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COVALENT ORGANOMETALLIC COMPOUNDS OF THE TRANSITION METALS

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INTRODUCTION

The ability to form organometallic compounds has for long been regarded as a characteristic property of metals. D. I. Mendeleev, describing the then undiscovered elements eka-boron and eka-silicon, stated that they should form organometallic compounds. The many attempts to prepare organic derivatives of metals of the transition periods were until recently always unsuccessful. The only exceptions were the polyphenyl derivatives of chromium discovered in the 1920's by Hein. Later, however, it was established that these have the peculiar sandwich structure characteristic of a variety of transition elements.

The lack of experimental success was attributed to the impossibility of existence of this type of compound. In the most complete monograph published at that time, Krause and von Grosse [1] provided theoretical justification for the assumption that the covalent bond between a transition metal and an organic radical is unstable. As an example, they examined the possibility of the existence of organometallic compounds of titanium. In their opinion, the bivalent titanium derivatives, formed by means of the valency *s* electrons, should be more stable than the quadrivalent titanium derivatives, whose formation should involve the valency *s* and *d* electrons of the transition metal.

Nesmeyanov [2] divided all the elements of the Periodic System into two classes, depending on the possibility of formation of stable alkyls and aryls. For transition metals, which have incomplete lower *d* levels in addition to valency *s* and *p* electrons, sandwich or diarene derivatives are more characteristic. Several excellent reviews and monographs dealing with the latter have recently been published.

In the last 10–12 years, increasing experimental evidence has appeared for the formation of σ bonds between transition metals and carbon. A number of truly covalent compounds of transition metals have been prepared, and these have attracted greater attention from research workers.

Alkyl and aryl derivatives of transition elements have been the subject of a review by Cotton [3], covering material up to 1955, and a section of a monograph by Zeiss [4], including some material up to 1960. This field of chemistry is making rapid progress, and it seemed to us useful to review briefly recent work on the organometallic compounds of the transition metals. The review deals with compounds containing a metal–carbon σ bond. The only π-cyclopentadienyl derivatives dealt with are those which, in addition to the π-cyclopentadienyl group, contain an organic radical covalently bound to the element.

In this review the alkyls and aryls of the transition metals are examined according to the groups of the Periodic System, starting with Group IV (titanium, zirconium, and hafnium). The compounds of vanadium, niobium, and

tantalum in Group V, chromium, molybdenum, and tungsten in Group VI, and manganese and rhenium in Group VII are characterised. In the case of Group VIII, only the compounds of iron, cobalt, and nickel are included. The review does not deal with the peculiar organometallic derivatives of the first "b" subgroup — copper, silver, and gold — or with the platinum subgroup.

GROUP IV

Titanium

Of the organometallic compounds of the transition metals of Group IV, the titanium derivatives have been most extensively studied. This has been due largely to the industrial use of catalysts of the Ziegler–Natta type for the polymerisation of alk-1-enes. The complex polymerisation catalysts of this type contain alkyl compounds of zinc, aluminium, and sodium together with halides of transition metals, chiefly titanium. Reaction between the components leads to halogen–alkyl exchange on the titanium atom and is accompanied by the reduction of quadrivalent titanium to lower-valency compounds.

The large number of papers on the study of various catalytic systems of this type served as the starting point for the development of the chemistry of organotitanium compounds, whose existence, up to 1952, had been regarded as impossible. Since the catalytic systems contained alkyl components, chiefly of aluminium, preparative work in the chemistry of organometallic compounds of titanium had a distinct bias towards aliphatic derivatives.

At the present time, the known alkyl compounds of titanium include products of the type R_nTiX_{4-n} (where n = 1, 2, 3, or 4, R = methyl, ethyl, or butyl, and X = Cl, Br, or I) obtained by alkylation of a quadrivalent titanium halide with the corresponding derivatives of lithium, zinc, aluminium, lead, and other metals.

The mono- and di-alkyl compounds have been most extensively studied. The exchange reaction between a titanium halide and an organoaluminium derivative of general formula R_nAlX_{3-n} is carried out in an inert atmosphere in solution in organic solvents (hexane, benzene, methylene chloride, etc.) at temperatures from -80° to 0°. To obtain the monoalkyl product, the reaction is carried out in an excess of TiX_4. Dialkyltitanium dihalides are obtained at a ratio of $TiX_4 : R_nAlX_{3-n}$ = 1 : 2. When the reaction is complete, the resulting organoaluminium compound $R_{n-1}AlX_{3-(n+1)}$ is converted into the insoluble or non-volatile state by the action of alkali or alkaline earth metal halides, and also higher ethers, phosphines, etc.[5,6]. The titanium mono- and di-alkyls are isolated by vacuum distillation of the reaction mixture. Thus methyltitanium trichloride is obtained by the exchange reaction of trimethylaluminium or of dimethylaluminium chloride with titanium tetrachloride in hexane solution[7]. The aluminium compound is added slowly to an excess of TiX_4 at room temperature

$$(CH_3)_2AlCl + TiCl_4 \rightleftarrows CH_3AlCl_2 + CH_3TiCl_3.$$

Sodium chloride is added to the reaction mixture to bind the organoaluminium compound in the complex $Na[AlCl_3(CH_3)]$, and the mixture is vacuum-distilled to give methyltitanium chloride in the form of dark violet crystals with m.p. 28.5° and b.p. 37° at 1 mmHg. Methyltitanium trichloride melts to form a yellow liquid, and is soluble in many organic solvents — hexane, benzene, and halogeno-derivatives — to give yellow solutions. Methyltitanium trichloride is monomolecular in benzene solution[5]. Dimethylzinc can be used instead of dimethylaluminium chloride and in this case the yield of product is 75% of the theoretical[7].

The monoethyl derivative was prepared in analogous fashion by the alkylation of an excess of $TiCl_4$ with tetraethyllead at -80°; the product has a lower thermal stability than the methyl derivative[8]. At 20° the ethyl derivative is a reddish liquid which decomposes in 24 h; iso-$C_4H_9TiCl_3$ is obtained by a method analogous to that for the methyl derivative but at a lower temperature[5].

Dimethyltitanium dichloride can be obtained from the monomethyl derivative by further methylation. Thus the action of trimethylaluminium on a hexane solution of CH_3TiCl_3 cooled to -80° gave almost black crystalline $(CH_3)_2TiCl_2$:

$$CH_3TiCl_3 + Al(CH_3)_3 \rightarrow (CH_3)_2TiCl_2 + (CH_3)_2AlCl.$$

Solutions of the latter in hexane are also pale yellow. Dimethyltitanium dichloride can be obtained by the disproportionation of methyltitanium trichloride with dicyclopentadienyldimethyltitanium at temperatures from -80° to 0° and a molar ratio of 1 : 2, and also by the reaction of dicyclopentadienyldimethyltitanium with titanium tetrachloride in hydrocarbon solutions[9]:

$$2(C_5H_5)_2Ti(CH_3)_2 + TiCl_4 \rightarrow 2(C_5H_5)_2Ti(CH_3)Cl + (CH_3)_2TiCl_2.$$

At a component ratio of 1 : 1 the reaction is

$$(C_5H_5)_2Ti(CH_3)_2 + TiCl_4 \rightarrow (C_5H_5)_2TiCl_2 + (CH_3)_2TiCl_2.$$

The dialkyl derivatives are less stable than the monoalkyl derivatives[10-13].

Tri- and tetra-methyltitanium can be obtained by the successive replacement of all the halogen atoms in a titanium halide by alkyl groups. Tetramethyltitanium is obtained in 50–70% yield from the ether addition compound in ethereal solution by the action of methyllithium or methylmagnesium chloride at temperatures from -50° to -80°.[14,15] It is obtained as glistening yellow crystals which distil with ether *in vacuo* at a temperature not exceeding 0°, and are stable at -78°.

$$TiCl_4 + 4CH_3Li \rightarrow (CH_3)_4Ti + 4LiCl.$$

Tetramethyltitanium was isolated in crystalline form from hexane solutions. After removal of ether, the hexane solution at temperatures between -30° and -50° gave glistening yellow needles of tetramethyltitanium, which forms methane on hydrolysis. Analysis of the product[16] gave the ratio $Ti : CH_4$ = 1 : 4.

Trimethyltitanium iodide $(CH_3)_3TiI$ is obtained by the exchange reaction of tetramethyltitanium in 2 : 1 ether — hexane solution with gaseous CF_3I at reduced temperature (-78°).[17] Methyl iodide is a side-product of the exchange reaction. When the temperature is raised to -50°, the solution becomes brown and does not give a positive Gilman reaction. Trimethyltitanium iodide is obtained as yellow needles by removal of the solvent. The compound is stable in the absence of oxygen at low temperatures. On hydrolysis of the product, the ratio of liberated methane to hydrogen iodide is 2.95 : 1.

In ether, titanium trichloride does not react appreciably with methyllithium, but the pale blue suspension of $TiCl_3$ in tetrahydrofuran or its pale brown suspension in dimethoxyethane react rapidly at temperatures between -50°

and -80° with an ethereal solution of methyllithium, to form lithium chloride and a dark green solution, evidently containing trimethyltitanium [14]. The possibility of formation of the bivalent and tervalent titanium compounds RTiX and $RTiX_2$ has also been reported briefly [13,18].

The interesting observation that organomagnesium compounds undergo isomerisation in the presence of small quantities of $TiCl_4$ is attributed to the intermediate formation of organotitanium compounds according to the scheme

$$(CH_3)_2CHMgBr + TiCl_4 \rightarrow (CH_3)_2CHTiCl_3 + MgClBr,$$
$$(CH_3)_2CHTiCl_3 \rightarrow CH_3CH{=}CH_2 + TiCl_3H,$$
$$CH_3CH{=}CH_2 + TiCl_3H \rightleftarrows CH_3CH_2CH_2TiCl_3,$$
$$CH_3CH_2CH_2TiCl_3 + RMgBr \rightleftarrows CH_3CH_2CH_2MgBr + RTiCl_3.$$

This is confirmed by the displacement of propene by the addition of other alkenes [19]

$$RCH{=}CH_2 + CH_3CH_2CH_2MgBr \xrightarrow{TiCl_4} RCH_2CH_2MgBr + CH_3CH{=}CH_2.$$

Repeated attempts to prepare aryl derivatives of titanium were unsuccessful for almost a century. The reactions of titanium tetrachloride with diphenylmercury, phenylsodium, and an aryl Grignard reagent, with heating of the components to 200°, always led to the formation of biphenyl and titanium trichloride [20]. The reaction of titanium tetrachloride with diphenylmercury took place according to the equation

$$TiCl_4 + (C_6H_5)_2Hg \rightarrow C_6H_5HgCl + TiCl_3 + {}^1/_2(C_6H_5)_2.$$

The formation of titanium trichloride and biphenyl might indicate decomposition of an unstable organotitanium compound formed initially.

The first aryl organotitanium compound isolated in pure form was phenyltitanium triisopropoxide, obtained by the reaction of titanium tetraisopropoxide with phenyllithium [21]

$$Ti(OC_3^iH_7)_4 + C_6H_5Li \rightarrow C_6H_5Ti(OC_3^iH_7)_3 + LiOC_3^iH_7.$$

This was the first compound to be prepared containing a carbon–titanium σ bond. The complex $C_6H_5Ti(OC_3^iH_7)_3 \cdot LiOC_3^iH_7 \cdot LiBr \cdot (C_2H_5)_2O$ is first formed, and this is decomposed by a slight excess of titanium tetrachloride:

$$C_6H_5Ti(OC_3^iH_7)_3 \cdot LiOC_3^iH_7 \cdot LiBr \cdot (C_2H_5)_2O + {}^1/_4TiCl_4 \rightarrow$$
$$\rightarrow C_6H_5Ti(OC_3^iH_7)_3 + LiCl + LiBr + (C_2H_5)_2O + {}^1/_4Ti(OC_3^iH_7)_4.$$

Unlike the alkyl derivatives, phenyltitanium triisopropoxide is an almost colourless compound with m.p.88–90°, stable in an inert atmosphere in the absence of moisture. It can be obtained in almost quantitative yield by the reaction of phenyllithium with $TiCl(OC_3^iH_7)_3$ in ether solution [22].

With change in the ratio of titanium tetraisopropoxide and phenyllithium from 1 : 1 to 1 : 2 and 1 : 4, the thermal stability of the resulting organotitanium compounds decreases considerably. It was concluded that, in compounds of general formula R_nTiX_{4-n}, the stability is determined chiefly by the value of n, but also depends on the electronegativity of R and X. It was found that stable compounds are formed only when $n \leqslant 2$ and X is sufficiently electronegative [23]. It was suggested that tetraphenyltitanium is extremely unstable, but yellow-orange crystals of this compound, fairly stable at low temperature, have recently been obtained by reaction of the ether addition compound of titanium tetrachloride with phenyllithium

$$TiCl_4 + 4C_6H_5Li \rightarrow (C_6H_5)_4Ti + 4LiCl.$$

The formation of phenyltitanium chlorides $(C_6H_5)_nTiX_{4-n}$ (where n = 1–2) as intermediate products was observed in the reaction of diphenylmercury with $TiCl_4$ in solutions of various organic solvents at ~ 90°. [24] The presence of the phenyl–titanium bond was proved by the reaction with mercuric chloride, leading to the formation of phenylmercury chloride, and also by oxidation to phenol and biphenyl. The possible disproportionation of the monophenyl derivative to the disubstituted product, and also its decomposition to biphenyl and titanium dichloride, were noted

$$2C_6H_5TiCl_3 \rightarrow (C_6H_5)_2TiCl_2 + TiCl_4,$$
$$(C_6H_5)_2TiCl_2 \rightarrow (C_6H_5)_2 + TiCl_2.$$

The replacement of all the chlorine atoms in $TiCl_4$ by phenyl groups, on reaction with phenyllithium in ether solution at -80°, gives glistening orange-yellow leaflets of tetraphenyltitanium. The formation of tetraphenyltitanium is proved by the reaction with mercuric chloride, leading to the quantitative separation of phenylmercury chloride. The reaction with cyclopentadiene leads to the replacement of two phenyl groups by cyclopentadienyl groups, with the formation of dicyclopentadienyldiphenyltitanium [25]

$$(C_6H_5)_4Ti + 2C_5H_6 \rightarrow (C_6H_5)_2Ti(C_5H_5)_2 + 2C_6H_6.$$

Tetraphenyltitanium, as predicted [23], is thermally unstable; with increase in temperature to -30° it decomposes with the formation of biphenyl and diphenyltitanium

$$(C_6H_5)_4Ti \rightarrow (C_6H_5)_2 + (C_6H_5)_2Ti.$$

The latter is a black pyrophoric substance, soluble in tetrahydrofuran and benzene. Its thermal stability is greater than that of its quadrivalent analogue.

A covalent titanium–radical bond is found in dicyclopentadienyl derivatives of the type π-$(C_5H_5)_2TiR_2$, where π-C_5H_5 is the cyclopentadienyl group or a monosubstituted cyclopentadienyl group joined to titanium in a π-$(C_5H_5)_2Ti$ sandwich, and R = CH_3, C_2H_5, or C_6H_4X. In these mixed organometallic compounds the electronic energy levels of the transition metal are filled by the π electrons of the sandwich group, leading to an increase in the stability of the compound as a whole and of the metal–carbon σ bonds in particular. The alkyl and aryl compounds were prepared by the action of the alkyls of Li, Mg, Zn, and Al on dicyclopentadienyltitanium dichloride. The dibromo-, diiodo-, dicyano-, dithiocyanato-, or dialkoxy-derivatives can be used instead of the dichloride.

$$\pi\text{-}(C_5H_5)_2TiCl_2 + RLi \rightarrow \pi\text{-}(C_5H_5)_2Ti(R)Cl + LiCl,$$
$$\pi\text{-}(C_5H_5)_2TiCl_2 + 2RLi \rightarrow \pi\text{-}(C_5H_5)_2TiR_2 + 2LiCl.$$

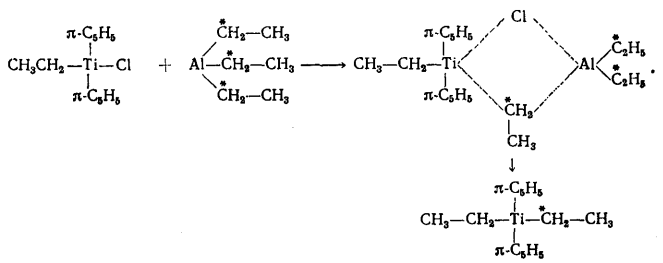
Products of complete and partial substitution $(C_5H_5)_2TiR_2$ and $(C_5H_5)_2Ti(R)X$ were obtained in this way [11,26–28]. Brief mention may be made of individual representatives of this type. The monomethyl derivative π-$(C_5H_5)_2Ti(CH_3)Cl$ forms red-orange crystals with m.p. 168–169°, soluble in water in the cold without decomposition. The first value given for the yield of this product was 1%; [26] the compound was later prepared in 90% yield [11,27]. The action of direct sunlight produces a rapid irreversible change in the compound. The monopropyl compound $(C_5H_5)_2Ti(C_3H_7)Cl$ begins to decompose at 160°; it is prepared from dicyclopentadienyltitanium dichloride and propyllithium.

Dicyclopentadienyldimethyltitanium $(C_5H_5)_2Ti(CH_3)_2$ forms orange needles with a characteristic odour and is prepared in analogous fashion in 95% yield [27]. It is stable to the action of water and oxygen, but darkens and decomposes rapidly on exposure to light.

The compound $(CH_3C_5H_4)_2Ti(CH_3)_2$ is obtained in 65% yield in the form of yellow crystals which are stable in air and in water but decompose on strong illumination or heating.

All these compounds can be used as catalysts for the polymerisation of alkenes, particularly in conjunction with organoaluminium compounds.

The reaction of ethyldicyclopentadienyltitanium chloride with ^{14}C-labelled triethylaluminium leads to further exchange of ethyl groups by the titanium and aluminium atoms



The resulting diethyl derivative decomposes at 40°, as indicated by the isolation of the labelled decomposition products — ethane and ethylene[20].

Diaryl derivatives of dicyclopentadienyltitanium π-$(C_5H_5)_2TiR_2$ were prepared with R = C_6H_5, m-$CH_3C_6H_4$, p-$CH_3C_6H_4$, and p-$(CH_3)_2NC_6H_4$. These compounds form yellow-orange crystals which melt with decomposition[29,30]. The most stable is π-$(C_5H_5)_2Ti(C_6H_5)_2$, which melts at 146–148° and is monomolecular in benzene solutions. All these compounds are readily soluble in organic solvents. Their thermal stability depends to a marked extent on the nature of the aryl group. Thus dicyclopentadienyldiphenyltitanium can be kept for several days at room temperature, whereas the p-dimethylaminophenyl derivative could not be isolated in pure form. With an excess of phenyllithium, the formation of dark-coloured complexes $Li[Ti(C_5H_5)_2(C_6H_5)_3]$ and $Li_2[Ti(C_5H_5)_2(C_6H_5)_4]$ is observed; hydrolysis of ethereal solutions of these compounds leads to regeneration of the original product.

$$(C_5H_5)_2Ti(C_6H_5)_2 + C_6H_5Li \rightarrow Li[Ti(C_5H_5)_2(C_6H_5)_3] \xrightarrow{H_2O} \xrightarrow{H_2O} (C_5H_5)_2Ti(C_6H_5)_2 + C_6H_6 + LiOH.$$

In addition to the dicyclopentadienyl compounds, monocyclopentadienyl derivatives of quadrivalent titanium, of the type π-$C_5H_5TiR_3$, with a titanium–radical bond, are known. These compounds are obtained by an exchange reaction, analogous to that described above, between monocyclopentadienyltitanium trichloride and alkali-metal alkyls or aryls. Thus the reaction of $C_5H_5TiCl_3$ with methyllithium gave the trimethyl compound $C_5H_5Ti(CH_3)_3$, which is stable at -70° and can be distilled at -20° and 0.5 mmHg.[31] At -80° the compound can be isolated from pentane solution in the form of lemon yellow crystals which are pyrophoric in air at room temperature[27].

The phenyl analogue $C_5H_5Ti(C_6H_5)_3$ is obtained in solution in analogous fashion by the use of phenyllithium. It is a yellow compound, stable in solution at -70°. With increase in temperature to room temperature it decomposes with formation of the bivalent titanium compound $C_5H_5TiC_6H_5$; the products of the decomposition carried out in ethereal solution contain also biphenyl and benzene[32]. The presence of phenyl–titanium bonds in these compounds was proved by the reaction with mercuric chloride. In the case of $C_5H_5Ti(C_6H_5)_3$, the quantity of phenylmercury chloride formed corresponds to three phenyl–titanium bonds, and in the case of the monophenyl compound, the yield of phenylmercury chloride amounts to 1 mole per mole of $C_5H_5TiC_6H_5$ taken. In both cases the cyclopentadienyl–titanium bond is unaffected, as indicated by the formation of cyclopentadienyltitanium trichloride in the products of the reaction with mercuric chloride. $C_5H_5TiC_6H_5$ is a black compound which is oxidised extremely readily in air and is soluble in benzene and tetrahydrofuran. It reacts at low temperatures with halogen-containing organic solvents ($CHCl_3$ and CCl_4).

Thermal stability. A distinctive feature of organotitanium compounds is their extremely low thermal stability. In the series of alkyl or aryl derivatives of the type $RnTiX_{4-n}$, compounds with a smaller number of organic groups and with more strongly electronegative groups X are the more stable[23]. Thus methyltitanium trichloride is stable at 20° for several days in the absence of air and moisture. The yellow dioxan addition compounds of R_2TiX_2 are stable at 20° for 24 h. Tetramethyltitanium is stable at -70°. The decomposition of methyltitanium trichloride has been studied in more detail. At about 100° the compound decomposes with the formation of $TiCl_3$, methane, and polymethylene. The $TiCl_3$ produced catalyses the decomposition, which takes place more readily in ether and hydrocarbons. The rate of decomposition of methyltitanium trichloride increases on irradiation or treatment with BF_3.[5] In a mixture of CCl_4 and ether, considerable quantities of methyl chloride are formed, as a result of the disproportionation of methyltitanium trichloride[7]. In a recent paper[33], the reactions of CH_3TiCl_3 with carbon tetrachloride in the presence of metallic mercury are interpreted as free-radical reactions. Evidence for this is provided by the formation of methylmercury chloride, hexachloroethane, and other products of the free-radical reaction.

With increase in temperature to room temperature, tetramethyltitanium decomposes spontaneously with the formation of a black precipitate and a metallic mirror[16]. The decomposition products are pyrophoric and possibly contain derivatives of bivalent titanium.

The same is observed in the case of the phenyl derivatives. The thermal decomposition of tetraphenyltitanium gives diphenyltitanium and biphenyl[24]. The thermal stability of diphenyltitanium is much greater than that of tetraphenyltitanium. The former decomposes at 200–250° *in vacuo* with the formation of biphenyl and metallic titanium.

The thermal stability of organotitanium compounds of the above types decreases sharply when one or two cyclopentadienyl groups, joined to the metal in a sandwich, are introduced into the molecule:

$$R_4Ti > R_3TiC_6H_5 > R_2Ti(C_6H_5)_2.$$

The monocyclopentadienyl derivatives of quadrivalent titanium $C_5H_5Ti(CH_3)_3$ and $C_5H_5Ti(C_6H_5)_3$ darken and decompose when warmed to room temperature in the light. Cyclopentadienyltriphenyltitanium decomposes in ethereal solution with the loss of two phenyl groups in the form of benzene and biphenyl:

$$C_5H_5Ti(C_6H_5)_3 \xrightarrow{ether} C_5H_5TiC_6H_5 + C_6H_6 + (C_6H_5)_2.$$

A bivalent titanium derivative is formed. The presence of the cyclopentadienyl and phenyl groups in this compound was proved by the reaction with mercuric chloride

$$C_6H_5TiC_6H_5 + HgCl_2 \rightarrow [C_6H_5TiCl] + C_6H_5HgCl,$$
$$[C_6H_5TiCl] + HgCl_2 \rightarrow C_6H_5TiCl_3 + Hg,$$
$$[C_6H_5TiCl] + 2HgCl_2 \rightarrow C_6H_5TiCl_3 + 2HgCl.$$

In the thermal decomposition of mixed dicyclopentadienyl derivatives of titanium under mild conditions, the titanium–radical σ bond is broken first[34]. When dicyclopentadienyldiphenyltitanium is heated in solution at ~90°, the two phenyl groups are removed successively in the form of free radicals:

$$(C_5H_5)_2Ti^{4+}(C_6H_5)_2 \rightarrow (C_5H_5)_2Ti^{3+}C_6H_5 + C_6H_5^{\cdot},$$
$$(C_5H_5)_2Ti^{3+}C_6H_5 \rightarrow (C_5H_5)_2Ti^{2+} + C_6H_5^{\cdot}.$$

A derivative of tervalent titanium is produced in the first stage of the process. The two cyclopentadienyl–titanium bonds are unaffected, as indicated by the conversion of the dark-coloured product of the thermal decomposition to the stable dichloride $(C_5H_5)_2TiCl_2$ by the action of halogen-containing compounds (CCl_4, $HgCl_2$, benzyl chloride, etc.)[35,36].

The low thermal stability of organotitanium compounds results from the electron-unsaturation of the structure of the central titanium atom. Stabilisation results when the *d* electron level is filled by donor atoms and the electronic structure shows maximum approach to that of the nearest inert gas (krypton). The least stable tetramethyltitanium has a deficit of ten electrons, whereas the more stable $(C_5H_5)_2TiR_2$ has a deficit of only four electrons. Filling of the *d* level of titanium may also be brought about by electron donors such as amines, phosphines, and ethers. Complexes obtained with the above ligands are more stable, Thus methyltitanium trichloride forms a tetrahydrofuran derivative which is soluble in organic solvents and very sensitive to oxygen and moisture, but which has a higher thermal stability (m.p.107–108°). It reacts with metallic mercury in CCl_4 medium by a free-radical mechanism to give methylmercury chloride[37]. Insoluble complexes of methyltitanium trichloride with triphenylphosphine and dioxan are known[5]. Dimethyltitanium dichloride also forms a dioxan derivative. An ammine of diphenyltitanium which is readily oxidised in air and is hydrolysed with the liberation of ammonia has been described[25]. Diphenyltitanium reacts with tetrahydrofuran to give a tetrahydrofuran derivative. The latter is a black substance which is readily oxidised with the formation of biphenyl and phenol. Its reaction with mercury derivatives is similar to that of diphenyltitanium.

Action of water, acids, and alcohols. The Ti–R σ bond is generally broken by the action of water, alcohols, and other hydroxyl-containing compounds. In the case of the simplest alkyl derivatives CH_3TiCl_3, $(CH_3)_2TiCl_2$, $(CH_3)_4Ti$, etc., the reaction takes place with the quantitative liberation of methane. The compounds $(C_5H_5)_2Ti(CH_3)X$, $(C_5H_5)_2Ti(CH_3)_2$, and $C_5H_5Ti(CH_3)_3$ are stable towards water but are decomposed quantitatively by dilute acids[27]. The phenyl derivatives react with water, aqueous acids, or alcohols, with the formation of benzene. The products of the hydrolysis of $C_6H_5Ti(OC_3^iH_7)_3$ contain isopropanol and benzene[23]. Diphenyltitanium reacts with dilute hydrochloric acid with the formation of hydrogen, benzene, and $TiCl_3$:

$$(C_6H_5)_2Ti + 2HCl \rightarrow 2C_6H_6 + TiCl_2,$$
$$TiCl_2 + HCl \rightarrow {}^1/_2H_2 + TiCl_3.$$

The reaction of $(C_6H_5)_2Ti$ with isopropanol gives benzene as the main product[24]. Cyclopentadienyltriphenyltitanium reacts with isopropanol to give benzene in quantities corresponding to three phenyl groups, the cyclopentadienyl–titanium bond being unaffected. Small quantities of acetone are also detected[32].

Dicyclopentadienyldiphenyltitanium is stable to water. Dilute inorganic acids at room temperature lead to quantitative rupture of the $Ti–C_6H_5$ bonds but do not affect the $(C_5H_5)_2Ti$ group. The action of hydrochloric acid gives benzene and dicyclopentadienyltitanium dichloride:

$$(C_5H_5)_2Ti(C_6H_5)_2 + 2HCl \rightarrow 2C_6H_6 + (C_5H_5)_2TiCl_2.$$

The reaction with alcohols takes place at elevated temperatures with the formation of benzene, acetone, and, apparently, a dicyclopentadienyltitanium dialkoxide[35].

Action of halogens and halogeno-derivatives. The reaction with halogen provides an analytical test for an alkyl–titanium σ bond. Quantitative formation of alkyl iodides has been observed with CH_3TiCl_3, $(CH_3)_4Ti$, and $(CH_3)_2Ti(C_5H_5)_2$:

$$(CH_3)_4Ti + 4I_2 \rightarrow 4CH_3I + TiI_4,$$
$$(C_6H_5)_2Ti(CH_3)_2 + 2I_2 \rightarrow (C_6H_5)_2TiI_2 + 2CH_3I.$$

In the case of the phenyl derivatives this reaction is incomplete. Thus the reaction of a benzene solution of diphenyltitanium with iodine at room temperature leads to the formation of 20% of iodobenzene and TiI_4.

The phenyl–titanium bonds in diphenyltitanium are readily broken by the action of chloroform or carbon tetrachloride. The reaction with chloroform takes place at room temperature, as indicated by a change in colour from black to yellowish brown. The reaction products are benzene, biphenyl, and titanium tetrachloride; derivatives of bivalent or tervalent titanium were not observed[25].

Cyclopentadienyltriphenyltitanium is decomposed by chloroform between -70° and -50° with the formation of almost the theoretical quantity of benzene and dicyclopentadienyltitanium dichloride[32].

The thermochemical and photochemical reactions of dicyclopentadienyldiphenyltitanium in chloroform solution give benzene and dicyclopentadienyltitanium dichloride in analogous fashion. With carbon tetrachloride, chlorobenzene is formed[35,36].

It was noted above that the reactions of methyltitanium trichloride with carbon tetrachloride gave appreciable quantities of methyl chloride[7,33,37].

The reaction of tetramethyltitanium with CF_3I gives methyl iodide in addition to trimethyltitanium iodide, but the mechanism of the reaction is not clear[17].

Action of metal halides. Metal halides react with the R–Ti bond. The action of the halides of tin, titanium, mercury, and other metals on a variety of organotitanium compounds has been noted. The action of $SnCl_4$

on methyltitanium trichloride leads to the formation of titanium tetrachloride and the methyl derivative of tin:

$$4CH_3TiCl_3 + SnCl_4 \rightarrow 4TiCl_4 + Sn(CH_3)_4.$$

The catalytic action of $TiCl_3$ on the decomposition of methyl derivatives of titanium was noted above. An analogous influence is shown by titanium dichloride. Titanium tetrachloride decomposes methyltitanium trichloride[7] and tetramethyltitanium[14]:

$$CH_3TiCl_3 + TiCl_4 \rightarrow 2TiCl_3 + CH_3Cl,$$
$$(CH_3)_4Ti + 3TiCl_4 \rightarrow [4CH_3TiCl_3] \rightarrow 4TiCl_3 + 4\dot{C}H_3.$$

Phenyltitanium triisopropoxide reacts with mercuric chloride to give heterolytic exchange of phenyl for halogen with the formation of phenylmercury chloride. Addition of titanium tetrachloride to the isopropoxide gave a catalyst for the intensive polymerisation of propene[38]. The reaction with $TiCl_4$ was studied in more detail in hexane or benzene medium at room temperature. Biphenyl, isopropoxytitanium trichloride, and a tervalent titanium compound were isolated from the reaction mixture:

$$C_6H_5Ti(OC_3'H_7)_3 + 2TiCl_4 \longrightarrow C_6H_5TiCl_2(OC_3'H_7) + 2C_3'H_7OTiCl_3.$$
$$\downarrow \quad \searrow$$
$$1/2(C_6H_5)_2 \quad + \quad \dot{C}_3'H_7OTiCl_2$$

The biphenyl isolated from the products of the reaction carried out in labelled benzene was almost inactive.

To prove the presence of a C–Ti σ bond, extensive use is made of the reaction with mercuric chloride, leading to formation of an unsymmetrical organomercury compound and titanium halides. Thus methyltitanium trichloride gives the methyl derivative of mercury[33]; phenylmercury chloride is the chief product of the reaction of phenyl compounds of titanium[24,32,34,35].

Oxidation. Oxidation is a characteristic reaction for the Ti–R bond. The oxidation of lower-valency titanium derivatives takes place very vigorously, often with spontaneous ignition. Thus diphenyltitanium, particularly in the finely divided state, ignites in air[24]. The oxidation of diphenyltitanium in benzene solution is complete in 1–2 h at room temperature; phenol and biphenyl are found among the reaction products. Special experiments on oxidation in labelled benzene medium showed that the products contained no tracer atoms from the solvent[25]. The products of the decomposition of tetramethyltitanium are pyrophoric[16], and cyclopentadienylphenyltitanium is vigorously oxidised[32].

In a series of quadrivalent derivatives, the stability to the action of oxygen increases with the introduction of cyclopentadienyl groups into the molecule. Methyltitanium trichloride reacts rapidly with the absorption of $\frac{1}{2}O_2$ per mole, the solution giving a precipitate which is coloured pale brown by impurities:

$$CH_3TiCl_3 + 1/2O_2 \rightarrow CH_3OTiCl_3.$$

This is followed by disproportionation of the alkoxytitanium trichloride:

$$3CH_3OTiCl_3 \rightarrow CH_3OTiCl_3 \cdot (CH_3O)_2TiCl_2 + TiCl_4.$$

Other alkyls and aryls of quadrivalent titanium — dialkyltitanium dihalides, tetramethyltitanium, the monophenyl derivatives $C_6H_5TiX_3$, and tetraphenyltitanium — are readily oxidised.

Alkyl or aryl derivatives of monocyclopentadienyltitanium are also oxidised vigorously; cyclopentadienyltrimethyltitanium is pyrophoric[31].

The dicyclopentadienyl compounds $(C_5H_5)_2TiR_2$ are more stable towards oxygen. In the solid state they are stable in air at low temperatures. In solution, oxidation is more rapid. Dicyclopentadienyldiphenyltitanium is readily oxidised by atmospheric oxygen in solutions in benzene, chloroform, and carbon tetrachloride at 50–60°.

Oxidation in isopropanol is accompanied by the formation of phenol, cyclopentadiene, acetone, and the oxidised organometallic compound. In CCl_4 medium, dicyclopentadienyltitanium dichloride is formed in addition to biphenyl, chlorobenzene, and carbonyl chloride; this indicates that reaction with the solvent, initiated by oxygen, takes place.

The sandwich group $(C_5H_5)_2Ti$ is unaffected under these conditions. Oxidation with aqueous hydrogen peroxide at 40–50° leads to complete decomposition of the original compound to CO and CO_2. Considerable quantities of acetophenone are found among the reaction products in addition to phenol[39].

Reduction. The discovery and study of polymerisation catalysts of the Ziegler–Natta type led to the development of work on the reduction of organotitanium compounds. The alkylation of titanium halides taking place in the systems formed by these catalysts leads to reduction of the quadrivalent titanium to the tervalent and bivalent states. The second component of the catalyst is an organometallic compound of lithium, magnesium, or, most frequently, aluminium. We shall not deal with the widely studied processes of formation and mechanism of action of "bridged" catalysts for the polymerisation of alk-1-enes, but merely point out that reduction of Ti^{4+} to Ti^{3+} often takes place in the synthesis of organotitanium compounds if the reaction is carried out at higher temperatures. The monosubstituted product $RTiCl_3$ forms $TiCl_3$ on decomposition:

$$RTiCl_3 \rightarrow R' + TiCl_3.$$

The reduction of the mono- and di-alkyl compounds is accompanied by the liberation of methane and ethane in the case of the methyl derivatives, and of ethane, ethylene, and butane in the case of the ethyl derivatives. This is due to disproportionation or dimerisation of the radicals.

The reactions of alkyl derivatives of titanium with hydrogen have been studied recently[27]. CH_3TiCl_3 and its mixtures with $(CH_3)_nAlCl_{3-n}$ do not react at all with H_2, whereas $(C_5H_5)_2Ti(CH_3)_2$ is reduced immediately in aliphatic and alicyclic hydrocarbons at room temperature, with the formation of two moles of methane and the sparingly soluble dark green dicyclopentadienyltitanium:

$$(C_5H_5)_2Ti(CH_3)_2 + H_2 \rightarrow (C_5H_5)_2Ti + 2CH_4.$$

No reaction with hydrogen takes place in halogen-containing solvents. Methyldicyclopentadienyltitanium chloride does not react with hydrogen at 20°. Dicyclopentadienyldiphenyltitanium in toluene is reduced appreciably only at 60°.

There is an interesting analogy between reduction under the influence of hydrogen or another organometallic compound and the thermal decomposition of titanium compounds with the formation of lower-valency derivatives.

Qualitative test for the C–Ti bond. The reaction with Michler's ketone provides a qualitative test

for a bond between a radical and a metal in the first three groups of the Periodic System. Alkyl derivatives of titanium also give a positive Gilman test. The final reaction products in the case of titanium compounds, however, differ from the analogous products for organoaluminium derivatives.

A slow positive reaction with Michler's ketone was observed for $C_6H_5Ti(OC_3^iH_7)_3$ and also for the products of the reaction of titanium tetraisopropoxide with phenyllithium in the proportions 1 : 2 and 1 : 4; the rate of the colour reaction increases with increase in the number of phenyl groups[23]. Phenyltitanium triisopropoxide reacts with benzophenone with the formation of triphenylmethanol. Diphenyltitanium gives a colour reaction with Michler's ketone.

Zirconium and Hafnium

There are isolated data on organometallic compounds of zirconium and hafnium. In Cotton's review[3] it is stated that zirconium tetrachloride does not react with diethylzinc and that metallic zirconium does not react with ethyl iodide or diethylmercury. According to recent data, however, exchange of radicals is observed in the systems formed by $ZrCl_4$ with R_2Hg or RMgX. $ZrCl_4$ reacts with diethylmercury and diphenylmercury[40] and with organolithium and organomagnesium compounds[41]. The reaction of phenylmagnesium chloride with $ZrCl_4$ gives biphenyl in 56% yield; $ZrCl_4$ or $Zr(OC_6H_5)_4$ reacts with methyllithium to give up to 70% of methane[42]. Hydrolysis of the reaction mixture gives hydrogen in addition to hydrocarbons. The reaction of a phenyl Grignard reagent with zirconium tetrachloride to give a compound of the type $RZrCl_3$ has recently been reported[43]. Hafnium and zirconium chlorides have been used as additives to aluminium triisobutoxide in order to study the resulting propene-polymerisation catalysts. The relative reactivity of the catalyst increases in the order

$$HfCl_4<ZrCl_4<TiCl_4<VOCl_3<VCl_4.$$

The formation of organometallic compounds of hafnium and zirconium by halogen–radical exchange reactions is probable in these cases. A brief report of the preparation of $Zr(C_5H_{11})_2$ from hydrides and diazohydrocarbons at low temperatures appeared in the patent literature[44].

GROUP V

Vanadium

The early papers cited in Cotton's review[3] contained no convincing proof of the formation of alkyl or aryl compounds of vanadium. The reaction of $VOCl_3$ with a Grignard reagent gives a dark green crystalline product which burns in air with a smoky flame and contains vanadium[45]. This substance was not studied more closely.

Recent papers contain reliable evidence of the formation of a phenyl–vanadium bond. Thus the reaction of ten moles of phenyllithium with one mole of the tetrahydrofuran addition compound of vanadium(II) chloride in ether in the cold, in the absence of moisture and air, gave the paramagnetic complex $4C_6H_5Li.V(C_6H_5)_2.3.5(C_2H_5)_2O$. The complex is very sensitive towards air and moisture. It loses ether *in vacuo* at 50°, and decomposes above 80° with the formation of biphenyl. Chemical reactions confirm the presence of a phenyl–vanadium σ bond. Decomposition by acids, water, or alcohols leads to the formation of benzene. The reaction with iodine gives iodobenzene and the reaction with mercuric chloride gives phenylmercury chloride. The tetrahydrofuran addition compound of vanadium chloride reacts with phenylmagnesium chloride to form a complex containing vanadium and magnesium[46]. Vanadium halides react with organometallic compounds of aluminium, mercury, and titanium with exchange of halogen atoms for phenyl groups. It was shown that triisobutylaluminium containing added halides of the transition metals of Groups IV–VI (Ti, V, Cr) form catalysts for the polymerisation of alk-1-enes, the greatest activity being shown by vanadium halides[47,48]. In the process, reduction of quadrivalent and quinquevalent vanadium to the bivalent and tervalent states is observed, together with the formation of a black precipitate which fumes in air and contains aluminium, vanadium, halogen, and a hydrocarbon radical. It was shown convincingly for the analogous systems formed by organometallic compounds of aluminium with titanium halides that the complexes with a "bridged" structure are intermediate products in the formation of true organotitanium compounds. The formation of individual derivatives in the case of vanadium halides might also be expected.

It was shown that diphenylmercury reacts in cyclohexane solution under ordinary conditions with vanadium halides and oxide halides, with the quantitative formation of phenylmercury chloride and a red solution of phenyl derivatives of vanadium:

$$(C_6H_5)_2Hg + VOCl_3 \rightleftarrows C_6H_5VOCl_2 + C_6H_5HgCl,$$
$$(C_6H_5)_2Hg + VCl_4 \rightleftarrows C_6H_5VCl_3 + C_6H_5HgCl.$$

Their formation is confirmed by spectroscopic data and also by hydrolysis, which leads to the formation of benzene. Benzene is also formed by the action of hydrogen bromide:

$$C_6H_5VOCl_2 + HBr \rightarrow C_6H_6 + VOCl_2Br.$$

The phenyl derivatives of vanadium were not isolated in pure form, since they are thermally unstable. Decomposition gives biphenyl, evidently as a result of disproportionation:

$$2C_6H_5VOCl_2 \rightleftarrows (C_6H_5)_2VOCl + VOCl_3,$$
$$(C_6H_5)_2VOCl \rightleftarrows (C_6H_5)_2 + VOCl.$$

It was proved that free phenyl radicals are not formed at this stage[49].

In the $(C_6H_5)_4Sn + VCl_4$ ($VOCl_3$) system, exchange of phenyl radicals is observed under more severe conditions (100°).[50] Rapid reduction of vanadium and formation of biphenyl was observed on the addition of $AlCl_3$, $AlBr_3$, or $Al(OC_4^iH_9)_3$. Diphenylzinc and CH_3TiCl_3 bring about partial reduction of vanadium from the quadrivalent to the bivalent state and give catalysts for the polymerisation of ethylene[47].

Phenyl derivatives of vanadium can be obtained by replacing the cyclopentadienyl group of $C_5H_5V(CO)_4$ by a phenyl group. If a current of hydrogen chloride, a mixture of HCl and O_2, and, finally, pure oxygen are passed in turn through a benzene solution of $C_5H_5V(CO)_4$, the colour changes from violet to pale blue. Removal of the solvent and distillation in a high vacuum gives $C_6H_5VOCl_2$, which is soluble in benzene, chloroform, ether, methylene chloride, and other organic solvents[51].

Replacement of the halogen in π-$(C_5H_5)_2VCl$ by a phenyl group by the action of an equimolar quantity of phenyllithium gave $(C_5H_5)_2VC_6H_5$ in pure form[52]. The same compound was obtained by the action of phenyllithium on π-$(C_5H_5)_2VCl_2$ in the molar ratio 2 : 1 in 1,2-dimethoxyethane solution at -50°. The solvent was removed *in vacuo* and the residue was extracted with petroleum ether. Black crystals of $(C_5H_5)_2VC_6H_5$ with m.p. 92° were isolated in 50% yield by freezing to -80°. Phenyldicyclopentadienylvanadium solution is stable in the absence of oxygen at room temperature for one week. The presence of phenyl–vanadium σ bond was proved by the formation of benzene on decomposition with HCl; the initial green colour of the solution changed to blue and then to green again, and crystals of $(C_5H_5)_2VCl$ separated from the reaction mixture:

$$(C_5H_5)_2\,V\,C_6H_5 + HCl \rightarrow C_6H_6 + (C_5H_5)_2VCl\,.$$

The vanadium derivatives are very sensitive towards oxygen.

Niobium and Tantalum

Data on the reactions of niobium and tantalum halides with aromatic hydrocarbons are contradictory[3]. The reactions of $NbCl_5$ and $TaCl_5$ with benzene, naphthalene, anthracene, and tetralin in a boiling solvent (benzene, CCl_4, or CS_2) led to the formation of compounds containing metal, halogen, and an organic residue[53]. The formulae RMX_4 or R_2MX_3 were ascribed to the products, but the latter were not isolated in pure form, with the exception of the complex $C_6H_6.NbCl_5$. Attempts to repeat these reactions with specially purified benzene were unsuccessful[54].

Reaction of a Grignard reagent with tantalum compounds gives red solutions, which are unstable towards water and oxygen and contain tantalum compounds in the dissolved state. Complete hydrolysis gives the oxide Ta_2O_5.[55]

The preparation of a complex of tetraphenylniobium with phenyllithium by the reaction of $NbBr_5$ with phenyllithium in ethereal solution has recently been reported[56]:

$$NbBr_5 + 8C_6H_5Li + 3(C_2H_5)_2O \xrightarrow[N_2]{} \underset{(I)}{Li_3Nb(C_6H_5)_7.3(C_2H_5)_2O} + 5LiBr + \frac{1}{2}(C_6H_5)_2.$$

The complex (I) crystallises as a black-violet compound which is pyrophoric in the dry state. The ether is removed in a high vacuum at room temperature. The substance is non-volatile, stable up to 40–50°, and is readily oxidised and hydrolysed. The magnetic moment is 1.66 β, which is characteristic of Nb^{4+}. The infrared spectra confirmed the presence of a phenyl–niobium σ bond; the formula $Nb(C_6H_5)_4.3C_6H_5Li.3(C_2H_5)_2O$ was ascribed to the substance.

GROUP VI

Chromium

Phenylchromium compounds became known as early as the 1920's, as a result of Hein's work. The compounds were prepared by the reaction of phenylmagnesium bromide with sublimed anhydrous chromium(III) chloride at -10°. Three series of compounds were isolated from the reaction mixture and these were named as derivatives of "triphenylchromium", "tetraphenylchromium", and "pentaphenylchromium". It appeared strange that all these compounds had the same orange colour, apparently indicating the same oxidation state. Reduction with lithium tetrahydroaluminate in all cases gave more biphenyl than benzene, and phenol was also obtained from the "penta"-derivative[57]. Reduction with $LiAlD_4$ showed that the biphenyl is formed at this stage and not by hydrolysis. It was thus established that each of these three products contains biphenyl, not phenyl, groups. The structure of Hein's polyphenylchromium compounds began to be explained in the light of a diarene π structure analogous to that of dibenzenechromium.

Measurement of the magnetic properties, the X-ray and infrared spectra, and analytical data proved that dibiphenylchromium iodide obtained by the Grignard reaction[58] was identical to that obtained from biphenyl and chromium(III) chloride in the presence of Friedel–Crafts catalysts[59].

Further work showed the possibility of the existence of true organometallic compounds of chromium. The formation of phenylchromium compounds of the type $C_6H_5CrCl_2$ or $(C_6H_5CrCl_2)_2CrCl$ as intermediate products was postulated in 1956.[60] In a description of the reaction of triphenylaluminium with $CrCl_3$, mention was made of the formation of the tetrahydrofuran addition compound of phenylchromium dichloride $C_6H_5CrCl_2.3THF$†.[61] Anhydrous chromium(III) chloride reacts with phenyllithium in ethereal solution to form a red solid (A)[62]:

$$CrCl_3 + 6C_6H_5Li \xrightarrow{\text{ether}} (C_6H_5)_3Cr\cdot 3C_6H_5Li\cdot 2.5\,(C_2H_5)_2O\,(A)\,.$$

The compound (A) is extremely sensitive to oxygen and moisture. Hydrolysis leads to the formation of benzene, and biphenyl is formed in the absence of oxygen. With iodine, biphenyl and iodobenzene are formed:

$$Li_3Cr\,(C_6H_5)_6 + {}^9/_2I_2 \longrightarrow 3\,LiI + CrI_3 + 3C_6H_5I + {}^3/_2\,(C_6H_5)_2\,.$$

The product (A) is paramagnetic (3.87 β and 3.61 β), which corresponds to tervalent chromium and confirms the presence of three phenyl–chromium σ bonds. The triphenylchromium complex can be obtained free from ether by dissolving compound (A) in benzene with subsequent crystallisation. Under normal conditions, the solutions absorb hydrogen and form the hydro-pentaphenyl derivative $Li_3[CrH(C_6H_5)_5].3(C_2H_5)_2O$ as shiny red crystals. Further treatment with hydrogen leads to the formation of complex products[63]. The reaction of $3C_6H_5Li.(C_6H_5)_3Cr\,.\,2.5(C_2H_5)_2O$ with lithium tetrahydroaluminate in ether in a current of pure dry argon gave a pyrophoric substance decomposing above 75°, and having the composition $Li_6CrAl_3H_{16}.\frac{1}{3}(C_2H_5)_2O$ (apparently a complex hydride of univalent chromium). The compound is insoluble in the usual solvents, readily deposits chromium, reduces azobenzene to aniline, and reacts with phenyllithium under ordinary conditions to give a hydride of composition $Li[AlH(C_6H_5)_3]$.[64]

Reaction of phenylmagnesium bromide with chromium(III) chloride in tetrahydrofuran solution at -20° gave the tetrahydrofuran addition compound $(C_6H_5)_3Cr.3THF$, which is readily hydrolysed to green $[Cr(H_2O)_6]^{3+}$ and reacts with mercuric chloride to give a quantitative yield of phenylmercury chloride[65,66]:

$$(C_6H_5)_3Cr\cdot 3THF + 3HgCl_2 \xrightarrow{THF} 3C_6H_5HgCl + CrCl_3\,.$$

† THF represents tetrahydrofuran.

On being heated *in vacuo*, and also as a result of the addition of diethyl ether, the precipitate loses all its tetrahydrofuran with formation of a black substance, which on hydrolysis in the absence of oxygen gives the π complexes dibenzenechromium and benzenebiphenylchromium[67]:

$$(C_6H_5)_3Cr\cdot 3THF \xrightarrow[H_2O]{heat} \pi\text{-}(C_6H_6)_2Cr + \pi\text{-}C_6H_6Cr(C_6H_5 - C_6H_5).$$

The double compound $(C_6H_5)_3Cr.3THF.3(MgBrCl.THF)$ (B) has also been isolated[68]. The action of ether on (B) gives the tetrahydrofuran addition compound of triphenylchromium. Drying *in vacuo* at 20–40° yields an extremely pyrophoric product, which on careful hydrolysis also gives a mixture of the π complexes dibenzenechromium and benzenebiphenylchromium. The π complexes can also be prepared by appropriate treatment of (B). The action of D_2O on the black intermediate product in an atmosphere of nitrogen gives a mixture of bismonodeuterobenzenechromium and biphenylmonodeuterobenzenechromium[69].

Carboxylation of the black intermediate product leads to the formation of carboxy-derivatives. Thus chromium(II) chloride in ethereal solution reacts with a phenyl Grignard reagent at -10°; after 4 h, saturation of the reaction mixture with carbon dioxide and hydrolysis with an aqueous solution of sodium tetraphenylborate give a red-orange precipitate having the composition[70]

$$(C_6H_5COOH)[(C_6H_5)_2Cr]^+(C_6H_5)_4B^-$$ (yield 12%, m.p. 144–147°).

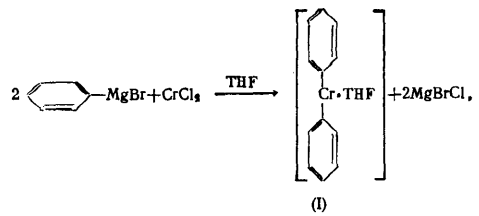
Substituted phenyl derivatives of chromium have recently been described. The action of *o*-methoxyphenyllithium on a chromium halide gives fine yellow crystals of bis-*o*-methoxyphenylchromium, which is pyrophoric in air, is slowly decomposed by alcohol, and has a low magnetic moment (0.55 β). Attempts to prepare this compound from the lithium derivative and the tetrahydrofuran addition compound of chromium(II) bromide led to formation of the red-brown crystalline complex $LiCr(o\text{-}CH_3OC_6H_4)_4.L$, where L is the solvent. This complex was also obtained by the disproportionation of bismethoxyphenylchromium with an ethereal solution of methoxyphenyllithium[71].

Tris-(ω-*NN*-diethylaminotolyl)chromium has been prepared by the reaction of chromium(III) chloride in ether with ω-*NN*-diethylaminotolyllithium. The compound forms glistening garnet red crystals which are comparatively stable in air and even more stable in alcoholic solution; it was assumed to have an inner-complex structure[72]. The analogous reaction with $p\text{-}N(CH_3)_2C_6H_4Li$ gave a yellow substance of composition

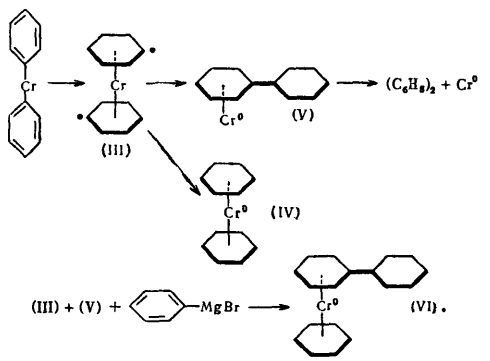
$$[p\text{-}N(CH_3)_2C_6H_4]_3Cr.3p\text{-}N(CH_3)_2C_6H_4Li.3THF$$ (Ref. 71),

which is sensitive to air and sparingly soluble in ether.

Tsutsui regards the formation of true phenylchromium compounds as an intermediate stage in the formation of the more stable arene π complexes. In his opinion[73] the reaction of chromium(II) chloride with a phenyl or mesityl Grignard reagent involves initially the formation of diphenyl- or dimesityl-chromium. Diphenylchromium was not isolated from the reaction products: it undergoes rapid rearrangement to dibenzenechromium and benzenebiphenylchromium. The true organochromium compounds formed initially undergo further rearrangement to the transition state — a π-radical hybrid — which may be stabilised in the form of the diradical sandwich π complex (III) or the half-sandwich π complex (V). In the process, the bivalent chromium is reduced to the zerovalent state.

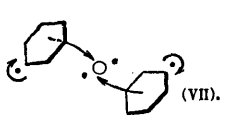


(I)



The π complexes (III) and (V) undergo rearrangement to sandwich compounds (IV) or (VI), with the stable electronic configuration of an inert gas, or else decompose with the formation of biphenyl, depending on the reaction conditions. Rearrangement to dibenzenechromium and benzenebiphenylchromium takes place as a result of hydrolysis or subsequent reaction with the Grignard reagent under the conditions of Hein's reaction. Decomposition to biphenyl takes place under more severe conditions.

Tsutsui suggests that the π-radical–electron hybridised complex (VII), in which the two phenyl groups are tilted relative to the chromium atom, is formed in an intermediate state between diphenylchromium and the π complex (III) or (V).



(VII).

In the case of dimesitylchromium, there is an increase in the strength of the mesityl–chromium σ bond. Dimesitylchromium is a stable compound, which can be isolated in the pure state and which does not undergo rearrangement to the π complex under any conditions[74]. This is due to steric hindrance to free rotation of the mesityl groups about the central chromium atom. Formation of π complex sandwich compounds cannot take place in this case, since it would require the two mesityl groups to be coplanar. For dimesitylchromium, only one reaction remains possible — formation of the biaryl under more severe experimental conditions — and bimesityl is in fact obtained in quantitative yield on boiling a tetrahydrofuran solution of dimesitylchromium.

The tetrahydrofuran addition compound of triphenylchromium, obtained by the reaction of phenylmagnesium bromide with chromium(III) chloride, can also be converted into a sandwich compound by rearrangement with the inter-

mediate formation of a π-radical hybrid complex, similar to diphenylchromium. At the instant of decomposition, which takes place by a free-radical mechanism, formation of a highly active "radical metal", which may attack the arene with formation of a stable π complex (IV) or (VI), is possible. The suggestion that a "radical metal" is formed in the reduction of a halide of a transition metal has been confirmed by new syntheses of diarene complexes[75]. Triethylaluminium has been used successfully as reducing agent for this purpose. The dimesitylene π complex of chromium has been obtained from mesitylene, chromium(III) chloride, and triethylaluminium in n-heptane solution at room temperature. The same method has been used to prepare the bridged dibenzenechromium 1,1'-($\beta\gamma$-diphenyltetramethylene)dibenzenechromium iodide[76].

Alkyl derivatives of chromium have not yet been isolated in the pure state. Mention of these compounds is made in a description of the reaction of methyllithium with chromium(II) chloride, which leads to the formation of a black solution, apparently of dimethylchromium. The reaction with chromium(III) chloride gives a brown-red solution, evidently of trimethylchromium[14].

σ-Trialkyl derivatives of chromium are of particular interest in connection with their use for the catalytic cyclisation of disubstituted acetylenes[77]. Triethylchromium cyclises diphenylacetylene to hexaphenylbenzene with the simultaneous formation of tetraphenylbenzene. In the presence of trimethylchromium, tetraphenylcyclopentadiene is obtained from diphenylacetylene. Condensation of disubstituted acetylenes also takes place with aryl derivatives of chromium. The tetrahydrofuran addition compound of triphenylchromium gives hexamethylbenzene and 1,2,3,4-tetramethylnaphthalene from but-2-yne, depending on the experimental conditions[78]. The intermediate formation of a complex of triphenylchromium with three molecules of the alkyne $R_3Cr.(H_3CC{:}CCCH_3)_3$ was postulated. The condensation of acetylene with triphenylchromium or triethylchromium in tetrahydrofuran solution gives only hexamethylbenzene. Trimethylchromium reacts exothermally with but-2-yne to give 2-mesitylbut-2-ene in addition to hexamethylbenzene[79]. The exothermic reaction of triphenylchromium with dimethyl acetylenedicarboxylate in tetrahydrofuran solution at room temperature leads to the attachment of two phenyl groups with the formation of dimethyl diphenylmaleate.

The addition of aryl groups with formation of derivatives of styrene or stilbene, and also condensation with ring closure, are explained as follows. The intermediate complex of the organochromium compound with acetylene is formed by the gradual replacement of solvent molecules. The final reaction products depend on the number of acetylene molecules coordinated to the triarylchromium molecule. The monosubstituted complex gives styrene or stilbene, and the disubstituted complex gives polycyclic aromatic hydrocarbons (e.g. naphthalene derivatives) if the *ortho*-position of the aryl is available for ring closure. The trisubstituted complexes given benzene derivatives.

Another important factor influencing the mechanism of the process is the effect of electron-repelling groups on the delocalisation of the π electrons of the alkynes. Thus in the presence of the electron-repelling [sic] methoxycarbonyl groups, the products of cyclic condensation are not obtained. The reaction of dimethyl acetylenedicarboxylate with triphenylchromium takes place with the addition of two aryl groups to the acetylene derivative.

Alkenes such as hexenes, isoprene, stilbene, and styrene do not react with triphenylchromium. If the alkene is able to form a complex with chromium derivatives, addition reactions are observed. These properties are shown by 2,2,1-bicyclic dienes, e.g. bicyclo[2,2,1]hepta-2,5-diene and conjugated alkenes (maleic anhydride). It has been shown that cyclisation of alkenes does not take place on phenylchromium complexes[80].

At the present time this field of study is developing rapidly, since by selecting suitable derivatives of the arylchromium and unsaturated compounds it is possible to extend the synthesis of a variety of condensed aromatic systems and other compounds.

Chromium derivatives obtained by reducing alkyl halides with chromium(II) perchlorate constitute a group apart. The reaction of benzyl chloride with an aqueous molar solution of chromium perchlorate in dilute perchloric acid gave a yellow-brown solution of the benzyl derivative of chromium $[Cr(CH_2C_6H_5)(H_2O)_5]^{2+}$. The solution oxidises in air with the formation of benzaldehyde. In the absence of air, 1,2-diphenylethane is formed, evidently by dimerisation of the benzyl radicals. The half-life at room temperature is about $1\frac{1}{2}$ days. A rapid reaction takes place with mercuric chloride with the formation of benzylmercury chloride and the chromium ion without change in the pH of the medium[81]:

$$[Cr(CH_2C_6H_5)(H_2O)_5]^{2+} + HgCl_2 + H_2O \longrightarrow C_6H_5HgCl + [Cr(H_2O)_6]^{3+} + Cl'.$$

Benzylpentaaquochromium(II) solutions are decomposed by sulphur dioxide but are stable towards carbon dioxide; reaction with hydrogen in the presence of palladium gives toluene.

Methyl chloride and methylene chloride are not reduced by chromium(II) perchlorate. Chloroform and carbon tetrachloride are very readily reduced under these conditions. In both cases the pale blue colour of bivalent chromium changes to red within a few minutes. Carbon tetrachloride reacts with chromium(II) perchlorate to form unstable solutions, which have not been more closely studied. It is suggested that the reduction of chloroform takes place according to the following mechanism

$$CHCl_3 + 2[Cr(H_2O)_6]^{2+} \rightarrow [CrCl(H_2O)_5]^{2+} + [Cr(CHCl_2)(H_2O)_5]^{2+} + 2H_2O,$$
$$CHCl_3 + Cr^{2+} + 5H_2O \rightarrow [CrCl(H_2O)_5]^{2+} + \dot{C}HCl_2,$$
$$\dot{C}HCl_2 + Cr^{2+} + 5H_2O \rightarrow [Cr(CHCl_2)(H_2O)_5]^{2+}.$$

The chloroform derivative was not isolated in the pure state. The bond between chromium and the $CHCl_2$ group is evidently similar to a covalent bond of weak polar character. Unlike the benzyl derivative, the chloroform derivative does not react with mercuric chloride, oxygen, or sulphur dioxide[82], but it is reduced by hydrogen in the presence of a palladium catalyst. No tetrachloroethane or dichloroethylene is formed on heating; instead, the chloride ion is liberated. No volatile organic compounds are obtained.

An increase in the strength of the transition metal σ bond, particularly that between chromium and carbon, is observed when a π-cyclopentadienyl group is introduced into the molecule. This is clearly illustrated for the case of organochromium compounds. Mixed cyclopentadienyl-nitrosyl derivatives of chromium with alkyl and aryl groups attached by σ bonds are known. These are obtained via the sodium derivative π-$C_5H_5Cr(NO)_2Na$ by reaction with alkyl or aryl halides:

$$\pi\text{-}C_5H_5Cr(NO)_2Na + RX \rightarrow \pi\text{-}C_5H_5Cr(NO)_2R.$$

This method was used to prepare methyl, ethyl, and cyclopentadienyl derivatives containing σ bonds, and also the compound with R = CH_2Cl.[83,84] These compounds are diamagnetic, coloured, crystalline, or oily (R = C_2H_5 or C_6H_5) substances which are readily soluble in organic solvents and can be sublimed in a high vacuum. They decompose slowly in air. The stability of the compounds decreases in the order $C_6H_5 > CH_3 > C_2H_5$.

Molybdenum and Tungsten

Molybdenum and tungsten halides react with phenyllithium or Grignard reagents; in a number of cases, only the dimerisation product biphenyl could be isolated[3]. Compounds of the type $(C_6H_5)_2Mo(OH, X)$, $C_6H_5MoO_2OH$, $C_6H_5Mo_2O_4H_4$, $(C_6H_5)_3Mo_2O_7H_7$, and $(C_6H_5)_2Mo_3O_9H_4$ may, however, be formed as intermediate products[84]. Analogous tungsten derivatives were obtained from WCl_6 or $W(OC_6H_5)_6$ with phenyl compounds of lithium or magnesium[85]. The properties of these molybdenum and tungsten compounds resemble those of the phenyl derivatives of chromium, but the former are less stable, so that they could not be isolated in the pure state.

Mixed π-cyclopentadienyl-carbonyl compounds of molybdenum and tungsten, containing a σ bond between the metal and the radical, have recently been reported. In these derivatives, stabilisation of the metal–carbon bond is due to the influence of the π-cyclopentadienyl group. σ-Substituted π-cyclopentadienyl-tricarbonyl compounds of molybdenum and tungsten have been obtained from the hydrides by reaction with diazomethane:

$$\pi\text{-}C_5H_5Mo(CO)_3H + CH_2N_2 \rightarrow \pi\text{-}C_5H_5Mo(CO)_3CH_3 + N_2,$$

or by reaction of the sodium salt of the π-cyclopentadienyl-tricarbonyl compound of the metal with alkyl halides[26,86]:

$$\pi\text{-}C_5H_5M(CO)_3Na + RI \rightarrow \pi\text{-}C_5H_5M(CO)_3R + NaI,$$

where R = methyl, ethyl, or isopropyl for M = Mo, and R = methyl or ethyl for M = W.

These compounds were isolated in 75–85% yield. They are relatively stable yellow crystalline substances with melting points from 80° to 150°. The stability of the compounds in air decreases in the order methyl > ethyl > isopropyl. The methyl compound of tungsten is more stable than that of molybdenum. All the compounds are insoluble in water and are slowly decomposed by acids and bases. Halogens bring about quantitative rupture of the alkyl–metal bond according to the equation

$$\pi\text{-}C_5H_5Mo(CO)_3CH_3 + I_2 \rightarrow \pi\text{-}C_5H_5Mo(CO)_3I + CH_3I.$$

The compounds react neither with $FeCl_2$ in tetrahydrofuran solution nor with maleic anhydride in benzene. Data obtained by infrared, ultraviolet, and nuclear magnetic resonance spectroscopy have established that all these derivatives have a cyclopentadienyl–metal π bond and a metal–radical σ bond.

The reaction of tungsten pentabromide with an ethereal solution of phenyllithium in a current of pure nitrogen gave crystalline tungsten compounds to which the formula $(C_6H_5)_3W.3C_6H_5Li.3(C_2H_5)_2O$ was at first ascribed[87]. This compound is a black substance which is readily soluble in benzene and readily ignites in air. According to recent data[88], the composition corresponds to the formula $(C_6H_5)_4W.2C_6H_5Li.3(C_2H_5)_2O$.

GROUP VII

Manganese and Rhenium

The stoichiometric coupling of a phenylmagnesium halide in the presence of manganese(II) chloride in ethereal solution gives biphenyl in quantitative yield[73]. Catalytic coupling (Kharasch's reaction) in the $C_6H_5MgX + C_6H_5X +$ + 3–5 mole % MnX_2 system produces 21% of biphenyl. The action of manganese bromide on ethylmagnesium bromide in the ratio 1 : 2 at 25° gave 63% of ethane and 29% of ethylene[42]. It was suggested that unstable intermediate organomanganese derivatives are formed, and this was confirmed by subsequent work. The reactions of phenylmagnesium iodide with manganese iodide in the ratio 3 : 1 in ethereal solution takes place with the formation of brown precipitates consisting of a mixture of the phenyl derivatives of manganese $(C_6H_5)_2Mn$ and C_6H_5MnI, which are unstable in air[3].

The reaction of alkyl and aryl Grignard reagents (methyl-, ethyl-, and benzyl-magnesium bromides, etc.) with manganese halides gives brownish oily liquids which are insoluble in organic solvents and unstable in air, and react readily with iodine in tetrahydrofuran or chloroform solution. With benzylmagnesium bromide, 1,2-diphenylethane was obtained. In other cases also, the manganese compounds could not be isolated in the pure state[89]. Replacement of the organomagnesium compound by RLi made it possible to obtain individual products. The reaction of methyllithium with manganese iodide gave methylmanganese iodide in the form of a brown oil, insoluble in ether:

$$CH_3Li + MnI_2 \rightarrow CH_3MnI + LiI.$$

Reaction with another molecule of methyllithium gives colourless amorphous dimethylmanganese:

$$CH_3MnI + CH_3Li \rightarrow (CH_3)_2Mn + LiI.$$

Dimethylmanganese was obtained as a spontaneously inflammable yellow powder, exploding on impact. It is evidently polymeric. Diphenylmanganese, like the dimethyl derivative, is polymeric, but it can be crystallised from tetrahydrofuran.

Dimethylmanganese readily reacts with manganese iodide according to the scheme

$$(CH_3)_2Mn + MnI_2 \rightarrow 2CH_3MnI.$$

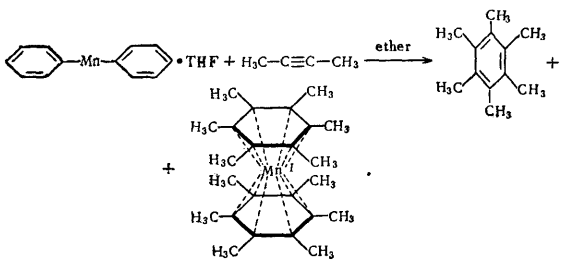
The reaction with excess of methyllithium gives the colourless amorphous complex $Li[Mn(CH_3)_3]$, insoluble in ether. This compound also reacts with MnI_2 to form dimethylmanganese and methylmanganese iodide:

$$(CH_3)_2Mn + CH_3Li \rightarrow Li[Mn(CH_3)_3],$$
$$Li[Mn(CH_3)_3] + MnI_2 \rightarrow (CH_3)_2Mn + CH_3MnI + LiI,$$
$$Li[Mn(CH_3)_3] + 2MnI_2 \rightarrow 3CH_3MnI + LiI.$$

Other complex products obtained were $Li[Mn(C_2H_5)_3]$ (a yellow amorphous powder, insoluble in ether), and also $Li[Mn(n\text{-}C_4H_9)_3]$, $Li[Mn(C_6H_5)_3]$, $Li[Mn(p\text{-}CH_3C_6H_4)_3]$, and $Li[Mn(p\text{-}CH_3OC_6H_4)_3]$.[89]

Diphenylmanganese can be obtained by the reaction of phenylmagnesium bromide with manganese chloride, or of phenyllithium with manganese iodide at -50° in tetrahydrofuran solution[90]. Dimethylmanganese forms a fairly stable pale yellow-green precipitate. Mesitylmagnesium bromide reacts with manganese chloride in the molar ratio 2 : 1 in

tetrahydrofuran solution to give a precipitate apparently consisting of dimesitylmanganese, but its structure has not been established. The substance is insoluble in organic solvents, very sensitive to the action of moisture and air, and does not react with alkynes, in particular but-2-yne. Diphenylmanganese similarly does not react with but-2-yne in tetrahydrofuran solution. When two volumes of diethyl ether are added to a tetrahydrofuran solution of diphenylmanganese, cyclic trimerisation of but-2-yne to hexamethylbenzene and the corresponding π complex takes place:



Mn^{II} is not as good an oxidising agent as Cr^{III}, so that the valency state of the manganese in this complex is unity, and this makes the complex isoelectronic with the zerovalent chromium complex[91]. The ability of phenylmanganese to coordinate solvent molecules is lower than that of the chromium compound[90]. Condensation with the formation of naphthalene derivatives is not observed. The fact that diphenylmanganese does not react with butyne in tetrahydrofuran solution is regarded as proof of the comparative stability of the phenyl–manganese bond. This is also illustrated by Tsutsui's data on the relative stabilities of the tetrahydrofuran addition compounds of diphenyl- and dimesityl-manganese[73]: the former decompose when the solvent is boiled, whereas the latter is quite stable at this temperature. This confirms Tsutsui's general hypothesis that the dimesityl derivatives of transition metals are generally more stable than the corresponding phenyl analogues.

Diphenyl- and dimethyl-manganese are decomposed by gaseous hydrogen. The solvent plays an important part in this process. In toluene, diphenylmanganese is unaffected when left to stand and agitated with hydrogen for 24 h, whereas in tetrahydrofuran at 20°, reaction begins rapidly with the formation of benzene and a black powder evidently consisting of the pyrophoric metal[27]. The quantity of hydrogen used corresponds to 0.85 mole per mole of substance; the reaction takes place according to the equation

$$(C_6H_5)_2Mn + H_2 \xrightarrow[20^\circ]{THF} Mn + 2C_6H_6.$$

The reduction of dimethylmanganese takes place in analogous fashion.

Stable organic derivatives of pentacarbonyl manganese, containing σ bonds, are known. The donor carbonyl groups joined to the metal increase the strength of the σ bond between manganese and substituents such as methyl, benzyl, and allyl, and also acetyl, benzoyl, and other acyls. The methyl derivative has been prepared by reaction of the sodium salt of pentacarbonyl manganese with dimethyl sulphate or methyl iodide[92]:

$$NaMn(CO)_5 + CH_3I \rightarrow CH_3Mn(CO)_5 + NaI.$$

Methylpentacarbonylmanganese forms colourless crystals which melt at 95°, are stable in air, and volatilise in a current of gas. The diamagnetic $CH_3Mn(CO)_5$ can be obtained by the action of diazomethane on the "carbonyl hydride"[94]:

$$HMn(CO)_5 + CH_2N_2 \rightarrow CH_3Mn(CO)_5 + N_2.$$

With carbon monoxide, methylpentacarbonylmanganese is converted into an acyl derivative, the process being reversible:

$$CH_3Mn(CO)_5 + CO \underset{t}{\overset{500\ atm,\ 20^\circ}{\rightleftharpoons}} CH_3COMn(CO)_5.$$

The acetyl derivative — a volatile white crystalline product of m.p. 54–55° — can be obtained in 51% yield by reaction of the sodium salt of pentacarbonyl manganese with acetyl chloride[92].

σ-Benzylpentacarbonylmanganese is prepared by a method analogous to that used for the methyl analogue. It is a pale yellow solid melting at 37.5–38.5°, stable to the action of air in the solid state, and less volatile in steam than the methyl derivative[92]. The phenyl-substituted product (m.p. 95–96°) has been obtained by the decarbonylation of benzoylpentacarbonylmanganese:

$$C_6H_5COMn(CO)_5 \rightarrow CO + C_6H_5Mn(CO)_5.$$

The presence of alkyl–manganese and acyl–manganese bonds is proved by the formation of the alkyl bromide or acyl bromide respectively on bromination[92].

σ-Allylpentacarbonylmanganese — an oily lemon yellow liquid which can be distilled *in vacuo* — has been obtained in 82% yield by the action of allyl chloride on the sodium salt of pentacarbonyl manganese in tetrahydrofuran solution[93]. It can be converted into π-allyltetracarbonylmanganese with the liberation of ~1 mole of carbon monoxide, by pyrolysis in a sealed tube at 80° for 12 h.

In Cotton's review[3] it is noted that methylmagnesium iodide in ether reacts vigorously with rhenium trichloride. After hydrolysis of the reaction mixture and removal of the solvent by distillation, fractionation at 60° gave trimethylrhenium in the form of a colourless oil, which burns with the formation of Re_2O_7. When this work was repeated, large quantities of methane and ethane were obtained[95] but no organorhenium compound was isolated. Like manganese, rhenium forms stable derivatives of the metal pentacarbonyl, containing an alkyl–metal σ bond[96].

GROUP VIII

Iron

Covalent compounds of Fe^{2+} and Fe^{3+} have not been isolated in the pure state. Their possible formation in solution during the reaction of iron halides with organometallic compounds of lithium, magnesium, zinc, etc. has been reported[3]. This is indicated by change in colour of the reaction solutions, absorption of hydrogen and acetylene[97], and reduction of the iron. The organic radicals of the organometallic reactants dimerise or disproportionate in the process. Thus the reaction of methyllithium with $FeCl_2$ at ordinary temperatures gives 56% of methane and 24% of ethane[42].

The greatest number of attempts to prepare iron derivatives has been made with the alkyl and aryl organomagnesium compounds. Ethylmagnesium bromide reacts with $FeCl_2$ at 35° to give 49% of ethane and 40% of ethylene. Phenylmercury iodide in the presence of the halides of iron and other metals of Group VIII ($RuCl_3$, $OsCl_3$) undergoes

53–99% conversion into biphenyl[42]. The action of iron(III) chloride on phenylmagnesium bromide in the molar ratio 2 : 1 under ordinary conditions gives chlorobenzene in 40% yield[28].

Reduction of the metal during the synthesis, noted above, may indicate decomposition of intermediate unstable organometallic compounds of iron. In the reaction with phenylmagnesium bromide, the Fe^{3+} is reduced to Fe^{2+}, and in a number of cases reduction to metallic iron takes place. Liberation of highly dispersed metal was observed when the temperature was raised above -40° in a reaction mixture having the composition $6C_6H_5MgBr + 2FeCl_3$.[98]

When the organomagnesium compound was replaced by C_2H_5ZnI, decomposition of the intermediate organoiron compounds did not take place. In this case the change in the ratio $Fe(OH)_2/Zn(OH)_2$ with time was studied by hydrolysed specimens of ethereal solutions of the reaction mixture $C_2H_5ZnI + FeI_2$. It was established that the ratio increased gradually and that after 6 h no ethylzinc iodide remained in solution. On hydrolysis of the final solutions, the quantity of ethane and $Fe(OH)_2$ corresponded to the formation of ethyliron iodide as intermediate product[99]:

$$2\,C_2H_5FeI + HI \xrightarrow{H_2O} 2C_2H_6 + Fe(OH)_2 + FeI_2.$$

This compound could not be isolated in the pure state.

Indirect indications of the possible formation of iron derivatives were obtained in the reaction of $FeCl_3$ or $FeCl_2$ with tetraethyllead, tetraethylsilicon, triphenylbismuth, etc.[101]. The reported formation of organoiron compounds by the reaction of pure iron with alkyl bromides is extremely doubtful[100].

Reports of the preparation of diaryl derivatives of iron by reaction of the corresponding mercury derivatives with iron powder at 120–125° [102] were found to be erroneous[103]. The tetrahydrofuran addition compounds of diphenyliron and dimesityliron are more stable, but these compounds are also decomposed at temperatures below -10°.[73]

The more stable mixed π-cyclopentadienyl compounds of the type π-$C_5H_5Fe(CO)_2R$, containing a σ bond between the metal and the methyl, ethyl, phenyl, or cyclopentadienyl groups, have been isolated in the pure state[26,104]. The methyl derivative was obtained in 50% yield by the reaction of a methylmagnesium halide with a halogeno-π-cyclopentadienyldicarbonyl compound of iron in ethereal solution:

$$\pi\text{-}C_5H_5Fe(CO)_2I + CH_3MgI \rightarrow \pi\text{-}C_5H_5Fe(CO)_2CH_3 + MgI_2.$$

The yield of this compound is increased to 70% in the reaction of an alkyl halide with the sodium salt of the π-cyclopentadienyl derivative. When ethyl iodide is used, the ethyl derivative is formed in 60% yield. The yield of the phenyl analogue is only 2–5%.

The action of cyclopentadienylsodium on the bromide π-$C_5H_5Fe(CO)_2Br$ in tetrahydrofuran solution gave the compound π-$C_5H_5Fe(CO)_2$-σ-C_5H_5, in which the second cyclopentadienyl group is joined to the metal atom by a simple σ bond.

These compounds are diamagnetic coloured products with definite melting points[26]. They are soluble in organic solvents, sublime readily in a high vacuum at 25–50°, and have characteristic odours. In solution, all the compounds are decomposed by air. The stability of the organoiron compounds decreases in the order phenyl > methyl > ethyl. These compounds are insoluble in water and do not react with it; they are decomposed by acids and bases. The action of acids gives the cation $[Fe(\pi\text{-}C_5H_5)(CO_2)]^{2+}$ (possibly hydrated), which yields characteristic Reinecke's salts. The action of iodine leads to quantitative formation of the iodide and the corresponding aryl or alkyl iodide. With the exception of the σ-cyclopentadienyl derivative, these compounds do not react with maleic anhydride. The reaction with the latter leads to a rapid change in colour, but the adduct obtained with maleic anhydride is unstable and cannot be isolated and identified.

Cobalt

Coupling of C_6H_5MgX takes place readily in the presence of added cobalt(II) chloride. The stoichiometric coupling of 0.03 mole of phenylmagnesium iodide with 0.01 mole of $CoCl_2$ gave 98% of biphenyl[42]. In the catalytic coupling, the yield of biphenyl is slightly lower and amounts to 86%.

The first papers on the preparation of organometallic compounds of cobalt of the type $RCoX_3$ and R_2CoX_2 appeared during 1949–1951. It was reported that the reaction of organomagnesium derivatives with cobalt bromide or iodide gave products with R representing methyl, ethyl, propyl, isopropyl, 1-naphthyl, and 2-naphthyl[105-107]. The compounds were obtained as coloured products decomposing at 65–160°. Some of their properties appeared to contradict the assumed formulae. For example, hydrolysis of a naphthyl derivative with water or dilute acids yielded chiefly binaphthyl. This gave the impression that the naphthyl groups were joined to one another in the same way as the phenyl groups in Hein's polyphenylchromium compounds. At the same time, doubt was cast on the possibility of formation of quadrivalent cobalt compounds under the conditions of the reducing medium in Grignard reactions[3].

The preparation of diallylcobalt, proposed as an additive to drying oils, has been reported in the patent literature[108,109], but there is no information on the methods of synthesis and the properties of this compound.

The formation of organometallic compounds of cobalt is indicated by the abnormal reactions of organomagnesium compounds in the presence of added cobalt salts. Kharasch and his coworkers have shown that the addition of 2–5 mole % of $CoCl_2$ to a Grignard reagent leads to a change in the mechanism of the reactions from ionic to free-radical[110-114]. An analogous but less marked effect is produced by iron(II) chloride and nickel(II) chloride. These results were attributed to the existence of intermediate unstable organocobalt compounds, which decompose with the formation of a cobalt subhalide; the latter brings about chain decomposition of the aryl or acyl halides:

$$RMgX + CoCl_2 \rightarrow RCoCl + MgXCl,$$

$$RCoCl \rightarrow R^{\cdot} + {}^{\cdot}CoCl,$$

$${}^{\cdot}CoCl + R'X \rightarrow R'^{\cdot} + CoXCl,$$

$$n\,R'^{\cdot} \rightarrow R'H + R'_2 + \text{other products.}$$

The conditions for the decomposition of RCoX may characterise the relative stability of the alkyl–cobalt and aryl–cobalt bonds. The reaction mixture of methylmagnesium bromide with added cobalt chloride loses its ability to bring about the dimerisation of phenyl radicals from bromobenzene after being heated for $1\frac{1}{2}$ h.[110] Coupling takes place quantitatively with a freshly prepared ethereal solution. Under the same conditions, phenylmagnesium bromide containing added $CoCl_2$, without preliminary heating, gives 98–99% of biphenyl from the phenyl radicals

of bromobenzene, but after heating for $1\frac{1}{2}$ h the yield of biphenyl amounts to only 50%. This indicates that the methyl–cobalt bond is less stable than the phenyl–cobalt bond. Contrary to Kharasch's opinion, however, the formation of symmetrical organocobalt compounds by the action of $CoCl_2$ on an organomagnesium compound is now considered more probable [115]:

$$2C_6H_5MgBr + CoCl_2 \rightarrow MgBr_2 + MgCl_2 + (C_6H_5)_2Co,$$

$$(C_6H_5)_2Co \rightarrow C_6H_6 + C_6H_4 + Co.$$

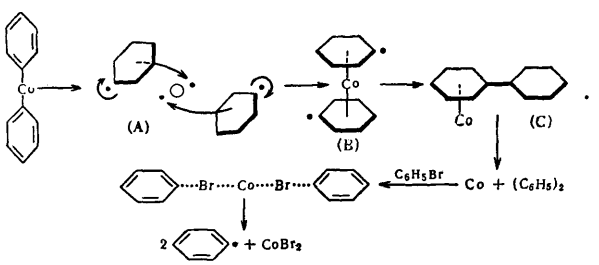
Decomposition of these compounds takes place with the separation of finely divided metallic cobalt, which brings about the chain reaction.

Proof of the existence of diaryls of cobalt is provided by the ability of phenylmagnesium bromide solutions containing CoX_2 to absorb hydrogen. The formation of benzene and cobalt hydride in the process is attributed to hydrogenation of the intermediate unstable diarylcobalt [97]:

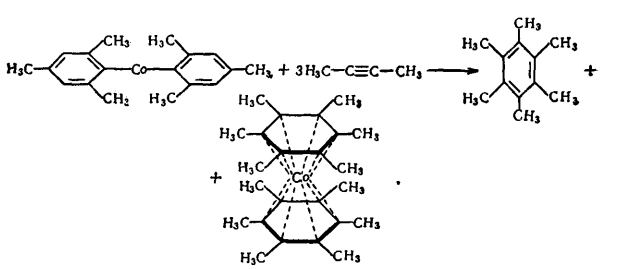
$$(C_6H_5)_2Co + 2H_2 \rightarrow CoH_2 + 2C_6H_6.$$

Finally, it has been possible to isolate diphenylcobalt and dimesitylcobalt in the form of the tetrahydrofuran addition compounds [74,90]. The dimesityl compound was obtained by the reaction of mesitylmagnesium bromide with cobalt chloride in tetrahydrofuran solution. The product is a yellow-green powder which is stable in the form of the tetrahydrofuran addition compound at -10° but which begins to decompose rapidly at room temperature. The presence of a mesityl–cobalt bond was proved by the quantitative formation of mesitylmercury chloride on reaction with mercuric chloride [90].

Tsutsui describes the conversion of the diarylcobalt compounds into the π complexes. The unstable diphenylcobalt formed initially undergoes gradual rearrangement with rotation of the aromatic rings via the π-radical hybrid (A) and the diradical π complex (B) to the half-sandwich π complex (C): [73]



Dimesitylcobalt catalyses the cyclic condensation of but-2-yne. The reaction takes place between -30° and -50° in tetrahydrofuran solution, with the formation of hexamethylbenzene (the yield varies in the range 50–100%, calculated on the organocobalt compound) and the π complex bishexamethylbenzenecobalt, the yield of which (20%) is independent of the alkyne concentration [91]:



The exceptional catalytic properties of dimesitylcobalt in this reaction are due to the unusual electronic structure of the π complex.

The organocobalt compounds confirm the general hypothesis that the complexes of organic derivatives of the transition metals are more stable than the diaryls. Stabilisation of the aryl–cobalt bond is observed in the complexes of a diarylcobalt with phosphines [116]. The *trans*-planar complexes of dimesitylcobalt and bismethylnaphthylcobalt with phenyldiethylphosphine $[C_6H_5P(C_2H_5)_2]_2CoR_2$ have a very small or no dipole moment, in conformity with their structure.

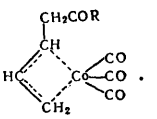
A methyl–cobalt bond is present in the mixed carbonyl of cobalt obtained by reaction of the sodium salt of the carbonyl with methyl iodide [117]:

$$Na[Co(CO)_4] + CH_3I \rightarrow CH_3Co(CO)_4 + NaI.$$

A number of interesting reactions of this unstable product have been described. Methyltetracarbonylcobalt readily undergoes rearrangement to acetyltricarbonylcobalt, and treatment of the latter with carbon monoxide leads to the formation of the acyltetracarbonylcobalt:

$$RCo(CO)_4 \rightleftarrows RCOCo(CO)_3 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} RCOCo(CO)_4.$$

Alkyl- and acyl-tetracarbonylcobalts react with conjugated dienes — butadiene, isoprene, cyclopentadiene, etc. — to form complexes of the type [118]



The same type of complex, with a bond between cobalt and the alkene, like that in the alkene complexes of platinum [119], has been obtained by reaction of the potassium salt of cobalt carbonyl with butadiene [120]. Study of the proton resonance, infrared, and ultraviolet spectra indicate that the compound is diamagnetic and contains no conjugated diene.

Nickel

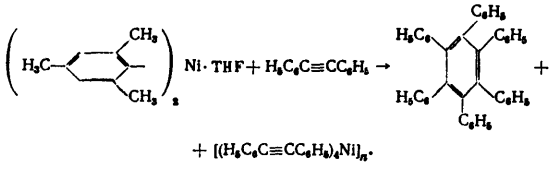
A great deal of indirect data indicates that the simplest organonickel compounds exist in solution, but these have not been isolated in the pure state [121–123]. The most noteworthy reaction is the coupling of phenyl Grignard reagents, which takes place readily in the presence of nickel salts. With aliphatic organomagnesium compounds, liberation of ethylene, acetylene, etc. is observed. In the presence of gaseous hydrogen, a freshly prepared reaction suspension of phenylmagnesium bromide in ether containing added $NiCl_2$ absorbs 2 moles of hydrogen per gramme-atom of nickel to give pyrophoric black nickel hydride [124]. It was suggested that the latter was produced by reduction of the hypothetical diphenylnickel formed in the initial stage:

$$NiCl_2 + 2C_6H_5MgBr \rightarrow (C_6H_5)_2Ni + MgCl_2 + MgBr_2,$$
$$(C_6H_5)_2Ni + H_2 \rightarrow 2C_6H_6 + NiH_2.$$

The instability of diphenylnickel is indicated by the following facts. If the reaction suspension containing $NiCl_2$ is kept for some time before the reaction of hydrogen, the yield of hydride is decreased considerably. After standing for 4 h at room temperature the system does not absorb hydrogen; no nickel hydride was found in the reaction products.

The formation of phenyl and mesityl compounds of nickel is indicated by the deep colour produced by the action of nickel chloride on the corresponding organomagnesium compound in tetrahydrofuran solution. The reddish brown colour is attributed to the tetrahydrofuran addition compounds of diphenylnickel and dimesitylnickel. Thus reaction of 0.01 mole of $NiCl_2$ in 50 ml of tetrahydrofuran with 0.02 mole of RMgBr between -30° and -70° gives tetrahydrofuran addition compounds which cannot be isolated in the pure state because of their low thermal stability. They begin to decompose at temperatures below -10°.[73]

The thermally unstable tetrahydrofuran addition compounds of R_2Ni are used in solution for the characteristic reactions involving cyclisation of disubstituted alkynes. Diethylnickel converts diphenylacetylene into tetraphenylcyclohexadiene[125]. Reaction of diphenylacetylene with the tetrahydrofuran addition compound of dimesitylnickel gives hexaphenylbenzene and a nickel-containing polymer. At an original component ratio of 1 : 4 the chief reaction product is the polymer, which is precipitated from solution as a dark orange, insoluble, amorphous precipitate:



$$+ [(H_5C_6C{\equiv}CC_6H_5)_4Ni]_n.$$

With increase in the ratio from 1 : 4 to 1 : 6, the chief reaction product becomes hexaphenylbenzene, which can be isolated in yields corresponding to 1.7–2.0 moles per mole of the organonickel compound[74,91]. Cyclisation of this type is attributed to the formation of an intermediate cyclobutadiene compound.

The complexes of R_2Ni with triethyl- or triphenyl-phosphines $(R'_3P)_2NiR_2$ and $(R'_3P)_2Ni(R)X$ are more stable. These compounds can be obtained by the reaction of the corresponding dihalide with an organomagnesium compound in liquid ammonia[116]. They are brightly coloured products, usually yellow-brown, with characteristic melting points. The derivatives with R = phenyl, *o*-tolyl, *o*-chloro- and *o*-bromo-phenyl, *o*-methoxyphenyl, mesityl, biphenylyl, pentachlorophenyl, and naphthyl, and R′ = phenyl, ethyl, propyl, and mixtures of these, have been isolated.

The thermal stability of these complexes depends to a marked extent on the nature of the radical from the organomagnesium compound, increasing in the order alkyl < phenyl < *m*- and *p*-substituted phenyl < *o*-substituted phenyl[126]. The alkyl complexes are less stable and have not been isolated in the pure state. The phenyl derivative decomposes rapidly in ethanol solution and melts with decomposition at 125–130°. The symmetrical mesityl compound melts at 148–150°, and the unsymmetrical compound sublimes *in vacuo* without decomposition at 150°.

The influence of *ortho*-substituents is due to steric hindrance to free rotation of the aryl groups about the nickel–carbon bond. The electronic systems of the aromatic rings undergo more energetic interaction with the *d* orbitals of the metal.

These compounds are diamagnetic and symmetrical, and have a low dipole moment. With the symmetrical and unsymmetrical derivatives, *trans*-planar arrangement of the groups relative to the nickel atom is observed. The chemical reactions indicate the mobility of the metal–radical bond, which is readily broken by hydrogen chloride with formation of a hydrocarbon and an unsymmetrical product:

$$trans\text{-}[(R'_3P)_2NiR_2] + HCl \rightarrow trans\text{-}[(R'_3P)_2Ni(R)Cl] + RH.$$

In the unsymmetrical derivatives, the chlorine atom is readily replaced by bromine or iodine atoms or nitro- or thiocyanato-groups[126].

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The above review shows that organic compounds of metals of the transition periods, containing a covalent metal–carbon bond, form a special class of compounds. Unlike the organometallic compounds of non-transition elements, which exhibit different characteristic chemical properties according to the groups of the Periodic System, the alkyls and aryls of the transition metals show a number of common chemical properties. Thus, for example, the covalent metal–carbon bond is readily broken by the action of hydroxyl-containing compounds, such as water, alcohols, acids, etc. The reaction of alkyls and aryls of the transition metals with halogens and halides is characteristic. These reactions are often used as analytical tests to prove the presence of an element–radical σ bond. Another typical property of most of these derivatives is their ready oxidation by oxygen and other oxidising agents.

The most characteristic property of these compounds — their thermal instability — is due to the presence of the incomplete electron sublevel of the central transition metal atom. The general characteristics of the electronic structure of the transition elements and the associated types of hybridisation involved in the formation of σ bonds have been examined more than once by Krause and von Grosse[1], Zeiss[4], Jaffé[127], and other workers.

The presence of vacant *d* sublevels in the transition metal atom makes possible the filling of these levels by various electron-donating ligands, such as amines, phosphines, ethers, and also carbonyl, nitrosyl, π-cyclopentadienyl, etc. These mixed sandwiches, carbonyls, or complexes with phosphines and other ligands are generally more stable to heat and also to oxidation and the action of other agents.

These compounds are of considerable interest in the study of the nature of the chemical bond. The intensified development of this field, however, is due not only to the theoretical importance of the subject but also to its considerable value in applied chemistry.

This review has not dealt with the exceptionally important problems associated with the use of catalytic systems based on organometallic derivatives of the transition metals. The mechanism of the stereoregular polymerisation of alk-1-enes depends to a marked extent on the properties of the intermediate covalent compounds of titanium, vanadium, and other transition metals[28,128,129]. Brief mention has been made of the interesting processes involving the cyclisation of disubstituted acetylenes with the participation of compounds of chromium, nickel, cobalt, etc.[77,78,91,130].

This young and rapidly developing field of chemistry dealing with the organometallic compounds of the transition metals promises to provide much of both theoretical and practical interest in the future.

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ADDITION OF α-CHLOROALKYL ETHERS TO UNSATURATED COMPOUNDS

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1. INTRODUCTION

In his review of the addition of alkyl halides to olefins Arbuzov[1] dealt in some detail with the El'tekov[2] and Kondakov[3,4] reaction, and Summers[5] reviewed the preparation and reactions of α-chloro-ethers, covering the literature up to 1955; however, in neither review did the addition of α-chloro-ethers to unsaturated compounds receive much attention. Nevertheless, in recent years much interesting work on the electrophilic addition of chloro-ethers to multiple bonds has appeared. In the present paper we have attempted to collect and classify the considerable material which has now accumulated on this subject.

2. ADDITION OF α-CHLOROALKYL ETHERS TO OLEFINS

α-Chloroalkyl ethers are much more reactive than alkyl halides, and they behave analogously to hydrogen halides. Cocker et al.[6] associate the activity of the labile chlorine atom in α-chloro-ethers with the simultaneous existence of a carbonium ion and an oxonium ion:

$$R-\overset{+}{C}H-\ddot{O}-R' \longleftrightarrow R-CH=\overset{+}{\ddot{O}}-R'.$$

Chloromethyl ether undergoes rapid hydrolysis and alcoholysis in aqueous and alcoholic solutions, yielding formaldehyde and a dialkoxymethane respectively. The rapidity of such processes has led many workers to conclude that the reactions are unimolecular, and this has been confirmed kinetically[7]. The rate-determining step is ionisation of the chloro-ether to produce a mesomeric carbonium ion, which rapidly adds on a hydroxide or alkoxide ion from the solvent:

$$CH_3-\ddot{O}-CH_2-Cl \xrightarrow[\text{slow}]{} CH_3-O-\overset{+}{C}H_2 + Cl^-,$$

$$ROH + CH_3O-\overset{+}{C}H_2 \xrightarrow[\text{fast}]{} CH_3OCH_2OR + H^+$$

(R = H or alkyl).

At room temperature in anhydrous solvents (or in the absence of a solvent), α-chloroalkyl ethers add to olefins in the presence of acidic catalysts by an ionic mechanism