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THE INFLUENCE OF COORDINATION ON THE REACTIVITY OF ORGANOMETALLIC COMPOUNDS

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I. INTRODUCTION

In attempting to answer the question implied in the title, it must first be recognised, as do Dewar and Thompson [1], that estimates of reactivity generally follow two main directions on the basis of: (a) different charge densities, bond orders, polarisability, etc.; or (b) a different in the energies of the reactants and of the transition state. From the standpoint of strict kinetics, only the second approach is legitimate. All constructs which ignore transition states are incorrect in principle. However, the second approach encounters serious theoretical difficulties [1], and in organometallic chemistry only the first has yet been practical, the approach of coarse correlations, giving only an approximate idea of the comparative reactivity of various compounds. The present work is not an exception in this sense.

The various reactivity series for the metal alkyls [2] are widely recognised as too generalised. It is evident that such series cannot be applied to reactions which differ in nature and in mechanism. In speaking about the comparative reactivity of organometallic compounds in a series of different reactions these reactions must be divided into groups similar in some features which play a decisive part. Practice shows that to a first approximation two types of organometallic reaction must be distinguished — additions to multiple bonds and substitutions. Neglect of these simple considerations necessarily leads to confusion both in the comparative evaluation of the reactivity of different compounds, and also in the evaluation of the influence of different complex-forming media on the activity of the same compound. To avoid this widespread error mainly substitutions will be considered.

Furthermore, following the now commonly accepted point of view, it must be assumed that in most such reactions the breaking of the metal–carbon bonds is heterolytic

for the rather active metals (Li, Mg, etc.). The energy of the heterolytic breaking of a non-ionic bond $A-B \rightarrow A^+ + B^-$ is greater than the energy of its homolytic dissociation, since to bring about such breaking it is necesary to do additional work in polarising the bond[3,4]:

$$D_H = E + I_A - E_B,$$

where D_H is the energy of heterolytic breaking of the bond A–B, E the bond energy, I_A the ionisation potential of A, and E_B the electron affinity of B. Eaborn[4] successfully used this approximation to evaluate the reactivity of different $\rangle$Si–X bonds in heterolytic substitutions of X. The application of this to metal–carbon bonds has apparently not been attempted.

The energy of heterolytic bond-breaking is extremely dependent on the solvolytic capability of the medium. With ionic bonds, solvation is the motive force for the destruction of the lattice during the dissolution of a substance in an ionising medium. With non-ionic, but sufficiently polar, bonds ionisation again cannot be neglected, but the energy of heterolytic breaking of the bond in a strongly solvating medium should obviously be less by some quantity proportional to the solvating ability of the medium, which is connected with the additional polarisation of the bond under the action of the solvent.

With organometallic compounds which contain rather polar bonds (M–C, M–H, M–Cl, etc.) this means that strong solvation should bring about additional polarisation of these bonds. However, the nature of this solvation is important.

Two fundamental types of solvating interaction must be distinguished[5,6]. Firstly, solvation can be a purely electrostatic interaction of the polar molecules of the solvent with molecules of the solute without the formation of any chemical bonds between them. Secondly, solvation can occur through bonds which have a donor–acceptor nature. Finally, there is specific solvation[5]. Electron-deficient cations form coordination complexes with solvents which possess electron-donor atoms; anions tend to form hydrogen bonds using the partially protonated hydrogen atoms of the solvent. In both instances we are concerned with specific solvation. Solvents which do not contain hydrogen atoms capable of forming hydrogen bonds are termed aprotic[5]. They are incapable of the specific solvation of anions but if electron-donor atoms (usually oxygen) are present they form coordination complexes with cations. After the appearance of Parker's review[5], the view became widely accepted that in a polar aprotic solvent medium the nucleophilic activity of anions in bimolecular substitutions (S_N2) of the anion–dipole type is greatly increased.

Among the factors which determine the increase in the reactivity of anions in S_N2 reactions are the following[5-7]: (1) the weak solvation of the anion, which makes it mobile in comparison with a strongly solvated counter-ion: (2) the breakdown of ion pairs (or ionic aggregates) due to the strong solvation of cations with the formation of "free" anions; and (3) the polarisation of a transition state, leading to the separation of the charges.

Most organometallic compounds do not have an ionic structure and do not form independent carbanions in solution. The validity of applying the concepts of the accelerating action of dipolar aprotic solvents on S_N2 reactions of anions to the reactions of organometallic compounds is not so obvious in this connection. It is characteristic that Parker[5] included in his review only certain reactions of alkali enolates having an ionic structure; he did not consider true organometallic compounds.

Tchoubar[6], in referring to the earlier work of Hammett[8], emphasises that an increase in the ionicity of a bond takes place precisely as a result of donor–acceptor interaction and that the characteristics of the medium such as dipole moment, dielectric constant, etc. play only a subordinate part in this increase. The conditions for dissociation into independent ions is here no longer obligatory, however, and Tchoubar in effect did not consider organometallic compounds.

Nevertheless, as will be shown below, the effect of aprotic electron-donor solvents and complex-forming anions in this field of chemistry is pronounced[9] and, with the reservations made at the beginning, of a rather general character.

II. INFLUENCE OF COORDINATION ON THE PHYSICAL PROPERTIES OF BONDS

In the specific solvation of an organometallic cation or of the positive end of a dipole there is a change in the valence state of the metal atom, which is inevitably accompanied by a change in the spatial configuration of the molecule, the interatomic distances, valence angles, etc. Digressing from that, the role which a dipolar aprotic solvent plays in a transition state nevertheless means that coordination facilitates an increase in the ionicity of the bonds in the initial compound. For ionic crystals this principle was formulated and generalised by Pauling[10]. It is supported by many experimental data, most of which relate, unfortunately, to inorganic materials.

A comparison of the quadrupole frequencies of ^{35}Cl in tin tetrachloride (24.296, 24.226, 24.140, and 23.720 MHz) and of the $SnCl_6^{2-}$ anion (15.61–15.73 MHz, depending on the nature of the cation) shows that chlorine is considerably more ionised in the complex anion than in the tetrachloride[11], which is consistent with the Mössbauer spectral data[12]. In the formation of the trimethyltin chloride complex with pyridine the Sn–Cl bond (2.37 Å) is lengthened (2.43 Å), and the complex has a planar configuration of the $(CH_3)_3Sn$ group, while the chlorine and nitrogen atoms are located at the vertices of a trigonal bipyramid[13,14]. The example of dibutyltin dichloride showed that the quadrupole splitting of the γ-transition of ^{119m}Sn depends strongly on the nature of the complex-forming solvent and its mole fraction[15]. It is characteristic that the increase in quadrupole splitting is continued up to a solvent : $(C_4H_9)_2SnCl_2$ molar ratio of 3, that is, even after the formation of an equimolecular complex. The polarisation of the Sn–Cl and Pb–Cl bonds in the formation of complexes of trialkyltin chlorides and trialkyl-lead chlorides with *NN*-dimethylacetamide and *NN*-dimethylformamide, with production of a bipyramidal structure also follows from the infrared and NMR spectra of these complexes[16].

A study of the proton resonance spectra of triethylaluminium, triethylgallium, and their ether addition compounds led Brownstein and coworkers[17] to conclude that in the complexes with ether the metal–carbon bonds were more "antibonding" in comparison with the initial metal alkyls. The decrease in the "electronegativity" of the aluminium atom on going from the trialkylaluminiums to complexes of the $MAlR_4$ type was also noted on the basis of their NMR spectra[18]. It is interesting that the tendency of the aluminium atom in such complexes to coordination is

not exhausted, and when they are dissolved in ether additional coordination with the ether takes place, accompanied by distortion of the AlR_4^- tetrahedron [19].

An increase in the bond length, which is usually associated with an increase in their ionicity [10], also follows from purely structural data. Thus the B–F bond, equal to 1.30 ± 0.02 Å in boron trifluoride is extended to 1.38–1.40 Å in the complexes of boron trifluoride with amines [20]. The bonds of mercury with halogens are lengthened on increasing its coordination number [21].

III. CHEMICAL CONSEQUENCES OF COORDINATION

The marked influence of electron-donor aprotic solvents on the course of various organometallic reactions has been repeatedly noted by many authors; however, the most varied assumptions have been made to explain these observations and until recently there has been no general approach to the appraisal of the role of the complex-forming media. The matter is also complicated by the fact that the same solvent often behaved differently towards different solutes. It is sufficient to mention that the addition of alkyl-lithiums to multiple bonds is often accelerated by complex-forming ethers, which is connected with the increase in the polarity of the C–Li bond in a complex with an ether [22,23], whereas the trialkylaluminium–ether addition compounds add to the alkenes with greater difficulty than the original alkylaluminiums [24]. Grignard reagents give lower yields of addition products with ketones in tetrahydrofuran [25], but they are especially effective in alkylation reactions in tetrahydrofuran [9]. Such behaviour often led to conflicting judgements. It is characteristic, for example, that in the celebrated monograph of Rochow and coworkers [2] it is stated directly that "under the influence of solvation bond polarity is decreased, thanks to the concentration of electrons with the electronegative donor atom of the solvent"†. The authors consider this question in direct association with the decrease in reactivity of the organometallic compounds during a fall in the polarity of the metal–carbon bond. However, analysis of the facts that have been accumulated at present shows this conclusion to be incorrect.

The increase in the polarity of metal–carbon bonds during coordination at the metal atom is confirmed by the acceleration of the heterolytic reactions of substitution and exchange in complex-forming media.

Ziegler [26] notes an increase in the rate of the "normal" Wurtz reaction:

$$RLi + R'X \rightarrow RR' + LiX,$$

in ether in comparison with a hydrocarbon medium and explains this phenomenon by the greater "ionising" ability of the ether. Eastham and Gibson [27] found that the rate of the reaction

$$C_4H_9Li + RBr \rightarrow LiBr + C_4H_9R,$$

is 10^3 times greater in the presence of ether [than in hexane (Ed. of Translation)], which the authors connect with the conversion of the hexameric butyl-lithium into a dimer on coordination with ether. According to Gilman and coworkers, the metallating ability of the alkyl-lithiums is higher in ether than in a hydrocarbon [28] and higher in tetrahydrofuran than in ether [29,30]. Gilman notes that the ease of metallation of fluorene and its analogues by the alkyl-lithiums in various ethers is proportional to the instability of their solutions in the ether concerned, but does not link this effect with a difference in the solvating ability of the solvent.

In recent years it has been found that a sharp increase in the nucleophilic activity of the alkyl-lithiums in substitutions also takes place in the formation of complexes with amines. Thus the complexes of butyl-lithium with *NNN'N'*-tetramethylethylenediamine and 1,4-diazobicyclo[2,2,2]octane metallise not only toluene, but also benzene more readily than butyl-lithium itself [31]; the reaction takes place even at room temperature.

Brown and coworkers [32] explain the increase in the reactivity of alkyl-lithiums in the presence of Lewis bases by a decrease in the degree of association of the initial compound. Actually, these authors showed that in the action of triethylamine on hexameric ethyl-lithium the latter dissociates into three molecules of coordinated dimer. The decrease in the degree of association of alkylmagnesium halides in a strongly solvating medium [33–35] is accompanied by their partial symmetrisation [34].

The general occurrence of a decrease in the degree of association is frequently considered to be the main reason for an increase in the reactivity of organometallic compounds. It is clear, however, that despite their plausibility, these concepts do not satisfactorily explain the nature of the action of the complex-forming media, since solvents capable of coordination markedly increase the reactivity of even those compounds which are monomers themselves (R_2Zn, [36] R_2Cd [37]).

The addition of Lewis bases to organolithium compounds increases their activity also in additions to multiple bonds [22,38–42].

It becomes more and more evident from recent data that the use of strongly solvating solvents accelerates nucleophilic substitutions of organomagnesium compounds. Thus the ease of the "normal" Wurtz reaction:

$$RMgX + R'X \rightarrow RR' + MgX_2,$$

is proportional to the solvating ability of the ether used as the solvent [43]. Whereas in diethyl ether the "normal" Wurtz reaction is brought about only for the allyl, benzyl, and greatly branched tertiary radicals [44], in dimethoxyethane the simplest aliphatic radicals readily undergo it [43].

According to Normant [45] the solvating ability of the medium ("basicity", in the expression of the author) is one of the deciding factors which determine the possibility of Grignard reactions with the halogen derivatives of alkenes and alkynes. The condensation of Grignard reagents with halogenoacetylenes:

$$RMgBr + Br{-}C{\equiv}CR' \rightarrow R{-}C{\equiv}C{-}R' + MgBr_2,$$

takes place only in a medium of hexamethyltriamidophosphate [hexamethylphosphoric triamide (Ed. of Translation)], but in less solvating solvents (ether or tetrahydrofuran) it does not occur. On the other hand, the Wurtz reaction with participation of unsaturated Grignard reagents and propargyl bromides occurs smoothly even in tetrahydrofuran [45].

† Reference 2, page 24 states: "Normally the effect of solvation is to decrease bond polarity by contribution of electrons from the electronegative donor atom of the solvent (the oxygen of ether, etc.) to the metal, but solvolytic dissociation into ion pairs also may occur". (Ed. of Translation).

Whereas a Wurtz reaction between heptynylmagnesium bromide and propargyl bromide catalysed by copper(I) chloride takes place in 115 h at 37° in diethyl ether, it needs only 1.5 h at the same temperature in tetrahydrofuran. The times for the analogous reaction with 1-chloropentyne are 65 h in ether and 1 h in tetrahydrofuran[46].

For the usual Grignard reagents in diethyl ether an exchange of radicals of the type:

$$RMgX+R'X \rightleftarrows R'MgX+RX,$$

is not characteristic and is observed only in certain specific instances. In a medium of the more solvating ethers even the simplest aliphatic and aromatic halides also take part in the exchange reaction[47-49]. The degree of exchange in the system n-$C_5H_{11}MgBr$ + CH_3I (0°, 1 h) in diethyl ether, diethoxyethane, ethoxymethoxyethane, diglyme, tetrahydrofuran, and dimethoxyethane, is respectively 5.7, 6.6, 12.7, 15.8, 17.5, and 38.5%. Aromatic iodides in dimethoxyethane medium exchange 52-75% after 3 h, giving the corresponding arylmagnesium halides[47].

Significantly, the completely unsolvated organomagnesium compounds which are obtainable in hydrocarbon medium[50] react with alkyl halides by a free radical mechanism[51]; the reaction products RMgX + R'X here are the products of the conversion of the free radicals R' and R''. The very nature of the breaking of the C–Mg bond (homolytic or heterolytic) in RMgX + R'X systems is thus determined by the nature of the solvent.

The accelerating action of electron-donor aprotic solvents appears especially clearly in metallating reactions. The simple replacement of ether for tetrahydrofuran makes the formation of Iotsich complexes strongly exothermic and rapid[9]. Metallation by alkylmagnesiums takes place very readily in hexamethyltriamidophosphate[52,53], where fluorene, indene, triphenylmethane, etc. are smoothly metallated. The usual Grignard reagents metallate fluorene only at 130°, but triphenylmethane is not metallated at all. Evidently, hexamethyltriamidophosphate ("hexametapol") $[(CH_3)_2N]_3PO$ is still the best solvent for metallating reactions: other complex-forming solvents are inferior to it in accelerating action[53].

Kinetic data on the metallation of hex-1-yne by ethylmagnesium bromide[33,54] are somewhat contradictory. On the one hand, replacing ether by tetrahydrofuran somewhat accelerates the reaction, but at the same time a reaction which is bimolecular in ether becomes termolecular[33]. However, in the presence of a tenfold excess of the hexyne the rate of its metallation by ethylmagnesium bromide falls with increase in the solvating ability of the ether in which the reaction is carried out[54]. It is possible that this exception from the general rule is due particularly to the presence of a large excess of acetylene, which changes the mechanism of the reaction.

It has been repeatedly noted that many alkylations of element–halogen bonds by Grignard reagents in a medium of tetrahydrofuran take place more rapidly and with better yields of organoelemental compounds than in ether[55-58]. This phenomenon, however, is frequently explained by the greater dissolving power of tetrahydrofuran or the possibility of working at a higher temperature. In reality, these factors hardly seem decisive; the main reason for the accelerating action of tetrahydrofuran is that in relation to a Grignard reagent it is a better complex-forming agent than ether. Really, dialkylthallium halides are alkylated to trialkylthalliums only by organolithium compounds and the usual Grignard reagents (in ether) are unsuitable for this purpose. In tetrahydrofuran the reaction takes place readily even at 0–5°; for example, triethylthallium is thus obtained[9,59]:

$$(C_2H_5)_2TlCl+C_2H_5MgBr \xrightarrow[0-5^\circ]{THF} (C_2H_5)_3Tl.$$

The sterically hindered alkylation of trichlorosilane by 1-naphthylmagnesium bromide in ether does not give any tri-(1-naphthyl)silane[60]: in tetrahydrofuran the latter is obtained with a yield < 30%,[33] and in an even more solvating ether – dimethoxyethane – the reaction proceeds under mild conditions and gives trinaphthylsilane with a yield > 70%:[9]

$$HSiCl_3+3\alpha\text{-}C_{10}H_7MgBr \xrightarrow{\text{dimethoxyethane}} (\alpha\text{-}C_{10}H_7)_3SiH+3MgBrCl.$$

The relatively inactive phenylethynylmagnesium bromide alkylates chlorotrimethylsilane only at 100° (after removal of ether)[60]; however, in tetrahydrofuran, and even more in dimethoxyethane, the reaction is exothermic at room temperature and the yields of trimethyl(phenylethynyl)silane are 47 and 77% respectively[9]:

$$(CH_3)_3SiCl+C_6H_5C\equiv CMgBr \rightarrow C_6H_5C\equiv CSi(CH_3)_3+MgBrCl.$$

In using dimethoxyethane as a solvent phenylmagnesium bromide can be used successfully instead of phenyl-lithium for obtaining pentaphenylantimony[9]:

$$(C_6H_5)_3SbCl_2+2C_6H_5MgBr \xrightarrow{\text{dimethoxyethane}} (C_6H_5)_5Sb+2MgBrCl.$$

Recently Ingold[61] reported that in the presence of dimethyl sulphoxide dialkylthallium halides are alkylated even by organomercury compounds.

As already noted, with alkyl-lithiums the coordination at the lithium atom facilitates both substitutions and also addition to multiple bonds. With organomagnesium compounds things are otherwise. Strongly solvated Grignard reagents give worse yields of addition products in reactions with ketones[25] and nitriles[62]; in some other instances only slight influence of solvation was observed[63].

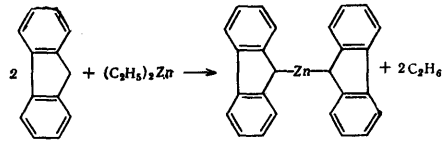
With organozinc compounds even such "classical" dipolar aprotic solvents as dimethylformamide and dimethyl sulphoxide can be used as strongly solvating media. In a non-complex-forming (hydrocarbon) medium diethylzinc hardly metallises phenylacetylene at all, whereas in hexamethyltriamidophosphate the reaction is violent[36]:

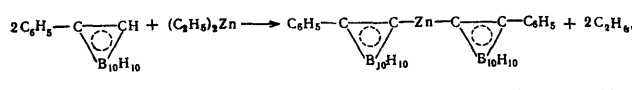
$$2C_6H_5C\equiv CH+(C_2H_5)_2Zn \rightarrow (C_6H_5C\equiv C)_2Zn+2C_2H_6.$$

The complex-forming solvents are arranged in the following series according to their accelerating action on this reaction (under the formula is given the time needed for half the theoretical amount of ethane to be liberated, in seconds)[36]:

$$\underset{8}{[(CH_3)_2N]_3PO} > \underset{200}{(CH_3)_2SO} > \underset{270}{(CH_3)_2NCHO} > \underset{7200}{CH_3OCH_2CH_2OCH_3} > \underset{\infty}{n\text{-}C_7H_{16}}.$$

Use of hexamethyltriamidophosphate allows even fluorene and phenylbarene to be readily metallised by diethylzinc:





The influence of electron-donor solvents on the reactivity of diethylcadmium is as perceptible again[37]. The

time for the half liberation of the theoretical amount of ethane in the reaction of diethylcadmium with phenylacetylene is 3 h 50 min in dimethylformamide, 1 h in dimethyl sulphoxide; it is characteristic that the difference in the accelerating action of these solvents for diethylcadmium is more significant than for diethylzinc. Whereas in ether diethylcadmium does not metallate phenylacetylene, in the presence of *NNN'N'*-tetramethylethylenediamine the reaction is almost explosive[37].

It was noted earlier[9] that no sharp distinction can be made between the solvation of an organometallic compound by donor–acceptor interaction with the solvent and the formation of stable complexes of the "reverse onia" type. Actually there are arguments in support of the idea that the reactivity of such complexes is higher than that of the original organometallic compounds[64]. Whereas neither potassium hydride nor butyl-lithium separately metallates alkylbenzenes their complex with one another $K[LiH(C_4H_9)]$ does so readily[65]. The alkylation of element–carbon bonds by trialkylaluminiums takes place more readily when the latter are bound in complexes with ethers or amines[66,67]. This also holds for the metallating ability of complexes of the $MAlR_4$ type in relation to alkynes: whereas trialkylaluminiums (except for triphenylaluminium[68]) add to the triple bond of alkynes the $MAlR_4$ complexes metallate them[69]. The complexes of alkylaluminiums with tertiary amines behave similarly[70].

It is significant that the addition of potassium chloride to unreacted mixtures of trimethylaluminium and silicon tetrachloride leads to the formation of tetramethylsilane[64]. The use, not of alkylaluminiums, but their complexes with alkali metal halides for the synthesis of organometallic compounds allows the process to be made more selective and with greater conversion of the alkyl groups[71,72].

The exchange of labelled mercury in $RHgX + Hg^*X_2$ systems is catalysed by halide anions and acetate ions, which form coordination complexes with the original organomercury compounds[73,74].

In the presence of iodide anions the breaking of Hg–C bonds in organomercury compounds with elemental iodine becomes a heterolytic reaction[75-87]. Beletskaya and coworkers suggested[76] that the decisive step in this exchange mechanism can be the formation of a complex of the organomercury compound with the iodide anion, which leads to the "relaxation" of the Hg–C bond. They later demonstrated the existence of such complexes with phenylmercury(II) chloride during a study on nucleophilic assistance in protodemercuration reactions[79]. The mechanism of assistance in reactions with multicentre transition states, with allowance for the effect of the medium, has also been considered by Dessy and Paulik[7].

It is evident that here the authors are dealing with the reduction of the energy of the heterolytic breaking of a metal–carbon bond under the influence of coordination at the mercury atom.

It has already been shown above that extension of the thesis of an increase in nucleophilic activity of organometallic compounds during complex formation in substitutions to additions can lead to erroneous conclusions. Such an ambiguous effect of coordination also appears in oxidations, carbonations, and some other reactions. Thus the coordination of diphenylmagnesium by ethers facilitates its oxidation by atmospheric oxygen[80], yet the rate of oxidation of a 2-phenylbis(biphenylene)alkylsodium falls sharply as the solvating ability of the solvent is increased[81]. Evidently, the strong specific solvation facilitates carbonation: alkali metal acetylides are smoothly carbonated (under pressure) in dimethylformamide[82] but hardly at all in ether. The carbonation of pentafluorophenylmagnesium halides in tetrahydrofuran gives pentafluorophenylbenzoic acid in 67% yield[83]. The same Grignard reagent in ether does not react with ethylene oxide but in tetrahydrofuran it smoothly forms 2-pentafluorophenylethanol (yield 82%)[84]. However, the information available about the influence of coordination on the ease of addition is clearly insufficient for any generalisations.

Summarising, the following general conclusions can be drawn:

1. Dipolar aprotic solvents form complexes of the donor–acceptor type with organometallic compounds, identical in many respects with the complexes of these compounds with anions ("reverse onia").

2. Both here and elsewhere there is an increase in the polarity of the bonds of a metal with more electropositive partners, including carbon, which lowers the energy of heterolytic breaking of metal–carbon bonds and makes a little-solvated carbanion (or carbanion end of a dipole) exceptionally active in heterolytic exchanges.

3. The influence of coordination on the course of additions is ambiguous, since here two opposing factors operate: (a) an increase in the nucleophilic nature of the metal–carbon bond; (b) a hindering of complex formation with an unsaturated compound, which prevents the necessary increase in the electrophilic nature of the multiple bond in the transitional state.

IV. FACTORS WHICH DETERMINE THE CHARACTER OF COORDINATION

The extent of the changes referred to above depends on the complex-forming (solvating) ability of the molecules of the donor in relation to a given organometallic compound. The problem of the methods for evaluating this ability is still not completely clear, however. From a comparison of given series of solvating solvents it becomes clear already that in relation to different compounds the different series of solvating abilities agree with one another only in the most general features, while differing considerably in details. It is quite evident, as Hamelin noted[85] for organomagnesium compounds, that interpretation only in terms of the basicity of the donor towards a proton is impossible since there is usually no direct correlation between the basicity of a ligand and its complex-forming ability in most of the examples considered. In relation to trialkylboron compounds the complex-forming ability of different amines ($NH_3 > EtNH_2 > Et_2NH > Et_3N$) is the reverse of their basicity in water ($NH_3 < EtNH_2 < Et_2NH < Et_3N$)[86]; the ability of aluminium hydride to coordinate decreases in the following series of solvents: tetrahydrofuran $>$ Et_3N $>$ $>$ EtOEt.[87] Unlike tetrahydrofuran and dimethoxyethane, the strongly basic triethylamine has no significant accelerating action on the exchange[48,49]:

$$RMgX + R'X \rightleftarrows R'MgX + RX$$

Different ethers which differ little in their "basicity", differ markedly in their ability to coordinate with ethylmagnesium bromide[34] and in their accelerating action on the reaction of organomagnesium compounds (see above).

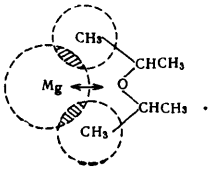
The examples given suffice to show that the basicity alone of a donor in relation to a proton is not a deciding

factor. Because of this, the use of the term "basicity", even with a series of reservations, is undesirable, since it creates the danger of misinterpretation. It is more correct to speak of the complex-forming ability of the donor (corresponding to the solvating ability of a medium) or of the affinity of a ligand for a particular cation or molecule, as is done, for example, by Ahrland and coworkers[88].

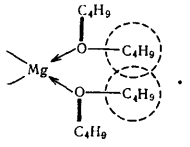
The non-correspondence between the proton-basicity of a donor and its coordination capability is due to a combination of factors, which must be considered in greater detail.

From the viewpoint of inductive effects tetrahydrofuran and diethyl ether should be donors of approximately equal strength; the fact that tetrahydrofuran is in reality a better complex-forming agent is usually explained by the absence of steric hindrance in coordination by this solvent[89].

The importance of the steric requirement in coordination has been stated repeatedly. Brown and coworkers[90] distinguish two types of steric hindrance during coordination — *B*- and *F*-strains. In the first the steric hindrances arise because of degree of branching close to the donor atom of the ligand; thus Hamelin[34] explains, for example, the low "basicity" of di-isopropyl ether in relation to a Grignard reagent:



In the second, equivalent to the *F*-strain of Brown and coworkers, solvation is hindered by the general steric hindrance of the ligand molecules arising during coordination[34]:



It is to be expected that the relation between the *B*- and *F*-factors will depend significantly on the dimensions of the metal atom: an increase in its covalent radius should intensify the role of *F*-strain and reduce the influence of *B*-strain. Clearly it is also necessary to consider the obstructions created by the replacing groups at the metal atom.

As well as the steric requirement of the substituents at the atoms of the donor and metal, the electron-donor properties of these substituents must be considered. Depending on the character of the substituent the donor–acceptor properties of the central atom can change within wide limits. Whereas, for example, trimethylantimony is a Lewis base, perfluorotrimethylantimony contains a coordination-unsaturated antimony atom capable of adding pyridine[91]. The feeble donor properties of diphenyl ether are undoubtedly due to the interaction of the unshared electron pairs of the oxygen with the π-electrons of the phenyl rings; in the absence of steric hindrance aryl derivatives of metals form, as a rule, more stable coordination complexes. Among recent studies mention may be made of the work of Noltes and van der Kerk[92], who showed that diphenylzinc forms coordination complexes more readily than dibutylzinc.

The replacement of hydrogen by a methyl group directly at a donor atom of a ligand significantly increases the ability of the latter to coordinate. In its capability for coordination dimethyl ether should significantly surpass diethyl and the higher ethers. This is also facilitated by the favourable steric conditions with the former. Actually, the heat of formation of the ether addition compound $(CH_3)_3Al{-}O(CH_3)_2$ is 19 kcal × × mole^{-1} [93] whereas that for the complex $(CH_3)_3Al{-}O(C_2H_5)_2$ is 11.2 kcal mole^{-1}.[94] An even more marked difference in the solvating ability of dimethyl and diethyl ethers appears in the formation of the naphthalene negative ion from sodium and naphthalene[95]: diethoxyethane has always been found to be a much less suitable solvent than dimethoxyethane[49,96].

A very important factor, which favours coordination, is the bidenticity of a donor and the possibility of forming a five-membered ring. Usually, bidentate ligands give more stable complexes and to a greater measure bring about all those changes mentioned above. Coordination complexes with ligands of this type have also been described for many organometallic compounds — for derivatives of beryllium[97], magnesium[98,99], zinc[100], cadmium[101], and boron and aluminium[24]. It is characteristic that dimethylcadmium with unidentate donors (tetrahydrofuran, pyridine) gives liquid 1 : 1 complexes which dissociate into the components even at low temperature, whereas analogous complexes with *NNN'N'*-tetramethylethylenediamine, 2,2'-bipyridyl, and 1,10-phenanthroline are solid and stable[101]. When the initial organometallic compound is associated (R_2Be, R_2Mg), coordination with bidentate ligands leads to the formation of monomeric complexes to a greater degree than for other complex-forming agents, which must also make a contribution to the general nucleophilic nature of the M–C bond. Thus, dimethylberyllium forms monomeric complexes with dimethoxyethane, *NNN'N'*-tetramethylethylenediamine, etc.[97]; the complex of dimethylmagnesium with this diamine can be distilled[98,99]. Unfortunately in studying the conditions for the formation of such complexes and their stability, most authors do not give any information about the interesting problems of their reactivity in comparison with that of the initial compounds.

Allowance must be made for the fact that the tendency of various metals (as ions or parts of molecules) to complex formation under equally severe conditions also depends on the nature of the donor atom of the ligand[88]. Most acceptor-metals form the most stable complexes when the donor atom belongs to the Second Period of the Periodic System (N, O, F). However, some metals (for example, mercury) give more stable complexes with elements of later periods (P, S, B, etc.). Transition metals such as cadmium, thallium, lead, and bismuth occupy an intermediate position and their affinity for one or another type of ligand depends on the specific conditions, including the nature of their environment. Boron is adjacent to these elements; characteristically[83,102], whereas the activity of the donors in relation to trimethylboron falls in the sequence N > P > As, in relation to borane (BH_3) this sequence alters (N < P ≫ As)‡.

Evidently information on the stability of complexes and on the affinity of ligands for different Lewis acids (including ions and polar molecules) can be used, with some limitations, also for evaluating the change in polarity of bonds and reactivity during coordination.

‡ $(CH_3)_3N$, $(CH_3)_3P$, and $(CH_3)_3As$ were used throughout.

With increase in the atomic number of the metal within the limits of Groups IIb–V there is an increase in the polarisability of the atomic core, which as a whole leads to an increase in the polarisation interaction between the atoms, and consequently to a decrease in the ionicity of the bond. It could evidently be expected that the relatively strong polarisation interaction would also level out to some extent the effect which is brought about by coordination. When the metal atom exhibits sufficiently mobile d-electrons (for example, atoms of metals of type $d^{10}s^2$) and the donor-atom has vacant d-orbitals, the d_π–d_π dative interaction between the atoms of the metal and the donor is an additional factor stimulating the formation of a complex. A consequence of this is, for example, that with increase in the atomic number of the metals in the zinc subgroup there is a rise in the tendency of their compounds to form complexes with derivatives of phosphorus, sulphur, and other elements having vacant d-levels.

It is evident that the reactivity of organocadmium and organomercury compounds will increase under the influence of complex-forming agents containing phosphorus and sulphur to a greater extent than that of the corresponding compounds of magnesium and zinc.

Hence at present it is possible to draw only the following tentative conclusions.

1. The influence of complex formation on the nucleophilic reactivity increases with effective charge at the nucleophilic atom, which, in turn, depends on the relative affinity of the given ligand for the compound concerned.

2. This affinity depends on: (a) the nature of the metal and of the donor atom of the ligand; (b) steric conditions; (c) the bidenticity of the ligand; (d) the inductive effects created by the substituents at the metal and the donor atom; (e) the Lewis basicity of the ligand; (f) factors which at present still cannot be understood. The action of all these factors may not be concordant, which in theoretical respects greatly complicates the problem of the degree and character of the different solvation effects and coordination phenomena.

3. Ideas about complex formation by metal ions (i.e. concepts from the chemistry of complex compounds) can evidently be transferred to complex formation by organometallic compounds, with definite limitations, and this allows a rough *a priori* appraisal to be made.

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PROGRESS IN THE FIELD OF THE CHEMISTRY OF STEROIDAL HETEROCYCLES

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