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_3, 71%; *p*-OCH_3, 68%.

Para-Substituted Benzyldichlorocarbonylbis(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^{-1}), *p*-chlorobenzyl complex **3b** (C=O 2069 cm^{-1}), and chlorocarbonylbis(triphenylphosphine)rhodium(I) (**4**) (C=O 1969 cm^{-1}); 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^{-1}), the acyl–alkyl rearrangement of para-substituted phenylacetyl complexes (C=O 1700 cm^{-1}), and the loss of para-substituted benzyl chloride from para-substituted benzyl complexes (C=O 2069 cm^{-1}) 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*)-(−)-α-trifluoromethylphenylacetyl chloride (**3**) was decarbonylated with stoichiometric amounts of chlorotris(triphenylphosphine)rhodium(I) (**1**), the α-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*)-α-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 β hydrogens are decarbonylated to alkyl chlorides whereas compounds containing a β hydrogen afford primarily olefins with one less carbon.[1] Rhodium(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

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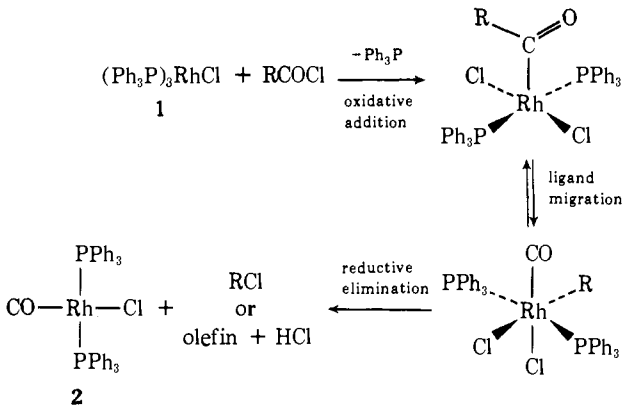
relatively unreactive chlorocarbonylbis(triphenylphosphine)rhodium(I) (**2**) provides a reusable source of in-



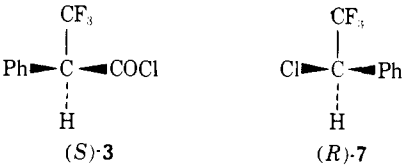
expensive low temperature catalyst.[2]

The stoichiometric decarbonylation of chiral aldehydes by **1** to form alkanes has been found to proceed with retention of configuration.[3] An intramolecular reaction was observed and a tight radical pair mechanism was proposed to account for the stereospecificity.[3] Reverse decarbonylation, "carbonyl insertion," occurs with predominant retention of configuration at the carbon–metal σ bond for iron,[4,5] manganese,[4] palladium,[6,7] and platinum,[7] and is generally accepted to proceed with retention in the case of transition metals. The ability of the common decarbonylation catalysts, palladium and rhodium, to abstract β hydrogens from a σ-bonded alkyl group prohibits both the synthesis of many alkyl–metal complexes and the decarbonylation of most available optically active acid halides to form alkyl halides.

Results and Discussion

The decarbonylation of an optically active α-substituted phenylacetyl chloride with no β hydrogens was undertaken. The synthesis, resolution, and absolute configuration of α-trifluoromethylphenylmethanol[8] and α-trifluoromethylphenylacetic acid[9] have been reported.

The *S* acid chloride was formed by treatment of optically active acid with thionyl chloride. Conversion of the alcohol (**4**) to the alkyl chloride (**7**) was accom-



plished by retention and inversion reagents (Figure 1, Table I). Treatment of the *S* methanol with thionyl chloride provided the (*S*)-chlorosulfite ester **5** which was

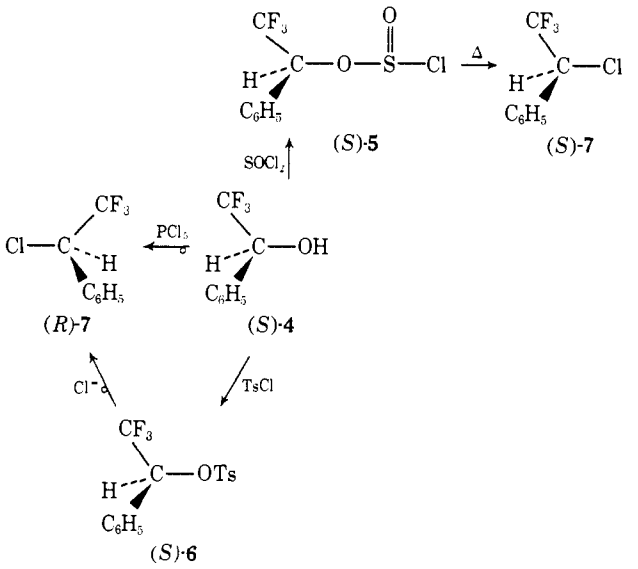


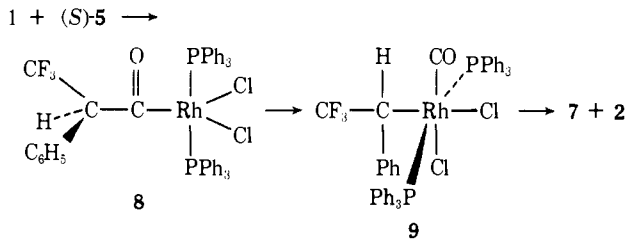
Figure 1. Preparation of optically active α-trifluoromethylbenzylchloride.

Table I. Conversion of α-Trifluoromethylphenylmethanol, $[\alpha]_D$ 31.8°, to Chloride

Reactant	Reagent	Product	$[\alpha]^{25}D$, deg
(*S*)-**4**	$SOCl_2$	(*S*)-**5**	75.3
(*S*)-**5**	Δ	(*S*)-**7**	44.4
(*S*)-**4**	PCl_5	(*R*)-**7**	−51.0
(*S*)-**6**	$(n\text{-Bu})_4N^+Cl^-$	(*R*)-**7**	−43.0

thermally decomposed to give the alkyl chloride (*R*)-**7**. Reaction of the *S* alcohol with tosyl chloride produced the *S* tosylate **6** which was allowed to react under SN2 conditions with chloride to provide (*R*)-**7**. In addition, the reaction of the *S* alcohol with phosphorus pentachloride yielded (*R*)-**7** with the largest magnitude of rotation, and was the method of choice (Table I).

When the optically active acid chloride (*S*)-**3** was treated with **1** in refluxing benzene, toluene, or acetonitrile, the alkyl chloride **7** was obtained. The reaction in acetonitrile was much faster than those in benzene or toluene. The chloride, obtained in 71% yield, was racemic. The intermediate acyl complex **8**, which



could be isolated, was optically active ($[\alpha]^{25}D$ −30.4°). When **8** was heated in refluxing benzene or toluene or heated *in vacuo* at 140°, again only racemic **7** was isolated.

In reactions carried out by heating (*R*)-**7** in refluxing benzene for 5 hr with various combinations of **1**, **2**, and triphenylphosphine, the alkyl chloride was recovered, unchanged, and unracemized, demonstrating that the product (**7**) was stereochemically stable under the reaction conditions. When **7** was stirred with the rhodium(I) carbonyl complex **2** for 5 days in chloroform,

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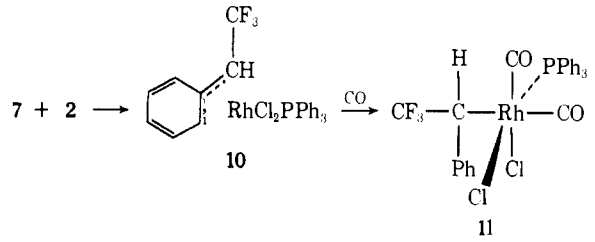
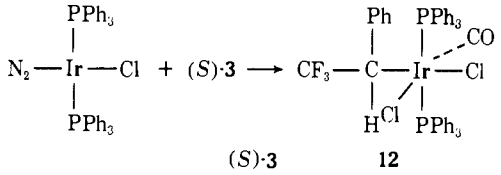
the π-benzyl complex **10** was obtained, which exhibited no carbonyl stretching bands in the infrared region. Treatment of **10** with carbon monoxide afforded the dicarbonyl σ complex **11** which had two distinct carbonyl absorptions.[10]

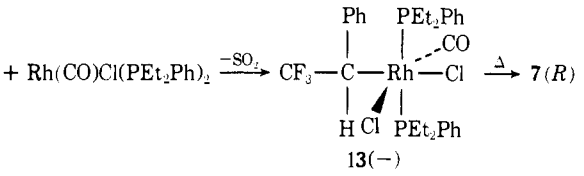


Although the alkylrhodium intermediate complex **9** could be isolated neither from the reaction of the acid chloride with **1** nor from the reaction of the alkyl chloride with **2**, the analogous isostructural d^8 iridium(*I*) complex has been reported to yield stable alkyliridium complexes if no β hydrogens are present on the alkyl group.[11,12] The addition takes place by prior formation of the acyl complex (**8**, Ir for Rh) which rapidly undergoes acyl–alkyl rearrangement to the d^6 alkyl complex.[11,12] Treatment of the acid chloride (*S*)-**3** with chlorodinitrogenbis(triphenylphosphine)-iridium(I) produced **12** ($[\alpha]^{25}D$ −5.8°). The low



rotation of this complex may be indicative of some racemization taking place in the acyl–alkyl rearrangement (or the actual rotation may indeed be low); however, the acyl–alkyl rearrangement does not occur with complete racemization.

Direct addition of **7** to rhodium complexes containing more basic phosphine ligands, chlorocarbonylbis(diethylphenylphosphine)[13] and chlorocarbonylbis(tri-*n*-butylphosphine)rhodium(I),[14] did not take place. An optically active alkylrhodium complex (**13**) could be



prepared by the addition of (+)-α-trifluoromethylbenzyl chlorosulfite ((*S*)-**5**) to chlorocarbonylbis(diethylphenylphosphine)rhodium(I). The benzyl complex **13** which had a negative sign of rotation was thermally decomposed to afford (*R*)-**7** in a 24% yield plus several products which could not be characterized. Thus, the overall reaction proceeding in two steps takes place with one inversion and one retention of configuration at carbon. Since the oxidative addition of this chlorosulfite ester to palladium(0) (with the loss of sulfur dioxide) takes place with inversion,[15] and since the insertion of sulfur dioxide into an iron–carbon σ bond also takes place with inversion,[16] we favor inversion of configuration at carbon in the formation of complex **13** and retention of configuration in the second step (**13** → **7**). The overall reaction takes place with 62% net inversion.

The racemization in the conversion of **3** to **7** probably occurs, therefore, in the acyl–alkyl rearrangement step. Even though an optically active iridium complex **12** (analogous to the rhodium complex **9**) was obtained from optically active **3**, *via* an acyl iridium complex (analogous to **8**), the optical purity of **12** is unknown as is the reliability of transference of stereochemical results and mechanisms between isoelectronic transition metal complexes of group VIII. The reaction of the acid chloride **3** with **1** showed by infrared that the alkyl complex **9** reached a steady-state concentration early in the reaction, remained until most of **8** had disappeared, and then diminished. It has been demonstrated[17] that phenylacetyl complexes of the type **8** rearrange to benzyl complexes of the type **9** reversibly. Thus, racemization could occur through an equilibrium attrition process, **8** ⇄ **9**.

The α substituent on the acid chloride had an important effect on both the ease of decarbonylation and the products obtained. When α-*tert*-butylphenylacetyl chloride was decarbonylated with chlorotris(triphenylphosphine)rhodium(I), the corresponding alkyl chloride was not produced; rather the π-benzyl complex was the predominant product. Substituents in the α position were also shown to be important in the decarbonylation of aldehydes.[3] Although aldehydes containing an α-methyl substituent afforded alkanes with 94% optical purity, those with an α-methoxy group gave products with only 6% optical purity.

Experimental Section

Preparation of α-Trifluoromethylphenylacetyl Chloride (3). To 3.80 g (0.0182 mol) of (*S*)-α-trifluoromethylphenylacetic acid[8] ($[\alpha]^{27}D$ −62.1°) was added 20 ml of thionyl chloride and the resulting mixture was heated to 80° for 4 hr. The thionyl chloride was removed at reduced pressure and the fraction boiling at 45–47° (1.5 mm) was collected to afford 3.30 g (81%) of acid chloride; $[\alpha]^{27}D$ −112° (*c* 4, $CHCl_3$).

To 2 ml of water was added 0.1 g of +**3** ($[\alpha]^{25}D$ +89.1°, prepared from the (+)-acid $[\alpha]^{25}D$ +56.2°) and the mixture was heated to the reflux temperature for 4 hr. After the mixture was cooled, white crystals of the acid were formed, which were collected by filtration and dried to afford the (+) acid with 97% overall retention: mp 90°; $[\alpha]^{25}D$ +54.3° (*c* 5, $CHCl_3$).

Preparation of Trifluoromethylphenylmethanol (4). To 50 ml of anhydrous ether was added 2.7 g (0.071 mol) of lithium aluminum hydride and the mixture was stirred for 10 min. To this was slowly added 25.0 g (0.144 mol) of trifluoroacetophenone in 25 ml of anhydrous ether. The mixture was stirred for 2 hr and neutralized with 2.7 ml of water, 2.7 ml of aqueous 15% soduim hydroxide, and 8.1 ml of water. The mixture was filtered and the precipitate was washed with 50 ml of ether and refiltered. The ether filtrate was evaporated and the residue was distilled at 80–82° (5 mm) to afford 17.3 g (71%) of the alcohol: lit.[18] bp 53–54.5° (2 mm); nmr (CCl_4) δ 3.9 (d, 1), 4.6 (m, 1), and 7.1 (m, 5).

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Preparation of Optically Active α-Trifluoromethylbenzyl Chloride (7). a. From Phosphorus Pentachloride. To 0.450 g (2.55 mmol) of the *S* alcohol[9] (*S*)-**4** ($[\alpha]^{25}D$ +30.10°, 94.5% optical purity) in 5 ml of chloroform was added, with cooling, 0.12 g (0.58 mmol) of phosphorus pentachloride and the mixture was slowly heated to the reflux temperature. After 2 hr at reflux, the solution was cooled and slowly poured in 25 ml of ice-cold saturated sodium chloride solution and stirred for 10 min. The chloroform layer was washed with water and a saturated sodium chloride solution, dried ($CaCl_2$), and concentrated by evaporation. The residue was distilled at 68–73° (10 mm) to afford 0.27 g (54%) of (*R*)-**7**: lit.[18] bp 70–71° (27 mm); $[\alpha]^{25}D$ −48.2° (*c* 10, $CHCl_3$); nmr (CCl_4) δ 5.08 (q, 1) and 7.2 (m, 5).

b. From Tosylate 6. To 1.10 g (6.25 mmol) of the *S* alcohol ((*S*)-**4** $[\alpha]^{25}D$ +30.10°) in 2 ml of pyridine was added 1.30 g (6.86 mmol) of *p*-toluenesulfonyl chloride and the mixture was stirred at room temperature for 24 hr. The mixture was slowly added to 100 ml of ice-cold 2 *N* hydrochloric acid and stirred for 5 min. The aqueous phase was discarded and the oily lower phase was taken up in ether and dried ($CaCl_2$). The ether was evaporated to afford 1.87 g (90.8%) of white fluffy needles of the tosylate (*S*)-**6**: mp 121–124°; $[\alpha]^{25}D$ +36.38° (*c* 10, acetone); nmr ($CDCl_3$) δ 2.40 (s, 3,), 5.72 (q, 1), 7.41 (s, 5), and 7.50 (q, 4).

To 1.71 g (5.15 mmol) of the *S* tosylate in 10 ml of dimethyl sulfoxide was added 4.10 g (0.148 mol) of tetra(*n*-butyl)ammonium chloride and the resulting mixture was stirred at 100° for 24 hr. The solution was then added to 40 ml of water and stirred. The aqueous solution was extracted with 3 × 10-ml portions of carbon tetrachloride and the combined extracts were washed with 3 × 10-ml portions of water. The carbon tetrachloride layer was dried ($CaCl_2$) and concentrated by evaporation to give a pale yellow oil. The oil was distilled at 70–72° (10 mm) to afford 0.29 g (32%) of (*R*)-**7** which was identified by vpc (10 ft SE-30 on Chromosorb W), $[\alpha]^{25}D$ −40.7° (*c* 10, $CHCl_3$).

c. From Thionyl Chloride. To 15 ml of freshly distilled thionyl chloride was added dropwise a solution of 15 ml of anhydrous ether and 0.35 g (2.0 mmol) of α-trifluoromethylbenzyl alcohol ((*S*)-**4** $[\alpha]^{25}D$ +31.80° (*c* 10, ether)). The resulting solution was stirred for 24 hr at room temperature. The thionyl chloride and ether were removed by vacuum distillation and the resulting pale yellow chlorosulfite ester **5** remained (0.49 g, 96%). Vpc analysis indicated the presence of sulfur dioxide and α-trifluoromethylbenzyl chloride. Mass spectral analysis did not provide a molecular ion but exhibited a strong peak at 64 (SO_2): nmr (CCl_4) δ 6.1 (m) and 7.3 (m); $[\alpha]^{25}D$ +75.32° (*c* 10, hexane). *Anal.* Calcd for $C_8H_6ClF_3O_2S$: C, 37.07; H, 2.33. Found: C, 37.45; H, 2.55.

A portion of the chlorosulfite ester was thermally decomposed during preparative gas chromatography (10 ft SE-30 on Chromosorb W, 175°) to afford α-trifluoromethylbenzyl chloride (*S*)-**7**: $[\alpha]^{25}\lambda$ (*c* 10, hexane); λ = 5892, α = 44.4°; λ = 5780, α = 46.3°; λ = 5460, α = 52.8°; λ = 4360, α = 95.28°; λ = 3650, α = 161.3°.

Stoichiometric Decarbonylation of 3. To a solution of 0.500 g (2.25 mmol) of the acid chloride (*S*)-**3** ($[\alpha]^{25}D$ −112°; 87.2% optical purity) in 15 ml of anhydrous benzene was added 2.10 g (2.27 mmol) of chlorotris(triphenylphosphine)rhodium(I) and the resulting solution was heated to the reflux temperature under nitrogen for 6 hr. The solution turned bright yellow and yellow crystals precipitated during the reaction. After cooling the reaction mixture to room temperature, 15 ml of hexane was added to precipitate any complex left in solution. The mixture was filtered and the filtrate was distilled at 73–75° (12 mm) to afford 0.31 g (71%) of **7**. Vpc analysis (10 ft SE-30 on Chromosorb W) indicated only **7** was present; $[\alpha]^{27}_{3650}$ +2.0° (*c* 5, CCl_4); 51.0% (+), 49.0% (−). A similar run in refluxing toluene for 4.5 hr afforded racemic **7**: $[\alpha]^{27}_{3650}$ +1.9 (*c* 5, CCl_4); 50.8% (+), 49.2% (−).

To 1.00 g (1.08 mmol) of **1** was added 8 ml of acetonitrile and 0.240 g (1.08 mmol) of (*S*)-**3** ($[\alpha]^{27}D$ −112°). The mixture was heated to the reflux temperature and 0.6-ml aliquots were removed, filtered, and analyzed by vpc (10 ft SE-30 on Chromosorb W) and polarimetry every 40 min. The analysis indicated the reaction was over after 40 min and the resulting chloride (**7**) was racemic; $[\alpha]^{25}D$ 0° (*c* 3, CH_3CN). After a total of 3 hr, the mixture was cooled and filtered and an infrared spectrum ($CHCl_3$) of the inorganic product indicated it to be **2** (Rh–CO, 1969 cm^{-1}).

Preparation of (*S*)-Dichloro(α-trifluoromethylphenylacetyl)bis(triphenylphosphine)rhodium(III) (8). To an ice-cold solution of 2.1 g (2.2 mmol) of **1** and 5 ml of dichloromethane was added 0.55 g (2.5 mmol) of (*S*)-**3** ($[\alpha]^{27}D$ −112°). The ice bath was removed and the mixture was allowed to stir for 1 hr. The dichloromethane was removed at reduced pressure and 20 ml of pentane was slowly added to precipitate orange crystals of the acyl complex **8**. The crystals were washed with 150 ml of pentane and dried *in vacuo* to yield 1.7 g (87%) of product: $[\alpha]^{27}D$ −30.4° (*c* 5, $CHCl_3$); ir ($CHCl_3$) 1720 and 1740 cm^{-1} (RCORh). *Anal.* Calcd for $C_{45}H_{36}Cl_2F_3OP_2Rh$: C, 61.05; H, 4.10. Found: C, 61.13; H, 4.27.

Decomposition of (*S*)-8. Acyl complex **8** (0.50 g, 0.56 mmol; $[\alpha]^{27}D$ 30.4°) was heated *in vacuo* at 140° and the volatile chloride was collected in a Dry Ice trap. Polarimetric analysis indicated the chloride **7** was racemic; $[\alpha]^{27}_{3650}$ +2.3° (*c* 5, $CHCl_3$). The acyl complex **8** (0.50 g; $[\alpha]^{27}D$ −30.4°) was heated to the reflux temperature in 5 ml of anhydrous benzene for 6.5 hr. The benzene was removed at reduced pressure; the chloride **7** which remained was collected at reduced pressure and was racemic; $[\alpha]^{27}_{3650}$ +0.7° (*c* 5, $CHCl_3$). In a similar manner, 0.50 g of the acyl complex (*S*)-**8** was heated to the reflux temperature in 5 ml of toluene for 5 hr. The chloride **7** produced was racemic; $[\alpha]^{27}_{3650}$ +1.2° (*c* 5, $CHCl_3$).

Reaction of (*R*)-7 with Rhodium Complexes. A solution of 0.065 g (0.360 mmol) of (*R*)-**7** and 0.010 g (0.014 mmol) of **2** in 2 ml of dry benzene was heated to the reflux temperature for 5 hr and then allowed to stand for an additional 19 hr. Essentially no isomerization had taken place: *t* = 0 hr, α = −45.6°; *t* = 24 hr, α = −44.4°. Other control reactions are listed in Table II.

Table II. Treatment of (*R*)-**7** with Rhodium Complexes

Initial rotation (**7**, mmol)	Catalyst (mmol)	Ph_3P (mmol)	Final rotation (**7**)
−45.6 (0.36)	**2** (0.014)		−44.4
−45.6 (0.36)	**1** (0.011)		−44.9
−172.6/365 nm (0.36)	**2** (0.32)	(0.36)	−168.1/365 nm

Addition of (*S*)-α-Trifluoromethylbenzyl Chlorosulfite (5) to Chlorocarbonylbis(diethylphenylphosphine)rhodium(I). A solution of 0.80 g of chlorocarbonylbis(diethylphenylphosphine)rhodium(I)[13] and 0.46 g (1.8 mmol) of the chlorosulfite ester (*S*)-**5** ($[\alpha]^{25}D$ +75.32° (*c* 10, hexane)) in 20 ml of anhydrous acetone was stirred for 2 hr at room temperature. The acetone was removed at reduced pressure and the residue was crystallized from dichloromethane–hexane to afford an alkylrhodium complex **13**: 0.90 g (79%); $[\alpha]^{25}D$ −12.1° (*c* 5, CH_2Cl_2); ir ($CHCl_3$) 2100 cm^{-1} (Rh^{III}–CO). Mass spectral analysis indicated the presence of a dichloromethane of solvation. *Anal.* Calcd for $C_{29}H_{36}Cl_2F_3OP_2Rh \cdot CH_2Cl_2$: C, 46.30; H, 4.89. Found: C, 46.88; H, 5.25.

Complex **13** (0.85 g, 1.3 mmol) was heated to 170° *in vacuo*. The volatile products were collected in a Dry Ice trap. Vpc analysis (10 ft SE-30 on Chromosorb W) indicated the presence of α-trifluoromethylbenzyl chloride and several other components. Preparative vpc of the reaction mixture afforded 0.06 g (0.31 mmol) of (*R*)-α-trifluoromethylbenzyl chloride (**7**); $[\alpha]^{25}_{3650}$ 100.5° (*c* 5, hexane).

Addition of α-Trifluoromethylbenzyl Chloride (7) to Chlorocarbonylbis(triphenylphosphine)rhodium(I). To 0.46 g (0.66 mmol) of **2** in 75 ml of chloroform was added 0.25 ml (two-fold excess) of racemic alkyl chloride and the solution was stirred for 5 days. The infrared carbonyl stretching frequency at 1969 cm^{-1} disappeared and the infrared was void of any carbonyl bands between 2200 and 1600 cm^{-1}. Removal of the solvent at reduced pressure and addition of pentane afforded rust colored crystals of **10** which were filtered and dried *in vacuo* and contained a molecule of **7** of solvation. *Anal.* Calcd for $C_{26}H_{21}Cl_2F_3PRh \cdot C_8H_6ClF_3$: C, 51.71; H, 3.45. Found: C, 51.75; H, 3.78.

Carbon monoxide was bubbled into a chloroform solution of the complex for 10 min and the infrared spectrum of the solution showed absorptions at 2095 and 2010 cm^{-1} corresponding to **8**.

Preparation of (−)-Dichloro(α-trifluoromethylbenzyl)carbonylbis(triphenylphosphine)iridium(III) (9). To 0.30 g (0.38 mmol) of chlorodinitrogenobis(triphenylphosphine)irridium(I)[11,12] (ir ($CHCl_3$) 2105 cm^{-1}, IrN_2) in 2 ml of oxygen-free benzene was added 0.10 g (0.45 mmol; $[\alpha]^{27}D$ −112°) of the acid chloride **3** and the mixture was stirred under nitrogen for 20 hr. The cream colored mixture was poured on 100 ml of hexane with vigorous stirring. The resulting powder was collected by suction filtration and was recrystallized from chloroform–ether to afford 0.20 g (71%) of the

alkyl complex **12**: mp 168–174°; $[\alpha]^{25}D$ 5.8° (*c* 2, $CHCl_3$); ir ($CHCl_3$) 2070 cm^{-1} ($Ir^{III}CO$). *Anal.* Calcd for $C_{45}H_{36}Cl_2F_3IrOP_2$: C, 55.45; H, 3.72. Found: C, 55.12; H, 4.01.

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Mechanism of Acid Chloride Decarbonylation with Chlorotris(triphenylphosphine)rhodium(I). Stereochemistry and Direction of Elimination

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Abstract: The decarbonylation of *erythro*- and *threo*-2,3-diphenylbutanoyl chloride with chlorotris(triphenylphosphine)rhodium(I) gave exclusively *trans*- and *cis*-methylstilbene, respectively. These results are best explained either by an acyl–alkyl rearrangement with retention and a cis β-hydride elimination, or a concerted cis elimination. The rates of the decarbonylation of dichloro(3-perdeuteriophenyl-3,3-dideuteriopropionyl)bis(triphenylphosphine)-rhodium(III) along with the undeuterated complex ($k_H = 3.34 \times 10^{-5}$ sec^{-1}, $k_D = 4.75 \times 10^{-6}$ sec^{-1}) showed a primary deuterium isotope effect of 7.04. Decarbonylation of 2-methylpentanoyl chloride, 2,2-dimethylpentanoyl chloride, 2-ethyl-3-methylbutanoyl chloride, and 2,3-dimethylbutanoyl chloride with *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) showed that this olefin-forming reaction preferred the Saytzeff elimination.

The homogeneous decarbonylation of carboxylic acid halides with chlorotris(triphenylphosphine)-rhodium(I) (**1**) takes place at room temperature.[1-4] When there is no β hydrogen on the acid halide, the product is an alkyl or aryl halide; when a β hydrogen is present, the products are the olefins and hydrogen halide. In the reaction, chlorotris(triphenylphosphine)rhodium(I) is converted to chlorocarbonylbis-(triphenylphosphine)rhodium(I) (**4**) and the reaction is stoichiometric with respect to the former. Chlorocarbonylbis(triphenylphosphine)rhodium(I) also catalyzes the homogeneous decarbonylation, but at a higher temperature.[3,5-9] The rhodium-catalyzed decarbonylation has the advantage over the palladium-catalyzed decarbonylation, since the major product from straight chain acid halides is the 1-olefin with small amounts of internal olefins resulting from isomerization. Palladium catalysis affords mainly internal olefins.[10,11]

The mechanism for the decarbonylation of acid chlorides by chlorotris(triphenylphosphine)rhodium(I) has been proposed to involve both acyl- and alkyl- or arylrhodium complexes[2-5] as shown in Figure 1. When catalytic amounts of **1** are used, the proposed mechanism involves the oxidative addition of an acid chloride to **4** at elevated temperatures to form **5**. In the next step, **5** can lose carbon monoxide to give **2**, followed by acyl–alkyl rearrangement to produce **3**. Finally, olefins are obtained by a β-hydride elimination reaction with the regeneration of the complex **4**.

Results and Discussion

Stereochemistry. In order to study the overall stereochemistry of β-hydrogen elimination, the *erythro*- and *threo*-2,3-diphenylbutanoyl chloride (**6** and **7**) obtained from the corresponding acids[12] were treated with **1** to form the appropriate acylrhodium complexes (Figure 2).

When the erythro acyl complex (**8e**) was stirred in benzene for 5 days at 30°, a 90% yield of *trans*-α-methylstilbene was obtained. In the case of the threo acyl complex (**8t**), similar reaction conditions resulted in a 90% yield of α-methylstilbenes; *cis*-α-methylstilbene comprised 90% of this mixture and *trans*-α-methylstilbene the remaining 10%. Thus the elimination takes place stereospecifically with overall cis elimination occurring. In the decarbonylation of both erythro and threo acid chlorides either the acyl–alkyl rearrangement and the β-hydride elimination occur stereospecifically, or a concerted stereospecific cis elimination occurs.

If the two-step process is followed, these results are consistent either with retention of configuration during the acyl to alkyl rearrangement (**2** → **3**) to afford an alkyl complex (*e.g.*, from the erythro isomer) followed by a cis β-hydrogen elimination or by inversion of configuration during this rearrangement to give alkyl complex (*e.g.*, **10** from the erythro isomer) followed by a trans elimination. The same arguments apply to the threo isomer in which either retention, cis elimination

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