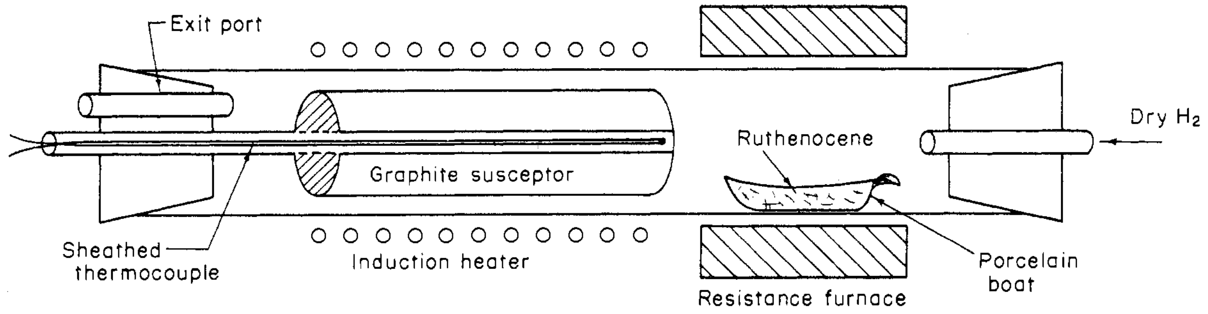

Fig. 1.—Metal vapor deposition apparatus.

film deposit may be due to temperature gradients along the graphite susceptor.

An X-ray diffraction powder diagram of the film deposit taken from the Vycor substrate indicated clean well-crystallized ruthenium metal. The X-ray parameters as shown in Table I agree exactly with standard ASTM data and no extraneous lines were found. The ruthenium metal film was compared with the $RuCl_3$ starting material by emission spectrographic analysis. A small amount of iron (about 0.01%) was found in both the metal film and the original $RuCl_3$. Palladium in the starting material (about 0.1%) was not detected in the vapor-deposited ruthenium, indicating that it is present in an amount less than 0.005%. Small amounts of silicon and boron from the Vycor substrate were also detected.

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR VAPOR-DEPOSITED RUTHENIUM FILM[a]

d, Å.	I	hkl
2.343	41	100
2.142	37	002
2.056	100	101
1.5808	23	102
1.3530	25	110
1.2189	24	103
1.1715	5	200
1.1434	26	112
1.1299	20	201
1.0705	4	004
1.0278	7	202
0.9738	6	104
0.9056	15	203
0.8857	6	210
0.8673	26	211
0.8395	18	114
0.8185	10	212
0.8043	15	105

[a] Radiation source used was Cu Kα.

Discussion

Deposition of films by dissociation of covalent cyclopentadienyl metal compounds or their derivatives suggests a potential source of pure metal. Metallocenes of the transition metals can be prepared in a pure state and exhibit appreciable vapor pressure at low temperatures (~100°), thus facilitating vapor transport in a gas stream. Ferrocene, for example, has a vapor pressure of 10 mm. at 100°.[4] Metallocenes in contrast to metal carbonyls offer the advantage of easier handling and eliminate the possibility of metal film contamination by oxides.

The hydrogen atmosphere appears to be a significant factor in obtaining a pure metallic deposit from a biscyclopentadiene compound. Recent thermal stability studies of a number of organic compounds by Johns[1] have shown that ferrocene decomposes to diferrocenyl at 454° in an inert atmosphere. In this reaction a carbon–hydrogen σ-bond is broken but the π-bonding of the ferrocene remains unchanged. In the patent by Bulloff[2] examples are cited of vacuum deposition of manganese, titanium, and vanadium mixed with their metal carbides. In this case decomposition of the metallocene took place at the hot surface where the deposit formed and not all of the metal–carbon bonds were broken. In the presence of a flow of hydrogen gas, we have shown that ruthenocene decomposed to give a film of pure ruthenium metal and a product or products removed in the gas stream.

Although the dissociation products other than the metal film were not identified in this study, we suggest the following mechanism for the reaction in the presence of hydrogen.

$$Ru(C_5H_5)_2 \longrightarrow Ru + 2C_5H_5\cdot$$
$$2C_5H_5\cdot + H_2 \longrightarrow 2C_5H_6$$

Further experiments will be necessary to establish the mechanism definitely.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Reaction of Copper(II) Chloride with Lithium Borohydride[1]

BY THEODORE J. KLINGEN[2]

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In this investigation the stoichiometry of the reduction of copper(II) chloride with lithium borohydride has been determined. This work provides evidence

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(2) Department of Chemistry, University of Mississippi, University, Miss. 38677.

that the reaction in diethyl ether at room temperature can be adequately explained on the basis of the equation

$$CuCl_2 + 2LiBH_4 \longrightarrow Cu + 2LiCl + B_2H_6 + H_2 \quad (1)$$

Also, it was found that if copper(II) chloride reacted with lithium borohydride in diethyl ether at −45°, a white nonvolatile compound, which has been identified as copper(I) borohydride,[3] was produced. The stoichiometry of this reaction was established as being that given by the equation

$$CuCl_2 + 2LiBH_4 \longrightarrow CuBH_4 + 2LiCl + {}^1/_2B_2H_6 + {}^1/_2H_2 \quad (2)$$

It was found that the copper(I) borohydride produced by this reaction decomposed at −12° to give diborane and hydrogen. The stoichiometry of this decomposition is given by the equation

$$CuBH_4 + Cu + {}^1/_2B_2H_6 + {}^1/_2H_2 \quad (3)$$

Experimental

Materials.—The diethyl ether used in these experiments was anhydrous, analytical reagent grade which was dried over lithium aluminohydride, vapor pressure 185 mm. at 0° (lit.[4] 183 mm.). The copper(II) chloride was prepared by dehydration of pure copper(II) chloride dihydrate by heating in a stream of dry hydrogen chloride. The purity of this compound was shown to be 99.95% copper(II) chloride by copper analysis. The lithium borohydride was purified by extraction with diethyl ether and its purity was determined by boron and hydrogen analysis to be 92.50% lithium borohydride.

TABLE II

STOICHIOMETRY OF THE REACTION OF $CuCl_2$ WITH $LiBH_4$ AT −45 AND −12°

			−45°		−12°		Room temp.	
	$CuCl_2$, mmoles	$LiBH_4$, mmoles	B_2H_6, mmoles	H_2, mmoles	B_2H_6, mmoles	H_2, mmoles	Cu, mg.-atoms	LiCl, mmoles
Theory[a]	2.30	4.60	1.15	1.15	1.15	1.15	2.30	4.60
Obsd.	2.30	4.54	0.98	1.20	1.07	1.33	2.30	4.47
Theory[a]	1.58	3.16	0.79	0.79	0.79	0.79	1.58	3.16
Obsd.	1.58	3.21	0.70	1.03	0.65	1.05	1.57	3.09

[a] The theoretical values were based on the copper(II) chloride taken and on eq. 2 and 3.

Reaction of Copper(II) Chloride with Excess Lithium Borohydride.—Copper(II) chloride reacted with lithium borohydride, taken in excess, in a diethyl ether slurry at room temperature. The reactions were carried out in a standard filtration unit attached to a high vacuum line. After the reaction ceased to generate gas (about 30 min.), the hydrogen and diborane formed were separated from the reaction product mixture and measured. The excess lithium borohydride was removed from the reaction products by extraction with diethyl ether. The excess lithium borohydride was hydrolyzed and the active hydrogen, boron, and (in some cases) the lithium were determined. The residue of the reaction product mixture was extracted in two of the experiments with methyl alcohol. The methyl borate ester formed in this extraction was analyzed for boron. The boron found in the methyl alcohol extraction could have been produced in the original reaction as either elemental boron or copper boride. The lithium chloride in the residue of the reaction product mixture, which was red in color, was extracted with distilled water and analyzed by determination of the chloride ion content. The copper in the water-insoluble residue was identified qualitatively by the X-ray powder diffraction method and determined quantitatively by electrodeposition from a nitric acid solution. The results of this experimental work are given in the observed value column of Table I.

TABLE I

STOICHIOMETRY OF THE REACTION OF $CuCl_2$ WITH $LiBH_4$ AT ROOM TEMPERATURE

	$CuCl_2$, mmoles	$LiBH_4$, mmoles	Cu, mg.-atoms	B_2H_6, mmoles	LiCl, mmoles	H_2, mmoles
Theory[a]	3.58	7.16	3.58	3.58	7.16	3.58
Obsd.	3.58	7.15	...[b]	3.17	...	5.04
Theory[a]	1.65	3.30	1.65	1.65	3.30	1.65
Obsd.	1.65	3.31	1.65	1.19	...	2.08
Theory[a]	1.68	3.36	1.68	1.68	3.36	1.68
Obsd.	1.68	3.34	1.68	1.19	3.28	1.81

[a] The theoretical values were based on the copper(II) chloride taken and on eq. 1. [b] An X-ray powder diffraction study was run on the copper from this reaction.

Reaction of Copper(II) Chloride with Lithium Borohydride at −45°.—In carrying out the reaction at −45° in diethyl ether solvent, it was found that in addition to hydrogen and diborane production, a white precipitate was formed. The hydrogen and diborane were separated from each other and measured. The white solid product which precipitated was found to be only slightly soluble in diethyl ether and to decompose in the absence of solvent at −12° to give hydrogen and diborane. The diborane and hydrogen produced by this decomposition were measured and found to be in agreement with the stoichiometry of eq. 3. Following decomposition of the low-temperature product, the excess lithium borohydride was then extracted with ether and analyzed for boron and hydrogen. The red residue in the reaction flask was analyzed for lithium chloride and copper in the same manner as described above for the room temperature reaction. The results of this phase of the investigation are shown in Table II.

Summary

The results obtained in this work agree well with the proposed stoichiometric equations, except that the hydrogen produced is always somewhat in excess of theory and the diborane is always slightly low. However, if one assumes catalytic decomposition of some of the diborane during the reaction to hydrogen, nearly perfect stoichiometry is obtained.

Acknowledgments.—The author wishes to express his appreciation to the late Dr. George W. Schaeffer for suggesting this problem and to Dr. Leo F. Hohnstedt of St. Louis University for his helpful comments on this note.

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(3) The unpublished data of R. H. Toeniskoetter and G. W. Schaeffer, St. Louis University, indicate that copper(I) chloride reacts with lithium borohydride at −45° in diethyl ether solution to produce a white nonvolatile compound without the evolution of diborane or hydrogen. This white solid was also found to decompose at −12° in accordance with eq. 3.

(4) R. T. Sanderson, "Vacuum Manipulations of Volatile Compounds," John Wiley and Sons, New York, N. Y., 1948.