The anhydride V, produced on gentle thermolysis of I, is hydrolyzed rapidly to II in acid or alkaline solution and thence to the parent acid III. The rate of the first hydrolysis step is 26 times faster than that of I at pH 2.0 and at higher pH's becomes too fast to measure by titration. Similarly the acid anhydride VI, obtained by pyrolysis of III, also hydrolyzes to III at a rate too fast to measure by titration or spectroscopy in the range pH 1 to 10. Thus both V and VI satisfy the kinetic requirement for their being intermediates in the hydrolysis of I to III.

The introduction of MeOD into a solution of V in $CDCl_3$ results in the immediate addition of methanol to phosphorus to give IV, shown by the appearance of a characteristic doublet at τ 6.13 in the nmr spectrum. In the presence of deuterated *p*-toluenesulfonic acid the same addition of methanol to phosphorus is followed by a slower replacement of the POEt signal by increased POMe resonance. In contrast, hydroxylamine at pH 5 or 7 rapidly converts V into a hydroxamic acid revealed by ferric chloride assay.[7] This reaction, characteristic of acyl phosphates,[3,8] is not given by the diesters I and VII or by the acid III under similar conditions. Nevertheless, hydroxamic acid is produced (with first-order kinetic rate) when I is slowly hydrolyzed in 4 *M* hydroxylamine buffer at pH 4.7. This is substantive evidence that V is an intermediate in the hydrolysis of I to II and, by analogy, that VI is formed in the hydrolysis of II to III.

Finally, the hydrolysis of carbonyl ^{18}O-enriched ester I provides the acid III with no significant loss of isotope. Also, the acid III after brief equilibration with ^{18}O-enriched water shows incorporation of isotope into all three phosphorus oxygens but not into the carboxyl group. These experiments establish that hydrolysis of I does not involve C–O cleavage at any stage in the formation of III.

We interpret these results to mean that the hydrolysis of I proceeds through successive intermediates V, II, and VI to the acid III, with alternate ring-closure and ring-opening processes. It may be significant that this route avoids any process which would violate the rules of pseudorotation.[9] Two possible transition states with apical orientation of the attacking oxygen are A and B. The specific acid nucleophilic catalysis mechanism A does not account for the observation (Figure 1) that the monoanion of ester II exhibits pH-independent hydrolysis in the range 3.5 to 5.5 and also that on protonation of the anion the hydrolysis rate increases only twofold. We prefer the concerted, four-center transition state B which is in accord with all the data presented here and has important stereochemical implications which will be discussed elsewhere in detail.

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G. Michael Blackburn, Michael J. Brown
Department of Chemistry, The University
Sheffield S3 7HF, England
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Stereochemical Nonrigidity in Phosphorus Trifluoride Substituents of Trifluoromethylcobalt Tetracarbonyl

Sir:

The study of stereochemically nonrigid compounds has become an important area of investigation in recent years. In the field of coordination chemistry, these studies have been directed particularly toward organometallic compounds containing cyclic polyolefins. In these compounds, hydrogen atoms, which on simple inspection appear to be unquestionably nonequivalent, frequently appear equivalent at room temperature on the nmr time scale. Low-temperature studies have allowed the investigation of the processes that allow this equivalence to occur.[1]

Some five-coordinate species are also thought to be stereochemically nonrigid. Both of the compounds PF_5[2] and $Fe(CO)_5$[3] have been shown to have a trigonal-bipyramid structure, yet F^{19} and C^{13} nmr studies[4,5] fail to show the expected nonequivalence between the axial and equatorial atoms. It has been postulated that a rapid internal inversion creates an average environment of the nuclei resulting in the apparent equivalence. However, variable-temperature studies have not given any confirmation of the mechanism for these compounds. Indeed, only rarely have studies given support for such a mechanism in five-coordinate systems[6] and never with five-coordinate transition metal carbonyl complexes.

We present here some clear-cut cases of stereochemical nonrigidity in the five-coordinate system of compounds $CF_3Co(PF_3)_x(CO)_{4-x}$. For the compound where $x = 1$, $CF_3Co(CO)_3(PF_3)$, fluorine nmr studies at room temperature produce spectra that can be accounted for on the basis of only one species. In the 30° spectrum of Figure 1, resonance centered 634 Hz downfield from the reference, $CFCl_3$, belongs to the methyl fluorines. This resonance is split into a doublet by the phosphorus with a J_{FCP} of 58 Hz, and this

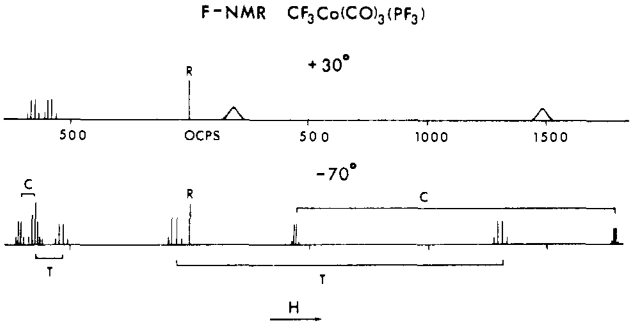

Figure 1. Fluorine nmr spectra of $CF_3Co(CO)_3(PF_3)$ at 30 and −70°—diagrammatic representation (reference, $CFCl_3$).

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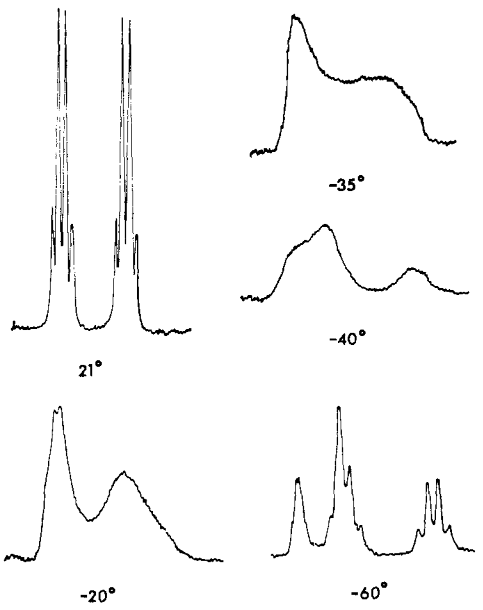

Figure 2. Spectral changes in methyl fluorine region at various intermediate temperatures.

doublet is split further into quartets by the phosphorus fluorines with a $J_{F_CF_P}$ of 6 Hz. The phosphorus fluorines exhibit their resonance centered 886 Hz upfield from $CFCl_3$. The direct phosphorus coupling causes a 1368-Hz splitting (typical for trifluorophosphine complexes). However, the F_P–F_C coupling is not resolved, as only broad bands are seen that are more than adequate to encompass the expected F–F coupling. Fluorine spectra of the methyl region at various temperatures are shown in Figure 2.

As the temperature is lowered, the resolution on the methyl fluorines is lost, and then all of the spectrum is generally broadened. At temperatures below −30°, the spectrum begins to give resolvable components, and by −70° a new high-resolution pattern is fully developed. This spectrum is centered around the previous areas of resonance, but contains peaks attributable to two isomers of $CF_3Co(CO)_3(PF_3)$ rather than one. As indicated in Figure 1, the −70° spectrum of the phosphorus fluorine regions shows two pairs of quartets. The J_{PF_P} and $J_{F_CF_P}$ are decidedly different. The methyl fluorines also yield two pairs of quartets, complicated slightly this time by the fact that two of the quartets overlap somewhat. The coupling constants found in the eight quartets are consistent with the presence of two isomers. These constants are summarized in Table I.

Table I. Chemical Shifts and Coupling Constants[a]

Species	Temp, °C	δF_C	δF_P	J_{FFC}	J_{PPFC}	J_{FFP}
$CF_3Co(CO)_3PF_3$	25	−634	886	58	6	1368
trans-$CF_3Co(CO)_3PF_3$	−70	−590	635	80	9	1351
cis-$CF_3Co(CO)_3PF_3$	−70	−659	1120	38	3	1373

[a] Reference $CFCl_3$.

A tentative assignment of the spectra to specific isomers can be made. On the general assumption that these species are trigonal bipyramid, then the trifluoromethyl groups can be assigned an axial position for both isomers. In substituted five-coordinate TBP species of the type $Fe(CO)_4L$, $Fe(CO)_3L_2$,[7] and $CF_3Co(CO)_4$,[8] the substituent has been assigned the axial position when that group is a poorer π-bonder than CO. It can be reasonably assumed that the CF_3 group assumes the axial position, but that PF_3 which is essentially equal to CO in π-bonding ability[9] will have no such restrictions placed on it. Thus with CF_3 axial and PF_3 either axial or equatorial, the appearance of spectra for two of four possible isomers is readily rationalized. It is generally found that *cis* coupling is decidedly less than *trans*,[10] and therefore the −70° spectrum in Figure 1 is assigned on the basis of this generalization.

The possible structures for the whole array of species of the type $CF_3Co(CO)_x(PF_3)_{4-x}$ will be discussed later in a full paper on this subject. All of the higher species behave in a comparable, but more complicated manner.

On the basis of the present assignment, both monophosphine isomers are present to a comparable extent. This means that for a double-well potential curve, the minimum energies for the two species are quite comparable.

The energy of activation for the conversion of one isomer to the other can be estimated through a study of the spectra as a function of temperature. A procedure analogous to that used by Muetterties and Phillips[11] was employed yielding an activation energy of about 11 kcal.

The compounds used in this study were prepared from $CF_3Co(CO)_4$ or $CF_3COCo(CO)_4$ and PF_3 by both thermal and irradiation techniques.[12] The individual compounds are isolated by gas–liquid partition chromatography.

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Carl A. Udovich, Ronald J. Clark
Department of Chemistry, Florida State University
Tallahassee, Florida 32306

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Acidity of Hydrocarbons. XXX. Kinetic Isotope Effects of the Cesium Cyclohexylamide Catalyzed Proton Exchange of Cyclohexane with Cyclohexylamine[1]

Sir:

In an earlier communication[2] we reported briefly a rate of cesium cyclohexylamide (CsCHA) catalyzed tritium exchange of cyclohexane relative to benzene.

(1) (a) Supported in part by Grant No. GM-12855 of the National Institutes of Health, U. S. Public Health Service. (b) Paper XXIX: A. Streitwieser, Jr., and F. Mares, *J. Am. Chem. Soc.*, 90, 2444 (1968).

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