University of North Dakota

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Organometallic Chemistry of Transition Metals

Interim Technical Report

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I. INTRODUCTION

A central problem of chemistry is the problem of the structure of chemical substances—that is, of the number and nature of the chemical bonds which can form between various kinds of atoms in molecules. Prediction of the properties, either chemical or physical, of a given substance will depend upon a knowledge of its structure. Since carbon is the element of central interest in organic chemistry, a complete understanding of the nature of the bonds which can form between carbon and other elements is of great importance to this branch of science.

If the present status of organic chemistry is considered from the above point of view, it is seen immediately that there is one area in which both theoretical and experimental knowledge are mostly lacking. There is relatively little data, and still less understanding, concerning bonds between carbon and the transition elements (that is, elements in whose atoms there is an incomplete inner electron shell). In the hundreds of thousands of known organic compounds, there occur bonds between carbon atoms and atoms of almost all non-transition elements. Abundant experimental data are available concerning substances in which there is, for example, a carbon-lithium, or carbon-lead, or carbon-chlorine bond. Theoretical descriptions of the behavior of such bonds can be offered in many cases. In contrast, only a handful of the known organic substances contain a bond between a carbon atom and an atom of a transition element. The principles which govern the formation of such bonds have not been put on any theoretical basis, and the experimental data are so limited as to offer no useful basis for even empirical generalizations.

It is because of the challenge offered by this relatively unknown area in the chemistry of carbon that the present program of research has been undertaken. The original proposal, dated February 5, 1952, presented the problem in broad terms, essentially as outlined above. The research contract subsequently offered, and accepted by the University of North Dakota, was written by the Office of

Naval Research in the same spirit as our proposal, and specifies simply that the University "shall conduct research on the reactions of active organometallic compounds with transition metals or their inorganic compounds, whether or not isolable organometallic products result". Such a broad specification allows the contractor much freedom in the research program. This fact is very much appreciated, since it indicates that the Office of Naval Research regards the project as properly one of long-range or "fundamental" investigation, and it is in this spirit that we have undertaken the work. From the beginning of the research, however, it has been kept in mind that such a contract leaves to the principal investigator the duty of avoiding aimless experimentation or scattered experiments carried out with no well-defined objective. Every effort has been made to keep the program directed steadily toward the development of useful basic experimental data on reactions of the type specified.

The main objective of the program for the period covered by the report has been to establish the stoichiometry of the reaction of organolithium compounds or of Grignard reagents with the halides of as many of the transition metals as possible. There is a certain amount of published work on the organic chemistry of various transition elements, and some of the results reported are very unusual. In many cases, however, it is impossible to form even a tentative opinion as to the nature of the chemical reactions involved, because of the lack of stoichiometric data. The practice has often been simply to treat an inorganic halide with a large excess of a Grignard reagent, and to isolate what products could be obtained from the resulting mixture. For example, the very curious organochromium compounds of F. Hein (see literature survey below) resulted from such a reaction between phenyl-magnesium bromide and chromium trichloride. Among the products were compounds, apparently, in which three, four, or five phenyl groups might be bonded to chromium; but the nature of the primary reaction cannot even be speculated on intelligently, because the number of moles of phenylmagnesium bromide actually involved in the reaction is unknown. It appeared that stoichiometric data, for this and many other

cases, would be essential to any attempt at elucidation of the chemistry involved.

Those investigations are reported below. They have not proceeded as rapidly as was anticipated, and this part of the program has dealt only with some of the transition elements of the fourth period of the periodic table—the transition elements of the 3d series. The main reason for this rather slow progress was the difficulty experienced in obtaining pure anhydrous inorganic starting materials. The halides of the transition metals are mostly well-known, but often as hydrated complexes. The preparation of those same halides in strictly anhydrous form, in a high state of purity, and in reasonable quantity, has proved in some cases to be troublesome. The literature of synthetic inorganic chemistry is often of little help in these cases, because of the lack of specific experimental directions, or for other reasons. For example, products obtained by heating hydrated salts have sometimes been reported and used as anhydrous halides, with no analysis given. Analysis will often show that such products are not pure, and probably contain oxygen. At least half the time of the first year of the project has been devoted to the development of supplies of suitable inorganic starting materials, especially anhydrous inorganic halides. This work has consisted in part of analysis and testing of materials supplied commercially, and in part of the preparation and analysis of our own samples and the evaluation of various methods for such preparations. The results of this preliminary labor are included as Part III of this report.

During the early phases of the work, it was also of course necessary to prepare a survey of the literature on the organometallic chemistry of these elements. This literature was familiar to us in general when the proposal was written, but the complete coverage of the field which was required in connection with the research itself proved to be a time-consuming undertaking, because of the large number of subjects under which search had to be made. The literature survey forms Part II of this report.

The experimental data on the reactions of halides of the transition metals with phenyllithium are given in Part IV, and these results are discussed briefly in Part V. Because the results are as yet incomplete, extensive discussion is not appropriate at this time. Some suggestions as to the future program are given in Part VI, which is followed by the summary, Part VII.

In conclusion of this introductory section, it is desirable to point out the importance of certain recently reported results from other laboratories to this research program. When the present project was first proposed, very few organic compounds of transition metals had been prepared. For instance, among fourth period elements, no organometallic compounds of titanium, vanadium, iron, cobalt, or nickel had been isolated, and there were only brief references to ill-defined scandium and manganese compounds. Only in the case of chromium had isolable substances, some apparently well-defined, been reported. Some suggestive results had been obtained, particularly with titanium, and in our proposal it is stated that "Titanium is the element which . . . should be investigated first . . . Although the work of Gilman and Jones did not yield isolable organotitanium compounds, their reaction of phenyllithium with titanium tetraethoxide seems interesting . . . Our initial experiments . . . might involve the use of organolithium compounds with various inorganic titanium compounds". This proposal was written late in 1950. The project did not start, however, until June 1, 1952, and during the time intervening two significant developments had appeared in the literature. One was a report of the isolation of an organotitanium compound, prepared from phenyllithium and titanium tetraisopropoxide— that is, by the same attack which we had expected would probably be most profitable. This work was reported in a brief communication by Herman and Nelson of the National Lead Company. Fortunately this communication appeared just as our research was starting, and we were able to avoid repetition of work which had already been done. We have, since then, been in touch with Drs. Nelson and Herman, who have been very cooperative in sending us information about their work, in advance of publication.

Also, in 1951, between the proposal and the initiation of the project, there was published the report of the preparation of dicyclopentadienyliron by a reaction of the type specified for study under this contract. This work was taken up immediately by several investigators, particularly by Wilkinson at Harvard, who prepared a whole series of "sandwich" compounds of this ferrocene type, including derivatives of titanium, vanadium, iron, cobalt, and nickel among the $3\underline{d}$ transition elements. Whether these compounds are "organometallic" or not is partly a question of definition, but in any case they certainly have a very important bearing on the general problem of bond formation between carbon and transition elements. It will be necessary to pay some attention to these compounds in future phases of our program. During this first year of our work, new information on these substances was being published so rapidly that it seemed best to defer any such experimental investigations of our own until the picture became a little clearer.

Thus, in a field in which there had been few new developments for some years prior to our proposal, there has in contrast been a considerable amount of publication during the past year. Some of these recent results have anticipated some of the work which we had proposed. However, these developments are encouraging in that they confirm the soundness of a proposal for research along these lines. It may be expected that continued investigations in this field will yield information, not only on yet other new and novel types of chemical substances, but also on problems of fundamental importance to the chemistry of carbon.

This report is an interim Technical Report, written to describe the progress made during the first year of a two-year contract. The contract is still in force, and the research is continuing.

II. SURVEY OF THE LITERATURE ON THE ORGANOMETALLIC CHEMISTRY OF

TRANSITION METALS OF THE 3d SERIES

(Arabic numerals in parentheses refer to literature references in the
bibliography, part VIII of the report.)

General

A chemical element is classified as transition or non-transition according
to whether or not its atom possesses unfilled orbitals in electron shells below
the valence shell. Non-transition elements have no such unused orbitals, and
bond formation by these elements is expected to involve no lower-lying orbitals.
Organic compounds of most of these elements have been prepared and studied, and
are on the whole well-defined substances in which the central element has the
valence which would be expected in view of its chemical properties.

A transition element is one in which there are unfilled orbitals below
the valence shell. This arrangement leaves orbitals in two shells available
for forming bonds to other atoms. There are several transition series in the
periodic table. In this report attention is concentrated on the series which
includes the elements from scandium through copper (the transition elements of
the 3d series.)

Most attempts to prepare organometallic derivatives of the transition metals
have employed the reaction of another organometallic, such as a Grignard reagent,
with an inorganic compound of the metal. The common product derived from such
a reaction is the compound which is the result of the coupling of the organic
radicals of the Grignard reagent, for instance, biphenyl from phenylmagnesium
bromide. That is, transition metal halides catalyze the decomposition of
Grignard reagents or other organometallics in a fashion such as

$$2RMgX \longrightarrow R-R$$

Relatively few compounds with a carbon-transition metal bond have been isolated
from such reactions, but Kharasch and Fields (68) studied this catalysis and
concluded that there is an organometallic intermediate formed in the coupling

reaction with Grignard reagents. If this is true then it may be said that organo-
metallic compounds of all the transition metals have been formed.

Formation of organometallic compounds of scandium, titanium, vanadium,
chromium, manganese, iron, cobalt, nickel, and copper has been reported. Up to
1950, however, no well-characterized simple compound had been described. Organo-
chromium compounds had been prepared and studied extensively by Hein, who re-
ported compounds in which the metal had the unexpected co-ordination numbers
three, four, or five. (As far as we can tell, this work has not been repeated
elsewhere—see below for details.)

In 1952, Herman and Nelson (56) reported the isolation and thorough charac-
terization of an organotitanium compound in which the titanium had the normal co-
valence of four. The compound was a crystalline material with a well-defined
melting point, and underwent many reactions typical of an organometallic bond
of low activity.

Since 1950 much interest has developed also in a new type of organic com-
pound of transition elements. Dicyclopentadienyliron (or "ferrocene", as it
will apparently be called), $(C_5H_5)_2Fe$, was originally prepared from cyclo-
pentadienylmagnesium bromide and ferric chloride. The molecule has two rings,
each with five equivalent C-H groupings, and an iron atom centrosymmetrically
placed between the two rings. Related compounds of nickel, titanium, zirconium,
vanadium, cobalt and ruthenium have been prepared and studied by Wilkinson and
co-workers at Harvard, in a research program which is still continuing.

Iron

The first attempt to prepare an organoiron compound was made by Wanklyn
and Carius (100) in 1861. From the reaction between ferrous iodide and diethyl-
zinc, they obtained a mixture of gases and metallic iron. The gases identified
were ethylene, ethane and hydrogen, the products one would expect if the re-
action proceeded by a radical mechanism. Bennett and Turner (1,2) found that

phenylmagnesium bromide with ferric chloride gave, besides biphenyl, a green
solid which contained iron, was soluble in benzene, and depressed the melting
point of biphenyl. No proof was given that the substance was a true organo-
metallic compound.

Job and Reich (63) reported the preparation of ethyliron iodide by the
action of ethylzinc iodide on ferrous iodide. The evidence for the existence of
an organoiron compound was the formation of ferrous hydroxide on hydrolysis of the
reaction mixture. Samples hydrolyzed as the reaction proceeded gave more ferrous
hydroxide and less zinc hydroxide. Champetier (11) reported that ferrous iodide
gave an organoiron compound with phenylzinc iodide, but not with phenylmagnesium
bromide. His proof also was based on the formation of ferrous hydroxide on
hydrolysis. Job and Champetier (61,62) noted the formation of an unstable organo-
iron compound in the reaction of phenylmagnesium bromide and iron perchlorate.
They did not isolate this compound.

An entirely different type of compound is that prepared by Kealy and Pauson
(66) from ferric chloride and cyclopentadienylmagnesium bromide. This product has
the formula $(C_5H_5)_2Fe$, and has been called "ferrocene". Miller, Tebboth, and
Tremaine (82) prepared the same compound from reduced iron and cyclopentadiene.
The properties of the material are similar to those of an aromatic hydrocarbon.
Wilkinson and co-workers at Harvard have studied the chemistry of this compound,
and of similar compounds of other metals. The iron compound is an orange solid,
m. p. 173-174^c, which is very stable toward acids and bases. It is insoluble in
water, 10% sodium hydroxide, or hot concentrated hydrochloric acid, but will
dissolve in organic solvents, dilute nitric acid, or concentrated sulfuric acid.
Woodward, Rosenblum, and Whiting (107) prepared many derivatives of ferrocene
which indicate that the compound acts as if it had two five-membered benzenoid
rings. When it was treated with acetyl chloride in the presence of $AlCl_3$, a red

crystalline diacetyl derivative, m. p. 130-131°, was formed. The diacetyl derivative would give a dioxime (decomposed above 200°), and a dicarboxylic acid (sublimed unchanged above 230°) which could be characterized by its dimethyl ester, m. p. 114-115°. Other derivatives are also mentioned. The acidity constants of ferrocene dicarboxylic acid and of benzoic acid are very similar; ferrocene dicarboxylic acid, pK_1 3.1×10^{-7}, pK_2 2.7×10^{-8}, benzoic acid pK 2.4×10^{-7}. Magnetic susceptibility determinations show that ferrocene is not paramagnetic, but that the cation which is produced by oxidation of ferrocene is paramagnetic and has one unpaired electron.

Wilkinson and co-workers (106) proposed a structure for ferrocene in which the two rings, each of five equivalent C-H groupings, are bonded to an iron atom which is centrosymmetrically placed between the two rings. X-ray examination of the molecule (14) confirms this structure.

Titanium

Cahours (8) was the first to report an attempt to prepare an organotitanium compound. He treated titanium tetrachloride with diethylzinc and obtained a black product of unknown composition. He also observed no reaction between the metal and methyl or ethyl iodide. Kohler (73) treated titanium tetrachloride with phenylphosphorous dichloride and observed no reaction. Schuman (93) obtained no organotitanium compounds from the reaction between diethylzinc and titanium tetrachloride, but Paterno and Peratoner (85) isolated a compound $TiCl_4 \cdot 2(C_2H_5)_2Zn$ from the same reaction. This product was decomposed vigorously by water, with the evolution of gas. Free zinc and a small quantity of oil was also recovered. The oil was reported to contain titanium, but analysis gave values for titanium which were 400% high for the value calculated for $(C_2H_5)_4Ti$. The authors stated that their titanium tetrachloride may not have been pure. Levy (75) made many attempts to prepare an organotitanium compound, but none were successful. The metal did not react with diethylmercury, diethylzinc or triethylaluminum. Titanium

tetrachloride and diethylmercury gave ethylmercuric chloride, titanium tri-
chloride, and an unidentified gas containing neither titanium nor chlorine.

Challenger, Pritchard and Jinks (10) treated titanium tetrachloride with
triphenylarsenic, -antimony, and -bismuth and also with phenylmagnesium bromide
and with α-naphthylmagnesium bromide. They did not get any organotitanium com-
pound from the reactions. The Grignard reagents yielded chiefly coupling prod-
ucts and a black solid containing trivalent titanium. Brown and Reid (6) iso-
lated a brown tarry substance from the reaction of titanium tetrachloride with
tetraethyllead. Negative results were also reported by Razuvaev and Bogdanov
(89) who treated titanium tetrachloride with diphenyl mercury, with phenylmagnesium
chloride, and with sodium and chlorobenzene.

Plets (88) reported the preparation of an organotitanium compound by
treatment of triethoxychlorotitanium or diethoxydichlorotitanium with butyl
chloride in the presence of metallic lithium. These compounds could not be
isolated because of their rapid hydrolysis. The chief argument for a carbon-
titanium bond is that iodine monochloride and the reaction products gave a small
amount of n-butyl iodide. The possibility of the n-butyl iodide arising from
n-butyl lithium in the reaction products seems to have been overlooked.

Gilman and Jones (21,65) reported the isolation of an orange precipitate
from the reaction of tetraethoxytitanium and phenyllithium. The orange solid
contained halogen and tetravalent titanium, but no reduced titanium. It gave a
color test, burned spontaneously in the air, and reacted violently with water.
Upon standing at room temperature the solid darkened and became a black mass
from which biphenyl (32% yield) was extracted as the only identified product.
The reaction between metallic titanium and diphenylmercury produced no reaction.
Titanium tetrachloride with phenyl or butyllithium gave no indication of an
organotitanium compound. The main product with phenyllithium was biphenyl (53%
yield).

Herman and Nelson (56) isolated a crystalline organotitanium compound from the following series of reactions: Isopropyl titanate was treated with phenyllithium in equimolar proportions to give a stable lithium complex of phenyltitanium triisopropoxide, which by chemical properties and elementary analysis seemed to have the formula $C_6H_5Ti(OC_3H_7)_3 \cdot LiOC_3H_7 \cdot LiBr \cdot (C_2H_5)_2O$. The complex was treated with titanium tetrachloride, which precipitated the lithium as the chloride and freed the organotitanium compound from the complex phenyltitanium triisopropoxide. The organotitanium compound has m. p. $88-90^\circ$, and was kept without decomposition for a year at 10°, under nitrogen. An ether solution gave a slowly developing Michler's ketone color test (23); phenyltitanium triisopropoxide reacted rapidly with oxygen to give a phenol derivative, reacted with water to give benzene, and reacted slowly with diphenyl ketone to give triphenylcarbinol, but it failed to give benzoic acid on treatment with solid carbon dioxide. These reactions are typical of an organometallic bond of low activity. Herman and Nelson studied the effects of various groups on the stability of organotitanium compounds of the type $R_nTiX_{(4-n)}$ (where R is alkyl or aryl and X is an anion). They found that the stability increased as R increased in "negativity". Aromatic R groups gave the most stable compounds. The smaller the value of n, the greater the stability. The stability of the compounds increased in the following order for different X groups: Fluoride, methoxy, chloride, butoxy. The ether solutions of the unisolated products obtained with phenylmagnesium bromide and alkyl titanates gave reactions similar to those obtained with the crystalline phenyltitanium triisopropoxide. The titanium-carbon bond was shown to decompose spontaneously to give phenyl radicals. This was illustrated by the ability of the material to catalyze the polymerization of styrene.

Wilkinson, Pauson, Birmingham and Cotton (105) have prepared an organic compound of titanium which is analogous to the iron compound ferrocene. Bis(cyclo-

pentadienyl)titanium dibromide was prepared by the reaction of excess cyclopenta-
dienylmagnesium bromide with titanium tetrachloride in toluene solution. It
forms dark red crystals with m. p. $240-243^{\circ}$. It is to some extent hydrolyzed by
water, giving a yellow solution which will give precipitates similar to other
bis(cyclopentadienyl)metal ions. Magnetic susceptibility measurements show
that bis(cyclopentadienyl)titanium dibromide is not paramagnetic.

Vanadium

Supniewski (97) reported that vanadium tri- and tetrahalides caused coupling
of the organic radicals of various organomagnesium halides. Phenylmagnesium
bromide and vanadium dichloride gave biphenyl in 40-50% yield. He found that
aliphatic Grignard reagents gave better yields of the coupling product. Vernon
(99) was the next to report on the reaction of phenylmagnesium bromide with the
halides and oxyhalides of vanadium. Biphenyl was recovered from the reaction
mixtures apparently in direct proportion to the amount of vanadium compound
used. In one case, that of vanadium oxytrichloride, an unstable organic solid,
which gave a positive test for vanadium, was isolated. Upon hydrolysis, this
solid yielded biphenyl. Other workers (70,80) also studied the reaction of
vanadium salts with phenylmagnesium bromide, but did not isolate organovanadium
compounds. Kirsanov and Sazanova (70) reported that they obtained an organo-
vanadium compound which could not be isolated.

Organic compounds of vanadium have been prepared and isolated by the re-
action of cyclopentadienylmagnesium bromide with vanadium tetrachloride (105).
These compounds are analogous to the iron compound ferrocene (66,82,106,107).
One compound is a dark green, rather unstable, ligroin-soluble dibromide. The
other is a pale green, ligroin-insoluble dichloride. Bis(cyclopentadienyl)-
vanadium dichloride is soluble in chloroform, ethyl acetate, and alcohol; it
decomposes on heating above 250°. In water it forms a green unstable solution
which gives precipitation reactions typical of bis(cyclopentadienyl)metal ions
with reagents such as chloroplatinic acid, potassium triiodide, picric acid, etc.

Magnetic susceptibility measurements indicate that bis(cyclopentadienyl)vanadium dichloride has one unpaired electron. There was no information on the molecular weight of the compound.

Chromium

Sand and Singer (92) were the first to attempt the preparation of an organochromium compound. They treated chromyl chloride with phenylmagnesium bromide, but failed to isolate any product of the desired type. Kondyrew and Fomin (74) and Bennett and Turner (1,2) found that the only products obtained by treating chromium halides with Grignard reagents were coupling products. Aliphatic Grignard reagents gave saturated and unsaturated hydrocarbons. The amount of biphenyl formed in the reaction of phenylmagnesium bromide with chromium trichloride was proportional to the amount of chromium trichloride used.

Hein and his co-workers (26-53) have reported the isolation of many organochromium compounds. These are polyphenyl compounds which are the products of the reaction of phenylmagnesium bromide and a halide or oxyhalide of chromium. An ethereal emulsion containing compounds of chromium was isolated from the acidification of the reaction mixture of phenylmagnesium bromide and chromium trichloride, and an orange-brown solid was isolated from this emulsion. The solid was soluble in chloroform, alcohols, and polar solvents, but was insoluble in ether. It was shown to be a mixture of bromides of a number of organochromium compounds. This crude mixture was purified by treating it with excess alcohol and mercuric chloride to obtain a complex corresponding to the formula $(C_6H_5)CrBr.HgCl_2$. The complex was extracted with alcohol, decomposed in pyridine with hydrogen sulfide, acidified with sulfuric acid and then extracted with chloroform and ether. The purified product corresponded in Cr content to the formula $(C_6H_5)_5CrBr.1/2(C_2H_5)_2O$. The product was unstable, and on exposure to light and air it decomposed with the formation of much biphenyl. This compound when treated with potassium hydroxide yielded $(C_6H_5)_5CrOH.4H_2O$, which is a very strong base.

Solutions of pentaphenylchromium hydroxide when treated with acids or neutral salts gave salts of $(C_6H_5)_4CrOH$, and not of $(C_6H_5)_5CrOH$ (with a few exceptions which include the acetate, chloroacetate, acid carbonate, and sulfate). The phenyl group which is lost appears as phenol, enough biphenyl to smell, an acidic material, and a solid soluble in organic solvents. Tetraphenyl- and triphenylchromium halides were also isolated from the crude product of the reaction between chromium trichloride and phenylmagnesium bromide. Tetraphenylchromium hydroxide was made from $(C_6H_5)_4CrI$ and silver hydroxide, and triphenylchromium hydroxide from a triphenylchromium halide and a base. The base strengths of these three polyphenylchromium hydroxides were measured and it was found that they decreased in the order $(C_6H_5)_3CrOH$, $(C_6H_5)_4CrOH$, $(C_6H_5)_5CrOH$, but that all were strong bases. Tetraphenylchromium was prepared by the electrolysis of $(C_6H_5)_4CrI$ in liquid ammonia at -40^0 to -50^0. The tetraphenylchromium was deposited upon the cathode as a red, smooth or crystalline deposit. It is quite unstable at room temperature and in air it becomes smeary, darkens, and evolves the odor of biphenyl. It will dissolve rapidly in alcohol or water and changes quantitatively into $(C_6H_5)_4CrOH$. The molecular weight of $(C_6H_5)_4Cr$ has not been determined. $(C_6H_5)_3Cr$ was prepared by a similar electrolysis reaction. It was deposited on the cathode as an amorphous brown yellow material which is unstable, splitting off biphenyl and forming $(C_6H_5)_3CrOH$ in air. $(C_6H_5)_3Cr$ was also obtained by treating $(C_6H_5)_3CrI$ with metallic sodium in liquid ammonia.

Only one solvent-free and uncomplexed organochromium compound with a co-ordination number of five, and one with a co-ordination number of three have been isolated. They are respectively penta(p-bromotriphenylene)chromium bromide, $[Br-(C_6H_4)_3]_5CrBr$, and triphenylchromium perchlorate, $(C_6H_5)_3CrClO_4$. Many such compounds in which chromium has a co-ordination number of four have been isolated, and analyses of these compounds check with the calculated values. All these organochromium hydroxides and many of their salts are of the same color, that of the dichromate ion, regardless of the apparent valence of the

chromium.

The only independent investigation of these compounds was made by Klemm and Neuber (72). They measured the paramagnetic susceptibility of compounds in which there were five, four and three groups bonded to the chromium atom. They found that all of the compounds from all three series gave a magnetic moment of 1.73 Bohr magnetons, independent of temperature, which indicates one unpaired electron in the molecule in every case. This would indicate that chromium is pentavalent in all of these compounds, thus making Hein's formulas in error or in need of revision. It is not clear from Klemm and Neuber's paper whether they obtained their organochromium compounds from Hein or whether they prepared the compounds independently. There is no other record of any independent confirmation of any of this work on organochromium compounds.

No reaction, of organochromium compounds with carbonyl or unsaturated groups in other molecules has been reported.

Scandium

The only reference to an organoscandium compound is by Plets (87), in which the preparation of triethylscandium mono-etherate from ethylmagnesium bromide and scandium trichloride is reported. The compound is a liquid which boils at 170-172°, oxidizes readily, and decomposes promptly in water.

Manganese

There are very few references to organometallic compounds of manganese in the literature. Gilman and Baillie (19) mention the preparation of phenyl-manganese iodide from manganous iodide and phenylmagnesium iodide. The product was a chocolate brown solid which gave both biphenyl and benzene on hydrolysis. It was inflammable and gave biphenyl on moderate pyrolysis. The solid analyzed for a mixture of phenylmanganese iodide and diphenylmanganese, although the authors state that it may not contain divalent manganese.

Plots (88) mentions that organic derivatives of manganese will form, but ho gives no experimental details.

Cobalt

The early work (22,68) on the reaction of Grignard reagents with the anhydrous halides of cobalt gave, in most cases, coupling products in nearly 100% yields.

$$2 \ RMgX \ + \ 2CoX_2 \longrightarrow R-R \ + \ 2MgX_2 \ + \ 2CoX$$
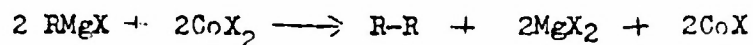
Ingles and Polya (60) were the first to report the isolation of an organocobalt compound. Organocobalt bromides and iodides were prepared from Grignard reagents, RMgX (R = 1- or 2- naphthyl; bromide or iodide), and cobalt halides in ethereal solution. The products were of the type $RCoX_3$, R_2CoX_2 and R_3CoX. They were all crystalline solids which decomposed over a range between 120-160°. They were analyzed for cobalt and halogen, and the results agreed well with the calculated values. The organocobalt compounds prepared from phenyl and from aliphatic Grignard reagents were impure.

Wilkinson (104) has prepared organic compounds of cobalt which are analogous to ferrocene. The compounds which were prepared are salts of the ion $(C_5H_5)_2Co^+$, which is called the cobalticinium ion. The ion was prepared from cobaltic acetylacetonate and cyclopentadienylmagnesium bromide in benzene.

The ion is very stable and is unaffected by boiling with either aqua regia or concentrated sulfuric acid, or with dilute alkalies alone or even in the presence of hydrogen peroxide. Fuming with perchloric acid will destroy the ion. Crystalline precipitates can be obtained with silicotungstic acid, picric acid, chloroplatinic acid, potassium triiodide or others. Cobalticinium hydroxide was made in aqueous solution by the action of silver oxide on the chloride solution. The ionization constant of the base is 8.2×10^{-3}. Magnetic susceptibility measurements on cobalticinium picrate show that the salts of the cobalticinium ion are not paramagnetic. Unsuccessful attempts were made by Page and Wilkinson (84)

to prepare cobalticene, $(C_5H_5)_2Co$, by controlled-potential electrolysis of a
neutral 0.001 M cobalticinium perchlorate solution.

Nickel

Job and Reich (64) were the first to report the preparation of an organo-
nickel compound. They treated phenylmagnesium bromide and an excess of $NiCl_2$
with ethylene, and then hydrolyzed the mixture. The products of the reaction
were ethane, ethylbenzene, styrolene and biphenyl. Since previous investigators
isolated only ethylbenzene from the reaction between ethylene and benzene in
the presence of $AlCl_3$, the authors concluded that an organonickel compound
is an intermediate in their reaction. No such compound was isolated.

Other authors (22,60,68) have attempted to prepare organonickel compounds
by treating the anhydrous halides of nickel with Grignard reagents. The results
have led almost exclusively to coupling products and not to organonickel com-
pounds.

Wilkinson, Pauson, Birmingham and Cotton (105) have prepared an organic
compound of nickel which is analogous to the organoiron compound ferrocene.
Dicyclopentadienylnickel was prepared by the reaction of cyclopentadienyl-
magnesium bromide with nickel acetylacetonate. It forms dark green crystals
from ligroin which decompose slowly even in the absence of air and light. It
sublimes above 130°, but decomposes below the melting point. The dicyclo-
pentadienylnickel ion, obtained by oxidation, gives precipitates with silico-
tungstic acid, potassium triiodide, etc. just as do the ferricinium (107) and
cobalticinium (104) ions. Aqueous solutions of this ion are rather unstable and
decompose in a few minutes. Magnetic susceptibility measurements show that
dicyclopentadienylnickel has two unpaired electrons.

Copper

Buckton (7) treated cuprous chloride with diethylzinc and obtained a

organometallic compounds of copper. The cuprous chloride was reduced to metallic copper. Wanklyn and Carius (100) attempted the same reaction with the same results. Franklyn and Duppa (17) treated copper metal with diethylmercury and obtained only a mixture of gases and no alkylcopper. In 1915 Kondyrew and Fomin (74) treated cuprous halides and cuprous cyanide with Grignard reagents. With aliphatic Grignard reagents the products were a mixture of saturated and unsaturated hydrocarbons. With aromatic Grignard reagents they obtained coupling products.

Reich (90) was the first to report the isolation of an organometallic compound of copper. He prepared phenylcopper by the action of phenylmagnesium bromide on cuprous iodide in dry ether. It was isolated as a gray powder which gave biphenyl in 95% yield on boiling with benzene. The compound when heated alone gave vapors of biphenyl and a red copper powder. With water the products were benzene and cuprous oxide. Ethylcopper was formed by a similar reaction, but it could not be isolated.

Gilman and Straley (24) also isolated phenylcopper as a white powder from the reaction between phenylmagnesium iodide and cuprous iodide at 0°. The phenylcopper was unstable and decomposed in air to form biphenyl. With water it gave 25-26% of biphenyl and up to 36% of benzene. With benzoyl chloride it gave benzophenone (55% yield); with allyl bromide, allylbenzene (31%); and with acetyl chloride, acetophenone (48%). p-Anisylcopper was also prepared, from p-anisylmagnesium bromide and cuprous iodide. This compound when treated with acetyl chloride in ether gave bi-p-anisyl. Ethylcopper was prepared from ethylmagnesium iodide and cuprous iodide. Treatment of this compound with benzoyl chloride in ether gave a 22% yield of propiophenone.

Bolth, Whaley, and Starkey (5,103) prepared a series of organocopper compounds from the corresponding diazonium borofluorides and metallic copper in dry

benzene or toluene. Phenyl-, p-nitrophenyl-, o-nitrophenyl-, m-nitrophenyl-, p-tolyl-, and p-sulfonamidophenylcopper were prepared in this way. No attempt was made to isolate the organocopper compounds; the reactions carried out with them were performed in solution. None of the compounds would give a Michler's ketone color test. Butyl bromide reacted with phenylcopper, but not with o-nitrophenylcopper. Other evidence of the presence of an organocopper compound was given by the reaction of phenyl- and o-nitrophenylcopper with chloroacetyl-chloride to give phenacyl- and o-nitrophenacyl chloride respectively.

Gilman, Jones, and Woods (20,25) prepared a solid organocopper compound from the reaction of a methyl Grignard reagent or methyllithium compound and a cuprous salt. This solid was unstable and decomposed to form copper and ethane. When dried in the air it exploded violently. The reaction of cuprous iodide and methyllithium produced a solution of methylcopper which gave a negative Michler's ketone color test. This yellow solution when reacted with benzoyl chloride gave a 56% yield of acetophenone.

III. ANHYDROUS HALIDES OF TRANSITION ELEMENTS OF THE 3d SERIES—
LITERATURE SUMMARY AND EXPERIMENTAL DATA

General

This portion of the report contains a collection of literature on the anhydrous halides of transition elements of the 3d series, and also the results of our own experimental work pertaining to the preparation of these substances. The collection of data is not a complete literature survey, but is intended to serve as a practical guide to the probable best methods of preparing these halides, and to such facts of their chemistry as seem to be of interest for our purposes. Information on color, boiling point, melting point, crystal structure, vapor density, solubility, magnetic susceptibility, and synthesis is given, where available.

Although the chemistry of metal halides in water solution is exhaustively reported in the chemical literature, exact data on anhydrous halides of elements such as these is in some cases difficult to locate, and this is particularly true of preparative methods. In the older literature preparations are often not given in sufficient detail to allow of duplication, and data which would establish the identity and purity of the product are often lacking. For this reason, it was necessary to spend much time in this investigation simply working out methods for preparation of starting materials. The methods we have found suitable are recorded here. None of them are new, but care has been taken to record the exact experimental procedures and to give analyses of all products, so that in the future, starting materials can be prepared without such delay and uncertainty.

Iron

The anhydrous halides of iron which have been prepared and which are available are $FeCl_2$, $FeCl_3$, $FeBr_2$, $FeBr_3$ and FeI_2. FeI_3 has not been isolated. Anhydrous $FeCl_3$ is available commercially (Eastman Kodak) at a fairly low price.

Chlorides of Iron

The synthesis of $FeCl_3$ is described by Tarr (98). This preparation involves heating iron wire in a stream of chlorine gas. The yield is almost quantitative, but the product obtained is not absolutely pure, since it contains small amounts of $FeCl_2$. It can be purified by sublimation in a stream of chlorine. $FeCl_3$ consists of brownish black crystals, sp. gr. 2.804, m. p. 282°, and b. p. 315°. It is soluble in water, alcohol, ether, and hydrochloric acid. Vapor density measurements show that it is dimeric at 440°, but monomeric above 750° (95). The crystal structure is of the hexagonal close packing type (59) in which each Fe atom is surrounded by six Cl atoms, three above and three below the Fe atom.

$FeCl_2$ was prepared by Gilman and Apperson (13) by the reaction of tetraethyllead with anhydrous $FeCl_3$ in ether. A 90% yield of $FeCl_2$ was reported, and analysis showed it to be of high purity. Lux (76) gives a preparation of $FeCl_2$ in which $FeCl_3$ is heated in an atmosphere of hydrogen at $300-350^o$. No analysis is given for the product. Many references in the literature report the preparation of $FeCl_2$ by the action of hydrogen chloride gas on iron wire, but with no details given. This method was tried in this laboratory with success in obtaining a product which had the correct chlorine content. However, this method was not suitable for the preparation of large quantities of $FeCl_2$, because the iron wire became coated with the product.

Experimental—Pure iron wire was placed in a Pyrex No. 172 ignition tube, which had been previously heated strongly in a furnace and cooled in a stream of dry nitrogen gas. The ignition tube was heated in a tube furnace and a stream of dry hydrogen chloride gas was substituted for the nitrogen. The furnace was heated to red heat, and the ferrous chloride formed in large, yellowish crystals on the inside of the Pyrex tube and on the iron wire.

Precautions were taken to insure that no moisture would enter the system, by placing drying tubes in the lines leading to and from the reaction tube. Only 0.1 g. of ferrous chloride was obtained from a reaction employing approximately 3.0 g. of iron wire and heating for five hours. <u>Anal.</u> Calc'd. for $FeCl_2$: Cl, 55.95. Found: Cl, 57.8.

$FeCl_2$ is a blue-green solid, m. p. $672°$ and b. p. $1030°$. It is soluble in water, alcohol, and acetone and insoluble in ether. In the vapor just above its boiling point, it consists of a mixture of $FeCl_2$ and Fe_2Cl_4 (95), but at $1300-1500°$ it is almost all $FeCl_2$. The crystal is of the cadmium chloride type (102), in which each Fe atom is surrounded by six Cl atoms at the corners of a regular octahedron.

Bromides and iodides of iron

Lux (76) prepared $FeBr_2$, $FeBr_3$ and FeI_2. The $FeBr_2$ was obtained by treatment of iron with hydrogen bromide gas. $FeBr_2$ occurs in the solid state as green crystals which decompose at $310°$. It is insoluble in water, but will dissolve in ammonium hydroxide. The crystal structure is of the lead iodide type (59) in which each Fe atom is surrounded by six Br atoms. $FeBr_3$ was prepared by heating iron and bromine in an evacuated tube. It is a very dark red deliquescent solid, which does not melt. It sublimes and then decomposes above $200°$. $FeBr_3$ is soluble in water, alcohol, and ether, and only slightly soluble in ammonia.

FeI_2 was prepared by heating iron wire in the presence of iodine vapor. The crystals are dark brownish red when they are freshly prepared, but they became grayish when exposed to air. The crystals are of the cadmium iodide type, m. p. $177°$. They are soluble in water.

Cobalt

The halides of cobalt which are available are $CoCl_2$, $CoBr_2$, and CoI_2, all of which were prepared by Biltz and Birk (3). $CoCl_3$ can be made (57) but

it is unstable and changes to $CoCl_2$ in light or in a vacuum.

$CoCl_2$ was prepared by preheating and drying either the hydrated or commercial $CoCl_2$ at 150^0, and then treating it with chlorine containing hydrogen chloride, at a little less than red heat. $CoCl_2$ is pale blue, m. p. 735^0, b. p. 1049^0 (95). It is soluble in water, alcohol, acetone, methyl acetate, acetonitrile, and pyridine (95). The crystal structure has six Cl atoms about each Co atom at the points of a regular octahedron. $CoBr_2$ was prepared by a process analogous to that for $CoCl_2$, but using hydrogen bromide in place of hydrogen chloride. It is formed as a bright green powder which is soluble in water, alcohol, acetone, and methyl acetate (95). The m. p. is 678^0 (95) and the sp. gr. is 4.91.

CoI_2 was prepared by heating spongy cobalt in a current of hydrogen iodide for 4-5 hours at 300^0, and then raising the temperature to a dark red. The spongy cobalt metal was obtained by heating cobalt oxalate strongly in a stream of hydrogen. CoI_2 is black, sp. gr. 5.68, and it is soluble in water and slightly soluble in alcohol and acetone.

Nickel

The three halides which are available were prepared by Biltz and Birk (3).

$NiCl_2$ was prepared by heating commercial or hydrated nickel chloride to 150^0, then heating the dried material in a chlorine-containing HCl stream at a little less than red heat. The compound sublimed in gold-colored crystals, sp. gr. 3.5. It is soluble in ammonium hydroxide and alcohol, slightly soluble in water, and insoluble in anhydrous ammonia. The crystal structure (95) is of the cadmium chloride type, in which each Ni atom is surrounded by six Cl atoms at the corners of a regular octahedron. The m. p. in a sealed tube is 1000^0 (95).

$NiBr_2$ was prepared in a manner analogous to that for $NiCl_2$. The dried

compound was heated in a stream of hydrogen bromide. The product is brownish yellow, and is soluble in alcohol, ether, and ammonium hydroxide, and only slightly soluble in water. The crystal structure is the same as for $NiCl_2$ (95).

NiI_2 was prepared by decomposing the hexammine of NiI_2. The hexammine was prepared by treating an aqueous solution of NiI_2 with concentrated ammonia, warming the solution, and then cooling it. The blue nickelous hexamminoiodide was deposited. This was slowly heated from 60^0 to 235^0 to drive off the ammonia. ($NiCl_2$ and $NiBr_2$ could also be prepared in this manner.) NiI_2 was produced as a black powder, soluble in water and alcohol. The crystal structure is the same as that of $NiCl_2$.

Manganese

The anhydrous halides of manganese which have been prepared and which are available are $MnCl_2$, $MnBr_2$ and MnI_2. Two other halides, $MnCl_3$ and $MnCl_4$, have been mentioned in the literature, but they are not available under normal laboratory conditions.

Manganous chloride

$MnCl_2$ was prepared by Kharasch and co-workers (69) by heating hydrated manganous chloride in an oven for eight hours at 120^C. This procedure was employed in the present investigation and gave satisfactory results.

Experimental-Hydrated manganous chloride was heated in an oven for two days at 160^0. It was then placed in an ignition tube, in a tube furnace, heated to fusion in a stream of hydrogen chloride gas, and then allowed to cool with the hydrogen chloride still flowing. Anal. Calc'd. for $MnCl_2$: Cl, 56.35. Found: Cl, 55.80, 55.98.

The anhydrous salt is rose colored. According to the literature it has sp. gr. 2.977 (77), m. p. 650^0, and b. p. 1190^0. It is soluble in water and alcohol (95), and insoluble in ether and ammonia. The results of magnetic

susceptibility studies (77) indicate that the compound is paramagnetic, but the observed paramagnetism is not as much as would be observed with a compound containing one unpaired electron. In the vapor, $MnCl_2$ is monomeric (95), while the crystal is of the $CdCl_2$ type (59).

Manganous bromide

Druce (13) prepared manganous bromide by adding excess $MnCO_3$ to a dry alcoholic solution of HBr. The crystals obtained had the formula $MnBr_2 \cdot C_2H_5CH$. When they were warmed in a stream of nitrogen, anhydrous $MnBr_2$ was formed. The compound is red, sp. gr. 4.39 (77), soluble in water, and insoluble in ammonia. The crystal is of the lead iodide type (59). Magnetic susceptibility measurements (77) show that the anhydrous salt has ferromagnetic properties at low temperatures.

Manganous iodide

Manganous iodide was prepared by Peters (86) by dehydrating the hydrated salt in a vacuum for ten days. This method was employed by us with good results in one case and poor in another.

Experimental-To 67.5 g. (0.58 moles) of sodium carbonate in 700 ml. of water was added 150 g. of 50% manganous nitrate solution. The precipitated manganous carbonate was filtered with suction and washed with water. To the solid manganous carbonate was added 350 g. of 47% hydriodic acid, which had been previously distilled in an atmosphere of carbon dioxide. The manganous iodide crystallized after evaporation of some of the water on a hot plate. The crystals were filtered through a sintered glass filter, recrystallized from a small amount of water, filtered, and placed in a vacuum desiccator for 10 days. Anal. Calc'd. for MnI_2: I, 82.20. Found: 82.17, 81.92.

The anhydrous salt is white, pink or brown depending upon the length of exposure to the air. Our product was pinkish white in vacuum. According to the literature, when heated to 80^0 the compound decomposes and

gives off iodine. It is soluble in water and ammonia and has sp. gr. 5.01. The crystal is of the CdI_2 type (59). The anhydrous salt, like the bromide, is ferromagnetic (95).

Chromium

Biltz and Birk (4) prepared and analyzed the following anhydrous halides of chromium: $CrCl_2$, $CrBr_2$, CrI_2, $CrCl_3$, $CrBr_3$ and CrI_3.

Chromic halides

Chromium trichloride can be prepared by heating chromium metal to red heat in a stream of chlorine. The $CrCl_3$ forms as violet crystals which can be sublimed at 800-900°. This is a rather slow process for preparation of any very large quantity of the halide, and the temperatures required are rather high. This is probably the only trustworthy process, however, for the preparation of $CrCl_3$ of high purity. The chromium metal must of course be pure and free from other metals such as iron.

Methods for the preparation of $CrCl_3$ from hydrated chromium trichloride have been described. Such methods would have the advantage of cheapness of starting materials, and, possibly, of allowing the reaction to be carried out at temperatures low enough so that glass equipment could be employed. In our hands, however, such methods do not produce pure $CrCl_3$. The Inorganic Syntheses (54 preparation, for example, gave a product which did not analyze correctly for halogen, and was contaminated with brown material which volatilized during attempts to sublime the $CrCl_3$.

Experimental—A 500-ml. distilling flask was equipped for the flash distillation of carbon tetrachloride, by dropping the carbon tetrachloride from a separatory funnel into the heated flask. The carbon tetrachloride vapors were then passed through a superheater which consisted of a coiled glass tube inserted in boiling water. The superheated carbon tetrachloride vapor was passed into another 500-ml. distilling flask which contained 37 g. of hydrated chromium trichloride. This reaction flask was heated in a furnace, and 100 g. of carbon

tetrachloride was passed in at the rate of one drop every 2 seconds. When the temperature of the furnace became about 650° the reaction was stopped. Anal. Calc'd. for $CrCl_3$: Cl, 67.14. Found: Cl, 54.22, 54.49. An attempt was made to sublime the product, but difficulty was encountered with large amounts of brown material with which it was contaminated.

Since "anhydrous chromium trichloride" is on the market from laboratory supply houses, we have also investigated the purity of samples of such material. Analysis has usually shown that these products are not $CrCl_3$. Furthermore, purification of such materials by sublimation is not usually possible, because of contamination with the volatile brown impurity. We have in hand now a sample of chromium trichloride from the Chemicals Procurement Company, and it is hoped that a satisfactory sample of $CrCl_3$ can be obtained from this material. It is not a pure sample (by chlorine analysis), but the amount of volatile impurity is apparently small enough that purification of the sample by sublimation may be possible.

$CrCl_3$ is very insoluble in water. The literature states that it may be made to dissolve by adding a small amount of $CrCl_2$, or by treating $CrCl_3$ with a reducing agent. For our analyses, the sample was fused with Na_2CO_3. $CrCl_3$ is also insoluble in aqueous acids, acetone, and carbon disulfide. The crystal structure is a layer lattice (59), in which each Cr atom is surrounded by six Cl atoms. In the vapor the compound is monomeric (77).

$CrBr_3$ was prepared (4) by heating chromium metal in a stream of bromine-containing nitrogen for 3 hours at 1100°. The product was brownish green, sp. gr. 4.25. It is soluble in alcohol, but insoluble in water. The crystal structure is very similar to that of $CrCl_3$.

CrI_3 was made in a corresponding manner (4). Chromium metal was heated with iodine, in an atmosphere of nitrogen, to 1200°. The product was then heated to 200° in a vacuum, to free it from the sublimed iodine which it contained.

CrI_3 is brownish green in color, sp. gr. 4.915. It is soluble in alcohol and acetone, but insoluble in chloroform. This compound is difficult to keep, because it decomposes on standing.

Chromous halides

Chromous chloride ($CrCl_2$) was prepared (4) by heating chromium metal in a stream of hydrogen chloride for two hours at 1150-1200°. The product was a grayish white crystalline material, soluble in water, slightly soluble in alcohol, and insoluble in ether. In the vapor the compound is a dimer (95).

$CrBr_2$ and CrI_2 were prepared (4) by reducing the corresponding chromic salts in a hydrogen bomb. The bromide was heated to 350-400°, and the iodide to 300-350°. The reaction took from 6 to 10 hours to complete. Chromous bromide is a white solid which turns to a yellow liquid when fused (95). It is soluble in water and alcohol and has sp. gr. 4.356. CrI_2 is grayish white, m. p. 790° and sp. gr. 5.2. It is very soluble in water.

Vanadium

The halides of vanadium which have been prepared are VCl_2, VCl_3, VCl_4, VBr_2, VBr_3, VI_2 and VI_3.

Vanadium chlorides

Vanadium tetrachloride was prepared by Mertes (78) by passing air-free chlorine over heated ferro-vanadium in a reaction tube. As the VCl_4 was formed it distilled out of the reaction tube, and was collected in a receiver. Some $FeCl_3$ is produced in this reaction, and it sometimes causes difficulties in the purification of the product. The use of pure vanadium metal instead of ferro-vanadium eliminates this difficulty. This is the procedure which we have employed, with good results.

Experimental--In a Pyrex No. 172 ignition tube, (a Vycor tube would be preferable) which had previously been heated in a furnace and cooled in a stream of dry carbon dioxide, there was placed 30 g. of 99.7% pure vanadium metal (Vanadium Corporation of America). Dry chlorine gas was allowed to

displace the carbon dioxide and the furnace was then heated to red heat with the chlorine flowing. The vanadium tetrachloride distilled into a collecting flask which was attached to the end of the Pyrex tube, and which was cooled in an ice bath. Approximately 72 g. of crude vanadium tetrachloride was obtained from a reaction which took seven hours. Approximately 10 g. of unused vanadium metal was recovered from the reaction chamber. The vanadium tetrachloride was purified by distillation from a Claisen flask in an apparatus protected by a drying tube. A "frog" was used to cut the fractions, in order to allow no moisture to enter the apparatus. The fraction boiling between $151-153^\circ$ was the product fraction.

Vanadium tetrachloride is a reddish brown liquid which hydrolyzes rapidly, m. p. -28°, b. p. 152°, sp. gr. 1.816 (95). The compound is unstable on standing, since it dissociates into VCl_3 and Cl_2 (95). Magnetic susceptibility measurements show that the VCl_4 molecule has one unpaired electron (77). In the vapor it is monomeric, but dissolved in CCl_4 it is a dimer. Electron diffraction studies (95) indicate that the molecule has a regular tetrahedral structure. In water VCl_4 is decomposed to HCl and $VOCl_2$, while it is soluble in absolute alcohol, ether, chloroform, and acetone.

Vanadium trichloride was prepared by Simons and Powell (96) by heating VCl_4 to 140° in an atmosphere of carbon dioxide for one week. This preparation we found to be satisfactory.

Experimental—A round bottom flask with a side arm was fitted with a Friedrichs condenser and a thermometer which extended to the bottom of the flask. The flask was filled half full of freshly distilled VCl_4 and the apparatus flushed with carbon dioxide and maintained thereafter under a pressure of about 5 p.s.i. of CO_2, while the contents were heated to 140° for ten days. Anal. Calc'd. for VCl_3: Cl, 67.63. Found: Cl, 66.66, 67.07.

VCl_3 is a violet solid which is very hygroscopic. Upon heating it does not melt, but disproportionates into VCl_2 and VCl_4 (95). The crystal is a layer lattice similar to $CrCl_3$ in which each vanadium atom is surrounded by six chlorine atoms. VCl_3 is very soluble in water, with which it reacts to form oxychlorides. It is soluble in alcohol, acetic acid, and ether, and insoluble in chloroform, toluene and carbon disulfide.

Vanadium dichloride was prepared by Ruff and Lickfett (91) by heating VCl_3 to 800° in a stream of pure dry nitrogen gas. The VCl_3 disproportionates to VCl_2 and VCl_4, and the VCl_4 is distilled out of the reaction vessel, leaving the dichloride as green crystals. This method was used in the present work.

Experimental-Anhydrous vanadium trichloride was placed in a Vycor tube and heated to 800° in a stream of pure dry nitrogen gas. After 4 hours all of the vanadium trichloride had been converted to the dichloride, which was left as shiny bright green crystals. Anal. Calc'd. for VCl_2: Cl, 58.20. Found: Cl, 58.02, 58.04, 58.05.

The solid VCl_2, on standing in air, takes up water quite slowly. When it is placed in water the crystals are not wet by the water, and dissolve slowly. VCl_2 is insoluble in ether. It can be sublimed by heating above 1000° (95).

Vanadium bromides

Vanadium tribromide was prepared by Meyer and Becka (79) by the action of bromine on powdered metallic vanadium. The reaction started at 40° and the product could be sublimed without dissociation. VBr_3 is a dark grey, deliquescent powder, which is soluble in water, alcohol, and ether, and insoluble in HBr.

Ephraim and Ammann (15) obtained light reddish brown crystals of vanadium dibromide by carefully reducing VBr_3 in a stream of hydrogen. The compound has sp. gr. 4.58, and a structure (59) similar to cadmium iodide, in which each vanadium atom is surrounded by six bromine atoms.

Vanadium iodides

Moretto (93) prepared two vanadium iodides, VI_2 and VI_3. Vanadium and iodine heated in a vacuum above 150° yielded VI_3, and when this was heated above 280° it dissociated into VI_2 and iodine. If there was an excess of iodine present, VI_2 would combine with it to reform VI_3 above 300°. Vanadium triiodide is a black powder, sp. gr. 4.2, which is very hygroscopic. It is soluble in water and ethyl alcohol, and is insoluble in benzene, carbon tetrachloride, and carbon disulfide. Vanadium diiodide , violet-rose colored solid with sp. gr. 5.0, which is wetted with difficulty by water, in which it dissolves slowly. VI_2 is soluble in ethyl alcohol, but not in benzene, carbon tetrachloride or carbon disulfide. This compound can be sublimed at $750-800^o$, but it dissociates to a large extent into vanadium and iodine.

Titanium

The halides of titanium which have been prepared are $TiCl_2$, $TiCl_3$, $TiCl_4$, $TiBr_2$, $TiBr_3$, $TiBr_4$, TiI_2, TiI_3 and TiI_4.

Titanium chlorides

Titanium tetrachloride is readily available commercially at a fairly low price. It has been made (95) by heating titanium metal in an atmosphere of chlorine, or more economically by heating titanium dioxide and carbon to red heat in an atmosphere of chlorine. It can be purified by fractional distillation. $TiCl_4$ is a colorless liquid, sp. gr. 1.726, m. p. -30°, b. p. 136°. It is hydrolyzed by water or moist air in which it gives off dense white fumes. In the vapor state it is monomeric (95).

$TiCl_3$ was prepared by Schumb and Sundstrom (94) by the reduction of $TiCl_4$ with hydrogen at 650°. The product is black in color, but on exposure to moist air it becomes violet. $TiCl_3$ will not melt, but will decompose at 440°. It is soluble in water, and is quite stable to exposure to the air. The crystal structure (71) is hexagonal close packing in which each Ti atom is surrounded by six chlorine atoms.

$TiCl_2$ was prepared (94) by heating $TiCl_3$ in a vacuum. The $TiCl_4$ formed was collected in the end of the tube, leaving the $TiCl_2$ as residue. The dichloride is black, sp. gr. 3.13. It is unstable in air, in which it oxidizes violently. It is decomposed in water, and is insoluble in carbon disulfide, ether, or chloroform.

Titanium bromides

The preparation of $TiBr_3$ and $TiBr_4$ is described by Young and Leaders (108,109). $TiBr_4$ was prepared by heating TiC_2 and carbon in a stream of bromine vapor carried by nitrogen or carbon dioxide. The product could be purified by distillation. $TiBr_4$ is an amber colored solid, m. p. 39^C, b. p. 230° (77). It decomposes in water, but it is soluble in chloroform, absolute alcohol, absolute ether, carbon tetrachloride, hydrobromic acid, and hydrochloric acid. In the vapor $TiBr_4$ is monomeric (95).

$TiBr_3$ was prepared (109) by reducing $TiBr_4$ with hydrogen at 750°. This preparation does not give very large amounts of product although the yield is high since any unreacted $TiBr_4$ can be recovered. $TiBr_3$ is a black compound which becomes violet when exposed to moisture. It is soluble in water, and when heated to 400° in a vacuum will disproportionate to $TiBr_2$ and $TiBr_4$.

$TiBr_2$ was prepared by Young and Schumb (110) by disproportionation of $TiBr_3$. It is a black powder which is very reactive. It catches fire when exposed to moist air, and when it is dissolved in water, there is evolution of hydrogen. On heating, $TiBr_2$ will decompose into titanium and titanium tribromide.

Titanium iodides

Fast (16) prepared the three iodides of titanium which are known. TiI_4 was prepared by the reaction of iodine and an excess of titanium at room temperature. When the reaction was complete the reaction flask was heated to 180° and pure TiI_4 was condensed into another bulb. TiI_4 is a red solid, m. p. 150°, b. p. above 360° (77). It is soluble in water, and monomeric in the vapor (95). TiI_2 was prepared by heating a mixture of TiI and Ti. It is a black solid which is

decomposed by water. TiI_3 was prepared by heating a mixture of TiI_4 and TiI_2, for several hours at 700°, cooling slowly, and removing excess TiI_4 by heating to 180°. TiI_3 is a violet solid which dissolves more slowly in water than the other two iodides. When heated in a vacuum TiI_3 will disproportionate to give the other two iodides.

Scandium

Only two scandium halides are available, the trichloride and the tribromide. Scandium trichloride was prepared by Meyer and Winter (81), by the action of a mixture of the vapor of sulfur chloride, S_2Cl_3, and chlorine on the heated oxide. It is a white solid which melts at 939° (77), and dissolves in water. It is insoluble in absolute alcohol. It can be sublimed at a temperature between 800 and 850^c (77). The crystal structure (71) of scandium trichloride is the same as that of ferric chloride, which is hexagonal close packing with six molecules per unit cell.

Hönigschmid (58) prepared scandium tribromide by heating a mixture of scandium oxide and carbon in a stream of bromine, and resubliming in a vacuum. It sublimes above 1000° (77), sp. gr. 3.91.

Copper

Cuprous halides

Anhydrous cuprous chloride, bromide, and iodide have been prepared. The preparation of the chloride and bromide is described by Keller and Wycoff (67). A solution of cupric chloride was treated with sodium sulfite, and the precipitated cuprous chloride was washed with glacial acetic acid, absolute alcohol, and absolute ether. Analysis of the product showed the correct copper and chlorine content. Cuprous bromide was prepared by the same method, but no analysis is given for the product. Anhydrous cuprous chloride is a white solid, m. p. 430°, b. p. 1367° (95), sp. gr. 3.53. It is soluble in hydrochloric acid, ammonium hydroxide, and alcohol, and slightly soluble in water. In the vapor it is dimeric (95), but not in the crystal (59). The

latter is of the zinc blend type in which each Cu atom has four Cl atoms as nearest neighbors and each Cl atom has four Cu atoms as nearest neighbors. Anhydrous cuprous bromide is a pale greenish yellow solid, sp. gr. 4.73, m. p. 4.83°, b. p. 1345°. It is insoluble in water or acetone, but will dissolve in hydrochloric acid, hydrobromic acid, and ammonium hydroxide. In the vapor it is dimerized (95), but in the crystal (59) it has the zinc blende arrangement like cuprous chloride. Cuprous iodide was prepared (77) by dissolving $CuSO_4$ in water, saturating the solution with sulfur dioxide, and adding potassium iodide. It settled out as a pale yellow solid which could be dried in a vacuum desiccator. The pure compound is white with m. p. 588°, b. p. 1293° (77). It is soluble in aqueous potassium iodide, but is insoluble in alcohol, aqueous acids, and water.

Cupric halides

Wells (101) described the preparation of anhydrous cupric chloride by heating the dihydrate to a moderate temperature in a stream of hydrogen chloride gas. He gave no analysis of the product. $CuCl_2$ is a brownish-yellow powder, m. p. 498° (95), sp. gr. 3.054. If heated to 993° it will lose chlorine, forming the cuprous salt. It is soluble in water and alcohol. The crystal is composed of a series of chains in which each copper atom is surrounded by four chlorine atoms and each chlorine atom has two copper atoms as nearest neighbors. Carter and Megson (9), and Helmholtz (55) have prepared anhydrous $CuBr_2$ by slow evaporation of solutions of the salt. Neither of these papers gives analyses of the products obtained. $CuBr_2$ is a black crystalline solid, m. p. 498°. When heated to red heat it breaks up into cuprous bromide and bromine. It is soluble in water, ammonia, alcohol, and acetone, and insoluble in benzene. The crystal structure (77) is very similar to that of cupric chloride. Cupric iodide is so unstable that efforts to prepare it give only cuprous iodide and iodine (95).

IV. EXPERIMENTAL DATA ON REACTIONS OF HALIDES OF SOME 3d TRANSITION ELEMENTS WITH PHENYLLITHIUM

Preparation of Phenyllithium

In all the reactions between phenyllithium and the anhydrous halides of the transition metals the phenyllithium solution was prepared in the following manner: A three-necked flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel was so arranged that it could be kept under an atmosphere of nitrogen. To 4.0 g. (0.57 g. atom) of lithium metal, cut into small pieces and placed in 165 ml. of dry ether, there was added a solution of 41.5 g. of bromobenzene in 65 ml. of ether, at such a rate that steady reflux was maintained. After the addition was complete, the solution was stirred for an additional hour. The stirring was then stopped and the solid material was allowed to settle out. The clear solution was decanted through glass wool, under nitrogen, into a calibrated dropping funnel. A 2-ml. aliquot of the phenyllithium solution was pipetted into water and titrated with 0.1 N sulfuric acid, with phenolphthalein as indicator. In most cases the solutions thus prepared were approximately 1 M.

General Procedure for Reaction of Phenyllithium with Anhydrous Halides

A solution or suspension of the anhydrous halide in 100 ml. of ether was placed in a three-necked flask equipped with a reflux condenser, a calibrated dropping funnel, and an all-glass mechanical stirrer with a semi-circular blade which fitted the contour of the bottom of the flask. This stirrer blade was necessary for efficient stirring, since there were heavy solids settling out of the reaction mixtures in many cases. The phenyllithium was added from the dropping funnel. The course of the reaction was followed as described in the section below. When the reaction was complete the reaction mixture was hydrolyzed by pouring it into an ice-cold ammonium chloride solution. The layers were separated, the ether layer was washed with water, and the aqueous

layer was extracted with ether. The organic layer and ether extracts were
dried with Drierite, and the solvent was removed on a steam bath. In all
cases biphenyl was the only product recovered from these reactions.

Methods of Determining the Stoichiometry

The methods employed for following the course of such reactions as these
include color tests, titrations, and carbonation. We employed the Michler's
ketone color test or acid-base titration of the reaction mixtures after
hydrolysis, or both.

The Michler's ketone test (23) is a sensitive color test for active or
moderately active organometallic compounds. It is positive for phenyllithium,
but a positive test would not be expected from such organometallic compounds
as might be formed from transition metals, since these should be relatively
unreactive in addition to the carbonyl double bond. The course of a reaction
involving phenyllithium and an inorganic halide can therefore, be followed by
adding standardized phenyllithium in increments, making a color test after
each addition, and determining the amount of phenyllithium necessary to
produce a positive test. The test is quite sensitive, and is produced by
a rather small excess of phenyllithium. The main drawback to such a pro-
cedure, which is quite similar to a titration, is that the end of a reaction
may be approached quite slowly, because of the low concentrations of reactants
present near the end point. In the presence of metals whose ions are greenish
or bluish in water solution, the test cannot be used. On the other hand, it
is interfered with by very few organic substances, and is rather specific for
organometallics of the types mentioned.

In the titration procedure, there is added an excess of standardized
phenyllithium solution, and thereafter aliquots of the reaction mixture are
withdrawn from time to time, hydrolyzed with water, and titrated with standard
sulfuric acid solution. In this case, since excess reagent is present, the
reaction may proceed to completion faster. The titration is, of course, not

specific for an active organometallic such as phenyllithium, and any basic
material present will be titrated. Thus it is necessary to interpret the
results with due consideration of what basic substances, other than lithium
hydroxide, might be formed during hydrolysis. Other difficulties encountered
are those which would in general be expected in acid-base titrations in which
there are present various transition metal ions--buffering effects, color
interference with visual indicators, and so on.

Reactions of Phenyllithium with Anhydrous Halides

Reaction of vanadium trichloride with phenyllithium

The phenyllithium solution was added to 7.0 g. (0.041 mole) of vanadium
trichloride in 100 ml. of ether, over a period of 45 minutes. A total of 0.27
moles of phenyllithium were added. Color tests could not be used in this ex-
periment because of the green color of the vanadyl ion which interfered with the
test. Titration of hydrolyzed aliquots, using a pH meter to determine the
end point, was the procedure employed.

The reaction mixture was heated to reflux for four days, after which it
was hydrolyzed and worked up as described above. The titrations showed that
0.16 moles of phenyllithium had been used, or that 3.98 moles of phenyllithium
were used for each mole of vanadium trichloride. Removal of the solvent
from the organic layer gave 8.0 g. of crude biphenyl, m. p. 62-66°. The
color of the reaction mixture varied from brown, after the addition of one
equivalent of phenyllithium, to purple, which was the color of the reaction
mixture after the addition of more than one equivalent of phenyllithium.

This reaction was repeated twice, using the same amounts of material, with
similar results. The yields of crude biphenyl were 11.5 g. and 6.0 g., and the
titrations showed phenyllithium-vanadium trichloride molar ratios of 4.07 and
3.98 respectively. This reaction was also run at the temperature of an ice-salt
bath for 5 hours, and the mixture worked up as usual. Removal of the solvent

under reduced pressure yielded 6.5 g. of crude biphenyl, m. p. 63-66°.

Reaction of vanadium dichloride with phenyllithium

The phenyllithium solution was added to 3.6 g. (.030 moles) of vanadium dichloride in 100 ml. of ether. A total of 2.6 equivalents of phenyllithium was added to the vanadium dichloride suspension. No noticeable amount of heat was evolved, and the color did not change from the original green. The reaction mixture was then refluxed for a total of 10 days. Titrations of aliquots taken during the course of the reaction indicated that the vanadium dichloride reacted very slowly. A final titration showed that 2.62 moles of phenyllithium had reacted with each mole of vanadium dichloride. There appeared to be a large amount of unreacted vanadium dichloride in the reaction mixture. There was isolated 2.8 g. of crude biphenyl, m. p. 63-66°, recovered from the dried organic layer after hydrolysis and working up of the reaction mixture.

Reaction of vanadium tetrachloride with phenyllithium

The phenyllithium was added to 7.8 g. (0.04 moles) of vanadium tetrachloride in 100 ml. of ether. The reaction was quite vigorous when phenyllithium was added to the vanadium tetrachloride solution. The solution was originally a dark brownish red, but it turned green after the addition of one equivalent and then back to brown. A light brown solid settled on the inner surface of the flask. After two equivalents the color was brown. The reaction mixture then darkened steadily, until after 7.6 equivalents had been added it was black with a purple tinge. The mixture was heated to reflux for three days. Aliquots were periodically hydrolyzed and titrated, using a pH meter to determine the end point. A final titration showed that 4.59 moles of phenyllithium reacted with each mole of vanadium tetrachloride. The reaction mixture was hydrolyzed on ice cold ammonium chloride and worked up as above. The dried organic layer yielded 7.0 g. of crude biphenyl, m. p. 60-64°.

Reaction of mangenous chloride with phenyllithium

The phenyllithium solution was added to 5.0 g. (0.040 moles) of mangenous chloride in 100 ml. of ether. The color of the manganous chloride-ether suspension was pink before the addition of phenyllithium. As the addition continued the color changed from pink through brown to tan. After 15 minutes it became yellow, and there was slight refluxing. A Michler's ketone color test was positive after the addition of 0.9 equivalent of phenyllithium, but after stirring for an hour and a half a color test was negative. After the addition of 1.25 equivalents of phenyllithium the color of the reaction mixture was bright yellow, and a color test was positive. The mixture was refluxed and stirred for two days. Color tests were all positive during this time. An aliquot was hydrolyzed and titrated and showed that .039 moles of phenyllithium were used or that 0.98 moles of phenyllithium reacted for each mole of mangenous chloride.

The reaction mixture was filtered, hydrolyzed and worked up as before. The filtered solids, when allowed to become dry on the filter paper, decomposed with the evolution of heat and dense white fumes. No open flame was observed. Removal of the solvent from the dried organic layer gave 2.3 grams of crude biphenyl, m. p. 63-66°.

This experiment was repeated using 7.5 g. (0.059 moles) of manganous chloride, to which was added 0.24 moles of phenyllithium. The color changes were the same except that with this excess of phenyllithium the reaction mixture became slightly greenish. The progress of the reaction was followed by hydrolyzing aliquots and titrating them with 0.1 N sulfuric acid, using a pH meter to determine the end point. After 3 days the titrations showed that 0.06 moles of phenyllithium had been used or that 1.00 mole of phenyllithium reacts with each mole of mangenous chloride. After hydrolysis, distillation of the dry ether layer gave 3.5 g. of crude biphenyl, m. p. 64-67°.

Another reaction was conducted at the temperature of an ice-salt bath.
Manganous chloride used was 12 g. (.087 moles). After 5 hours an aliquot was
hydrolyzed and titrated, and it showed that only 0.28 moles of phenyllithium
reacted with each mole of manganous chloride. The reaction mixture was hydrolyz-
ed and worked up as before. The dried ether layer was distilled under reduced
pressure to yield 1.5 g. of crude biphenyl, m. p. 61-64°.

Reaction of manganous bromide with phenyllithium

The phenyllithium solution was added to 12.4 g. (0.058 moles) of manganous
bromide in 100 ml. of ether. Before the addition of phenyllithium the manganous
bromide-ether suspension was tan, but after the addition of a few ml. of phenyl-
lithium the color changed to green. Slight refluxing occurred. A dark green
solid formed on the side of the reaction flask where the phenyllithium was enter-
ing the flask. A Michler's ketone color test was negative after the addition of
0.9, 1.1, and 1.9 equivalents of phenyllithium. A positive test was obtained
after the addition of 2.1 equivalents of phenyllithium and the test remained
positive after refluxing the mixture for one day. An aliquot was titrated with
0.1 N sulfuric acid, using phenolphthalein as indicator. This showed that 1.75
moles of phenyllithium had reacted with each mole of manganous bromide. The re-
action mixture was green, with rust-colored solid in it. The solids were filter-
ed and the filtrate was hydrolyzed and worked up as usual. The filtered solid,
when dry, decomposed with the evolution of heat and dense white fumes. A sample
of the residue from the decomposition gave a positive test for carbon. Distil-
lation of the dried organic layer gave 3.9 g. of crude biphenyl, m. p. 67-68°.

This experiment was repeated. The color changes in the reaction mixture
were the same. Color tests were not used, but aliquots were hydrolyzed and
titrated to determine the progress of the reaction. After three days, titrations
showed that 1.56 moles of phenyllithium reacted with each mole of manganous
bromide.

Reaction of ferrous chloride with phenyllithium

The phenyllithium solution was added to 9.5 g. (0.074 moles) of ferrous chloride in 100 ml. of ether. The ferrous chloride solution was greenish yellow before the addition of phenyllithium, but became darker and finally black after a few ml. had been added. Titration of hydrolyzed aliquots of the reaction mixture gave inconsistent results, so color tests were used to determine the amount of phenyllithium used. The reaction mixture was heated to reflux, and color tests were taken at appropriate intervals during the addition of phenyllithium. The tests were all negative after allowing the reaction mixture to run for a few hours after each addition. A total of 0.23 moles of phenyllithium was added, and after 3 days a color test was negative, showing that more than 3 equivalents of phenyllithium reacted with each mole of ferrous chloride.

This experiment was repeated with 6.6 g. (0.052 moles) of ferrous chloride. A negative color test was obtained after 4.7 equivalents of phenyllithium had been added. This was after fifteen days in which the reaction mixture was stirred and refluxed during the day and allowed to stand at night. A total of 5.6 equivalents of phenyllithium was then added, and after $2\frac{1}{2}$ days of similar treatment a color test was still positive.

A third experiment was performed in which 0.24 moles of phenyllithium was added to 0.164 moles of ferrous chloride. The reaction mixture was refluxed for six hours and a color test was negative. The reaction mixture was hydrolyzed on an ice cold ammonium chloride solution, and worked up as usual. The dried organic layer yielded 15.0 g. of crude biphenyl.

Reaction of ferric chloride with phenyllithium

The phenyllithium solution was added to 9.0 g. (0.055 moles) of ferric chloride in 125 ml. of ether. The ferric chloride solution was initially brown. After the addition of a few ml. of phenyllithium, a yellow solid settled from the reaction mixture, while the ether solution remained dark brown. As addition

continued the reaction mixture became darker, and after one and one-half equiva-
lents of phenyllithium had been added the color had become black. Color tests
were negative until 4.1 equivalents of phenyllithium had been added. After
three days, during which the reaction mixture was refluxed and stirred, the
color test was still positive.

This experiment was repeated using 6.5 g. (0.039 moles) of ferric chloride.
After 3.7 equivalents of phenyllithium was added a color test was negative,
but after 4.2 equivalents had been added, the color tests were positive during
a three day period during which the reaction mixture was stirred and refluxed.

A third experiment was performed in which 3.9 equivalents of phenyllithium
was added. A color test was positive immediately. After a total of 4.05 moles
of phenyllithium had been added, the reaction mixture was refluxed for an hour,
hydrolyzed on ice cold ammonium chloride, and worked up as usual. Distillation
of the dried organic layer yielded 9.7 g. of crude biphenyl.

V. DISCUSSION

In the series of experiments to determine the stoichiometry of the reactions between phenyllithium and the anhydrous halides of the transition metals, three of the seven compounds studied gave phenyllithium-halide ratios which were whole numbers, while the other four gave fractional ratios.

Vanadium trichloride, ferric chloride, and manganous chloride all gave whole-number ratios. In the case of ferric chloride and manganous chloride, the reaction was quite rapid, and the final ratios were arrived at in a few hours. Vanadium trichloride reacted quite rapidly with the first three equivalents of phenyllithium, and then quite slowly with the fourth.

Manganous bromide reacted rapidly with phenyllithium to a point, and then the reaction seemed to stop. Two experiments gave ratios of 1.75 to 1 and 1.56 to 1, and in both cases these ratios were reached in a few hours, after which no change occurred for 3 days. Vanadium tetrachloride reacted rapidly with four equivalents of phenyllithium, but then continued to react further. Two experiments gave ratios of 4.59 to 1 and 4.24 to 1 after 4 and 5 days respectively. Ferrous chloride behaved similarly in that it reacted quickly with 2 equivalents of phenyllithium, and then the reaction became quite slow. After 4 days 3 equivalents of phenyllithium had been used, and after seventeen days the ratio of phenyllithium to ferrous chloride had gone beyond 4.7 to 1. Vanadium dichloride reacted very slowly with phenyllithium, with no apparent leveling-off point in the phenyllithium-halide ratio as the reaction progressed. After 10 days much unreacted vanadium dichloride could be seen in the reaction mixture indicating either that the reaction would proceed further, because all the halide had not been used, or possibly that none of the original halide had been used, that the halide was acting simply as a catalyst in the reaction.

Solubility of the various halides in ether seemed to have little effect on the reactions, except in the speed of the reaction. The halides which were in-

soluble in ether reacted a little more slowly and less vigorously, but even among these there were differences. Of the four insoluble halides studied, vanadium dichloride was the only one which failed to react with phenyllithium within an hour in refluxing ether.

The length of time is another factor determining the stoichiometry of these reactions. In these experiments, the reactants were allowed to stir and reflux until it appeared that no more phenyllithium would react. In the case of vanadium dichloride and ferrous chloride it seemed that the reaction would continue as long as the reactants were in contact. If continued long enough, the reactions involving the other halides might proceed further, but if so they would be very slow.

The yields of biphenyl from the reactions ranged from 53% in the case of $MnBr_2$ to 91% for $MnCl_2$ (see Table). If Gilman and Lichtenwalter (22) were correct in their suggestion that the extent of coupling is a rough measure of the thermal stability of an intermediately formed organometallic compound, then it appears as if the organometallic compound obtained with $MnBr_2$ would be the most likely to be stable.

Since this series of studies is not complete, it is not very profitable to attempt, at this time, to discuss the possible reasons for the results above. It is hoped that, if such data can be gathered for all the 3d transition elements, comparison of the results may make clear the reasons for some of the differences in behavior.

TABLE I

REACTION OF PHENYLLITHIUM WITH ANHYDROUS HALIDES OF 3d TRANSITION ELEMENTS

Halide	Molar ratio (Phenyllithium-halide)	Method used to determine ratio	Contact time, days	Reflux time, hours	Biphenyl yield based on phenyllithium used, percent
VCl_2	2.62 – 1	titration	9	77	65
	1.45 – 1	titration	10	97	_____
VCl_3	3.58 – 1	titration	4	14	58
	3.98 – 1	titration	4	20	>57
	4.07 – 1	titration	6	27	_____
VCl_4	4.59 – 1	titration	4	21	61
	4.24 – 1	titration	5	39	_____
$FeCl_2$	>3.0 – 1	color test	4	23	_____
	>4.7 – 1; <5.6 – 1	color test	17	133	_____
	>1.5 – 1	color test	1	4	82
$FeCl_3$	>3.7 – 1; <4.2 – 1	color test	4	35	_____
	>3.7 – 1; <4.15 – 1	color test	5	35	_____
	>3.9 – 1; <4.05 – 1	color test	2/24	1	69
$MnCl_2$	0.98 – 1	color test and titration	2	10	86
	1.00 – 1	titration	3	14	91
	0.28 – 1	titration	5/24	_____ *	78
$MnBr_2$	1.75 – 1	color test and titration	3	7	53
	1.56 – 1	titration	4	33	_____

*Experiment performed in ice-salt bath.

VI. SUMMARY

1. A survey of the literature on the organometallic chemistry of the transition metals of the third period is given.

2. A collection of literature data on the anhydrous halides of the transition metals of the third period is given, and results of our work on the preparation of these substances is described.

3. A study of the stoichiometry of the reaction between phenyllithium and seven anhydrous halides of transition metals is described.

VII. FUTURE PROGRAM

The program of investigation for the remainder of this contract is as follows:

(1). Continue the investigations of the stoichiometry of the reactions of phenyllithium with transition metal halides, as described above, and attempt   to complete these studies for the 3d transition elements (with Sc a possible exception)

(2). Investigate the behavior of halides of the ferrocene type, when treated with organolithium compounds. It seems evident that a project concerned with the organometallic chemistry of transition metals should take notice of the new developments in the field of "sandwich" compounds. From our point of view, one of the most interesting cases is the case of titanium because for this element both a sandwich compound (105) and a typical covalent organometallic (56) have been reported. It seems desirable to investigate this situation further, in the hope of producing evidence which will throw light on the question of the nature of bonds which titanium can form to various organic structures.

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