was added. All crystalline material dissolved slowly forming an intensely orange-red solution. After addition was complete, the reaction mixture was allowed to warm to room temperature. As the temperature gradually increased, a dense, orange-yellow crystalline material precipitated. At room temperature, evolution of gas became pronounced. The dichloromethane was quickly decanted and the crystalline material was washed with two 30-ml aliquots of cool dichloromethane. A small portion of the product was dissolved in a minimum amount of warm dichloromethane and filtered. Coarse orange crystals formed slowly at refrigerator temperature.

When this product is not immediately isolated after its formation and is allowed to remain in the reaction mixture at room temperature, it redissolves with evolution of carbon monoxide. The resulting reaction mixture is a deep red, transparent solution.

Reaction of $Cl_2Sn[Fe(CO)_4SiCl_3]_2$ with $(C_2H_5)_4NCl$.—A mixture of 0.88 g of $Cl_2Sn[Fe(CO)_4SiCl_3]_2$ (1.1 mmol) and 0.18 g of $(C_2H_5)_4NCl$ (1.1 mmol) in 20 ml of dichloromethane was stirred at room temperature until evolution of gas ceased. The solution changed slowly from yellow to red and a total of 29.4 cm^3 of gas at 25° and 695 mm pressure (at STP 24.5 cm^3, 1.1 mmol) was collected. The solvent was removed at reduced pressure leaving a red, oily material which was washed with several aliquots of pentane. The transparent, red, oily residue was dissolved in 40 ml of dichloromethane. Hexane was added to the top of the dark red solution, resulting in two liquid layers. Over a period of 3–4 weeks the hexane diffused into the dichloromethane and some red crystals, surrounded by an oily material formed. These were isolated and dried. When this crystalline material was heated, it slowly turned yellow. At 145° some melting activity was observed and above 160° it decomposed. Its infrared spectrum showed bands at 2096 (m), 2045 (s), 2030 (ms), and 1938 cm^{-1} (w) (dichloromethane).

Anal. Calcd for $C_{15}H_{20}Cl_9Fe_2NO_7SnSi_2$: C, 19.3; H, 2.2; Cl, 34.2; N, 1.5. Found: C, 19.9–20.2; H, 3.4–3.5; Cl, 35.6–36.3; N, 2.0–2.5.

$C_6H_5Cl_2Sn(Cl_3SiFe)Fe(CO)_4$.—A solution of 42.7 g of $(C_2H_5)_3NH^+[Cl_3SiFe(CO)_4]^-$ (1.06 mol) in 50 ml of dichloromethane was slowly added to a magnetically stirred solution of 50 ml of dichloromethane containing 36.2 g of $C_2H_5SnCl_3$ (0.120 mol) at −78°. After addition was complete, the reaction mixture was allowed to warm to room temperature. The solvent was removed at reduced pressure, leaving a yellow, oily material. This was extracted with hexane and filtered. The clear, yellow filtrate was cooled to −78° to form a cream-colored, microcrystalline material.

Acknowledgment.—We thank the National Research Council of Canada for financial support and Drs. W. J. Jacobs and R. B. Stewart for carrying out some supplementary experiments.

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Kinetics and Mechanism of Oxidative Addition Reactions. II. Reactions of Benzyl and Allyl Halides with π-Cyclopentadienyl(triphenylphosphine)carbonylrhodium[1]

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The oxidative addition reactions of benzyl and allyl halides to $C_5H_5Rh(CO)P(C_6H_5)_3$ (**1**) yield products of the form $C_5H_5RhX(COR)P(C_6H_5)_3$. The reactions of the benzyl halides $C_6H_5CH_2X$ display simple kinetics, first order with respect to each reagent, and become progressively faster in the order $Cl \ll Br < I$. Reactions of allyl halides are more complex, but a mechanism is proposed to account for both the kinetics and the structures of the products. Investigation of a number of other electrophiles suggests that **1** will react cleanly only with reactive alkyl halides which lack other complicating functional groups.

Introduction

The oxidative additions of CH_3I and C_2H_5I to the compound $C_5H_5Rh(CO)P(C_6H_5)_3$ were shown[1] to involve a nucleophilic attack by the metal atom on the alkyl halide, the reactions being first order in each reagent. We have now extended this reaction to a number of other electrophiles. In this paper we describe these reactions and report the kinetics of the reactions with benzyl and allyl halides.

Experimental Section

Alkyl halides (Aldrich, Eastman, or BDH) were distilled under vacuum before use in kinetic runs. No impurities were detected by nmr. Dichloromethane was fractionated twice under nitrogen before use. All reactions were performed under an atmosphere of nitrogen. The preparation of $C_5H_5Rh(CO)P(C_6H_5)_3$ (**1**) has been described.[1] Products were prepared by one of two methods as follows.

Method A.—Compound **1** (100–200 mg) was dissolved with a stoichiometric amount of alkyl halide in 1–2 ml of CH_2Cl_2 and 1–2 ml of hexane. The mixture was allowed to stand at room temperature for a suitable time (Table I). Some of the products crystallized slowly from the reaction mixture, giving a useful preliminary purification. Recrystallization from CH_2Cl_2–hexane gave the product as red prisms or needles.

Method B.—Compound **1** (100–200 mg) was dissolved in CH_2Cl_2 (1–2 ml) with a large excess (1–2 ml) of alkyl halide. After a suitable reaction time the solvent and excess alkyl halide were removed under vacuum and the product was recrystallized as above.

Infrared data were obtained with a Perkin-Elmer Model 337 spectrophotometer, equipped with a Hewlett-Packard Model 7127A external recorder. Nmr spectra were recorded on Varian A56/60A and HA100 instruments and data are presented in Table II. Analytical data (Table I) were obtained by the microanalytical laboratory of this department.

Kinetics were based on the disappearance of the infrared carbonyl stretching band of **1** (at 1942 cm^{-1} in CH_2Cl_2).[1] All kinetics were carried out under pseudo-first-order conditions, using at least a tenfold excess of alkyl halide. Rate data are listed in Table III.

Results and Discussion

Compound **1** reacts with benzyl and allyl halides and

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[1] Part I: A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, **9**, 2658 (1970).

TABLE I
PREPARATIVE, INFRARED, AND ANALYTICAL DATA

No.	Compound	Method of prepn	Reaction time, hr	Yield, %	Mp,[a] °C	ν_{CO}, cm^{-1} (CH_2Cl_2)	% calcd C	% calcd H	% found C	% found H
2	$C_5H_5RhI(P(C_6H_5)_3)COCH_3$[b]	B			170–175	1666, 1643	...	...	...	...
3	$C_5H_5RhI(P(C_6H_5)_3)COC_2H_5$[b]	B			167–171	1660, 1654	...	...	...	...
4	$C_5H_5RhI(P(C_6H_5)_3)COCH_2C_6H_5 \cdot 0.5S$[c]	A	24	70	141–144	1659, 1653[d]	52.6	3.9	52.6	3.6
5	$C_5H_5RhBr(P(C_6H_5)_3)COCH_2C_6H_5 \cdot 0.5S$[c]	A	24	80	141–142	1659–1663[d]	56.3	4.2	56.4	4.4
6	$C_5H_5RhCl(P(C_6H_5)_3)COCH_2C_6H_5 \cdot S$[c,e]	B	1000	55	122–128	1662, 1654[d]	57.4	4.4	56.8	4.8
7	$C_5H_5RhI(P(C_6H_5)_3)COC_3H_5$	B	0.5	76	150–152	1660	51.8	4.0	51.8	4.1
8	$C_5H_5RhBr(P(C_6H_5)_3)COC_3H_5$[f]	B	2.5	72	148–153	1664, 1639 sh	56.0	4.4	55.8	4.4
9	$C_5H_5RhCl(P(C_6H_5)_3)COC_3H_5$[g]	B	100	69	133–138	1666, 1640 sh	60.6	4.7	60.5	4.7
10	$C_5H_5RhCl(P(C_6H_5)_3)COC_4H_7$	B	68	60	125–128	1670 sh, 1655	61.3	5.0	61.5	4.8
11	$[C_5H_5Rh(\pi\text{-}C_3H_5)P(C_6H_5)_3]^+Cl^- \cdot 0.5S$[c]	*h*	*h*	*h*	127–129	...	60.1	4.8	60.1	5.0
12	$C_5H_5RhBr(P(C_6H_5)_3)COCH_2CO_2C_2H_5 \cdot 0.5S$[c]	A	100	82	142–146	1731, 1661	51.3	4.2	51.2	4.1
13	$[C_5H_5RhBr(P(C_6H_5)_3)COCH_2]_2C_6H_4 \cdot S$[c]	A	100	80	123.5–124	1660	54.1	4.0	53.7	4.4
14	$C_5H_5RhCl(P(C_6H_5)_3)COCH_2CHCHC_6H_5$	A	150	50	136–139	1661	61.6	4.6	62.0	4.3

[a] Determined on a Kofler hot stage. All compounds decomposed at or near the melting point. [b] Data taken from ref 1. [c] S signifies solvent (CH_2Cl_2) of crystallization in **4**, **5**, **6**, **11**, **12**, and **13**. [d] The acyl CO bands of **4**, **5**, and **6** were broad, with two flattened maxima separated by about 5 cm^{-1}. [e] Cl analysis: calcd, 15.9%; found, 16.2%. [f] Br analysis: calcd, 13.8%; found, 13.9%. [g] Cl analysis: calcd, 6.6%; found, 6.6%. [h] See text.

TABLE II
^{1}H NMR SPECTRA[a]

No.	Compound	$\tau_{C_5H_5}$[b]	τ_{RhCOCH_2}	Shape	δ_{AB}, ppm	J_{AB}, Hz	Other peaks
1	$C_5H_5Rh(CO)P(C_6H_5)_3$	4.86					
2	$C_5H_5RhI(P(C_6H_5)_3)COCH_3$[c]	4.76	7.08	s (CH_3)			
3	$C_5H_5RhI(P(C_6H_5)_3)COC_2H_5$[c]	4.77	6.76	ABX_3	0.40	17	τ_{CH_3} 9.26 (t); $J_{H-C-C-H} = 7.4$ Hz
4	$C_5H_5RhI(P(C_6H_5)_3)COCH_2C_6H_5$[d]	4.88	5.42	AB	0.38	15.6	
5	$C_5H_5RhBr(P(C_6H_5)_3)COCH_2C_6H_5$[c,d]	4.94	5.49	AB	0.58	14.1	
6	$C_5H_5RhCl(P(C_6H_5)_3)COCH_2C_6H_5$[d]	4.95	5.58	AB	0.65	15.6	
7	$C_5H_5RhI(P(C_6H_5)_3)COC_3H_5$	4.81	6.07	*e*	*e*	*e*	$\tau_{CH=}$ 4.3 (m); $\tau_{=CH_2}$ 4.9 (m), 5.1 (m)
8	$C_5H_5RhBr(P(C_6H_5)_3)COC_3H_5$[c]	4.81	6.05	*e*	*e*	*e*	$\tau_{CH=}$ 4.25 (m); $\tau_{=CH_2}$ 4.9 (m), 5.11 (m)
9	$C_5H_5RhCl(P(C_6H_5)_3)COC_3H_5$	4.91	6.20	*e*	*e*	*e*	$\tau_{CH=}$ 4.3 (m); $\tau_{=CH_2}$ 5.0 (m), 5.2 (m)
10	$C_5H_5RhCl(P(C_6H_5)_3)COC_4H_7$	4.92	6.20	br, d	*e*	*e*	$\tau_{CH=CH}$ 4.73 (m); τ_{CH_3} 8.53 (br, d)
11	$[C_5H_5Rh(P(C_6H_5)_3)\text{-}\pi\text{-}C_3H_5]Cl$[d]	4.32					vbr peaks at 5.7 (d), 7.0 (s), 8.3 (t)
12	$C_5H_5RhBr(P(C_6H_5)_3)COCH_2CO_2C_2H_5$	4.71	5.82	AB	0.39	16.5	$\tau_{CH_2CH_3}$ 5.96 (q); $\tau_{CH_2CH_3}$ 8.84 (t); $J_{H-C-C-H} = 7.1$ Hz

[a] All compounds run in $CDCl_3$ (except **11**; CD_2Cl_2) at 30–40° with TMS reference. Compounds **2**, **4**, **6**, **11**, and **12** were run at 60 MHz only. The others were run at 100 MHz or both to check assignments. All compounds showed complex aromatic multiplets in the region τ 2.2–2.8. All peak intensities were checked by integration. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; v, very [b] The C_5H_5 peak of **1** appears as a triplet ($J_{H-P} = J_{H-Rh} = 0.6$ Hz). [f] In all other compounds the C_5H_5 peak is a double doublet, the larger coupling being due to phosphorus.[g] Compounds **3**, **5**, **7**, **8**, and **10** were examined in detail, and in each case the couplings were $J_{H-P} = 1.8$ Hz and $J_{H-Rh} = 0.7$ Hz. [c] The spectra of **2**, **3**, **5**, and **8** are reproduced in Figure 1. [d] Compounds **4**, **5**, **6**, and **11** showed peaks near τ 4.7 for the expected amount of CH_2Cl_2 of crystallization (Table I). [e] Not fully resolved; see text. [f] H. G. Shuster-Woldan and F. Basolo, *J. Amer. Chem. Soc.*, **88**, 1657 (1966). [g] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, in press.

TABLE III
RATES OF REACTIONS OF $C_5H_5Rh(CO)P(C_6H_5)_3$ WITH BENZYL HALIDES AND ALLYL IODIDE IN CH_2Cl_2 AT 25°[a]

Halide	[Halide], *M*	10^4k_{obsd}, sec^{-1}	10^4k_2, *M*$^{-1}$ sec^{-1}
$C_6H_5CH_2I$	0.166	7.37	44
	0.237	10.7	45
	0.402	16.0	40
$C_6H_5CH_2Br$	0.247	0.658	2.67
	0.579	1.57	2.71
	0.740	2.00	2.70
$C_6H_5CH_2Cl$	0.654	0.0038	0.0058
	1.829	0.0095	0.0052
C_3H_5I	0.217	7.3	34
	0.284	9.8	35
	0.426	13.3	31

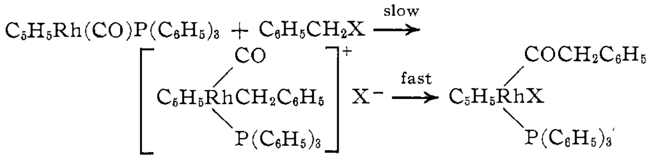
[a] All reactions performed under pseudo-first-order conditions. Under the same conditions the second-order rate constants k_2 for methyl and ethyl iodides were as follows: CH_3I, 35×10^{-4} M^{-1} sec^{-1}; C_2H_5I, 0.03×10^{-4} M^{-1} sec^{-1}.[1]

some related compounds in an oxidative addition process

$$C_5H_5Rh(CO)P(C_6H_5)_3 + RX \longrightarrow C_5H_5RhX(COR)P(C_6H_5)_3$$

The products of these reactions are air-stable, crystalline solids, which have been characterized by elemental analysis and infrared and nmr spectroscopy.

Benzyl Halides.—The benzyl halide reactions displayed simple kinetics, first order in both **1** and benzyl halide. Benzyl iodide reacts slightly faster than methyl iodide, while the bromide and chloride react progressively more slowly, as would be expected from normal leaving group behavior.[2] The mechanism is presumably analogous to that proposed for CH_3I and C_2H_5I[1]



$$C_5H_5Rh(CO)P(C_6H_5)_3 + C_6H_5CH_2X \xrightarrow{\text{slow}} \left[C_5H_5Rh(CO)(CH_2C_6H_5)P(C_6H_5)_3\right]^+ X^- \xrightarrow{\text{fast}} C_5H_5RhX(COCH_2C_6H_5)P(C_6H_5)_3$$

The very slow reaction of the chloride (nearly 10^4 times slower than the iodide) is probably due at least in part

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(2) E. S. Gould, "Structure and Mechanism in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 260.

to the poor stabilization of the high-energy chloride ion by the weakly polar solvent dichloromethane. In view of the retarding effects of chloride and of α-alkyl groups (C_2H_5I was found[1] to react about 10^3 times more slowly than CH_3I), it is not surprising that no reaction is observed between $((C_6H_5)_3P)_2Rh(CO)Cl$ and C_2H_5Cl[3] or between $C_5H_5Rh(CO)P(C_6H_5)_3$ and n-C_3H_7Cl.[4] The isolation of 55% of the benzyl chloride product **6** after 6 weeks of reaction illustrates the great stability of these products.

An interesting feature of the benzyl halide products is the magnetic nonequivalence of the methylene protons in the phenylacetyl groups. The rhodium atom in all these products is bonded to four different ligands, and provided that the coordinating atoms do not lie in a plane, there cannot be a plane of symmetry which includes the Rh–CO–CH_2R system. Each of the benzyl products **4**, **5**, and **6** showed a clear AB pattern for the methylene protons, illustrated for the bromide (**5**) in Figure 1b. A similar pattern is observed for the corresponding methylene protons of $C_5H_5RhBr(P(C_6H_5)_3)COCH_2CO_2C_2H_5$ (**12**) and $C_5H_5RhI(P(C_6H_5)_3)COCH_2CH_3$ (**3**); in the latter, the methylene protons couple equally to the methyl protons, which appear as a sharp triplet (Figure 1c). Magnetic nonequivalence of similar origin has been observed in other related compounds.[4,5]

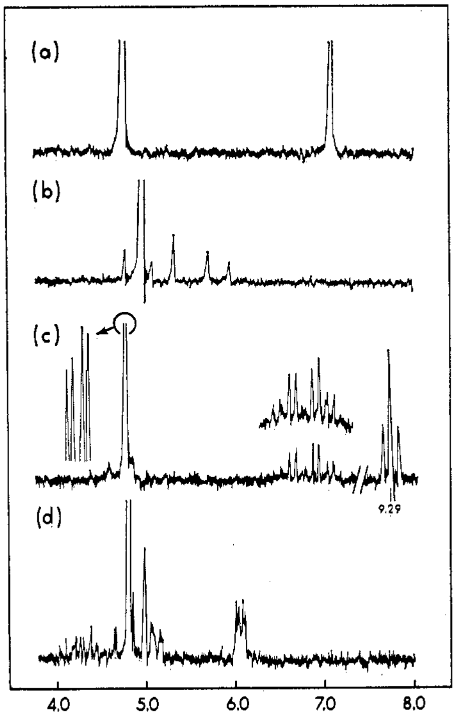

Figure 1.—The ^1H nmr spectra in $CDCl_3$: (a) $C_5H_5RhI(P(C_6H_5)_3)COCH_3$ (**2**), 60 MHz; (b) $C_6H_5RhBr(P(C_6H_5)_3)COCH_2C_6H_5$ (**5**), 60 MHz; (c) $C_5H_5RhI(P(C_6H_5)_3)COC_2H_5$ (**3**), 100 MHz; (d) $C_5H_5RhBr(P(C_6H_5)_3)COC_3H_5$ (**8**), 100 MHz.

The acyl carbonyl stretching bands in these compounds are broad and in some cases split into two separate bands. This phenomenon also arises from the low symmetry of the molecules and has been discussed previously in terms of a conformational effect.[1,4]

Allyl Halides.—The reactions of **1** with allyl halides are complicated by two possible factors—the isomerization of the allyl group and the formation of π-allyl complexes. Allyl iodide reacts to give a good yield of the "normal" product **7**, and the reaction shows simple second-order kinetics, the addition being slightly slower than that of CH_3I. During the reaction, however, a new band is observed at 2067 cm^{-1}, which is the expected position for the proposed intermediate $[C_5H_5Rh(\sigma\text{-}C_3H_5)(CO)P(C_6H_5)_3]^+I^-$.[1] This band appears very rapidly on mixing the reagents and then disappears at about the same rate as the starting material band at 1942 cm^{-1}. In the case of methyl iodide the nucleophilic attack on the halide was shown[1] to be rate determining

$$\begin{tikzcd}
C_5H_5Rh(CO)P(C_6H_5)_3 + CH_3I \arrow[r, "\text{slow}"] & {[C_5H_5RhCH_3(CO)P(C_6H_5)_3]^+I^-} \arrow[d, "\text{fast}"] \\
 & C_5H_5RhI(COCH_3)P(C_6H_5)_3
\end{tikzcd}$$

With allyl iodide, however, it appears that the first stage is a rapid equilibrium and the second is rate determining

$$\begin{tikzcd}
C_5H_5Rh(CO)P(C_6H_5)_3 + C_3H_5I \arrow[r, shift left, "K_{\text{eq}},\ \text{fast}"] & {[C_5H_5Rh(\sigma\text{-}C_3H_5)(CO)P(C_6H_5)_3]^+I^-} \arrow[l, shift left] \arrow[d, "\text{slow}", "k'"'] \\
 & C_5H_5RhI(COC_3H_5)P(C_6H_5)_3
\end{tikzcd}$$

If this is correct, the observed rate constant k_{obsd} is really a composite given by $k_{\text{obsd}} = k_{\text{eq}}k'[C_3H_5I]$, where K_{eq} is the equilibrium constant for the first stage and k' is the rate constant for the second stage.

Allyl bromide and allyl chloride also react with **1** to give good yields of the normal products **8** and **9**. In each case, however, a small amount of by-product is formed (*ca.* 2% for the bromide and 5% for the chloride). In each case this product crystallized from the reaction mixture as bright yellow needles, while both starting material and normal product are red. These compounds have no CO stretching bands and appear to be the π-allyl derivatives $[C_5H_5Rh(\pi\text{-}C_3H_5)P(C_6H_5)_3]^+X^-$, probably formed by elimination of CO from the ionic intermediate. This formulation is supported for the chloride by analysis and by its nmr spectrum, which showed the expected downfield shift of the C_5H_5 resonance due to the positive charge. The C_3H_5 protons gave broad signals. These compounds may be better prepared by reaction of the allyl halides with $C_5H_5Rh(C_2H_4)P(C_6H_5)_3$.[6]

The nmr spectra of the normal allyl products **7**, **8**, and **9** are closely similar to those reported for the related compounds $C_5H_5Mo(CO)_2(P(C_6H_5)_3)COC_3H_5$.[7] Some of the chemical shift and coupling parameters are almost identical. In the rhodium compounds reported here, however, there seem to be secondary effects which make the spectra highly complex (Figure 1d). The methylene protons $COCH_2$–, for example, are reported for the molybdenum compound as a doublet but appear in **8** as

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

(4) A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, **9**, 423 (1970).

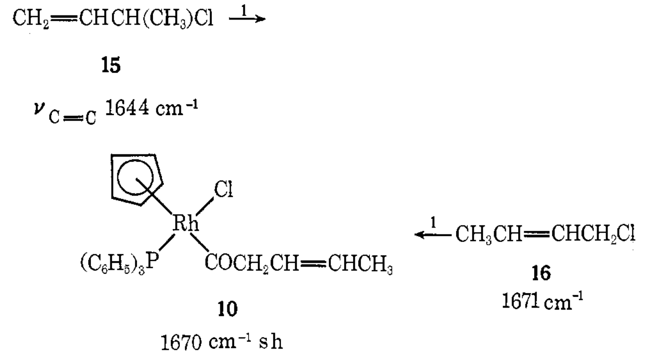
(5) H. Brunner and E. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **8**, 616 (1969); K. H. Pannell, *Chem. Commun.*, 1346 (1969); Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jap.*, **43**, 143 (1970).

(6) A. J. Oliver and W. A. G. Graham, unpublished results.

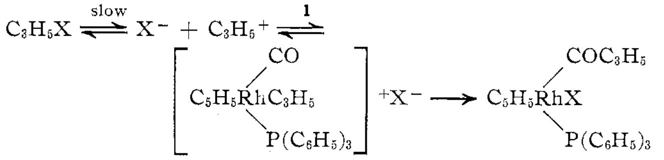
(7) P. J. Craig and M. Green, *J. Chem. Soc. A*, 157 (1969).

about 16 lines, not fully resolved.[8] Because of the complexity of the spectra we cannot present any definite analysis.

Compound **1** reacted with both α- and *trans*-γ-methylallyl chlorides. In each case the infrared and nmr spectra of the crude product revealed the presence of only one isomer **10**. The assignment of this structure to compound **10** is based on the following observations. (i) The nmr spectrum is, like those of the allyl compounds, similar to that of the molybdenum analog,[7] although rather more complex. (ii) The peak in the nmr spectrum at τ 6.28, which is assigned to the Rh–CO–C*H* system, integrates for 2H and shows a pattern similar to that of **9**, with no sign of coupling to a geminal methyl group. (iii) The acyl CO stretching band shows a shoulder at 1670 cm^{-1}, which is probably due to $\nu_{C=C}$ in an RCH=CHR′ system (compare **16**), in contrast to compounds **8** and **9** which have shoulders near 1640 cm^{-1} ($\nu_{C=C}$ in $RCH=CH_2$; compare **15**). The position of this presumed C=C band suggests that the double bond is trans,[9] but the nmr spectrum was not sufficiently clear to decide this question, and the assignment is only tentative.



The kinetics of the allyl bromide and chloride reactions were complex. The rate plots which we obtained suggested that the rate-determining step was SN1 dissociation of the allyl halide, with subsequent attack on the alkenyl cation by the rhodium atom



$$C_3H_5X \xrightleftharpoons{\text{slow}} X^- + C_3H_5^+ \xrightleftharpoons{\mathbf{1}} \left[C_5H_5Rh(CO)(C_3H_5)(P(C_6H_5)_3) \right]^+ X^- \longrightarrow C_5H_5RhX(COC_3H_5)(P(C_6H_5)_3)$$

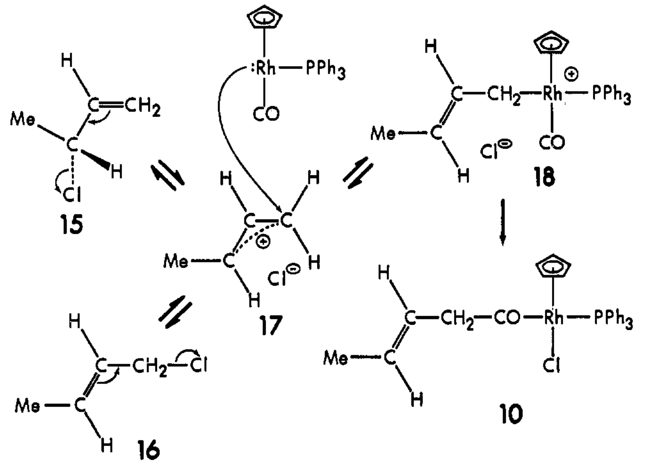
This SN1 mechanism is reasonable[10] in view of the moderate nucleophilicity of **1**[1] and is supported by two observations.

(i) The rates were independent of the concentration of **1** in the early stages of the reactions but tended toward first-order dependence later on, when this concentration became sufficiently low for halide ion to compete effectively.

(ii) During the reactions of **1** with the butenyl halides, the excess halides in solution were found to isomerize. This was detected by the growth of the expected C=C stretching band in the infrared spectrum and was confirmed by nmr. Compound **1** (8 mg) and α-methylallyl chloride (**15**, 660 mg, 400-fold excess) were sealed with 1 drop of TMS in an nmr tube and kept at 25°. By infrared analysis the half-life of the oxidative addition is about 21 hr under these conditions. The halide was found to isomerize steadily to crotyl chloride, showing about 30% reaction in 14 days. The reverse reaction (**16** → **15**) went about 5% in the same time. These rates are comparable with those observed for the zero-order oxidative additions to **1**. This type of rearrangement has been extensively studied in various solvents.[10]

The overall reactions of allyl bromide and allyl chloride were slower than those of the iodide by factors of the order of 10 and 10^2, respectively, and those of both α- and γ-methylallyl chlorides were slightly slower than the reactions of the unsubstituted C_3H_5Cl. We contemplate no further work on the bromide and chloride systems.

Stereochemistry of the Product $C_5H_5RhCl(P(C_6H_5)_3)$-COC_4H_7 (10).—The attack by the rhodium atom on the cations formed from the butenyl chlorides would be expected to occur predominantly at the primary end, in view of the marked steric selectivity observed for this type of nucleophile.[1] This implies that the intermediate **18** will be the γ-methyl compound regardless of whether the halide was **15** or **16**, which accounts for the fact that both **15** and **16** give the same product **10**. The suggested trans configuration of the double bond in **10** may also be determined at this point in the reaction. Both **15**[11] and **16** might be predicted to give rise mainly to the transoid carbonium ion **17**, which on attack at the primary end would yield the *trans*-but-2-enyl intermediate **18**. This in turn should give the *trans*-pent-3-enoyl product **10** provided that no isomerization occurs during the ligand migration, which has been shown to be the case for the related *cis*-but-2-enyl-molybdenum system.[7]



Further Reactions.—In order to investigate the preparative possibilities of this type of reaction we tried reactions of **1** in CH_2Cl_2 at room temperature with a number of compounds which are generally electrophilic. The results may be summarized as follows.

(i) $BrCH_2CO_2C_2H_5$, $ClCH_2CH=CHC_6H_5$, and *p*-$BrCH_2C_6H_4CH_2Br$ reacted smoothly and normally (although the product of the last was very unwilling to

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[8] The observed 16 lines could be due to an AB pattern (δ 0.03 ppm, J = 4.8 Hz) with major coupling to the vicinal proton (J_{CH_2-CH} = 6.8 Hz) and further small couplings to one or both of the terminal CH_2 protons (J = 0.5–1 Hz).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1962, p 32.

[10] R. H. deWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

[11] W. G. Young, S. H. Sharman, and S. Winstein, *J. Amer. Chem. Soc.*, **82**, 1376 (1960); D. Bethell and V. Gold, "Carbonium Ions—An Introduction," Academic Press, New York, N. Y., 1967, p 178; P. B. D. de la Mare, "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 51.

crystallize). The products are, respectively, $C_5H_5Rh\text{-}Br(COCH_2CO_2C_2H_5)P(C_6H_5)_3$ (**12**), $C_5H_5RhCl(CH_2\text{-}CH{=}CHC_6H_5)P(C_6H_5)_3$ (**14**), and $[C_5H_5RhBr(P(C_6H_5)_3)CH_2]_2C_6H_4$ (**13**). Analytical data are listed in Table I and the nmr spectrum of **12** is recorded in Table II.

(ii) $BrCH_2CO_2H$, ICH_2CO_2H, $ClCH_2COC_6H_5$, $BrCH_2COC_6H_5$, and $BrCH(CH_3)C_6H_5$ reacted readily but gave complex mixtures of products with many carbonyl stretching bands. The haloacetic acids reacted rapidly even at −78° and still gave complex mixtures.

(iii) IC_6H_5, $p\text{-}IC_6H_4NO_2$, propiolactone, $ICH_2CH_2CO_2H$, $BrCH_2C{\equiv}CH$, and $(CH_3)_4N^+Cl^-$ reacted, but the major products had no carbonyl stretching bands. The iodides in particular tended to give at least some of the dihalide $C_5H_5RhX_2P(C_6H_5)_3$.

(iv) $p\text{-}CH_3OSO_2C_6H_4CH_3$, propylene oxide, and $(CH_3CO)_2O$ showed no observable reaction in 1 week at room temperature.

Thus it appears that the reaction is applicable only to reactive halides which lack other complicating functional groups.

Conclusion

In part I of this series[1] we presented evidence (which we believe to be convincing) that the first step in the reactions of alkyl iodides with $C_5H_5Rh(CO)P(C_6H_5)_3$ and related compounds was a simple nucleophilic attack by the metal atom on the α carbon of the alkyl halide to displace halide ion. The reactions described in this paper support this conclusion. Since the first paper was submitted, evidence of inversion at carbon in a related reaction has been presented,[12] which again adds support to an SN2 mechanism.[13] Pearson and Muir, however, have shown[14] that in one case at least oxidative addition of alkyl halides can occur by a concerted three-center process. Thus it appears that two different mechanisms are possible. The actual pathway may be determined by the substrate.

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[12] J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970).

[13] A reviewer has suggested that we should mention the concerted and/or termolecular mechanism suggested by Douek and Wilkinson.[8] We find the arguments of these authors unconvincing and believe that a simple bimolecular displacment of halide ion operates in our system at least.

[14] R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970).

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Silyltricarbonyl-π-cyclopentadienylchromium, -molybdenum, and -tungsten[1,2]

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The new compounds $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$, $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$, and $H_3SiW(CO)_3(\pi\text{-}C_5H_5)$ were synthesized by the reaction of H_3SiBr with $KM'(CO)_3(\pi\text{-}C_5H_5)$ (where M′ = Cr, Mo, W). The thermal stability of the compounds was examined. The silicon–transition metal bond was cleaved at room temperature by water and hydrogen chloride and at slightly elevated temperatures by dimethylamine. Trimethylamine and dimethylamine formed adducts which were stable at room temperature.

The synthesis of $H_3CM'(CO)_3(\pi\text{-}C_5H_5)$ (where M′ = Cr, Mo, W) was reported in 1956 by Piper and Wilkinson.[3] Since that time, similar compounds containing the groups F_3C,[4] Cl_3Si,[5] and $(CH_3)_3Si$[6] have been characterized. The chief purpose of this present investigation, preliminary results of which have been reported previously,[7] was to study selected chemical properties of the parent molecules $H_3SiCr(CO)_3(\pi\text{-}C_5H_5)$, $H_3SiMo(CO)_3(\pi\text{-}C_5H_5)$, and $H_3SiW(CO)_3(\pi\text{-}C_5H_5)$, in order to obtain information concerning the nature of the silicon–transition metal linkage.

Results and Discussion

I. Synthesis of the Silicon–Transition Metal Bond.—The synthesis of a number of compounds containing silicon linked to chromium, molybdenum, or tungsten has been reported by several workers. Jetz and Graham[5] reported the synthesis of $Cl_3SiMo(CO)_3(\pi\text{-}C_5H_5)$ from trichlorosilane and bis(tricarbonyl-π-cyclopentadienylmolybdenum) as the first compound containing a silicon–molybdenum linkage. In 1967 Cardin, Keppie, Kingston, and Lappert[6] reported the syntheses of $(H_3C)_3SiMo(CO)_3(\pi\text{-}C_5H_5)$ and of $(H_3C)_3SiW(CO)_3(\pi\text{-}C_5H_5)$ in tetrahydrofuran from the appropriate complex metal hydride and $(H_3C)_3SiN(CH_3)_2$, *viz.*, $HMo(CO)_3(\pi\text{-}C_5H_5) + (H_3C)_3SiN(CH_3)_2 \rightarrow (H_3C)_3SiMo(CO)_3(\pi\text{-}C_5H_5) + HN(CH_3)_2$. Patil and Graham,[8] in a very comprehensive paper in which they reported several germanium, tin, and lead compounds containing the $M'(CO)_3(\pi\text{-}C_5H_5)^-$ anion (where M′ = Cr, Mo, W), mentioned briefly that the interaction of the complex anion with a silicon halide did not lead to the desired

[1] This report is based on portions of a dissertation submitted by P. J. R. to the Graduate College of the University of Oklahoma in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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