several times, yielded 6.0 g. of product insoluble in common organic solvents.

*Anal.* Calcd. for $(C_{13}H_{13}O_3AsPb)_x$ (XI or XII): C, 31.3; H, 2.61; As, 15.0; Pb, 41.5. Found: C, 28.48; H, 2.72; As, 13.87; Pb 41.8.

This product boiled together with glacial acetic acid yielded diphenyllead diacetate.

**Acknowledgment.**—The author is grateful to C. DiPietro of the Analytical Group of this Division for the elemental analyses.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH,
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# The Determination of Complex Formation in Mixed Solvents by Gas Chromatography. The Tetrahydrofuran Complexes of Lithium Aluminum Hydride, Magnesium Bromide, and Several Grignard Reagents[1]

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AND SUNIL KUMAR PODDER

*Received September 11, 1961*

A gas chromatographic method has been used to obtain relative partial pressures of solutions containing mixed volatile solvents. The data, analyzed by a method previously used by McCauley, *et al.*, yield the stoichiometry of complexes formed by tetrahydrofuran with ethyl ether solutions of lithium aluminum hydride, magnesium bromide, and several Grignard reagents. The complexes indicated are $LiAlH_4 \cdot 2THF$, $R_2Mg \cdot MgBr_2 \cdot 2THF$, and $MgBr_2 \cdot 3/2THF$. A dioxane complex $R_2Mg \cdot MgBr_2 \cdot 2C_4H_8O_2$ also is indicated. The latter two are apparent complexes existing in heterogeneous mixtures of liquid and solid.

The partial pressures exerted by volatile components in a multicomponent system provide a direct measure of the activity of the volatile components. Conclusions regarding complexing between a given volatile component and other components of the system may be made by analysis of the appropriate partial pressure–composition isotherms. One of the most direct methods of analysis of such data is the determination of the displacement of the partial pressure–composition isotherm in the presence, and in the absence, of a solute.[3] The previous studies were carried out using vacuum line systems and involved direct manometric measurements. Since only the total pressure was measured, application has been limited to those systems in which the complexing agent is the only appreciably volatile component in the system. The use of gas chromatography for the determination of relative partial pressures removes the restriction that only the complexing agent be appreciably volatile.

A constant volume, constant temperature, sample of a vapor in equilibrium with a solution contains an amount of each component of the solution which is proportional to the partial pressure of each component. The gas chromatogram of the sample will have a peak area for a given component (or for symmetrical peaks, a peak height) which will be proportional to the amount of that component. Thus the chromatogram for a constant volume, constant temperature, sample will have an area (or peak height) which will be directly proportional to the partial pressure of the component giving the peak.

## Experimental

**Apparatus.**—A diagram of the apparatus used is shown in Fig. 1. It consisted of a manostated reflux vessel, gas sampling valve, and a gas chromatograph.

A prototype of the Burrell Model K-5 gas chromatograph was used. Polypropylene glycol, supported on diatomaceous earth, was used as a column packing; the col-

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[1] Based in part on a thesis submitted by L. V. Guild in June, 1960, in partial fulfillment of the requirements for the degree of Master of Science.

[2] Chemistry Department, University of Cincinnati, Cincinnati, Ohio.

[3] (a) D. A. McCauley, B. H. Shoemaker, and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950); (b) H. C. Brown and H. W. Pearsall, *J. Am. Chem. Soc.*, **74**, 191 (1952); (c) E. T. McBee, O. R. Pierce, and D. D. Meyer, *ibid.*, **77**, 83 (1955); (d) H. C. Brown, P. F. Stehle, and P. A. Tierney, *ibid.*, **79**, 2020 (1957); (e) C. W. Heitsch and J. B. Verkade, *Inorg. Chem.*, **1**, 392 (1962).

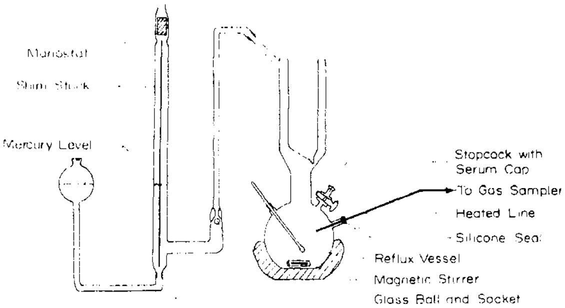

Fig. 1.—Reaction vessel and manostat.

umn temperature was 98-99°. Helium was used as the carrier gas.

The reflux vessel consisted of a 125-ml. flat bottom florence flask connected to a Dry Ice-acetone cooled finger condenser having an off-center drip tip. The flask had three side arms. A thermometer was inserted into one side arm through a Tygon sleeve. A capillary stopcock was sealed to the second side arm, and the outer end was sealed with a serum stopper. Samples were introduced by means of a hypodermic syringe with a needle sufficiently small to pass through the stopcock. A sampling tube, which was made of 17 gage hypodermic tubing, passed through a silicone seal in the third side arm and extended into the vapor above the refluxing solution. The sampling tube was wrapped with electrical heating tape and maintained at a temperature sufficiently high to prevent condensation of the vapor sample. A glass enclosed magnetic stirring bar was added through one of the side arms prior to the addition of the sample. The flask was heated with a Glas-Col heating mantle. The finger condenser was filled with a Dry Ice-acetone slurry, which was maintained at a constant level during the experiment.

The temperature of the refluxing mixture was kept constant as the cosolvent was added during the experiment by adjusting the pressure in the system. The manostat, shown in Fig. 1, consisted of a glass enclosed column, the height of which could be controlled by a mercury leveling bulb. A small ground glass ball and ground socket acted as a one-way float valve which permitted gas from the reflux vessel to enter the bottom of the mercury column. The top of the mercury column was open to the atmosphere. A thin metal strip of shim stock divided the mercury column vertically and helped to prevent bumping and to keep a more nearly constant pressure on the refluxing liquid. A metal baffle at the top of the glass cylinder prevented the escape of mercury from the manostat during operation. A slow flow of helium, introduced through the sampling tube, kept the pressure from dropping below the pressure set by the manostat.

The gas sampling valve[4,5] used an arrangement of six low volume Hoke toggle valves that permitted the following operations: (1) evacuation of the sample chamber while passing a slow stream of helium through the reflux vessel, (2) connection of the sample chamber to the reflux vessel, thus allowing a vapor sample to enter the sample chamber, (3) transfer of the sample to the chromatographic column by passing helium through the sample chamber and into the column. The sample chamber was kept in a constant temperature bath at 50° in order to prevent condensation of the vapor sample.

**Reagents.**—**Ethyl ether** (Mallinckrodt analytical reagent grade anhydrous ether) was stored over sodium. **Tetrahydrofuran** was distilled from ferrous sulfate solution, dried over calcium chloride, treated with a small amount of lithium aluminum hydride, or a Grignard reagent, then distilled and stored over sodium. **Dioxane** was refluxed with aqueous hydrochloric acid, dried over calcium chloride, then distilled from sodium. All **Grignard reagents** were prepared by the usual method in a nitrogen atmosphere and were stored under nitrogen in serum-capped amber colored glass bottles. They were used within a few days after their preparation. The ratios of bromide to basic magnesium were as follows: $C_6H_5CH_2MgBr$, 120; $C_6H_5MgBr$, 1.04; $C_2H_5MgBr$, 1.11. The ether solution of **magnesium bromide** was prepared by treating magnesium turnings in ethyl ether with liquid bromine. Precautions against side reactions were taken as suggested by Rowley.[6] The solution obtained, *i.e.*, the lower or more concentrated layer of the two liquid phases obtained, was slightly brown in color; its composition was 38% by weight magnesium bromide. The ether solution of **lithium aluminum hydride** was prepared as described elsewhere[7]; analysis by the iodine-sodium thiosulfate method of Felkin[8] gave results which agreed with the amount of hydrogen evolved upon reaction with alcohol.

**Procedure.**—The oven dried reflux vessel was purged with dry nitrogen and then placed in the system as shown in Fig. 1. After further purging with nitrogen the cold finger condenser was filled with a Dry Ice-acetone slurry. The ether solution then was added from a hypodermic syringe through the serum stopper on the capillary stopcock. When the solution had been brought to reflux, an appropriate quantity of cosolvent was added from a hypodermic syringe. After refluxing again had become steady a sample of the vapor was taken and sent through the gas chromatograph. More cosolvent then was added and the process repeated. In this way the amount of cosolvent in the vapor was obtained as a function of the amount of cosolvent in the solution.

## Results and Discussion

The relative concentrations (relative peak heights) of tetrahydrofuran in the vapor as a function of the solvent composition for solutions of $LiAlH_4$ in ethyl ether-tetrahydrofuran mixtures are shown in Fig. 2. Further pertinent information about the conditions and results of these experiments are shown in Table I. The straight line portions of the curves are nearly parallel to the Henry's law line (*i.e.*, the line for the system with no hydride), and because the breaks

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[4] This valve was suggested to us by D. Smith, Phillips Petroleum Company; other sampling valves now described in the literature would also be satisfactory.

[5] See, for example, G. L. Pratt and J. H. Purnell, *Anal. Chem.*, **32**, 1213 (1960).

[6] H. H. Rowley, *J. Am. Chem. Soc.*, **58**, 1337 (1936).

[7] G. B. Smith, D. H. McDaniel, E. Biehl, and C. A. Hollingsworth, *ibid.*, **82**, 3560 (1960).

[8] H. Felkin, *Bull. soc. chim. France*, **5**, 347 (1952).

TABLE I

COMPOSITIONS OF THE SOLUTIONS AND THE INDICATED COMPLEXING

| Figure and curve | Solute A | Molarity of A | Cosolvent B | Original solvent (mole %) Ether | Pentane | Bound B per A |
|---|---|---|---|---|---|---|
| 2,a | None | .. | THF | 100 | 0 | .. |
| 2,b | $LiAlH_4$ | 0.22 | THF | 100 | 0 | 2.2 |
| 2,c | $LiAlH_4$ | .38 | THF | 100 | 0 | 2.1 |
| 2,d | $LiAlH_4$ | .75 | THF | 100 | 0 | 2.0 |
| 3,a | $C_6H_5MgBr$ | .47 | THF | 36 | 64 | 1.2 |
| 3,b | $LiAlH_4$ | .22 | THF | 11 | 89 | 2.1 |
| 3,c | $LiAlH_4$ | .38 | THF | 18 | 82 | 2.4 |
| 3,d | $LiAlH_4$ | .75 | THF | 36 | 64 | 2.0 |
| 4,a | None | .. | THF | 100 | 0 | .... |
| 4,b | $C_6H_5CH_2MgBr$ | .35 | THF | 100 | 0 | 0.9 |
| 4,c | $C_6H_5MgBr$ | .50 | THF | 100 | 0 | 1.1 |
| 4,d | $C_2H_5MgBr$ | .63 | THF | 100 | 0 | 1.1 |
| 5,a | $C_2H_5MgBr$ | .63 | Dioxane | 100 | 0 | 1.2 |
| 5,b | $MgBr_2$ | .45 | THF | 100 | 0 | 1.4 |

in the curves are fairly sharp the intercepts of the straight lines (extended) with the abscissa can be interpreted as giving, to a good approximation, the amount of tetrahydrofuran that is bound to the solute. The shape of the experimental curves indicates the existence of an equilibrium of some type, such as

$$LiAlH_4 \cdot n\ \text{ether} + 2THF \rightleftharpoons LiAlH_4 \cdot (n - r)\text{ether} \cdot 2THF + r\ \text{ether} \quad (1)$$

In order to have systems with lower ether activities and, thus, possibly to obtain curves with sharper breaks, systems in which most of the ether was replaced by pentane were studied. The results of these experiments are shown in Fig. 3. These systems were not true solutions. Rather the solute was in the form of a gelatinous precipitate, or paste. The fact that the breaks in the curves were not much sharper suggests that much of the ether remained with the solute in the precipitate. The amount of tetrahydrofuran bound to the solute is not changed by the presence of pentane and the existence of a heterogeneous system.

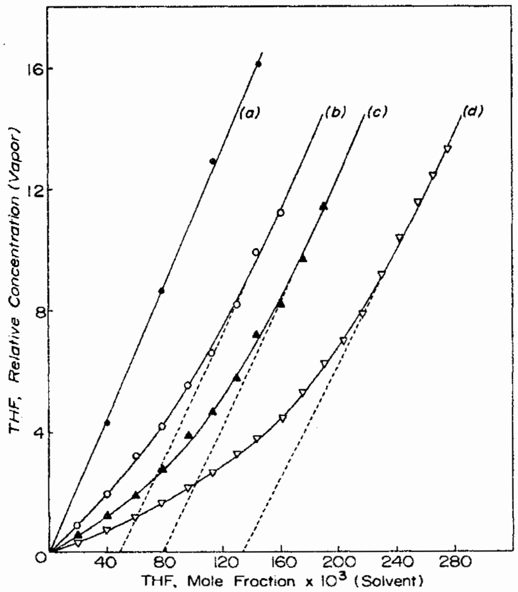


Fig. 2.—Relative concentration of tetrahydrofuran in the vapor *vs.* its mole fraction in the liquid. Curves are labeled as shown in Table I.

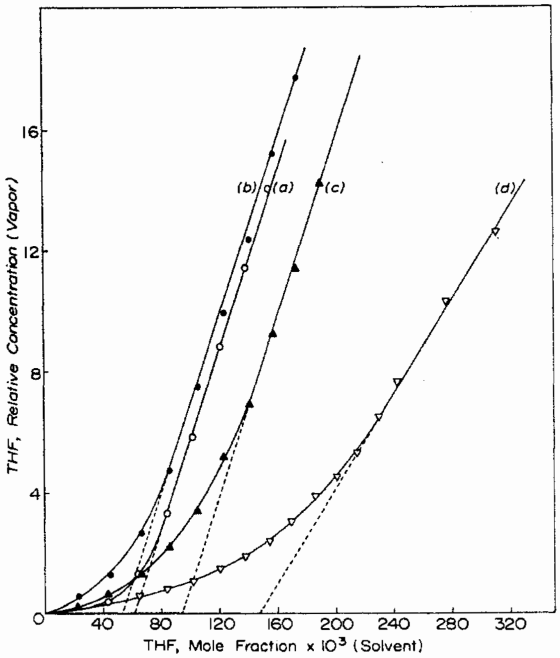


Fig. 3.—Relative concentration of tetrahydrofuran in the vapor *vs.* its mole fraction in the liquid. Curves are labeled as shown in Table I.

Figure 4 gives the curves obtained for $C_6H_5CH_2MgBr$, $C_6H_5MgBr$, and $C_2H_5MgBr$ in ether with tetrahydrofuran. Figure 5 shows the curve for $MgBr_2$ in ether with tetrahydrofuran and $C_2H_5MgBr$ in ether with dioxane. All of the

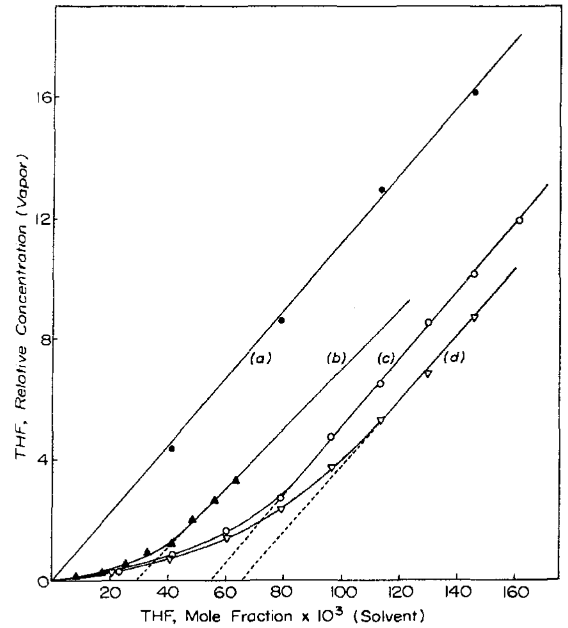


Fig. 4.—Relative concentration of tetrahydrofuran in the vapor *vs.* its mole fraction in the liquid. Curves are labeled as shown in Table I.

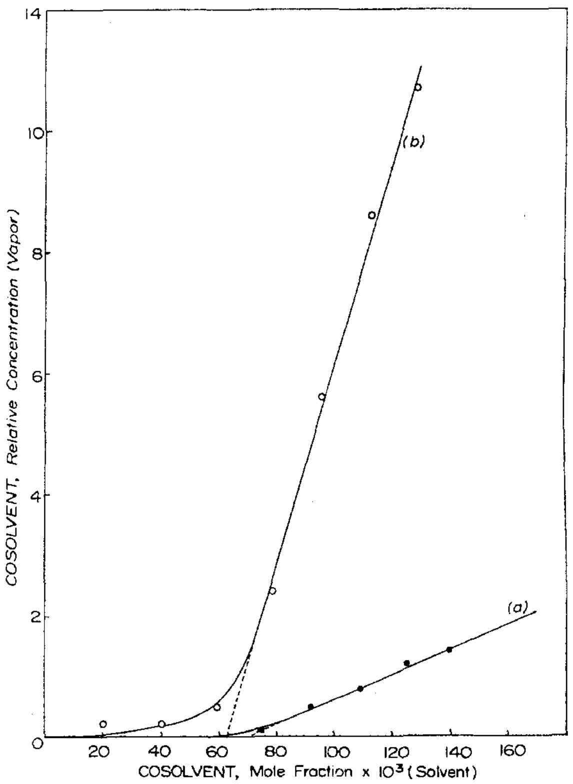


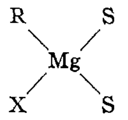
Fig. 5.—Relative concentration of cosolvent in the vapor *vs.* its mole fraction in the liquid. Curves are labeled as shown in Table I.

Grignard reagents produced precipitates when tetrahydrofuran was added, but the precipitation was slow, and it was possible to complete the experiment before much solid had separated out. When the solution had stood for a longer time or when excess tetrahydrofuran was added a larger amount of solid precipitated. The bromide to basic magnesium ratio in the solid was about ten times that in the original Grignard reagents.

In the case of magnesium bromide in ether and tetrahydrofuran and of $C_2H_5MgBr$ in ether and dioxane the precipitation was much more rapid. The results obtained for these cases, therefore refer to a heterogeneous mixture of solution and solid, and the numbers in column seven of Table I give only the total bound cosolvent and do not indicate how this bound cosolvent is distributed between the liquid and solid phases.

These empirical formulas are in close agreement with the results: $LiAlH_4 \cdot 2THF$ in solution; $RMgBr \cdot THF$ in solution with a small amount of $MgBr_2 \cdot 3/2THF$ precipitated; $MgBr_2 \cdot 3/2THF$ and $RMgBr \cdot C_4H_8O_2$ in a heterogeneous mixture of solid and liquid.

The complexes of the Grignard reagent are of special significance with regard to postulated structures for this reagent. The two most commonly recurring formulas are



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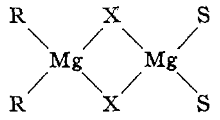

II

Structure II has recently been given strong support by evidence of (1) identity of chemical reactivity of equimolar mixtures of ethylmagnesium and magnesium bromides in ether,[9,10] (2) existence of non-equivalent magnesium atoms in such a mixture,[11,12] (3) existence of a 1:1 complex between ethylmagnesium and magnesium bromides.[13] The manner of bridging and the degree of solvation have not been established for the solution species. This work suggests a stoichiometry of solvation consistent with structure II. The evidence is not conclusive because it has not been established that $n = r = 1$ in the complexing equilibrium, which might be represented by

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(9) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, **21**, 1063 (1956).

(10) R. E. Dessy, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **79**, 358 (1957).

(11) R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *ibid.*, **79**, 3476 (1957).

(12) R. E. Dessy and G. S. Handler, *ibid.*, **80**, 5824 (1958).

(13) R. E. Dessy, *J. Org. Chem.*, **25**, 2260 (1960).

$$\mathrm{RMgX}\cdot n\ \mathrm{ether} + \mathrm{THF} \rightleftharpoons \mathrm{RMgX}\cdot(n - r)\mathrm{ether}\cdot\mathrm{THF} + r\ \mathrm{ether}$$

However, there is no cogent reason for believing that $n \neq r \neq 1$.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY,
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# Synthesis and Characterization of Some Diacidotetraamminerhodium(III) Compounds[1]

BY SUSAN A. JOHNSON[2] AND FRED BASOLO

*Received February 23, 1962*

The syntheses of salts of the complex cations $[\mathrm{RhA}_m\mathrm{Cl}_2]^+$, where A = $\mathrm{NH_3}$, en, *m*-bn, *d,l*-bn, tetrameen, tren, or trien,[3] are described. Similarly, preparations are given for salts of the type $[\mathrm{Rh(en)_2X_2}]^+$, where X = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{NO_2^-}$, or $\mathrm{N_3^-}$, and for those of the type $[\mathrm{Rh(en)_2XCl}]^{+n}$ where X = $\mathrm{SCN^-}$, $\mathrm{NO_2^-}$, or $\mathrm{NH_3}$. In most cases it was possible to isolate both the *cis* and *trans* isomers. Proof of structure for the isomers of $[\mathrm{Rh(en)_2Cl_2}]^+$ was obtained by resolution of the *cis* form. In all other cases structural assignment was based on measurements of absorption spectra. For the $[\mathrm{RhA}_m\mathrm{Cl}_2]^+$ systems there was the supporting evidence that the rates of hydrolysis of the *trans* isomers are not base-catalyzed, whereas the *cis* isomers hydrolyze more rapidly in alkaline solution.

## Introduction

Although extensive investigations have been carried out on the synthesis, properties, and reactive behavior of the diacidotetraamminecobalt(III) complex cations (*i.e.*, species of the type $[\mathrm{CoA}_m\mathrm{X}_2]^+$, where $\mathrm{A}_m$ signifies coördination of four of the six octahedral positions by amine nitrogens and may be comprised of four unidentate, two bidentate, or one quadridentate ligand, and X is a univalent anion such as $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{SCN^-}$, $\mathrm{NO_2^-}$, $\mathrm{N_3^-}$, $\mathrm{OH^-}$, etc.), very little work has appeared in reference to analogous complexes of the congener Rh(III). The available information on diacidotetraamminerhodium(III) cations consists of reports of synthesis of half a dozen such complexes, some of which the present authors have found to be of questionable accuracy. In every case only one of the two possible geometric isomers was reported and its structure was never established. References to the previous work were given in a preliminary communication.[4]

The successful synthesis of the diacidotetraamminerhodium(III) salts reported here will enable us to draw quantitative behaviorial comparisons between the corresponding cobalt(III) and rhodium(III) complexes in regard to the kinetics and mechanisms of hydrolysis, isomerization, and racemization. Results of these comparisons will be reported later. This paper is intended to describe methods of synthesis and characterization of a variety of previously unknown diacidotetraamminerhodium(III) compounds.

## Experimental and Results

Hydrated rhodium chloride ($\mathrm{RhCl_3\cdot 3H_2O}$) was generally used as the starting material for the preparation of dichlorotetraamminerhodium(III) complexes. Details of its preparation starting with Rh metal have been described elsewhere.[5]

***trans*-Dichlorotetraamminerhodium(III) Salts.**—The method reported by Lebedinski[6] for the synthesis of $[\mathrm{Rh(NH_3)_4Cl_2}]\mathrm{NO_3}$ was tried several times without success, the only isolable product of the reaction being $[\mathrm{Rh(NH_3)_3Cl_3}]$. The desired complex was isolated as a by-product

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)315. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] National Institutes of Health Fellow, 1960–1961.

[3] The symbols used are en = ethylenediamine, *m*-bn = *meso*-butylenediamine, *d,l*-bn = *d,l*-butylenediamine, tetrameen = C-tetramethylethylenediamine, tren = β,β′,β″-triaminoethylamine, and trien = triethylenetetramine.

[4] S. Anderson and F. Basolo, *J. Am. Chem. Soc.*, **82**, 4423 (1960).

[5] S. N. Anderson and F. Basolo, *Inorg. Syn.*, **7**, in press.

[6] W. W. Lebedinski, *Izv. Inst. Izučeniju Platiny*, **12**, 67 (1935).