Mechanism of Decarbonylation of Acid Chlorides with Chlorotris(triphenylphosphine)rhodium(I) Structure and Stereochemistry

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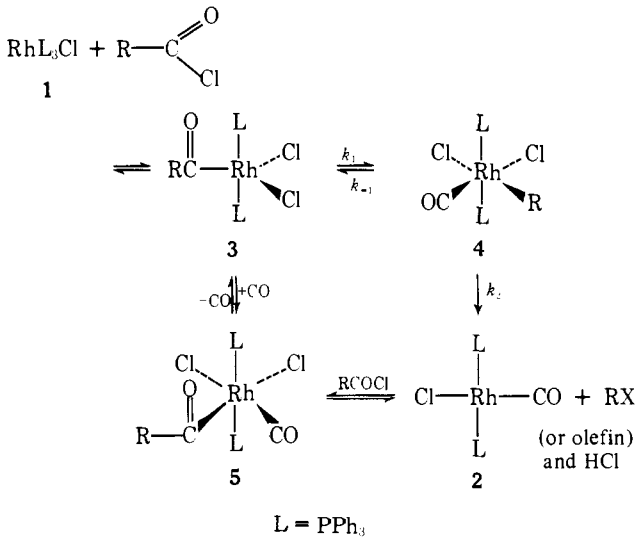
Abstract: The stoichiometric decarbonylation of *S*-(+)-α-deuteriophenylacetyl chloride with chlorotris(triphenylphosphine)rhodium(I) resulted in the formation of *trans*-carbonylchlorobis(triphenylphosphine)rhodium(I) and *S*-(+)-benzyl-α-*d* chloride with an overall stereospecificity of 20–27%. The decarbonylation of acid chlorides using chlorine-36 labeled $Rh^{36}Cl(PPh_3)_3$ gave an *even* distribution of ^{36}Cl among the products, alkyl chloride, the carbonylrhodium(I) complex, and unreacted starting material, in agreement with a rapid equilibrium in the formation of the rhodium(III)-acyl complex and an equivalence of the chlorine atoms in the acyl complex. The structure of the rhodium(III)-acyl complex was elucidated by infrared, ^{31}P NMR, and x-ray crystallographic studies. The stoichiometric decarbonylation of 3,3-dideuterio-3-perdeuteriophenylpropionyl chloride afforded a mixture of all possible d_0, d_1, d_2, and d_3 perdeuteriophenylethenes but the catalytic decarbonylation gave 1-deuterio-1-perdeuteriophenylethene as the exclusive organic product. The hydrogen isotope exchange is a result of inter- and intramolecular hydride transfer mechanisms. A reinvestigation of the rates of decarbonylation showed a deuterium isotope effect of 1.2. These results favor a mechanism in which a rapid pre-equilibrium between the acyl- and alkylrhodium complexes is followed by the rate-limiting step, a concerted cis elimination of rhodium hydride.

The stoichiometric decarbonylation of acid chlorides with chlorotris(triphenylphosphine)rhodium(I) (**1**) takes place under mild conditions;[1-5] at higher temperatures the reaction is catalytic. A convenient method for the regeneration of catalyst **1** from *trans*-carbonylchlorobis(triphenylphosphine)rhodium(I) (**2**), the end product of the stoichiometric decarbonylation, provides a reusable source of the otherwise expensive catalyst.[6] Acid chlorides which contain β hydrogens produce olefins upon decarbonylation, while alkyl chlorides are formed from acid chlorides with no β hydrogens.

The key steps in the mechanism of decarbonylation involve initially the facile oxidative addition of the acid halide to **1**

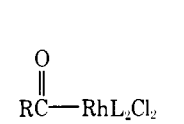


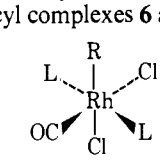
giving the five-coordinate acylrhodium(III) complex **3**. The subsequent acyl-alkyl rearrangement of **3** leads to a six-coordinate alkylrhodium(III) complex **4** which undergoes reductive elimination to give the alkyl halides (or olefin) and **2**.[2,5,7-9]

In the decarbonylation of para-substituted benzoyl chlorides and para-substituted phenylacetyl chlorides, both the acyl- (**3**) and alkyl(or aryl)rhodium(III) (**4**) complexes have been isolated.[7,10] The kinetics for each of the consecutive steps (**3** ⇄ **4** and **4** → **2**) leading to the formation of aryl or benzyl chlorides and **2** have been measured.[7] The equilibrium in the acyl-alkyl (**3** ⇄ **4**) rearrangement depends on the nature of the migrating group.[11,12] When the migrating group is methyl, the reaction proceeds only in one direction and methyl migration on to the carbonyl ligand predominates to give the acyl complex. In the case of phenyl, the reaction proceeds in the opposite direction yielding the aryl complex. The benzyl group, however, shows an intermediate reversible behavior.[7]

Acid halides which possess β hydrogens undergo decarbonylation with **1** to give olefin and **2.** The decarbonylation of *erythro*- and *threo*-2,3-diphenylbutanoyl chlorides gives exclusively *trans*- and *cis*-methylstilbenes, respectively.[9] The observed stereospecificity can be explained by two mechanistic sequences (Scheme I): an acyl-alkyl rearrangement with *retention* of configuration at carbon followed by a cis β elimination or an acyl-alkyl rearrangement with *inversion* of configuration at carbon followed by a trans β elimination. For the two-step mechanism, the retention cis-elimination pathway was favored on the basis of the retention of configuration observed in the decarbonylation of aldehydes with rhodium,[11,13] in cis metal hydride elimination[14,15] and in acyl-alkyl rearrangements[17-21] in other systems.

The reported[9] primary deuterium isotope effect of **7,** however, in the decarbonylation of the acyl complexes **6** and **7** was





6, R = $C_6H_5CH_2CH_2$
7, R = $C_6D_5CD_2CH_2$
9, R = $C_6H_5CHDCHD$

8, R = $C_6D_5CD_2CH_2$
10, R = C_6H_5CHDHD

considered to be more consistent with a rate-determining concerted cis-elimination reaction of **7** (without the intervention of the intermediate alkyl complex **8**) as opposed to the two-step mechanism (in which the decomposition of **8** must be rate determining).

Recently, however, it was reported that the decarbonylation of *erythro*- and *threo*-2,3-dideuterio-3-phenylpropionyl chloride with **1** yielded styrene-d_0, -d_1, and -d_2. A reversible

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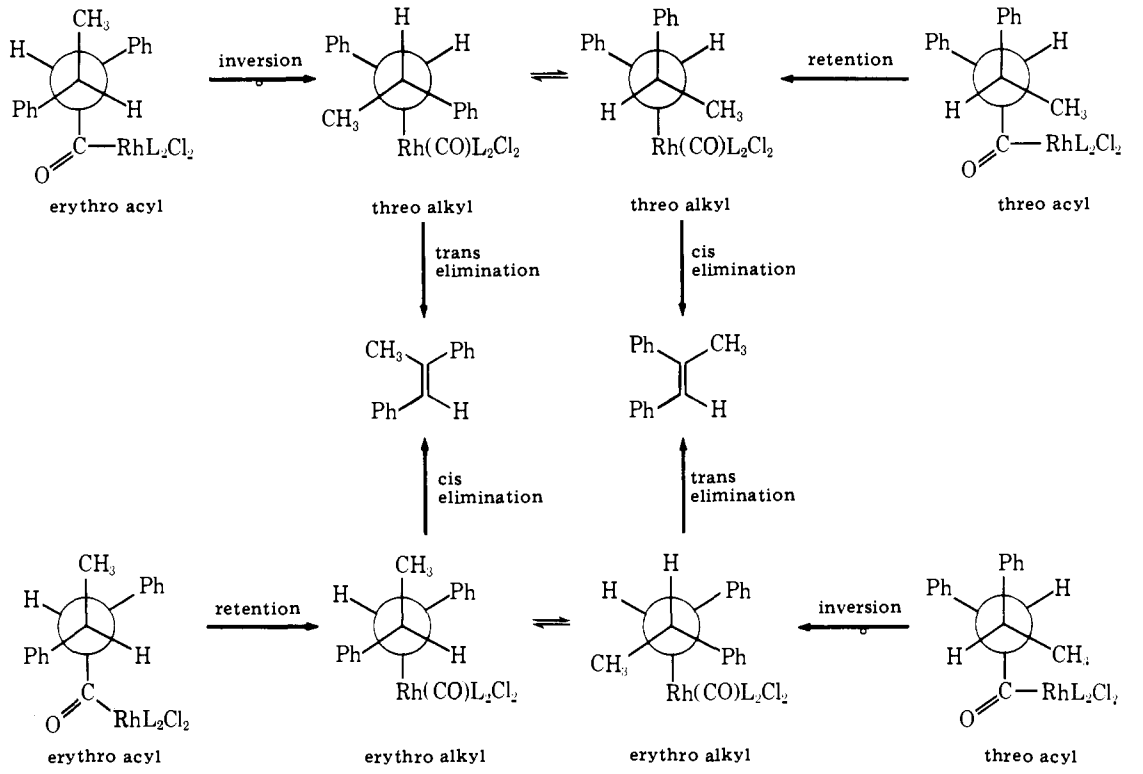
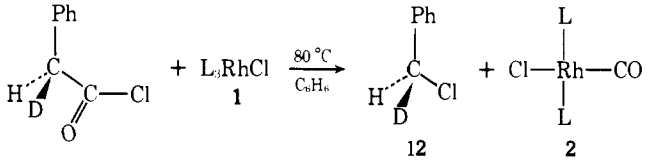
Scheme I



β-elimination mechanism involving the alkyl complex **10** was proposed to account for the nonstereospecific nature of the reaction.[22] The same mechanism also accounts for the observation that pentacarbonyl(*threo*- and *erythro*-2,3-dimethylvaleryl)manganese(I) decomposes thermally to give identical mixtures of olefins.[23]

Results and Discussion

Stereochemistry of Decarbonylation. When *S*-(+)-α-deuteriophenylacetyl chloride (**11**) of known optical purity was treated with chlorotris(triphenylphosphine)rhodium(I) (**1**)

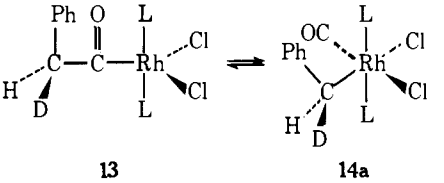


S(+)-11

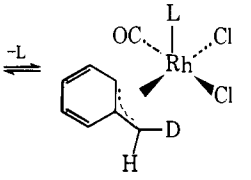
L = PPh_3

in refluxing benzene, carbonylchlorobis(triphenylphosphine)rhodium(I) (**2**) and benzyl-α-*d* chloride (**12**) were obtained. A predominance of **12** with 20–27% net retention of configuration at carbon was observed.

The extensive racemization in the decarbonylation of *S*(+)-**11** with **1** was disappointing in view of the remarkable stereospecificity observed in the decarbonylation of aldehydes with the same rhodium complex.[11,13,25] In reactions carried out by heating *S*(+)-**12** in refluxing benzene for 5 h with either **1** or **2** and triphenylphosphine, the alkyl chloride was recovered, unchanged and unracemized, demonstrating that **12** was stereochemically stable under the reaction conditions. Furthermore, when benzyl chloride was stirred with **2** either in chloroform at 25 °C for 196 h or in refluxing benzene for 24 h, only the starting materials were recovered; no π-benzyl complex **14b** was isolated. The observed loss of configuration at carbon cannot be attributed to the σ–π rearrangement **14a** $\rightleftarrows$ **14b** since, in order for **14b** to lose its optical activity, the benzyl group must undergo a 180° rotation, reattaching its



13 14a



14b

opposite face to rhodium. In an analogous palladium system, the π-benzyl ligand retains its configuration during the rearrangement.[26] The racemization which accompanies the decarbonylation of optically active α-trifluoromethylphenylacetyl chloride to α-trifluoromethylbenzyl chloride and **2** has been attributed to the acyl $\rightleftarrows$ alkyl rearrangement rather than the subsequent step, the conversion of the benzyl rhodium complex to the benzyl chloride and **2**. Moreover, kinetic studies on the rearrangement of achiral complexes **13** $\rightleftarrows$ **14a** showed that the reaction is characterized by a low ρ value and a small entropy of activation, suggesting that the rearrangement proceeds either by a tight radical pair or at least with little charge development and with little change in restriction in going to the transition state. A number of successive acyl $\rightleftarrows$ alkyl rearrangements prior to the rate-limiting step could, by attrition, lead to a high degree of racemization even if only a small degree of racemization took place at each step, regardless of the racemization mechanism.

Stoichiometric and Catalytic Decarbonylation of 3,3-Dideuterio-3-perdeuteriophenylpropionyl Chloride. When a solution of dichloro(3,3-dideuterio-3-perdeuteriophenylpropionyl)bis(trisphenylphosphine)rhodium(III) (**7**) in α-methylnaphthalene was decarbonylated at 100 °C and 30 mm Hg, a mixture of styrenes was condensed from the gas phase.

Table I. ^{31}P NMR Spectral Parameters for Rhodium Complexes in Chloroform-*d* Solution (R = $PhCH_2CH_2$)

Complex	Temp, K	δP, ppm	J(Rh–P),[b] Hz
$RCO-RhL_2Cl_2$	313	−23.2	−108
	298	−23.2	−108
	218	−23.2	−108
$RCO-RhL_2Br_2$	298	−23.7	−106
$RCO-RhL_2BrCl$	298	−23.5	−107

[a] The negative chemical shifts are downfield from 85% H_3PO_4. Uncertainties of the measurements are ±0.1 ppm and ±1 Hz. [b] For the sign determination and absolute sign convention, see ref 34.

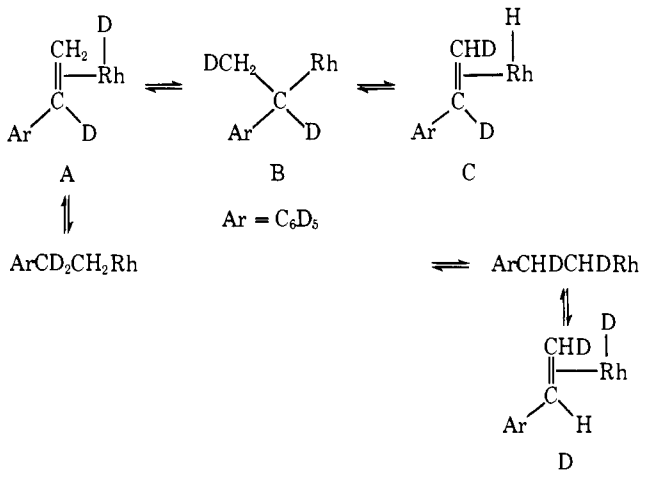
NMR[27] (Table II) and mass spectral analysis[28] of the condensate revealed the presence of $C_6D_5CH=CH_2$, $C_6D_5CD=CH_2$, $C_6D_5C_2D_2H$, *cis* + *trans*-$C_6D_5CH=CHD$ and $C_6D_5CD=CD_2$ in 34, 42, 15, 6, and 3% yields, respectively.

It is noteworthy that a relatively high ratio of d_0 to d_3 product was formed. In order to verify that no deuterium scrambling occurred during the oxidative addition of 3,3-dideuterio-3-perdeuteriophenylpropionyl chloride (**15**) to **1**, adduct **7** was carbonylated at 1 atm and 25 °C.[2] Under these

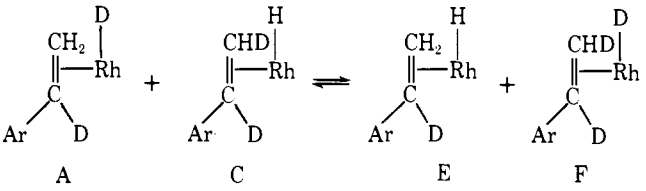
$$C_6D_5CD_2CH_2\overset{O}{\overset{\|}{C}}-RhL_2Cl_2 \xrightarrow{CO} C_6D_5CD_2CH_2COCl + 2$$

7 15

conditions **7** was smoothly converted to **15** and **2.** Since no deuterium scrambling was detected in the recovered **15,** the scrambling must have taken place during one of the subsequent steps. No hydrogen-isotope exchange was detected in the stoichiometric decarbonylation of phenylpropionyl chloride with chlorotris(tri-2,6-dideuteriophenylphosphine)rhodium(I) (**16**) or when styrene was subjected to the action of **16.** Moreover, the fact that styrene-d_0 was obtained (in addition to styrene-d_1 and -d_2) in the decarbonylation of **9** in chloroform-*d*[22] ruled out a possible exchange with the solvent. The observation that $C_6D_5CH=CH_2$ was one of the major reaction products in the decarbonylation of **7** cannot be accounted for on the basis of *intramolecular* elimination-readdition of rhodium hydride/deuteride species across the double bond. Such a mechanism predicts the formation of styrenes substituted at the vinyl group with one or two deuterium atoms only. Thus, the formation of perdeuteriophenylethene could be rationalized only by assuming the participation of *intermolecular* hydride transfer mechanism. This process may occur via dissociation of the various π-complexed styrenes A, C, or D from their coordination sites, followed by liberation of solvated



Rh-H or Rh-D species which could react with the free styrenes present. The rate of this process should be much faster than the rate of distillation of the styrenes from the reacting system. Alternatively, a bimolecular ligand exchange process which does not require the presence of free styrenes cannot be excluded:



Intramolecular addition-elimination of Rh-H or Rh-D in the new hydrido π complexes E and F would eventually lead to a mixture of $C_6D_5CH=CH_2$ and $C_6D_5CD=CD_2$. The prevailing formation of the former is very likely kinetically controlled. A deuterium isotope effect combined with a statistical factor favoring hydrogen abstraction in the secondary alkyl complex B leads to accumulation of perdeuteriophenylethene.

Previously, a large deuterium isotope effect was reported[9] for this system. In view of the extensive deuterium scrambling observed in this study, a reinvestigation of the kinetics was undertaken. The homogeneous decarbonylation of **6** in 1,2-dichloroethane was examined by following the appearance of the carbonyl band of **2** at 1986 cm^{-1} in the infrared at 75 °C. A complex kinetic behavior, 7/8 order in **2,** was observed. The rate of decarbonylation of **6** increased in the presence of excess 3-phenylpropionyl chloride, indicating that a prior equilibrium **6** ⇄ $PhCH_2CH_2COCl + Rh(PPh_3)_2Cl$ was taking place. A small deuterium isotope effect $k^H_{obsd}/k^D_{obsd} = 1.21 \pm 0.1$ was

Table II. ^1H NMR Spectra of Deuterated Styrenes

	Chemical shifts[a]					
	H_a, Ar =		H_b, Ar =		H_c, Ar =	
Styrene	m-$O_2NC_6H_4$	C_6D_5	m-$O_2NC_6H_4$	C_6D_5	m-$O_2NC_6H_4$	C_6D_5
Ar, H_c; H_a, H_b	6.756 (dd) J_{ab} = 10.7 J_{ac} = 17.5	6.721 (dd) J_{ab} = 10.8 J_{ac} = 17.6	5.866 (dd) J_{bc} = 0.60	5.729 (dd) J_{bc} = 1.09	5.420 (dd) J_{bc} = 0.60	5.241 (dd)
Ar, H; D, H			5.867 (dd) J_{HD} = 2.7	5.725 J_{HD} = 2.70	5.422 (dd) J_{HD} = 1.5	5.233 (d)
Ar, H; H, D	*b*	*b*			5.406 (d) J_{ac} = 17.5	5.209 (d) J_{ac} = 17.6
Ar, D; H, H	*b*	*b*	5.848 (d) J_{ab} = 10.7	5.708 (d) J_{ab} = 10.8		

[a] Chemical shifts were measured in $CDCl_3$ relative to TMS. Coupling constants are given in Hz. Chemical shifts are accurate to within ±0.1 Hz. Multiplicities are given in parentheses. [b] Broad weak absorptions due to H_a in that region precluded full analysis.

Table III. Summary of Results of Isotope Labeling Experiments

Compd	Specific radio activity, (cpm/mmol) × 10^{-4}	Adjusted value
LiCl* reference	20.0 ± 0.6	20.0 ± 0.6[a]
LiCl* recovered after exchange	13.8 ± 0.4	13.8 ± 0.4[b]
$PhCH_2Cl$* (19*r)	20.3 ± 0.6	20.3 ± 0.6
$PhCH_2Cl$* (19*)	4.10 ± 0.12	5.97 ± 0.52[c] (29.5 ± 3.4%) of value of 19*r
$Rh(PPh_3)_2(CO)(Cl^*)$ (2*r)	15.4 ± 0.5	15.4 ± 0.5
$Rh(PPh_3)_2(CO)Cl^*$ (2*)	4.61 ± 0.14	4.61 ± 0.14 (29.9 ± 1.9%) of value of 2*r

[a] This value represents 100% of the available isotope label. It does not mean that all chlorine atoms are physically labeled. [b] This value is 69 ± 4% of the original activity. The complex 1* thus obtained also has 69 ± 4% of the chlorine atoms "isotopically labeled". [c] Since the product 19* was obtained from the decarbonylation of phenylacetyl chloride with 1* which was only 69% "labeled", an adjustment factor (0.69) was included.

measured for the decarbonylation reaction. These results are consistent with the observed deuterium scrambling. Repetition of the experimental conditions described in the previous report[9] showed that in the benzene solvent used in that determination, the solubility of the acyl complexes is rather limited, leading to a heterogeneous system. Since the usual deuterium scrambling was observed under these conditions, the reported difference in rates for the decarbonylation of **6** and **7** possibly was due to a difference in the crystals which caused different rates of dissolution.

In order to demonstrate that the intermolecular hydride-transfer mechanism was responsible for the d_0 and d_3 products, the decarbonylation of **7** was carried out in the presence of *m*-nitrostyrene (**17**). NMR and mass spectral analysis of the recovered nitrostyrene showed that preferential monodeuteration at the α position took place.

$$7 + ArCH{=}CH_2 \rightarrow \underset{17}{} \quad \underset{(56\%)}{17}$$
$$+ ArCD{=}CH_2 + \underset{(20\%)}{cis\text{-}} + \underset{(11\%)}{trans\text{-}}ArCH{=}CHD$$
$$+ ArC_2D_2H + \underset{(13\%)}{C_6D_5CH{=}CH_2} + \underset{(72\%)}{} + \underset{(28\%)}{C_6D_5CD{=}CH_2} + 2$$
$$Ar = m\text{-}O_2N\text{-}C_6H_4$$

This result indicates that the preferred direction of addition of Rh–D species to **17** is Markownikoff, leading to a primary alkyl derivative followed by elimination of Rh–H. A similar deuterium transfer from deuteriocarbonyltris(triphenylphosphine)rhodium(I) to 1-pentene has been observed,[30] although the position of the deuterium labeling in the alkene was not established.

The extent of the hydrogen isotope exchange can be greatly diminished only if the concentration of the rhodium hydride species is kept at a relatively low level. Such a situation exists in the catalytic reaction. Decarbonylation of **15** with **2** at 190 °C and 1 atm gave rise to a mixture of 86 and 14% DCl and HCl, respectively. When the reaction was carried out such that the olefin and the deuterium chloride gas were removed as soon as they were formed, *pure l-deuterio-l-perdeuteriophenylethene was formed as the exclusive organic product.*

Direct experimental evidence for the presence of the intermediate alkylrhodium complexes was obtained from infrared studies of the decarbonylation of dichloro(3-phenylpropionyl)bis(triphenylphosphine)rhodium(III) (**6**) and dichloro(2,3-diphenylbutanoyl)bis(triphenylphosphine)rhodium(III) at higher temperature. A sharp band at 2080 cm^{-1} was detected at 90 °C during the course of decarbonylation of these acyl complexes, which is characteristic of the C–O stretching mode of carbon monoxide coordinated to a six-coordinated rhodium(III) complex.[7] A similar observation was reported by Dunham and Baird.[22] Thus, the results of this investigation of the decarbonylation of **7** are more consistent with a pre-equilibrium **7** ⇄ **8** followed by the decomposition of the latter in a rate-limiting step than with a concerted cis-elimination mechanism, in which **3** goes to olefin directly.

Isotopic Labeling Studies. In order to determine whether halogen scrambling occurs in the decarbonylation of acid halides, chlorotris(triphenylphosphine)rhodium(I) which contained chlorine-36 was used for the decarbonylation of phenylacetyl chloride (**18**), the fate of the chlorine-36 isotope being followed by scintillation counting. $Rh^{36}Cl(PPh_3)$ (**1***) was prepared from rhodium(III) trichloride[31] in the presence of lithium chloride-^{36}Cl. The extent of transfer of chlorine-36 from lithium chloride-^{36}Cl to **1*** was 69 ± 4% based on the loss of radioactivity of the recovered $Li^{36}Cl$.[32]

Reference (r) samples benzyl chloride (**19*r**) and *trans*-carbonylchlorobis(triphenylphosphine)rhodium(I) (**2*r**) were obtained respectively from the displacement reaction of benzyl tosylate by lithium chloride-^{36}Cl in dimethylformamide and the carbonylation of **1*** in ether. The decarbonylation of

$$RhCl_3{\cdot}3H_2O + LiCl^* \xrightarrow[EtOH]{PPh_3} \underset{1^*}{Rh(PPh_3)_3Cl^*} + LiCl^*$$

$$\underset{18}{PhCH_2\overset{O}{\overset{\|}{C}}Cl} + \underset{1^*}{Rh(PPh_3)_3Cl^*} \xrightarrow[80\ ^\circ C]{benzene} \underset{19^*}{PhCH_2Cl^*} + \underset{2^*}{Rh(PPh_3)_2(CO)Cl^*} + PPh_3$$

$$PhCH_2OH \longrightarrow PhCH_2OSO_2C_6H_4CH_3\text{-}p \xrightarrow[DMF]{LiCl^*} \underset{19r^*}{PhCH_2Cl^*}$$

$$Rh(PPh_3)_3Cl^* \xrightarrow[Et_2O]{CO} \underset{2r^*}{Rh(PPh_3)_2(CO)Cl^*}$$

phenylacetyl chloride (**18**) with **1*** (mole ratio of **18**/**1*** 2:1) yielded benzyl chloride (**19***) and **2*** (Table III) which exhibited radioactivity amounting to one-third of the values of the respective reference samples (**19*r** and **2*r**). Thus, the decarbonylation of phenylacetyl chloride (**18**) with **1*** resulted in equal distribution of chlorine-36 among the products, benzyl chloride (**19***), **2***, and unreacted **18**. Similarly, *p*-methylbenzoyl chloride (**20**) and racemic α-trifluoromethylphenylacetyl chloride (**21**) underwent decarbonylation in the presence of **1*** to yield the respective alkyl halides which showed radioactivity. Again, approximately one-third of the original radioactivity in **1*** was retained in **2*** (Table IV). 3-

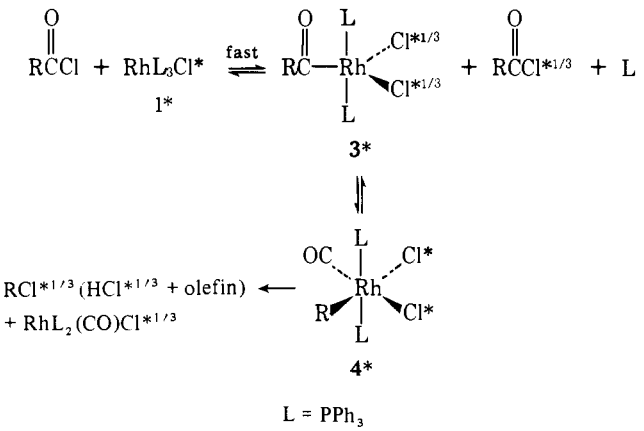
Table IV. Stoichiometric Decarbonylation of *p*-Methylbenzoyl Chloride (20) and ±α-Trifluoromethylphenylacetyl Chloride (21)

Acid chloride	Solvent	Reaction Temp, °C	Reaction Time, h	Specific radioactivity, cpm/mmol Chloride	$RhCl(CO)(PPh_3)_2$ Original[a]	$RhCl(CO)(PPh_3)_2$ Final	^{36}Cl retained on rhodium,[b] %
20	C_6H_5CN	190	2	p-MeC_6H_4Cl 7662	51101 ± 4618	18415	36 ± 0.4
21	C_6H_6	Reflux	6	$Ph(CF_3)CHCl$ 52120	142003 ± 11626	50025	35.5 ± 3

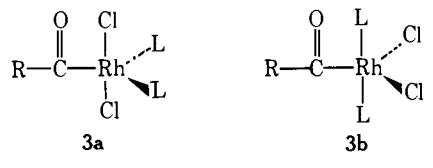
[a] Specific activity of $RhCl(CO)(PPh_3)_2$ expected if all chlorine-36 were retained on the rhodium after the reaction. [b] Calculation was based on $(CO)(PPh_3)_2Rh^{36}Cl$ which was obtained from the carbonylation of the $(PPh_3)_3Rh^{36}Cl$ used in decarbonylation.

Phenylpropionyl chloride underwent analogous decarbonylation with **1*** to afford styrene, radioactive hydrogen chloride, and **2***. The organorhodium product **2*** retained 27 ± 3% of the original amount of radioactivity.

The equal incorporation of chlorine-36 in the alkyl chloride product and in **2*** (one-third each of the original radioactivity) suggests that the two chlorine atoms in the intermediate acylrhodium complex (**3**) are equivalent or rapidly equilibrate. The fact that each of these decarbonylation products (alkyl chloride and **2***) contained only one-third of the original radioactivity (instead of one-half) implies a rapid equilibration step among the three species (acid chloride, **1** and **3**) prior to acyl-alkyl rearrangement (**3** ⇄ **4**) and subsequent decarbonylation.



^{31}P Nuclear Magnetic Resonance and X-Ray Crystallographic Studies. Results of the isotope labeling studies suggest two alternatives. Either the chlorines in **3** are not equivalent but rapidly equilibrate, or one of two geometric isomers **3a** or **3b** is formed, assuming stereochemical rigidity of the complex in solution. The same labeling results also are consistent with the facile interconversion of **3a** with **3b** (e.g., the Berry pseudorotation process[33]).



The phosphorus-31 spectra of the acylrhodium complexes (**3**) consist of a sharp doublet, and the results (Table I) indicate that **3** is stereochemically rigid in the range of 218–313 K. No line broadening was observed which might indicate an equilibration process. The phosphorus chemical shift appears to be only slightly dependent on the nature of the halogen atoms. The insensitivity of the phosphorus–rhodium coupling constant to halogen substitution[34] and the magnitude of the coupling constant J(Rh-P) suggests that both phosphorus atoms are cis to the halogens and are themselves occupying the apical positions of the trigonal bipyramidal framework,[35] thus supporting structure **3b**. Final confirmation of this structure comes from a preliminary x-ray structure determination[36] of a complex prepared by the oxidative addition of 3-phenylpropionyl chloride to **1**. The refinement, stopped at a stage where $R = 0.20$, clearly shows the trigonal bipyramidal arrangement in which the two phosphines are in apical positions (Figure 1).

The bulkiness of the triphenylphosphine ligands can seemingly be best accommodated in trans diapical positions.

Conclusion

The decarbonylation of acid chlorides having no β-hydrogen atoms proceeds with low net retention of configuration on carbon. Since the acyl ⇄ alkyl rearrangement is believed to take place with retention of configuration on carbon, the reductive elimination step must occur with the same stereochemistry. By microscopic reversibility, the oxidative addition of alkyl halides to d^8 Rh(I) complex **2** should also proceed with retention of configuration on carbon. This conclusion is in contrast with the high degree of net inversion of configuration on carbon observed in the oxidative addition to d^{10} Pd(0) phosphine complexes.[24,26] The decarbonylation of acyl chlorides bearing β-deuterium atoms is nonstereoselective, the deuterium label being scrambled by inter- and intramolecular hydride transfer mechanism. On the other hand, the decarbonylation of *erythro*- and *threo*-2,3-diphenylbutanoyl chlorides is highly stereospecific, giving rise to *trans*- and *cis*-methylstilbenes, respectively. These observations imply that the addition of rhodium hydride species across the double bond as well the reverse reaction are nonregioselective concerted processes with cis stereochemistry. The oxidative addition of acyl chlorides to ^{36}Cl isotopically labeled **1** gives an even distribution of the ^{36}Cl isotope among the unreacted starting material, the product alkyl chloride (or HCl + olefin), and the carbonylrhodium(I) complex. This result points out that a rapid equilibrium is established between the acyl chloride and a trigonal bipyramidal oxidative addition product **3a** which possesses C_{2v} symmetry. The intermediate alkyl complex **4** belongs to the same symmetry group.

Experimental Section

Chlorotris(triphenylphosphine)rhodium(I) (**1**) was prepared by a published procedure.[31] *trans*-Carbonylchlorobis(triphenylphosphine)rhodium(I) (**2**) was obtained from the carbonylation of **1**.[38] *p*-Methylbenzoyl chloride,[7] α-trifluoromethylphenylacetyl chloride,[8] and 3-phenylpropionyl chloride[9] were prepared from the corresponding carboxylic acids with oxalyl chloride or thionyl chloride.

Synthesis of Chiral α-Deuteriophenylacetyl Chloride. Chlorination of Optically Active Chloro(α-deuteriophenylacetyl)bis(triphenylphosphine)palladium(II). Optically active chloro(α-deuteriophenylacetyl)bis(triphenylphosphine)palladium(II) was prepared by the oxidative addition of *R*-(−)-benzyl-α-*d* chloride ($[\alpha]^{25}D$ −1.28 ± 0.02°, neat, l = 0.1) to carbonyltris(triphenylphosphine)-palladium(0)[39] according to an earlier report from these laboratories.[24] To a 200-mL methylene chloride suspension of 15.1 g (19.2 mmol) of optically active chloro(α-deuteriophenylacetyl)bis(triphenylphosphine)palladium(II) cooled to −78 °C under nitrogen was

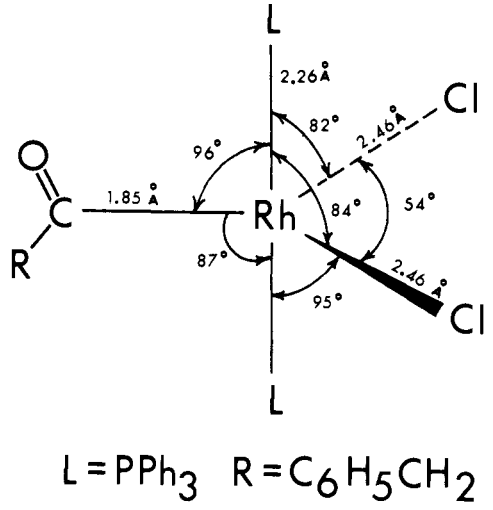


Figure 1.

added 13.0 mL of a 1.37 M solution of chlorine in carbon tetrachloride. The mixture was stirred at 25 °C for 10 min and diluted with an equal volume of pentane and the yellow complex was isolated by filtration under nitrogen. The yellow complex was treated with an additional 3 mL of the chlorine–carbon tetrachloride solution to ensure complete transformation to dichlorobis(triphenylphosphine)palladium(II). The filtrate was concentrated to a yellow oil under nitrogen. Distillation at reduced pressure (bp 41–48 °C (0.35–0.40 mm Hg)) afforded pure *S*-(+)-α-deuteriophenylacetyl chloride. Yield, 1.26 g (8.09 mmol, 45.5%); $[\alpha]^{25}D$ +2.14 ± 0.02° (neat, l = 0.1), 73.3% optically pure.[24]

Stoichiometric Decarbonylation of *S*-(+)-α-Deuteriophenylacetyl Chloride with Chlorotris(triphenylphosphine)rhodium(I). A mixture of 0.584 g (3.76 mmol) of *S*-(+)-α-deuteriophenylacetyl chloride, $[\alpha]^{25}D$ +2.14° (neat, l = 0.1) (73% optically pure), and 3.47 g (3.75 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 30 mL of deaerated, anhydrous benzene was heated at reflux under nitrogen for 24 h. After cooling, the mixture was mixed with an equal volume of hexane and filtration separated the bright yellow *trans*-carbonylchlorobis(triphenylphosphine)rhodium(I) complex (100%; IR ($CHCl_3$) 1985 cm^{-1}) and a filtrate which was concentrated to a yellow mass. Extraction (6 × 10 mL) with pentane and concentration of the combined pentane extracts yielded a yellow oil which was purified by distillation (24 °C (0.8 mm Hg)) to afford 113 mg (0.889 mmol, 23.7%) of benzyl-α-*d* chloride, identifiable by its NMR and mass spectra. The optical purity of benzyl-α-*d* chloride was determined by enantiomer dilution to be 15% with preponderance in the *S* enantiomer.

A duplicate run was carried out using 0.674 g (4.33 mmol) of the optically active acid chloride and 7.00 g (4.33 mmol) of chlorotris(triphenylphosphine)rhodium(I) in 30 mL of benzene at reflux under nitrogen for 5 h. The isolated *trans*-carbonylchlorobis(triphenylphosphine)rhodium(I) (100%) was identified by its IR spectrum (IR ($CHCl_3$) 1985 cm^{-1}) and the purified benzyl-α-*d* chloride (155 mg, 1.21 mmol, 28.2%) was determined to be 20% optically pure.

Enantiomer Dilution for the Determination of Optical Purity of Chiral Benzyl-α-*d* Chloride. A sample of optically active benzyl-α-*d* chloride of known quantity and optical purity was used as the reference. To this reference was added a known quantity of the purified reaction product which was partially optically active benzyl-α-*d* chloride. The rotation of the resulting mixture was taken. The contribution of the added sample to the lowering of the optical rotation of the reference was then calculated as follows. Define:

$[\alpha]$ as the specific rotation of the final mixture of benzyl-α-*d* chloride

$[\alpha]_0$ the specific rotation of the reference sample

X_2 the optical purity of the final mixture (based on maximum rotation of $[\alpha]^{25}D$ 1.53°)[24]

X_1 the optical purity of the reference

S_1, S_2 the mole fraction of the *S* enantiomer in the reference and in the final mixture, respectively

R_1, R_2 the mole fraction of the *R* enantiomer in the reference and in the final mixture, respectively

$$S_1 = (1 + X_1)/2$$

$$S_2 = (1 + X_2)/2$$

$$R_1 = (1 - X_1)/2$$

$$R_2 = (1 - X_2)/2$$

Let:

S_{m_1}, S_{m_2} be the numbers of millimoles of the *S* enantiomer in the reference and in the final mixture, respectively

R_{m_1}, R_{m_2} be the number of millimoles of the *R* enantiomer in the reference and in the final mixture, respectively

W_1, W_2 be the weight of the reference and of the final mixture, respectively

Then:

$S_{m_1} = S_1 W_1$
$S_{m_2} = S_2 W_2$
$R_{m_1} = R_1 W_1$
$R_{m_2} = R_2 W_2$
Increment of *S* enantiomer $S' = S_{m_2} - S_{m_1}$
Increment of *R* enantiomer $R' = R_{m_2} - R_{m_1}$

The optical purity of the added sample can be calculated from the formula $(S' - R')/(S' + R') \times 100\%$.

Sample calculation:

$[\alpha]_1 = 1.13°$
$[\alpha]_2 = 1.03°$
$X_1 = 73.9 \pm 1.0\%$
$X_2 = 67.3 \pm 1.0\%$

$S_1 = 0.869$ $S_2 = 0.837$

$R_1 = 0.131$ $R_2 = 0.163$

$S_{m_1} = 5.584$ $S_{m_2} = 6.0448$

$R_{m_1} = 0.842$ $R_{m_2} = 1.1772$

$S' = 0.459$ $\dfrac{S' - R'}{S' + R'} = \dfrac{0.122}{0.796} = 0.15$

$R' = 0.337$

Preparation of 3,3-Dideuterio-3-perdeuteriophenylpropionyl Chloride. The preparation of 3,3-dideuterio-3-perdeuteriophenylpropionyl chloride was carried out according to a previous report.[9] Bp 51–56 °C (0.3 mm Hg); NMR ($CDCl_3$) δ 3.18 ppm (s, $C_6D_5CD_2CH_2CO$).

Preparation of Acylrhodium(III) Complexes. Dichloro(acyl)bis(triphenylphosphine)rhodium(III) complexes were prepared by the oxidative addition of acyl chlorides to chlorotris(triphenylphosphine)rhodium(I) (**1**). Dibromo(3-phenylpropionyl)bis(triphenylphosphine)rhodium(III) was obtained from the reaction of 3-phenylpropionyl bromide and bromotris(triphenylphosphine)rhodium(I). Bromochloro(3-phenylpropionyl)bis(triphenylphosphine)rhodium(III) was prepared by the oxidative addition of either the acid chloride to bromotris(triphenylphosphine)rhodium(I) or the acid bromide to chlorotris(triphenylphosphine)rhodium(I).

The preparation of dichloro(3-phenylpropionyl)bis(triphenylphosphine)rhodium(III) illustrates the general procedure: A 20-mL methylene chloride solution of 1.00 g (1.08 mmol) of chlorotris(triphenylphosphine)rhodium(I) and 0.455 g (2.70 mmol, 2.50 equiv) of 3-phenylpropionyl chloride was stirred under nitrogen at 25 °C for 24 h. Mixing with 200 mL of 95% ethanol gave a golden yellow complex which was isolated by filtration and dried in vacuo (0.1 mm) to yield 0.827 g (0.995 mmol, 92.0%) of product. Anal. Calcd for $C_{45}H_{39}Cl_2OP_2Rh$: C, 65.00; H, 4.73. Found: C, 64.50; H, 4.46.

All acylrhodium(III) complexes exhibit a strong absorption at 1710 cm^{-1} (KBr or $CHCl_3$) in the IR spectrum. Far-IR spectra taken in Nujol mull between polystyrene cell windows showed characteristic Rh–halogen stretching frequencies as follows: dichloro complex 354 (vs), 219 (s), 295 (w), 244 (s), 189 (s); dibromo complex 267 (vs), 221

(s), 186 (s); bromochloro complex 315 (s), 294 (sh), 218 (s).

Preparation of Chlorotris(triarylphosphine)rhodium(I) (aryl = 2,6-dideuteriophenyl). A 50-mL ethanol slurry of 0.566 g (2.15 mmol) of rhodium(III) trichloride trihydrate and 2.34 g (8.74 mmol, 4.06 equiv) of triarylphosphine was heated under argon at reflux for 15 h. The brick-red complex was isolated by filtration and washed with ethanol and ether to yield 1.59 g (1.68 mmol, 78.1%) of product. Anal. Calcd for $C_{54}H_{27}D_{18}ClP_3Rh$: C, 68.75; H, 4.81. Found: C, 68.39; H, 4.68.

Attempted Hydrogen–Deuterium Exchange between Styrene and Chlorotris(triarylphosphine)rhodium(I) (aryl = 2,6-dideuteriophenyl). A 10-mL benzene solution of 0.497 g (0.526 mmol) of chlorotris(triarylphosphine)rhodium(I) and 0.302 g (2.91 mmol) of styrene was heated at reflux under nitrogen for 50 h. The volatile components were transferred at 30 °C (3 mm Hg) to a receiver cooled in liquid nitrogen. Solvent removal gave an oil which was shown by NMR analysis to be only styrene. No deuterium incorporation was detected.

Stoichiometric Decarbonylation of β-Phenylpropionyl Chloride with Chlorotris(triarylphosphine)rhodium(I) (aryl = 2,6-dideuteriophenyl). A 25-mL benzene solution of 1.08 g (1.14 mmol) of chlorotris(triarylphosphine)rhodium(I) and 0.434 g (2.57 mmol, 2.25 equiv) of β-phenylpropionyl chloride was heated at reflux under nitrogen for 50 h. The volatile components were transferred at 0.1 mm Hg to a receiver cooled at liquid nitrogen temperature. Concentration of the distillate gave an oil which was shown by NMR analysis to be only styrene-d_0. No deuterium incorporation was detected.

Decarbonylation of Dichloro(3,3-dideuterio-3-perdeuteriophenylpropionyl)bis(triphenylphosphine)rhodium(III) (7). Complex **7** (400 mg, 0.48 mmol) was placed in a 10-mL round-bottomed flask equipped with a gas inlet capillary which extended to within 1 mm from the bottom of the flask. The complex was covered with 3 mL of α-methylnaphthalene, which had been passed through an alumina column and distilled. A slow stream of argon was continuously bubbled through the suspension. The temperature was raised to 100 °C and the pressure was kept at 30 mm Hg. Complete dissolution of the complex was observed. Heating was continued for 5 h and the product was collected in a receiver maintained at −78 °C. The styrenes collected in the receiver (18 mg, 35%) were analyzed with PFT NMR on a Bruker HX-90E (Table II). Mass spectrum (20 eV) *m/e* (rel intensity) 113 (0.1), 112 (0.7), 111 (3.9), 110 (10.4), 109 (8.0), 108 (1.4), 107 (0.4). The mass spectrum of styrene taken at 20 eV was used as the basis for computing[28] the isotopic composition of the perdeuteriophenylethene. *m/e* (rel intensity) 105 (7.59), 104 (85.0), 103 (13.29), 102 (0.50). The computation yielded the following isotopic composition of the perdeuteriophenylethenes: $C_6D_5C_2H_3$ (34%), $C_6D_5C_2H_2D$ (48%), $C_6D_5C_2HD_2$ (15%), and $C_6D_5C_2D_3$ (3%). The precision in this measurement was ±1.5%. The $C_6D_5C_2H_2D$ isomeric composition was 87% $C_6D_5CD{=}CH_2$ and 13% *cis-* + *trans*-$C_6D_5CH{=}CHD$ according to NMR analysis. The flask was cooled to 25 °C and the residue was diluted with 10 mL of pentane. The yellow precipitate was filtered and washed well with ether and dried to afford 328.6 mg (99%) of chlorocarbonylbis(triphenylphosphine)-rhodium(I); IR (KBr) 1970 cm^{-1} (C≡O).

Carbonylation of Dichloro(3,3-dideuterio-3-perdeuteriophenylpropionyl)bis(triphenylphosphine)rhodium(III) (7). A solution of 405 mg (0.487 mmol) of dichloro(3,3-dideuterio-3-perdeuteriophenylpropionyl)bis(triphenylphosphine)rhodium(III) in 15 mL of benzene was stirred under 1 atm of CO at 25 °C. The color turned gradually from orange-brown to yellow, and a yellow precipitate was formed. After 34 h 5 mL of ethanol was added and the reaction mixture was filtered. The yellow precipitate was washed with ether and dried and was identified as chlorocarbonylbis(triphenylphosphine)rhodium(I); IR (KBr) 1970 cm^{-1} (C≡O). An additional crop of the yellow complex was obtained from the concentrated filtrate; the combined yield was 317 mg (0.459 mmol, 94%). The mother liquor was combined with the ether washings and concentrated in vacuo. Distillation of the residue on a Kugelrohr at 100 °C (0.2 mm) afforded 73 mg (0.39 mmol, 81%) of ethyl-3,3-dideuterio-3-perdeuterio phenylpropionate as a colorless oil. NMR ($CDCl_3$) δ 4.18 (q, 2 H, J = 8 Hz, CH_2-CH_3), 2.86 (bs, 2 H, CH_2-CD_2), 1.30 (t, 3 H, J = 8 Hz, CH_3). Mass spectrum (70 eV) *m/e* 185 (M+), 99% D.

Decarbonylation of Dichloro(3,3-dideuterio-3-perdeuteriophenylpropionyl)bis(triphenylphosphine)rhodium(III) (7) in the Presence of 3-Nitrostyrene (17). To a solution of 902 mg (1.084 mmol) of dichloro(3,3-dideuterio-3-perdeuteriophenylpropionyl)bis(triphenylphosphine)rhodium(III) in 20 mL of benzene was added 423 mg (2.84 mmol) of 3-nitrostyrene and the mixture was heated to the reflux temperature under argon for 7 h. Upon cooling to 25 °C a yellow precipitate of chlorocarbonylbis(triphenylphosphine)rhodium(III) was formed; more complex precipitated upon addition of 30 mL of pentane. The precipitate was filtered and the filtrate was concentrated at atmospheric pressure to remove most of the pentane, followed by distillation of the benzene at 30 °C (210 mm Hg). After most of the solvent was removed, the residue was distilled, bulb-to-bulb, at 25 °C (0.2 mm Hg) to afford 55 mg of styrene which consisted according to NMR analysis of 72% perdeuteriophenylethene and 28% 1-deuterio-1-perdeuteriophenylethene. The remainder of the yellow residue was distilled on a Kugelrohr at 138 °C (0.2 mm) to afford 420 mg of pale yellow oil characterized as a mixture of deuterated 3-nitrostyrenes. Mass spectrum (70 eV) *m/e* (rel intensity) 151 (16), 150 (39), and 149 (70). (The relative intensities are corrected for $M^+ + 1$ intensity obtained from the mass spectrum of 3-nitrostyrene (70 eV) *m/e* 150 (6), 149 (38) (M^+).) NMR data are given in Table II.

Catalytic Decarbonylation for 3,3-Dideuterio-3-perdeuteriophenylpropionyl Chloride (15) with Chlorocarbonylbis(triphenylphosphine)rhodium(I). (a) At 470 mm Hg. To a solution of 500 mg (2.85 mmol) of 3,3-dideuterio-3-perdeuteriophenylpropionyl chloride in 1.5 mL of α-methylnaphthalene was added 27.7 mg (0.04 mmol) of chlorocarbonylbis(triphenylphosphine)rhodium(I). A slow stream of argon was passed continuously through the reaction mixture, and the temperature was raised to 190 °C while the pressure was kept at 470 mm Hg. Vigorous gas evolution was observed, and the distilled product was collected in a receiver cooled to −78 °C. Heating was continued for 4 h. The collected styrene (127 mg, 40.5%) was characterized by NMR to be 1-deuterio-1-perdeuteriophenylethene (>95%).

(b) At 1 atm. A solution of 1.0 g (5.7 mmol) of 3,3-dideuteriophenylpropionyl chloride and 27.7 mg (0.04 mmol) of chlorocarbonylbis(triphenylphosphine)rhodium(I) in 3 mL of α-methylnaphthalene was heated to 190 °C while a slow stream of argon was passed through the reaction mixture. The flask was connected to a receiver maintained at −123 °C (*n*-propyl chloride slush) which in turn was connected to a tube filled with molecular sieves (3A, 8–12 mesh). The train was terminated with a mercury bubbler. During the course of the reaction, the reflux of styrene was noticed which slowly ceased due to polymerization. The condensed hydrochloric acid was transferred on a vacuum line to an IR gas cell. Typical resolved HCl and DCl absorptions centered around 2910 and 2105 cm^{-1} were observed. Mass spectral analysis (70 eV) of the gas mixture showed the presence of DCl and HCl in 86 and 14%, respectively.

High-Temperature Infrared Studies. All decarbonylations were carried out at 90 ± 2 °C, using a Perkin-Elmer 421 infrared spectrometer fitted with a variable temperature IR cell compartment (Barnes Model VTC-104). The acylrhodium complexes under investigation were dichloro(3-phenylpropionyl)bis(triphenylphosphine)rhodium(III)[9] and dichloro(2,3-diphenylbutanoyl)bis(triphenylphosphine)rhodium(III).[5] Both complexes absorb at 1710 cm^{-1} and undergo decarbonylation to give *trans*-carbonylchlorobis(triphenylphosphine)rhodium(I) which absorbs at 1980 cm^{-1} (CH_2ClCH_2Cl).

Initially, a solution of the acylrhodium(III) complex in 1,2-dichloroethane was transferred to the sample cell which was then placed in the variable temperature cell compartment. The temperature inside the variable temperature compartment was measured by using a copper–constantan thermocouple, located in close proximity of the sample cell, in conjunction with a thermocouple potentiometer (Biddle Model 723161). The IR cell compartment was slowly heated to attain 90 ± 2 °C. Infrared spectra taken at 20, 35, and 50 °C showed no appearance of the 1980-cm^{-1} absorption of the product rhodium(I) complex and no decrease in intensity of the 1710-cm^{-1} absorption of the acylrhodium(III) complex. At 90 ± 2 °C, infrared spectra in the range of 2500–1600 cm^{-1} were taken at 3-min intervals until the total disappearance (ca. 45 min) of the 1710-cm^{-1} (acylrhodium) absorption. During the course of decarbonylation, a small sharp peak appeared and persisted at 2080 cm^{-1}. Toward the end of decarbonylation the 2080-cm^{-1} peak disappeared.

Kinetic Procedure. The decarbonylation of **6** or **7** was carried out at 75 °C and was followed by monitoring the increase in the carbonyl stretching mode of *trans*-$Rh(CO)Cl(PPh_3)_2$ (**2**) at 1986 cm^{-1}. Compound **2** obeyed Beer's law in 1,2-dichloroethane at 75 °C up to 0.005 M; the molar extinction coefficient was 1130 ± 10 M^{-1} cm^{-1}.

Kinetic measurements were performed as previously described[7] except that the sample cell (thickness 0.1 cm) was modified such that it could be easily filled at 75 °C without removing it from the variable temperature chamber. The initial concentrations for both **6** and **7** were 0.005 M. The order of the reaction with respect to **2** was determined by plotting [absorbance][7/8] vs. time. A straight line with a slope taken from the average of five separate determinations was obtained.

Preparation of Lithium Chloride-^{36}Cl. Titration of Lithium Hydroxide with Hydrochloric Acid-^{36}Cl. A radioactive sample of hydrochloric acid-^{36}Cl (0.61 mL, 2 M, 41 μCi/mL) was diluted with ca. 15 mL of a 10 M hydrochloric acid solution and 30 mL of distilled water. The dilute acid solution was titrated with a solution of 4.72 g of lithium hydroxide in 130 mL of water. A pH meter was used to indicate the end point of 7.0.

The solution of lithium chloride was mixed with 300 mL of benzene and was azeotropically distilled until no more water was collected in the Dean-Stark trap. The crystalline lithium chloride was isolated by filtration. After overdrying at 120 °C for 1.5 h, the white crystals were cooled under nitrogen to yield 8.55 g (0.197 mol); specific radioactivity ($2.00 \pm 0.06 \times 10^7$ cpm/mmol).

Preparation of Benzyl Tosylate. Reaction of Sodium Benzyl Alcoholate with *p*-Toluenesulfonyl Chloride. A modified literature procedure[40] was followed. A solution of 9.0 mL (87 mmol) of benzyl alcohol in 100 mL of anhydrous ether was added dropwise to 2.3 g (96 mmol) of sodium hydride powder under nitrogen. The mixture was stirred at reflux for 1 h and then cooled to −30 °C before the dropwise addition of a solution of 17.5 g (89 mmol) of tosyl chloride in 100 mL of anhydrous ether. The mixture was allowed to warm to 25 °C within 2.5 h and was stirred at 25 °C for additional 2 h.

Filtration with a minimal exposure to moisture separated a clear ethereal filtrate from a gelatinous mass. The ethereal filtrate was evaporated to yield a fluffy white solid which was washed with prechilled pentane. NMR analysis showed the characteristics of benzyl tosylate: NMR ($CDCl_3$) δ 2.43 (s, 3 H, Ar-CH_3), 5.06 (s, 2 H, $C_6H_5CH_2O$), 7.30 (s, 5 H, $C_6H_5CH_2O$), 7.31 and 7.81 ppm (AA′ BB′q, aromatic). Yield 11.5 g (44 mmol, 51%); the low yield was due to difficulty in filtration.

Preparation of Benzyl Chloride-^{36}Cl. Reaction of Benzyl Tosylate with Lithium Chloride-^{36}Cl. A solution of 0.400 g (1.53 mmol) of benzyl tosylate and 0.230 g (5.29 mmol, 3.47 equiv) of lithium chloride-^{36}Cl (specific radioactivity, 2.00×10^5 cpm/mmol) in 5 mL of deaerated, anhydrous dimethylformamide was stirred under nitrogen at 25 °C for 9 h. The solution was mixed with 100 mL of water and was extracted four times with 10-mL portions of methylene chloride. The combined organic extracts were then washed three times with 5 N hydrochloric acid followed with water and aqueous sodium bicarbonate. The organic phase was dried over magnesium sulfate and concentrated to an oil which was purified by preparative GLC (185 °C, 10 ft × 0.375 in., 20% FFAP on Chromosorb W 60/80) and identified as benzyl chloride by retention time comparison with an authentic sample. Yield 32.4 mg (0.254 mmol, 16.5%); specific radioactivity (2.03 ± 0.06) $\times 10^5$ cpm/mol.

Preparation of Chlorotris(triphenylphosphine)rhodium(I)-^{36}Cl. An ethanolic slurry of 0.922 g (3.50 mmol) of rhodium(III) trichloride trihydrate, 1.25 g (28.9 mmol, 8.25 equiv) of lithium chloride-^{36}Cl (specific radioactivity, 2.00×10^5 cpm/mmol), and 5.09 g (19.4 mmol, 5.55 equiv) of triphenylphosphine was heated under nitrogen at reflux for 8 h. The reddish brown complex was isolated by filtration and was washed thoroughly with ethanol and then ether to yield 2.94 g (3.18 mmol, 90.8%) of product. Anal. Calcd for $C_{54}H_{45}{}^{36}ClP_3Rh$: C, 70.10; H, 4.90. Found: C, 70.52; H, 5.09.

The filtrate was concentrated and partitioned between 50 mL of methylene chloride and 100 mL of water. The aqueous layer was separated, mixed with 100 mL of benzene, and then azeotropically distilled until no more water was collected in the Dean-Stark trap. The crystalline lithium chloride, isolated by filtration under nitrogen, had a specific radioactivity of (1.38 ± 0.04) $\times 10^5$ cpm/mmol, 69 ± 4% of the activity of the original lithium chloride-^{36}Cl. Recovery 1.08 g (86.0%).

Preparation of Carbonylchlorobis(triphenylphosphine)rhodium(I)-^{36}Cl. Carbonylation of Chlorotris(triphenylphosphine)rhodium(I)-^{36}Cl. Carbon monoxide was bubbled through a slurry of 73.4 mg (79.2 μmol) of chlorotris(triphenylphosphine)rhodium(1)-^{36}Cl in 3 mL of anhydrous benzene. In 2 min, the initial reddish brown slurry turned into a clear yellow solution which eventually yielded a precipitate. The benzene solvent was partially evaporated and the mixture was mixed with ether. The crystalline yellow complex was isolated by filtration and washed with ether to yield 40.6 mg (58.6 μmol, 79.8%) of product; IR ($CHCl_3$) 1985 cm^{-1} (Rh(I)-CO). Anal. Calcd for $C_{37}H_{30}{}^{36}ClOP_2Rh$: C, 64.23; H, 4.37. Found: C, 65.00; H, 4.73. Specific radioactivity (1.57 ± 0.05) 10^5 cpm/μmol.

Stoichiometric Decarbonylation of Phenylacetyl Chloride with Chlorotris(triphenylphosphine)rhodium(I)-^{36}Cl. A mixture of 0.907 g (0.979 mmol) of chlorotris(triphenylphosphine)rhodium(I)-^{36}Cl and 0.311 g (2.02 mmol, 2.06 equiv) of phenylacetyl chloride in 20 mL of deaerated anhydrous benzene was heated to reflux in 10 min under nitrogen. At 50 °C, the mixture became a clear brown solution. At reflux, the solution turned opaque and a yellow complex began to form. After 7 h at reflux, the mixture was cooled and treated with 5 mL of methanol and 30 mL of pentane. The bright yellow complex of *trans*-carbonylchlorobis(triphenylphosphine)rhodium(I) was isolated by filtration: IR ($CHCl_3$) 1985 cm^{-1}; specific radioactivity (4.61 ± 0.14) $\times 10^4$ cpm/mmol. Anal. Calcd for $C_{37}H_{30}{}^{36}ClOP_2Rh$: C, 64.23; H, 4.37. Found: C, 63.46; H, 5.04.

The filtrate was concentrated and extracted four times with 10-mL portions of pentane. The combined pentane extracts were concentrated to an oil which was purified by GLC (185 °C, 10 ft × 0.375 in., 20% FFAP on Chromosorb W 60/80.) The recovered benzyl chloride (5.3 mg) had a specific radioactivity of (5.97 ± 0.52) $\times 10^4$ cpm/mmol.

Determination of Chlorine-36 Radioactivity. The determination of chlorine-36 radioactivity was carried out using a Beckman Model LS-150 liquid scintillation system. The chlorine-36 radioactivity was measured in terms of number of counts of β emissions per minute. Each sample of chlorotris(triphenylphosphine)rhodium(I)-^{36}Cl (**1***), *trans*-carbonylchlorobis(triphenylphosphine)rhodium(I)-^{36}Cl (**2*** and **2***r), and benzyl chloride-^{36}Cl (**16*** and **16r***) was prepared in toluene cocktail containing PPO and naphthalene. The samples of lithium chloride-^{36}Cl were prepared in dioxane cocktail. Each sample was placed in the counting system and radioactivity counts were taken over 100 min. The accuracy of counts was ±3%.

Phosphorus-31 NMR Studies. The NMR spectra were recorded on a Bruker PFT-90-MHz variable frequency spectrometer. All results were for a field strength such that the proton signal from TMS would be observed at 90 MHz. For all spectral measurements, the samples were sealed in 10-mm spinning sample tubes. A capillary of 85% H_3PO_4 was sealed in the tubes as an external standard. Each sample was 400 mg in 1.5 mL of spectrograde deuteriochloroform and the solution was purged with high-purity nitrogen gas.

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References and Notes

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Specific Effects of Chloride Ion in the Hydrolysis of a K-Region Arene Oxide

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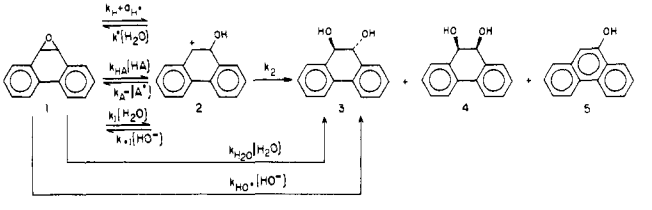
Abstract: The pH–rate profiles for the hydrolysis of phenanthrene 9,10-oxide (**1**) in 1 M KCl, 0.1 M $NaClO_4$, and 1 M $NaClO_4$ solutions in the pH range 4–10 have been determined. The pH–rate profiles indicated that only two mechanisms for hydrolysis of phenanthrene 9,10-oxide in 0.1 M and 1 M $NaClO_4$ solutions are operative in the pH range studied. An acid-catalyzed reaction predominates below pH ~7, and a spontaneous reaction of the epoxide with solvent operates at pH above ~7. The pH–rate profile for the hydrolysis of phenanthrene oxide in 1 M KCl was more complicated, and was explained in part by a specific effect of added chloride ion. A plateau and inflection point in the pH–rate profile were attributed to nucleophilic addition of chloride ion to the epoxide to form an intermediate chlorohydrin. The plateau at pH > 9 results from a reversal of the pH-dependent equilibrium between chlorohydrin and epoxide such that the rate-limiting step becomes the spontaneous reaction of epoxide with solvent. Product analyses throughout the pH range studied were consistent with the mechanism proposed. General acid catalysis in the hydrolysis of **1** by acetic acid and dihydrogen phosphate ion was also studied in $NaClO_4$ and KCl solutions. Variable catalytic constants for general acid catalysis in the hydrolysis of **1** when the solutions were kept at constant ionic strength by KCl were also attributed to specific effects of chloride ion.

K-region arene oxides derived from carcinogenic aromatic hydrocarbons possess both mutagenic[2a,b] and weak carcinogenic activity, and have therefore been implicated as potential causative agents in the carcinogenicity of the parent hydrocarbons.[3] Intermediate arene oxides are further transformed by both enzymatic and nonenzymatic pathways, and knowledge of the solvolytic and nucleophilic reactions of such arene oxides are essential to understanding the more complex processes by which they react under biological conditions.

The elegant kinetic work of Bruice et al.[4] on the hydrolysis of arene oxides throughout the pH range has greatly aided in the understanding of the various mechanisms by which arene oxides can hydrolyze. Many kinetic studies on oxide hydrolyses have been carried out in aqueous solutions containing potassium chloride, and consequently product studies have been carried out in solutions that also contain the same electrolyte.[4,5] We now report that *potassium chloride induces specific effects in the hydrolysis of a typical K-region arene oxide, phenanthrene 9,10-oxide* (**1**).

The pH–rate profile for the hydrolysis of **1** in 1 M KCl solution from pH 3 to 14 has been previously determined.[5b,c] We have verified the kinetic observations reported previously, and the profile for the hydrolysis of **1** in the pH range 4–10 is given in Figure 1. The profile had been interpreted in terms of the

Scheme I



general mechanisms outlined in Scheme I. Different rate-limiting steps were assigned to the approximate pH regions 4–5.5, 5.5–7.2, and 8.5–11.5. In the pH region 4–5.5, the dominant reaction is the hydronium-ion-catalyzed process ($k_{H^+}a_{H^+}$). The rate profile in the region 5.5–7.2 was interpreted in terms of general acid catalysis by water ($k_1[H_2O]$), and nucleophilic addition of water to **1** ($k_{H_2O}[H_2O]$) was suggested as being the most reasonable mechanism for hydrolysis at pH 8.5–11.5. An inflection point at pH ~7.2 was attributed to the change in mechanism from general acid catalysis by water to nucleophilic addition of water to **1**.

Although other mechanisms were considered that were consistent with the pH–rate profile, the series of mechanisms presented above were most consistent with the product distri-