

manner analogous to the preparation of the $(\text{NMe})_2(\text{CH}_2)_3$ bridged derivative by using 5.6 g (7.9 mmol) of $[\text{Ni}((\text{MeNEthi})_2\text{Me}_2[16]\text{tetraeneN}_4)](\text{PF}_6)_2$ in 250 mL of acetonitrile, 0.36 g (15.8 mmol) of sodium in 25 mL of methanol, and 3.59 g (7.9 mmol) of 1,8-bis(*p*-toluenesulfonato)octane in 250 mL of acetonitrile. After the solution of the ditosylate was added, the mixture was refluxed for 18 under nitrogen. The dark solution was rotary evaporated to dryness, and the resulting product was dissolved in 25 mL of acetonitrile, and filtered through celite to remove sodium *p*-toluenesulfonate. The filtrate was chromatographed on a column of Woelm neutral alumina, eluting with acetonitrile. The orange-yellow band was collected and rotary evaporated to a small volume. The addition of methanol caused crystallization of the orange product.

(2,3,10,11,19,25-Hexamethyl-3,10,14,17,20,24-hexaazabicyclo[10.7.6]hexacos-1,11,13,17,19,24-hexaene- κ^4 N)nickel(II) Hexafluorophosphate $[\text{Ni}((\text{CH}_2)_6(\text{MeNEthi})_2[15]\text{tetraeneN}_4)](\text{PF}_6)_2$. This 15-membered macrocyclic dry cave complex was prepared by dissolving 5.0 g (7.19 mmol) of $[\text{Ni}((\text{MeOEthi})_2\text{Me}_2[15]\text{tetraeneN}_4)](\text{PF}_6)_2$ in 500 mL of acetonitrile and slowly dripping in a solution of 1.04 g (7.19 mmol) of *N,N'*-dimethyl-1,6-hexanediamine in 500 mL of acetonitrile. The solution turned a dark brown-red and was rotary evaporated to give a viscous dark red oil which was dissolved in a minimum amount of acetone and chromatographed on an alumina column (3-in. diameter, 12-15-in. length) eluting slowly with a 1:1 mixture of acetone and dichloromethane. The light yellow band was collected, leaving numerous dark bands at the top of the column, and rotary evaporated to dryness, and the resulting product was slurried with absolute ethanol. The product was isolated, washed with ether, and dried in vacuo.

[3,10,13,19-Tetramethyl-2,11-dimethylene-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacos-12,19,20,25-hexaenato(2-)- κ^4 N]nickel(II) $[\text{Ni}((\text{CH}_2)_6(1\text{-MeN-vinyl})[16]\text{hexaenatoN}_4(2-))]_2$. All operations were carried out in a drybox. To a solution of 3.00 g of $[\text{Ni}((\text{CH}_2)_6(\text{MeNEthi})_2[15]\text{tetraeneN}_4)](\text{PF}_6)_2$ in 25 mL of CH_3CN was added a solution of 1.00 g of potassium *tert*-butoxide in 20 mL of methanol. An immediate color change from yellow-orange to red-violet was observed. The solvent was removed under vacuum, and the residue was extracted with 75 mL of benzene. Inorganic salts were removed by filtration. The benzene was then removed under vacuum, and the purple solid was slurried in heptane or acetonitrile. The product was isolated by suction filtration and was dried in vacuo at room temperature. Anal. Calcd. for $\text{NiC}_{26}\text{H}_{42}\text{N}_6$: C, 62.79; H, 8.51; N, 16.90. Found: C, 63.37; H, 8.79; N, 16.28.

[3-(1-(Methylamino)ethylidene)-11-(1-methyl-2-piperidinylidene)-12,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene- κ^4 N]-

nickel(II) Hexafluorophosphate-Acetonitrile $[\text{Ni}(\text{Me}_2(\text{MAE})(\text{MPip})[16]\text{tetraeneN}_4)](\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}$. A 1.51-g sample (0.0284 mol) of sodium methoxide in 10 mL of methanol was added to a 250-mL solution of 10 g (0.0142 mol) of (3,11-bis((1-methylamino)ethylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene)nickel(II) hexafluorophosphate in acetonitrile. The resulting red solution and another containing 5.44 g (0.0142 mol) of 1,3-ditosylpropane in 250 mL of acetonitrile were simultaneously dripped into 500 mL of refluxing acetonitrile, under an atmosphere of nitrogen, over a period of 5-6 h. The dark yellow solution was filtered to remove sodium tosylate and evaporated to a volume of 50 mL. Chromatography of this solution on a 25-cm Woelm neutral alumina column with acetonitrile eluent gave a single mobile yellow band which was collected and evaporated to dryness. The yellow-brown powder was recrystallized from acetonitrile saturated with ammonium hexafluorophosphate to yield large yellow-orange crystals containing one molecule of acetonitrile per complex, as solvent of crystallization; yield 4.8 g (45%). Anal. Calcd. for $\text{Ni}(\text{C}_{23}\text{H}_{38}\text{N}_6)(\text{PF}_6)_2 \cdot \text{CH}_3\text{N}$: C, 38.09; H, 5.24; N, 12.44; Ni, 7.45. Found: C, 38.36; H, 5.24; N, 12.31; Ni, 7.27.

2,3,10,11,20,26-Hexamethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacos-1,11,13,18,20,25-hexaene-N₄ Hexafluorophosphate $[\text{H}_3((\text{CH}_2)_6(\text{MeNEthi})_2\text{Me}_2[16]\text{tetraeneN}_4)](\text{PF}_6)_3$. Hydrogen chloride gas was bubbled through a solution of 5.00 g (6.33 mmol) of $[\text{Ni}((\text{CH}_2)_6(\text{MeNEthi})_2\text{Me}_2[16]\text{tetraeneN}_4)](\text{PF}_6)_2$ in acetonitrile for approximately 10 min. The color of the solution did not turn deep blue as it did for most other dry cave complexes, but eventually it turned turquoise. The solvent was stripped by use of the rotary evaporator, and the residue was dissolved in 100 mL of water and 10 mL of absolute ethanol. To this solution was added a solution of 10.3 g of ammonium hexafluorophosphate in 50 mL of water. Aliquots were added over a period of about 1 h. The cream colored solid formed was isolated by suction filtration, washed with ether, and dried in vacuo; yield 3.28 g (59%) of an off-white solid. The compound so isolated analyzed as a dihydrate. Anal. Calcd.: $\text{C}_{26}\text{H}_{51}\text{N}_6\text{P}_3\text{F}_{18}\text{O}_2$: C, 34.14; H, 5.62; N, 9.19. Found: C, 33.95; H, 5.40; N, 9.13. The water could be removed under vacuum at $\sim 60^\circ\text{C}$ overnight, as evidenced by the disappearance of the band due to the O-H stretching mode from the infrared spectrum.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. Dr. Charles Cottrell was most helpful in the NMR studies and Mr. Richard Weisenberger determined the mass spectra. These contributions are deeply appreciated.

Reaction of α,β -Unsaturated Acid Chlorides with Tris(triphenylphosphine)chlororhodium(I): Formation of Phosphonium Salts¹

J. A. Kampmeier,* S. H. Harris,² and R. M. Rodehorst

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. Received July 9, 1980

Abstract: The reaction of (*E*)-cinnamoyl chloride and tris(triphenylphosphine)chlororhodium(I) in equivalent amounts in dichloroethane at 85°C gives styryltriphenylphosphonium chloride and bis(triphenylphosphine)chlorocarbonylrhodium in good yields. (*E*)-2-Butenoyl chloride gives 1-propenyltriphenylphosphonium chloride, and (*E*)-2-heptenoyl chloride gives a mixture of 1- and 2-hexenyltriphenylphosphonium chlorides. 3-Methyl-2-butenoyl chloride gives only isobutylene. None of these α,β -unsaturated acid chlorides give the expected 1-chloro-1-alkene. Control experiments showed that the phosphonium salts are not formed by secondary reactions. Bis(triphenylphosphine)styryldichlorocarbonylrhodium was shown to be an intermediate in the formation of styryltriphenylphosphonium chloride. A study of the kinetics of decomposition of this intermediate showed that dissociation of chloride ion is the rate-determining step. The observed rate law is $-\text{d}[\text{intermediate}]/\text{dt} = k[\text{intermediate}]k'[\text{PPh}_3]/(k'[\text{Cl}^-] + k[\text{PPh}_3])$. The significance of these observations for an understanding of the details of the "reductive elimination" reaction is discussed.

Wilkinson's catalyst (1) is known to be an effective stoichiometric reagent for the decarbonylation of acid chlorides under

mild conditions and a catalyst for this process at elevated temperatures.^{3,4} In the absence of a $\beta\text{-C-H}$ bond in the substrate,

Table I. Products from the Reaction of R₁R₂C=CHCOCl with RhCl(PPh₃)₃^a

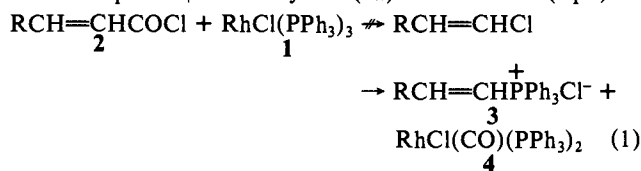
R ₁	R ₂	RhCl(CO)- (PPh ₃) ₃ ^b	R ₁ R ₂ C= CHP ⁺ Ph ₃ Cl ^{-b}	"volatiles" ^b	react time, h	solvent
Ph	H	0.84	0.77	0.007 ^c	17	C ₂ H ₄ Cl ₂ ^d
Ph	H	0.63	0.22	0.11 ^c	24	CH ₃ CN
Ph	H	0.93	0.64	0.04 ^c	24	C ₆ H ₆
CH ₃	H	0.81	0.78	<0.01	7	C ₂ H ₄ Cl ₂ ^d
CH ₃	H	0.52	0.44	<0.01	4	CH ₃ CN
CH ₃	H	0.55	0.55	<0.01	24	C ₆ H ₆
<i>n</i> -C ₄ H ₉	H	0.98	0.87 ^e	0.01 ^f	24	C ₂ H ₄ Cl ₂ ^d
<i>n</i> -C ₄ H ₉	H	0.77	0.42 ^e	0.12 ^f	4	CH ₃ CN
CH ₃	CH ₃	0.63	<0.01	0.59 ^g	120	C ₂ H ₄ Cl ₂ ^d
CH ₃	CH ₃	0.89	<0.01	0.59 ^g	120	CH ₃ CN
H	H	0.82	<0.01		24	C ₂ H ₄ Cl ₂ ^d

^a [RCOCl]₀ = 0.05 M; [RCOCl]₀/[RhCl(PPh₃)₃]₀ = 1; under N₂; when R₁ ≠ R₂, *E* isomer was used. ^b Moles of product/mole of [RCOCl]₀. ^c Styrene. ^d 1,2-Dichloroethane. ^e Mixture of 1- and 2-isomers. ^f 1-Hexyne. ^g Isobutylene.

this reaction gives useful yields of alkyl chlorides; in the presence of a β-hydrogen, the corresponding olefin is the major product. This paper reports a novel decarbonylation of α,β-unsaturated acid chlorides (2) with RhCl(PPh₃)₃ to give substituted vinyltriphenylphosphonium chlorides (3). Observations relating to the mechanism of this reaction are presented.

Results

In a typical experiment, (*E*)-cinnamoyl chloride (2a) reacts with an equimolar amount of Wilkinson's catalyst (1) in dichloroethane at 85 °C under N₂ to give styryltriphenylphosphonium chloride (3a) in 77% isolated yield and an 84% isolated yield of RhCl(CO)(PPh₃)₂ (4). A small amount of styrene is also observed, but the expected β-chlorostyrene (5a) is not formed (eq 1).



2, 3, 5: (a) R = Ph, (b) R = CH₃, (c) R = *n*-C₄H₉

In similar fashion (*E*)-2-butenoyl chloride (2b) and (*E*)-2-heptenoyl chloride (2c) give 1-propenyltriphenylphosphonium chloride (3b) and a mixture of 1-hexenyltriphenylphosphonium chloride (3c) and the corresponding 2-hexenyl isomer, respectively. In neither case is the corresponding 1-chloroalkene (5b,c) formed. The allylic phosphonium salt, 2-hexenyltriphenyl phosphonium chloride, was shown to be the result of isomerization of the vinylphosphonium salt under the reaction conditions. Hexenoyl chloride also gives a small amount of 1-hexyne. The formation of phosphonium salts is not particularly sensitive to solvent changes. As judged by NMR data, the phosphonium salts (5) are all *E* isomers.

The reaction failed to give isolable vinylphosphonium salt or vinyl chloride with acryloyl chloride; the corresponding vinylphosphonium bromide was shown to be unstable to the reaction conditions, and the reaction of acryloyl chloride was not investigated more closely. 3-Methyl-2-butenoyl chloride also gives neither a vinylphosphonium salt nor a vinyl chloride; the corresponding olefin, isobutylene, is the only significant organic product, and the reaction is many times slower than the reactions of the less substituted substrates. All of these reactions give reasonable yields of the carbonylated organometallic RhCl(CO)(PPh₃)₂. These product studies are summarized in Table I.

A molecule of triphenylphosphine is liberated in the first step of the reaction of Wilkinson's catalyst (1) with acid chlorides.^{3,4}

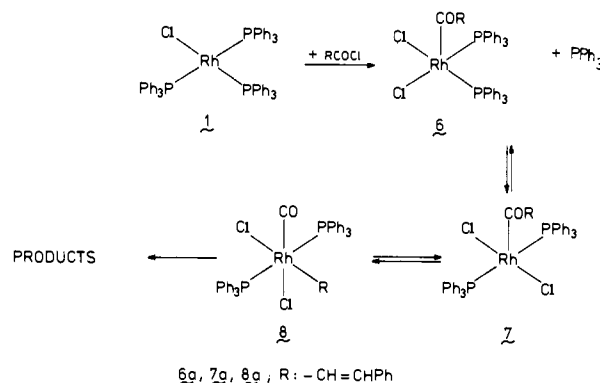
(1) This work has been presented in short form: Abstracts of the IXth International Meeting on Organometallic Chemistry, Dijon, France, 1979, C40.

(2) Taken in part from Ph.D. Thesis of S. H. Harris, University of Rochester, 1979.

(3) Tsuji, J.; Ohno, K. *Synthesis* 1969, 1, 157.

(4) Baird, M. C. In "The Chemistry of Acid Derivatives", Supplement B, Part 2; Patai, S., Ed.: Wiley: New York, 1979; p 825, and references cited there.

Scheme I



It is tempting to propose that the expected vinyl chlorides are, indeed, formed but are consumed by this free phosphine to give the phosphonium salts in secondary reactions involving an addition-elimination mechanism.⁵ Authentic samples of each of the vinyl chlorides corresponding to the acid chlorides in Table I were prepared; gas chromatographic analysis of authentic mixtures showed that a 1% yield of each of these products would have been detected. In addition, several reactions in the styryl series were followed by NMR; the absorptions of styrylphosphonium salt appeared directly without discernable intervention of β-chlorostyrene. A host of control experiments were performed in which β-chlorostyrene and triphenylphosphine were heated in the absence and in the presence of obvious rhodium species such as RhCl(PPh₃)₃ and RhCl(CO)(PPh₃)₂; styryltriphenylphosphonium salt was never observed and β-chlorostyrene was recovered. Triphenylphosphine and cinnamoyl chloride also do not react in the absence of 1 to give styryltriphenylphosphonium chloride. In the most searching control experiments, cinnamoyl chloride was reacted with RhCl(PPh₃)₃ in the presence of added 1-chloro-1-propene (5b) and 1-hexene. Styryltriphenylphosphonium salt was formed in each reaction, guaranteeing that the reaction conditions had been reproduced, but neither 1-propenyltriphenylphosphonium salt (3b) nor 1- or 2-hexenyltriphenylphosphonium salt (3c) was formed. In a similar test, 1-heptenoyl chloride was decarbonylated to give a mixture of 1- and 2-hexenyltriphenylphosphonium salts in the presence of added 1-propyne; no 1-propenylphosphonium salt was formed. These crossover controls exclude mechanistic hypotheses involving the initial formation of the vinylchlorides (5), alkenes, or alkynes, followed by a secondary reaction of these products under the reaction conditions to give phosphonium salts. Thus, the phosphonium salts are primary reaction products formed directly from the organometallic intermediates involved in the decarbonylation sequence.

There is general agreement about the overall form of the mechanism of decarbonylation of acid chlorides by Wilkinson's catalyst.^{3,4,6} This agreement is based on the spectroscopic ob-

(5) Rappoport, Z. *Adv. Phys. Org. Chem.* 1969, 7, 1.

servation and isolation of several intermediates on the reaction pathway, as outlined in Scheme I. The slow step is the product forming step, $8 \rightarrow$ products. The reaction of cinnamoyl chloride with $\text{RhCl}(\text{PPh}_3)_3$ follows this same general scheme because an analogous series of intermediate complexes can be detected and followed by IR or NMR spectroscopy. Thus, successive IR spectra of a reaction in progress between **1** and cinnamoyl chloride show a very rapid decrease of the acid chloride (**2a**) absorption at 1750 cm^{-1} and a concomitant increase in the absorptions of the acyl complexes **6a** and **7a** at 1705 and 1680 cm^{-1} . This is followed by a slower increase in the absorption of the carbonyl complex **8a** at 2070 cm^{-1} and a simultaneous decrease in the absorptions due to the acyl complexes. The disappearance of **8a** to give products (**3a** and **4**) is very slow, and, indeed, **8a** can be isolated in pure form without difficulty. ^1H NMR observations reveal the same sequence of intermediates. ^{31}P NMR or IR observations, starting with **8a**, show an initial equilibration to give a mixture of **6a**, **7a**, and **8a**, followed by slow disappearance of the mixture to give products **3a** and **4**. These observations and the spectroscopic assignments are in agreement with reports in the literature for reactions of other acid chlorides.⁶

Complex **8a** was isolated and studied directly. As mentioned above, **8a** equilibrates with **6a** and **7a** in solution at room temperature; **8a** is the major isomer. When **8** ($\text{R} = \text{CH}=\text{CHC}_6\text{H}_4\text{CH}_3\text{-}p$) is heated at 85°C in dichloroethane solution, a complicated mixture of reactions takes place to give regenerated *p*-methylcinnamoyl chloride (31%), *p*-methylstyrene (31%), (*p*-methylstyryl)triphenylphosphonium chloride, (33%) and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (40%). (The *p*-methyl group is a useful label for NMR studies.) This complicated set of reactions presumably reflects the fact that the forward reaction of **8** to give phosphonium salt and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ requires 1 equiv of phosphine at some stage. In the absence of free phosphine, the rate of this forward reaction is suppressed and side reactions of the complexes **6**, **7**, and **8** are relatively more important. In an attempt to distinguish intra- and intermolecular pathways for the forward reaction of **8a** to give phosphonium salt, **8a** (with triphenylphosphine ligands) was reacted with 1 equiv of tri-*p*-tolylphosphine to give a 53% isolated yield of a mixture of styryltriarylphosphonium chlorides showing approximately 40% incorporation of the added tri-*p*-tolylphosphine. Since the exchange of tri-*p*-tolylphosphine with styryltriphenylphosphonium salt was shown to be too slow to be the source of the observed exchange, the exchange of phosphine ligands in **8a** (via **6a** and **7a**) must precede the formation of products. The slight deviation of the product composition from the statistical value of 33% may simply reflect the fact that tri-*p*-tolylphosphine is a better ligand to rhodium than triphenylphosphine. In any case, this prior exchange spoils this attempt to distinguish intra- and intermolecular pathways for the formation of phosphonium salt from **8a**.

Plots of the log of the initial rates of disappearance of **8a** vs. $\log [\text{8a}]_0$ in the presence of excess phosphine gave a slope of 1. First-order plots of the disappearance of **8a** in the presence of excess phosphine were linear for several half-lives and k_{obsd} was independent of $[\text{PPh}_3]_0$ (see Table III). Thus, the rate law in the presence of a large excess of phosphine is $\text{rate} \propto [\text{8a}]^1[\text{PPh}_3]^0$. The reaction could be monitored by either UV or IR spectroscopy. The IR measurement records only the decrease in $[\text{8a}]$ since no other species in solution absorbs at 2070 cm^{-1} . The UV method monitors the concentration of all the rhodium(III) complexes in solution. Since these two methods gave the same first-order rate constants, the equilibrium $\text{8a} \rightleftharpoons \text{6a} + \text{7a}$ must be fast with respect to the rate of reaction to give products, as indicated previously by qualitative spectroscopic observations.

A first-order plot of the disappearance of **8a** in the presence of only 1 equiv of phosphine showed considerable downward curvature, ruling out a simple first-order decomposition of **8a** to give products. Studies of initial rates of reaction of **8a** with equivalent concentrations of phosphine in the presence of variable

added amounts of alkyltriphenylphosphonium chloride suggested an inverse first-order dependence on phosphonium chloride. The addition of 1-propenyltriphenylphosphonium hexafluorophosphate actually increased the rate, probably reflecting the increased ionic strength of the medium. Therefore, the inhibition observed with added phosphonium chloride is due to chloride ion and not to the phosphonium ion. At high concentrations of added chloride ion and low concentrations of phosphine, the initial rates depended on $[\text{PPh}_3]^1$. Second-order plots were obtained for the reaction of **8a** with equivalent concentrations of phosphine in the presence of excess alkyltriphenylphosphonium chloride; the observed rate constants showed an inverse first-order dependence on the concentration of added phosphonium chloride (see Table III); thus, the rate law at low phosphine concentration in the presence of excess chloride ion is $\text{rate} \propto [\text{8a}][\text{PPh}_3]/[\text{Cl}^-]$. These reactions could only be followed for the first 1–2 half-lives because of a reaction of chloride ion with the product $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ to give an absorbing species which increasingly interfered with the UV analysis as the reaction proceeded. A general rate law can be deduced from the observed kinetic behavior under the limiting conditions: $\text{rate} \propto [\text{8a}][\text{PPh}_3]/([\text{Cl}^-] + [\text{PPh}_3])$. At high concentrations of phosphine or chloride ion, the denominator simplifies to $[\text{PPh}_3]$ and $[\text{Cl}^-]$, respectively, giving the observed form of the rate laws under these limiting conditions.

The behavior of 3-methyl-2-butenoyl chloride is qualitatively different from that of the other acid chlorides. As indicated previously, the reaction is very much slower and gives only isobutylene; no phosphonium salt is observed. The absence of an IR absorption in the region near 2070 cm^{-1} shows that complex **8** ($\text{R} = \text{CH}=\text{CMe}_2$) is not present in appreciable concentrations in the course of the reaction, presumably because of the unfavorable steric crowding in **8** caused by the dialkyl substitution in the β -position. Thus, the rate of formation of phosphonium salt is suppressed, and a slow protolytic cleavage⁷ of one of the organorhodium complexes by adventitious HCl to give isobutylene can compete. This slow cleavage is presumably also the source of the styrene observed in the reactions of cinnamoyl chloride. The details of these cleavages are not clear. In an attempt to trace the source of the "new" hydrogen in isobutylene, 2-methyl-2-butenoyl chloride was reacted with **1** in deuterated acetonitrile to give isobutylene (80% d_0 , 20% d_1). Intermediate isobutenyl radicals or carbanions should have been rapidly quenched by CD_3CN to give only isobutylene- d_1 , contrary to observation. Thus, a protolytic cleavage of an organorhodium complex by traces of acid in the reaction mixture is the most reasonable source of isobutylene. The small amount of d_1 product probably reflects an exchange of HCl with CD_3CN under the reaction conditions to give some DCl.

Discussion

The formation of phosphonium salts has occasionally been observed in some other organometallic reactions⁸ but had not been previously reported in decarbonylation reactions involving $\text{RhCl}(\text{PPh}_3)_3$. Reactions of **1** with α,β -unsaturated acid chlorides are not described in the literature. Thus, the reactions reported in this paper are new and represent exceptions to the generalization that acid chlorides are decarbonylated by $\text{RhCl}(\text{PPh}_3)_3$ to give alkyl chlorides (or olefins). While this work was in progress, Weinberg and Baird reported⁹ the formation of methyltriphenylphosphonium chloride from the decomposition of **8** ($\text{R} = \text{CH}_3$). (We have noted that benzyltriphenylphosphonium chloride is formed in significant amounts during the decarbonylation of phenylacetylchloride by **1** under commonly used conditions,¹⁰ but

(7) cf.: Labinger, J. A.; Hart, D. W.; Seibert, W. E.; Schwartz, J. J. *Am. Chem. Soc.* **1975**, *91*, 3851. Bootz, B. L.; Lloyd, A. D. *J. Organomet. Chem.* **1972**, *35*, 195. Michman, M.; Bolog, M. *Ibid.* **1971**, *31*, 395.

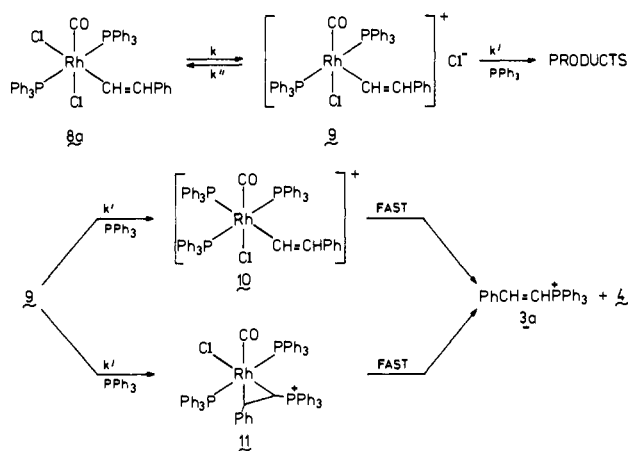
(8) (a) Horner, L.; Mummertney, G.; Masser, H.; Beck, P. *Chem. Ber.* **1966**, *99*, 2782. (b) Cassar, L.; Foa, M. *J. Organomet. Chem.* **1974**, *74*, 75. (c) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1960**, 1718 (cf. Cotton, F. A. *J. Am. Chem. Soc.* **1961**, *83*, 344). (d) Ziegler, C. B.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2941.

(9) Weinberg, E. L.; Baird, M. C. *J. Organomet. Chem.* **1979**, *179*, C 61.

(10) Stille, J. K.; Regan, M. T. *J. Am. Chem. Soc.* **1974**, *96*, 1508.

(6) Egglestone, D. C.; Baird, M. C.; Lock, C. J. L.; Turner, G. J. *Chem. Soc., Dalton Trans.* **1977**, 1576.

Scheme II



in this case it is easy to show by NMR studies that this product is simply a secondary product formed by the reaction of benzyl chloride with triphenylphosphine under the decarbonylation conditions.¹¹)

More importantly, the vinyltriphenylphosphonium salts seem to be the wrong "reductive elimination" products and, therefore, invite a consideration of the mechanistic details of this important step in the reaction sequence. The observed rate law can be rewritten as the product of two terms

$$\text{rate} = k[8a] \cdot k'[PPh_3] / (k'[Cl^-] + k[PPh_3])$$

The first term, $k[8a]$, describes the rate of formation of a reactive intermediate. The second term describes the fraction of this intermediate which proceeds to products. Thus, a rate-determining loss of chloride ion to give a cationic rhodium complex is implicated in the rate-determining step;¹² the rhodium cation is captured either by chloride ion to give **8a** again or by phosphine to give products (Scheme II). Therefore, the apparent "reductive elimination" is not a simple concerted unimolecular decomposition of **8a** to give $RhCl(CO)(PPh_3)_2$ and styryltriphenylphosphonium chloride.

Unfortunately, the nature of the actual product-forming step is not revealed by our kinetic experiments. Cation **9** is ambident, and the forward reaction with phosphine could involve attack either at the metal to give a six-coordinate cationic rhodium complex **10** or at the carbon of the vinyl group to give **11** (see Scheme II). Either complex, **10** or **11**, might be unstable with respect to loss of phosphonium salt and, therefore, decompose rapidly to products; either process conforms to the observed rate law. (Complex **11**, of course, is just one way of describing the result of nucleophilic attack by phosphine at carbon. Several other formulations are possible, and, in fact, there is no requirement that there be an intermediate on this pathway involving reaction at carbon.)

Chloride ion is also present in solution and is also a nucleophile but must attack **9** exclusively at the metal to regenerate **8a** since reaction at carbon would give β -chlorostyrene, contrary to observation. If phosphonium salt is formed by nucleophilic attack at carbon, then the facts require that phosphine and chloride ion show different selectivities for the carbon and the metal centers. A better resolution of this question will have to wait for experiments with other nucleophilic traps for the cationic complex **9** or the identification of other complexes on the path from **8a** to products.

It is worth noting that nucleophilic attack by phosphine on a ligand has been observed or proposed in reactions of several other metal complexes. Thus, examples of attack at both ligand and metal have been observed for the reaction of phosphine with cationic complexes containing π -bonded olefinic ligands.¹³ A variety of

nucleophiles, including phosphine, react with organometallic carbene complexes at carbon.¹⁴ Bergman and Huggins recently proposed¹⁵ a reversible addition of triphenylphosphine to the double bond of a σ -bonded alkenyl-nickel complex. Weinberg and Baird suggested⁹ that methyltriphenylphosphonium chloride was formed by nucleophilic attack by phosphine on the methyl group of **8** ($R = CH_3$).

Finally, it seems worthwhile to ask why phosphonium salts are formed in these reactions of vinyl substrates but not in other decarbonylation reactions. The simplest hypothesis is that the σ -vinyl-rhodium bond is appreciably stronger than σ -alkyl bonds,¹⁶ thereby suppressing the rate of all concerted reductive elimination reactions in the vinyl systems. Thus, an alternative path, involving ionization and subsequent nucleophilic attack by phosphine at carbon, takes over. As noted above, this is acceptable only if the two nucleophiles, chloride ion and phosphine, behave differently in their reactions with **9**.

Another possibility is that both phosphine and chloride ion react with the cationic complex **9** at the metal to give a new complex **10** or starting complex **8a**, respectively. As discussed above, the new complex **10** might then reductively eliminate phosphonium salt in a concerted reaction. If so, then one must ask why complex **8** ($R = CH_2Ph$) eliminates benzyl chloride and not benzyltriphenylphosphonium salt while **10** chooses to eliminate phosphonium salt instead of β -chlorostyrene.

It may be that elimination of the chloro compound is stereoelectronically inhibited in the styryl case. For example, it seems likely that the cis Rh-Cl bond must interact with the π or π^* system of the styryl ligand in order to reductively eliminate β -chlorostyrene. However, the styryl ligand is "sandwiched" between two large phosphine ligands; i.e. the π - π^* system is held orthogonal to the Rh-Cl bond, thereby prohibiting elimination of the vinyl chloride. The phosphine ligand, however, is in the right position for the Rh-P bond to interact with the π or π^* system. This stereoelectronic requirement, imposed by the π - π^* system, is not present in the benzyl system and the inherently more favorable extrusion of the chloro compound is therefore observed. A choice between these possibilities will clearly require further studies. Nevertheless, it does seem clear that the formation of products from **8** is more complex than has been previously suggested.

Experimental Section

Melting points were performed in a bath with a heating rate of $1^\circ/\text{min}$ for the final 30° period; melting points and boiling points are uncorrected. Analytical vapor-phase chromatography was performed either on a Perkin-Elmer Model 900 instrument with flame ionization detectors or on a Hewlett-Packard 5700 A instrument with thermal conductivity detectors. Preparative VPC was performed on a F and M series 700 instrument. The columns used were as follows: A, $1/8$ in. \times 10 ft, 10% FFAP in Chromasorb P, 60/80; B, $1/8$ in. \times 10 ft, 10% Apiezon L on Chromasorb W (AW-DMCS), 80/100; E, $1/8$ in. \times 20 ft, 10% DNBP on Chromasorb P, 60/80; F, $1/8$ in. \times 6 ft, Poropak Q. Peak areas were determined by triangulation.

Nuclear magnetic resonance (NMR) spectra were obtained on a JEOL-JNM-MH-100 instrument in $CDCl_3$ solution with use of tetramethylsilane as internal standard. Phosphorus NMR studies were performed on a JEOL-JNM-PS-100 Fourier Transform NMR instrument as was 1H FTNMR. Infrared spectra were obtained from a Perkin-Elmer 137 or 467 instrument, calibrated to polystyrene (1601 cm^{-1}). Mass spectra were performed on a Dupont 490B mass spectral analyzer, with GC-mass spectra performed in conjunction with a Varian Series 1400

(11) Kampmeier, J. A.; Rodehorst, R. M.; Philip, J. B., Jr., unpublished observations.

(12) cf.: Ettore, R. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 45. Appleton, T. G.; Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1974**, *65*, 275. Hall, P. W.; Puddephatt, R. J.; Tipper, C. F. H. *Ibid.* **1975**, *84*, 407.

(13) Ligand: McCleverty, J. A.; Murray, A. J. *J. Organomet. Chem.* **1978**, *149*, C29. Sweigart, D. A.; Wilker, C. N. *J. Chem. Soc., Chem. Commun.* **1977**, 304. Birney, D. M.; Crane, A. M.; Sweigart, D. A. *J. Organomet. Chem.* **1978**, *152*, 187. Whitesides, T. H.; Arhart, R. W.; Slaven, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 2791. Salzer, A. *Inorg. Chim. Acta* **1976**, *17*, 221. John, G. R.; Kane-Maquire, L. A. P. *J. Organomet. Chem.* **1976**, *120*, C45, C47. Metal: Brown, D. A.; Crawla, S. K.; Glass, W. K. *Inorg. Chim. Acta* **1976**, *19*, L31. Bailey, N. A.; Kita, W. G.; McCleverty, J. A.; Murray, A. J.; Mann, B. E.; Walker, N. W. *J. Chem. Soc., Chem. Commun.* **1974**, 592. Powell, P.; Russel, L. J.; Styles, E.; Brown, A. J.; Howarth, O. W.; Moore, P. *J. Organomet. Chem.* **1978**, *149*, C1.

(14) Fischer, H.; Fischer, E. O.; Kreiter, C. G. *Chem. Ber.* **1974**, *107*, 2459. Casey, C. P.; Polichnewski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097.

(15) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4410.

(16) Baird, M. C. *J. Organomet. Chem.* **1974**, *64*, 289.

instrument with flame ionization detectors. Ultraviolet spectra were performed on a Cary 118 spectrometer with use of matched 1.0-cm quartz cells. Combustion analyses were performed by Chemalytics, Inc., Tempe, AZ.

Reagents and Chemicals. Spectro grade **1,2-dichloroethane** (Eastman) was washed with equal volumes of 10% KOH, water, and brine. The excess water was removed by azeotropic distillation and the remaining solvent refluxed with CaH_2 under nitrogen. The center cut, bp 84 °C, was collected and distilled from CaH_2 under nitrogen prior to use. Spectro grade **acetonitrile** (Mallinckrodt) was refluxed with CaH_2 under nitrogen and distilled; the center cut, bp 82–83 °C, was redistilled from CaH_2 prior to use. Reagent grade **benzene** was washed with small portions of concentrated H_2SO_4 until no color remained in the acid layer and then washed with water, 10% NaOH, water, and brine. After being dried with CaCl_2 , it was refluxed with CaH_2 and distilled under nitrogen to give a center cut; bp 81 °C. **Acid chlorides** were prepared from the corresponding acids by reaction with thionyl chloride and were carefully distilled before use. **Crotonyl chloride**: bp 66–67 °C (120 mm) (lit.¹⁷ 124–125 °C (760 mm); IR (film) 1770 (s), 1634 (s), 965 (m) cm^{-1} ; NMR δ 2.01 (3 H, dd, $J = 7, 2$ Hz), 6.11 (1 H, dq, $J = 12, 2$ Hz), 7.26 (1 H, dq, $J = 12, 7$ Hz).

(E)-Cinnamoyl chloride: bp 101–102 °C (3 mm) (lit.¹⁸ 101 °C (21 mm); IR (CHCl_3) 1754 (s), 1626 (s) cm^{-1} ; NMR δ 6.67 (1 H, d, $J = 16$ Hz), 7.57 (5 H, m), 7.88, (1 H, d, $J = 16$ Hz).

3-Methyl-2-butenoyl chloride: bp 67–68 °C (45 mm) (lit.¹⁹ 59–60 °C (30 mm); IR (film) 1767 (s), 1600 (s), 832 (m) cm^{-1} ; NMR δ 1.98 (3 H, s), 2.18 (3 H, s), 6.07 (1 H, br s).

(E)-2-Heptenoyl chloride: bp 59–60 °C (6 mm); IR (film) 1755 (s), 1625 (s), 980 (m) cm^{-1} ; NMR δ 0.92 (2 H, t, $J = 7$ Hz), 1.44 (4 H, m), 2.32 (2 H, dt, $J = 7, 7$ Hz), 6.08 (1 H, d, $J = 16$ Hz), 7.16 (1 H, dt, $J = 16, 7$ Hz).

(E)-p-Methylcinnamoyl chloride (recrystallized from pentane): mp 70–71 °C (lit.²⁰ 70 °C); NMR δ 2.36 (3 H, s), 6.08 (1 H, d, $J = 16$ Hz), 7.12 (2 H, d, $J = 8$ Hz), 7.35 (2 H, d, $J = 8$ Hz), 7.68 (1 H, d, $J = 16$ Hz).

1-Chloro-1-propene. Ethylene glycol (200 mL), KOH (75 g, 1.5 mol), and 112 g (1 mol) of 1,2-dichloropropane (Aldrich) were combined, stirred, and heated to 90 °C for 24 h. The organics were distilled at this bath temperature and dried with CaCl_2 . Careful distillation through a 30 × 1.5-cm column packed with 3-mm glass beads gave 19.6 g (26%) of a mixture of (*Z*)- and (*E*)-1-chloro-1-propene: bp 32–36 °C (760 mm) [lit.²¹ 37 °C (738 mm) *E*; 30.8 °C (738 mm) *Z*]; IR (film) 3070 (m), 1650 (s), 1445 (s), 939 (s), 885 (m), 789 (m), 750 (s), 683 (s) cm^{-1} ; NMR δ 1.72 (d, $J = 7$ Hz), 1.77 (3 H, d, $J = 7$ Hz), 5.96 (2 H, m). The mixture was 60% (*E*)-1-chloro-1-propene by VPC (column A, 30 °C).

1-Chloro-1-hexene was prepared by the literature method;²² bp 121–127 °C (lit.²² 121 °C, *Z*; 128 °C, *E*); NMR δ 0.90 (3 H, t, $J = 6$ Hz), 1.36 (4 H, m), 2.08 (2 H, m), 5.60–6.10 (2 H, m); IR (film) 3021 (w), 2899 (s), 1623 (m), 1445 (m), 943 (m), 732 (s, br), 709 (m) cm^{-1} . The *Z*:*E* ratio was 45:55 by VPC (column A, 100 °C). For confirmation, the longer retention time isomer was collected by VPC ($1/4$ in. × 10 ft, 10% SE-30 on Chromasorb P, 60/80): IR (film) 3021 (w), 2899 (s), 1623 (m), 1445 (m), 939 (s) (*E*); 732 (s, br) (*C*-Cl) cm^{-1} .

(E*Z*)- β -Chlorostyrene was obtained from Frinton Laboratories and passed through a column of basic aluminum oxide before use.

Styryltriphenylphosphonium Chloride (3a). A flask was charged with 1.5 g (11 mmol) (*EZ*)- β -chlorostyrene (Frinton), 1.5 g (12 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1.8 g (7 mmol) of triphenylphosphine, and 20 mL of benzonitrile. The mixture was refluxed under nitrogen for 4 h and then poured into 100 mL of water. The organic materials were azeotropically distilled, and the green aqueous layer was extracted thoroughly with 50 mL of chloroform. The chloroform layer was dried with Na_2SO_4 and concentrated to yield a solid. This solid was dissolved in a minimal amount of chloroform and was precipitated with ether to give 0.42 g (14%) of styryltriphenylphosphonium chloride as a white solid: mp 201.5–204 °C dec; IR (KBr) 1605 (s), 1570 (m), 1480 (m), 1440 (s), 1116 (s), 1005 (s), 865 (s), 830 (m), 755 (s, br), 700 (s) cm^{-1} ; NMR δ 7.05 (1 H, dd, $J = 17, 24$ Hz), 7.80 (20 H, m), 8.73 (1 H, dd, $J = 17, 20$ Hz). Recrystallization from 4 mL of 3:1 benzene–chloroform gave an analytical sample; mp 202–204 °C dec. Calcd for $\text{C}_{26}\text{H}_{37}\text{ClP}$: C, 78.00; H, 5.50; Cl, 8.75. Found: C, 77.67; H, 5.82; Cl, 8.22.

(E)-1-Propenyltriphenylphosphonium chloride was prepared by a literature method;²³ mp 232–233 °C (lit.²³ 235–236 °C); IR (KBr) 3030 (w), 1630 (m), 1580 (m), 1480 (m), 1440 (s), 1114 (s), 100 (m), 817 (s), 768 (s), 724 (s), 690 (br) cm^{-1} ; NMR δ 2.34 (3 H, dd, $J = 2, 6$ Hz), 6.76 (1 H, dd, q , $J = 24, 17, 6$ Hz), 7.4–8.0 (16 H, m).

1-Propenyltriphenylphosphonium hexafluorophosphate. A flask was charged with 8 mL of ethanol and 253 mg (0.1 mmol) of AgPF_6 (Ventron) under nitrogen. After 15 min of stirring, 338 mg (0.1 mmol) of 1-propenyltriphenylphosphonium chloride in 4 mL of ethanol was added. A white precipitate formed immediately. The solution was stirred an additional hour, and 50 mL of methylene chloride was added. The solution was filtered and concentrated and the precipitated solid was recrystallized from 5:5:10 benzene–acetone–ether to yield 285 mg (64%) of 1-propenyltriphenylphosphonium hexafluorophosphate: mp 191–193 °C; NMR δ 2.34 (3 H, br d, $J = 4$ Hz), 6.80 (1 H, m), 7.36 (1 H, m), 7.84 (15 H, m); IR (KBr) 3050 (w), 2950 (m), 1605 (m), 1580 (m), 1480 (m), 1435 (s), 1310 (s), 1100 (s), 991 (s), 820 (s), 745 (s), 685 (s), 500 (s, m) cm^{-1} .

(2-Methyl-1-propenyl)triphenylphosphonium Chloride. Methallyl chloride (30 mL, 0.3 mol) was placed in a flask with 10 g (38 mmol) of triphenylphosphine. The mixture was refluxed under nitrogen for 24 h. Ether (20 mL) was added to the slurry and the solid collected by filtration to yield 9.55 g (71%) of a mixture of allyl and vinyl phosphonium salts: NMR δ 1.64 (br s), 1.76 (d, $J = 3$ Hz), 2.46 (s), 4.80 (d, $J = 16$ Hz), 4.94 (d, $J = 4$ Hz), 5.08 (d, $J = 4$ Hz), 6.56 (d, $J = 2.1$ Hz), 7.82 (aromatic). One gram of this solid was refluxed with 0.1 mL of 40% methanolic Triton-B in 5 mL of acetonitrile. After 2 h, the solvent was removed at reduced pressure. The resulting solid was recrystallized from acetone–ether to yield 0.54 g of (2-methyl-1-propenyl)triphenylphosphonium chloride: mp 201–203 °C; IR (KBr) 2882 (m,w), 1605 (s), 1572 (sh), 1480 (m), 1440 (s), 1104 (s), 994 (m), 881 (m), 822 (m), 752 (br s), 719 (s), 690 (br s) cm^{-1} ; NMR δ 1.76 (3 H, d, $J = 3$ Hz), 2.46 (3 H, s), 6.59 (1 H, br d, $J = 23$ Hz), 7.78 (15 H, m). Anal. Calcd for $\text{C}_{22}\text{H}_{33}\text{ClP}$: C, 75.00; H, 6.25; Cl, 10.00; P, 8.80. Found: C, 75.48; H, 6.52; Cl, 9.70; P, 8.59.

1- and 2-Hexenyltriphenylphosphonium Chlorides. Into a flask fitted with a condenser was placed 1.0 g (3.8 mmol) of triphenylphosphine and 3 mL (21.2 mmol) of *E*-1-chloro-2-hexene.^{24,25} The flask was flushed with nitrogen and the contents refluxed under nitrogen for 24 h. After the solution cooled, 1 mL of ether was added to give an oil and an upper liquid phase. The liquid phase was decanted to leave 1.15 g (79%) of a mixture of 1- and 2-hexenyltriphenylphosphonium chlorides as a yellow oil (repeated attempts to crystallize this material failed): IR (CHCl_3) 1623 (w), 1600 (m), 1480 (m), 1440 (s), 1122 (s), 1007 (m), 979 (m) cm^{-1} ; NMR δ 0.72 (t, $J = 7$ Hz), 0.90–2.10 (envelope), 2.59 (m), 4.60 (dd, $J = 15.7$ Hz), 5.36 (m), 5.82 (m), 7.80 (aromatic). By analogy to the propenyl phosphonium salts, the peak at δ 4.60 is due to the CH_2PPH_3 of the allyl isomer and the peak at δ 2.59 is due to the $\text{CH}_2\text{-CH=CH}$ of the vinyl isomer. Integration of these two peaks shows an 8:1 ratio of allyl to vinyl. The mixture of hexenyl phosphonium salts (allyl to vinyl 8:1) (1.27 g, 3.3 mmol) was placed in a flask with 5 mL of dry acetonitrile and three drops of 40% methanolic Triton-B.²³ The solution was flushed with nitrogen and refluxed. Samples were removed at 2, 4, 8, and 12 h time intervals. The solvent was removed by rotary evaporation, and these samples were analyzed by NMR. The only observed change was in the relative areas of the resonances at δ 4.60 (allyl) and 2.59 (vinyl). The ratio changes smoothly to a constant ratio of 2.5:1 of allyl to vinyl after 12 h. Again, repeated attempts to crystallize the oil failed.

Vinyltriphenylphosphonium bromide was prepared by the literature method;²⁶ mp 180–190 °C dec (lit.²⁶ 189–190 °C); NMR δ 6.12 (1 H dd, $J = 18, 24$ Hz), 7.12 (1 H, dd, $J = 12, 48$ Hz), 7.5–8.5 (16 H, m); IR (KBr) 3015 (w), 1580 (m), 1480 (m), 1435 (s), 1380 (m), 1115 (s), 1001 (s), 990 (s), 735 (s, br), 695 (s), 600 (m), 540 (s), 500 (s) cm^{-1} .

RhCl(PPh_3)₃ was prepared by the literature method;²⁷ mp 134–137 °C dec (lit.²⁷ 157–158 °C; 134 °C²⁸); IR (KBr) 3030 (w), 1600 (w), 1470 (m), 1440 (s), 1075 (m), 740 (s), 695 (s), 525 (s), 510 (s), 300 (w) cm^{-1} .

RhCl₂(styryl)(CO)(PPh₃)₂ (8a). $\text{RhCl}(\text{PPh}_3)_3$ (954 mg, 1.04 mmol), and 171 mg (1.04 mmol) of cinnamoyl chloride were added to a two-neck flask. After two vacuum-nitrogen cycles, 8 mL of purified chloroform

(17) Fuson, R. C.; Christ, R. E.; Whitman, G. M. *J. Am. Chem. Soc.* **1936**, *58*, 2450.

(18) Jones, L. W.; Mason, J. P. *J. Am. Chem. Soc.* **1927**, *49*, 2528.

(19) Smith, L. I.; Engelhardt, V. A. *J. Am. Chem. Soc.* **1949**, *71*, 2671.

(20) Rasschaert, A.; Janssens, W.; Sloothmarkers, P. *J. Bull. Soc. Chim. Belg.* **1966**, *75*, 449.

(21) Smith, H. A.; King, W. H. *J. Am. Chem. Soc.* **1950**, *72*, 95.

(22) Normant, J. *Bull. Soc. Chim. Fr.* **1963**, 1873.

(23) Keough, P. T.; Grayson, M. *J. Org. Chem.* **1964**, *29*, 631.

(24) Collington, E. W.; Meyers, A. I. *J. Org. Chem.* **1971**, *36*, 3044.

(25) Hurd, C. D.; McNamee, R. W. *J. Am. Chem. Soc.* **1932**, *54*, 1648.

(26) Schweizer, E. E.; Bach, R. D. *J. Org. Chem.* **1964**, *29*, 1746.

(27) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

(28) Hudson, B.; Taylor, P. C.; Webster, D. E.; Wells, P. B. *Discuss. Faraday Soc.* **1968**, *45*, 39.

was added by syringe, and the solution was degassed with two vacuum-nitrogen cycles. The mixture was stirred for 30 min at room temperature and then placed in a refrigerator (-10°C) for 4 days. The solution was then poured into 100 mL of ether and 100 mL of pentane. This solution was kept at -10°C overnight and was then filtered to yield 826.7 mg of a yellow powder. The ether-pentane solution was evaporated, 2 mL of methylene chloride and 100 mL of pentane were added, and the resulting precipitate was collected to yield 71.4 mg of more material. The combined yield was 898.1 mg (94%) of **8a**: mp $183.5\text{--}185.5^\circ\text{C}$ dec; IR (KBr) 2080 (s), 1480 (m), 1430 (s), 1075 (s), 740 (s), 690 (s), 510 (s, br), 321 (w), 275 (w) cm^{-1} . Anal. Calcd for $\text{C}_{45}\text{H}_{37}\text{Cl}_2\text{OP}_2\text{Rh}\cdot\text{CHCl}_3$: C, 57.08; H, 3.91; Cl, 19.80. Found: C, 57.34; H, 4.11; Cl, 20.46.

$\text{RhCl}_2(p\text{-Me-styryl})(\text{CO})(\text{PPh}_3)_2$. This was prepared analogously to the styryl complex from 300 mg (0.3 mmol) of $\text{RhCl}(\text{PPh}_3)_3$ and 72 mg (0.4 mmol) of *p*-methylcinnamoyl chloride in 2 mL of chloroform. After 4 days at -10°C , the solution was poured into 50 mL of 1:1 pentane-ether to yield 247 mg (86%) of (*p*-methylstyryl)dichlorocarbonylbis(triphenylphosphine)rhodium: mp $180\text{--}185^\circ\text{C}$ dec; IR (KBr) 2079 (s), 1690 (m, br), 1582 (m), 1550 (m), 1480 (m), 1440 (s), 1090 (s), 990 (s), 810 (w), 750 (s), 700 (s), 520 (s) cm^{-1} . Anal. Calcd for $\text{C}_{46}\text{H}_{39}\text{Cl}_2\text{OP}_2\text{Rh}\cdot\text{CHCl}_3$: C, 60.71; H, 4.30; Cl, 15.20. Found: C, 59.93; H, 4.58; Cl, 15.56. Found: C, 59.64; H, 4.58; Cl, 15.28.

Decarbonylation Procedure. This general procedure was used for all acid chloride decarbonylations and for the control reactions. It is described for cinnamoyl chloride.

A reaction tube (or a flask with a stopcock side arm and condenser) was charged with $\text{RhCl}(\text{PPh}_3)_3$ (250 mg, 0.27 mmol) and 45 mg (0.28 mmol) of cinnamoyl chloride. The tube was evacuated, and then nitrogen was admitted rapidly; the process was repeated. Pure acetonitrile (or other solvent) (5 mL) was added by syringe; volatile acid chlorides were also introduced at this time. The pressure was reduced until the solvent boiled at room temperature. Then nitrogen was admitted rapidly. The degassing cycle was repeated, the contents of the tube were frozen at -78°C , and the tube was sealed and placed in an oil bath at 85°C . The reaction time was generally 24 h, at which time the tube was cooled to -10°C . The tube was opened, a VPC standard, in this case 20 μL decane, was introduced, and the solution was bulb-to-bulb distilled at 0.025-mm pressure. With use of prepared samples of authentic materials, less than 10% loss was observed in this distillation. The distillate was analyzed by VPC, and the volatiles were identified by comparison of retention times and mass spectra with authentic materials. The mass spectra (GCMS) agreed in position and intensity ($\pm 10\%$) with those of prepared samples. Styrene (0.028 mmol, 10.4%) was produced and determined by VPC peak-height comparisons with a sample of 0.027 mmol of styrene and 20 μL of decane.

The residue from the distillation was recrystallized from 2 mL of dichloroethane to yield 122 mg (65.5%) of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. This product was routinely identified by IR comparison with that of an authentic sample; the spectra agreed with respect to position and relative intensity for all absorptions.

The filtrate from the recrystallization was chromatographed on silica gel (J. T. Baker, 40–140 mesh) with use of acetone as eluant to remove residual rhodium compounds and acetone-methanol (1:1) to elute the phosphonium salts. After evaporation of the solvent, the salts were identified by IR and NMR comparisons to those of authentic samples. The yield of styryltriphenylphosphonium chloride in this experiment was 24.3 mg (22%).

For reactions with 3-methyl-2-butenoyl chloride, crotonyl chloride, and acryloyl chloride, reaction solutions were directly injected onto the VPC column, without bulb-to-bulb distillation. Table II gives analytical conditions and mass spectral data for observed and suspected reaction products.

Control Experiments. A. $\text{RhCl}(\text{PPh}_3)_3$ (50 mg, 0.054 mmol), 8 mg (0.054 mmol) of cinnamoyl chloride, 2 mL of dichloroethane, 12 μL (0.096 mmol) of β -chlorostyrene, and 20 μL of decane were heated at 85°C for 8 h. The usual workup showed 0.018 mmol (33%) of styrene, 91% recovery of β -chlorostyrene by comparison to the aliquot of the initial reaction mixture, $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (24.4 mg, 65%), and styryltriphenylphosphonium chloride (8.5 mg, 39%).

B. $\text{RhCl}(\text{PPh}_3)_3$ (50 mg, 0.054 mmol), 36.8 mg of styryltriphenylphosphonium chloride, 5 μL (0.054 mmol) of crotonyl chloride, and 1.5 mL of dichloroethane refluxed for 1 h. Analysis showed <1% 1-chloro-1-propene. Cooling to -10°C overnight gave 20.3 mg (55%) of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and 35.4 mg of a phosphonium salt: NMR δ 2.36 (br d, $J = 6$ Hz), 7.02 (dd, $J = 16.22$ Hz), 7.80 (m), 8.75 (dd, $J = 16.20$ Hz). Integration of the absorbance at δ 2.36 (propenyl) vs. 8.75 (styryl) gave 7.1 mg (31%) of 1-propenyltriphenylphosphonium chloride and 28.3 mg (77% recovery) of the styryl salt.

C. A reaction tube was charged with 100 mg (0.108 mmol) of $\text{RhCl}(\text{PPh}_3)_3$, 17 mg (0.108 mmol) of cinnamoyl chloride, 36 mg of 1.3:1

Table II

compd	column (temp, $^\circ\text{C}$)	<i>m/e</i> (rel intensity) ^b
1-chloropropene	A (60)	<i>a</i>
acetylene	F (80–180)	<i>a</i>
1-chlorohexene	A (90)	<i>a</i>
1-hexyne	A (85)	82 (42), 81 (10), 79 (9), 67 (100), 65 (10), 60 (8), 54 (16), 53 (15)
2-methyl-1-chloropropene	A (85)	<i>a</i>
isobutene	E (70)	56 (69), 55 (13), 41 (100), 40 (15), 39 (42)
styrene	B (120)	104 (100), 103 (49), 77 (38), 76 (23), 65 (9), 63 (16), 50 (20)
β -chlorostyrene	B (150)	<i>a</i>

^a Product not detected; a 1% yield was easily detectable.

^b From GCMS taken at 70 eV.

1-hexenyltriphenylphosphonium chloride:2-hexenyltriphenylphosphonium chloride, and 3 mL pure dichloroethane and heated to 85°C for 19 h. Analysis showed 32% styrene, <1% β -chlorostyrene, 52 mg (75%) of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, and 46.8 mg of a phosphonium salt: NMR δ 0.8–2.0 (m), 2.76 (m), 4.70 (dd, $J = 8, 15$ Hz), 5.30 (m), 5.80 (m), 7.04 (dd, $J = 16, 24$ Hz), 7.80 (m), 8.68 (dd, $J = 16, 20$ Hz). Integration of the aliphatic to aromatic protons for the isolated salt showed it to be 23.4 mg (56%) of styryl phosphonium chloride and 23.4 mg (65% recovery) of 1- and 2-hexenylphosphonium chloride, in a 1:2.5 vinyl:allyl ratio.

D. A reaction tube was charged with 100 mg (0.108 mmol) of $\text{RhCl}(\text{PPh}_3)_3$, 17 mg (0.1 mmol) of cinnamoyl chloride, 40 mg (0.108 mmol) of vinyltriphenylphosphonium bromide, and 3 mL of dichloroethane heated for 24 h at 85°C . Analysis gave 0.007 mmol (7%) of styrene, 51.6 mg (74%) of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, and 47.9 mg (109%) of styryltriphenylphosphonium chloride: NMR δ 6.96 (1 H, dd, $J = 16, 24$ Hz), 7.3–8.0 (20 H, m), 8.45 (1 H, dd, $J = 16, 20$ Hz). By NMR comparison to a known mixture, it was found that less than 10% of the phosphonium salt was vinyltriphenylphosphonium bromide.

E. A flask was charged with 200 mg (1.45 mmol) of β -chlorostyrene (*Z* 45%, *E* 55%; by VPC) and 400 mg (1.53 mmol) of triphenylphosphine; the mixture was refluxed under nitrogen for 24 h and analyzed by NMR: δ 6.24 (d, $J = 8$ Hz), 6.64 (d, $J = 8$ Hz), 6.64 (d, $J = 16$ Hz), 6.88 (d, $J = 16$ Hz), 7.1–8.0 (aromatic, m). The absorbances due to the styryl phosphonium salt at δ 6.98 and 8.76 were not observed. A known mixture showed that 10% yield of the phosphonium salt was readily detectable. In a similar experiment, 21 mg (0.12 mmol) of cinnamoyl chloride and 32 mg (0.12 mmol) of triphenylphosphine were heated in 2.5 mL of CDCl_3 for 72 h. The absorbances due to styryltriphenylphosphonium salt could not be detected by NMR studies.

F. β -Chlorostyrene (8.5 mg, 0.06 mmol), 0.054 mmol of $\text{RhCl}(\text{PPh}_3)_3$ or $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, and 2 mL of purified acetonitrile were refluxed for 24 h and then analyzed by TLC (silica gel, acetone-methanol, 5:1). The reaction solution showed no spot for phosphonium salt; a 1% yield was detectable.

G. $\text{RhCl}(\text{PPh}_3)_3$ (250 mg, 0.27 mmol), cinnamoyl chloride (44.8 mg, 0.27 mmol), in 1 mL of pure dichloroethane, and 4 mL more of dichloroethane were refluxed for 15 min, and then 200 μL (2.8 mmol) of 1-chloro-1-propene was added and the solution refluxed for 48 h. Workup gave 104 mg (0.15 mmol, 56%) of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, 0.044 mmol (16.5%) of styrene, and 36.1 mg (0.09 mmol) of styryltriphenylphosphonium chloride: NMR δ 7.05 (1 H, dd, $J = 17, 24$ Hz), 7.80 (20 H, m), 8.73 (1 H, dd, $J = 17, 20$ Hz). The methyl doublet at δ 2.36 for the propenyl phosphonium salt is readily observable in a prepared 10:1 molar mixture of styryl to propenyl phosphonium chlorides. This corresponds to less than 0.3% conversion of 1-chloro-1-propene to its salt.

H. Phenylacetylene (11 μL , 0.108 mmol), 0.108 mmol of $\text{RhCl}(\text{PPh}_3)_3$ or $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, and 1 mL of CDCl_3 were refluxed under nitrogen for 3 h; the NMR spectrum showed no styryl phosphonium salt resonances at δ 6.98 and 8.76. Thin-layer chromatography (silica gel, acetone-methanol, 6:1) of the reaction solution compared to a prepared solution of styryltriphenylphosphonium chloride showed that less than 1% of this salt was formed.

I. $\text{RhCl}(\text{PPh}_3)_3$ (250 mg, 0.27 mmol), 4 mL of purified dichloroethane, and 39.7 mg (0.27 mmol) of *trans*-2-heptenoyl chloride were stirred for 5 min to give an orange solution. Propyne (Matheson) (30 mg, 0.75 mmol) in 1 mL of dichloroethane was added, and the solution was refluxed for 2 h. Workup gave 137.6 mg (0.199 mmol), 74% of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, less than 1% of hexyne and 1-chloro-1-hexene, and

50 mg (0.131 mmol, 54.6%) of a mixture of 1- and 2-hexenyl phosphonium salts: NMR δ 0.76 (6 H, t, $J = 7$ Hz), 1.0–2.0 (10 H, m), 2.72 (2 H, m), 4.68 (2 H, dd, $J = 3, 7, 12$ Hz), 5.36 (1 H, m), 6.9–7.0 (1 H, m), 7.80 (31 H, m). The allyl:vinyl ratio of the phosphonium salts was 3.3:1. Comparison of this NMR to that of a 10:1 molar mixture of 1- and 2-hexenyl phosphonium salts and 1-propenylphosphonium chloride clearly shows the methyl doublet at δ 2.36 for the latter compound. Thus, less than 1% of the added propyne is converted to 1-propenyltriphenylphosphonium chloride.

J. A reaction tube is charged with 100 mg (0.1 mmol) of $\text{RhCl}(\text{PPh}_3)_3$, 17 mg (0.1 mmol) of cinnamoyl chloride, 100 μL (1 mmol) of 1-hexene, and 3 mL of purified dichloroethane and heated at 85 °C for 24 h. Workup gave 0.025 mmol (25%) of styrene, 63.3 mg (0.092 mmol, 92%) of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, and 20.6 mg (0.052 mmol, 52%) of styryltriphenylphosphonium chloride: NMR δ 7.09 (1 H, dd, $J = 17, 24$ Hz), 7.3–8.3 (20 H, m), 8.92 (1 H, dd, $J = 17, 20$ Hz). Addition of 0.02 mmol of a mixture of 1- and 2-hexenyltriphenylphosphonium chloride to the compound obtained above clearly shows the methyl triplet at δ 0.79 is due to the added salt. This means less than 2% of the hexene was converted to the hexenylphosphonium salts.

Decomposition of $\text{RhCl}_2(p\text{-methylstyryl})(\text{CO})(\text{PPh}_3)_2$. A solution of 50 mg (0.052 mmol) of the complex in 1 mL of dichloroethane was heated at 85 °C for 24 h in a sealed tube. The tube was opened, 20 μL of decane was added, and the solution was bulb-to-bulb distilled. The distillate was refluxed with 2 mL of 10% KOH and the aqueous layer acidified with concentrated HCl. Extraction of this solution with three 10-mL portions of ether, drying with Na_2SO_4 , and removal of the solvent gave 2.6 mg (31%) of *p*-methylcinnamic acid, identified by mass spectral comparison (70 eV) with an authentic sample; m/e (relative intensity): 162 (100), 161 (50), 147 (29), 146 (29), 117 (26), 116 (26), 115 (53), 92 (26). The original distillate, after base treatment, was analyzed by VPC (column B, 100 °C) to give a 31% yield of *p*-methylstyrene. A GCMS (70 mV) result was identical with that for an authentic sample; m/e (relative intensity): 118 (100), 117 (72), 115 (19), 103 (9), 91 (23), 77 (6), 65 (7), 63 (7). Recrystallization of the residue from the bulb-to-bulb distillation gave 14.7 mg (40.3%) of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. Column chromatography of the mother liquor from the recrystallization in the usual manner gave 7.0 mg (33%) of (*p*-methylstyryl)triphenylphosphonium chloride: NMR δ 2.37 (3 H, s), 6.97 (1 H, dd, $J = 16, 22$ Hz), 7.3–7.8 (19 H, m), 8.56 (1 H, dd, $J = 16, 20$ Hz).

After a similar experiment starting with **8a** in CDCl_3 was completed, the NMR spectrum after 12 h at 90 °C showed the doublet at δ 6.7 characteristic of cinnamoyl chloride. Addition of a few drops of methanol caused this peak to disappear and a new doublet, δ 6.4 ($J = 15$ Hz), characteristic of methyl cinnamate to appear. Parallel IR observations showed the disappearance of the acid chloride (1730 cm^{-1}) and appearance of the ester (1700 cm^{-1}) band.

Reaction of $\text{RhCl}_2(\text{styryl})(\text{CO})(\text{PPh}_3)_2$ with (*p*-Tolyl) $_3\text{P}$. A solution of 220 mg (0.27 mmol) of $\text{RhCl}_2(\text{styryl})(\text{CO})(\text{PPh}_3)_2$ and 82 mg (0.27 mmol) of tri-*p*-tolylphosphine (Alfa) in 5 mL of pure dichloroethane was refluxed for 2 h and bulb-to-bulb distilled. Styrene (0.034 mmol, 12.5%) was observed by VPC (column B, 110 °C). The residue from the distillation was chromatographed on silica gel. Elution with benzene gave 182 mg (92%) of a $\text{Rh}(\text{I})\text{-CO}$ product: IR (KBr) 1960 (s), 1480 (m), 1440 (s), 1260 (s), 1090 (s), 800 (2), 750 (s), 690 (s), 520 (s, br) cm^{-1} ; NMR δ 2.34 (s), 2.38 (s), 7.0–7.8 (m). Both IR and NMR spectra showed incorporation of the tolylphosphine. The two singlets, δ 2.34 and 2.38, could be due to mono- and disubstituted $\text{Rh}(\text{I})$ complexes. Integration of these singlets vs. the aromatic protons gave 44% incorporation. Elution with acetone-methanol (1:1) gave 60 mg (53.3%) of a phosphonium salt: NMR δ 2.53 (s), 7.14 (dd, $J = 16, 24$ Hz), 7.3–8.0 (m), 8.73 (dd, $J = 16, 20$ Hz); IR (KBr) 1595 (s), 1570 (m), 1480 (m), 1440 (s), 1110 (s), 1000 (m), 860 (m), 820 (m), 810 (m), 750 (s), 730 (s), 690 (s), 525 (s, br) cm^{-1} . Comparison of the integrations at δ 2.53 and 8.73 gave a value of 40% incorporation of $\text{P}(p\text{-tolyl})_3$. In a control experiment, styryltriphenylphosphonium chloride (150 mg, 0.375 mmol) and 114 mg (0.375 mmol) of tri-*p*-tolylphosphine were combined in 8 mL of dichloroethane, and the solution was refluxed under nitrogen for 4 h. Column chromatography in the usual manner gave 172 mg of a mixture of phosphonium salts: NMR δ 2.42 (s), 2.46 (s), 4.06 (d, $J = 4$ Hz), 7.12 (dd, $J = 17, 24$ Hz), 7.3–8.3 (m), 8.82 (dd, $J = 17, 20$ Hz). The absorbance at δ 4.06 is due to the diphosphonium salt of the solvent. With the use of integrations of the peaks at δ 8.82, 4.06, 2.42, and 2.46 a value of 6% phosphine exchange was calculated.

Decarbonylation of 3,3-Dimethylacryloyl Chloride in CD_3CN . A reaction tube was charged with 100 mg (0.108 mmol) of **1**, 11 μL (0.108 mmol) of 3,3-dimethylacryloyl chloride, and 2 mL of purified CD_3CN (Aldrich) and heated to 85 °C for 4 days. Pentene, 10 μL , was added. Vapor-phase chromatography (column E, 60 °C) showed 0.068 mmol (61%) of isobutene, which was 20%- d_1 by mass spectroscopy [m/e at 70

eV (relative intensity): 55 (34), 56 (100), 57 (25)] and was referenced to isobutene- d_0 . Collection of the yellow precipitate yielded 67.3 mg (90%) of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$: IR (KBr) 1960 (s), 1480 (m), 1440 (s), 1090 (s), 745 (s), 690 (s), 575 (s), 520 (s), 510 (s) cm^{-1} .

Spectroscopic Observations. A. The ^{31}P NMR spectrum of a solution of ca. 50 mg of **8a** in 1 mL of CDCl_3 after 30 min at 30 °C showed the following peaks (relative to $(\text{MeO})_3\text{PO}$): δ 13.55 (d, $J = 88$ Hz, **8a**), 22.06 (d, $J = 104$ Hz, **7a**), 25.10 (d, $J = 136$ Hz, **6a**). After heating for 4.5 h at 85 °C, only traces of the doublets centered at δ 22.06 and 25.10 (**7a** and **6a**) remained; the absorption at 13.55 due to **8a** was less intense. New absorptions were observed at δ 19.37 (s, **3a**), and 26.56 (d, $J = 103$ Hz, **4**); two unidentified absorptions were observed at δ 23.41 and 24.11.

B. The experiment above was repeated with added PPh_3 . After 30 min at 30 °C, the spectrum was the same as above with additional absorptions at δ -7.68 (s, PPh_3) and 23.95 (unidentified). After 4.5 h at 85 °C, the spectrum showed δ 13.55 (d, $J = 87$ Hz, **8a**), 19.40 (s, **3a**), 22.06 (d, $J = 107$ Hz, **7a**) 23.45 and 24.11 (unidentified), 26.66 (s, OPPh_3). An independent experiment showed that the spectrum of **4** is not observable under these conditions because of rapid exchange with free PPh_3 .

C. $\text{RhCl}(\text{PPh}_3)_3$, 0.12 mmol, was dissolved in 5 mL of pure CHCl_3 ; cinnamoyl chloride (0.12 mmol) was added, and the IR spectrum was scanned at various times. The first scan showed carbonyl absorptions (cm^{-1}) due to **2a** (1750 weak shoulder), **6a** and **7a** (1705 and 1680, strong), and **8a** (2080, weak). In the first 20 min, the absorption due to **2a** disappeared rapidly. The absorptions due to **6a** and **7a** gradually decreased and that due to **8a** increased; a weak absorption appeared at 1960 cm^{-1} . The solution was then heated at 80 °C and the IR recorded at intervals. The absorptions due to **6a**, **7a**, and **8a** gradually disappeared as a strong absorption for **4** (1960) grew over a period of 19 h.

KBr spectra of **8a** showed only 2080- cm^{-1} absorption in the carbonyl region. Solution spectra of **8a** in CHCl_3 showed **8a** (2080), **7a** (1680), and **6a** (1705). The absorption due to **8a** decreased as absorptions due to **7a** and **6a** increased over a period of 10 min to give a final spectrum of **8a** (strong), **7a** (medium), and **6a** (weak).

D. $\text{RhCl}(\text{PPh}_3)_3$, 0.12 mmol, was dissolved in 3 mL of CDCl_3 , and 0.12 mmol cinnamoyl chloride was added. The ^1H NMR spectrum was recorded with time. Cinnamoyl chloride (δ 6.67, $J = 16$ Hz) was barely discernable in the first spectrum (30 s), and an absorption assigned to **6a** and **7a** was apparent at δ 8.3 (d, $J = 15$ Hz). In the course of 30 min at 30 °C, the doublet at δ 8.3 was replaced by the absorption of **8a** [δ 5.6 (d, $J = 16$ Hz), δ 6.5 (m)]. The sample was then heated to 80 °C. In the course of 20 h, the absorptions due to **8a** were replaced by the absorptions of **3a** [δ 8.45 (dd, $J = 16, 19$ Hz), 6.90 (dd, $J = 16, 22$ Hz)] and styrene [δ 5.6 (d), 5.1 (d)].

Kinetic Procedure. Solutions of **8a** and **4** in dichloroethane followed Beer's law at 330 nm in the concentration range 10^{-4} – 2×10^{-5} M. A working graph relating the absorbance of solutions containing both **8a** and **4** to the absorbance of **8a** was constructed with use of the equation

$$A_{\text{total}} = A(1-x)[\mathbf{8a}] + x[\mathbf{4}]$$

At equivalent concentrations, the absorbance of **8a** at 330 nm is more than 10 times greater than that of **4**.

Auxiliary working graphs were prepared to correct for absorption at 330 nm due to added triphenylphosphine or phosphonium salt. Solutions of **8a** also obeyed Beer's law in the IR studies. Matched 0.5-mm NaCl cells were used, and the region 2200–2000 cm^{-1} was scanned slowly.

The general procedure for the kinetics is described for one representative run. Complex **8a** (18.9 mg, 0.02 mmol) was placed in a 25-mL flask with a stopcock side arm. To this was added 524 mg (2 mmol) of triphenylphosphine. After two vacuum-nitrogen cycles, 2.0 mL of purified dichloroethane was added by a pipet and the solution stirred and degassed. Samples were removed and placed into 6-mm Pyrex reaction tubes, prepared by careful washing, baking at 110 °C for several days, and flushing with nitrogen just before use. Septa were placed on the reaction tubes, and the contents were frozen at -78 °C; the tubes were sealed, warmed to room temperature, and placed into a stirred oil bath maintained at 84.7 ± 0.1 °C. After appropriate times, sample tubes were removed and quenched by freezing at -78 °C. The tubes are warmed to room temperature, and 50- μL aliquots were diluted to 5 mL with solvent for UV analysis. For IR analysis, the solutions were used directly.

The rate constant was obtained with use of a linear least-squares, iterative computer program supplied by Professor L. E. Friedrich of the University of Rochester. The equation for first-order kinetics was $(A_0 - A_\infty)/(A_0 - A_t) = e^{-kt}$, where A_0 and A_∞ were obtained from the working concentration-absorbance graph, described earlier. Alternatively, for long reaction times these values can be computed directly from the observed data; when this is done, the values obtained agree with the predicted values. The A_∞ values were not obtained experimentally because the $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ complex reacts slowly with solvent to form

Table III. Rate Constants for the Disappearance of 8a under Various Conditions^a

k_{obsd}	conditions
$(4.6 \pm 0.3) \times 10^{-5b}$	$[\text{8a}] : [\text{PPh}_3] = 50^d$
$(4.9 \pm 0.8) \times 10^{-5b}$	$[\text{8a}] : [\text{PPh}_3] = 50^d$
$(5.0 \pm 0.3) \times 10^{-5b}$	$[\text{8a}] : [\text{PPh}_3] = 100^d$
$(4.7 \pm 0.2) \times 10^{-5b}$	$[\text{8a}] : [\text{PPh}_3] = 100^e$
$(4.2 \pm 0.2) \times 10^{-3c}$	$[\text{8a}] : [\text{PPh}_3] : [\text{RP}^+\text{Ph}_3\text{Cl}^-]^f = 1:1:15^d$
$(3.0 \pm 0.4) \times 10^{-3c}$	$[\text{8a}] : [\text{PPh}_3] : [\text{RP}^+\text{Ph}_3\text{Cl}^-]^f = 1:1:20^d$

^a In 1,2-dichloroethane at 85 °C. ^b k_{obsd} values given in s^{-1} .
^c k_{obsd} values given in $\text{M}^{-1} \text{s}^{-1}$. ^d Followed by UV spectroscopy at 330 nm. ^e Followed by IR spectroscopy at 2070 cm^{-1} .
^f $[\text{RP}^+\text{Ph}_3\text{Cl}^-]$ = allyltriphenylphosphonium chloride.

an absorbing species. The equation $1/A = kt + 1/A_0$ was used to calculate second-order rate constants with $[\text{8a}]_0 = [\text{PPh}_3]_0$. The results are shown in Table III.

Initial Rates. A. A 25-mL two-neck flask with a side arm was charged with 18.9 mg (0.02 mmol) of complex **8a** and 262 mg (1.0 mmol) of triphenylphosphine. After the flask was evacuated and flushed with nitrogen, 2.0 mL of dichloroethane was added. A phosphine stock solution was prepared from 262 mg of triphenylphosphine and 2.0 mL of solvent. Reaction solutions were prepared by diluting aliquots of the rhodium solution with the phosphine stock solution in order to maintain a constant phosphine concentration. The solutions were placed in nitrogen-flushed reaction tubes, sealed, and heated at 84.7 ± 0.1 °C for 1.0 h. The UV absorbance was obtained, and the concentration was determined from the working graph. A plot of initial rate vs. $[\text{8a}]_0$ gave a slope of 1.

B. $\text{RhCl}_2(\text{styryl})(\text{CO})(\text{PPh}_3)_2$ (39.8 mg, 0.04 mmol) and 10.8 mg (0.04 mmol) of triphenylphosphine were placed in a flask with side arm. After a nitrogen-vacuum cycle, 4.0 mL of dichloroethane was added. Portions of this solution, 0.4 mL, were added to nitrogen-flushed flasks containing the following amounts of allyltriphenylphosphonium chloride: 27 mg (0.08 mmol), 20.3 mg (0.06 mmol), 13.5 mg (0.04 mmol), 6.7 mg (0.02 mmol), and no salt. After being degassed, the solutions were placed in the reaction tubes and heated for 1.0 h, as described in the previous experiment. A plot of initial rate vs. $[\text{RP}^+\text{Ph}_3\text{Cl}^-]_0$ gave a steep initial slope and a slope of -1 in the region $[\text{RP}^+\text{Ph}_3\text{Cl}^-]_0 = 0.05\text{--}0.2$ M.

C. The styryl complex (39.8 mg, 0.04 mmol) and 270 mg (0.8 mmol) of allyltriphenylphosphonium chloride were added to a flask, which had been evacuated and flushed with nitrogen. Dichloroethane, 4.0 mL, was admitted. A 0.4 M phosphine solution was prepared from 104.8 mg (0.4 mmol) of triphenylphosphine and 1 mL of solvent. Aliquots of the stock rhodium complex solution, 0.2 mL, were mixed with varying amounts of the phosphine solution to give the following phosphine concentrations: 0.01 M, 0.02 M, 0.04 M, and 0.05 M. These new solutions are degassed and reacted for 1 h at 84.7 ± 0.1 °C in the usual manner. The amount of reaction is determined by UV spectroscopy with use of the working graph. A plot of the initial rates vs. $[\text{PPh}_3]_0$ gave a slope of 1 in the region $[\text{PPh}_3]_0 = 0.01\text{--}0.04$ M.

Acknowledgment. We are grateful to Johnson-Matthey, Inc., for a generous loan of RhCl_3 and to the National Science Foundation (Grant No. NSF-7308798) for financial support. S.H.H. was the recipient of Sherman Clarke and Elon H. Hooker Fellowships from the University of Rochester. We appreciate stimulating discussions with R. H. Grubbs and C. P. Casey and thank D. K. Wedegaertner for the ^{31}P NMR experiments.

A Closed Three-Center Carbon-Hydrogen-Metal Interaction. A Neutron Diffraction Study of $\text{HFe}_4(\eta^2\text{-CH})(\text{CO})_{12}$

M. A. Beno,^{1a} Jack M. Williams,^{*1a} M. Tachikawa,^{1b} and E. L. Muetterties^{*1b}

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, Chemistry Department, Brookhaven National Laboratory, Upton, Long Island 11973, and the Department of Chemistry, University of California, Berkeley, California 94720. Received July 2, 1980

Abstract: The crystal and molecular structure of $\text{HFe}_4(\eta^2\text{-CH})(\text{CO})_{12}$ has been determined at 173 K by X-ray diffraction and at 26 K by neutron diffraction techniques. The complex crystallized in the monoclinic space group $P2_1/c$ [C_{2h}^5 , No. 14] with unit-cell dimensions of $a = 8.694$ (1) Å, $b = 32.920$ (6) Å, $c = 13.757$ (3) Å, $\beta = 112.95$ (1)°, and $V = 3625.7$ Å³ at 26 K with $Z = 8$. Full-matrix least-squares refinement of the neutron data gave $R(F_o) = 0.060$ and $R_w(F_o) = 0.079$ for all 5663 data. The "goodness-of-fit", with a data to parameter ratio of 10.1:1, was 1.876. The only significant structural differences in the two unique molecules of the asymmetric unit were the intermolecular contacts. The iron atoms were arranged in a "butterfly" conformation with a C-H group nestled between the wings. The most significant structural finding was a true C-H-Fe three-center interaction, containing both a very short Fe-H distance of 1.753 (4) Å (1.747 (4) Å, second molecule) and the longest reported C-H bond distance, 1.191 (4) Å (1.176 (4) Å). These results have been discussed in relation to the origin and nature of this C-H-Fe three-center interaction, the "activation" of C-H bonds in catalysis, and possible η^2 bonding of a C-H fragment at a metal surface.

Introduction

In some hydrogenation reactions of carbon monoxide, the sequence comprises dissociative CO chemisorption to give a surface carbide atom that is subsequently hydrogenated.² A question of substance in our research which compares the coordination chemistry of metal clusters and metal surfaces has been whether

a cluster carbide atom might exhibit reactivity toward hydrogen. Recently, the transformation of $\text{Fe}_4\text{C}(\text{CO})_{12}^{2-}$ to $\text{Fe}_4\text{C}(\text{CO})_{12}$ followed by hydrogen addition to give $\text{HFe}_4(\eta^2\text{-CH})(\text{CO})_{12}$ has incisively demonstrated the reactivity of exposed, low coordinate cluster carbide carbon atoms.³ We describe here the full molecular structure of the end product of these key transformations, $\text{HFe}_4(\eta^2\text{-CH})(\text{CO})_{12}$, and discuss the stereochemical significance

(1) (a) Argonne National Laboratory. (b) University of California.
 (2) See discussion by E. L. Muetterties and J. Stein, *Chem. Rev.*, **79**, 479 (1979), and references therein.

(3) M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, **102**, 4541 (1980).