TABLE I

SELECTED IR DATA FOR Pt COMPLEXES (CM^{-1})

$(NH_3)_2Pt(CH_3CH_2CN)_2(ClO_4)_2$	$(NH_3)_2Pt(CH_3CN)_2(ClO_4)_2$
621 (singlet)	623 (singlet)
800–1000 (no peaks)	800–1000 (no peaks)
1090 (singlet)	1090 (singlet)
1348 and 1364 (NH_3 sym def)	1343 and 1363 (NH_3 sym def)

nmr spectrum of the solution exhibited the triplet due to bound CH_3CN. The central peak of this triplet was integrated with respect to the ^{13}C satellite of bulk CH_3CN and the value of the solvation number was found to be 1.95 ± 0.1. Thus two acetonitrile molecules had displaced the two propionitrile molecules. This result confirms the existing evidence that acetonitrile displaces propionitrile completely from the Pt coordination shell.[7] The position of the CH_3CH_2CN methyl triplet, 64, 72, and 80 cps downfield from TMS, showed that this resonance was due to free propionitrile. Furthermore, when the methyl peak of CH_3CH_2CN was integrated with respect to the ^{13}C satellite of bulk CH_3CN, the number of free CH_3CH_2CN molecules was calculated using eq 1. The ratio of the propionitrile to

$$\frac{\text{free } CH_3CH_2CN}{\text{free } CH_3CN} = \frac{\text{area of } CH_3CH_2CN}{(178.5)(\text{area of } ^{13}C)} \tag{1}$$

^{13}C areas was 1.73. Thus 0.254 mol of free CH_3CH_2CN was found, in reasonable agreement with the 0.216 mol expected.

The ^{195}Pt–^{1}H coupling is transmitted through four bonds. The value of the coupling constant, 12.1 cps, is smaller than those reported for coupling through two or three bonds.[8-15] Lewis, *et al.*,[10] used values of coupling constants to assign bonding sites in Pt–acac complexes. The basis for their assignments was that coupling constants should decrease as the interacting nuclei are separated by more bonds. Thus, it becomes important to determine coupling constants for a variety of systems. The coupling in the Pt–CH_3CN system is slightly larger than that of other systems where the interaction is through four bonds.[16,17] In fact, four-bond Pt–H couplings range from our 12.1 cps down to 2 cps.[10] The persistence of the coupling up to the boiling point (81°) indicated that the acetonitrile molecules were strongly bonded to the platinum. This was consistent with the observation of no broadening of the bound triplet even at the higher temperatures and indicated that the solvent-exchange rate was too slow to be measurable by this method.

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The Mass Spectrum of Trifluorosilyltetracarbonylcobalt[1a]

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Recently published reports[2,3] on the infrared spectrum and force constants of trifluorosilyltetracarbonylcobalt, $SiF_3Co(CO)_4$, have suggested that there might be significant $(d \rightarrow d)\pi$ bonding between the silicon and cobalt in this and other silicon tetracarbonylcobalt compounds. This paper reports the fragmentation pattern of $SiF_3Co(CO)_4$ and the appearance potential measurement of selected ions from which the standard heats of formation of the positive ions of $SiF_3Co(CO)_4$, $\Delta H_f°(SiF_3Co(CO)_4)$, and the silicon–cobalt bond energy in $SiF_3Co(CO)_4$ have been calculated.

Experimental Section

Trifluorosilyltetracarbonylcobalt was prepared from $HSiF_3$ and $Co_2(CO)_8$.[4] The identity and purity of the compound were ascertained by partial elemental analysis, Dumas molecular weight determination, and infrared and mass spectral measurements. Decomposition was minimized by storage of the compound at the temperature of boiling liquid nitrogen. Trifluorosilyltetracarbonylcobalt was introduced into the mass spectrometer by the following procedure. The tube containing $SiF_3Co(CO)_4$ was warmed slowly from −196 to −78° and traces of any volatile materials, *e.g.*, CO and SiF_4, were removed by evacuation; the sample tube was then warmed slowly to 0°, distilling $SiF_3Co(CO)_4$ into the mass spectrometer.

All of the mass spectral data were obtained on a modified 12-107 Bendix TOF mass spectrometer previously described.[5] The reasons for the selection of this mass spectrometer have been cited elsewhere.[6] A fresh sample of $SiF_3Co(CO)_4$ was introduced into the mass spectrometer for each measurement, since some thermal decomposition did occur on standing at room temperature.

Results and Discussion

Fragmentation Patterns.—The fragmentation pattern of $SiF_3Co(CO)_4$, corrected for the background in the mass spectrometer, is given in Table I. Some of the salient features of the mass spectrum are the moderately intense parent ion current at *m/e* 256 and the fact that CO is fragmented from the parent ion more readily than F. Like other transition metal carbonyls,[7,8]

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TABLE I

FRAGMENTATION PATTERN[a] OF $^{28}SiF_3Co(CO)_4$ BASED ON PER CENT OF TOTAL ION CURRENT

m/e	Ion	% $I_i/\Sigma I_i$
256	$SiF_3Co(CO)_4^+$	2.8
237	$SiF_2Co(CO)_4^+$	0.5
228	$SiF_3Co(CO)_3^+$	4.0
209	$SiF_2Co(CO)_3^+$	0.3
200[b]	$SiF_3Co(CO)_2^+$	3.4
181	$SiF_2Co(CO)_2^+$	0.1
172	$SiF_3Co(CO)^+$	2.6
144	SiF_3Co^+	12.5
125	SiF_2Co^+	0.4
115	$Co(CO)_2^+$	12.1
87	$Co(CO)^+$	17.6
85	SiF_3^+	3.5
78	CoF^+	0.8
71	CoC^+	2.2
66	SiF_2^+	1.3
59	Co^+	23.3
57.5	$Co(CO)_2^{2+}$	2.1
47	SiF^+	1.8
43.5	$Co(CO)^{2+}$	0.8
28	CO^+	7.9

[a] Ionizing voltage 70 V; ionizing current 0.125 μA; instrument operated in pulsed mode with ion lens on. [b] *m/e* 200 has been corrected for presence of Hg in the background of the mass spectrometer.

$SiF_3Co(CO)_4$ loses CO moieties from the molecular ion in a series of sequential eliminations. The rearrangement ion at *m/e* 78, FCo^+, appears to have been formed from the SiF_3Co^+ ion by elimination of the now well-authenticated[9] SiF_2 radical. In a similar reaction, elimination of SiF_2 from the ion $CH_3SiF_2Co^+$ by a methyl migration led to the formation of the rearrangement ion CH_3Co^+.[10] Absorption in the CO stretching region of the gas-phase infrared spectrum of CH_3SiF_2-$Co(CO)_4$ suggests the presence of small quantities of $CH_3Co(CO)_4$ which can be regarded as being formed by the elimination of SiF_2 from $CH_3SiF_2Co(CO)_4$.[11] Thus, it is suggested that SiF_2 elimination might be a general reaction of organometallic compounds containing the silicon difluoride moiety, and, hence, certain organometallic compounds may be a convenient source of SiF_2 radicals.

Differentiation between Si- and CO-containing ions was made by comparison of the expected effect of the Si and CO isotopes on the ratios of the $M + 1$ and $M + 2$ for the *m/e* ratios $M = 144, 125, 115, 87$, and 28. The correct chemical composition of the ion currents is cited in column 2 of Table I. The doubly charged ion species $Co(CO)_2^{2+}$ and $Co(CO)^{2+}$, observed in the spectrum of $SiF_3Co(CO)_4$, have also been noted in the mass spectra of $HCo(CO)_4$[6] and $CH_3SiF_2Co(CO)_4$[10] but not in the spectrum of $Co_2(CO)_8$[12] or in the spectra of the phosphorus trifluoride derivatives of $HCo(CO)_4$.[6]

While instrumentational limitations prevented a detailed study of the negative ions of $SiF_3Co(CO)_4$, several were observed. These were (in decreasing abundance at 70 V) $SiF_3Co(CO)_3^-$, $SiF_3Co(CO)_2^-$, and $SiF_3Co(CO)^-$.

Appearance Potentials and Thermochemical Results.—The values of the appearance potentials and the thermochemical properties of the ions of $SiF_3Co(CO)_4$ are shown in Table II. In the thermochemical values reported here, it has been assumed that the ions did not contain excess kinetic or electronic energy. This assumption was not experimentally verified; therefore, the value reported for the heat of formation of $SiF_3Co(CO)_4$ should be taken as a lower limit, while the values cited as heats of formation of the positive ions and the F_3Si–$Co(CO)_4$ bond dissociation energy must be considered as upper limits. Field and Franklin[13] have discussed the relationships between the measured appearance potentials and bond dissociation energies and between the heats of formation of the ions and compounds, as well as the errors encountered in these measurements. Bond energies and heats of formation

TABLE II

APPEARANCE POTENTIALS[a] AND THERMOCHEMICAL RESULTS FOR $^{28}SiF_3Co(CO)_4$

Ion (*m/e*)	Neutral species	Appearance potential EV	Appearance potential kcal/mol	$\Delta H_f°$(ion), kcal/mol	$\Delta H_f°(SiF_3Co(CO)_4)$[b] kcal/mol
$SiF_3Co(CO)_4^+$ (256)	...	9.7 ± 0.1[c]	224	−257	...
$SiF_3Co(CO)_3^+$ (228)	CO	10.4 ± 0.1	240	−215	...
$SiF_3Co(CO)_2^+$ (200)[d]	2CO	...	...	...	...
$SiF_3Co(CO)^+$ (172)	3CO	13.8 ± 0.2	318	−84	...
SiF_3Co^+ (144)	4CO	15.1 ± 0.1	348	−27	...
$Co(CO)_2^+$ (115)	SiF_3 + 2CO	14.0 ± 0.2	323	138[e]	−491 ± 10[h]
$Co(CO)^+$ (87)	SiF_3 + 3CO	15.9 ± 0.2	367	203[e]	−496 ± 10[h]
SiF_3^+ (85)		16.3 ± 0.3	376	54[f]	
CoF^+ (78)	SiF_2 + 4CO	21.0 ± 0.3	484	248	...
Co^+ (59)	SiF_3 + 4CO	17.8 ± 0.2	410	287[g]	−482 ± 10[h]

[a] Average of seven independent measurements determined by Warren's method of extrapolated differences: J. W. Warren, *Nature*, **165,** 811 (1950). Calibrating gases: Ar (I = 15.8 V), Kr (I = 14.0 V), and Xe (I = 12.1 V). [b] Average value for $\Delta H_f°(SiF_3Co(CO)_4)$ = −490 ± 10 kcal/mol. [c] Standard deviation of the mean. [d] No value for the appearance potential of $SiF_3Co(CO)_2$; *m/e* 200 is reported because of interference from the Hg background in the mass spectrometer. [e] Reference 12. [f] Reference 15. [g] Reference 14. [h] Error includes the error of the appearance potential measurement and an estimate of the error in the heat of formation of the positive ion.

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can be calculated from appearance potential measurements, provided the ion source reaction is known or can be reasonably assumed and appropriate supporting thermochemical values are available. The pertinent equations are (for a hypothetical ion source reaction, $R_1R_2 \rightarrow R_1^+ + R_2$)

$$AP \geqq \Delta H_f^\circ(R_1^+) + \Delta H_f^\circ(R_2) - \Delta H_f^\circ(R_1R_2)$$

and

$$AP \geqq I(R_1) + D(R_1\text{–}R_2)$$

where AP is appearance potential, I is ionization potential, ΔH_f° is standard heat of formation, and D is bond dissociation energy. The inequality holds when any of the products contain excess energy. The ancillary values employed in these calculations were (in kcal/mol): $\Delta H_f^\circ(Co^+) = 287$,[14] $\Delta H_f^\circ(CO) = -26.4$,[14] $\Delta H_f^\circ(SiF_3) = -253$,[15] $\Delta H_f^\circ(SiF_3^+) = 54$,[15] $\Delta H_f^\circ(SiF_2) = -139$,[12] $I(SiF_3) = 307$,[15] $\Delta H_f^\circ(Co(CO)_4) = -132$,[12] $\Delta H_f^\circ(Co(CO)^+) = 203$,[12] and $\Delta H_f^\circ(Co(CO)_2^+) = 138$.[12]

In Table II it is noted that the appearance potential of SiF_3^+ is 16.3 ± 0.3 V. Dibeler and Mohler have reported[16] the appearance potential of SiF_3^+ from SiF_4 as 16.1 ± 0.2 V. Since SiF_4 is one of the decomposition products of $SiF_3Co(CO)_4$ and in view of the agreement between the appearance potentials, it appears that the SiF_3^+ ion arises from SiF_4 and not the carbonyl. At least the AP of SiF_3^+ from SiF_4 is lower than the AP of SiF_3^+ from $SiF_3Co(CO)_4$.

The differences between the sum of the heats of formation of $Co(CO)_4$ and SiF_3 and the heat of formation of $SiF_3Co(CO)_4$ is the bond dissociation energy of the Si–Co bond in this compound. The heat of formation of $SiF_3Co(CO)_4$ (−490 ± 10 kcal/mol) is 53 kcal/mol more negative than $\Delta H_f^\circ(CH_3SiF_2Co(CO)_4)$ (−437 ± 12 kcal/mol).[10] However, the bond dissociation energy $D(F_3Si\text{–}Co(CO)_4)$ (105 ± 12 kcal/mol) is 22 kcal/mol less than $D(CH_3SiF_2\text{–}Co(CO)_4)$ (127 ± 15 kcal/mol).[10] The relative difference in Si–Co bond dissociation energy is believed to be significant because the factors which give rise to the errors in the absolute values of the bond energy are essentially the same in both compounds. This difference suggests that there may be a greater degree of $(d \rightarrow d)\pi$ bonding between silicon and cobalt in $CH_3SiF_2Co(CO)_4$ than in $SiF_3Co(CO)_4$. The reason for this result can qualitatively be ascribed to the greater electron density in the silicon 3d orbital of $SiF_3Co(CO)_4$ arising from greater $(p \rightarrow d)\pi$ bonding between silicon and fluorine. The reduction in the π-electron density of the silicon when a fluorine atom is replaced by a methyl moiety might be expected to increase the amount of $(d \rightarrow d)\pi$ bonding between cobalt and silicon. It is interesting to note that greater $(d \rightarrow d)\pi$ bonding between cobalt and silicon in $CH_3SiF_2Co(CO)_4$, compared to $SiF_3Co(CO)_4$, is also suggested by the values reported[3] for $(k_e - k_a)$ of these compounds where k_e and k_a are the force constants for the equatorial and axial carbonyl ligands, respectively.

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Reactions of Coordinated Ligands. The Reaction of Isothiocyanatopentaamminecobalt(III) Ion with Hydrogen Peroxide in Acid Solution

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The kinetics and stoichiometry of the reaction of $Co(NH_3)_5NCS^{2+}$ with H_2O_2 at temperatures between 25 and 97° has recently been reported.[1] In the course of our studies on the oxidation, reduction, and addition reactions of the coordinated thiocyanate ion in complexes primarily of the type *cis*- and *trans*-$Co(en)_2XNCS^{n+}$, where X = Cl, Br, NO_2, NH_3, and NCS, we have also investigated the behavior of $Co(NH_3)_5NCS^{2+}$ with H_2O_2 and here report some of our observations.

Experimental Section

Reagents and Preparations.—Except as indicated "Analar" reagents were used throughout without further purification. $[Co(NH_3)_5NCS](ClO_4)_2$ was prepared as described by Werner and Muller.[2] The crude perchlorate was recrystallized from water containing $NaClO_4$ until pure. *Anal.* Calcd for $[Co(NH_3)_5NCS](ClO_4)_2$: Co, 14.70. Found: Co, 14.64. The compounds $[Co(NH_3)_6]Cl_3$,[3] $[Co(NH_3)_5H_2O]_2(C_2O_4)_3$,[4] and $[Co(NH_3)_5CN]Cl_2$[5] were obtained by the methods described in the references cited. The salts were recrystallized from a minimum of water at room temperature and analyzed spectrophotometrically. Molar extinction coefficients (ε) of the pure complexes were measured on a Unicam SP800 or a Cary 14 spectrophotometer employing solutions of approximately 10^{-3} M concentration and matched cells of path lengths 1.0, 2.0, and 5.0 cm. The cell compartment was thermostated at 25.0° in all cases. Values of λ_{max} (ε) for each complex used in these studies are as follows (Å, M^{-1} cm^{-1}): $[Co(NH_3)_5NCS]^{2+}$, 4960 (208), 3050 (1770); $[Co(NH_3)_6]^{3+}$, 4740 (53.3), 3390 (47.8); $[Co(NH_3)_5H_2O]^{3+}$, 4890 (48.4), 3420 (53.5); $[Co(NH_3)_5CN]^{2+}$, 4410 (53.4), 3270 (51.5).

Stock solutions of hydrogen peroxide were prepared from Baker hydrogen peroxide (30%) containing 0.05% $Na_4P_2O_7 \cdot 10H_2O$ as preservative and the peroxide content was determined iodimetrically following Vogel's[6] procedure. Stock solutions of hydrogen peroxide (∼9.0 M) were stored in the refrigerator when not in use and restandardized periodically.

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