5140 *Organometallics* **2005,** *24,* 5140−5146

Theoretical Studies of Cycloaddition Reactions of Cationic Aluminum β-Diketiminate Alkyl Complexes with Alkenes and Alkynes

Alireza Ariafard and Zhenyang Lin*

Department of Chemistry and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Richard F. Jordan*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Received July 10, 2005

Cycloaddition reactions of cationic $\{HC(CHNX)_2\}Al(R)^+$ aluminum β-diketiminate complexes (X = variable substituent) with alkenes and alkynes to form bicyclic diimine species, $\{\kappa^3\text{-}N,N,C\text{-}HC(CH{=}NX)_2(CR_2CR_2)\}Al(R)^+$ and $\{\kappa^3\text{-}N,N,C\text{-}HC(CH{=}NX)_2(CR{=}CR)\}Al(R)^+$, respectively, were studied by density functional theory. Alkenes and alkynes form $\{HC(CHNMe)_2\}Al(Me)(substrate)^+$ adducts with binding energies ranging from 11.4 (ethylene) to 19.4 (2-butyne) kcal/mol. Alkene and alkyne coordination is stronger than CH_2Cl_2 coordination to $\{HC(CHNMe)_2\}Al(Me)^+$ by 0.4 (ethylene) to 8.4 (2-butyne) kcal/mol. Alkynes bind more strongly than sterically similar alkenes, and alkyl substituents on the alkenes and alkynes enhance binding. Electron-withdrawing groups on the diketiminate nitrogens (X) enhance alkene and alkyne coordination. These trends reflect the fact that the Al−substrate binding is dominated by substrate-to-Al σ-donation. Cycloaddition of $\{HC(CHNX)_2\}Al(Me)(alkene)^+$ species proceeds by a concerted asynchronous process through an unsymmetrical transition state in which the new Al−C bond is almost fully formed, the C═C bond is lengthened ca. halfway between the reactant and product distances, the Al−N and C−C distances within the diketiminate ring are lengthened but the C−N bonds are shortened, and the new C−C distance is long. Alkyl substituents on the alkene and electron-withdrawing substituents on the diketiminate nitrogens disfavor cycloaddition of $\{HC(CHNX)_2\}Al(Me)(alkene)^+$. These substituents enhance the interaction between the alkene HOMO and the $\{HC(CHNX)_2\}Al(Me)(alkene)^+$ LUMO+1 (Al $3p_z$), which stabilizes the $\{HC(CHNX)_2\}Al(Me)(alkene)^+$ species, and decrease the interaction between the $\{HC(CHNX)_2\}Al(Me)^+$ HOMO and the alkene LUMO, which destabilizes the cycloadduct. Cycloaddition of $\{HC(CHNX)_2\}Al(Me)(alkyne)^+$ species is more exothermic than cycloaddition of analogous alkene adducts because the newly formed C−C and Al−C bonds in the $\{\kappa^3\text{-}N,N,C\text{-}HC(CH{=}NX)_2(CR{=}CR)\}Al(R)^+$ alkyne cycloadducts involve sp^2-hybridized carbons and are stronger than those in the alkene cycloadducts, which involve sp^3-hybridized carbons.

Introduction

Cationic aluminum alkyl complexes are interesting because the charge may result in enhanced electrophilic character and different reactivity compared to neutral aluminum species.[1−4] Jordan et al. investigated the chemistry of cationic aluminum β-diketiminate complexes of general type $\{HC(CMeNAr)_2\}Al(R)^+$ (Ar = 2,6-$^iPr_2$-Ph, counterion = $B(C_6F_5)_4^-$, eqs 1−4).[5] The reaction of $\{HC(CMeNAr)_2\}Al(^iBu)_2$ (**1a**) with Ph_3C^+ proceeds by β-hydride abstraction and yields the monoalkyl complex $\{HC(CMeNAr)_2\}Al(^iBu)^+$ (**2a**, eq 1). The isobutylene

---

* To whom correspondence should be addressed. E-mail: chzlin@ust.hk; rfjordan@uchicago.edu.

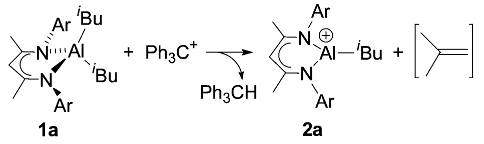
(1) (a) Atwood, D. A. *Coord. Chem. Rev.* **1998**, *176*, 407. (b) Atwood, D. A.; Yearwood, B. C. *J. Organomet. Chem.* **2000**, *600*, 186. (c) Liu, S.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Organomet. Chem.* **2000**, *596*, 109. (d) Jegier, J. A.; Atwood, D. A. *Inorg. Chem.* **1997**, *36*, 2034. (e) Atwood, D.; Jegier, J. *Inorg. Chem.* **1996**, *35*, 4277. (f) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc.* **1995**, *117*, 6779. (g) Atwood, D.; Jegier, J. *Chem. Commun.* **1996**, 1507. (h) Munoz-Hernandez, M.-A.; Sannigrahi, B.; Atwood, D. A. *J. Am. Chem. Soc.* **1999**, *121*, 6747. (d) Jegier, J. A.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Chem. Soc., Dalton Trans.* **1999**, 2583.

(2) (a) Bochmann, M.; Dawson, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2226. (b) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908. (c) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (d) Lancaster, S. J.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **1999**, 1533.

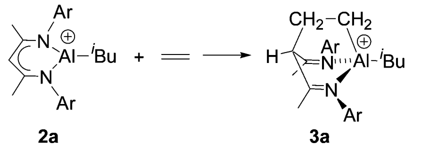
(3) (a) Cosle'dan, F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 705. (b) Pappalardo, D.; Tedesco, C.; Pellecchia, C. *Eur. J. Inorg. Chem.* **2002**, 621. (c) Baugh, L. S.; Sissano, J. A. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1633. (d) Cui, C. M.; Giesbrecht, G. R.; Schmidt, J. A. R.; Arnold, J. *Inorg. Chim. Acta* **2003**, *351*, 404. (e) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1472. (f) Dagorne, S.; Lavanant, L.; Welter, R.; Chassenieux, C.; Haquette, P.; Jaouen, G. *Organometallics* **2003**, *18*, 3732. (g) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523. (h) Lewinski, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789.

10.1021/om050577v CCC: $30.25

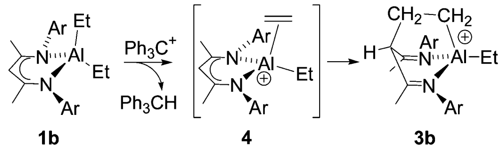
coproduct is polymerized under the reaction conditions, presumably by a cationic mechanism. Complex **2a** reacts with ethylene by a cycloaddition process to yield the bicyclic β-diimine complex **3a** (eq 2). The reaction of diethyl complex **1b** with Ph_3C^+ affords the analogous bicyclic cation **3b** directly (eq 3), via β-hydride abstraction to produce $\{HC(CMeNAr)_2\}Al(Et)(ethylene)^+$ (**4**, not observed) followed by cycloaddition. Interestingly, these cycloaddition reactions are reversible. For example, as shown in eq 4, **3b** reacts with 2-butyne to yield bicyclic complex **5**, presumably by initial extrusion of ethylene followed by trapping of $\{HC(CMeNAr)_2\}Al(Et)^+$ by 2-butyne cycloaddition.[6]



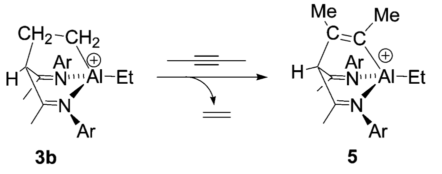
(1)



(2)



(3)



(4)

In this article, we employ density functional theory calculations to study the factors that influence these cycloaddition reactions. Earlier theoretical studies of cationic aluminum alkyls focused on their alkene insertion and β-H transfer chemistry.[7]

Computational Details

Density functional theory calculations at the B3LYP level[8] were used to study the cycloaddition reactions. The effective core potentials of Hay and Wadt with double-ζ valance basis sets (LanL2DZ)[9] were used for Al and Si. The 6-31G[10] basis set was used for C, H, F, and N. Polarization functions were added for Al ($\zeta_d = 0.198$), Si ($\zeta_d = 0.262$), F ($\zeta_d = 1.496$), N ($\zeta_d = 0.864$), and those C atoms that are involved in the cycloaddition reactions and those that are part of the β-diketiminate-Al chelate ring ($\zeta_d = 0.6$).[11] Frequency calculations at the same level of theory and basis sets were performed to identify all stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). Calculations of intrinsic reaction coordinates (IRC)[12] were used on the transition states to confirm that such structures connect the two corresponding minima. All calculations were performed with the Gaussian 03 software package.[13] Mulliken population analyses were carried out using the MullPop program.[14]

Results and Discussion

$\{HC(CMeNAr)_2\}Al(R)(L)^+$ Species. Experimental studies of $\{HC(CMeNAr)_2\}Al(R)^+$ species were performed in chlorocarbon solvents, in which the formation of $\{HC(CMeNAr)_2\}Al(R)(ClR)^+$ solvent adducts is probable.[15] The reaction of a $\{HC(CMeNAr)_2\}Al(R)^+$ or $\{HC(CMeNAr)_2\}Al(R)(ClR)^+$ species with an alkene or alkyne likely proceeds by initial complexation of the substrate followed by cycloaddition. Therefore, we first investigated the energetics of alkene and alkyne coordination to $\{HC(CHNX)_2\}Al(Me)^+$ model species, by calculating the reaction energies for displacement of CH_2Cl_2 from

---

[4] (a) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125. (b) Ihara, E.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277. (c) Korolev, A. V.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 11605. (d) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673. (e) Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 8291. (f) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274.

[5] Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384.

[6] For related reactions of transition metal species see: (a) Weiss, M. C.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 3389. (b) Weiss, M. C.; Gordon, G. C.; Goedken, V. L. *J. Am. Chem. Soc.* **1979**, *101*, 857. (c) Koford, P.; Moore, P.; Alcock, N. W.; Clase, H. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1261. (d) Koford, P.; Alcock, N. W.; Moore, P. *Acta Chem. Scand.* **1993**, *47*, 1083. (e) Cotton, F. A.; Czuchajowska-Wiesinger, J. *Gazz. Chem. Ital.* **1992**, *122*, 321. (f) Setsune, J.; Saito, Y.; Ishimaru, Y.; Ikeda, M.; Kitao, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 639. (g) Setsune, J.; Ikeda, M.; Kitao, T. *J. Am. Chem. Soc.* **1987**, *109*, 6515. (h) Riley, D. P.; Sone, J. A.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 767. (i) Cotton, F. A.; Czuchajowska, J. *J. Am. Chem. Soc.* **1991**, *113*, 3427. (j) Russel, D. A.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1743. (k) Russel, D. A.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1749. (l) Barlex, D. M.; Jarvis, A. C.; Kemmitt, R. D. W.; Kimura, B. Y. *J. Chem. Soc., Dalton Trans.* **1972**, 2549. (m) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3771.

[7] (a) Talarico, G.; Budzelaar, P. H. M.; Gal, A. W. *J. Comput. Chem.* **2000**, *21*, 398. (b) Talarico, G.; Budzelaar, P. H. M. *Organometallics* **2000**, *19*, 5691. (c) Meier, R. J.; Koglin, E. *Macromol. Theory Simul.* **2004**, *13*, 133. (d) Reinhold, M.; McGrady, R. J.; Meier, R. J. *J. Chem. Soc., Dalton Trans.* **1999**, 487. (e) Meier, R. J.; Koglin, E. *J. Phys. Chem. A* **2001**, *105*, 3867.

[8] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (c) Lee, C.; Yang, W.; Parr, G. *Phys. Rev.* **1988**, *B37*, 785.

[9] (a) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

[10] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[11] Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier Science Pub. Co.: Amsterdam, 1984.

[12] (a) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161. (b) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

[13] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B05; Gaussian, Inc.: Pittsburgh, PA, 2003.

[14] *MullPop*, a program written by Reinaldo Pis Diez at the National University of La Plata, Argentina.

[15] (a) Delpech, F.; Guzei, I. A.; Jordan, R. F. *Organometallics* **2002**, *21*, 1167. (b) Korolev, A. V.; Delpech, F.; Dagorne, S.; Guzei, I. A.; Jordan, R. F. *Organometallics* **2001**, *20*, 3367.

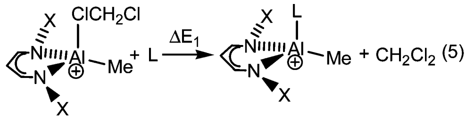
Table 1. Reaction Energies Calculated for Eqs 5 and 6, where X = Me

L	ΔE_1 (kcal/mol)	ΔE_2 (kcal/mol)
$H_2C{=}CH_2$	−0.4	11.4
$Me_2C{=}CH_2$	−6.2	17.2
trans-MeHC=CMeH	−2.3	13.4
$Me_2C{=}CMe_2$	−5.3	16.4
$HC{\equiv}CH$	−2.7	13.7
$MeC{\equiv}CMe$	−8.4	19.4

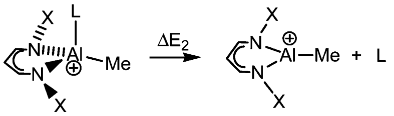
Table 2. Reaction Energies Calculated for Eqs 5 and 6, where L = Ethylene

X	ΔE_1 (kcal/mol)	ΔE_2 (kcal/mol)
CF_3	−2.9	19.4
SiF_3	−1.9	17.8
H	−0.5	12.1
SiH_3	−1.3	12.2
Ph	−0.1	9.6
^tBu	−1.6	8.5

$\{HC(CHNX)_2\}Al(Me)(Cl_2CH_2)^+$ by substrate (ΔE_1, eq 5) and for ethylene dissociation from $\{HC(CHNX)_2\}Al(Me)(CH_2{=}CH_2)^+$ (ΔE_2, eq 6). The results of these calculations are summarized in Tables 1 and 2.



6Me: X = Me, L = $H_2C{=}CH_2$
6CF₃: X = CF_3, L = $H_2C{=}CH_2$
6SiF₃: X = SiF_3, L = $H_2C{=}CH_2$
6H: X = H, L = $H_2C{=}CH_2$
6SiH₃: X = SiH_3, L = $H_2C{=}CH_2$
6Ph: X = Ph, L = $H_2C{=}CH_2$
6tBu: X = ^tBu, L = $H_2C{=}CH_2$
7Me: X = Me, L = $Me_2C{=}CH_2$
8Me: X = Me, L = $HC{\equiv}CH$
9Me: X = Me, L = $MeC{\equiv}CMe$



(6)

Several trends are apparent from Tables 1 and 2. First, the alkene and alkyne complexes are predicted to be slightly more stable than the CH_2Cl_2 adducts, and alkynes bind more strongly than sterically similar alkenes. For example, displacement of CH_2Cl_2 from $\{HC(CHNMe)_2\}Al(Me)(Cl_2CH_2)^+$ by ethylene and acetylene is exothermic by 0.4 and 2.7 kcal/mol, respectively. Second, alkyl substituents on the alkenes and alkynes enhance substrate binding. For example, isobutylene binds to $\{HC(CHNMe)_2\}Al(Me)^+$ more strongly than ethylene by 5.8 kcal/mol, and 2-butyne binds more strongly than acetylene by 5.7 kcal/mol. Third, as summarized in Table 2, the substituents on the diketiminate nitrogen atoms (X) strongly influence the binding energies. Electron-withdrawing N-substituents such as CF_3 or SiF_3 enhance alkene and alkyne coordination, while electron-donating N-substituents such as ^tBu weaken the binding of these substrates. These trends reflect the fact that the Al−substrate binding is dominated by substrate-to-Al σ-donation and that no significant back-bonding to the substrate π* orbitals is present.[16]

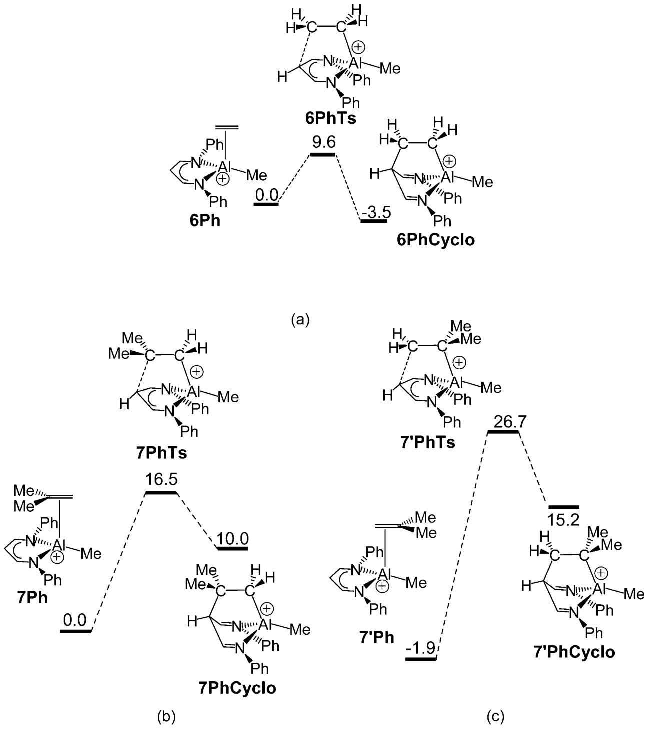
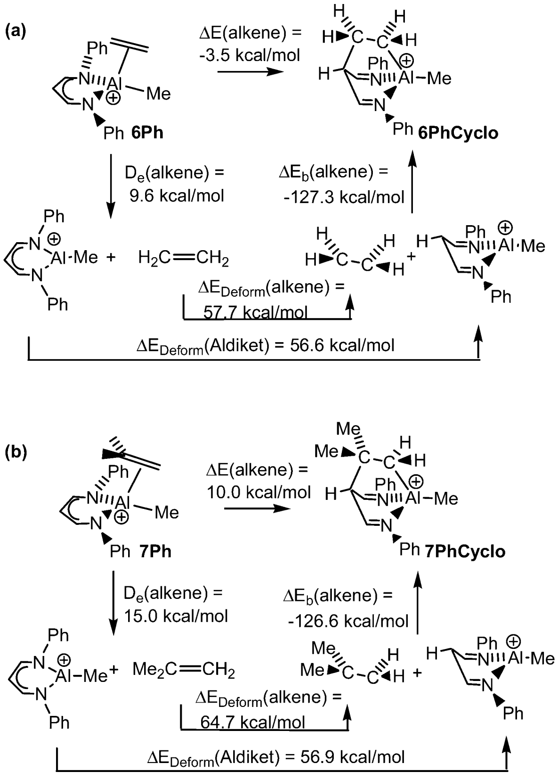


Figure 1. Energy profiles for the cycloaddition reactions of **6Ph** (a), **7Ph** (b), and **7′Ph** (c). The calculated relative energies are given in kcal/mol.

Scheme 1



Alkene Cycloaddition Reactions. Since the alkene adducts are more stable than the solvent adducts, we use the alkene adducts as the starting points in the

---

[16] The entropy contribution is expected to be similar for each case and should not influence these trends in binding strength.

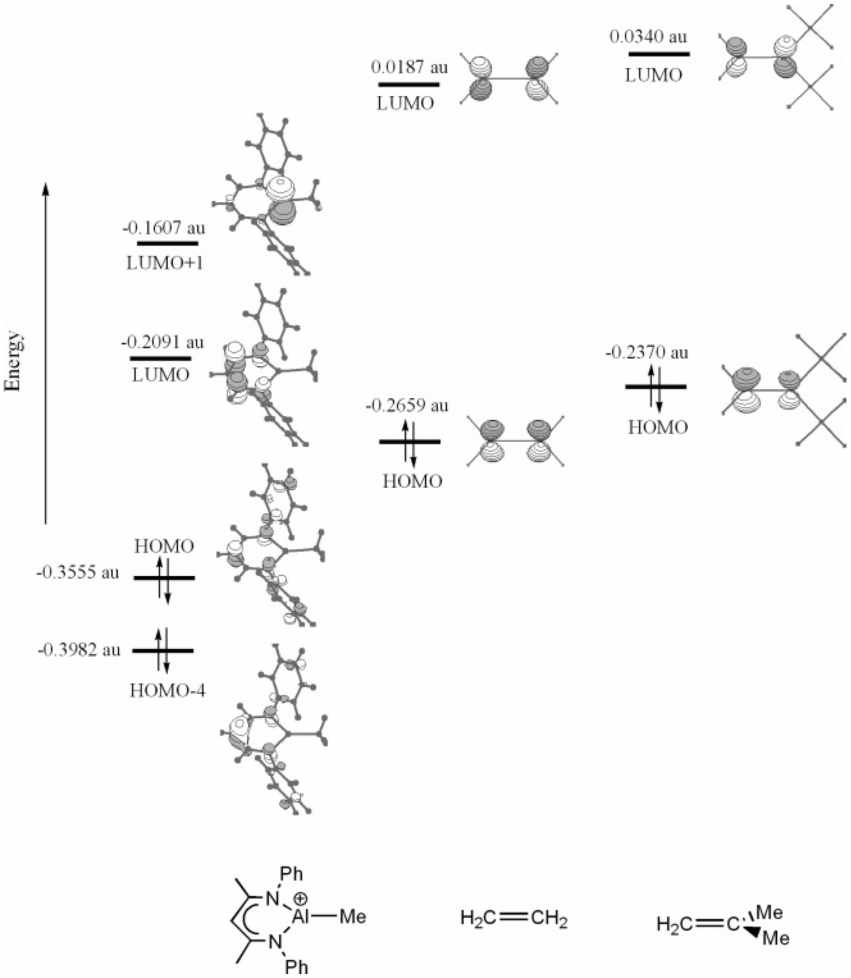


Figure 2. Frontier orbitals of the $\{HC(CHNPh)_2\}Al(Me)^+$ cation, $H_2C{=}CH_2$ and $H_2C{=}CMe_2$. Energies are given in atomic units (au).

discussion below. Energy profiles for cycloaddition of the model alkene complexes $\{HC(CHNPh)_2\}Al(Me)(ethylene)^+$ (**6Ph**) and $\{HC(CHNPh)_2\}Al(Me)(isobutylene)^+$ (**7Ph** and **7′Ph**) are compared in Figure 1. **7Ph** and **7′Ph** are isomers that differ in the orientation of the isobutylene ligand. Cycloaddition of **6Ph** to **6PhCyclo** is exothermic by 3.5 kcal/mol and has a barrier of only 9.6 kcal/mol (Figure 1a). In contrast, the cycloaddition reactions of **7Ph** and **7′Ph** are both endothermic and have higher barriers (Figure 1b,c). These results are consistent with the observed facile cycloadditions in eqs 2 and 3 and the lack of cycloaddition in eq 1.

To probe the origins of the difference in cycloaddition reactivity of **6Ph** and **7Ph**, the energy decomposition scheme in Scheme 1 was investigated.[17] Scheme 1 shows that the difference in the reaction energies for **6Ph** and **7Ph** results from a significant difference in the binding energies of the starting adducts (D_e(alkene)) and a difference in the alkene deformation energies $\Delta E_{\mathrm{Deform}}$(alkene). Figure 2 shows spatial plots and orbital energies for the frontier orbitals of $\{HC(CHNPh)_2\}Al(Me)^+$, ethylene, and isobutylene. Alkene coordination involves interaction of the alkene HOMO with the $\{HC(CHNPh)_2\}Al(Me)^+$ LUMO+1, which is essentially the Al $3p_z$ orbital. The better energy matching in the isobutylene case results in a larger D_e(alkene) value. The higher deformation energy for isobutylene versus ethylene results from the increase in steric repulsion between the two Me groups[18] and from a greater destabilization of isobutylene HOMO compared to the ethylene HOMO upon deformation.[19]

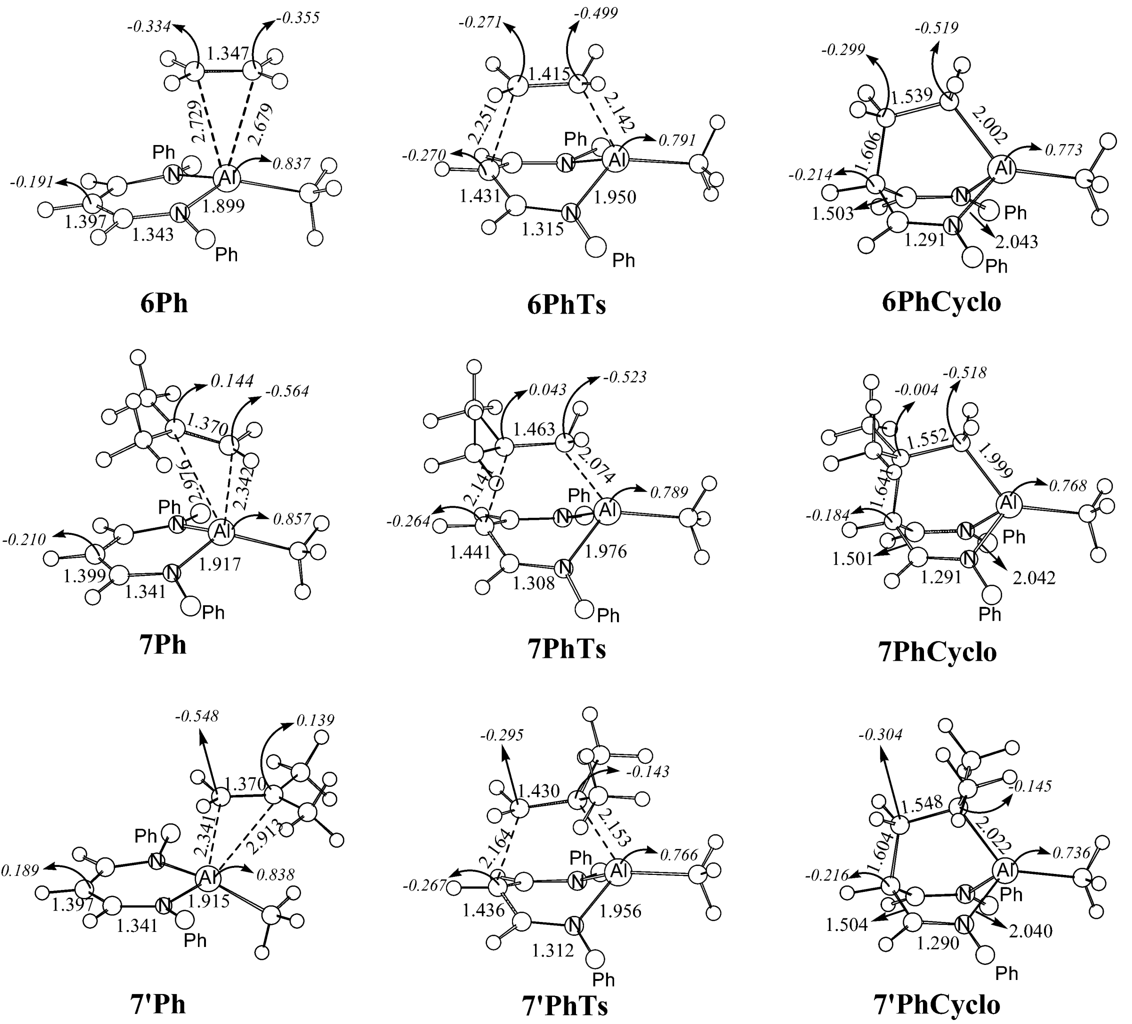
Alkene cycloaddition involves formation of a new C−C bond and cleavage of the alkene π bond via net nucleophilic attack of the β-diketiminate C2 carbon on the coordinated alkene. A key factor that is expected to influence the relative stabilities of **6PhCyclo** and **7PhCyclo** is the interaction between the filled frontier orbitals of $\{HC(CHNPh)_2\}Al(Me)^+$ that contain significant orbital density at the β-diketiminate C2 carbon and the alkene LUMO. As shown in Figure 2, the $\{HC(CHNPh)_2\}Al(Me)^+$ cation has two high-lying filled orbitals (HOMO and HOMO-4) with significant coefficients at the β-diketiminate C2 carbon, due to mixing of the N-*Ph* π systems with the β-diketiminate orbitals. N-Substituents that form only σ bonds with N give rise to only one such orbital. The ethylene LUMO (π^*) is lower in energy than the isobutylene LUMO and hence interacts more effectively with the $\{HC(CHNPh)_2\}Al(Me)^+$ HOMO and HOMO−4 orbitals, contributing to

---

(17) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

(18) The closest H- - -H contact between the two isobutylene Me groups decreases from ca. 2.583 Å in **7Ph** to ca. 2.499 Å in **7PhCyclo**.

(19) The HOMO of the deformed isobutylene is raised in energy by 0.0214 au (atomic units) when compared with that of isobutylene. The HOMO of the deformed ethylene is raised in energy by 0.0180 au when compared with that of ethylene.



6Ph **6PhTs** **6PhCyclo**

7Ph **7PhTs** **7PhCyclo**

7'Ph **7'PhTs** **7'PhCyclo**

Figure 3. B3LYP-optimized structures for **6Ph**, **7Ph**, and **7′Ph**, their cycloaddition products **6PhCyclo**, **7PhCyclo**, and **7′PhCyclo**, and the transition states **6PhTs**, **7PhTs**, and **7′PhTs** that link these species. Selected bond distances are given in Å. Mulliken atomic charges for selected atoms are also given (in italics).

the greater exothermicity for cycloaddition of **6Ph** versus **7Ph** (Figure 1).

B3LYP-optimized structures for **6Ph**, **7Ph**, and **7′Ph**, the corresponding cycloaddition products **6PhCyclo**, **7PhCyclo**, and **7′PhCyclo**, and the transition states **6PhTs**, **7PhTs**, and **7′PhTs** that link these species are shown in Figure 3. Mulliken charges for selected atoms in these species are also given in Figure 3. The net charge transfer to the two alkene vinyl carbons upon going from **6Ph** to **6PhCylco** (0.129*e*) is greater than that for conversion of **7Ph** to **7PhCylco** (0.102*e*) or **7′Ph** to **7′PhCylco** (0.040*e*). Additionally, the lengthening of the alkene C=C bond upon going from **6Ph** to **6PhCylco** (0.192 Å) is greater than that for conversion of **7Ph** to **7PhCyclo** (0.182 Å) or **7′Ph** to **7′PhCyclo** (0.178 Å). These differences are consistent with a stronger interaction between the $\{HC(CHNPh)_2\}Al(Me)^+$ HOMO and HOMO−4 orbitals and the alkene LUMO in the case of **6Ph**.

The transition states **6PhTs**, **7PhTs**, and **7′PhTs** (Figure 3) are similar and are very unsymmetrical. In all three cases the new Al−C bond is almost fully formed, the C=C bond is lengthened ca. halfway between the reactant and product distances, and the new C−C distance is long. Within the diketiminate ring, the Al−N and C−C distances are lengthened, while the C−N bonds are shortened (Figure 3). From these results, it is concluded that the cycloaddition reactions are concerted but asynchronous, with the Al−C bond formation and the diketiminate reorganization happening earlier than the C−C bond formation.

The atomic charges and structural data in Figure 3 provide insight to why cycloaddition of **7′Ph** is disfavored relative to **7Ph**. In both **7′Ph** and **7Ph**, the alkene *C*Me$_2$=CH$_2$ carbon (C$_{int}$) carries a significant positive charge, while the CMe$_2$=*C*H$_2$ carbon (C$_{term}$) has a large negative charge. In **7Ph**, C$_{int}$ is positioned close to the nucleophilic *β*-diketiminate C2 carbon, and C$_{term}$ is positioned close to the positively charged Al center. However, in **7′Ph**, this arrangement is reversed, resulting in a higher barrier to cycloaddition. The closest H- - -H contact between the two isobutylene Me groups is 2.582 Å in **7PhTs** and 2.608 Å in **7′PhTs**, suggesting that differences in steric crowding between the Me groups do not contribute to the different stabilities of the two transition states.

Influence of N-Substituents. Model $\{HC(CHNX)_2\}Al(Me)(ethylene)^+$ complexes (**6X**) that contain different N-substituents (X) were investigated to probe how the properties of the *β*-diketiminate ligand influence cycloaddition reactivity. As noted above and summarized in Table 2, electron-withdrawing N-substituents en-

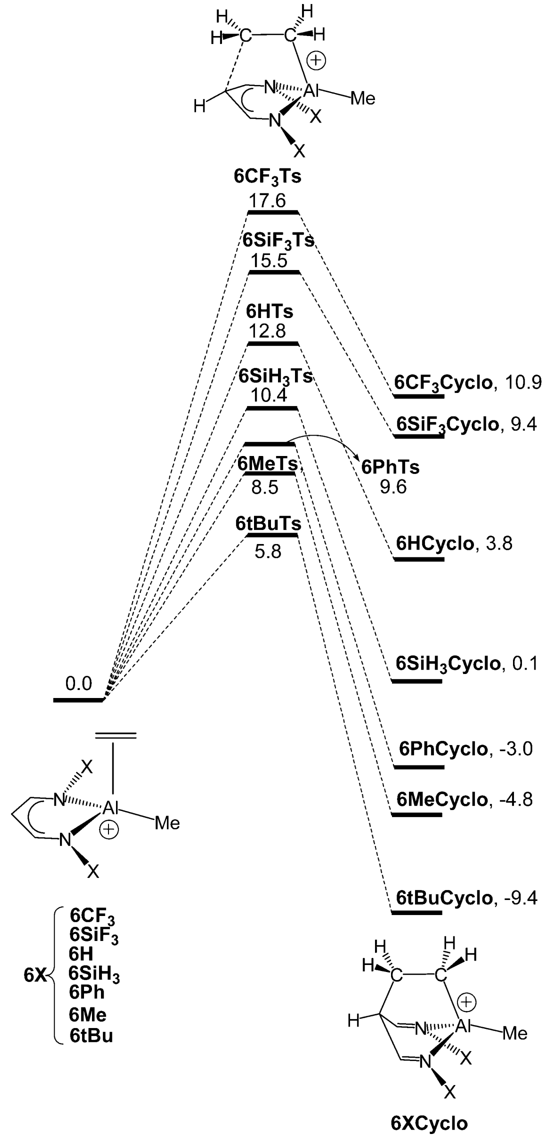


Figure 4. Energy profiles for ethylene cycloaddition of $\{HC(CHNX)_2\}Al(Me)^+$ species that contain different N-substituents (X). The calculated relative energies are given in kcal/mol.

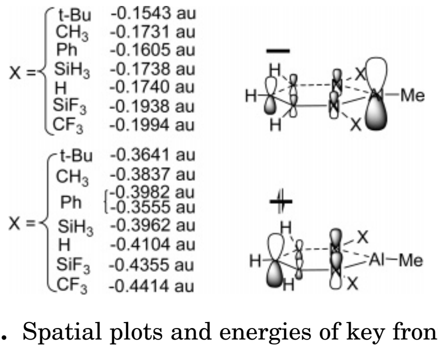


Figure 5. Spatial plots and energies of key frontier orbitals of $\{HC(CHNX)_2\}Al(Me)^+$ species that contain different N-substituents (X). Energies are given in atomic units (au).

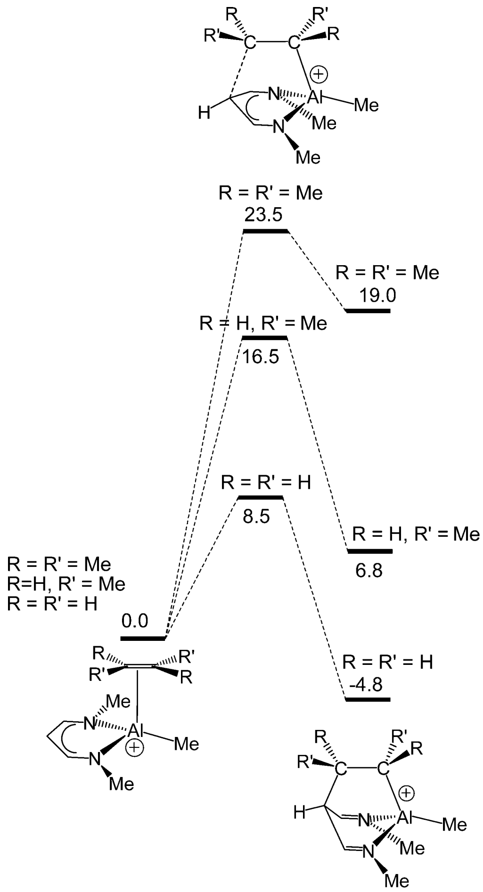
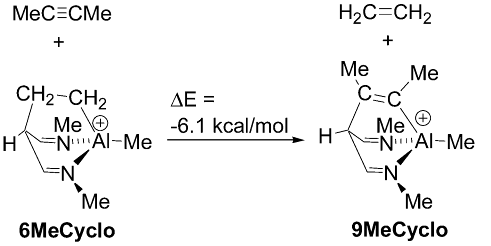


Figure 6. Energy profiles for cycloaddition $\{HC(CHNMe)_2\}$-$Al(Me)(alkene)^+$ species containing $CH_2{=}CH_2$, *trans*-$CHMe{=}CHMe$, or $CMe_2{=}CMe_2$. The calculated relative energies are given in kcal/mol.

hance ethylene binding to $\{HC(CHNX)_2\}Al(Me)^+$. However, as shown in Figure 4, electron-withdrawing substituents also strongly disfavor cycloaddition. These trends can be rationalized by the orbital interaction arguments developed above. The energies of the key frontier orbitals of $\{HC(CHNX)_2\}Al(Me)^+$ are given in Figure 5. Electron-withdrawing N-substituents stabilize the $\{HC(CHNX)_2\}Al(Me)^+$ LUMO+1 and thus enhance its interaction with the ethylene HOMO, stabilizing the corresponding **6X** complexes and increasing the insertion barrier. The difference in barrier heights for **6CF$_3$** versus **6tBu** corresponds almost exactly to the difference in ethylene binding energies (ΔE_2, Table 2). Electron-withdrawing N-substituents also stabilize the $\{HC(CHNX)_2\}Al(Me)^+$ HOMO, which decreases its interaction with the ethylene LUMO and disfavors the cycloaddition product.

Influence of Alkene Substituents. The influence of methyl substituents on the alkene was investigated using the model complex $\{HC(CHNMe)_2\}Al(Me)^+$. As shown in Figure 6, incorporation of methyl groups on the alkene increases the endothermicity and the barrier for cycloaddition. Following the discussion above, the methyl substituents increase the alkene HOMO and LUMO energies, which favors the π complex and disfavors the cycloaddition product. Steric repulsion among the Me groups becomes important for highly methylated alkenes.

Alkyne Cycloaddition. Equation 4 shows that the reaction of **3b** with 2-butyne yields cycloadduct **5** with release of ethylene. Consistent with this observation, the analogous reaction of **6MeCyclo** (eq 7) is calculated to be exothermic by 6.1 kcal/mol. These results suggest that alkyne cycloaddition is more exothermic than alkene cycloaddition.



(7)

Energy profiles for cycloaddition of the model alkyne complexes $\{HC(CHNMe)_2\}Al(Me)(HC{\equiv}CH)^+$ (**8Me**) and $\{HC(CHNMe)_2\}Al(Me)(MeC{\equiv}CMe)^+$ (**9Me**) are compared in Figure 7. Cycloaddition of **8Me** is exothermic by 19.2 kcal/mol. The incorporation of the Me groups on the alkyne in **9Me** strongly decreases the exothermicity and increases the barrier for cycloaddition. As for alkene cycloadditions, the methyl substituents in **9Me** raise the substrate HOMO and LUMO orbital energies, enhancing the alkyne binding in the starting substrate complex and destabilizing the bicyclic product.

To understand why alkyne cycloaddition is favored over alkene cycloaddition (eqs 4, 7), we compared the cycloaddition of **8Me** and **6Me** using the energy decomposition scheme in Scheme 2. The higher exothermicity of cycloaddition of **8Me** (19.2 kcal/mol) compared to **6Me** (4.8 kcal/mol) results primarily from the ΔE_b(substrate) term. The newly formed C−C and Al−C bonds in **8MeCyclo** involve sp^2-hybridized carbons and thus are stronger than those in **6MeCyclo**, which involve sp^3-hybridized carbons. This difference overwhelms the differences in substrate binding energies (D_e(substrate)) and $\{HC(CHNMe)_2\}Al(Me)^+$ deformation energies (ΔE_{deform}(Aldiket)), which favor cycloaddition of **8Me**.

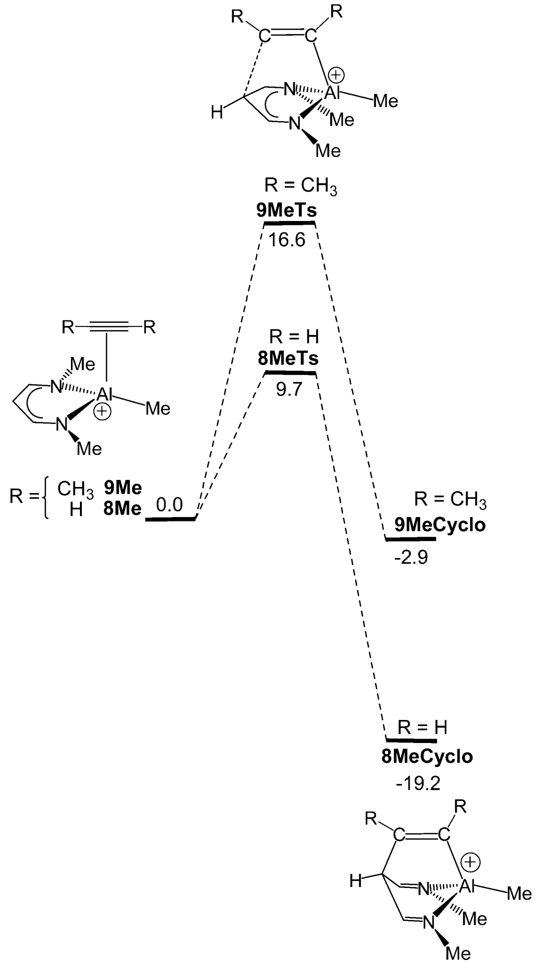
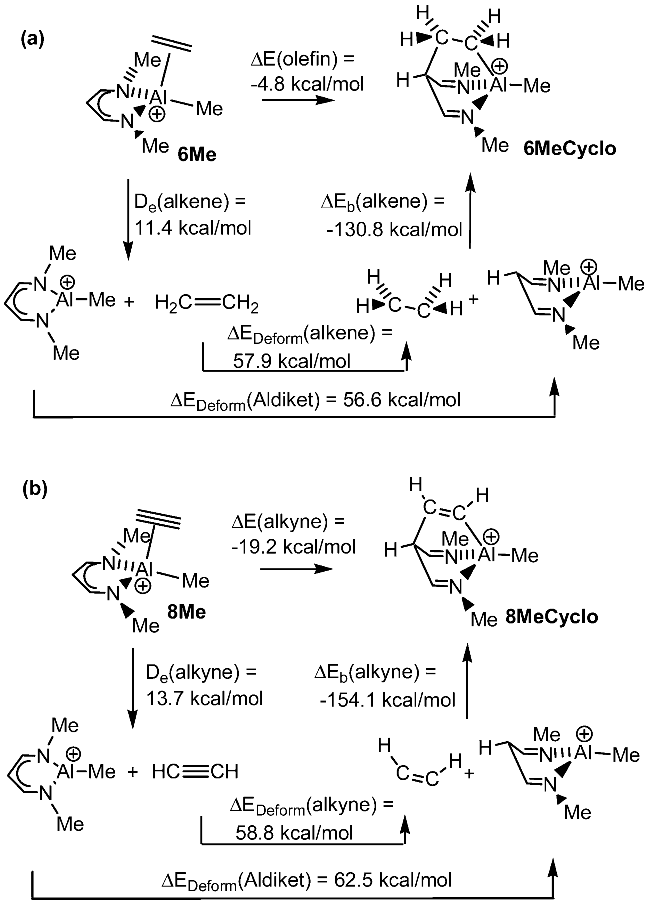


Figure 7. Energy profiles for cycloaddition of $\{HC(CHNMe)_2\}Al(Me)(HC{\equiv}CH)^+$ (**8Me**) and $\{HC(CHNMe)_2\}Al(Me)(MeC{\equiv}CMe)^+$ (**9Me**). The calculated relative energies are given in kcal/mol.

Scheme 2



Cycloaddition versus Insertion. Earlier density functional theory calculations on ethylene insertion in the Al−alkyl bonds of cationic aluminum alkyl complexes predicted insertion barriers of greater than 25 kcal/mol,[7] which is significantly higher than the barriers for cycloaddition determined in this work. These results are consistent with the experimental observation that $\{HC(CMeNAr)_2\}Al(R)^+$ species react with alkenes by cycloaddition rather than insertion into the Al−R bond. An important implication of this result is that nonreactive ancillary ligands will be required to favor reactions at the Al-alkyl group.

Acknowledgment. This work was supported by the Research Grant Council of Hong Kong (HKUST 6023/04P and DAG03/04.SC15), the University Grants Committee of Hong Kong through the Area of Excellence Scheme (Aoe), and the U.S. National Science Foundation (CHE-0212210).

Supporting Information Available: Cartesian coordinates of all the calculated structures reported in this article are available free of charge via the Internet at http://pubs.acs.org.

OM050577V