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Reactions of Transition Metals in the Atomic State

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The formation of organometallic compounds and π complexes by the direct action of the atomic metal on organic and inorganic compounds is surveyed. The mechanism of these reactions is examined, and practicable recommendations are given for conducting them. A list of 100 references is included.

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I. INTRODUCTION

During recent years research has been vigorously pursued on the reactions of various metals in the atomic state, as well as on individual valency-unsaturated species. The possibility of using atomic metals for preparative purposes has been studied[1-4]. Condensation of the vapours of magnesium and a monomer—styrene, α-methylstyrene, isoprene, acrylonitrile—together at $-196^{\circ}C$ yields yellow–orange frozen solutions. Thawing is accompanied by vigorous polymerisation, which is often explosive. Among polymerisation initiators—magnesium, zinc, cadmium, calcium, mercury—atomic magnesium has proved the most active[3,4]. Tin and lead do not exhibit activity, and in the ternary systems with a monomer and magnesium, inhibition of polymerisation has even been observed. Electron spin resonance has shown[2] that polymerisation is initiated by a radical formed by the reaction

$$CH_2{=}CH + Mg \rightarrow \overset{\oplus}{M}g{-}\overset{\ominus}{C}H_2{-}\dot{C}H \quad (1)$$
$$\qquad\qquad\quad | \qquad\qquad\qquad\quad |$$
$$\qquad\quad CN \qquad\qquad\quad CN$$

Such radicals, frozen in excess of the monomer on the cooled walls, initiate polymerisation at temperatures far below the melting point of the monomer. Extension of the fundamental reaction to the vapours of carbon[5] and transition metals[6] has now led to the establishment of a new field in the synthetic chemistry of organometallic compounds.

The Reviewers have now made a general survey of this problem, paying attention to theoretical aspects, assessing experimental methods and equipment, with the introduction of an actively and constantly extending range of compounds into reaction (1), and prospects for employing this reaction in synthetic organometallic and applied chemistry. Existing reviews[6-8] are devoted to particular problems or else give inadequate coverage of the most recent results.

Hitherto studied reactions of organic and inorganic compounds with transition metals in the atomic state can be divided into those involving addition and those involving oxidative incorporation of the metal at various bonds. The classification of organometallic compounds of transition metals according to types of ligands is at present regarded as more convenient. In reporting the factual material, however, we have slightly modified the classification by taking as basis the maximum possible number of electrons that the compound used in the synthesis is able to donate to the metal.

II. TYPES OF REACTIONS

1. Addition of Atomic Metals

(*a*) Reactions with eight-membered carbocyclic $h^8\pi$ donors (cyclo-octatetraene)

Hardly any reactions with cyclo-octatetraene have been reported, apart from a brief mention[9] of the synthesis of dicyclo-octatetraeneuranium. The cocondensation of gaseous iron with the hydrocarbon in the presence of trifluorophosphine forms $C_8H_8Fe(PF_3)_3$, the low yield of which is probably due to slight polymerisation of cyclo-octatetraene on reaction with atomic metals[10]. However, the synthesis of $(C_8H_8)_2M$ (where M = U, Th, Pu) from the dispersed metals and cyclo-octatetraene[11] indicates that these compounds can be obtained also by low-temperature cocondensation from the gaseous metals.

(*b*) Reactions with seven-membered carbocyclic $h^7\pi$ donors

Cycloheptatriene behaves differently towards different atomic metals. Thus the cocondensation of chromium vapour with cycloheptatriene gives a mixture of products, among which the complex $(C_7H_8)_2Cr$ and the component $C_{14}H_{17}Cr$ have been detected mass-spectrometrically[12-14]. The h^4-cyclohepta-1,4-diene-h^7-cycloheptatrienylchromium complex, corresponding to the compound $C_{14}H_{17}Cr$, had been described earlier[15]. The condensation of chromium vapour with cycloheptatriene and trifluorophosphine leads to the isolation of $C_7H_8Cr(PF_3)_3$,[12,14] but the cocondensation of cycloheptatriene with atomic molybdenum or tungsten gives the h^5-cycloheptadienyl-h^7-cycloheptatrienyl derivative, in which the former ligand is easily exchanged for cyclopentadienyl[16,17]. Iron vapour reacts smoothly with cycloheptatriene to give a good yield of $C_7H_9FeC_7H_7$,[13,18] in which the cycloheptadienyl and tropylium systems are coordinated to the iron atom and exhibit dynamic behaviour $C_7H_7 \rightleftharpoons C_7H_9$ in solution. The nuclear magnetic resonance and mass spectra of the product have been determined, and an X-ray structural analysis has been made[18]. Cobalt reacts with cycloheptatriene in the presence of trifluorophosphine to give an allyl derivative, h^3-cycloheptenyltetrakistrifluorophosphinecobalt, and tristrifluorophosphinecobalt hydride[19].

(*c*) Reactions with six-membered carbocyclic $h^6\pi$ donors (arenes)

The use of atomic metals has opened up wide prospects for synthesising diarene complexes of various metals, as well as complexes of functionally substituted benzene derivatives.

Diarene complexes of titanium $Aren_2Ti$ [where Aren = C_6H_6, $C_6H_5CH_3$, $C_6H_3(CH_3)_3$] have been obtained for the first time[20,21]. Dibenzenetitanium comprises reddish-orange crystals that are extremely sensitive to air; they sublime readily at 80°C (10^{-3} mmHg) and begin to decompose above this temperature. The structure of diarene complexes of titanium has been proved by the ^1H n.m.r., infrared, mass, and photoelectronic spectra[21]. In contrast to other methods, the yield of an organometallic compound obtained from the gaseous metal is a measure of the stability of the compound, since it is determined also by the reverse decomposition to the metal and the ligand. In some cases, however, the yield probably depends also on secondary processes. It is interesting to trace the variation in the yield (calculated on the metal vaporised) in a series of diarene complexes of vanadium[22-24]:

$(C_6H_6)_2V$ (60%), $(C_6H_5CF_3)_2V$ (22%), $(C_6H_5F)_2V$ (13%), $(C_6H_5Cl)_2V$ (7%), $(p\text{-}C_6H_4F_2)_2V$ (1%).

Hexafluorobenzene forms with vanadium vapour an extremely reactive and explosive complex[22].

An immense number of diarene compounds of chromium have been obtained by the direct method. The first such derivative was dibenzenechromium[25,26], obtained in ~60% yield (calculated on the metal vaporised) by the interaction of chromium and benzene vapours. By removing the need for intermediate reagents, use of the metal in its most reactive form permits partial avoidance of the transalkylation and elimination processes that accompany Fischer reduction[27,28].

The compounds obtained include dibenzenechromium derivatives substituted by CH_3, C_2H_5, Cl, F,[12] $[CH_2]_nCOOR$ ($n = 0-2$),[29,30] t-C_4H_9,[19] iso-C_3H_7,[31] CF_3,[24] and C_6H_5[32] with various substituents[23,33-35]. Diarenechromium complexes have been obtained from polysubstituted arenes containing *o*-COOR,[36] *p*-F,[12] *m*-iso-C_3H_7,[31] *m*- and *p*-CF_3, and *o*-Cl.[24] Complexes have been prepared having different substituents in the ring (H, F, Cl, CH_3, CF_3) and different numbers of these substituents in the rings[33]. The ^{19}F n.m.r. spectra have been compared with those of the original organic molecules[33], and the ^{13}C n.m.r. spectra have been determined[34]. The synthesis of bisborazinechromium was reported[37], but no confirmation has subsequently appeared in the literature.

Mixed complexes can be obtained by the cocondensation of chromium vapour with a mixture of compounds:

$$Cr + Aren + nL \rightarrow (Aren)Cr(L)_n \quad n = 1, 3;\ L = Aren',\ PF_3 \qquad (2)$$

Thus the complex $C_6H_6CrC_6HF_5$, stable in air, has been obtained from a mixture of benzene and pentafluorobenzene[38]. The acidic hydrogen atom in the second ligand is very readily replaced by a lithium atom on metallation with t-butyl-lithium in ethereal solution; various derivatives of the type $C_6H_5CrC_6H_5X$ could be obtained by replacing the lithium, with X = $Si(CH_3)_3$, Co_2Li, $C(CH_3)_2OH$, $CpFe(CO)_2$, $CpFeC_5H_4CHOH$.[36] Cocondensation of chromium vapour with a mixture of benzene and hexafluorobenzene gives $C_6H_6CrC_6F_6$.[32] Timms[19] obtained a series of mixed complexes $ArenCr(PF_3)_3$, where Aren = C_6H_6, C_6H_5F, 1,4-$C_6H_4F_2$, 1,3,5-$C_6H_3F_3$, 1,2,3,5-$C_5H_2F_4$, C_6HF_5, C_6F_6. The cocondensation of chromium vapour solely with hexafluorobenzene gives an extremely reactive, explosive complex[22,24].

Work on the preparation of diarene and mixed complexes of chromium, as well as vanadium complexes, reveals a tendency for the yield of the addition product to decrease with increase in the electron-accepting properties of the groups in the ring. However, certain complexes of chromium with halogenobenzenes are obtained in higher yield than are the complexes with benzene itself[12]. In a series of compounds of general formula $ArenCr(PF_3)_3$ maximum and minimum yields were obtained when the arene was respectively *p*-difluorobenzene and hexafluorobenzene[19]. An interesting distribution of yields is exhibited[24] by the compounds $[p\text{-}(CF_3)_2C_6H_4]_2Cr$ (38%), $(o\text{-}ClC_6H_4CF_3)_2Cr$ (33%), $[m\text{-}(CF_3)_2C_6H_4]_2Cr$ (17%), and $(C_6H_5CF_3)_2Cr$ (26%). The high yields of the diarene complexes of chromium containing two electron-accepting substituents in the benzene ring of the ligand are combined with unusual stability of these compounds in air. The decrease in the yields of complexes of polyhalogenated arenes is explained by an increasing tendency for dehalogenation to occur, but the high yield of $p\text{-}C_6H_4F_2Cr(PF_3)_3$ in comparison with $C_6H_6Cr(PF_3)_3$ by kinetic factors[19].

The cocondensation of chromium vapour with pyridine and trifluorophosphine produces a mixture of the two volatile compounds $\pi\text{-}C_5H_5NCr(PF_3)_3$ and $\sigma\text{-}C_5H_5NCr(PF_3)_3$[19,32]. The former is a true π complex of pyridine; it is stable in air for a short time. Its decomposition is promoted by moist air[19].

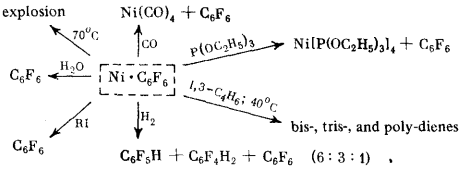
Elimination of electron-accepting groups (bromo, iodo, cyano) under the influence of the atomic metal is sometimes observed[33,37] in the preparation of diarene complexes by the cocondensation of chromium vapour with arenes. This is accompanied by resinification of the organic compound with formation of bound hydrocarbon products and chromium compounds in an oxidised state. Thus an almost theoretical yield of chromium tribromide is obtained by the cocondensation of chromium vapour with bromobenzene[33]. Analogous elimination of electron-accepting substituents from the benzene ring takes place in the Fischer preparation of diarenechromium derivatives[27,28]. The elimination is probably due to enhanced mobility of the substituent in the form of an anion in the actual diarene complex owing to transfer of electron density from the metal to the electron-accepting group.

Diarene compounds are not formed by the action of gaseous manganese on arenes[19]. The cocondensation of manganese vapour with a mixture of an arene and cyclopentadiene gives mixed complexes $ArenMnC_5H_4R$, where Aren = C_6H_6, $C_6H_5CH_3$, 1,3,5-$C_6H_3(CH_3)_3$, and R = H, CH_3.[19] Hydrogen begins to be evolved only at −120°C.[13,19] Since the reaction was conducted by feeding cyclopentadiene to the reaction vessel after the cocondensation of manganese and benzene, cyclopentadienyl derivatives are obviously not preliminary products. The yield of $C_6H_6MnC_5H_5$ calculated on the manganese vaporised is 2−3%,[13] whereas the yield of the same product from the reaction between manganese(II) chloride, phenylmagnesium bromide, and sodiocyclopentadiene is only 0.4%.[39] Direct synthesis is more convenient for the preparation of arenocene complexes of manganese, since this metal can be evaporated from a resistance vaporiser at a rate of 20−100 mg-atoms h^{-1}.[6]

The cocondensation of iron vapour with benzene obviously forms dibenzeneiron[25,31,40], but this explodes when the reaction mixture warms up to −50°C. If cyclopentadiene is added to this cocondensate at −196°C, a 40%

yield of ferrocene is formed on thawing out[25], but $C_6H_6FeC_5H_5$ is not formed. When the cocondensate of iron with benzene heats up to room temperature in an atmosphere of hydrogen, part of the benzene is hydrogenated to cyclohexane. Toluenebistrifluorophosphineiron has been isolated[40] from the cocondensation of iron vapour with toluene followed by addition of trifluorophosphine at −196°C. If buta-1,3-diene is used instead of trifluorophosphine, buta-1,3-dienetolueneiron is formed[40]. According to Timms[19] the stable eighteen-electron complex h^6-mesitylene-h^4-1,3,5-trimethylcyclohexa-1,3-dieneiron-(0) is formed by the cocondensation of iron vapour with mesitylene, but the formation of a diene ligand from this hydrocarbon is difficult to understand. With cyclohexa-1,3-diene iron vapour gives h^6-benzene-h^4-cyclohexa-1,3-dieneiron(0). When the cocondensate is heated to −20°C, the hydrocarbon undergoes catalytic disproportionation to cyclohexane and benzene.

Gaseous nickel does not react with benzene under conditions of direct synthesis. The nickel atom is not incorporated at a carbon–fluorine bond when atomic nickel acts on hexafluorobenzene[22], but an unstable, extremely reactive, and explosive complex of zerovalent nickel is formed. Proof of its formation is provided by its reactions



(3)

At low temperatures nickel probably gives unstable intermediate complexes with arenes. On heating or removal of the ligand atomic nickel undergoes aggregation to a highly active mass[24,41,42]. Like nickel, cobalt forms with hexafluorobenzene a complex that decomposes at −10°C.[22] Furthermore, mixed complexes of cobalt and nickel have been obtained, analogous to the iron compounds ArenFe.$(PF_3)_2$ and ArenFe-1,3-C_4H_6.[40]

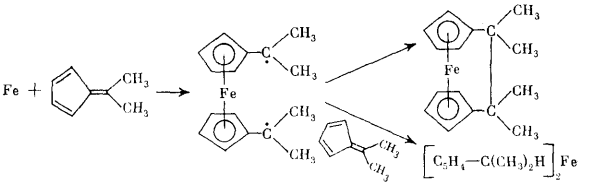
The reactions of atomic molybdenum and tungsten have been studied by two teams of investigators. Diarene complexes of molybdenum have been obtained with Aren = C_6H_6, $C_6H_5CH_3$, 1,3,5-$C_6H_3(CH_3)_3$,[20] $C_6H_5OCH_3$, $C_6H_5N(CH_3)_2$, C_6H_5F, C_6H_5Cl, and $C_6H_5COOCH_3$; and of tungsten with Aren = C_6H_6, $C_6H_5CH_3$, o-$C_6H_4(CH_3)_2$, $C_6H_5OCH_3$, C_6H_5F.[43]

Attempts to obtain arene derivatives of lanthanides (samarium, erbium) did not give definite results[9]. The volatile products obtained were not identified.

(*d*) Reactions with five-membered carbocyclic $h^5\pi$ donors (cyclopentadienyls, etc.)

These reactions are interesting if only because cyclopentadiene possesses a "spare" hydrogen atom for the formation of an h^5-C_5H_5–Metal bond. Cyclopentadiene therefore behaves differently depending on the nature of the metal.

The synthesis of ferrocene by the cocondensation of freshly distilled cyclopentadiene and iron vapour, in 60% yield based on the iron vaporised, was first reported by Timms[25]. Under these conditions nickel gave an 80% yield of h^5-cyclopentadienyl-h^3-cyclopentenylnickel. No subsequent communications have appeared on the synthesis of ferrocene, but in a review[6] Timms referred to Skell in connection with such a synthesis†. More recently the preparation of a mixture of 1,1′-di-isopropylferrocene and ferrocenophan has been reported[44] by the cocondensation of the vapours of iron and dimethylfulvene, for which the mechanism



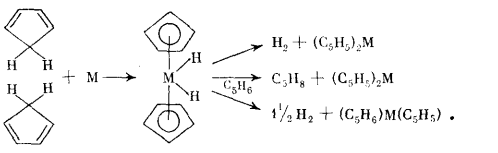
(4)

was suggested. Although the presence of bound ferrocene was not clearly demonstrated[44], the process is of great interest.

Hydrogen evolution is observed in the reaction of atomic chromium with monomeric cyclopentadiene[12], and a 50% yield of dicyclopentadienylchromium is obtained. The hydrogenation product cyclopentene is detected among the reaction products[12]. In the case of atomic cobalt the reaction with cyclopentadiene involves the formation of h^4-cyclopentadiene-h^5-cyclopentadienylcobalt in 50% yield calculated on the metal vaporised[6].

Manganese does not react with cyclopentadiene under conditions of direct synthesis (the mixed arene–cyclopentadienyl complexes have been discussed above). Especially interesting reactions occurred in the action of atomic molybdenum and tungsten on monomeric cyclopentadiene[45], when the di-h^5-cyclopentadienylmetal dihydrides were formed. The characteristics of the products agreed well with those of the compounds obtained in the traditional way[46]. The cocondensation of molybdenum or tungsten vapour with an equimolecular mixture of benzene (or an alkylbenzene) and cyclopentadiene gives a mixture of 20% of a diarene complex, 25% of a dihydride, and 55% of a monohydride[47]. The h^6-arene-h^5-cyclopentadienylmolybdenum monohydride obtained sublimes readily under 1 μmHg at 65°C. Preliminary results[47] on the action of atomic molybdenum and tungsten on indene indicate formation of a mixture of the di-indenylmetal, di-indenyl dihydride, and di-indenyl monohydride.

Thus results on the reactions of metal vapours—iron, chromium, cobalt, molybdenum, tungsten—with cyclopentadiene can be summarised on the hypothesis that all the reactions have the mechanism

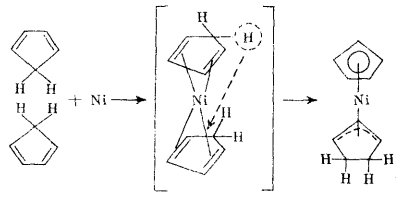


(5)

A possible alternative is intramolecular dehydrogenation–hydrogenation of the h^4-cyclopentadiene ligands with their

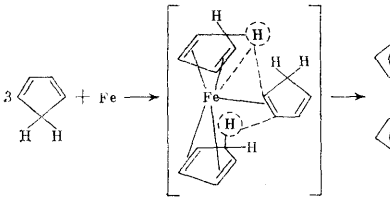
† The paper to which Timms[6] refers does not actually mention ferrocene[100].

aromatisation:



(6)

The coordinated double bond of a third cyclopentadiene molecule may also undergo intramolecular hydrogenation, facilitated by cooperation of the metal atom:



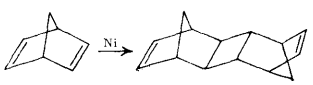
(7)

The mechanism of migration of the hydrogen atom is probably analogous to the hydride rearrangement. The stability of hydro-derivatives of transition metals (such as rhenium, niobium, tantalum, molybdenum, and tungsten) increases[48] with the atomic weight of the metal; hence, according to the above hypothesis, the same dependence should exist for the intermediate hydride complexes formed in the reaction of metal vapours with cyclopentadiene. It therefore seems to us possible that stable hydride complexes may be isolated when the vapours of other "heavy" transition metals undergo cocondensation with cyclopentadiene.

The cocondensation of nickel vapour with the *closo*-carborane $C_2B_9H_{11}$ gives the well known complex $(C_2B_9H_{11})_2Ni$.[19]

(*e*) Reactions with dialkene $h^4\pi$ donors

Reactions with cyclic dienes. The action of atomic nickel on cyclo-octa-1,5-diene gives the complex $(C_8H_{12})_2Ni^0$ [49] described earlier by Wilke[50], whereas with norbornadiene the *exo-trans-exo*-dimer is formed[49]



(8)

instead of an organometallic product. With atomic metals the former hydrocarbon gives several isostructural complexes $(C_8H_{12})_2M$, where M = Pt,[51] Fe.[10] The iron complex was synthesised at −120°C, iron being sputtered into a solution of the hydrocarbon in methylcyclohexane (other solvents have also been used). Formation of the complex is proved by its reaction with 2,2′-bipyridyl[10]:

$$(1,5\text{-}C_8H_{12})_2Fe + 2,2'\text{-Bipy} + HPF_6 \rightarrow (Bipy)_2Fe(PF_6)_2 + 2\,(1,5\text{-}C_8H_{12}). \quad (9)$$

The action of trimethyl phosphite on the complex $(C_8H_{12})_2Fe$ entails[52] isomerisation of the ring with the formation of $1,3\text{-}C_8H_{12}Fe[P(OCH_3)_3]_3$; such isomerisation is not observed when carbon monoxide, phosphorus trifluoride, or t-butyl isocyanide is used instead of the phosphite.

Bubbling nitrogen through an ethereal solution of the complex $(1,5\text{-}C_8H_{12})_2Fe$ and 1,2-bisdiphenylphosphinoethane gives[52] a nitrogen-containing complex $N_2FeP(C_6H_5)_2.CH_2CH_2P(C_6H_5)_2$. The complex $(1,5\text{-}C_8H_{12})_2Fe$ is a 16-electron compound; this governs its properties. It comprises pyrophoric crystals, which at −40°C decompose rapidly with the separation of iron. In solution in cyclo-octa-1,5-diene the complex is stable right up to 0°C. The ligands in the complex are easily replaced by cyclo-octatetraene, cycloheptatriene, and buta-1,3-diene[10].

Complexes isostructural with $(1,5\text{-}C_8H_{12})_2Fe$ have been obtained with cobalt, nickel, and platinum[53], among which the most stable is the cobalt complex, decomposing at −10°C. The action of atomic chromium has been studied on cyclo-octa-1,3- and -1,5-dienes[54,13]. Cocondensation of the former diene with atomic chromium in the presence of carbon monoxide involves isomerisation into the 1,5-diene, as in the reactions with molybdenum and tungsten hexacarbonyls[55]. Replacing carbon monoxide by trifluorophosphine yields[54] two compounds:

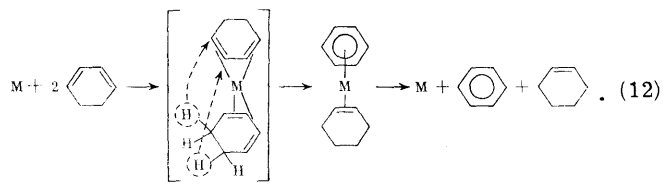
$$1,5\text{-}C_8H_{12} + PF_3 + Cr \rightarrow (1,5\text{-}C_8H_{12})Cr(PF_3)_4 + C_8H_{11}Cr(PF_3)_3H. \quad (10)$$

The expected cyclo-octa-1,5-dienetetrakistrifluorophosphinechromium (yield 1%) is accompanied by $C_8H_{11}Cr.(PF_3)_3H$ (yield 3%), a red solid formed also by the action of atomic chromium on cyclo-octa-1,3-diene in the presence of phosphorus trifluoride[54]. Furthermore, the complex $1,5\text{-}C_8H_{12}Cr(PF_3)_4$ undergoes the reaction

$$3(1,5\text{-}C_8H_{12})Cr(PF_3)_4 \xrightarrow{85^\circ C} Cr(PF_3)_6 + 2C_8H_{11}Cr(PF_3)_3H + 1,5\text{-}C_8H_{12} \quad (11)$$

when heated[54]. X-Ray examination shows[54] that $C_8H_{11}Cr.(PF_3)_3H$ is h^4-cyclo-octadienylhydrotristrifluorophosphinechromium, with the hydride hydrogen not localised on the chromium. The signal at τ = 22.4 ppm in the ^1H n.m.r. spectrum (in deuterotoluene at −50°C) is regarded as evidence of the presence of hydride hydrogen. A π-allyl hydride mechanism is postulated[54] for migration of the hydrogen atom to the ring.

An interesting reaction is the catalytic disproportionation of cyclic dienes on cocondensation with chromium, iron, cobalt, and nickel in the vapour state. It is assumed that an intermediate complex is formed[16]:

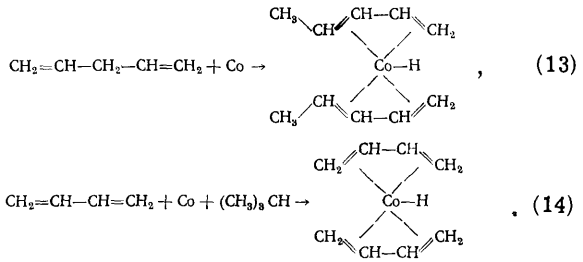


(12)

Reactions with acyclic dienes. Products of the action of atomic metals on acyclic dienes are not always clearly defined, but there is evidence that organometallic compounds are formed. Skell and his coworkers have undertaken a series of investigations[12,16,49,56] on the reactions between atomic metals and unsaturated hydrocarbons. Whereas with atomic aluminium the main reaction is addition at the double bond (σ bond),[56] atomic nickel forms π complexes having a pure π bond[49]. Deuterolysis of the reaction products from transition metals with dienes gives the original acyclic dienes. A certain quantity of deuterium detected in them is attributed to π-allyl hydride rearrangement. The cocondensation of atomic nickel with buta-1,3-diene leaves a grey residue, probably containing bridging butadiene ligands[49], from which a volatile yellow

liquid was isolated (yield 2%) that proved to be bisbuta-1,3-dienenickel(0). Dissolution of this complex in liquid butadiene at −20°C gives a dark red organonickel compound $C_{12}H_{18}Ni$, identical with the dodeca-2,6,10-triene-*centro*-nickel(0) obtained by Wilke[50], hydrogenation of which forms n-dodecane.

Gaseous cobalt is a highly active catalyst for the isomerisation of alk-1-enes into non-terminal alkenes and of non-conjugated into conjugated compounds[16]. Such catalytic reactions, as well as certain polymerisation processes, are terminated by the formation of stable complexes of cobalt and certain other metals. Thus relatively stable complexes of cobalt are formed by the reactions[16]

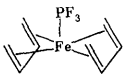


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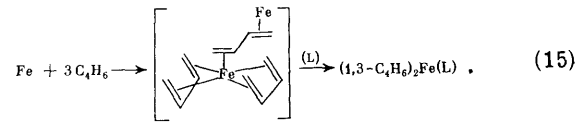
(14)

Formation of a hydride complex by the latter reaction takes place in the presence of compounds that readily liberate hydrogen.

The cocondensation of platinum vapour with buta-1,3-diene[51] gives a product that catalyses hydrogenation of excess of the butadiene at −78°C. Atomic iron on cocondensation with buta-1,3-diene yields a dark substance probably containing bridging butadiene ligands[40]. When the cocondensate was warmed up to −78°C and trifluorophosphine or carbon monoxide added, complexes $(1,3\text{-}C_4H_6)_2FeL$ were obtained, in which L = PF_3, CO, or $P(OCH_3)_3$. It is suggested[57] that the trifluorophosphine group is present in an axial position in the $(1,3\text{-}C_4H_6)_2.FePF_3$ molecule



The complex of chromium with buta-1,3-diene is obtained[57] by a reaction analogous to formation of the iron complex $(1,3\text{-}C_4H_6)_2Fe$. Crystals of the complex $1,3\text{-}C_4H_6Cr(CO)_4$ decompose above 0°C.[57] Such complexes are assumed to be formed by the reaction



(15)

L = PF_3, CO, $P(OCH_3)_3$

The use of trimethyl phosphite in reaction (15) gives not only the compound $1,3\text{-}C_4H_6FeP(OCH_3)_3$ but also another complex $1,3\text{-}C_4H_6Fe[P(OCH_3)_3]_3$. In an attempt to obtain $[2,3\text{-}(CH_3)_2C_4H_4]_3Fe$ it proved impossible to isolate only $2,3\text{-}(CH_3)_2C_4H_4Fe[P(OCH_3)_3]_3$.[58]

The cocondensation of molybdenum and tungsten vapours with buta-1,3-diene gave the previously unknown trisbuta-1,3-diene complexes[59], which sublimed readily and were stable in air. X-Ray examination showed[16] that the molybdenum or tungsten atom was equidistant from all the carbon atoms.

(*f*) Reactions with three-electron π and π donors

Reactions with inorganic compounds. When chromium vapour undergoes cocondensation with nitric oxide[6] the metal is oxidised to non-volatile compounds. Several compounds containing mixed ligands, including nitrosyl, have been obtained. Thus the yield of $PF_3Mn.(NO)_3$ is 25%, although this compound is not formed by the usual synthesis under pressure; in an atmosphere of carbon monoxide (1 atm at 20°C) it is converted quantitatively into $COMn(NO)_3$. Mixed ligands have been obtained[31] with cobalt and iron, e.g. $NOCo(PF_3)_2$. Thus an attempt to obtain the already known $Co(NO)_3$ by the cocondensation of cobalt vapour and nitric oxide gave a compound that was insoluble in inorganic solvents[31], whereas $Co(NO)_3$ is readily soluble. No final conclusion was reached on the structure of the product.

Reactions with organic compounds. Timms has shown[19] that, with tetra-allyltin used as source of allyl radicals, a 20–30% yield of di-h^3-allylnickel can be obtained by cocondensation with the atomic metal. Tri-h^3-allyliron could not be isolated under similar conditions. When the reaction was conducted in the presence of phosphorus trifluoride, however, a paramagnetic compound $h^3\text{-}C_3H_5Fe(PF_3)_3$ separated that contained a seventeen-electron shell and was stable in air[19]. Di-h^3-allylbistrifluorophosphineiron, which contains an eighteen-electron shell, is obtained only in insignificant quantities.

Atomic cobalt acts on propene in the presence of phosphorus trifluoride to form a mixture[19] of $h^3\text{-}C_3H_5Co(PF_3)_3$ and $HCo(PF_3)_4$.

(*g*) Reactions with two-electron n and π donors

Reactions with inorganic compounds. Reactions with phosphorus trifluoride and with carbon monoxide have been most widely studied. It is difficult to obtain carbonyl derivatives by cocondensation with metal vapours because solid carbon monoxide has a high vapour pressure at −196°C. They are therefore obtained at lower temperatures (down to that of liquid helium) or by exchange reactions at relatively high temperatures, in which carbon monoxide interacts with intermediate compounds, acting as a stabilising ligand. The compounds $Ni(PF_3)_4$, $Pd(PF_3)_4$, $Cr(PF_3)_6$, and $[Co(PF_3)_4]_2$ have been obtained in yields respectively of 100%, 70%, 65%, and 50%.[6,8,25,29] The cocondensation of iron vapour with phosphorus trifluoride gives a mixture of 25% of $Fe(PF_3)_5$ and 25% of the dinuclear complex $(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$; the unstable compound $[Co(PF_3)_4]_2$ could not be definitely characterised. The previously known compound $(PF_3)_3.Co(PF_2)_2Co(PF_3)_3$[60] is not formed in this reaction. Like cobalt, iron forms a dinuclear complex[59] containing difluorophosphino-bridges.

The complexes $Ni(PF_2Cl)_4$ and $M[P(CH_3)_3]_4$ have been obtained with chlorodifluorophosphine and with trimethylphosphine, where M = Ni, Co, Pd.[59] The cocondensation of iron vapour with trimethylphosphine gave the previously unknown complex $Fe[P(CH_3)_3]_5$,[59] an extremely reactive solid. This compound is assumed to result from secondary reactions occurring on heating. The cocondensate of iron vapour and trimethylphosphine at −196°C is green, whereas the compound isolated is yellowish red. Nickel will form several complexes with phosphine[6,59]. The cocondensation of nickel vapour with phosphine at −196°C

is accompanied by hydrogen evolution, which intensifies when the cocondensate heats up to room temperature. Tetraphosphinenickel could not be isolated because of the instability of the complex: only the mixed complex $Ni(PF_3)_2(PH_3)_2$ is obtained; it decomposes slowly above 0°C, but in the presence of phosphorus trifluoride is quantitatively converted into $Ni(PF_3)_4$.[59]

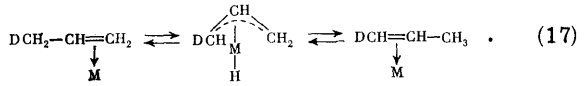
An interesting reaction, unique of its kind, occurs between nickel vapour and carbon dioxide:

$$Ni + CO_2 \rightarrow NiO + CO + Ni(CO)_4 \quad . \qquad (16)$$

The tetracarbonyl is formed in 10% yield[8]. The formation of $Ni(CS)_4$ as an analogue of the tetracarbonyl is confirmed by infrared spectroscopy and mass spectrometry[61].

Many papers have appeared recently on the use of vibrational spectroscopy to study the action of atomic metals on various substances. Cocondensation of the metal with the substance has been conducted in an argon matrix at the temperature of liquid helium. This has proved the formation of carbonyls of various metals—nickel, chromium, manganese, iron, cobalt, europium, holmium, praseodymium, rhodium, neodymium, palladium, platinum, copper, silver, and iridium[13,62-71]—as well as carbonyls of intermediate composition. The formation of aluminium carbonyls $Al_x(CO)_2$ indicates[72] that carbonyl derivatives can be obtained with most metals. Complexes of nickel and palladium with molecular nitrogen $Ni(N_2)_n$ and $Pd(N_2)_m$, where $n = 1-4$ and $m = 1, 3$, are formed[73-75] at the temperature of liquid helium.

Reactions with alkenes. Skell and his coworkers[12,49,51,56] have shown how the character of the metal–alkene bond changes on passing from aluminium to chromium and then to nickel and cobalt. Deuterolysis of the organometallic products and analysis of the substances isolated has enabled the character of this bond to be deduced. True π complexes are assumed to be formed with nickel, and a certain proportion of σ bonding is postulated in the case of complexes of chromium with alkenes. It is often impossible to isolate individual compounds from the cocondensation of transition-metal vapours with alkenes, but the latter undergo various processes of catalytic conversion. Nickel and cobalt are the most active. The cocondensation of nickel and but-1-ene is accompanied by catalytic isomerisation into but-2-ene.[49] Similar isomerisation is observed[12] in the cocondensation of but-1-ene with chromium. The cocondensation of platinum with propene gives a grey substance, in which they are assumed[51] to be present in the proportions 1 : 1. π-Allyl hydride rearrangement as a mechanism of isomerisation of alkenes is confirmed by the selective cocondensation of nickel with 2- and 3-deuteropropenes[16]:



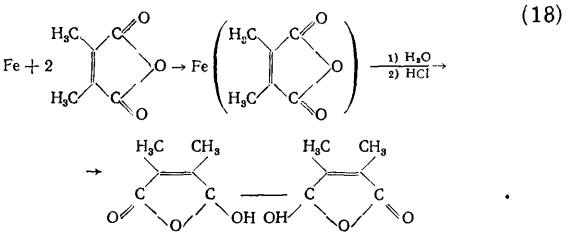
(17)

This mechanism makes it clear why the quantity of 2-deuteropropene in the initial mixture remains unchanged, and why 1-deuteropropene appears after the reaction.

Attempts to prepare alkene–metal complexes isostructural with the known compound $(C_2H_4)_3Ni$ succeeded in yielding $(C_2H_4)_3Co$ and $(C_2H_4)_3Pd$ (decomposing at −60 and −30°C respectively)[53,76]. Alkene complexes of iron and chromium have not been detected. Bicyclo[2,2,1]heptane gave coloured complexes of palladium, chromium, and cobalt; the palladium complex $(C_7H_{10})_3Pd$ breaks down only at +5°C.[76]

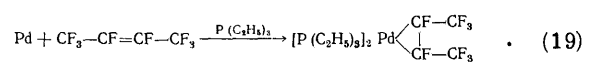
The formation of π complexes by the cocondensation of silver and copper vapours with ethylene or perdeuteroethylene has been confirmed by electron spin resonance[77]. Gold atoms did not form complexes with ethylene. The formation of copper complexees $(C_2H_4)nCu$, with $n = 1-3$, has been proved by vibrational spectroscopy.

Iron vapour reacts with dimethylmaleic anhydride[13]:



(18)

The pyrophoric product (yield 10–15%) does not react with carbon monoxide. Hydrolysis of this compound of unknown structure leads to the linking of two anhydride molecules. The cocondensation of palladium vapour with perfluorobut-2-ene in the presence of triethylphosphine involves an interesting reaction[24]:



(19)

Reactions with alkynes. Reactions of this type have been little studied. The cocondensation of nickel with alkynes gives mixtures of 1,2,4- and 1,3,5-trialkylbenzenes[49]. Trimerisation of alkynes is observed[12] also under the influence of atomic chromium. But-2-yne forms hexamethylbenzene, but terminal alkynes (but-1-yne, pent-1-yne) give mixtures of isomeric 1,2,4- and 1,3,5-trialkylbenzenes[12]. The low yield of these products does not indicate catalytic conversion, but analysis of the reaction products shows the presence of diarene complexes. Such complexes could have been postulated as intermediate compounds, promoting trimerisation of the alkynes. Obviously, only one arene ring is formed, which is attached for a certain time interval to the chromium.

Styrene undergoes polymerisation on cocondensation with iron vapour[58]. If the cocondensate heats up in an atmosphere of carbon monoxide to −20°C, a mixture of derivatives $C_6H_5CH:CH_2Fe(CO)_n$ is formed in which $n = 3-5$. Hardly any trimerisation of styrene takes place: the yield of triphenyl is ~1%.[58]

Molecular spectroscopy has been used[79] to investigate the action of nickel, palladium, and platinum on alkynes (hex-1-yne, 3-chloropropyne), but no concrete conclusions were reached on the formation of a definite type of complexes.

2. Incorporation of Atomic Metals

(*a*) Incorporation of atomic metals at carbon–halogen bonds

On cocondensation with an allyl halide atomic nickel gives the π-allylnickel halide[80]. The yield of the bromide is 80%, and that of the chloride 75%, but the product is contaminated with a mixture of C_{10-15} hydrocarbons. The cocondensation of platinum vapour with allyl chloride gives a yellow solid that decomposes at 160–170°C; reaction with triphenylphosphine forms $[C_3H_5PtCl.(C_6H_5)_3P]_x$, a

compound known previously. The action of platinum on allyl chloride is assumed[51] to give a polymeric compound $(C_3H_5PtCl)_x$. The most widely reported reactions with nickel and palladium involve oxidative incorporation of the metal at the bond between an aryl, alkyl, or acyl carbon atom and the halogen:

$$M + RHal \rightarrow RMHal$$
$$M=Ni, Pd;\quad Hal=Cl, Br, I;\quad R=C_6F_5, C_6H_5, CF_3, CH_3, C_3F_7, C_3H_7. \qquad (20)$$

The stability of the products is largely determined by the radical R.[81,82] Pentafluorophenylpalladium bromide (yield 13%) was a stable, greasy, orange-brown compound, which separated at room temperature and atmospheric pressure. It is stable in air for a short time. Its properties confirm its structure:

$$C_6F_5PdBr + Cl_2 \rightarrow C_6F_5Cl + PdClBr\ , \qquad (21)$$

$$C_6F_5PdBr \xrightarrow[\text{(in benzene)}]{\Delta} C_6F_5{-}C_6F_5 + PdBr_2 + Pd\ . \qquad (22)$$

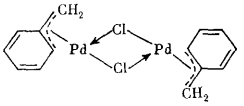
The freshly prepared bromide is able to react instantaneously with triphenylphosphine at room temperature, forming pentafluorophenylbistriphenylphosphinepalladium bromide as a white solid[81]. Pentafluorophenylpalladium bromide exists as a polymer in the solid state and as a dimer in solution. It reacts readily with various phosphine derivatives even at low temperatures. The PR_3 groups are assumed[83] to enter the *trans* position. Since compounds of type RMX are for the most part unstable, they have been isolated as complexes with phosphines[81-84]. Nickel and palladium exhibit great similarity of behaviour in reactions of incorporation, but the resulting nickel compounds are always less stable than the corresponding palladium compounds. Study of a large number of compounds has shown that incorporation of atomic palladium at a carbon–halogen bond becomes less easy according to the nature of the halogen in the sequence I > Br > Cl. The stability of the RPdHal compounds depends on the nature of R and diminishes in the sequence[24,84]

$$C_6F_5 > CF_3 \approx C_2F_5 \approx n\text{-}C_3F_7 > C_6H_5 > CH_3 \approx C_2H_5 \approx CF_2Br \approx iso\text{-}C_3F_7$$[24,84].

All arylpalladium halides decompose thermally to the biaryl, palladium, and the palladium dihalide.

Metals can be incorporated at carbon–halogen bonds also in acyl halides[84]. The products RCOMHal decompose readily with decarbonylation[24,84]. The stability of the compounds RCOMHal diminishes according to the nature of R in the sequence $n\text{-}C_3F_7 > CF_3 > C_6F_5 > C_6H_5 > CH_3 > C_3H_7$.[84]

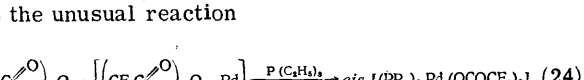
The incorporation of palladium into benzyl chloride



(23)

is of great interest[85]. The product (yield 50%) is stable, decomposing in the solid state only at 100–110°C, but in solution at 40°C. Such surprising stability, and also the spectral characteristics, indicate the presence of a π-allyl type of bond. There are data suggesting strong distortion of the benzene structure.

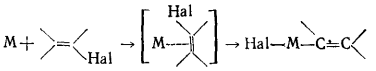
The cocondensation of palladium with trifluoroacetic anhydride followed by the addition of triethylphosphine involves the unusual reaction



(24)

which is not finally understood[83]. The product is the salt-like bistriethylphosphinepalladium bistrifluoroacetate. A complex of a molecule of trifluoroacetic anhydride with a palladium atom is assumed to be formed as intermediate, but its structure is not yet clear.

The literature contains a brief mention[24] of reactions of platinum and titanium vapours yielding compounds of type RMX. Platinum gives the quite stable pentafluorophenylplatinum bromide, which reacts with triphenylphosphine. The *cis*- and *trans*-adducts are thus obtained, whereas the nickel and palladium analogues give only the *trans*-complexes. The compound "C_6F_5TiBr" is extremely unstable, and such a structure has only been postulated[24]. The cocondensate of titanium with bromopentafluorobenzene is able to cause the vigorous, almost explosive polymerisation of buta-1,3-diene at −78°C. The compound "C_6H_5TiBr" could not be stabilised by reaction with triphenylphosphine. An unsuccessful attempt was made[24] to incorporate palladium atoms at the C–CN bond in benzonitrile and benzilonitrile. Stereochemical aspects of incorporation in optically active compounds (1,1,1-trifluoro-, 2-chloro-, and 2-phenyl-ethanol) have been studied, and the results may be expected shortly[24]. The character of the bond (π or σ) in complexes of nickel, palladium, and platinum with halogenated alkenes



has been investigated[24].

No examples have been reported of the incorporation of transition-metal atoms at carbon–fluorine bonds. However, the formation of complexes of metals with hexafluorobenzene[22] involves vigorous decomposition of the cocondensate, probably owing to the exothermal character of the formation of metal–fluorine bonds. Incorporation of a metal at a carbon–fluorine bond occurs in the cocondensation of calcium with hexafluorobenzene[86].

(*b*) Dehalogenation with transition-metal atoms

One of the first reactions of this type was conducted by Timms[87,88], by the cocondensation of copper vapour with boron trichloride:

$$Cu + 2BCl_3 \rightarrow 2CuCl + B_2Cl_4\ .$$

With the proportions $Cu : BCl_3 = 1 : 6$ a 40% yield of B_2Cl_4 is obtained, which increases to 70% when the proportions are 1 : 20. In the cocondensation of copper vapour with methylboron dichloride in the proportions 1 : 6 the yield of $(CH_3)_2B_2Cl_2$ is 35% calculated on the copper vaporised.

Gold on cocondensation with ethyl bromide[19,32] gives products—butane, ethane, and ethylene—of the dimerisation and disproportionation of the ethyl radical, together with gold(I) bromide. Ethyl chloride does not react with gold. The cocondensation of nickel with ethyl bromide[19] forms a mixture of hydrocarbons—ethylene, ethane, and butane—in the molecular proportions 1 : 1 : 6; the residue contains much free nickel and a small quantity of its dibromide. The yield of hydrocarbons based on the nickel vaporised is only 10%: i.e. nickel is not such an effective dehalogenating metal as copper, gold, and silver. These three atomic metals are more selective reagents than are the alkali metals[19]: the

product of the reaction of the optically active s-butyl chloride with copper and silver vapours retains 70% of the activity[19], whereas sodium gives the completely inactive 3,4-dimethylhexane.

It is of practical interest to obtain adducts of nickel with solvents[24,41,42]. On cocondensation with oxolan nickel gives a stable adduct, which is a good reagent for binding alkyl halides. Thus allyl bromide or benzyl chloride can be bound by means of the nickel–oxolan adduct at 40°C.

3. Reactions of Atomic Transition Metals with Compounds containing Active Hydrogen

(*a*) Synthesis of acetylacetonates

The preparation of chromium and iron acetylacetonates by cocondensation of the metal vapours with pentane-2,4-dione in the presence of oxygen was first reported by von Gustorf[89]. The yields of $CrAcac_3$ and $FeAcac_3$ were respectively 32% and 24%. In the absence of oxygen, compounds of the type $MAcac_2$ were obtained[13,63] with manganese, nickel, copper, iron, zinc, tin, and palladium in respective yields of 30%, 36%, 10%, 25%, 28%, 11%, and 10%. The aluminium complex $AlAcac_3$ has also been obtained, as well as acetylacetonates $MAcac_3$ of the rare-earth metals—erbium, dysprosium, and holmium[63].

(*b*) Reactions with alcohols

Chromium vapour reacts with methanol to form the methoxide $Cr(OCH_3)_3$ in 28% yield[13]. Reaction goes readily with isopropyl and t-butyl alcohols, but sparing solubility results in difficulties in purifying the products.

(*c*) Reactions with acids

Chromium reacts with hydrogen chloride at −196°C with the liberation of one mole of hydrogen per gram-atom of chromium vaporised[16]. Cocondensation with acetic acid yields a mixture of bi- and ter-valent salts, the relative composition of which depends on the experimental conditions[13].

(*d*) Reactions with water

Chromium reacts with water at −196°C to liberate half a mole of hydrogen, and the other half appearing on heating[16]. Atomic molybdenum and tungsten do not react with water at −196°C.

III. MECHANISM OF THE COCONDENSATION OF ATOMIC METALS WITH ORGANIC AND INORGANIC SUBSTANCES

No published assessment is available on the mechanism of the condensation of metal vapours with various substances (vapour-phase synthesis). The Reviewers feel it possible to consider this process by applying equilibrium thermodynamics to the direct synthesis of dibenzenechromium. An earlier thermodynamic calculation showed[90] that the equilibrium constant of the decomposition of dibenzenechromium

$$(C_6H_6)_2Cr\ (g) \rightleftarrows Cr\ (s) + 2C_6H_6\ (g) \qquad (25)$$

increases with rise in temperature from 298 to 1000 K. Furthermore, calculation over the ranges 298–800 K and 10^{-5}–10^{7} atm showed that only at 10^{7} atm does the Gibbs free energy of process (25) change sign, i.e. that the equilibrium shifts towards formation of the complex.

To elucidate the mechanism of direct synthesis, which may be either a gas-phase or a gas–solid reaction, we can calculate the changes in Gibbs free energy ΔG (in kcal mole^{-1}) for the possible reactions under these conditions (chromium was regarded in the calculations as an ideal gas):

$$Cr\ (s) + 2C_6H_6\ (g) \overset{298\ K}{\rightleftarrows} (C_6H_6)_2Cr\ (g) \quad (\Delta G = 27.2) \qquad (26)$$

$$Cr\ (s) + 2C_6H_6\ (g) \overset{298\ K}{\rightleftarrows} (C_6H_6)_2Cr\ (s) \quad (\Delta G = 18.9) \qquad (27)$$

$$Cr\ (g) + 2C_6H_6\ (g) \overset{298\ K}{\rightleftarrows} (C_6H_6)_2Cr\ (g) \quad (\Delta G = -57.4) \qquad (28)$$

$$Cr\ (g) + 2C_6H_6\ (g) \overset{298\ K}{\rightleftarrows} (C_6H_6)_2Cr\ (s) \quad (\Delta G = -65.5) \qquad (29)$$

$$Cr\ (g) + 2C_6H_6\ (l) \overset{298\ K}{\rightleftarrows} (C_6H_6)_2Cr\ (s) \quad (\Delta G = -62) \qquad (30)$$

$$Cr\ (s) + 2C_6H_6\ (s) \overset{77\ K}{\rightleftarrows} (C_6H_6)_2Cr\ (s) \quad (\Delta G = 16.4) \qquad (31)$$

$$Cr\ (g) + 2C_6H_6\ (s) \overset{77\ K}{\rightleftarrows} (C_6H_6)_2Cr\ (s) \quad (\Delta G = -70) \qquad (32)$$

$$Cr\ (g) + 2C_6H_6\ (g) \overset{1000\ K}{\rightleftarrows} (C_6H_6)_2Cr\ (g) \quad (\Delta G = -30.3)\ . \qquad (33)$$

It thus becomes clear that reactions (28)–(30), (32), and (33) must be regarded as thermodynamically probable. Experimental observations indicate that equilibria (26), (27), and (31) are displaced to the left, since on the termination of synthesis the reaction vessel contains metallic chromium as a powder formed by the aggregation of atomic chromium and unable to react with benzene under normal conditions. Furthermore, the thermodynamically permitted reactions (28), (29), and (33) require a three-body collision, whose probability z_3 is almost zero: its ratio to the probability z_2 of a bimolecular gas-phase reaction is $0.01p$, where p (atm) is the pressure at 300 K;[91] since under conditions of direct synthesis $p = 10^{-4}$–10^{-6} mmHg (i.e. 10^{-6}–10^{-8} atm), it becomes obvious that the probability of a three-body collision $z_3 = (10^{-8}$–$10^{-10})z_2$ is extremely small. As the free path of metal atoms at such pressures exceeds considerably the dimensions of all the reaction vessels used, direct synthesis must obviously be regarded as a gas–solid (metal–benzene) reaction (32). From this several conclusions may be reached concerning the mechanism of direct synthesis.

A metal atom incident on the surface of a condensed organic or inorganic substance will obviously lose its energy at the first collision with molecules of the latter (this can be deduced from the estimated kinetic energy of the atom). The local heating of the condensed phase facilitates diffusion of the metal atom and of molecules of the latter, which promotes the three-dimensional orientation favourable for interaction in the matrix. Intense vaporisation of the metal increases the probability of mutual encounter of the metal atoms and their aggregation. With inadequate dissipation of heat and the freezing of a thick layer on the walls of the reaction vessel, moreover, the substance may melt (reaction 30). The gas–liquid reaction is permitted thermodynamically, but the probability of mutual encounter and aggregation of metal atoms will be especially high under these conditions. In the condensed state the metal no longer reacts. This may explain the diminished yield of organometallic compound

(relative to the theoretical yield based on the metal vaporised) and the formation of a metal powder, although the yield is governed, of course, also by the reverse decomposition of the organometallic compound to the metal and the organic compound.

The isolation of the metal atoms in the matrix can be assessed by means of the ratio of the number M of matrix atoms or molecules to the number R of metal atoms in the matrix. The spectroscopy of atoms isolated in a matrix[92] indicates that good isolation of atomic metals is achieved with $M/R \geqslant 300$. However, such data apply to a matrix which is inert with respect to the metal. Work on direct synthesis usually employs ratios of $M/R = 6-100$, since a large excess of the substance is obviously unnecessary, because of interaction with the atomic metal.

Further cooling of the walls of the reaction vessel (to the temperature of liquid helium) confers great "rigidity" on the matrix, and thereby impedes diffusion of the metal atoms and diminishes the probability of their aggregation. Furthermore, compounds that are unstable at the temperature of liquid nitrogen can be recorded spectroscopically at the lower temperature.

The above estimate provides a better understanding of the relation of direct synthesis to the thermal decomposition of organometallic compounds, e.g. a diarenechromium, which in turn enables us to assess the stability of an organometallic compound from its yield. The phase in which the metal separates plays an important part in displacing the equilibrium in thermal decomposition. Thus when chromium atoms are adsorbed on a solid (substrate) or when they aggregate to form a solid phase of metallic chromium, the synthesis–decomposition equilibrium should shift towards breakdown of the diarenechromium, because of the low mobility of chromium atoms in the solid phase. Calculation for the gas-phase reaction (33) at 1000 K shows, however, that the equilibrium is again displaced towards synthesis of dibenzenechromium if the chromium is in the gaseous state. In direct synthesis the chromium atom incident on the layer of condensed substance is more mobile than the chromium atom in contact with the substrate in the case of thermal decomposition, and the translational motion of the atom can be regarded as terminated only on formation of the organometallic compound or as a result of mutual aggregation of the atoms.

Analogous calculations can be made for the formation of ferrocene from atomic iron and cyclopentadiene:

$$Fe\ (g) + 3C_5H_6\ (g) \overset{298\ K}{\rightleftharpoons} (C_5H_5)_2Fe\ (g) + C_5H_8\ (g)\ (\Delta G = -112) \qquad (7)$$

$$Fe\ (g) + 2C_5H_6\ (g) \overset{298\ K}{\rightleftharpoons} (C_5H_5)_2Fe\ (g) + H_2\ (\Delta G = -97) \qquad (34)$$

$$Fe\ (g) + 2C_5H_6\ (g) \overset{298\ K}{\rightleftharpoons} (C_5H_5)_2Fe\ (g) + 2H\ (\Delta G = +1). \qquad (35)$$

The free energies of these reactions at 77 K could not be calculated, unlike the case of the synthesis of dibenzenechromium, owing to the absence of thermodynamic characteristics for solid cyclopentadiene and of data on the temperature dependence of its heat capacity. However, these calculations suggest that reactions (7) and (34) will be thermodynamically feasible, involving as transition state a hydride or an eighteen-electron complex of iron (II, 1*d*). The existence of such an intermediate eighteen-electron iron complex [Eqn. (7) in II, 1*d*] can be regarded as proved by the presence in the reaction mixture of cyclopentene in equimolecular proportions to the ferrocene isolated[93].

IV. APPARATUS FOR DIRECT SYNTHESES

1. Vacuum System and Reaction Vessel

An ordinary high-vacuum system (Fig. 1), having fore vacuum and diffusion pumps, was used for the direct syntheses‡. The rate of evacuation can be increased by supplementing these with a booster pump, but normally this is not required, since the walls of the reaction vessel, cooled to −196°C, provide effective cryogenic evacuation of the substance supplied to the reaction vessel, by freezing it and thereby maintaining a high vacuum in the system.

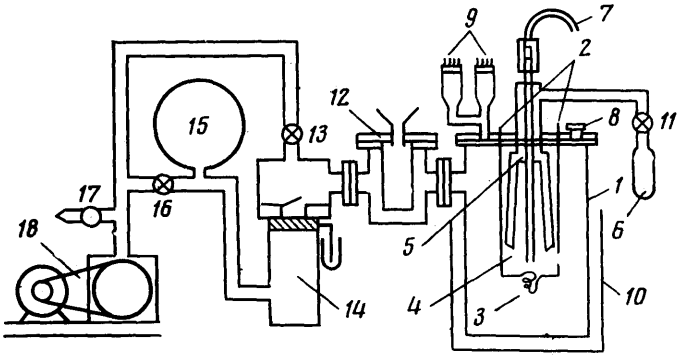


Figure 1. Diagram of apparatus for direct synthesis: 1) reaction vessel; 2) current leads; 3) vaporiser coil; 4) tube for supply of metal; 5) tube for supply of compound; 6) ampoule containing compound; 7) ampoule containing metal fragments; 8) viewing window; 9) manometric valves; 10) Dewar vessel; 11, 13, 16, 17) vacuum taps; 12) trap; 14) VA-01-1 vacuum unit; 15) ballast volume; 18) preliminary vacuum pump.

One or two traps filled with liquid nitrogen are placed between the high-vacuum system and the reaction vessel. They comprise detachable Dewar vessels. The reaction vessel with a flanged coupling and a copper or aluminium gasket is connected to the high-vacuum system through traps. Of the two forms of reaction vessel—with rigid coupling or rotating—the latter uses the same principle as in the rotary vaporiser, which is used in chemical laboratories for the vacuum evaporation of solvents. A complication in the present case is to make a stuffing box capable of rotation and operating in the pressure range $10^{-5}-10^{-6}$ mmHg (Fig. 2)§.

‡ In our laboratory the apparatus was based on a standard VA-01-1 vacuum unit. It is convenient to use as the ballast volume the inner vessel of an ASD-15 Dewar flask. Such a metal ballast volume is safe in operation and has a large capacity (15 litres).

§ The firm G.V. Planer Ltd. (Great Britain) manufactures equipment with a rotating glass reaction vessel (diameter 100 mm) and a resistance vaporiser; an electron-beam gun of type EBSI/H is also produced by the same firm.

The overall arrangement of the apparatus is straightforward, and solving the design problem of the rigidly fixed vessel presents no great difficulty. Cooling the walls of the reaction vessel gives rise to certain difficulties, since the use of glass Dewar vessels under these conditions is complicated by the relatively large diameter of the reaction vessel. The latter should therefore have a double or triple jacket (with the outer vessels connected to the vacuum system, while the inner vessel serves for pouring the liquid nitrogen) or else the reaction vessel should be immersed in a reservoir of liquid nitrogen, for which purpose a tank cast from foam plastic can be recommended. All the various forms of apparatus differ in the ways in which they solve the problem of vaporising the metal and feeding the organic or inorganic substance to the reaction vessel.

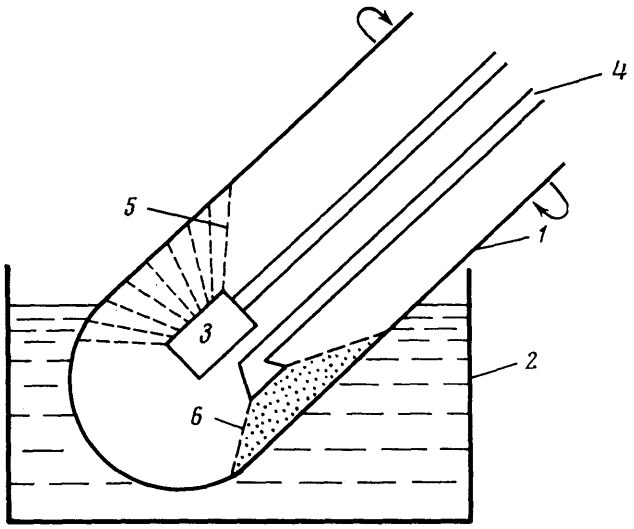


Figure 2. Diagram of rotating reaction vessel: 1) reaction vessel; 2) Dewar vessel; 3) electron gun; 4) delivery of compound; 5) metal vapour; 6) vapour of compound.

2. Vaporisation of the Metal in a Vacuum

The technology of the vacuum evaporation of metals is now well developed. Among the main methods for vaporising a metal—(*a*) from a resistance-heated vaporiser, (*b*) by induction heating of the metal in a container, (*c*) by electron bombardment of a specimen of the metal, and (*d*) by a laser beam—method (*a*) is the simplest and most practicable, but its application is restricted by the difficulty of vaprosing refractory metals. Processes (*b*) and (*c*) have the greatest prospects and are most convenient.

(*a*) Vaporisation from a resistance-heated vaporiser

In this process the metal vapour is obtained from a resistance-heated vaporiser basket made of tungsten or molybdenum wire (diameter 1–1.5 mm). The required shape is conferred on the vaporiser by means of a threaded conical mandrel (tungsten wire is wound on the cone while being heated in a flame). Such an evaporator is fixed in the clips of the current leads, which are situated in the flanged lid of the reaction vessel and are usually cooled with water.

The difficulty with a resistance evaporator is that the molten metal begins to flow along the coil and to "short" it, when vaporisation almost ceases and the coil burns out; at the same time the unmelted solid metal has a low vapour pressure and its rate of vaporisation is very small. Wetting of the coil with the molten metal can be avoided by using crucibles comprising the same vaporisers as before, but coated with aluminium or beryllium oxide[94]; such a coating is applied from an aqueous suspension of alumina¶. Use of a resistance evaporator permits the vaporisation of transition metals of the first series, copper, silver, gold, palladium, uranium, and also lanthanides. The employment of crucibles coated with aluminium oxide is restricted by the possibility of interaction with the molten metal. Such interaction takes place with chromium, and more electropositive metals cannot be vaporised from such a crucible.

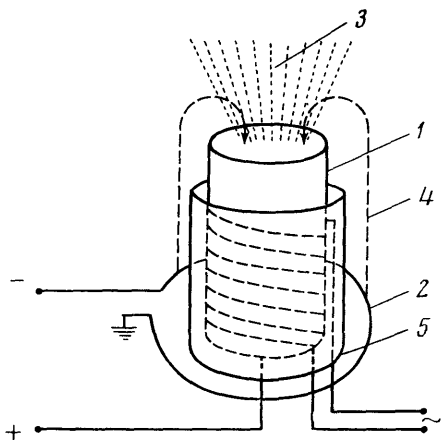


Figure 3. Diagram of electron gun: 1) crucible containing metal specimen (having a high positive potential) preheated by a coil; 2) preheated tungsten wire; 3) metal vapour; 4) flux of electrons; 5) cylindrical shield (having a slight negative potential).

Vaporisation can be effected by other modifications of this method. (i) The vaporiser may consist of a tungsten rod (diameter 3–4 mm) on which are wound in parallel a wire of the metal to be evaporated and a thin tungsten wire (diameter 0.3–0.5 mm). (ii) In the exploding wire method [57] a wire descending from a special container short-circuits the contacts and burns up, with production of a high density of metal vapour; here, however, polyatomic

¶ The crucible coating can be applied as a paste—aluminium in a silicate cement—the coated crucibles first being dried at 200°C and then annealed in a vacuum.

metal particles are formed. (iii) The vaporiser can be made from rolled molybdenum, tungsten, or niobium–tantalum alloy (combustion boat).

The source of supply for resistance vaporisers is an adjustable transformer capable of giving currents up to 100–150 A at voltages of 6–12 V.

(*b*) Induction heating

This method has advantages over the resistance heating of a metal specimen, but is hardly used at all in apparatus for the direct synthesis of organometallic compounds. It also has its problems in connection with the need to use a high-frequency oscillator [95].

(*c*) Electron bombardment

An electron gun is used in which the electrons emitted by a tungsten filament are focussed on a specimen of the metal to be vaporised. A compact design of electron gun has been proposed by the English firm G.V. Planer Ltd. (type EBSI/H) (Fig. 3).

Choice of power for the electron gun must be based on the enthalpy of vaporisation of the metal, the desired rate of evaporation, and also the inevitable accompanying energy losses. If the power is insufficient, the metal specimen may be preheated by a different method, e.g. resistance heating.

(*a*) Laser vaporisation

Use of a laser beam to vaporise metals in direct syntheses has been reported by von Gustorf [13,57]. A carbon dioxide laser of power 1.2 kW was focussed into a spot of diameter 1–2 mm. Vaporisation of metals of high melting point was effected from a heated crucible into which the laser beam was directed.

The dependence of the reflecting power of the metal on the wavelength must be taken into account for optimum utilisation of the laser energy. The most acute problem in the use of a laser is the "window" in the reaction vessel. Thus, whereas with other methods of heating metals a "window" is necessary only for periodic observations, being closed for the remaining time and not coated with a film of the condensed metal, in the present method the "window" should be open continuously for passage of the laser beam. A "sluice" is arranged to protect the "window" from sputtering in the evacuated reaction vessel: the pressure in the "sluice" is maintained at 0.1–0.01 mmHg by a jet of argon, which blows away metal atoms (of very small volume) travelling in the direction of the "window" [13].

3. Supply of Organic or Inorganic Substance

The supply of gases to the reaction vessel is structurally very simple, being effected through orifices in a tube placed at the centre of the vessel. The supply is controlled by means of a finely adjustable tap. Volatile liquids are supplied in the same way as gases, but organic compounds of high boiling point must be heated in an ampoule, and the whole tube along which they pass to the reaction must be warmed (to prevent their condensation inside the tube). A gaseous substance is uniformly distributed in the reaction vessel, and condenses on the walls. Delivery can be simplified by uniformly spraying the substance into the reaction vessel, since a gas–solid (metal–condensate) reaction takes place.

A sublimer is introduced into the reaction vessel for the delivery of solids. The substance may also be supplied dissolved in an inert solvent (C_{10-12} saturated hydrocarbons, etc. [10,19]).

4. Isolation of Organometallic Compounds Formed by Direct Synthesis

Methods of isolation depend on the nature of the compound obtained. Certain structural units should therefore be provided in the apparatus.

Volatile reaction products distil from the reaction vessel into a trap. For such purposes the easily detachable vessel is usually disconnected from the vacuum system and connected to another system, into whose trap the reaction product distils. Equipment fitted with a parallel evacuation line from the reaction vessel may also be used: this line is used for distilling off products while the main vacuum line is closed.

Use of such a system to isolate less volatile products is complicated by their condensation in the vacuum tubes and taps. An interchangeable flange with a receiver ("finger") cooled in liquid nitrogen can be employed for this purpose. When synthesis is complete, the main flange is replaced by the flange with the cooled receiver, on whose surface the reaction products sublime from the walls of the reaction vessel.

Various chemical reactions can be conducted at either room or low temperatures in order to isolate certain organometallic compounds. Diarenechromium complexes, for example, can be oxidised in the presence of water to the diarenechromium hydroxides, which can then be converted into the iodides or into neutral complexes [29,30]. Many examples have been reported of the isolation and proof of formation of unstable products of the cocondensation of atomic metals with organic compounds. The isolation of organometallic compounds RMHal (where M = Ni, Pd) as adducts with phosphines $RMHal.2PR_3$ is typical of such reactions.

To prove the formation of unstable compounds increasing use is being made of the spectroscopic recording (directly on the cooled caesium iodide window of the infrared spectrometer) of compounds formed by the low-temperature cocondensation of metal vapours with organic and inorganic substances [41,52,53].

V. POSSIBILITIES AND PROSPECTS

In the near future the technique of low-temperature cocondensation should take its place in chemical laboratories. It provides unusual opportunities for obtaining Grignard reagents by the cocondensation of magnesium vapour with halogenated organic compounds, and also for preparing an especially active magnesium mass by cocondensation with an inert solvent. Such a mass will give Grignard reagents with the most inert halogenated aromatic compounds. For example [24] the cocondensation of magnesium vapour with oxolan forms a complex that can be used for the synthesis of Grignard reagents:

$$\mathrm{Mg + Oxol} \xrightarrow{196^\circ C} \mathrm{[Mg.Oxol]} - \begin{cases} \xrightarrow{C_6H_5Cl;\ 25^\circ C} C_6H_5MgCl\ (80\%) \\ \xrightarrow{C_6F_5Br;\ 80^\circ C} C_6F_5MgBr\ (80\%) \\ \xrightarrow{CF_3Br;\ 80^\circ C} CF_3MgBr\ (1\%) \end{cases} \quad (36)$$

It is of practical interest to prepare a similar active mass of nickel. Thus the cocondensation of nickel vapour with oxolan produces a stable adduct, which is a very good reagent for binding alkyl halides [24,41,42]:

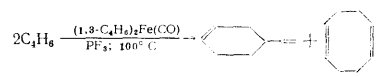
$$2C_3H_5Br + \text{Ni-Oxol} \xrightarrow{40^\circ C} C_3H_5{-}C_3H_5 + NiBr_2 \quad (37)$$

$$2C_6H_5CH_2Cl + \text{Ni-Oxol} \xrightarrow{40^\circ C} (C_6H_5CH_2)_2 + NiCl_2 . \quad (38)$$

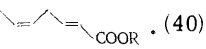
Such solvate complexes of metals are only now beginning to be investigated, but the results already obtained are extremely encouraging.

Complexes formed in cocondensation with atomic metals are often good catalysts for various processes. In the presence of phosphines at 100°C, for example, $(1,3\text{-}C_4H_6)_2$. .FeCO [13] catalyses the dimerisation of dienes and other reactions:

$$2C_4H_6 \xrightarrow[PF_3;\ 100^\circ C]{(1,3\text{-}C_4H_6)_2Fe(CO)} \quad (39)$$



$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH{-}COOR \xrightarrow[P(C_6H_5)_3]{(1,3\text{-}C_4H_6)_2Fe(CO)} \quad (40)$$



Extremely promising and interesting work has been done [96, 97] on the oligomerisation of butadiene catalysed by products of the cocondensation of vapours of transition metals—titanium, nickel, chromium, manganese, iron, cobalt, vanadium—with butadiene in benzene or toluene in the presence and in the absence of dimeric diethylaluminium chloride. With titanium and iron in the presence of $[(C_2H_5)_2AlCl]_2$ oligomerisation involved 100% conversion; nickel, chromium, vanadium, and manganese also showed great catalytic activity (respectively 90%, 60%, 43%, and 40%); but cobalt was relatively inactive (10%). On oligomerisation in the absence of aluminium complex the greatest catalytic activity was developed by iron, cobalt, nickel, and chromium (90%, 88%, 75%, and 62% respectively), whereas titanium was inactive (10%).

A simple and perhaps more economic process—cocondensation of metal vapours with organic compounds—may be used to prepare catalysts [97]. Titanium can be vaporised by an electron gun at a rate of 70 kg h^{-1}, which makes it possible to produce the catalysts on an industrial scale [98].

Direct synthesis enables especially pure organometallic compounds to be obtained. Thus whereas the usual Fischer preparation of bisethylbenzenechromium yields many homologues with different numbers of alkyl substituents, for example, the cocondensation of chromium vapour with ethylbenzene gives the individual compound bisethylbenzenechromium [99], which is very important in the use of organochromium compounds to obtain chromium films. The technical process requires substances of constant characteristics—boiling point, vapour pressure, viscosity, density, etc.—and use of this method enables standard substances to be obtained for the analysis of various mixtures of organometallic compounds, as well as for obtaining accurate spectral and other characteristics of particular compounds.

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