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Isomerization of and Chloride Migration in Representative Complexed 1-Chloro-2-methyl-1-propenylmetals

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ABSTRACT: *A computational study of the title compounds, in which the metal functionality is lithium or dimethylboryl, each complexed with NH_3, compares effects of complexation upon the title compounds with ammonia against those experimentally observed with TMEDA. Previous similar calculations predicted intermediates formed with loss of stereospecificity but did not consider complexation effects, which were reported to increase the yield of the stereospecific reactions. In contrast, when ammonia is included to model complexation by TMEDA, an ionized form of the title compounds is generally favored that is capable of maintaining stereochemistry. This form is a Met-Cl associated intermediate, in which Cl^- has migrated from carbon to become associated with Met.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 623–630, 1998

INTRODUCTION

The reactions of α-chloroalkenylmetals [1a] are of great interest synthetically, due to their stereospecificity under certain conditions [1–3], and mechanistically, due to apparent nucleophilic substitutions at the sp^2-hybridized carbon. Metal-assisted ionization (MAI) [1, 3a, b, 4], in which weakening of the carbon-halogen bond is assisted by the metal atom bonded to carbon, has been used [1, 3] to explain (1) the more facile C–Cl ionization in α-chloroalkenylmetals compared to haloalkenes, (2) their increased reactivity with nucleophiles, (3) inversion of stereochemistry in their reactions with nucleophiles, and (4) their increased ease of isomerization. MAI reportedly accounts for each of these phenomena as follows: (1) In the MAI mechanism, a form (**a**, Scheme 1), in which chlorine is covalently bonded to carbon, is predicted to dissociate into another form (**b**), in which the C–Cl bond is ionized and chlorine becomes associated with the metal atom, the Met-Cl associated form; this process facilitates ionization. (2) Nucleophilic attack occurs upon form **b** in Scheme 1 more easily than upon the covalent form **a**. (3) Chloride blocks the nucleophile from attacking on the side from which it departs, so it is forced to attack on the opposite side, leading to inversion of stereochemistry. (4) The increased ease of isomerization is provided by the use of route $\mathbf{a} \rightarrow \mathbf{b} \rightarrow \mathbf{b}' \rightarrow \mathbf{a}'$ rather than the direct route $\mathbf{a} \rightarrow \mathbf{a}'$. However, two additional conditions must be met if MAI is to explain successfully the stereospecificity and the ease of the reactions of α-chloroalkenylmetals with nucleophiles [3a, b] as well as their ease of ionization and isomerization: (1) the energy of activation should be lower for MAI ($\mathbf{a} \rightarrow \mathbf{b}$) than for direct isomerization ($\mathbf{a} \rightarrow \mathbf{a}'$), and (2) the Met-Cl associated forms **b** and the transition states leading to and from them must be capable of maintaining stereochemistry.

Previous theoretical investigations [1] of isomerization of the compounds explored two possible

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Dedicated to Prof. Robert R. Holmes on the occasion of his 70th birthday.

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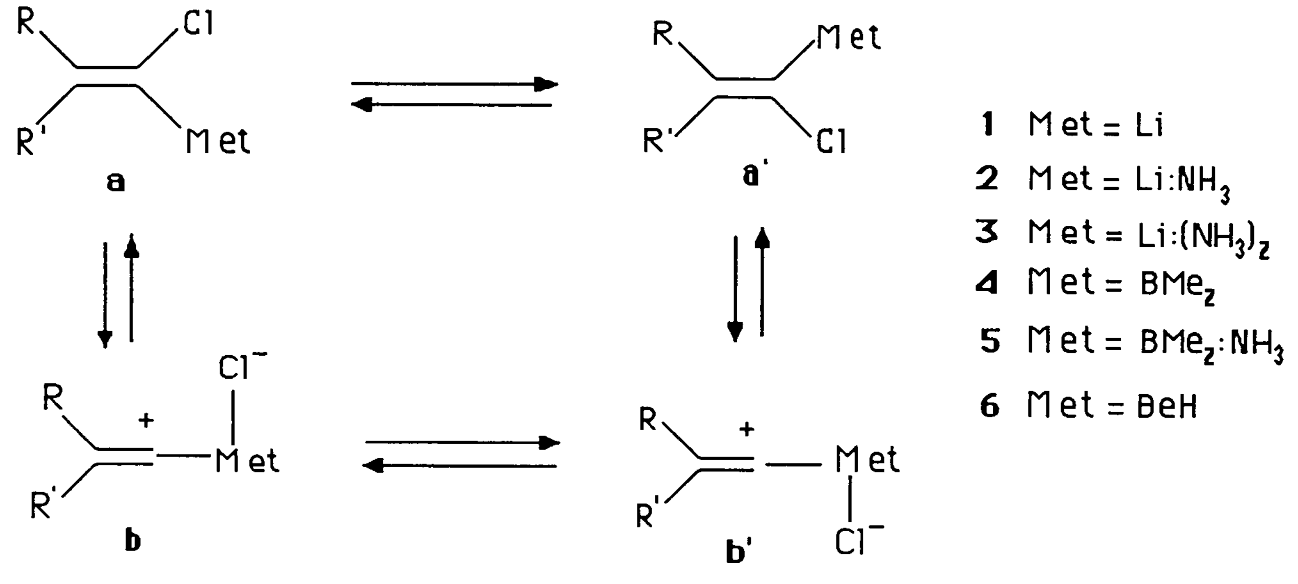

SCHEME 1

pathways (Scheme 1). One was direct isomerization of the covalent C–Cl bonded form **a** → **a**′. A second possible route for isomerization goes through the Cl-Met associated form **b** resulting from MAI [1, 3a, b, 4] (**a** → **b** → **b**′ → **a**′). These calculations [1], as well as calculations by others [5] on similar systems and giving similar results, modeled gas-phase reactions and provided no information regarding the effects of complexation and solvation. However, the effects of changing different reaction conditions (temperature, solvent, TMEDA addition, etc.) have been studied in depth and are detailed in Ref. 1b. It was reported that the presence of TMEDA increases the yield of the reaction (Met = Li) considerably [1b], so the complexation of the α-haloalkenylmetals with one or more molecules of NH_3 to include the effects of TMEDA should better model the reaction conditions. Hence, it seems desirable to investigate computationally the complexed α-haloalkenylmetals, as well as their isomerization and C–Cl ionization. Accordingly, we have probed the stereochemical integrity of the complexed intermediates by examining computationally the isomerization and C–Cl ionization in each of the systems, Met = $Li{:}NH_3$, $Li{:}(NH_3)_2$, and $BMe_2{:}NH_3$, by using MNDO.

RESULTS AND DISCUSSION

Structures, Heats of Formation, and Stereochemistry

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 covalently bonded to carbon (**a** → **a**′), and isomerization of the forms in which chlorine is associated with the metal (**b** → **b**′). The heats of formation for the ground-state structures and for the transition-state structures are given in Table 1. Energies of activation for the transformations are given in Table 2. ORTEP plots of the stationary points are given in Figures 1–3.

For each α-chloroisobutenylmetal, the C–Cl bonded compound **a** has the lowest heat of formation of any stationary point found on the potential energy surface. The Cl-Met associated forms, which are complexed with NH_3, **2b**, **3b**, and **5b**, are 26.65 kcal/mol (Met = $Li{:}NH_3$), 26.05 kcal/mol (Met = $Li{:}(NH_3)_2$), and 44.28 kcal/mol (Met = $BMe_2{:}NH_3$) less stable than their C–Cl bonded analogs **2a**, **3a**, and **5a**, respectively. These differences are significantly greater than those in these uncomplexed systems 23.11 kcal/mol (Met = Li, **1b** − **1a**) and 26.17 kcal/mol (Met = BMe_2, **4b** − **4a**).

In order for the MAI pathway to be viable, each structure involved must be capable of maintaining stereochemistry. In the formation of **2b** or **3b** from **2a** or **3a**, the C–Cl bond of **a** is heterolytically broken, and chloride remains in the molecular plane (Figures 1c and 2c). Therefore, a stereospecific reaction involving nucleophilic attack upon **b** is possible. In **5b** (Met = $BMe_2{:}NH_3$), Cl does not remain in the molecular plane but rotates out to form a 68° ClC1C2C3 dihedral angle (Figure 3c) with only a very small barrier to formation for **5b**′, so that retention of stereochemistry in this system might be doubtful. These theoretical results are unlike those of the cor-

TABLE 1 MNDO Heats of Formation (kcal/mol) for C–Cl Bonded (**a**) and Met-Cl Associated (**b**) Forms of Representative 1-Chloro-2-methyl-1-propenylmetals and for the Transition-State Structures Corresponding to *Cis-Trans* Isomerizations (**a** → **a**′ and **b** → **b**′) and to Interconversions (**a** → **b**) for Each

	Met					
	Li$(NH_3)_x$			*BMe*$_2(NH_3)_x$		*BeH*[a]
Structure	**1**[a], *x* = *0*	**2**, *x* = *1*	**3**, *x* = *2*	**4**[a], *x* = *0*	**5**, *x* = *1*	**6**
a(C–Cl bonded)	−22.07	−49.35	−69.93	−39.22	−48.09	−26.64
TS(**a** → **a**′)	20.58	−6.61	−28.11	−2.92	−2.79	13.97
TS(**a** → **b**)	4.72	−21.90	−43.25	−12.07	−2.62	−7.67
b(Met-Cl assoc.)	1.04	−22.70	−43.88	−13.05	−3.81	−16.75
TS(**b** → **b**′)	—	−20.83	−38.56	—	−3.42	−8.57
b − **a**	23.11	26.65	26.05	26.17	44.28	9.89

[a] Data from Ref. 1d.

TABLE 2 Energies (kcal/mol) of Activation for Isomerization and Ionization of Representative 1-Chloro-2-methyl-1-propenylmetals

			E_a			
Met	*Compound*	*x*	**a** → **a**′	**a** → **b**	**b** → **b**′	**b** → **a**
Li$(NH_3)_x$	**1**[a]	0	42.7	26.8	—	3.68
	2	1	42.7	27.5	1.9	0.80
	3	2	41.8	26.7	5.3	0.63
BMe$_2(NH_3)_x$	**4**[a]	0	36.3	27.2	—	0.98
	5	1	45.3	45.5	0.4	1.19
BeH[a]	**6**	0	40.6	19.0	8.2	9.08

[a] Data from Ref. 1d.

responding uncomplexed system **4** [1d] in which stereochemistry was completely lost by Cl rotating to be perpendicular to the molecular plane.

Thus, the structures of the Cl-Met associated forms **b** complexed with ammonia are similar in that they all retain the stereochemistry of their bonded forms **a**. This similarity in the complexed systems is in sharp contrast to the corresponding results of calculations on the uncomplexed molecules **1b, 4b, 6b,** in which the structures of **b** (Met = Li, BMe$_2$, BeH) are all very different, and only the beryllium derivative **6b** retains the stereochemistry of **6a** [1d]. However, the capability of stereospecific reaction in these systems is supported by experimental reports of retention of stereochemistry in numerous cases with electrophiles, and in some cases with nucleophiles, specifically those in which Met = Li [3], B [2a, b, d, e], Si [2f, g, h], Al [2c], Cu [3d, e], and often using a complexing agent [2b, f, g, 3d, e], such as TMEDA. Thus, the calculations presented in this report, which include association with ammonia and indicate retention of stereochemistry, more accurately match experimental results than do the previously reported ones that do not include complexation with ammonia. The inversion of the uncomplexed form has not been studied experimentally, so a comparison of theoretical results with experimental results is not possible for the inversion pathway.

Transition-State Structures

In order to explore the viability and stereospecificity of the isomerization pathway involving metal assistance (**a** → **b** → **b**′ → **a**′), it was desirable to calculate the transition-state structures. 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. Therefore, the reaction **a** → **b** might be considered a migration of chloride from carbon to the metal, rather than a true ionization. The TS(**a** → **b**) was located and characterized and is given for each of the complexed lithio (Figures 1d and 2d) and dimethylboryl (Figure 3d) systems.

Each of the transition-state structures TS(**2b** → **2b**′), TS(**3b** → **3b**′), and TS(**5b** → **5b**′) has a plane of symmetry with one end of the double bond rotated by 90° (Figures 1e, 2e, and 3e) and is predicted to provide a system capable of maintaining stereochemical integrity, similar to that of the beryllio system (**2b** → **2b**′, Met = BeH) [1d]. In the uncomplexed systems [1d], stereochemical reactions involving the lithium **1b** and boryl **4b** derivatives are not possible due to symmetry in each, which causes loss of the stereochemical information of the substrate.

Pathway Comparisons

Another requirement in order for the pathway involving MAI to be viable is that its overall E_a should be lower than that for simple isomerization. In order to predict whether the lower-energy pathway for interconversion of **a** and **a**′ is simple isomerization (**a** → **a**′) or involves MAI (**a** → **b** → **b**′ → **a**′), it is necessary to compute and compare the heats of formation ΔH_fs and the energies of activation E_as of each step constituting the transformations. The ΔH_fs are given in Table 1, and the E_as are given in Table 2.

Complexation with NH$_3$ has little effect on the energies of activation E_a for direct isomerization **a** → **a**′ in the lithium derivatives (42.7 and 41.8 kcal/mol versus 42.7 kcal/mol), but it increases the E_a in the boryl system (45.3 kcal/mol versus 36.3 kcal/mol). In each transition-state structure for **a** → **a**′, the plane containing Met-C-Cl is perpendicular to

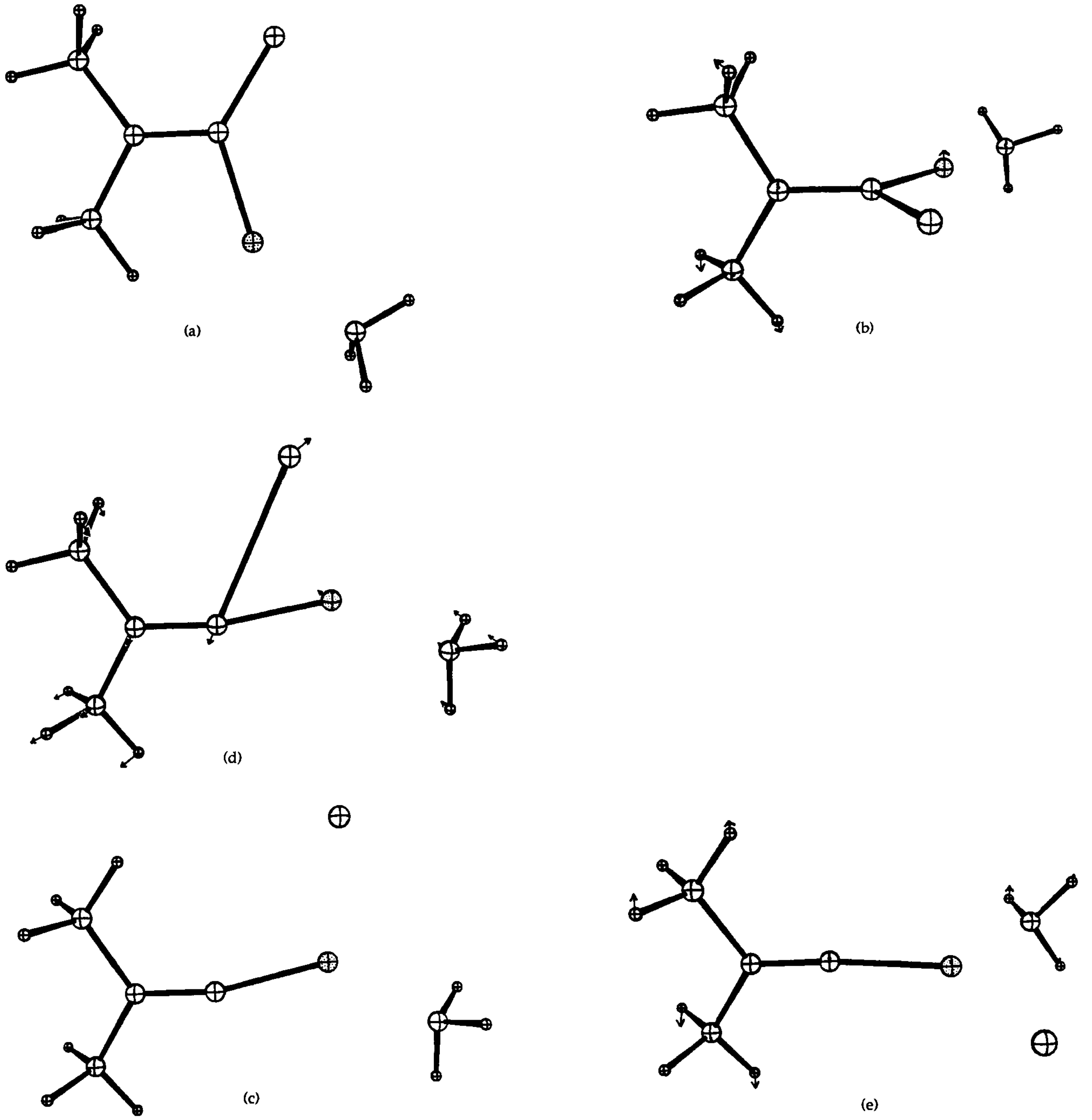

FIGURE 1 ORTEP plots for stable species and transition states derived from 1-chloro-2-methyl-1-propenyllithium complexed with NH_3. Arrows designate by length and direction the contribution of individual atomic motions to the transition coordinate: (a) C–Cl bonded form **2a**; (b) transition state for conversion of **2a** to **2a**′, TS(**2a** → **2a**′); (c) Li–Cl associated form **2b**; (d) transition state for conversion of **2a** to **2b**, TS(**2a** → **2b**); (e) transition state for conversion of **2b** to **2b**′, TS(**2b** → **2b**′). The lithium atom is filled with dots in each.

the plane containing Me-C-Me (Figures 1b, 2b, and 3b). Complexation with ammonia has little effect on the E_a of the **a** → **b** ionization in the lithium derivatives (27.5 and 26.7 kcal/mol versus 26.8 kcal/mol) and makes it less favorable in the boryl derivatives (45.5 kcal/mol versus 27.2 kcal/mol). The transition-state structures corresponding to these rearrangements are shown in Figures 1d, 2d, and 3d and are as expected for these calculations.

The E_a for bond reformation **b** → **a** is much less than that for ionization in all systems. Complexation reduces the E_a in the lithium derivatives slightly

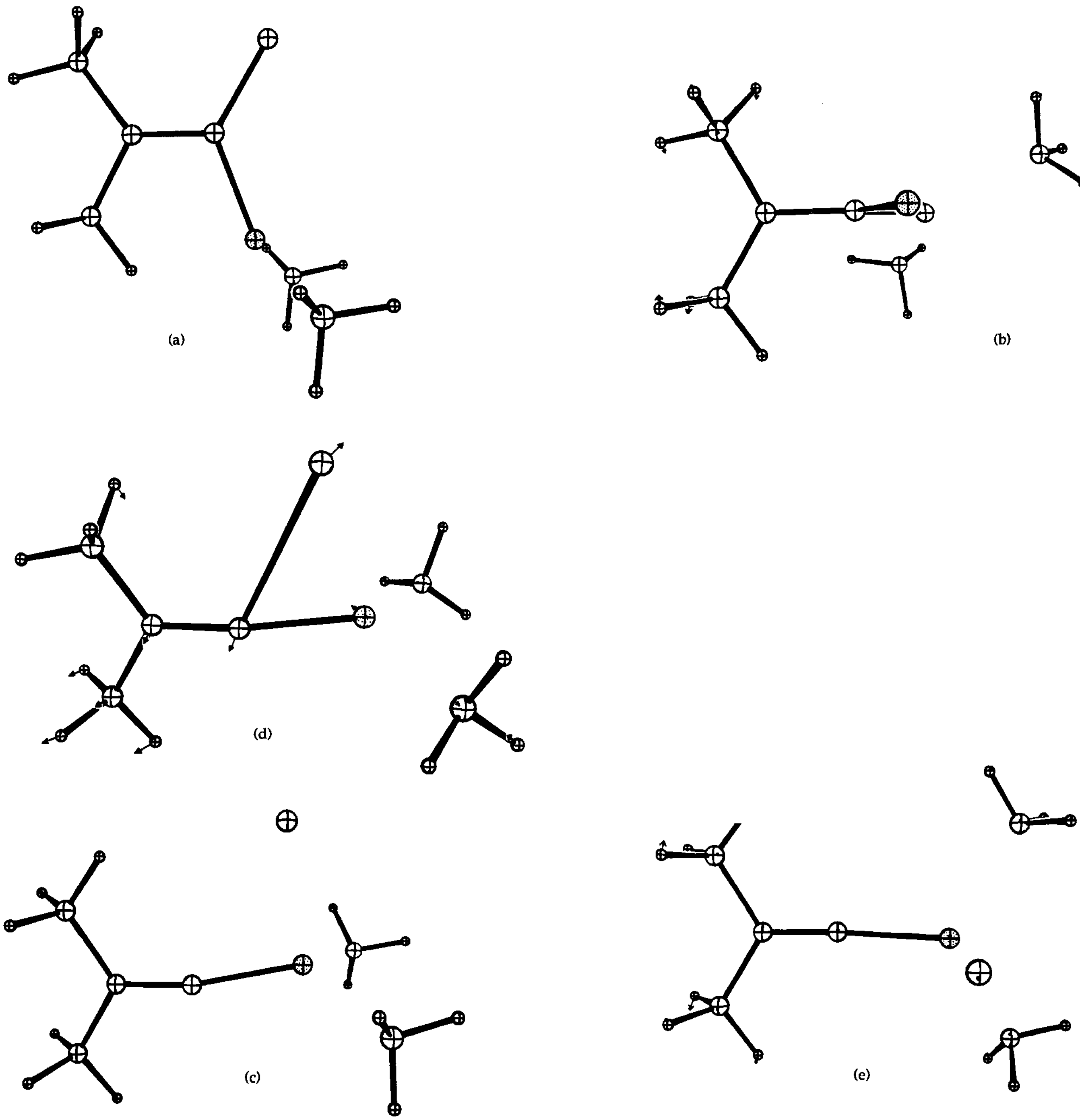

FIGURE 2 Plots analogous to those of Figure 1 for species from 1-chloro-2-methyl-1-propenyllithium complexed with two NH_3 molecules: (a) C–Cl bonded form **3a**; (b) TS(**3a** → **3a**′); (c) Li–Cl associated form **3b**; (d) TS(**3a** → **3b**); (e) TS(**3b** → **3b**′).

(0.80 and 0.63 kcal/mol versus 3.68 kcal/mol) and has little effect on the boryl system (1.19 kcal/mol versus 0.98 kcal/mol). The corresponding transition-state structures are analogous to those for **a** → **b**, which are given in Figures 1d, 2d, and 3d.

In each of **2b**, **3b**, and **5b**, there is a small barrier to rotation of Cl^- from one side of the molecular plane to the other (1.9 kcal/mol, 5.3 kcal/mol, and 0.4 kcal/mol, respectively), which results in isomerization of the ionized structure. This barrier is similar to that of the BeH system **6b** → **6b**′ reported earlier [1d] (~8.2 kcal/mol, a more significant, but still relatively small, barrier). These barriers could explain the low-temperature stereochemical integrity observed experimentally [2c] and support the involvement of metal-assisted ionization in the stereospecific reactions of α-haloalkenylmetals.

Thus, for both of the complexed lithio systems,

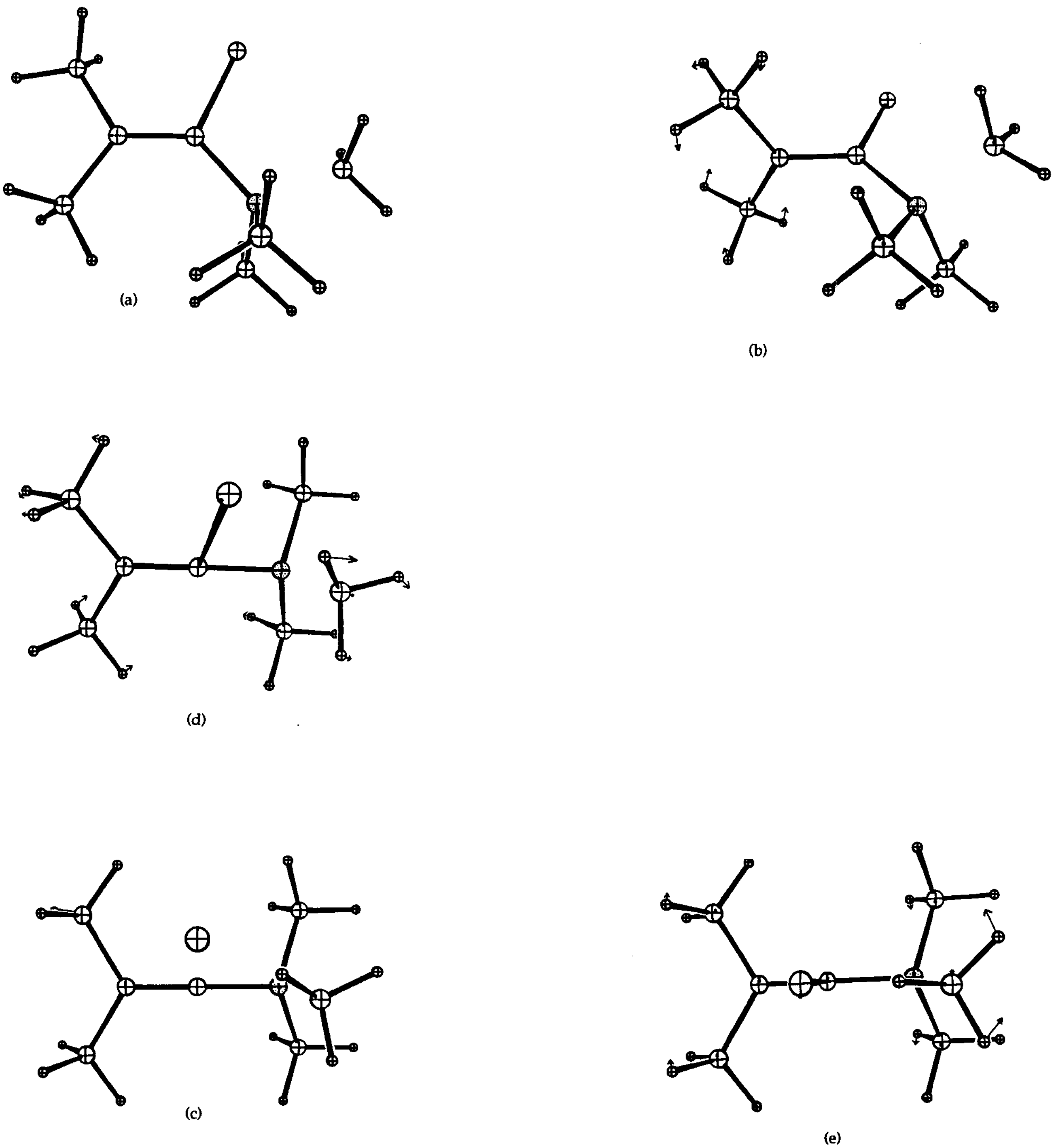

FIGURE 3 Plots analogous to those of Figure 1 for species from 1-chloro-2-methyl-1-propenyldimethylborane complexed with NH_3: (a) C–Cl bonded form **5a**; (b) TS(**5a** → **5a′**); (c) B–Cl bonded form **5b**; (d) TS(**5a** → **5b**); (e) TS(**5b** → **5b′**). The boron atom is filled with dots in each.

the barrier for ionization followed by isomerization and bond reformation (**a** → **b** → **b′** → **a′**; Met = Li:NH_3, 28.5 kcal/mol and Met = Li:$(NH_3)_2$, 31.4 kcal/mol) is significantly less (14.2 and 10.4 kcal/mol less, respectively) than that for direct isomerization (**a** → **a′**; Met = Li:NH_3, 42.7 kcal/mol and Met = Li:$(NH_3)_2$, 41.8 kcal/mol). This is compared to the uncomplexed system (Met = Li), in which the pathway involving MAI was predicted to be more favorable by 16.0 kcal/mol but in which stereochemistry would be lost. For the complexed boryl system, the barrier for ionization followed by isomerization (**a** → **b** → **b**′; Met = $BMe_2{:}NH_3$, 45.5 kcal/mol) is approximately equal to that for direct isomerization (**a** → **a**′; Met = $BMe_2{:}NH_3$, 45.3 kcal/mol). This is compared to the uncomplexed system (Met = BMe_2), in which MAI was predicted to be favored by 9.1 kcal/mol but in which stereochemistry would be lost. Thus, the results for the lithio systems support the pathway involving ionization, while the uncomplexed boryl system supports MAI by a lower E_a and the complexed system by stereospecificity.

THEORETICAL PROCEDURES

The calculations were carried out by using the MNDO molecular orbital method and parameters in AMPAC as described earlier [1c]. 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 insure that the transition state corresponded to the desired reaction. Others have reported that MNDO has been tested in treating structures such as these [6] and that generally the method gives results consistent with sophisticated ab initio calculations [6c, e]. Others have found the method to be remarkably successful in predicting the preferred mode of lithium complexation [6d, e].

CONCLUSION

This work is pertinent to the effects of aggregation, solvent, and complexing agents that come into play in these systems [7] and that were not included in previous calculations. In the lithio systems, the effects of complexation with ammonia have little effect on the barrier to the ionic pathway or the predicted preference of the pathway involving metal-assisted ionization beyond that predicted in the uncomplexed system. However, in the complexed lithio systems, the ionized forms **b** are predicted to have structures that would be capable of maintaining the stereochemistry of **a**, in contrast to the uncomplexed system in which stereochemistry was predicted to be lost. In the boryl system, mixed results are obtained. Complexation makes **b** just barely capable of maintaining stereochemistry, although it was predicted not to be capable at all in the uncomplexed system; complexation also makes the two pathways, MAI and direct isomerization, have about equal E_as, whereas MAI was favored considerably in the uncomplexed system.

In the complexed lithio systems, both requirements necessary for MAI to be a viable pathway for the reaction with nucleophiles are met: (1) in **b**, chloride blocks the nucleophile from attacking the side of the molecule from which Cl originated, and (2) the capability of the Met-Cl associated forms **b** to maintain stereochemistry is ascertained.

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