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Oxidation of Organometallic Compounds by Transition Metal Salts

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The mechanisms of one- and two-electron oxidation of organometallic compounds by transition metal salts are considered. It is shown that organometallic compounds can be oxidised as a result of dielectric electron transfer but usually unstable transition metal compounds are formed as intermediates in the reactions. The mechanisms of the thermal and catalytic decomposition of certain types of organometallic compounds are discussed in this connection.
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I. INTRODUCTION

The reactions of organometallic compounds with transition metal salts have continuously attracted the attention of investigators because many of them are of preparative value. Recently interest in such reactions has increased still further in connection with their involvement in complex processes catalyses by transition metal complexes.

Various reactions occur when organometallic compounds interact with transition metals salts. These include in the first place the transmetallation reaction as a result of which a new organometallic compound is formed:

$$RMX_n + M'X_n \rightarrow RM'X_{m-1} + MX_{n+1} . \quad (1)$$

Since this review is devoted to reactions involving the oxidation of organometallic compounds, we shall consider only those in which unstable organometallic intermediates, decomposing with formation of the products R_2, RH, and R(-H), are formed.

According to modern ideas, organic compounds of transition metals can decompose via the free-radical mechanism (2) and via the so-called bimolecular mechanism (3) in which free radicals are not formed:

$$RM'X_{m-1} \rightarrow R^{\cdot} + M'X_{m-1} ,$$
$$2R^{\cdot} \rightarrow RH + R(-H) , \quad (2)$$
$$2R^{\cdot} \rightarrow R_2 ;$$

$$2RM'X_{m-1} \rightarrow RH + R(-H) + 2M'X_{m-1} ,$$
$$2RM'X_{m-1} \rightarrow R_2 + 2M'X_{m-1} . \quad (3)$$

Whereas the free-radical mechanism of the decomposition of organometallic compounds is understood in all its aspects, the question of the essential features of the bimolecular mechanism is not quite so clear and there is not even a unanimous view concerning the nature of the reactions occurring. For example, it is not clear how the organometallic compounds decompose in this instance, whether the process is homolytic and occurs within a radical cage or whether it is heterolytic

and involves, for example, the hydride elimination stage whose products are RH and R(−H). This uncertainty has resulted in the lack of a single terminology used to designate this mechanism. It is referred to as the bimolecular mechanism, the latent radical mechanism, and sometimes the latent ionic mechanism, but these terms merely confirm the absence of free radicals.

When organometallic compounds interact with metal salts, free radicals can be formed not only as a result of the homolytic decomposition of the product of the transmetallation reaction (2) but also in the one-electron oxidation of the organometallic compounds. The radicals formed in this instance, as in mechanism (2), dimerise, disproportionate, or react with the solvent:

$$RMX_n + M'X_m \rightarrow [(RMX_n)^+ (M'X_m)^-] \rightarrow R^\cdot + MX_{n+1} + M'X_{m-1} ,$$
$$2R^\cdot \rightarrow R_2 ,$$
$$2R^\cdot \rightarrow RH + R(-H) . \qquad (4)$$

This pathway, leading to the oxidation of organometallic compounds, is fundamentally different from mechanism (2) discussed above. On the other hand, they are difficult to distinguish because the reaction results in the formation of free radicals and the same products. Finally, when organometallic compounds interact with metal salts, there is a possibility of two-electron oxidation to carbonium ions R^+, which react with nucleophilic species via mechanism (5). Carbonium ions can be formed in these reactions in a wide variety of ways: in the intramolecular decomposition of $RM'X_{m-1}$ [mechanism (5), pathway *a*] produced as a result of transmetallation in accordance with Eqn.(1), in the oxidation of the radicals $R^\cdot$ [mechanism (5), pathway *b*] generated via pathways (2) and (4), or in the direct two-electron oxidation of the initial organometallic compound [mechanism (5), pathway *c*]:

$$RM'X_{m-1} \xrightarrow{a} R^+ + M'X_{m-2} + X^- ,$$
$$R^\cdot + M'X_m \xrightarrow{b} R^+ + M'X_{m-1} + X^- ,$$
$$RMX_n + M'X_m \xrightarrow{c} R^+ + MX_{n+1} + M'X_{m-2} + X^- ,$$
$$R^+ + Nu^-(X^-) \rightarrow RNu(RX) . \qquad (5)$$

We may note that free carbonium ions are not always formed in the two-electron oxidation of organometallic compounds—for example, when electron transfer takes place with the simultaneous transfer of a nucleophilic ligand:

$$RM'X_{m-1} \xrightarrow{a} RX + M'X_{m-2} ,$$
$$R^\cdot + M'X_m \xrightarrow{b} RX + M'X_{m-1} ,$$
$$RMX_n + M'X_m \xrightarrow{c} RX + MX_{n+1} + M'X_{m-2} . \qquad (6)$$

There is also a possibility of a rarely encountered activation of the intramolecular transfer of a second electron as a result of the attack by the nucleophile (Nu) on the radical-cation intermediate:

$$RMX_n + M'X_m \rightarrow (RMX_n)^+ + M'X_{m-1} + X^- ,$$
$$(RMX_n)^+ + Nu^- \rightarrow RNu + MX_n . \qquad (7)$$

This review deals with the above mechanisms of the oxidation of organometallic compounds by metal salts. To facilitate exposition, the data for reactions involving the oxidation of organometallic compounds by silver(I), copper(I), and copper(II) salts as well as Group VIII metal salts are considered as far as possible in separate sections. This is mainly because specific mechanisms have been proposed for each oxidant and numerous examples of their reactions have been studied. Analogous problems are dealt with also in recently published reviews[1,2].

In our view, the thermal decomposition reactions of organic derivatives of silver, copper(I), and other transition metals also merit attention. Interest in these processes is due to two causes. Firstly, they may constitute the stage in which the intrinsic oxidation of the organic group R occurs. This happens when the oxidation of an organometallic compound by the metal salt begins with the transmetallation reaction and an intermediate RM is formed. Secondly, these reactions are oxidation processes of a specific type for which independent mechanisms have been proposed. We shall adhere to these standpoints in considering the wide variety of decomposition reactions of organometallic compounds. Thus we shall regard the homolytic decomposition of organometallic compounds as a one-electron oxidation process. This is not a formal approach, since the carbanion bound to the metal cation is indeed oxidised in the course of the reaction, being converted into a radical. Similarly the decomposition of the compounds RM with formation of R^+ or intramolecular decomposition of R_2M with formation of R_2, RH, and R(−H) should be regarded as two-electron oxidation processes. These reactions are considered in detail in the last section of the present review.

II. ONE-ELECTRON OXIDATION OF ORGANOMETALLIC COMPOUNDS BY TRANSITION METAL SALTS

Particularly numerous reactions with transition metal salts are known for organomagnesium compounds RMgX. In many instances, especially for R = Ar, this reaction can serve as a preparative method for the synthesis of biaryls, since in the synthesis of a symmetrical product this reaction is simpler than the Wurtz–Fittig reaction.

The reaction (with a nearly quantitative yield of biaryl) was first carried out in 1914:[3]

$$p\text{-}MeC_6H_4MgBr \xrightarrow[80-85\%]{CrCl_3} (p\text{-}MeC_6H_4)_2 .$$

In subsequent years the number of examples of similar reactions increased and studies were mainly carried out in order to elucidate the influence of the nature of the metal salt on the yield of product. It was shown[4] that the yield of biphenyl (%) varies as follows as a function of the nature of the oxidant in the reactions of PhMgI with metal salts in ether:

$FeCl_2$	98	$PdCl_2$	98
$CoBr_2$	98	$OsCl_3$	53
$NiBr_2$	100	$IrCl_3$	28
$RuCl_3$	99	$PtCl_4$	5
$RhCl_3$	97	—	—

According to Tsutsui[5], the yield of the dimerisation product (%) in the reaction of ArMgX with various metal chlorides in tetrahydrofuran (THF) varies within a very wide range:

$FeCl_2$	47	$MnCl_2$	21
$CoCl_2$	86	$CrCl_3$	7
$NiCl_2$	72	$CuCl_2$	6

Biaryls are formed when arylmagnesium bromides are treated with thallium(I) bromide[6], uranyl nitrate[7], titanium tetrachloride and vanadium oxide trichloride[8], and chromium(IV) t-butoxide[9]. Depending on the nature of the aryl group, the yield of the dimerisation product varies for the majority of salts from 25 to 100%.[8]

When transition metal salts act on alkylmagnesium halides, the main products become olefins and alkanes and not coupling products[10]. The yields of the products of these reactions have been reported[11]. Cotton[12] proposed the following

classification of the reactions taking into account the preferential formation of particular products: mainly alkanes in group I reactions, disproportionation products in group II reactions, and alkanes and olefins together with coupling products in group III reactions, while group IV reactions include those whose products are the dimers Alk_2. According to this classification, transition metal salts are involved mainly in reactions to the following types:

group I: $TiCl_4$, $Ti(OR)_4$, $ZrCl_4$, $TaCl_5$;
group II: $CrCl_3$, $MnBr_2$, $FeCl_2$, TlCl, Cu_2Cl_2, $CuCl_2$;
group III: AgX, $AuCl_3$.

Group IV reactions are those of silver and copper salts with organomagnesium and organolithium compounds without a β-hydrogen atom.

The mechanisms of the reactions of transition metal salts with aryl- and alkylmagnesium halides are usually regarded as consecutive transmetallation and decomposition of the organometallic intermediate by a radical mechanism or without the involvement of free radicals. It is believed[11] that the decomposition of the organometallic intermediate can be unimolecular [radical mechanism (2)] or bimolecular [without the involvement of radicals—mechanism (3)]. The decomposition of aliphatic organometallic derivatives containing a β-hydrogen atom apparently takes place via a hydride abstraction stage. This case will be examined below.

A detailed study of the products of the reactions of organomagnesium compounds with transition metal salts was first undertaken by Smith[13] in order to elucidate the mechanism of the decomposition of organometallic intermediates. It was found that, when cobalt(II) bromide reacts with PhMgBr, benzene (42%) and biphenyl (45%) are formed, whereas in the case of p-MeC_6H_4MgBr the products are toluene (55%) and bitolyl (33%). On the other hand, when a mixture of these Grignard reagents (PhMgBr and p-MeC_6H_4. .MgBr) is treated with $CoBr_2$, an asymmetric biaryl resulting from cross-coupling is formed together with the above products, the relative yields of the biaryls (%) differing from the statistical distribution: PhH (53)†, Ph_2 (30), PhMe (55), (p-$MeC_6H_4)_2$ (18), and PhC_6H_4Me (15). This result alone provides grounds for the hypothesis that the biaryls are not formed from free radicals.

When $CoBr_2$ reacts with a mixture of aryl and alkyl Grignard reagents (PhMgBr and EtMgBr), mainly benzene, ethane, and ethylene are formed, whereas the amount of cross-coupling products obtained is small[13]: PhH (81)†, Ph_2 (16), PhEt (5), EtH (52), C_2H_4 (47), and BuH (1).

In addition, the ratio of the alkanes and alkenes formed is smaller than in the reaction of individual alkylmagnesium bromides. In its turn the amount of benzene formed in this instance is greater than in the reaction of PhMgBr with $CoBr_2$ while that of biphenyl is actually smaller. According to Smith[13], this can be associated with the additional disproportionation reaction between the phenyl and alkyl derivatives of cobalt(II).

The results presented undoubtedly indicate a bimolecular mechanism of the decomposition of the intermediates or at least an appreciable contribution of this reaction pathway to the overall process. The data obtained by Wittig for the reactions of 2,2'-dilithiobiphenyl [14] or o-dilithiobenzene [15] with transition metal salts agree with this view. Thus o-dilithiobenzene gives rise to biphenyl and triphenylene (in an overall yield up to 25%), their relative yields depending on the nature of the salt employed. We may note that dehydrobenzene is not formed in this reaction and triphenylene could not therefore be produced as a result of its trimerisation.

The only product of the reaction of PhMgBr with cobalt(III) and manganese(III) acetylacetonates is biphenyl[16], whose yield is independent of the added α-methylstyrene. The operation of the bimolecular mechanism is apparently due to the fairly high stability of the aryl derivatives of cobalt(III) and manganese(III).[12,17]

In principle, a free-radical mechanism is also possible for the reactions of organomagnesium compounds RMgX with transition metal salts. Both the formation of the hydrocarbons RH in a series of reactions as well as the presence of deuterium in the products of the reaction of PhMgBr with various salts in a mixture of deuterated benzene and ether can serve as confirmation of this postulate[18]. The radicals can be formed in these reactions on homolytic decomposition of the transmetallation product or as a result of the one-electron oxidation of the organomagnesium compound. The available data are usually insufficient to make an unambiguous choice between the possible pathways leading to the formation of the reaction products. It has been shown convincingly in only one study[19] that radicals are formed in the reaction of alkyl-lithium with $TiCl_4$ as a result of electron transfer and not on decomposition of $RTiCl_3$, because the above compound is stable under the experimental conditions.

Like the aryl derivatives, aliphatic organomagnesium compounds react with transition metal salts apparently with formation of unstable organometallic compounds. It has been shown[20] that, when EtMgBr is treated in THF with palladium(II), copper(II), and copper(I) salts, the ratio of the products formed (ethane and ethylene) is close to unity. On treatment with iron(II), iron(III), cobalt(II), nickel(II), and manganese(II) salts, the ethane : ethylene ratio varies in the range 2–5,[20,21] but in the presence of styrene the yields of ethane and ethylene become identical and the yield of butane increases. According to the authors[20], styrene plays the role of a π-ligand and stabilises the organometallic intermediate; this reduces the probability of the homolytic decomposition, as a result of which the reaction proceeds via a bimolecular mechanism.

In the reaction involving the oxidation of two organomagnesium compounds (RmgX and R'MgX) containing a β-hydrogen atom the yield of the cross-coupling products is appreciable only for copper and silver salts, while in the remaining instances disproportionation products are formed. It is of interest to note that the ratio of alkanes and alkenes formed from RMgX depends on the nature of the R'MgX. Thus, in the interaction of ethyl- and n-propyl-magnesium bromides with palladium chloride, the ratio $C_2H_4/C_2H_6 = C_3H_6/C_3H_8 = 0.9$, while in the reaction of ethyl- and isopropyl-magnesium bromides $C_2H_4/C_2H_6 = 0.4$ and $C_3H_6/C_3H_8 = 2.6$, i.e. the alkane is formed mainly from the ethyl group, while the olefin is formed from the propyl group. An analogous behaviour has been observed for other transition metal salts, but the differences between the ratios of products are not so significant.

Two possible mechanisms of the formation of alkanes and alkenes in these reactions were considered[20]:

(1) the hydride mechanism[21]:

$$RCH_2CH_2M \rightarrow RCH{=}CH_2 + MH \quad ,$$
$$RCH_2CH_2M + MH \rightarrow RCH_2CH_3 + 2M \quad ;$$

(2) the bimolecular mechanism:

$$2RCH_2CH_2M \rightarrow RCH{=}CH_2 + RCH_2CH_3 + 2M \quad .$$

The authors[20] believe that organometallic intermediates formed in many reactions decompose with participation of the

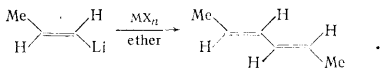
† The yields of the reaction products are calculated taking into account the overall concentration of Grignard reagents.

metal hydride. Reactions of organometallic compounds with copper(I) and silver salts, particularly in the case of secondary and tertiary derivatives, are an exception[22].

One of the distinctive features of vinyl Grignard reagents or organolithium compounds in reactions with transition metal salts is their tendency to form dimerisation products. However, the yield of the latter depends greatly on the nature of the metal salt. Thus the yield of hexa-2,4-diene in the reaction of *trans*-propenyl-lithium in ether varies as follows as a function of the salt[23]:

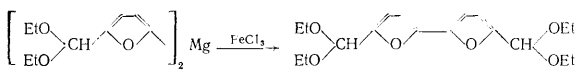
MX_n	$ZrCl_4$	$CrCl_2$	VCl_3	$PdCl_2$	$FeCl_2$	$CrCl_3 \cdot 3THF$	$MnBr_2$	$CoCl_2$	$(Ph_3P)_2PtCl_2$	MoCl
Yield, %	2	9	24	24	25	47	49	73	115	176

The reaction is to a large extent stereospecific even in those cases when the yield of hexa-2,4-diene is low. The reaction mechanism apparently involves the bimolecular decomposition of vinyl derivatives of metals. According to the authors[23], the high stereospecificity of the reaction is due to the involvement of the π-bond in the stabilisation of the configuration of the transition state:



Biaryls are apparently formed in reactions of aryl Grignard reagents with transition metal salts also on bimolecular decomposition of the intermediates. For example, the fact that the yield of biphenyl reaches 70% in the interaction of PhMgBr with $FeCl_3$ in ether at −80 °C, while chlorobenzene and an appreciable amount of tarry products are formed at the usual temperatures is consistent with this view[24]. One cannot rule out the possibility that at room temperature the intermediate undergoes the usual homolytic decomposition and not bimolecular decomposition and the phenyl radicals formed are oxidised to chlorobenzene. Such a decrease of the relative yield of the dimer with increase of temperature was observed for the reaction of $CoBr_2$ with a neophyl Grignard reagent without a β-hydrogen atom[25].

Organomagnesium derivatives of the furyl series are oxidised by transition metal salts with formation of dimerisation products. Thus treatment of bis(2-diethoxymethyl-5-furyl)-magnesium with iron(III) chloride results in a quantitative yield of bis-2,2′-diethoxymethyl-5,5′-bifuryl[26]:



Organoaluminium compounds react fairly readily with transition metal salts. When triethylaluminium is treated with cobalt(II) chloride in ether, ethane and ethylene are formed in nearly unimolecular proportions (51.5 : 48).[27] At a higher temperature, for example on refluxing in methylcyclohexane, the yield of the alkane increases to 69%, which may be associated with the homolytic decomposition of the organocobalt intermediate. When trimethylaluminium interacts with cobalt(II) acetylacetonate in benzene, methane and ethane are mainly formed (in proportions of 3 : 1) together with a small amount of toluene[28]. The authors[28] believe that toluene is the product of heterolytic substitution in which the intermediate $CH_3Co(acac)_2$ participates, and it is most probably formed on radical methylation of benzene.

The reactions of triethylaluminium with cobalt(III), chromium(III), and iron(III) acetylacetonate complexes have been investigated in fair detail[29,30], because these systems are used to initiate the polymerisation of monomers. The formation of nickel(I) compounds has been detected by EPR in the reaction involving a nickel(II) complex.[31]

Organometallic compounds having a more covalent C–M bond than the compounds of alkali and alkaline earth metal metals also react fairly readily with transition metal salts. For example, Razuvaev and coworkers have shown that, when diphenylmercury is refluxed with iron(III), cobalt(II), manganese(II), and nickel(II) chlorides in dioxan, ethylcellosolve, or pyridine, the product is benzene. Biphenyl was not detected among the products[32,33]. The intermediates formed apparently decompose under the reaction conditions via a free-radical mechanism and the phenyl radicals react with the solvent. At a lower temperature the stability of the intermediates increases and, as already shown for reactions with active organometallic compounds, a bimolecular decomposition mechanism operates in this instance and a biphenyl is formed.

In the reaction of diphenylmercury with highest-valence vanadium compounds ($VOCl_3$ and VCl_4) in cyclohexane, biphenyl is formed[34], i.e. the intermediates decompose via a bimolecular mechanism. This is also indicated by the finding that, for the equimolar reactant ratio, these reactions do not induce the polymerisation of ethylene. However, in the presence of an excess of diphenylmercury relative to the oxidant, polyethylene with a low molecular weight is formed, which the authors[34] believe to be due to the homolytic decomposition of vanadium derivatives containing several phenyl groups.

When dibenzylmercury or benzylmercury chloride is oxidised with iron(III), cobalt(II), and copper(II) chlorides, benzyl chloride is formed[35]:

$$PhCH_2HgCl + FeCl_3 \rightarrow PhCH_2Cl + HgCl_2 + FeCl_2 \quad .$$

The authors[35] believe that the reaction has a latent ionic mechanism (free radicals are not formed in the reaction). These two-electron oxidation reactions will be examined in greater detail below.

The reactions of di-isopropylmercury with titanium(IV), iron(III), cobalt(II), and tin(IV) chlorides result in the formation of isopropyl radicals, because the acrylonitrile added to the reaction mixture polymerises under these conditions[36]. However, it is difficult to agree with the authors[36] that this is evidence for the one-electron transfer mechanism because the radicals might have been formed as a result of the homolysis of the intermediate formed.

The main product of the reaction of di(*p*-tolyl)mercury with $Pd(OAc)_2$ or of *p*-tolylmercury acetate with $PdCl_2$ is bitolyl[37]. Heterocyclic organomercury compounds react similarly[38]. The formation of biaryls in the reaction of substituted arylmercury salts with palladium(II) chloride proceeds equally well in the presence of both electron-donating and electron-accepting substituents[39]. The reaction was patented as a method of synthesis of biaryls as a result of the oxidative coupling of organomercury salts and was modified in such a way that the palladium(II) salts functioned as the catalyst and the oxidant was $CuCl_2$:[39]

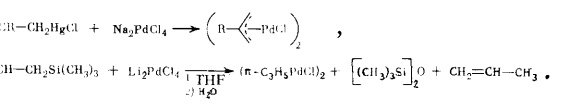
$$p\text{-}MeC_6H_4HgCl \xrightarrow[AcOH]{PdCl_2\text{-}CuCl_2} (p\text{-}MeC_6H_4)_2 \quad .$$

The interaction of arylboronic acids with palladium salts should be included among the oxidative coupling reactions of the type considered[40]. A common feature of all these reactions is that they apparently proceed via a transmetallation stage and subsequent bimolecular decomposition of organopalladium intermediates:

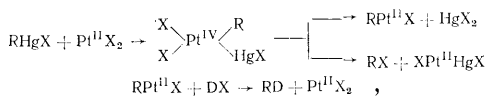
$$RHgX + PdX_2 \rightarrow RPdX + HgX_2 \quad ,$$
$$2RPdX \rightarrow R_2 + PdX_2 + Pd \quad .$$

When the organopalladium intermediate is relatively stable, the reaction stops at the transmetallation stage. For example, when allyl derivatives of metals are treated with palladium(II)

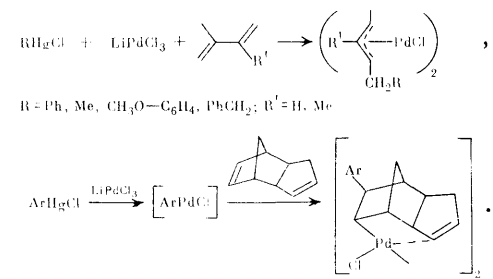
chloride, a stable dimer of π-allylpalladium dichloride is formed[41,42]:



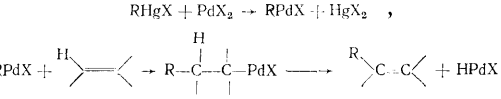
On the other hand, if the palladium intermediate is unstable, its formation can be inferred from the products formed following the addition of special reagents or on reaction with the solvent. For example, it has been shown that[43] the protolysis of alkylsilanes is catalysed by palladium(II) and platinum(IV) salts. Transmetallation leads to the formation in the reaction of organometallic intermediates, which undergo protolysis. The formation of platinum intermediates in the reaction of RHgBr (R = Me, Et, or Bu) with K_2PtX_4 (X = Cl or Br) may be postulated analogously[44]. The reaction was carried out in a D_2O–MeCOOD mixture, in which organomercury compounds are stable, but, after the addition of platinum salts, deuterated hydrocarbons and alkyl halides were formed. It has been suggested that the reaction proceeds via an oxidative addition stage:



Olefins are specific agents trapping the unstable organopalladium intermediates. The reaction involving addition to a multiple bond results in the formation of a new organopalladium compound which can be isolated if it is sufficiently stable[45–47]:



The reaction continues in an interesting manner when the organopalladium intermediate is not stabilised by ligands and contains a β-hydrogen atom. The elimination of palladium hydride then results in the formation of a substituted olefin[46]:

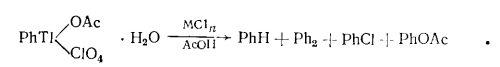


This reaction, discovered by Heck and given his name, is of preparative value as a method of arylating olefins[46,48–50].

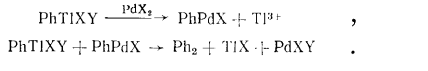
Another compound whose reaction can serve as a test for the formation of palladium intermediates is carbon monoxide. For example, alkyl carboxylates and ketones are formed in alcohol in the presence of CO.[51] However, in the presence of a very large excess of the olefin or CO, the bimolecular decomposition of intermediates is not fully suppressed, although the yield of a dimeric product diminishes[51,52].

Apparently there exists also another pathway in the reaction of organometallic compounds with palladium(II) salts in which there is no transmetallation stage. Thus the composition and yield of the products of the reaction of bis(allylpalladiumchloride) with organic derivatives of Group IVB elements depend on the nature of the metal[53]. It has therefore been suggested that the oxidation proceeds in the complex of R_4M with $(\pi\text{-}C_3H_5PdCl)_2$.

In the reaction of the organothallium compound $PhTl(OAc)_2 \cdot ClO_4 \cdot H_2O$ with $PdCl_2$, benzene and biphenyl are formed on refluxing in acetic acid[54]. If the same reaction is carried out in the presence of catalytic amounts of other transition metal chlorides (117 °C, 5 h), then chlorobenzene and phenyl acetate are formed together with biphenyl[55]:



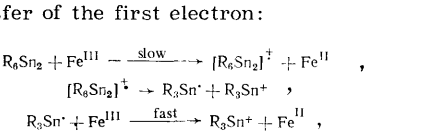
We may note that, with the exception of biphenyl, all these products might be formed in the presence of metal salts either as a result of acetolysis or as a result of the oxidative elimination of thallium. The mechanism of the formation of biphenyl, whose yield depends on the nature of the catalyst employed, is more complex. It is believed[55] that the poor reproducibility of the yield of biphenyl in the reactions involving iron(II), thallium(III), and copper(II) chlorides indicates a radical reaction mechanism. Presumably the intermediate $PhMCl_{n-1}$, formed as a result of transmetallation, undergoes homolytic decomposition and the catalyst is regenerated when MCl_{n-1} is oxidised with tervalent thallium. At the same time one cannot rule out the possibility of the formation of biphenyl also without the involvement of free radicals, as has been suggested, for example, for the reaction of organothallium compounds with $PdCl_2$:[55]



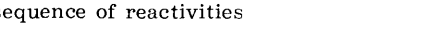
This reaction pathway resembles very closely the bimolecular decomposition of organometallic compounds discussed above and formally constitutes two-electron oxidation.

It is seen from the data presented above that the commonest mechanism of the oxidation of organometallic compounds by a transition metal salt involves consecutive transmetallation stages and thermal decomposition of the intermediates formed. However, there exist processes in which oxidation takes place as a result of intermolecular electron transfer. Such reactions are particularly characteristic of organobimetallic compounds and π-bonded transition metal compounds—for example the oxidation of distannanes R_3SnSnR_3 (R = Me, Bu, or Ph) by compounds of iron(III) perchlorate with phenanthroline[56] or other complex-forming agents[57] in acetonitrile:

The reaction is of second order overall and of first order with respect to each reactant and the slow stage is apparently the transfer of the first electron:

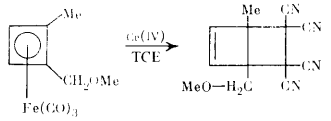


The observed sequence of reactivities

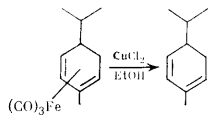


reflects the electron-donating capacity of these compounds relative to the oxidant. The satisfactory linear correlation between $\lg k_2$ and $E^0(Fe^{III}L_n/Fe^{II}L_n)$ with a slope $\alpha = 0.44$ suggests that electron transfer proceeds via an outer-sphere mechanism[56]. Processes such as the interaction of silver

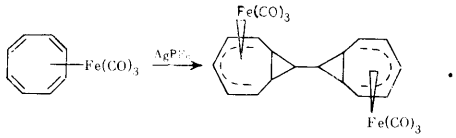
salts with the distannanes R_6Sn_2 [58] and diplumbanes[59] or the oxidation of π-bonded transition metal compounds should apparently be considered within the framework of the oxidation-reduction mechanism. Thus the oxidation of substituted cyclobutadieneiron tricarbonyl by cerium(IV) leads to the formation of a substituted cyclobutadiene, which can be trapped by tetracyanoethylene (TCE):[60]



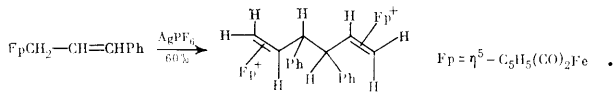
The dienyl complexes of $Fe(CO)_3$ are oxidised similarly by copper(II) chloride[61]:



Whereas the iron atom is oxidised in the above reactions of dienyl complexes of $Fe(CO)_3$, in the interaction of the η^4-cyclo-octatetraenyl complex with silver hexafluorophosphate only the organic ligand is oxidised and a new organometallic compound is formed[62]:



The oxidation of allyl σ-derivatives of cyclopentadienyliron dicarbonyl is the same type of reaction[63]:



We may note that in this case both the organic group and the organometallic fragment are oxidised. The intermediate formation of allyl radicals in this reaction has been confirmed by the finding that the π-olefin cation (Fp^+-π-CH_2=CR^1-CR^2R^3H), which is a product of the reaction of the radical with a solvent, is formed together with the dimer.

III. OXIDATION OF ORGANOMETALLIC COMPOUNDS BY SILVER AND COPPER SALTS

We shall consider the reactions involving the oxidation of organometallic compounds by salts of the copper subgroup metals: Cu, Ag, and Au. These reactions are of interest because many of them, particularly those involving copper(I) salts, are widely used in organic synthesis[63].

1. Reactions of Organometallic Compounds with Univalent Silver Salts

It is well known that the interaction of organometallic compounds with silver salts results in the formation of organosilver compounds which are usually unstable and yield on decomposition the radical coupling products[65]. Thus the reactions of Grignard reagents RMgX (for example, with R = Ar, $PhCH_2$, or Bu) with silver salts lead to the formation of the hydrocarbon R_2, whose yield is frequently quantitative[66,67]. Apart from the coupling product R_2, the reactions of isobutyl- and s-butyl-magnesium bromides results in the formation of a small amount of butene and butane[68]. It has been shown that the reaction of $RPbEt_3$ (R = p-$CF_3C_6H_4$, p-$Me_2NC_6H_4$, PhCH=CH, etc.) involves the cleavage of the bond and the formation of an organosilver compound which then decomposes to R_2.[69] The reactions of benzyl and allyl derivatives of lead result directly in the formation of R_2. The intermediate formation of organosilver compounds cannot be detected in this instance because they are extremely unstable. In the reaction of vinyl derivatives of lead, mono-olefins are obtained together with hydrocarbons[70,71].

Thus the reactions of organometallic compounds with silver salts as a rule begin with transmetallation. This view gives rise to no doubts at the present time and the problem therefore consists in establishing the mechanism of the thermal decomposition of the organosilver compounds. Numerous investigations in this field have shown that RAg can decompose via a bimolecular mechanism, i.e. without the involvement of free radicals[22,72,73], and via a free-radical mechanism[69,74-77]. The relative contributions of these reaction pathways are in general determined both by the nature of the group R and by the reaction conditions. We shall consider the problem in relation to the thermal decomposition reactions of alkyl, vinyl, and aryl derivatives of silver.

The radical mechanism of the thermal decomposition of organosilver compounds was first proposed for ethylsilver[78] and was subsequently confirmed as a result of a study of the kinetics of this reaction[74]. The main evidence in support of the formation of radicals is that the amount of ethane formed is greater than that of ethylene:

$$C_2H_5Ag \xrightarrow{EtOH} C_2H_6 + C_2H_4 + C_4H_{10} \quad .$$

The ratios of the yields of C_2H_6, C_2H_4, and C_4H_{10} are 2.5 : 0.38 : 0.37.[74] There is no doubt that ethane is a product of the reaction of the ethyl radical with the solvent#. An analogous behaviour has been observed in the reaction of Et_4Pb with $AgNO_3$ in which ethylsilver is obtained as an intermediate, while ethane, ethylene, and butane are formed in ratios of 53.2 : 9.9 : 36.2.[72]

At the same time, there are data which do not agree with the free-radical mechanism of these reactions. For example, the reaction of tetramethyl-lead with $AgNO_3$ results in the formation of ethane; methane has not been detected among the reaction products[78]. Furthermore, styrene, methyl methacrylate, or acrylonitrile added to the reaction mixture do not polymerise under the reaction conditions[76].

A widely used procedure, with the aid of which investigators have frequently attempted to determine the mechanism of the decomposition of organosilver compounds, consists in carrying out simultaneously the reactions of the silver salt with two different Grignard reagents and subsequent analysis of the reaction products. Thus the interaction of silver bromide in THF with ethylmagnesium bromide mixed with other alkylmagnesium bromides results in the formation of the following coupling products[79]:

$$EtMgBr + RMgBr \xrightarrow[THF,\ 2°C]{AgBr} C_4H_{10} + EtR + R_2 \quad .$$

R	n-C_4H_{10}, %	EtR, %	R_2, %	Σ, %
Et	46	46	--	92
Pr	47	37	12	96
iso-Pr	41	28	10	79
t-Bu	36	5	19	60

The data presented show that in the case of normal alkylmagnesium bromides the overall yield of coupling products is also quantitative. The amount is somewhat smaller in the

It has been shown that the radical abstracts hydrogen from the hydroxy-group of the alcohol but in the decomposition of methylsilver more hydrogen is abstracted from the α-CH bond[77].

reaction with Grignard reagents having a branched group R, which is apparently associated with the formation of alkanes and alkenes in side reactions. It is also striking that, with increase of the degree of branching in the group R in the Grignard reagent, the yield of cross-coupling products diminishes from 46% to 5%, while the yield of homocoupling products R_2 not only does not diminish but actually increases. These data are difficult to account for from the standpoint of the free-radical mechanism.

The most convincing evidence for the possibility of a bimolecular mechanism of the decomposition of alkyl derivatives of silver has been obtained by Clinton and Kochi[80], who investigated the reaction of tetraethyl-lead with silver triflate in THF. It was found that the ratio of the ethane, ethylene, and butane formed in this instance depends on the concentration of the silver salt and that in the presence of oxygen the yield of ethane is significantly reduced, while that of butane remains almost unaltered. Evidently ethane is formed predominantly via a radical pathway, while butane results from the bimolecular reaction

$$2EtAg \rightarrow BuH + 2Ag \quad .$$

In contrast to free alkyl derivatives of silver, the tributylphosphine complex of n-butylsilver is more stable and decomposes in ether with formation of octane (93%) and insignificant amounts of butane (5%) and butene (2%).[22] According to the authors[22], the C–Ag bond dissociates in this instance with simultaneous formation of a new C–C bond, while the contribution of the radical reaction pathway is insignificant. Furthermore, silver(I) hydride is apparently not involved in the formation of the disproportionation product, because the yield of butane is higher than that of butene. However, one cannot rule out the possibility that the thermal decomposition of s-BuAg(PBu_3) does in fact proceed via a stage involving the formation of AgH, since all the products (butane, butene, and octane) are obtained in comparable amounts and, furthermore, the amount of butene is greater than that of butane:

$$\underset{29\%}{\text{s-BuAg}(PBu_3)} \rightarrow \underset{35\%}{BuH} + \underset{30\%}{C_4H_8} + C_8H_{18} + Ag + PBu_3 \quad ,$$

$$RAg(PBu_3) \rightarrow R(-H) + HAg(PBu_3) \quad ,$$

$$RAg(PBu_3) + HAg(PBu_3) \rightarrow RH + Ag + PBu_3 \quad ,$$

$$2RAg(PBu_3) \rightarrow R_2 + Ag + PBu_3 \quad ,$$

$$2HAg(PBu_3) \rightarrow H_2 + Ag + PBu_3 \quad .$$

It is seen from the data presented that the alkyl derivatives of silver can decompose via both radical and bimolecular mechanisms. Vinyl organosilver compounds decompose similarly. For example, the interaction of triethylisobutenyl-lead with silver nitrate at very low temperatures yields a relatively unstable isobutenyl derivative of silver. At temperatures above −20 °C isobutene is formed preferentially together with a small amount of 2,5-dimethylhexa-2,4-diene (10%).[70] The detection of the olefin among the reaction products undoubtedly demonstrates the formation of free radicals in the decomposition of the corresponding silver compound. The author[70] proposed the following chain mechanism of the process with participation of the ethoxy-radical:

$$Et_3PbCH{=}CMe_2 \xrightarrow{AgX} Me_2C{=}CHAg \quad ,$$

$$Me_2C{=}CHAg \rightarrow Me_2C{=}CH^{\cdot} + Ag \quad ,$$

$$2Me_2C{=}CH^{\cdot} \rightarrow Me_2C{=}CH{-}CH{=}CMe_2 \quad ,$$

$$Me_2C{=}CH^{\cdot} + EtOH \rightarrow Me_2C{=}CH_2 + EtO^{\cdot} \quad ,$$

$$Et_3PbCH{=}CMe_2 + EtO^{\cdot} \rightarrow Et_3PbOEt + Me_2C{=}CH^{\cdot} \quad .$$

An analogous mechanism has been proposed for the reaction of tetravinyl-lead with silver nitrate[71§]. The hypothesis of the radical chain mechanism is based on the finding that, with decrease of the concentration of $AgNO_3$, the yield of isobutene increases[70]. However, Tamura and Kochi[79] showed that the metallic silver formed in the decomposition process can be oxidised by the nitrate ion and the effect of the $AgNO_3$ concentration observed by Glockling[70] might be partly due to this reaction. Thus the decomposition of vinylsilver is a radical process.

On the other hand, the tributylphosphine complexes of 1-propenyl- and 2-butenyl-silver decompose via the bimolecular mechanism, judging from stereochemical data, since the only reaction product, resulting from the coupling of the radicals, is formed with retention of the configuration of the sp^2-hybridised carbon atom[82].

We shall consider the decomposition reactions of aromatic derivatives of silver primarily in order to demonstrate the possibility of the occurrence of the radical and bimolecular mechanisms for this class of compounds and to discuss certain problems concerning the nature of the bimolecular mechanism.

It has been shown that in the joint decomposition of phenyl- and tolyl-silver in pyridine at 50–80 °C, the cross-coupling product is formed in a statistical proportion and that the addition of quinone diminishes appreciably the yield of not only ArH but also Ar_2.[75] There is no doubt that the decomposition of ArHg results in the formation of free radicals in this instance, apparently owing to the high reaction temperature.

In contrast to this, the reaction of silver bromide with a mixture of phenyl- and anisyl-magnesium bromides in ether leads to proportions of products which differ from the statistical distribution[83]:

$$PhMgBr + p\text{-}MeOC_6H_4MgBr \xrightarrow{AgBr} \underset{22\%}{Ph_2} + \underset{18.2\%}{PhC_6H_4OMe} + \underset{4.7\%}{(MeOC_6H_4)_2} \quad .$$

Furthermore, the relative yields of products depend on the concentration of the Grignard reagent. The authors[83] believe that ArAg decomposes via a radical pathway, but we think that the data presented actually support the bimolecular reaction mechanism.

The reactions of silver nitrate with tetraphenyl derivatives of tin and lead merit special attention[73]. Whereas in the first reaction the main product is benzene (80.6%) with only 5.2% of biphenyl, in the second case the main product is biphenyl (70.2%) and only trace amounts of benzene are produced. The observed differences between the compositions of the reaction products are undoubtedly associated with the different conditions in the decomposition of phenylsilver. Presumably the steady-state concentration of phenylsilver in the reaction of Ph_4Pb, which is much faster than the reaction of Ph_4Sn,[73] is high and the bimolecular decomposition of PhAg is therefore more probable. On the other hand, in the reaction of Ph_4Sn with $AgNO_3$ phenylsilver decomposes mainly via a radical mechanism and benzene is formed¶.

We believe that benzene can be formed also as a result of the catalytic decomposition of PhAg by silver nitrate. This view is confirmed indirectly by the finding that the complex

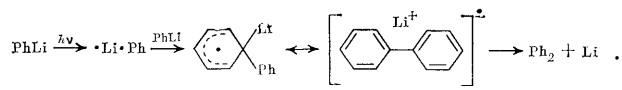
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§ A radical chain mechanism has also been proposed for the decomposition of RMe_2SiCH_2Ag (R = Me or Ph).[81]

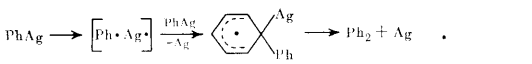
¶ The formation of benzene in this reaction can hardly be attributed to the radical chain mechanism considered above for vinyl derivatives of lead, because organotin compounds show a smaller tendency, compared with lead compounds, to enter into S_H2 reactions[84].

$5PhAg.2AgNO_3$ decomposes rapidly at room temperature, while pure phenylsilver is stable even in the course of a whole day[85]. Generally speaking, this is by no means a common phenomenon where the metal salt initiates the decomposition of an organic derivative of the same metal, particularly when the latter is in the same oxidation state. An attempt may be made to account for this finding by taking into account certain characteristics of silver compounds. The effect of silver nitrates in this reaction can be twofold: firstly, the Ag^+ cation is in principle capable of oxidising PhAg with formation of phenyl radicals, whereupon the reaction product is benzene, and, secondly, silver nitrate can prevent the formation of dimeric (polymeric) associated species, which are known for organosilver compounds[65]. We draw special attention to the possible role of the formation of associated species, because the latter can influence in a most unusual manner the pathway leading to the decomposition of organometallic compounds. On the other hand, the formation of associated species can increase the stability of the organosilver compound irrespective of decomposition. On the other hand, the decomposition of the associated species should lead to the formation of a dimer R_2, which is usually explained from the standpoint of the bimolecular mechanism.

Van Tamelen's mechanism, proposed for the photochemical decomposition of phenyl-lithium in ether[86], can involve an unusual mode of bimolecular decomposition of PhAg:

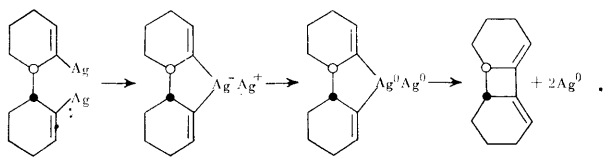


At first sight this photochemical reaction has little in common with the decomposition of PhAg, but these processes have the common feature that free radicals are not formed and the only product is biphenyl. By analogy with van Tamelen's mechanism, one can put forward the following mechanism for the decomposition of phenylsilver:



Evidently the formation of dimers can favour this course of reaction.

Another model for the decomposition of organosilver compounds without the involvement of free radicals has been considered by Moore et al.[87] These workers suggested that the intramolecular coupling products are formed in the decomposition of *d,l*-2,2′-disilver-3,3-bicyclohexenyl as a result of the following oxidation-reduction processes†:



In essence, this mechanism postulates the formation of intermediates whose structure is analogous to that of the organic cuprates R_2CuLi.

In conclusion of this section on the action of silver salts on organometallic compounds we may note that certain organic derivatives of non-metallic elements, for example, boron[88,89], react analogously. The reaction yields the corresponding silver compounds whose decomposition leads to the formation of coupling products.

Gold(I) salts have analogous chemical properties to those of silver salts; for example, their reaction with organoboron compounds results in the formation of the dimerisation products R_2 [89,90]

2. Reactions of Organometallic Compounds with Copper Salts

The reactions of organometallic compounds of the type RM with copper salts are undoubtedly more common and have been more thoroughly investigated than the reactions with silver salts. This is not surprising bearing in mind not only the wide variety of the products formed but also the definite synthetic value of these reactions. Depending on the oxidation state of copper, the hydrocarbon R_2 or RH and R(-H), as well as two-electron oxidation products, for example, organic halides in reactions with copper(II) halides, can be formed.

Leaving aside for the moment the details of the mechanisms of the interaction of organometallic compounds with copper salts, we may note that all these reactions usually proceed via a transmetallation stage. However, the intermediates formed are relatively stable only in the case of copper(I) compounds and they can be sometimes actually isolated at the usual temperature[85,91,92]. On the other hand, if the intermediates are very unstable, and this happens much more frequently, then their formation can sometimes be confirmed indirectly[93]. For example, Clinton and Kochi[94] established that the acetolysis of tetraethyl-lead is catalysed by copper(I) salts. The study of this phenomenon in a deuterated solvent showed that the kinetic isotope effect (KIE) in the reaction differs from that in the non-catalysed reaction (in the absence of copper salts, ethane-d_1 is formed six times more slowly than in the catalysed reaction). The results demonstrate convincingly the intermediate formation in the catalysed reaction of ethylcopper, which undergoes protolysis.

The oxidation of organometallic compounds by copper(II) salts proceeds similarly via a transmetallation stage. Although the corresponding intermediates have never been obtained, this view has now become firmly established. The mechanism of oxidation via a one-electron transfer stage appears unlikely in view of the low oxidising capacity of copper(II) salts[95] (admittedly the oxidation of carbanions may prove to be an exception to this rule). This can be illustrated fairly clearly by comparing the reactions involving the oxidation of tetraalkyl-lead by copper(II) chloride and the anion $IrCl_6^{2-}$, which is a one-electron oxidant:

$$R_4Pb + 2CuCl_2 \rightarrow RCl + R_3PbCl + 2CuCl \quad ,$$

$$R_4Pb + 2IrCl_6^{2-} \rightarrow RCl + R_3PbCl + 2IrCl_5^{2-} \quad .$$

The same product, namely alkyl chloride, is formed in both processes but there are significant differences between the reaction kinetics[96,97]. Whereas in the oxidation of tetraethyl-lead by $IrCl_6^{2-}$ the rate of reaction exceeds by a factor greater than 1000 the rate of oxidation of Me_4Pb, the opposite relation is observed in the reaction with $CuCl_2$—Me_4Pb proved to be 44 times more active than Et_4Pb. There is no doubt that these differences are due to the high steric hindrance by the bulky Et_3Pb group in the transmetallation reaction. Furthermore, in the oxidation of a mixed compound of the type $Et_{4-n}Me_nPb$ (n = 1–3) by $IrCl_6^{2-}$, the ethyl group shows a greater tendency to be split off, and not the methyl group as usually happens in electrophilic substitution.

† The open and filled circles denote carbon atoms having different configurations.

Combined analysis of the results of studies of the reactions of copper salts with organometallic compounds permits the differentiation of three main problems: (1) the mechanism of the formation and decomposition of organic derivatives of copper(I); (2) the mechanism of the reaction of organometallic compounds with copper(II) salts; (3) the possible pathways leads to the formation of the products of the two-electron oxidation of organometallic compounds by copper salts. All these problems are considered in subsequent sections.

3. Thermal Decomposition of Organocopper Compounds

Numerous studies on the thermal decomposition of organocopper compounds have been published recently. In these reactions the organic derivatives of copper(I) partly resemble the organosilver compounds, although, depending on the nature of the organic group in the RCu or RAg molecules and the reaction conditions, certain differences are also observed. Thus, in the thermal decomposition of alkylcopper, alkanes and alkenes are formed in maximum amounts rather than the coupling products R_2 as was the case for the silver compound. Alkanes and alkenes are virtually the only decomposition products of alkylcopper stabilised by trialkylphosphines and their ratio may be the same[30]. For example, butane and but-1-ene in proportions of 49 : 51, hydrogen (10%), and less than 0.1% of octane are formed in the thermal decomposition of the tributylphosphine complexes of butylcopper in ether[21,82]. The decomposition of 5-hexenylcopper-(I) in a complex with tributylphosphine in ether gives rise to 44% of hex-1-ene, 52% of hexa-1,5-diene, and only 3.5% of cyclic hydrocarbons[81]. In this case the reaction does not have a radical mechanism, since it is known that the cyclisation of hexenyl radicals is faster than the abstraction of hydrogen from the solvent[98,99]. Furthermore, it has been shown that the rate of decomposition of alkylcopper is not influenced by the addition of "radical trapping agents" such as styrene[21,82,100,101]. To explain the results, a mechanism has been proposed for the thermal decomposition with participation of copper hydride[21,100]:

$$\text{i. } \mathrm{BuCu \cdot P(n\text{-}Bu)_3} \rightarrow \mathrm{CH_2{=}CH_2} + \mathrm{CH_2{=}CH_2} + \mathrm{HCu \cdot P(n\text{-}Bu)_3} \quad ,$$

$$\mathrm{BuCu \cdot P(n\text{-}Bu)_3} + \mathrm{HCu \cdot P(n\text{-}Bu)_3} \rightarrow \mathrm{BuH} + 2\mathrm{Cu} + 2\mathrm{P(n\text{-}Bu)_3} \quad .$$

Analysis of the products formed in the decomposition of a mixture of RCu and R'Cu (R = Et, and R' = Pr or iso-Pr) showed that there are two independent decomposition pathways:

$$\mathrm{EtCu + PrCu \text{ or iso-PrCu} \xrightarrow{\begin{matrix} a \\ b \end{matrix}} \begin{matrix} \rightarrow C_2H_6 + C_3H_6 + 2Cu \\ \rightarrow C_2H_4 + C_3H_8 + 2Cu \end{matrix}} \quad .$$

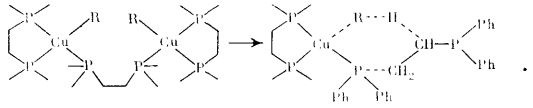
Pathway *a* proves to be dominant in the case of PrCu, while pathway *b* is dominant for iso-PrCu, which has been explained[78] by the easier reduction of secondary derivatives by copper hydride compared with the primary derivatives.

There exists the view that copper hydride is formed in the thermal decomposition of alkylcopper as a result of the β-elimination of the hydride ion[21], similarly to the formation of hydrides of other transition metals on decomposition of unstable organometallic compounds[102]. However, it is difficult to explain from this standpoint why the olefin is formed mainly from the ethyl fragment in the decomposition of a mixture of ethylcopper and isopropylcopper[78], since the hydride ion is usually abstracted from the carbon atom with the smallest number of hydrogen atoms. We believe that the thermal decomposition reactions are in reality of the radical type but occur within the complex. In fact, if the decomposition takes place within a binuclear complex formed in the solution, for example, on elimination of a phosphine ligand, then the heterolysis of the C–C bond will occur more readily in the case of isopropylcopper; in its turn the radical formed abstracts a β-hydrogen from another organic group#.

One may point to a certain analogy between the reaction mechanism discussed above and the mechanism proposed by Miyashita and Yamamoto[104], who investigated the thermal decomposition of the 1,2-bis(diphenylphosphino)ethane complex of RCu (R = Me, Et, Pr, or iso-Bu). It was found that this reaction does not proceed entirely in the usual manner—biphenylvinylphosphine is formed together with an alkane:

$$(\mathrm{RCu})_2(\mathrm{dppe})_3 \xrightarrow{\mathrm{THF}} \mathrm{Ph_2PCu(dppe)} + \mathrm{RH} + \mathrm{Ph_2PCH{=}CH_2} + \mathrm{RCu(dppe)} \; ;$$
$$\mathrm{dppe} = \mathrm{Ph_2PCH_2CH_2PPh_2} \quad .$$

The authors[104] believe that an intramolecular reaction with a phosphine ligand in which there is a concerted transfer of hydrogen and the cleavage of a carbon–phosphorus bond, takes place in this instance:



An interesting feature of the decomposition reaction of alkylcopper and possibly of other copper(I) derivatives is that the process can be catalysed by metals and not only by copper and silver but also by palladium[100]. Thus the decomposition of alkylcopper is an autocatalytic process and the induction period observed in this reaction diminishes following the addition of metals which can be arranged in the following sequence in terms of their activities: Cu > Ag > Pd. The formation of the paramagnetic dinuclear organocopper intermediate $[\mathrm{EtCu^{I}.Cu^{0}}]$ was demonstrated by EPR in the decomposition of ethylcopper in THF. The authors[100] proposed the following mechanism of the catalytic process involving the species:

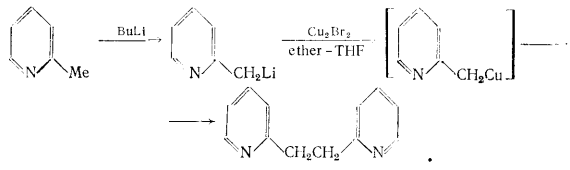
$$\mathrm{RCu^{I}} + \mathrm{Cu^{0}} \rightarrow [\mathrm{RCu^{I}Cu^{0}}] \quad ,$$

$$[\mathrm{RCu^{I}Cu^{0}}] \xrightarrow{\text{fast}} \mathrm{R(-H)} + [\mathrm{Cu^{0}}] \cdot \mathrm{CuH} \quad ,$$

$$\mathrm{RCu^{I}} + \mathrm{CuH} \rightarrow \mathrm{RH} + 2\mathrm{Cu^{0}} \text{ etc.}$$

However, we believe that the catalytic decomposition of alkylcopper can also occur on the surface of the metal. The copper atoms formed in the reaction are incorporated in the metal lattice and the resulting energy gain, equal to the heat of condensation, is the decisive factor in this catalytic reaction.

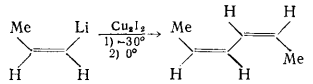
Benzyl derivatives of copper(I) are particularly unstable and readily decompose during preparation with formation of the dimer R_2. This reaction is used, for example, in the dehydrodimerisation of picolines[105,106]:



Since benzyl radicals usually dimerise and do not abstract hydrogen from the solvent, the formation of R_2 in the decomposition of benzyl derivatives of copper(I) is no longer a criterion of a bimolecular reaction mechanism. The homolytic dissociation of a carbon–metal bond can occur in this reaction with equal success.

The radical abstraction of a β-hydrogen atom is known to occur, for example, in the reaction of organomercury compounds with $CCl_3^{\cdot}$.[103]

Dienes are formed in the decomposition of vinyl derivatives of copper as in the case of silver compounds. The reaction is more stereospecific both in the presence and in the absence of tributylphosphine[23,82,107]. This is usually regarded as an argument against a radical reaction pathway:



Judging from the formation of the hydrocarbon ArH, the decomposition of the aryl derivatives of copper ArCu takes place in many instances via a radical mechanism[75]. The thermal decomposition of 2-dimethylaminophenylcopper in dimethylformamide (DMF) apparently takes place in this way, since *N*,*N*-dimethylaniline is formed in this reaction together with 2,2′-bis(dimethylamino)diphenyl (40%).[108] Even in the complex with 1,2-bis(diphenylphosphino)ethane this compound decomposes with participation of radicals and diphenylvinylphosphine is formed in addition to *N*,*N*-dimethylaniline [109] (see the analogous reaction for alkyl compounds of copper[104]).

At the same time there exist data showing that aryl derivatives of copper(I) can decompose without the participation of free radicals[111,112]. This applies particularly to the decomposition of various cluster compounds. Thus the decomposition of the octanuclear cluster $(m\text{-}CF_3C_6H_4)_8Cu_8$ yields biaryl and a cluster assumed to be of the type R_4Cu_8.[113,114] However, this cluster apparently decomposes via a radical mechanism, since trifluoromethylbenzene is then formed[114].

The dimer 2,2′-bis(dimethylamino)biphenyl is formed in a yield exceeding 90% on decomposition of $(2\text{-}Me_2NC_6H_4)_4Cu_6Cl_2$, while the decomposition of the corresponding non-cluster compound yields mainly *N*,*N*-dimethylaniline[108]. The steric proximity of the aryl group in this hexanuclear cluster promotes this reaction pathway[115]. The relative positions of the groups Ar and R (Ar = $2\text{-}Me_2NC_6H_4$, R = PhC≡C) determine similarly the decomposition of the cluster $Ar_4R_2Cu_6$. The only product of this reaction is ArR and there are not even traces of R_2 and Ar_2.[116,117]

The data presented show that the formation of cluster intermediates is important for the decomposition of organocopper compounds with formation of radical coupling products. The finding that the yield of 1-phenyl-1-propyne reaches 75% in the joint decomposition of methyl- and phenylethyl-copper in ether[118], i.e. greatly exceeds the yield expected for statistical coupling of the radicals, can be explained from this standpoint[1].

IV. THERMAL DECOMPOSITION OF ORGANIC COMPOUNDS OF OTHER METALS

To complete the overall picture of the state of research into the thermal decomposition of organic derivatives of metals, particularly those of the copper subgroup, we shall consider data for the decomposition of compounds of other transition metals. The decomposition of alkylgold(I) stabilised by triphenylphosphine, in both the solid phase and in solution in decalin at a temperature close to 100 °C, leads to the formation of products of the radical dimerisation and disproportionation reactions[119]. Thus ethane and a very small amount of methane are formed from methylgold, butane (90%), ethane (1.4%), and ethylene (0.7%) are formed from ethylgold, propane (28%), propene (34%), and only traces of 2,3-dimethylbutane are formed from isopropylgold, while t-butylgold gives rise to isobutane (13%), isobutene (48%), and a certain amount of unidentified products.

Thus it can be seen that the thermal decomposition reactions of primary derivatives of alkylgold resemble those of the silver derivatives, while the reactions of the secondary and tertiary derivatives take place analogously to the decomposition of the copper compounds. The study of the kinetics of the decomposition of the triphenylphosphine complex of methylgold in decalin showed that the reaction is of first order with respect to $MeAu.PPh_3$. This suggested that the rate-determining stage is the elimination of the triphenylphosphine ligand:

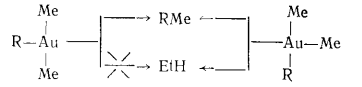
$$MeAu \cdot L \xrightarrow{k_1} MeAu + L \ ,$$
$$MeAu \cdot L + MeAu \rightarrow EtH + 2Au + L \ .$$

In contrast to alkyl derivatives of gold(I), the thermal decomposition of trialkylgold takes place as reductive elimination[120,121], for which various mechanisms have been proposed depending on the nature of the solvent:

$$Me_3AuL \rightarrow EtH + MeAuL \ .$$

The study of the products of the thermolysis of equimolar mixtures of Me_3AuPPh_3 and $(CD_3)_3AuPPh_3$ showed that at 80 °C in decalin and chlorobenzene the decomposition reaction is unimolecular, because a statistical average distribution of products is obtained ($C_2H_6 : CH_3CD_3 : C_2D_6 = 1 : 2 : 1$). On the other hand, in polar solvents [dimethyl sulphoxide (DMSO) and DMF] at a low concentration of trialkylgold the reaction proceeds almost exclusively via an intramolecular mechanism and the yield of the cross-coupling product reaches only 5% in this instance. The results of the study of the decomposition reaction of $CD_3Me_2AuPPh_3$ also agree with this conclusion; in chlorobenzene the yields of EtH, $MeCD_3$, and C_2D_6 are in the proportions 49 : 46 : 6, while in DMSO these ratios are 25 : 75 : 0.

It has been shown for *cis*- and *trans*-RMe_2AuPPh_3 (R = Et or Pr)[121] that the yield of ethane in the decomposition of the *cis*-isomer in decalin greatly exceeds that in the case of the *trans*-isomer, which agrees with an intramolecular process occurring as stereospecific *cis*-elimination:



In contrast to this, in the decomposition of *cis*- and *trans*-$CD_3Me_2AuPPh_3$ in decalin, the composition of the products is independent of the isomer undergoing decomposition which indicates the intermolecular nature of the reaction. Thus the mechanism of the thermal decomposition of trialkylgold is largely determined by the nature of not only the solvent but also of the alkyl group.

The phosphine complexes of dialkylgold salts decompose similarly—via intermolecular reductive elimination[122]:

$$[R_2Au(PPh_3)_2]O_3SCF_3 \rightarrow R_2 + Au(PPh_3)_2O_3SCF_3 \ ,$$
$$R = Me, Et, Bu \ .$$

A characteristic feature of the majority of the thermal decomposition reactions of organometallic compounds of transition metals is inhibition of the process following the addition of complex-forming agents. For example, it is known that alkylcopper is absolutely unstable at room temperature, while some of its phosphine complexes are fairly stable under these conditions[104]. The rate of the decomposition reaction of phosphine complexes of trialkylgold[121] and salts of dialkylgold[122] examined above diminishes appreciably after the addition of substituted phosphines. An analogous effect of added phosphines is manifested in the reductive

elimination of triethylphosphine complexes of methylarylnickel:[123]

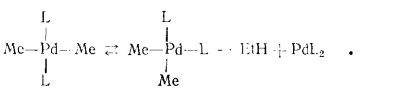
$$(Et_3P)_2NiArMe \rightarrow ArMe + (Et_3P)_2Ni \quad .$$

It is usually assumed that the addition of complex-forming agents prevents the formation of coordination-unsaturated intermediates, while the electronic structure favours the decomposition reaction. This has been confirmed, for example, in a thermographic study[124] of the decomposition of the complexes C_6F_5CoL (L = Schiff base) with various ligands Q (Q = H_2O, NH_3, Py, etc.). It was shown that the formation of perfluorobiphenyl in this reaction is always preceded by the ligand elimination stage, i.e. the process takes place in stages:

$$RCoLQ \rightarrow RCoL + Q \quad ,$$
$$RCoL \rightarrow CoL + 1/2R_2 \quad .$$

For some ligands, the elimination of Q takes place at temperatures lower than that required for further decomposition of RCoL. Other ligands are so strongly coordinated to the metal atom that their elimination requires a higher temperature at which both reactions—the elimination of Q and the formation of R_2—take place simultaneously.

Another explanation of the influence of added ligands on the decomposition of metal complexes has been given in a study[125] of the intramolecular decomposition of phosphine complexes of dimethylpalladium leading to the formation of ethane. It was found that this reaction occurs only for *cis*-complexes, while the decomposition of *trans*-complexes proceeds via the *trans–cis* isomerisation stage. The latter process is facilitated in the presence of polar solvents and added ligands:



Thus the influence of added ligands on the decomposition of metal complexes may be associated with the acceleration of the *trans–cis* isomerisation and also with the increase of the concentration of active species having the *cis*-configuration.

However, processes are known in which added complex-forming agents facilitate the thermal decomposition of complexes already having the *cis*-configuration. Thus the intramolecular reductive elimination reaction of *cis*-$PtAr_2L_2$ in toluene at 60 °C is accelerated in the presence of free triarylphosphine[126]:

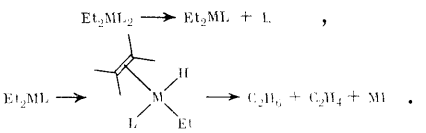
$$PtAr_2L_2 \rightarrow Ar_2 + PtL_2 \quad ,$$
Ar = Ph, *p*-MeC_6H_4; L = PPh_3, $(p\text{-}MeC_6H_4)_3P$.

The kinetics of this reaction have been studied in very great detail, but the mechanism of the influence of triphenylphosphine on the rate of the process remains unelucidated.

We shall consider a further two types of thermal decomposition reactions of organic compounds of transition metals. One of these consists of reductive elimination reactions leading to the formation of alkanes and alkenes, an example of which is provided by the decomposition of dialkyl complexes of cobalt(III),[127] palladium(II),[128] platinum(II),[129] and iron(II):[130,131]

$$MR_2L_n \rightarrow RH + R(-H) + ML_n \quad .$$

Studies of the kinetics of the decomposition of $CoR_2(acac).(PR'_3)_2$,[127] $Et_2Pd(PR'_3)_2$,[128] and $Et_2Pt(PEt_3)_2$ [129] showed that the reactions are of first kinetic order, i.e. are intramolecular. On the basis of these results as well as data for the influence of the nature of the group R on the thermal stability of organometallic compounds, a reaction mechanism has been proposed, according to which the decomposition of the compounds is preceded by the ligand displacement stage and the formation of a metal hydride complex:



Judging from the values of the kinetic isotope effect in the reactions of R_2ML_n with R = Et and CD_3CH_2, any of these stages can be the rate-determining step[129].

Another reaction which has attracted the attention of investigators recently is the thermal decomposition of organometallic compounds involving the transfer of an α-hydrogen atom[132,133]. It was shown, for example, that the decomposition of pentabenzyltantalum proceeds precisely in this manner[134]:

$$(PhCH_2)_5Ta \rightarrow PhCH_3 + (PhCH{=})_5Ta_2 \quad .$$

This reaction is apparently intramolecular and takes place without the formation of free radicals, because α-deuterotoluene is not formed when the decomposition of $(PhCH_2)_5Ta$ is carried out in C_6D_6 and the reaction is not accelerated in the presence of radical initiators.

V. ONE-ELECTRON OXIDATION OF ORGANOMETALLIC COMPOUNDS BY COPPER(II) SALTS

The mechanism of the reactions of organometallic compounds with copper(II) salts differs significantly from the mechanism of the reactions with copper(I) salts. Bawn and Whitby[76] investigated the reaction of tetramethyl-lead with coppper(II) nitrate in ethanol and showed that it results in the formation of ethane and methane in proportions of 1 : 0.47. They put forward the hypothesis that the reaction proceeds in stages. The first stage is of the oxidation-reduction type and leads to the formation of radicals and a copper(I) salt:

$$Cu^{2+} + Me_4Pb \rightarrow Cu^+ + Me_3Pb^+ + Me^\cdot \quad ,$$
$$2Me^\cdot \rightarrow EtH \quad .$$

In the second stage the interaction of $(CH_3)_4Pb$ with Cu^+ leads to the formation of an organocopper compound which undergoes thermal decomposition:

$$Cu^+ + Me_4Pb \rightarrow MeCu + Me_3Pb^+ \quad ,$$
$$MeCu \xrightarrow{EtOH} MeH + Cu^0 \quad .$$

An analogous reaction mechanism was subsequently examined for the interaction of organolithium compounds with copper(II) chloride[135].

Despite the fact that subsequent studies showed that the mechanism of Bawn and Whitby is largely correct, in its initial version[76], proposed for the methyl system, there was a clear contradiction. In fact, in the first stage of this mechanism[76] methyl radicals dimerise, while in the second stage they abstract hydrogen from the solvent (although it would seem that this process should be the only one occurring if the reaction does indeed involve the formation of free methyl radicals). Furthermore, it is known that the decomposition of alkyl derivatives of copper(I), even those containing a β-hydrogen atom, results in the formation of a considerable amount of a radical coupling product (see Section III), whereas according to the mechanism of Bawn and Whitby only methane is obtained at this stage.

Studies[136,137] which established that the butane formed in the reaction of tetraethyl-lead with copper(II) nitrate is obtained on decomposition of ethylcopper are remarkable in

this connection. This conclusion is based on the finding that butane is not formed in the presence of *p*-dimethylaminobenzylidenerhodanine (A) [which forms complexes with copper(I) salts], while in the absence of the rhodanine its yield is 17%:

$$Et_4Pb \xrightarrow{Cu(NO_3)_2} EtH + C_2H_4 + BuH + Et_3PbNO_3 + Cu^0$$

In the absence of A	77%	6%	17%	
In the presence of A	86%	14%	0%	

Furthermore, it has been shown in special experiments that[136,137] the decomposition of ethylcopper leads to the formation of butane:

$$\underset{74\%}{EtCu} \rightarrow \underset{74\%}{EtH} + \underset{0\%}{C_2H_4} + \underset{26\%}{BuH} + Cu^0 \quad .$$

The data presented are also of interest from the point of view that they demonstrate the formation of ethylcopper only as a result of the reaction of the initial organometallic compound with copper(I) nitrate. This makes it possible to reject the mechanism of Thiele and Kohler[138], who believe that the reactions of organometallic compounds with copper(II) salts proceed via a stage involving the total transmetallation and subsequent decomposition of the copper(II) derivative[138]:

$$Alk_2Zn + CuCl_2 \rightarrow ZnCl_2 + Alk_2Cu \quad ,$$
$$Alk_2Cu \rightarrow AlkCu + Alk^{\cdot} \quad .$$

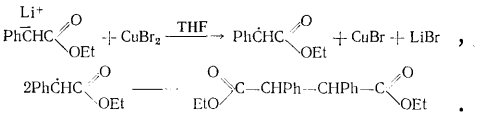
This mechanism is unlikely also because it is difficult to imagine the formation of dialkylcopper by-passing the stage involving the formation of a mixed derivative RCuX. If the latter compound had in fact been obtained, then, by virtue of its instability, it would have decomposed before being able to react with another molecule of dialkylzinc. However, its decomposition should occur with the cleavage of the R–Cu bond, in contrast to dialkylcopper, and cannot lead to the formation of alkylcopper:

$$RCuX \rightarrow R^{\cdot} + CuX \quad .$$

Thus the main feature distinguishing the mechanism of the interaction of organometallic compounds with copper(II) salts is the formation of free radicals. Their generation in these reactions was demonstrated by introducing "radical trapping agents" such as diphenylpicrylhydrazyl[136] or by initiating the polymerisation of monomers added to the reaction mixture[76,136]. In all cases the yield of the products of the radical reactions, mainly alkanes, diminished under these conditions.

The formation of free radicals is also indicated by the nature of the products obtained. Thus, when triethylaluminium is refluxed with copper(I) and copper(II) chlorides in cyclohexane, ethane and ethylene are formed in proportions of ~2 : 1 together with a small amount of butane (2–9%).[27] The composition of the mixture of products depends little on the oxidation state of copper in the salt used. In the reaction of organolead compounds of the type of R_4Pb with copper(II) salts, several products are formed whose ratio depends on the nature of R and X. Thus the interaction of tetraphenyl-lead or tetraphenyltin with copper(II) nitrate in ethanol results in the quantitative formation of benzene[73], tetramethyl-lead gives rise to methane (21.2%) together with ethane (74.6%),[73,135] while the reaction of tetraethyl-lead leads to the formation of ethane, ethylene, and butane in the same proportions as in the reaction with silver nitrate (26.3% EtH, 16.7% C_2H_4, and 52.5% BuH).[73,76,136]

At the same time reactions of organometallic compounds are known in which the yield of radical coupling products is greater—for example, the oxidation of the lithium enolates of acetate esters, acetic acid derivatives[139], and ketones[140]. These reactions are usually regarded as electron transfer from the enolate to the copper(II) halide with subsequent dimerisation of the radicals:



The coupling of radicals in reactions of diphenylmethyl[141,142] and fluorenyl derivatives of lithium[142] with copper(II) halides apparently proceeds analogously. This pathway most probably operates when fairly stable radicals are formed in the reaction. For the usual reactions of organometallic compounds, a hypothetical mechanism postulating the involvement of organic copper(II) chlorocuprates of the type $[RCuCl_3]^{2-}$ in the coupling reaction has been proposed[20].

Organic compounds of copper(II) are known to be exceptionally unstable; any attempt to prepare them led to the formation of radicals. On the other hand, one cannot rule out the possibility of an increase of the stability of RCuCl as a result of coordination to ligands, for example, the chloride ion. The number of examples of such stabilisation of organometallic compounds is fairly large; it is sufficient to mention that the majority of σ-linked transition metal compounds are stable by virtue of such coordination. The existence of copper(I) cuprates of the type of R_2CuM, widely used in organic synthesis[64], has also played a considerable role in the development of ideas about the organic copper(II) chlorocuprates.

The mechanism of the coupling of organometallic compounds with participation of chlorocuprates has been invoked to account for the results of the study of the reaction of RMgBr with Li_2CuCl_4 in THF.[20] Its products are the dimers R_2 and organic chloro-derivatives RCl; the products do not contain the hydrocarbons RH. The ratio of R_2 and RCl depends on the reactant concentrations and the yield of the dimeric products increases with increasing RMgBr concentration.

[EtMgBr]/[Cu^{2+}]	BuH, %	EtCl, %
0.6	50.6	49.4
1.2	53.9	46.1
2.9	73.7	26.3

The yield and proportions of the products are not influenced by the addition of styrene, which rules out the possibility of the formation of free radicals in this reaction. The authors[20] proposed the following reaction scheme, in which organic chlorocuprates decompose via a bimolecular mechanism with formation of a dimeric product:

$$(Cu^{II}Cl_4)^{2-} + RMgBr \rightarrow [RCuCl_3]^{2-} + MgBrCl \quad ,$$
$$2\,[RCuCl_3]^{2-} \rightarrow R_2 + 2\,(Cu^{I}Cl_2)^{-} + 2Cl^{-} \quad .$$

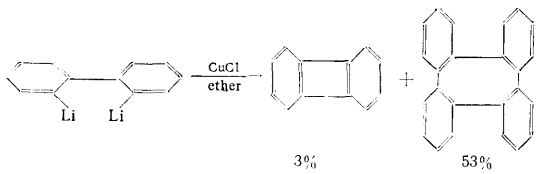
Yet another possibility of the formation of coupling products in these reactions should be noted. According to Whitesides et al.[143], treatment of the homocuprate Bu_2CuLi in THF with the copper(II) chloride complex of tetramethylethylenediamine (TMEDA) leads to the formation of octane:

$$Bu_2CuLi \xrightarrow[THF]{CuCl_2 \cdot TMEDA} Bu{-}Bu \quad .$$

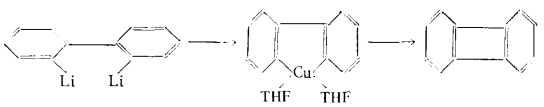
One cannot therefore rule out the possibility that organic cuprates, whose subsequent oxidation leads to the formation of dimeric products, are formed in the reactions of organic compounds of lithium and possibly also magnesium with copper(II) salts.

The involvement of cuprates can be postulated in the reaction of 2,2′-dilithiobiphenyl with copper(II) chloride in ether[64], while diphenylene and tetraphenylene are formed

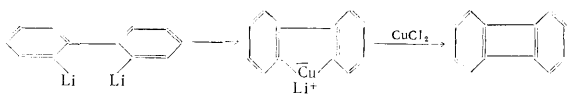
together with biphenyl and *o*-quaterphenyl:[14,144–146]



When a 1 : 1 mixture of ether and THF is used as the solvent, the yield of diphenylene increases to 36% and that of tetraphenylene falls to 24%. According to the authors[146], THF stabilises the intermediate R_2Cu, which increases the contribution of the decomposition via the intramolecular mechanism:



However, it is most likely that cuprates are formed, whose oxidation leads to intramolecular coupling:



The formation of the remaining products—tetraphenylene and *o*-quaterphenyl—can be account for analogously.

In our view, cuprates can also be involved in the reactions of vinyl derivatives of aluminium with copper(II) chlorides, because dienes are formed in this reaction with retention of the configuration at the carbon atom[147]. If free vinyl radicals participated in the reaction, the geometrical configuration might be distorted somewhat, but in the first place this would involve the abstraction of hydrogen from the solvent molecule with formation of an olefin.

There exists yet another possibility of the formation of coupling products in the oxidation of organometallic compounds by a copper(II) salt. It is known that organic copper(I) compounds, formed in these reactions as intermediates, give rise to associated species having the polymeric 3*c*–2*e* structure. This specific feature of the structure of the organometallic compounds can favour the formation of the dimers R_2 in the subsequent oxidation reaction[1]. This applies particularly to the oxidation of ethynyl derivatives of metals in which copper acetylides, existing only in a polymeric form, are formed. For example, in the interaction of copper(II) halides with ethynyl Grignard reagents[148] or with the corresponding derivatives of gold, silver, and copper[149,150], the yield of the dimeric product is as a rule quantitative:

$$RC{\equiv}CM + CuCl_2 \xrightarrow[M=Cu,\ Ag,\ Au]{THF} RC{\equiv}C{-}C{\equiv}CR + CuCl + MCl \ .$$

Another product of the reactions of organometallic compounds with copper(II) halides is an organic halide. It is evidently the product of the two-electron oxidation of the organometallic compound, since a carbonium ion linked to a halide ion is then formed from the carbanion R^- in RM. There exist various views on the mechanism and the formation of such halides; the next section is devoted to the consideration of this question and in general to the two-electron oxidation of organometallic compounds.

VI. TWO-ELECTRON OXIDATION OF ORGANOMETALLIC COMPOUNDS

A greater number of possible mechanisms have been considered for the two-electron oxidation of organometallic compounds than for the one-electron oxidation. In principle, such oxidation can occur in stages as a result of the successive transfer of two electrons from the organic group R:

$$RMX_n \xrightarrow{-e^-} R^\cdot + MX_n^+ \ ,$$
$$R^\cdot \xrightarrow{-e^-} R^+ \xrightarrow{Nu^-} RNu \ .$$

However, it has been suggested for certain reactions that the conversion of RM into RNu takes place in a single stage via a heterolytic mechanism, which can be formally regarded as nucleophilic substitution:

$$RMX_n + Nu^- \longrightarrow RNu + MX_{n-1} + X^- \ .$$

The role of the transition metal salt in these processes can be most varied: it can participate in the transmetallation reaction, can manifest the properties of an oxidant, and can even catalyse the single-stage two-electron oxidation.

1. Oxidation by Bivalent Copper Salts

The two-electron oxidation takes place particularly frequently in the reactions of organometallic compounds with copper(II) salts, for example with copper(II) halides. It was shown in Section V that the primary product of these reactions may be free radicals and one can therefore suggest that these are in fact the species oxidised by the copper(II) salt with formation of the two-electron oxidation product RX:

$$RMX_n + CuX_2 \longrightarrow [RCuX] + MX_{n+1} \ ,$$
$$RCuX \longrightarrow R^\cdot + CuX \ ,$$
$$R^\cdot + CuX_2 \longrightarrow RX + CuX \ .$$

The studies by Kochi and coworkers[151–153], which established that the radicals are very effectively oxidised by copper(II) salts, greatly promoted the development of such ideas. It has been shown for alkyl radicals that their oxidation by copper(II) acetate leads to the formation of carbonium ions, which are stabilised either by eliminating a proton with formation of an olefin or by interacting with the solvent to form solvolytic products. The reaction with copper(II) chloride yields bromoalkanes, i.e. the radicals are oxidised with simultaneous "ligand transfer". It has been suggested that the oxidation of the radicals leads to the intermediate formation of an unstable copper(III) compound§, which is converted into RX by oxidative substitution[152]:

$$R^\cdot + CuX_2 \rightleftarrows [RCuX_2] \ ,$$
$$[RCuX_2] \rightleftarrows R^+CuX_2^- \rightarrow RX + CuX \ .$$

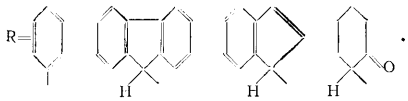
In agreement with these data, organic halides are formed in the reaction of organometallic compounds with copper(II) halides, while the reaction with copper acetate leads to acetates and olefins (in the case of alkyl derivatives of metals). For example, it has been frequently noted that the reaction of R_2Hg or RHgX (R = Ph, $PhCH_2$, ferrocenyl, etc.) with copper(II) halides results in the formation of halogenoderivatives RX or solvolytic products[33,35,156–165]. Using an excess of copper(II) bromide in dimethylformamide and most

§ The hypothesis of the intermediate formation of unstable copper(III) compounds has been recently confirmed in a study of the oxidation of radicals by a peptide complex of copper(II).[154]

varied radicals R [Bu, Ph, $PhCH_2$, C_6F_5, $C_6F_5CH_2$, $(CF_3)_2CH$, $PhCOCH_2$, CCl_3], it is possible to obtain organic bromides in nearly quantitative yields[160].

The interaction of organotin compounds $RSnMe_3$ with $CuBr_2$ in methylene chloride similarly results in the formation of the corresponding bromides RBr, whose yield is also quantitative [161]:

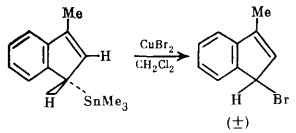
$$RSnMe_3 + 2CuBr_2 \rightarrow RBr + Me_3SnBr + 2CuBr ,$$

R=  .

This reaction is remarkable in the sense that with its aid organic bromides containing electron-accepting groups such as 9-fluorenyl, indenyl, and 2-cyclohexanonyl have been obtained. The point is that fairly stable free radicals are formed as intermediates in the oxidation of the corresponding organometallic compounds. In the case of more active derivatives of lithium or magnesium, radicals are not usually oxidised but dimerise, since the copper(II) halide reacts preferentially with the initial organometallic compound (see Section V). However, in the reactions of covalent derivatives of tin the radicals are oxidised to organic bromides.

It follows from the foregoing that both two-electron and one-electron oxidation is possible in the interaction of copper(II) salts with organic derivatives of metals RM and in general with organic derivatives of the elements, whose chemical properties are similar to those of organometallic compounds and the relative contributions of the two reaction pathways for derivatives of a single element depend on the nature of R and X in CuX_2. This can be seen in relation to the reactions of readily oxidised oxidisable organoboron compounds. Thus treatment of trialkylboranes[161] and phenylboronic[162], thienylboronic[163], ferrocenylboronic[164], and cymantrenylboronic acids[165] with copper(II) halides leads to the formation of organic halides only. In contrast to this, the interaction of organoboron compounds of copper(II) acetate usually results in the formation of one-electron oxidation products—the corresponding dimers[164-168]. The intermediate formation of an organic copper(I) compound, which decomposes in benzene with formation of R_2 and the product RH of the interaction of radicals with the solvent, was detected in the reaction of cymantrenylboronic acid[167]. The two-electron oxidation by copper(II) acetate is known for trialkylboranes, the products of the reactions of which are olefins[161], and for ferrocenylboronic acid, the oxidation of which gives a 59% yield of acetoxyferrocene[168].

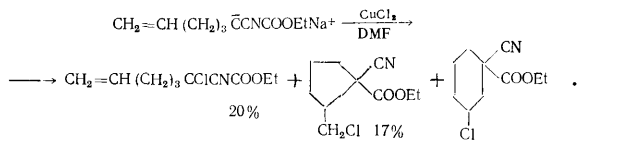
The involvement of free radicals in the reactions of organometallic compounds has not been confirmed solely by the formation of one-electron oxidation products, stereochemical evidence also being available. Thus the formation of free radicals in the reaction of $CuBr_2$ with alkyl derivatives of mercury has been demonstrated[169]. It was found that, regardless of which diastereoisomer of 3,3-dimethyl-1,2-dideuterobutylmercury chloride is introduced into the reaction, a mixture of deuterated neohexyl bromides with the same contents of the *threo*- and *erythro*-isomers is alway formed. The same stereochemical approach has been used to demonstrate the formation of radicals in the oxidation of organotin compounds—the racemic 1-bromo-3-methylindene was obtained in the reaction of the optically active *S*-(+)-3-methylindenyltrimethyltin with $CuBr_2$:[160]



(±)

There is no doubt that the loss of stereochemical configuration occurred in the indenyl radical formation stage.

The cyclisation of the hexenyl radical has been used as a test for its formation in reactions of the sodium enolate of the ethyl ester of 2-cyanohept-6-enoic acid with CuX_2 (X = Cl, SO_4, OAc, PhCOO, or p-$NO_2C_6H_4COO$) in DMF.[170] Derivatives of cyclopentane- and cyclohexane-carboxylic acids were detected in the reaction mixture:



The majority of investigators agree that the oxidation of organometallic compounds by copper(II) salts usually occurs with participation of free radicals, but it has been suggested that free radicals are not formed in some of the reactions. The reaction of Grignard reagents with the chlorocuprate Li_2CuCl_4 in THF, which has already been considered, apparently belongs to processes of this type[20]. Its products are the dimers R_2 and the chloro-derivatives RCl, which is obtained, according to the authors[20], in the oxidation of the intermediate organic chlorocuprate:

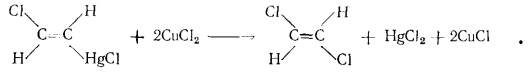
$$RMgBr + (CuCl_4)^{2-} \rightarrow [RCuCl_3]^{2-} + MgBrCl ,$$
$$[RCuCl_3]^{2-} + (CuCl_4)^{2-} \rightarrow RCl + 2(CuCl_2)^- + 2Cl^- .$$

The observed increase of the yield of RCl with increase of the Li_2CuCl_4 concentration agrees with this view. By analysing the overall kinetic reaction mechanism, it is possible to show that such dependence of the yield of RCl on the Li_2CuCl_4 concentration is possible only when RCl is obtained as a result of the oxidation of $[RCuCl_3]^{2-}$ and not of the radical R$^{\cdot}$ formed in the homolysis of this intermediate.

Kinetic analysis also leads to serious objections to the possibility of the formation of RCl as a result of the intramolecular decomposition of the intermediate RCuCl via the mechanism

$$RCu^{II}Cl \rightarrow RCl + Cu^0 .$$

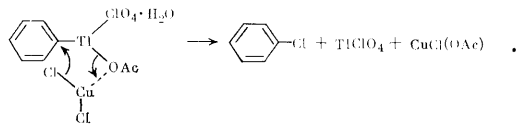
This pathway to the formation of two-electron products of organometallic compounds has been considered in a study[155] of the reaction of *trans*-β-chlorovinylmercury chloride with copper(II) chloride:



According to the authors[155], free radicals are not formed in this reaction, since it takes place with retention of the geometrical configuration at the carbon atom—*trans*-dichloroethylene is obtained from *trans*-β-chlorovinylmercury chloride, while *cis*-dichloroethylene is obtained from the *cis*-isomer[171]. However, this test for the formation of radicals is not very reliable, because it postulates that the loss of configuration in the vinyl radical occurs faster than its oxidation by copper(II) chloride. This cannot be claimed *a priori*, particularly if account is taken of the fact that the vinyl radicals invert much more slowly than alkyl radicals.

Finally, we shall consider the heterolytic mechanism of the two-electron oxidation of organometallic compounds by copper(II) halides which has been proposed for the oxidation of organic derivatives of thallium(III). According to this mechanism, the formation of organic halides proceeds in a

single step involving the elimination of thallium with reduction of thallium(III) to thallium(I), catalysed by the copper(II) salt[55,156,172]:



Formally this process can be regarded as substitution via the S_NC mechanism, but this is not the usual nucleophilic substitution because its driving force is the ability of thallium(III) to act as a two-electron oxidant. Furthermore, the role of the copper(II) salt in this mechanism is not clear.

One must note that the products of the one-electron oxidation ArH and Ar_2 are also formed in this reaction and the yields of all the products vary as a function of the nature of Ar and the anion X in the copper(II) salt. Thus, when $PhTl(OAc)ClO_4$ is treated with copper(II) chloride in acetic acid, the main product is chlorobenzene (yield 56–59%), but a small amount of benzene and biphenyl (2–4%) is also formed. On the other hand, mainly anisole (30–65%) and only 2% of chloroanisole are obtained from p-$MeOC_6H_4Tl(OAc)ClO_4$, while bianisyl is absent. The interaction of $PhTl(OAc)ClO_4$ with copper(II) acetate results in the formation of only benzene (13%) and biphenyl (2%).[156] The reaction with copper(I) or copper(II) cyanide leads to benzonitrile[53], while phenyl thiocyanate is formed in 42% yield in the reaction with copper(II) thiocyanate[171]. It is interesting that in the latter case the addition of potassium thiocyanate diminishes the yield of PhSCN and the yield of benzene then increases from 0 to 19%. However, the observed effect of the common ion has not been explained[173].

We may note that even copper(I) halides initiate the decomposition of organic compounds of thallium(III). Thus the interaction of CuBr with β-methoxyphenylethylthallium diacetate in acetonitrile yields the corresponding bromo-derivative[174] and it has been established with the aid of radical traps that free radicals are involved in its formation[175]. It is believed that the copper(I) halide behaves as the reductant in this reaction, converting the thallium(III) compound into an intermediate containing thallium(II).[176] The latter decomposes with formation of a radical which is oxidised further by the copper(II) halide:

$$R{-}C(OMe)HCH_2{-}Tl^{III}(OAc)_2 \xrightarrow{CuX^-} [R{-}C(OMe)HCH_2{-}Tl^{II}(OAc)_2]^- \cdot \rightarrow R{-}C(OMe)HCH_2^{\bullet} + Tl^{I}(OAc)_2^- ,$$

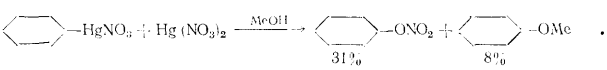
$$R{-}C(OMe)HCH_2^{\bullet} + CuX_2 \longrightarrow R{-}C(OMe)HCH_2X + CuX .$$

However, the radical reaction pathway obtains at 80 °C. Under milder conditions, the reaction has a predominantly ionic mechanism. It has been shown in relation to *erythro*-n-$C_8H_{17}CH(OMe)CHDTl(OAc)_2$ that at 60 °C the reaction takes place with inversion of configuration[176].

The data presented show that the oxidation of phenyl compounds of thallium(III) by copper(II) salts differs from the oxidation of derivatives of other metals—particularly by the fact that one-electron oxidation products can be obtained in considerable amounts in reactions with copper(II) halides. The cause of these differences is associated with the fact that the thallium in these compounds exists in the highest valence state and is a powerful electron acceptor. However, the true mechanism of these reactions is so far not clear and the substitution mechanism put forward by Ichikawa and coworkers[55,156,172] is to a large extent hypothetical.

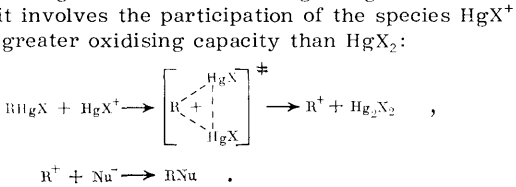
2. Oxidation of Mercury Salts

Certain electrophilic substitution reactions of organometallic compounds with bivalent mercury salts are accompanied by the formation of two-electron oxidation products. In a number of instances the process is dominant. For example, the interaction of benzylmercury nitrate with mercury(II) nitrate results in the formation of benzyl nitrate and benzyl ethyl ether in methanol and of benzyl alcohol, benzyl nitrate, and benzaldehyde in water[177,178]. The reaction with cyclohexylmercury nitrate in methanol takes place similarly, the corresponding nitrate and ether also being obtained:



According to Ichikawa and Ouchi[179], the reaction of organomercury acetates with mercury acetates likewise leads to the formation of organic acetates and a mercury(I) salt.

So far little is known about the mechanism of these reactions. It is most likely that it involves a special type of oxidative demetallation (see subsection 5 below), in which the organic group is oxidised with the simultaneous participation of the two mercury atoms. Since the rate of reaction increases following the addition of strong inorganic acids[179], presumably it involves the participation of the species HgX^+, which has a greater oxidising capacity than HgX_2:



It was noted that the interaction of propylboronic acid with mercury(II) chloride in water leads to the formation of propyl chloride and calomel together with propylmercury chloride[180]. The authors[180] believe that propyl chloride is obtained on oxidation of the transmetallation product—propylmercury chloride:

$$PrB(OH)_2 + HgCl_2 + H_2O \rightarrow PrHgCl + B(OH)_3 + HCl ,$$
$$PrHgCl + HgCl_2 \rightarrow PrCl + Hg_2Cl_2 .$$

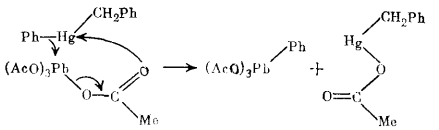
When organic derivatives of titanium(IV) ($MeTiCl_3$ [181] or Cp_2TiPh_2 [182]) react with mercury(II) chloride, calomel is formed as one of the products. According to the authors[182], the organotitanium compound decomposes and the new organic derivative of titanium(II) formed is oxidised by mercury(II) chloride:

$$Cp_2TiPh_2 + HgCl_2 \xrightarrow{CCl_4} Cp_2TiCl_2 + PhHgCl + PhCl + Ph_2 + Hg_2Cl_2 ,$$
$$Cp_2TiPh_2 \rightarrow Cp_2Ti + 2Ph^{\bullet},$$
$$n\,Ph^{\bullet} \xrightarrow{CCl_4} PhCl + Ph_2,$$
$$Cp_2Ti + HgCl_2 \rightarrow Cp_2TiCl_2 + Hg_2Cl_2 .$$

3. Oxidation by Lead-Tetra-acetate

The oxidation of organometallic compounds, particularly mercury derivatives, by lead tetra-acetate was first carried out by Criegee et al.[183] The reaction of alkyl derivatives of mercury leads to the formation of the corresponding alkyl acetates, both primary and secondary acetates being formed from primary alkylmercury acetates, which indicates the intermediate formation of carbonium ions. Thus the acetates derived from benzyldimethylmethanol and t-pentyl alcohol were isolated in the oxidation of dineophyl- and dineopentylmercury instead of the corresponding neophyl and neopentyl acetates[183]. The interaction of a fully asymmetric compound

(benzylphenylmercury) with lead tetra-acetate in benzene at room temperature results in electrophilic substitution and the elimination of the phenyl group, which is most nucleophilic[183]:

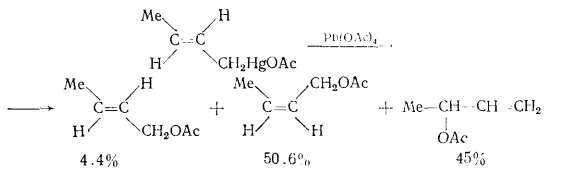


It has come to be believed that an organolead compound is always formed in the first stage of these reactions and then decomposes with formation of a two-electron oxidation product[183,184]:

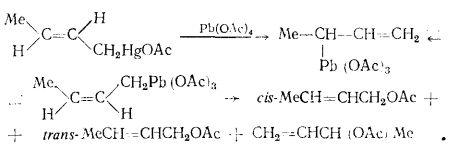
$$(PhCH_2)_2Hg \xrightarrow{Pb(OAc)_4} PhCH_2Pb(OAc)_3 \xrightarrow{-Pb(OAc)_2} PhCH_2OAc .$$

In the case of alkyl derivatives of metals, it is usually impossible to isolate the corresponding lead(IV) compound under the reaction conditions. Only the quantitative formation of $Et_2Pb(OAc)_2$ in the reaction of Et_2Hg with $Pb(OAc)_4$ in chloroform at room temperature has been described[185], but in benzene the above compound is not obtained on interaction of Et_4Sn with $Pb(OAc)_4$, ethyl acetate being produced in 78% yield[186].

All three possible isomers of the organic acetate are formed on oxidation of *trans*-crotylmercury acetate[185]:



However, the fact that much more of *cis*-crotyl acetate is formed than of the *trans*-isomer suggests that free carbonium ions do not participate in the reaction. It is most difficult to account for the preferential formation of the thermodynamically less stable *cis*-crotyl acetate. According to Kitching et al.[187], this reaction includes the following stages: transmetallation via the S_E2' (or S_Ei') mechanism, intramolecular metallotropic rearrangement of the intermediate, and oxidative demetallation of the organolead compounds formed:



The capacity of organic compounds of lead(IV) for decomposition without the oxidative demetallation mechanism depends on the nature of not only the organic group but also the anions present in solution. Thus, when potassium iodide[188] or PhMgBr [189] is added to a solution of the stable $PhPb(OAc)_3$, acid anion exchange takes place and the resulting intermediate decomposes with formation of halogenobenzenes and lead(II) salts.

It is noteworthy that the formation of products of two-electron oxidation in these reactions can occur both on oxidative demetallation of $RPb(OAc)_3$ and as a result of homolytic decomposition with cleavage of the R–Pb bond and subsequent oxidation of the radical R$^{\cdot}$ by the excess lead tetra-acetate. Presumably the oxidation of organic compounds of thallium(III) by lead tetra-acetates proceeds via one of these pathways[190]:

$$ArTl(OOCCF_3)_2 \xrightarrow[Cl_3CCOOH]{Pb(OAc)_4} ArOOCF_3 + Tl^{I} + Pb^{II} .$$

Another view on the mechanism of the formation of radicals in these reactions has been expressed in a study[191] of the oxidation of alkyl derivatives of mercury and tin by lead tetra-acetate. The reaction proceeds fairly readily on refluxing in acetic acid but the yield of the acetates is high only in the case of benzyl derivatives¶:

$$\text{n-PrHgOAc} \xrightarrow[6.5\%]{Pb(OAc)_4} \text{n-PrOAc} + \textit{cis}\text{-PrOAc} ,$$

$$\text{iso-BuHgOAc} \xrightarrow[10\%]{Pb(OAc)_4} \text{iso-BuOAc} + \text{s-BuOAc} + \text{t-BuOAc} ,$$

$$PhCH_2HgOAc \xrightarrow[82\%]{Pb(OAc)_4} PhCH_2OAc ,$$

$$(PhCH_2)_3SnCl \xrightarrow[77\%]{Pb(OAc)_4} PhCH_2OAc + PhCH_2Cl .$$

The authors[191] proposed a mechanism involving the one-electron oxidation of the organometallic compound with subsequent oxidation of the radicals and the formation of organic acetates. However, this alternative transmetallation oxidation reaction is not supported by any evidence.

On the other hand, the oxidation of trialkylboranes by lead tetra-acetate in benzene apparently proceeds via an electron transfer stage[193]. The point is that secondary radicals and not primary radicals, as is usually the case in transmetallation reactions, are preferentially split off in this reaction. For example, the amount of n-hexyl acetate formed in the reaction of bicyclohexyl-n-hexylborane with $Pb(OAc)_4$ is 10 times smaller than that of cyclohexyl acetate. This is apparently due to the preferential decomposition of the radical-cation with formation of a more stable secondary radical:

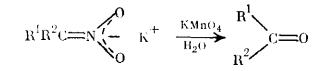
$$[C_6H_{13}(C_6H_{11})_2B]^{\cdot+} \rightarrow C_6H_{11}^{\cdot} + C_6H_{13}C_6H_{11}B^{+} .$$

4. Oxidation by Compounds of Other Metals

The oxidation of organometallic compounds by chromium trioxide apparently also proceeds via an electron transfer stage since transmetallation is hardly possible in this instance. When PhHgI and $PhCH_2HgCl$ are treated with chromium trioxide in a 1 : 1 $AcOH/Ac_2O$ mixture or in the complex $CrO_3.2Py$ in dichloromethane, iodobenzene and benzyl chloride are formed. Benzaldehyde has also been detected in the case of $PhCH_2HgCl$.[194] Tetra-alkyl derivatives of tin react with chromium trioxide in acetic acid to form aldehydes and acids[195]. The reactions of organic boronic acids with chromic acid (with CrO_3 in water) lead to the formation of an alcohol[196]:

$$\text{t-BuB(OH)}_2 + CrO_3 \xrightarrow{H_2O} \text{t-BuOH} + Cr^{III} + H_3BO_3 .$$

The oxidation of potassium salts of nitroparaffins by potassium permanganate belongs to processes of the same type[196]:



This reaction has been suggested as a method of synthesis of aldehydes and ketones.

The oxidation of tetra-alkyltin by phenanthroline complexes of iron(III) [197] and the reactions of alkyl derivatives of lead[96], tin[198], mercury[199], and platinum[200] as well as benzylcobaloxime[201] with the $IrCl_6^{2-}$ anion, which is a one-electron

¶ A high yield of alkyl acetates is observed in the reaction of $Pb(OAc)_4$ with organoaluminium compounds obtained as a result of the addition of $LiAlH_4$ to olefins in the presence of $TiCl_4$.[192] Since the reaction is not accompanied by isomerisation, it is of interest from the synthetic standpoint.

oxidant, are examples of oxidation reactions of organometallic compounds which undoubtedly proceed via a one-electron transfer stage. The products of these reactions are chloro-derivatives formed as a result of the multistage two-electron oxidation with the intermediate formation of radicals. A clear confirmation of the one-electron transfer mechanism of these reactions is finding that on oxidation of, for example, a mixed lead compound $Et_{4-n}Me_nPb$, the ethyl group is split off preferentially[96] and not the methyl group as is usually the case in electrophilic substitution. Furthermore, the partial [rate?] factor for this process is independent of the number of ethyl groups in the molecule of the organolead compound, which is apparently associated with the preferential decomposition of the radical-cation via the mechanism

$$[(Et_{4-n}Me_n)Pb]^{+\cdot} \rightarrow Et^{\cdot} + (Et_{3-n}Me_n)Pb^{+} \quad .$$

The intermediate formation of radicals in the reaction of R_4Pb with $IrCl_6^{2-}$ has been demonstrated with the aid of "radical trapping agents" of the type of nitrosoisobutane[96]. Since only alkyl chlorides are formed in the reaction, one must suppose that the radicals are oxidised very rapidly.

An additional confirmation of the one-electron transfer mechanism is provided by the satisfactory linear correlation between the logarithms of the rate constants for the oxidation of organometallic compounds and their ionisation potentials[96,202,203] as well as the [absorption] frequencies corresponding to charge transfer to the complex from tetracyanoethylene[203,204]. Analysis of these correlations from the standpoint of the Marcus theory demonstrated that these reactions have an electron transfer mechanism[196,201]. It has been shown, for example, that the reaction of R_4Sn with phenanthroline complexes of iron(III) takes place as an outer-sphere transfer, while the oxidation of R_4Sn by $IrCl_6^{2-}$ involves an inner-sphere electron transfer.

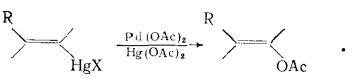
The reaction of benzylchromium $[PhCH_2Cr(H_2O)_5]^{2+}$ with iron(III), cobalt(III), and copper(II) salts, which leads to the formation of typical oxidation products of the benzyl fragment, namely benzaldehyde, benzyl alcohol, and bibenzyl, has an interesting mechanism[205]. However, kinetic study showed that the rate of this process is not determined by the electron transfer stage, since the reaction is of first order with respect to the benzylchromium cation and of zero order with respect to the oxidant. The authors[205] suggest that the rate-limiting stage of the process is the homolysis of the benzylchromium cation and that the radical fragments formed are oxidised in the rapid stage.

Using a combination of two oxidants [a palladium salt in a catalytic amount and one of the oxidants in the series comprising chromium(VI) salts, $Pb(OAc)_4$, $NaClO_3$, $KMnO_4$, $NaNO_3$, and $NaNO_2$], it was possible to achieve an interesting two-electron oxidation of phenylmercury salts. The reaction products in the presence of freshly added nucleophiles Nu^- are substituted benzenes PhNu, while in the absence of oxidants the main product of the stoichiometric reaction is biphenyl[206]:

$$PhHgOAc \xrightarrow[K_2Cr_2O_7]{Pd(OAc)_2} \underset{50\%}{PhOAc} + \underset{6\%}{Ph_2} \quad ,$$

$$PhHgOAc \xrightarrow[LiOAc]{Pd(OAc)_2} \underset{\sim 5\%}{PhOAc} + \underset{95\%}{Ph_2} \quad .$$

It has been suggested that transmetallation results in the formation of a phenylpalladium(II) salt which is subsequently oxidised by the main oxidant. The catalytic cycle terminates by the addition of the nucleophile Nu^- to the phenylcarbonium ion formed. The vinylmercury salts are similarly oxidised by mercury(II) acetate, the reaction being catalysed by palladium(II) acetate[207]. The reaction proved to be a convenient preparative method of synthesising substituted enol acetates:



Another possible reaction mechanism is the oxidation of C_6H_5HgX or C_6H_5PdX with a palladium(IV) salt[206], obtained by the reaction of the palladium(II) salt with the main oxidant. In his analysis of this possibility, Henry[206] drew attention to the fact that, in the oxidation of an oxidant weaker than palladium(IV) such as copper perchlorate, alkyl chlorides are formed from alkyl derivatives of palladium(II), while radical coupling products are obtained from aromatic derivatives of palladium(II). Since it is difficult to suppose that PhPdX is oxidised with greater difficulty than AlkPdX, it follows from the data presented that the PhPdX oxidation reaction competes with the coupling reaction only when sufficiently strong oxidants are employed.

5. Oxidative Demetallation Reactions

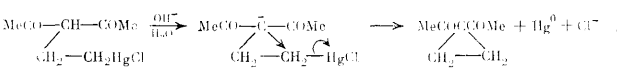
The decomposition of unstable organic compounds of metals with formation of two-electron oxidation products is of special interest. The reaction involving the elimination of mercury from organomercury cations in the presence of acids is an example of such a process[179,208–210]:

$$RHgOAc \xrightarrow{HClO_4} RHg^{+} \quad ,$$

$$R\overset{\curvearrowright}{-}Hg^{+} \longrightarrow R^{+} + Hg^{0} \quad ,$$

$$R^{+} + AcOH \longrightarrow ROAc \quad .$$

A mercury elimination reaction under the influence of bases is known[211]:



This reaction is unusual, since the carbanion formed in it formally substitutes the $HgCl^-$ group by an intramolecular nucleophilic mechanism.

The acetolysis of mercury benzylmercaptide is of a type similar to that of the processes considered[212]:

$$PhCH_2SHgOAc \xrightarrow[90-100^{\circ}]{AcOH} PhCH_2OAc + (PhCH_2)_2 + HgS \quad .$$

The intermediate formation of the benzyl cation in this reaction has been demonstrated by trapping it with mesitylene.

The decomposition of phenylthallium bromides and iodides is in essence an oxidative demetallation reaction[213,214]:

$$PhTlBr_2 \rightarrow PhBr + TlBr \quad ,$$

$$PhTlI_2 \rightarrow PhI + TlI \quad .$$

This reaction has been suggested as a method of synthesis of aryl iodides. It has been postulated that iodobenzene is formed in the interaction of $Ph_2TlOCOCF_3$ with I_2 not only on electrophilic substitution but also as a result of oxidative demetallation[215]:

$$Ph_2Tl(OCOCF_3) + I_2 \rightarrow PhTlIOCOCF_3 + PhI \quad ,$$

$$PhTlIOCOCF_3 \rightarrow PhI + TlOCOCF_3 \quad .$$

The same pathway apparently obtains in the reactions of bismuth(V) and bismuth(III) compounds[180]:

$$Ph_3Bi(OH)_2 \rightarrow Ph_2BiOH + PhOH \quad .$$

The intramolecular decomposition of unstable organopalladium intermediates, formed in the interaction of palladium(II) salts with organometallic compounds, also constitutes an oxidative demetallation reaction, because it yields metallic palladium. For example, when $PdCl_2$ interacts with β-chloromercuriethanol or β-chloromercuriethyl acetate, acetaldehyde and vinyl acetate are formed respectively[216]:

$$HO{-}CH_2CH_2HgCl \xrightarrow{PdCl_2} \left[ClPd{-}CH_2{-}\underset{H}{CH}{-}OH\right] \rightarrow MeCHO + Pd^0 ,$$

$$MeCO{-}CH_2CH_2HgCl \xrightarrow{PdCl_2} \left[ClPd{-}CH_2{-}\underset{H}{CH}{-}\underset{O}{OCMe}\right] \rightarrow CH_2{=}CH{-}OAc + Pd^0 .$$

The nature of the products formed suggests that the decomposition of the organopalladium intermediate entails the generation of carbonium ions, which are stabilised as a result of a hydride shift (on formation of acetaldehyde) or the elimination of a proton (on formation of vinyl acetate).

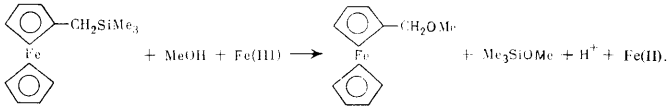
The decomposition of organometallic compounds accompanied by the intramolecular oxidation of the organic group is naturally possible only for compounds containing a metal capable of effecting two-electron oxidation. There is no doubt that this process depends both on the nature of the organic group and on the coordination environment of the metal atom. For example, the mode of the decomposition reaction of β-methoxyphenylethylthallium diacetate in aqueous methanol in the presence of perchloric acid depends on the concentration of the added chloride ions[217]. Whereas at low Cl^- concentrations oxidative demetallation, accompanied by the migration of the phenyl group, takes place and the rate of reaction increases with increasing Cl^- concentration, i.e.

$$PhCH(OMe)CH_2Tl(OAc)_2 \xrightarrow[MeOH]{Cl^-,H+} PhCH_2{-}CH(OMe)_2 + Tl^I ,$$

at high Cl^- concentrations, where the acetate ions are fully substituted by chloride ions, the product is styrene and the rate of reaction is independent of the Cl^- concentration and is determined solely by the acidity of the medium:

$$PhCH(OMe)CH_2Tl(OAc)_2 \xrightarrow{Cl^-} PhCH(OMe)CH_2TlCl_2 \rightarrow$$
$$\xrightarrow{H+} PhCH(\overset{+}{O}Me)CH_2TlCl_2 \rightarrow PhCH{=}CH_2 + Tl^{III} .$$

An interesting instance of oxidative demetallation has been observed by Kumada and coworkers[218,219] in studies of the solvolysis of ferrocenylmethyl derivatives of silicon and germanium in methanol, initiated by iron(II) salts:



According to the authors, methoxymethylferrocene is formed as a result of consecutive intermolecular and intramolecular electron transfers:

$$FcCH_2MMe_3 + Fe^{III} \rightarrow Fc^+{-}CH_2MMe_3 + Fe^{II} ,$$
$$Fc^+CH_2MMe_3 + CH_3OH \xrightarrow{slow} Fc{-}\dot{C}H_2 + MeOMMe_3 + H^+ ,$$
$$FcCH_2^{\cdot} + Fe^{III} \rightarrow [Fc^+{-}CH_2^{\cdot}] + Fe^{II} ,$$
$$[Fc^+{-}CH_2^{\cdot}] + MeOH \rightarrow FcCH_2OMe + H^+ .$$

The absence of a correlation between the rate constants for the solvolytic reaction and the oxidation-reduction potentials of substituted ferrocene derivatives indicates, according to the authors[218], that the rate-determining stage of the process is nucleophilic attack by methanol on the metal atom in the ferrocenium ion.

We shall consider yet another pathway leading to the formation of the two-electron oxidation products, which is possible for organic derivatives of transition metals, particularly for alkylcobaloximes. According to Anderson et al.[220], the one-electron oxidation of organocobalt compounds results in the formation of an intermediate containing a metal atom in a higher valence state. As a result of this, the electron density at the α-carbon atom is reduced so much that the carbon–cobalt bond is broken on nucleophilic substitution via the S_N2 mechanism:

$$RCo^{III}L_2 \xrightarrow{-e^-} [RCo^{IV}L_2] \xrightarrow[-Co^{II}L_2]{Nu^-} RNu .$$

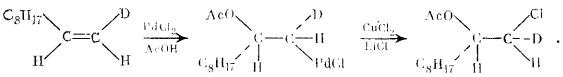
The studies of the composition of products as a function of the nature of the nucleophilic species present in solution and competing for the intermediate formed[201] as well as stereochemical data in general confirm this view. Thus it has been shown that the oxidation of (+)-*S*-(1-methylheptyl)bis(dimethylglyoximato)pyridinecobalt(III) with a two-fold excess of $IrCl_6^{2-}$ in the presence of bromide ions results in the formation of (−)-*S*-1-methylheptyl bromide in 37% yield and with an optical purity in excess of 50%,[220] i.e. the configuration at the carbon atom is inverted. However, in this formulation of the experiment one cannot rule out the possibility that the active agent in the reaction might have been the bromine formed on oxidation of Br^-. This deficiency was taken into account in a study[221] where 1-methylheptylbis(dimethylglyoximato)cobalt was oxidised at a low temperature with a cerium(IV) salt and then chloride ions were added to the reaction mixture:

$$RCo^{III}(dmgH)_2 \xrightarrow[MeOH]{CAN,\ -60^\circ} RCo^{IV}(dmgH)_2 \xrightarrow{Cl^-} RCl ,$$

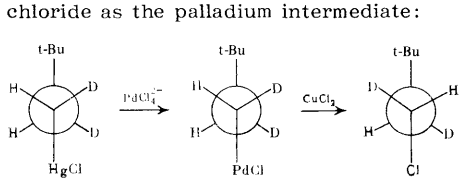
$dmgH_2 = CH_3C(=NOH)C(=NOH)CH_3$, CAN = cerium ammonium nitrate

The degree of inversion of the configuration was 90 ± 10%.

It is noteworthy that the mechanism of the oxidation of organometallic compounds examined above, which includes a nucleophilic substitution stage activated by electron transfer, has been widely used recently to account for the inversion of the stereochemical configuration in electrophilic substitution reactions involving transition metals[222]. Apparently the inversion of configuration on cleavage of the C–Pd bond with copper(II) chloride, which has been observed by Backvall[223], can be explained from the same standpoint.



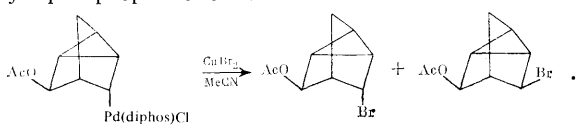
Presumably the palladium intermediate formed, whose *threo*-configuration is determined by the stereochemistry of the oxypalladisation reaction[224,225], is oxidised by $CuCl_2$ and attack by Cl^- comes from the side opposite that of the metal. It is possible to explain similarly the inversion of configuration observed in the oxidation of *threo*-3,3-dimethylbutyl-1,2-d_2-mercury chloride with copper(II) chloride in the presence of $PdCl_4^{2-}$.[226] It is believed that this reaction involves the formation of *threo*-3,3-dimethylbutyl-1,2-d_2-palladium chloride as the palladium intermediate:



Thus it is seen from the above examples that the oxidation of organopalladium compounds by copper(II) halides can bypass the transmetallation stage. Henry, who investigated

the oxidation of but-2-ene by copper(II) chloride in the presence of $PdCl_2$, reaches the same conclusion[227].

On the other hand, judging from the stereochemical results of certain reactions of organopalladium compounds with copper(II) halides, the latter proceed like those involving non-transition metal compounds, i.e. via stages involving transmetallation and the intermediate formation of radicals. An example of such reactions is provided by the interaction of *endo*-norticyclenylpalladium(II) with $CuBr_2$, which leads to the formation of the *endo*- and *exo*-isomers in approximately equal proportions[169]:



Interesting reactions occur in the oxidation by copper(II) chloride of alkyl and aryl alkyl σ-derivatives of iron [η^5-Cp.$(CO)_2$FeR]. For example, the reaction of the benzyl derivatives with $CuCl_2$ in CH_2Cl_2 results in the formation of benzyl chloride only[228]:

$$\eta^5\text{-CpFe(CO)}_2\text{CH}_2\text{Ph} + \text{CuCl}_2 \rightarrow \eta^5\text{-CpFe(CO)}_2\text{Cl} + \text{PhCH}_2\text{Cl} + 2\text{CuCl} \quad .$$

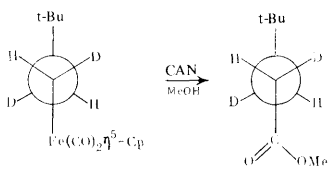
This reaction can be modelled by the electrochemical oxidation of $RFe(CO)_2\eta^5$-Cp (R = Me, $PhCH_2$, or $PhCH_2CH_2$) in the presence of chloride ions, whereupon the corresponding chloro-derivatives are also formed. It has been shown in relation to *threo*-PhCHDCHD-Fe$(CO)_2\eta^5$-Cp [228] that the electrochemical oxidation takes place with the preferential retention of configuration. Since the label is distributed between both carbon atoms of the ethyl fragment in the oxidation of the ^{13}C- labelled β-phenylethyl derivative, presumably a phenonium ion is formed in the reaction and the observed stereochemical result (retention of configuration) is due to attack by a chloride ion from the side of the iron atom.

When the same iron complexes are oxidised in alcohol and not in CH_2Cl_2, particularly in the presence of CO, carbonylation products (alkyl carboxylates) are formed[229]:

$$RFe(CO)_2\eta^5\text{-Cp} \xrightarrow[R'OH,CO]{CuCl} RCOOR' \quad ;$$

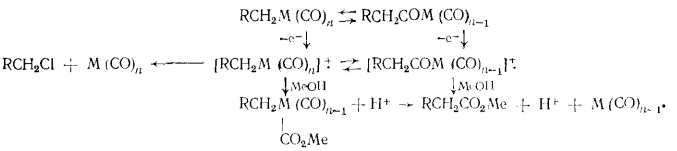
R = $PhCH_2CH_2$, cyclo-$C_6H_{11}CH_2$, cyclo-C_6H_{11} .

A similar reaction takes place in the oxidation of *erythro*-3,3-dimethylbutyl-1,2-d_2-Fe(CO)η^5-Cp by cerium ammonium nitrate in methanol[230]:



The stereochemistry of this process and also the reaction with $CuCl_2$ considered above[229] shows that the oxidation of the complex causes the insertion of CO in the C—Fe bond, which takes place with retention of configuration, after which nucleophilic attack on the alcohol takes place.

The oxidation of *p*-fluorobenzyl (R) derivatives of molybdenum, chromium, iron, manganese, namely π-$Cp(CO)_3$MoR, π-$Cp(CO)_3$CrR, π-$Cp(CO)_2$FeR, and $RMn(CO)_5$, by cerium(IV) salts in methanol in the presence of LiCl was considered from the same standpoints[231]. Apart from *p*-fluorobenzyl chloride, methyl *p*-fluorophenylacetate is formed in the reaction, the ratio of the yields of the products depending on the nature of the metal atom. The following mechanism accounts for the possible pathways leading to their formation:



Finally we shall turn to the coupling reactions which occur in the oxidation of transition metal compounds $R^1R^2ML_n$ and lead to the formation of the dimer R^1R^2. We have already encountered one example of such reactions when the oxidation of the cuprates R_2CuLi by copper(II) halides was considered[143]. The $Ar_4Cu_6X_2$ clusters are oxidised similarly[232]. Here we should like to examine these reactions in greater detail and note the role which they can play in complex processes involving transition metal complexes, particularly in the cross-coupling reaction.

Morell and Kochi were some of the first investigators who drew attention to the intramolecular coupling reactions occurring in the oxidation of organometallic compounds. They observed that the intramolecular decomposition of the complexes $[Et_3P]_2[MeArNi]$ is accelerated in the presence of ArBr or O_2.[123,233]

$$(Et_3P)_2Ni\begin{matrix}Ar\\Me\end{matrix} \rightarrow ArMe + (Et_3P)_2Ni \quad .$$

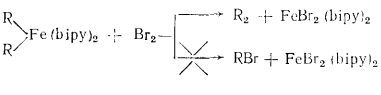
On the basis of these data, it was suggested that the reductive elimination can be activated by electron transfer from the complex to ArX and that ArX yields an oxidative addition product in the mechanism proposed for the decomposition:

$$L_2NiArCH_2 + ArX \rightleftharpoons [L_2NiArCH_2]^{\ddagger} + Ar^{\cdot}_{\ddagger} \quad ,$$
$$[L_2NiArCH_2]^{\ddagger} \rightarrow ArCH_2 + L_2Ni \quad ,$$
$$L_2Ni^{\ddagger} + ArX^{\mp} \rightarrow L_2NiArX \quad .$$

Generally speaking, this hypothesis was not confirmed, but data exist showing that intermediates capable of reductive elimination can be formed in the oxidation of transition metal complexes. Thus only coupling products are formed in the oxidation of dialkyl derivatives of iron(II) by a wide variety of reagents, such as Na_2IrCl_6 or thallium(III), cerium(IV), and cobalt(III) triflates[234]:

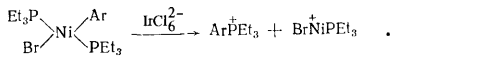
$$R_2Fe(bipy)_2 + 2IrCl_6^{2-} \rightarrow R_2 + FeCl_2(bipy)_2 + 2IrCl_6^{3-} \quad .$$

This reaction is not intermolecular and proceeds without the involvement of free radicals, because the decomposition of a mixture of the diethyl and dimethyl complexes does not result in the formation of propane. Halogens behave in a very unusual manner in the reaction considered—they exhibit exclusively oxidising properties and alkanes are formed in this instance instead of alkyl halides[130,234]:



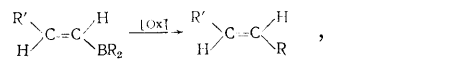
The above oxidative coupling reactions involving transition metal complexes can be modelled by electrochemical oxidation on platinum. Thus the electrolysis of triethylphosphine complexes of diarylnickel in acetonitrile leads to the formation of biaryl, whose yield reaches 94% in the case of $(PEt_3)_2Ni(o\text{-}MeC_6H_4)_2$. Some of the intermediates formed in the one-electron oxidation of the complexes have been detected with the aid of cyclic voltamperometry at −50 °C.[235]

An interesting coupling reaction occurs in the oxidation of the phosphine complexes of arylnickel bromide by Na_2IrCl_6, $Ce(CF_3COO)_4$, and $CuBr_2$:[234]



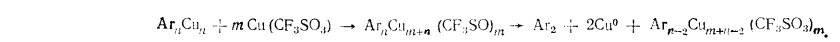
It has been shown for o-$MeC_6H_4NiBr(PEt_3)_2$ that a phosphonium cation is formed from the $[o\text{-}MeC_6H_4NiBr(PEt_3)_2]^+$ species, for which the corresponding EPR spectrum has been obtained at −50 °C. The same species was detected with the aid of CO and the formation of the cation $[ArCONiBr.(PEt_3)_2]^+$ was detected by EPR.

The stereospecific oxidation of alkenyldialkylboranes by $Pb(OAc)_4$, $PhI(OAc)_2$,[236] and $Pd(OAc)_2$,[237] leading to the formation of substituted olefins



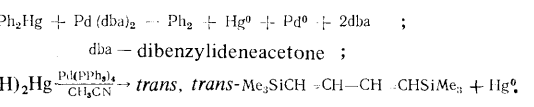
constitutes an interesting case of oxidative coupling of radicals. The Zweifel reaction, in which iodine is used as the oxidant, is a prototype of these processes[238].

The above coupling reactions, promoted by electron transfer, in essence do not differ in any way from the intramolecular thermal decomposition of organometallic compounds (reductive elimination reactions) examined in Section IV. The role of the oxidant in these reactions reduces to effecting a transition of the complex to an oxidation state which favours the occurrence of the reductive elimination reaction. However, there exist a multiplicity of reactions in which coupling takes place under the influence of compounds which function exclusively as catalysts. For example, the decomposition of the cluster compound arylcopper(I) (Ar_4Cu_4) is catalysed by copper(I) triflate. According to van Koten et al.[239], the coupling in such clusters takes place as a result of the intramolecular electron transfer in the complex formed by the reactants:



The decomposition of the clusters $R_4Cu_6X_2$ (X = Br, I, or CF_3SO_3) is promoted similarly by the addition of copper(II) salts[108,232] or copper(I) triflate[239].

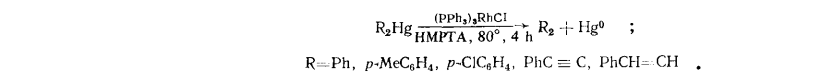
Another example of such reactions is the decomposition of R_2Hg in the presence of palladium and platinum complexes in which the metal is in a low valence state[240,241]:



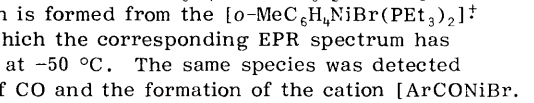
dba — dibenzylideneacetone ;

It has now been established that $Pd(PPh_3)_4$ or $Pt(PPh_3)_3$ are initially inserted in the C–Hg bond in these reactions, exhibiting the properties of a nucleophilic carbenoid. In a number of instances, when R_2Hg contains the powerful electron-accepting groups R = CF_3 and C_6H_5,[242] the insertion products can be isolated and characterised by physicochemical methods. However, the intermediates are usually unstable and undergo the elimination of mercury and reductive elimination with formation of a coupling product.

The decomposition reactions of the compounds R_2Hg catalysed by rhodium(I) complexes apparently have an analogous mechanism[243]:



We may note that similar reactions are known for organomercury salts. Thus biaryls are formed from ArHgCl on treatment with rhodium(I) complexes in the presence of LiCl.[244] The carbenoid insertion of the rhodium(I) atom in the C–Hg bond apparently takes place in this instance and Ar_2 is formed as a result of reductive elimination:



As in the instances considered above, mercury is the oxidant in this catalytic process, its oxidation state changing from +2 to 0 in the course of the reaction.

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