



**Table I.** Analytical Data for Complexes of the Types **2a**, **2b**, and **3a**

	Calcd (Found)		
	C	H	N
RhCl <sub>2</sub> (COC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	60.87 (60.76)	4.04 (4.21)	1.65 (1.63)
RhCl <sub>2</sub> (COC <sub>6</sub> H <sub>4</sub> Cl)(PPh <sub>3</sub> ) <sub>2</sub>	61.68 (61.12)	4.09 (4.25)	
RhCl <sub>2</sub> (COC <sub>6</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	64.27 (64.76)	4.39 (4.33)	
RhCl <sub>2</sub> (COC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	63.40 (63.60)	4.48 (4.59)	
RhCl <sub>2</sub> (COCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	61.27 (60.19)	4.21 (4.31)	1.62 (1.73)
RhCl <sub>2</sub> (COCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl)(PPh <sub>3</sub> ) <sub>2</sub>	62.07 (61.33)	4.26 (4.58)	
RhCl <sub>2</sub> (COCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	64.6 (63.2)	4.56 (4.50)	
RhCl <sub>2</sub> (COCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	63.77 (64.31)	4.64 (4.50)	
RhCl <sub>2</sub> (CO)(C <sub>6</sub> H <sub>4</sub> Cl)(PPh <sub>3</sub> ) <sub>2</sub>	61.68 (62.02)	4.09 (4.21)	
RhCl <sub>2</sub> (CO)(C <sub>6</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	64.27 (64.67)	4.39 (4.59)	
RhCl <sub>2</sub> (CO)(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	64.64 (63.73)	4.56 (4.45)	
RhCl <sub>2</sub> (CO)(C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	63.40 (63.34)	4.48 (4.90)	

**Table II.** Infrared Frequencies (cm<sup>-1</sup>, 1,2-Dichloroethane) for Complexes of Types **2a**, **2b**, **3a**, and **3b**

	$\nu(>C=O)$	$\nu(C\equiv O)$	$\nu(Rh-Cl)^a$
RhCl <sub>2</sub> (COC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	1669		
RhCl <sub>2</sub> (COC <sub>6</sub> H <sub>4</sub> Cl)(PPh <sub>3</sub> ) <sub>2</sub>	1650		
RhCl <sub>2</sub> (COC <sub>6</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	1666		
RhCl <sub>2</sub> (COC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	1667		
RhCl <sub>2</sub> (COCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	1679		
RhCl <sub>2</sub> (COCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl)(PPh <sub>3</sub> ) <sub>2</sub>	1714		
RhCl <sub>2</sub> (COCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	1708		
RhCl <sub>2</sub> (COCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	1692		
RhCl <sub>2</sub> (CO)(C <sub>6</sub> H <sub>4</sub> Cl)(PPh <sub>3</sub> ) <sub>2</sub>		2074	318, 280
RhCl <sub>2</sub> (CO)(C <sub>6</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub>		2074	320, 283
RhCl <sub>2</sub> (CO)(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>		2074	320, 288
RhCl <sub>2</sub> (CO)(C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>		2074	318, 280
RhCl <sub>2</sub> (CO)(CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>		2069	
RhCl <sub>2</sub> (CO)(CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cl)(PPh <sub>3</sub> ) <sub>2</sub>		2069	
RhCl <sub>2</sub> (CO)(CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub>		2069	
RhCl <sub>2</sub> (CO)(CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>		2069	

<sup>a</sup> Only measured for complexes of the type **3a**.

complexes always occurs at 300 nm, regardless of the para substituent on the phenyl ring. These intermediate complexes have solubility characteristics similar to the parent chlorotris(triphenylphosphine)rhodium(I) (**1**) in that they are soluble in dichloromethane to about 20 g/l. at 25°, and in benzene or toluene to about 2 g/l. at 25°, but much less soluble in acetic acid, acetone, and methanol. In paraffins and cyclohexane, the complexes are virtually insoluble.

While the acyl complex **2** has been depicted in Scheme I as a monomeric complex, a dimeric structure can also be envisioned for this type of five-coordinate intermediate, with bridging occurring through the chlorine atoms. Benzoyl complexes **2a** are too reactive to allow for determination of molecular weight; however, vapor pressure osmometer measurements for the more stable phenylacetyl complex (**2b**, R = C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>) indicate that at least this acyl complex is monomeric.

The phenylacetyl complexes **2b** were prepared by allowing an excess of para-substituted phenylacetyl chloride to react with **1** in dichloromethane at 0°, and then adding pentane after 30 sec to precipitate the desired phenylacetyl complex **2b** as yellow crystals. The crystals were washed with ether, and recrystallized at low temperature from acetone-pentane to afford the analytically pure complexes (Table I). These acyl complexes exhibited absorption in the infrared characteristic of the carbon-oxygen double bond stretching of an acyl group in a transition metal complex.<sup>11,19</sup> The absorption maxima show some dependence on the nature of the para substituent on the phenyl ring of the benzyl group (Table II). The wavelength of maximum absorption of these complexes in the ultraviolet occurs at 300 nm.

The molecular weight of phenylacetyldichlorobis-(triphenylphosphine)rhodium(III) (**2b**, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) in chloroform was shown by vapor pressure osmometry to be 761 (calculated 817), indicating that this five-coordinate acyl intermediate is monomeric in solution and not a bridged dimer.

The phenyl complexes **3a** were isolated by allowing an excess of the para-substituted benzoyl chloride to react with **1** in benzene at 30°, and then quenching the reaction with pentane after 2 days, causing the desired phenyl complex to precipitate as yellow crystals. Low temperature recrystallization from chloroform-ethanol yielded analytically pure complexes (Table I). The infrared spectra of the phenyl complexes contain an absorption at 2074 cm<sup>-1</sup> which is characteristic of the carbon-oxygen stretching mode of carbon monoxide coordinated to a six-coordinate rhodium(III) complex.<sup>11</sup> In the ultraviolet these carbonyls have absorption maxima at 333 nm.

Octahedral rhodium complexes with two chlorine atoms in trans position are known to have two rhodium-chlorine stretching frequencies, one near 339 cm<sup>-1</sup> and the other near 313 cm<sup>-1</sup>.<sup>20,21</sup> In the case of a chlorine trans to a phosphine, the rhodium-chlorine stretching consists of a single band between 278 and 264 cm<sup>-1</sup>. All of the para-substituted phenyldichlorocarbonylbis-(triphenylphosphine)rhodium(III) complexes had two absorptions in the far-infrared, at 283 and 320 cm<sup>-1</sup>, indicating that all of these six-coordinate rhodium(III) complexes were of the same stereochemistry. The observed far-infrared spectra show that in these phenyl complexes the chlorines must be cis and since neither chlorine is trans to a phosphine, the phosphines must be trans. These assignments allow the stereochemistry of **3a** to be established as shown in Scheme I. The fact that these para-substituted rhodium(III) phenyl complexes are all of the same stereochemistry is in contrast to the results reported for the analogous para-substituted iridium(III) benzoyl complexes,<sup>22</sup> in which the stereochemistry of the six-coordinate benzoyl complexes was dependent upon the nature of the para substituent in the phenyl ring of the benzoyl group.

Isolation of the benzyl complexes **3b** presented the most difficulty. First attempts to isolate para-substituted benzyl complexes involved allowing an excess of *p*-chlorophenylacetyl chloride to react with **1** in

(20) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 597 (1969).

(21) P. R. Brookes and B. L. Shaw, *J. Chem. Soc. A*, 1079 (1967).

(22) M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, **93**, 1368 (1971).

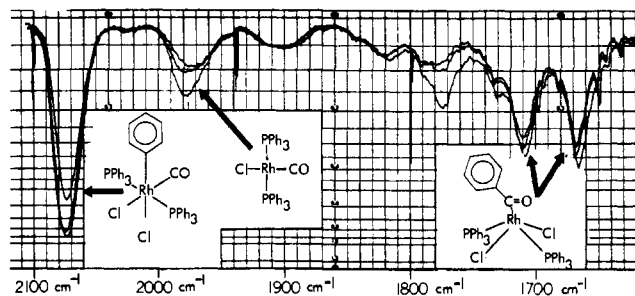


Figure 1. Infrared spectra of intermediate complexes in the decarbonylation of benzoyl chloride by chlorotris(triphenylphosphine)rhodium(I) (1).

dichloromethane. Any variation in reaction temperature and reaction time had no significant effect on the amount of **3b** produced in this reaction. The isolated product was a mixture of **2b**, **3b**, and **4** that never contained more than 5% of the benzyl complex **3b**. However, when chloroform was used as the solvent and an excess of *p*-chlorophenylacetyl chloride was allowed to react with **1** at 0° for 3 min, followed by the addition of pentane to quench the reaction, the *p*-chlorobenzyl complex **3b** constituted 80% of the product mixture. Apparently the acyl-alkyl rearrangement (**2b** → **3b**) is faster in chloroform than in dichloromethane, resulting in a greater accumulation of the *p*-chlorobenzyl complex **3b** in chloroform. The ability of solvents such as dichloromethane and 1,2-dichloroethane to solvate the vacant coordination site in the five-coordinate acyl intermediate **2** more effectively than chloroform may account for this.<sup>11</sup>

The infrared spectra of the benzyl complexes contain absorptions at 2069 cm<sup>-1</sup> which are characteristic of the carbon-oxygen stretching mode of carbon monoxide coordinated to six-coordinate rhodium(III) complexes.<sup>11</sup> In the ultraviolet region these carbonyl complexes have absorption maxima at 333 nm.

**Reaction Kinetics.** The rearrangement of the para-substituted benzoyl complexes **2a** to the para-substituted phenyl complexes **3a** in 1,2-dichloroethane was followed by monitoring the first-order disappearance of the acyl band near 1670 cm<sup>-1</sup> in the infrared (Figure 1). The fact that the phenyl complexes **3a** can be isolated pure without any contamination of the benzoyl complexes **2a**, as determined by examination of the carbonyl region of the infrared spectrum, is evidence that this rearrangement is irreversible under the reaction conditions. The substituent effects measured at 24.7° show that electron-withdrawing groups enhance the rate of this rearrangement (Table III). The effect of changing the halogens in the benzoyl complex on the rate of this acyl-alkyl rearrangement was determined. If electronic effects are an important factor, bromine could donate electrons either through polarization or back-bonding to rhodium more effectively than chlorine,<sup>23</sup> and the dibromo benzoyl complex should rearrange more rapidly than the dichloro benzoyl complex. The dichloro benzoyl complex, however, rearranges approximately twice as fast as the dibromo benzoyl complex (Table III) which is consistent with a more rapid migration to the more positive metal center.

The rearrangement of the para-substituted phenyl-

(23) B. E. Douglas and D. H. McDaniel, "Concepts and Models of Inorganic Chemistry," Blaisdell, Waltham, Mass., 1965, p 418.

acetyl complexes **2b** to the para-substituted benzyl complexes **3b** in 1,2-dichloroethane was followed by monitoring the first-order disappearance of the acyl band near 1700 cm<sup>-1</sup> in the infrared. The position of equilibrium in an acyl-alkyl rearrangement depends on the nature of the migrating group.<sup>11,24</sup> When the migrating group is methyl, the reaction only proceeds in one direction and methyl migration onto the carbon monoxide occurs to form an acyl complex. When the group is phenyl, the reaction only proceeds in the opposite direction to yield an aryl complex. It was anticipated that the benzyl group should have characteristics intermediate between that of a methyl group and a phenyl group, and that possibly the acyl-alkyl rearrangement of a benzyl group would be reversible. The results obtained in this kinetic study show that the acyl-alkyl rearrangement is indeed reversible for a benzyl group (Table V). The kinetic treatment of this complex reaction sequence simplifies readily because the benzyl complex can justifiably be termed a steady-state intermediate in the conversion of a phenylacetyl complex **2b** to benzyl chloride and **4**. In the case of every para substituent studied, the concentration of the intermediate benzyl complex (**3b**), as determined by analysis of the carbonyl region of the infrared spectrum, was approximately 1% of the mixture of the phenylacetyl complex **2b**, benzyl complex **3b**, and chloro-carbonylbis(triphenylphosphine)rhodium(I) (**4**). Since the rearrangement of the phenylacetyl complex **2b** to form the benzyl complex **3b** is reversible, the equilibrium constant for this acyl-alkyl rearrangement is incorporated in the observed rate constant for the first-order disappearance of the phenylacetyl complex **2b**. The substituent effects for this rearrangement, measured at 42.4°, show that electron-donating groups enhance the rate of this rearrangement (Table III).

The  $\rho$  values measured for the rearrangement of the para-substituted benzoyl complexes **2a** and the para-substituted phenylacetyl complexes **2b** are 0.265 and -0.612, respectively. For benzyl radical reactions in which charge is being developed on the benzylic carbon  $\rho$  values fall between -0.3 and -1.5,<sup>25-30</sup> while for reactions involving benzyl cations the  $\rho$  values fall between -4.5 and -6.5.<sup>31-37</sup> The magnitude of  $\rho$  values for reactions involving direct attack on a phenyl ring depends on whether a radical intermediate or a carbenium ion is involved. Electrophilic substitution provides suitable models of reactions that proceed through a carbenium ion delocalized  $\sigma$  complex. The

(24) I. C. Douek and G. Wilkinson, *J. Chem. Soc. A*, 2604 (1969).

(25) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **93**, 4536 (1971).

(26) P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960).

(27) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

(28) G. A. Russell and R. C. Williamson, Jr., *J. Amer. Chem. Soc.*, **86**, 2357 (1964).

(29) L. Huang and K. H. Lee, *J. Chem. Soc. C*, 935 (1966).

(30) R. P. Gilliom and B. F. Ward, Jr., *J. Amer. Chem. Soc.*, **87**, 3944 (1965).

(31) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(32) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(33) H. C. Brown and Y. Okamoto, *J. Org. Chem.*, **22**, 485 (1957).

(34) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Amer. Chem. Soc.*, **89**, 370 (1967).

(35) V. J. Shiner, Jr., E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, **90**, 418 (1968).

(36) D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969).

(37) See ref 25 and references cited therein.

$\rho$  values for nitration and chlorination are  $-6.53$  and  $-11.35$ , respectively.<sup>31</sup> Free radical substitution of chlorine for bromine on an aromatic ring serves as a good example of a reaction having an electron delocalized  $\sigma$  complex transition state, and has a  $\rho$  value of  $-0.19$ .<sup>38</sup> While the magnitude of  $\rho$  in the rearrangement of both para-substituted benzoyl complexes **2a** and the para-substituted phenylacetyl complexes **2b** is low enough to fall in the range observed for reactions involving radical intermediates the sign of  $\rho$  indicates the type of charge imbalance, however small, in the transition state.

In light of the fact that phosphines are known to coordinate with rhodium to form transition metal complexes, the possibility of added triphenylphosphine occupying the vacant coordination site in the five-coordinate acyl complexes **2** and thus retarding the rate of the acyl-alkyl rearrangements was examined. The rates of rearrangement of both the benzoyl complex (**2a**, R = C<sub>6</sub>H<sub>5</sub>) and the phenylacetyl complex (**2b**, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) are unchanged by the addition of triphenylphosphine (Table III). This result can be com-

**Table III.** First-Order Rate Constants for the Rearrangement of the Acyl Complexes **2a** and **2b** to the Corresponding Phenyl and Benzyl Complexes **3a** and **3b** in 1,2-Dichloroethane

R	$10^4 k$ , sec <sup>-1</sup>	Standard deviation	Temp, °C
<i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	3.50	0.20	24.7
C <sub>6</sub> H <sub>5</sub>	4.56	0.38	24.7
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	5.27	0.20	24.7
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	6.80	0.35	24.7
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	10.2	0.20	32.9
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	20.0	0.28	37.9
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	34.0	0.38	42.4
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	63.0	1.10	48.1
C <sub>6</sub> H <sub>5</sub>	6.40	0.13	26.3
C <sub>6</sub> H <sub>5</sub> <sup>a</sup>	6.33	0.09	26.3
C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	3.13	0.02	26.3
<i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	7.70	0.10	42.4
C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	5.44	0.06	42.4
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	3.86	0.07	42.4
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> <sup>a</sup>	3.78	0.05	42.4
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	1.77	0.04	42.4
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	7.09	0.16	47.4
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	11.9	0.13	52.7
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	19.1	0.13	57.4

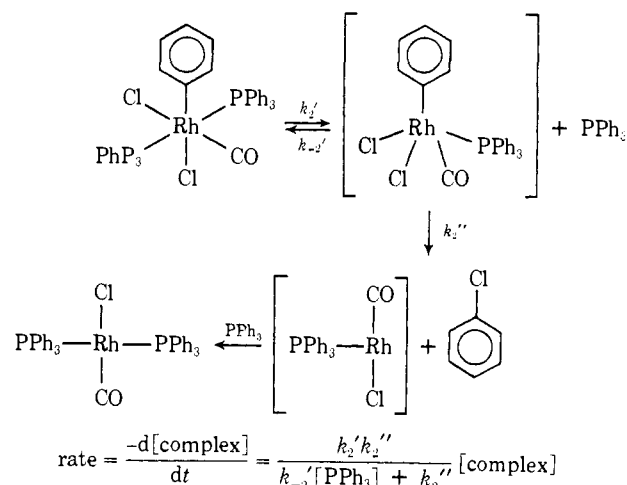
<sup>a</sup> 1,2-Dichloroethane-triphenylphosphine ( $2.0 \times 10^{-2}$  M) was the solvent. <sup>b</sup> Benzoyldibromobis(triphenylphosphine)rhodium(III).

pared with a small retarding effect of added triphenylphosphine observed for the acyl-alkyl rearrangement in an analogous iridium(III) benzyl system.<sup>19</sup>

The loss of para-substituted chlorobenzenes from the para-substituted phenyl complexes **3a** in 1,2-dichloroethane and toluene was followed by monitoring the first-order disappearance of the absorption at 333 nm in the ultraviolet spectra. This reaction was also monitored in one instance by infrared ( $2068\text{ cm}^{-1}$ ) and the rate constants obtained by both methods are identical within experimental error (Table IV). This reaction is irreversible since the para-substituted chlorobenzenes, formed as products, will not oxidatively add to **4**.<sup>11</sup> This was the only reaction studied that could be followed by monitoring the ultraviolet absorption of

the complex under study. The acyl absorption at 300 nm and the alkyl absorption at 333 nm overlap so that ultraviolet spectrometry could not be used to follow the kinetics of the acyl-alkyl rearrangements or the loss of para-substituted benzyl chlorides from the para-substituted benzyl complexes **3b**. Due to the increased sensitivity of the ultraviolet method this reaction could be followed in toluene as well as 1,2-dichloroethane. In both solvents electron-donating substituents enhance the rate of reaction (Table IV). It was noticed during the preparation of these phenyl complexes **3a** that the extra mole of triphenylphosphine that was liberated from **1** and free in solution inhibited the subsequent loss of chlorobenzene from the phenyl complexes **3a**. Under the conditions used in the synthesis of the phenyl complexes **3a**, reaction times of several weeks did not result in the loss of chlorobenzenes. However, in kinetic studies, in the absence of triphenylphosphine, these same phenyl complexes **3a** have a half-life of approximately 3 hr at 30° in toluene. The effect of added triphenylphosphine on the rate of this reaction was determined quantitatively (Table IV). A mechanism involving reversible dissociation of triphenylphosphine from the phenyl complex **3a** to form a five-coordinate steady-state intermediate accounts for these results (Scheme II). The inverse dependence of added

**Scheme II**



triphenylphosphine appears in the rate equation for this mechanism. There is ample precedent for the reversible dissociation of triphenylphosphine from six-coordinate rhodium(III) complexes.<sup>12,39</sup>

The loss of para-substituted benzyl chlorides from the para-substituted benzyl complexes **3b** in 1,2-dichloroethane was followed by monitoring the first-order disappearance of the absorption at  $2069\text{ cm}^{-1}$  in the infrared spectra of these benzyl complexes. The benzyl complexes **3b** could not be isolated in analytical purity; however, in chloroform, a weakly coordinating solvent, the benzyl complexes were isolated as a mixture consisting of 10% phenylacetyl complexes **2b**, 80% benzyl complexes **3b**, and 10% chlorocarbonylbis(triphenylphosphine)rhodium(I) (**4**). When this mixture of complexes was dissolved in 1,2-dichloroethane at 25° the very labile benzyl complex **3b** ( $2069\text{ cm}^{-1}$ ) disappeared rapidly, with a concurrent increase in the

(38) G. H. Williams, "Homolytic Aromatic Substitution," 1st ed, Pergamon Press, New York, N. Y., 1960, p 21.

(39) P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Amer. Chem. Soc.*, **94**, 3240 (1972).

absorption in the infrared at  $1969\text{ cm}^{-1}$ , representing the appearance of **4**. Unexpectedly, the concentration of the phenylacetyl complex **2b** ( $1700\text{ cm}^{-1}$ ) also increased, indicating that the benzyl complex **3b** disappeared by two different routes: migration of the benzyl group back onto carbon monoxide to re-form the phenylacetyl complex **2b**, and loss of benzyl chloride to form **4**. Using entropy of activation data calculated for the rearrangement of the *p*-chlorophenylacetyl complex **2b** to form the *p*-chlorobenzyl complex **3b** in 1,2-dichloroethane, the rate constant for this acyl-alkyl rearrangement was extrapolated to  $25^\circ$ . The rearrangement of the five-coordinate acyl intermediate is too slow, possibly due to the effective solvation of the vacant coordination site by 1,2-dichloroethane, to interfere with the measurement of the kinetics of the decomposition of the relatively labile *p*-chlorobenzyl complex **3b**. Since the *p*-chlorobenzyl complex is consumed by two different pathways the rate of disappearance of the *p*-chlorobenzyl complex is faster than the rate of appearance of **4**. The difference in these two rates is the rate at which the *p*-chlorobenzyl complex **3b** reverts to the *p*-chlorophenylacetyl complex **2b** (Table V). The intermediate *p*-chlorobenzyl complex has approximately an equal chance of reverting back to *p*-chlorophenylacetyl complex or losing *p*-chlorobenzyl chloride. The rearrangement of the *p*-chlorophenylacetyl complex **2b** is slower than the loss of the *p*-chlorobenzyl chloride from the *p*-chlorobenzyl complex **3b** by a factor of 20. Thus, the rearrangement of the phenylacetyl complexes is too slow to interfere with measurement of the kinetics of the disappearance of the benzyl complexes at least during the first 2 half-lives. Under the reaction conditions of this kinetic study, the para-substituted benzyl chlorides formed as products will not oxidatively add to **4**. It has been reported that at  $170^\circ$  benzyl chloride will react with **4** forming a  $\pi$ -benzylic complex resulting from the loss of carbon monoxide rather than a simple oxidative addition to form a benzyl complex.<sup>40</sup>

Substituent effects measured at  $25.0^\circ$  show that electron-withdrawing groups enhance the rate of this reaction (Table IV). The magnitude of  $\rho$  for both the loss of para-substituted chlorobenzenes from the para-substituted phenyl complexes **3a** and the loss of para-substituted benzyl chlorides from the para-substituted benzyl complexes **3b** is low enough to fall in the range observed for radical reactions.

In contrast to the marked retarding influence of added triphenylphosphine on the loss of chlorobenzene from the phenyl complex **3a**, added triphenylphosphine has no effect on the rate of loss of benzyl chloride from the benzyl complex **3b**. It appears that the two reactions occur by different mechanisms. At  $25^\circ$  the benzyl complex loses benzyl chloride approximately 20 times faster than the phenyl complex loses chlorobenzene. The benzyl complex does not decompose by a dissociative mechanism because the loss of benzyl chloride from the six-coordinate benzyl complex occurs faster than the dissociation of triphenylphosphine. The loss of chlorobenzene from the phenyl complex has a rather large positive entropy of activation (9.0 eu) which would be expected for a reaction proceeding by the dissociative mechanism shown in Scheme II.

(40) C. O'Connor, *J. Inorg. Nucl. Chem.*, **32**, 2299 (1970).

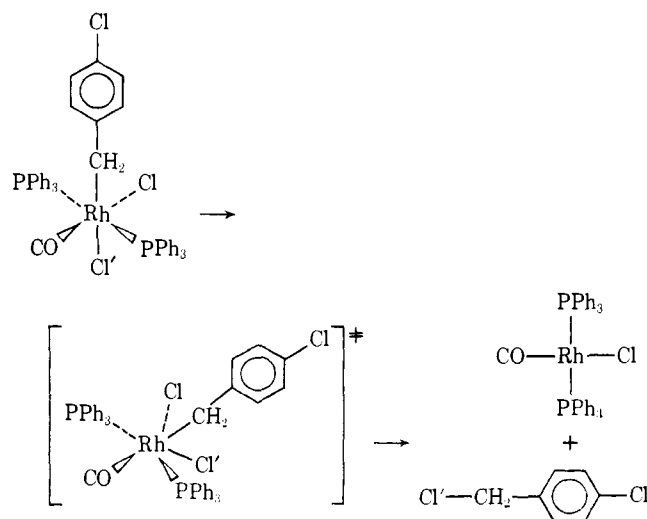
Table IV. First-Order Rate Constants for the Loss of RCl from Phenyl and Benzyl Complexes (**3a** and **3b**) in 1,2-Dichloroethane

R	$10^4k$ , sec <sup>-1</sup>	Standard deviation	Temp, °C
<i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>a</sup>	12.2	0.33	32.9
<i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>b</sup>	11.7	0.41	32.9
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	9.50	0.23	32.9
C <sub>6</sub> H <sub>5</sub>	5.30	0.093	32.9
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	1.88	0.015	32.9
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	3.71	0.095	37.9
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	6.89	0.83	42.4
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	17.0	0.75	49.2
C <sub>6</sub> H <sub>5</sub>	4.27	0.10	27.6
C <sub>6</sub> H <sub>5</sub> <sup>c</sup>	0.428	0.01	27.6
C <sub>6</sub> H <sub>5</sub> <sup>d</sup>	0.102	0.004	27.6
<i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>e</sup>	5.31	0.28	42.4
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> <sup>e</sup>	2.18	0.21	42.4
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> <sup>e</sup>	0.976	0.032	42.4
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	17.0	0.11	25.0
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	9.59	0.07	25.0
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> <sup>f</sup>	9.39	0.06	25.0
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	1.06	0.01	7.1
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	2.16	0.01	12.8
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	5.03	0.03	18.6
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	21.5	0.10	31.2

<sup>a</sup> Followed by ultraviolet spectroscopy. <sup>b</sup> Followed by infrared spectroscopy. <sup>c</sup> 1,2-Dichloroethane-triphenylphosphine ( $11.5 \times 10^{-6}\text{ M}$ ) was the solvent. <sup>d</sup> 1,2-Dichloroethane-triphenylphosphine ( $30.0 \times 10^{-6}\text{ M}$ ) was the solvent. <sup>e</sup> Toluene was the solvent. <sup>f</sup> 1,2-Dichloroethane-triphenylphosphine ( $2.0 \times 10^{-2}\text{ M}$ ) was the solvent.

However, the loss of benzyl chloride from the benzyl complex has a negative entropy of activation ( $-3.6\text{ eu}$ ). It has been established that the reverse reaction, oxidative addition of an alkyl halide, occurs in a trans manner. If it can be assumed that the loss of RCl from complexes of the type **3** must also occur by trans stereochemistry the fact that benzyl complexes and phenyl complexes react by different mechanisms can be explained in the following way. The benzyl group must have a smaller steric requirement and therefore can pass through the plane of the complex more easily to become bonded to the trans chlorine (Scheme III).

Scheme III



The phenyl complex, being unable to do this, must react by the dissociative mechanism. However, these arguments are not valid if the cis chlorine is undergoing the elimination. The ease of elimination in the benzyl

case could also be attributed to its ability to form a  $\pi$ -allyl complex.

A summary of the kinetic data (Table V) shows that

**Table V.** Summary of Kinetics

$\begin{array}{c} \text{R} \\   \\ \text{C}=\text{O} \\   \\ \text{PPH}_3-\text{Rh}-\text{Cl} \\   \quad   \\ \text{Cl} \quad \text{PPH}_3 \end{array} \xrightleftharpoons[k_{-1}]{k_1} \begin{array}{c} \text{R} \\   \\ \text{CO} \\   \\ \text{PPH}_3-\text{Rh} \\   \quad   \\ \text{PPH}_3 \quad \text{Cl} \end{array} \xrightarrow{k_2} \begin{array}{c} \text{PPH}_3 \\   \\ \text{Cl}-\text{Rh}-\text{CO} \\   \\ \text{PPH}_3 \end{array} + \text{RCl}$				
First-order rate constant ( $10^4 k$ , $\text{sec}^{-1}$ ) at $25^\circ$				
R	$k_1$	$k_{-1}$	$k_2$	
$p\text{-ClC}_6\text{H}_4$	5.27	0.0	0.59	
$p\text{-ClC}_6\text{H}_4\text{CH}_2$	0.50	6.84	9.59	
R	$\rho(k_1)$	$\rho(k_2)$		
$p\text{-XC}_6\text{H}_4$	0.265	-1.64		
$p\text{-XC}_6\text{H}_4\text{CH}_2$	-0.612	0.452		
R	$(k_1)$		$(k_2)$	
	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
$p\text{-ClC}_6\text{H}_4$	22.8	2.1	25.9	9.0
$p\text{-ClC}_6\text{H}_4\text{CH}_2$	21.3	-6.8	20.5	-3.6

when  $\text{R} = p\text{-ClC}_6\text{H}_4$ , the acyl-alkyl rearrangement ( $2a \rightarrow 3a$ ) is approximately ten times as fast as the loss of  $\text{RCl}$  from  $3a$ . However, when  $\text{R} = p\text{-ClC}_6\text{H}_4\text{CH}_2$ , the acyl-alkyl rearrangement ( $2b \rightarrow 3b$ ) is approximately 20 times slower than the loss of  $\text{RCl}$  from  $3b$ . Thus, the rate-determining step is different for the two  $\text{R}$  groups.

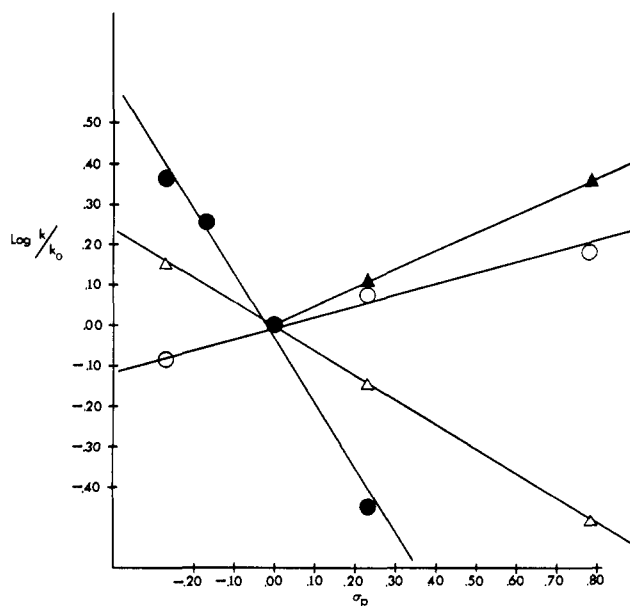
The substituent effects observed for these four steps have the following three characteristics in common: the magnitude of  $\rho$  is always low enough to fall in the range observed for reactions involving radical intermediates; Hammett plots reveal a better correlation with  $\sigma$  than with  $\sigma^+$ , indicating the absence of a strong resonance contribution to stabilization;<sup>31,41</sup> no maxima or minima are observed in any of the Hammett plots, which is to say the reactions follow the same sequence as the  $\sigma$  values (Figure 2). As found in other organometallic systems, the sign of  $\rho$  in reactions such as these is a function of many factors and varies in an unpredictable manner in the reactions studied.<sup>19,42</sup> Activation parameter data for the four reactions does not fall into any discernible pattern; however, for  $\text{R} = p\text{-ClC}_6\text{H}_4\text{CH}_2$  more negative entropies and enthalpies of activation are observed than in the same step for  $\text{R} = p\text{-ClC}_6\text{H}_4$ .

## Experimental Section

**Preparation of Para-Substituted Phenylacetyl Chlorides.** The general method of preparation of the para-substituted phenylacetyl chlorides is illustrated with phenylacetyl chloride. To 5.01 g (0.0367 mol) of phenylacetic acid was added 4.37 g (0.0367 mol) of thionyl chloride under nitrogen. The evolution of gases in the exothermic reaction was spontaneous. Occasional swirling of the reaction vessel during the first 2 hr of gas evolution helped bring the solid acid into contact with the thionyl chloride. At the end of the period of spontaneous gas evolution (ca. 20 hr) the reaction flask was warmed to  $35\text{--}40^\circ$  at which time the evolution of gas again occurred. The reaction flask was maintained at this temperature until gas evolution was negligible. A volume of dry

(41) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957).

(42) M. Kubota and B. M. Loeffler, *Inorg. Chem.*, **11**, 469 (1972).



**Figure 2.** Hammett plot: (O) rearrangement of benzoyl complexes,  $2$  ( $\text{R} = p\text{-XC}_6\text{H}_4$ ), to phenyl complexes,  $3$  ( $\text{R} = p\text{-XC}_6\text{H}_4$ ); (●) loss of para-substituted chlorobenzenes from phenyl complexes,  $3$  ( $\text{R} = p\text{-XC}_6\text{H}_4$ ); (Δ) rearrangement of phenylacetyl complexes,  $2$  ( $\text{R} = p\text{-XC}_6\text{H}_4\text{CH}_2$ ), to benzyl complexes,  $3$  ( $\text{R} = p\text{-XC}_6\text{H}_4\text{CH}_2$ ); (▲) loss of para-substituted benzyl chlorides from benzyl complexes,  $3$  ( $\text{R} = p\text{-XC}_6\text{H}_4\text{CH}_2$ ).

benzene equal to approximately 25% of the volume of the reaction mixture was added and the thionyl chloride and benzene were removed under reduced pressure. The product was then distilled by increasing the pot temperature to  $75\text{--}80^\circ$  (1 mm). A yield of 4.59 g (80%) of colorless, liquid phenylacetyl chloride was obtained, bp  $55\text{--}57^\circ$  (1 mm). The only modification of this procedure made in the synthesis of the less volatile para-substituted phenylacetyl chlorides was the use of a diffusion pump in the distillation. The pressure was reduced to  $10\ \mu$  to avoid extensive decomposition of these less volatile acid chlorides during distillation.

**Para-Substituted Benzoyldichlorobis(triphenylphosphine)rhodium(III) Complexes (2a).** The general procedure for the preparation of the para-substituted benzoyl complexes is illustrated with benzoyl chloride. To a solution of 0.229 g (0.247 mmol) of chlorotris(triphenylphosphine)rhodium(I) ( $1$ ) in 15 ml of dichloromethane was added 3.63 g (3.00 ml, 26.0 mmol) of benzoyl chloride by means of a syringe. The reaction mixture was stirred at  $30^\circ$  for 3 min and was then quenched by the addition of 100 ml of pentane. The precipitated product was filtered and the yellow precipitate was washed with 3–5-ml portions of ether to yield 0.124 g (63%) of fine yellow precipitate. The yields of the other benzoyl complexes were  $p\text{-NO}_2$ , 69%;  $p\text{-Cl}$ , 61%;  $p\text{-OCH}_3$ , 65%.

**Para-Substituted Phenylacetyldichlorobis(triphenylphosphine)rhodium(III) Complexes (2b).** The general procedure for the preparation of para-substituted phenylacetyl complexes is illustrated with  $p$ -chlorophenylacetyl chloride. To a solution of 1.09 g (0.00122 mol) of chlorotris(triphenylphosphine)rhodium(I) ( $1$ ) in 75 ml of dichloromethane cooled to  $0^\circ$  was added 4.64 g (4.00 ml, 0.0251 mol) of  $p$ -chlorophenylacetyl chloride by means of a syringe. After the solution was stirred at  $0^\circ$  for 30 sec the reaction was quenched by the addition of 250 ml of pentane. The mixture was filtered and the yellow precipitate was washed with 10–15-ml portions of ether to remove excess triphenylphosphine, and was then recrystallized at low temperature ( $0^\circ$ ) from acetone-pentane to yield 0.73 g (70%) of product. The yields of the other phenylacetyl complexes were  $p\text{-NO}_2$ , 71%;  $p\text{-H}$ , 68%;  $p\text{-OCH}_3$ , 73%.

**Para-Substituted Phenylidichlorocarbonylbis(triphenylphosphine)rhodium(III) Complexes (3a).** The general procedure for the preparation of para-substituted phenyl complexes is illustrated with benzoyl chloride. To a solution of 0.503 g (0.540 mmol) of chlorotris(triphenylphosphine)rhodium(I) ( $1$ ) in 20 ml of benzene was added 0.50 ml (4.3 mmol) of benzoyl chloride. The reaction mixture was stirred at  $30^\circ$  for 48 hr after which time the reaction was quenched by the addition of 100 ml of pentane. The precipitated product was filtered and the fine yellow precipitate was washed with

3-5-ml portions of ether to remove excess triphenylphosphine. Low temperature (0°) recrystallization from chloroform-ethanol yielded 0.305 g (70%) of analytically pure phenyl complex. The yields of the other phenyl complexes were *p*-Cl, 73%; *p*-CH<sub>3</sub>, 71%; *p*-OCH<sub>3</sub>, 68%.

**Para-Substituted Benzoyldichlorocarbonylbis(triphenylphosphine)rhodium(III) Complexes (3b).** The general procedure for the preparation of para-substituted benzyl complexes is illustrated with *p*-chlorophenylacetyl chloride. To a solution of 1.01 g (0.00112 mol) of chlorotris(triphenylphosphine)rhodium(I) (1) in 75 ml of chloroform cooled to 0° was added a solution of 5.02 g (4.22 ml, 0.0261 mol) of *p*-chlorophenylacetyl chloride by means of a syringe. After the solution was stirred at 0° for 3 min the reaction was quenched by the addition of 250 ml of pentane. The mixture was filtered and the yellow precipitate was washed with 10-15-ml portions of ether to remove the excess triphenylphosphine and yield 0.75 g of product mixture. Analysis of the carbonyl region of the infrared spectrum of the product indicated a mixture of *p*-chlorophenylacetyl complex **2b** (C=O 1714 cm<sup>-1</sup>), *p*-chlorobenzyl complex **3b** (C=O 2069 cm<sup>-1</sup>), and chlorocarbonylbis(triphenylphosphine)rhodium(I) (4) (C=O 1969 cm<sup>-1</sup>); the *p*-chlorobenzyl complex **3b** represented 80% of the mixture.

**Kinetic Procedures.** The acyl-alkyl rearrangement of para-substituted benzoyl complexes (C=O 1670 cm<sup>-1</sup>), the acyl-alkyl rearrangement of para-substituted phenylacetyl complexes (C=O 1700 cm<sup>-1</sup>), and the loss of para-substituted benzyl chloride from para-substituted benzyl complexes (C=O 2069 cm<sup>-1</sup>) were followed by monitoring the decay of the appropriate carbonyl absorption in the infrared. The loss of para-substituted chlorobenzenes from para-substituted phenyl complexes was followed by monitoring the decay of the absorption at 333 nm in the ultraviolet.

A Perkin-Elmer 521 infrared spectrometer fitted with a variable-temperature chamber (Barnes Model VTC-104) and a Cary 14 ultraviolet spectrometer fitted with a simple water-jacketed cell holder were used in these studies. Beer's law plots showed that the concentration of the intermediate complexes was linearly related to the observed carbonyl absorbance. The solvent, 1,2-

dichloroethane, was placed in a capped vial and brought to the reaction temperature in an oil bath or low-temperature water bath. In the case of infrared studies the sample cell was brought to the reaction temperature in a variable-temperature chamber. (Barnes Model VTC-104) while for ultraviolet studies the sample cell was brought to the reaction temperature in a simple water-jacketed cell holder. An aliquot of solvent was removed and added to a weighed amount of complex (typical concentrations for the infrared studies were 0.02 *M*). The solution was then transferred to the sample cell and the cell was rapidly placed in either the variable-temperature chamber (infrared) or the water-jacketed cell holder (ultraviolet). The temperature inside the variable-temperature chamber was measured by using a copper-constantin thermocouple, located in close proximity to the sample cell in conjunction with a thermocouple potentiometer (Biddle Model 723161). The ultraviolet or infrared absorption was monitored continuously at the wavelength of maximum absorption of the intermediate complex under study, rather than scanning through the wavelength of maximum absorption at regular time intervals. The latter method is inherently less accurate because of the uncertainty in the added variables which include scan rate and pen response. Limiting absorbances were determined by sealing an aliquot of solution in an ampoule and placing it in an oil bath maintained at 50° for 2 weeks. In each case the rate constants were the average of three or four separate determinations. Exposure of the reaction solutions to air had no effect on the results. Changes in the concentration of the complexes had no effect on the rate constant, indicating that these are truly first-order reactions.

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## Mechanism of Decarbonylation of Acid Chlorides by Chlorotris(triphenylphosphine)rhodium(I). Stereochemistry

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**Abstract:** When (*S*)-(-)- $\alpha$ -trifluoromethylphenylacetyl chloride (**3**) was decarbonylated with stoichiometric amounts of chlorotris(triphenylphosphine)rhodium(I) (**1**), the  $\alpha$ -trifluoromethylbenzyl chloride (**7**) obtained in a 71% yield was racemic. Optically active benzyl chloride (**7**) was not racemized under the reaction conditions. Since racemization could have taken place either in the rearrangement of the intermediate acylrhodium(III) complex (**8**) to the benzylrhodium(III) complex (**9**) or in the decomposition of **9** to the benzyl chloride (**7**) and chlorocarbonylbis(triphenylphosphine)rhodium(I) (**2**), the synthesis of an optically active intermediate similar to **9** was carried out. Although the optically active acyl complex (**8**) could be prepared, its decomposition always gave the final product without the isolation of the intermediate. Reaction of (*S*)- $\alpha$ -trifluoromethylbenzyl chlorosulfite and chlorocarbonylbis(diethylphenylphosphine)rhodium(I) did afford, with the loss of sulfur dioxide, an optically active intermediate **13** analogous to the intermediate benzylrhodium(III) complex (**9**). Decomposition of **13** gave (*R*)-**7** with 62% net inversion in the two steps. Thus, racemization in the decarbonylation probably takes place in the acyl to alkyl rearrangement step.

The decarbonylation of acid halides and aldehydes with transition metal catalysts, particularly rhodium(I), is a synthetically useful reaction; acid chlorides with no  $\beta$  hydrogens are decarbonylated to alkyl chlorides whereas compounds containing a  $\beta$  hydrogen afford primarily olefins with one less carbon.<sup>1</sup> Rho-

dium(I) is an especially effective catalyst for both low-temperature stoichiometric decarbonylations and for the higher temperature catalytic reaction. A convenient method for the regeneration of the very reactive chlorotris(triphenylphosphine)rhodium(I) (**1**) from the

(1) J. Tsuji in "Organic Synthesis by Metal Carbonyls," Vol. 2, Interscience, New York, N. Y., in press; J. Tsuji and K. Ohno, *Syn-*

*thesis*, **1**, 157, 1969; J. Tsuji in "Advances in Organic Chemistry, Methods and Results," Vol. 6, Interscience, New York, N. Y., 1969, pp 109-255.