CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

The Reactions of Cyclopentadienyl(dimethylphenylphosphine)carbonylrhodium with Halogens and Organic Halides

BY A. J. OLIVER AND W. A. G. GRAHAM

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At low temperatures $C_5H_5Rh(CO)L$, **1** ($L = P(CH_3)_2C_6H_5$), reacts with Cl_2, Br_2, CH_3COBr, and CF_3COCl forming isolable $[C_5H_5Rh(CO)LX]^+X^-$ or $[C_5H_5Rh(CO)L(COR)]^+X^-$ which were converted to their more stable tetraphenylboron salts. At room temperature the ionic dihalides lose CO forming neutral $C_5H_5RhLX_2$. Alkyl halides (CH_3Cl, CH_3Br, CH_3I, C_3H_5Cl) react with **1** forming *acyl* derivatives $C_5H_5RhL(COR)X$ in a reaction thought to proceed *via* ionic $[C_5H_5Rh(CO)LR]^+X^-$.

Introduction

The reaction of metal carbonyls with halogens under suitable conditions often results in loss of one of the carbon monoxide ligands and its replacement by two halogen ligands. Such reactions constitute a well-known class designated by the term "oxidative elimination."[1-3] In some cases, an ionic halide forms as an intermediate which may or may not be isolable. The reaction is by no means limited to halogens, and a variety of compounds, including certain organic halides, undergo a similar reaction.[4,5] Only a few oxidative-elimination reactions have been carried out on $C_5H_5Rh(CO)_2$. Reactions with iodine and with perfluoroalkyl iodides[6] have been reported, and tetrahalides of germanium and tin afford products of the type $C_5H_5Rh(CO)XMX_3$.[7] The latter are analogous to compounds prepared from $C_5H_5Co(CO)_2$.[8]

It seemed reasonable to suppose that initial replacement of carbon monoxide by phosphine would increase the stability of Rh(III) products in such oxidation reactions. The formation of complexes $C_5H_5Rh(CO)PR_3$ has been reported for a variety of phosphines,[9] although there has been no study of the reactions of such compounds. We have chosen the previously unreported complex with phenyldimethylphosphine for a study of oxidative-elimination processes involving halogens and pseudohalides; this particular phosphine was selected so that the formation of any compound containing an asymmetric center at rhodium[10] could be monitored using the chemical shift separation of the two methyl resonances in the nmr spectrum.

Experimental Section

All reactions were carried out under a nitrogen atmosphere and solid products were handled with minimum exposure to the air. Pentane and hexane were dried over sodium or 9.5% sodium–lead alloy and dichloromethane was dried over anhydrous magnesium sulfate. Other solvents and reagents were used as obtained from commercial sources. Cyclopentadienyldicarbonylrhodium was prepared by a slight modification of the method of Fischer and Bittler;[11] a ratio of sodium cyclopentadienide to chlorodicarbonylrhodium dimer of 4:1 was used with no decrease in yield compared to higher ratios.

Microanalyses (Table I) were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Bonn, Germany, and by the microanalytical laboratory of this department. Infrared spectra were measured with a Perkin-Elmer 337 grating spectrometer and recorded in expanded form on a Hewlett-Packard 7127A recorder. Spectra were calibrated using a carbon monoxide gas cell for the terminal carbonyl region and a polystyrene film for acyl carbonyl spectra. Nmr measurements were made on Varian A56/60A and HA100 instruments.

Preparation of $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$.—Cyclopentadienyldicarbonylrhodium (1.27 g, 5.7 mmol) was dissolved in hexane (50 ml) and phenyldimethylphosphine (1.0 g, 7.2 mmol) was added. The mixture was stirred for 6 hr at room temperature, filtered, and cooled to −15°. Fine orange crystals of product slowly formed and were filtered off and dried under vacuum (yield 1.2 g, 63%).

Preparation of $[C_5H_5RhP(CH_3)_2C_6H_5(CO)Cl]^+Cl^-$.—A solution of $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ (0.33 g, 1.0 mmol) in 10 ml of dichloromethane was cooled to liquid nitrogen temperature and chlorine (0.07 g, 1.0 mmol) was distilled in. The mixture was slowly warmed to −78° and hexane (15 ml) was added to precipitate a bright yellow solid. The solution was decanted and the solid was washed twice with 10-ml portions of hexane, while maintaining the temperature close to −78°. After drying under high vacuum for several hours, the yield of product was 0.35 g (86%).

A similar procedure was used to prepare $[C_5H_5RhP(CH_3)_2C_6H_5(CO)Br]^+Br^-$; 24 hr was allowed for the reaction with bromine at −78°.

Reaction of the phosphine adduct with CH_3COBr and CF_3COCl in similar fashion afforded $[C_5H_5RhP(CH_3)_2C_5H_5(CO)(COCH_3)]^+Br^-$ and $[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+Cl^-$; these reactions were carried out at −23° for 12 hr, and during the work-up procedure the temperature was maintained near −23°.

Preparation of $[C_5H_5RhP(CH_3)_2C_6H_5(CO)Cl]^+[B(C_6H_5)_4]^-$.—The chloride $[C_5H_5RhP(CH_3)_2C_6H_5(CO)Cl]^+Cl^-$ (0.20 g, 0.49 mmol) was quickly dissolved in methanol (10 ml) and a solution of sodium tetraphenylboron (0.25 g, 0.73 mmol) in 5 ml of methanol was immediately added. The mixture was stirred for 30 min and the bright yellow precipitate which formed was filtered off. This was washed twice with 3-ml portions of methanol and once with 3 ml of pentane and dried under vacuum. The weight of the product was 0.27 g (80%).

The compounds $[C_5H_5RhP(CH_3)_2C_6H_5(CO)Br]^+[B(C_6H_5)_4]^-$,

(1) J. Lewis and S. B. Wild, *J. Chem. Soc., A*, 69 (1966).

(2) Other authors[3] describe reactions of this type as an oxidative addition to a coordinatively saturated complex, with accompanying loss of a neutral ligand.

(3) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **87**, 4008 (1965); *Advan. Organometal. Chem.*, **7**, 53 (1968).

(4) The reactions of allyl halides with $C_5H_5Co(CO)_2$ are particularly relevant to the present work: (a) E. O. Fischer and R. D. Fischer, *Z. Naturforsch.*, **16a**, 475 (1961); (b) R. F. Heck, *J. Org. Chem.*, **28**, 604 (1963).

(5) K. Noack, *J. Organometal. Chem.* (Amsterdam), **13**, 411 (1968).

(6) (a) R. B. King, *Inorg. Chem.*, **5**, 82 (1966); (b) J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4200 (1964).

(7) A. J. Oliver and W. A. G. Graham, unpublished work.

(8) R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 523 (1968).

(9) H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.*, **88**, 1657 (1966).

(10) M. R. Churchill, *Inorg. Chem.*, **4**, 1734 (1965).

(11) E. O. Fischer and K. Bittler, *Z. Naturforsch.*, **16b**, 225 (1961).

TABLE I

ANALYTICAL DATA, MELTING POINTS, COLORS, AND YIELDS

Compound	Mp, °C[a]	Color	% yield	Calcd % C	Calcd % H	Calcd % X	Calcd % P	Found % C	Found % H	Found % X	Found % P
$C_5H_5RhP(CH_3)_2C_6H_5(CO)$	78–80	Orange	63	50.32	4.83	...	...	50.21	4.83	...	...
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)Cl]^+Cl^-$	*b*	Yellow	86	...	...	...	...	...	...	...	...
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)Cl]^+B(C_6H_5)_4^-$	94–97 dec	Pale yellow	80	66.25	5.27	...	...	66.11	5.21	...	...
$C_5H_5RhP(CH_3)_2C_6H_5Cl_2$	245–248	Dark red	86	41.41	4.28	18.81	8.21	41.23	4.40	18.66	8.08
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)Br]^+Br^-$	95–97	Orange	98	34.04	3.26	32.35	...	33.96	3.53	32.51	...
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)Br]^+B(C_6H_5)_4^-$	87–92 dec	Yellow-orange	90	62.24	4.95	...	...	62.21	4.89	...	...
$C_5H_5RhP(CH_3)_2C_6H_5Br_2$	222–226 dec	Dark red	80	33.51	3.46	34.30	6.65	33.14	3.63	34.46	6.53
$C_5H_5RhP(CH_3)_2C_5H_5I_2$	204–206	Black	73	27.88	2.88	45.35	5.53	27.77	3.04	45.45	5.39
$C_5H_5RhP(CH_3)_2C_6H_5C_3F_7I$	123–125	Orange	59	31.92	2.68	...	...	31.76	2.91	...	...
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+Br^-$	*b*	Yellow	83	...	...	...	...	...	...	...	...
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+B(C_6H_5)_4^-$	98–100 dec	Yellow	70	68.98	5.64	...	...	68.77	5.77	...	...
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+Cl^-$	*b*	Pale yellow	86	...	...	...	...	...	...	...	...
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+B(C_6H_5)_4^-$	102–103 dec	White	80	64.02	4.84	...	...	63.96	4.85	...	...
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)Cl$	92–94	Dark red	48	46.84	4.98	9.22	4.16[c]	47.13	4.87	8.98	4.06[c]
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)CH_3]^+B(C_6H_5)_4^-$	130 dec	White	96	70.08	5.88	...	4.63	70.10	5.91	...	4.85
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)Br$	118–122	Dark red	51	41.99	4.46	18.62	3.73[c]	41.98	4.21	18.50	3.89[c]
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)I$	113–115	Dark red	71	37.84	4.02	26.65	6.51	36.40	4.04	27.32	6.52
$C_5H_5CoP(CH_3)_2C_6H_5(COCH_3)I$	98–100	Black	76	41.69	4.20	...	...	41.51	4.51	...	...
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_2CHCH_2)Cl$	109–112	Dark red	46	49.72	5.15	...	...	49.37	5.27	...	...
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(CH_2CHCH_2)]^+B(C_6H_5)_4^-$	106–108 dec	Pale yellow	91	70.90	5.95	...	...	70.73	6.37	...	...

[a] All melting points were determined using Kofler hot-stage apparatus. [b] Compound decomposes below room temperature. [c] Refers to O not P analysis.

$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+[B(C_6H_5)_4]^-$, and **$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+[B(C_6H_5)_4]^-$** were prepared by the procedure outlined above from the corresponding halide salts.

Preparation of $C_5H_5RhP(CH_3)_2C_6H_5Cl_2$.—The ionic halide $[C_5H_5RhP(CH_3)_2C_6H_5(CO)Cl]^+Cl^-$ (0.20 g, 0.49 mmol) was placed in 10 ml of dichloromethane and stirred for 6 hr. Hexane (20 ml) was added and the mixture was cooled to yield $C_5H_5RhP(CH_3)_2C_6H_5Cl_2$ (0.16 g, 86%).

The corresponding dibromide **$C_5H_5RhP(CH_3)_2C_6H_5Br_2$** was also prepared by this method from $[C_5H_5RhP(CH_3)_2C_6H_5(CO)Br]^+Br^-$; however, a reaction time of 3 days was necessary for complete conversion in this case.

Preparation of $C_5H_5RhP(CH_3)_2C_6H_5I_2$.—A sample of $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ (0.22 g, 0.66 mmol) was dissolved in 20 ml of dichloromethane and iodine (0.17 g, 0.66 mmol) was added. After 1 hr, the solution was concentrated to 5 ml, 10 ml of pentane was added, and the mixture was cooled to −10°. The fine black needles of product which formed were collected and dried (yield 0.27 g, 73%).

Preparation of $C_5H_5RhP(CH_3)_2C_6H_5C_3F_7I$.—Perfluoropropyl iodide (2.0 g, 6.8 mmol) was added to $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ (0.50 g, 1.5 mmol) dissolved in 10 ml of hexane and the mixture was allowed to stand for 24 hr. The orange microcrystalline precipitate was collected, washed with two 10-ml portions of hexane, and dried (yield 0.53 g, 59%).

Preparation of $C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)Cl$.—A sample of $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ (0.44 g, 1.3 mmol) was placed in a Carius tube and about 2 ml of methyl chloride was condensed into the tube. After sealing, the tube was left at room temperature for 4 days. Excess methyl chloride was removed under reduced pressure, and the product was collected and recrystallized twice from dichloromethane–pentane (yield 0.24 g, 48%).

Reactions with methyl bromide and allyl chloride were carried out by a similar procedure for a period of 24 hr; the products were **$C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)Br$** and **$C_5H_5RhP(CH_3)_2C_6H_5(COCH_2CHCH_2)Cl$**, respectively.

Preparation of $[C_5H_5RhP(CH_3)_2C_6H_5(CO)CH_3]^+[B(C_6H_5)_4]^-$.—A solution of sodium tetraphenylboron (0.25 g, 0.73 mmol) in 5 ml of methanol was added slowly to $C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)Cl$ (0.19 g, 0.5 mmol) in 10 ml of methanol. A pale orange precipitate formed immediately, but this quickly became white. After stirring for 1 hr the precipitate was filtered off and washed twice with 5-ml portions of methanol and once with 5 ml of pentane. After drying under vacuum, the yield of microcrystalline white product was 0.32 g (96%).

The same procedure was used to form the very pale yellow **$[C_5H_5RhP(CH_3)_2C_6H_5(CO)CH_2CHCH_2]^+[B(C_6H_5)_4]^-$** from **$C_5H_5RhP(CH_3)_2C_6H_5(COCH_2CHCH_2)Cl$**.

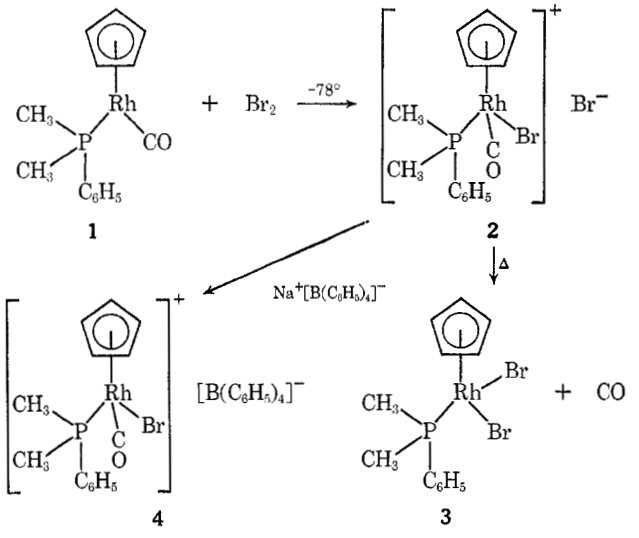
Preparation of $C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)I$.—Methyl iodide (0.34 g, 2.4 mmol) was added to a solution of $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ (0.33 g, 1.0 mmol) in 20 ml of methylene chloride, and the mixture was stirred for 1 hr. The solution was concentrated to about 1 ml and hexane was added very slowly to yield dark red crystals (0.34 g, 71%).

The cobalt derivative **$C_5H_5CoP(CH_3)_2C_6H_5(COCH_3)I$** was prepared by a similar method from $C_5H_5Co(CO)P(CH_3)_2C_6H_5$. The latter was formed by refluxing $C_5H_5Co(CO)_2$ with excess phosphine in hexane solution.

Discussion

Bromine reacts at low temperatures with $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ (1) to form an ionic derivative (2); on warming to room temperature and above, the ionic form loses carbon monoxide with formation of the neutral dibromide (3). The intermediate cation is

SCHEME I



stabilized by conversion to its tetraphenylboron salt (4) by rapid reaction in methanol.

Chlorine reacts similarly but the ionic derivative decomposes too rapidly to obtain an nmr spectrum. In dichloromethane solution at room temperature, infrared spectra indicate that the ionic chlorine derivative has a half-life of about 2 min. The corresponding ionic bromide decomposes more slowly as a solid or in solution. The tetraphenylboron salts of both cations are more stable, decomposing over a period of a few days at room temperature, but they are apparently stable if stored at −15°.

On warming, both bromide and chloride ionic derivatives give high yields of nonionic dihalides. The intermediate formation of ionic halogen compounds has been observed in the preparation of other nonionic halides.[3,4] Iodine and perfluoropropyl iodide presumably react in similar fashion to chlorine and bromine but only the neutral species $C_5H_5RhP(CH_3)_2C_6H_5I_2$ and $C_5H_5RhP(CH_3)_2C_6H_5C_3F_7I$ could be isolated. Similar replacement of carbon monoxide has been noted for cyclopentadienyldicarbonylrhodium.[6] Likewise $C_5H_5CoP(C_6H_5)_3I_2$ has been formed by carbonyl replacement from $C_5H_5Co(CO)P(C_6H_5)_3$.[6a] Closely related derivatives have also been prepared by reaction of pentamethylcyclopentadienylrhodium dihalide dimer with triphenylphosphine.[12]

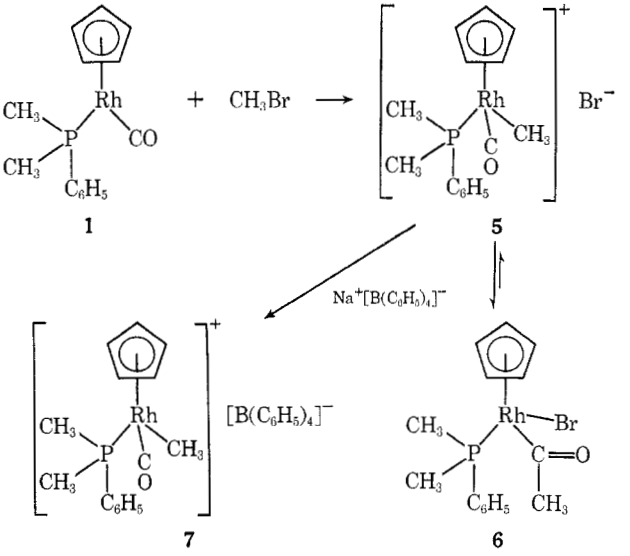
Acetyl bromide and trifluoroacetyl chloride react as pseudohalides to give ionic products at low temperature.

$$1 + CF_3COCl \longrightarrow [C_5H_5RhP(CH_3)_2C_6H_5(CO)COCF_3]^+Cl^-$$

These ionic compounds decompose a little below room temperature, forming complex mixtures. Formation of tetraphenylboron derivatives only slightly increases the stability of these compounds but does give an easy method of purification. A similar derivative could not be obtained from acetyl chloride although an infrared spectrum of the reaction mixture at −23° showed the presence of a small quantity of the desired product.

Most interesting is the reaction of $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ (1) with alkyl halides to yield the *acyl* complexes $C_5H_5RhP(CH_3)_2C_6H_5(COR)X$ (6). A kinetic study of this reaction is in progress.[13] We believe that the ionic intermediate $[C_5H_5Rh(CO)P(CH_3)_2C_6H_5R]^+X^-$ [14] (5) is initially formed with subsequent nucleophilic attack of the halide ion and simultaneous migration of the alkyl group to the carbonyl group. Such an intermediate must have some

SCHEME II



stability as shown by the existence of $[C_5H_5RhP(CH_3)_2C_6H_5(CO)CH_3]^+[B(C_6H_5)_4]^-$ (7). Indeed, the ease of formation of this compound could possibly be explained by the presence of an equilibrium between ionic and nonionic forms (5 and 6). Also, infrared spectral data indicate that reaction of the above tetraphenylboron salt with tetraphenylarsonium chloride re-forms the neutral acyl compound.

The existence of an ionic intermediate which is made neutral by halide ion attack is reminiscent of the reaction of allyl iodide with $C_5H_5Co(CO)_2$.[4b] In the latter reaction, however, both derivatives could be isolated.

A very limited number of alkyl halides undergo this reaction; the steric requirement of the alkyl group seems to be an important factor. An infrared study of small-scale reactions indicated that benzyl derivatives could also be formed, although no acyl carbonyl bands appeared from *n*-propyl chloride or *t*-butyl chloride reactions. From iodobenzene and trimethyltin iodide, only the nonionic diiodide could be obtained and this in good yield in the latter case. Preparation of the derivatives $C_5H_5CoP(C_6H_5)_3R_2$ by Yamazaki and

(12) J. W. Kang and P. M. Maitlis, *J. Am. Chem. Soc.*, **90**, 3259 (1968).

(13) A. J. Hart-Davis and W. A. G. Graham, to be submitted for publication. The similar reaction of analogous cobalt derivatives is also under study.

(14) Recent work on iridium systems in this laboratory yields such ionic products which are completely stable at room temperature.

TABLE II

INFRARED SPECTRA[a]

Compound	Carbonyl str freq, cm^{-1}			
$C_5H_5RhP(CH_3)_2C_6H_5(CO)$		1933[b]		
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)Cl]^+Cl^-$	2115 m, sh	2100 s		
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)Cl]^+B(C_6H_5)_4^-$		2105		
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)Br]^+Br^-$	2109 m, sh	2095 s		
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)Br]^+B(C_6H_5)_4^-$		2099		
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+Br^-$	2079 m, sh	2061 s	1710 m	1689 w, sh
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+B(C_6H_5)_4^-$	2089 w, sh	2066 s	1715 m	
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+Cl^-$		2081 s	1699 m	
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+B(C_6H_5)_4^-$		2090 s	1701 m	
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)Cl$			1668 m	1644 m
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)CH_3]^+B(C_6H_5)_4^-$		2068		
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)Br$			1665 m	1643 m
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)I$			1662 m	1643 m
$C_5H_5CoP(CH_3)_2C_6H_5(COCH_3)I$			1650 s	1629 m, sh
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_2CHCH_2)Cl$			1660 s	1638 m, sh
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)CH_2CHCH_2]^+B(C_6H_5)_4^-$		2065		

[a] In dichloromethane solution. [b] 1952 cm^{-1} in cyclohexane solution.

Hagihara[15] resulted in products only for R = CH_3 or $CH_2C_6H_5$, thus leading these authors to a similar conclusion regarding steric effects. For the rhodium compounds reported here this is consistent with the idea of initial formation of an Rh–R bond and subsequent migration of R to the carbonyl group. If the alkyl group were to bond directly to the CO carbon (*e.g.*, in a four-center mechanism), considerable easing of steric problems would be expected and the dependence of compound formation on the group R would be less easily accounted for.

It is known that attack of nucleophiles such as carbon monoxide, triphenylphosphine, or iodide ion[16] on $CH_3Mn(CO)_5$ causes methyl migration to yield an acyl derivative. Such attack is analogous to the attack of halide ions on the proposed cationic intermediate $C_5H_5RhP(CH_3)_2C_6H_5(CO)CH_3^+$. In the rhodium system, however, attack should be even more facile due to electrostatic attraction. Indeed, the similarity of these two systems may be taken further by considering the preparations of the methyl derivatives from methyl halides. Both involve attack of a nucleophilic species $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ or $Mn(CO)_5^-$ on carbon. In the former example the halide ion produced remains in solution for further reaction and in the latter the halide ion would be precipitated out, normally as the sodium salt. This mechanism can also be compared with the low-temperature bromination of iron carbonyl,[5] although in the present case compounds containing an acyl carbonyl are the more stable products.

Infrared Spectra.—The starting material $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$, formally a Rh(I) compound, has a relatively low carbonyl stretching frequency which is rather sensitive to solvent (Table II). All reactions reported here yield Rh(III) and thus in the compounds where carbon monoxide remains coordinated a typical increase in frequency is observed. When the carbon monoxide becomes placed in an acyl position, the frequency drops, as expected, but remains consistent with previously known examples[17,18] of rhodium–acyl moieties. Splitting of the carbonyl bands into two components is observed in most cases. This is attributable to the extremely asymmetric nature of these molecules.[19,20]

Nmr Spectra.—All spectra show at least three sets of resonances due to the phenyl and methyl protons of the phosphorus ligand and the π-cyclopentadienyl system attached to rhodium. Both ^{31}P and ^{103}Rh have 100% abundance in nuclei with spin $^1/_2$ and thus peaks in the spectra can be expected to exhibit a double doublet structure. The phenyl resonances show typical complex structures and thus only the chemical shift of the most intense line is reported for each compound in Table III. The methyl and cyclopentadienyl resonances do in most cases appear as the expected double doublet with phosphorus assumed to have the greater coupling constant in both cases. This seems very reasonable for the methyl groups directly attached to phosphorus but for the cyclopentadienyl system this interpretation is based on the results of Schuster-Woldan and Basolo.[9] Spectral measurements on the compound $C_5H_5RhP(C_6H_5)_3(CH_3)_2$[21] also agree in this relative assignment, although the magnitude of the reported couplings[21] is much larger. In the Rh(I) compound $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ the phosphorus and rhodium couplings to the cyclopentadienyl ring are of the same order with the result that a triplet is observed, just as in the compound $C_5H_5Rh(CO)P(C_6H_5)_3$.[9] Oxidation to Rh(III) increases the phosphorus coupling in much the same ways as it is increased by a phosphite ligand in the Rh(I) complex.[9] Little can be inferred from the small changes in $\tau_{C_5H_5}$ except to note the deshielding present in the ionic halides in chloroform solution.

The two methyl groups as noted above are expected

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TABLE III

^{1}H NMR SPECTRA[a]

Compound	Solvent	$\tau_{C_6H_5}$	$\tau_{C_5H_5}$	τ_X[b]	τ_{CH_3}	$\Delta\tau$[c]	$J_{P-C_5H_5}$	$J_{Rh-C_5H_5}$	J_{P-X}[b]	J_{Rh-X}[b]	J_{P-CH_3}	J_{Rh-CH_3}
$C_5H_5RhP(CH_3)_2C_6H_5(CO)$	$CDCl_3$	2.57	4.72	...	8.19	...	0.6	0.6	...	...	9.7	1.6
$C_5H_5RhP(CH_3)_2C_6H_5Cl_2$	$CDCl_3$	2.48	4.70	...	7.98	...	1.8	0.5	...	...	13.1	0.7
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)Br]^+Br^-$	$CDCl_3$	2.42	3.57	...	7.37	0.10	1.5	0.4	...	...	12.6	0[d]
$C_5H_5RhP(CH_3)_2C_6H_5Br_2$	$CDCl_3$	2.50	4.70	...	7.85	...	1.7	0.4	...	...	12.3	0.7
$C_5H_5RhP(CH_3)_2C_6H_5I_2$	$CDCl_3$	2.50	4.63	...	7.65	...	1.8	0[d]	...	...	11.6	0.7
$C_5H_5RhP(CH_3)_2C_6H_5C_8F_7I$[e]	$CDCl_3$	2.52	4.75	...	7.89	0.18	1.5	0	...	...	10.6	0
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+Br^-$[f]	$CDCl_3$	2.48	3.92	7.48	7.61	0.11	1.0	0.4	0	0	11.9	1.2
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+B(C_6H_5)_4^-$	CD_2Cl_2	3.07	4.68	7.58	8.13	0.07	1.1	0.4	0	0	11.6	1.1
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+Cl^-$[g]	$CDCl_3$	2.44	3.66	...	7.41	0.07	0	0	...	...	12.4	0
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+B(C_6H_5)_4^-$	CD_2Cl_2	3.10	4.87	...	8.27	0.04	1.2	0.4	...	...	11.5	1.1
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)Cl$	$CDCl_3$	2.20	4.84	7.18	8.17	0.17[h]	1.5	0.6	0.4	0	11.7	1.0
$[C_5H_5RhP(CH_3)_2C_6H_5(CO)CH_3]^+B(C_6H_5)_4^-$	CD_2Cl_2	3.08	4.85	9.18	8.35	0.04	1.3	0.4	5.1	2.2	11.2	1.1
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)Br$	$CDCl_3$	2.53	4.70	7.08	8.08	0.10[h]	1.6	0.6	0.4	0	11.4	1.1
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)I$	$CDCl_3$	2.55	4.75	7.02	7.99	0.02[h]	1.6	0.6	0	0	11.2	1.3
$C_5H_5RhP(CH_3)_2C_6H_5(COCH_2CHCH_2)Cl$	$CDCl_3$	2.56	4.82		8.18	0.16[i]	1.4	0.6	...	...	11.8	1.2
$[C_5H_5RhP(CH_3)_2C_6H_5(CH_2CHCH_2)(CO)]^+B(C_6H_5)_4^-$	$CDCl_3$	3.11	4.88		8.32	0.03	1.1	0.4	...	...	11.4	1.2

[a] Measured at 60 Mc at 40°. [b] X refers to protons of methyl groups not directly bonded to phosphorus. [c] $\Delta\tau$ refers to the chemical shift separation of the two phosphorus methyl groups due to the asymmetric center on rhodium. [d] A value of 0 normally indicated a coupling constant of <0.4 cps which could not be resolved by the spectrometer used. [e] This compound showed some broadening of the resonance lines presumably due to fluorine coupling. [f] Spectrum obtained at 0°. [g] Spectrum obtained at −20°; poorly resolved. [h] Spectrum also measured at 100 Mc in order to differentiate chemical shift separations from rhodium coupling. [i] Chemical shift separation dependent on temperature; at −40°, τ_{sepn} = 0.23.

to appear in the nmr spectrum as double doublets; however, the difference in magnetic environment of each group due to the asymmetry at rhodium, in most derivatives reported here, introduces a chemical shift separation ($\Delta\tau$). Thus a group of eight equally intense lines should be observed. This was experimentally verified but did introduce the problem of correctly interpreting separations as chemical shifts or coupling constants. Three representative spectra of $C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)X$, where X = Cl, Br, or I, were observed at 100 Mc as well as 60 Mc, thus providing unambiguous assignments in these cases and allowing fairly confident assignments to be made for the other compounds. Values of J_{P-CH_3} (Table III) are greater in the Rh(III) derivatives than in the Rh(I) starting material; this is in accord with the view that the effective electronegativity of Rh(III) is greater. Decreasing J_{P-CH_3} along the series of chloro-, bromo-, and iodorhodium(III) derivatives can similarly be rationalized.

Other resonances observed were attributed to acyl groups which appeared at chemical shifts expected for such groups,[18] and in the compound $[C_5H_5RhP(CH_3)_2C_6H_5(CO)CH_3]^+[B(C_6H_5)_4]^-$ a methyl group is directly attached to rhodium. The observed chemical shift and coupling constants compare very favorably with such compounds as $RhCl_2CH_3(CO)[P(C_6H_5)_3]_2$,[18] where τ_{CH_3} = 9.15, J_{P-H} = 5.0 cps, and J_{Rh-H} = 2.1 cps. The spectra exhibited by the allyl derivatives were insufficiently resolved for solution of the nmr parameters. Relative peak areas were found to be correct for all compounds. The only exception was the ionic σ-allyl complex, where integration was not possible, for the allyl protons showed their presence only by small deviations from a straight base line. The other protons in the molecule integrated correctly.

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