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NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME ELECTRON-DEFICIENT COMPOUNDS: BORON HYDRIDES, DIMERS OF ALKYLALUMINIUMS, AND ORGANOLITHIUM COMPLEXES

I. B. Golovanov and A. K. Piskunov

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INTRODUCTION

Many compounds are known in which the number of chemical bonds exceeds the number of electron pairs: boron hydrides [1]; the dimers of the alkyl compounds of aluminium [2], beryllium [3], organolithium complexes [4], etc.[5,6]. Compounds of this type have become known as electron--deficient.

By use of the nuclear magnetic resonance (NMR) method information has been obtained about the structure of these compounds and also about the electron distribution and about its symmetry for certain nuclei. The most important results of the study of electron-deficient compounds by the NMR method are considered below.

Before discussing the NMR results some questions of the qualitative theory of electron-deficient bonds [1,5-7] are considered.

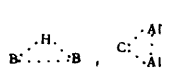
I. QUALITATIVE QUANTUM-MECHANICAL IDEAS ABOUT THE FORMATION OF ELECTRON-DEFICIENT BONDS

The presence of a metal atom with vacant orbitals on which the bond-establishing electrons can be promoted without a large expenditure of energy, and of an atom or group of atoms which do not possess unshared electron pairs are general for most electron-deficient compounds. The conditions for the formation of donor–acceptor bonds do not exist.

Compounds with electron-deficient bonds have been insufficiently studied, but it can be maintained that the principal features of the structures of these compounds are clear. Thus, the data on diamagnetic susceptibilities [2] suggest that the bonds cannot be "one-electron". Each of the bridge bonds has less energy than if it were "normal" and its length also differs from the "normal". Some examples from the compounds that have been most studied are given in Table 1.

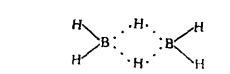
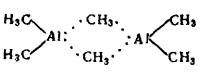
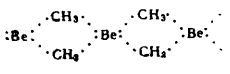
The bridge bonds B...H, Be...C, and Al...C are longer than the corresponding terminal bonds. The latter have the same length as the "usual" bonds.

The experimental values for the metal–metal distances in these compounds are close to those for the M_2 molecules. Attempts were therefore made to explain the bonding in such complexes by the formation of "protonated double bonds" [2]. Next considerations were advanced in support of the formation of polycentric orbitals [13] of the type:



Apparently a short M–M distance is necessary for the formation of localised three-centre orbitals.

TABLE 1.

Structure of the compounds	Heats of formation of the complexes (Ref. 5), kcal	r_{M-M}, sum of covalent radii (Refs. 11 and 12), Å	r_{C-C}, sum of intermolecular radii, Å
 $r_{BB}=1.78$ Å[a] $r_{BH_K}=1.19$ Å $r_{BH_M}=1.34$ Å $\angle H_K BH_K=121.5°$ $\angle H_M BH_M=100°$	32	1.82	3.8
 $r_{Al-Al}=2.55$[a] $r_{Al-C_K}=1.99$Å $r_{Al-C_M}=2.24$Å $\angle C_M AlC_M=70°$	20	2.86	3.8
 $r_{Be-C}=1.93$Å $\angle Be-C-Be=66°$ $r_{Be-Be}=2.10$Å	—	2.26	3.8

The C–C distance in complexes is usually close to the van der Waals distance and the C atoms can be considered as non-bonded from the point of view of valency.

A characteristic feature is that the M–C–M angle is less than 90°, which suggests that the orbitals of the metal atoms form a bond with one orbital of the carbon atom and also that the metal atoms interact with one another. Apparently the formation of such bonds becomes hindered as the size of the metal atom is increased.

Electron-deficient bonds can differ in degree of polarity. In diborane, for example, the B...H bonds are close to covalent and in the dimer of phenyllithium they are apparently strongly polar. This can suggest starting from the characteristics of the atoms which form the bond. Table 2 gives some facts about the atoms, the bonds between which are discussed below.

Although electronegativity is a very crude characteristic of ionic character of the bonds, nevertheless it allows us to state, for example, that the C–Li bond should be more polar than B–H, etc.; therefore for organolithium complexes the contribution of the ionic state must also be considered.

Spectrographic data about the atomic levels also somewhat elucidate the problem of the use of free orbitals. Actually it is most favourable to use those orbitals for which the energy of promotion is less, and also the energy of the orbital itself is less. When the atoms are of similar size, the strength of the bond in the complex will be greater for that atom whose vacant levels are close to the occupied level with lower energy. For example, the aluminium and lithium atoms are similar in size and therefore it could be expected that the C–Li bond would be stronger than the C–Al bond. The available information about the energy of the C...Li bond confirms this hypothesis [16,17].

TABLE 2.

Property	Atoms				
	Li	Be	B	Al	C
Position of the atomic levels (occupied and lower free)[14] E, eV	—3.6...— —5.4...—	— —	— —	— —	— —
Electronegativity[15]	0.95	1.5	2.0	1.5	2.5
Covalent radii [11,12]	1.34	0.96	0.84	1.26	0.77

Theoretically the formation of electron-deficient compounds with predominantly covalent bonds can be considered as the usual problem for quantum chemistry involving a few electrons in the field of a few centres, in which the number of atomic orbitals from which the molecular orbitals are constructed is greater than the number of electrons which participate in the bonds [1,5-7].

As the simplest example, let us consider the molecular ion $[A-B-C]^+$, the bonding in which is provided by a pair of electrons. We will consider that the atoms A, B, and C are disposed along a straight line, there is no exchange between A and C, and the overlap can always be neglected.

Then within the framework of the simplest method of LCAO MO, [18] by expressing the molecular orbital in the form

$$\psi = a_1\psi_A + a_2\psi_B + a_3\psi_C,$$

we obtain the secular equation for determining the energy:

$$\begin{vmatrix} \alpha_A - E & \beta_1 & 0 \\ \beta_1 & \alpha_B - E & \beta_2 \\ 0 & \beta_2 & \alpha_C - E \end{vmatrix} = 0.$$

When the atoms A and C are greatly different and the interaction of atom B with one of them (for example, with A) is considerably greater than that with the other, that is, $\beta_1 \gg \beta_2$, then this is equivalent to dealing with the system $[A-B]^-$ ion C^+.

The energy of an electron in the molecular orbital (we assume that $\alpha_A - \alpha_B \ll \beta$) will then be:

$$E = \frac{\alpha_A + \alpha_B}{2} + \beta.$$

When atoms A and C are the same and the ion C^+ has approached to the closest distance, then since A–B is equal in length to A–C, the secular equations will have the form:

$$\begin{vmatrix} \alpha_A - E & \beta & 0 \\ \beta & \alpha_B - E & \beta \\ 0 & \beta & \alpha_A - E \end{vmatrix} = 0$$

and the energies of the molecular orbitals will be:

$$E_1 = \frac{\alpha_A + \alpha_B}{2} + \sqrt{2}\beta,$$

$$E_2 = \alpha_A,$$

$$E_3 = \frac{\alpha_A + \alpha_B}{2} - \sqrt{2}\beta.$$

The gain in energy which is obtained in the formation of the electron-deficient compound $(A-B-A')^+$, is calculated as the difference in energy of the ion $(A-B-A')^+$ when a free orbital is used and the energy of the system consisting of the isolated molecule AB and the ion A^+ when the A orbital is not used:

$$\Delta E = 2\left(\frac{\alpha_A + \alpha_B}{2} + \sqrt{2}\beta\right) - 2\left(\frac{\alpha_A + \alpha_B}{2} + \beta\right) = 0.82\beta,$$

where ΔE is the delocalisation energy of the electron.

We note that this result is obtained with the following assumptions: (1) the atoms A and A′ are similar in properties or the same, (2) the overlaps A–B and B–A′ are the same (that is, the A–B and B–A′ bond lengths are the same), (3) the energy of promotion of the electrons in the valence state equals zero. As noted, this requirement is satisfied by some of the compounds considered above.

It can be assumed that the orbitals used by atom B should be the same in the A and A′ directions, that is, there should be known local symmetry in the structure of the complex. When atom B gives one orbital then its overlap with the atoms A and A′ should be the same.

Polycentric orbitals should be formed when there is conjugation and in electron-deficient molecules. In reality, when n orbitals are used for the formation of the "usual" two-centre bonds then $n/2$ bonding and $n/2$ anti-bonding orbitals are obtained from them. n electrons are distributed in the bonding orbitals, but the anti-bonding orbitals remain vacant. If there were more than n electrons then they would occupy some of the anti-bonding orbitals. When n orbitals are used for the formation of three-centre bonds they give $n/3$ bonding orbitals. The others will be non-bonding or anti-bonding. $2n/3$ of the electrons will be distributed in the bonding orbitals, and the remaining electrons would occupy the anti-bonding orbitals. Evidently electron-deficient compounds will be short of just those electrons which should have occupied the anti-bonding orbitals.

Besides the bonding in the complex where there is formation of polycentric orbitals with bonds close to covalent, as considered above there is a possibility of the formation of complexes due to polar bonds.

For any two-atom molecule A–B the molecular orbital can be presented in the form $\psi = a_1\psi_a + a_2\psi_b$ and the energy of the occupied orbital is

$$E = \frac{\alpha_1 + \alpha_2}{2} + \beta,$$

where

$$\alpha_i = \int \psi_i^* H \psi_i \, d\tau; \quad \beta = \int \psi_1^* H \psi_2 \, d\tau.$$

When the A–B bond is strongly polar, then the complex $(A-B)_2$ is formed. For simplicity we will consider it to be symmetrical, with the lengths of the bonds close to those for the monomeric molecule AB.

To describe the complex $(A-B)_2$ for the initial atomic orbitals we can select symmetrical orbitals, the form and symbolic representation of which are shown in Table 3.

The molecular orbitals are selected in the form: $\psi = \sum_i c_i\sigma_i$, in which the lowest energy is determined from the equation:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0,$$

where

$$H_{11} = \int \sigma_1 H \sigma_1 d\tau = \int \frac{1}{\sqrt{2}}(\psi_{A_1} + \psi_{A_2}) H \frac{1}{\sqrt{2}}(\psi_{A_1} + \psi_{A_2}) d\tau =$$

$$= \frac{1}{2}\left[\int \psi_{A_1} H \psi_{A_1} d\tau + 2\int \psi_{A_1} H \psi_{A_2} d\tau + \int \psi_{A_2} H \psi_{A_2} d\tau\right] =$$

$$= \int \psi_{A_1} H \psi_{A_1} d\tau + \int \psi_{A_1} H \psi_{A_2} d\tau = \alpha_1 + \beta' = (1 + k_1)\alpha_1, \qquad k_1 > 0$$

$$H_{22} = \int \sigma_2 H \sigma_2 d\tau = (1 + k_2)\alpha_2, \quad k > 0$$

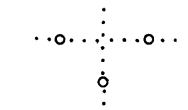
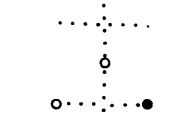
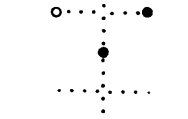
$$H_{12} = \int \sigma_1 H \sigma_2 d\tau = 2\beta$$

Since all the bond lengths in the diameter are the same, the solution will be:

$$E_1 = \frac{(1 + k_1)\alpha_1 + (1 + k_2)\alpha_2}{2} + 2\beta,$$

$$E_2 = \frac{(1 + k_1)\alpha_1 + (1 + k_2)\alpha_2}{2} - 2\beta.$$

TABLE 3.

Orbital	Atoms	
$\frac{1}{\sqrt{2}}(\psi_{A_1}+\psi_{A_2})=\sigma_1$		a_{1g}
$\frac{1}{\sqrt{2}}(\psi_{B_1}+\psi_{B_2})=\sigma_2$		a_{1g}
$\frac{1}{\sqrt{2}}(\psi_{A_1}-\psi_{A_2})=\sigma_3$		b_{1u}
$\frac{1}{\sqrt{2}}(\psi_{B_1}-\psi_{B_2})=\sigma_4$		b_{1u}

We find other solutions from the equations:

$$\mathbf{H}\psi_3 = E_3\psi_3 \quad \psi_3 = \sigma_3$$
$$\mathbf{H}\psi_4 = E_4\psi_4 \quad \psi_4 = \sigma_4$$
$$E_3 = \int \sigma_3 \mathbf{H}\, \sigma_3 d\tau = (1-k_1)\alpha_1, \quad k_1 > 0,$$
$$E_4 = \int \sigma_4 \mathbf{H}\, \sigma_4 d\tau = (1-k_2)\alpha_2, \quad k_2 > 0.$$

We assume that

$$|(1-k_1)\alpha_1| > |(1-k_2)\alpha_2|.$$

The occupied orbitals have the energies:

$$E_1 = \frac{(1+k_1)\alpha_1 + (1+k_2)\alpha_2}{2} + 2\beta,$$
$$E_3 = (1-k_1)\alpha_1.$$

The difference in energy between the dimer and the two monomeric A–B molecules is:

$$\Delta E = (1-k_1)\alpha_1 - (1-k_2)\alpha_2.$$

Hence, when $k_1 = k_2 = 0$,

$$\Delta E = \alpha_1 - \alpha_2.$$

Thus the above analysis shows the possibility of complexes being formed without use of free orbitals due to polar interaction. We note that in this a complex from polar molecules acquires the properties of a covalent compound: the dipole moment of the complex equals zero, there is a molecular orbital envoloping all the nuclei, etc.

In this instance the part played by overlap is small, not because there is little overlap of the atomic bonding orbitals, but on account of the low electron density in these orbitals and because the increase in overlap due to the utilisation of more directed vacant orbitals changes nothing (the overlap of "empty" orbitals does not give bonds). A similar situation occurs in some organometallic compounds and also in the formation of intramolecular hydrogen bonds [2,19]. Accurate calculations [20,21] made for H_3^+ and B_2H_6 confirm the correctness of what has been stated for the formation of non-polar bridge bonds.

On the basis of the above, it can be stated that the bonding in electron-deficient compounds is due to: (1) the delocalisation of electrons in the formation of polycentric orbitals with the utilisation of the free orbitals of the metal atom, or (2) strong polar interaction in the formation of structures with alternating charges of different polarity; polycentric orbitals can be formed here without utilisation of the free orbitals of the metal atom.

II. WHAT IS UNDERSTOOD BY THE EXPRESSIONS "ENERGETICALLY FAVOURABLE ORBITAL" AND "UTILISATION OF VACANT ORBITALS"

In speaking about "energetically favourable free orbital" we mean that the energy for the promotion of an electron in a valence state is moderate and can be restored in the formation of chemical bonds of the given atom with others. The use of this definite orbital ("free orbital") signifies that in it there is some electron density, that is, the most favourable polycentric molecular orbitals are obtained when this particular free orbital takes part in their formation. In the MO LCAO language this signifies that when a molecular orbital can be written in the form $\psi_M = \sum_k a_k \psi_k$, then the coefficient in the "favourable" orbital is not zero.

Often no mention is made in the literature of what is understood by these expressions [6,7,22]. For example, Hoffmann [23] considers that when the free $3p$ orbital of aluminium is used in compounds of the $[Al(C_2H_5)_3]_2$ type, the CH_2 bridging group should be in weaker fields than the terminal, since then the electrons of atom C will be distributed in two aluminium orbitals. This statement signifies that some charge is transferred from the CH_2 bridging group to the "favourable" orbitals of the aluminium atoms. However, this would be correct were it to be shown that in using the free orbitals of the aluminium atom there is a "flowing in" of charge into its free orbitals from other atoms or atomic groups, but the use of these free orbitals by the electrons of the aluminium atom for the purpose of creating more directed orbitals is unfavourable. Such an analysis has not been made. The reverse effect occurs in boron hydrides. With diborane [24] the bridging protons are in stronger fields than the terminal protons, that is, charge is transferred from the boron to the bridging protons, however, it is thought that in the formation of polycentric molecular orbitals the free p orbitals of a boron atom are used. That being so the free orbitals of the atom are used by "its own" electrons.

One of the fundamental problems in the study of bonds in electron-deficient compounds is that of the participation of the free orbitals of the metal atom in the formation of the polycentric molecular orbitals.

In the subsequent discussion of NMR results attention will be drawn to the experiments which confirm the use of free p orbitals of boron, aluminium, and lithium atoms.

III. NMR SPECTRA OF BORON HYDRIDES

There have been many detailed articles [1,25] about the investigation of the structure and properties of the boron hydrides, therefore we will limit the discussion to only the NMR results obtained for these compounds.

The study of the boron hydrides by the NMR method began as soon as their most important peculiarities had been revealed. However, the use of the NMR method gave more than confirmation of the results obtained earlier.

1. Proton Magnetic Resonance (PMR) Spectra

The PMR spectra of the boron hydrides are very complex owing to splitting, which is connected with the interaction of the protons with the ^{11}B and ^{10}B nuclei. As an

example, Fig. 1 gives the PMR spectra of diborane, pentaborane, and decaborane. The asymmetric form of the PMR spectrum for diborane rules out the possibility of an "ethane-like" structure existing.

When the method of double nuclear resonance is used a simplified spectrum is obtained[26]. Esentially, in addition to the high-frequency field bringing about the transition of the ^1H nucleus, a strong field, corresponding to the frequency of the transitions of the ^{11}B nucleus is imposed. This leads to saturation of the ^{11}B signals. At saturation the ^{11}B nucleus appears to cease to interact with protons and the splitting due to the $^{11}B-^1H$ interaction ceases. Fig. 2 shows the PMR spectra of the same compounds as in Fig. 1 obtained by the double resonance method.

The diborane spectrum shows the presence of two types of protons. The ratio of the intensities of the signals suggests that one group consists of two hydrogen atoms, and the other of four. This confirms the "bridge" structure of diborane.

The molecule of pentaborane, B_5H_9, has a tetragonal pyramidal structure[27]. The boron atom situated at the apex of the pyramid is combined with one proton and each boron atom lying at the base of the pyramid is linked with one terminal hydrogen atom and two bridging hydrogen atoms. The NMR spectrum should in principle give three groups of lines with 1 : 4 : 4 ratio of intensities. The PMR spectrum observed experimentally (Fig. 1*b*) consists of four

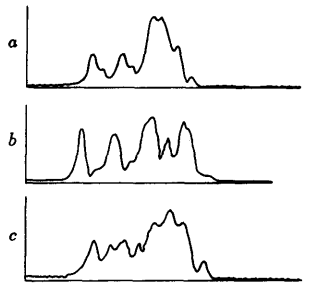


Fig. 1. PMR spectra of boron hydrides[24] (f_{res} = 30 MHz): *a*) diborane; *b*) pentaborane-9; *c*) decaborane.

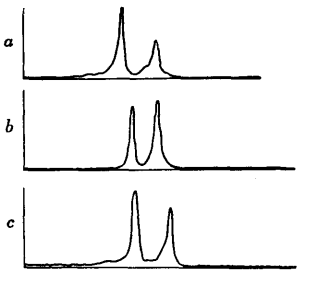


Fig. 2. PMR spectra of boron hydrides (f_{res} = 30 MHz) obtained on saturation of ^{11}B at the frequency 9.65257 MHz: *a*) diborane; *b*) pentaborane; *c*) decaborane.

intense lines (the signal of the terminal protons, bound to the boron atoms at the base of the pyramid, split owing to interaction with ^{11}B), four weak lines, somewhat displaced into the region of stronger fields (the line from the proton at the apex of the pyramid is split because of interaction with ^{11}B) and finally a group of lines from bridging protons, which is superimposed on the spectrum of the terminal protons. By using the double resonance method, on saturating the ^{11}B nuclei lying in the base a spectrum consisting of two lines of different intensities is observed. This indicates that the number of terminal and bridging protons connected with the boron atoms in the base of the pyramid are the same. In saturation of the ^{11}B "vertex" nucleus a signal from the proton bound to it is observed; the signal is positioned between the signals from the terminal and bridging protons lying in the base of the pyramid.

The PMR spectra of pentaborane-11, decaborane, etc. have been described in detail[28-33]. The analysis of the spectra confirmed the earlier findings concerning the peculiarities of the structure of these compounds.

The PMR spectra were obtained for the pure compounds and not solutions, external standards were not used, and in the overwhelming majority of the instances the spectra were not calibrated. The internal chemical shift was measured for diborane: the NMR bridging protons are shifted into the strong field region by 4.3×10^{-6} relative to the terminal protons. This suggests that the negative charge on the bridging protons is greater than that on the terminal, and when terminal B–H bonds are considered close to covalent bonds then the bridging bonds have a significant percentage of ionicity. Actually by using the wave functions of diborane obtained by Jamadjaki[21] it is easy to show that the excess of negative charge on the bridging proton compared with the terminal is $\sim 0.25\,e$. On each of the boron atoms there is a positive charge of $\sim +0.24\,e$. It is evident that such a charge distribution corresponds to the model of Pitzer and Gutowsky[2] which explains the bond by the formation of a B–B "protonated double bond", since the appearance of a signal from the bridging protons in weak fields would then be expected.

Kern and Lipscomb[34] made an approximate calculation of the magnetic screening for bridging and terminal protons in diborane and obtained qualitative agreement with the experimental results. They showed that the bridging protons are situated in strong fields and the internal chemical shift was found to be 3.2×10^{-6}.

2. ^{11}B NMR Spectra

The NMR spectra of the boron hydrides showed the presence of non-equivalent nuclei of ^{11}B and protons and gave additional confirmation of the correctness of the structures found by other methods.

The ^{11}B NMR spectrum of diborane consists of nine lines[24] (Fig. 3). Due to the strong interaction with the terminal protons the ^{11}B lines give a triplet $J_{^{11}B-^1H_K}$ = = 137 Hz), but the interaction with the bridging protons gives an additional triplet splitting of each of the three lines ($J_{^{11}B-H_M}$ = 48 Hz). Analysis of the spectrum confirms the non-equivalency of the two groups of protons and shows the equivalency of the boron nuclei.

The pentaborane-9 spectrum consists of two lines with intensity ratio $\simeq$ 4 : 1 (Fig. 4). The interaction of the boron atoms lying at the base of the pyramid with the

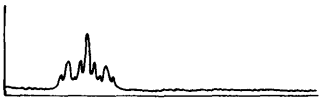


Fig. 3. ^{11}B NMR spectrum of diborane[24] (f_{res} = 12.3 MHz).

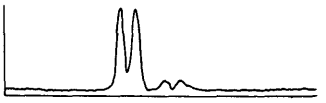


Fig. 4. ^{11}B NMR spectrum of pentaborane[24] (f_{res} = 12.3 MHz).

bridging protons is not shown clearly but the lines are appreciably broader than in diborane. Possibly one of the reasons for the broadening of the ^{11}B NMR lines is the interaction of the ^{11}B nucleus with the bridging proton.

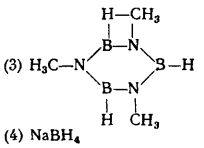
The ^{11}B NMR spectrum of other boron hydrides has been described in detail[30-33,35,36] and since the interpretation of the spectra is usually given for confirmation of their structure, we will restrict the discussion to diborane and pentaborane-9.

The study of ^{11}B NMR has been carried out more thoroughly than the NMR of the protons. We now have much information about the chemical shifts of ^{11}B and about the $^{11}B-^{1}H$ spin–spin interaction. Table 4 gives data on the chemical shifts and spin–spin interactions for some boron-containing compounds[36].

As Table 4 shows, the ^{11}B shift in diborane relative to $B(OCH_3)_3$ is very small. It can evidently be assumed that the boron atom in compounds such as $B(OCH_3)_3$, is "stripped".

However, such a hypothesis would not be correct for other boron compounds (for example, for diborane), since it has been noted that with change in the hybridisation of

TABLE 4.

Compound	$\delta=\frac{H_{specimen}-H_{std}}{H_{std}}\times 10^6$		$J_{^{11}B-^{1}H}$, Hz	
	base	apex	base	apex
(1) $B(OCH_3)_3$	0			
(2) $B(OC_2H_5)_3$	+0.6			
(3) 	−14.3		134	
(4) $NaBH_4$	+61.0		81	
(5) B_2H_6	+0.5		137($H_{terminal}$) 48(H_{bridge})	
(6) B_4H_9	+25.0		132	
	+59.9		156	
	+30.8			
(7) B_5H_9	+30.8	+69.6	168	176
(8) $B_{10}H_{14}$	+6.9	+53.9	124	159
	+19.5		128	
(9) B_5H_{11}	−16.2	+49.8	134	142
	+ 0.7		162	

the boron atom (on transition from sp^2 to sp^3) the paramagnetic contribution to the screening constant decreases[35,36].

Without evaluating the changes in the paramagnetic contribution it is impossible to draw any conclusions about the electron density at the ^{11}B nucleus.

The spin–spin constants of the $^{11}B-^{1}H$ interaction for the boron hydrides can be explained qualitatively on the basis of the hypothesis of Gutowsky and coworkers[37] that the spin–spin interaction between ^{1}H and other nuclei will depend on the fraction of s character in the hybrid orbital bound to the hydrogen atom. Hence the interaction constant between ^{1}H and the sp^2 hybridisation of the boron atom should be greater than that between ^{1}H and the sp^3 hybridised atom. The results in Table 4 confirm this hypothesis. Thus, for compound (3), in which the hybrid boron orbitals are close to sp^2, the quantity $J_{^{11}B-^{1}H}$ is 134 Hz, but for $NaBH_4$ where the hybridisation of the boron atom is close to sp^4, $J_{^{11}B-^{1}H}$ = 81 Hz.

When the spin–spin interaction constant $J_{^{11}B-^{1}H}$ reflects the influence of the s character of the hybrid orbitals of the boron atom, then the hybrid orbitals of the boron atom in hydrides are intermediate between sp^2 and sp^3. With diborane a difference in the hybridisation of the orbitals of the boron bound with the terminal and the bridging protons appears quite distinctly (137 and 48 Hz). In the last the contribution of p character is greater.

The information on spin–spin interaction shows that the B–H bonds (even bridging) are predominantly covalent. Were they strongly polar, then it is evident that the $J_{^{11}B-^{1}H}$ spin–spin interaction would be close to zero, as it is for $B(OCH_3)_3$.

3. Saturation of the ^{11}B NMR Signals

The ^{11}B nucleus is known to have a nuclear quadrupole moment, and the interaction of nuclear quadrupole with the "lattice" and with other nuclei diminishes[26] with the spin–lattice relaxation time T_1, and with the spin–spin relaxation time T_2. The optimal conditions for recording the spectra are short T_1 (since the signal intensity $\propto \sqrt{T_2/T_1}$) and long T_2 (since the signal decay $\propto 1/T_2$). The difference in the line breadths or their intensities can give some information about the electron environment of the ^{11}B nucleus.

Actually in many ^{11}B NMR spectra of boron hydrides the peak area of the NMR signals of the ^{11}B nuclei in non-equivalent positions give only approximately the number of nuclei found in the corresponding positions. The explanation is that the ^{11}B nuclei are in electronic surrounding with unusual symmetry and the interaction of the quadrupole moment ^{11}B with the electric field alters the spin–lattice relaxation time differently for nuclei situated in different positions. For example, the ^{11}B NMR signal of the BH_4^- ion is easily saturated (T_1 is large) and this is the result of the symmetry of the electronic environment of the ^{11}B nucleus, which decreases the interaction of the ^{11}B quadrupole moment with the lattice. The position for exchange is similar.

The study of "relative ease of saturation" for the boron hydrides gave the following results: the BH_2 groups in tetraborane-10 are saturated more readily than the BH groups[38]; the apex boron atom in pentaborane-9 is saturated more readily than the boron atoms lying at the base

of the pyramid, etc. [33,39]. In both instances the saturation at these nuclei is easier because of the high symmetry of the electron environment.

It was found for hexaborane-10 that the ^{11}B nuclei lying in the base are saturated much more easily than those at the vertices and this is difficult to explain by the presence of a symmetrical electron environment, due to the structure of the compound itself. Evidently this is brought about by the exchange of "bridging" hydrogen atoms, as the symmetry of the electron environment increases in similar intramolecular rearrangements. Exchange leads to the absence of $J_{^{11}B-H_M}$ spin–spin interaction noted earlier for pentaborane-9 and for other compounds [39].

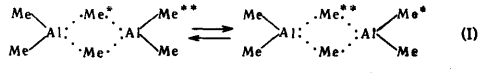
IV. NMR OF ORGANOALUMINIUM COMPOUNDS

Some organoaluminium compounds are electron-deficient. For example, there are the dimers of trimethylaluminium and triethylaluminium, the polymers of $Al(OPr^i)_3$, etc. [2,40].

The difference between the organoaluminium compounds and the boron compounds is that the polarity of the bonds can play a greater part in the formation of bridge bonds in them. Actually, in accordance with the electronegativity rules [15] the polarity of the C–Al bonds is ~ 30%. Furthermore, in the formation of polycentric orbitals with participation of the free 3*p* orbitals, the energy of the Al...C bridging bonds should be appreciably less than for B–H, since the energy for promoting in the valence state for the aluminium atom is greater than that for boron (see Table 2). And finally, in the formation of dimers by the alkylaluminiums steric hindrance to complex formation may arise [2].

1. PMR Spectra

It was established earlier that trimethylaluminium exists as a dimer in the solid state (its structure is shown in Table 1). In benzene solutions [2] and in the gaseous state [41] trimethylaluminium also exists as a dimer, but in early work on PMR, the spectrum of $[Al(CH_3)_3]_2$ appeared as a single line [26,42]. This can be explained either by the equivalence of all groups in the dimer, or by rapid exchange:



(I)

Miller and Pritchard [43] showed that at ordinary temperatures there is an exchange between bridging and terminal CH_3 groups. On cooling a solution of trimethylaluminium in cyclopentane to -75° a spectrum is obtained which consists of two lines with an intensity ratio of 2:1. The form of the spectrum is shown in Fig. 5. The shifts of the bridging and terminal methyl groups relative to the signal of cyclopentane are respectively 1.04×10^{-6} and 2.17×10^{-6}. At elevated temperatures the signal from the bridging groups broadened and merged with the signal from the terminal groups.

The activation energy for the transition mentioned, calculated from the temperature dependence of the form of the spectrum lay within the limits 6–14 kcal mole^{-1}. The heat of dissociation of the dimer [5] is 20.2 kcal mole^{-1}, and apparently trimethylaluminium does not dissociate into the monomer during change (I). It is thought [43] that the formation of a transitional state can rule out rupture of one

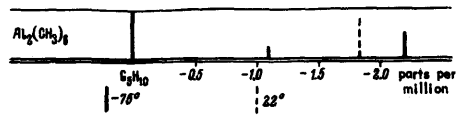
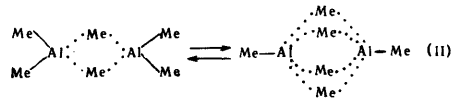


Fig. 5. PMR spectrum of the dimer of trimethylaluminium [44].

Al–C bond or the formation of new Al...C bonds for the transitional structure, that is,



(II)

Hyperfine splitting due to the $^{27}Al-^1H$ interaction was not observed.. The PMR lines are very broad (~ 6 Hz).

For dichlorotetramethyldialuminium $Al_2Cl_2(CH_3)_4$ the PMR lines have a breadth of ~ 1 Hz (f_{res} = 40 MHz), but here in the temperature interval -85–0° the $^{27}Al-^1H$ spin–spin interaction was not observed [44].

The absence of hyperfine splitting is easily explained by the great polarity of the C–Al bonds or by the fact that in the hybrid Al orbital the 3*s* state "impurity" is small.

The PMR spectrum of $[Al(C_2H_5)_3]_2$ shows that all the CH_2 groups are equivalent [23,45]. If the "usual" association were assumed, the non-equivalency of the CH_2 groups would be expected:

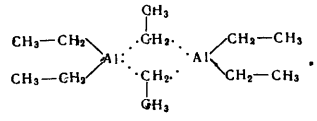
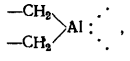
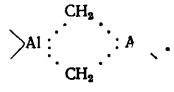


Fig. 6 shows the PMR spectrum. The methylene group signal appears at the "mean" value of the field: between the positions expected at a stronger field for



and the position for the bridging CH_2 groups in the configuration:



Hoffmann considers [23] that the NMR signal of the bridging groups should be expected in a weaker field, since then the electrons of the C–Al bond will be distributed on two orbitals of the aluminium.

The hypothetical positions of the signals of the outer ethyl groups (or the bridging groups) can be judged from the spectra of compounds with –Al–CH_2– groups which

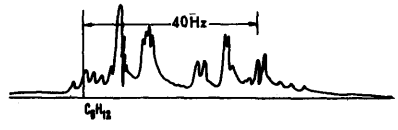
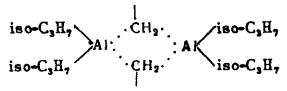


Fig. 6. PMR spectrum of the dimer of triethylaluminium [44] (f_{res} = 40 MHz).

either are not associated, for example[46], $AlPr^i_3$, or contain an ethyl group only in the bridge bond, for example,



For the CH_2 groups in these instances[23] a frequency difference of 17.6 Hz is obtained (at f_{res} = 40 MHz), in which the bridging methylene group gives a signal in weaker fields than the terminal groups. But because a single line is observed for triethylaluminium, it is thought[23] that here there is an alkyl exchange. Assuming that the shift between the terminal and bridging $-CH_2-$ groups should be ~ 17 Hz it can be concluded that the Al...C bridging bond is unstable and has a life of $\tau \ll 10^{-2}$ s.

However, the instability of the Al...C bonds cannot be considered to be finally established, since the NMR spectra at low temperatures have not been investigated (as they have for trimethylaluminium[43]), and there have also been no studies of the applicability of the "static" model, proposed earlier by Pitzer and Gutowsky[2] (bonding in the complex by the formation of Al...H bonds is suggested, as shown in Fig. 7). This model is reasonable from the standpoint of "geometry" and to explain the same position of the signals for the methylene groups there is no need to invoke the existence of exchange.

The data about the PMR spectra of other compounds (diethylaluminium hydride, etc.[23,44,45]) are fragmentary and will not be discussed here.

2. ^{27}Al NMR

The ^{27}Al nucleus has a comparatively large quadrupole moment ($Q = 0.149 \times 10^{-24}$ e cm^{-2}) and if its electronic environment does not have sufficient symmetry then owing to the interaction of the quadrupole moment with the electric field T_2 decreases and the aluminium line broadens. The ^{27}Al NMR usually is very broad but since the range of shifts for ^{27}Al is great not only the line breadth but also the chemical shifts can be measured with an accuracy of $\pm 10 \times 10^{-6}$. Some data[47] for the NMR of aluminium compounds are given in Table 5.

The spectra of the compounds mentioned in Table 5 were taken at a frequency of f_{res} = 7.2 MHz.

The narrow lines of the ^{27}Al NMR show compounds having electric field symmetry around the ^{27}Al nucleus close to the tetradhedral $Al(CH_3)_3$, $AlCl_3$, and solutions of the polymer $Al(OPr^i)_3$.

Pure trimethylaluminium gives a wider ^{27}Al NMR line than $AlCl_3$, and this can be explained by the dimer

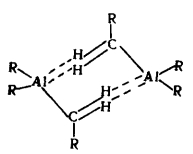


Fig. 7. Structure of the dimer of triethylaluminium according to Pitzer and Gutowsky[2].

TABLE 5.

Compound	$\delta = \frac{H_{specimen} - H_{std}}{H_{std}} \times 10^6$	Line breadth, G
$Al(N_2O)_6^{+3}$	0	0.05
$[Al(CH_3)_3]_2$	−156	0.4
$[Al(C_2H_5)_3]_2$	−171	1.5
$Al(iso\text{-}C_4H_9)_3$	−220	5.4
$Al(O—iso\text{-}C_4H_9)_3$ (Solution in heptane)	−7	0.09
$[AlCl_3]_2$	−94	0.3
$H—Al(iso\text{-}C_4H_9)_2$	−162	8.9

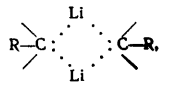
$[Al(CH_3)_3]_2$ being formed by the setting up of Al...H bonds[47], that is, a hydrogen atom of the methyl group, and not the carbon, takes part in the intermolecular bond. This is not in agreement with the X-ray data, but accords well with the Raman and infrared spectra[2] where it is found that the symmetry of $[AlCl_3]_2$ is higher than that of $[Al(CH_3)_3]_2$.

The dimer of triethylaluminium gives a relatively "narrow" line, evidently because the gradient of the electric field at the ^{27}Al nucleus diminishes on formation of the A...H bonds. Were exchange to exist, an NMR line almost coinciding in breadth with the trimethylaluminium line would be expected. For the molecule-monomers, for example, $AlPr^i_3$, the symmetry of the electronic environment of the ^{27}Al nucleus is lower and the line becomes significantly wider.

The chemical shifts of the compounds discussed have not been interpreted.

V. NMR OF ORGANOLITHIUM COMPOUNDS

It has been found[4] that organolithium compounds are strongly associated, and with ethyllithium even in the vapour the molecules exist predominantly in the form of tetramers and hexamers[48]. The considerably branched molecule of $(CH_3)_3CLi$ gives tetramer complexes in benzene solution[49]. The simplest dimer associate was found in an ethereal solution of phenyllithium[50]. However, not one of the papers we have read reports the observation of monomeric molecules of organolithium compounds. It is suggested[2,50] that the intermolecular bonds in the complexes arise because of the strong polarity of the C–Li bonds. From the infrared spectra[51] and the chemical properties of the substances (solubility in non-polar solvents, electrical conductivity, etc.) its was proposed that multicentric molecular orbitals and C...Li bridge bonds are formed in the organolithium complexes:



and the 2p orbitals of the lithium atom participate in the formation of the multicentric orbitals. The proposed C...Li bonds are essentially covalent.

The difference between the lithium atom and the atoms of boron and aluminium is that the 2p orbitals of the lithium atom are not used in the normal state (and therefore information about the participation of any of the 2p orbitals in bonds is needed for the solution of problems). In addition allowance must be made for polarity of the bonds playing an important part in the formation of complexes.

1. PMR Spectra

Table 6 gives some information about the PMR spectra of some organolithium compounds.

Figs. 8–10 show PMR spectra of methyl-, ethyl-, and phenyl-lithium.

The results for the chemical shifts of PMR for the CH_2 group cannot be explained in terms of electronegativity by the rules found earlier for alkylmetals [54]. The large shift of the CH_2 line in the region of strong fields can be explained if it is assumed that the C–Li bond is strongly polar. In reality the shift of the CH_2 group in $(R-Li)_n$ complexes relative to the CH_2 group in normal hydrocarbons is [26] $\sim 2.6 \times 10^{-6}$. To obtain such a shift the charge on the 1s cloud of the hydrogen atom must be increased by 0.2 e. When it is assumed that the charge is transferred from the lithium atom to the CH_2 group and there distributed in accordance with the electronegativity of the atoms, then there should be a charge of $\sim 0.7\ e$ on the CH_2 group.

The NMR results for alkyl compounds of normal structure show that outside the dependence on the complexity of the complex, the CH_2 group directly bound with the lithium atom is always found in the same electronic environment, although for different complexes some differences could be expected. For example, for the tetramer and hexamer of ethyllithium structures in the form of "bookcases" [layers (Ed. of Translation)] of dimers joined by C...Li bonds have been suggested [55] and also the structures [4] shown in Fig. 11. However, with the "bookcases" for the hexamer there should be a difference in the shifts of the CH_2 groups for different "layers" of the bookcase. Probably, for the structure proposed by Brown and coworkers [4] in the tetramer and hexamer there should be different electronic environments for the CH_2 groups.

When alkyl exchange is not taken into account the structures proposed above do not explain the PMR results, besides which these structures are highly stressed due to the mutual repulsion of the non-valence bonded atoms [52], which was noted earlier for the example of the triethylaluminium complexes [2]. Evidently as for $[Al(C_2H_5)_3]_2$ complexes [2], C_2H_5Li can exist in solution thanks to the formation of Li...H bonds [52] (Fig. 12). Such a structure also exists for the hexamer.

The size of the chemical shift of the CH_2 group, as for other structures is readily explained by the high polarity of the C...Li bond. The equivalence of the methylene groups is also evident, since the Li...H bonds are identical. The

TABLE 6*.

Substance	Solvent	Concentration, N	Association factor	$\delta = \frac{H_{specimen} - H_{C_6H_6}}{H_{C_6H_6}} \times 10^6$
CH_3Li	$(C_2H_5)_2O$	0.6—0.8		9.05±0.05
C_2H_5Li [4,52]	C_6H_6		6	8.11±0.05
	C_6H_{12}	0.5—0.8		8.11±0.08
	$(C_2H_5)_2O$	0.85—2.40		8.10
$n\text{-}C_4H_9Li$ [52]	C_6H_{14}	0.6—1.18		8.10
$C_{12}H_{25}Li$ [52]	C_6H_6	0.6		8.10
	C_6H_{12}	0.6		8.10
C_6H_5Li [50,53]	$(C_2H_5)_2O$		2	shift of the most intense line relative to benzene is 0.2
$t\text{-}C_4H_9Li$ [49]			4	6.16 (δ_{CH_3})

* $J_{^1H^7Li} \simeq 0$.

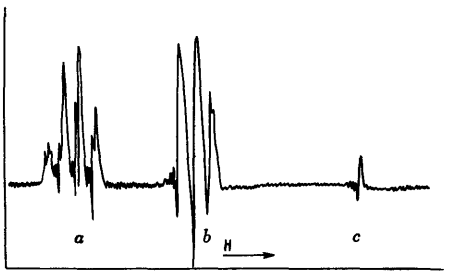


Fig. 8. PMR spectra of methyllithium in diethyl ether: *a*) lines of the CH_2 group of the ether; *b*) lines of the CH_3 group of the ether; *c*) lines of the CH_3 group of methyllithium (breadth $\simeq$ 1.4 Hz, f_{res} = 22.68 MHz).

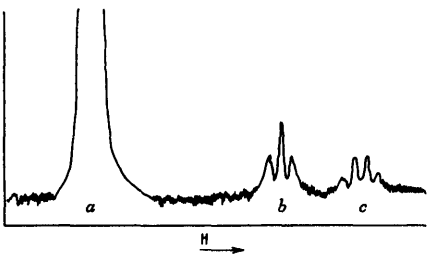


Fig. 9. PMR spectrum of ethyllithium in benzene (f_{res} = = 25 MHz): *a*) benzene line; *b*) CH_3 group of ethyllithium; *c*) CH_2 group of ethyllithium.

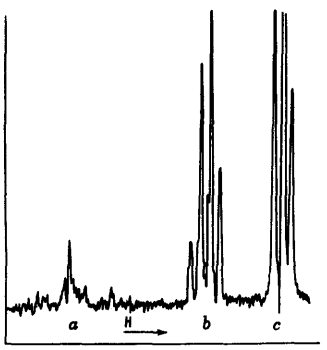


Fig. 10. PMR spectrum of phenyllithium in diethyl ether [53] (f_{res} = 25 MHz): *a*) phenyllithium lines; *b*) CH_2 group of the ether; *c*) CH_3 group of the ether.

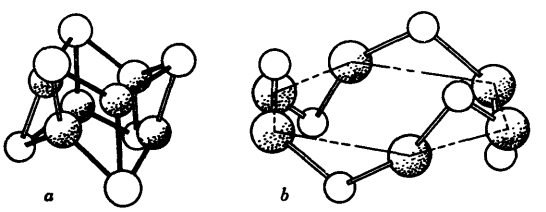


Fig. 11. Structure of the ethyllithium hexamer [4] (lithium atoms omitted). The alkyl exchange between the structures (*a*), postulated to explain the breadth of the ^7Li lines, is suggested as possible because of the formation of intermediate structures (*b*).

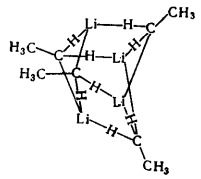


Fig. 12. Hypothetical structure of the tetramer of ethyllithium [52].

Li...H bonds are preferentially polarised bonds in which there is apparently some overlap of the 1s orbitals of the hydrogen atom with the 2s orbitals of the lithium atom. A feature of these bonds is that the free 2s orbital of the hydrogen atom agrees in energy [14] with the free 2p orbital of the lithium atom and on transfer of the 2s electron of the lithium atom to the 2p level, the electron can use the 2s orbitals of neighbouring hydrogen atoms without expenditure of energy [52].

The chemical shifts of the PMR lines for $(CH_3)_3CLi$ and C_6H_5Li were not interpreted.

All authors note the absence of $^7Li-^1H$ spin–spin interaction. This is associated either with alkyl exchange or with the great polarity of the C–Li bond (the latter is the more probable).

X-Ray analysis [55] of crystalline C_2H_5Li showed that the ethyllithium molecules form tetramers in the crystals. Apparently the dissolution of ethyllithium in non-polar solvents is due to the comparatively slight interaction of the tetramers with one another. The retention of the form of the tetramer in solution should give different shifts for the NMR lines of the methylene group protons. It can therefore be assumed that the complex changes its configuration to some extent during dissolution.

2. ^7Li NMR Spectra

The ^7Li nucleus has a quadrupole moment ($Q = 4.2 \times \times 10^{-26}$ e cm^{-2}) and therefore the breadth of the ^7Li line can be considerable owing to the interaction of the quadrupole moment with the "lattice". However, the ^7Li NMR lines of solutions of a series of compounds give narrow lines. Some of the NMR results are given in Table 7.

Brown and coworkers [4] explain the narrow ^7Li NMR lines by the exchange of radicals as for trimethylaluminium [43]. However, the line breadth is unaltered on cooling to -75° (and ether solutions to -100°) therefore it can be assumed that the narrow ^7Li line is due to the symmetry of the electron environment and not to exchange. Actually if it is assumed that the structure shown in Fig. 12 is stable, then the absence of electric field gradients at the ^7Li nucleus is the result of the compensating action of the neighbouring H, C, and Li atoms.

TABLE 7.

Substance	Solvent	ΔH_{Li}, Hz ($t = 27°$)	ΔH_{Li}, Hz ($t = -75°$)
C_2N_5Li [4]	C_6H_6	$\sim 10^{-3}$	
C_2H_5Li [5]	C_6H_6	$<6 \cdot 10^{-3}$	
	C_6H_5	$<6 \cdot 10^{-3}$	
	$(C_2H_5)_2O$	$<6 \cdot 10^{-3}$	$<6 \cdot 10^{-3}$
$n\text{-}C_4H_9Li$ [52]	C_6H_{14}	$<6 \cdot 10^{-3}$	$<6 \cdot 10^{-3}$
$C_{12}H_{25}Li$ [52]	C_6H_6	$<6 \cdot 10^{-3}$	
	C_6H_{13}	$<6 \cdot 10^{-3}$	
$C_6H_5 \cdot CH_2Li$ [53]	$(C_2H_5)_2O$	$<6 \cdot 10^{-3}$	$<6 \cdot 10^{-3}$

We note that the strongly polar C–Li and Li...H bonds will give a narrow ^7Li NMR line for almost any configuration of the complex. The alkyl exchange postulated for the explanation of the small line breadths [4] of ^7Li lines apparently does not occur, since even at low temperatures a narrow line is observed. It is especially difficult to admit the possibility of exchange for such compounds as dodecyllithium.

Apparently in these compounds the ^7Li nucleus is almost in an environment of 1s electrons, that is, the C–Li and Li...H bonds are strongly polar.

This hypothesis is supported by comparison with the NMR results [47] for ^{27}Al. When it is assumed that for compounds of the $(Li-R)_n$ type in solutions the correlation time, viscosity, etc. are just the same as for $[Al(CH_3)_3]_2$ (which is probably not true, as there are changes in the direction of the broadening of the ^7Li line) then the ratio of the line breadths should determine the ratios of the squares of the quadrupole moments [56] and the ^7Li NMR lines should have a breadth of more than 2×10^{-1} Hz. Comparison with the experimentally observed line breadths allows the conclusion to be drawn that the ^7Li nucleus has an electronic environment of high symmetry. Evidently there is very little utilisation of free orbitals and the lithium in these compounds is in a form close to Li^+. This suggestion explains the PMR results, the line breadths, and the absence of spin–spin interaction.

The chemical shifts in ^7Li were observed in only one work [4], but definite conclusions were not drawn, since the standard was a solution of lithium bromide in water. The shift of $\sim 1 \times 10^{-6}$ of the lithium lines (ethyllithium) towards weaker fields relative to lithium bromide does not seem significant since the transfer of electrons from the water molecule to the free orbitals of Li^+ is possible (in the formation of a hydrated ion).

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The examples considered show that the bonds in organo--lithium, -aluminium, and -boron complexes differ considerably: from close to covalent to strongly polar bonds. Therefore to formulate the principles of electron-deficient bonding it is necessary to consider both polar interaction and also the possibility of using free orbitals. The principle formulated by Rundle [6,7] does not take polar interactions into account.

It is interesting to note that at first glance allowance for polar interactions can explain many experimental facts. For example, Pitzer and Gutowsky [2] suggested that when the bonds in the alkylaluminium dimers are predominantly polar then all the alkylmetals in which the metal atoms have less electronegativity are associated and those with greater electronegativity are monomers. This suggestion is equivalent to saying that M–C bonds for metals of low electronegativity are strongly polar. Such a compound will give complexes with formation of polar bonds, spin–spin interaction in these complexes will be absent, and the chemical shift of M relative to the M^+ ion will be small. In metals with high electronegativity the C–M bond will be predominantly covalent, there will be spin–spin interaction, etc. Cryoscopic and NMR data confirm this hypothesis.

TABLE 8.

Compound	Electronegativity of the M atom (Ref. 15)	Association factor	J_{M-CH_3}, Hz	J_{M-CH_3}, Hz
$C_2H_5{}^7Li$	0.95	6	0	0
$(CH_3)_3{}^{27}Al$	1.5	2[3]	0	0
$(C_2H_5)_3{}^{27}Al$	1.5	2[3]	0	0
$(CH_3)_3Ga$	1.6	unstable dimer[87]	—	—
$(CH_3)_3In$	1.7	1[6]	—	—
$(CH_3)_2{}^{111}Cd$	1.7	1		50.2±0.4 [88]
$(C_2H_5)_2{}^{111}Cd$	1.7	1	49.4±0.8 51.2±0.8	59.8±0.8 57.2±0.8
$(CH_3)_2{}^{199}Hg$	1.8	1	—	102 [89]
$(C_2H_5)_2{}^{199}Hg$	1.8	1	120 115.2	91 [89] 87.6 [60]
$(C_2H_5)_4{}^{207}Pb$	1.8	1	125.0	41.0[60]
$(CH_3)_4{}^{119}Sn$	1.9	1	—	54.2±0.3 [88] 51.9±0.3
$(C_2H_5)_4{}^{119}Sn$	1.9	1	51.4±0.8 49.1±0.8	69.8±0.8 66.8±0.8
$(CH_3)_2{}^{125}Te$	2.1		20.7[61]	
$(C_2H_5)_2{}^{125}Te$	2.1		exists, but the spectrum is complex and has not been interpreted[61]	
$(CH_3)_2{}^{77}Se$	2.4		—	11.2±0.3 [88]
$(C_2H_5)_2{}^{77}Se$	2.4		<15	15

Table 8 gives some cryoscopic and NMR results for various groups of organometallic compounds.

Pitzer and Gutowsky's views are also confirmed for alkylmetal complexes.

As for boron hydrides, it is almost impossible to confirm the use of all the 2*p* orbitals in the formation of bonds, but quantum mechanical calculations show the correctness of this hypothesis.

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