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Theoretical Studies of Metallo (Li and Na)−Ene Reaction Mechanisms

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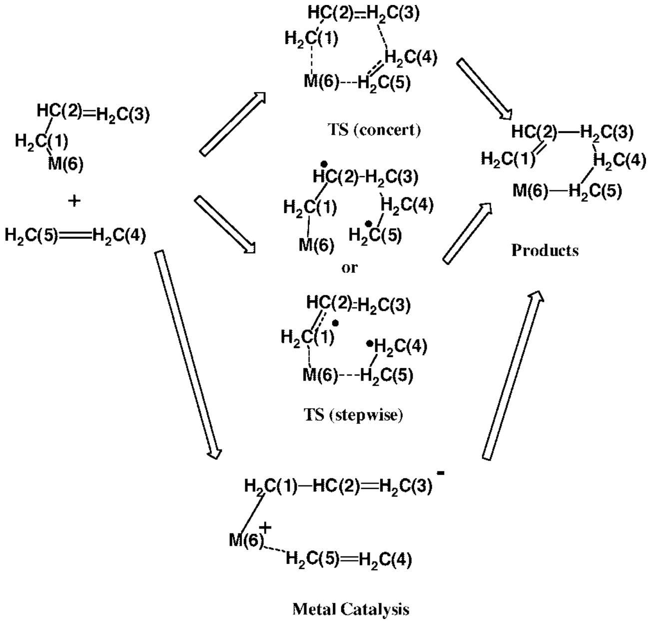
The reaction mechanisms of allyl−lithium and allyl−sodium with ethylene were studied by ab initio molecular orbital (MO) methods. The reaction mechanisms were analyzed by a CiLC-IRC method on the basis of ab initio CASSCF MOs. The ene reaction pathways of allyl−Li and allyl−Na with ethylene were located. The complex between allyl−metal and ethylene for both systems is found in the first step of the reaction, and then the metal migration and new C−C bond formation occur synchronously through the transition state. The complexation energies are −13.2 and −9.6 kcal/mol for Li and Na systems, respectively. The activation energy barriers from the reactants are 3.5 kcal/mol for the Li system and 2.0 kcal/mol for the Na system at the MRMP2 calculation level. These barriers are significantly lower than that of the ene reaction of propene with ethylene as the parent reaction. The CiLC-IRC analysis shows that the reaction of allyl−metal with ethylene is a concerted ene reaction mechanism, not a metal catalysis and/or a stepwise reaction.

1. Introduction

Pericyclic reactions may be the most important class of organic reactions. The mechanisms of the reactions have been the subject of the most heated and interesting controversies. The mechanisms of the concerted pericyclic path and stepwise path, involving a diradical or zwitterions, have been discussed. The ene reactions are one of the most interesting pericyclic reactions, and also have been the subject of controversies.[1−11] Although the ene reaction of propene with ethylene as the simplest reaction has not been observed experimentally, the reaction mechanism is important as the parent reaction. The reaction has been studied[11−14] by some theoretical methods. The concerted pericyclic mechanism for the reaction of propene with ethylene was proposed by ab initio MO and density functional methods. Recently, we[11] proposed that the stepwise pathway for the reaction of propene with ethylene is more favorable than the concerted one by the multireference molecular orbital methods. On the other hand, metallo-ene reactions have been studied experimentally. The metallo-ene and/or closely related addition of allyl−lithium,[15] −magnesium,[16−18] −zinc,[19−24] −aluminum,[25] and −boron reagents[26,27] to alkenes, acethylene, allenes, and enol ethers have been reported.

The most of the objects of these studies are regio- and stereoselectivity for the reaction, and some studies discussed as metal catalytic reaction mechanisms. The mechanisms of metallo-ene reactions were not well-known theoretically. For the metallo-ene reactions, it is important where the mechanism is a real concerted ene reaction, a stepwise reaction, or metal catalysis reaction. Some stationary points of cyclic reactions of allyl−lithium and ethylene were calculated[28] by single-reference molecular orbital levels. However, the multireference MO calculation levels are sometimes very important for the pericyclic reaction mechanisms including diradical states as stepwise process. Especially, the electronic state of the migration metal atom is also interesting in the mechanism as shown in the parent reaction, and is important to be treated by the multireference MO methods. Therefore, in this paper, the potential energies of metallo-ene reactions of allyl−lithium and −sodium with ethylene were presented with multireference MO levels. These reaction mechanisms were analyzed by a CiLC-IRC method on the basis of a multireference MO method.



2. Theoretical Treatment

The equilibrium and transition state geometries for the reactions treated here were determined using a CASSCF method[29] with analytically calculated energy gradients and the 6-31G(d,p) basis set.[30,31] Six active orbitals with six electrons relating to the reactions as corresponding to the ene reaction of propylene and ethylene in our previous paper[11] were included. Namely, these active orbitals correspond to the π and π^* orbitals of allyl and ethylene and σ and σ^*

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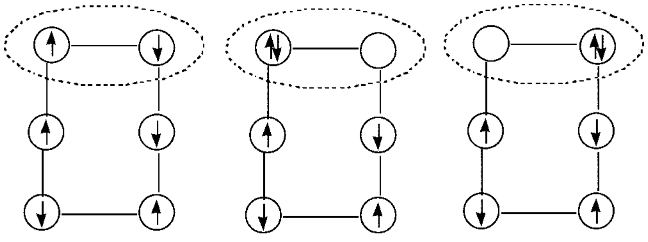
orbitals of Li−C bond for the reactants, and the orbitals relate to the products. All configurations in active spaces were generated. A vibrational analysis was performed at each stationary point found to confirm its identity as an energy minimum or a transition structures. Additional calculations were performed to obtain improved energy comparison calculations with the CASSCF optimized structures with electron correlations incorporated through the multiconfigurational second order perturbation theories (MRMP2)[32] with the 6-31G(d,p) and the 6-311+G(d,p) basis sets.[33] The intrinsic reaction coordinate (IRC)[34,35] was followed from the transition state toward both reactants and products.

To interpret the mechanisms for the reactions, a CiLC (configuration interaction/localized molecular orbital/CASSCF) analysis was carried out following a method described elsewhere.[36−38] In brief, the method is as follows: (1) The CASSCF is calculated to obtain a starting set of orbitals for the localization procedure. (2) The CASSCF-optimized orbitals are then localized, and all CASSCF-optimized MOs in the active spaces are subjected to the Boys localization procedure.[39] The calculated localized orbitals are atomic in nature. (3) Using the localized MOs as a basis, a full configuration interaction (CI) in the active spaces with determinants level is used to generate electronic structures and their relative weights in the atomic-like wave functions. The total energy calculated by the CI method in the process corresponds to that by the CASSCF calculation. The calculation procedures are repeated along the pathway, which we call a CiLC-IRC for the procedure. In the notation of the valence-bond-like model, the electronic structures of a bond on the basis of CiLC calculation were presented roughly as one singlet coupling term and two polarization terms. The representation with the three terms (one singlet coupling and two polarization terms) for a bond has been successful[40,41] to explain the bond formations and bond extinction along a chemical reaction path.



Singlet Coupling **Polarization A** **Polarization B**

The calculations of the CiL-IRC analysis were performed with the GAMESS program package,[42] and the others were made with the use of the Gaussian03 program package.[43]

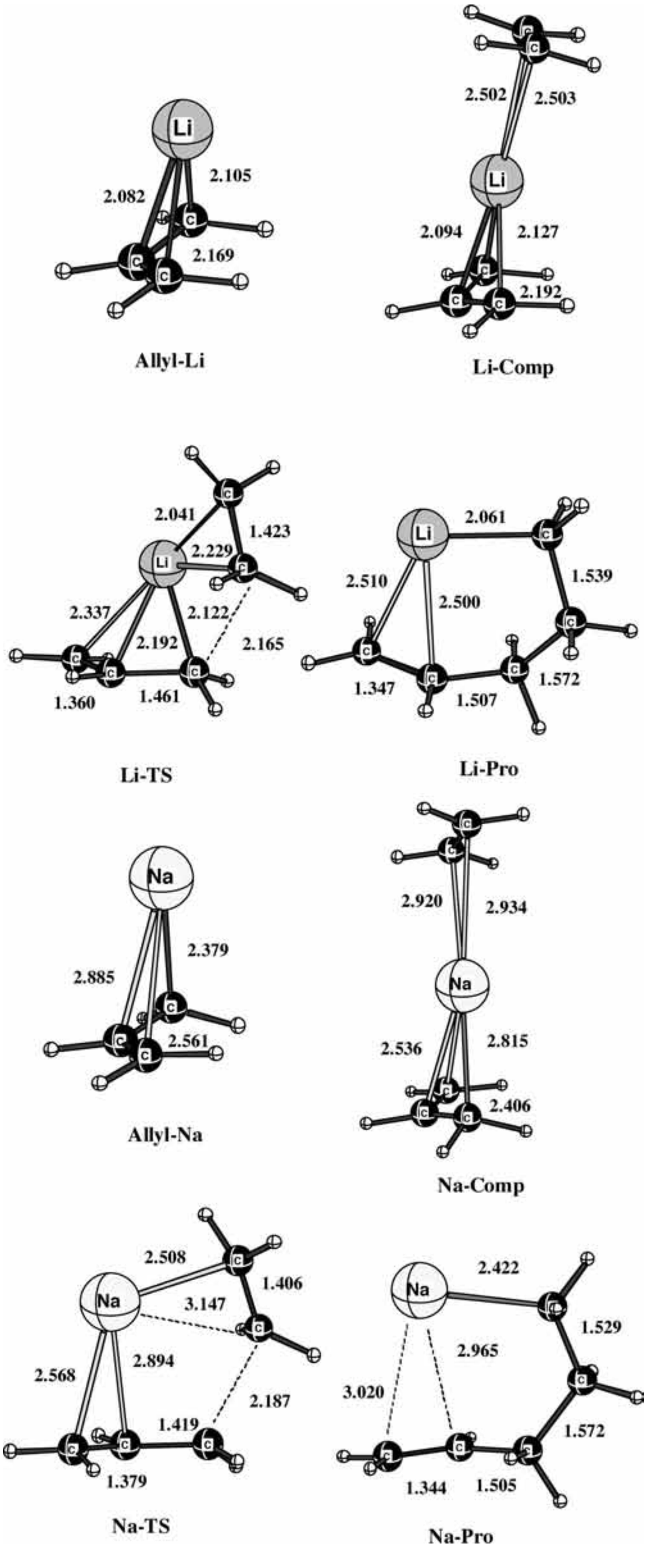


Figure 1. Geometric parameters of the complexes, transition states, and products of the reaction of allyl−metal with ethylene using the CASSCF/6-31G(d,p) method. All bond lengths are in Å.

3. Results and Discussion

3.1. Geometry and Potential Energy. The stationary points of the reactions of allyl−lithium and −sodium with ethylene are shown in Figure 1. The structure of allyl−lithium is the complex between the allyl and Li metal atom and is not analogous to propene. The structure has C_1 symmetry, only slightly different from C_s symmetry. Although the C_s symmetry structure obtained by our CASSCF calculation has one negative eigenvalue for the force constant matrix because of nonmixing of a′ and a″ orbitals of Li atom from the symmetry for the active space, the real structure probably has C_s symmetry. In fact, the CASSCF(4,7) level[44] calculation including three isolated vacant orbitals of Li atom gave the stable C_s symmetry structure. However, the energy difference between C_1 and C_s symmetry structures is only 0.008 kcal/mol. For the C_1 symmetry structures such as the transition state and product for the reaction, the inclusion of the extra active spaces is not important. The complex (Li-Comp) between allyl−Li and ethylene has also C_1 symmetry and the complex with C_s symmetry has one negative eigenvalue

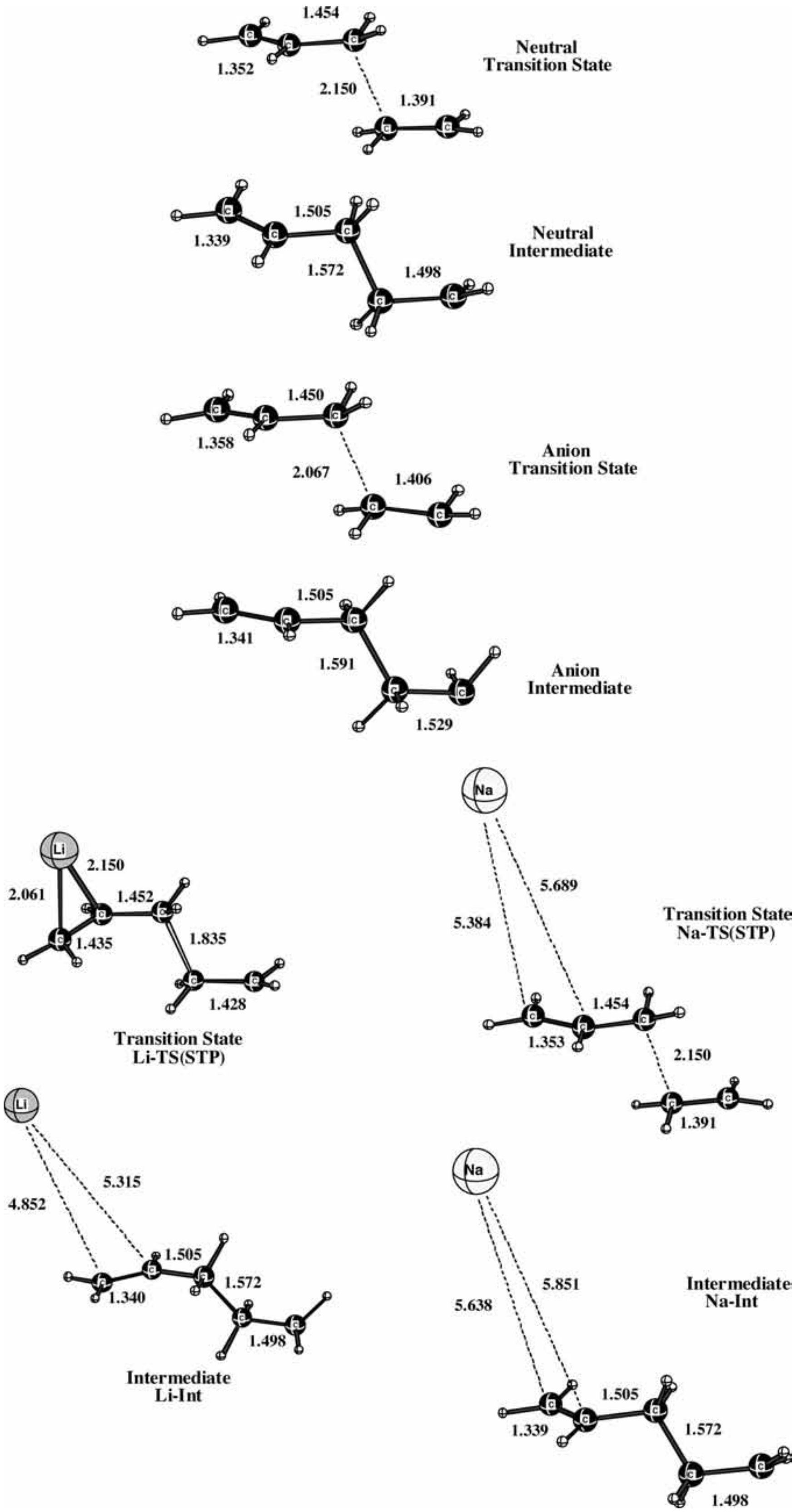


Figure 2. Geometric parameters of the transition states, and intermediates of the reactions 1 and 2 and the stepwise reactions of allyl−metal with ethylene using the CASSCF/6-31G(d,p) method. All bond lengths are in Å.

for the force constant matrix. However, the energy difference between the complexes with the C_s and C_1 symmetry is only 0.007 kcal/mol at the CASSCF/6-31G(d,p) level. Accordingly the difference of the structures by the symmetry is negligible energetically. The bond distances of Li−C(ethylene part) of Li-Comp are larger than those of Li−C(allyl part). The complexation energy is about 13 kcal/mol at the MRMP2/6-311+(d,p) level. Consequently, Li-Comp is a weak complex between allyl−Li and ethylene. For the transition state, the bond distance of Li−C_5 (of ethylene) is close to the Li−C_5

TABLE 1: Relative Energies (kcal/mol) for the Reactions of Allyl−Li and Allyl−Na with Ethylene[a]

	CASSCF		MRMP2	
	6-31G (d,p)	6-311+G (d,p)	6-31G (d,p)	6-311+G (d,p)
allyl−Li + $H_2C{=}CH_2$	0.0	0.0	0.0	0.0
Li-Comp	−8.97	−7.24	−15.28	−13.24
Li-TS	17.63	20.09	2.55	3.45
Li-Pro	−8.97	−4.87	−14.87	−12.16
Li-TS(STP)	49.66	51.54	31.88	30.35
Li-Int	19.09	23.36	27.37	31.59
allyl−Na + $H_2C{=}CH_2$	0.0	0.0	0.0	0.0
Na-Comp	−6.45	−5.09	−11.15	−9.55
Na-TS	18.23	21.26	0.23	2.03
Na-Pro	−11.30	−7.68	−18.66	−15.70
Na-TS(STP)	23.91	27.62	25.85	28.95
Na-Int	0.09	4.01	6.83	11.32

[a] The zero point correction is not included.

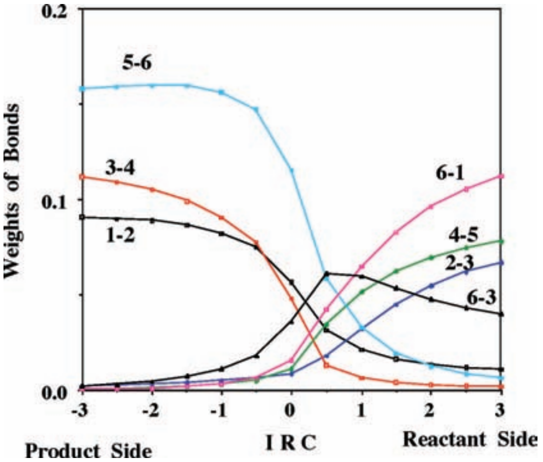


Figure 3. Weights of bonds of CiLC calculation along the IRC pathway of the reaction of allyl−Li with ethylene. The units are bohr amu$^{1/2}$.

bond distance of the product (Li-Pro) and the distance of new C_3−C_4 bond is a little shorter by 0.076 Å than that[11] of the concerted type transition state of ene reaction of propene with ethylene. Also from the comparison of other geometrical parameters with the concerted transition state of the ene reaction of propene with ethylene, the transition state (Li-TS) of the reaction is a later transition state. This corresponds to the Hammond postulation,[45] because the heat of reaction of this reaction is less than that of the ene reaction of propene with ethylene. The other interesting point at the transition state is that the Li−C_1 bond distance of Li-TS is about 0.2 Å longer than the Li−C_3 bond distance. If this reaction is a typical concerted ene reaction, the Li atom migrates from the C_1 atom (not the C_3 atom) to the C_5 atom. Accordingly, the bond nature of Li−C_1 and Li−C_3 is interesting in the mechanism. The electronic states of both bonds will be discussed in the following section. The activation energy barrier at the transition state is quite low, only 3 kcal/mol from the reactant at the MRMP2 level. This barrier is about 48 kcal/mol lower than that of the concerted ene reaction of propene and ethylene. This probably comes from the difference of the bond breaking energies of one allyl−π bond and π bond of propene and from the energy difference of the Li−C and H(migrating)−C bonds.

For the reaction of allyl−Na and ethylene, the stable structure of allyl−Na is C_1 symmetry and the structure with C_s symmetry has one negative eigenvalue for the force constant matrix. The energy difference between the C_1 and C_s symmetry structures is only 0.98 kcal/mol. For the complex between allyl−Na and ethylene, the structure with C_s symmetry has one negative eigenvalue for the force constant matrix and one (Na-Comp) with C_1 symmetry has no negative eigenvalue. The energy difference of the C_1 and C_s symmetry structures of Na-Comp is only 0.69 kcal/mol at the CASSCF level. From the comparison of the geometrical parameters for Li and Na reaction systems, the transition state (Na-TS) is earlier than Li-TS. This also corresponds to the Hammond postulation[45] from the difference of the heat of reactions of Li and Na systems. For the transition state, the activation energy barriers from the reactants (allyl−metal and ethylene) are 17.6 and 18.2 kcal/mol for Li and Na systems at the CASSCF level, respectively. These energy barriers are the middle of the energy barriers of C−C bond formation for reaction 1 [allyl radical + ethylene: $\Delta E^{\ddagger} = 21.7$ kcal/mol] and reaction 2 [allyl anion + ethylene: $\Delta E^{\ddagger} = 15.9$ kcal/mol], and the geometries of the transition states and intermediates are shown in Figure 2.

$$H_2CCHCH_2\ (\text{neutral}) + H_2C{=}CH_2 \rightarrow H_2C{=}CH{-}CH_2{-}CH_2{-}CH_2 \quad (1)$$

$$H_2CCHCH_2^-\ (\text{anion}) + H_2C{=}CH_2 \rightarrow H_2C{=}CH{-}CH_2{-}CH_2{-}CH_2^- \quad (2)$$

$$M^+\text{--}C_3H_5^- + H_2C{=}CH_2 \rightarrow M^+\text{--}C_5H_9^- \quad (3)$$

Accordingly, the reactions treated here are not pure metal-catalysis as reaction 3. These energy barriers reduce to 3.5 and 2.0 kcal/mol for Li and Na systems by the MRMP2/6-311+G(d,p) level, respectively.

We tried to search the stepwise transition state for both systems, but we could not find them on the approaching path of ethylene from the same side of metal for π orbitals of allyl. On the approaching path of ethylene from the reverse side of metal for π orbitals of allyl, the transition states and intermediate products for Li and Na systems were located as shown in Figure 2. For the transition state (Li-TS(STP)) of Li system, the structure is similar to the stepwise one of the ene reaction type. Along the IRC pathway after the transition state as shown in the intermediate (Li-Int), Li atom removes far from the C_1 atom (also C_2 and C_3). The energy barrier of Li-TS(STP) is extremely high (about 50 kcal/mol at the CASSCF and 32 kcal/mol at the MRMP2; see Table 1). Consequently, the stepwise pathway for the reaction of allyl−Li and ethylene does not occur. For the transition state (Na-TS(STP)) of Na system, the structure looks like the transition state of reaction 1 plus a Na atom; namely, the distance between Na and C_1 (also C_2 and/or C_3) is extremely long. The energy barrier is also higher than the concerted one. After the transition state, the structure of the intermediate (Na-Int) is also that of reaction 1 plus Na atom.

For the concerted type, the heat of reaction for the Li system is −12.2 kcal/mol, and about 3.5 kcal/mol less than that for the Na system. Therefore two reactions are similar energetically.

3.2. Reaction Mechanisms. To study the electronic mechanisms of the reaction of allyl−Li with ethylene, the variations of the weights of the related bonds along the reaction pathway by the CiLC analysis are shown in Figure 3. In the figure, x−y indicates the bond between x and y atoms

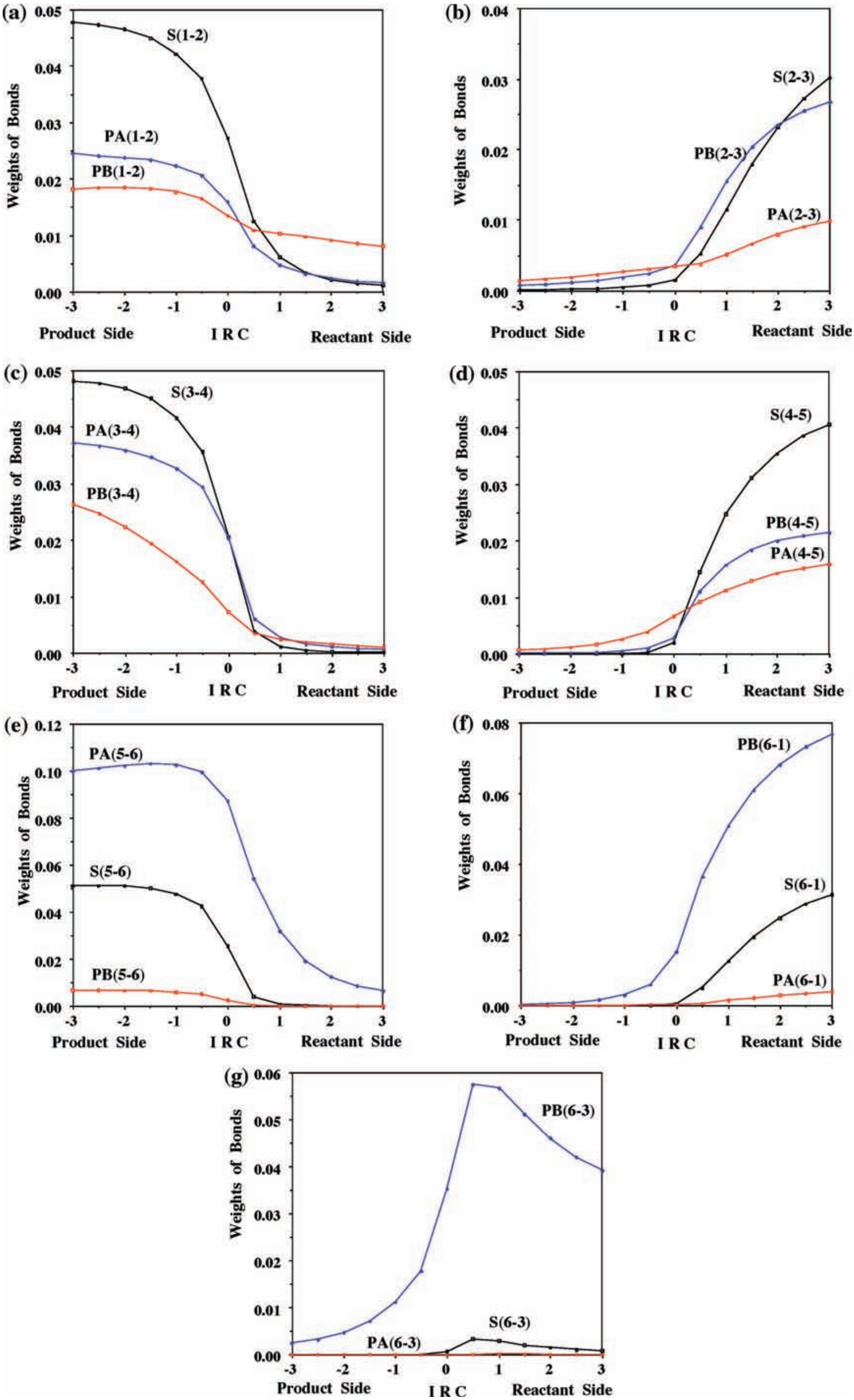


Figure 4. Weights of singlet coupling and polarization terms for each bond by CiLC calculation along the IRC pathway of the reaction of allyl−Li with ethylene. The units are bohr amu$^{1/2}$.

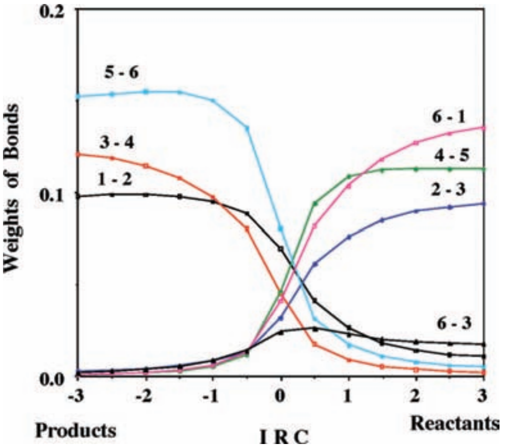


Figure 5. Weights of bonds of CiLC calculation along the IRC pathway of the reaction of allyl−Na with ethylene. The units are bohr amu$^{1/2}$.

(orbitals). The variations of the weights of the singlet coupling (S($x-y$)) and the polarization terms (PA($x-y$) and PB($x-y$)) of each bond are shown in Figure 4, where PA($x-y$) means the polarization term that the electron pair localizes to x atom (orbital) and PB($x-y$) means the polarization term that the electron pair localizes to y atom (orbital). The bond formation and the bond breaking occurs at the region (a little reactant side from the transition state) between 0 and 1 bohr (amu)$^{1/2}$ on the IRC pathway as shown in Figure 3. The reaction occurs almost synchronous, but not at one time. That is to say, the π bond exchange between C_2-C_3 and C_2-C_1 occurs first, and also the Li migration (the σ bond exchange of Li−C_1 and Li−C_5) occurs. After then, the C_3-C_4 σ bond is formed. Consequently, it is considered that the driving force of the reaction is probably the π bond exchange between C_2-C_3 and C_2-C_1. A more interesting point from the CiLC analysis is the variation of the weight of Li−C_3 bond. The weight of the Li−C_1 bond is larger than that of the Li−C_3 bond for the reactant side. At the region of the bond formation and the bond breaking, the weight of Li−C_3 bond is larger than that of the Li−C_1 bond. This corresponds to these bond distances at the transition state structure as pointed out in the previous section. Specifically, the bond distance of the Li−C_1 at the transition state is longer than that of the Li−C_3. If a Li atom migrates to the C_1 atom, this reaction is not the "typical concerted ene reaction". However, the nature of both bonds is different at the composition of bonds as shown in Figure 4f,g. The Li−C_1 bond comprises the polarization term of PB(6−1) and the singlet coupling term of S(6−1), and the Li−C_3 bond almost comprises the polarization term of PB(6−3). Consequently, Li−C_1 includes the covalent bond nature and Li−C_3 has only the ionic character. As shown in Figure 4e, although the Li−C_5 bond is polarized a lot, it includes the covalent bond nature as the Li−C_1 bond. From Figure 4b, the electron pair of the C_2-C_3 bond localizes to the C_3 atom (p_π orbital). The C_3-C_4 bond formation occurs at the latter stage (Figure 2) including ionic character as shown from the ratio of the weights of the singlet coupling and the polarization terms (Figure 4c). The formed C_1-C_2 π bond has typical covalent character as shown in Figure 4a and the deformed C_4-C_5 π bond has also typical covalent nature as shown in Figure 4d. Accordingly, it is considered that the reaction of allyl−lithium with ethylene can be classified as "the concerted ene reaction" in the pericyclic reaction.

To compare the reaction mechanisms of the Li and Na systems, the variations of the weights of the related bonds of the reaction of allyl−Na with ethylene along the IRC pathway by the CiLC analysis are shown in Figure 5. The variations of the weights of the singlet coupling and the polarization terms of each bond are also shown in Figure 6. From the comparison of Figures 3 and 5, the bond formation and the bond breaking occurs at the region of near the transition state, and the region is narrower (more synchronous) than that of the Li system. The bond exchange between C_2-C_3 and C_1-C_2 and the Na migration between C_1 and C_5 atoms occur slightly earlier than the C_3-C_4 bond formation. The weight of the Na−C_3 bond is not much large at the region of near the transition state such as that of the Li system. This corresponds also to the bond distance of Na−C_3 at the transition state structure (Na-TS). The character of Na−C_3 interaction is also similar to that of Li−C_3 as shown in Figure 6g. The bonds of Na−C_5 and Na−C_1 have also ionic character (see Figure 6e,f). Although the electron pair of the C_2-C_3 bond for the Li system localizes to the C_3 atom for the reactant side, the C_2-C_3 bond for the Na system localizes only slightly to C_3 atom as shown in Figure 6b. Also the C_3-C_4 bond is formed with ionic character from Figure 6c. The bonds of C_1-C_2 (π) and C_3-C_4 (σ) were formed with covalent character as shown in Figure 6a,c. In the comparison with the Li system, the reaction of allyl−sodium with ethylene occurs with less polarized mechanisms and also the concerted ene reaction mechanism.

4. Conclusions

The potential energy surfaces of the metallo-ene reactions of allyl−lithium and allyl−sodium with ethylene were calculated by ab initio CASSCF and MRMP2 calculation levels. The complexes between allyl−metals and ethylene are formed at the first step in the reaction, and then the metal migration and the new C−C bond formation occur through the transition state. The complexation energy of allyl−Li and ethylene is −13.3 kcal/mol at the MRMP2/6-311+G(d,p) level, and more stable by 3.7 kcal/mol than that of allyl−Na and ethylene. For the transition state, the activation energy barriers from the reactants (allyl−metal and ethylene) are 17.6 and 18.2 kcal/mol for the Li and Na systems at the CASSCF level, respectively. These energy barriers are reduced to 3.5 and 2.0 kcal/mol for the Li and Na systems by the MRMP2/6-311+G(d,p) level, respectively. The energy barriers are much lower than that of the concerted type ene reaction of propene and ethylene. This comes from the weak bond energy between metal atom and carbon atom. That is to say, the metal-migration reaction has a lower activation energy than the hydrogen migration. The heat of reaction for the Li system is −12.2 kcal/mol, and about 3.5 kcal/mol less than that for the Na system. Therefore two reactions are similar energetically.

To study the reaction mechanisms from the variation of the electronic states of each bond along the IRC pathway, the CiLC-IRC analysis was performed. For the Li system, the reaction, the bond formation and bond breaking, occurs almost synchronous. Although the weight of the Li−C_3 bond increases at the region of the transition state, the nature of the Li−C_3 bond is different from that of the Li−C_1 (or Li−C_5) bond. The Li−C_3 bond comprises almost all of the polarization term, and the Li−C_1 bond comprises the polarization term and the small weight of the single coupling term. Consequently, it is considered that the reaction of allyl−Li and ethylene is the "concerted ene reaction mech-

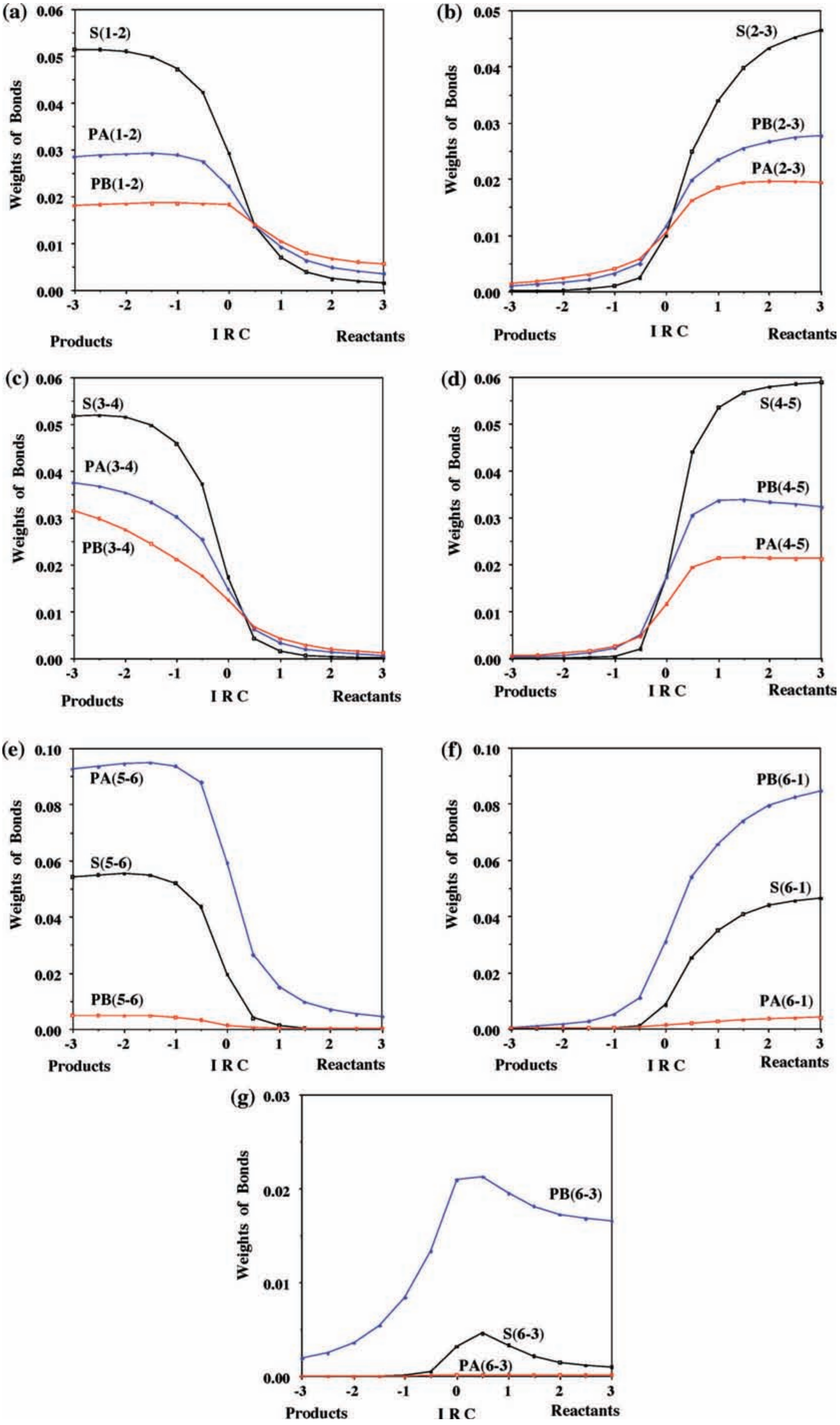


Figure 6. Weights of singlet coupling and polarization terms for each bond by CiLC calculation along the IRC pathway of the reaction of allyl−Na with ethylene. The units are bohr amu$^{1/2}$.

anism”. For the Na system, the reaction mechanism is also similar to that of the Li system and classified to the concerted ene reaction mechanism.

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