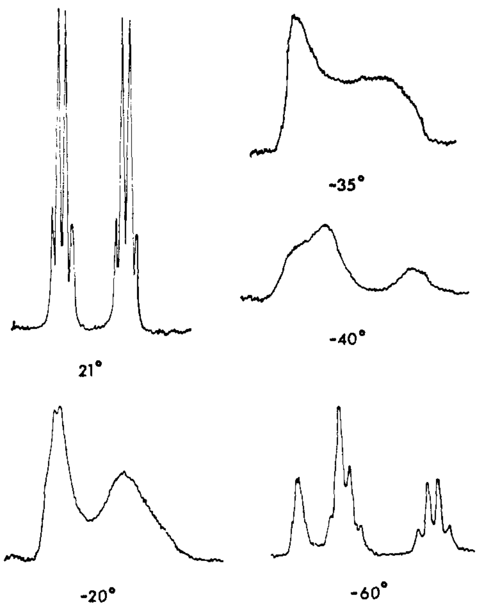

Figure 2. Spectral changes in methyl fluorine region at various intermediate temperatures.

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_{FF_C}	J_{PPF_C}	J_{FF_P}
$CF_3Co(CO)_3PF_3$	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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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.

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(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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Table I. Rates for Tritiodeprotonation with CsCHA at 50°

Run no.	[CsCHA], *M*	Compound	k_T, sec^{-1}	k_T/k_{PhH}
RAC 36	0.055	Benzene	$(2.16 \pm 0.10) \times 10^{-2}$	
		Cyclohexane	$(2.40 \pm 0.10) \times 10^{-10}$	$(1.11 \pm 0.07) \times 10^{-8}$
RAC 37[a]	0.066	Benzene	$(2.80 \pm 0.06) \times 10^{-2}$	
		Cyclohexane	$(2.93 \pm 0.10) \times 10^{-10}$	$(1.05 \pm 0.04) \times 10^{-8}$
WRY 6	0.05	Benzene	$(2.13 \pm 0.21) \times 10^{-2}$	
		p-Di-*t*-butylbenzene	$(1.94 \pm 0.15) \times 10^{-4}$	$(9.1 \pm 1.1) \times 10^{-3}$
		Cyclohexane	$(2.07 \pm 0.19) \times 10^{-10}$	$(0.97 \pm 0.13) \times 10^{-8}$
WRY 7[a]		*p*-Di-*t*-butylbenzene	$(2.40 \pm 0.12) \times 10^{-4}$	$((9.1 \pm 1.1) \times 10^{-3})$[b]
		Cyclohexane	$(3.31 \pm 0.15) \times 10^{-10}$	$(1.26 \pm 0.18) \times 10^{-8}$

[a] Activity of cyclohexylamine was about 10–12 mCi/mol. [b] Activity of cyclohexylamine was about 100 mCi/mol.

Table II. Comparison of Cyclohexane with Cyclohexane-d_{12}

Run WRY 7		Run WRY 10	
Compound	k_{rel}	Compound	k_{rel}
Cyclopentane	(1.00)	Cyclopentane	(1.00)
Cyclohexane	0.175 ± 0.008	Cyclohexane-d_{12}[a]	0.036 ± 0.001
Cycloheptane	0.133 ± 0.017	Cycloheptane	0.128 ± 0.004

[a] Contained 93.6% D, 6.4% H, by low-voltage mass spectrometry.

We now report the reproducibility of this result and a primary isotope effect that support a normal carbanion mechanism for the cyclohexane exchange.[3] The four runs summarized in Table I were accomplished by two different researchers several years apart, using somewhat different procedures. The mixture of hydrocarbons and CsCHA in N-tritiated cyclohexylamine was prepared within a bifurcated reactor[4] on a vacuum line; in the earlier work kinetic points were ejected at intervals using argon pressure whereas in the later work the solution was transferred to sealed tubes.[5] The cyclohexane exchanges were carried to <0.1% of completion and each kinetic point required careful purification by gas chromatography before the liquid scintillation counting. Rate constants were obtained using appropriate least-squares computer analyses. Reproducible results were obtained giving cyclohexane a reactivity $(1.10 \pm 0.09) \times 10^{-8}$ that of benzene (Table I). This reproducibility argues against any reaction mechanism involving adventitious radicals.[6] The most reasonable alternative mechanism is a straightforward proton removal giving cyclohexylcesium as a reactive intermediate, a mechanism directly analogous to that established for benzene itself.[7]

The primary isotope effect was determined by separately comparing cyclohexane and cyclohexane-d_{12} with cyclopentane and cycloheptane. Since we actually follow small extents of reaction, the radioactivity of cyclopentane plotted against the radioactivity of cyclohexane in each kinetic aliquot gives a straight line whose slope is five-sixths of the relative rate. Such relative reactivities are summarized in Table II. Cyclohexane-d_{12} is clearly less reactive than cyclohexane, and the C_5/C_7 rate ratios, 7.5 ± 1.0 and 7.8 ± 0.2, respectively, agree well in the two runs. The relative reactivity of cyclohexane-d_{12} compared to cyclohexane corresponds to $k_H/k_D = 6.5 \pm 0.6$ when corrected for the small amount of hydrogen in the deuterated compound.[8] This isotope effect includes the secondary isotope effect of the other eleven deuteriums, but their contribution is expected to be comparatively small, especially since there seems to be no large change in hybridization at the reactive carbon atom.[9] The essentially normal magnitude of this primary isotope effect has two important implications: internal return[10–12] is not important and the isotope effect for the reverse reaction of cyclohexylcesium with cyclohexylamine must have a comparable magnitude; that is, this reverse reaction is not of diffusion-controlled velocity—cyclohexylcesium must survive several collisions with solvent before reacting.[13] These properties undoubtedly also apply to the CsCHA exchange of other cycloalkanes. The reactivities of cyclopentane and cycloheptane that also result from the present study are discussed elsewhere.[14]

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(5) For further details see R. A. Caldwell, Ph.D. Dissertation, University of California, Berkeley, 1964, and W. R. Young, Ph.D. Dissertation, University of California, Berkeley, 1967.

(6) Note that the use of a tenfold change in radioactivity concentration gave no significant change in relative rate; hence, there can be no significant contribution by radical chain reactions initiated by radiation decomposition.

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(8) In the carbanion mechanism, removal of a proton or deuteron gives cyclohexylcesium which reacts with solvent to give mostly cyclohexane with some cyclohexane-*t*. A straightforward kinetic analysis shows that *for small extents of reaction* (~0.1%) the rates of tritium incorporation into cyclohexane and cyclohexane-*d* are indeed a direct measure of the rates of proton and deuteron removal, respectively, or k_H/k_D, where these rate constants refer to the forward rate of hydrogen isotope removal to give the carbanion intermediate.

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