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A Theoretical Study of the Electronic Structures of Several Methyl Compounds of Group I, II, and III Elements

Katsutoshi OHKUBO, Hidetoshi SHIMADA, and Masahide OKADA
Faculty of Engineering, Kumamoto University, Kurokami-machi, Kumamoto

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The electronic states of the group I, II, and III methyl compounds were investigated using the extended Hückel method, with particular reference to the nature of the bond of metal-carbon. First, the monomers of the group I methyl compounds indicated remarkable electron-localizations on the carbon atom in CH_3. $(CH_3Li)_4$ was found to be a possible tetramer, its total energy being lower by 0.34 eV per CH_3Li unit than that of the CH_3-Li-monomer in spite of the unstability of $(CH_3Li)_2$. Second, $(CH_3)_4Be_2$ was more stable than $(CH_3)_2Be$ by *ca.* 4.04 eV per $(CH_3)_2Be$ unit. Third, the stability of $(CH_3)_3B$ in the form of a monomer was understood well by the fact that its π-bond nature is so much in comparison with that of $(CH_3)_3Al$. Finally, the reactivities in a series of the groups were discussed briefly in connection with the electronic states.

The reactivities of organometallic compounds, in particular those of compounds containing group I, II, and III elements have hitherto attracted many authors' attention.[1-13] An interesting proposal suggested by Gilman[1] and Rocho[2]: the reactivities have a direct relationship with the electronegativities of the metals. However, some obscurities still remain as a result of the lack of information concerning the molecular structures of the compounds.

Recently, the molecular structures of organometallic compounds have been observed in connection with the bridge-type polymerization of the compounds.[14,15] Many X-ray and spectrophotometric studies have been performed in making experimental analyses of the dimer- or polymer-structures of C_2H_5-Li,[16,17] *n*-C_4H_9Li,[18] $(CH_3)_2Be$,[19,20] $(C_2H_5)_2Mg$,[20] $(CH_3)_3Al$,[21,22] and a characteristic monomer of (C-

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5) H. Gilman and J. W. Morton, "Organic Reactions," Vol. VI, Chap. 7; Vol. VIII, Chap. 6 (1951).
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$H_3)_3B$.[23,24] These studies suggested the striking features of the compounds mentioned above, namely, the so-called "*five-coordinate carbon*" or "*electron-deficient bridged bond*" of such compounds as the methyllithium tetramer,[25] the dimethylberyllium polymer,[19] and the trimethylaluminum dimer.[21,22] More recently, as to the molecular structures of the electron-deficient compounds, some molecular orbital calculations[26-29] have been performed with particular reference to the natures of the bond, such as the metal-carbon and metal-metal bonds, in $(CH_3Li)_4$,[26] $(CH_3)_6B_2$,[26] and $(CH_3)_6Al_2$.[26] In regard to the contributions of the π-type bonding (hyperconjugation) of alkyls to the formation of the bridged bond mentioned above, these calculations have provided the interesting information that the π-type bonding of the above polymer appears to be approximately the same as that of its monomer and less than 10% of the metal-carbon σ-bond in the compounds.

In the present paper, an extended Hückel molecular orbital calculation will be carried out for the methyl compounds of group I (Li, Na, K, Rb), group II (Be, Mg, Ca), and group III elements (B, Al). The main purpose of this study is to make an extensive consideration of the electronic states of the compounds in connection with their reactivities.[1,2]

Method of Calculations

The extended Hückel method proposed by Hoffmann[30] was used to make calculations for several methyl compounds of group I, II, and III elements: CH_3Li, $(CH_3Li)_2$, $(CH_3Li)_4$, CH_3Na, CH_3K, CH_3Rb, $(CH_3)_2Be$, $(CH_3)_4Be_2$, $(CH_3)_2Mg$, $(CH_3)_2Ca$, $(CH_3)_3B$, $(CH_3)_3Al$, and $(CH_3)_6Al_2$. The values of the orbital exponents of the elements were taken from those evaluated by Clementi,[31] while the following valence-state ionization potentials (vsip)[32,33] were employed for the diagonal H-matrix elements: H_{ii}(eV)$=-13.6$ (H 1s), -5.39 (Li 2s), -3.54 (Li 2p), -5.14 (Na 3s), -3.04 (Na 3p), -4.34 (K 4s), -2.17 (K 4p), -4.18 (Rb 5s), -2.60 (Rb 5p), -9.92 (Be 2s), -5.96 (Be 2p), -8.95 (Mg 3s), -4.52 (Mg 3p), -7.09 (Ca 4s), -3.96 (Ca 4p), -14.91 (B 2s), -8.42 (B 2p), -12.27 (Al 3s), -6.47 (Al 3p), -21.01 (C 2s), and -11.27 (C 2p). The Wolfsberg-Helmholtz approximation[34] was employed for the off-diagonal matrix elements (H_{ij}) as:

$$H_{ij} = K(H_{ii} + H_{jj})S_{ij}/2$$

where the value of the parameter, K, was taken to be 1.75.[30] The bond lengths of the group I methyl compounds were taken to be Li–C=2.19 Å,[35] Na–C=2.70 Å, K–C=3.10 Å, and Rb–C=3.29 Å. The atomic coordinates of $(CH_3Li)_2$ and $(CH_3Li)_4$ were calculated from the pertinent bond distances and bond angles.[14] The bond angles of carbon-metal-carbon for the group II methyl compounds were taken to be linear, assuming the $D_{\infty h}$-structures, and the following bond lengths were used: Be–C=1.98 Å, Mg–C=2.45 Å, and Ca–C=2.82 Å. The molecular structures of the group III methyl compounds were assumed to be D_{3h},[36] and the bond lengths of B–C and Al–C were set as 1.80 Å[37] and 2.28 Å[38] respectively. For the calculations of the dimer structures of $(CH_3)_4Be_2$ and $(CH_3)_6Al_2$, the bond lengths of Be–C,[39] Al–C_b,[40] and Al–C_t[41] were taken to be 1.93 Å,[42] 2.24 Å,[14] and 2.00 Å[14] respectively. In all the calculations, the bond distance of C–H was taken to be 1.09 Å for the sake of simplicity.

Results and Discussion

The Electronic States of the Group I Methyl Compounds. Among organometallic compounds of group I elements, lithium compounds can be distinguised by their associations[4] in such organic solvents as ether and tetrahydrofuran. From their experimental works, Brown *et al.*[42] and others[43-45] emphasized the hexamer structures of alkyllithiums, while

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35) This length was derived from that of $(CH_3Li)_4$ reported in Ref. 14.
36) The angle of CBC in $(CH_3)_3B$ was reported as 119.4°± 0.3° by Ref. 23.
37) In Ref. 23, the mean bond length of B–C was reported to be 1.5783±0.0011 Å. We modified this value slightly.
38) The bond lengths of Al–C in $(CH_3)_6Al_2$ were determined to be 2.24 Å[21] (2.14±0.01 Å[22]) for the bridged distance and 1.99 Å[21] (1.97±0.01 Å[22]) for the exterior distance. We used approximate values as estimated from Ref. 21.
39) The same interatomic distance of Be–C was applied to those of the Be-terminal C and the Be- bridged C.
40) The C_b and C_t notations denote a bridged carbon and a terminal one respectively.
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Table 1. Electronic states of group I methyl compounds

Compound	Bond[a] length (Å)	P(M-C)[d] S(M-C)[b]	P(M-C)[c]	s(M)-s(C)	s(M)-p(C)	N(M-C)[e]	M(M-C)[f]	Energy (eV) HO[g]	LV[h]	Total
CH_3Li	2.19	0.191	0.232	−0.190	0.384	0.064	−0.152	−11.90	−4.77	−133.98
LiCl[i]	3.31	0.278	0.086	−0.034	0.140		0.032	−13.39	−5.09	−128.41
CH_3Na	2.70	0.121	0.294	−0.140	0.416	0.0424	−0.122	−11.66	−4.70	−133.11
NaCl[i]	3.65	0.160	0.052	−0.018	0.082		0.008	−13.39	−5.02	−128.39
CH_3K	3.10	0.057	0.142	−0.146	0.272	0.0248	−0.190	−11.60	−4.07	−132.37
KCl[i]	4.05	0.113	0.022	−0.008	0.034		0.002	−13.39	−4.27	−128.38
CH_3Rb	3.29	0.026	0.096	−0.094	0.224	0.0154	−0.054	−11.61	−3.84	−132.20
RbCl[i]	4.25	0.056	0.014	−0.004	0.018		0.0006	−13.39	−4.16	−128.38

a) Atomic distance of metal—carbon or metal—chlorine.
b) Total orbital overlap between metal (M) and carbon (C).
c) Bond order density between M and C.
d) Bond order density of M-C. s(M)-s(C) and s(M)-p(C) mean the bond order density between s-M orbital and s-C one and that between s-M orbital and p-C one in $sp\sigma$-bond of M-C, respectively.
e) AO bond population between the orbitals of M and C presented in d).
f) Total bond population between M and C.
g) This HO level is depended on the p-C orbital presended in d), while for the chlorides, it is depended on the p-lone pair orbital of Cl.
h) This level indicates the energy of the lowest vacant s-M orbital.
i) They are listed for the comparison's sake.

Weiner and his co-workers[46] supported the tetramer structures. The association of the lithium compounds may be attributed to very small contributions of orbital overlaps (including "*hyperconjugation*") between the lithium atom and carbon to the formation of their stable molecules. As to the other metal compounds, however, there is little information about their electronic states except that there is a tendency[47,48] for their slight covalent natures to increase with a decrease in their atomic numbers. These characteristics should be reflected in the total orbital overlap (S(M–C)) defined by the sum of orbital overlaps, the bond order density (P(M–C)), and the total bond population (M(M–C)). These values and, in addition, the energy levels (HO and LV) are shown in Table 1, while the atomic- and bond-populations are given in Fig. 1. As may be seen in Table 1, S(M–C) supports the previous idea as to the tendency[47,48] of the bond nature; moreover, P(M–C) suggests that the σ-bond of M–C is formed by the bonding orbital of s(M)–p(C) and the anti-bonding orbital of s(M)–s(C). The electrons of the M–C bond localize remarkably on the carbon atom, which is over the unit charge (see Fig. 1). In this case, the contribution of "*hyperconjugation*" can hardly be expected because of the negative π-bond character of the compounds. It is of interest here to pay attention to the bond nature of the metal halides for the sake of comparison. Notwithstanding the fact that the interatomic distances of M–Cl are larger than those of M–C, the halides indicate a more covalent nature of the bond than do the methyl derivatives. This reflects a negative contribution of the hyperconjugation of CH_3 group such as has been described above; a striking covalency of the lithium compounds is also seen, a covalency which may be attributed to the small radius of the Li ion and the larger effective nuclear charge of Li caused by the scanty shielding effect of the electrons on Li.

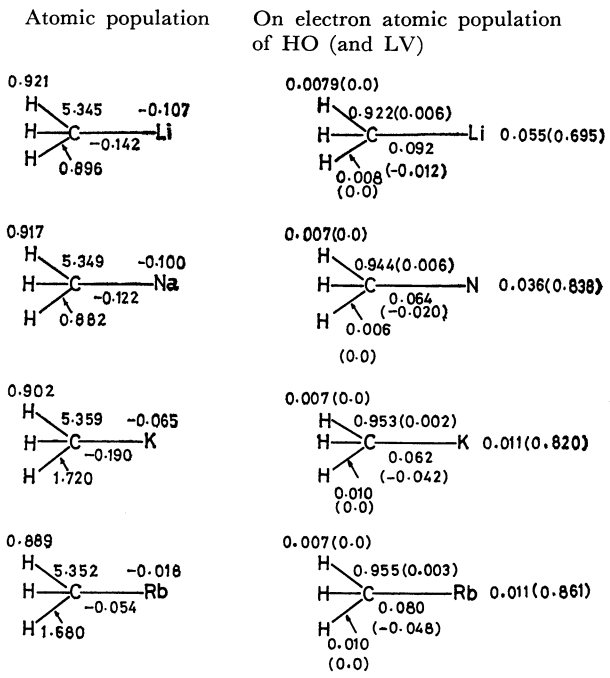

Fig. 1. Atomic population of the group I methyl compounds. (Values in parentheses are those of S-M orbitals.)

In regard to the associated polymer of alkyllithium, the present calculations give the interesting information that $(CH_3Li)_2$ is less stable than CH_3Li by *ca.* 0.25 eV per CH_3Li unit, while $(CH_3Li)_4$ is more stable by 0.34 eV per CH_3Li unit, neglecting core repulsions and electron-electron interactions (see Table 2). From this point of view, from their detailed calculations of the total energy, Cowley and White[29] have demonstrated the stability of $(CH_3Li)_4$ in comparison with

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Table 2. Atomic and overlap populations for the methyllithium monomer, dimer, and tetramer

Compound	Atom	EHMO	Bond	EHMO	Total energy (eV) EHMO	Total energy (eV) SCF[a]
CH_3Li	Li	−0.107	Li-C	−0.152	−133.98	−282.32
	C	5.345	C-H	0.896		
	H	0.921				
$(CH_3Li)_2$	Li	−0.156	Li-Li	0.122	−267.45	—
	C	5.330	Li-C	−0.128		
	H	0.942	Li-C′	−0.102		
			C-H	0.902		
$(CH_3Li)_4$	Li	−0.282	Li-Li	−0.092	−537.26	−1241.75
	C	5.388	Li-C	−0.092		
	H	0.996	Li-C′	−0.054		
			C-H	0.964		

a) These data were cited from Ref. 29 for comparison.

Table 3. Overlap populations and energy states of group II methyl compounds

Compound	Bond	M(X-Y)[a]	Energy (eV) HO[b]	Energy (eV) LV[c]	Energy (eV) Total
$(CH_3)_2Be$	Be-C	0.106	−11.83	−4.32	−266.88
	C-H	0.886			
$(CH_3)_2Be_2$	Be-C_b	0.282	−12.31	−11.25	−541.84
	Be-C_t	0.346			
	Be-Be	0.274			
	C_b-H	0.718			
	C_t-H	0.728			
$(CH_3)_2Mg$	Mg-C	0.174	−11.80	−4.49	−266.30
	C-H	0.856			
CH_3MgBr[d]	Mg-C	0.308	−12.22	−6.78	−256.17
	Mg-Br	0.118			
	C-H	0.820			
$(CH_3)_2Ca$	Ca-C	0.104	−11.68	−5.19	−264.61
	C-H	0.836			

a) Total bond population of X-Y.
b) HO-orbital except that of Be-derivative is mainly depended on p-C orbital in $sp\sigma$-bond of M-C.
c) LV-level indicates that of the lowest vacant s-M orbital except Be-derivatives.
d) This was listed for the comparison's sake (Geometry is shown in Fig. 2).

that of CH_3Li (28.12 eV per CH_3Li unit). On the other hand, the electron population on the lowest vacant s-metal orbital[49] and that on the bond of metal-carbon at the highest occupied level[50] (see Fig. 1) may support a trend of the reactivities[1,2] such as RLi<RNa<RK<RRb<RCs for the addition reactions with carbonyl groups, because the larger value of the former may reflect the reactivity of the metal cation to the nucleophiles, while that of the latter may suggest a measure of the resistance to the cleavage of the M–C bond.

The Electronic States of Group II Methyl Compounds. Before speaking about the electronic states of the compounds, it may be mentioned that beryllium compounds usually have striking covalent natures which can be attributed to the small size of the metal (its metallic radius, 0.89 Å, is much smaller than Li's 1.22 Å), and have a far less electropositive character than Li in all aspects of their chemical behavior, while compounds of Ca, Ba, Sr, and Ra are all essentially ionic, though some Mg compounds show a covalent nature. Generally, the polymer structures of beryllium compounds such as the bridged $(BeCl_2)_n$ are well accepted; Mg compounds also have a polymer chain similar to that of Be compounds.[20] However, it can hardly be expected that a polymer chain exists in other group II metal compounds because of the striking ionic nature of the compounds. The energetic states and the overlap population (M(X–Y)) of the group II methyl compounds are summarized in Table 3. As Table 3 shows, M(X–Y) does not indicate reliable information about the polymeric character of Be and Mg derivatives. However, the characteristic covalency of Be compounds is reflected in the relatively large S(Be–C) value of 0.254 as compared with those of S(Mg–C) and S(Ca–C) (0.030 and 0.034 respectively), considering that S(Be–C) relates directly to (Be–C), which is immediately influenced by the selected ionization potentials (vsip) of Be and C. On the other hand, the total energies of $(CH_3)_2Be$ and $(CH_3)_4Be_2$ suggest, interestingly, that $(CH_3)_4Be_2$ is more stable than $(CH_3)_2Be$; the stabilized energy is about 4.04 eV per $(CH_3)_2Be$ unit. Moreover, the AO populations of the p_z-Be orbitals of both $(CH_3)_2Be$ and $(CH_3)_4$-

49) The value of this population indicates the electron-vacancy of the orbitals.
50) The highest occupied orbital is the $2p$-carbon one used for the formation of the σ-bond of M–C.

Table 4. Electronic states of group III methyl compounds

Compound	Bond	M(M-C)[a]	N_M(S)[b]	N_M(X)[b]	N_M(Y)[b]	N_M(Z)[b]	Energy (eV) HO	Energy (eV) LV[c]	Energy (eV) Total
$(CH_3)_3B$	B-C	0.536	0.710	0.241	0.241	0.209	−11.99	−4.62	−404.33
	C-H	0.828 (0.812)	(0.522)	(0.522)	(0.410)		(−12.30)	(−6.23)	
$(CH_3)_3Al$	Al-C	0.402	0.819	0.239	0.239	0.018	−12.01	−5.89	−402.16
	C-H	0.834 (0.603)	(0.165)	(0.165)	(0.052)		(−12.14)	(−5.01)	
$(CH_3)_6Al_2$	Al-C_b	0.322 (0.313)							
	Al-C_t	0.246 (0.704)							
	Al-Al	0.422 (0.468)	0.813	0.680	0.500	0.735	−11.32	−11.17	−799.81
	C_b-H	0.728 (0.790)							
	C_t-H	0.740 (0.800)							

a) Overlap population of metal-carbon.
b) AO population of the metal. D_3-ligand plane of the compound is on X-Y cross section, and the notations, X, Y, and Z, denote the p_x, p_y, and p_z-orbitals of metal, respectively.
c) This level corresponds to that of p_z-metal orbital.
Data in parentheses are those in Refs. 26 and 29 for dimethyl-boron or aluminum and dimethyl aluminum dimer, respectively.

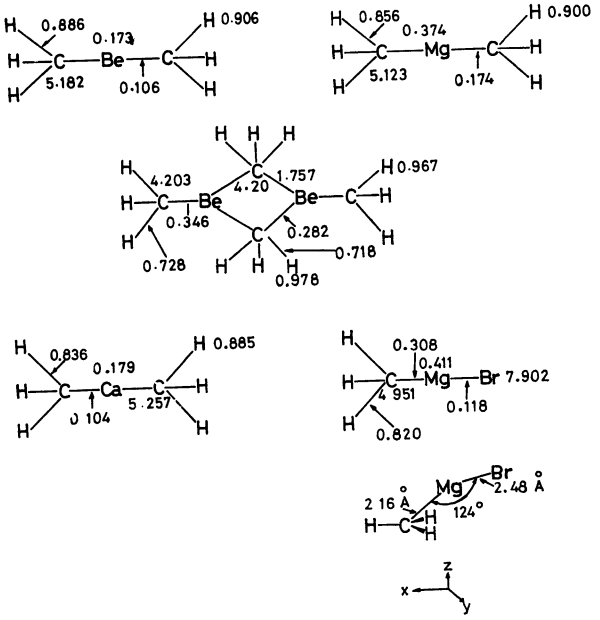

Fig. 2. Atomic populations of group II methyl compounds.

Be_2 (0.043 and 0.047 respectively) also predict the stability of the dimer, because the electrons on the p_z-orbital contribute to the stabilization of the dimer through the π-bond of Be–C. Under these circumstances, the relatively strong bond of Be–Be is enough to compensate for the weak bond of Be–C_b (see Fig. 2). However, the π-bond of Be–Be contributes little to this bond formation (less than 1.0%[51] of the total overlap). The above considerations may be understood from the data listed in Table 5. Furthermore, another striking feature of the dimer is also reflected in the atomic charge of the metal; that is, the bridged Be-atom (+0.24) is less positive than the Be in the monomer (+0.83). The charges of the metals (Be=+0.83, Mg=+0.63, and Ca=+0.82, as estimated from the atomic populations in Fig. 2) are, however, not in good agreement with such a trend of the reactivities[1,2] as RBe<RMg<RCa in the carbonyl group-addition reaction, probably because the behavior of RM (M=metal) in the reaction system can hardly be evidenced only from the electronic states of RM-monomers; that is, the interaction between the carbonyl groups and the monomer or dimer of RM was not taken into consideration at the molecular level. In connection with the stabilized dimer of $(CH_3)_4Be_2$, the energy state of the dimeric methyl beryllium is illustrated in Fig. 3.

Electronic States of the Group III Methyl Compounds. The most characteristic feature of the compounds of this series is the dimerization of the lower trialkyls of Al in spite of the stable monomers of trialkyls of B, Ga, In, and Tl in vapor and in solution.[52] Therefore, it is of interest to investigate the difference in the electronic states between trialkyl boron and trialkyl aluminum. The data as to these compounds are listed in Table 4. The smaller metal-carbon overlap population of $(CH_3)_3Al$ than that of $(CH_3)_3B$ first indicates less stability in $(CH_3)_3Al$. The most remarkable feature of $(CH_3)_3Al$ appears in the small AO population of the p_z-Al orbital (used for the π-bond of Al–C) as compared with $(CH_3)_3B$. This indicates the weak π-bond of Al–C. Considering the large contribution of the π-bond to the stabilization of the molecule, the remarkably small π-bond nature of Al–C (see Table 5) suggests the improbable existence of the trialkyl aluminum monomer. These circumstances are reflected in the slight different atomic populations of $(CH_3)_3B$ and $(CH_3)_3Al$, as is indicated in Fig. 4. However, the total energy of $(CH_3)_6Al_2$ failed to suggest its stability, as is indicated in Table 4. It is plausible here to focus on the lowest vacant p_z-

51) The π-bond character formed by the p_z-orbitals of the two Be atoms was 0.23% of the total overlap, neglecting the contribution of p_x-orbitals.
52) N. Muller and A. L. Otermat, *Inorg. Chem.*, **4**, 296 (1965).

$(CH_3)_2Be$		$(CH_3)_4Be_2$
		6.306 eV $0.84(X_{Be_1}-X_{Be_2})+0.64(X_{C_{15}}-X_{C_{10}})$[a]
		0.652 $1.00(Z_{Be_2}-Z_{Be_1})$
$1.22S_{Be_9}-0.40(Y_{C_1}-Y_{C_5})-0.37(S_{C_1}+S_{C_5})$	−0.015	−1.068 $0.63(S_{Be_2}-S_{Be_1})$
$1.04X_{Be_9}-0.34(X_{C_1}+X_{C_5})$	−4.423	−4.253 $-0.58(S_{Be_1}+S_{Be_2})+0.35(Y_{C_3}-Y_{C_4})$
$1.04Z_{Be_9}-0.34(Z_{C_1}+Z_{C_5})$		−4.621 $-0.63(Z_{Be_1}+Z_{Be_2})+0.37(Z_{C_3}+Z_{C_4})$
		−10.807 $0.44(X_{C_3}+X_{C_4})+0.41(Y_{C_3}+Y_{C_4})+0.33(Y_{C_{11}}+Y_{C_1})$
		−11.085 $0.51(Y_{C_{11}}+Y_{C_{15}})+0.37(X_{C_3}+X_{C_4})$
		−11.253 $-0.49(Y_{C_{11}}-Y_{C_{15}})-0.35(X_{C_3}-X_{C_4})$
$0.64(Y_{C_1}+Y_{C_5})-0.20Y_{Be_9}+0.11(S_{C_1}+S_{C_5})$	−11.834	−12.315 $0.37(Y_{C_{11}}-Y_{C_{15}})+0.37(X_{C_3}-X_{C_4})+0.33(Y_{C_3}-Y_{C_4})$
		−12.850 $0.34(Y_{Be_1}+Y_{Be_2})+0.30(Y_{C_{11}}+Y_{C_{15}})+0.24(S_{C_{11}}-S_{C_{15}})$
		−12.983 $0.34(Y_{Be_2}-Y_{Be_1})$

a) The notations, X_{Be_1} and X_{Be_2}, denote the the p_x-Be orbitals of Be_1 and Be_2, respectively, and so on. Small coefficients below 10^{-1} and the values of H were neglected for the sake of simplicity.

Fig. 3 Energy diagrams of $(CH_3)_2Be$ and $(CH_3)_4Be_2$.

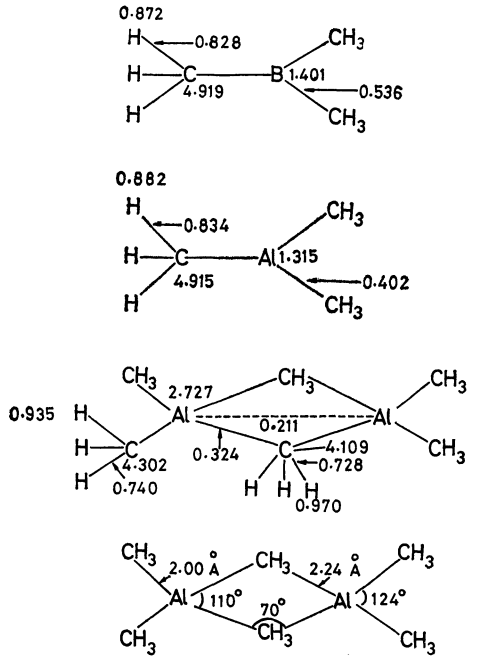

Fig. 4. Atomic and bond populations of $(CH_3)_3B$, $(CH_3)_3Al$ and $(CH_3)_6Al_2$.

Table 5. Overlap populations of σ- and π-bonds

Compound	N(M-C)[a] σ	π	Total
CH_3Li	−0.136	−0.016	−0.152
CH_3Na	−0.112	−0.010	−0.122
CH_3K	−0.038	−0.004	−0.042
CH_3Rb			
$(CH_3)_2Be$	0.070	0.036	0.106
$(CH_3)_4Be_2$	—[b]	0.012[c]	0.282(Be-C_b)
	—[b]	0.018[c]	0.346(Be-C_t)
	—[b]	0.0006[c]	0.274(Be-Be)
$(CH_3)_2Mg$	0.176	−0.002	0.174
$(CH_3)_2Ca$	0.106	−0.002	0.104
$(CH_3)_3B$	0.482	0.054	0.536
$(CH_3)_3Al$	0.398	0.006	0.402

a) Total bond population of metal-carbon.
b) Separation of the bond character into σ and π is not possible.
c) π-Bond overlap of p_z-orbitals on M and C (see Fig. 3).

metal orbital in connection with the reactivity of the compounds, because the electron-vacancy of the boron- or aluminum-orbital (M_B(LV) or M_{Al} (LV) respectively) may play an important role in the reaction with nucleophiles. M_B(LV) and M_{Al}(LV) are 0.880 and 0.991 respectively. Therefore, the appreciable vacancies of the orbitals on both metals may suggest the effectiveness of the orbitals for the attack of nucleophiles. In this point of view, Gilman[1] has reported the order of the reactivity for the attack of nucleophiles as RB<RAl. Finally, the π- and σ-overlap population of M–C in a series of the group I, II, and III methyl compounds are recorded in Table 5 for the sake of comparison.

The results obtained from the present study may be summarized as follows:

a) The striking nature of the covalency of lithium compounds appeared in the large total orbital-overlap. In all Group I methyl compounds, the electron-localization occurred on the C-atom in CH_3 over the C-unit charge. As to the stabilization of the alkyllithium polymer, $(CH_3Li)_4$ was more stable than CH_3Li in the order of *ca.* 0.34 eV per unit, although $(CH_3Li)_2$ was less stable than CH_3Li (*ca.* 0.25 eV per CH_3Li unit).

b) The dimer structure of $(CH_3)_4Be_2$ was stabilized in the energy of 4.04 eV per $(CH_3)_3Be$ unit, and the contribution of the σ-type Be–Be bond to the stabilization was relatively large, while that of the π-type bond was very small.

c) The π-bond character of the monomer of $(CH_3)_3Al$ was about 1/9 that of $(CH_3)_3B$; this would well explain the stability of trialkyl boron monomers.

The present calculations were carried out on the FACOM 230.60 computer at the Computer Center of the University of Kyushu.