at 498 (vvs) cm^{-1} is broadened and shifted to 481 (vvs) cm^{-1} in $TiCl_4$(l). *In conclusion, infrared data for I in* CH_2Cl_2 *are consistent with the presence of noncoordinated* $[(CH_3)_2N]_2BCl$ *and* $TiCl_4$. Low concentrations of I in CH_2Cl_2 afford yellow solutions while high concentrations yield red solutions. Also, cooling solutions containing low concentrations of I (yellow) from 25 to −78° results in the appearance of a red color. These color changes indicate the presence of low concentrations of intermediate complexes in solution as suggested by

$$\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3 \longrightarrow \{[(CH_3)_2N]_2BCl\}_{2-x}\{TiCl_4\}_{3-y} + x[(CH_3)_2N]_2BCl + yTiCl_4$$

The red coloration most likely is a result of these suggested intermediate complexes. Lack of observed infrared absorptions for such species is attributed to coincidence of frequencies arising from both associated and dissociated products.

Summary

The coordination complex $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ is formed by treatment of $TiCl_4$ with $[(CH_3)_2N]_2BCl$. Evaluation of infrared data for this complex in the solid state indicates the involvement of $[(CH_3)_2N]_2BCl$ as a nitrogen bidentate ligand bridging two molecules of $TiCl_4$. Dissociation of this complex *in vacuo* and in CH_2Cl_2 occurs to afford $TiCl_4$ and $[(CH_3)_2N]_2BCl$; these dissociations are accompanied by small amounts of intermolecular exchange affording $(CH_3)_2NBCl_2$ and $Cl_3TiN(CH_3)_2$.

Experimental Section

The preparation and purification of $[(CH_3)_2N]_2BCl$, $(CH_3)_2NBCl_2$, $TiCl_4$, and $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$ have been described in a previous paper.[1a] Samples of the complex were ground in an agate mortar under a dry nitrogen atmosphere in a glove box, mixed with Nujol (previously dried over sodium) or Flurolube (previously dried over Linde Molecular Sieve Type 4A), and enclosed between KBr plates. Dichloromethane solutions of the complex were syringed into 0.1-mm matched liquid cells equipped with KBr optics. Dichloromethane was previously dried over CaH_2 and distilled in a vacuum line. Vapor-phase spectra of the volatile components in equilibrium with the solid complex were determined at various temperatures by immersing the condensation finger of the gas cell in heated dibutyl phthalate. The temperature of dibutyl phthalate was measured before and after the recording of each vapor-phase infrared spectrum to establish the temperature interval. All infrared measurements were carried out with a Perkin-Elmer Model 337 grating spectrophotometer.

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The Mass Spectra of Trifluorophosphinecarbonylcobalt Hydrides[1]

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Abstract: A mass spectral study has been carried out on the series of compounds: $HCo(CO)_x(PF_3)_{4-x}$, where $x = 0$ to 4. These studies, which included the measurement of the fragmentation patterns and appearance potentials of the five compounds, showed that the Co–CO and Co–PF_3 bond energies are essentially identical (56 ± 15 kcal/mole) and are much greater than the H–Co bond energy (4 ± 15 kcal/mole). The heats of formation of these compounds, calculated from the appearance potential data, become more negative by approximately 200 kcal/mole for each CO moiety that is replaced by PF_3. Since this variation is the difference between the heats of formation of PF_3 and CO, the nature of the Co–PF_3 and Co–CO bonds must be quite similar. The values for $\Delta H_f°(HCo(CO)_x(PF_3)_{4-x})$ are (in kcal/mole): -173 ± 11, -381 ± 9, -579 ± 10, -783 ± 9, and -978 ± 14 for $x = 4$ to 0, respectively. Comparison of the relative intensity of the hydrogen-containing ions with ions that have lost a hydrogen atom in the mass spectra of these cobalt hydrides shows that ions containing H–Co bonds are more abundant until two or more of the covalently bonded ligands (CO or PF_3) are lost from the parent ion. This type of fragmentation can be explained by an interaction between the equatorial ligands around the Co atom and the axial hydrogen atom.

A number of mass spectral studies of metal carbonyl compounds have been reported in the literature recently.[2-9] While a few publications[6,10] have dealt with the mass spectra of substituted metal carbonyls, a mass spectral study, including both appearance potential and fragmentation data, of a complete series of substituted metal carbonyls has not been reported.

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(1) Part of the report is based on a portion of the thesis to be submitted by S. K. Gondal to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. It is supported in part by the Advanced Research Projects Agency, Office of the Secretary of Defense.

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This investigation describes the mass spectra of five cobalt hydrides, $HCo(CO)_x(PF_3)_{4-x}$ ($x = 0$ to 4), four of which have phosphorus trifluoride substituted completely or in part for carbon monoxide. The fragmentation patterns of these compounds have been correlated with a proposed structure, and appearance potential data have been used to calculate the heats of formation of the positive ions of these five cobalt hydrides, the values of the hydrogen–cobalt, cobalt–carbon monoxide, and cobalt–phosphorus trifluoride bond energies, and the standard heats of formation of the compounds.

Experimental Section

Details of the preparation, separation, purification, and physical properties of these compounds are described elsewhere.[11,12] The compounds having both carbonyl and phosphorus trifluoride ligands were prepared by the reaction of $CH_3SiH_2Co(CO)_4$ with PF_5 and also by the reaction of $Co_2(CO)_8$ with a mixture of CH_3SiH_3 and PF_5. The desired products were separated by vacuum distillation and low-temperature gas chromatography. Tetracarbonylcobalt hydride, $HCo(CO)_4$, was obtained by the standard reaction of dicobaltoctacarbonyl with pyridine, followed by the addition of aqueous sulfuric acid, and $HCo(PF_4)_4$ was prepared by treating the mixture of compounds containing both CO and PF_3 groups prepared by the above reaction with excess PF_3, as described by Clark.[13] The mass and infrared spectra were employed to check the purity of the compound under investigation.

All mass spectral data reported here were obtained on a modified Bendix 12-107 Time-of-Flight mass spectrometer which has been previously described.[14] This instrument was preferred because of its relatively cool ion source (35 ± 5°) and the fact that the mass spectral data (fragmentation patterns and ionization efficiency curves) could be obtained very rapidly. Recording the data rapidly reduces the chance of any products formed by decomposition on the filament of the mass spectrometer from diffusing into the ion source and interfering with the recorded mass spectrum. In these studies the fragmentation pattern data were obtained in less than 2 min and the ionization efficiency curves for two ions (an ion from the sample of interest and the internal standard used to calibrate the voltage scale, either Kr, Xe, or Ar) were obtained simultaneously in less than 1 min. The disadvantage of obtaining data this rapidly is that statistical fluctuations in the ion currents are emphasized, resulting in larger error limits. As an accuracy check, a second rare gas was always introduced into the mass spectrometer with the standard and sample, and its ionization potential was measured immediately following the determination of the appearance potential of the sample and compared to the spectroscopic ionization potential of the rare gas. A fresh sample of the compound being investigated was introduced into the mass spectrometer for each measurement. Winters and Kiser have reported[4] that some metal carbonyl compounds decompose in the mass spectrometer causing a contamination problem; thus, as a precautionary measure, the ion source, electron multiplier, and Philips vacuum gauge were routinely cleaned and the mass spectrometer filament replaced after every 4 hr of operation. The data recorded on replica measurements before and after the general cleaning and filament changes agreed within limits quoted below. It was impossible to determine whether or not the ions reported possessed excess kinetic energy; therefore, the appearance potentials reported here may be greater than the true potentials. Because of this fact, the values reported for the bond energies and the heats of formation of the positive ions should be taken as upper limits and the values cited for the standard heats of formation of the compound should be viewed as lower limits.

Results and Discussion

Table I. Fragmentation Patterns of $HCo(CO)_x(PF_3)_{4-x}$ Based on Per Cent of Total Ion Current, $I_i/\Sigma I_i$[a]

		x				
m/e	Ion	4	3	2	1	0
412	$HCo(PF_3)_4^+$	...	...	...	...	2.9
352	$HCo(CO)(PF_3)_3^+$	...	...	...	1.7	...
324	$HCo(PF_3)_3^+$	...	...	...	0.6	3.9
323	$Co(PF_3)_3^+$	...	...	...	...	1.6
305	$HCo(PF_2)(PF_3)_2^+$	...	...	...	...	2.8
292	$HCo(CO)_2(PF_3)_2^+$	...	...	3.1	...	...
264	$HCo(CO)(PF_3)_2^+$	...	...	3.4	3.0	...
263	$Co(CO)(PF_3)_2^+$	...	...	0.2	1.0	...
236	$HCo(PF_3)_2^+$	...	...	0.2	1.3	5.7
235	$Co(PF_3)_2^+$	...	...	0.3	1.7	7.3
232	$HCo(CO)_3(PF_3)^+$	...	2.0	...	...	...
217	$HCo(PF_2)(PF_3)^+$	...	...	...	0.3	3.7
216	$Co(PF_2)(PF_3)^+$	...	...	...	...	0.5
204	$HCo(CO)_2(PF_3)^+$	...	3.9	3.5	0.4	...
203	$Co(CO)_2(PF_3)^+$	...	0.6	1.1	...	...
176	$HCo(CO)(PF_3)^+$	...	1.7	3.7	4.0	...
175	$Co(CO)(PF_3)^+$	...	3.8	7.5	7.7	...
172	$HCo(CO)_4^+$	4.5	...	...	...	...
148	$HCo(PF_3)^+$	...	1.0	1.9	3.1	6.0
147	$Co(PF_3)^+$	...	4.1	8.7	14.3	25.9
144	$HCo(CO)_3^+$	7.6	0.9	...	...	...
143	$Co(CO)_3^+$	2.2	1.1	...	...	...
129	$HCo(PF_2)^+$	...	...	...	0.4	1.7
128	$Co(PF_2)^+$	...	...	...	0.7	1.3
116	$HCo(CO)_2^+$	3.7	3.0	2.0	...	...
115	$Co(CO)_2^+$	15.6	10.4	7.0	...	...
110	$HCo(PF)^+$	...	...	...	...	0.05
109	$Co(PF)^+$	...	...	...	0.3	0.5
88	$HCo(CO)^+$	1.6	4.2	3.9	4.1	...
87	$Co(CO)^+$	17.8	17.0	15.8	10.9	...
78	CoF^+	...	1.1	1.6	3.0	4.1
71	CoC^+	2.2	1.6	1.2	0.9	...
69	PF_2^+	...	3.9	3.9	8.7	4.7
60	HCo^+	1.0	1.6	1.8	2.2	2.7
59	Co^+	19.5	21.7	21.9	22.6	24.3
57.5	$Co(CO)_2^{2+}$	2.2	...	...	...	...
43.5	$Co(CO)^{2+}$	1.3	...	...	...	...
28	CO^+	20.8	16.5	7.1	5.7	...

[a] Electron energy, 70 V; ionizing current, 0.125 μA; instrument operated in the pulsed mode with the ion lens on.

Fragmentation Patterns. Mass spectral fragmentation patterns for the five cobalt hydrides, corrected for residual background in the mass spectrometer, are shown in Table I. In addition to the ions reported in Table I, other ions with relatively minor abundance (less than 0.05% of the total ion current) were also observed. These were fragment ions which were formed by the loss of an oxygen atom from one of the carbon monoxide ligands or by loss of a fluorine atom from one of the phosphorus trifluoride moieties. All of the compounds have a moderately intense molecular weight ion, and the abundance of these ions fluctuates in a wavelike manner as phosphorus trifluoride is substituted for carbon monoxide. There is a continuous increase in the intensity of the $HCo(PF_3)_x^+$ and $Co(PF_3)_x^+$ fragment ions as phosphorus trifluoride is substituted for carbon monoxide in the compounds, while the ion current intensities of the $HCo(CO)_x^+$ (except where $x = 1$), $Co(CO)_x^+$, and CO^+ species decrease with increasing substitution of PF_3. The interesting rearrangement ion at m/e 78, CoF^+, increases in intensity with increasing PF_3 substitution and appears to be formed by decomposition of $HCoPF_3^+$ with the elimination of the elements of HPF_2. Since metastable ions cannot be observed in our TOF mass spectrometer, the evidence for this decomposition mechanism was gleaned from a study of the clastograms (a plot of the fragmentation pattern *vs.* electron energy) in a manner

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(11) S. K. Gondal, A. G. MacDiarmid, M. V. McDowell, and F. E. Saalfeld, part I, submitted for publication.

(12) S. K. Gondal, A. G. MacDiarmid, M. V. McDowell, and F. E. Saalfeld, part II, submitted for publication.

(13) R. J. Clark, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract L-149.

(14) F. E. Saalfeld and M. V. McDowell, *Inorg. Chem.*, **6**, 96 (1967).

similar to that used by Winters and Kiser to elucidate the decomposition mechanism of the metal carbonyls.[4,5]

The ion current observed at *m/e* 88 could be due to either PF_3^+ or $HCoCO^+$. Unfortunately, the resolution of our mass spectrometer was not sufficient to resolve these peaks, but it is pointed out that a small (approximately 1% of the *m/e* 88 peak) isotopic peak (presumably due to ^{13}C) was observed at *m/e* 89. Because of the weakness of this isotope peak, it was impossible to measure the intensity of this ion with sufficient accuracy to prove its identity from known isotopic abundances. However, both P and F are monoisotopic and therefore no isotope peak should be observed; further, the appearance potential of the ion observed at *m/e* 88 was significantly greater than the ionization potential of PF_3. In view of these facts and since no *m/e* 88 is observed in the spectrum of $HCo(PF_3)_4$, it is felt that the ion observed at *m/e* 88 is $HCo(CO)^+$ rather than PF_3^+.

The similarities of the mass spectra of metal carbonyls and metal–phosphorus trifluoride systems have been reported by Kiser, *et al.*,[15] who also pointed out a significant difference in the two classes of compounds: the metal carbonyls form rather intense, doubly charged positive ions, whereas the metal–phosphorus trifluorides do not. This trend was also observed in these cobalt hydrides where doubly charged ions were observed only in the spectrum of $HCo(CO)_4$.

A comparison of the relative intensity of the hydrogen-containing ions to those that have lost a hydrogen atom in the spectra of these five compounds shows that ions containing the H–Co bond are more abundant when none or only one of the covalently bonded ligands (either CO or PF_3) is lost from the parent ion. None of the parent ions of these cobalt hydride compounds loses a hydrogen atom, a trend which has also been noted in the mass spectra of polynuclear metal carbonyl hydrides[7] where the hydrogen atoms are in bridging positions. The structure of $HCo(CO)_4$ proposed by Green and Jones[16] is essentially a trigonal bipyramid where the equatorial carbonyl groups are bent toward the axial hydrogen atom. If the phosphorus trifluoride substituted compounds have a structure similar to $HCo(CO)_4$, then the fragmentation patterns described above for $HCo(CO)_x(PF_3)_{4-x}$ can be explained by an interaction between the equatorial ligands (either CO or PF_3) and the axial hydrogen atom. Such an interaction has been previously suggested by Edgell.[17,18] The compounds $HCo(CO)_x(PF_3)_{4-x}$ are likely to have the same molecular structure as $HCo(CO)_4$ since other metal carbonyl structures have been found to be the same before and after phosphorus trifluoride has been substituted for CO.[19]

In the negative ion spectra of these five cobalt hydride compounds several ions were observed, but, because of the poor mass separation of the $HCo(CO)_x(PF_3)_{4-x}^-$ and the $Co(CO)_x(PF_3)_{4-x}^-$ ions on the photographic record, we were unable to differentiate between these two ion types. Thus, the mass assignments given below should be viewed as being either $HCo(CO)_x(PF_3)_{4-x}^-$ or $Co(CO)_x(PF_3)_{4-x}^-$. Tentative mass assignments for the negative ions formed at 70 V from these cobalt compounds are (in decreasing order of abundance) shown in Table II. These ions are apparently formed by ion-pair processes, and, although it was impossible to assign numerical values to the intensities of these negative ions, several salient features are noted. First, a parent ion is not observed but a parent minus hydrogen ion appears in the spectrum of each compound. Second, the most intense ion current in each spectrum is the ion species which has lost one ligand (either CO or PF_3). This type of negative ion fragmentation behavior has been noted by Winters and Kiser[20] in the negative ion spectra of other transition metal carbonyls. The parent minus hydrogen atom ion is the second most intense ion current in the spectrum of all of the cobalt compounds, with the exception of $HCo(CO)_2(PF_3)_2$, where it is the third most intense ion. In general, the intensities of the negative ions increased with increasing substitution of PF_3. Owing to instrumental limitations, it was not possible to study the appearance potentials of the negative ions produced from these interesting compounds; however, our mass spectrometer is now being modified and we will report the appearance potentials of these compounds in the near future.

Table II

$HCo(CO)_4$	$HCo(CO)_3^-$, $Co(CO)_4^-$, $Co(CO)_2^-$
$HCo(CO)_3(PF_3)$	$HCo(CO)_2(PF_3)_2^-$, $Co(CO)_3(PF_3)_2^-$, $Co(PF_3)^-$, $Co(CO)(PF_3)^-$, $HCo(CO)_3^-$
$HCo(CO)_2(PF_3)_2$	$HCo(CO)(PF_3)_2^-$, $Co(CO)_2(PF_3)^-$, $Co(CO)_2(PF_3)_2^-$, $Co(CO)(PF_3)^-$, $Co(PF_3)^-$
$HCo(CO)(PF_3)_3$	$HCo(CO)(PF_3)_2^-$, $Co(CO)(PF_3)_3^-$, $HCo(PF_3)_3^-$, $Co(CO)(PF_3)^-$, $Co(PF_3)^-$, $Co(PF_3)_2^-$
$HCo(PF_3)_4$	$HCo(PF_3)_3^-$, $Co(PF_3)_4^-$, $Co(PF_3)_2^-$, $Co(PF_3)^-$

Appearance Potentials. The appearance potentials of the positive ions of the five cobalt hydrides are given in Table III. These compounds undergo unimolecular decomposition in a series of successive eliminations of either carbon monoxide or phosphorus trifluoride similar to the decomposition of other metal carbonyls observed by Winters and Kiser.[2–5] Several features of the data in Table III are noteworthy. The appearance potential of a given ion appears to be the same regardless of the progenitor molecule. Two exceptions to this observation are the ions $HCo(PF_3)_3^+$ from $HCo(CO)(PF_3)_3$ and $HCo(PF_3)_4$ and $HCo(CO)_2^+$ from $HCo(CO)_3(PF_3)$. The reason for this is not apparent; however, the possibility of these ions containing excess kinetic energy cannot be ruled out. It is interesting that there is not a smooth trend in the ionization potentials of these compounds as phosphorus trifluoride is substituted for carbon monoxide. In comparing the ionization potential and abundance of the molecular ions in these compounds, it is seen that, when the ionization potential of the molecule decreases (Table III), the intensity of the molecular ion (Table I) increases, and *vice versa*. For example, the ionization potential

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Table III. Appearance Potentials[a] (in eV) for the Positive Ions of $HCo(CO)_x(PF_3)_{4-x}$

	x				
Ion	4	3	2	1	0
$HCo(PF_3)_4^+$	...	...	...	...	9.2 ± 0.2^b
$HCo(CO)(PF_3)_3^+$	...	...	...	10.2 ± 0.1^b	...
$HCo(PF_3)_3^+$	...	...	...	11.1 ± 0.2	10.4 ± 0.2
$HCo(CO)_2(PF_3)_2^+$	...	...	9.6 ± 0.2^b	...	...
$HCo(CO)(PF_3)_2^+$	...	...	10.3 ± 0.3	10.4 ± 0.3	...
$HCo(PF_3)_2^+$	...	...	...	12.6 ± 0.2	12.7 ± 0.2
$Co(PF_3)_2^+$	...	...	...	14.5 ± 0.2	14.3 ± 0.3
$HCo(CO)_3(PF_3)^+$	...	9.8 ± 0.2^b	...	...	...
$HCo(CO)_2(PF_3)^+$	...	10.3 ± 0.3	10.1 ± 0.2	...	...
$Co(CO)_2(PF_3)^+$	...	...	...	...	...
$HCo(CO)(PF_3)^+$	...	12.5 ± 0.3	12.4 ± 0.2	12.3 ± 0.3	...
$Co(CO)(PF_3)^+$	...	14.3 ± 0.3	14.0 ± 0.3	14.1 ± 0.3	...
$HCo(CO)_4^+$	8.7 ± 0.1^b	...	...	...	...
$HCo(PF_3)^+$	...	13.8 ± 0.2	13.6 ± 0.3	13.6 ± 0.2	14.4 ± 0.3
$Co(PF_3)^+$	...	15.7 ± 0.2	15.9 ± 0.2	15.7 ± 0.5	15.8 ± 0.3
$HCo(CO)_3^+$	9.4 ± 0.2	9.9 ± 0.2	...	...	...
$Co(CO)_3^+$	12.1 ± 0.3	12.1 ± 0.2	...	...	...
$HCo(CO)_2^+$	11.2 ± 0.2	12.4 ± 0.3	11.6 ± 0.2	...	...
$Co(CO)_2^+$	12.9 ± 0.3	14.0 ± 0.2	13.6 ± 0.2	...	...
$HCo(CO)^+$	12.8 ± 0.3	12.1 ± 0.2	12.3 ± 0.2	12.0 ± 0.2	...
$Co(CO)^+$	15.0 ± 0.3	15.5 ± 0.2	15.3 ± 0.3	15.9 ± 0.2	...
HCo^+	15.2 ± 0.3	14.6 ± 0.3	14.9 ± 0.3	15.6 ± 0.3	16.0 ± 0.3
Co^+	17.8 ± 0.3	17.8 ± 0.3	18.2 ± 0.3	17.8 ± 0.3	17.8 ± 0.3

[a] Average of seven independent measurements determined by Warren's method of extrapolated differences: J. W. Warren, *Nature*, **165**, 810 (1950). Calibrating gases: Ar ($I = 15.8$ V), Kr ($I = 14.0$ V), and Xe ($I = 12.1$ V). [b] Standard deviation of the mean.

of $HCo(CO)_2(PF_3)_2$ is 9.6 V and the intensity of this ion is 3.1% of the total ion current, but, when one additional phosphorus trifluoride is substituted for a carbon monoxide to give $HCo(CO)(PF_3)_3$, the ionization potential increases to 10.2 V and the intensity of the molecular weight ion decreases to 1.7%. The reason for the undulation of ionization is not obvious although a possible explanation[21] might be that the highest occupied molecular orbital in these five cobalt hydrides is occupied to different extents from the metal and ligand orbitals. The exact nature of this type of variation could be related to the geometrical position of the PF_3 substitution.

As was mentioned previously, the ion observed at *m/e* 88 could be either $HCoCO^+$ or PF_3^+. The appearance potential of this ion varies from 12.0 to 12.8 V in these hydrides (Table III), and, since the ionization potential of PF_3 is 11.5 ± 0.1 V,[22] outside the experimental error limits, this ion cannot be PF_3 produced by thermal decomposition. The PF_3^+ could arise by a fragmentation mechanism from the parent ion, but arguments presented previously appear to negate this possibility.

Thermochemical Properties. Thermochemical values, such as the heats of formation of the compounds or of the positive ions, and bond energies can be calculated from appearance potential measurements if the ion source reaction is known or can be reasonably assumed and appropriate ancillary data are available. The value of the appearance potential is, to a good approximation, equal to the heat of reaction, and Hess's law of elementary thermodynamics can be used to calculate the unknown heats of formation.[23] In this study the following supporting data were employed in the calculations (in kcal/mole): $\Delta H_f°(H) = 52.1$;[24] $\Delta H_f°(Co^+) = 287$;[24] $\Delta H_f°(CO) = -26.4$;[24] $\Delta H_f°(PF_3) = -226.0$;[25] $\Delta H_f°(Co(CO)_3^+) = 70$;[4] $\Delta H_f°(CoCO_2^+) = 138$;[4] $\Delta H_f°(Co(CO)^+) = 203$.[4] Using these data with the appearance potentials in Table III, the heats of formation of the compounds and their positive ions have been calculated and are summarized in Table IV. The heats of formation of $HCo(CO)_4$, $HCo(CO)_3(PF_3)$, $HCo(CO)_2(PF_3)_2$, $HCo(CO)(PF_3)_3$, and $HCo(PF_3)_4$ are (in kcal/mole): -173 ± 11, -381 ± 9, -579 ± 10, -783 ± 9, and -978 ± 14, respectively. It is seen that the heat of formation of the compounds becomes approximately 200 kcal/mole more negative each time a phosphorus trifluoride molecule is substituted for carbon monoxide. Since this variation is, within the experimental error, the difference between the heats of formation of phosphorus trifluoride and carbon monoxide (-226.0[25] and -26.4,[24] respectively), the nature of the cobalt-to-carbon and cobalt-to-phosphorus bonds in these compounds must be quite similar. A similar situation appears to exist in the case of nickel tetracarbonyl and its phosphorus trifluoride analog. Fischer, Cotton, and Wilkinson[26] have reported $\Delta H_f°(Ni(CO)_4)$ to be -145.1 kcal/mole, while Kiser, *et al.*,[15] have calculated a value of -948 kcal/mole for $\Delta H_f°(Ni(PF_3)_4)$ from appearance potential measurements. The difference in these values, 803 kcal/mole, is essentially four times the difference in the heats of formation of phosphorus trifluoride and carbon monoxide, suggesting that the nature of bonding in $Ni(CO)_4$ and $Ni(PF_3)_4$ is also quite similar.

The heats of formation of $HCo(CO)_2(PF_3)_2$, shown in column 4 of Table IV, calculated from the appearance potential of various ions ($Co(CO)_2^+$, $Co(CO)^+$, and

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[21] We are grateful to a referee for pointing out this possible interpretation of the data.

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Table IV. Heats of Formation of $HCo(CO)_x(PF_3)_{4-x}$ Positive Ions (in kcal/mole)

	x				
Ion	4	3	2	1	0
$HCo(PF_3)_4^+$	...	...	...	...	−766
$HCo(CO)(PF_3)_3^+$	...	...	...	−547	...
$HCo(PF_3)_3^+$	...	...	...	−500	−512
$HCo(CO)_2(PF_3)_2^+$	...	...	−358	...	...
$HCo(CO)(PF_3)_2^+$	...	...	−315	−317	...
$HCo(PF_3)_2^+$	...	...	...	−240	−233
$Co(PF_3)_2^+$	...	...	...	−248	−248[c] (−977)
$HCo(CO)_3(PF_3)^+$	...	−155	...	...	...
$HCo(CO)_2(PF_3)^+$	...	−117	−120	...	...
$Co(CO)_2(PF_3)^+$	...	...	...	...	...
$HCo(CO)(PF_3)^+$	...	−40	−40	−47	...
$Co(CO)(PF_3)^+$	...	−51	−56	−57	...
$HCo(CO)_4^+$	28	...	...	...	...
$HCo(PF_3)^+$	...	16	13	9	32
$Co(PF_3)^+$	...	8	14	6	9[c] (−981)[b]
$HCo(CO)_3^+$	71	73	...	...	...
$Co(CO)_3^+$	70[a] (−183)[b]	70[a] (−383)[b]	...	...	...
$HCo(CO)_2^+$	139	157	141	...	...
$Co(CO)_2^+$	138[a] (−160)[b]	138[a] (−385)[b]	138[a] (−575)[b]	...	...
$HCo(CO)^+$	202	176	183	172	...
$Co(CO)^+$	203[a] (−170)[b]	203[a] (−381)[b]	203[a] (−576)[b]	203[a] (−790)[b]	...
HCo^+	284	260	269	282	295
Co^+	287[a] (−177)[b]	287[a] (−376)[b]	287[a] (−585)[b]	287[a] (−775)[b]	287[a] (−975)[b]
Av $\Delta H_f°[HCo(CO)_x(PF_3)_{4-x}]$	(−173 ± 11[d])[b]	(−381 ± 9[d])[b]	(−579 ± 10[d])[b]	(−783 ± 9[d])[b]	(−978 ± 14[d])[b]

[a] Literature ref 4 and 21. [b] Numbers in parentheses are heats of formation of a given compound, $HCo(CO)_x(PF_3)_{4-x}$, calculated using the literature value of the heat of formation of the appropriate ion. Final value in the heat of formation column is the average of the values in the parentheses. [c] Value of the heat of formation of the ion is obtained from the heat of formation of that ion determined previously from the other compounds in this study and employed to calculate the $\Delta H_f°(HCo(PF_3)_4)$. [d] The error terms reported include the error in the appearance potential measurement and the estimated error in the $\Delta H_f°$ of the positive ions used in the calculations.

Co^+), are in agreement with each other. This internal agreement supports Winters and Kiser's value[4] of −132 kcal/mole for $\Delta H_f°(\cdot Co(CO)_4)$. The value of $\Delta H_f°(HCo(CO)_2(PF_3)_2)$ calculated from the spectroscopic determination of $\Delta H_f°(Co^+)$ and the measured appearance potential is in agreement with heats of formation of $HCo(CO)_2(PF_3)_2$ calculated from the appearance potentials of the ions at *m/e* 115 and 87 and mass spectrometric evaluation of $\Delta H_f°(Co(CO)_2^+)$ and $\Delta H_f°(Co(CO)^+$ which depend on the value of $\Delta H_f°(Co(CO)_4)$ reported by Winters and Kiser.[4] The same observation is noted for $HCo(CO)_4$, $HCo(CO)_3(PF_3)$, and $HCo(CO)(PF_3)_3$. The bond dissociation energy of the cobalt–carbon monoxide and cobalt–phosphorus trifluoride bonds, calculated using the appearance potential data cited in Table III and a standard mass spectrometric equation,[27] are equal. This fact is not surprising in view of the similarity in the nature of cobalt–carbon and cobalt–phosphorus bonds suggested by the values of the heats of formation of the compounds. In order to calculate the bond energies it was necessary to estimate the ionization potential of the CoCO radical. This was accomplished by noting that the ionization potential of $Co(CO)_4$ was 8.3 V,[28] while the ionization potential of Co is 7.87 V.[29] The difference between these values, ~0.4 V, was extrapolated to give an estimated value for the ionization potential of CoCO of 8.0 V. While this extrapolation may be questionable, it appears to be legitimate under the circumstances. The values of the bond energies are: *E*(Co–CO) = *E*(Co–PF_3) = 56 ± 15 kcal/mole and *E*(Co–H) = 4 ± 15 kcal/mole, where the error limits quoted are estimates of the accuracy of the energy reported and reflect the uncertainty in the experimental data and the estimation discussed above. King and Lippincott[30] have reported values of 59 and 53 kcal/mole for Fe–C and Ni–C bond energies in the two group VIII carbonyls, $Fe(CO)_5$ and $Ni(CO)_4$. It may be fortuitous that the value reported for the Co–C bond energy, 56 ± 15 kcal/mole, is exactly the expected result; however, the agreement is gratifying and lends some support to the assumptions made in the calculation of this result. The fact that the Co–H bond energy is only 4 kcal/mole is most surprising in light of the Co–H stretching vibration of 1934 cm^{-1} (5.5 kcal/mole) reported by Edgell and Summitt.[31] However, in view of the large error placed on the value cited for the Co–H bond energy, it is felt that the value reported here should stand as a first estimate. Certainly, the mass spectrometric value for the Co–H supports the claim of Edgell, *et al.*, that "the hydrogen is expected to be weakly bound to the $Co(CO)_4$ skeleton."

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