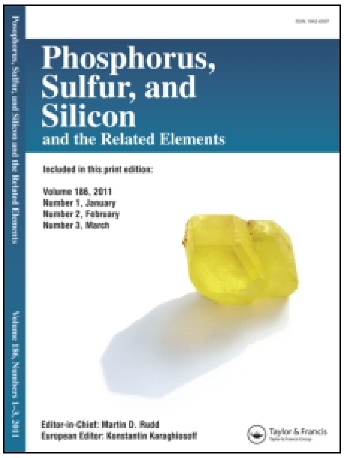

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1,2-Metallobridging and the Antiperiplanar Effect. Thermodynamic Preference for the *Z*-Configuration in Imidoyl(Alkali Metals) and their Phosphorus Analogs

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1,2-METALLOBRIDGING AND THE ANTIPERIPLANAR EFFECT. THERMODYNAMIC PREFERENCE FOR THE *Z*-CONFIGURATION IN IMIDOYL(ALKALI METALS) AND THEIR PHOSPHORUS ANALOGS

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We showed that imidoyl- and phosphaethenyl(alkali metals) would thermodynamically prefer the Z-configuration. The bond model analysis of the electronic structures showed that the Z-preference should originate from 1,2-metallobridging by the delocalization of lone pairs on N or P to vacant p-orbitals of the alkali metals and from the antiperiplanar effect of the delocalization from $\sigma_{\mathrm{C—M}}$ *to* $\sigma^*_{\mathrm{N(P)—R}^2}$ *and from* $n_{\mathrm{N(P)}}$ *to the* $C—R^1$*. The Z-preference increases by more electron-withdrawing groups at the carbon atom of the double bond. However, substitution at the nitrogen/phosphorus results in E-preference because of 1,4-chelation of the lone pair of the substituents to alkali metals. Most of halogen derivatives were not stable and eliminate metal halides.*

Keywords: 1,2-metallobridging; antiperiplanar effect; bond metal analysis; imioloyl (alkali metals); phosphaethenyl (alkali metals); Z-preference

Recently, we suggested[1] that the 1,2-bridged structure[2] of alkoxymethyl(alkali metals) is important in ethylation reactions with methyl ethers[3] in the presence of butyllithium and potassium *t*-butoxide (Schlosser Base).[4] We explored the general importance of the 1,2-bridged structure to examine the possibility of alkali metal bridging between the doubly bonded atoms in the molecular plane, and its effect on the relative stability of *Z*-/*E*-isomers. In this article, we show that the 1,2-bridging and the antiperiplanar effect lead to a thermodynamic preference for the *Z*-configuration of imidoyl- and phosphaethenyl(alkali metals) against steric repulsion.

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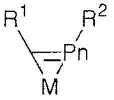
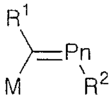


Z-isomer



E-isomer

1a Pn = N; M = Li; R^1,R^2 = Me

1b Pn = P; M = Li; R^1,R^2 = Me

2a Pn = N; M = Na; R^1,R^2 = Me

2b Pn = P; M = Na; R^1,R^2 = Me

3a Pn = N; M = K; R^1,R^2 = Me

3b Pn = P; M = K; R^1,R^2 = Me

4a Pn = N; M = Li; R^1= SiH_3, R^2 = Me

4b Pn = P; M = Li; R^1= SiH_3, R^2 = Me

5a Pn = N; M = Li; R^1= OMe, R^2 = Me

5b Pn = P; M = Li; R^1= OMe, R^2 = Me

6a Pn = N; M = Li; R^1= SMe, R^2 = Me

6b Pn = P; M = Li; R^1= SMe, R^2 = Me

7a Pn = N; M = Li; R^1= F, R^2 = Me

7b Pn = P; M = Li; R^1= F, R^2 = Me

8a Pn = N; M = Li; R^1= Cl, R^2 = Me

8b Pn = P; M = Li; R^1= Cl, R^2 = Me

9a Pn = N; M = Li; R^1= Me, R^2 = SiH_3

9b Pn = P; M = Li; R^1= Me, R^2 = SiH_3

10a Pn = N; M = Li; R^1= Me, R^2 = NH_2

10b Pn = P; M = Li; R^1= Me, R^2 = NH_2

11a Pn = N; M = Li; R^1= Me, R^2 = PH_2

11b Pn = P; M = Li; R^1= Me, R^2 = PH_2

12a Pn = N; M = Li; R^1= Me, R^2 = OMe

12b Pn = P; M = Li; R^1= Me, R^2 = OMe

13a Pn = N; M = Li; R^1= Me, R^2 = SMe.

13b Pn = P; M = Li; R^1= Me, R^2 = SMe

14a Pn = N; M = Li; R^1= Me, R^2 = F

14b Pn = P; M = Li; R^1= Me, R^2 = F

15a Pn = N; M = Li; R^1= Me, R^2 = Cl

15b Pn = P; M = Li; R^1= Me, R^2 = Cl

RESULTS AND DISCUSSION

Initially, we optimized the structures of four model compounds of both the *E*- and *Z*-isomers of **1a** and **1b** at the RHF/6-31G* level using the GAUSSIAN98 program.[5] The optimized structures are shown in Figure 1. Both the *Z*-isomers, ***Z*-1a** and ***Z*-1b**, are more stable by 14.1 and 3.1 kcal · mol^{-1}, respectively, than the *E*-isomers. The most noticeable feature of ***Z*-1a** is that the lithium atom forms a three-membered ring of $\underbrace{\text{Li—N—C}}$. The bond angles of ∠Li—N—C and ∠Li—C—N are very acute (73.4° and 66.2° respectively). The phosphorus analog ***Z*-1b** has a similar feature. The bond angles of ∠Li—P—C and ∠Li—C—P are also very acute (55.5° and 80.7° respectively). On the other hand, the *E*-isomers have obtuse angles of ∠Li—C—N = 116° in ***E*-1a** and

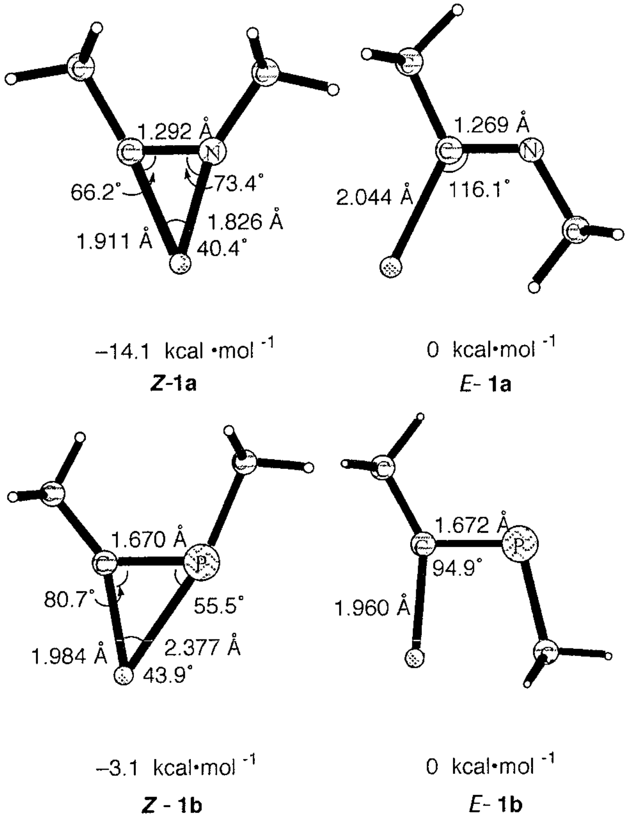


FIGURE 1 Optimized structures of **1**.

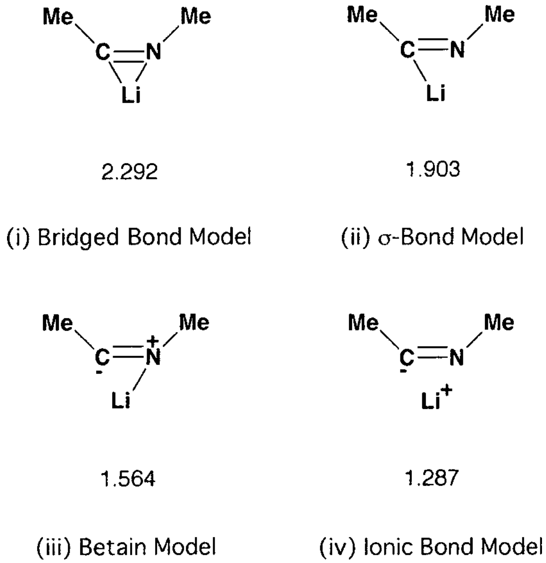


FIGURE 2 Bond models and Lewis index.

∠Li—C—P = 95° in ***E*-1b**. The angle in the phosphorus derivative is much narrower. These results demonstrate the general importance of metallobridge structures and the thermodynamic preference for the *Z*-configuration.

We subjected the electronic structure of ***Z*-1a** to the bond model analysis[6]* on the basis of the four models (Figure 2). The bridged bond model (i) has a three-membered ring including the lithium atom.

---

*The single Slater determinant Ψ for the electronic structure can be expanded into electron configurations:

$$\Psi = C_G\Phi_G + \Sigma C_T\Phi_T + \cdots$$

In the ground configuration (Φ_G), a pair of electrons occupies a bonding orbital of a chemical bond (a nonbonding orbital of an unshared electron pair). Interaction between bonds is accompanied by electron delocalization. This is expressed by mixing an electron-transferred configuration (Φ_T) where an electron shifts from a bonding orbital of one bond to an antibonding orbital of another.

The bond orbitals of the hybrid atomic orbitals are optimized to give the maximum value for Lewis index, the coefficient of the ground configuration (C_G).

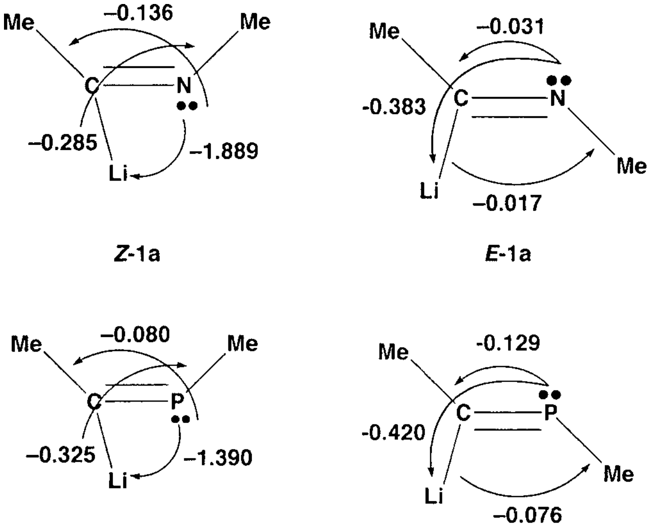
To estimate the interactions between the bond orbitals i and j, we used the interbond energy IBE[7] which is derived from the following equation:

$$\mathrm{IBE}_{ij} = \mathrm{P}_{ij}(\mathrm{H}_{ij} + \mathrm{F}_{ij})$$

where P_{ij}, H_{ij}, and F_{ij} are the elements of the density, Fock and core Hamiltonian matrices, respectively.

Lithium atom is divalent, connected to both of the carbon and the nitrogen. The σ bond model (ii) has normal bonds. Lithium is bonded only to the carbon atom and the nitrogen has a lone pair. For the betain model (iii), lithium is bonded to the nitrogen rather than to the carbon. The ionic bond model (iv) is an ion pair of a lithium cation and an imidoyl anion. Lewis index (LI).[6] Indicates the weight of the Lewis structure (represented by a bond model) in the whole electronic structure of one molecule. The calculated LI values of the bond models are shown in Figure 2. The bond model with the highest LI is the bridged bond model (i) (2.292). The bridged bond model (i) may be the most appropriate picture for **Z-1a**. However, we used the second appropriate σ bond model (ii) to scrutinize the origins of the thermodynamic preference for the *Z*-isomer by comparison with the *E*-isomer. Note that the σ bond model (ii), where normal connectivity is retained at the carbon atom of the imidoyl group, has a larger LI than the betain model (iii).

Figure 3 summarizes the interbond energy of **1**. The greatest difference between **Z-1a** and ***E*-1a** was found in electron delocalization due to strong coordination of the heteroatom to the Lewis acidic and cationic lithium atom. The interbond energy between the lone pair on nitrogen and the vacant p orbital on the metal is greater in **Z-1a** (IBE = −1.889 a.u.). The electrostatic interaction also contributes to the attraction between the lithium ion and the nitrogen atom. These make the bond



Z-1a *E*-1a

Z-1b *E*-1b

FIGURE 3 Interbond energy (IBE/a.u.) of **1** at the RHF/6-31G* level.

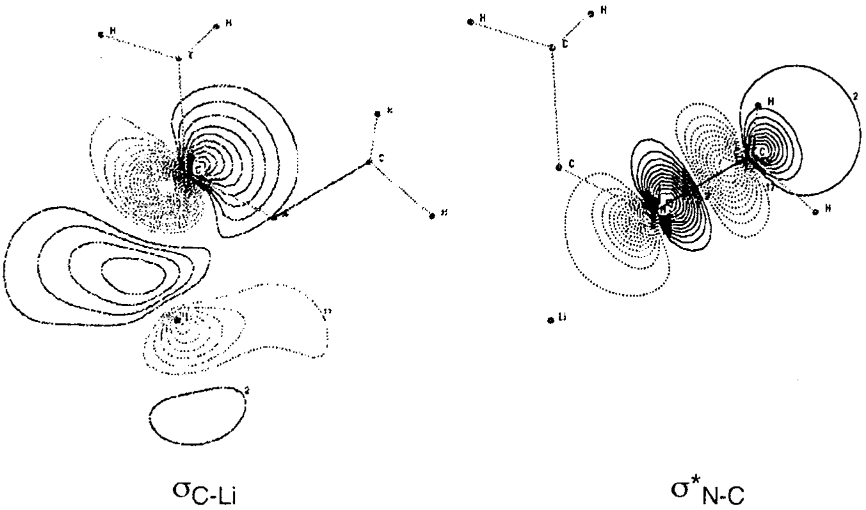


FIGURE 4 Contour plot of $\sigma_{\mathrm{C-Li}}$ and $\sigma^*_{\mathrm{N-C}}$.

angles acute, and form a metallobridged three-membered ring. The delocalization from σ_{CLi} to $\sigma^*_{\mathrm{N-CH3}}$ (IBE = −0.285 a.u.) and n_{N} to the vicinal $\sigma^*_{\mathrm{C-CH3}}$ (IBE = −0.136 a.u.) also significantly favors the *Z*-configuration due to the antiperiplanar relation. The σ_{CLi} bond extends appreciably outward from the ring (Figure 4), as is observed for CH_3OCH_2Li, and facilitates good overlap with the $\sigma^*_{\mathrm{N-CH3}}$ orbital in parallel.

Substitution of nitrogen by phosphorus gave almost the same result. However, the difference in energy is smaller than in the nitrogen analogs. Due to the low Lewis basicity of phosphorus, the Lewis acid-base coordination is weakened (IBE = −1.390 a.u.), but is still predominant. The antiperiplanar delocalization from σ_{CLi} to $\sigma^*_{\mathrm{P-CH3}}$ (IBE = −0.325 a.u.) is more essential because the energy (0.477 a.u.) of $\sigma^*_{\mathrm{P-CH3}}$ is lower than that (0.713 a.u.) of $\sigma^*_{\mathrm{N-CH3}}$. The delocalization from np to $\sigma^*_{\mathrm{C-CH3}}$ (IBE = −0.080 a.u.) is less considerable because the lone pair on phosphorus overlap with $\sigma^*_{\mathrm{C-CH3}}$ ($S_{n\sigma*} = 0.091$) less than n_{N} in **Z-1a** ($S_{n\sigma*} = 0.105$).

We further examined effects of the metal atom on the *Z*-preference. Heavier alkali metals, sodium and potassium, possess lower Lewis acidity than lithium. The 1,2-metallobridging should be considerably disfavored by the heavier metals. Decrease in the *Z*-preference of **2** and **3** was predicted and confirmed (Table I). The IBE value between the lone pair on nitrogen and the vacant p orbital on the metal decreases on going from −1.889 a.u. for **Z-1a** (M = Li); −1.321 a.u. for **Z-2a** (M = Na); −0.802 a.u. for **Z-3a** (M = K). On the other hand, the

TABLE I Calculated Energy Differences (ΔE) Between *Z*- and *E*-Isomers (RHF/6-31G*, ZPE Corrected) and Interbond Energies (IBE) of *Z*-Isomers

Compd.	ΔE/kcal $\cdot$ mol^{-1a}	IBE$_{(\mathrm{nPn}\rightarrow \mathrm{p^*M})}$ /a.u.	IBE$_{(\sigma \mathrm{C—M}\rightarrow {}^*\mathrm{Pn–C})}$ /a.u.	IBE$_{(\mathrm{nPn}\rightarrow \sigma^*\mathrm{C–C})}$ /a.u.
Z-1a	−14.1	−1.889	−0.285	−0.136
Z-1b	−3.1	−1.390	−0.325	−0.096
Z-2a	−4.7	−1.320	−0.360	−0.214
Z-2b	−2.7	−0.802	−0.396	−0.121
Z-3a	−5.7	−0.921	−0.317	−0.193
Z-3b	−4.0	−0.622	−0.427	−0.104

[a] E(*Z*-isomer)-E(*E*-isomer).

antiperiplanar delocalization from σCM to $\sigma^*_{\mathrm{N—CH3}}$ (IBE = −0.360 a.u. for **Z-2a**, M = Na; IBE = −0.317 a.u. for **Z-3a**, M = K) occurs more than that from σ_{CLi} to $\sigma^*_{\mathrm{N—CH3}}$ in **Z-1a** (IBE = −0.285 a.u.). This is the case with the delocalization from nN to $\sigma^*_{\mathrm{C—CH3}}$ (IBE = −0.214 a.u. for **Z-2a** and IBE = −0.193 a.u. for **Z-3a**: cf. IBE = −0.136 a.u. for **Z-1a**). The antiperiplanar effect is important for the *Z*-preference for M = Na, K, but not important for the dependence of the *Z*-preference on the metals. Electrostatic attraction contributes more to the *Z*-preference on the substitution with heavier alkali metals (the calculated total atomic charge: Li (0.370 in **Z-1a**) $<$ Na (0.525 in **Z-2a**) $<$ K (0.694 in **Z-3a**)). This is not in agreement with the decrease in the *Z*-preference. So, the electrostatic interaction is not important for the dependence of the *Z*-preference on the metals. The bond model analysis of the phosphorus analogs showed similar features. The IBE values are −1.390 a.u. (**Z-1b**), −0.802 a.u. (**Z-2b**), −0.622 a.u. (**Z-3b**) for the Lewis acid-base interaction; −0.325 a.u. (**Z-1b**), −0.396 a.u. (**Z-2b**), −0.427 a.u. (**Z-3b**) for the delocalization from σ_{CM} to $\sigma^*_{\mathrm{P—CH3}}$; −0.096 a.u. (**Z-1b**), −0.121 a.u. (**Z-2b**), −0.104 a.u. (**Z-3b**) for the delocalization from np to $\sigma^*_{\mathrm{C—CH3}}$. As a result, the 1,2-metallobridging by the Lewis acid-base interaction and the antiperiplanar effect is important for the *Z*-preference, while 1,2-chelation is predominant in the decrease in the *Z*-preference of heavy metal derivatives.

The results of the bond model analysis showed that the antiperiplanar delocalization from $\mathrm{n_N}$ to $\sigma^*_{\mathrm{C—CH3}}$ should favor the *Z*-configuration. Substitution of the methyl group in **Z-1a** by a more electronegative substituent was predicted to enhance the *Z*-preference. This prediction was confirmed by our calculations of the prototypes **4–6** (Table II). The *Z*-preference increases with OMe and SMe substitution, but decreases with more electropositive $\mathrm{SiH_3}$ substitution. We further attempted to examine halogen substitution **7** and **8**. However, the imidoyl isomers

TABLE II Calculated Energy Differences (ΔE) Between *Z*- and *E*-Isomers (RHF/6-31G*, ZPE Corrected)

Compd. (Pn = N)	ΔE/kcal $\cdot$ mol^{-1a}	Compd (Pn = P)	ΔE/kcal $\cdot$ mol^{-1a}
1a	−14.1	**1b**	−3.1
4a	−13.4	**4b**	−1.7
5a	−21.6	**5b**	−6.6
6a	−27.1	**6b**	−4.0
7a	−10.2	**7b**	1.2
8a	[b]	**8b**	−4.6
9a	[b]	**9b**	−0.1
10a	7.2	**10b**	17.9
11a	−4.7	**11b**	8.5
12a	8.1	**12b**	15.3
13a	−3.8	**13b**	11.2
14a	[c]	**14b**	14.1
15a	[b]	**15b**	[b]

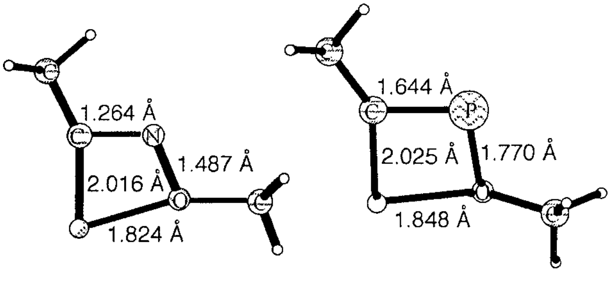
[a] E(*Z*-isomer)-E(*E*-isomer).

[b] The *E*-isomer was not located. See text.

[c] Both isomers were not located. See text.

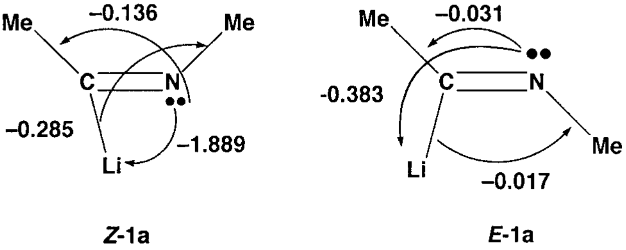
***E*-7a** and ***E*-8a** are very labile to liberate LiF and LiCl, respectively. We could not locate their optimized structures. *Z*-l-fluoro- and *Z*-l-chlorophosphaethenyllithium are more stable than the corresponding *E*-isomers by 4.6 and 0.1 kcal · mol^{-1} respectively.

The antiperiplanar delocalization from $\sigma_{\mathrm{C-Li}}$ to $\sigma^*_{\mathrm{N-CH3}}$ more stabilizes **Z-1a** than the one from n_N to $\sigma^*_{\mathrm{C-CH3}}$. It was more promising that substitution at the nitrogen/phosphorus atom by an electronegative atom substituent would increase the *Z*-preference. However, most of the compounds studied here showed *E*-preference (Table II), because of 1,4-chelation of the substituent hetero atom to Li (Figure 5). Only *Z*-*N*-phosphinoacetimidolithium **11a** and *Z*-*N*-methylthioacetimidolithium **13a** are more stable by 4.7 kcal · mol^{-1} and 3.8 kcal · mol^{-1} than their



E-**10a** *E*-**10b**

FIGURE 5 Structures of some *E*-isomer preferred compounds.



Interbond Energy (IBE, in a.u.) of **1a**.

E-isomers due to relatively weak chelation of the P and S atoms. The halogen-substituted substrates are very facile to liberate lithium salts. Only *Z*-*P*-chloro-1-methylphosphaethynyllithium **15a** was located as a stable isomer.

Yoshifuji[8] recently reported that the kinetically transmetallated product of the *E*-isomer of 1-phenylthio-2-(2,4,6-tri-*t*-butylphenyl)-2-phosphaethenyllithium was transformed exclusively to the *Z*-isomer in good agreement with our results. Niecke reported the X-ray analysis of *Z*-*P*-mesityl-1-chlorophosphaethenyllithium. However, it is solvated by two molecules of dimethoxyethane and has no metallobridge structure.[9] The solvation may lead to weaken the metallobridge. The antiperiplanar effect contributes to the preference of the stereoisomers in solution.

CONCLUSION

We showed that imidoyl- and phosphaethenyl(alkali metals) would thermodynamically prefer the *Z*-configuration. The *Z*-preference should originate from 1,2-metallobridging by the delocalization of lone pairs on N or P to vacant p-orbitals of the alkali metals and from the antiperiplanar effect of the delocalization from σ_{C-M} to $\sigma^*_{N(P)-R^2}$ and from $n_{N(P)}$ to the C—R^1 bond. Heavier alkali metals reduce the *Z*-preference due to weak Lewis acidity. The *Z*-preference is enhanced by electron-withdrawing groups (MeO and MeS) at the carbon atom of the double bond. However, fluorine substitution led to facile elimination of LiF from **7**. On the other hand, substitution at the nitrogen/phosphorus mostly results in *E*-preference because of 1,4-chelation of the lone pair of the substituents to alkali metals. Only *N*-phosphinoacetimidolithium **11** and *N*-methylthioacetimidolithium **13** show the *Z*-preference due to the poor ability of chelation of P and S among the substrates calculated here. For halogen substitution, local energy minima were not located except **15a** due to the facile elimination of lithium salts.

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