

Fig. 5.—A speculation as to the structure of the silver 9-methyladenine (or silver adenosine) precipitate.

On reconsideration, however, this result may not be so surprising. Equation 10 is not expected to apply accurately to the substances studied here. They are not structurally very similar to the nitrogen bases which were correlated by eq. 8 in the original paper.<sup>10</sup> The formation of a precipitate and the necessity of comparing different reaction types (eq. 3 and 4) is an additional complicating factor. However, eq. 10 might be approximately applicable. Figure 2 shows that at pH 7 and at any fixed  $r_b$  around 0.5, the equilibrium silver ion concentration for displacing an N-9 hydrogen is about  $10^{-4}$  of that for displacing an amino hydrogen. Take 10 for the  $pK_a$  of an N-9 NH bond; eq. 10 then predicts a  $pK_a$  of  $10 + (4/0.7) \approx 16$  for an amino hydrogen. There are no measurements available, but our chemical intuition is not repelled by this estimate.

In part, the driving force of the reactions studied here is the formation of polymeric species, either soluble or as precipitates, due to the presence of several basic

nitrogen atoms in a purine ring system. This is not a decisive factor however in making a displacement of an amino hydrogen possible. Simpson has observed proton displacement of amino hydrogens of purines and pyrimidines by the monofunctional methylmercury cation to give soluble complexes.<sup>11</sup> Eichorn and Clark<sup>12</sup> have presented evidence that mercuric ion can replace a proton from the amino group of adenosine on cytidine.

There remains the perplexing question of why the silver to purine ratio for amino binding (deoxyadenosine and 9-methyladenine) is 3:2 rather than 1:1. A number of speculations can be put forth but, in the absence of further evidence, it is not profitable to do so. However, we wish to record the suggestion displayed in Fig. 5. Here, two silvers are used in the way that hydrogens are used in the hydrogen-bonded base pairs of nucleic acids. This type of ring formation would provide an additional driving force for the displacement of the amino hydrogens. The uptake of an additional silver per base pair (by N-3 in the figure but it could just as well be N-7) is necessary in order to get an insoluble, polymeric species.

**Acknowledgment.**—This research has been supported by the Atomic Energy Commission (Contract AT-11-1-180) and the United States Public Health Service (GM-10991). R. J. is a Predoctoral Fellow of the Public Health Service and K. G. is the recipient of a summer undergraduate research grant from the California Foundation for Biochemical Research.

(11) R. B. Simpson, *J. Am. Chem. Soc.*, **86**, 2059 (1964).

(12) G. L. Eichorn and P. Clark, *ibid.*, **85**, 4020 (1963).

[CONTRIBUTION FROM THE RESEARCH CENTER OF THE HERCULES POWDER COMPANY, WILMINGTON, DELAWARE]

## Alkyliridium and Alkylrhodium Dihalocarbonylbis(trialkyl- or triarylphosphines)

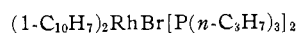
BY R. F. HECK

RECEIVED FEBRUARY 20, 1964

Rhodium and iridium halocarbonylbis(trialkyl- or triarylphosphines) react readily with active organic halides producing alkylrhodium and alkyliridium dihalocarbonylbis(trialkyl- or triarylphosphines) in good yields. Methylrhodium chloriodocarbonylbis(tri-*n*-butylphosphine) absorbs carbon monoxide at atmospheric pressure and 30° to form the corresponding acetyl derivative. Carbon tetrachloride oxidizes  $\text{RhCl}(\text{CO})[\text{P}(\text{C}_2\text{H}_5)_3]_2$  to  $\text{RhCl}_2(\text{CO})[\text{P}(\text{C}_2\text{H}_5)_3]_2$ . Bromine and iodine add to  $\text{RhCl}(\text{CO})[\text{P}(\text{n-C}_4\text{H}_9)_3]_2$  to form the mixed trihalides,  $\text{RhClBr}_2(\text{CO})[\text{P}(\text{n-C}_4\text{H}_9)_3]_2$  and  $\text{RhClI}_2(\text{CO})[\text{P}(\text{n-C}_4\text{H}_9)_3]_2$ , respectively.

### Introduction

Only two examples of  $\sigma$ -bonded organorhodium compounds have been reported. Chatt<sup>1</sup> in 1963 found that bis(1-naphthyl)rhodium bromobis(tri-*n*-propylphosphine) could be prepared in 3% yield by the reaction of 1-naphthylmagnesium bromide with rhodium tribromotris(tri-*n*-propylphosphine). A similar com-



pound was also prepared with diethylphenylphosphine in place of the tri-*n*-propylphosphine. No  $\sigma$ -bonded organoiridium compounds have been described in the literature although Chatt has referred to unpublished

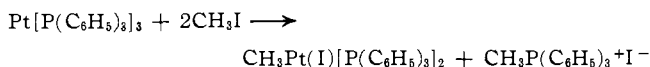
work on such compounds.<sup>1</sup> Both iridium and rhodium form stable  $\pi$ -bonded organometallic derivatives.

The report of Vaska<sup>2</sup> that  $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$  has a great tendency to add covalent molecules, such as halogens, halogen halides, and hydrogen, suggested that it might be possible to add alkyl halides to this complex also and form alkyliridium derivatives.<sup>2</sup> The addition of alkyl halides to electron-deficient metals or metal compounds is well known with nontransition metals but there are only a few reported examples of transition metals undergoing the reaction. Two pertinent examples are the platinum tris(triphenylphosphine) reaction with methyl iodide, giving methylplatinum iodobis(triphenylphosphine),<sup>3</sup> and the reaction

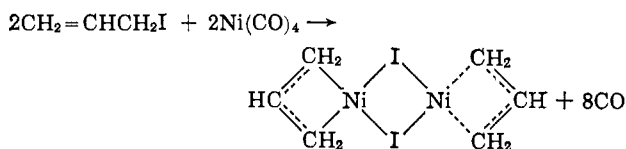
(2) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962); **83**, 2784 (1961).

(3) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

(1) J. Chatt and A. E. Underhill, *J. Chem. Soc.*, 2088 (1963).



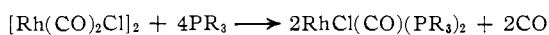
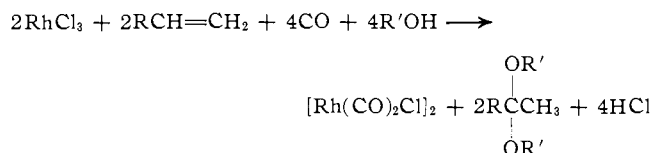
of nickel carbonyl with allyl iodide, forming  $\pi$ -allyl-nickel iodide dimer.<sup>4</sup> In this paper are reported the



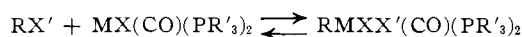
reactions of various alkyl halide derivatives with  $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$  and with the related rhodium derivatives,  $\text{RhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$ ,  $\text{RhI}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$ , and  $\text{RhCl}(\text{CO})[\text{P}(\text{C}_2\text{H}_5)_3]_2$ .

### Results

The iridium complex  $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$  was prepared by the method of Vaska<sup>2</sup> while the rhodium complexes,  $\text{RhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$ ,  $\text{RhI}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$ , and  $\text{RhCl}(\text{CO})[\text{P}(\text{C}_2\text{H}_5)_3]_2$ , were prepared by a modification of the usual method,<sup>5,6</sup> which eliminates the need to isolate  $[\text{RhCl}(\text{CO})_2]_2$  or  $[\text{RhI}(\text{CO})_2]_2$ . Methanol solutions of the appropriate rhodium trihalide were reduced with 1-pentene at 30–60° under a carbon monoxide atmosphere. Addition of 2 moles of the phosphine formed the bis(phosphine) derivative in high yield.



Solutions or slurries of  $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$  or of the related rhodium derivatives react readily with active organic halides in inert solvents, generally giving nicely crystalline, air-stable, pale yellow to red complexes. Successful reactions were carried out with methyl iodide, allyl iodide, benzyl chloride, and methyl iodoacetate. Less reactive halides such as ethyl iodide do not appear to give stable products or, at least, the products are unstable under the conditions required for their formation. When stable products were formed, analyses showed that alkylmetal dihalocarbonylbis(phosphines) were produced, apparently by a three-centered addition of the halide to the metal compound. A list of the compounds prepared appears



in Table I. Great difficulty has been experienced in obtaining good analyses of these derivatives although they all crystallized nicely and were apparently air-stable. The reasons for this difficulty may be that, because the reactions are reversible, starting material cannot be completely removed from the products, or

(4) E. O. Fischer and G. Bürger, *Chem. Ber.*, **94**, 2409 (1961).

(5) W. Hieber, H. Hensinger, and O. Vohler, *ibid.*, **90**, 2425 (1957).

(6) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

TABLE I

ALKYLIRIDIUM AND ALKYL RHODIUM DIHALOCARBONYLBIS(TRIALKYL- OR TRIARYL-PHOSPHINES) AND RELATED ACYL AND TRIHALO DERIVATIVES

Compound	Halide prepared from	M.p., °C.	Color	$\nu_{\text{CO}}$ , $\text{cm}^{-1}$	Formula	Analyses, %	
						Calcd.	Found
$\text{CH}_3\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	$\text{CH}_3\text{I}$	268–269 dec.	Pale yellow	2060 <sup>a</sup>	$\text{C}_{33}\text{H}_{38}\text{OClIrP}_2$	49.49	49.15
$\text{CH}_3\text{OCOCCH}_2\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	$\text{CH}_3\text{OCOCCH}_2\text{I}$	248–249	Pale yellow	2060, 1710 <sup>b</sup>	$\text{C}_{40}\text{H}_{38}\text{O}_3\text{ClIrP}_2$	49.02	49.10
$\text{CH}_2=\text{CHCH}_2\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	$\text{CH}_2=\text{CHCH}_2\text{I}$	155	Tan	2048 <sup>c</sup>	$\text{C}_{40}\text{H}_{38}\text{OClIrP}_2$	50.66	50.70
$\text{CH}_2=\text{CHCH}_2\text{IrCl}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$	$\text{CH}_2=\text{CHCH}_2\text{Cl}$	214	Tan	2048 <sup>c</sup>	$\text{C}_{40}\text{H}_{38}\text{OCl}_2\text{IrP}_2$	56.07	54.58
$\text{RhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	...	40–41	Yellow	1955 <sup>d</sup>	$\text{C}_{25}\text{H}_{54}\text{OClP}_2\text{Rh}$	52.58	52.56
$\text{CH}_3\text{RhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	$\text{CH}_3\text{I}$	85–88	Pale yellow	2045 <sup>e</sup>	$\text{C}_{28}\text{H}_{54}\text{OClP}_2\text{Rh}$	43.80	44.00
$\text{CH}_3\text{OCOCCH}_2\text{RhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	$\text{CH}_3\text{OCOCCH}_2\text{I}$	104–105	Yellow	2055, 1710 <sup>b</sup>	$\text{C}_{28}\text{H}_{58}\text{O}_3\text{ClP}_2\text{Rh}$	43.62	42.90
$\text{CH}_3\text{OCOCCH}_2\text{RhI}_2(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	$\text{CH}_3\text{OCOCCH}_2\text{I}$	90–92	Red	2055, 1695 <sup>a</sup>	$\text{C}_{28}\text{H}_{58}\text{O}_3\text{I}_2\text{P}_2\text{Rh}$	38.99	38.42
$\text{C}_6\text{H}_5\text{CH}_2\text{RhClBr}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	109–110.5	Pale yellow	...	$\text{C}_{32}\text{H}_{61}\text{OClBrP}_2\text{Rh}$	51.79	52.77
$\text{CH}_3\text{CORhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	...	82.2–85.0	Orange	2070, 1670 <sup>b</sup>	$\text{C}_{27}\text{H}_{57}\text{O}_2\text{ClP}_2\text{Rh}$	43.76	42.90
$\text{CH}_3\text{CORhI}_2(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	...	76–78	Orange	2070, 1665 <sup>a</sup>	$\text{C}_{27}\text{H}_{57}\text{O}_2\text{I}_2\text{P}_2\text{Rh}$	38.95	39.91
$\text{RhCl}_3(\text{CO})[\text{P}(n\text{-C}_2\text{H}_5)_3]_2$	$\text{CCl}_4$	143–144	Bright yellow	2078 <sup>c</sup>	$\text{C}_{13}\text{H}_{30}\text{OCl}_3\text{PRh}$	32.95	33.13
$\text{RhClBr}_2(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	$\text{Br}_2$	109–110	Orange	2060 <sup>b</sup>	$\text{C}_{25}\text{H}_{54}\text{OClBr}_2\text{P}_2\text{Rh}$	41.08	40.80
$\text{RhClI}_2(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	$\text{I}_2$	111.5–113	Red-brown	2055 <sup>c</sup>	$\text{C}_{25}\text{H}_{54}\text{OClI}_2\text{P}_2\text{Rh}$	36.40	36.30

<sup>a</sup> Chloroform solution. <sup>b</sup> Methylene chloride solution. <sup>c</sup> *Anal.* Calcd.: I, 17.8. Found: I, 17.2. <sup>d</sup> *Anal.* Calcd.: Cl, 22.5. Found: Cl, 22.3.

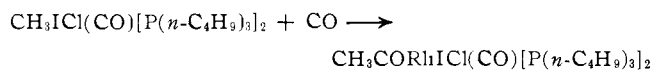
that some disproportionation may be occurring during recrystallization when two different halogens are attached to the metal. A third possible reaction which could be responsible for making purification difficult is that metal trihalocarbonylbis(phosphines) are being formed as by-products and that these are difficult to separate from the monoalkyls. This reaction has been observed in the addition of carbon tetrachloride and allyl iodide to  $\text{RhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$ . In the former example, only rhodium trichlorocarbonylbis(tri-*n*-butylphosphine) could be isolated, while with allyl iodide, an inseparable mixture of allyldihalo- and trihalorhodium derivatives was formed.

The reversibility of the alkyl halide addition reaction was clearly shown in the reaction of  $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$  with allyl chloride. The adduct was readily formed with an excess of allyl chloride present, as evidenced by the disappearance of the yellow color of the starting compound and the infrared spectrum changes. Colorless crystals of the product can be isolated by evaporation of the solution at 25° or below. Attempts to recrystallize the product, however, in the absence of allyl chloride led to the dissociation of the complex and the yellow starting material was gradually re-formed.

The course of the alkyl halide addition reactions is easily followed by observing the shift of the carbonyl stretching band in the infrared spectrum of the reacting mixtures. Generally the carbonyl absorption of the starting carbonyl is shifted to higher frequency by 50–100  $\text{cm}^{-1}$  by the formation of alkylmetal dihalocarbonylbis(phosphines).

The formation of rhodium trihalocarbonylbis(triphenylphosphines) by the halogenation of the corresponding rhodium monohalide was first reported by Vallarino.<sup>7</sup> Chlorine and iodine could both be added satisfactorily but bromine did not yield the expected product.<sup>7</sup> With the bis(tri-*n*-butylphosphine) derivative, bromine added as well as iodine did. No definite evidence for the presence of more than one isomer was found in the few examples studied although other isomers may have been present.

Methylrhodium iodocarbonylbis(tri-*n*-butylphosphine) in methylene chloride solution slowly absorbs about 1 mole of carbon monoxide at atmospheric pressure and 25° to form the corresponding acetyl derivative. The orange crystalline acetyl complex has an



acyl carbonyl absorption at 1670  $\text{cm}^{-1}$  as well as a coordinated carbonyl band at 2070  $\text{cm}^{-1}$ . The carbonylation reaction was accompanied by side reactions, and, as in the other examples mentioned above, difficulty was experienced in obtaining good analyses of the product. Methylrhodium diiodocarbonylbis(tri-*n*-butylphosphine) reacts with CO in the same manner. The methyliridium iodochlorocarbonylbis(triphenylphosphine), on the other hand, did not take up CO under the same conditions, although it probably would under higher pressures at higher temperatures.

The addition of covalent compounds to coordinately unsaturated metal compounds is probably a much

more common reaction than is generally supposed. We are currently investigating apparently related reactions of some cobalt(I) derivatives.

## Experimental

**Rhodium Chlorocarbonylbis(tri-*n*-butylphosphine).**—In a capable Pyrex bottle of about 150-ml. capacity were placed 3.0 g. of rhodium trichloride trihydrate (Fischer Scientific Co.) and a magnetic stirring bar. The bottle was capped with a self-sealing, rubber-lined, metal cap with holes in the metal for hypodermic injections. After the bottle was evacuated and pressured several times with carbon monoxide, 20 ml. of methanol and 3.0 ml. of 1-pentene were injected and the solution was stirred magnetically in a 60° bath. The carbon monoxide pressure was raised to 30 p.s.i. and kept at this pressure until the dark red reaction mixture had turned to a bright yellow. About 5 hr. was required. The solution was then cooled in ice water, vented to atmospheric pressure, and 8.0 ml. of tri-*n*-butylphosphine (Food Machinery and Chemical Corp.) was injected with venting of the carbon monoxide formed. After standing a few minutes, the solvent was evaporated at room temperature on the vacuum pump. The yellow viscous liquid residue obtained was dissolved in 40 ml. of pentane and decanted from a small amount of a colorless oil which did not dissolve. The pentane solution was evaporated to 15 ml. and, on cooling in Dry Ice, yellow prisms of the product separated. A second recrystallization from 15 ml. of pentane gave 5.45 g. of pure product, the properties and analyses of which are given in Table I.

The same method was applied for the preparation of  $\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ . The addition of a methanol solution of triphenylphosphine instead of tri-*n*-butylphosphine to the  $(\text{Rh}(\text{CO})_2\text{Cl})_2$  solution gave a yellow crystalline precipitate of the  $\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ . A single recrystallization of this material from chloroform-ethanol gave the pure product in high yield. Triethylphosphine gave  $\text{RhCl}(\text{CO})[\text{P}(\text{C}_2\text{H}_5)_3]_2$  by the same procedure as a yellow powder, m.p. 53–58° dec. Using rhodium triiodide (K & K Laboratories) in place of the trichloride led to the formation of the corresponding monoiodo derivative, also in good yield. The  $\text{RhI}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$  was obtained as a yellow-brown liquid,  $\nu_{\text{CO}}$  1970  $\text{cm}^{-1}$ , which could not be crystallized; and  $\text{RhI}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$ ,  $\nu_{\text{CO}}$  1985  $\text{cm}^{-1}$ , was obtained as yellow-brown needles, m.p. 177–180°.

The rhodium halocarbonyltriarylphosphine complexes seem to be air-stable, while the trialkylphosphine derivatives gradually darken in air. The latter can be kept indefinitely under nitrogen at 0°, however.

**General Method for the Preparation of Alkylrhodium and Alkyliridium Dihalocarbonylbis(trialkyl- or triarylphosphines).**—Best results have been obtained without solvent by mixing the iridium or rhodium halocarbonylbis(phosphine) derivative with a several mole excess of the alkyl halide and leaving the mixture under nitrogen at room temperature until the infrared spectrum of a small sample in methylene chloride solution shows that the reaction is complete. Carbon tetrachloride must not be used as a solvent, because it rapidly oxidizes any unreacted monohalide to the trihalide, giving a false indication of completion of the reaction. Generally, the reactions are complete in a few minutes to several hours in this procedure, depending upon the halide and upon the metal complex used. Leaving the reactions for much longer than necessary or heating them may cause the formation of trihalo derivatives at the expense of the alkyls. The triarylphosphine derivatives can usually be isolated merely by adding ether or pentane to the reaction mixture and filtering off the insoluble products. The trialkylphosphine derivatives are more soluble and the excess halide is best evaporated *in vacuo* first and then the product can be recrystallized from pentane, ether-pentane, or methanol. With the higher boiling halides which do not evaporate readily, it is best to use only a 2 or 3 mole excess of the halide with a little methylene chloride as solvent for the reaction. With solvent the reaction may be much slower but the product can be more easily isolated by crystallization after the evaporation of the solvent if a large excess of the halide is not present.

**Methyliridium Chloroiodocarbonylbis(triphenylphosphine).**—A mixture of 0.5 g. of  $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2$  and 3.0 ml. of methyl iodide in a capped nitrogen-filled tube was allowed to react for

(7) L. Vallarino, *J. Inorg. Nucl. Chem.*, **8**, 288 (1958).

about 15 hr. The addition of 5.0 ml. of pentane to the reaction mixture completed the precipitation of the product. The nearly colorless solid was separated by centrifuging and dried *in vacuo*. The compound was purified by dissolving it in 50 ml. of boiling chloroform, filtering, and concentrating to about 30 ml. and then adding 100 ml. of ether. The compound soon crystallized. Another crystallization by the same procedure gave 0.5 g. of very pale yellow needles with the properties given in Table I.

**Methylrhodium Chloriodocarbonylbis(tri-*n*-butylphosphine).**—A solution of 3.0 g. of  $\text{RhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$  in 3.0 ml. of methyl iodide under nitrogen in a capped tube was allowed to react for 15 hr. at room temperature. The excess methyl iodide was evaporated *in vacuo* and the residue was recrystallized first from pentane containing a little ether with cooling to  $-80^\circ$ , then from hexane with cooling to  $0^\circ$ . There was obtained 2.43 g. of pale yellow prisms. Another crystallization from pentane with cooling to  $-80^\circ$  gave the samples whose properties are reported in Table I.

**Acetylrhodium Chloriodocarbonylbis(tri-*n*-butylphosphine).**—A solution of 1.0 g. of  $\text{CH}_3\text{RhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$  in 10 ml. of purified tetrahydrofuran was stirred magnetically in a  $30^\circ$  bath under 1 atm. of carbon monoxide until gas absorption stopped. A total of 45.0 ml. of gas was absorbed in about 48 hr. and the reaction stopped. The solvent was then removed *in vacuo* at  $30^\circ$  and the dark residue was extracted with warm methanol. The methanol solution was decanted from a dark oil which separated first. On cooling, orange crystals separated from the methanol solution. Another crystallization from methanol and one from pentane gave about 0.2 g. of material with the properties listed in Table I. The reaction was also carried out under 30 p.s.i. of CO and in methylene chloride, instead of in tetrahydrofuran, but the gas volume change could not be accurately measured because of the high vapor pressure of the methylene chloride at  $30^\circ$ .

**Rhodium Trichlorocarbonylbis(triethylphosphine).**—A solution of 1.0 g. of  $\text{RhCl}(\text{CO})[\text{P}(\text{C}_2\text{H}_5)_3]_2$  in 5.0 ml. of carbon tetrachloride was allowed to react at room temperature for 15 hr. in a capped tube under nitrogen. The infrared spectrum showed that the starting compound had completely reacted by then. Evaporation of the unreacted carbon tetrachloride at room temperature left a partially crystalline residue. Addition of pentane caused complete crystallization of the residue. Then crystallization from ether with cooling to  $-80^\circ$  gave 0.2 g. of bright yellow prisms with the properties indicated in Table I.

Methyl trichloroacetate reacted with  $\text{RhCl}(\text{CO})[\text{P}(\text{C}_2\text{H}_5)_3]_2$  in a completely analogous way to give the same product. The fate of the methyl trichloroacetate or of the carbon tetrachloride in the above reaction was not determined.

**Rhodium Chlorodibromocarbonylbis(tri-*n*-butylphosphine).**—In a capped tube under nitrogen, 0.5 g. of  $\text{RhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$  was dissolved in 2.0 ml. of methylene chloride. A solution of 2.0 g. of bromine in 2 ml. of methylene chloride was injected. After reacting for 1 hr., the solvent was evaporated and pentane and a little ether were added to dissolve the product. On cooling to  $-80^\circ$ , the product crystallized. Recrystallization, three times from methanol, yielded 0.3 g. of orange prisms. The properties are given in Table I.

**Rhodium Chlorodiodocarbonylbis(tri-*n*-butylphosphine).**—A solution of 0.5 g. of  $\text{RhCl}(\text{CO})[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$  in 2 ml. of ether was treated with a solution of 0.3 g. of iodine in 2 ml. of ether under nitrogen. After standing overnight, the solvent was removed *in vacuo* and the product was recrystallized three times from an ether-pentane solution with cooling to  $-80^\circ$ . There was obtained 0.48 g. of red-brown crystals with the properties shown in Table I.

**Infrared Spectra.**—All infrared spectra were taken on a Perkin-Elmer Model 237B Grating Infracord. Each spectrum was calibrated with a polystyrene film and the readings reported should therefore be accurate to  $\pm 5.0 \text{ cm.}^{-1}$ .

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

## Synthetic and Electron Spin Resonance Studies of Six-Coordinate Complexes Related by Electron-Transfer Reactions

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RECEIVED MARCH 30, 1964

A new series of six-coordinate complexes of the general type  $[\text{MS}_z\text{C}_6\text{R}_6]^z$  with  $\text{R} = \text{CF}_3$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ,  $z = 0, -1, -2$ ) and  $\text{R} = \text{CN}$  ( $\text{M} = \text{Cr}, \text{V}$ ,  $z = -2$ ;  $\text{M} = \text{Cr}$ ;  $z = -3$ ) has been prepared. These complexes are similar to related bis complexes<sup>1-4</sup> in that they contain metals stabilized in several different oxidation states and complexes of given R and M can be interconverted by simple oxidation-reduction reactions. The syntheses of all compounds are described in detail, and chemical stabilities are discussed in terms of polarographic half-wave potentials. The results of magnetic susceptibility, electron spin resonance, and infrared studies are discussed. Electron spin resonance results show the presence of a strong trigonal component in the octahedral ligand field in complexes with a doublet ground state, and are not in agreement with the conventional  $d_0^1$  or  $(a_1^*)^1$  ground state. Probable electronic structures of these complexes are discussed.

### Introduction

In a continuing series of investigations being carried out in these laboratories, the synthesis and characterization of a large number of four-coordinate complexes of the transition elements in which the metal is coordinated only by sulfur have been achieved.<sup>1-4</sup> These complexes are of the general formulation  $[\text{MS}_4\text{C}_4\text{R}_4]^z$  in which the metal is coordinated by the bidentate *cis*-1,2-disubstituted ethylene-1,2-dithiolato group  $\text{R}_2\text{C}_2\text{S}_2$ , in which  $\text{R} = \text{CF}_3, \text{CN}, \text{C}_6\text{H}_5$ . One of the

most significant results of these investigations is the discovery that these planar complexes undergo reversible and unusually facile electron-transfer reactions which have permitted the synthesis of a wide variety of complexes with total charge  $z = 0, -1, -2$ . These complexes have been investigated by several physical methods including electron spin resonance and the probable electronic structures of several complexes with  $z = -1, -2$  have been discussed.<sup>2-4</sup>

The existence of electron-transfer reactions in the four-coordinate series of complexes suggested that a similar set of reactions might exist among six-coordinate tris complexes of the type  $[\text{MS}_6\text{C}_6\text{R}_6]^z$ . The recent synthesis of  $[\text{MoS}_6\text{C}_6(\text{CF}_3)_6]$  by King<sup>5</sup> is especially pertinent in view of the early isolation in the

(1) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963).

(2) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 3049 (1963).

(4) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

(5) R. B. King, *ibid.*, **2**, 641 (1963).