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A theoretical study of isomerization of and chloride migration in representative 1-chloro-2-methyl-1-propenylmetals

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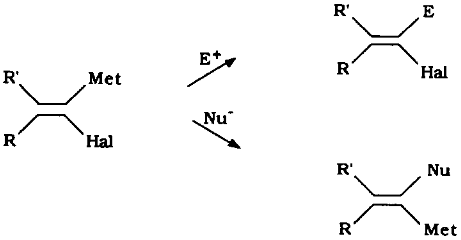
Abstract

An MNDO modified neglect of differential overlap study of the title compounds, in which the metal functionality is lithium, beryllium hydride, or dimethylboryl, addresses the existence and stereochemical integrity of a Met–Cl associated intermediate, in which Cl^- has migrated from carbon to become associated with Met. Each such intermediate was located and characterized, and they are about 23.1 kcal mol^{-1}; and about 26.2 kcal mol^{-1} respectively, less stable than the C–Cl bonded isomer. Only the beryllium hydride derivative is calculated to maintain stereochemical integrity of the Met–Cl associated form, with an approximately 8.2 kcal mol^{-1} barrier to *cis–trans* isomerization. The lithium compound is linear in the pertinent region, and therefore any stereochemical information possessed by the substrate is lost. A similar conclusion is reached for the boryl analog, since the structure is twisted 90° about the C–B bond so that the B–Cl bond is perpendicular to the molecular plane, generating a plane of symmetry. The results support the Met–Cl associated form as an intermediate in reactions with nucleophiles, which implicates metal-assisted ionization of the C–Cl bond in those cases.

Key words: Lithium; Beryllium; Boron; MNDO calculations; Correlation calculations; Alkene reactivity

1. Introduction

The reactions of α-haloalkenylmetals are synthetically useful [1–4] and mechanistically intriguing since those with electrophiles proceed with retention of stereochemistry about the double bond [2], and those with nucleophiles [2d,3,4] proceed with inversion of stereochemistry [2d,4] (see eqn. (1)), see eqn. (2).

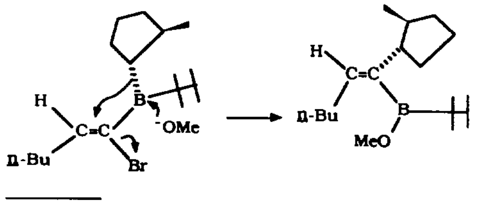


(1)

(2)

Although the stereochemistry is not known in all cases, there are examples of these reactions with a fairly wide range of metals. While there are some exceptions to the stereospecificity rule in the reactions with nucleophiles, most [5*] of these can be explained by steric effects [6a] or intramolecular complexation [6b]. It is interesting that the same stereospecificity is observed in the reactions of the analogous 1-metallo-1-halocyclopropanes: retention with electrophiles [7] and inversion with nucleophiles [4a,8]. In this cyclic system also, there are exceptions due to steric effects [8b,9] and intramolecular complexation [8d,e,10].

Two mechanisms have been proposed in order to account for inversion of stereochemistry, which accompanies nucleophilic attack upon α-haloalkenylmetals. Nucleophilic attack concurrent with loss of halide has been postulated in a reaction involving migration of an internal nucleophile [2a,f,11] (see eqn. (3)).



(3)

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[*] A reference number with an asterisk indicates a note in the list of references.

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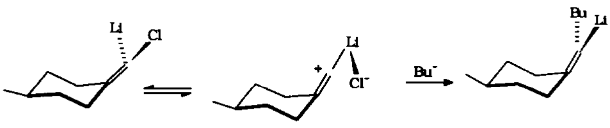
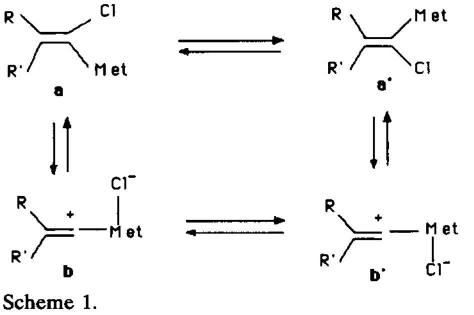
However, this is essentially an S_N2 reaction at an sp^2-hybridized carbon atom, which is usually considered not possible. Thus, although inversion in reactions of 1-metallo-1-halocyclopropanes could be explained by an S_N2 mechanism, such a reaction for α-haloalkenylmetals is difficult to envisage if one considers the bonds to be the traditional covalent type shown in eqn. (3).

Walborsky and Duraisamy [4a] and Duraisamy and Walborsky [4b] proposed a mechanism involving metal-assisted ionization (MAI), in which weakening of the carbon–halogen bond is assisted by the metal atom attached to carbon [4b]:



(4)

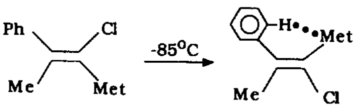
They coined the term "metal-assisted ionization" [4b] to explain the more facile C–Cl ionization of α-haloalkenylmetals [4b,11,12] compared to haloalkenes. However, many of the essentials were presented in the earlier papers of Köbrich and coworkers [2b,4c]. In this mechanism, a form in which chlorine is bonded to carbon is predicted to dissociate into a form in which chlorine is associated with lithium, creating a Li–Cl associated form. Although it is not a central issue to this study, the C–Li bond of each of these compounds probably has an ionic structure, based on previous calculations of other similar structures [13]. Walborsky and Duraisamy [4a] and Duraisamy and Walborsky [4b] proposed the latter Li–Cl associated form to be the reacting species. Nucleophilic attack upon the Li–Cl associated form could explain the stereospecificity of the reaction, since attack would be blocked from the front by chloride and would be forced to take place from the back side (eqn. (4)) [4]. A crucial requirement for the viability of this mechanism is that the Li–Cl associated form must be capable of maintaining its stereochemistry, *i.e.* there must be a barrier for rotation of chloride from one side of the molecule to the other.



1 Met = Li
2 Met = BeH
3 Met = BMe$_2$

Scheme 1.

The capability of the Li–Cl associated form to maintain stereochemistry is also pertinent to the pathway for isomerization proposed by Köbrich and Ansar [4c]. Köbrich *et al.* [2c] reported that the (Z) isomer of lithiated chloromethylstyrene converts spontaneously and irreversibly to the (E) isomer when warmed to −85 °C. Neither the mechanism nor the reason for the greater stability of the (E) isomer has been understood. Calculations [14] on such systems predicted that the greater stability is due to a favorable agostic-type interaction between the metal atom and the *ortho* hydrogen on phenyl:



(5)

One obvious route for isomerization would be direct isomerization of the Walborsky–Duraisamy covalent C–Cl bonded form **a** → **a'** (Scheme 1). A second possible route for isomerization would go through the Cl–Met associated form resulting from MAI [4] (**a** → **b** → **b'** → **a'**).

Thus the existence of an Li–Cl associated form capable of maintaining stereochemistry is pertinent to both the isomerization of α-haloalkenylmetals and their reactions with nucleophiles. Computational studies of the beryllio derivatives have appeared [14b], but these did not include investigation of pathways for isomerization or ionization. Typical molecular orbital computational methods model gas-phase reactions and therefore, are not necessarily applicable to an ionization in solution. However, such calculations have been applied with excellent results to similar reactions in simpler systems [13]. Therefore they seem appropriate for this migration mechanism. Hence, it seemed desirable to investigate computationally the lithio and boryl analogs, as well as the isomerization and C–Cl ionization of the lithio, boryl, and beryllio derivatives. Accordingly, we have probed the stereochemical integrity of such an intermediate by investigating computationally the isomerization and C–Cl ionization in each of three representative systems (Met = Li, BeH, or BMe$_2$) by using modified neglect of differential overlap (MNDO).

2. Theoretical procedures

The calculations were carried out by using the MNDO [15] molecular orbital method and parameters in MOPAC [16]. The program was adapted to run on our IBM 3081 computer and equipped with additional parameters [16b,17]. Deficiencies in the MNDO parametrization for lithium have been noted [18a,b,e].

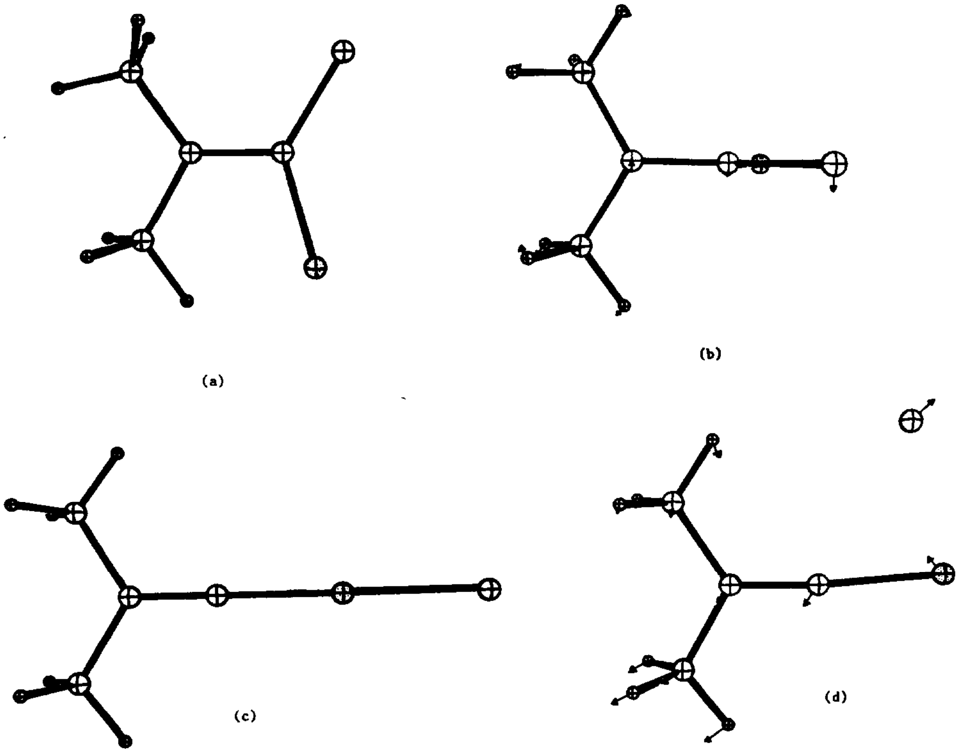


Fig. 1. ORTEP plots for stable species and transition states derived from α-chloroisobutenyllithium. The arrows designate by length and direction the contribution of individual atomic motions to the transition coordinate: (a) C–Cl bonded form **1a**; (b) transition state for conversion of **1a** to **1a'**, TS(**1a** → **1a'**); (c) Li–Cl associated form **1b**; and (d) transition state for conversion of **1a** to **1b**, TS (**1a** → **1b**). The lithium atom is dotted in each.

It has been reported that the MNDO lithium parameters [16b,17] have been extensively tested and that generally the method gives results consistent with sophisticated *ab-initio* calculations [18c,e]. The method has also been found to be remarkably successful in predicting the preferred mode of lithium complexation [18d,e]. In addition, when comparing isomers with a very similar bonding arrangement, such as in this study, cancellation of many problems [18a,e], such as overestimation of C–Li bond energies [18a,f] can often be anticipated. The geometries of stable species were found by minimizing the total energy; except where noted, all geometrical variables were allowed to optimize. Each transition state was located by using the SADDLE subroutine and characterized as such by calculating and diagonalizing the force constant matrix, thus establishing that it had one and only one negative eigenvalue. The corresponding eigenvector (transition coordinate) was also examined to ensure that the transition state corresponded to the desired reaction.

TABLE 1. MNDO heats of formation for C–Cl bonded (**a**) and Met–Cl associated (**b**) forms of three α-chloroisobutenylmetals and for the transition-state structures corresponding to *cis–trans* isomerizations (**a** → **a'** and **b** → **b'**) and to interconversions (**a** → **b**) for each

Structure	Heat of formation (kcal mol^{-1})		
	Met = Li	Met = BeH	Met = BMe_2
a(C–Cl bonded)	−22.07	−26.64	−39.22
TS (**a** → **a'**)	20.58	13.97	−2.92
TS (**a** → **b**)	4.72	−7.67	−12.07
b (Met–Cl associated)	1.04	−16.75	−13.05
TS (**b** → **b'**)	–	−8.57	–

3. Results and discussion

3.1. Ground-state structures

Using a model system (R,R' = Me), we have located and characterized the ground-state structures for **a** and **b**, as well as the transition-state structures corresponding to interconversion (**a** → **b**), isomerization of the forms with chlorine bonded to carbon (**a** → **a'**), and isomerization of the forms in which chlorine is associated to the metal (**b** → **b'**). ORTEP plots of the stationary points are given in Figs. 1–3. The heats of formation for the ground-state structures and for the transition-state structures are given in Table 1. For each α-chloroisobutenylmetal, the C–Cl bonded compound

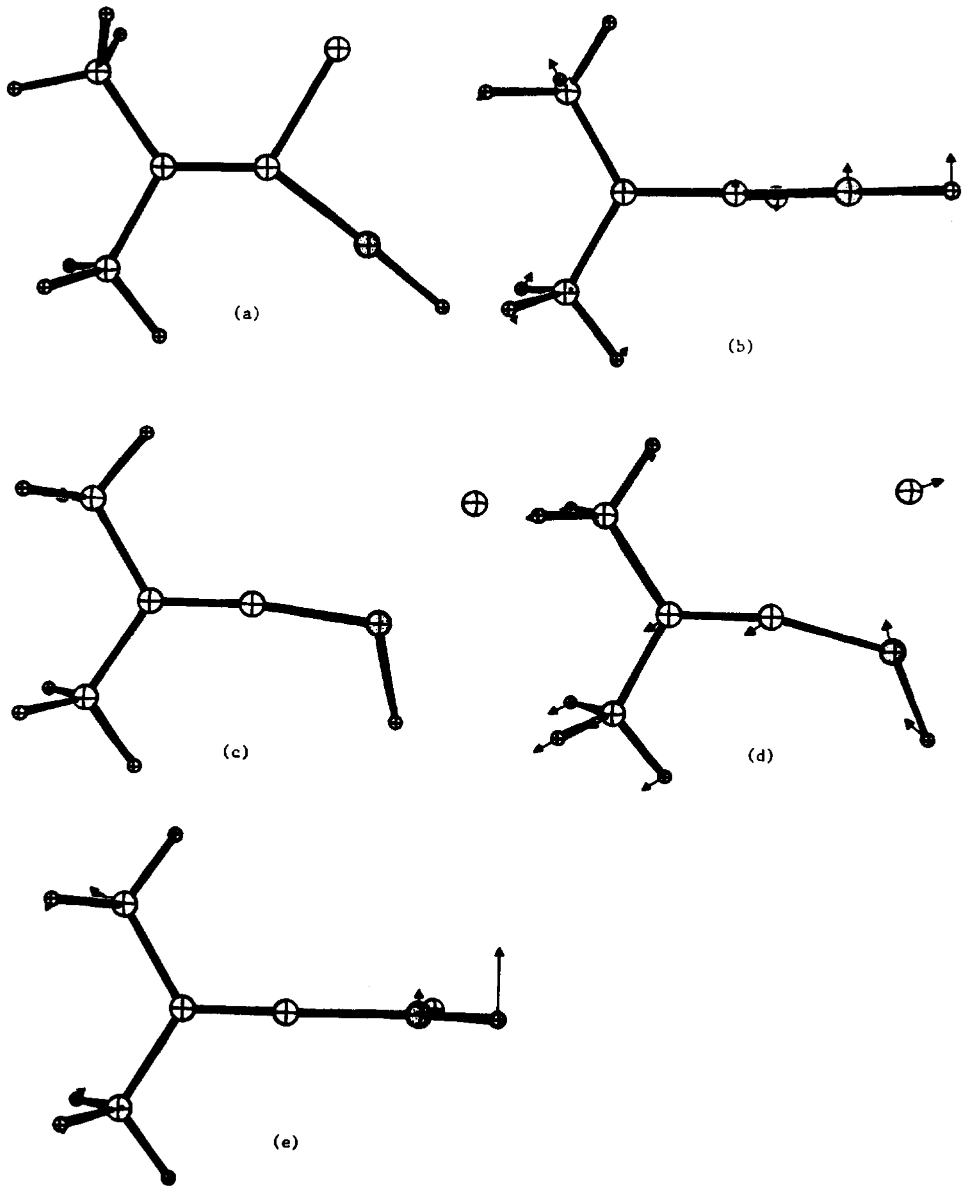


Fig. 2. Plots analogous to those in Fig. 1 for species from α-chloroisobutenylberyllium hydride: (a) C–Cl bonded form **2a**; (b) TS(**2a** → **2a′**); (c) Be–Cl associated form **2b**; (d) TS(**2a** → **2b**); (e) TS(**2b** → **2b′**). The beryllium atom is dotted in each.

TABLE 2. Calculated bond lengths in compounds **a** and **b**

Met	Bond length (Å)							
	a			**b**		Met–Cl in **a** [a]		
	C–Cl	C–Met	Met–Cl	C–Met	Met–Cl	Experiment	Calculation	C–Met in **d** [b]
H	1.750	–		–	–	–		
Li	1.773	1.825	3.305	1.911	2.220	2.02	2.188	1.814
BeH	1.810	1.658	2.586	1.671	1.998	1.77	1.913	1.622
BMe_2	1.778	1.544	2.638	1.486	1.899	1.715	1.761	1.533

[a] Compounds **c** are LiCl [20], $BeCl_2$ [21] and BCl_3 [22].

[b] Compounds **d** are the isobutenylmetals.

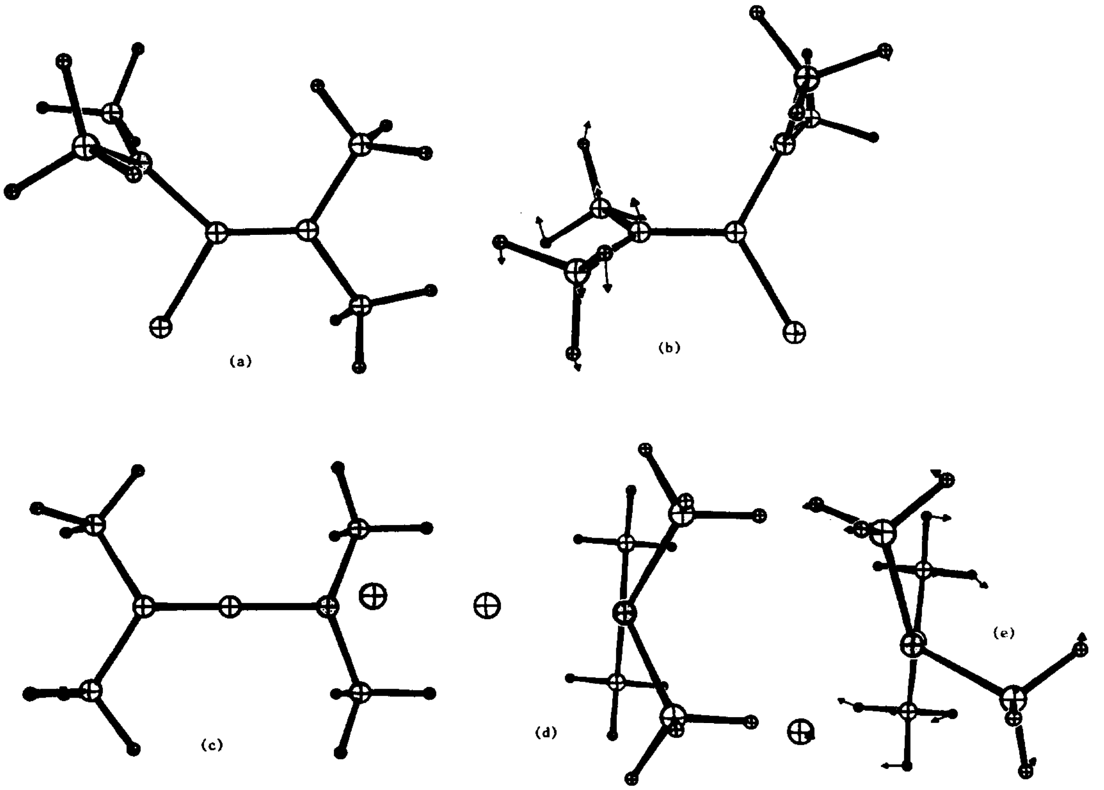


Fig. 3. Plots analogous to those in Fig. 1 for species from α-chloroisobutenyldimethylborane: (a) C–Cl bonded form **3a**; (b) TS(**3a** → **3a'**); (c) B–Cl bonded form **3b**; (d) **3b** rotated 90°; (e) TS(**3a** → **3b**). The boron atom is dotted in each.

a has the lowest heat of formation of any stationary point found on the potential energy surface.

The calculated C–Cl bond length (Table 2) is longer in **1a** (1.773 Å), **2a** (1.810 Å), and **3a** (1.778 Å) than in isobutenyl chloride (calculated 1.750 Å; experiment [19*] 1.72 Å), in agreement with weakening of the bond by the presence of Li. The carbon–metal bond distances in **a** are slightly longer than those calculated for the corresponding isobutenylmetals **d** (Table 2). However, the Met–Cl interatomic distances are far too great for a carbene–MetCl complex. Conversely, the geometry is in agreement with considerable "carbenoid" character, which has been cited as responsible for the electrophilic nature of these compounds [13b,d–g].

Structures **1b** and **2b** have longer C–Cl and C–Met bonds (Table 2 and Figs. 1 and 2) than their counterparts **1a** and **1d** and **2a** and **2d**. This agrees with the structure of a singlet carbene–alkali halide complex, reported earlier for similar systems [13b,d,e,f,g] and described as having "carbanionoid" character. The MetCl interatomic distances are only slightly longer than those of the uncomplexed MetCl compounds, and are therefore also in the range suitable for this type of structure.

The carbene–ClMet complexed forms **1b**, **2b** and **3b** are 23.11 kcal mol (Met = Li), 9.89 kcal mol^{-1} (Met = BeH) and 26.17 kcal mol^{-1} (Met = BMe_2) less stable than the C–Cl bonded isomers **1a**, **2a** and **3a** respectively. This is similar to other systems [13] in which Met–Cl associated forms were calculated to be significantly less stable than their C–Cl bonded isomers. The Met–Cl bond lengths calculated for compounds **b** are only slightly longer than those calculated for the model compounds **c** (Table 2). The value calculated for the Met–Cl bond in each model **c** is significantly longer than that found experimentally in the gas-phase ion pairs (Table 2).

The C–Met interatomic distances of **1b** and **2b** are greater than those of **1a** and **2a**, indicating that the C–Met bonds in structures **1b** and **2b** are weaker than those in **a**. The C–B bond in **3b** is shorter than that in **3a** or in the model compound **3d**, probably because there is some hyperconjugation in which the electron density of the B–Cl bond is donated into the empty p orbital of carbon. This gives the B–C bond some double-bond character, as discussed below. The carbon–metal bond distances in **1b** and **2b** are also longer than those calculated for the corresponding isobutenylmetals **d** (Table 2).

3.2. Structure and stereochemical considerations

The C–C–Li, C–C–Be and C–C–B bond angles in the structures of the Cl–Met associated forms **b** do not have similar values. One reason may be the increasing steric requirements of metals with higher valencies. However, since the three metal derivatives are so dissimilar in their structures of **b**, they cannot be discussed as a group.

The lithium derivative **1b** (Fig. 1(c)) has a linear structure with carbon complexed to lithium chloride in an "end-on" fashion [23], which is similar to structures reported [13b,d,e,f] for various compounds $CH_2HalMet$. The linear geometry of this intermediate would prevent any stereochemistry from being transmitted from the reactant to the product by a mechanism involving nucleophilic attack upon **1b**.

In contrast, the beryllium hydride derivative **2b** has a geometry and barrier to isomerization such that it could maintain stereochemical integrity. Compound **2b** (Fig. 2(c)) has a near-linear structure with carbon complexed to BeHCl in a slightly "bent" fashion [23]. The structure **2b** has a C=C–Be angle of about 172° and a C–Be–Cl bond angle of about 123°. The barrier to rotation of Cl from one side of the molecular plane to the other is about 8.2 kcal mol^{-1} and could explain the low temperature stereochemical integrity observed experimentally [2b]. (A very low barrier for the analogous rearrangement in CHF_2Li was predicted previously [13f]). In the formation of **2b** from **2a**, the C–Cl bond of **2a** is heterolytically broken, chloride remains in the molecular plane, and the ion moves out to be associated with the beryllium atom. Since **2b** retains the stereochemistry of **2a**, a stereospecific reaction involving nucleophilic attack upon **2b** is possible. Thus the results from the beryllium hydride system support the involvement of MAI in the stereospecific reactions of α-haloalkenylmetals.

The structure of the boron derivative **3b** (Figs. 3(c) and 3(d)) is only very slightly bent (C=C–B angle, 179.3°). Furthermore, the orientation of BMe_2Cl in **3b** is twisted by 90° such that the B–Cl bond is perpendicular to the molecular plane. This twisting allows overlap from the B–Cl bond into the empty p orbital on the adjacent carbon. Additional evidence for this overlap is the shorter C–B bond length in **3b** (1.486 Å) than in **3a** (1.544 Å), which is opposite to the relationship in **a** *vs.* **b** in the lithio or beryllio systems. The twisting about the C–B bond also generates a plane of symmetry in **3b** which would prevent stereochemistry from being transmitted from **a** to **b** by a mechanism involving this compound. Even if **3b** were not symmetrical (if the two alkyl groups bound to the alkenyl carbon atom were not identical), then stereochemistry could not be retained by this intermediate since the 90° twisting described above could proceed in either direction and isomerize the alkene.

3.3. Transition-state characteristics

Each transition state structure TS(**a** → **b**) corresponds to a reaction pathway in which the C–Cl bond is broken and Cl moves out to be associated with the metal. In structures **b**, chloride is associated with the metal [4]. Therefore, the reaction **a** → **b** might be considered a migration of chloride from carbon to the metal, rather than a true ionization. TS(**a** → **b**) was located and characterized and is given for each of the lithio (Fig. 1(d)), beryllio (Fig. 2(d)) and dimethylboryl (Fig. 3(e)) systems. The lithio form TS(**1a** → **1b**) is somewhat curious in that all bonds of the pertinent carbon atom extend into a single hemisphere (Fig. 1(d)), as determined in similar systems by other methods [13b,c,d,e]. In comparison, the structure for TS(**2a** → **2b**) (Fig. 2(d)) has a more expected structure; this is probably because it lies more closely to the half-way point on a direct pathway between **2a** and **2b**. The boryl form TS(**3a** → **3b**) also lies more closely to the half-way point on a direct pathway between **3a** and **3b**. However, this transition-state structure bears little resemblance to those of the lithio or beryllio systems. This can be attributed to the differences between the structures in which Cl^- is associated with the metal — the twisted structure of **3b** *vs.* the planar structure of **1b** and **2b**.

The energies E_a of activation (Table 1) for the migration of chloride from carbon to the metal are as follows: **1a** → **1b**, Met = Li, 26.79 kcal mol^{-1}; **2a** → **2b**, Met = Be, 18.97 kcal mol^{-1}; **3a** → **3b**, Met = BMe_2, 27.15 kcal mol^{-1}. The E_a for bond reformation are much less, as one might expect: **1b** → **1a**, Met = Li, 3.68 kcal mol^{-1}; **2b** → **2a**, Met = BeH, 9.08 kcal mol^{-1}; **3b** → **3a**, Met = BMe_2, 0.98 kcal mol^{-1}. Activation energies for isomerization of the Cl–C bonded form of each derivative are as follows: **1a** → **1a′**, Met = Li, 42.65 kcal mol^{-1}; **2a** → **2a′**, Met = BeH, 40.61 kcal mol^{-1}; **3a** → **3a′**, Met = BMe_2, 36.30 kcal mol^{-1} (Table 1). In each case, the transition-state structure for **a** → **a′** has a plane of symmetry with one end of the double bond perpendicular to the other (Figs. 1(b), 2(b) and 3(b)).

The three metal derivatives cannot be considered as a group in discussing **b** → **b′** since they are so dissimilar in their structures of **b**. However, **1b** and **3b** are similar in at least two ways. First, as discussed above, stereochemical reactions involving the lithium derivative **1b** and boryl derivative **3b** are not possible owing to symmetry in each which causes loss of the stereochemical information of the substrate. Second, isomerization about the π bond is calculated not to be a viable process in either of these systems. The lithio derivative **1b** is linear in the pertinent region and therefore possess no *cis–trans* stereochemistry. Isomerization (**3b** → **3b**′) of the boryl compound goes through the C–Cl bonded form **3a** (Figs. 1(c), 3(c) and 3(d)). This unexpected result arises apparently because structure **3b** is twisted by 90° about the C–B bond, relative to structure **3a**. Isomerization can result from rotation in either direction. The E_a for this conversion, which is essentially bond reformation followed by ionization, is 0.98 kcal mol^{-1}.

Only isomerization of the beryllio derivative (**2b** → **2b**′, Met = BeH) is predicted to provide a system capable of maintaining stereochemical integrity (Fig. 2(c)). The energy of activation for this isomerization is 8.18 kcal mol^{-1}, a relatively small barrier. The transition state structure TS(**2b** → **2b**′) has a plane of symmetry with one end of the double bond rotated by 90° (Fig. 2(e)), as expected.

3.4. *Comparison with other studies*

It is useful to compare the structures of the energy minima found in our studies with those in previous studies of similar compounds [13]. In the highest level *ab-initio* calculations carried out on the CCl_3Li system [13h], the “classical” structure analogous to **1a**, with C–Cl and C–Li bonds, was 12 kcal mol^{-1} lower than the carbene–ClLi complexed form **1b**. Compound **1a** is 23.1 kcal mol^{-1} lower in energy than **1b** by our calculations. Two of the stationary points, both energy minima, located in an earlier study [13c] of that system correspond roughly to our **1a** and **1b** respectively, with the former 2.6–4.1 kcal mol^{-1} lower than the latter, depending upon the method used.

In each structure **1a** and **1b**, our calculations predict a shorter C–Li bond than that predicted by using *ab initio* methods for either Cl_3CLi [13] or vinyllithium [24] (Table 2). However, it is known that MNDO has a tendency to overestimate those bond strengths, which would yield shorter bond lengths [18]. Conversely, the MNDO carbon–lithium bond lengths in both **1a** and **1b** are significantly longer than that calculated for vinyllithium [24] or for isobutenyllithium (Table 2) using MNDO, in agreement with previous calculations [13e].

Studies of CH_2FLi [13b,d,e,g] have been reported. Ground state structures similar to **1a** and **1b** were located, with the latter lower in energy by amounts from 23.6 kcal mol^{-1} [13d] to 27.5 kcal mol^{-1} [13e] in the higher level studies. This compares quite well with that obtained in our study (23.1 kcal mol^{-1}). Calculations for the structure corresponding to **1b** yielded a geometry (C–Li–F bond angle, of 180°) which was also more like that predicted for **1b** in our study than that of CCl_3Li.

The phenomenon exhibited by the structure of TS(**1a** → **1b**) in which “all four valencies of carbon extend into a single hemisphere” [13d] (Fig. 1(d)) was observed earlier in *ab-initio* calculations of ground-state structures [13b,d,e] and of a transition-state structure [13e] of H_2CLiF. This was also observed to a lesser extent in CCl_3Li [13c]. The small energy of activation predicted by our calculations for the bond reformation process **1b** → **1a** (3.68 kcal mol^{-1}) is in accord with that predicted by *ab-initio* calculations (1 kcal mol^{-1}) [13e] for C–F bond re-formation in H_2CLiF.

3.5. *Isomerization pathway*

The location of the Met–Cl associated form leads us to consider its involvement in the *cis–trans* isomerization. Location and characterization of the transition states corresponding to isomerization directly from one C–Cl bonded form to the other (**a** → **a**′) and from one Met–Cl associated form to the other (**b** → **b**′) are of interest to determine whether the activation energy for the former pathway is lower than the overall activation energy for the pathway involving metal assistance. However, such consideration of transition states corresponding to isomerization of Met–Cl associated forms was impractical in the lithio and boryl derivatives. The Li–Cl associated form of the former is linear as mentioned above, and isomerization of the B–Cl associated form **3b** → **3b**′ does not take place directly but goes through the C–Cl bonded form **3b** → **3a** → **3b**′. Only the beryllio derivative has a geometry suitable for such an investigation. In the beryllio system, the barrier calculated for isomerization of the C–Cl bonded form (40.61 kcal mol^{-1}) is higher than that for ionization–isomerization–bond reformation (18.97 kcal mol^{-1}). In addition, the effects of solvation and complexation should lower the energy barrier involving ionization more than that for simple isomerization. All these factors support the pathway involving ionization.

3.6. *Consideration of metal-assisted ionization*

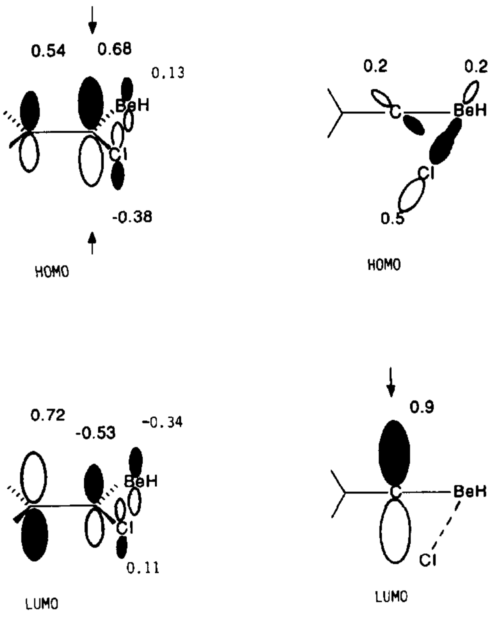
In the Walborsky–Duraisamy MAI, weakening of the carbon–halogen bond caused by the metal atom attached to the carbon is predicted [4b]. The longer C–Cl bond lengths in **1a**–**3a** than in isobutenyl chloride and the predicted involvement of structures **b** in the systems studied support this theory. The calculated C–Cl force constants in **1a** (629 cm^{-1}) and **2a** (732 cm^{-1}) were much lower than those calculated for the parent compound, isobutenyl chloride (877 cm^{-1}). That for **3a** was higher (977 cm^{-1}). The lower calculated

C–Cl force constants for **1a** and **2a** than for the parent compound and the high degree of ionic character in **a** are also consistent with weakening of the C–Cl bond upon metallation at the α position. Such reduction of the C–Cl force constant upon α metallation has been observed experimentally [25].

3.7. Nucleophilic ("carbanionoid") and electrophilic ("carbenoid") character of a and b

The idealized highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of **2a** and **2b** are compared in Fig. 4. The HOMO of **2a** is a π orbital with the largest atomic orbital at C(1), while that of **2b** is a highly polarized σ_{BeCl} orbital. The LUMO of **2a** is a π^* orbital with the largest atomic orbital at C(2), while that of **2b** is essentially a π orbital at C(1). The HOMOs of the CH_2FLi system [13a] and of the other $CH_2HalMet$ systems [13g] are similar to that of **2a** and were cited as responsible for "carbanionoid" character. The LUMOs [13g] were similar to that of **2b** and were cited as responsible for "carbenoid" character.

The preferred site of electrophilic attack in the HOMO and of nucleophilic attack in the LUMO is expected to be at the larger atomic orbital of each [13a,26]. Examination of the HOMOs of **2a** and **2b** (Fig. 4) reveals that attack by an electrophile at the largest atomic orbital of **2a**, centered on C(1), could lead to the observed product, while the corresponding attack upon **2b** would not be expected to yield the product [27]. Hence, one can conclude that the C–Cl bonded form of a compound such as **2a** is the reacting species with electrophiles. The negative electronic charges at C(1) in **1a** and **2a** support this conclusion (Table 3). A similar analysis of nucleophilic attack upon the LUMOs of **2a** and **2b** leads to the conclusion that only the LUMO of the latter could reasonably be expected to give the observed product. The LUMO of **2b**, essentially an empty p orbital at C(1), is responsible for the electrophilic character of these compounds. This analysis invokes the carbene–MetCl complex as an intermediate in the reactions of such compounds with nucleophiles. It also accounts nicely for the observed stereospecificity. The positive electronic charges at C(1) in **1a** and **2a** support this theory (Table 3). Hence, our calculations support the involvement of MAI in the reactions of such compounds with nucleophiles [4] as well as in the isomerization of the α-haloalkenylmetals.



1b 2b

Fig. 4. Idealized frontier molecular orbitals of compounds **2a** and **2b**. The arrows show preferred positions of attack of an electrophile upon the HOMO or a nucleophile upon the LUMO.

TABLE 3. Calculated electronic charges at C(1) in **a**, **b** and **d**

Met	Electronic charge		
	a	**b**	**d** [a]
H	0.02	—	—
Li	−0.12	0.34	−0.24
BeH	−0.16	0.34	−0.28
BMe_2	−0.02	0.44	−0.10

[a] Compounds **d** are the isobutenylmetals.

3.8. Solvent effects

The effects of aggregation, solvent, and complexing agents which undoubtedly come into play in these systems [27] are neglected in these calculations. However, the interactions that we invoke in the mechanistic rationalizations are also expected to occur when the carbenoids are aggregated, complexed, or solvated. Such effects would undoubtedly lower the barrier to the ionic pathway and increase further the predicted preference of the pathway involving MAI.

4. Conclusion

The results for the beryllium hydride derivative indicate that the Met–Cl associated form possesses stereochemistry and other characteristics necessary for stereospecific nucleophilic attack at the α-carbon. Metallation α to chlorine is calculated to weaken, lengthen, and increase the ionic character of the C–Cl bond. These results support the involvement of MAI in stereospecific reactions with nucleophiles. The barrier for direct isomerization of the C–Cl bonded form is calculated to be about 22 kcal mol^{-1} higher than that for the ionization–isomerization–bond reformation pathway, which supports MAI involvement in the more favored pathway. The effects of solvation, aggregation, or complexation should stabilize the associated form more than the C–Cl bonded form owing to a greater charge dispersal in the former form, which should favor the pathway involving ionization more than that of simple isomerization and increase the energy difference between the two pathways beyond that predicted by this study.

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