ALKYLS AND ARYLS OF TRANSITION METALS

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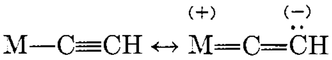
I. Introduction

The alkyl and aryl derivatives of transition metals constitute one of the several classes of compounds in which transition elements are bonded to carbon atoms. The type of bond existing in the alkyl and aryl derivatives—essentially an ordinary σ-bond—is the simplest and also the least stable. The various principal types of carbon compounds of transition metals, excluding carbides, are the following: (*1*) carbonyls, cyanides and cyanide complexes, isocyanides, and acetylides; (*2*) olefin complexes; (*3*) metal–cyclopentadienyl compounds; (*4*) the alkyls and aryls.

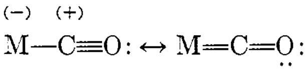
In class 1 the carbonyls may be regarded as the parent compounds in the sense that they exemplify most clearly a type of bonding which probably occurs in all of the others to a greater or lesser extent. That type of bonding is believed to consist (116) of a primary dative σ-bond supplemented by π-bonding varying in extent from one compound to another. Although this view is probably an oversimplification, it has been of use in correlating a great amount of data. In the carbonyls, the pronounced shortening of the metal–carbon bond distances relative to those expected from the sum of covalent radii has been taken to indicate that the π-bonding is quite extensive. On the other hand, the metal–carbon bond force constants in carbonyls are in just the range to be expected for single electron-pair bonds between the elements concerned (145). There is x-ray evidence (133) that organic isocyanides form bonds to transition elements which are very similar to those in the metal carbonyls. The postulate of some carbonyl-type bonding in cyanides and cyanide complexes (122) has no experimental foundation and is based primarily on the fact that certain similarities between the cyanide ion and the carbon monoxide molecule make the assumption reasonable. However, the cyanide complexes may well be nearly totally ionic.

Nast (119, 120) has recently shown that some elements toward the end of the first transition series form compounds with acetylene which bear certain formal resemblances to the compounds of these elements with cyanides, isocyanides, and carbon monoxide. He regards the bonding in these compounds as being of a nature similar to that in the carbonyls. Thus he suggests (119) that the acetylides are stabilized by resonance principally between structures Ia, analogous to those (Ib) postulated for the carbonyls.



$$\mathrm{M{-}C{\equiv}CH} \leftrightarrow \overset{(+)}{\mathrm{M}}{=}\mathrm{C}{=}\overset{(-)}{\ddot{\mathrm{C}}}\mathrm{H}$$

Ia



$$\overset{(-)}{\mathrm{M}}{-}\overset{(+)}{\mathrm{C}}{\equiv}\mathrm{O}{:} \leftrightarrow \mathrm{M}{=}\mathrm{C}{=}\underset{\cdot\cdot}{\mathrm{O}}{:}$$

Ib

While the second canonical structure is of importance in carbonyls because it provides a means of reducing the negative charge placed on the metal in the first, there is no such charge separation in the first canonical structure for the acetylide. It is much more likely that double bonding between metal and carbon in the acetylides arises from the overlap of suitable filled *d*-orbitals of the metal with filled πp-orbitals of the acetylide group, not by back donation as pictured above. While on Nast's hypothesis the acetylides are classed with the carbonyls, it is quite possible that they are most nearly related to the alkyls and aryls, being just examples of the latter type in which π-bonding between metal and carbon is very effective. They have, however, been omitted from detailed consideration in this review. Some details may be found in the paper by Nast (119) cited above. The important point here is that in none of these compounds, with the possible exception of the acetylides, is there essentially an ordinary electron-pair covalent bond.

The nature of the bonding in olefin–platinum(II) complexes, class 2, has recently been elucidated by Chatt (16, 17). It quite definitely does not involve any simple σ-bonds. Rather, it consists of a primary μ-bond in which πp-electrons from ethylene are donated to one of the dsp^2 hybrid orbitals of the platinum atom, and π-bonding which results from overlap of filled *dp* hybrid orbitals of the metal with the πp antibonding orbitals of the ethylene.

At present, three types of linkage of a metal atom to the cyclopentadienyl group (class 3) are known. These are (*1*) compounds in which a more or less metallic element is bonded covalently to a single carbon atom in the C_5H_5 ring. Examples are $(C_5H_5)_2Si(CH_3)_2$ (28) and possibly also $(C_5H_5)_2Hg$. No transition metal forms a compound of this type, but all of them form one or the other of the following types. (*2*) Ionic compounds in which the $C_5H_5^-$ anion exists as such. These are formed in general by very electropositive metals, as sodium, potassium, calcium, magnesium, etc., and among the transition metals by scandium, yttrium, lanthanum, and the rare earths, and by manganese (8, 19, 163). (*3*) The bis-cyclopentadienyl compounds, in which the metal atom is bonded to the C_5H_5 ring by a singular type of delocalized and essentially covalent bond (118). When two rings are present, the compounds have the well-known "sandwich" geometry. It appears that any metal which can provide two half-filled *d*-orbitals with the required symmetry properties will form a bis-cyclopentadienyl compound unless for some reason ionic bonding, as with the group III elements, the rare earths, and manganese, is more favorable. Thus all of the transition elements which do not form ionic cyclopentadienides form bis-cyclopentadienyl compounds. Some of the transition elements also form compounds which contain only one C_5H_5 ring bonded to the metal in the same manner as in the bis-cyclopentadienyl compounds. There are then other groups such as carbon monoxide, nitric oxide, etc., also attached to the metal (25, 126). Again the point to be emphasized is that transition metal–cyclopentadienyl compounds do not contain simple, localized covalent bonds from metal to a particular carbon atom.

The division of the principal transition metal–carbon compounds into four classes is made therefore on the basis of the nature of the bond between the metal and the carbon atom(s) of the carbon-containing group. Generally, the differences in bond type are clear-cut, although the acetylides possibly lie on the borderline of classes 1 and 4.

The preceding discussion has been given to clarify the relation of the alkyls and aryls, which are the subject of this review, to the other classes of transition metal–carbon compounds. Several reasons prompted the writing of this review. The field has never before been reviewed exhaustively and critically. Krause and von Grosse (102) in 1937 summarized only the positive results available at that time. An attempt has been made to make the bibliography in this review exhaustive. There has recently been a reawakening of interest in the field and it is worthwhile to summarize newer work and set it in context. Finally, the already extensive chemistry of the bis-cyclopentadienyl compounds is perhaps better appreciated against the background of the classical organometallic chemistry of the transition elements. While there is justification for restricting attention entirely to alkyls and aryls, the restriction of the discussion to transition metals is artificial in certain respects. Particularly, the impression that there is any sharp line of demarcation between the elements of Group VIII and those of Group IB is to be avoided. While in several places the alkyls and aryls of the Group IB metals have been discussed because of their natural relevance to the point, specific detailed consideration of their chemistry has been omitted. A good summary of this subject has been given by Sidgwick (148).

A final word concerning the use of the term "organometallic" compound or derivative is required. In the sequel these terms are used exclusively to mean an alkyl or aryl derivative of a metal. Thus, for example, the statement that "no organometallic compounds of element X have been isolated" means merely that no derivatives of the type under consideration in this review have been isolated. It is quite possible that element X may form cyclopentadienyl derivatives, olefin or acetylene compounds, etc.

II. Survey of Experimental Work

A. GROUP III METALS AND THE LANTHANIDES

Plets (128) has reported the preparation of etherates of triethylscandium and triethylyttrium. These he claims to have obtained by reaction of an ethereal suspension of scandium trichloride or yttrium trichloride with an ether solution of ethylmagnesium bromide, the reaction mixture being at first cooled in ice but later heated under reflux for about half an hour. The reactions were carried out under nitrogen. According to this author, the products, which were pale yellow oils, were separated by distillation in a current of nitrogen. Certain physical and chemical properties, including analyses, were also reported. However, this work is questionable for the following reasons:

(*1*) The percentage yields reported were calculated by the author to be 66 per cent and 75 per cent for scandium and yttrium, respectively. However, in these calculations the fact that *three* ethyl groups are required per molecule of the product was overlooked. The correct yields, calculated from the weights given by Plets, turn out to be about 200 per cent of the yields theoretically possible. (*2*) An attempt to repeat this work in the case of scandium failed (18). (*3*) Attempts to prepare erbium (4) and lanthanum (35, 87) alkyls under similar conditions were unsuccessful.

The best positive evidence for the formation of organometallic compounds by a metal of this group is the reaction of methyl radicals with a lanthanum mirror in an experiment utilizing the Paneth technique (137). This observation led Gilman and Jones (35) to attempt the preparation of organolanthanum compounds by several standard procedures. They found that metallic lanthanum failed to react with iodobenzene in ether or benzene. After heating the metal with diphenylmercury at 135°C. for 100 days in a sealed tube, the reaction mixture was treated with carbon dioxide and extracted with benzene, which removed all organic matter. A 15 per cent yield of biphenyl was obtained, but no benzoic acid or lanthanum was found in this benzene extract. Since free mercury was produced, the biphenyl can be attributed to decomposition of the diphenylmercury. However, failure to isolate benzoic acid is not necessarily evidence against formation of a phenyl–lanthanum bond, as shown by later studies on phenyl–titanium bonds.

No reaction was observed between an ether solution of phenyllithium and anhydrous lanthanum chloride suspended therein. On replacing the ether with benzene and refluxing the new reaction mixture, a gradual blackening occurred. Various tests on the products gave no definite indication of the presence of organolanthanum compounds. Lanthanum chloride suspended in an ether solution of methyllithium produced methane and a dark syrupy precipitate; however, no organolanthanum compounds were obtained either by extraction or by distillation at 30 mm. pressure. No reaction appeared to take place between lanthanum trichloride and ethylmagnesium bromide in ether. After removal of the solvent the residue was heated but no distillate was obtained.

Transient existence of some sort of methyllanthanum compound might be postulated to explain the production of methane in one of the above experiments, but the existence of any organolanthanum compounds sufficiently stable to permit their isolation under such conditions seems doubtful.

There are no reported studies on the other elements of this group.

B. GROUP IV METALS

1. *Titanium*

After nearly a century of fruitless efforts by many workers (10, 13, 14, 35, 42, 99, 106, 124, 129, 135, 144) Herman and Nelson (70, 71) succeeded in isolating and characterizing a compound containing a titanium–carbon bond. Shortly thereafter, Summers and Uloth (149) reported the preparation of a second highly interesting type of organotitanium compound.

Although previous work had not led to the isolation of any organotitanium compounds, there were indications that such compounds had at least transient existence in various reaction mixtures of titanium salts with solutions of other organometallic compounds, especially those of magnesium and lithium. Herman and Nelson made a careful study of such systems, and the following discussion is based on their work, unless otherwise noted.

It was first shown that the interaction of phenylmagnesium bromide with butyl titanate, $(C_4H_9O)_4Ti$, leads to the formation of a moderately stable phenyl–titanium bond *in situ.* (The reaction mixture was maintained at a temperature of about 8°C. during the course of the reaction and was never refluxed.) An equimolar mixture of these substances in ether gave a slowly developing but eventually strong color test with Michler's ketone (42). Since a prompt positive test is given by phenylmagnesium bromide, it is reasonable to assume that this compound had disappeared and a new organometallic compound of lower reactivity had been formed. This conclusion was substantiated by the fact that carbonation of the reaction mixture produced only a 0–2 per cent yield of benzoic acid, whereas phenylmagnesium bromide is known to give an approximately 70 per cent yield under the same conditions. The appearance in the reaction mixture of colors attributable to titanous compounds and the observation that small amounts of a freshly prepared reaction mixture of phenylmagnesium bromide and butyl titanate induced the polymerization of styrene nearly as effectively as does benzoyl peroxide led to the conclusion that the phenyl–titanium bond decomposes spontaneously according to equation 2. As con-

$$C_6H_5Ti\equiv \rightarrow C_6H_5\cdot + \equiv Ti\cdot \qquad (2)$$

siderations in Section II,H will show, it is doubtful that free phenyl radicals are formed. It is more likely that biphenyl is produced in a bimolecular reaction

$$2C_6H_5Ti\equiv \rightarrow C_6H_5C_6H_5 + 2\equiv Ti\cdot \qquad (3)$$

(equation 3) and that polymerization of the styrene is initiated by the $\equiv Ti\cdot$ radical.

This spontaneous decomposition was followed over a period of many days at room temperature by determining the percentage of total titanium in the titanous state at a given time. An initial decomposition rate of 5–6 per cent per day was found. In the case of a reaction mixture of methylmagnesium bromide and butyl titanate, the suggested unimolecular decomposition (equation 2) was confirmed. This mixture, like its phenyl analog, gave a delayed but eventually strong color test, thus showing the presence of the methyl–titanium bond. On standing, this mixture produced, in addition to titanous compounds, methane resulting from attack of the solvent by methyl radicals initially formed. It was observed that, within experimental error, the formation of Ti(III) and of methane proceeded at the same rate.

The actual isolation of the phenyltitanium compound was achieved using phenyllithium. On adding this reagent to an ether solution of isopropyl titanate, the temperature of the reaction mixture being kept at 8–15°C., a transient orange color was produced, and finally a white crystalline solid separated. This precipitate was washed and dried under nitrogen and in the cold. Analysis led to the following formulation: $C_6H_5Ti(OC_3H_7)_3 \cdot LiOC_3H_7 \cdot LiBr \cdot (C_2H_5)_2O$, with the ether content somewhat variable. It is interesting to note that Gilman and Jones (35) had previously carried out the same type of reaction between phenyllithium and ethyl titanate, $(C_2H_5O)_4Ti$, and observed that after addition of about two-thirds of the phenyllithium, an orange, crystalline precipitate suddenly appeared. They showed it to contain lithium, halogen, and titanium in the tetravalent state only, and observed that it reacted violently with water and inflamed spontaneously in air. They reported, however, that they could not obtain a purified sample for analysis, since the compound darkened rather rapidly on warming to room temperature. Furthermore, while the complex obtained by Herman and Nelson using isopropyl titanate is stable for prolonged periods of time, these authors found that with isobutyl and *n*-propyl titanates no complex precipitated. These results clearly show that it is unsound to assume the non-existence of organometallic compounds of a given element purely on the basis of failure to isolate such compounds within a limited range of reactants and experimental conditions.

The final product obtained by Herman and Nelson, phenyltitanium triisopropoxide, was prepared by treating the lithium-containing complex with aluminum chloride or titanium tetrachloride (equation 4) to cause precipitation of the lithium as lithium bromide or lithium chloride (both practically insoluble in ether). It was found most convenient to carry out this reaction *in situ*, treating

$$C_6H_5Ti(OC_3H_7)_3 \cdot LiOC_3H_7 \cdot LiBr \cdot (C_2H_5)_2O + \tfrac{1}{4}TiCl_4 \rightarrow C_6H_5Ti(OC_3H_7)_3 + LiCl + LiBr + \tfrac{1}{4}Ti(OC_3H_7)_4 + (C_2H_5)_2O \qquad (4)$$

the ether slurry of the complex directly with a 10 per cent excess of titanium tetrachloride. The yield was 53 per cent of theory.

Phenyltitanium triisopropoxide is a white crystalline substance of rather surprising stability. It melts at 88–90°C. and shows no darkening after storage at 10°C. for over a year. In agreement with the results obtained on mixtures of phenylmagnesium bromide and butyl titanate, it gives a delayed but strong color test with Michler's ketone, but fails to undergo carbonative splitting on treatment with dry ice. On heating at 100–120°C. it is decomposed, giving a violet titanous product.

In their second paper (71), Herman and Nelson reported some further studies of the stability of titanium–carbon bonds, in which the varied parameters were: (*1*) the alkyl or aryl group, R; (*2*) the number, *n*, of such groups attached to the titanium atom; and (*3*) the nature of the other groups, X, bonded to the titanium atom. The general formula for the titanium species existing in the reaction mixtures can thus be written $R_nTiX_{(4-n)}$. Studies were first made on the system $(C_4H_9O)_4Ti$–C_6H_5MgBr–ether at 18–20°C., with the mole ratio $C_6H_5MgBr/(C_4H_9O)_4Ti$ taking the values 0.25:1, 1:1, 2:1, 3:1, and 4:1. Representative solutions were then subjected to the following tests: (*1*) The organometallic test mentioned above. (*2*) Fresh solution was treated with dry ice, hydrolyzed, and the yield of benzoic acid determined. (*3*) Fresh solution was hydrolyzed directly and the yield of benzene determined. (*4*) Fresh solution was treated with oxygen and the amount of phenol present in the hydrolysis products determined. (*5*) The rate of spontaneous decomposition of these solutions was measured from the percentage of total titanium present as Ti(III) after hydrolysis. The results of these experiments are summarized in table 1.

Conclusions were drawn as to the effect of *n* on the stability of organotitanium compounds. In each of the five solutions, the fact that all of the phenylmagnesium bromide had been consumed was indicated by the 0 per cent yield of benzoic acid on carbonation. The positive color test and the yields of benzene and phenol show the presence of phenyl–titanium bonds. Since solution A (of 0.25:1 mole ratio) showed an initial decomposition rate of zero, and in fact showed essentially no decomposition over a period of 24 days, it seemed reasonable to suppose that here only a monophenyltitanium compound was formed and that this is relatively stable. On the other hand, solution B (of 1:1 mole ratio) showed an appreciable rate of decomposition, leading to the conclusion that diphenyl-

TABLE 1

Properties of butyl titanate–phenylmagnesium bromide systems

Solution	A	B	C	D	E
Mole ratio, $\frac{C_6H_5MgBr}{(C_4H_9O)_4Ti}$	0.25:1	1:1	2:1	3:1	4:1
1. Color test	Very weak	Weak	Strong, rapid	Very strong, rapid	Very strong, rapid
2. Benzoic acid found	None	None	None	None	None
3. Benzene, per cent yield		65	76		34
4. Phenol, per cent yield	23	23–25	22		
5. Initial rate of decomposition, per cent per day	~0	~4.7	~6.1	Complete in 3 hr.	Instantaneous decomposition
Color of solution	Yellow-green	Green to dark amber	Dark	Very dark with black solid	Black solution and considerable solid

and possibly higher polyphenyltitanium compounds were formed (as a result of consecutive competitive reactions) and that these decompose rather rapidly, perhaps inducing the decomposition of the predominating monophenyl compound in the process.

The existence of the diphenyltitanium alkoxide species is proved by the 76 per cent yield of benzene on hydrolysis of solution C, since the number of phenyl groups bonded to each titanium atom must thus average at least 1.5, and the rapid decomposition supports the conclusion that the introduction of a second phenyl–titanium bond results in considerable instability of the $R_nTiX_{(4-n)}$ molecule.

The extremely rapid and complete decomposition of solutions D and E implies that tri- and tetraphenyltitanium species are of such low stability as to exist only as short-lived intermediates. Furthermore, the evolution of hydrogen when samples of these solutions were hydrolyzed for titanium analysis suggests the presence of Ti(II) and possibly the existence of diphenyltitanium. The general conclusion reached by Herman and Nelson from these studies is that the increase of n, the number of phenyl groups bonded to one titanium atom, beyond one, drastically reduces the stability of the $R_nTiX_{(4-n)}$ molecule.

In a second series of experiments, the effect of the particular group, R, was studied by following the spontaneous decomposition of reaction mixtures in which the mole ratio of the various Grignard compounds to butyl titanate was 1:1. Stability was found to increase in the following order: butyl < methyl < acetylenyl < *p*-anisyl < phenyl < α-naphthyl < indenyl. The significance of this order will be discussed in Section III, but it may be stated here that the indenyl group almost certainly constitutes a special case, since it is known to form compounds of the bis-cyclopentadienyl type with other transition elements (26, 123).

The results of a study of the effect of the group X on the stability of systems containing TiX_4 and phenylmagnesium bromide in 1:1 mole ratio were not clean-cut but suggested the order of stability to be butoxy $\simeq$ isobutoxy $\simeq$ propyl $\simeq$ isopropyl > methoxy, chloride > fluoride.

In view of the failure of previous workers to isolate any alkyl- or aryltitanium compounds using in the main titanium tetrahalides or titanium metal as starting materials, Herman and Nelson suggested that their compound owed its existence to the special ability of the electronegative oxygen atoms in the butoxy groups to permit a transition to the four-covalent state (70). Normally the transition from the ground state of the titanium atom, d^2s^2, to the lowest excited state in which there are four unpaired electrons, d^3s, is forbidden because for such a transition $\Delta l = 2$. However, under the influence of a strong electrostatic field, such as the oxygen atoms would provide, the transition would be allowed and it was assumed that stable compounds of the type $R_nTiX_{(4-n)}$ may exist where X is a highly electronegative group such as OR′ or Cl, R is a relatively electronegative aryl or alkyl group, and n is 1 or at most 2.

Jaffe (81), however, believes this argument to be fallacious on several grounds. First, while the electronic state most likely involved in tetravalent titanium is $3d^34s$, it is a valence state (V_4 in the notation of Mulliken) and hence cannot be assigned any particular multiplicity or l value, and the transition from $3d^24s^2$ to $3d^34s$ is forbidden only for certain multiplicities and angular momenta, not for all. Since the reactions start, not with gaseous titanium atoms in the ground state but with combined titanium atoms in a V_4 state, no transition is involved in compound formation. Finally, should, for any reason, such a transition be necessary, the field of *any* four atoms surrounding another atom at bond distances is sufficiently strong to produce the perturbation required to make the forbidden transition allowed. The electronegativity of the atoms probably does not contribute much in that respect.

Summers and Uloth (149) studied the reaction of bis-cyclopentadienyltitanium halides (162) with several lithium aryls and prepared compounds containing two titanium–carbon bonds according to the following general reaction:

$$(C_5H_5)_2TiX_2 + 2LiR \rightarrow (C_5H_5)_2TiR_2 + 2LiX \tag{5}$$

In particular, compounds in which R is phenyl, *p*-tolyl, and *p*-dimethylaminophenyl were prepared and purified. Cryoscopic measurements showed them to be monomeric. They are orange-yellow in color and soluble in organic solvents. All three derivatives are relatively stable; the diphenyl and di-*p*-tolyl compounds can be stored for some days at room temperature, although there was apparently some slow decomposition.

Attempts to prepare analogous compounds containing α-naphthyl and *o*-tolyl groups gave crude crystalline products which decomposed during attempts at recrystallization. A further interesting observation made by Summers and Uloth was that diphenylbis-cyclopentadienyltitanium dissolves in an ether solution of phenyllithium, apparently with the consumption of the latter substance, producing a dark orange-brown or nearly black solution. On hydrolysis of this solution, the diphenylbis-cyclopentadienyltitanium can be recovered. It was postulated that further uptake of phenyl anions occurs so that there is formed in solution $(C_5H_5)_2Ti(C_6H_5)_3^-$ and possibly also $(C_5H_5)_2Ti(C_6H_5)_4^{--}$.

2. Zirconium and hafnium

No organozirconium compound has been isolated, although some studies indicate the existence of organozirconium species as intermediates of low stability. Zirconium tetrachloride does not appear to react with diethylzinc (73). Metallic zirconium undergoes no reaction with ethyl iodide or diethylmercury, nor does zirconium tetrachloride react with diethyl- or diphenylmercury when these mixtures are heated to 200°C. in sealed tubes (125). Little or no reaction was observed between zirconium tetrachloride and methane or acetylene (153).

Gilman and Jones (35) studied the reactions of zirconium tetrachloride with several organolithium and organomagnesium compounds. The general procedure was to mix the reactants at about -10°C. and then allow the reaction mixture to warm to room temperature. In general, there was no reaction at the low temperature, but the mixture darkened on warming. No evidence of any persisting organozirconium compounds was obtained. However, with phenylmagnesium bromide, a yield of 56 per cent of biphenyl was obtained after hydrolysis, and the addition of methyllithium to zirconium tetrachloride and zirconium tetraphenoxide produced high yields (50–70 per cent) of methane. Furthermore, hydrolysis of some of the reaction mixtures produced hydrogen as well as hydrocarbons. Bearing in mind the recent studies on titanium, these observations permit the assumption that unstable organozirconium compounds are formed. Presumably they quickly decompose, producing zirconium in lower valence states and either phenyl radicals which couple to produce biphenyl or methyl radicals which abstract hydrogen from the solvent to produce methane.

It seems likely that more precise information on the stability of the zirconium–carbon bond could now be obtained by studies similar to those made by Herman and Nelson (70, 71) on titanium systems, although the literature indicates that analogous zirconium systems may be somewhat less amenable to such investigations.

No research concerning organohafnium compounds has been reported.

C. GROUP V METALS

The reactions of various compounds of vanadium, niobium, and tantalum, particularly the halides, with Grignard reagents have been examined by several workers. The halides vanadium trichloride, vanadium tribromide, and vanadium tetrachloride react vigorously (115, 150) with ice-cold solutions of phenylmagnesium bromide. The reaction mixtures, on hydrolysis, afforded some benzene, about 40 per cent yields of biphenyl, but no organovanadium compounds. Higher yields of the corresponding RR compounds were obtained with several aliphatic Grignard reagents (150). However, in these experiments the solutions were deliberately heated to as much as 100°C.; thus it is not surprising that no organometallic compounds were isolated, even if they had formed initially. Methylmagnesium iodide gave a 50 per cent yield of ethane in an almost explosively violent reaction. These studies were extended (154) to cover the reactions of VCl_2, $VOCl_3$, V_2O_3, V_2O_4, and V_2O_5 with phenylmagnesium bromide. Again, while the temperature was held below 10°C. during the addition of the vanadium compound to the Grignard reagent, the reaction mixture was refluxed prior to hydrolysis. Since with all of the halides and the oxyhalide the reaction was spontaneous and very vigorous, and since it might have been expected that any possible organovanadium compounds would be thermally unstable,[1] it is difficult to understand why this procedure was consistently followed. The oxides apparently did not react with the Grignard solution. VCl_2, like the other halides, did not produce any isolable organovanadium compound under the experimental conditions. However, in one run with $VOCl_3$ a dark green, crystalline material was found adhering to the walls of the flask at the point where the $VOCl_3$ had been introduced. It was rather unstable toward air and burned in flashes of sooty yellow flame, leaving a white residue which contained vanadium.

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[1] This work was done after Hein's earlier papers on phenylchromium compounds had appeared. Hein (48) clearly stated that the secret of his success where others had failed lay in keeping the reaction mixture cool (below 0°C.) at all times.

It reacted with water to generate biphenyl, but could not be recrystallized from organic solvents; no analysis was reported.

$(\text{iso-}C_5H_{11}O)_3VO$ was found to react with both phenylmagnesium bromide and methylmagnesium iodide, causing coupling of the organic radicals, but no organovanadium compounds were obtained (97).

The only reported study of the interaction of a tantalum compound with Grignard reagents consists in the observation (1, 2) that on treating tantalum pentachloride with phenyl- and ethylmagnesium bromides, colored solutions result which are quite unstable toward air and traces of water, and which generate tantalum pentoxide on complete hydrolysis.

Several other less likely but possible routes to organo derivatives of the elements of this group have been explored, entirely without success. Thus 40-mesh vanadium metal failed to react with a variety of alkyl and aryl halides, even after remaining in contact for eight months (154). Vanadium metal refluxed with phenylmagnesium bromide solution reacted only slightly or not at all, there being no evidence of compound formation (154). The reaction of vanadium tetrabromide with $Bi(p\text{-}C_6H_5CH_3)_3$ did not lead to any organovanadium compound (154). When vanadium tetrachloride and diphenylmercury were mixed and refluxed for 6 hr., much hydrogen chloride was evolved, but only phenylmercury chloride and $VOCl_2 \cdot 2H_2O$ were isolated (115).

It has been reported that vanadium tetrachloride, niobium pentachloride, and tantalum pentachloride react with a number of aromatic hydrocarbons to yield organic derivatives of these metals. In each case, however, the claims have subsequently been challenged.

Mertes and Fleck (114) reported that when vanadium tetrachloride is added to benzene the mixture assumes a color darker than that of the tetrachloride itself, and that, on standing, a precipitate settles out and hydrogen chloride is evolved. The precipitate, after filtration and washing with fresh benzene, was purple in color, was stable toward dry air, and dissolved in water with a hissing sound to produce a brown solution. When the reaction was allowed to proceed for six weeks, they obtained a substance to which the formula $C_6H_4 \cdot 2VCl_3$ was assigned. Shorter reaction times led to a substance formulated as $C_6H_5V_2Cl_5$. When carbon tetrachloride solutions of vanadium tetrachloride and anthracene were mixed, a precipitate was immediately formed and hydrogen chloride was evolved. When this precipitate was quickly filtered off it was found to have a composition corresponding to $C_{14}H_9V_2Cl_5$. If the reaction mixture was refluxed for 2 hr. before isolating the precipitate, its composition corresponded to $C_{14}H_{10} \cdot 2(C_{14}H_9V_2Cl_5)$.

Meyer and Taube (115) conducted further experiments of this type and concluded that no definite organovanadium compounds are isolable. They pointed out that, although the formulas assigned by Mertes and Fleck are completely *ad hoc*, the agreement with analytical data is not good. In the case of the substances derived from benzene, the discrepancies are sometimes as large as 10 absolute per cent. They verified the fact that on refluxing vanadium tetrachloride in benzene much hydrogen chloride is evolved and a black mass separates. When this mass was extracted with chloroform, a strongly yellow solution containing no vanadium was obtained. The mass was then extracted with ether, giving a green to blue solution which deposited dark blue needles. These readily lost ether over sulfuric acid, having then the composition $VOCl_2 \cdot 2H_2O$. After these extractions, a highly insoluble black residue still remained which varied in vanadium content from 15 to 22 per cent.

Funk and Niederländer (31) found that like vanadium tetrachloride, the pentachlorides of niobium and tantalum react with various aromatic hydrocarbons, generating hydrogen chloride and giving rise to substances containing metal, chlorine, and organic matter. The reaction conditions and the compounds produced are summarized in table 2. In every case the formulas are assigned on the basis of analyses for metal and chlorine only. For these compounds, however, the agreement of the analytical results with the assigned formulas is excellent, despite the fact that, excepting the addition compound $C_6H_6 \cdot NbCl_5$, none of them were obtained in crystalline form.

TABLE 2

Reactions of niobium and tantalum pentachlorides with aromatic hydrocarbons

Salt	Hydrocarbon	Solvent	Reaction Conditions	Postulated Formula	Color	Remarks
$NbCl_5$........	Benzene	Benzene	Boil; time not stated	$C_6H_6 \cdot 3NbCl_5$	Yellow-brown; crystalline	$C_6H_6 \cdot NbCl_5$ and $C_6H_6 \cdot 2NbCl_5$ also postulated
$NbCl_5$........	Naphthalene	Molten naphthalene	Minimum reaction time	$NbCl_4 \cdot C_{10}H_7$	Red-brown	No simple addition compound
$NbCl_5$........	Naphthalene	Molten naphthalene	Long heating	$NbCl_3 \cdot (C_{10}H_7)_2$	Black	
$NbCl_4 \cdot C_{10}H_7$..	Naphthalene	Carbon tetrachloride	Boil 8-10 hr.	$NbCl_3 \cdot (C_{10}H_7)_2$	Black	
$NbCl_5$........	Anthracene	Carbon disulfide	Mix cold solutions	$NbCl_4 \cdot C_{14}H_9$	Intense yellow; brown-yellow when dry	Immediate precipitate on mixing solutions
$TaCl_5$........	Benzene	Benzene	Boil 6–8 hr.	$TaCl_4 \cdot C_6H_5$	Yellow	No simple addition compound
$TaCl_5$........	Naphthalene	Molten naphthalene	Short reaction time; immediate removal of excess naphthalene	$TaCl_5 \cdot C_{10}H_8$	Yellow powder	
$TaCl_5$........	Naphthalene	Molten naphthalene	Short reaction time	$TaCl_4 \cdot C_{10}H_7$	Red-brown powder	
$TaCl_5$........	Naphthalene	Molten naphthalene	Boil 6 hr.	$TaCl_3 \cdot (C_{10}H_7)_2$	Black	
$TaCl_5$........	Anthracene	Carbon disulfide	Mix ice-cold solutions	$TaCl_5 \cdot C_{14}H_{10}$	Pale yellow	
$TaCl_5$........	Anthracene	Carbon disulfide	Mix warm solutions	$TaCl_4 \cdot C_{14}H_9$	Green yellow	
$TaCl_5$........	Anthracene	Carbon disulfide	Boil several hours	$TaCl_3 \cdot (C_{14}H_9)_2$	Blue	
$TaCl_5$........	Tetralin	Tetralin	Short gentle warming	$TaCl_4 \cdot C_{10}H_{11}$	Yellow	
$TaCl_5$........	Tetralin	Tetralin	Boil 1 hr.	$TaCl_3 \cdot (C_{10}H_{11})_2$	Yellow	

Very little in the way of physical and chemical properties of the compounds was reported. They were observed to char on heating. Their reactions with aqueous ammonia make it possible to discriminate between the addition compounds and those formulated as organometallic halides. The former are converted to colorless residues, whereas the latter give strongly colored residues. Brown-yellow $NbCl_4 \cdot C_{14}H_9$, for example, is converted into a yellow, halogen-free substance which by boiling with hydrochloric acid was shown to contain one ammonia molecule per atom of niobium. The same procedure showed that the dark-brown intermediate obtained on treatment of $TaCl_3 \cdot 2(C_{10}H_7)_2$ with aqueous ammonia contained one molecule of ammonia per two atoms of tantalum. The authors suggested that the aqueous ammonia converted the organometallic halides into ammonium salts of organometallic oxyacids.

Previously Funk and Niederländer (30) had prepared phenol derivatives of niobium and tantalum by an analogous procedure and formulated the products as phenolates, e.g., $Me(OC_6H_5)_4Cl$, where Me = niobium or tantalum. These products were colored and similar in appearance to the hydrocarbon derivatives, but differed in being decolorized on treatment with aqueous ammonia. After preparing the hydrocarbon derivatives, the authors expressed the opinion that the previously prepared phenol derivatives also contained carbon–metal rather than oxygen–metal bonds. This seems rather doubtful. Later on, Funk and Baumann (29) prepared other phenol derivatives, but formulated them as phenolates without any further comment.

von Grosse (103), however, reports that when he attempted to repeat the preparation of $C_6H_5TaCl_4$, using the purest benzene and tantalum pentachloride, he observed no evolution of hydrogen chloride or other evidence of reaction, even after adding some hydrogen chloride as a "promoter."

D. GROUP VI METALS

1. Chromium

The chemistry of the polyphenylchromium compounds of Hein has long constituted one of the most fascinating but perplexing phases of organometallic chemistry. The reactions and properties of these substances seem, at face value, so completely unorthodox, and the isolation of the compounds so tedious that there has been scepticism, covert and overt (117), as to the validity of Hein's claims. Until quite recently, no preparation of any of these compounds had been reported except by Hein himself. However, Zeiss and Tsutsui (167) have now recorded confirmation of a large part of Hein's experimental work.

Undiscouraged by either the failure of previous workers (5) or by the several assertions that organometallic compounds of transition metals in general (110, 168) and those of chromium in particular (168) could not be made, Hein systematically sought for the proper conditions under which organochromium compounds might be isolated. Assuming that should such compounds exist, they would undoubtedly be thermally unstable, and would thus be decomposed before they could be isolated if the attempted preparation were carried out as it had been previously—with or without initial cooling, followed by refluxing of the reaction mixture—he slowly added sublimed chromic chloride to phenylmagnesium bromide in ether, maintaining the reaction mixture at −10°C. throughout (47, 48). The whole mass, after standing at −10°C. for perhaps 24 hr., was poured into an ice slush of dilute sulfuric acid. The crude, red-brown phenylchromium compounds went into the ether layer in the form of an emulsion.

The crude product obtained after the ether was stripped was inhomogeneous and partially dissolved in alcohol. From the alcoholic solution, on addition of alcoholic mercuric chloride, a precipitate of $(C_6H_5)_5CrBr \cdot HgCl_2$ was obtained from which the orange pentaphenylchromium bromide, $(C_6H_5)_5CrBr$, was prepared. A molecular weight determination showed it to be monomeric. Yields were at best about 20 per cent. Pentaphenylchromium bromide is rather unstable, and on exposure to air and light it decomposes, producing much biphenyl. The formulation of the compound as pentaphenylchromium bromide is due to Hein (throughout most of this discussion his nomenclature will be followed as a matter of convenience).

Pentaphenylchromium bromide is salt-like in character (48), a solution giving instantaneously a precipitate of silver bromide when silver nitrate is added. On treatment with moist silver oxide a strongly basic solution is produced which, on addition of silver nitrate, gives an immediate precipitate of silver hydroxide. Pentaphenylchromium hydroxide was obtained in pure crystalline form (48) as the tetrahydrate, $(C_6H_5)_5CrOH \cdot 4H_2O$, by treating pentaphenylchromium bromide with potassium hydroxide and extracting the base with chloroform. The orange tetrahydrate loses two molecules of water over mild drying agents, remaining orange, and loses all four over phosphorus pentoxide, turning olive-green. The changes were found to be reversible and the heats of hydration were measured (62). Pentaphenylchromium hydroxide was shown to be a strong monobasic base, comparable in conductivity in absolute methanol to the alkali metal hydroxides. It precipitates silver ion as silver hydroxide, liberates ammonia from ammonium salts, gives green-blue colors with aromatic nitro compounds, etc.

When an alcoholic solution of the anhydrous base, $(C_6H_5)_5CrOH$, was added to a solution of Reinecke's salt, $NH_4[Cr(CNS)_4(NH_3)_2]$, a precipitate appeared but it contained only four phenyl groups. Similarly, treatment of the base with potassium iodide, potassium bromide, perchloric acid, and ammonium dichromate led to salts of monovalent tetraphenylchromium (49). In late experiments (65) the base was neutralized with about forty different acids and phenols. Nearly all of these gave the so-called "abnormal" neutralization reaction (formation of a tetraphenylchromium salt) except with acetic acid, chloroacetic acid, sulfuric acid, and carbon dioxide, which reacted in the normal manner to form pentaphenylchromium salts. A few of the phenols also appeared to give the "normal" neutralization reaction.

It was shown by molecular weight determinations that the tetraphenylchromium group was present monomerically and not, for example, as $(C_6H_5)_4Cr$-$OCr(C_6H_5)_4$. The fate of the phenyl group which is lost was next investigated. When hydrated pentaphenylchromium hydroxide reacts with a potassium halide (the resulting tetraphenylchromium salt is extracted into chloroform), the cleaved phenyl group appears entirely as phenol (66). Equation 6 was suggested by Hein to represent the reaction. The evolution of hydrogen required by the equation was not observed,

$$(C_6H_5)_5CrOH + H_2O + KX \rightarrow (C_6H_5)_4CrX + KOH + C_6H_5OH + (H) \quad (6)$$

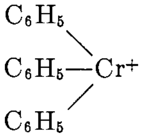
however. It was established that had hydrogen actually been set free it could not have escaped detection and furthermore that it was not consumed in side reactions. There seemed then no other alternative but to assume that it remained attached in some mysterious manner to the tetraphenylchromium group.

Tetraphenylchromium hydroxide may be prepared in several ways (64). On treatment of a chloroform solution of tetraphenylchromium iodide with an aqueous slurry of silver oxide, the orange color characteristic of the tetraphenylchromium group is found to pass into the aqueous layer; $(C_6H_5)_4CrOH \cdot 3H_2O$ can be isolated in 40 per cent yield. A methanol solution of tetraphenylchromium iodide may be shaken with silver oxide, filtered, and the product precipitated with ether. Finally, a solution of tetraphenylchromium hydroxide is obtained when an alcoholic solution of tetraphenylchromium iodide is electrolyzed. Tetraphenylchromium hydroxide in aqueous methanol has all the properties of a strong base, and its electrical conductivity in such solutions is comparable to that of sodium hydroxide. It reacts with acids and salts metathetically to produce tetraphenylchromium salts, which are identical with those obtained in the abnormal neutralization of pentaphenylchromium hydroxide.

It appears that in the initial preparative reaction both pentaphenyl and triphenylchromium salts are produced. The latter are formed in smaller quantities, but apparently independently and not as decomposition products of the pentaphenylchromium species (50). There is no indication of the production of tetraphenyl salts in this reaction. Triphenylchromium salts were isolated (50) in the following way. After treating crude pentaphenylchromium bromide with potassium hydroxide and crystallizing out the pentaphenylchromium hydroxide, the aqueous layer still remained orange. When it was concentrated, a precipitate of pentaphenylchromium carbonate was obtained. Further concentration produced a strongly alkaline, red-black, syrupy mass, which redissolved in water. From this water solution Reinecke's salt precipitated the triphenylchromium cation as $(C_6H_5)_3Cr[Cr(CNS)_4(NH_3)_2] \cdot 2H_2O$. Over concentrated sulfuric acid both molecules of water were lost, and molecular weight determinations showed the triphenylchromium group to exist as a monomer. Triphenylchromium iodide and perchlorate were also prepared. All were orange in color.

By electrolyzing liquid ammonia solutions of triphenylchromium iodide and tetraphenylchromium iodide, free triphenylchromium and tetraphenylchromium were prepared (54, 55). Both were exceedingly unstable orange substances. They dissolved in nitromethane and pyridine. The molecular weight of tetraphenylchromium in pyridine solution (55) was determined and showed that there was little or no association of the tetraphenylchromium groups, although complexing with the solvent is quite possible. On treating the radicals with hydrogen chloride and methanol the corresponding chlorides were regenerated quantitatively. Tetraphenylchromium is also deposited cathodically when pentaphenylchromium hydroxide is electrolyzed in liquid ammonia, a phenyl group thus being eliminated as in the "abnormal" neutralization of the base. The properties of these free phenylchromium radicals were found to be quite different from those of other pseudo-metallic radicals such as the tetraalkylammonium radicals. They do not form amalgams with the mercury cathode nor do they dissolve in liquid ammonia. When tetraphenylchromium was dissolved in aqueous methanol, tetraphenylchromium hydroxide was produced, but no evolution of hydrogen was observed. Although this was in no way surprising, since the solubility of hydrogen in the reaction medium was about six times greater than the amount actually produced, Hein chose to believe that the hydrogen attached itself to the tetraphenylchromium ion, as he had been forced to assume in the abnormal neutralization of pentaphenylchromium hydroxide.

It has been mentioned in most cases that the compounds were orange. The similarity in color of all the phenylchromium compounds is indeed quite striking. All except the anhydrous pentaphenylchromium hydroxide are virtually indistinguishable in color. On Hein's formulation (I, II, and III) the valence states of chromium in the penta-, tetra-, and triphenylchromium compounds would be 6, 5, and 4, respectively, values which are difficult to reconcile with the almost identical color of all of them. Klemm and Neuber (98) measured the magnetic susceptibilities of a number of representative compounds of the three series and found that all of them possessed magnetic moments of ca. 1.7 BM, and obeyed Curie's law. Since the chromium atom has six electrons in the 4*s* and 3*d* orbitals, it was assumed that all of the compounds contained chromium(V). Although quinquevalent chromium compounds are otherwise very rare, the authors attempted a reformulation of the phenylchromium compounds so as to provide for the presence of a Cr(V) atom in each case. Two new formulations suggested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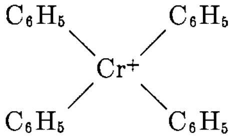
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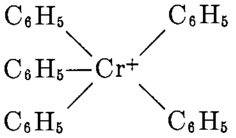
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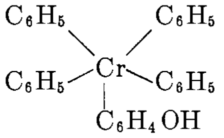
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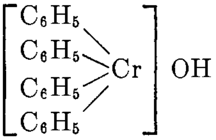
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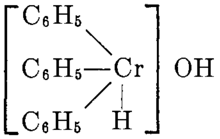
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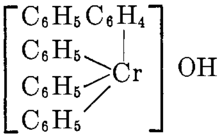
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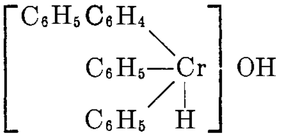
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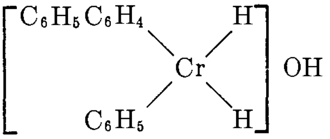

IX

are shown in formulas IV–VI and VII–IX. Both of these involved changes of composition which were within the errors of Hein's analytical data. Formulas IV–VI were then rejected by Klemm and Neuber, chiefly because the structure for pentaphenylchromium hydroxide would indicate an acidic rather than strongly basic nature for that compound. Perhaps the most striking feature of formulas VII–IX is the presence of hydrogen atoms bonded to chromium. These are held by definite covalent bonds, not by any sort of loose association such as had been postulated by Hein. This appears highly artificial and unlikely, since the chemistry of the compounds gives no indication of the presence of either acidic hydrogen as in carbonyl hydrides or of hydridic hydrogen. None of the phenylchromium compounds were particularly sensitive to water. Also, the presence of biphenyl, and especially of precisely one biphenyl group in each compound, is difficult to accept without some further justification. Thus, although the magnetic data definitely ruled out Hein's original formulation, the true structures of the compounds could scarcely be said to have been any better understood.

In late 1954 Zeiss and Tsutsui (167) reported definite corroboration of the key aspects of Hein's experimental work and also made several illuminating suggestions as to the constitution of the compounds. Thus pentaphenylchromium bromide, pentaphenylchromium hydroxide, tetraphenylchromium iodide, and triphenylchromium iodide were prepared, using Hein's methods with only minor modifications. Pentaphenylchromium bromide, the so-called "raw bromide" of Hein, was found by these authors also to be an amorphous mixture, but they also observed that it showed O—H infrared absorption. Pentaphenylchromium hydroxide was isolated as the orange crystalline tetrahydrate, having a melting point of 104–105°C., which is the same value reported by Hein (48). Tetraphenylchromium iodide and triphenylchromium iodide were found to be identical in all properties with Hein's compounds. These two compounds also showed almost identical ultraviolet absorption.

Recalling the utility of lithium aluminum hydride in the determination of the structure of other organometallic compounds, e.g., diphenylmercury, which was reduced by lithium aluminum hydride in ether to give benzene as the sole organic product, Zeiss and Tsutsui applied this reduction to the polyphenylchromium compounds which they had isolated. Their results are summarized in table 3.

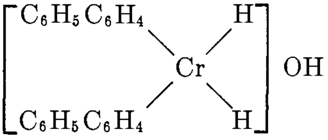
TABLE 3

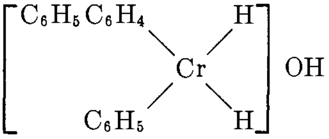
Reduction of polyphenylchromium compounds by lithium aluminum hydride

Compound Reduced	Moles of Product per Mole of Compound				Compound Reduced	Moles of Product per Mole of Compound			
	C_6H_6	$(C_3H_5)_2$	C_6H_5OH	Others		C_6H_6	$(C_6H_5)_2$	C_6H_5OH	Others
$(C_6H_5)_5CrBr$	0.17	1.08		~0.016 terphenyl	$(C_6H_4)_3CrI$	0.03	0.61		
$(C_6H_5)_5CrOH$	0	0.96	0.47		C_6H_6	0.31			
$(C_6H_5)_4CrI$	0	1.52							

The work was not intended to be quantitative, but qualitatively it clearly shows any formulation in which all phenyl groups are present as such to be untenable. It indicates that the compounds actually do contain biphenyl groups, as postulated by Klemm and Neuber. Of very great significance is the occurrence of phenol in the reduction products of pentaphenylchromium hydroxide, for the authors were then able to explain the so-called "abnormal" salt formation of pentaphenylchromium hydroxide by reformulating this compound as tetraphenylchromium phenoxide. This idea is quite in accord with other aspects of the behavior of the compound, such as cathodic deposition of tetraphenylchromium on electrolysis, its similarity in color to the tetraphenylchromium salts, its strongly basic nature (phenoxide ion is a strong base), and the elimination of a "phenyl" group as phenol in the "abnormal" neutralization reaction. It does, however, leave in doubt the constitution of pentaphenylchromium bromide, which has one unpaired electron and an ionic bromine atom, and then makes the "normal" salt formation by the "pentaphenyl" base which was observed in a very few cases rather puzzling.

The question of how many biphenyl groups are present in the tetra- and triphenylchromium salts and of how they are bound so that both series have a magnetic moment corresponding to one unpaired electron was next considered. Firstly, as the results in table 3 show that only biphenyl is present in the "tetraphenyl"-chromium compounds, the Klemm–Neuber formulations must be modified to Xa and Xb for "triphenyl"- and "tetraphenyl"-chromium hydroxide,


Xa


Xb

respectively. In possible contradiction to this conclusion stands an observation by Hein and H. Pauling (57) that while the thermal decomposition of tetraphenylchromium iodide into biphenyl is essentially complete at higher temperatures, at 100°C., after a quantity of biphenyl corresponding almost exactly to that calculated for the conversion of tetraphenyl- to triphenylchromium iodide had come off, no further production of biphenyl occurred. However, they did not definitely identify triphenylchromium iodide as the product.

Studies of the reduction of triphenyl- and tetraphenylchromium by lithium aluminum deuteride made by Zeiss and Tsutsui, the results of which are summarized in table 4, throw further light on the question of structure. The compounds were treated with the reagents indicated in the table, the biphenyl was sublimed and burned to water, the water reduced over zinc, and the deuterium determined in a mass spectrometer. From the first two entries in the table it is clear that the free hydrocarbons are formed not later than the reaction of the compound with $LiAlH(D)_4$. If the compounds have the structures Xa and Xb, and the hydrogenation of the organic moieties is effected entirely by the re-

TABLE 4

Reduction of polyphenylchromium compounds by lithium aluminum deuteride

Compound Reduced	Millimoles	Reductant	Hydrolytic Agent	Millimoles of Biphenyl	Atom per cent Deuterium*
$(C_6H_4)_4CrI$	0.195	$LiAlH_4$	D_2O	0.079†	0
$(C_6H_6)_4CrI$	0.107	$LiAlD_4$	D_2O	0.054†	5.0
$(C_6H_5)_3CrI$	0.70	$LiAlD_4$	D_2O	0.58‡	6.7§ 6.6
$(C_6H_5)_2$		$LiAlD_4$	H_2O		0

* $\frac{\text{Atoms of D} \times 100}{\text{Total atoms D and H}}$.

† No benzene detected.

‡ Benzene (0.21 millimole) was found but not analyzed.

§ Duplicate analyses.

ductant, then the atom percentages of deuterium in the biphenyl would in each case be 10, so that it might be assumed that, in fact, some biphenyl is completed by hydrogen intramolecularly and the rest (about half) by hydrogen from the reductant. Zeiss and Tsutsui, however, question the presence of hydrogen atoms in the phenylchromium compounds for reasons similar to those which have already been cited here, and suggest the following "sandwich" type structure (figure 1), geometrically similar to the structures of the bis-cyclopentadienyl compounds (20), for "tetraphenyl"-chromium iodide. "Triphenyl"-chromium iodide would be similarly constituted, with one biphenyl group replaced by a benzene ring.[2] They propose to explain the presence of only one unpaired electron in the molecule by assuming that each of the two phenyl groups bound to the chromium donates all six of its π-electrons to metal orbitals, thus filling them to just one short of the krypton configuration. The authors acknowledge that the hydrogen–deuterium exchange which must then be postulated to explain the

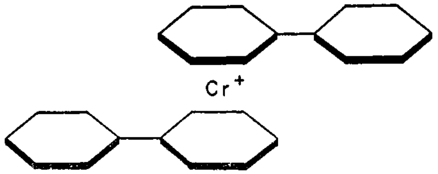


FIG. 1. The structure proposed for $C_{24}H_{20}CrI$ by Zeiss and Tsutsui

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[2] While the production of benzene only in the reduction of diphenylmercury with lithium aluminum hydride probably demonstrates the absence of $C_6H_5C_6H_5$— groups in that compound, failure to isolate benzene from the reduction of "tetraphenyl"-chromium iodide tends to prove by analogy the absence of phenyl groups in that compound only if it contains RC_6H_5–metal bonds of the same type as those in diphenylmercury, i.e., presumably simple, two-center bonds from metal to a particular carbon atom. However, the "sandwich" structure proposed does *not* contain bonds analogous to those in diphenylmercury, and it is not clear that the existence of two biphenyl groups in a compound of the postulated structure is demonstrated by the reduction experiments. The author is indebted to Dr. E. O. Brimm for bringing this important point to his attention.

deuterium distribution in the products of the reduction with lithium aluminum deuteride is somewhat surprising, but they believe it to be less anomalous than the presence of curiously unreactive hydrogen bonded to chromium as in the Klemm–Neuber structures. They cite the ferricinium ion, $(C_5H_5)_2Fe^+$, as a precedent for such an electronic arrangement. Although E. O. Fischer (138) maintains that in bis-cyclopentadienylmetal compounds all π-electrons are contributed to metal orbitals, Cotton and Wilkinson (20) have pointed out that the weight of evidence is against this idea. In fact, the properties of all the bis-cyclopentadienyl derivatives can only be explained by assuming that such extensive dative bonding is unnecessary and does not occur to any appreciable extent. Such extensive donation of electrons in this case would involve an unprecedented degree of charge separation, but it has not been made clear how any lower degree of dative bonding would explain the magnetic data. It is, however, best to await a decision from x-ray studies which are in progress (166) as to the geometric structure of $C_{24}H_{20}CrI$ before attempting to speculate on the electronic structure.

Hein and collaborators (51, 63, 67, 68) also investigated the possibility of preparing analogous organochromium compounds with other aryl groups, with varying degrees of success. By far the best results were obtained with *p*-tolyl compounds. These appeared to be basically analogous to the phenyl derivatives but less stable. The *o*-tolyl analogs were formed in still poorer yields and were considerably less stable and hence more difficult to purify. Xylyl Grignard reagents in general afforded no definite products. No product could be isolated with cyclohexyl groups. Reactions involving halogen-substituted phenyl groups were generally very complicated, producing quantities of polyphenyls, although in a few cases some definite organochromium compounds were isolated in very small yields. For example, *p*-bromophenylmagnesium bromide afforded a minute yield of $(p\text{-}BrC_6H_4)_4CrBr$ and several other derivatives.

There have been several studies to determine the type of chromium compounds besides the simple halides which will react with phenylmagnesium bromide to produce phenylchromium compounds (51, 53, 58, 60). As a general rule, it appears that compounds containing all halogen atoms or other acidic residues in the inner coördination sphere do react, while chromium compounds and complexes not fulfilling this requirement do not.

2. Molybdenum and tungsten

Several attempts to prepare organometallic derivatives of molybdenum and tungsten led only to coupling of the radicals of the Grignard reagent (11, 32, 74, 156). Hein and Melms-Bode, in 1938, reported (52) very briefly that molybdenum pentachloride and molybdenum tribromide reacted with phenyllithium, and tripyridomolybdenum tribromide with either phenyllithium or a phenyl Grignard reagent, to produce phenylmolybdenum compounds. The formation is not so ready as with chromium, and the stability of the resulting compounds is not so great. The compounds mentioned, none of which were obtained crystalline, were the following:

$(C_6H_5)_2Mo(OH,Br)$ $C_6H_5MoO_2OH$ $C_6H_5Mo_2O_5H_4$
$(C_6H_5)_3Mo_2O_7H_7$ $(C_6H_5)_2Mo_3O_9H_4$

Hein and Nebe (56) in 1940 reported in a short note the preparation of tungsten derivatives similar to the molybdenum compounds. Either $W(OC_6H_5)_6$ or WCl_6 reacts with phenyllithium or a phenyl Grignard reagent to produce an amorphous brown substance bearing considerable resemblance to the crude phenylmolybdenum products. The crude product was freed from tungsten oxyacids by extraction with ammonium bicarbonate. The compounds reported to have been isolated were $C_6H_5WO_{3.5}H_2$, $(C_6H_5W)_2O_7H_4$, and $(C_6H_5)_3W_2O_8H_7$. In color, general appearance, and properties they resembled the molybdenum compounds and like them were less stable than the phenylchromium compounds.

E. GROUP VII METALS

The preparation of a crude mixture of phenylmanganese compounds has been reported summarily (34, 38, 96). It was stated that when phenylmagnesium iodide in ether and manganous iodide in 3:1 mole ratio were stirred together for 12 hr., a chocolate-brown precipitate was formed which, after washing with ether to remove excess Grignard reagent and magnesium salts, analyzed as a mixture of diphenylmanganese and phenylmanganese iodide. It was stated (33) to be quite unstable and to require handling in an atmosphere of dry nitrogen.

No studies of organotechnicium compounds have been reported.

Druce (23) has described the preparation and some properties of trimethylrhenium. He found that rhenium trichloride reacted vigorously with methylmagnesium iodide in ether. The reaction mixture was hydrolyzed with dilute hydrochloric acid and from the yellow ether layer a fraction boiling at $\sim 60°C.$ was collected. The analysis for rhenium corresponded to $(CH_3)_3Re$. The compound was an almost colorless oil, somewhat heavier than water with which it was immiscible. It burned to give a cloud of Re_2O_7. An unsuccessful attempt to duplicate this work was made (36). It was observed that the reaction produced considerable quantities of methane and ethane, in one case equivalent to 91 per cent of the methylmagnesium iodide used, but no methylrhenium compound could be isolated. It was suggested (36) that a possible cause of failure in this attempt was the presence in the rhenium of impurities (iron, copper, etc.) in trace amounts which quickly decomposed the methylmagnesium iodide in a manner similar to the catalytic coupling reaction (see Section II,H).

F. GROUP VIII METALS EXCLUDING PLATINUM

1. Iron

A considerable amount of early work (5, 6, 100, 101, 121, 155) on the interaction of ferric and ferrous halides with a variety of Grignard reagents led only to the complete reduction of the iron halide to metallic iron with concomitant production of coupling products and other hydrocarbons derived from the organic groups of the Grignard reagents.

A careful and representative study is that of Champetier (15), who reported that when ferric chloride was added to an ether solution of phenylmagnesium bromide a violent reaction occurred and a black precipitate formed. The reaction ceased when 1 mole of ferric chloride per 3 moles of phenylmagnesium bromide had been added. The ether solution was found to contain biphenyl and magnesium halides, and the black sediment was a highly active form of metallic iron. The overall reaction was formulated as shown in equation 7.

$$6C_6H_5MgBr + 2FeCl_3 \rightarrow 3C_6H_5C_6H_5 + 2Fe + 3MgCl_2 + 3MgBr_2 \quad (7)$$

It was subsequently shown (40) that after 1 hr. a virtually stoichiometric yield of biphenyl is obtained. Champetier stated that there was no evidence for an organoiron intermediate in his experiments at room temperature. However, at −40°C. he found that the black precipitate did not appear immediately, but rather the solution became brown and only when allowed to warm up did it decompose, precipitating iron.

Job and Reich (84) felt that the use of a preparative agent less violent than the Grignard reagent would increase the possibility of isolating an organoiron product. They therefore studied the reaction between ferrous iodide and ethylzinc iodide. When a solution of ferrous iodide in ether was added to an equimolar quantity of the zinc reagent, the solution remained clear. The temperature was raised to the boiling point of ether and held there for 6 hr., and the reaction mixture was then hydrolyzed with water. A green precipitate consisting entirely of ferrous hydroxide was obtained. Furthermore, when a reaction mixture was sampled periodically, the proportion of ferrous hydroxide to zinc hydroxide in the hydrolyzed samples was found to increase steadily, until after approximately 6 hr. only ferrous hydroxide was obtained. The quantities of ethane and ferrous hydroxide formed in the final hydrolysis corresponded rigorously to equation 8.

$$2C_2H_5FeI + 2H_2O \rightarrow 2C_2H_6 + FeI_2 + Fe(OH)_2 \quad (8)$$

Job and Reich thus claimed that, although the compound ethylferrous iodide was not sufficiently stable to permit its isolation, its existence in ether solution had been demonstrated. This claim has been disputed (89), the results of the hydrolysis experiments being ascribed to the difference in solubility between ferrous and zinc hydroxides. However, since at room temperature ferrous hydroxide is about 2500 times as soluble as zinc hydroxide, this objection is unfounded. Also, the steady increase in the proportion of ferrous hydroxide in the precipitated hydroxides accords well with the supposition of Job and Reich. Subsequently Champetier (15) concluded, on the basis of hydrolysis experiments, that ferrous iodide reacts with phenylzinc chloride to produce phenylferrous iodide, but again it was not possible to isolate the product.

Krause and Wendt (105) reported that when ferric chloride is added to phenylmagnesium bromide, with air carefully excluded by a blanket of nitrogen, a greenish yellow reaction product is obtained, while the brown color of ferric chloride in the ether simultaneously disappears. This green-yellow substance was insoluble in ether, but dissolved in deaerated alcohol to give an intensely green solution which on exposure to air turned an equally intense red. On treatment with water, the green solution gave ferrous hydroxide and the red solution gave ferric hydroxide. When the green solid under ether was exposed to air, a red solution was quickly formed. This red solution could be reversibly reduced and reoxidized by triethylaluminum and air, respectively. No stoichiometric phenyliron compound was isolated, however.

Solutions of iron halides in Grignard reagents have been shown to absorb various gases, including hydrogen (160) and acetylene (82, 83), and mechanisms involving organoiron compounds have been postulated.

Recently it has been reported (4) that iron powder of high purity, carefully washed and dried, reacts with pure ethyl bromide, the action ceasing after 10–15 min. Upon concentration of the liquid, red-orange crystals, said to be $(C_2H_5)_2FeBr \cdot C_2H_5FeBr_2$, were obtained in about 10 per cent yield. The product was soluble in ether and benzene and was decomposed by water to give bromide and ferric ions. It was also stated that amyl and phenyl bromides reacted similarly. Independent corroboration of these results and definite information as to the composition of the product would be highly desirable.

The reaction of alkyls and aryls of various other elements with iron carbonyl (59) and with ferric chloride (109, 135) gave no evidence of the formation of organoiron compounds.

2. Cobalt

Some organocobalt compounds have been isolated and partially characterized (9, 76, 77, 130). Ingles and Polya found that when α- and β-naphthylmagnesium iodides and bromides were added to ether solutions of cobaltous iodide or bromide, and the reaction mixture refluxed for 15 min., dark green precipitates formed. These were filtered off, dried in vacuum, and extracted with benzene, giving green or blue-green solutions which deteriorated on storage. Addition of light petroleum or dioxane to these benzene solutions generally afforded compounds of the types $RCoX_3$, R_2CoX_2 and also $R_3Co_2X_5$, which can be formulated as an equimolar mixture of the first two, i.e., $RCoX_3 \cdot R_2CoX_2$. The compounds were purified by reprecipitation from ether. The substances originally extracted with benzene are not the same as the final products, since the latter are nearly insoluble in benzene. They are also insoluble in light petroleum, slightly soluble

TABLE 5

Preparation and some properties of naphthylcobalt compounds

Product	Decomposition Temperature	Color	Reactants		Precipitating Agent	Yield
			Grignard	Cobalt Salt		
	°C.					*per cent*
$(1-C_{10}H_7)CoI_3$..........	150–160	Yellow-green	$1-C_{10}H_7MgI$	CoI_2	Light petroleum	60
			$1-C_{10}H_7MgI$	$CoBr_2$	Light petroleum	2
			$1-C_{10}H_7MgBr$	CoI_2	Light petroleum	25
$(1-C_{10}H_7)_2CoI_2$..........	~150	Reddish brown	$1-C_{10}H_7MgI$	CoI_2	Dioxane	<1
			$1-C_{10}H_7MgI$	$CoBr_2$	Dioxane	<1
			$1-C_{10}H_7MgBr$	CoI_2	Dioxane	<1
$(1-C_{10}H_7)CoBr_3$.........	~120	Blue	$1-C_{10}H_7MgBr$	$CoBr_2$	Light petroleum	2
$(1-C_{10}H_7)_2CoBr_2$........	~120	Blue	$1-C_{10}H_7MgBr$	$CoBr_2$	Dioxane	<1
$(2-C_{10}H_7)CoI_3$..........	~160	Yellow-green	$2-C_{10}H_7MgI$	CoI_2	Light petroleum	<1
			$2-C_{10}H_7MgI$	$CoBr_2$	Light petroleum	<1
			$2-C_{10}H_7MgBr$	CoI_2	Light petroleum	47
$(2-C_{10}H_7)_2CoI_2$..........	~90	Reddish brown	$2-C_{10}H_7MgI$	CoI_2	Dioxane	<1
			$2-C_{10}H_7MgI$	$CoBr_2$	Dioxane	<1
			$2-C_{10}H_7MgBr$	CoI_2	Dioxane	<1
$(2-C_{10}H_7)CoBr_3$........	150–160	Blue	$2-C_{10}H_7MgBr$	$CoBr_2$	Light petroleum	9
$(2-C_{10}H_7)_2CoBr_2$........	65	Blue	$2-C_{10}H_7MgBr$	$CoBr_2$	Dioxane	<1

in chloroform and in dioxane with decomposition, and soluble in ether. The various combinations of reactants studied, the products, and the yields are summarized in table 5.

The structure of these compounds is a matter of considerable uncertainty. All of the formulas are assigned on the basis of analyses for cobalt and halogen only, but these data are in good agreement with the assigned formulas. It will be noted that if the structures are written with the naphthyl groups and the halogen atoms individually bonded to cobalt, in each case the compound will contain Co(IV). The only known examples of cobalt(IV) compounds (147) are the binuclear peroxo-bridged complexes, which also contain a cobalt(III) atom, and they certainly do not arise in a reducing medium such as a Grignard reagent. It was found that on treatment with water or dilute acids the compounds generated mainly binaphthyls; this result, it was said, shows that they are organometallic. However, the usual product of hydrolysis of an organometallic metal–carbon bond, R—M, is RH not R—R, the latter being frequently the product of thermal or spontaneous decomposition. Furthermore it was observed that after the hydrolysis cobalt was present both as cobaltous hydroxide and as cobalt salts. An equation (equation 9) can be written describing the hydrolysis of, say, $RCoX_3$ which accounts for the production of RR, $Co(OH)_2$ and CoX_2, but it is seen that hydrogen is also produced. No mention of gas evolution was made

$$2RCoX_3 + H_2O \rightarrow RR + \tfrac{3}{2}CoX_2 + \tfrac{1}{2}Co(OH)_2 + \tfrac{1}{2}H_2 \qquad (9)$$

by the authors. However, decomposition of R_2CoX_2 to RR would not require the agency of water or acid and would not generate cobaltous hydroxide without also producing hydrogen. Clearly, further study of these hydrolyses is needed and might provide valuable clues to the structures of the compounds.

It was also observed that the compounds decomposed on heating without melting, but the products were apparently not identified. On sublimation in a vacuum, decomposition again occurred with the liberation of free halogen. Two further significant observations with regard to the naphthyl compounds may be mentioned. It was found that in the preparative reaction no metallic cobalt was produced. It was also noted that through degradation with dioxane the organocobalt compounds all tended toward an empirical formula of the type R_3CoX, although no compound of this composition was isolated in a pure state. Magnetic and crystallographic data on the naphthylcobalt compounds are not yet available.

Further studies were conducted (77) using Grignard reagents derived from methyl iodide, ethyl iodide, propyl iodide, isopropyl iodide, and phenyl bromide in which an analogous preparative procedure was followed. The products, obtained in yields of only 4–8 per cent, had approximately the correct cobalt–halogen ratios required by the types obtained in the naphthyl series, but the absolute values were low. It was possible to explain the discrepancies by assuming association of one or two molecules of benzene with the compound and in one case, where 1-chloronaphthalene was used in place of benzene for extraction, a compound of empirical formula $C_2H_5CoI_3 \cdot C_{10}H_7Cl$ was isolated. In general, the phenyl and aliphatic compounds were impure and require further study. Analogous experiments with iron and nickel halides were unsuccessful.

Diallylcobalt, $(CH_2{=}CHCH_2)_2Co$, has been patented as an addition agent in drying oils (164, 165), but no information about the preparation or properties of the compound are given.

Solutions of cobaltous chloride in phenylmagnesium bromide have been found to absorb hydrogen, forming CoH_2; the course and stoichiometry of the reaction provide circumstantial evidence of the existence of diphenylcobalt (160). A discussion of the analogous reaction involving nickel chloride is presented below. The role of cobaltous chloride in catalytically altering the course of Grignard reactions is discussed in detail in Section II,H.

3. Nickel

No organonickel compound has ever been isolated. Essentially the only evidence for the existence of organonickel derivatives lies in the behavior of Grignard solutions to which nickel chloride has been added (86, 143, 159, 160). Weichselfelder and Thiede (160), for example, observed that freshly prepared reaction mixtures consisting of nickel chloride suspended in an ether solution of phenylmagnesium bromide in twofold molar proportion absorb 2 moles of hydrogen per mole of nickel, giving a black pyrophoric precipitate. However, the precipitate is found to have the composition NiH_2 after drying in a stream of hydrogen. With this much information, the following reaction schemes seemed plausible (equations 10).

$$
\begin{array}{ll}
(1) & NiCl_2 + 2C_6H_5MgBr \rightarrow (C_6H_5)_2Ni + MgCl_2 + MgBr_2 \\
(2a) & (C_6H_5)_2Ni + 2H_2 \rightarrow 2C_6H_6 + NiH_2 \\
(2b) & (C_6H_5)_2Ni + 2H_2 \rightarrow C_6H_5C_6H_5 + NiH_4 \xrightarrow{\text{drying}} NiH_2 + H_2 \\
(2c) & (C_6H_5)_2Ni \rightarrow C_6H_5C_6H_5 + Ni \xrightarrow{2H_2} NiH_4 \xrightarrow{\text{drying}} NiH_2 + H_2
\end{array}
\qquad (10)
$$

A determination of the hydrogen content of the nickel hydride without removing it from the reaction mixture showed that the compound NiH_4 never arises, thus eliminating the alternatives 2b and 2c. A mechanism in which the nickel is reduced directly to metal without the appearance of diphenylnickel would also necessitate the initial formation of NiH_4 with loss of hydrogen on drying and is therefore eliminated. Thus the correct mechanism is probably as represented in equation 1, followed by 2a, and there is then good circumstantial evidence for the existence in solution of diphenylnickel.

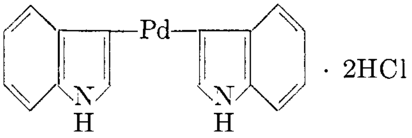
There is abundant evidence that diphenylnickel is very unstable. Thus when the reaction mixture is permitted to stand for 1 hr. and then hydrolyzed, essentially quantitative yields of biphenyl and nickel are obtained (40). Weichselfelder and Thiede attempted to isolate the diphenylnickel, using a variety of techniques and reaction conditions, but without success (160). Weichselfelder and Kossodo (159) showed that when the reaction mixture of nickel chloride and phenylmagnesium bromide was permitted to stand for increasing lengths of time before treatment with hydrogen, the absorption of hydrogen over the quantity required to produce NiH_2 decreased, becoming zero for a mixture which had aged 4 hr. The NiH_2 was assumed to have arisen from the uptake of hydrogen by the highly reactive nickel deposited on decomposition of the diphenylnickel.

Various unsaturated gaseous compounds are absorbed by reaction mixtures consisting of nickel chloride and a Grignard reagent, particularly phenyl Grignards. Among those which have been studied (85, 86) are carbon monoxide, nitric oxide, ethylene, and acetylene. In most cases it has been reported that the gases are absorbed in integral mole ratios to the nickel present, but little knowledge of the probable organonickel intermediates is to be gleaned from this work.

4. Other elements

Concerning the remaining six elements, with the exception of platinum, which is discussed in Section II,G, there is only one report of an attempt to prepare or at least ascertain the stability of organo derivatives, a discussion of which will be deferred to Section II,H on coupling reactions.

Compounds of palladium with indole (22) and pyrrole (142) have been prepared and formulated with palladium–carbon bonds. For the pyrrole compound the analyses do not, in fact, correspond to the formulas proposed, and we shall consider here only the indole derivative which, it is said, was prepared by adding a cold, saturated aqueous solution of indole to a 5 per cent aqueous solution of palladous chloride. After a few hours a dark precipitate separated, for which formula XI was proposed. However, in an attempt to repeat this work (18) it was found that immediately on mixing the solutions a rusty-red precipitate formed which had the composition $C_8H_6NPdCl_2$. Regardless of this difference in experience, the question of how the indole is attached to the palladium remains. The assumption of a carbon–palladium linkage is quite arbitrary, since at least four other possibilities suggest themselves, *viz.*: (*1*) a bond to nitrogen; (*2*) an amine-type donor bond; (*3*) an olefin-type donor bond as in platinum–olefin complexes; (4) a "sandwich" type bond as in bis-cyclopentadienyl compounds. Thus this compound cannot in the light of present evidence be regarded as an organopalladium compound.


XI

All of the Group VIII elements will be considered further in Section II,H on coupling reactions.

G. PLATINUM

The first organoplatinum compound, trimethylplatinum iodide, was reported by Pope and Peachey (131, 132) in 1907. This was prepared by slow addition of an ether slurry of anhydrous platinic chloride to a solution of methylmagnesium iodide in ether. Cooling was provided to moderate the exothermic reaction, and after standing for a few hours, the mixture was hydrolyzed; the product was extracted with benzene and crystallized from that solvent in the form of an orange, crystalline powder. The reaction is represented by equation 11.

$$3CH_3MgI + PtCl_4 \rightarrow (CH_3)_3PtI + MgI_2 + 2MgCl_2 \qquad (11)$$

A reinvestigation of this reaction has been reported by Gilman, Lichtenwalter, and Benkeser (39, 41, 107), in which it was found that in addition to the main reaction, represented by equation 11, producing trimethylplatinum iodide, numerous side-reactions leading to other methylplatinum derivatives also occur. Among these additional products, which formed in yields of only a few tenths of a per cent, were tetramethylplatinum, dimethylplatinum diiodide, methylplatinum triiodide, methylplatinum pentaiodide, and several other substances which were apparently homogeneous, but were not characterized. In view of the unusual structures of the trimethylplatinum halides and of tetramethylplatinum (*vida infra*), physical and structural studies of these compounds would be valuable. The structure of the black compound, formulated on the basis of analyses as methylplatinum pentaiodide, would be especially interesting, since there is no reported example of a platinum(VI) compound, nor is one likely to arise from a platinum(IV) compound in the reducing medium of a Grignard reagent. The preparative method of Pope and Peachey was slightly modified and a 45 per cent yield of trimethylplatinum iodide was reported.

Pope and Peachey (132) converted trimethylplatinum iodide into a series of derivatives of the trimethylplatinum group, including the chloride, nitrate, hydrated sulfate, $[(CH_3)_3Pt]_2SO_4 \cdot 2H_2O$, and hydroxide, $(CH_3)_3PtOH$, which they regarded as the parent base of the series of salts. It is interesting that the halides and the hydroxide are soluble in most organic solvents and quite insoluble in water, whereas the nitrate and sulfate are soluble only in a few polar organic media and highly soluble in water.

Gilman and coworkers (39, 41, 107) also succeeded in preparing two completely methylated platinum compounds. In addition to the very tiny amounts of tetramethylplatinum obtained as by-products in the preparation of trimethylplatinum iodide, the latter on treatment with methylsodium is converted to tetramethylplatinum in 46 per cent yield. This substance is a colorless solid, is soluble in many common organic media, but possesses no definite melting or decomposition point. On refluxing trimethylplatinum iodide with potassium in benzene, it is converted, in 60 per cent yield, to hexamethyldiplatinum, a colorless substance, soluble in several common organic solvents, and insoluble in water. It decomposes in a shower of sparks on heating. Several of the trimethylplatinum derivatives also explode when heated.

Since the preparation and handling of anhydrous platinic chloride is somewhat tedious, Foss and Gibson (27) sought a more convenient starting material. Experience with the preparation of dialkylgold compounds led them to study the action of methylmagnesium iodide on *cis*- and *trans*-dipyridinotetrachloroplatinum. It was found that while the *trans* isomer gave rise to no methylplatinum compounds, *cis*-dipyridinotetrachloroplatinum, suspended in a mixture of benzene and ether, reacted smoothly with the Grignard reagent, giving, in 70 per cent yield, a compound having the empirical formula $Py(CH_3)_3PtI$. This compound can then be converted into trimethylplatinum iodide, the overall yield being about 63 per cent.

Trimethylplatinum iodide has also been prepared by the action of a methylmagnesium iodide reagent containing excess methyl iodide on platinum(II) complexes. Thus when Gel'man (45) prepared trimethylplatinum iodide from Zeise's salt, $K[(C_2H_4)PtCl_3]$, she claimed to have proven that the platinum atom in Zeise's salt was quadrivalent. However, Chatt and Duncanson (17) pointed out that her Grignard reagent contained a substantial excess of methyl iodide and suggested the following reaction sequence to account for the result.

$$K[(C_2H_4)PtCl_3] + 2CH_3MgI \rightarrow C_2H_4 + (CH_3)_2Pt + KCl + MgCl_2 + MgI_2$$

$$(CH_3)_2Pt + CH_3I \rightarrow (CH_3)_3PtI \qquad (12)$$

They supported this proposal by preparing trimethylplatinum iodide, using the same quantities of reagents with Na_2PtCl_4 substituted for the Zeise's salt.

Before proceeding to a more detailed consideration of the chemistry of polymethylplatinum compounds, which involves questions of stereochemistry and coördination number, let us examine the available x-ray structural data. Powder photographs (21) showed that trimethylplatinum chloride has a body-centered cubic lattice, but although the symmetry was consistent with a tetrahedral disposition of the four groups around the platinum atom, in view of the strong tendency of platinum(IV) to demand six-coördination, the tetrahedral model was questionable. A more complete analysis by Rundle and Sturdivant (141) indicated that the molecule is tetrameric and that the platinum atom is in fact six-coördinated. The structure proposed is shown in figure 2. Although the great scattering of the platinum atoms obscured that of the carbon atoms, the platinum–platinum distance of 3.73 Å. is too great to permit platinum–platinum bonding and the distance between the tetrahedra formed by the groups of four platinum atoms is so great as to "practically demand" the proposed structure. The platinum–platinum bridging through the chlorine atoms is comparable to many other examples of metal–metal bridging via halogen atoms, notably in aluminum chloride (Al_2Cl_6).

Rundle and Sturdivant (141) also examined tetramethylplatinum and, again on the basis of the location of the platinum atoms, concluded that this molecule is a tetramer also. However, in this case the bridging is effected by a methyl group. Although this is the only known example of an alkyl group functioning as a three-way bridge, in view of the existence of two-way methyl and ethyl bridges in the aluminum alkyls (127) and the fact that the functioning of a methyl group as a three-way bridge may be readily explained on Rundle's theory of "partial bonds" (139), the tetrameric structure of tetramethylplatinum seems reasonably certain.

Tetramethylplatinum, when freshly crystallized from benzene, contains half a mole of benzene of crystallization which is quickly lost by efflorescence. Rundle and Holman (140) showed that the presence of this benzene in the lattice in no way disturbs the tetrameric groups. Thus $(CH_3)_4Pt \cdot 0.5C_6H_6$ shows the molecular weight of the tetramer in benzene solution, and shows the same principal x-ray reflections as the unsolvated compound. Tetramethylplatinum has the same ultraviolet spectrum in hexane as in benzene. Apparently the benzene is retained only by van der Waals forces, augmented by good crystal packing of the polarizable benzene molecules.

The dipole moments of trimethylplatinum iodide, bromide, and chloride were measured in benzene solution and found to be 1.1, 0.98, and 0.97 Debye units, respectively (146). Assuming that the iodide and bromide are also tetrameric in solution, all three compounds should have a zero permanent dipole. However, in computing these results, no correction for atomic polarization was made. Since in molecules such as these atomic polarization could easily account for an apparent electric moment of 1 Debye, these data are quite in accord with the tetrameric structure, for if the molecules were tetrahedral they might well be expected to have rather large permanent moments.

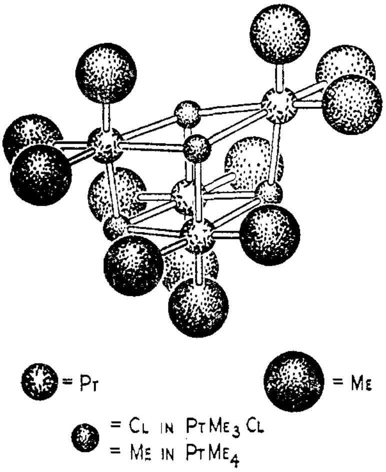
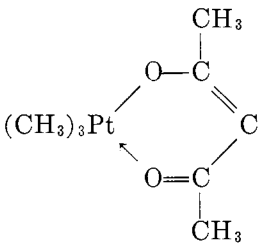


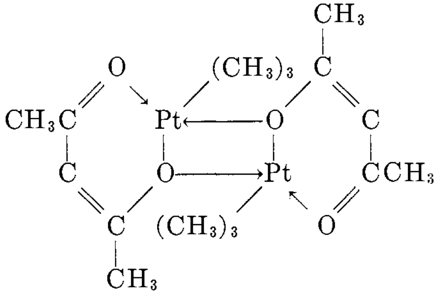
FIG. 2. The structure of trimethylplatinum chloride. Reproduced by permission from the article by R. E. Rundle and J. H. Sturdivant (J. Am. Chem. Soc. **69**, 1564 (1947)).

The assumption that the bromide and iodide of trimethylplatinum also possess tetrameric structures deserves further comment. The evidence that, in solution, they do is indicative rather than conclusive. The similarity in dipole moment data is consistent with this idea. Cryoscopically and ebullioscopically, trimethylplatinum iodide shows association factors of about 4.4. However, trimethylplatinum iodide crystallizes in the monoclinic system (12) with $a{:}b{:}c = 1.778{:}1{:}1.826$ and 116°02′, while trimethylplatinum chloride forms isometric rhombohedra (12), indicating that at present the assumption must be made with reservations in the case of the crystalline compounds.

While x-ray investigation of hexamethyldiplatinum is not conclusive, it appears that the molecule is at least dimeric but no larger than $[(CH_3)_3Pt]_{12}$, although the possibility of continuous chains was not excluded (75). However, a molecular weight determination in freezing benzene (39) is in excellent agreement with the dimeric formula, $(CH_3)_6Pt_2$. It is probable that again there is methyl bridging, perhaps to give the platinum atoms six-coördination, although a direct platinum–platinum bond is not positively excluded by the experimental data.

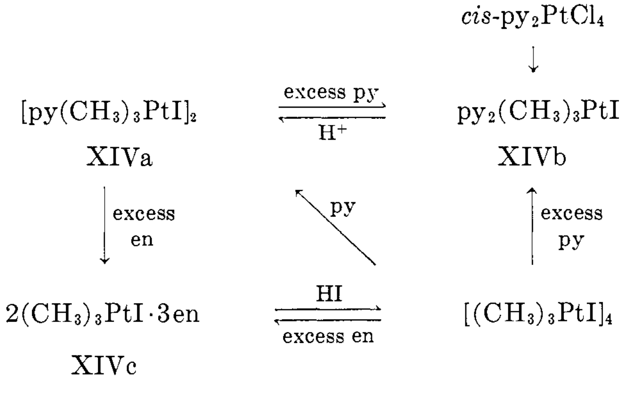
Trimethylplatinum iodide reacts with acetylacetone, dipropionylmethane, benzoylacetone, and ethyl acetoacetate to form dimerized chelate derivatives (111, 113). A 3 per cent solution of the acetylacetonate, for example, shows a molecular weight nearly twice that for the monomeric formula (XII). A structure such as XIII was postulated to account for the dimerization, which is in keeping with the demand of platinum(IV) for sixfold coördination.


XII

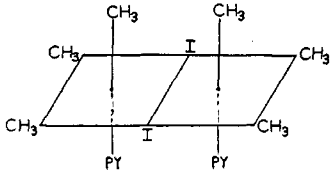

XIII

According to Wiltshire (112), when trimethylplatinum acetylacetonate is dissolved in aqueous acetic acid and potassium iodide is added, a compound of the formula $(CH_3)_3PtI$ is obtained. However, this compound is white instead of orange and gives association factors, both cryoscopically and ebullioscopically, in benzene of 2.3–2.5, whereas orange $(CH_3)_3PtI$, prepared according to Pope and Peachey, showed association factors of about 4.4 in parallel experiments. Both the white and the orange forms were found to crystallize from benzene in the same crystal habit and to be indistinguishable under the microscope.

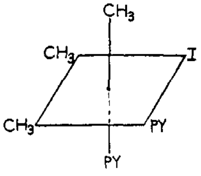
A variety of amine complexes of trimethylplatinum iodide have been prepared (27, 69, 108). Those containing pyridine (py) and ethylenediamine (en) are particularly interesting. Foss and Gibson (27), in connection with their synthesis of trimethylplatinum iodide from *cis*-py_2PtCl_4, investigated the reactions summarized in the following scheme:



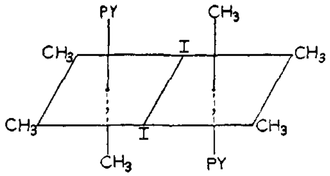
A stereochemical interpretation was proposed. Assuming that trimethylplatinum iodide has the same tetrameric structure as the chloride—and the molecular weight and dipole moment data favor this assumption—it is clear that the formation of a dimeric or monomeric complex will involve splitting of platinum–iodine linkages in the tetramer, with the freed positions in the octahedral coordination sphere of platinum being then occupied by the amine molecules. If it is further assumed that in the process no rearrangement of the three initially mutually *cis* methyl groups occurs, then, stereochemically, XIVa probably has the structure XVa, where the four-membered ring of platinum and iodine atoms was originally one face of the cubic tetramer. Further splitting and replacement of iodine by pyridine in XVa would produce XVb, the *cis* form of XIVb. In *cis*-dipyridinotetrachloroplatinum three methyl groups can replace three mutually *cis* chlorine atoms, whereas this is not possible with *trans*-dipyridinotetrachloroplatinum. If we again assume a minimum of reorientation, it is clear that the *cis* isomer can react with the methyl Grignard to produce XIVb, while the *trans* isomer cannot. The dimerization of XIVb, stereochemically XVb, could produce either XVa or XVc. Since this dimer is identical with that obtained from the splitting of trimethylplatinum iodide, it is probably XVa. The structure of XIVc is an open question. XVIa was first proposed (108), but Foss and Gibson (27) favor XVIb on the grounds that ethylenediamine shows a strong tendency to chelate wherever possible.



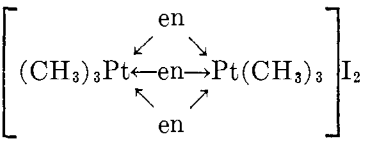
XVa



XVb



XVc



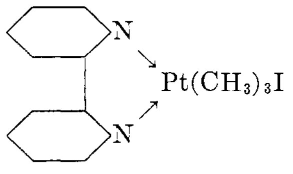
$$\left[\begin{array}{c} en \\ \swarrow \quad \searrow \\ (CH_3)_3Pt\leftarrow en\rightarrow Pt(CH_3)_3 \\ \nwarrow \quad \nearrow \\ en \end{array}\right]I_2$$

XVIa

$[en(CH_3)_3Pt\leftarrow en\rightarrow Pt(CH_3)_3en]I_2$

XVIb

Other amino derivatives which have been reported, followed by the appropriate references, are:



(108)

$en_2Pt(CH_3)_3I$ (45)

$enPt(CH_3)_3I$ (108)

$(CH_3)_3Pt(NH_3)_2I$ (132)

$(CH_3)_3Pt(NH_3)_3I$ (44, 45)

The chemistry of organoplatinum compounds is almost entirely that of the methyl derivatives. However, some fragmentary studies concerning compounds with other organic radicals have been reported by Lichtenwalter (107). When platinum tetrachloride is added to phenylmagnesium iodide, it is found that about ten equivalents of the Grignard reagent are required in order that the solution give a positive color test which is characteristic of the Grignard compound. An insoluble white complex is formed in the reaction. On hydrolysis, this generates an amorphous brown solid containing organic matter, platinum, and iodine, which Lichtenwalter stated to be a mixture of phenylplatinum compounds, although no individual ones could be isolated. This mixture was found to be slightly soluble in benzene, alcohol, and chloroform, and very soluble in dioxane, and various fractions were obtained varying in platinum content from 30 to 48 per cent.

The reaction of platinum dichloride with methylmagnesium iodide produced a difficultly soluble, amorphous brown powder, the analyses of which were said to correspond to the formula $(CH_3)_2PtI_2$. It seems extremely unlikely that a compound of platinum(IV) would be produced from platinum dichloride by the action of a Grignard reagent, unless, as in the cases previously cited, an excess of methyl iodide was present. Unfortunately no experimental details were reported. Platinum dichloride was also found to react with α-naphthylmagnesium bromide to form di-α-naphthylplatinum, obtained as a brown powder.

H. COUPLING REACTIONS

A coupling reaction may be defined as one in which two molecules of a Grignard compound, RMgX, give rise to one molecule of the compound RR in the presence of a heavy metal halide. Organolithium compounds may also be used, but transition metal halides have been applied almost exclusively with Grignards. There are two types of coupling reaction, which will be called stoichiometric and catalytic, respectively, depending upon whether the heavy metal halide is present in large quantity and completely consumed in the coupling reaction or whether a small amount of it (say 3 mole per cent) suffices to effect the coupling. This discussion of coupling reactions is included because, if certain assumptions as to the mechanism can be made, then they indirectly provide information about the relative stabilities of some organo derivatives of transition metals. The stoichiometric coupling reaction will be discussed first.

Many examples of the stoichiometric reaction have been encountered in the foregoing discussion. A clear example (5) is the production, in essentially quantitative yield, of biphenyl upon refluxing a solution of phenylmagnesium bromide with chromium chloride.

$$2C_6H_5MgBr + 2CrCl_3 \rightarrow C_6H_5C_6H_5 + MgCl_2 + MgBr_2 + 2CrCl_2 \qquad (13)$$

Gilman and Lichtenwalter (40) have pointed out that when a metal halide reacts with an RMgX compound, the following possibilities exist:

(1) Metathesis to produce a stable organometallic compound:

$$m\text{RMgX} + \text{MX}_n = m\text{MgX}_2 + \text{R}_m\text{MX}_{(n-m)} \qquad m \leqslant n \qquad (14)$$

(2) Metathesis to produce an unstable organometallic compound which decomposes to give RR.
(3) Production by metathesis of an organometallic compound which is so unstable as to immediately decompose, *in situ*, so that only the overall coupling reaction is observed.

The three cases actually merge, one into the next. The assumption in case 3 that an organometallic intermediate does actually exist, however short-lived it may be, has not of course been proven to be universally valid, but seems justified by many examples of case 2 in which the stability of the organometallic compound obtained is very small indeed. Krause and Wendt (104), for example, isolated phenylsilver in an impure state and observed that when dried it spontaneously decomposed in a puff of white smoke, yielding biphenyl and metallic silver, and that even when kept under ether it decomposed completely to the same products within a few hours. The silver alkyls are still less stable, being immediately decomposed at −18°C. (43, 136).

A study of the coupling reactions of all eight of the Group VIII elements with phenylmagnesium iodide has been made (40, 107), and the extent of the coupling interpreted as a rough measure of the stability of the intermediate organometallic derivatives. The general experimental procedure consisted in adding the anhydrous metal halide to a clear, cold, well-stirred solution of phenylmagnesium iodide in ether. The reaction was allowed to proceed for 1 hr. before the reaction mixture was hydrolyzed with an iced solution of ammonium chloride. The runs were repeated several times with concordant results which are assembled in table 6. It appears that under the experimental conditions the phenyl derivatives of the first six elements are quite unstable and short-lived. In the case of platinum, which forms stable methyl derivatives, practically no biphenyl was obtained, but crude phenylplatinum compounds were isolated. These have been discussed in the previous section. If, as postulated and borne out here by platinum and the first six elements, the extent of the coupling is a rough index of the stability of organometallic intermediates, the low yields of biphenyl with osmium and iridium trichlorides as coupling agents signify that organoösmium and organoiridium compounds should be moderately stable and perhaps isolable. In fact, a small amount of tarry organic matter containing osmium remained after removal of the biphenyl, and with iridium(III) chloride, although it reacted very slowly (requiring about three weeks at room temperature before

TABLE 6

Yields of biphenyl in coupling reactions of Group VIII metals

Metallic Halide	Quantity of Metallic Halide	C_4H_4MgI	Yield of Biphenyl	Metallic Halide	Quantity of Metallic Halide	C_6H_5MgI	Yield of Biphenyl
	moles	*moles*	*per cent*		*moles*	*moles*	*per cent*
$FeCl_3$	0.01	0.03	98	$PdCl_2$	0.00566	0.0163	98
$CoBr_2$	0.01	0.03	98	$OsCl_3$	0.00275	0.07	53
$NiBr_2$	0.03	0.095	100	$IrCl_4$	0.003	0.01	28
$RuCl_3$	0.0036	0.108	99	$PtCl_4$	0.006	0.06	~5
$RhCl_3$	0.0036	0.013	97				

giving a negative test for phenylmagnesium iodide), an inhomogeneous, amorphous, brown solid was isolated, which burned, leaving a residue of iridium metal.

The catalytic coupling reaction is perhaps best introduced by means of an example. When bromobenzene is added slowly to phenylmagnesium bromide containing about 3 mole per cent of cobaltous chloride, a vigorous exothermic reaction occurs in which biphenyl is produced in virtually quantitative yield (based on phenylmagnesium bromide) (90). This is quite remarkable, since (*1*) arylmagnesium halides do not react with aryl halides, (*2*) metallic halides do not react with aryl halides, (*3*) metallic halides alone couple only a stoichiometrically related amount of an aryl Grignard reagent, as has been mentioned. It was also shown (90) that the biphenyl is formed almost entirely from the phenylmagnesium bromide and that the bromobenzene is consumed, giving rise to benzene, a trace of biphenyl, and other higher polyphenyls. To account for these results, the following scheme was postulated (90):

$$\begin{array}{ll}
\text{(a)} & C_6H_5MgBr + CoCl_2 \rightarrow C_6H_5CoCl + MgClBr \\
\text{(b)} & 2C_6H_5CoCl \rightarrow C_6H_5C_6H_5 + CoCl\cdot \\
\text{(c)} & CoCl\cdot + C_6H_5Br \rightarrow CoClBr + C_6H_5\cdot \\
\text{(d)} & xC_6H_5\cdot \rightarrow C_6H_6 + C_6H_5C_6H_5 + \text{higher polyphenyls}
\end{array} \qquad (15)$$

The effect of cobalt chloride or bromide in catalytic amounts on a great number of other reactions involving Grignard reagents was investigated by Kharasch and coworkers (90, 92, 95, 152); in every case it was found that the presence of the cobaltous halide altered the course of the reaction. Other transition metal halides were found to behave similarly but not as consistently as the cobaltous halides (91). The explanations proposed have the common feature of assuming that something analogous to steps (a) and (b) of reaction 15 always occurs. That is, the Grignard compound reacts with the cobaltous halide to form an RCoX compound which decomposes to yield a coupled product, RR, when R is aryl or a free radical, R•, and a cobalt subhalide, CoX•′, which is assumed to be the carrier in a chain reaction. The subhalide is constantly regenerated to CoX_2 as, for example, in step c of reaction 15. If the proposed reaction sequence is correct up to the point at which the RCoX compound breaks down, then at least one experiment in this body of work provides qualitative information as to the relative stabilities of alkyl–cobalt and aryl–cobalt bonds.

It was observed (90) that when a reaction mixture consisting of methylmagnesium bromide and a few mole per cent of cobaltous chloride was heated for 1.5 hr. prior to addition of bromobenzene no coupling reaction occurred, although with freshly prepared methylmagnesium bromide containing cobaltous chloride a vigorous coupling reaction occurs. In a parallel experiment it was found that when preheated phenylmagnesium bromide is used, the yield is still about 50 per cent of that obtained using a freshly prepared reagent. These results were regarded as showing methylcobaltous chloride to be less stable than phenylcobaltous chloride.

However, Wilds and McCormack (161) have questioned the general type of mechanism proposed by Kharasch and coworkers and have postulated finely divided cobalt as the chain carrier in a mechanism whose initial steps they illustrate by the example shown in equation 16. With regard to the experiment cited above, in which phenyl and methylmagnesium bromides containing

$$\begin{array}{ll}\text{(a)} & 2C_2H_5MgBr + CoCl_2 \rightarrow MgBr_2 + MgCl_2 + (C_2H_5)_2Co \\ \text{(b)} & (C_2H_5)_2Co \rightarrow C_2H_6 + C_2H_4 + Co\end{array} \qquad (16)$$

cobaltous chloride were preheated, Wilds and McCormack state that it is unlikely that either C_6H_5CoCl or CH_3CoCl would survive; to explain the result on the basis of their mechanism, they site observations (24, 85) that colloidal cobalt prepared using an alkyl Grignard reagent is more easily flocculated than that from a phenyl Grignard reagent, which seems to stabilize the colloidal solution. Until the question of mechanism is settled, this experiment cannot be said to demonstrate the greater stability of phenyl–metal *versus* alkyl–metal bonds.

The use of the term "coupling reaction" is strictly justified only when the group R in the Grignard compounds, RMgX, is aryl, for when R represents an alkyl group, methyl or ethyl particularly, coupling is not the sole course of the reaction and in many cases does not occur at all, although the course of the reaction is almost certainly the same (37) up to the stage at which an organometallic intermediate breaks down. Recently Gilman, Jones, and Woods (37) have published comprehensive data on the products of stoichiometric coupling reactions of alkyl Grignard reagents and alkyllithium compounds. These data, together with the result of a catalytic coupling reaction, are displayed in tables 7 and 8.

It is seen that all of the reactions may be divided into four general classes, *viz.*: (I) Those in which the major product is a paraffin, RH; (II) those in which both disproportionation products, paraffin and olefin, are obtained in substantial quantities, but no coupled products; (III) those in which both coupled and disproportionation products are obtained in appreciable quantities; (IV) those in which only coupled products are obtained. All coupling reactions involving phenyl Grignard reagents may also be included in class IV, since biphenyl in considerable amount has invariably been the sole product isolated and in many cases is produced quantitatively.

Because ethyl radicals are not easily produced in solution at ordinary temperatures (157), it is not known definitely what their decomposition products would be. Gas-phase studies have shown, however, that the activation energy of the reaction

$$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot \qquad (17)$$

is about 39.5 kcal. (78), whereas the reaction

$$C_2H_5\cdot + RH \rightarrow C_2H_6 + R\cdot \qquad (18)$$

where RH is some low-molecular-weight alkane, proceeds about as readily as does the corresponding reaction with methyl radicals, for which the activation energies are in the range of 4 to 9 kcal. (156). Hence it would seem very probable that free ethyl radicals in a solvent containing alkyl groups, such as ether, would

TABLE 7

*Results of coupling reactions with Grignard reagents**

Class	Grignard reagent $C_nH_{2n+1}MgX$	Metal Salt	Mole ratio $RMgX/MX_n$	Products† and Yields Based on Grignard Reagent		
				RR	C_nH_{2n+2}	C_nH_{2n}
				per cent	*per cent*	*per cent*
I	C_2H_5MgBr	$TiCl_4$	4	0	52	9
	C_2H_5MgBr	$Ti(OC_2H_5)_4$	4	0	58	
	C_2H_5MgBr	$ZrCl_4$	4	0	48	3
	C_2H_5MgBr	$TaCl_5$	5	0	48	2
	C_2H_5MgBr	$TaCl_5$	1	0	51	7
IIa	C_2H_5MgBr	$CrCl_3$	3	0	42	33
	C_2H_5MgBr	$MnBr_2$	2	0	63	29
	C_2H_5MgBr	$FeCl_3$	2	0	49	40
IIb	C_2H_5MgBr	$TlCl$	1	0	34	32
	C_2H_5MgBr	$CuCl$	1	0	46	45
	C_2H_5MgBr	$CuCl_2$	1	0	33	28
III	C_2H_5MgBr	$AgCl$, $AgBr$, AgI	1	43-56	7-22	7-20
	C_2H_5MgBr	$AuCl_3$	3	11	15	6
I	$(CH_3)_2Mg$	$ZrCl_4$	4		74	
	CH_3MgI	$ZrCl_4$	2		53	
	CH_3MgCl	$TaCl_5$	5		62	
	$(CH_3)_2Mg$	$CrCl_3$	3		62	
IV	$(CH_3)_2Mg$	$AgBr$	1	88		
IV	$(CH_3)_2Mg$	CuI	1	83		
	CH_3MgCl	$CuCl_2$	1	70		
	$(CH_3)_2Mg$	$CuCl_2$	1	74		
I	$n\text{-}C_4H_9MgBr$	Catalytic: 5 mole per cent $CoCl_2$ + C_6H_5Br		0	83 combined	

* Data from the work of Gilman, Jones, and Woods (37) with the exception of the last entry, which is from Kharasch, Lewis, and Reynolds (93).

† For all entries but the last, all gaseous hydrocarbons produced in yields greater than 1 per cent are listed.

TABLE 8

*Stoichiometric coupling reactions with methyllithium**

Group	Metal Salt	Mole Ratio CH_3Li/MX_n	Products†		Group	Metal Salt	Mole Ratio CH_3Li/MX_n	Products†	
			CH_4	C_2H_6				CH_4	C_2H_6
			per cent	*per cent*				*per cent*	*per cent*
I	$TiCl_4$	4	64	0	II	$AuCl_3$	3	17	64
	$Ti(OC_2H_5)_4$	4	59	0		$FeCl_3$	2	56	24
	$ZrCl_4$	4	56	0		$NiCl_2$	2	36	38
	$ZrCl_4$	2	50	0					
	$Zr(OC_6H_5)_4$	4	70	0	IV	$AgBr$	1	0	86
	$TaCl_5$	5	72	0		$CuCl$	1	0	80
	$MnBr_2$	2	78	0		CuI	1	0	80
	$CrCl_3$	3	73	0		$CuCl_2$	1	0	80
	$CeCl_3$	3	20	0					
	$LaCl_3$	3	14	0					

* Data from the work of Gilman, Jones, and Woods (37).

† All gaseous hydrocarbons produced in yields greater than 1 per cent are listed.

react largely to produce ethane. Free methyl radicals in solution are known to abstract hydrogen, producing methane, but have not been observed to couple in appreciable quantities (157). Phenyl radicals in solution *always* attack the solvent but do not couple, and in solvents containing alkyl groups the sole product is benzene (72, 158).

Following a suggestion by Gilman, Jones, and Woods (37) that in some cases the decomposition of the intermediate may be unimolecular and in others bimolecular, it appears possible to correlate all of the available data on coupling reactions and at the same time to derive information about the relative stabilities of aryl–transition metal bonds and alkyl–transition metal bonds. Bearing in mind the above facts about the behavior of free radicals in solution, three basic mechanisms for the decomposition of the organometallic intermediates (which are assumed to be formed in each case) are postulated.

If the bond between carbon and metal in the organometallic intermediate is very weak, the decomposition is unimolecular, thus producing a free radical, R•.

$$\mathrm{RMX}_n \rightarrow \mathrm{R}\cdot + \mathrm{MX}_n \tag{19}$$

If the carbon–metal bond is relatively strong, the decomposition of the intermediate is bimolecular. The product of this bimolecular reaction may be either a coupled product, RR, or products of disproportionation.

$$\begin{array}{ll}\text{(a)} & 2\mathrm{RMX}_n \rightarrow \mathrm{RR} + 2\mathrm{MX}_n \\ \text{(b)} & 2\mathrm{RMX}_n \rightarrow \underset{\text{Paraffin}}{(\mathrm{R} + \mathrm{H})} + \underset{\text{Olefin}}{(\mathrm{R} - \mathrm{H})} + 2\mathrm{MX}_n\end{array} \tag{20}$$

If the R—M bond is of intermediate stability, both unimolecular and bimolecular processes may occur, and it is also possible that both bimolecular processes might occur in the same system, if the two transition states are energetically similar. Since there is no *a priori* reason to assume that a bi-organo intermediate, say R_2M, would, on decomposition, produce a coupled product, and because in coupling reactions with silver salts it is well established that the intermediates are monoalkyl- or monoarylsilver molecules (7, 88), such an hypothesis is eliminated from consideration.

The four classes of results listed above can be accounted for on the basis of the proposed mechanistic possibilities in the following way. Taking first the two extreme cases, class I reactions involve the unimolecular decomposition of RMX_n (equation 19), with the radical R• which is produced decomposing primarily by abstraction of hydrogen from the solvent to form RH, although a small amount of disproportionation can, and as table 7 shows, does occur when R• is $C_2H_5\cdot$. Reactions in class IV must proceed entirely by the bimolecular mechanism (20a). Reactions in class II can be further subdivided into those which produce RH and olefin in essentially equal quantities (class IIb), and those which, while producing considerable amounts of both, definitely produce a preponderance of RH (class IIa). It may be assumed that in the latter case the stability of the R—M bond in the intermediate is such that while a certain amount of unimolecular dissociation occurs, giving rise only to RH, the predominating mechanism is the bimolecular decomposition 20b, which produces equimolar quantities of paraffin and olefin. In reactions of class IIb giving disproportionation products in equimolar quantities, the R—M bond is sufficiently stable so that no unimolecular decomposition occurs and the reaction proceeds entirely by the bimolecular mechanism 20b. Reactions of class III proceed by both bimolecular mechanisms and thus produce both RR and an equimolar mixture of the disproportionation products.

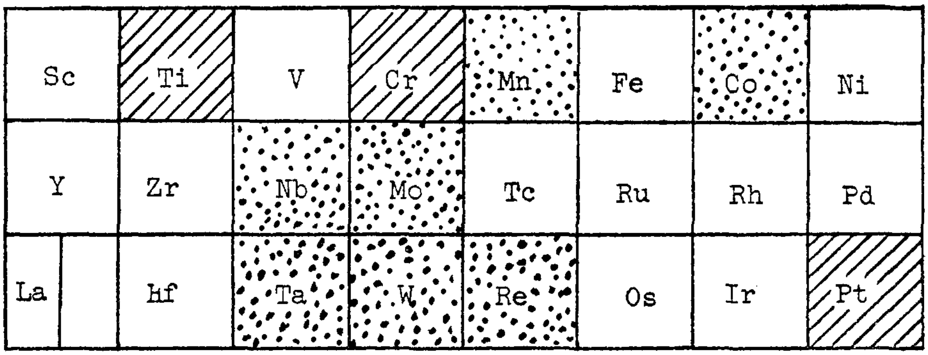
If these proposals are valid, it is then possible to draw certain qualitative conclusions about the relative strengths of R—M bonds in organometallic species of low stability. The stability of the R—M bond is a function both of the radical, R, and the metal, M, concerned. It seems, first, that quite generally, alkyl groups form less stable bonds to any given metal than does the phenyl group, for the data in tables 7 and 8 show that alkyl–metal compounds have a great tendency to decompose wholly or in part by the unimolecular mechanism (equation 19), whereas, regardless of the metal concerned, phenyl–metal intermediates decompose only bimolecularly. It will be noticed that only the alkyls of copper, silver, gold, and thallium decompose entirely by bimolecular processes. It is reasonable to believe that this results from an intrinsically greater tendency for these metals to form bonds to carbon, since thallium alkyls and aryls have been isolated and copper, silver, and gold form derivatives sufficiently stable to be isolated or at least studied in solution (148).

Although the interpretation of coupling reactions which has been presented is believed to be fundamentally correct and to constitute *prima facie* evidence that alkyl–metal bonds are generally less stable than aryl–metal bonds, particularly where transition metals and metals of Group IB are concerned, it must be emphasized that any more detailed interpretation is obviated by various complicating factors. In detailed studies of the coupling reactions of silver halides, it has been shown that the electronegativity of the group R is important (88) (but not in such a way as to effect the conclusions drawn here) and that the halogen in the Grignard compound affects the rate of formation of the organometallic intermediate (7). Interpretation of catalytic coupling reactions of alkyl- and aryllithium compounds is complicated by the occurrence of metal–halogen interchange between RLi and the alkyl or aryl halide required (94). Finally, the reaction medium, particularly the reactivity of the alkylation agent, may also affect the stabilities of the organometallic intermediates in a manner not clearly understood, as witnessed, for example, by the greater stability of ethyliron iodide when produced from ethylzinc iodide than when produced from reaction of the ferrous iodide with an ethyl Grignard.

Among the organo derivatives of the Group IB elements, copper, silver, and gold, the greater stability of the aryls is quite apparent (148). As will be seen, there are theoretical grounds for expecting this greater stability of aryls.

III. THEORY

Figure 3 shows the region of the periodic system under consideration in this review. The elements lying therein are divided into three classes: (*1*) those of



Sc	▨ Ti	V	▨ Cr	░ Mn	Fe	░ Co	Ni
Y	Zr	░ Nb	░ Mo	Tc	Ru	Rh	Pd
La	Hf	░ Ta	░ W	░ Re	Os	Ir	▨ Pt

FIG. 3. Transition elements forming alkyls and aryls. ▨, one or more well-established compounds; ░, some positive results requiring further confirmation; ☐, positive results very inconclusive or non-existent.

which at least one well-established alkyl or aryl has been isolated; (*2*) those for which positive evidence of the existence of isolable alkyl or aryl derivatives is at hand, but which require further study or confirmation; (*3*) finally, the remaining elements for which the existence of isolable, well-defined (at least in composition) alkyl or aryl derivatives is extremely meager or non-existent.

It will be apparent from this overall picture of alkyls and aryls of transition metals that the often-heard generalization that they are very much less stable and accessible than those of non-transition elements is quite true. The underlying reasons for this are of interest. von Grosse (46) in 1926 suggested that the fact that the valence electrons of transition metals are derived from shells of different principal quantum number might be in some way of importance. Undoubtedly there is some common feature or features of the electronic structures of transition metals which is particularly responsible. Jaffé (80) has shown that the instability may be attributed to the intrinsically low ability of transition elements to form strong σ-bonds with carbon in its usual states of hybridization. His calculations were based on the so-called "magic formula" of Mulliken, in which the energy of a chemical bond is expressed as a relatively simple function of the overlap integral and the ionization potentials of the atoms concerned. Jaffé also considered ionic resonance energy calculated from electronegativity differences. Although certain essential quantities, even in such a simplified treatment, are very difficult to calculate precisely, sufficiently accurate estimations can be made to provide meaningful results. Thus the strength of the bonds is analyzed into two factors: (*1*) the covalent contribution, involving ionization potentials and the overlap integral, and (*2*) the ionic resonance energy. It was found that the covalent contribution for the bonds from carbon in the sp^3 hybrid state to metals of the first transition series was only about 50–60 per cent of that for the dozen or so non-transition elements flanking them on either side. The ionic resonance energies were not very high either. While with potassium and calcium the overlap integrals are somewhat less favorable than with the transition metals, the electronegativity differences for potassium–carbon and calcium–carbon bonds are about four times higher than the general average for the transition metal–carbon bonds. At the other end of the first transition series, through the elements nickel, copper, and zinc, although the electronegativity difference remains extremely small, there is a very appreciable increase in the covalent contribution.

Jaffé (79) also found from calculation of the relevant overlap integrals that bond energies generally decrease with increasing atomic weight within any group in the periodic system. That this is indeed true is well illustrated by the Group IB metals, which resemble the transition metals very closely in their organometallic chemistry. The stability of alkyl and aryl derivatives of copper, silver, and gold decreases very markedly in that order.

An examination of the experimental data shows that among the transition metals and also those of Group IB where the *d*-electrons are still available for π-bonding, aryl derivatives are considerably more stable than the alkyls. This is clearly evident in the data of Herman and Nelson (71) on titanium and in the well-known behavior of the Group IB organometallics (148), and is borne out by the results of coupling reactions (see Section II, H). The singular stability of the methylplatinum compounds is quite possibly a result of the polymeric structures of these substances, which may at the same time determine steric requirements for the organic group, which are met only by methyl. This superior stability of aryl *vs.* alkyl derivatives is to be expected on theoretical grounds. According to Jaffé (79), the mean metal–carbon bond dissociation energy is affected by the nature of the organic radical through (*1*) the state of hybridization of the carbon atom, (*2*) the π-electron resonance energy, and (*3*) the rearrangement energy of the radical. On increasing the amount of *s* character in the carbon hybrid orbitals, the overlap integrals, the ionic resonance energy, and the ionization potential of the carbon atom are all affected so as to increase the strength of the metal–carbon bond. In the alkyls the hybridization is sp^3, while in aryls it is sp^2. Since all the transition metals have low-lying *d*-orbitals, the formation of delocalized π-bonds with the π-electrons of aryl radicals will contribute to the bond strength. The estimation of rearrangement energies is rather difficult, but it is certain that this quantity is smaller for the cyclic aromatic systems than for aliphatic radicals. Hence, all major factors considered combine to make aryl–metal compounds more stable than their alkyl analogs. For the same reasons, bonds to acetylenyl radicals will also have greater stability, and this is borne out by the recent success of Nast (119, 120) in isolating acetylenyl derivatives of some transition and Group IB metals.

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IV. REFERENCES

(1) AFANASYEV, B. N.: Chemistry & Industry **59**, 631 (1940).
(2) AFANASYEV, B. N.: Z. anorg. u. allgem. Chem. **245**, 381 (1941).

(3) Afanasyev, B. N., and Tsyganova, P. A.: J. Gen. Chem. (U.S.S.R.) **18**, 306 (1944); Chem. Abstracts **42**, 6743 (1948).

(4) Afanasyev, B. N., and Tsyganova, P. A.: J. Gen. Chem. (U.S.S.R.) **21**, 485 (1951); Chem. Abstracts **45**, 6109 (1951).

(5) Bennett, G. M., and Turner, E. E.: J. Chem. Soc. **1914**, 1057.

(6) Bennett, G. M., and Turner, E. E.: J. Proc. Roy. Soc. N. S. Wales **53**, 100 (1919).

(7) Bickley, E. A., and Gardner, J. H.: J. Org. Chem. **5**, 126 (1940).

(8) Birmingham, J. M., and Wilkinson, G.: J. Am. Chem. Soc. **76**, 6210 (1954).

(9) Briggs, D. A. E., and Polya, J. B.: J. Chem. Soc. **1951**, 1615.

(10) Browne, O. H., and Reid, E. E.: J. Am. Chem. Soc. **49**, 830 (1927).

(11) Brydowna, W.: Bull. soc. chim. France [4] **39**, 1771 (1926).

(12) Burovaya, E. E.: Trudy Inst. Krist., Akad. Nauk S.S.S.R. No. **5**, 197 (1949): Chem. Abstracts **47**, 3749 (1953).

(13) Cahours, A.: Ann. **122**, 48 (1862).

(14) Challenger, F., and Pritchard, F.: J. Chem. Soc. **125**, 864 (1924).

(15) Champetier, G.: Bull. soc. chim. France [4] **47**, 1131 (1930).

(16) Chatt, J.: J. Chem. Soc. **1949**, 3348.

(17) Chatt, J., and Duncanson, L. A.: J. Chem. Soc. **1953**, 2939.

(18) Cotton, F. A.: Unpublished work.

(19) Cotton, F. A., Birmingham, J. M., and Wilkinson, G.: J. Nuc. Inorg. Chem., in press.

(20) Cotton, F. A., and Wilkinson, G.: Z. Naturforsch. **9b**, 453 (1954).

(21) Cox, E. G., and Webster, K. C.: Z. Krist. **90**, 561 (1935).

(22) Delavigne, L.: Gazz. chim. ital. **68**, 271 (1938).

(23) Druce, J. G. F.: J. Chem. Soc. **1934**, 1129.

(24) Dupont, G., and Piganiol, P.: Bull. soc. chim. France [5] **6**, 322 (1939).

(25) Fischer, E. O., and Hafner, W.: Z. Naturforsch. **9b**, 503 (1954).

(26) Fischer, E. O., Seus, D., and Jira, R.: Z. Naturforsch. **8b**, 692 (1953).

(27) Foss, M. E., and Gibson, C. S.: J. Chem. Soc. **1951**, 299.

(28) Frisch, K. C.: J. Am. Chem. Soc. **75**, 6050 (1953).

(29) Funk, H., and Baumann, W.: Z. anorg. u. allgem. Chem. **231**, 264 (1937).

(30) Funk, H., and Niederländer, K.: Ber. **61**, 249 (1928).

(31) Funk, H., and Niederländer, K.: Ber. **61**, 1385 (1928).

(32) Gazopoulos, I.: Prakt. Akad. Athenon. **7**, 180 (1932): Chem. Abstracts **28**, 4726 (1934).

(33) Gilman, H.: Private communication.

(34) Gilman, H., and Bailie, J. C.: J. Org. Chem. **2**, 87 (1937).

(35) Gilman, H., and Jones, R. G.: J. Org. Chem. **10**, 505 (1945).

(36) Gilman, H., Jones, R. G., Moore, F. W., and Kolbezen, M. J.: J. Am. Chem. Soc. **63**, 2525 (1941).

(37) Gilman, H., Jones, R. G., and Woods, L. A.: J. Am. Chem. Soc. **76**, 3615 (1954).

(38) Gilman, H., and Kirby, R. H.: J. Am. Chem. Soc. **63**, 2046 (1941).

(39) Gilman, H., and Lichtenwalter, M.: J. Am. Chem. Soc. **60**, 3085 (1938).

(40) Gilman, H., and Lichtenwalter, M.: J. Am. Chem. Soc. **61**, 957 (1939).

(41) Gilman, H., Lichtenwalter, M., and Benkeser, R. A.: J. Am. Chem. Soc. **75**, 2063 (1953).

(42) Gilman, H., and Schulze, F.: J. Am. Chem. Soc. **47**, 2002 (1925).

(43) Gilman, H., and Straley, J. M.: Rec. trav. chim. **55**, 825 (1936).

(44) Gel'man, A. D., and Gorushkina, E. A.: Doklady Akad. Nauk S.S.S.R. **57**, 43 (1947).

(45) Gel'man, A. D., and Gorushkina, E. A.: Doklady Akad. Nauk S.S.S.R. **57**, 259 (1947).

(46) Grosse, A. von: Z. anorg. u. allgem. Chem. **152**, 145 (1926).

(47) Hein, F.: Ber. **52**, 195 (1919).

(48) Hein, F.: Ber. **54**, 1905 (1921).

(49) HEIN, F.: Ber. **54**, 2708 (1921).
(50) HEIN, F.: Ber. **54**, 2727 (1921).
(51) HEIN, F.: J. prakt. Chem. **132**, 59 (1931).
(52) HEIN, F.: Z. anorg. u. allgem. Chem. **51**, 503 (1938).
(53) HEIN, F.: J. prakt. Chem. **153**, 160 (1939).
(54) HEIN, F., AND EISSNER, W.: Ber. **59**, 362 (1926).
(55) HEIN, F., AND MARKERT, E.: Ber. **61**, 2255 (1928).
(56) HEIN, F., AND NEBE, E.: Naturwissenschaften **28**, 93 (1940).
(57) HEIN, F., AND PAULING, H.: Z. anorg. u. allgem. Chem. **273**, 209 (1953).
(58) HEIN, F., AND PINTUS, F.: Ber. **60**, 2388 (1927).
(59) HEIN, F., AND PLOBOTH, H.: Z. anorg. u. allgem. Chem. **248**, 84 (1941).
(60) HEIN, F., RESCHKE, J., AND PINTUS, F.: Ber. **60**, 679 (1927).
(61) HEIN, F., RESCHKE, J., AND PINTUS, F.: Ber. **60**, 749 (1927).
(62) HEIN, F., AND RETTER, W.: Z. physik. Chem. **156A**, 81 (1931).
(63) HEIN, F., AND RETTER, W.: Ber. **71**, 1966 (1938).
(64) HEIN, F., AND SCHWARTZKOPFF, O.: Ber. **57**, 8 (1924).
(65) HEIN, F., SCHWARTZKOPFF, O., HOYER, K., EISSNER, W., KLAR, K., AND CLAUSS, W.: Ber. **61**, 730 (1928).
(66) HEIN, F., SCHWARTZKOPFF, O., HOYER, K., KLAR, K., EISSNER, W., CLAUSS, W., AND JUST, W.: Ber. **62**, 1151 (1929).
(67) HEIN, F., AND SPAETE, R.: Ber. **57**, 899 (1924).
(68) HEIN, F., AND SPAETE, R.: Ber. **59**, 751 (1926).
(69) HELLMAN, A.: Unpublished work cited by F. Hein in *Chemische Koordinations Lehre*, p. 432ff. S. Hirzel Verlag, Leipzig (1950).
(70) HERMAN, D. F., AND NELSON, W. K.: J. Am. Chem. Soc. **75**, 3877 (1953).
(71) HERMAN, D. F., AND NELSON, W. K.: J. Am. Chem. Soc. **75**, 3882 (1953).
(72) HEY, D. H.: J. Chem. Soc. **1934**, 1966.
(73) HINSBERG, O.: Ann. **239**, 253 (1887).
(74) IBRAHIM, I.: Thesis, Berlin, 1932.
(75) ILLUMINATI, G., AND RUNDLE, R. E.: J. Am. Chem. Soc. **71**, 3575 (1949).
(76) INGLES, D. L.: Ph.D. Thesis, University of Tasmania.
(77) INGLES, D. L., AND POLYA, J. B.: J. Chem. Soc. **1949**, 2280.
(78) IVIN, K. J., WIJNEN, M. J. H., AND STEACIE, E. W. R.: J. Chem. Phys. **56**, 967 (1952).
(79) JAFFÉ, H. H.: J. Chem. Phys., in press.
(80) JAFFÉ, H. H., AND DOAK, G. O.: J. Chem. Phys. **21**, 196 (1953).
(81) JAFFÉ, H. H.: Personal communication.
(82) JOB, A., AND CHAMPETIER, G.: Compt. rend. **189**, 1089 (1929).
(83) JOB, A., AND CHAMPETIER, G.: Bull. soc. chim. France [4] **47**, 279 (1930).
(84) JOB, A., AND REICH, R.: Compt. rend. **174**, 1358 (1922).
(85) JOB, A., AND REICH, R.: Compt. rend. **177**, 1439 (1923).
(86) JOB, A., AND REICH, R.: Compt. rend. **179**, 330 (1924).
(87) JONES, R. G.: Iowa State Coll. J. Sci. **17**, 88 (1942).
(88) JOSEPH, L., AND GARDNER, J. H.: J. Org. Chem. **5**, 61 (1940).
(89) KEALY, T. J., AND PAUSON, P. L.: Nature **168**, 1039 (1951).
(90) KHARASCH, M. S., AND FIELDS, E. K.: J. Am. Chem. Soc. **63**, 2316 (1941).
(91) KHARASCH, M. S., KLEIGER, S. C., MARTIN, J. A., AND MAYO, F. R.: J. Am. Chem. Soc. **63**, 2305 (1941).
(92) KHARASCH, M. S., AND KLEIMAN, M.: J. Am. Chem. Soc. **65**, 491 (1943) and following papers.
(93) KHARASCH, M. S., LEWIS, D. W., AND REYNOLDS, W. B.: J. Am. Chem. Soc. **65**, 499 (1943).
(94) Reference 93, p. 500.
(95) KHARASCH, M. S., AND SAYLES, D. C.: J. Am. Chem. Soc. **64**, 2972 (1942).
(96) KIRBY, R. H.: Iowa State Coll. J. Sci. **12**, 137 (1937).

(97) Kirsanov, A. V., and Sazonova, T. V.: J. Gen. Chem. (U.S.S.R.) **5**, 956 (1935); Chem. Abstracts **30**, 1025 (1936).

(98) Klemm, W., and Neuber, A.: Z. anorg. u. allgem. Chem. **227**, 261 (1936).

(99) Köhler, H.: Ber. **13**, 1626 (1880).

(100) Kondyrew, N., and Fomin, D.: J. soc. phys.-chim. russe **46**, 620 (1914).

(101) Kondyrew, N., and Fomin, D.: J. soc. phys.-chim. russe **47**, 190 (1915).

(102) Krause, E., and Grosse, A. von: *Die Chemie der Metall-organischen Verbindungen.* Verlag Gebrüder Borntraeger, Berlin (1937).

(103) Reference 102, p. 767.

(104) Krause, E., and Wendt, B.: Ber. **56**, 2064 (1923).

(105) Krause, E., and Wendt, B.: Reference 102, p. 784.

(106) Levy, L.: Ann. chim. et phys. [6] **25**, 433 (1892).

(107) Lichtenwalter, M.: Iowa State Coll. J. Sci. **14**, 57 (1939).

(108) Lile, W. J., and Menzies, R. C.: J. Chem. Soc. **1949**, 1168.

(109) Manulkin, Z. M.: J. Gen. Chem. (U.S.S.R.) **18**, 299 (1948); Chem. Abstracts **42**, 6742 (1948).

(110) Mendeleyev, D. I.: Quoted in reference 48.

(111) Menzies, R. C.: J. Chem. Soc. **1928**, 565.

(112) Menzies, R. C., and Overton, H.: J. Chem. Soc. **1933**, 1290.

(113) Menzies, R. C., and Wiltshire, E. R.: J. Chem. Soc. **1933**, 21.

(114) Mertes, A. T., and Fleck, H.: J. Ind. Eng. Chem. **7**, 1037 (1915).

(115) Meyer, J., and Taube, W.: Z. anorg. u. allgem. Chem. **222**, 167 (1935).

(116) Moeller, T.: *Inorganic Chemistry*, p. 702. John Wiley and Sons, Inc., New York (1952).

(117) Reference 116, p. 709.

(118) Moffitt, W. E.: J. Am. Chem. Soc. **76**, 3386 (1954).

(119) Nast, R.: Z. Naturforsch. **8b**, 381 (1953).

(120) Nast, R.: Private communication.

(121) Oddo, B.: Gazz. chim. ital. **44**, 268 (1914).

(122) Pauling, L.: *The Nature of the Chemical Bond*, 2nd edition, p. 254. Cornell University Press, Ithaca, New York (1945).

(123) Pauson, P. L., and Wilkinson, G.: J. Am. Chem. Soc. **76**, 2024 (1954).

(124) Peterno, E., and Peratoner, A.: Ber. **22**, 467 (1889).

(125) Peters, W.: Ber. **41**, 3173 (1908).

(126) Piper, T. S., Cotton, F. A., and Wilkinson, G.: J. Nuc. Inorg. Chem., in press.

(127) Pitzer, K. S., and Gutowsky, H. S.: J. Am. Chem. Soc. **68**, 2204 (1946).

(128) Plets, V. M.: Compt. rend. acad. sci. (U.S.S.R.) **20**, 27 (1938).

(129) Plets, V. M.: J. Gen. Chem. (U.S.S.R.) **8**, 1298 (1938); Chem Abstracts **33**, 4193 (1939).

(130) Polya, J. G., and Ingles, D. L.: Nature **164**, 447 (1949).

(131) Pope, W. J., and Peachey, S. J.: Proc. Chem. Soc. **23**, 86 (1907).

(132) Pope, W. J., and Peachey, S. J.: J. Chem. Soc., Trans. **95**, 571 (1909).

(133) Powell, H. M., and Bartindale, G. W. R.: J. Chem. Soc. **1945**, 799.

(134) Razuvaev, G. A., and Bogdanov, I. F.: J. Gen. Chem. (U.S.S.R.) **3**, 367 (1933); Chem. Abstracts **28**, 2340 (1934).

(135) Razuvaev, G. A., and Fedotov, M. S.: J. Gen. Chem. (U.S.S.R.) **22**, 484 (1952); Chem. Abstracts **47**, 2723 (1953).

(136) Reich, R.: Compt. rend. **177**, 322 (1923).

(137) Rice, F. O., and Rice, K. K.: *The Aliphatic Free Radicals*, p. 58. The Johns Hopkins Press, Baltimore (1935).

(138) Ruch, E., and Fischer, E. O.: Z. Naturforsch. **7b**, 676 (1952).

(139) Rundle, R. E.: J. Am. Chem. Soc. **69**, 1328 (1947).

(140) Rundle, R. E., and Holman, E. J.: J. Am. Chem. Soc. **71**, 3264 (1949).

(141) Rundle, R. E., and Sturdivant, J. H.: J. Am. Chem. Soc. **69**, 1561 (1947).

(142) SACCARDI, P., AND DELAVIGNE, L.: Gazz. chim. ital. **67**, 611 (1937).
(143) SCHLENK, W., AND WEICHSELFELDER, T.: Ber. **56**, 2230 (1923).
(144) SCHUMANN, A.: Ber. **21**, 1079 (1888).
(145) SHELINE, R. K., AND PITZER, K. S.: J. Am. Chem. Soc. **72**, 1107 (1950).
(146) SHIDLOVSKAYA, A. N., AND SYRKIN, J. K.: Compt. rend. acad. Sci. U.R.S.S. **55**, 231 (1947).
(147) SIDGWICK, V. N.: *The Chemical Elements and their Compounds*, p. 1420. Oxford University Press, London (1950).
(148) Reference 147, p. 113.
(149) SUMMERS, R., AND ULOTH, R. H.: J. Am. Chem. Soc. **76**, 2278 (1954).
(150) SUPNIEWSKI, J.: Roczniki Chem. **7**, 172 (1927); Chem. Abstracts **22**, 766 (1928).
(151) TURNER, E. E.: Proc. Chem. Soc. (London) **30**, 4 (1914).
(152) URRY, W. H., AND KHARASCH, M. S.: J. Am. Chem. Soc. **66**, 1438 (1944).
(153) VENABLE, F. P., AND DEITZ, R O.: J. Elisha Mitchell Sci. Soc. **38**, Nos. 1 & 2, 74 (1922).
(154) VERNON, C. C.: J. Am. Chem. Soc. **53**, 3831 (1931).
(155) WANKLYN, J. A., AND CARIUS, L.: Ann. **120**, 69 (1861).
(156) WATERS, W. A.: *The Chemistry of the Free Radicals*, p. 130. Oxford University Press, London (1946).
(157) Reference 156, p. 137.
(158) WATERS, W. A.: J. Chem. Soc. **1937**, 113.
(159) WEICHSELFELDER, T., AND KOSSODO, M.: Ber. **62B**, 769 (1929).
(160) WEICHSELFELDER, T., AND THIEDE, B.: Ann. **447**, 64 (1926).
(161) WILDS, A. L., AND MCCORMACK, W. B.: J. Org. Chem. **14**, 45 (1945).
(162) WILKINSON, G., AND BIRMINGHAM, J. M.: J. Am. Chem. Soc. **76**, 4281 (1954).
(163) WILKINSON, G., AND COTTON, F. A.: Chemistry & Industry **1954**, 307.
(164) WILLIAMS, G. M.: U. S. patent 2,441,738; Chem. Abstracts **42**, 5688 (1948).
(165) WILLIAMS, G. M.: U. S. patent 2,528,937; Chem. Abstracts **45**, 3170 (1951).
(166) ZEISS, H. H.: Private communication.
(167) ZEISS, H. H., AND TSUTSUI, M.: Abstracts of Papers Presented at the 126th Meeting of the American Chemical Society, New York, September, 1954, p. 29-O.
(168) ZELTNER, J.: J. prakt. Chem. [2] **77**, 394 (1908).