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Metal Carbonyl–Phosphorus Trifluoride Systems. XIII. Fluorine Nuclear Magnetic Resonance Studies on $R_fCo(PF_3)_x(CO)_{4-x}$ Compounds ($R_f = CF_3, C_2F_5, C_3F_7$)[1]

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A fluorine NMR study has been done on the $R_fCo(PF_3)_x(CO)_{4-x}$ species ($R_f = CF_3$, C_2F_5, C_3F_7, $x = 1$–4). All of the species are stereochemically nonrigid at room temperature. In many cases, temperatures approaching −100 °C are required to freeze out the motion. However, even this temperature did not always yield the limiting structure. Two types of dynamic processes have been found: one occurring between different isomers and the other between nonequivalent sites in a single isomer. All of the data are most simply explained by assuming a trigonal-bipyramidal structure with an axial perfluoroalkyl group. In the $CF_3Co(PF_3)_x(CO)_{4-x}$ series when $x = 1$, there are nearly equal proportions of isomers having axial and equatorial PF_3 groups. The equatorial isomer is increasingly favored for $x = 2$ and 3. For the species $R_fCo(PF_3)(CO)_3$ of the perfluoroethyl and perfluoropropyl species, the isomer with an axial PF_3 group is strongly favored over the equatorial. For the di- and trisubstituted compounds of this latter series, the isomer with all PF_3 ligands equatorial is sufficiently disfavored that it is not seen at all.

Introduction

The stereochemical nonrigidity of five-coordinate compounds, particularly those in their lower oxidation states, seems now to be a ubiquitous aspect of their structural character.[3] In studies on the species $R_fCo(PF_3)_x(CO)_{4-x}$, where $R_f = CF_3$, C_2F_5, and C_3F_7 and $x = 1$–4, the nonrigidity has been clearly demonstrated,[4-6] particularly in the case of $CF_3Co(PF_3)(CO)_3$.[4] At the time of publication of the work on the trifluoromethyl compound,[4] our NMR equipment was not adequate to give us enough confidence to publish the data[6] on the species having a greater degree of NMR complexity. We have now reprepared the species and taken new NMR data on modern equipment. The earlier data[4,6] have by and large been reconfirmed and expanded upon and it is the results of this study that we wish to report.

Experimental Section

The compounds were reprepared using essentially the same procedures as before. The species with a lower PF_3 content disproportionate at a moderate rate. Therefore it was necessary to separate them by gas chromatography under the mildest conditions possible. Also, it was found necessary to store the sealed samples at low temperatures for the same reason. The spectra of the disproportionation products are readily recognizable and are generally sufficiently resolved from the spectrum of the main product to be tolerated in small amounts. On the other hand, trace amounts of decomposition yielded paramagnetic impurities which resulted in poor resolution. Vacuum distillation followed by sealing under vacuum resulted in high-quality spectra when the operations were carefully done.

The NMR samples were run as roughly 10% solutions in an approximately equal-volume mixture of $CFCl_3$ and $CFHCl_2$, using a few percent of $CF_3C_6H_5$ as internal lock and reference. Alternatively, $C_2F_4Br_2$ and $CFHCl_2$, with a lock on the upfield half of the fluorine spectrum of the latter, could be used. The fluorine peak of $C_2F_4Br_2$ broadened too much below −80 °C to be used as lock, but it still served as a good solvent. Spectra were run on a Bruker HFX-90 at 84.66 MHz. The temperature-measuring and -controlling thermocouple was placed just below the NMR tube. It was calibrated by a thermocouple immersed in a blank tube and is felt to be accurate to ±2 °C. For reference purposes, $CFCl_3$ is 63.43 ppm downfield of $CF_3C_6H_5$, and the upfield peak of $CFHCl_2$ is 17.68 ppm upfield of $CF_3C_6H_5$. All chemical shifts are reported as positive downfield of $CF_3C_6H_5$.

Results

There are a number of possible isomers for the various compositions of the system $R_fCo(PF_3)_x(CO)_{4-x}$. Five-coordinate compounds can be either trigonal bipyramidal (TBP) or square-based pyramidal (SBP) with these species most commonly being TBP.[7] The various isomers within such a structure are shown in Figure 1. It is generally found that in these TBP structures a ligand or group like CF_3, which would π bond less than CO (or PF_3), will occupy an axial site.[7] This reduces further the number of isomers but leaves two isomers for each mixed carbonyl–trifluorophosphine composition.

The infrared data[5] in the carbonyl stretching region are not always definitive concerning the number of isomers. For the tricarbonyl, if two isomers are present, five bands are expected. For a single isomer, either three or two bands are expected. Three ir ^{12}CO stretching frequencies, however, are clearly distinguished from the various weak ^{13}CO bands. Therefore, if two isomers are present, there must be a high degree of accidental degeneracy among the bands. For the dicarbonyl, where two stretching bands are expected for either isomer, three bands are seen. The third band indicates the presence of two isomers, but again, one band of the four expected bands is not observed. For the monocarbonyl a shoulder on the major band implies a second isomer.

The room-temperature NMR data indicate a single isomer for each member of the series. The fluorine spectra in the PF_3 region for the mono-, di-, and trisubstituted compounds are similar in appearance to species containing one, two, and three equivalent PF_3 groups.[8] Further, the coupling of the phosphorus atoms to either the CF_3 group or the α fluorines of the C_2F_5 and C_3F_7 groups is indicative of equivalent fluorines. The room-temperature data are given in Table I.

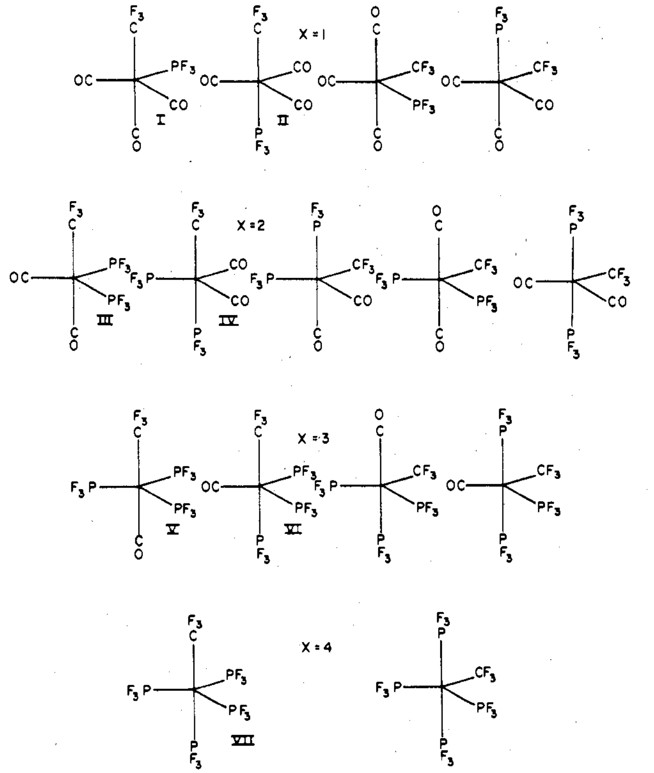

Figure 1. Possible trigonal-bipyramidal isomers of the $CF_3Co(PF_3)_x(CO)_{4-x}$ species. The numbered isomers on the left are those with the CF_3 group axial.

Table I

	$\delta(F_{c\alpha})^a$	$\delta(F_P)^a$	$^1J_{PF}$, Hz	$^3J_{PF_c}$, Hz	$^4J_{FF}$, Hz
$CF_3Co(PF_3)(CO)_3$	74.40	47.76	1371	59	6
$CF_3Co(PF_3)_2(CO)_2$	76.79	47.07	1337	47	
$CF_3Co(PF_3)_3(CO)$	79.17	47.32	1395	41	4
$CF_3Co(PF_3)_4$	81.61	50.11	1319	46	6
$C_2F_5Co(PF_3)(CO)_3{}^b$	8.44	49.66	1371	63	6
$C_2F_5Co(PF_3)_2(CO)_2$	9.11	49.03	1348	63	
$C_2F_8Co(PF_3)_3(CO)$	11.27	49.68	1342	57	
$C_2F_5Co(PF_3)_4$	16.14	51.40	1329	51	
$C_3F_7Co(PF_3)(CO)_3{}^c$	13.12	49.63	1373	62	6
$C_3F_7Co(PF_3)_2(CO)_2{}^d$	13.69	49.02	1348	65^e	6

[a] Chemical shifts downfield relative to $CF_3C_6H_5$. [b] For $C_2F_5Co(CO)_4$: $\delta(F_{c\alpha})$ 7.02, $\delta(F_{c\gamma})$ −18.46. [c] $\delta(F_{c\gamma})$ −15.85, $\delta(F_{c\beta})$ −50.46. [d] $\delta(F_{c\gamma})$ −15.77, $\delta(F_{c\beta})$ −49.86. [e] For the compounds $C_3F_7Co(PF_3)_3(CO)$ and $C_3F_7Co(PF_3)_4$, the $^3J_{PF}$ values are 56 and 52 Hz, respectively.

Several factors, however, argue that these room-temperature NMR data represent a time average of several isomers rather than the low-temperature limit or a single isomer. First, the ir data in some cases point toward more than one isomer being present for each chromatographically purified species. Second, there are solvolysis reaction results that argue in favor of the presence of two isomers.[5] Third, it is hard to imagine a single consistent structural type among either the TBP or SBP stereochemistries that would yield equivalent PF_3 groups throughout an $R_fCo(PF_3)_x(CO)_{4-x}$ series with x up to 4. Finally, the low-temperature NMR data to be discussed below are proof of a dynamic process.

Trifluoromethyl Compounds.[6b] The data for the $CF_3Co(PF_3)(CO)_3$ compound have been reported earlier.[4] The results obtained on the newly prepared compound run on a 90-MHz instrument agree closely with those found earlier. The only changes are those to be expected from a 50% increase in the field. At room temperature or slightly above, the spectrum consists of a doublet of quartets for both the methyl and phosphine fluorines. The $^3J_{PF_c}$ and $^1J_{PF}$ coupling constants are 59 and 1371 Hz, respectively. Both portions of the spectrum broaden as the temperature is lowered, with the PF_3 fluorines broadening at somewhat higher temperatures than the methyl fluorines. By −70 °C, the limiting spectrum is fully developed. In the PF_3 region, the doublet of quartets that existed at room temperature has been replaced by two sets of doublets of quartets. In the CF_3 region, the same thing occurs. There is, however, some slight overlap among the peaks. The values of the coupling constants found show clearly that two different isomers are being frozen out.[9] It seems reasonable to assign the two isomers structures I and II, respectively. For the two species, the $^3J_{PF_c}$ coupling constants are 40 and 80 Hz, and $^1J_{PF}$ are 1373 and 1351 Hz. If one assumes that $^3J_{PF_c}$ follows the same trends as in the compound $Fe(PF_3)_2(CO)_3$,[10] where the trends in coupling are cis < vicinal < trans, then the 40-Hz coupling would be assigned to the equatorial isomer I and the 80-Hz coupling to the axial isomer II. The time-averaged room-temperature coupling constant is about halfway between the values of the two limiting constants. Thus at high temperature there are nearly equal quantities of the two isomers. At low temperature, there are roughly equal areas under the peaks of the two isomers. It therefore appears that the isomers have almost identical energies and that there is very limited population shift over the temperature range studied. The $^4J_{FF}$ coupling constants also follow the same trend in magnitude as the $^3J_{PF_c}$ constants. For the isomer assigned to I, a value of 3 Hz is found; for II, a value of 9 Hz is found. The room-temperature time-averaged value of 6 Hz again argues that little shift in the equilibrium position has occurred.

The fluorine spectrum of the compound $CF_3Co(PF_3)_2(CO)_2$ is again time-averaged showing equivalent PF_3 groups. The PF_3 spectrum has the characteristic mirror-imaged second-order[8] pattern of two equivalent PF_3 groups. Unfortunately, the added complication of further coupling to the CF_3 group makes it difficult to obtain the various time-averaged coupling parameters. The perfluoromethyl fluorines are split into a triplet of heptets. Representative spectra at various temperatures are shown in Figure 2. The spectrum in the perfluoromethyl region begins to broaden at 10 °C reaching a maximum broadness at −20 °C. At −40 °C, the perfluoromethyl fluorines have sharpened into two sets of triplets of multiplets with phosphorus–fluorine coupling in the major one being about 38 Hz and in the minor one about 61 Hz. As the temperature is lowered further, the minor triplet rebroadens somewhat and resharpens into a doublet of doublets with couplings of 74 and 33 Hz. This seems to be the limiting structure. Since peaks of the doublet of doublets are broad, poorly resolved multiplets, the coupling constants are hard to obtain with accuracy. Since we have taken no phosphorus NMR data, it is not possible to determine if the chemical shifts between the axial and equatorial phosphorus atoms are sufficiently large relative to $^2J_{PP'}$ to yield the truly first-order

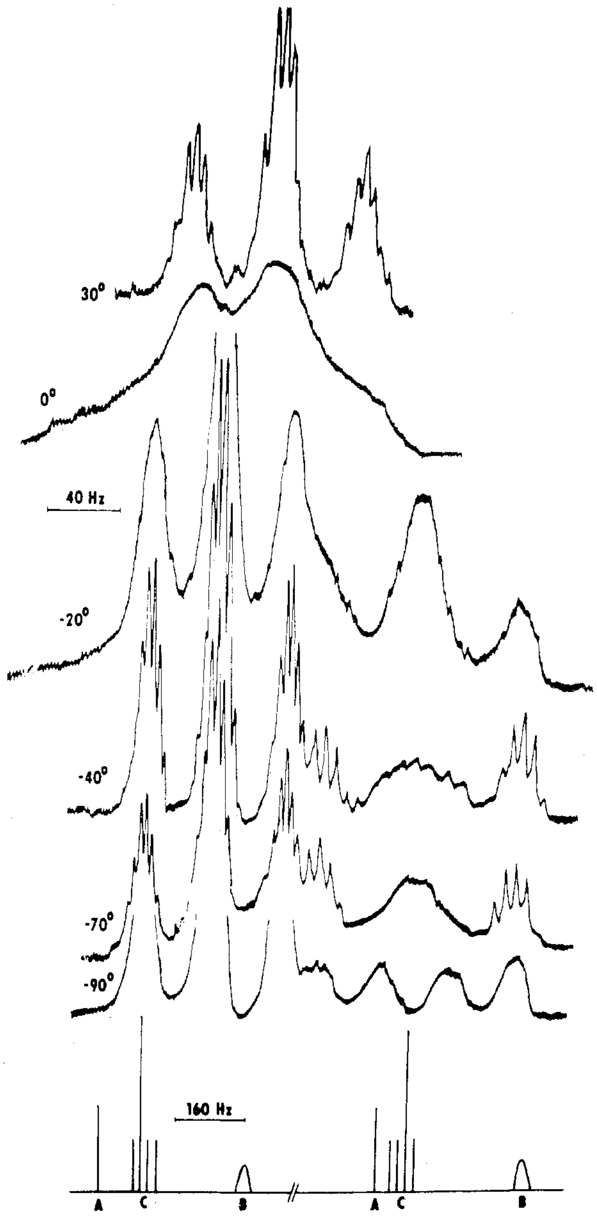

Figure 2. Representative tracings of 84.66-MHz fluorine NMR spectra of $CF_3Co(PF_3)_2(CO)_2$ at various temperatures. All but the bottom one represents the CF_3 region. The bottom spectrum is a schematic representation of the PF_3 region at −90 °C showing three types of fluorine atoms.

low-temperature spectrum that we have assumed is present.

The limiting isomers probably have the structures of species III and IV in Figure 1. The major isomer with its triplet of multiplets is most likely to have diequatorial phosphines. The $^3J_{PF_c}$ of 38 Hz is quite similar to that seen for the equatorial isomer of the monophosphine. The $^4J_{FF}$ coupling constant of 3 Hz is also the same. The minor isomer, in which the perfluoromethyl fluorines are split into a doublet of doublets, is probably the equatorial–axial species IV. The $^3J_{PF_c}$ coupling constants of 33 and 74 Hz are similar to the cis and trans values of the monophosphine.

In the high-temperature time-averaged spectrum, the $^3J_{PF_c}$ value is 47 Hz. If one makes a calculation assuming 38-Hz cis coupling in the diequatorial isomer and 33- and 74-Hz coupling in the axial–equatorial isomer, one finds between 40 and 45% of the diequatorial isomer. This calculation is not very accurate since it is quite sensitive to the exact values taken for the limiting coupling constants. At the low-temperature limit, area integration shows that the diequatorial isomer is definitely the major isomer and the equatorial–axial species is the minor one. There appears to be a definite population shift with temperature, the diequatorial species being favored as the temperature is lowered.

The occurrence of a triplet at intermediate temperatures for the minor equatorial–axial isomer is possibly only an artifact of the line shape phenomenon as it pertains to a minor isomer. However, other more probable explanations will be explored in the Discussion.

The spectrum in the PF_3 region is compatible with the above interpretation. At room temperature, the spectrum is a mirror-imaged pattern of peaks. At the low-temperature limit, there are three sets of peaks: one a mirror-imaged set of peaks centered at 43.74 ppm relative to $CF_3C_6H_5$, a second centered at 45.65 ppm, and a third centered at 53.74 ppm. The values of 43.75 and 45.65 ppm are similar to the value found for an equatorial PF_3 in $CF_3Co(PF_3)(CO)_3$. Likewise, 53.75 ppm is similar to the chemical shift of the monophosphine axial isomer. The spectrum is shown schematically in Figure 2. Isomer III, having two equivalent PF_3 groups, should exhibit a mirror-imaged pattern of peaks. Isomer IV would have a resonance in both the axial and equatorial regions. The single peaks A and B, broadened in the real spectrum, correspond to these axial and equatorial PF_3 groups. The broadening is probably due to unresolved phosphorus and fluorine coupling between the nonequivalent PF_3 ligands. Based on the second-order pattern, the resonance C of Figure 2 can be assigned to the diequatorial species. Assuming that resonance B belongs to the equatorial PF_3 of species IV, then the downfield resonance A belongs to the axial PF_3. As in the monophosphine, the equatorial PF_3 groups have been assigned to the upfield peaks, and the axial PF_3 group was assigned to the downfield peaks. This assignment, made on the basis of coupling constants in the monophosphine and coupling patterns in the disubstituted compound, should be noted. It will be used in the interpretation of the spectra of the perfluoroethyl and -propyl compounds. Support is also provided by work with $HCo(PF_3)_4$ in which the fluorine resonance of the axial PF_3 also occurs downfield of the equatorial.[11]

The room-temperature spectrum of $CF_3Co(PF_3)_3(CO)$ is that of a time-averaged species with equivalent PF_3 groups. In the PF_3 region, the pattern is a complex, broad, mirror-imaged doublet separated by about 1300 Hz with each half being spread over 300–400 Hz. The spectrum in the CF_3 region consists of a quartet of multiplets, each multiplet presumably a 10-line pattern in which the outer lines are not resolved. The $^3J_{PF_c}$ coupling constant of the quartet is 41 Hz with $^4J_{FF}$ fine structure of 5 Hz. As the temperature is lowered, broadening occurs, and by −76 °C a new spectrum is seen. Downfield from the original quartet is found a new quartet with $^3J_{PF_c}$ of 38 Hz and $^4J_{FF}$ of about 3.5 Hz. Based on the coupling pattern this spectrum is readily assigned to the triequatorial isomer V in Figure 1. This isomer is the major species. On the high-field side of this quartet are seen two multiplets that are a portion of the spectrum of the minor isomer—presumably species VI. Between −76 and −110 °C the spectrum of the minor isomer broadens and resharpens. The splitting between these multiplets changes from about 50 Hz at −76 °C to about 40 Hz. Conclusions concerning the minor isomer must be considered incomplete until data can be obtained at a strong enough field so that the remainder of the spectrum which overlaps the spectrum of the major isomer can be resolved. However, the behavior is similar to that found for $CF_3Co(PF_3)_2(CO)_2$. The PF_3 groups in the minor isomer at intermediate temperatures around −76 °C are still effectively time-averaged and as such show a coupling of 50 Hz which compares favorably with an average of 51 Hz expected for two 38-Hz cis couplings and one 78-Hz trans coupling for isomer

VI. The −110 °C coupling of 40 Hz then could be the outermost portion of a doublet of triplets with 75–80-Hz trans coupling and about 38-Hz cis coupling.

For $CF_3Co(PF_3)_4$, the room-temperature data are suggestive of equivalent PF_3 groups. The PF_3 fluorine region has a complex, mirror-imaged second-order pattern. The CF_3 fluorine region is a quintet of multiplets with $^3J_{\mathrm{PF_c}}$ and $^4J_{\mathrm{FF}}$ couplings of 46 and 5.5 Hz, respectively. Although this could be a square-based pyramid with the CF_3 group at the apical site, the low-temperature data argue in favor of a TBP structure. The CF_3 quintet broadens and the fine structure is lost by −76 °C, and by −110 °C a new pattern is developed that is badly overlapping. The low-temperature spectrum can be interpreted in terms of three equivalent equatorial PF_3 groups with 35-Hz cis coupling and one axial PF_3 group with 72-Hz trans coupling. The original quintet has become a hextet of multiplets. Since the cis coupling is about half that of the trans, this particular overlap pattern should be expected. The PF_3 region is somewhat clearer. A mirror-imaged doublet of peaks centered at 47.30 ppm relative to $CF_3C_6H_5$ is indicative of three equivalent PF_3 groups. Downfield 8 ppm is found another doublet of multiplets having about one-third the area of the major doublet. This downfield doublet can be assigned to the axial PF_3 group. The $^1J_{\mathrm{PF}}$ for each set of peaks is approximately 1300 Hz. This low-temperature pattern is consistent with isomer VII of Figure 1.

Throughout the series, the species can be consistently assigned a TBP structure with the CF_3 group occupying only an axial site. No other structure interpretation is as simple or consistent as the TBP assignment above. The PF_3 group occupies both axial and equatorial sites with a tendency toward equatorial developing in the higher phosphines.

Pentafluoroethyl and Heptafluoropropyl Compounds.[6b] The spectral characteristics of the pentafluoroethyl and heptafluoropropyl compounds are quite similar. The latter will generally be discussed only when there are significant differences.

The presence of the perfluoroethyl or perfluoropropyl group adds a new dimension to our considerations. In $C_2F_5Co(CO)_4$, the occurrence of the bulky ethyl group breaks the strict C_{3v} symmetry of the parent carbonyl.[12] This is shown in the infrared spectrum by the splitting of the E vibrational mode. Four ir-active bands are seen rather than the three expected for C_{3v} symmetry. This same effect[13] is seen when comparing $CF_3Mn(CO)_5$ to $C_2F_5Mn(CO)_5$. The effect is obviously a steric one in the manganese compounds since the same splitting could also theoretically occur in the trifluoromethyl species where the CF_3 group could cause the $Mn(CO)_5$ symmetry to be lower than C_{4v} local symmetry.

The presence of the bulky C_2F_5 group in the cobalt compounds could have steric effects in the TBP structure (R_f group axial) not found with the CF_3 compounds. In addition to the possibility of both axial and equatorial sites for PF_3 substitution as shown in Figure 1, the bulky C_2F_5 group could cause, for instance, three equivalent equatorial PF_3 ligands to become nonequivalent in a 2:1 ratio. However, we have no definitive evidence for a steric phenomenon based on this latter effect but only one based on the axial–equatorial site inequivalence found earlier with the methyl compounds.

The room-temperature infrared data[5] show that, other than an additional splitting in $C_2F_5Co(CO)_4$, the remaining carbonyls of the series $C_2F_5Co(PF_3)_x(CO)_{4-x}$ are totally analogous to their trifluoromethyl analogues, implying a similar behavior.

The fluorine NMR data on all of the species in the $C_2F_5Co(PF_3)_x(CO)_{4-x}$ system (as well as the $C_3F_7Co(PF_3)_x(CO)_{4-x}$ system) imply either that the compounds exist as a single isomer with equivalent PF_3 groups or that the isomers are time averaged. The room-temperature data are given in Table I. The substitution of CO by PF_3 causes only a very slight shift in the chemical shift of the α, β, and γ fluorines in the C_2F_5 and C_3F_7 groups. Our basic spectra compare well with those in the literature.[14] The phosphorus coupling is greatest to the α fluorines, less to the β, and barely discernible to the γ fluorines.

In the compound $C_2F_5Co(PF_3)(CO)_3$, the spectral characteristics are such as to show that a dynamic process is occurring. In the PF_3 region, as the temperature is lowered, the peaks broaden somewhat reaching a maximum around −40 °C. At the low-temperature limit, two isomers are frozen out in quite different proportions—about 4:1 for the ethyl and 8:1 for the propyl. The resonance for the minor isomer occurs about 8 ppm upfield of the major. For C_2F_5, δ equals 51.36 ppm for the major and 43.01 ppm for the minor isomer. For C_3F_7, the values are 51.21 and 42.94 ppm. The spectrum of the α-CF_2 region broadens slightly over the same temperature region and then resharpens by −80 °C. The amount of broadening is never very large. At maximum broadness, the peaks are only about twice as wide as those found at either high or low temperatures.

We interpret the data in the following way. At the lowest temperature, two isomers exist in about a 4:1 ratio. The major isomer has a $^1J_{\mathrm{PF}}$ of 1363 Hz and the minor 1392 Hz. For the $^4J_{\mathrm{FF}}$, the values are 6.5 and 4.9 for the major and minor isomers. In both cases, the relative magnitudes are such that by comparison[4] with $CF_3Co(PF_3)(CO)_3$, the major isomer should be assigned to the axial isomer I. The relative chemical shifts of the major and minor isomers confirm this assignment. As in the perfluoromethyl compounds, the resonances of the fluorines for the equatorial phosphine occur well upfield of the fluorines of the axial phosphine. An enhancement of the axial isomer is what one would predict for the steric effect of a bulky perfluoroethyl group.

Unfortunately, the methylene region is of no help in confirming this assignment. The room-temperature value of $^3J_{\mathrm{PF_c}}$ was reduced from 61 Hz to an ultimate value of 54 Hz at about −100 °C. A corresponding reduction is found for the propyl compound. A spectrum for the minor isomer is not seen in the CF_2 region owing possibly to its spectral broadness or to the possibility that it is buried under the spectrum of the major isomer. It is also possible that it has not yet been frozen out, although the slight broadening and resharpening referred to earlier may well indicate the contrary.

The trend in the value of $^3J_{\mathrm{PF_c}}$ is still bothersome. The change in the coupling constant indicates a population shift among the two isomers. If this population shift is occurring, then our previous data on coupling constants imply that there is an enhancement of the equatorial isomer. A similar enhancement of a minor isomer has been observed in the disubstituted phosphine of the cyclohexadieneiron carbonyl system.[15] An examination of the trends in the chemical shifts and coupling constants in the high- and low-temperature regions yields support to the view that a population shift has occurred. However, the conclusions are not firmly based since there are not enough data in either temperature range for accurate extrapolations. Also, as pointed out by a referee, this trend could be explicable in terms of a change in the rotamer population of the C_2F_5 group.[16]

The spectrum of $C_2F_5Co(PF_3)_2(CO)_2$ in the PF_3 region at room temperature is a mirror-imaged doublet of about 1300-Hz separation that is normally seen for equivalent PF_3 groups. Again, because of the additional coupling to the perfluoroalkyl fluorines, it cannot be resolved adequately to obtain the various second-order parameters. The methylene region is a 1:2:1 triplet of multiplets. The $^3J_{\mathrm{PF_c}}$ is 65 Hz, but the fine structure due to the CF_3 group or the phosphine fluorines is not resolvable. As the temperature is lowered, there is little change in the methylene fluorine resonance, but the phosphine fluorine pattern undergoes a major change.

The phosphorus fluorine resonances broaden and reach their maximum broadness at about −70 °C. By −90 °C, a spectrum has begun to reappear. Unfortunately, the sample began precipitating from our best solvent system before it could be completely sharpened up. A doublet of about 1300-Hz splitting is seen centered at 53.30 ppm downfield from $CF_3C_6H_5$ and a second doublet is centered at 45.65 ppm. The areas of the two sets of resonances are approximately equal (by the cut and weigh method).

Based on a comparison of the chemical shifts with those of the methyl compound, the downfield doublet would be assigned to the axial PF_3 and the upfield doublet to the equatorial PF_3. Since these peaks are quite broad, the resonance for the diequatorial compound could well be hidden under the peaks for the equatorial–axial isomer. However, since the areas are nearly equal, we feel that the equilibrium mixture is predominantly isomer IV (equatorial–axial) and at most a very minor amount of isomer III.

The only change in the methylene triplet is the appearance of what appears to be a weak, broad multiplet between the upfield peaks in the triplet. This is probably due to a small amount of $C_2F_5Co(PF_3)(CO)_3$ impurity which is also seen in the PF_3 region. The frequencies of these minor peaks agree with those found earlier for the monophosphine. The fact that the triplet has not changed is not surprising since the resonances being averaged are separated by an order of magnitude less than those in the PF_3 region. Presumably, a further lowering of the temperature would give us the expected spectral changes if the compound did not come out of solution.

The spectrum of $C_2F_5Co(PF_3)_3(CO)$ at room temperature is similar to the disubstituted compound. The spectrum is more complex since the third PF_3 group creates an $AA'A''X_3X'_3X''_3$ system with additional second-order couplings causing, in general, broadening. Again, it is clear that at room temperature the three PF_3 ligands are either equivalent or time averaged. Isomer V would allow the former to be true, but the fact that all other compounds discussed thus far seem to be time averaged would make it likely that $CF_3CF_2Co(PF_3)_3(CO)$ would also contain more than one type of PF_3 group.

The value of the 57-Hz $^3J_{PF_c}$ coupling constant between the methylene fluorines and the phosphorus atoms cannot be used to determine the concentrations of isomers V and VI without some assessment of the limiting cis and trans values.

The low-temperature spectrum at −90 °C is too broad to be used for anything but an indication of the final situation. The PF_3 region has two very broad sets of doublets in the region projected for axial and equatorial fluorines. The ratio of the downfield (axial) to upfield area is approximately 1:2, indicative of a sample predominating in the axial–diequatorial isomer VI. However, the methylene region again is too complex and broad for confirmation. In addition at −90 °C, the spectrum in the CF_2 region probably does not represent the limiting structure.

The spectrum of $C_2F_5Co(PF_3)_4$ at room temperature contained resonances for the CF_3 fluorines, a quintet for the CF_2 fluorines with a $^3J_{PF_c}$ of 50 Hz, and a very broad mirror-imaged pattern for the PF_3 groups. Both the CF_2 fluorine pattern and the PF_3 pattern are indicative of equivalent PF_3 groups. For the structure to be TBP, the spectrum must be time averaged. Interestingly, *if* the cis and trans $^3J_{PF_c}$ coupling constants of about 40 and 80 Hz in the $CF_3Co(PF_3)_x(CO)_{4-x}$ series are transferable to the corresponding methylene group in the perfluoroethyl compounds, then the $^3J_{PF_c}$ of 50 Hz is what one would calculate for three cis and one trans couplings.

On lowering the temperature, the PF_3 region broadens and yields ultimately at −90 °C two sets of doublets, each quite broad. A smaller area in the downfield axial region and a larger area in the equatorial region presumably represents the 1:3 axial:equatorial ratio of a TBP structure. However, again the spectrum of the CF_2 region does not appear to represent the limiting structure. Due to coupling to effectively equivalent PF_3 groups, it is a quintet.

Discussion

The results presented here show conclusively that all of the compounds of the $R_fCo(PF_3)_x(CO)_{4-x}$ system are stereochemically nonrigid. In some cases, the dynamic process occurs between different isomers of the same compound, and in other cases, the process occurs between nonequivalent sites on a single isomer.

The simplest explanation of the stereochemistries is that the compounds are trigonal bipyramidal throughout with the R_f group occupying an axial site and the CO and PF_3 ligands occupying the remaining axial and the three equatorial sites. The $R_fCo(PF_3)_4$ species are shown to have C_{3v} symmetry at low temperatures similar to $HCo(PF_3)_4$.[11,17] The greater repulsion of the perfluoroalkyl will surely tend to push the PF_3 back from their nearly tetrahedral arrangement[17] in $HCo(PF_3)_4$ (H on a face) to a structure rather closely approximating trigonal bipyramidal.

The perfluoroalkyl group has a pronounced effect on the nature of the isomer population in the various compounds. When CF_3 is the perfluoroalkyl group occupying the axial site, the monophosphine contains nearly equal quantities of axial and equatorial isomers both at high and low temperatures. The compound $CF_3Co(PF_3)_2(CO)_2$ at low temperatures contains even a higher percentage of the diequatorial isomer. The trisubstituted phosphine appears to continue the trend in favor of the triequatorial isomer. However, the presence of the perfluoroethyl or propyl group in the axial site appears to introduce a steric effect on the equatorial site presumably caused by the bulk of the ligand. For the $R_fCo(PF_3)(CO)_3$ species of the perfluoroethyl and propyl series, the low-temperature spectra show that the axial isomer predominates over the equatorial in 4:1 and 8:1 ratios, respectively. For the disubstituted compounds of both systems, there is no definitive evidence for the diequatorial isomer—only the equatorial–axial species. However, a small quantity of the diequatorial isomer could be lost in the broad spectra.

The changing isomer population between the CF_3 and the C_2F_5 and C_3F_7 compounds does not reflect a strong energetic difference. It takes only a few kilocalories of energy difference to make a radical change in isomer population. Thus one concludes that although the bulky perfluoroethyl or propyl group interferes somewhat with the ability of PF_3 to occupy the equatorial sites, CO and PF_3 are still sufficiently similar that radical changes in the energetics are not created.

Another interesting trend that is found among these species is that, as the R_f group becomes more bulky, the temperature necessary to freeze out the motion is lower. This temperature effect caused considerable difficulty, making it impossible to reach the low-temperature limit with some species in certain spectral regions. This effect of crowding has been observed before, for instance by Osborn.[18]

The basic Berry mechanism[19] seems adequate to explain the dynamic process, although the turnstile mechanism would also serve equally well.[20] By either mechanism, the perfluoroalkyl group would end up in an equatorial site. Since there is no spectral evidence for such a species, it must be assumed that the isomers with equatorial alkyl groups would be high-energy intermediates of very low concentration. In the next inversion, the perfluoroalkyl group would probably return to its favored axial position.

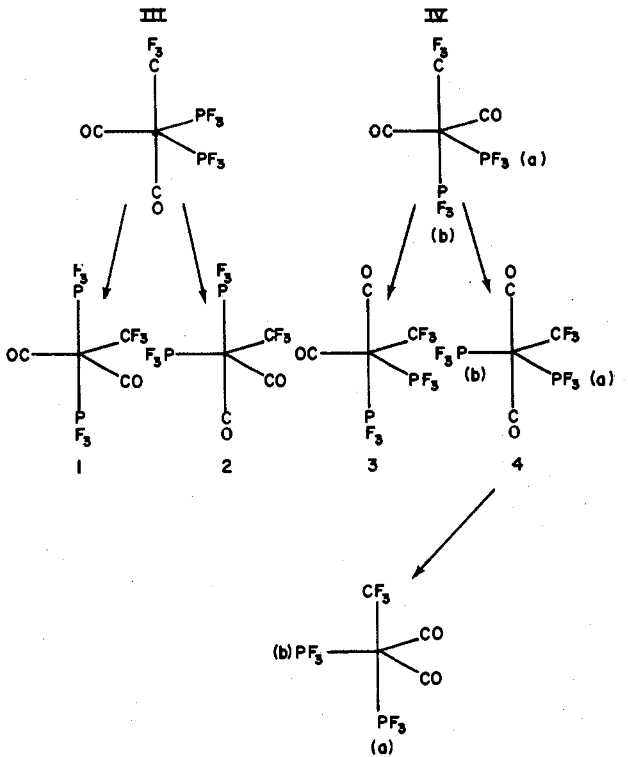

Figure 3. Trigonal-bipyramidal isomers of $CF_3Co(PF_3)_2(CO)_2$ having an axial CF_3 group plus the Berry inversion intermediates. This figure shows how the PF_3 groups in isomer IV could be exchanged via intermediate **4** without involving isomer III.

In the compounds of $CF_3Co(PF_3)_2(CO)_2$ and $CF_3Co(PF_3)_3CO$, the application of the Berry mechanism seems slightly more complex. In these species, the minor isomer still appears to be equilibrating while the major isomer is frozen out. It is possible that the effect is merely an artifact of the line-broadening phenomenon. Such an effect cannot be ruled out without the appropriate line shape calculation. However, the sharpness of the outer multiplets of the minor isomer makes it seem quite unlikely that the appearance of the spectrum for this species is merely some accident.

A far more probable explanation is that there are two intramolecular rearrangements operating in the system that have different activation energies and hence different temperature behaviors. The mechanism (or mechanisms) explaining such behavior would also have to explain the fact that, at low temperatures, while the equatorial and axial PF_3 groups of isomer III are equilibrating, they never attain the diequatorial configuration (IV). At the temperature being considered, the spectrum of the diequatorial isomer indicates that it is no longer involved in a dynamic process.

Obviously, more data are necessary before such a dual mechanism could be completely delineated. However, one possible mechanism by which it could occur will be discussed. In Figure 3 are shown the two TBP structures of $CF_3Co(PF_3)_2(CO)_2$. According to the Berry mechanism, each structure has two different groups in the equatorial plane to act as pivotal points. The four intermediates shown in Figure 3 are then produced. (These are classed as intermediates since there is no evidence from NMR for species having perfluoroalkyl groups in the equatorial plane.) Of these intermediates, **2** and **3** are the same and allow for the isomers to interchange. As also seen in the figure, intermediate **4** allows for the interchange of the axial and equatorial PF_3 groups of isomer IV. If intermediate **4** has a significantly lower energy than the other three intermediates or a lower activation energy is required to reach it, then it is quite possible that isomer IV could still be exchanging while III is frozen.

Two possible reasons can be cited in support of the lower energy of intermediate **4**. On steric grounds, the bulky PF_3 group is favored in the equatorial position over the axial positions. *If* PF_3 is acting as a slightly better π-bonding ligand than CO in these complexes, it would also be favored in the equatorial position. The higher concentration of the diequatorial isomer compared to that of the equatorial–axial isomer also favors such a proposal for the stabilization of intermediate **4**.

The room-temperature carbonyl stretching frequency data[5] for the di- and triphosphine compounds of the ethyl and propyl alkyl implied that two isomers are present. The low-temperature NMR data give evidence for only one. An obvious explanation is that one isomer is being depopulated as the temperature is lowered. We plan a variable-temperature ir study soon to explore this point.

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Registry No. I, 22925-61-7; II, 22925-60-6; III, 58342-02-2; IV, 58342-03-3; V, 58342-04-4; VI, 58341-99-4; VII, 58342-00-0; $C_2F_5Co(CO)_4$, 18703-18-9; $C_2F_5Co(PF_3)(CO)_3$, 23254-15-1; $C_2F_5Co(PF_3)_2(CO)_2$, 23254-14-0; $C_2F_5Co(PF_3)_3(CO)$, 23254-13-9; $C_2F_5Co(PF_3)_4$, 58281-45-1; $C_3F_7Co(PF_3)(CO)_3$, 23254-17-3; $C_3F_7Co(PF_3)_2(CO)_2$, 23738-91-2; $C_3F_7Co(PF_3)_3(CO)$, 23254-16-2; $C_3F_7Co(PF_3)_4$, 58281-46-2.

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