

these assumptions for the experimental reagent concentrations are given in the fourth column of Table III.

The experimental results of the initial rate studies are shown in the third column of Table III. These results are in good agreement with those expected on the basis of mechanism 5 if $\text{Co}_2(\text{CO})_7\text{Ph}_2\text{C}_2$ accumulates (fourth column) and in very poor agreement with the requirements of any of the other interpretations (fifth and sixth columns). Therefore, it is concluded that the mechanism of reaction 1 is that given by eq 5.

Because the values for k_1 shown in Table II are obtained by extrapolation, they are not highly accurate; the evaluation at 30° is rendered more inaccurate by the fact that the faster kinetic runs gave relatively severely curved pseudo-first-order rate plots. The temperature dependence given yields estimates for $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ of $16 \pm 2 \text{ kcal mol}^{-1}$ and $-14 \pm 7 \text{ eu}$, respectively. In contrast, the activation parameters reported for CO exchange are $\Delta H_{\text{ex}}^\ddagger = 23 \pm 2 \text{ kcal mol}^{-1}$ and $\Delta S_{\text{ex}}^\ddagger = 13 \pm 4 \text{ eu}$. Since mechanism 5 suggests that k_1 should also be the rate constant for CO exchange and hence that the same activation parameters should be obtained in both studies, the poor agreement is somewhat disconcerting.

Moreover, the disagreement is too great to be reasonably ascribed solely to experimental error. This point is perhaps best appreciated by a consideration of the rate constants themselves. Over the temperature range $+5$ to -20° , two different reports^{7,8} have given consistent values for the first-order rate constant for CO exchange, while, as noted above, the values for k_1 shown in Table II are in good agreement with the result of earlier studies³ of reaction 1. Nevertheless, extrapolation of the CO exchange results to 20° gives an

estimate of $23 \times 10^{-8} \text{ sec}^{-1}$ for the value of k_1 at this temperature.

This apparent discrepancy between the results of the CO-exchange studies and those of the alkyne-substitution studies can be given a plausible explanation. It need only be supposed that *dicobalt heptacarbonyl* also undergoes CO exchange, so that, on the average, more than one molecule of carbon monoxide is exchanged for every event of CO dissociation giving dicobalt heptacarbonyl. Independent evidence exists for the occurrence of reactions 4 (*vide supra*), and these constitute a mechanism of the necessary type if the forward reaction of (4b) is presumed to be sufficiently rapid. (Since the rate of tetracobalt dodecacarbonyl production is proportional to the *equilibrium* constant for (4b) this proposal does not conflict with the observed characteristics of reaction 3. On the other hand, the hypothesis that the rate-determining step of (1) is the reaction of the alkyne with $\text{Co}_2(\text{CO})_6$ can be excluded, since this leads to the prediction that α is proportional to the square of the carbon monoxide concentration.)

That the temperature dependence of k_1 leads to a negative value of $\Delta S_1^\ddagger$ is unexpected. However, in view of the uncertainty associated with this value, the unknown role of the dicobalt octacarbonyl isomeric equilibrium in contributing to this value, and the absence of evidence on the structure (or structures) of dicobalt heptacarbonyl, speculation on this result is unwarranted.

Acknowledgment.—Support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO COMPANY, ST. LOUIS, MISSOURI 63166

Tertiary Phosphine Complexes of Rhodium(I) and Rhodium(III) Chlorides

By G. M. INTILLE

Received June 8, 1971

The most complete series of tertiary phosphine complexes of rhodium yet reported has been prepared. Depending on the particular phosphine and the method of preparation, several different types of complexes may be formed. These include, $\text{RhCl}_3(\text{PR}_3)_3$, $\text{RhCl}(\text{PR}_3)_3$, $\text{RhHCl}_2(\text{PR}_3)_3$, $\text{RhH}_2\text{Cl}(\text{PR}_3)_3$, $\text{RhHCl}_2(\text{PR}_3)_2$, $[\text{RhCl}_2(\text{PR}_3)_2]_2$, $\text{RhClCO}(\text{PR}_3)_2$, $\text{RhCl}_3\text{CO}(\text{PR}_3)_2$, and $\text{RhHCl}_2\text{CO}(\text{PR}_3)_2$. The chemistry involved in the preparation and interconversion of each of these types or classes of complexes is discussed. Their properties, proof of structure, and factors affecting their relative stabilities are also given.

Introduction

A large amount of work has been reported on tertiary phosphine-group VIII transition metal complexes, especially those of triphenylphosphine.¹ The catalytic activity of this type of compound is well known,^{2,3} and they have recently become the object of a great deal of interest by industry particularly with respect to their

use as selective homogeneous catalysts. Because of this the preparation of a series of tertiary phosphine-rhodium chloride complexes was undertaken in the hope that subtle changes could be made in the properties of the compounds while still retaining the same overall features throughout the series. The reaction of rhodium halides with various phosphines, however, results in many different types of complexes, in varying yields, depending on conditions and the properties of the particular phosphine. Although several investigators, most notably Chatt and Shaw, have reported studies

(1) W. P. Griffith, "The Chemistry of Rarer Platinum Metals," Macmillan, New York, N. Y., 1961, and references therein.

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

(3) D. Evans, J. Osborn, and G. Wilkinson, *ibid.*, A, 3133 (1968).

TABLE I
ELEMENTAL ANALYSES

Compd	% calcd				% found			
	C	H	P	Cl	C	H	P	Cl
<i>mer</i> -RhCl ₃ (PMe ₃) ₃	24.70	6.22	21.23	24.31	24.57	6.05	21.10	24.40
<i>mer</i> -RhCl ₃ (PEt ₃) ₃	38.35	8.04	16.48	18.86	38.34	7.90	16.62	18.72
<i>mer</i> -RhCl ₃ (P(<i>n</i> -Pr) ₃) ₃	47.00	9.20	13.46	15.41	46.97	9.20	13.35	...
<i>mer</i> -RhCl ₃ (P(<i>n</i> -Bu) ₃) ₃	52.97	10.00	11.38	13.03	53.07	9.97	...	13.02
<i>mer</i> -RhCl ₃ (P(<i>n</i> -Oct) ₃) ₃	65.45	11.67	7.03	8.05	65.61	11.53	7.12	...
<i>mer</i> -RhCl ₃ (P(<i>i</i> -Pr) ₃) ₃	47.00	9.20	13.46	15.41	46.88	9.35	13.33	15.49
<i>mer</i> -RhCl ₃ (P(<i>i</i> -Bu) ₃) ₃	52.97	10.00	11.35	13.03	52.92	10.15	11.26	...
<i>mer</i> -RhCl ₃ (P(<i>c</i> -Hx) ₃) ₃	61.73	9.49	8.84	10.12	61.75	9.40	8.99	10.13
<i>mer</i> -RhCl ₃ (PBz ₃) ₃	67.41	5.65	8.27	9.47	67.57	5.55	8.51	9.21
<i>mer</i> -RhCl ₃ (PMe ₂ Ph) ₃	46.21	5.33	14.89	17.05	46.12	5.35	...	...
<i>mer</i> -RhCl ₃ (PEt ₂ Ph) ₃	50.90	6.40	13.12	15.02	50.78	6.55	...	...
<i>mer</i> -RhCl ₃ (PMePh ₂) ₃	57.83	4.85	11.47	13.13	57.85	4.72	...	...
<i>mer</i> -RhCl ₃ (PEtPh ₂) ₃	59.20	5.32	10.90	12.48	58.95	5.02	...	...
<i>fac</i> -RhCl ₃ (PMe ₃) ₃	24.70	6.22	21.23	24.31	24.61	6.48	20.91	24.37
<i>fac</i> -RhCl ₃ (PEt ₃) ₃	38.35	8.04	16.48	18.86	38.01	8.28	16.56	...
<i>fac</i> -RhCl ₃ (PMe ₂ Ph) ₃	46.21	5.33	14.89	17.05	46.37	5.05	...	...
RhCl(PMe ₃) ₃	29.48	7.42	25.34	9.67	29.58	7.08	25.37	9.78
RhCl(PEt ₃) ₃	43.86	9.20	18.85	7.19	43.74	9.25	18.93	6.96
RhCl(P(<i>n</i> -Pr) ₃) ₃	52.38	10.25	15.00	5.72	52.49	10.22	...	5.88
RhCl(P(<i>i</i> -Pr) ₃) ₃	52.38	10.25	15.00	5.72	52.52	10.03	15.19	5.97
RhCl(PMe ₂ Ph) ₃	52.14	6.01	16.80	6.41	52.44	5.89	...	6.65
β -RhHCl ₂ (PMe ₃) ₃	26.81	7.00	23.05	17.59	26.62	7.27	22.91	17.65
β -RhCl ₂ (PEt ₃) ₃	40.84	8.76	17.59	13.39	40.69	8.65	17.59	13.18
α -RhHCl ₂ (PMe ₂ Ph) ₃	48.91	5.81	15.76	12.03	48.84	5.68	...	11.79
β -RhHCl ₂ (PMe ₂ Ph) ₃	48.91	5.81	15.76	12.03	48.60	5.68	...	11.80
α -RhHCl ₂ (PEtPh ₂) ₃	61.70	5.67	11.36	8.67	61.78	5.55	...	...
β -RhHCl ₂ (PEtPh ₂) ₃	61.70	5.67	11.36	8.67	61.56	5.57	...	...
RhHCl ₂ (P(<i>i</i> -Pr) ₃) ₂	43.64	8.75	12.50	14.31	43.65	8.77	12.41	14.39
Rh ₂ Cl ₆ (PMe ₃) ₄	19.93	5.02	17.13	29.42	19.78	5.24	17.35	29.25
Rh ₂ Cl ₆ (PEt ₃) ₄	32.34	6.78	13.90	23.86	32.35	5.75	13.75	...
Rh ₂ Cl ₆ (P(<i>n</i> -Pr) ₃) ₄	40.81	7.99	11.69	20.07	41.05	8.06	...	...
Rh ₂ Cl ₆ (P(<i>n</i> -Bu) ₃) ₄	46.95	8.86	10.09	17.32	46.72	8.68	...	...
Rh ₂ Cl ₆ (P(<i>n</i> -Pent) ₃) ₄	51.61	9.53	8.87	15.23	51.47	9.80	...	...
Rh ₂ Cl ₆ (P(<i>c</i> -Hx) ₃) ₄	56.14	8.63	8.04	13.81	56.92	8.91	...	...
Rh ₂ Cl ₆ (PBz ₃) ₄	61.66	5.17	7.57	13.00	61.71	5.29	...	...
Rh ₂ Cl ₆ (PMe ₂ Ph) ₄	39.57	4.56	12.75	21.90	39.28	4.84	...	...
RhClCO(PMe ₃) ₂	26.39	5.69	19.44	11.13	26.44	5.89	19.33	11.47
RhClCO(PEt ₃) ₂	36.89	7.74	15.85	9.07	36.57	7.45	15.63	9.24
RhCl ₃ CO(PEt ₃) ₂	31.22	6.55	13.42	23.04	30.91	6.47	13.22	21.98
RhClCO(P(<i>n</i> -Pr) ₃) ₂	46.87	8.69	12.72	7.28	46.68	8.81	...	7.17
RhCl ₃ CO(P(<i>n</i> -Pr) ₃) ₂	40.91	7.59	11.10	19.06	41.19	7.61	...	18.80
RhClCO(P(<i>n</i> -Bu) ₃) ₂	54.31	6.56	11.20	6.41	54.49	6.26	...	6.14
RhCl ₃ CO(P(<i>n</i> -Bu) ₃) ₂	48.17	5.81	9.93	17.05	48.38	6.11	...	17.38
RhClCO(P(<i>i</i> -Pr) ₃) ₂	46.87	8.69	12.72	7.28	46.51	8.71	13.02	7.10
RhCl ₃ CO(P(<i>i</i> -Pr) ₃) ₂	40.91	7.59	11.10	19.06	41.26	8.07	10.97	18.86
RhClCO(P(<i>c</i> -Hx) ₃) ₂	61.10	9.14	8.51	4.87	61.40	9.49	...	...
RhCl ₃ CO(P(<i>c</i> -Hx) ₃) ₂	55.67	8.33	7.76	13.32	55.85	8.56	...	...
RhClCO(PBz ₃) ₂	66.63	5.46	7.99	4.57	66.62	5.70	...	...
RhCl ₃ CO(PBz ₃) ₂	61.04	5.00	7.32	12.57	61.13	5.31	...	...
RhClCO(PMe ₂ Ph) ₂	46.12	5.00	13.99	8.00	45.90	5.02	...	...
RhCl ₃ CO(PMe ₂ Ph) ₂	39.75	4.31	12.06	20.70	39.41	4.41	...	...
RhClCO(PEt ₂ Ph) ₂	50.57	6.06	12.41	7.10	50.51	6.04	...	...
RhCl ₃ CO(PEt ₂ Ph) ₂	44.27	5.30	10.87	18.66	44.05	5.42	...	...
RhClCO(PEtPh ₂) ₂	58.55	5.08	10.41	5.95	58.40	4.82	...	...
RhCl ₃ CO(PEtPh ₂) ₂	52.31	4.54	9.30	15.97	51.99	4.21	...	...

of particular rhodium-phosphine complexes,⁴⁻¹⁷ most have dealt with only one or two of the various types of compounds or dealt with only a limited number of dif-

ferent phosphines or have overlooked minor side products. In this work an attempt was made to isolate and characterize as many of these products as possible in order to explain why various tertiary phosphines behave so differently and to clarify the chemistry involved in the interconversion of the various types of complexes. In total, in addition to improving on some preparations which have previously been reported, 38 previously unknown compounds were synthesized.

Experimental Section

Reagents.—Tertiary phosphines were obtained from Strem Chemicals Inc., Danvers, Mass., and were used as received without further purification. Rhodium chloride trihydrate was obtained from Engelhard Industries, Newark, N. J. All other solvents and reagents were commercially available and were of reagent grade or better. Solvents in general were deaerated

- (4) J. Chatt and B. L. Shaw, *J. Chem. Soc. A*, 1437 (1966).
- (5) J. Chatt, N. P. Johnson, and B. L. Shaw, *ibid.*, 2508 (1964).
- (6) A. J. Deeming and B. L. Shaw, *ibid.*, A, 579 (1969).
- (7) P. R. Brooks and B. L. Shaw, *ibid.*, A, 1079 (1967).
- (8) J. Chatt and B. L. Shaw, *Chem. Ind. (London)*, 290 (1960).
- (9) J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc. A*, 1674 (1969).
- (10) M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).
- (11) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1054 (1968).
- (12) R. T. Heck, *J. Amer. Chem. Soc.*, **86**, 2796 (1964).
- (13) M. A. Bennett and P. A. Songstaff, *Chem. Ind. (London)*, 846 (1965).
- (14) L. Vallarino, *J. Inorg. Nucl. Chem.*, **8**, 288 (1968).
- (15) J. J. Levison and S. D. Robinson, *Chem. Commun.*, 1405 (1968).
- (16) S. O. Grim and R. A. Ferrence, *Inorg. Chim. Acta*, 277 (1969).
- (17) A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc. A*, 1670 (1966).

and dried over molecular sieves before use. Most preparations, especially those involving free phosphines, were conducted in a nitrogen atmosphere.¹⁸

Infrared Spectra.—Spectra were taken with a Beckman IR-12 grating infrared spectrophotometer either in Nujol mulls, as cesium iodide pellets, or in chloroform or methylene chloride solutions.

Nmr Spectra.—A Varian A-60A spectrometer operated at approximately 30° was used to obtain nmr spectra. Carbon tetrachloride, deuteriochloroform, deuteriomethylene chloride, or deuteriobenzene was used as solvent. In all cases tetramethylsilane was used as an internal standard.

Elemental Analyses.—All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. These are presented in Table I.

Preparation of Complexes. *mer*-Trichlorotris(trimethylphosphine)rhodium(III), *mer*-RhCl₃(PMe₃)₃. (Method A).—This complex was prepared by dissolving RhCl₃·3H₂O (5.0 mmol) in ethanol and evaporating to dryness twice to remove water. The solid was taken up in 100 ml of ethanol-benzene and excess trimethylphosphine (40.0 mmol) was added. The solution was stirred overnight at ambient conditions and evaporated to a small volume. Addition of hexane and cooling caused formation of a good yield of orange crystals (mp 230–245°).

In similar fashion *mer*-trichlorotris(triethylphosphine)rhodium(III), *mer*-RhCl₃(PEt₃)₃, was obtained as orange crystals (mp 100–120°).

mer-Trichlorotris(*tri-n*-propylphosphine)rhodium(III), *mer*-RhCl₃(P(*n*-Pr)₃)₃. (Method B).—Excess *tri-n*-propylphosphine (30.0 mmol) was added to 100 ml of 0.03 *M* rhodium trichloride. This was evaporated to dryness and redissolved in 15 ml of benzene. Addition of hexane and cooling caused precipitation of orange crystals (mp 170–175°).

In a similar fashion *mer*-trichlorotris(*tri-n*-butylphosphine)rhodium(III), *mer*-RhCl₃(P(*n*-Bu)₃)₃, as orange crystals (mp 135–140°), *mer*-trichlorotris(*tri-n*-octylphosphine)rhodium(III), *mer*-RhCl₃(P(*n*-Oct)₃)₃, as dark yellow crystals (mp –20°), and *mer*-trichlorotris(triisobutylphosphine)rhodium(III), *mer*-RhCl₃(P(*i*-Bu)₃)₃, as orange crystals (mp 30–35°) were prepared.

mer-Trichlorotris(triisopropylphosphine)rhodium(III), *mer*-RhCl₃(P(*i*-Pr)₃)₃. Method C.—A rhodium trichloride slurry in benzene (10.0 g-atoms of rhodium) was allowed to react with exactly a stoichiometric amount of triisopropylphosphine at 0°. Evaporation of solvent and addition of hexane caused precipitation of dark orange solid (mp 40–50°).

In a similar manner *mer*-trichlorotris(dimethylphenylphosphine)rhodium(III), *mer*-RhCl₃(PMe₂Ph)₃, as orange crystals (mp 215–220°), *mer*-trichlorotris(diethylphenylphosphine)rhodium(III), *mer*-RhCl₃(PEtPh₂)₃, as yellow crystals (mp 185–190°), *mer*-trichlorotris(methyldiphenylphosphine)rhodium(III), *mer*-RhCl₃(PMePh₂)₃, as orange crystals (mp 170–173°), and *mer*-trichlorotris(ethyldiphenylphosphine)rhodium(III), *mer*-RhCl₃(PEtPh₂)₃, as orange crystals (mp 140–145°), were formed.

mer-Trichlorotris(tricyclohexylphosphine)rhodium(III), *mer*-RhCl₃(P(*c*-Hx)₃)₃. Method D.—Rhodium trichloride (5.0 mmol) dissolved in 100 ml of methanol on slow addition of excess tricyclohexylphosphine (35.0 mmol) gave red crystals (mp 200–210°). Similarly, *mer*-trichlorotris(tribenzylphosphine)rhodium(III), *mer*-RhCl₃(PBz₃)₃, was obtained as yellow crystals (mp 150–161°).

fac-Trichlorotris(trimethylphosphine)rhodium(III), *fac*-RhCl₃(PMe₃)₃. Method E.—Rhodium trichloride (5.0 mmol) was dissolved in ethanol and evaporated to dryness twice to remove water. The solid was taken up in 100 ml of methylene chloride-ethanol and excess trimethylphosphine (30.0 mmol) was added to the suspension, stirred overnight at room temperature, and evaporated to dryness. The residue was washed with benzene, redissolved in chloroform, evaporated to dryness, and reworked with benzene. A poor yield of yellow-orange crystals remained (mp 160–170°).

Similarly prepared were *fac*-trichlorotris(triethylphosphine)rhodium(III), *fac*-RhCl₃(PEt₃)₃, as yellow crystals (mp 160–170°), and *fac*-trichlorotris(dimethylphenylphosphine)rhodium(III), *fac*-RhCl₃(PMe₂Ph)₃, as yellow crystals (mp 210–215°).

(18) Extreme care must be used in working with the lighter tertiary phosphines which are highly volatile, air sensitive, and toxic. Trimethylphosphine is an extremely odorous compound which ignites on contact with air.

The latter required extraction with tetrahydrofuran to obtain a pure product.

Di-μ-chloro-tetrachlorotetrakis(trimethylphosphine)dirhodium(III), Rh₂Cl₆(PMe₃)₄. Method F.—RhCl₃(PMe₃)₃ (2.0 mmol) dissolved in 100 ml of chloroform-ethanol was allowed to stand several days exposed to air. Cubic, deep red-orange crystals formed and were washed with hexane (mp 250–254°).

Similarly prepared were the triethyl (deep red crystals, mp 250–255°), *tri-n*-propyl (red crystals, mp 185–190°), *tri-n*-butyl (red crystals, mp 183–186°), *tri-n*-pentyl (brown powder, mp 125–135°), tricyclohexyl (red crystals, mp 205–210°), and dimethylphenyl (red crystals, mp 220–225°) derivatives of similar structure.

Chlorotris(trimethylphosphine)rhodium(I), RhCl(PMe₃)₃.

Method G.—Ethylene at 1 atm was bubbled through 100 ml of a refluxing 0.05 *M* ethanol-benzene solution of rhodium trichloride for 24 hr. The solution was cooled and excess trimethylphosphine (30.0 mmol) was added. Nitrogen was vigorously bubbled through the solution for 2 days with additional solvent added as needed to replace that lost by evaporation. The dark red solution was filtered and the filtrate was evaporated to dryness and pumped on under high vacuum. The solid was redissolved and the last three steps repeated to yield a red powder (mp 205–210°).

Similar preparations yielded chlorotris(triethylphosphine)rhodium(I), RhCl(PEt₃)₃, as a brown-red powder (mp 185–195°), chlorotris(*tri-n*-propylphosphine)rhodium(I), RhCl(P(*n*-Pr)₃)₃, as a brown powder (mp 120–130°), chlorotris(triisopropylphosphine)rhodium(I), RhCl(P(*i*-Pr)₃)₃, as brown crystals (mp 30–35°), and chlorotris(dimethylphenylphosphine)rhodium(I), RhCl(PMe₂Ph)₃, as a brown-red powder (mp 170–175°).

Hydridodichlorotris(trimethylphosphine)rhodium(III), RhHCl₂(PMe₃)₃. Method H.—To a 0.02 *M* benzene solution of RhCl(PMe₃)₃ a stoichiometric amount of aqueous hydrochloric acid in ethanol was added. The solution changed to a light red color and the ir analysis indicated immediate formation of a hydride (M–H 1960 cm^{–1}). Quickly evaporating to a small volume causes a poor yield of yellow crystals (mp 210–219°). Excess hydrochloric acid or prolonged reaction results in formation of RhCl₃(PMe₃)₃.

A similar method is used to obtain hydridodichlorotris(dimethylphenylphosphine)rhodium(III), RhHCl₂(PMe₂Ph)₃, as yellow crystals (mp 215–220°). With this phosphine two isomers may be obtained. The β form is obtained as above, and the α form is obtained by prolonged reaction with hydrochloric acid prior to the isolation of the product. The α isomer is collected as yellow-orange crystals (mp 160–165°). The β form of hydridodichlorotris(triethylphosphine)rhodium(I), RhHCl₂(PEt₃)₃, was similarly obtained as yellow-orange crystals (mp 140–200°) but the α form which was indicated by the ir spectrum (M–H 2090 cm^{–1}) could not be obtained pure. Both α-hydridodichlorotris(ethyldiphenylphosphine)rhodium(III), RhHCl₂(PEtPh₂)₃ (yellow crystals (mp 215–220°), and α-hydridodichlorotris(diethylphenylphosphine)rhodium(III), RhHCl₂(PEtPh₂)₃ (yellow crystals, mp 140–145°), were obtained by direct reaction of rhodium trichloride in ethanol and the phosphine. The β form of RhHCl₂(PEtPh₂)₃ was obtained by treatment of RhCl(PEtPh₂)₃ with hydrochloric acid to give yellow crystals (mp 180–185°).

Chlorocarbonylbis(trimethylphosphine)rhodium(I), RhClCO(PMe₃)₂. Method J.—A 0.02 *M* solution of RhCl₃(PMe₃)₃ or Rh₂Cl₆(PMe₃)₄ in benzene was treated with carbon monoxide at 1 atm for several hours. The red solution lightened to pale yellow. Evaporation to a small volume followed by addition of ethanol caused the yellow precipitate to form. Other complexes prepared in this fashion included the *tri-n*-pentyl-, *tri-n*-octyl-, tribenzyl-, and dimethylphenylphosphine derivatives.

Method K.—RhCl(PMe₃)₃ (2.0 mmol) in ethanol-benzene solution (100 ml) immediately formed a yellow precipitate on contact with carbon monoxide. All derivatives for which the starting product RhCl(PR₃)₃ was available could be obtained in this manner.

Method L.—[RhCl(CO)₂]₂ formed by the action of carbon monoxide on ethanol solutions of rhodium trichloride when treated with excess phosphine yielded the corresponding derivative.

Trichlorocarbonylbis(triethylphosphine)rhodium(III), RhCl₃CO(PEt₃)₂. Method M.—Treatment of RhCl₃(PEt₃)₃ or Rh₂Cl₆(PEt₃)₄ with carbon monoxide in ethanol for a short period of time results in a mixture of monochloro- and trichlorocarbonyls (identified by ir spectra). Treatment of this mixture with chlorine in carbon tetrachloride resulted in complete conversion

to the trichloro complex. Evaporation to a small volume and cooling resulted in a good yield of yellow crystals. Similar preparations were used for the other trichlororhodium analogs.

Hydridodichlorocarbonylbis(triisopropylphosphine)rhodium(III), $\text{RhHCl}_2\text{CO}(\text{P}(i\text{-Pr})_3)_2$. Method N.—Carbon monoxide was bubbled through a 0.02 M ethanol-chloroform solution of $\text{RhHCl}_2(\text{P}(i\text{-Pr})_3)_2$. Addition of ethanol and cooling caused precipitation of a yellow-orange solid. This was a mixture of the desired product and $\text{RhClCO}(\text{P}(i\text{-Pr})_3)_2$ (identified by ir band at 1948 cm^{-1}). Analyses done on several of these mixtures which had varying amounts of the 1948-cm^{-1} impurity were consistent with mixtures of various proportions estimated by their ir spectra. Attempts to extract the 1948-cm^{-1} product always resulted in formation of more of it, probably due to loss of HCl.

Results and Discussion

Table II summarizes the compounds that have been

TABLE II
COMPLEXES PREPARED IN THIS WORK^a

R_3	$\text{mer-RhCl}_3(\text{PR}_3)_3$	$\text{fac-RhCl}_3(\text{PR}_3)_3$	$\text{RhCl}(\text{PR}_3)_3$	$\alpha\text{-RhHCl}_2(\text{PR}_3)_3$	$\beta\text{-RhHCl}_2(\text{PR}_3)_3$	$\text{RhHCl}_2(\text{PR}_3)_2$	$\text{RhCl}_2(\text{PR}_3)_4$	$\text{trans-RhClCO}(\text{PR}_3)_2$	$\text{trans-RhCl}_2\text{CO}(\text{PR}_3)_2$	$\text{trans-RhHCl}_2\text{CO}(\text{PR}_3)_2$
Me_3	2A	1E	2G		1H		1F	2J	1M	
Et_3	2A	2E	1G	1H	1H		2F	2K	2M	1N
$n\text{-Pr}_3$	2B		1G				2F	1K	1M	
$n\text{-Bu}_3$	2B						2F	2L	1M	1N
$n\text{-Pent}_3$							1F	1J		
$n\text{-Oct}_3$	1B							1J		
$i\text{-Pr}_3$	1C		1G			1A		1K	1M	1N
$i\text{-Bu}_3$	1B									
$c\text{-Hx}_3$	1D						1F	1L	1M	1N
Bz_3	1D						1F	1J	1M	
Me_2Ph	2C	2E	1G	1H	1H		1F	2J	1M	
Et_2Ph	2C			2H	2B			2L	2M	
MePh_2	3							2K	2M	1N
EtPh_2		3	3	3	3	3		2K	2M	1N
Ph_3	3	3	3	3	3			3	3	

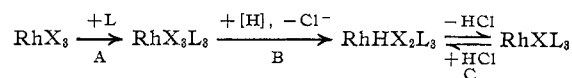
^a Letter indicates method of preparation. 1 = new compound; 2 = modified preparation of previously reported compound; 3 = prepared as previously reported.

prepared. These are discussed individually according to type of compound below.

RhX_3L_3 .—In general, the most common product from the direct reaction of rhodium trichloride with excess tertiary phosphine was *mer*- $\text{RhCl}_3(\text{PR}_3)_3$.¹⁹ For most trialkylphosphines this is the major product obtained from alcohol solutions. The two exceptions to this were tri-*n*-pentyl- and triisopropylphosphines. The failure to obtain the *n*-pentyl complex was probably due more to difficulty in crystallizing the product than to difficulty in forming it. The isopropyl derivative, however, can be obtained but is not the major product. The major product in this case is instead $\text{RhHCl}_2(\text{PR}_3)_2$. The reason for this singularity is not clear. Steric factors are probably not the cause since both triisobutyl- and tricyclohexylphosphines, both of which should be more sterically hindered, behave normally.

An excess of triarylphosphine, on the other hand, gives a reduced species $\text{RhCl}(\text{PR}_3)_3$ as the major product.¹ Mixed arylalkylphosphines yield a hydrido complex, $\text{RhHCl}_2(\text{PR}_3)_3$. No exceptions were formed to this general behavior which is in accordance with the mechanism postulated by Sacco, *et al.*,¹⁷ that the reac-

tion occurs in three steps



With more basic (trialkyl) phosphines, the reaction stops at the first step. With less basic (triphenyl) phosphines, it goes completely to the third step. With phosphines of intermediate basicity (alkylaryl) it stops at the second step. Recently, Shaw and others²⁰ have postulated that this is due to steric rather than electronic factors. In order to obtain the RhX_3L_3 complexes for triaryl- or mixed alkylarylphosphines, conditions must be carefully controlled and excess phosphine avoided. Even then only poor yields were obtained. Once prepared, however, these complexes exhibit moderate stability comparable to that of the trialkyl analogs.

$\text{Rh}(\text{PR}_3)_3\text{Cl}_3$ may exist as one of two possible isomers. In the meridional isomer two of the phosphines are *trans* to each other, while in the facial isomer all are *cis*. The *mer* isomer is therefore sterically preferred especially with the larger phosphines. This is borne out by our



inability to prepare the facial isomer for any but the smaller trimethyl-, triethyl-, and dimethylphenylphosphines. Isolation of these three was facilitated by the difference in polarity between these isomers. In more polar solvents, formation of the *fac* isomer becomes favored. Thus, while in benzene very little *fac* isomer is obtained, in methylene chloride a 40% yield may be obtained for the trimethyl derivative. The assignments of these isomers has been substantiated by nmr as will be discussed below.

RhXL_3 .—While triphenylphosphine reduces rhodium trichloride to the monochlororhodium(I) species, formation of this derivative by direct reaction for other phosphines is not possible. These complexes may however be prepared by previously reducing the Rh(III) with a volatile olefin such as ethylene. Addition of excess phosphine to the so-formed prerduced compounds followed by pumping off of the olefin under high vacuum has led to pure compounds. This method worked well for the more volatile phosphines but with the heavier ones purification was more difficult, probably due to difficulty in removing unreacted phosphines. The only other compound of this type was prepared by Sacco's¹⁷ method of addition of aniline to the hydridodichloro complex.

RhHX_2L_3 .—This type of hydridodichloro complex could be obtained *via* one of two methods. As noted above, the mixed alkylarylphosphine complexes of this type could be made by direct reaction of the metal halide and the phosphine. The trimethyl- and triethylphosphines as well as the mixed phosphines could also be prepared by oxidative addition of HCl to the square-planar rhodium(I) complex $\text{RhCl}(\text{PR}_3)_3$. The tri-*n*-propylrhodium(I) derivative, however, on reac-

(19) In this work, for simplicity, the only halogen employed was chloride.

(20) C. Masters, B. L. Shaw, and R. E. Stainbank, *Chem. Commun.*, 209 (1971).

tion with HCl was oxidized instead to the trichloro complex $\text{RhCl}_3(\text{PR}_3)_3$. The triisopropyl derivative lost a phosphine ligand forming the five-coordinate species $\text{RhHCl}_2(\text{PR}_3)_2$.

The six-coordinate $\text{RhHCl}_2(\text{PR}_3)_3$ may exist in several isomeric forms. Nmr evidence presented below for the dimethylphenyl derivative indicates a meridional distribution of phosphines. This leaves the two possible isomers.



By analogy with the corresponding iridium complexes, $\text{IrHCl}_2(\text{PR}_3)_3$,²¹ the hydride trans to a phosphine should exhibit a lower M-H stretching frequency than one trans to a chloride. Oxidative addition of HCl to $\text{RhCl}(\text{PR}_3)_3$ gives initially the β complex (M-H, 1980 cm^{-1}). When left standing in solution this gradually rearranged to yield the α form (for PEt_3 , M-H 2090 cm^{-1} ; for PMe_2Ph , M-H 2105 cm^{-1}).²² These results argue strongly for a cis-addition mechanism for the oxidative addition of HCl, followed by a slower rearrangement to the trans product (*i.e.*, the product which would be obtained from a trans addition). Cis addition is known to occur in the reaction of H_2 with $\text{RhCl}(\text{PPh}_3)_3$ to produce *cis*- $\text{RhH}_2\text{Cl}(\text{PPh}_3)_3$ (M-H 2012, 2082 cm^{-1}).¹ Table III gives the infrared prop-

TABLE III
IR PROPERTIES OF $\text{RhHCl}_2(\text{PR}_3)_3$ COMPLEXES

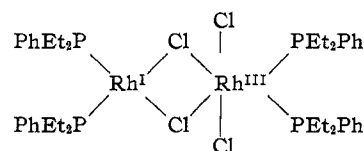
Compd	M-H str, ^a cm^{-1}	Compd	M-H str, ^a cm^{-1}
β - $\text{RhHCl}_2(\text{PMe}_3)_3$	1960	α - $\text{RhHCl}_2(\text{PEt}_2\text{Ph})_3$	2115
α - $\text{RhHCl}_2(\text{PEt}_3)_3$	2090 ^b	α - $\text{RhHCl}_2(\text{PEtPh}_2)_3$	2120
β - $\text{RhHCl}_2(\text{PEt}_3)_3$	1980	β - $\text{RhHCl}_2(\text{PEtPh}_2)_3$	1982
α - $\text{RhHCl}_2(\text{PMe}_2\text{Ph})_3$	2105	α - $\text{RhHCl}_2(\text{PPh}_3)_3$ ¹⁷	2220
β - $\text{RhHCl}_2(\text{PMe}_2\text{Ph})_3$	1980	β - $\text{RhHCl}_2(\text{PPh}_3)_3$ ¹⁷	2120

^a CsI pellets. ^b Ethanol-chloroform solution.

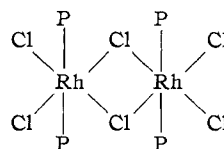
erties of complexes of this type which were prepared.

RhHX_2L_2 .—This unusual complex is the main product from the prolonged reaction of triisopropylphosphine with $\text{RhX}_3 \cdot 3\text{H}_2\text{O}$. This complex was puzzling since it did not have a detectable M-H stretch in the infrared region of 1900–2300 cm^{-1} . It is either too weak to be detected or obscured for some other reason. In addition, an nmr hydride band could not be found either. It was postulated as a hydride because on reaction with carbon monoxide in chloroform the carbonyl hydride $\text{RhHCl}_2\text{CO}(\text{PR}_3)_2$ was formed along with $\text{RhClCO}(\text{PR}_3)_2$. The latter probably comes from the former by loss of HCl. The formation of the hydride could not have resulted from reaction with this solvent and as is discussed below is not subsequently formed from some other carbonyl-containing precursor. Therefore, the hydrogen must have already been present as a hydride in the starting complex. Simultaneously with this work a similar complex, $\text{RhHCl}_2(\text{P}(\text{tert-Bu})(n\text{-Pr})_2)_2$, was fully characterized by Shaw, *et al.*,²³ who also re-

ported the nmr spectrum. The hydride had the extremely high τ value of 41.4. This is beyond the range at which we looked. A compound isolated by Sacco¹⁷ which he postulates as having the a bridging Rh(I)–Rh(III) structure, shown below, perhaps might also be better postulated as a hydride, $\text{RhHCl}_2(\text{PEt}_2\text{Ph})_2$.



Binuclear Complexes.—Very stable chlorine-bridging binuclear species are formed with most of the various phosphines when limiting phosphine is present. The most satisfactory way to obtain the binuclear complexes was to crystallize them slowly from solutions of RhX_3L_3 which had been exposed to air. Presumably, one phosphine is lost, perhaps *via* oxidation to the phosphine oxide leaving an unoccupied coordination site which is satisfied by bridging chlorines. The nmr spectra of the trimethyl and dimethylphenyl derivatives discussed below tend to suggest a trans arrangement of the phosphine ligands. Limited solubility, however, precludes making a definite assignment on this basis. The trans isomer would be the sterically favored one.



This structure, however, is in apparent conflict with the results obtained by Shaw,⁵ who has reported a dipole moment for the *n*-butyl derivative of 11.5 D. Since large single crystals of the benzyl derivative were available, a preliminary single-crystal X-ray analysis was performed on it. The space group was found to be $P2_1/c$ with $a = 13.2 \text{ \AA}$, $b = 19.7 \text{ \AA}$, $c = 14.6 \text{ \AA}$, and $\beta = 102^\circ$. The density determined by flotation was $1.45 \pm 0.05 \text{ g/cm}^3$ compared to a calculated value of 1.463 g/cm^3 for two dimeric units per unit cell. Assuming no disorder, the only dimeric structure with which these data are consistent is one in which the dimer is centrosymmetric. Therefore, regardless of whether the phosphines were *cis* or *trans*, the dimer must still have a zero moment. This also eliminates a bent structure as is common in Rh(I) bridging species. This means that the moment measured in solution must have arisen from dissociation of the dimer into monomeric units which presumably have a solvent molecule occupying the sixth coordination position. If this is the case, the *trans* structure is no longer in conflict with a high measured dipole moment. We, therefore, feel that the structure depicted is the most likely one for all of these derivatives, at least in the solid state.

Reaction with CO.—The determination of the structure of many of the compounds discussed above was assisted by noting the products formed in their reaction with carbon monoxide. The reaction of the rhodium(I) complexes $\text{RhCl}(\text{PR}_3)_3$ with CO gave quite cleanly the well-known $\text{RhClCO}(\text{PR}_3)_2$. These compounds could also be obtained by direct reaction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with CO and excess phosphine or by reaction of the phosphine with rhodium carbonyl chloride dimer,

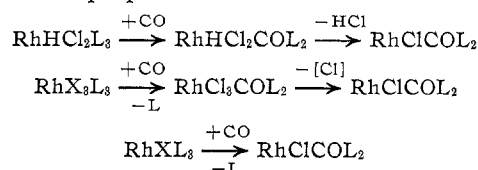
(21) J. Chatt and B. L. Shaw, *Chem. Ind. (London)*, 931 (1960).

(22) The α form of the triethyl derivative could not be isolated. Attempts to isolate a solid resulted instead in $\text{RhCl}_3(\text{PEt}_3)_3$.

(23) C. Masters, W. S. McDonald, S. Roper, and B. L. Shaw, *Chem. Commun.*, 210 (1971).

[RhCl(CO)₂]₂. In all cases the only product is the trans isomer. Treatment of the rhodium(III) complexes, either the monomers or dimers, with CO resulted in a more complicated product mix. The trimethyl-, tri-*n*-pentyl-, tri-*n*-octyl-, tribenzyl-, and dimethylphenylphosphine derivatives were completely reduced by CO yielding only the monochlorocarbonyl complex. The triethyl-, diethylphenyl-, and ethyldiphenyl complexes yielded a mixture of the monochloro complex and the trichloro complex, RhCl₃CO(PR₃)₂. The tri-*n*-butyl derivative was not reduced at all giving only the trichlorocarbonyl. Reaction of CO with the triisopropyl complex yielded a mixture of both the monochloro complex and the hydridodichloro complex RhHCl₂CO(PR₃)₂. The latter type of complex is also obtained along with the rhodium(I) monochloride by reaction of CO with RhHCl₂(PET₃)₃. Independent experiments have shown that under reaction conditions RhHCl₂CO(PET₃)₂ could not be formed from RhClCO(PET₃)₂ or RhCl₃CO(PET₃)₂. Therefore, the hydride must already be present in the starting complex for the hydridocarbonyl to form. Because of this the formation of the triisopropyl derivative RhHCl₂CO(P(*i*-Pr)₃)₂ was construed as evidence for the formulation of RhHCl₂P(*i*-Pr)₃ as a hydride, not as a Rh(I)-Rh(III) dimer.

The following mechanisms for the reactions of CO are therefore proposed



A list of the carbonyl complexes which were prepared is given in Table IV.

TABLE IV
IR DATA FOR CARBONYL COMPLEXES

Compd	Str, cm ⁻¹	M-H
RhClCO(PMe ₃) ₂	1958 ^a	
RhCl ₃ CO(PMe ₃) ₂ ^c	2055 ^b	
RhClCO(PET ₃) ₂	1960 ^a	
RhCl ₃ CO(PET ₃) ₂	2060 ^a	
RhHCl ₂ (PET ₃) ₂ ^c	2050 ^b	2095
RhClCO(P(<i>n</i> -Pr) ₃) ₂	1958 ^a	
RhCl ₃ CO(P(<i>n</i> -Pr) ₃) ₂	2070 ^a	
RhClCO(P(<i>n</i> -Bu) ₃) ₂	1955 ^a	
RhCl ₃ CO(P(<i>n</i> -Bu) ₃) ₂	2078 ^a	
RhClCO(P(<i>n</i> -Pent) ₃) ₂ ^c	1955 ^b	
RhClCO(P(<i>n</i> -Oct) ₃) ₂ ^c	1940 ^b	
RhClCO(P(<i>i</i> -Pr) ₃) ₂	1948 ^a	
RhCl ₃ CO(P(<i>i</i> -Pr) ₃) ₂	2060 ^a	
RhHCl ₂ CO(P(<i>i</i> -Pr) ₃) ₂ ^c	2037	2119
RhClCO(P(<i>c</i> -Hx) ₃) ₂	1950 ^a	
RhCl ₃ CO(P(<i>c</i> -Hx) ₃) ₂	2055 ^a	
RhClCO(PBz ₃) ₂	1970 ^a	
RhCl ₃ CO(PBz ₃) ₂	2095 ^a	
RhClCO(PMe ₂ Ph) ₂	1963 ^a	
RhCl ₃ CO(PMe ₂ Ph) ₂	2085 ^a	
RhClCO(PET ₂ Ph) ₂	1953 ^a	
RhCl ₃ CO(PET ₂ Ph) ₂	2089 ^a	
RhClCO(PETPh ₂) ₂	1960 ^a	
RhCl ₃ CO(PETPh ₂) ₂	2107 ^a	

^a CsI pellets. ^b Ethanol-chloroform solutions. ^c Not isolated as pure solids.

Nmr.—The nmr spectra are in general characteristic of the particular phosphine, but only minor differences can be detected, in most cases, between various types

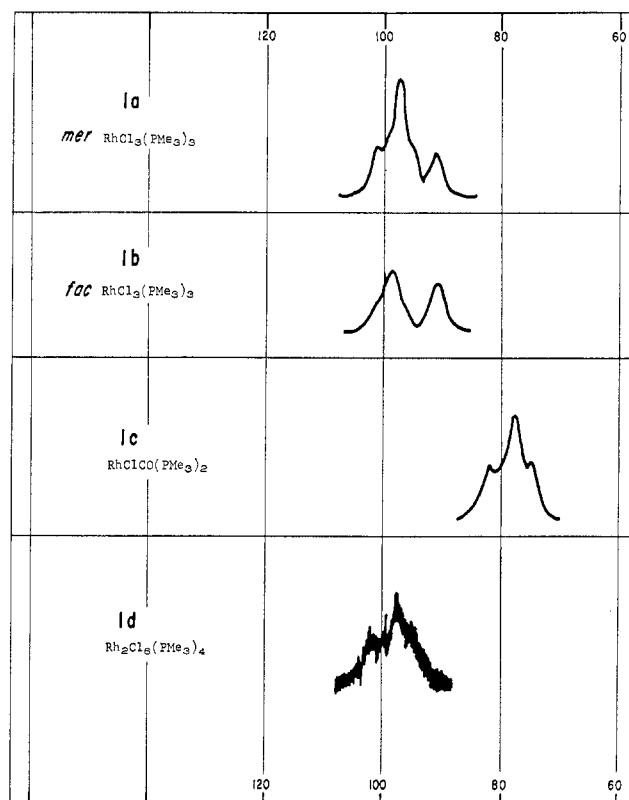


Figure 1.—Nmr spectra of trimethylphosphine complexes.

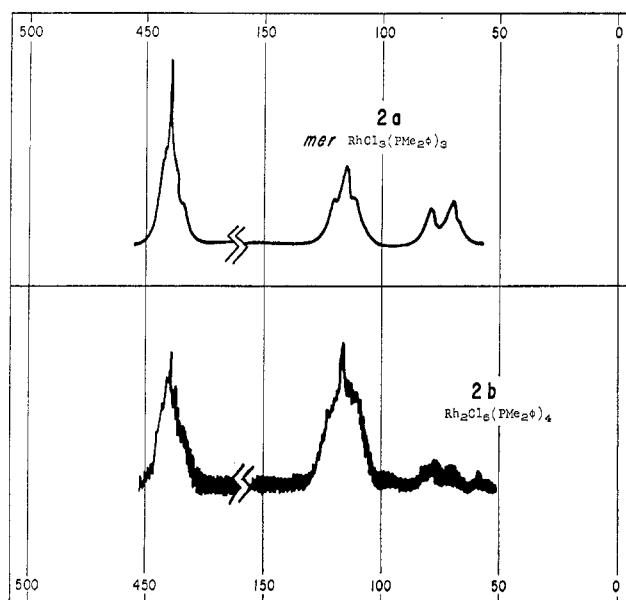


Figure 2.—Nmr spectra of dimethylphenylphosphine complexes.

of compounds for a given phosphine. The exceptions to this are the complexes of the phosphines which have a methyl substituent, PMe₃ and PMe₂Ph. Shaw and coworkers²⁴⁻²⁶ have already shown the usefulness of proton nmr for the determination of structural isomers by observation of the phenomenon of "virtual coupling" of trans phosphines. Due probably to overlap of the same metal orbital, the phosphorus atoms of trans phosphines couple with the α hydrogens with equal strength. Thus, an α hydrogen is split into a

(24) P. R. Brooks and B. L. Shaw, *J. Chem. Soc. A*, 1079 (1967).

(25) J. M. Jenkins and B. L. Shaw, *ibid.*, A, 1407 (1966).

(26) J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *ibid.*, A, 1787 (1966).

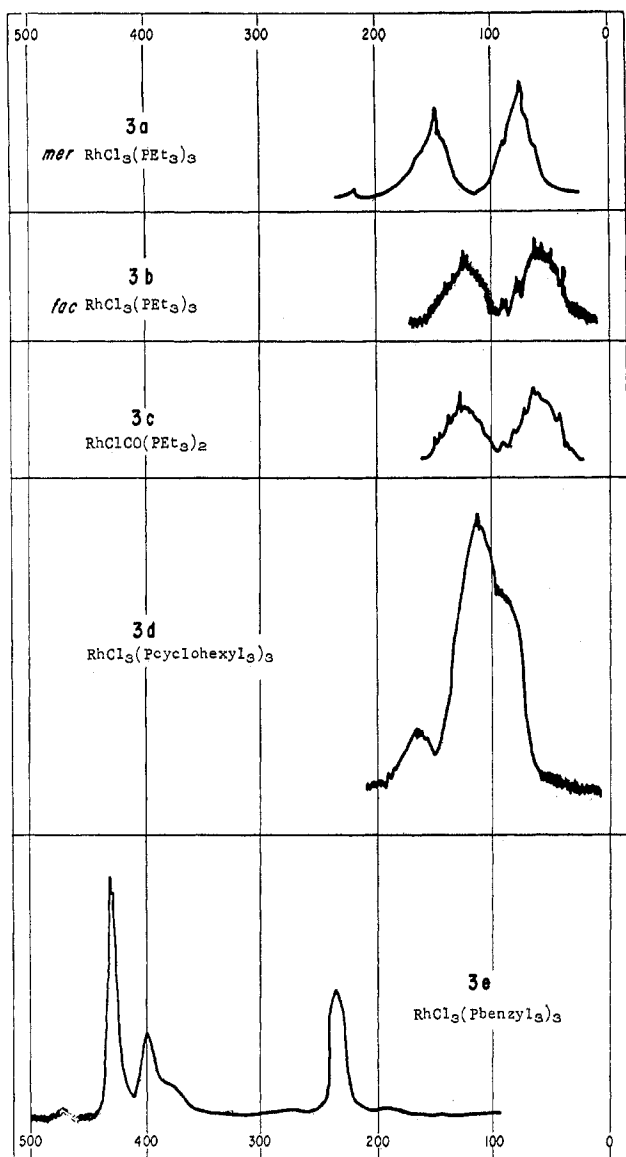


Figure 3.—Nmr spectra of trialkylphosphine complexes.

triplet by the two phosphorus atoms rather than the expected doublet (^{31}P , $S = 1/2$). Figures 1 and 2 give the proton nmr spectra for several of the different types of complexes for PMe_3 and PMe_2Ph phosphines, respectively. Figure 1a is the spectrum for *mer*- $\text{RhCl}_3(\text{PMe}_3)_3$ which is a 1:2:1 triplet and a 1:1 doublet which overlap. The triplet is at τ 8.39, $J(\text{P}_{\text{trans}}-\text{H}) \cong 8.0$ Hz,²⁷ and the doublet at τ 8.42, $J(\text{P}_{\text{cis}}-\text{H}) \cong 8.5$ Hz. This is consistent with both *cis* and *trans* phosphines being present in a 1:2 ratio. *fac*- $\text{RhCl}_3(\text{PMe}_3)_3$, Figure 1b, exhibits a doublet at τ 8.42, $J(\text{P}_{\text{cis}}-\text{H}) \cong 8.5$ Hz. The unequal area of these two peaks is due to a small amount of *mer* impurity which is present. This spectrum is consistent with all *cis* phosphines. *trans*- $\text{RhClCO}(\text{PMe}_3)_2$, Figure 1c, exhibits only a well-defined 1:2:1 triplet, shifted slightly [probably because this is a rhodium(I) species rather than rhodium(III)], at τ 8.70, $J(\text{P}_{\text{trans}}-\text{H}) \cong 7.5$ Hz. The spectrum of the sparingly soluble $\text{Rh}_2\text{Cl}_6(\text{PMe}_3)_4$, Figure 1d, is quite noisy but looks more like a triplet than a doublet and is centered closer to τ 8.39 characteristic of the *trans* phosphines.

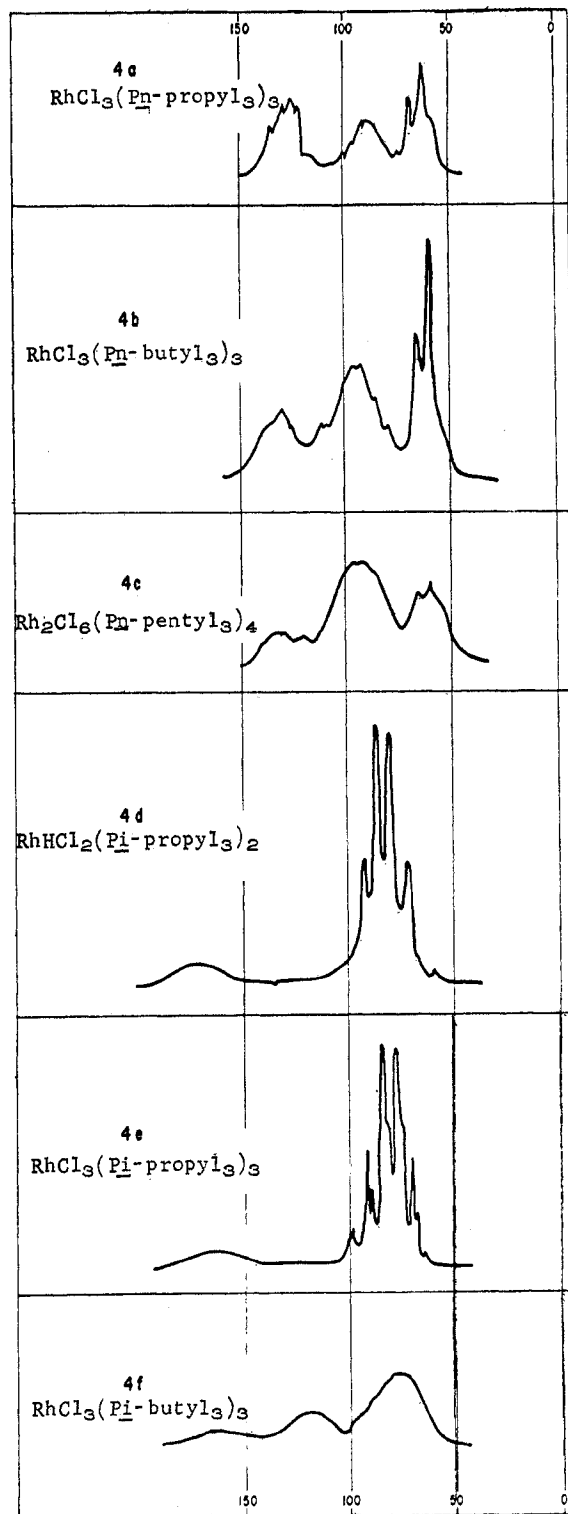
(27) $J(\text{P}-\text{H})$ is defined as the separation of the outermost lines.

Figure 4.—Nmr spectra of trialkylphosphine complexes.

This then suggests the structure which has been discussed above.

Similar assignments have been made by Shaw⁷ for the PMe_2Ph complex *mer*- $\text{RhCl}_3(\text{PMe}_2\text{Ph})_3$, Figure 2a, and are in this case even more clear-cut since the doublets and triplets do not overlap. Again, both the position and the shape of the methyl hydrogen resonance for $\text{Rh}_2\text{Cl}_6(\text{PMe}_2\text{Ph})_4$, Figure 2b, are more consistent with *trans* phosphines than with *cis*. The nmr spectra for other selected complexes are given in Figures 3 and 4.

Conclusion

Some fairly general procedures have been worked out for the preparation of several different types of complexes for a variety of phosphine ligands. Unfortunately, the differences in the electronic and steric properties of the various tertiary phosphines are so large as to preclude any completely general procedures. In spite of this, however, several series of complexes were prepared. There do not seem to be any really discernible trends within these groups with respect to stability, color, melting points, or carbonyl stretching frequencies.

Several interesting anomalies were noted. Whereas most of the rhodium(III) species appear to be six-coordinate as expected, the five-coordinate $\text{RhHCl}_2(\text{P}(i\text{-Pr})_3)_2$ is the most stable complex of this ligand. It was

also of interest to note that this compound is capable of decarbonylating both alcohols and carboxylic acids to form $\text{RhClCO}(\text{P}(i\text{-Pr})_3)_2$.

The oxidative addition of HCl to $\text{RhCl}(\text{PR}_3)_3$ to yield the hydride compound $\text{RhHCl}_3(\text{PR}_3)_3$ was observed to proceed *via* a cis addition followed by a less rapid rearrangement to the product which would occur from trans addition.

Finally, evidence has been obtained for the structure of the dinuclear complexes. These are postulated as the dinuclear, chlorine-bridged isomer with all trans phosphines.

Acknowledgment.—The author is indebted to Dr. D. Dahm for the single-crystal X-ray data and to Drs. D. E. Morris, H. B. Tinker, and D. Forster, of this laboratory, for helpful discussions.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND 02912, AND CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

Spectroscopic Studies of Metal-Metal Bonding. III. Vibrational Spectra and Analyses of $\text{M}[\text{Co}(\text{CO})_4]_2$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$)

By ROBERT J. ZIEGLER,¹ JAMES M. BURLITCH,² SUSAN E. HAYES, AND WILLIAM M. RISEN, JR.*³

Received August 2, 1971

The vibrational spectra of the recently studied $\text{Zn}[\text{Co}(\text{CO})_4]_2$ and its congeners $\text{Cd}[\text{Co}(\text{CO})_4]_2$ and $\text{Hg}[\text{Co}(\text{CO})_4]_2$ have been measured in the infrared (33–4500 cm^{-1}) and laser-Raman ($\Delta\omega = 0\text{--}4000 \text{ cm}^{-1}$) regions. The infrared and Raman fundamentals are assigned on the basis of D_{3d} symmetry, under which no coincidences are allowed, but infrared-Raman band "pairs" are observed which are separated by interactions across the metal-metal system. The normal-coordinate analyses of these species also demonstrate significant coupling across the trinuclear M-M'-M bond and permit evaluation of vibrational coupling of coterminal metal-metal bonds as well as the strengths of the M-Co bonds. The metal-metal force constants are nearly identical, although they fall in the order $k(\text{Zn-Co}) \geq k(\text{Cd-Co}) \geq k(\text{Hg-Co})$. This result is discussed in terms of the reported trends in $k(\text{M-Co})$ from very approximate treatments and reported mass spectral results.

Introduction

The Hg , Cd , and Zn derivatives of $\text{Co}(\text{CO})_4^-$, $\text{M}[\text{Co}(\text{CO})_4]_2$, have occupied an interesting position in the study of metal-metal bonded compounds. Their relatively early known existence^{4,5} has made them the subject of several vibrational spectroscopic investigations,^{6–12} of which the earliest^{6–8} were attempts to elucidate the structures of the compounds. Subsequent X-ray crystallographic determinations^{13,14} confirmed the spectroscopic conclusions of a linear, un-

supported Co-M-Co bonding framework. The more recent interest in the nature of metal-metal bonding in such systems has prompted reports^{15–19} of the low-frequency vibrational spectra of the $\text{M}[\text{Co}(\text{CO})_4]_2$ compounds, with particular emphasis on those bands which primarily involve M-Co stretching vibrations. Using vibrational frequency data and localized mode calculations with varying approximations in the calculations, several authors^{7,15,16,20} have reported for these compounds metal-metal "force constants" which range from a high⁷ of 2.6 and 2.3 $\text{mdyn}/\text{\AA}$ for $k(\text{Hg-Co})$ and $k(\text{Cd-Co})$, respectively, to a low²⁰ of 0.77 $\text{mdyn}/\text{\AA}$ for $k(\text{Cd-Co})$. The several approximate treatments give the order of force constants to be $k(\text{Hg-Co}) > k(\text{Cd-Co})$ or $k(\text{Zn-Co}) > k(\text{Hg-Co}) > k(\text{Cd-Co})$.

Recently J. M. B.^{21,22} reported studies of the ionic dissociation reactions and the mass spectra of the

(1) Abstracted in part from the Ph.D. thesis of R. J. Z., Brown University, to be submitted for publication.

(2) Fellow of the Alfred P. Sloan Foundation, 1970–1972.

(3) Author to whom correspondence should be addressed at Brown University.

(4) W. Hieber and U. Teller, *Z. Anorg. Allg. Chem.*, **249**, 43 (1942).

(5) (a) W. Hieber, E. O. Fischer, and E. Böckly, *ibid.*, **269**, 308 (1952);

(b) W. Hieber and R. Breu, *Chem. Ber.*, **90**, 1259 (1957).

(6) G. Bor and L. Markó, *Spectrochim. Acta*, **16**, 1105 (1960).

(7) H. Stammreich, K. Kawai, O. Sala, and P. Krumholz, *J. Chem. Phys.*, **35**, 2175 (1961).

(8) K. Noack, *Helv. Chim. Acta*, **47**, 1555 (1964).

(9) L. M. Bower and M. H. B. Stiddard, *J. Organometal. Chem.*, **13**, 235 (1968).

(10) G. Bor, *Inorg. Chim. Acta*, **3**, 196 (1969).

(11) A. R. Manning, *J. Chem. Soc. A*, 1018 (1968).

(12) A. R. Manning and J. R. Miller, *ibid.*, **A**, 8352 (1970).

(13) B. Lee, J. M. Burlitch, and J. L. Hoard, *J. Amer. Chem. Soc.*, **89**, 3682 (1967).

(14) G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc. A*, 1005 (1968).

(15) P. N. Brier, A. A. Chalmers, J. Lewis, and S. B. Wild, *ibid.*, **A**, 1889 (1967).

(16) D. M. Adams, J. B. Cornell, J. L. Dawes, and R. D. W. Kemmitt, *Inorg. Nucl. Chem. Lett.*, **3**, 437 (1967).

(17) W. F. Edgell, A. T. Watts, J. Lyford, and W. M. Risen, Jr., *J. Amer. Chem. Soc.*, **88**, 1815 (1966).

(18) W. P. Griffith and A. J. Wickham, *J. Chem. Soc. A*, 834 (1969).

(19) D. M. Adams, J. N. Crosby, and R. D. W. Kemmitt, *ibid.*, **A**, 3056 (1968).

(20) T. G. Spiro, *Progr. Inorg. Chem.*, **11**, 1 (1970).

(21) J. M. Burlitch, *J. Amer. Chem. Soc.*, **91**, 4562 (1969).

(22) J. M. Burlitch and A. Ferrari, *Inorg. Chem.*, **9**, 563 (1970).