Contribution from the Department of Chemistry,
Florida State University, Tallahassee, Florida 32306

Metal Carbonyl–Trifluorophosphine Systems. VII. Cobalt Carbonyl Hydrides and Perfluoroalkyls[1a]

By CARL A. UDOVICH and RONALD J. CLARK

Received October 8, 1968

Cobalt carbonyl compounds of the type $RCo(CO)_4$, where R is H, CF_3, C_2F_5, or C_3F_7, react readily with PF_3 to yield all possible substitution compositions of the type $RCo(PF_3)_x(CO)_{4-x}$. The hydride substitution takes place quite rapidly and spontaneously even at −20°. The perfluoroalkyls react more slowly than the hydrides, but the substitution is readily induced by ultraviolet light or slight heating and pressure. The various compositions can be isolated by gas–liquid partition chromatography. The materials are colorless or light yellow liquids, having melting points well below room temperature. Their thermal stability increases as the degree of substitution increases. The lower hydride species readily disproportionate, but the higher substitution products of the hydrides and all substituents of the alkyls can be kept chromatographically pure. The infrared spectra of these species indicate that they contain nonseparable isomers. Solvolysis studies support this hypothesis.

Introduction

This paper is a continuation of the studies of the substitution of phosphorus trifluoride into metal carbonyls. Work by Clark and coworkers[1] and by Kruck and his coworkers[2] has shown the great similarity between these two ligands toward lower valent transition metals.

This work is part of a continuing study of five-coordination. The similarity between PF_3 and CO allows nearly random exchange which allows the preparation of series of related five-coordinate species through substitution into parent compounds such as $HCo(CO)_4$ and $R_fCo(CO)_4$ where R_f represents a lower perfluoroalkyl homolog.

Of interest is the stereochemical relationship between the hydride group and other groups such as the perfluoroalkyl moiety. Early experiments suggested that $HCo(CO)_4$ behaved as a pseudonickel tetracarbonyl with tetrahedral geometry. Current work, however, suggests that the hydrogen atom is occupying a coordination site.[3] A comparison of corresponding compounds in the series $HCo(PF_3)_x(CO)_{4-x}$ and $R_fCo(PF_3)_x(CO)_{4-x}$ should shed some light on the matter. The latter must have normal five-coordinate structures.

Of the trifluorophosphine species in this series, work has been published on two, $HCo(PF_3)_4$[4] and $HCo(CO)(PF_3)_3$.[5] The work on this latter compound was published after the present work was underway and evoked some considerable interest on our part. The preparative procedure departed from Kruck's carbon monoxide free synthesis which has allowed him to prepare numerous totally substituted trifluorophosphine analogs of metal carbonyls. In his preparation of $HCo(CO)(PF_3)_3$, several approaches were employed. These entailed reactions such as

$$Co_2(CO)_8 + H_2 + 6PF_3 \xrightarrow{Pt} HCo(CO)(PF_3)_3 + 6CO$$

The product of the reaction was reported to be pure $HCo(CO)(PF_3)_3$—a direct reaction product. In our experience with mixed CO–PF_3 systems, it has *never* been possible to isolate any of these species pure from reactions whenever CO and PF_3 are both present—mixtures have always occurred. It is usually easy to sort out data such as infrared spectra from the mixtures, but the separation of the species has always required highly efficient techniques such as gas–liquid partition chromatography.

Experimental Section

Hydride Derivatives.—Mixtures of the $HCo(PF_3)_x(CO)_{4-x}$ species were prepared through the reaction of $HCo(CO)_4$ and PF_3. This direct replacement reaction occurs extremely rapidly. Samples of $HCo(CO)_4$ which had been prepared as described earlier[6] were distilled into a 500-ml flask at −195°. The desired amount of PF_3 was condensed into the flask and the vessel was allowed to warm to −20°. The contents were stirred for 1–2 hr at this temperature. The reaction was either terminated at this point or the flask was warmed to room temperature and allowed to react further depending upon the degree of reaction that was wanted.

The product distribution was controlled primarily by the PF_3:$HCo(CO)_4$ ratio and secondarily by the time of reaction. Since the first 2 mol of PF_3 can be consumed essentially quantitatively during the first few minutes of reaction, time was not a good control variable. It was found that the preparation of mixtures predominating in mono- and disubstitution requires careful control of the ratio. The amount of $HCo(CO)_4$ that had been vacuum distilled into the flask was measured by allowing it to melt into a small side arm whose volume had been previously determined. The volume of liquid $HCo(CO)_4$ was noted quickly when the sample was allowed to warm barely to its melting point of −20° and then the flask was quickly recooled to at least −78°. After the calculated quantity of PF_3 had been added, the reaction was allowed to take place at −20°. For the substitution of only one or two groups, the vessel was not

---

[1] (a) Part VI: W. J. Miles, Jr., and R. J. Clark, *Inorg. Chem.*, **7**, 1801 (1968); (b) earlier papers in the series.

[2] Th. Kruck, *Angew. Chem., Intern. Ed. Engl.*, **6**, 53 (1967).

[3] A. P. Ginsberg, *Transition Metal Chem.*, **1**, 112 (1965).

[4] Th. Kruck, W. Lang, and A. Engelmann, *Angew. Chem., Intern. Ed. Engl.*, **4**, 148 (1965).

[5] Th. Kruck and W. Lang, *Chem. Ber.*, **98**, 3060 (1965).

[6] R. J. Clark, S. E. Whiddon, and R. E. Serfass, *J. Organometal. Chem.* (Amsterdam), **11**, 637 (1968).

allowed to warm to room temperature for any length of time in order to avoid the formatioin of excessive quantities of dark polymeric materials. With higher PF_3:$HCo(CO)_4$ ratios, the flask could be warmed to room temperature after the initial reaction period at lower temperature was complete.

For the preparation of mixtures rich in tetrasubstitution, the flask was stirred for 1 hr or more at room temperature; then it was cooled to −195°, the evolved CO was removed under vacuum, and the flask was returned to room temperature for further reaction. This was repeated several times over the course of 12–24 hr.

The hydride samples were separated by gas–liquid partition chromatography using an Autoprep A-700. A 7 m × 0.25 in. copper or polyethylene column loaded with 40% DC-702 silicone oil on Chromasorb P was used with helium as the carrier gas. The unusually high loading was important in the separation of the mono- and diphosphine complexes. The temperature of the column, the injection port, the detector, and the collector were all kept between room temperature and 50°. Disproportionation of the mono- and disubstituted complexes became unreasonable at higher temperatures. Injection quantities of 25 μl could be used for clean separation of the tetra- and trisubstituted hydrides. The separation of the less substituted complexes was good enough to allow considerably larger injections. The components were trapped at −78°. The higher substituents were dried by distilling them through 4A Molecular Sieves. The lower products were stored at either −78 or −195° before use to prevent disproportionation.

Perfluoroalkyl Derivatives.—Trifluoroacetylcobalt tetracarbonyl was made by essentially the same procedure as that used by Hieber, *et al.*[7] The sodium salt $NaCo(CO)_4$ was allowed to react with $(CF_3CO)_2O$ in diethyl ether at 0° rather than dimethyl ether at −50°. The ether was removed from the acetyl compound under vacuum at −30°. The $CF_3COCo(CO)_4$ was purified by distilling it through 4A Molecular Sieves at room temperature.

Mixtures of the $CF_3Co(PF_3)_x(CO)_{4-x}$ species were prepared by a variety of techniques, each of which yielded a different mixture composition. It was not necessary to decarbonylate the acetyl parent before the PF_3 substitution reaction was allowed to occur. To prepare mixtures in which x is predominantly 3 and 4, 0.5 ml of $CF_3COCo(CO)_4$ was distilled into a 500-ml flask at −195° and 300 ml of PF_3 under standard conditions was added. The flask was irradiated by an A-H6 uv lamp for 2 hr and the mixture of cobalt compounds was recovered from the PF_3 and CO by simple vacuum manipulation. For x equals predominantly 2, 0.5 ml of $CF_3COCo(CO)_4$ was distilled into a 50-ml pressure vessel at −195° and sufficient PF_3 was added to yield a pressure of 200–400 psi at room temperature. The vessel was warmed to 45–50° for 12–24 hr and the mixture of complexes was recovered. Mixtures containing predominantly monosubstitution products were prepared by another variation. The perfluoroacetyl compound (0.5 ml) was distilled into a 500 ml flask containing about 15 g of 4A Molecular Sieves and sufficient PF_3 was added to yield a pressure of 500 Torr at room temperature. The vessel was allowed to stand at room temperature for 24 hr and the mixture of complexes was isolated.

We had some difficulty in getting the decarbonylation reaction of $CF_3COCo(CO)_4$ into $CF_3Co(CO)_4$ to take place. The reported procedure[7] resulted in excessive decomposition in our hands. The procedure used to prepare $CF_3Co(CO)_3(PF_3)$ discussed above suggests that the decarbonylation reaction will take place at room temperature over 4A Molecular Sieves. This was attempted by distilling 0.5 ml of $CF_3COCo(CO)_4$ into a flask containing 15 g of activated sieves. After 24 hr at room temperature, decarbonylation was complete and the recovery was essentially quantitative.

The $CF_3Co(PF_3)_x(CO)_{4-x}$ mixtures were separated on the same 40% DC-702 silicone oil column that was used for hydrides. The conditions of separation were the same.

The compounds $C_2F_5COCo(CO)_4$ and $C_3F_7COCo(CO)_4$ were produced from $NaCo(CO)_4$ and the appropriate acyl chloride.[7,8] The product was purified in the same manner as the previous acetyl compound. Decarbonylation and substitution occurred simultaneously under the influence of uv irradiation in the presence of PF_3. Using quantities comparable to the acetyl case, a composition predominating in $R_fCo(CO)_3(PF_3)$ resulted after about 15 min of irradiation and material predominating in di- and trisubstituted species resulted after 45 min. The totally substituted species occurred as minor products in the 45-min irradiations and as more major products in longer times. The tri- and tetraphosphine species had similar retention times using our present columns.

Equilibrium Constants.—A mildly accurate evaluation of the species distribution at equilibrium with CO and PF_3 was made for the hydride system. Two approaches were taken. In the first, various known CO:PF_3 gas ratios were established in a 10-cm gas cell and 0.5–1.0 μl of a cobalt hydride compound was injected into the cell. Reaction was initiated either by a series of 5-min irradiations with a 300-W uv lamp or by allowing the vessel to stand for much longer times. The spectra were run after various periods of time. The composition of the cobalt species was determined by calibrating the spectra against samples of the pure species and known mixtures. The calibration spectra had to be run quickly to avoid significant amounts of disproportionation. Equilibrium was approached from both directions.

In the second approach, small quantities of complexes were injected into a vessel containing the desired PF_3–CO gas mixture. This was equilibrated for 24–72 hr at room temperature. The ligand gas and the metal complexes were separated by vacuum manipulation and the complex composition was determined by infrared analysis in hexane. Alternately, when the most stable species $HCo(PF_3)_4$ and $HCo(CO)(PF_3)_3$ were involved, analysis was done by glpc. In each of the above examples, the relative quantities of ligand gas to complex were such that the reaction would not appreciably change the gas composition. The ligand gas ratio was determined by the initial pressures of the various gases.

General spectra were run on a P-E 521 spectrometer in 0.1-mm liquid cells in hexane. The spectrometer was calibrated with gaseous DCl for the carbonyl region and NH_3 for the P–F region. Metal analysis was done by atomic absorption on a P-E 303. The samples were run directly in an absolute ethanol solution. Molecular weights were determined by vapor density measurements.

The phosphorus trifluoride used in this work was obtained from Ozark-Mahoning Co. and purified as described earlier.[1]

Anal. Calcd for $HCo(CO)_3(PF_3)$: mol wt, 232. Found: mol wt, 236. Calcd for $HCo(CO)_2(PF_3)_2$: Co, 20.2; mol wt, 292. Found: Co, 20.8; mol wt, 287. Calcd for $HCo(CO)(PF_3)_3$: Co, 16.7; mol wt, 352. Found: Co, 16.8; mol wt, 354.

Results

Both $HCo(CO)_4$ and the $R_fCo(CO)_4$ compounds react with PF_3 to form complete series of species of the $HCo(PF_3)_x(CO)_{4-x}$ and $R_fCo(PF_3)_x(CO)_{4-x}$. The hydride species are prepared by the direct interaction between $HCo(CO)_4$ and PF_3, whereas the perfluoroalkyl species are prepared by a more indirect interaction between $R_fCOCo(CO)_4$ and PF_3.

The basic identification of the compounds comes by a study of the species using gas–liquid partition chromatography and infrared spectroscopy as a function of the extent of reaction. Using the assumption that the replacement of carbonyl groups by phosphorus trifluoride will be sequential, the various new species

---

(7) W. Hieber and E. Lindner, *Chem. Ber.*, **95**, 2042 (1962).

(8) W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961).

can be identified as they are formed by controlling the extent to which the reaction is allowed to proceed. The degree of reaction is controlled by the use of the variables time, temperature, and relative proportions of reactants.

In the case of the hydrides, the parent carbonyl $HCo(CO)_4$ is essentially impossible to inject into the gas–liquid partition chromatograph, and, if injected, it is eluted from the columns only in traces even at room temperature. Mainly gaseous decomposition products are formed. The reaction of $HCo(CO)_4$ with PF_3 is the fastest substitution reaction that the authors have ever encountered. After a quantity of hydride such as 1 ml of liquid reacts with PF_3 for only a few minutes at $-20°$, new products are found in the gas–liquid partition chromatograph. As the extent of reaction increases, the species with shorter retention times are systematically formed at the expense of those with longer retention times. Thus the hydrides are identified in Table I with $HCo(CO)_3(PF_3)$ having the longest retention time of the substituents down to $HCo(PF_3)_4$ having the shortest. These species follow the precedent established in other systems in which the higher substitution species have the shorter retention times.

Table I

Relative Retention Times of the $RCo(PF_3)_x(CO)_{4-x}$ Species

	R group			
Species	H	CF_3	C_2F_5	C_3F
$RCo(CO)_4$	1.00	1.00	1.00	1.00
$RCo(CO)_3(PF_3)$	0.63	0.57	0.53	0.52
$RCo(CO)_2(PF_3)_2$	0.41	0.38	0.31	0.30
$RCo(CO)(PF_3)_3$	0.29	0.26	0.25	0.24
$RCo(PF_3)_4$	0.25	0.22	. . .[a]	0.19[a]

[a] These species were not isolated, although they can easily be prepared in the mixtures.

The metal analysis and vapor density molecular weights on the hydride species agree closely with the expected values and add confirmation to the assignment made by other methods.

These hydride species can be isolated on a small scale by preparative glpc. Generally, they are pure when reinjected into the chromatograph immediately after isolation. A notable exception is the species identified as $HCo(CO)_3(PF_3)$, which disproportionates too fast to be kept in high purity.

The formation of the substituted trifluoromethylcobalt carbonyl compounds is slightly more indirect than the hydrides. It follows the general reaction

$$CF_3COCo(CO)_4 + xPF_3 \rightarrow CF_3Co(PF_3)_x(CO)_{4-x} + (x + 1)CO$$

An over-all composition of x equaling approximately 1 requires only standing at room temperature over the surface of molecular sieves for 24 hr; for x equal to about 2, high pressure and a little heating are used; and for x equal to 3–4, uv irradiation is best. It should be emphasized that these compositional ranges are not mutually exclusive but are matters of experimental convenience. The complete reaction consists of both decarbonylation and substitution. It would seem that the decarbonylation is either the first reaction or takes place quite rapidly after the first stage of substitution. There is no indication of the presence of PF_3-substituted acetyl species of the type $CF_3COCo(PF_3)_x(CO)_{4-x}$.

The ethyl and propyl compounds were prepared by the uv method but in this case the reaction was somewhat faster. There was no evidence whatsoever for substituted acyl compounds.

The identity of the alkyl species, all of which are stable in the gas–liquid partition chromatograph, can be essentially unambiguously established by the sequence of formation approach that is used for the hydrides and other systems that have been studied. Also, an infrared comparison between the various alkyls and the analyzed hydrides shows that these systems are undoubtedly closely related and adds further confirmation to the assignment.

A fluorine nmr study that will be reported shortly fully confirms the compositional assignments.

The infrared spectra for these species in hexane are shown in Table II. The gas-phase spectra were also run for several of the hydride species and these spectra agree well with those obtained by MacDiarmid[9] on these species using a radically different preparative approach. The gas-phase spectra are similar to the liquid-phase spectra in many respects, but a couple of differences should be noted. The corresponding bands have shifted about 8 cm^{-1} to higher frequencies in the gas phase. In addition, a few features are seen in the liquid spectra that are not seen in the gas spectra. In the species $HCo(CO)(PF_3)_3$, a very weak shoulder is seen at 2062 cm^{-1} on the low-frequency side of the main band. (This compound is stable to disproportionation for several hours and can be prepared in high purity.) This band is not at the expected frequency for a C^{13} absorption. At a glance it appears so weak that one might prefer to attribute this band to an impurity. However, it appears in the spectra in exactly the same way in every preparation which leads the authors to think that the band is something inherent in $HCo(CO)(PF_3)_3$. It might be noted that application of curve analysis using either Gaussian or Lorentzian curves, in which one assumes peaks of the same inherent width, indicates that this small band *could* be a component of appreciable concentration. The curves are illustrated in Figure 1. Since one does not know the relative absorptivities for the two bands, extensive speculation is not profitable. The nature of these peaks is such that the two monocarbonyls, $HCo(CO)(PF_3)_3$ and $Fe(CO)(PF_3)_4$, may well be similar. In the latter, two isomers are clearly indicated.[10]

The same type of situation occurs in the dicarbonyl $HCo(CO)_2(PF_3)_2$. Two bands are seen, as expected, for the dicarbonyl in gas spectra, whereas a third is always present at medium intensity in the liquid spectra. This band, at 2036 cm^{-1}, unfortunately corresponds closely

---

(9) A. G. MacDiarmid, private communication.

(10) R. J. Clark, *Inorg. Chem.*, 3, 1395 (1964).

TABLE II

INFRARED SPECTRA OF $\mathrm{RCo(PF_3)_x(CO)_{4-x}}$ SPECIES (CM^{-1})

$\mathrm{HCo(PF_3)_4}$	$\mathrm{HCo(CO)\ (PF_3)_3}$	$\mathrm{HCo(CO)_2(PF_3)_2}$	$\mathrm{HCo(CO)_3(PF_3)}$[a]
	2071 s	2086 s	2102 m
. . .	2062 sh	2050 s	2051 m
	2023 w[c]	2035 m	2035 s
		2019 vw[c]	2003 w[c]
		2015 vw[c]	
1978 w	1962 w		1929 w
	929 m	1945 w	904 w
	894 s	904 m	874 s
	859 s	885 m	857 w
		876 sh	
		856 m	
$\mathrm{CF_3Co(PF_3)_4}$	$\mathrm{CF_3Co(CO)(PF_3)_3}$	$\mathrm{CF_3Co(CO)_2(PF_3)_2}$	$\mathrm{CF_3Co(CO)_3(PF_3)}$
	2071 s	2096 s	2116 w
. . .	2057 vw	2080 vw[c]	2052 vs
	2024 vw[c]	2060 s	2014 vw[c]
		2050 vs	
		2025 vw[c]	
		2015 vw[c]	
1072 m	1061 m, b	1078 m	1081 m
1059 m		1055 m	1049 m
		1048 sh	
931 w	925 w	918 m	912 w
925 m	903 m	904 s	893 m
912 w	865 s	894 m	879 w
861 s		865 s	864 vw
$\mathrm{C_2F_5Co(PF_3)_4}$	$\mathrm{C_2F_5Co(CO)(PF_3)_3}$	$\mathrm{C_2F_5Co(CO)_2(PF_3)_2}$	$\mathrm{C_2F_5Co(CO)_3(PF_3)}$
	2065 s	2094 w	2114 w
. . .	2049 vw	2091 m	2055 s
	2017 vw[c]	2077 vw[c]	2048 s
		2058 w	2017 vw[c]
		2047 vs	2009 vw[c]
		2012 vw[c]	
. . .[b]	1280 w	1296 w	1200 w
	1198 m	1286 w	1195 w
	1048 w	1202 m	1055 w
		1059 m	
	940 vw	920 m	910 w
	923 w	887 s	884 w
. . .	909 m	863 m	872 w
	887 s		
	857 s		
n-$\mathrm{C_3F_7Co(PF_3)_4}$	n-$\mathrm{C_3F_7Co(CO)(PF_3)_3}$	n-$\mathrm{C_3F_7Co(CO)_2(PF_3)_2}$	n-$\mathrm{C_3F_7Co(CO)(_3PF_3)}$
	2069 sh	2094 w	2115 w
. . .[b]	2065 s	2091 w	2055 s
	2047 w	2077 vw[c]	2048 m
	2017 vw[c]	2058 w	2019 vw[c]
		2047 vs	
		2012 vw[c]	

[a] This species is too unstable to assign clearly, especially in the P–F region. [b] These species were not isolated although they could be prepared readily. [c] Indicates probable C^{13} mode.

to a band belonging to $\mathrm{HCo(CO)_3(PF_3)}$. Since disproportionation of the dicarbonyl to the tri- and monocarbonyls will occur, this source for the band must be eliminated before one can properly evoke any phenomena such as mixed isomers. This is difficult to do. The approach that was taken was to study the liquid spectra of the $\mathrm{HCo(PF_3)_x(CO)_{4-x}}$ species that had been equilibrated with various $\mathrm{PF_3}$:CO ratios. As one increases the $\mathrm{PF_3}$:CO ratio, the composition will shift away from the tricarbonyl toward di- and monocarbonyls. (The equilibrium constants will be discussed shortly.) Thus if the 2036-cm^{-1} peak belongs to only the tricarbonyl, the 2101-cm^{-1} peak (unique to the tricarbonyl) and the 2036-cm^{-1} peak will both diminish relative to the 2049-cm^{-1} peak of the dicarbonyl. On the other hand, if the 2036-cm^{-1} peak belongs to both the tri- and dicarbonyls, then the 2101-cm^{-1} peak will tend to disappear while the 2049- and 2036-cm^{-1} peaks settle into a constant ratio characteristic of the dicarbonyl. Of the two alternatives, the latter appears to be taking place. However, the whole problem is complicated by the need to separate

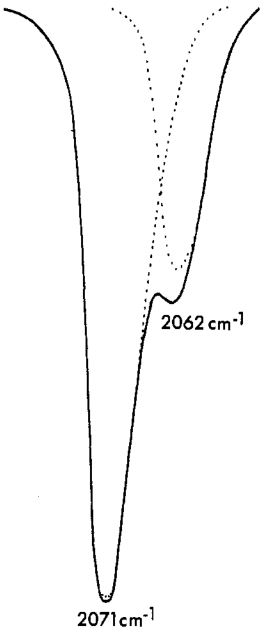

Figure 1.—Expanded infrared spectrum of $HCo(CO)(PF_3)_3$ in hexane.

the complexes from the gaseous equilibrium in order to run the liquid spectrum. The instability of this cobalt hydride species to disproportionation, dimerization, and oxidation makes it fruitless to argue seriously about the number of bands present in the purified species.

The perfluoroalkyl derivatives show spectra comparable to those of the hydrides. These species disproportionate much more slowly than the hydrides so once they are prepared chromatographically pure, they are still chromatographically pure after a fair amount of handling. Each of the three monocarbonyls shows basically the same spectrum, a strong band at about 2065–2071 cm^{-1} and a much weaker band about 16 cm^{-1} at lower frequency. Also, 46–48 cm^{-1} below the strong band, a weak band appears that seems appropriate for a C^{13} absorption.

The dicarbonylperfluoroalkyls have infrared spectra that are also analogous to those of the corresponding hydrides. Since the alkyls are much more stable toward disproportionation than the hydrides, the assignments are much less speculative than in the latter. Each of the alkyls shows three main bands in the carbonyl region in the neighborhood of 2095, 2060, and 2050 cm^{-1}. The 2095-cm^{-1} band is split into a doublet in the ethyl and propyl derivatives. The relative intensities of the three bands in each alkyl varies more than one might expect as one simply varies an R group on a single type of species. This variation strongly suggests that more than one isomer is present in each chromatographically pure composition. A variable-temperature fluorine nmr study currently in progress on the $R_fCo(PF_3)_x(CO)_{4-x}$ species confirms the infrared evidence of an isomer equilibrium in these compounds.

The infrared spectra of the present $R_fCo(CO)_4$ species are close to those reported in the literature.[7,8] However, it was found that the strong band that occurs at about 2055 cm^{-1} in various compounds was split in the ethyl and propyl derivatives. No sign of a splitting could be found in the methyl derivative even under the highest resolution. The explanation is probably the same as that for related phenomena observed with $R_fMn(CO)_5$ species.[11] In the present case the 2055-cm^{-1} band is probably a degenerate E mode in the C_{3v} symmetry. The asymmetry of the ethyl and propyl derivatives causes this to be split.

The limited solvolysis studies on $CF_3Co(CO)_2(PF_3)_2$ produces some dramatic changes in the spectra as shown in Figure 2. One effect of solvolysis is to shift the band location about 10 cm^{-1} to lower frequency as each $-OCH_3$ group is added.[12] More significant, however, are the relative band intensities. As shown in Figure 2, the relative intensity of the band starting at 2050 cm^{-1} is unchanged. The band commencing at 2096 cm^{-1} is reduced by perhaps 50% and the band at 2060 cm^{-1} becomes quite weak. All of these data can be interpreted by assuming that one dicarbonyl species had bands originally at 2096 and 2050 cm^{-1} and the other had bands at 2096 and 2060 cm^{-1}. On solvolysis, the first set is only shifted whereas the second set is shifted and also reduced drastically owing to a change in the composition of the mixture.

The hydride species $HCo(PF_3)_x(CO)_{4-x}$ are in fairly rapid equilibrium with the ligand gases PF_3 and CO. Thus one can attempt the evaluation of the equilibrium constants of the four reactions starting with $HCo(CO)_4 + PF_3 \rightarrow HCo(CO)_3(PF_3) + CO$. The random scrambling among the species for the four stages of reaction yields values of K_1, K_2, K_3, and K_4 of 4.0, 1.5, 0.66, and 0.25, respectively. The value of K_1 for the reaction shown above is not readily evaluated owing to the extreme instability of $HCo(CO)_4$ toward decomposition to $Co_2(CO)_8$. The current best values of K_2, K_3, and K_4 are 75, 10, and 0.25, respectively. The first equilibrium constants are well removed from the random values.

The properties of the hydride species have been described previously. They are all colorless, volatile liquids, having the ability to disproportionate or rescramble into the full array of species. The tricarbonyl does so to an appreciable extent in minutes and the monocarbonyl in hours. The tendency to dimerize decreases rapidly down the series. As in all PF_3 species, they are stable to attack by solvents like hexane and benzene but react rapidly with solvents such as acetone and alcohols. The alkyl species are yellow liquids and are considerably more stable to disproportionation than the hydrides. The melting points of all intermediates are well below those of the parent carbonyls and they are usually below −78°.

---

[11] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).
[12] R. J. Clark and K. A. Morgan, *Inorg. Chim. Acta*, **2**, 93 (1968).

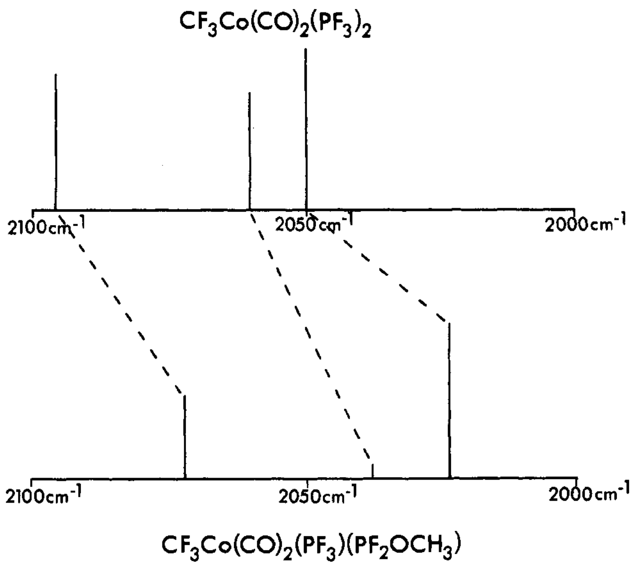

Figure 2.—Spectral change in $CF_3Co(CO)_2(PF_3)_2$ on monosolvolysis with methanol.

Discussion

The structures of these species are of considerable interest although little can be said definitively. The hydrides are certainly not pseudotetrahedral species since their spectra do not resemble those of the $Ni(CO)_x(PF_3)_{4-x}$ species in either the carbonyl or the P–F regions. This has already been noted by Kruck[4] in comparing $Ni(PF_3)_4$ and $HCo(PF_3)_4$, and he surmised, no doubt correctly, that the species are trigonal bipyramid. The resemblance in the spectra between the related $R_fCo(PF_3)_x(CO)_{4-x}$ and $HCo(PF_3)_x(CO)_{4-x}$ species clearly implies that the hydrides must have the same five-coordinate structure as the alkyls. The question as to the location of the hydride atom and the trifluoralkyl group is still open, although they are generally assumed to be axial.[2,3,7,8] The proton nmr spectra are quite broad and have not aided as yet in determining these stereochemical features. Fluorine work which is under extensive investigation currently on the alkyls is consistent with the idea of an axial CF_3 group (and also the presence of an isomeric equilibrium as discussed below).

The carbonyl infrared spectra of both the hydride and alkyl series can be interpreted in terms of the presence of nonisolable isomers. This phenomenon is becoming common in five-coordinate mixed carbonyl–phosphorus trifluoride systems.[13] Most species are prepared chromatographically pure on long, highly efficient columns and are shown to be relatively stable. The numerous bands at similar frequencies in species of different degrees of substitution must be accidental. There is a precedent for metal carbonyl–phosphorus trifluoride systems to have bands at similar frequencies.[14] This is presumably due to the nearly identical bonding properties of CO and PF_3.

The solvolysis work with $CF_3Co(CO)_2(PF_3)_2$ strongly suggests that the relative proportion of two isomers is capable of changing through a rapid internal inversion process as the ligand PF_3 is changed into PF_2OCH_3, etc. The implication of this and related solvolysis work toward isomer composition and the phenomenon of internal inversion will be discussed fully in a forthcoming paper on the $Fe(CO)_x(PF_3)_{5-x}$ system and its solvolysis reaction.[13]

The number of bands present in the infrared spectra of any chromatographically pure mono- or dicarbonyl or their solvolysis products is always too large for a single species and generally too small for the number of isomers potentially capable of being present. We assume that the poorer π-bonding ligands—the original H or R_f group and then the solvolysis product PF_2OCH_3—will each seek the axial location and this will reduce the number of isomers that is possible in the system. When the number of possibilities is reduced in this fashion, the spectra can be tentatively assigned as in Figure 2.

Two further points on the hydride system are particularly noteworthy. One is the speed of the substitution reaction. The uptake of PF_3 by $HCo(CO)_4$ is extremely rapid even at low temperature and it could well be approaching contact time for the gas–liquid reaction during at least the first two stages of reaction. This is consistent with what Heck[15] observed with the first stage of substitution with triphenylphosphine into $HCo(CO)_4$. The reason for this rapid exchange is not clear, but it may be consistent with the speed of CO exchange observed by Basolo[16] in related systems. Since these are strong acids, the reactions could be essentially autocatalytic by a protonation step in a fashion similar to that observed with iron pentacarbonyl.[16] It was found that protonation considerably increased the speed of carbonyl exchange. Although we have made no kinetic measurements, our qualitative observations have made us suspect that the rate of reaction although always fast may vary significantly between certain preparations. If so, the rapid reaction might also be attributable to trace impurities such as acids or water or possibly to the catalytic effect of variable amounts of dimerization products such as $Co_2(CO)_8$.

The other point worthy of special note is the significant deviation from random scrambling in the distribution of the ligands CO and PF_3. Phosphorus trifluoride is the preferred ligand in the bound state particularly in the early stages of substitution. In other systems for which data have been taken—$Ni(CO)_x(PF_3)_{4-x}$ and $Co(NO)(CO)_x(PF_3)_{3-x}$—the systems do not deviate nearly as much from randomness. In the other two systems, all ligands have had very good π-bonding

---

(13) References 1 and 10 give some of the limited data. Work by Udovich and Clark, in press, will explore this phenomenon in depth with the iron system.

(14) R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, **4**, 1771 (1965).

(15) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 657 (1963).

(16) F. Basolo, A. T. Brault, and A. J. Poë, *J. Chem. Soc.*, 676 (1964).

abilities. In the present case with the hydride present, the cobalt will favor the best π-bonding ligand. It has been suggested by Cotton[17] and Horrocks[18] among others that PF_3 is slightly better at π bonding than CO. This might explain the preference for PF_3. We are attempting to test this idea.

The equilibrium constant data, combined with the rapid reaction rates, clearly demonstrate that $HCo(CO)(PF_3)_3$ should never result as a single product from a reaction involving only cobalt hydrides and the ligand gases CO and PF_3. Calculations show that major concentrations of the other species will also be present in most $CO:PF_3$ mole ratios. Kruck's work[4] in the isolation of $HCo(CO)(PF_3)_3$ must then force one to the conclusion that the hydrogen fluoride impurity either added deliberately or in the form of impure phosphorus trifluoride must play some rather unique role in the formation of the monocarbonyl.

Acknowledgment.—The authors gratefully acknowledge the Atomic Energy Commission (Grant AT-(40-1)-3352) for financial support during the course of this work. We also wish to thank Dr. Fred Basolo and Dr. Alan MacDiarmid for useful discussions.

(17) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84,** 4432 (1962).
(18) W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, **2,** 723 (1963).

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

Vibrational Spectra and Structure of Some Silicon-Containing Compounds. II. Hexachlorodisiloxane

By J. R. DURIG and K. L. HELLAMS[1]

Received August 9, 1968

The Raman spectrum of liquid hexachlorodisiloxane $[(SiCl_3)_2O]$ was recorded with both Toronto arc and He–Ne laser excitation. Quantitative depolarization values were measured for all lines of reasonable intensity. The mid-infrared spectrum was recorded of a contact film and the far-infrared spectrum was recorded to 33 cm^{-1} of solutions in both benzene and cyclohexane. The spectra have been interpreted in detail and it was found that D_{3h} or D_{3d} symmetry selection rules are most satisfactory for spectral interpretation. Such high symmetry is indicative of a very large Si–O–Si angle; however, the spectra clearly indicate that the molecule is not linear. The assignments are tabulated and discussed in detail.

Introduction

The surprisingly large Si–O–Si bond angles reported for disiloxanes and related molecules[2–4] have stimulated particular interest in the vibrational spectra of these molecules.[5–24] The majority of these spectra (Raman and infrared) display a simplicity suggestive of the operation of selection rules of high symmetry. Indeed the vibrational spectra of disiloxane and disiloxane-d_6 have been observed to follow the selection rules of D_{3d} symmetry.[13] The vibrational spectra of hexamethyldisiloxane which have been studied repeatedly[7,12,14,18,20–22,24] furnish another case in point. Scott, *et al.*, have selected frequencies "that appear well established" for this molecule and assigned them to the fundamental modes of vibration according to C_{2v} symmetry; such an assignment scheme requires numerous accidental degeneracies.

In order that a disiloxane derivative have a symmetry higher than C_{2v}, the Si–O–Si bond angle must approach linearity. To explain the wide Si–O–Si bond angles observed, $d\pi$–$p\pi$ interaction between silicon and oxygen atoms has been suggested. Since such interaction might be enhanced by electronegative sub-

(1) Taken from the thesis submitted by K. L. Hellams to the Department of Chemistry in partial fulfillment for the Ph.D. degree; presented at the 23rd Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Sept 4, 1968.
(2) M. Yokoi, *Bull. Chem. Soc. Japan*, **30,** 100 (1957).
(3) M. Yokoi, *ibid.*, **30,** 106 (1957).
(4) K. Yamasaki, A. Kotera, M. Yokoi, and Y. Ueda, *J. Chem. Phys.*, **18,** 1414 (1950).
(5) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **42,** 2496 (1964).
(6) A. L. Smith, *Spectrochim. Acta*, **19,** 849 (1963).
(7) D. W. Scott, J. F. Messerly, S. S. Tadd, G. B. Guthrie, I. A. Hossenlopp, R. T. Moore, A. Osborn, W. T. Berg, and J. P. McCullough, *J. Phys. Chem.*, **65,** 1320 (1961).
(8) H. Kriegsmann, *Z. Anorg. Allgem. Chem.*, **299,** 78 (1959).
(9) A. N. Lazarev, M. G. Voronkov, and T. F. Tenisheva, *Opt. i Spektroskopiya*, **5,** 365 (1958).
(10) D. C. McKean, *Spectrochim. Acta*, **13,** 38 (1958).
(11) H. Kriegsmann and K. H. Schowta, *Z. Physik. Chem.* (Leipzig), **209,** 261 (1958).
(12) H. Kriegsmann, *Z. Elektrochem.*, **61,** 1088 (1957).
(13) R. C. Lord, D. W. Robinson, and W. C. Schumb, *J. Am. Chem. Soc.*, **78,** 1327 (1956).
(14) Ya. M. Slobodin, Ya. E. Shmulyakovskii, and K. A. Rzhedzinskaya, *Dokl. Akad. Nauk SSSR*, **105,** 958 (1955).
(15) C. C. Certo, J. L. Lauer, and H. C. Beachell, *J. Chem. Phys.*, **22,** 1 (1954).
(16) R. Sh. Malkovich and V. A. Kolesova, *Zh. Fiz. Khim.*, **28,** 926 (1954).
(17) R. Ulbrich, *Z. Naturforsch.*, **9b,** 380 (1954).
(18) A. P. Kreshkov, Yu. Ya. Mikabailenko, and G. F. Yakimovich, *Zh. Fiz. Khim.*, **28,** 537 (1954).
(19) L. Savidon, *Bull. Soc. Chim. France*, **20,** 411 (1953).
(20) H. Murato and M. Kumada, *J. Chem. Phys.*, **21,** 945 (1953).
(21) I. Simon and H. O. Mahon, *ibid.*, **20,** 905 (1952).
(22) E. Richards and H. W. Thompson, *J. Chem. Soc.*, 124 (1949).
(23) J. Goubeau and R. Warnick, *Z. Anorg. Chem.*, **259,** 233 (1949).
(24) N. Wright and M. J. Hunter, *J. Am. Chem. Soc.*, **69,** 803 (1947).