Br)	8.35 (Br)

[a] °C, in sealed tube under nitrogen. [b] Molar conductance values (S cm^2 mol^{-1}) for 10^{-3} M nitromethane solutions at 25 °C. [c] Decomposes. [d] μ_{eff} (20 °C) = 2.25 μ_B. % P: calcd, 13.79; found, 13.7. [e] μ_{eff} (20 °C) = 2.15 μ_B. % P: calcd, 13.93; found, 13.9. [f] Plot of Λ_e vs. $N^{1/2}$ in nitromethane at 25 °C gives, according to the Onsager equation $\Lambda_0 = \Lambda_e + AN^{1/2}$, Λ_0 = 82.5 S cm^2 $equiv^{-1}$ and A = 175 S cm^2 $equiv^{-1}$ $N^{-1/2}$. [g] μ_{eff} (20 °C) = 2.30 μ_B.

hydrogen. The pale yellow precipitate formed was filtered off, washed with isopropyl alcohol, and dried in vacuo (yield 80%).

(b) A suspension of $CoH(HPPh_2)_4$ (1.6 g, 2 mmol) in ethanol (20 mL) was treated with aqueous $HClO_4$ (2 mmol). The mixture was stirred until the red original product turned pale yellow. The precipitate was filtered, washed with ethanol, and dried in vacuo (yield 80%).

$[Co(PPh_2)(HPPh_2)_3]Y$ (Y = ClO_4, BF_4). $CoY_2{\cdot}6H_2O$ (1 mmol) was dissolved in isopropyl alcohol (20 mL) and $HPPh_2$ (0.9 g, 5 mmol) was added. After 30 min of stirring, yellow crystals precipitated which were washed with isopropyl alcohol and recrystallized from dichloromethane–isopropyl alcohol (yield 70%).

***trans*-$[CoHX(HPPh_2)_4]Y$ (Y = ClO_4, BF_4; X = Br, I, NCS).** (a) $HPPh_2$ (1.9 g, 10 mmol) was added to an isopropyl alcohol solution (20 mL) containing equimolar amounts of $CoY_2{\cdot}6H_2O$ (1 mmol) and the appropriate cobalt(II) halide or thiocyanate. After being stirred for 10 min at 40 °C, the green mixtures turned yellow. The yellow crude products (brown in the case of X = I) were removed by filtration, washed with isopropyl alcohol, and dried in vacuo (yield 50–70%).

(b) The halides were also obtained by addition of the corresponding acid HX in aqueous solution (3 mmol) to a suspension of $[Co(PPh_2)(HPPh_2)_3]Y$ (2 mmol) in isopropyl alcohol (20 mL). Ready reaction occurs with formation of the yellow product (yield 80%). ν_{CN} for $[CoH(NCS)(HPPh_2)_4]BF_4$ falls at 2090 cm^{-1}.

***trans*-$[CoH(CN)(HPPh_2)_4]BF_4$.** To a suspension of $[Co(PPh_2)(HPPh_2)_3]BF_4$ (0.9 g, 1 mmol) in isopropyl alcohol (20 mL), in which also 50 mg of sodium cyanide (1 mmol) was dissolved, aqueous HBF_4 (1 mmol) was added. On stirring, the red suspension, which was initially obtained, turned pale yellow within 24 h. The pale yellow crystals were removed by filtration washed with isopropyl alcohol, and dried in vacuo (yield 80%). ν_{CN} falls at 2100 cm^{-1}.

$[CoBr(HPPh_2)_4]BF_4$. A 0.22-g sample of anhydrous cobalt bromide (1 mmol) and 0.34 g of $Co(BF_4)_2{\cdot}6H_2O$ (1 mmol) were dissolved in 20 mL of isopropyl alcohol, and the solution was cooled to 0 °C. To this solution was added 1.9 g of $HPPh_2$ (10 mmol) and the resulting green mixture was briefly stirred at 0 °C. The green crystals were rapidly filtered and washed with cooled isopropyl alcohol. The compound was not purified; attempted recrystallization from dichloromethane–isopropyl alcohol readily gave the corresponding $[CoHBr(HPPh_2)_4]BF_4$ derivative described above (yield 50%).

Results and Discussion

The diphenylphosphine–$CoY_2{\cdot}6H_2O$ (Y = ClO_4, BF_4) system in isopropyl alcohol (molar ratio 5:1) slowly absorbs hydrogen at room temperature and pressure to yield the yellow $[CoH_2(HPPh_2)_4]Y$ compounds.[1b] For the cation, a cis arrangement of the two hydride groups is inferred from IR spectra, which show two bands in the Co–H stretching region, at 1910 and 1945 cm^{-1}. The same complexes could be easily obtained by protonation of $[CoH(HPPh_2)_4]$[5] with mineral acids containing weakly coordinating anions (i.e., fluoboric and perchloric acid).

The complexes *cis*-$[CoH_2(HPPh_2)_4]Y$ are fairly unstable and slowly give green products in the solid state; when dissolved in common organic solvents under an inert atmosphere, they give green solutions with hydrogen evolution. By exposure of these solutions to hydrogen, the original yellow color is restored, thus suggesting the occurrence of a reductive elimination–oxidative addition equilibrium of the type

$$[CoH_2(HPPh_2)_4]^+ \rightleftarrows [Co(HPPh_2)_4]^+ + H_2$$

A quite similar behavior has been described recently for some *cis*-$[CoH_2(P(OR)_3)_4]^+$ complexes by Muetterties et al.[6]

As reported previously,[1] the existence of this equilibrium offers a simple route to cobalt(I) derivatives: so, in the presence of carbon monoxide or of conjugated dienes, elimination of H_2 rapidly occurs to yield the corresponding cobalt(I) derivatives $[Co(CO)(HPPh_2)_4]^+$ or $[Co(diene)(HPPh_2)_3]^+$ (diene = 1,3-butadiene, isoprene, 1,3-cyclohexadiene).

Attempts have been made to elucidate the stoichiometry of the reaction between H_2 and the isopropyl alcohol solutions of $CoY_2{\cdot}6H_2O$ plus $HPPh_2$. We have observed that most of the cobalt(II) originally present was converted into *cis*-$[CoH_2(HPPh_2)_4]Y$ (yield as solid product about 80%), thus ruling out a dismutative route Co(II) → $^1/_2$Co(I) + $^1/_2$Co(III), followed by the oxidative addition of H_2 to the Co(I) intermediate. In the case of the CoY_2–$P(CH_3)_2Ph$ system, which similarly reacts with H_2 in isopropyl alcohol to give the *cis*-$[CoH_2(P(CH_3)_2Ph)_4]^+$ cations,[1] GLC analyses of the reaction mixtures reveal the presence of stoichiometric amounts of acetone. By contrast, in the case of the CoY_2–$HPPh_2$–H_2 system, even in isopropyl alcohol, no acetone is formed, while formation of oxidation products of the diphenylphosphine (phosphine oxide and/or phosphinic acid) was invariably observed. It seems reasonable that in both cases the *cis*-$[CoH_2(phosphine)_4]Y$ derivatives could arise from an oxidative addition of H_2 on a hypothetical $[Co(phosphine)_4]^+$ intermediate[7], the formation of which from cobalt(II) occurs with oxidation of the alcohol (as in the case of dimethylphenylphosphine) or of the phosphine itself (as in the case of diphenylphosphine).

Under an inert atmosphere, $HPPh_2$ immediately reacts with alcoholic solutions of $CoY_2{\cdot}6H_2O$ (molar ratio 5:1) to give red solutions, which slowly deposit a yellow crystalline product. Elemental analyses, which indicate a Co:phosphine:Y ratio of 1:4:1, and magnetic data (μ_{eff} at room temperature around 2.2 μ_B) suggest for the above complexes a low-spin square-planar structure for $[Co(PPh_2)(HPPh_2)_3]Y$, with one diphenylphosphido group bound to the cobalt.

Further support for the presence of the phosphido group comes from pH titration data, which show that the formation of $[Co(PPh_2)(HPPh_2)_3]Y$ occurs with production of 1 equiv of acid/mol of cobalt.

The monomeric nature of the complex has been confirmed by Hayter's method[8] (see Table I). The ability of diphenylphosphine to give complexes derived from the anionic 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] $C_p = A + BT$

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