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Promoting of Non-transition Metal Alkylation with Organyl Halides in the Presence of Binary Systems Based on an Organometallic Compound and a Transition Metal Compound: I. Hypothetical Stepwise Scheme and Verification of the System Efficiency

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Abstract—A hypothetical scheme has been proposed for the alkylation of non-transition metals with organyl halides in the presence of binary systems consisting of an organometallic compound and a transition metal compound. The scheme implies catalysis by transition metal atoms, small clusters, and subhalides adsorbed on the surface of metal to be alkylated. These particles are formed during the process as a result of interaction between the binary system components. The alkylation of commercial zinc powder with ethyl bromide has been used as a model reaction to demonstrate that the binary system ethylzinc bromide–copper(I) iodide is superior in its efficiency and experimental simplicity to all other examined methods for stimulation of the alkylation of elements with organyl halides yielding organometallic compounds.

Keywords: zinc, ethyl bromide, alkylation, stimulation, mechanism

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Alkyl derivatives of non-transition metals are widely used in laboratory and large-scale syntheses [1]. One of the most important practical applications of organometallic compounds is preparation of materials for electronics. In this case, high requirements are imposed on their purity [2]. The main impurities in organometallic compounds are the initial reactants, side products, and equipment materials. Therefore, the impurity composition of organometallic compounds may essentially vary depending on the preparation method [2–5]. The purest samples are obtained by so-called direct synthesis [4, 5] based on the alkylation of metals with organic halogen compounds. Hence, the direct synthesis attracts the strongest interest from the viewpoint of obtaining highly pure organometallic compounds. However, only electropositive alkali metals and magnesium react with alkyl halides relatively readily. The alkylation of other elements generally requires additional stimulation. Despite a wide range of known stimulation methods, in most cases it is impossible to attain a combination of high performance of the direct synthesis with its simplicity and manufacturability. Taking into account the above stated, the goal of the present study was to develop a new efficient method for promoting the non-transition metal alkylation with organyl halides, which would ensure relatively simple and high-yield preparation of practically important organometallic compounds containing no difficultly removable impurities. The subjects for the study were the syntheses of organozinc and organocadmium compounds by reactions of the metals with alkyl halides. Highly pure alkyl derivatives of zinc and cadmium attract interest from the technological viewpoint [2, 6–10, 11]. However, no convenient, highly efficient, and manufacturable methods for their preparation have been reported [8, 9].

To the best of the author knowledge, the present paper is the first to consider in much detail a hypothetical mechanism of a new version of stimulation of the direct synthesis of organometallic compounds in the presence of binary systems consisting of an organometallic compound and a transition metal compound. Also, the efficiency of the new version was tested experimentally. Some synthetic potentialities of the proposed stimulation version in the alkylation of zinc and cadmium have already been reported in [12–14]. The results of these studies have been obtained on the basis of the data discussed in the present contribution.

Hypothetic stepwise scheme of the direct synthesis of organometallic compounds in the presence of binary systems. The known stepwise schemes of the direct synthesis of organo-metallic compounds describe the constant-rate state of the process, though the direct synthesis generally involves an induction period. The latter amounts to a few minutes to several days or even months and is often comparable with the duration of the constant-rate process. For example, an induction period was observed in the alkylation of Li, Na, Mg, Ca, Zn, Al, Si, Ge, Sn, and Pb with organyl halides. Mechanisms of the known stimulation methods, side reactions, and concomitant physical processes were not usually considered. Therefore, we propose a new hypothetical stimulation version. It consists of the addition of two necessary components to the initial reaction mixture: a transition metal compound, e.g., halide, and an alkyl derivative of a non-transition metal. The latter may be the desired product of the direct synthesis. In the further treatment such stimulating systems will be referred to as binary systems. The development of the stimulation method was based on the following well-known concepts. First, under normal conditions metal surface is covered by a thin passivating film which can be detected only by special methods. This film creates a barrier to heterogeneous reaction of metals with other reactants. Second, metal atoms and small clusters are extremely reactive. In particular, they readily react with organyl halides even at 77 K and lower temperatures to give insertion products into the carbon–halogen bond.

The stepwise scheme of the direct synthesis of organometallic compounds in the presence of binary systems may be represented as a series of sequential/parallel macro steps: (1) interaction of the binary system components with each other; (2) mass transfer of the products formed thereby to the metal surface (to be alkylated) and their adsorption thereon; (3) decomposition of the passivating film on the metal surface; (4) generation of the active metal surface; and (5) formation of the target organometallic compound.

Interaction of the binary system components (transmetalation) yields a labile alkyl derivative of transition metal (RM).

$$\mathrm{ML + RMgX \rightleftarrows RM + MgXL.}$$

Here, ML is a transition metal derivative, and RMgX is the organometallic compound in the binary system (alkylmagnesium derivative is given as an example).

Depending on the solubility of ML in the reaction medium, the process can occur in the bulk solution and/or on the surface of the undissolved transition metal derivative particles, as well as on the surface of the non-transition metal being alkylated. Labile alkyl derivative of transition metal RM can be decomposed even on the surface of undissolved ML particles or in the bulk solution to produce eventually transition metal atoms and molecular organic products. Transition metal atoms and RM molecules are in turn capable of forming complexes with with organometal component of the binary system ($\mathrm{M \cdots RMgX}$) [15, 16] and *ate* complex ($\mathrm{RM \cdots RMgX}$). The feasibility of the reduction of transition metal compounds to zero-valence metals with various organometallic compounds follows from published data. For example, Cu, Ag, Au, Ti, V, Cr, Mo, W, Fe, Co, Ni, Pd, Pt, and Os halides and other derivatives are reduced to the corresponding metals with organic derivatives of non-transition metals belonging to Groups I–IV of the periodic table.

The first macro step is accompanied by mass transfer of the products formed in the reaction between the binary system components and of the components themselves to the non-transition metal surface, followed by their adsorption on that surface (second macro step). Simultaneously, passivating film on the non-transition metal surface decomposes. This macro step may include several pathways. The passivating film can be etched by the organic halide and by the organometallic compound of the binary system. The mechanism of the reaction of organyl halide with a metal coated with a passivating film, which is responsible for the initial step (induction period) of the direct synthesis was not considered in the literature. Presumably, it also includes steps similar to those typical of metal oxidation and corrosion (see, e.g., [10]), and it may be represented as shown in Fig. 1. The resulting defects in the crystal structure of the passivating film eventually give rise to unstable compounds and film dissolution.

The decomposition of the passivating film under the action of organyl halide (Fig. 1) includes the following steps: (1) diffusion of organyl halide molecules from the bulk solution to the passivating

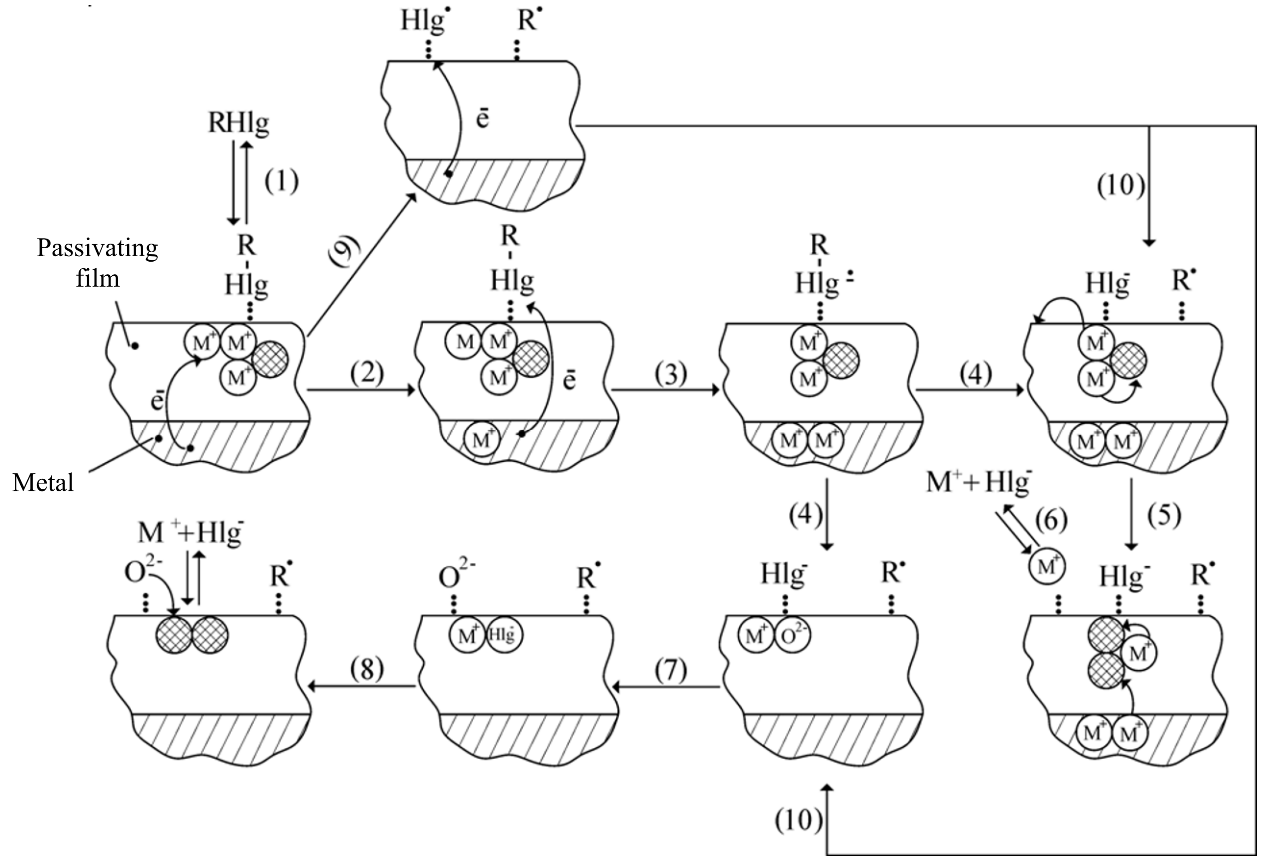


Fig. 1. Scheme of decomposition of the passivating film on the surface of non-transition metal by the action of organyl halide. Hatched circles denote vacancies; M^+ is metal ion; M is the reduced metal.

film surface and adsorption thereon; (2) electron transfer from the metal through the passivating film by the action of organyl halide and capture of electrons by metal ions (reduction of the metal); (3) capture of electrons by organyl halide molecules with formation of radical anions; (4) fast and irreversible dissociation of radical anions into organic radical and halide ion; (5) metal ions transfer to the outer surface and their reaction with halide ions with formation of metal halide; (6) dissolution of metal halide; (7) replacement of lattice oxygen in the passivating film by halogen (this is possible if the halide is more stable than the corresponding oxide); (8) dissolution of the halide formed in the preceding step; (9) possible dissociative adsorption of organyl halide on the passivating film surface; and (10) metal oxidation with halogen atoms generated in the preceding step.

Step (2) is one of the key ones. According to the existing theory, the electron work function of a metal coated with an oxide or semiconductor film should not change appreciably provided that the film thickness does not exceed the Debye length [11, 17]. The latter is estimated as 100 nm for oxide films [17]. Etching of the passivating film on the non-transition metal surface by organometallic compound may be described as follows. Some reactive organometallic compounds are capable of reacting with oxides. This reaction underlies methods of preparation of a number of organic compounds of Hg, B, Si, Sn, Pb, As, Sb, Bi, and transition metals. Furthermore, it is known that solutions of organic compounds of groups I–IV non-transition metals are characterized by a complex composition; they include a number of metal-containing particles: monomeric molecules of completely or partially alkylated metals, metal halides, various associates, and ionic metal-containing species. All these species are solvated and are involved in equilibria which have been understood only in general terms even for the most explored systems such as Grignard reagents (see, e.g., [18, 19]). Therefore, organometallic compounds in solution can act as a source of cations whose adsorption on the passivating film surface generates a positive charge facilitating electron transfer from the metal particle to the surface through the passivating film. In addition, positively charged ions are stronger oxidants than, e.g., alkyl halides. In particular, it is known that RZn^+ ions are reduced at a less negative potential than ethyl iodide [20]. In this case, decomposition of the passivating film is determined by the reduction of metal cations in the film as a result of capture of electrons transferred from the bulk metal to the cation adsorbed on the outer film surface. Taking into account the high oxidizing ability of cations, it may be expected that organometallic compound in the binary system may be a more efficient etching agent toward the passivating film even than alkyl iodides which are the strongest oxidants among alkyl halides. Apart from organic halide and organometallic compound of the binary system, etching agents may be other oxidants that could be generated in the reaction medium during the process. Such agents may be, e.g., halogen atoms and molecules and transition metal adatoms and clusters.

Hereafter the active surface stands for the non-transition metal surface free of the passivating film and containing potentially catalytically active species. These species are primarily assumed to be transition metal adatoms and small clusters. The macro step corresponding to active surface generation is likely to begin concurrently with the passivating film decomposition as shown in Fig. 2. Transition metal adatoms can also be generated as a result of reduction of the initial transition metal compound (ML) with the non-transition metal (Fig. 2b). In fact, transition metal halides and other compounds can be reduced with non-transition metals not only in aqueous (see, e.g., electrochemical series of redox couples [10]) but also in nonaqueous media [10, 21, 22]. Isolated adsorbed transition metal atoms appearing on the non-transition metal surface are capable of being involved in a number of known concurrent processes, such as migration across the surface, adatom aggregation, chemisorption, and desorption into the bulk solution. Adsorbed species are localized mainly on steps at the surface terrace boundaries and crystal structure defects, i.e., sites where electron density distribution differs from that of an ideal crystal. Finally, adatoms can participate in the emergence and growth of transition metal phase nuclei on the passivating film surface and active surface of the non-transition metal (Fig. 2c) [10, 23, 24]. Decomposition of the alkyl transition metal derivative (RM), its *ate* complex ($RM \cdots RMgX$), and the $M \cdots RMgX$ complex can also occur in the bulk liquid phase (Fig. 2a). Generally speaking, transition metal atoms thus formed can initiate emergence and growth of transition metal nuclei in the bulk mixture. However, it is known that the energy of formation of a critical nucleus in heterogeneous nucleation of a new phase is always lower than in homogeneous nucleation [10, 24]. Therefore, transition metal atoms generated in the bulk solution are likely to be eventually captured by the non-transition metal surface. Thus, transition metal atoms are continuously supplied to the adlayer on the non-transition metal surface and continuously removed therefrom due to incorporation into the crystal structure of transition metal phase nuclei. It may be expected that the final step in the formation of the active non-transition metal surface is establishment of a quasi-stationary concentration of transition metal adatoms.

Presumably, the macro step of formation of the target organometallic compound includes a catalytic path involving transition metal adatoms on the non-transition metal surface (Fig. 3). Transition metal adatoms may be both isolated and included into associates or small clusters. I believe that the mechanism of catalytic action of transition metal adatoms is based on their high reactivity toward organyl halides. The reaction of adatoms with organyl halide molecule leads to their insertion at the carbon–halogen bond. The labile insertion product undergoes decomposition into organic radical and transition metal subhalide. Also, abstraction of halogen from the organyl halide molecule by transition metal adatom cannot be ruled out. In order to interface steps of the catalytic process with each other, further reduction of the transition metal subhalide is necessary. The reduction can be accomplished by the non-transition metal with regeneration of adatom and formation of surface non-transition metal halide. The feasibility of this process has been discussed above while considering the preceding macro step. Surface non-transition metal halide is then attacked by the organic radical, yielding the target mixed organometallic compound.

Other paths leading to the formation of the target organometallic compound are also possible. For example, it is believed that metal subhalides are highly reactive toward organic halides. These concepts were used to analyze the Kharasch reaction mechanism [25]. It is also known that organopolymagnesium halides RMg_nHlg readily react with organic chlorides [26].

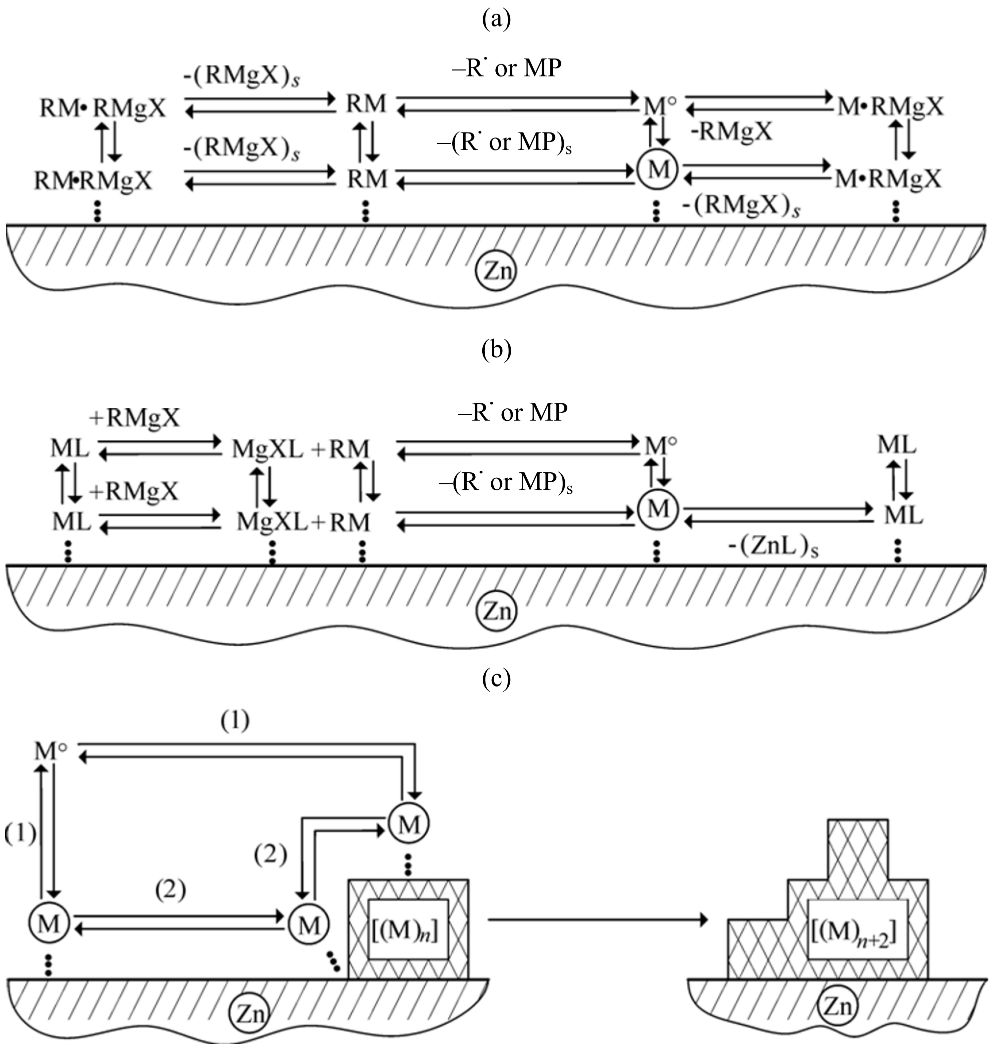


Fig. 2. Scheme of formation of active surface of the non-transition metal. (a, b) appearance of transition metal adatoms on the surface of the non-transition metal; (c) generation and subsequent growth of transition metal phase nuclei; (1) adsorption, (2) surface diffusion; ML stands for a transition metal compound; RMgX is a Grignard reagent; MgXL is a magnesium salt; RM is an alkyl derivative of transition metal; RM···RMgX is an *ate* complex; M is a transition metal adatom; M^0 is a transition metal atom; M···RMgX is a transition metal complex with Grignard reagent; $(M)_n$ is a transition metal phase nucleus; R˙ is an alkyl radical; MP is a molecular product. Hereinafter (in figure captions and text) the subscript “s” denotes a surface species.

$$PhMg_nCl + (n-1)PhCl \rightarrow nPhMgCl.$$

Finally, steps involving partially halogenated metals are considered to be crucial in a number of direct electrolytic syntheses of organic compounds of Zn, Cd, Hg, In, Tl, Sn, Pb, and other metals [20, 27].

$$(MHlg)_s + (RHlg)_s \rightarrow (RMHlg)_s + (Hlg)_s,$$

Therefore, not only adatoms and small clusters but also transition metal subhalides may be catalytically active in the direct synthesis of organometallic compounds. Most probable paths of the reaction of transition metal subhalide with an organyl halide [steps (1), (3), etc.] are shown in Scheme 1.

The process can involve either all *n* catalytic cycles (*n* is the oxidation state of transition metal) or only a part of them, depending on the ratio of the rates of competing reactions: that of transition metal subhalide with organyl halide and reduction of the subhalide with non-transition metal. Each catalytic cycle produces organic radical R˙ and surface non-transition metal halide $(ZnHlg)_S$, which react with each other to afford the target organometallic compound, RZnHlg.

Verification of the efficiency of binary systems. High stimulating efficiency of binary systems in the alkylation of metals with organyl halides is not obvious a priori. Transition metals and their com-

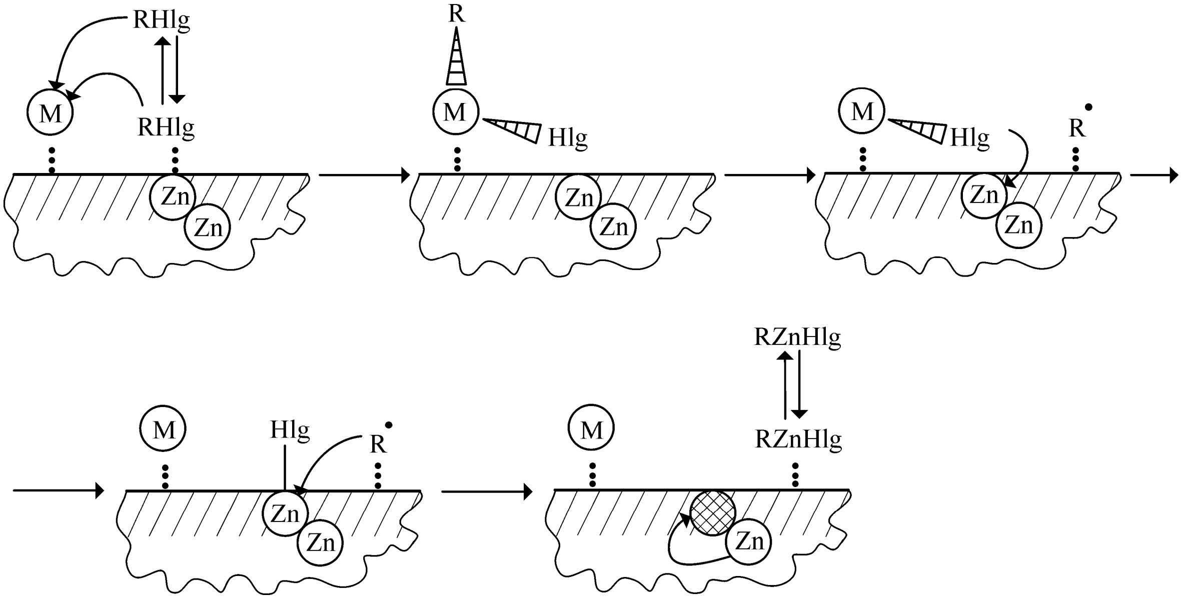


Fig. 3. Catalytic path of the formation of the target organometallic compound with participation of transition metal adatoms. Hatched circles denote vacancies, and M stands for transition metal adatoms.

pounds are known to promote or catalyze a number of side reactions leading to hydrocarbons, in particular thermal decomposition and dehydrohalogenation of organyl halides, their reactions with organometallic compounds (cross-coupling and Kharasch reaction), thermal decomposition of organometallic compounds, and oxidation of organometallic compounds with transition metal compounds. Moreover, the hypothetical scheme of the catalytic cycle involving transition metal adatoms implies that adatoms should be regenerated mainly via reduction of the surface transition metal halide with the non-transition metal. This process may compete with the adatom regeneration by the action of the target organometallic compound or organometallic compound constituting the binary system.

$$(\mathrm{CuHlg})_s + \mathrm{RMHlg} \rightleftarrows (\mathrm{CuR})_s + \mathrm{MHlg}_2, \quad (1)$$

$$(\mathrm{CuR})_s \rightarrow (\mathrm{Cu})_s + (\mathrm{R}^{\bullet})_s. \quad (2)$$

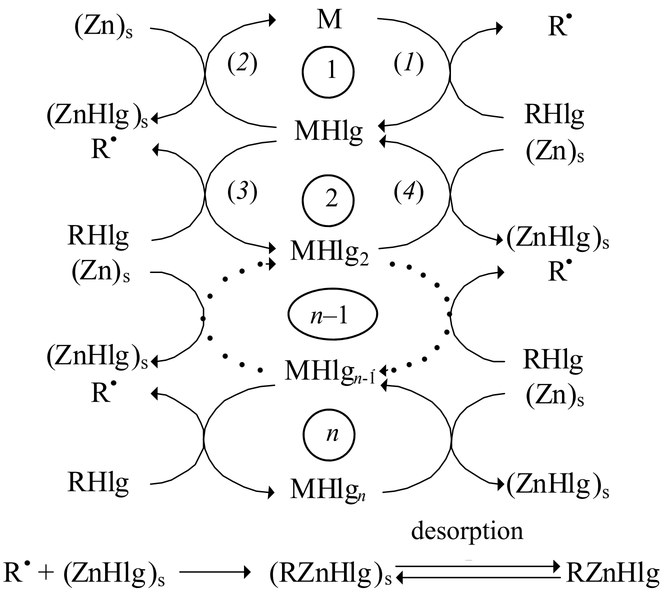
Here, M is the non-transition metal atom.

If the above path is operative, the most probable products are non-transition metal halide and a mixture of hydrocarbons resulting from transformations of alkyl radicals $\mathrm{R}^{\bullet}$. Therefore, the yield of the target organometallic compound in the direct synthesis in the presence of binary systems may appear to be lower even when the path of formation of organometallic compounds catalyzed by transition metal adatoms is operative.

However, even trial experiments on the alkylation of commercial zinc powder with ethyl bromide in the presence of the ethylzinc bromide–copper(I) iodide binary system showed that ethylzinc bromide (target organometallic compound) was formed at an appreciable rate at 38°C under forced stirring of the reaction mixture.

$$\mathrm{EtBr} + \mathrm{Zn} \rightarrow \mathrm{EtZnBr}. \quad (3)$$

The results of those experiments carried out under solvent-free conditions in the absence of other additives are given in Fig. 4. Figure 4a indicates the existence of an induction period. The duration of the latter was estimated according to the procedure for topochemical processes (see, e.g., [28]), by extrapolation of the kinetic curves until intersection with the time axis. It ranged from 11 to 50 min for the experiments illustrated by Fig. 4 (average duration 24 min for six runs). The developed process goes at an almost constant rate up to a high conversion of the reactants, and the kinetic curves are satisfactorily fitted with a linear correlation. The maximum conversion of zinc in curves *1* and *2* (Fig. 4b) was of 96 and 92%, respectively, and the conversion of ethyl bromide in the experiment corresponding to kinetic curve *3* in Fig. 4b attained 45–64%. Kinetic measurements at higher conversions of ethyl bromide were complicated by crystallization of the reaction mixture in the sampler while withdrawing samples from the reactor. Therefore, in further experiments the kinetic curves



Scheme 1. Here, M is a transition metal adatom; MHlg, $MHlg_2$, and $MHlg_{n-1}$ are transition metal subhalides adsorbed on the surface of the non-transition metal; *n* is the oxidation state of the transition metal.

were plotted up to a conversion of organyl halide not exceeding 50–60%. Almost no evolution of gaseous products was observed. This indicated the following. First, the contribution of side reactions leading to hydrocarbons (see above) was not appreciable. Second, the path of regeneration of potentially catalytically active transition metal adatom by the action of organometallic compound [reactions (1), (2)] was insignificant. Estimation of the observed order of the reaction [29] with respect to ethyl bromide by the kinetic curves obtained in four runs (curve *4* in Fig. 4b) gave a value close to zero (0.01±0.63). No reaction occurred over a period of 6 h in the absence of the binary system or any of its components, other conditions being the same.

Furthermore, preliminarily experiments showed that prolonged heating of a mixture of 34 g (0.31 mol) of ethyl bromide, 50 g (0.76 mol) of zinc powder, 2.8 g (0.016 mol) of ethylzinc bromide, and 12.4 g (0.065 mol) of copper(I) iodide under reflux in a round-bottom reactor equipped with a reflux condenser (without additional stirring) was accompanied by increase in the intensity of the red–brown color of the mixture. This clearly indicated reduction of copper(I) iodide to copper metal by the action of ethylzinc bromide during the alkylation of zinc with ethyl bromide. An attempt was also made to estimate the rate of transmetalation (4) of copper(I) iodide with ethylzinc bromide in ethyl bromide at 38°C under vigorous stirring, i.e., under the conditions analogous to the alkylation of zinc with ethyl bromide.

$$\mathrm{EtZnBr + CuI \rightleftarrows EtCu + ZnBrI}, \qquad (4)$$

$$\mathrm{EtCu \rightarrow Cu^0 + \text{mixture of gaseous hydrocarbons}}. \qquad (5)$$

The initial reaction mixture contained 15.69 g (0.09 mol) of ethylzinc bromide, 22.85 g (0.12 mol) of copper(I) iodide, and 63.16 g (0.58 mol) of ethyl bromide. It was found that the heterogeneous reaction [copper(I) iodide is almost insoluble in ethyl bromide] was very slow: the conversion of ethylzinc bromide attained ≈2% in 5 h. The volume of the evolved gaseous products was 20 mL (reduced to normal conditions). A bright copper metal ring appeared at the liquid–gas–ampule wall boundary in samples of the reaction mixture in a few minutes after withdrawal. These findings indicated transmetalation (4) and subsequent decomposition of ethylcopper thus formed [reaction (5)], as well as an appreciable solubility of ethylcopper or its *ate* complex with the organozinc compound (EtCu · · · EtZnBr) in ethyl bromide; this means that transfer of copper-containing particles to the zinc surface under conditions of its alkylation with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide is possible.

A large number of stimulation methods for the direct synthesis of organometallic compounds have

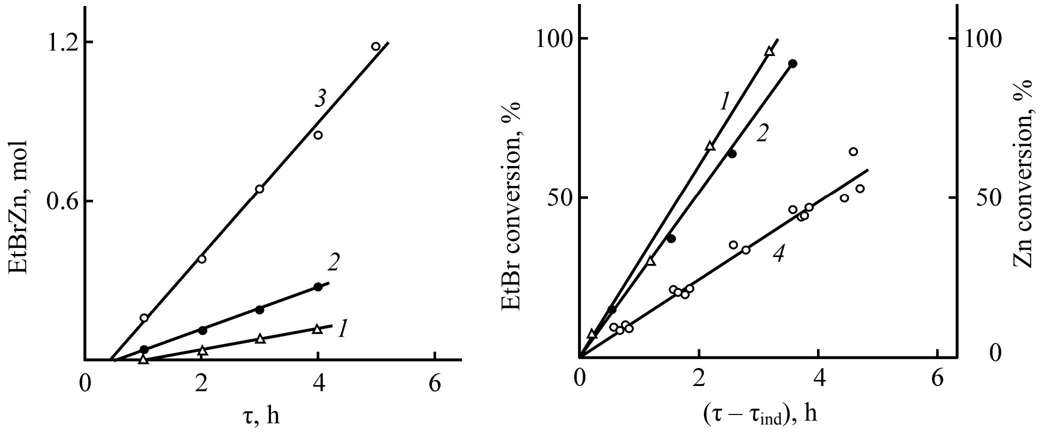


Fig. 4. Alkylation of zinc powder with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide [38°C; 0.033 mol of CuI; agitation speed 500 rpm]: (*1*) Zn, 0.13 mol; EtBr, 1.65 mol; EtZnBr, 0.06 mol; (*2*) Zn, 0.30 mol; EtBr, 1.65 mol; EtZnBr, 0.06 mol; (*3*) Zn, 1.84 mol; EtBr, 1.84 mol; EtZnBr, 0.07 mol; (*4*) averaged data for four runs with 1.84 mol of EtBr. Zn: 0.98, 1.84, 1.84, and 3.77 mol; EtZnBr: 0.07, 0.07, 0.43, and 0.07 mol, respectively; τ is the reaction time, and τ_{ind} is the induction period.

been reported in the literature (see table). It was interesting to compare the stimulating efficiencies of the proposed binary systems and known methods. However, it was impossible to perform even rough qualitative tests of so large number of known methods in the present study, and only a few of them were selected for comparison. The choice was made so that the maximum number of groups of known methods was covered (denoted by numbers 1 to *5* in the table). The main selection criterion was experimental simplicity. Laborious methods involving the use of specially prepared highly reactive metals (group 2) were not tested.

The indicative reaction was alkylation of zinc with ethyl bromide (3). Under the examined conditions, commercial zinc powder underwent appreciable oxidative dissolution only in the presence of the ethylzinc bromide–copper(I) iodide system (Fig. 4) or when the reaction was carried out in *N*,*N*-dimethylformamide or dimethyl sulfoxide, including their combination with transition and non-transition metal salts [KI, NaI, $Hg(NO_3)_2$, CuCl, $AgNO_3$]. The reaction of zinc powder with ethyl bromide did not start (1) without stimulation, (2) under UV irradiation, (3) in the presence of ethyl iodide, (4) in the presence of ethylzinc bromide, (5) in dimethyl sulfate, (6) in the presence of $MgSO_4 \cdot 7H_2O$, $ZnCl_2$, ZnI_2, $CdBr_2 \cdot 4H_2O$, CdI_2, HgI_2, $SnCl_4$, $SnSO_4 \cdot 2H_2O$, or CuI, or (7) in the presence of dimethyl sulfate–CuCl, EtZnBr–I_2, or EtZnBr–copper powder.

The zinc/copper couple did not react with ethyl bromide over a period of 50 h under forced vigorous stirring. However, organozinc compounds were formed in the reaction of the zinc/copper couple with ethyl bromide in the following cases: (1) under UV irradiation or under UV irradiation in the presence of $ZnCl_2$, (2) in the presence of ethyl iodide, (3) in the presence of ethylzinc bromide, and (4) in the presence of $MgSO_4{\cdot}7H_2O$, $ZnCl_2$, ZnI_2, $CdBr_2{\cdot}4H_2O$, CdI_2, $SnCl_4$, $SnSO_4{\cdot}2H_2O$, or $FeCl_3{\cdot}6H_2O$ (each salt was taken individually). Therefore, the binary system ethylzinc bromide–copper(I) iodide considerably exceeds in efficiency and experimental simplicity the zinc/copper couple and all other tested versions of stimulation of the alkylation of zinc with ethyl bromide. The effect of EtZnBr–CuI is comparable with those of such electron-donor solvents as DMF and DMSO. However, it should be noted that the use of hygroscopic high-boiling DMF, DMSO, or other similar solvents could appreciably complicate isolation of the resulting organometallic compounds.

In summary, the obtained results indicate high stimulating efficiency and experimentally simple use of the binary system ethyl zinc bromide–copper(I) iodide in the direct synthesis of ethylzinc bromide in the absence of a solvent. The experimental findings [a short induction period, reduction of copper(I) iodide to copper metal with ethylzinc bromide, solubility of ethylcopper in the reaction mixture, insufficiency of only one component of the binary mixture to stimulate the alkylation process, the lack of gaseous by-products] are very consistent with the proposed hypothetical scheme for stimulation of the direct synthesis of organometallic compounds in the presence of binary systems.

Known methods of stimulation of the direct synthesis of organometallic compounds by reaction of elements with organyl halides

Stimulation method and its versions	Alkylated elements
1. Physical activation	
1.1. Ultrasonic treatment	Li, Mg, Zn, Al, Ga
1.2. Mechanical activation	Mg, Sn
1.3. UV irradiation	Mg, Hg, Sn
1.4. Ionizing irradiation	Ge, Sn
1.5. Electrolysis of solutions of organyl halides under cathodic or anodic polarization of the element to be alkylated	Zn, Cd, Hg, Ga, In, Tl, Ge, Sn, Pb, P, As, Sb, Bi, S, Se, Ti, Zr, Hf , Ni, Pd
2. Use of highly reactive metals prepared by different methods	
2.1. Liquid metal atomization with a nebulizing fluid jet or inert gas	Be, Zn, Al, Ga, In, Tl
2.2. Electrolytic deposition	Mg, Ba, Zn
2.3. Application of mechanical fields to metal powder, turnings, or foil	Mg, Zn, Al
2.4. Joint condensation of metal vapor and organic solvent at low temperature (77 K and lower)	Mg, Zn, Cd, Al, In, Ge, Sn, Pb, Ni
2.5. Joint vacuum deposition of metal vapor and organic solvent onto a surface cooled to a low temperature	Mg, Ca, Ga, Sn, Ti, Ni, Pd, Pt
2.6. Reduction of metal halides with alkali metals (or naphthalene sodium salt) in organic solvents	Mg, Zn, Cd, Al, In, Tl, Sn, Pb, Sm, Yb, Ni, Pd, Pt
2.7. Preliminary treatment of metals with solutions of acid, alkali, or salt, halogen, hydrogen halide, organometallic compound, etc.	Mg, Zn, Al, Ga, Si, Sn, Cu
3. Use of alloys or couples with other metals	
3.1. With non-transition metals (Li, Na, K, Mg, Ca, Zn, Cd, Hg)	Li, Mg, Ca, Zn, Cd, Hg, Al, Ga, In, Sn, Pb, P, As, Sb, Te, Sm, Yb
3.2. With transition metals (Cu, Ag, Au, Ti, Zr, Nb, Ta, Fe, Co, Ni, Pd, Pt)	Li, Mg, Zn, Hg, Al, Si, Ge, Sn
3.3. Triple and multicomponent alloys	Zn, Al, Ga, Si, Ge, Sn, Pb
4. Addition of chemical substances	
4.1. Elemental halogens (iodine, bromine, chlorine)	Li, Be, Mg, Ca, Ba, Zn, Hg, Al, Ga, Si, Sn, Pb, As, Mn
4.2. Highly reactive organyl halides (iodides or bromides)	Li, Mg, Zn, Al, Sn, Pb
4.3. Hydrogen halides	Si, Ge, Sn
4.4. Non-transition metals (Li, Na, Mg, Zn, Hg, Al, Sn, Pb, Sb, Bi)	Zn, Al, Ga, In, Si, Sn, Pb
4.5. Transition metals (Cu, Ag, Au, Fe, Pt)	Zn, Si, Ge, Pb, As, Sb, Bi
4.6. Alloys and mixtures of two or more metals	Si, Ge, Pb
4.7. Organic compounds of non-transition metals (Li, Be, Mg, Ca, Zn, Cd, Al, Sn, Pb)	Li, Be, Mg, Ca, Zn, Al, Sn, Pb
4.8. Salts (commonly halides) Na, K, Cs, Be, Mg, Zn, Cd, Hg, B, Al, Sn, As, Sb, Bi, Cu, Ag, Au, Ti, Fe, Co, Pt, ammonium	Be, Mg, Zn, Hg, Al, Si, Ge, Sn, Pb, As, Se, Te, Mn
4.9. Li, Na, Mg, and Ca hydrides	Mg
4.10. Electron-donor compounds containing Groups V and VI elements (N, P, As, Sb, O, S, Se, Te)	Li, Na, Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Al, Ga, In, Sn, Pb, As, Se, Te, Cu, Ce, Pr, Nd, Sm, Eu, Ho, Yb, Mn
5. Stimulation methods implying a combination of two or more of the above listed versions (see entry nos. 1–4 in this table)	Mg, Ba, Zn, Cd, Hg, Al, Ga, In, Si, Ge, Sn, Pb, Sm, Yb, Mn

EXPERIMENTAL

The following reagents were used without additional purification: zinc powder PTs-10 (TU 48-4015-1/0-81), copper powder (TsMTU 4451-54), silver(I) nitrate (pure, GOST 8422-66), calcium chloride (pure, GOST 4461-77), cadmium(II) bromide tetrahydrate (pure, GOST 16871-71), cadmium(II) iodide (pure, GOST 8421-79), copper(I) chloride (pure, TU 6-09-02-429-75), copper(I) iodide (pure, TU 6-09-02-437-87), copper(II) oxide (analytical grade, GOST 165-39-71), iron(III) chloride hexahydrate (pure, GOST 4147-74), mercury(II) nitrate (pure, GOST 4520-68), potassium iodide (pure, GOST 4038-74), magnesium sulfate heptahydrate (analytical grade, GOST 4523-77), sodium iodide (pure, GOST 1277-63), tin(IV) chloride (pure, TU 6-09-3182-75), tin(II) sulfate dihydrate (pure, TU 6-09-1502-75), zinc(II) iodide (pure, TU 6-09-4573-78), crystalline iodine (ultrapure 20-3, TU 6-09-2545-72), dimethyl sulfoxide (chemically pure, MRTU 6-09-5697-68), dimethyl sulfate (pure, MRTU 6-09-4995-69), acetone (GOST 2768-79), ethylenediaminetetraacetic acid disodium salt (analytical grade, GOST 10652-73), dithizone (pure, GOST 10165-79), aqueous HCl (pure, GOST 3118-77), sulfuric acid (pure, GOST 4204-77).

Zinc turnings were prepared mechanically from sheet zinc 0 (GOST 989-62). Mercury(II) iodide was prepared as described in [30]. Zinc(II) chloride was prepared by dehydration of $ZnCl_2 \cdot 1.5H_2O$ (pure, GOST 4526-67) [30]. Dimethylformamide (pure, GOST 5703-70) was purified from traces of water and formic acid by shaking with potassium hydroxide followed by distillation over calcium oxide [31]. Argon (pure, GOST 10157-79) was passed prior to use in succession through drying columns charged with calcium chloride, magnesium sulfate, silica gel, and phosphorus(V) oxide. Ethyl iodide (pure, TU 6-09-4117-83) was additionally purified by distillation through a glass packed column (20 theoretical plates) under atmospheric pressure at a reflux ratio of 15 to 20. Ethyl bromide (pure, GOST 20181-74) was purified from diethyl ether, ethanol, and water according to known procedure [32] and was then distilled through a glass packed column (30 theoretical plates) under atmospheric pressure at a reflux ratio of 15 to 20. The zinc/copper couple was prepared from zinc turnings and copper(II) oxide. A mixture of 240 g of zinc turnings and 20 g of copper(II) oxide powder was placed into a 500 mL glass round-bottom flask and carefully heated with an open fire in a stream of hydrogen up to a temperature approaching the zinc melting point. The flask was intermittently shaken to avoid sintering of zinc turnings. The mixture was heated until it turned uniformly grey–brown and its volume decreased approximately threefold. The mixture was left to cool down in a slow stream of hydrogen, and the product was used immediately after the synthesis.

A solution of ethylzinc bromide in ethyl bromide was prepared according to the following procedure. A glass round-bottom reactor equipped with a stirrer, reflux condenser, and thermometer was charged with zinc powder and copper(I) iodide. The reactor was evacuated and filled with argon, and ethyl bromide and a small amount of a solution of ethylzinc bromide in ethyl bromide were added. Usually the initial mixture had the following composition: zinc, 120–246 g (1.84–3.77 mol); ethyl bromide, 200 g (1.84 mol); ethylzinc bromide, 12.20–17.44 g (0.07–0.10 mol); copper(I) iodide, 6.25 g (0.033 mol). The reflux condenser was capped with a drying tube. The synthesis was conducted under atmospheric pressure with vigorous stirring during 5–8 h, maintaining the temperature not higher than 45–50°C. When the reaction was complete, the stirrer was removed from the reactor, the reflux condenser was replaced by a direct one, and unreacted ethyl bromide was distilled off under reduced pressure. The reactor was cooled and left overnight under argon. Ethyl bromide was added to the crystallized mixture, a stirrer and reflux condenser were installed back, and the mixture was heated on a water bath under stirring to dissolve ethylzinc bromide. Stirring and heating were then turned off, the mixture was allowed to settle down, and the liquid phase was separated and placed into a separate flask. A sample of crystalline ethylzinc bromide was stored under argon in a hermetically closed vessel in the dark.

Alkylation of zinc with ethyl bromide. The reaction was carried out in a glass round-bottom reactor equipped with a stirrer with an oil seal, thermometer, and reflux condenser caped with a drying tube which was connected with a gasometer flask to monitor evolution of gaseous products. The Teflon stirrer arm had a half-moon shape to fit the reactor bottom. The reactor was heated on a water or oil bath. The reactor was charged with solid initial components (zinc powder, zinc/copper couple, copper powder, and crystalline salts), evacuated, and filled with argon. Liquid components (ethyl bromide, ethyl iodide, solvent, additives) were then added, and stirring and heating were turned on. In the experiments with addition of ethylzinc bromide, after attainment of a required temperature, a solution of EtZnBr in ethyl bromide was quickly added dropwise, and the end of its addition was assumed to be the initial moment. In the other experiments, the reaction was assumed to begin when the required temperature was reached. Samples were withdrawn from the reaction mixture at definite time intervals to monitor the reaction kinetics. The first sample was withdrawn at the reaction start. Samples were subject to preliminary treatment, and the concentration of zinc ions therein was determined by titration. Experiments under UV irradiation were carried out in a quartz reactor equipped with a reflux condenser, electrical heater, and thermometer. The mixture was irradiated with a DRT-375 mercury lamp (TU 16-535.280-74) in the following mode: irradiation for 2 h, 45 min timeout, and so on. The distance from the radiation source to the reactor was of 10–15 cm.

Different stimulation methods were tested in part under reflux without forced stirring. The initial mixtures contained the following components: zinc or zinc/copper couple, 0.4–3.73 mol; ethyl bromide, 0.30–2.11 mol; solvent (dimethyl sulfoxide, dimethylformamide, or dimethyl sulfate), 0.18–0.85 mol; ethylzinc bromide, 0.02–0.51 mol; salt, 0.3–0.8 g. Ethyl iodide was added as an equimolar mixture with ethyl bromide. In the reactions with addition of ethylzinc bromide in combination with iodine (0.01 mol) or copper powder (0.38 mol), the initial mixtures contained zinc powder (3.67 mol), ethyl bromide (1.74 mol), and ethylzinc bromide (0.17 mol). The observation duration was 10 to 50 h to make sure that no reaction occurred.

Reaction of copper(I) iodide with a solution of ethylzinc bromide in ethyl bromide. The reaction was carried out in a cylindrical flat-bottom reactor equipped with a jacket, thermometer, magnetic stirrer, and reflux condenser capped with a drying tube which was connected with a gasometer flask. The reactor was charged with copper(I) iodide, evacuated, and filled with argon. A solution of ethylzinc bromide in ethyl bromide was then added, and the mixture was stirred on heating by passing water heated to a required temperature through the jacket. Samples were withdrawn from the reaction mixture at definite time intervals, and the concentration of zinc therein was determined after appropriate treatment. The first sample was withdrawn as the reaction started. The volume of the evolved gaseous products was reduced to normal conditions according to standard procedure [32].

Concentration of zinc in the samples withdrawn from the reaction mixtures was determined (after appropriate treatment) by titration with a solution of EDTA disodium salt [33] with an accuracy of ±2%. Samples were preliminarily treated as follows. An ampule containing a known amount of the reaction mixture (without dispersed particles) was cooled with an ice–salt mixture, and 5 mL of acetone was added. When gaseous products no longer evolved, ~1 mL of distilled water was carefully added dropwise, and the ampule was left to stand for 30 min. The precipitate was dissolved by adding 0.1 mol/L aqueous HCl. The content of the ampule was quantitatively transferred into a volumetric flask and adjusted to 500 mL by adding distilled water. Samples were withdrawn from the volumetric flask, and the concentration of zinc ions therein was determined.

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