

Diradical Mechanisms for the Cycloaddition Reactions of 1,3-Butadiene, Benzene, Thiophene, Ethylene, and Acetylene on a Si(111)-7×7 Surface

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Abstract: The cycloaddition chemistry of several representative unsaturated hydrocarbons (1,3-butadiene, benzene, ethylene, and acetylene) and a heterocyclic aromatic (thiophene) on a Si(111)-7×7 surface has been explored by means of density functional cluster model calculations. It is shown that (i) 1,3-butadiene, benzene, and thiophene can undergo both [4+2]-like and [2+2]-like cycloadditions onto a rest atom–adatom pair, with the former process being favored over the latter both thermodynamically and kinetically; (ii) ethylene and acetylene undergo [2+2] cycloaddition-like chemisorptions onto a rest atom–adatom pair; and (iii) all of these reactions adopt diradical mechanisms. This is in contrast to the [4+2] cycloaddition-like chemisorptions of conjugated dienes on a Si(100) surface and to the prototype [4+2] cycloadditions in organic chemistry, which were believed to adopt concerted reaction pathways. Of particular interest is the [4+2]-like cycloaddition of *s-trans*-1,3-butadiene, whose stereochemistry is retained during its chemisorption on the Si(111) surface.

Introduction

In recent years, organic functionalization of surfaces of group IV semiconductors is of great interest because of its potential applications in microelectronic technology. So far, great efforts have been made to investigate the interaction and reaction of various types of organic molecules, such as unsaturated hydrocarbons, heterocyclic aromatics, ketones, alcohols, amines, and so on, with the surfaces of group IV semiconductors.¹ Among them, the most intensively investigated is the attachment of unsaturated hydrocarbons (e.g., alkenes, dienes, and benzenes) and allied heteroaromatics (e.g., thiophene, furan, and pyridine) on the two representative Si surfaces, Si(100)-2×1 and Si(111)-7×7.¹ Especially, in the study of these substances reacting with the Si(100)-2×1 surface, close interplays between experimentalists and theoreticians in the past few years have remarkably and rapidly improved our understanding of the nature of the interactions.¹ In contrast to the intensive experimental investigations reported on the corresponding interactions with the Si(111)-7×7 surface, matching theoretical investigations are relatively scarce, probably due to the structural heterogeneity of the Si(111)-7×7 surface. In this paper, we report the results of our density functional cluster model calculations on the mechanisms for the reactions of representative unsaturated

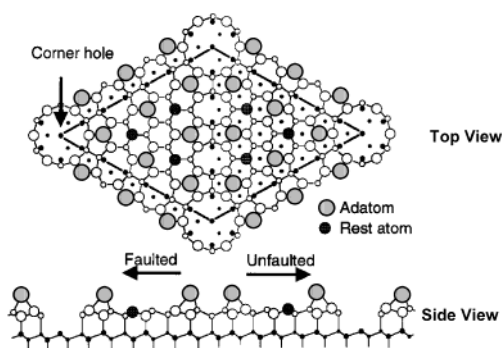


Figure 1. Atomic arrangement of Si(111)-7×7 surface.

hydrocarbons and heterocyclic aromatics such as 1,3-butadiene, benzene, thiophene, ethylene, and acetylene with the Si(111)-7×7 surface.

The reconstructed Si(111)-7×7 surface adopts the dimer-adatom-stacking fault (DAS) structure,² as is schematically displayed in Figure 1. Its large 7×7 surface unit cell contains seven chemically distinguishable types of surface atoms, including three corner adatoms, three center adatoms, and three rest atoms at both the faulted and the unfaulted halves, as well as one rest atom at the bottom of the deep corner hole, with a total of 19 dangling bonds (DBs). Such structural inhomogeneity confers this silicon surface high flexibility to various mechanically interesting chemical reactions.¹ In contrast, the structure of the reconstructed Si(100)-2×1 surface is much

(1) For recent reviews on chemical functionalization of the surfaces of group IV semiconductors, see: (a) Waltenburg, H. N.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 1589. (b) Hamers, R. J.; Wang, Y. *Chem. Rev.* **1996**, *96*, 1261. (c) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413. (d) Buriak, J. M. *Chem. Commun.* **1999**, 1051. (e) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. S.; Russell, J. N., Jr. *Acc. Chem. Res.* **2000**, *33*, 617. (f) Lu, X.; Lin, M. C. *Int. Rev. Phys. Chem.* **2002**, *21*, 137. (g) Bent, S. F. *J. Phys. Chem. B* **2002**, *106*, 2830. (h) Bent, S. F. *Surf. Sci.* **2002**, *500*, 879.

(2) (a) Takayanagi, K.; Tanishiro, Y.; Takahashi, M.; Takahashi, S. *J. Vac. Sci. Technol., A* **1985**, *3*, 1502. (b) Hamers, R. J.; Tromp, R. M.; Demuth, J. E. *Phys. Rev. Lett.* **1986**, *56*, 1972. (c) Wolkow, R.; Avouris, Ph. *Phys. Rev. Lett.* **1988**, *60*, 1049.

simpler; that is, adjacent silicon atoms on the surface are paired up to form dimers that are asymmetric at low temperatures.³ The bonding within a surface dimer can be described in terms of a strong σ bond and a weaker π bond, analogous to the bonding within the C=C double bond of simple alkenes.⁴ Such similarity led to experimental observations and theoretical findings that the dimer of the Si(100) surface does undergo the Diels–Alder reactions (i.e., [4+2] cycloaddition reactions) with 1,3-dienes,^{5,6} benzene,^{7,8} thiophene,^{9,10} and similar aromatics.^{10,11}

Adsorption of benzene and thiophene on the Si(111)- 7×7 surface has been investigated by various analytical techniques, including TPD (temperature programmed desorption), HREELS (high-resolution electron energy loss spectroscopy), LEED (low-energy electron diffraction), XPS (X-ray photoelectron spectroscopy), UPS (ultraviolet photoelectron spectroscopy), and STM (scanning tunneling microscopy).^{9a,12,13} TPD experiments revealed that almost all chemisorbed benzene and thiophene can be desorbed molecularly upon heating at elevated temperatures.^{12,13} Both molecules have been assumed to undergo [4+2] cycloaddition-like chemisorption on the Si(111)- 7×7 surface,^{9a,12,13}

wherein a rest atom–adatom pair assumes the role of a “dienophile”. Semiempirical quantum chemical and ab initio cluster model calculations^{13a,14} confirmed that the [4+2] cycloaddition-like product for thiophene^{13a} and benzene¹⁴ chemisorption is thermodynamically the most stable. Thus, it is very interesting that the Si(100) and Si(111) surfaces, which are structurally and electronically different, display a similar regioselectivity toward these cyclic aromatics. Previous density functional cluster model calculations^{8b,10a} have revealed that the [4+2] cycloadditions of benzene and thiophene onto the Si(100) surface adopt a concerted reaction pathway, similar to the prototype Diels–Alder (DA) reactions widely used in synthetic organic chemistry. Whether a similar reaction mechanism would be followed on the Si(111) surface remains unclear.

Besides its high reactivity toward cyclic aromatics, a Si(111)- 7×7 surface was found experimentally to also be quite reactive toward the simplest unsaturated hydrocarbons, ethylene¹⁵ and acetylene.¹⁶ STM and XPS experiments indicated that surface states assigned to rest atoms and adatoms were sensitively quenched upon adsorption of ethylene or acetylene, implying that both surface sites were involved in the adsorption.^{15,16} Accordingly, it was proposed that ethylene or acetylene was di- σ bonded onto an adjacent rest atom–adatom pair. This is somewhat similar to their adsorption on the Si(100)- 2×1 surface, where ethylene¹⁷ and acetylene^{18,19} were found to be di- σ bonded onto Si=Si dimers probably following stepwise, diradical

- (3) Tromp, R. M.; Hamers, R. J.; Demuth, J. E. *Phys. Rev. Lett.* **1985**, *55*, 1303.
- (4) Appelbaum, J. A.; Baraff, G. A.; Hamann, D. R. *Phys. Rev. B* **1976**, *14*, 588.
- (5) For examples of recent experiments on the adsorption of 1,3-dienes on Si(100), see: (a) Hovis, J. S.; Liu, H. B.; Hamers R. J. *J. Phys. Chem. B* **1998**, *102*, 6873. (b) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Chem. Phys.* **1998**, *108*, 4599.
- (6) (a) Konecny, R.; Doren, D. J. *Surf. Sci.* **1998**, *417*, 169. (b) Choi, C. H.; Gordon, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 11311.
- (7) For examples of recent experiments on the adsorption of benzene on Si(100), see: (a) Hofer, W. A.; Fisher, A. J.; Lopinski, G. P.; Wolkow, R. A. *Phys. Rev. B* **2001**, *61*, 085314. (b) Alavi, S.; Rousseau, R.; Patitsas, S. N.; Lopinski, G. P.; Wolkow, R. A.; Seideman, T. *Phys. Rev. Lett.* **2000**, *85*, 5327. (c) Stauffer, M.; Birkenheuer, U.; Belling, T.; Nortemann, F.; Rösch, N.; Widdra, W.; Kostov, K. L.; Moritz, T.; Menzel, D. *J. Chem. Phys.* **2000**, *112*, 2498. (d) Self, K. W.; Pelzel, R. I.; Owen, J. H. G.; Yan, C.; Widdra, W.; Weinberg, W. H. *J. Vac. Sci. Technol., A* **1998**, *16*, 1031. (e) Lopinski, G. P.; Fortier, T. M.; Moffatt, D. J.; Wolkow, R. A. *J. Vac. Sci. Technol., A* **1998**, *16*, 1037. (f) Borovsky, B.; Krueger, M.; Ganz, E. *Phys. Rev. B* **1998**, *57*, R4269. (g) Gokhale, S.; Trischberger, P.; Menzel, D.; Widdra, W.; Droge, H.; Steinruck, H. P.; Birkenheuer, U.; Gutdeutsch, U.; Rösch, N. *J. Chem. Phys.* **1998**, *108*, 5554.
- (8) (a) Silvestrelli, P. L.; Ancillotto, F.; Toigo, F. *Phys. Rev. B* **2000**, *62*, 1596. (b) Alavi, S.; Rousseau, R.; Seideman, T. *J. Chem. Phys.* **2000**, *113*, 4412. (c) Birkenheuer, U.; Gutdeutsch, U.; Rösch, N. *Surf. Sci.* **1998**, *409*, 213. (d) Wolkow, R. A.; Lopinski, G. P.; Moffatt, D. J. *Surf. Sci.* **1998**, *416*, L1107. (e) Jeong, H. D.; Ryu, S.; Lee, Y. S.; Kim, S. *Surf. Sci.* **1995**, *344*, L1226.
- (9) For examples of recent experiments on the adsorption of thiophene on Si(100), see: (a) Rousseau, G. B. D.; Dhanak, V.; Kadodwala, M. *Surf. Sci.* **2001**, *494*, 251. (b) Qiao, M. H.; Cao, Y.; Tao, F.; Liu, Q.; Deng, J. F.; Xu, G. Q. *J. Phys. Chem. B* **2000**, *104*, 11211. (c) Jeong, H. D.; Lee, Y. S.; Kim, S. *J. Chem. Phys.* **1996**, *105*, 5200.
- (10) (a) Lu, X.; Xu, X.; Wang, N.; Zhang, Q.; Lin, M. C. *J. Phys. Chem. B* **2001**, *105*, 10069. (b) Lu, X.; Lin, M. C.; Xu, X.; Wang, N.; Zhang, Q. *PhysChemComm* **2001**, 13.
- (11) Lu, X.; Xu, X.; Wang, N.; Zhang, Q. *New J. Chem.* **2002**, *26*, 160.
- (12) For examples of recent experiments on the adsorption of benzene on Si(111), see: (a) Tomimoto, H.; Takehara, T.; Fukawa, K.; Sumii, R.; Sekitani, T.; Tanaka, K. *Surf. Sci.* **2003**, *526*, 343. (b) Kawasaki, T.; Sakai, D.; Kishimoto, H.; Akbar, A. A.; Ogawa, T.; Oshima, C. *Surf. Interface Anal.* **2001**, *31*, 126. (c) Cao, Y.; Wei, X. M.; Chin, W. S.; Lai, Y. H.; Deng, J. F.; Bernasek, S. L.; Xu, G. Q. *J. Phys. Chem. B* **1999**, *103*, 5698. (d) Carbone, M.; Piancastelli, M. N.; Casaletto, M. P.; Zanoni, R.; Comtet, G.; Dujardin, G.; Hellner, L. *Phys. Rev. B* **2000**, *61*, 8531. (e) Carbone, M.; Piancastelli, M. N.; Zanoni, R.; Comtet, G.; Dujardin, G.; Hellner, L. *Surf. Sci.* **1998**, *407*, 275. (f) Taguchi, Y.; Ohta, Y.; Katsumi, T.; Ichikawa, K.; Aita, O. *J. Electron Spectrosc. Relat. Phenom.* **1998**, *88*, 671. (g) Brown, D. E.; Moffatt, D. J.; Wolkow, R. A. *Science* **1998**, *279*, 542. (h) Wolkow, R. A.; Moffatt, D. J. *J. Chem. Phys.* **1995**, *103*, 10696. (i) Macpherson, C. D.; Hu, D. Q.; Leung, K. T. *Solid State Commun.* **1991**, *80*, 217. (j) Taguchi, Y.; Fujisawa, M.; Nishijima, M. *Chem. Phys. Lett.* **1991**, *78*, 363.
- (13) (a) Cao, Y.; Yong, K. S.; Wang, Z. H.; Deng, J. F.; Lai, Y. H.; Xu, G. Q. *J. Chem. Phys.* **2001**, *115*, 3287. (b) Cao, Y.; Yong, K. S.; Wang, Z. Q.; Chin, W. S.; Lai, Y. H.; Deng, J. F.; Xu, G. Q. *J. Am. Chem. Soc.* **2000**, *122*, 1812. (c) Letarte, S.; Adnot, A.; Roy, D. *Surf. Sci.* **2000**, *448*, 212. (d) Macpherson, C. D.; Leung, K. T. *Phys. Rev. B* **1995**, *51*, 17995. (e) Macpherson, C. D.; Hu, D. Q.; Leung, K. T. *Surf. Sci.* **1992**, *276*, 156. (f) Hu, D. Q.; Macpherson, C. D.; Leung, K. T. *Solid State Commun.* **1991**, *78*, 1077.
- (14) (a) Wang, Z. H.; Cao, Y.; Xu, G. Q. *Chem. Phys. Lett.* **2001**, *338*, 7. (b) Li, Y. C.; Wang, W. N.; Cao, Y.; Fan, K. N. *Acta Chim. Sin.* **2002**, *60*, 653.
- (15) For experiments on the adsorption of ethylene on Si(111), see: (a) Rochet, F.; Jolly, F.; Bourmel, F.; Dufour, G.; Sirotti, F.; Cantin, J. L. *Phys. Rev. B* **1998**, *58*, 11029. (b) Kusunoki, I.; Takagaki, T.; Ishidzuka, S.; Igarai, Y.; Takaoka, T. *Surf. Sci.* **1997**, *380*, 131. (c) Carbone, M.; Zanoni, R.; Piancastelli, M. N.; Comtet, G.; Dujardin, G.; Hellner, L.; Mayner, A. *J. Electron Spectrosc. Relat. Phenom.* **1995**, *76*, 271. (d) Piancastelli, M. N.; Motta, N.; Sgarlata, A.; Balzarotti, A.; Decrescenzi, M. *Phys. Rev. B* **1993**, *48*, 17892. (e) Yshinobu, J.; Tsuda, H.; Onchi, M.; Nishijima, M. *Solid State Commun.* **1986**, *60*, 861.
- (16) For experiments on the adsorption of acetylene on Si(111), see: (a) De Renzi, V.; Biagi, R.; del Pennino, U. *Appl. Surf. Sci.* **2001**, *184*, 90. (b) De Renzi, V.; Biagi, R.; del Pennino, U. *Phys. Rev. B* **2001**, *64*, 155305. (c) Rochet, F.; Dufour, G.; Prieto, P.; Sirotti, F.; Stedile, F. C. *Phys. Rev. B* **1997**, *57*, 6738. (d) Yoshinobu, J.; Fukushi, D.; Uda, M.; Nomura, E.; Aono, M. *Phys. Rev. B* **1992**, *46*, 9520. (e) Yshinobu, J.; Tsuda, H.; Onchi, M.; Nishijima, M. *Chem. Phys. Lett.* **1986**, *130*, 170.
- (17) For examples of recent experiments on the adsorption of ethylene on Si(100), see: (a) Yeom, H. W.; Baek, S. Y.; Kim, J. W.; Lee, H. S.; Koh, H. *Phys. Rev. B* **2002**, *66*, 115308. (b) Nagao, M.; Yamashita, Y.; Machida, S.; Hamaguchi, K.; Yasui, F.; Mukai, K.; Yoshinobu, J. *Surf. Sci.* **2002**, *513*, 413. (c) Shimomura, M.; Munakata, M.; Iwasaki, A.; Ikeda, M.; Abukawa, T.; Sato, K.; Kawawa, T.; Shimizu, H.; Nagashima, N.; Kono, S. *Surf. Sci.* **2002**, *504*, 19. (d) Casaletto, M. P.; Zanoni, R.; Carbone, M.; Piancastelli, M. N.; Aballe, L.; Weiss, K.; Horn, K. *Phys. Rev. B* **2000**, *62*, 17128. (e) Matsui, F.; Yeom, H. W.; Matsuda, I.; Ohta, T. *Phys. Rev. B* **2000**, *62*, 5036. (f) Ikeda, M.; Maruoka, T.; Nagashima, N. *Surf. Sci.* **1998**, *416*, 240. (g) Matsui, F.; Yeom, H. W.; Imanishi, A.; Isawa, K.; Matsuda, I.; Ohta, T. *Surf. Sci.* **1998**, *401*, L413. (h) Liu, H. B.; Hamers, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 7593. (i) Ness, H.; Fisher, A. J. *Phys. Rev. B* **1997**, *55*, 10081.
- (18) For examples of recent experiments on the adsorption of acetylene on Si(100), see: (a) Terborg, R.; Polcik, M.; Hoeft, J. T.; Kittel, M.; Sayago, D. I.; Toomes, R. L.; Woodruff, D. P. *Phys. Rev. B* **2002**, *66*, 085333. (b) Kim, W.; Kim, H.; Lee, G.; Chung, J.; You, S. Y.; Hong, Y. K.; Koo, J. Y. *Surf. Sci.* **2002**, *514*, 376. (c) Kim, W.; Kim, H.; Lee, G.; Hong, Y. K.; Lee, K.; Hwang, C.; Kim, D. H.; Koo, J. Y. *Phys. Rev. B* **2001**, *64*, 193313. (d) Mezheny, S.; Lyubintsky, I.; Choyce, W. J.; Wolkow, R. A.; Yates, J. T. *Chem. Phys. Lett.* **2001**, *344*, 7. (e) Terborg, R.; Baumgartel, P.; Lindsay, R.; Schaff, O.; Giessel, T.; Hoeft, J. T.; Polcik, M.; Toomes, R. L.; Kulkarni, S.; Bradshaw, A. M.; Woodruff, D. P. *Phys. Rev. B* **2000**, *61*, 16697. (f) Xu, S. H.; Keefe, M.; Yang, Y.; Chen, C.; Yu, M.; Lapeyre, G. J.; Rotenberg, E.; Denlinger, J.; Yates, J. T. *Phys. Rev. Lett.* **2000**, *84*, 939. (g) Xu, S. H.; Yang, Y.; Keefe, M.; Lapeyre, G. J.; Rotenberg, E. *Phys. Rev. B* **1999**, *60*, 11586. (h) Li, L.; Tindall, C.; Takaoka, O.; Hasegawa, Y.; Sakurai, T. *Phys. Rev. B* **1997**, *56*, 4648.
- (19) In addition to the adsorption geometry specified in this manuscript, multiple adsorption geometries have been found for acetylene adsorption on the Si(100) surface,

mechanisms.^{17h,20,21} No theoretical study has been reported on the adsorption of ethylene and acetylene on the Si(111)-7×7 surface. Semiempirical quantum chemical calculations were reported regarding acetylene adsorption on an ideal Si(111) surface,²² which is structurally much different from the thermodynamically most stable Si(111)-7×7 surface. It is unclear whether the adsorption of ethylene and acetylene on the Si(111)-7×7 surface would also adopt a diradical mechanism. On the other hand, controversy exists on whether their adsorption would induce severe surface reconstruction.^{17,18}

The purpose of the present theoretical work is to explore mechanisms for the cycloaddition reactions of representative unsaturated hydrocarbons and heterocyclic aromatics such as 1,3-butadiene, benzene, thiophene, ethylene, and acetylene with the Si(111)-7×7 surface. It is noteworthy that neither experiment nor theoretical calculation has been reported on the adsorption of the simplest conjugated diene, 1,3-butadiene, on the Si(111)-7×7 surface.

Computational Details

We used a Si₁₆H₁₈ cluster model (Figure 2a) to represent the adjacent adatom–rest atom pair on a faulted half of a Si(111)-7×7 surface unit cell. This model had been used in our previous theoretical investigations of the dissociative chemisorptions of CH₃OH and NH₃ on the same surface;^{1f,23} merits and demerits of such a cluster model were discussed already.²³ The hybrid density functional (U)B3LYP method,²⁴ together with the effective-core-potential LANL2DZ basis set for the Si atom,²⁵ the standard 6-31+G* basis set for the C atom,²⁶ and the D95 basis set for the H atom,²⁷ was used to investigate the energetics of the reactions. Specifically, the UB3LYP method was used for the calculation of intermediates and transition states, as well as the Si₁₆H₁₈ cluster model, which are mostly singlet-diradical. Geometry optimizations with no constrained degrees of freedom were performed using analytical gradients and the Bery algorithm. Reported energies are ZPE(zero-point energy)-corrected. All calculations were performed with the Gaussian 98 package.²⁸

Results and Discussion

A. 1,3-Butadiene. 1,3-Butadiene always adopts two conformations, *s-trans*- and *s-cis*-orientations, wherein the latter is less favored in energy. We first consider the cycloaddition of *s-trans*-1,3-butadiene on the Si₁₆H₁₈ cluster model, for which the predicted intermediate, transition states, and products are depicted in Figure 2.

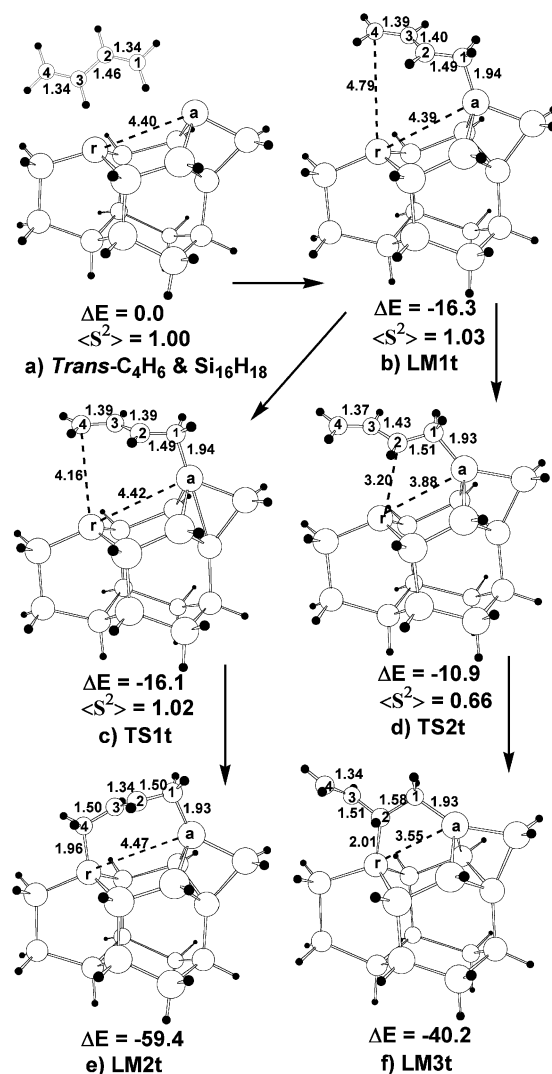


Figure 2. Optimized geometries (distance in Å) for the reactants, intermediates, transition states, and products of the cycloaddition of *trans*-1,3-butadiene on the Si₁₆H₁₈ cluster model. Energies (ΔE in kcal/mol) relative to isolated reactants and the $\langle S^2 \rangle$ values for the wave functions of these stationary points are also given.

As shown in Figure 2, the addition of *s-trans*-1,3-butadiene onto the cluster model is initiated by a barrierless attack of the C1 atom to the adatom of the surface model, forming a mono- σ bonded and singlet-diradical intermediate *LM1t*; the predicted formation energy is -16.3 kcal/mol. In *LM1t*, both the rest atom and the allylic group in the as-adsorbed butadiene are radical-like and subject to further radical–radical combination. Two possible pathways for such radical–radical combination can be envisaged: they are between either C4 or C2 of the as-adsorbed butadiene and the rest atom. The former process leads to the formation of a [4+2] cycloaddition-like product *LM2t*, and the latter leads to that of a [2+2] cycloaddition-like product *LM3t*. The predicted formation energies for *LM2t* and *LM3t* are -59.4 and -40.2 kcal/mol, respectively, indicating that the [4+2] cycloaddition-like pathway is thermodynamically favorable over the [2+2] cycloaddition one. Furthermore, two transition states, *TS1t* for the [4+2] cycloaddition-like process and *TS2t* for the [2+2] cycloaddition-like process, have been located. The transition state *TS1t* is found to be only 0.2 kcal/mol higher in energy than the intermediate *LM1t*, but 5.2 kcal/

- (20) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 4082.
 (21) Lu, X. *J. Am. Chem. Soc.* **2003**, *125*, 6384.
 (22) (a) Weiner, B.; Carmer, C. S.; Frenklach, M. *Phys. Rev. B* **1991**, *43*, 1678.
 (b) Chu, S. Y.; Anderson, A. B. *Surf. Sci.* **1988**, *194*, 55.
 (23) Lu, X.; Xu, X.; Wang, N.; Zhang, Q.; Lin, M. C. *Chem. Phys. Lett.* **2002**, *355*, 365.
 (24) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1989**, *37*, 785.
 (25) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
 (26) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
 (27) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; pp 1–28.
 (28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

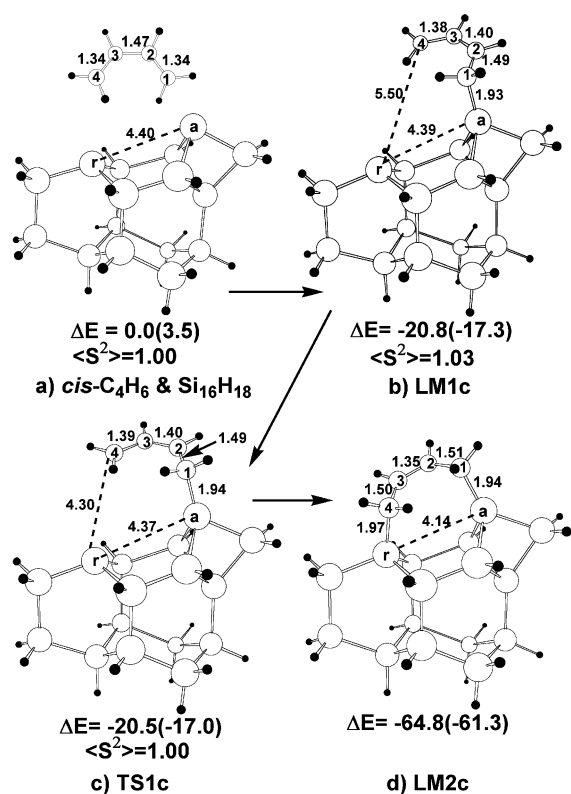


Figure 3. Optimized geometries (distance in Å) for the reactants, intermediate, transition state, and product of the cycloaddition of *cis*-1,3-butadiene on the Si₁₆H₁₈ cluster model. Energies (ΔE in kcal/mol) relative to isolated reactants and the <S²> values for the wave functions of these stationary points are also given. Energies relative to isolated *trans*-1,3-butadiene and the Si₁₆H₁₈ cluster model are given in parentheses.

mol lower than **TS2t**. It is evident that the [4+2] cycloaddition-like adsorption is overall barrierless and kinetically favorable over the [2+2] cycloaddition-like adsorption.

The above analysis clearly demonstrates that the adsorption of *s-trans*-1,3-butadiene on the Si(111)-7×7 surface would selectively give rise to the formation of the [4+2] cycloaddition-like product **LM2t** without a barrier, in which the stereochemistry of the *s-trans*-1,3-butadiene is retained. It is the unique electronic and geometric structures of Si(111) that facilitate *s-trans*-1,3-butadiene to undergo such a stereoselective cycloaddition. It should be mentioned that Wang et al. reported favorable [4+2] trans cycloaddition of ethyl vinyl ketone (EVK) on the X=X dimers (X = Si, Ge) of the Si(100) and Ge(100) surfaces.²⁹

At this stage, it is reasonable to deduce that, for the adsorption of *s-cis*-1,3-butadiene, an analogous [4+2] cycloaddition-like pathway would be favored over the [2+2] one. We thus calculated only the [4+2] cycloaddition-like pathway for *s-cis*-1,3-butadiene, which is depicted in Figure 3. The adsorption of *s-cis*-1,3-butadiene is also initiated by the barrierless formation of the singlet-diradical intermediate **LM1c**, which is predicted to be 20.8 kcal/mol lower than the isolated reactants, *s-cis*-1,3-butadiene and the Si₁₆H₁₈ cluster model. A transition state **TS1c**, which is only 0.3 kcal/mol higher than **LM1c** in energy, is located for further radical–radical combination within **LM1c**. The final product of such a stepwise [4+2] cycloaddition-like

process is **LM2c**, in which the stereochemistry of *s-cis*-1,3-butadiene is retained. The formation energy of **LM2c** is predicted to be -61.8 kcal/mol with respect to the isolated reactants, *s-cis*-1,3-butadiene and the Si₁₆H₁₈ cluster model.

To summarize, the (U)B3LYP cluster model calculations unambiguously reveal that both the *s-trans*- and the *s-cis*-conformations of 1,3-butadiene undergo barrierlessly the [4+2] cycloaddition-like adsorption on a rest atom–adatom pair in a Si(111)-7×7 surface by following a stepwise, diradical pathway. This is different from the adsorption of conjugated dienes on the Si(100)-2×1 surface, for which previous ab initio cluster model calculations predicted barrierless and concerted pathways.^{8b,10a}

B. Benzene. Similar to the adsorption of 1,3-butadiene, the adsorption of benzene on a rest atom–adatom pair in a Si(111)-7×7 surface also follows a stepwise, diradical mechanism. Both the [4+2] cycloaddition and the [2+2] cycloaddition pathways predicted by our (U)B3LYP cluster model calculations are depicted in Figure 4. A transition state **TS1b** is located for the formation of the mono-σ bonded, singlet-diradical intermediate **LM1b**. **TS1b** and **LM1b** are predicted to be by 9.2 and 6.7 kcal/mol, respectively, higher in energy than the isolated reactants, benzene and the Si₁₆H₁₈ cluster model. This is reasonable as the formation of the C1–Si_a bond in **LM1b** destroys the aromaticity of benzene. From **LM1b**, two transition states, **TS2b** and **TS3b**, have been located for the [4+2] cycloaddition-like and [2+2] cycloaddition-like pathways, respectively; their energies are higher by 1.0 and 5.4 kcal/mol, respectively, than that of intermediate **LM1b**. Furthermore, the [4+2] cycloaddition-like product **LM2b** is predicted to be 15.8 kcal/mol lower in energy than the [2+2] cycloaddition-like product **LM3b**. Accordingly, the [4+2] cycloaddition-like pathway is both thermodynamically and kinetically favorable over the [2+2] cycloaddition-like pathway. The adsorption of benzene on a rest atom–adatom pair of the Si(111)-7×7 surface should preferentially give rise to the [4+2] cycloaddition-like product **LM2b**. The overall activation barrier for the adsorption of benzene is 9.2 kcal/mol. This value might have been overestimated because of spin contamination.^{30–32} Yet the predicted adsorption energy of -21.5 kcal/mol is in quite good agreement with the experimental estimation^{12ij} of 21.9 ± 0.5 kcal/mol. This is reasonable as the [4+2] cycloaddition-like product **LM2b** adopts close-shell wave functions without spin contamination. The good agreement of the predicted adsorption energy with the experimental value justifies our choice of the Si₁₆H₁₈ cluster model.

C. Thiophene. In organic chemistry, thiophene behaves as a cisoid conjugated diene for [4+2] cycloadditions with dienophiles and is less reactive than 1,3-butadiene but more reactive than benzene in the [4+2] cycloaddition reactions. As shown above, both 1,3-butadiene and benzene prefer the [4+2] cycloaddition-like adsorption over the [2+2] cycloaddition-like adsorptions. It can be inferred that the adsorption of thiophene on the Si(111) surface also prefers a [4+2] cycloaddition-like

(30) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036.

(31) (a) Nendel, M.; Tolbert, L. M.; Herring, L. E.; Islam, M. N.; Houk, K. N. *J. Org. Chem.* **1999**, *64*, 976. (b) Tian, J.; Houk, K. N.; Klamer, F. G. *J. Phys. Chem. A* **1998**, *102*, 7662. (c) Firestone, R. A. *Heterocycles* **1987**, *25*, 61.

(32) Johnson, B. G.; Gonzalez, C. A.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1994**, *221*, 100.

(29) Wang, G. T.; Mui, C.; Musgrave, C. B.; Bent, S. F. *J. Am. Chem. Soc.* **2002**, *124*, 8990.

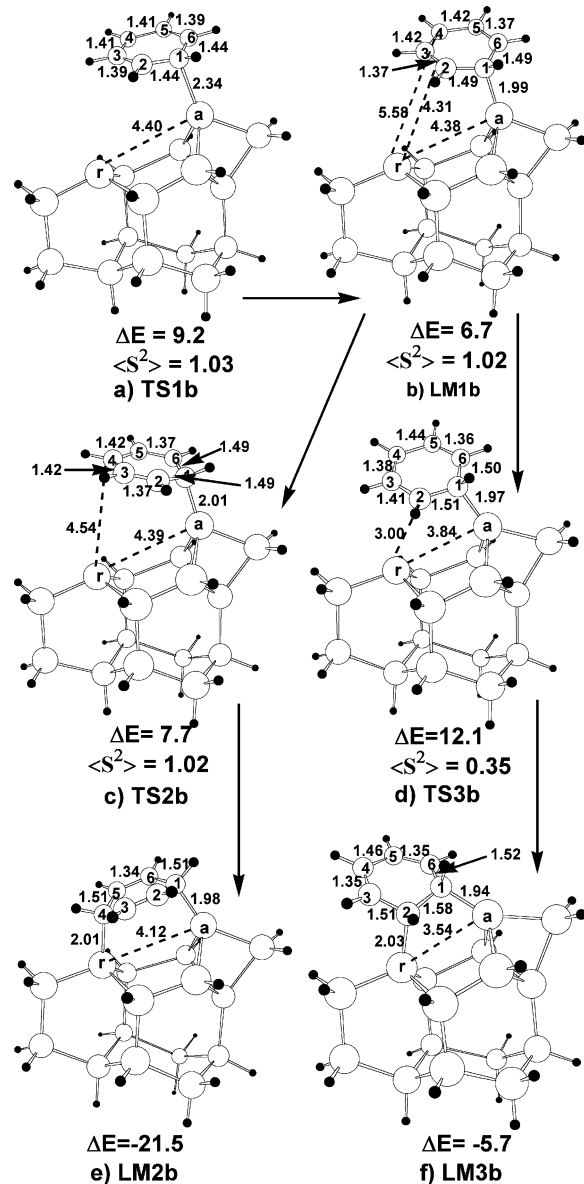


Figure 4. Optimized geometries (distance in Å) for the reactants, intermediates, transition states, and products of the cycloaddition of benzene on the Si₁₆H₁₈ cluster model. Energies (ΔE in kcal/mol) relative to the isolated reactants and the $\langle S^2 \rangle$ values for the wave functions of these stationary points are also presented.

pathway, which has been considered solely in the computations. The predicted reaction pathway is given in Figure 5.

As in the case of benzene, the adsorption of thiophene is initiated by the formation of a mono- σ bonded and singlet-diradical intermediate **LM1S** that requires overcoming an activation barrier of 5.4 kcal/mol at the transition state **TS1S**. **LM1S** is found to be lower in energy than isolated reactants by 4.6 kcal/mol. The endothermicity for the formation energy of **LM1S** can also be ascribed to the aromaticity of thiophene, which is destroyed by the formation of the C2–Si_a bond. It is interesting to compare **LM1S** with the mono- σ bonded intermediate **LM1b** formed in the adsorption pathway of benzene. Benzene has a higher aromaticity than does thiophene. The estimated resonance energies for benzene and thiophene are 28.3 and 16.5 kcal/mol, respectively.³³ The activation of benzene

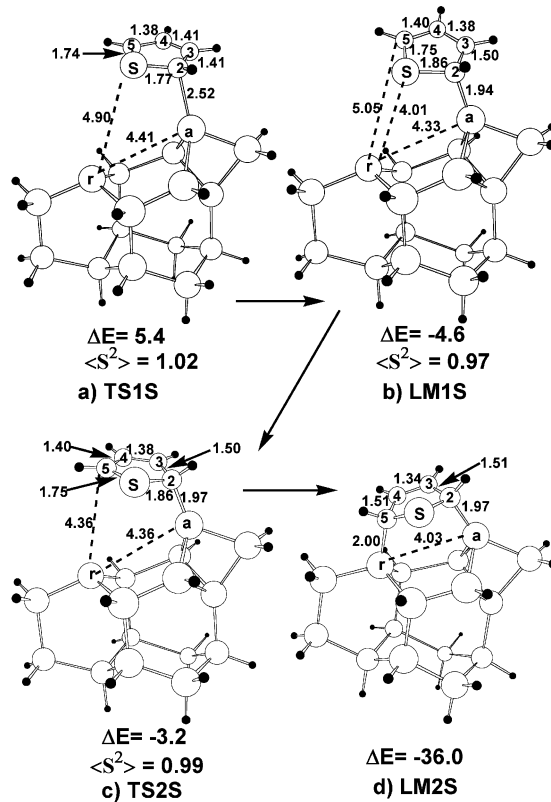


Figure 5. Optimized geometries (distance in Å) for the transition states, intermediate, and product of the cycloaddition of thiophene on the Si₁₆H₁₈ cluster model. Energies (ΔE , unit in kcal/mol) relative to the isolated reactants and the $\langle S^2 \rangle$ values for the wave functions of these stationary points are also given.

would be more difficult than that of thiophene. This is confirmed by our prediction that the formation of the mono- σ bonded intermediate **LM1S** for thiophene is both kinetically and thermodynamically easier than that of **LM1b** for benzene. More interesting is that the difference (11.3 kcal/mol) in the formation energy of **LM1S** and **LM1b** agrees excellently with the resonance energy gap (11.8 kcal/mol) of thiophene and benzene. A similar formation energy versus resonance energy relationship has previously been observed for the [4+2] cycloaddition of six- and five-membered ring aromatics on the Si(100) surface.^{10b}

As shown in Figure 5, the second step in the [4+2]-like cycloaddition of thiophene on the rest atom–adatom pair is a radical–radical combination forming the C5–Si_r bond. The transition state **TS2S** for this step is 1.4 kcal/mol higher in energy than the intermediate **LM1S**. The predicted formation energy for the [4+2] cycloaddition-like product **LM2S** is –36.0 kcal/mol. This value is comparable with the previously predicted adsorption energy (–34.3 kcal/mol)^{10a} for the [4+2] cycloaddition-like chemisorption of thiophene on the Si(100) surface.

D. Ethylene. Ethylene is predicted to undergo [2+2] cycloaddition-like adsorption on a rest atom–adatom pair, as shown in Figure 6. The predicted formation energy for the [2+2] cycloaddition-like product **LM1e** is –47.9 kcal/mol with respect to the isolated reactants, ethylene and the Si₁₆H₁₈ cluster model. Further detailed potential energy surface scanning reveals neither an intermediate nor a transition state along a diradical reaction pathway, in which adsorption is initiated by the barrierless formation of the C1–Si_a bond followed by the formation of the C2–Si_r bond. Thus, the [2+2] cycloaddition-like adsorption

(33) Dewar, M. J. S.; Holder, A. J. *Heterocycles* **1989**, *28*, 1135.

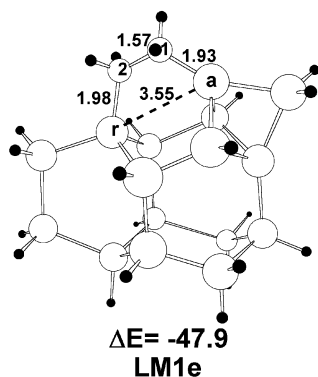


Figure 6. Optimized geometry (distance in Å) for the product of the cycloaddition of ethylene on the Si₁₆H₁₈ cluster model. The energy (ΔE , unit in kcal/mol) relative to the isolated reactants is presented.

of ethylene is quite facile on a rest atom–adatom pair of the Si(111)-7×7 surface without inducing severe substrate reconstruction. Similar [2+2] cycloaddition was found to occur on the Si(100)-2×1 surface, for which our previous B3LYP/6-31G* cluster model calculations predicted a diradical mechanism.²¹

E. Acetylene. Similar to the adsorption of ethylene, acetylene is predicted to undergo the [2+2] cycloaddition-like adsorption on a rest atom–adatom pair of the Si(111)-7×7 surface. However, the predicted reaction pathway (see Figure 7) for acetylene adsorption is more complicated than that for ethylene.

By forcing the acetylene molecule to approach the adatom site, we located a transition state **TS1a** preceding the formation of a mono- σ bonded and singlet-diradical intermediate **LM1a**. The predicted activation energy for the formation of **LM1a** from free acetylene is 3.7 kcal/mol at **TS1a**. The predicted formation energy for **LM1a** is -13.9 kcal/mol relative to the isolated reactants. From **LM1a**, intramolecular rotation of the H–C2 bond within the adsorbed acetylene is required to give rise to the second mono- σ bonded, singlet-diradical intermediate **LM2a**, so as to be prepared for further radical–radical combination. Such an intramolecular rotation has to overcome a barrier height of 3.9 kcal/mol (at **TS2a**) with respect to **LM1a**. **LM2a** is found to be by 12.2 and 1.7 kcal/mol lower in energy than the isolated reactants and the first intermediate **LM1a**, respectively. Following **LM2a**, a third transition state **TS3a**, which is only 0.7 kcal/mol higher in energy than **LM2a**, is located for ring-closing (radical–radical combination), that gives rise to the final [2+2] cycloaddition product **LM3a**. The predicted formation energy for **LM3a** is -66.5 kcal/mol relative to the isolated reactants.

In summary, the adsorption of acetylene on the Si(111) surface adopts a stepwise, diradical pathway, in which the rate-determining step is the first step, that is, the formation of the singlet-diradical intermediate **LM1a**, with an overall barrier height of 3.7 kcal/mol, as is schematically shown in Figure 8. This differs subtly from the stepwise, diradical pathway for acetylene adsorption on the Si(100) surface, in which the first step is the barrierless formation of a π -complex.²⁰

Concluding Remarks

We report the first theoretical investigation of the mechanisms for reactions of unsaturated hydrocarbons and the allied heterocyclic aromatics with the Si(111)-7×7 surface. Our density functional cluster model calculations predict stepwise, diradical pathways for these reactions. It is shown that the

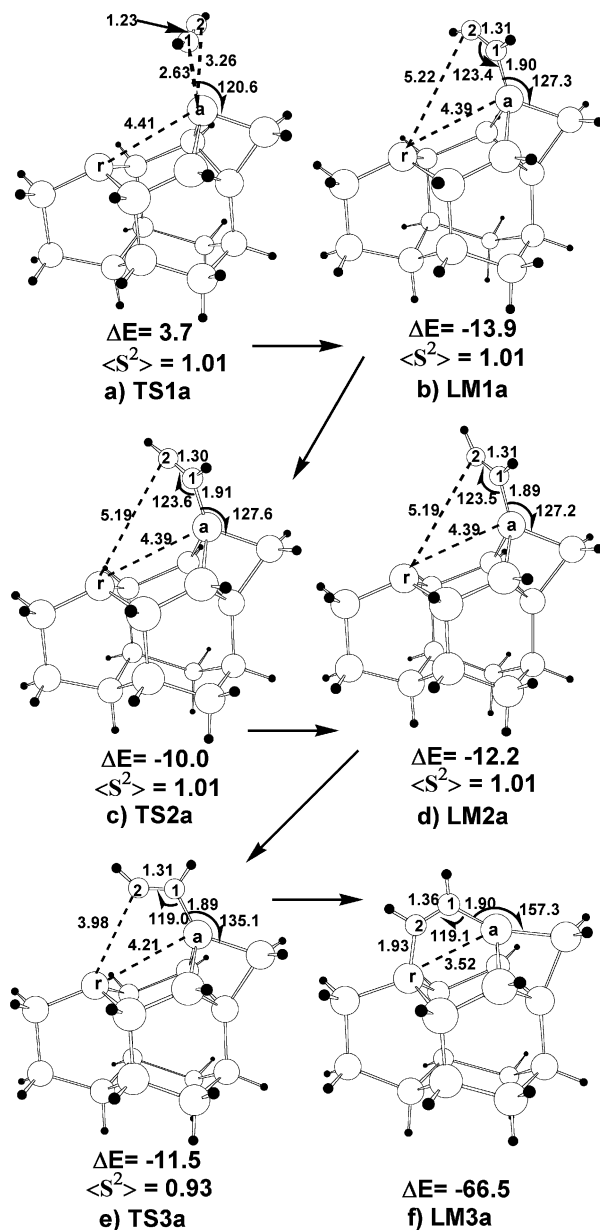


Figure 7. Optimized geometries (distance in Å and bond angle in deg) for the transition states, intermediates, and product of the cycloaddition of acetylene on the Si₁₆H₁₈ cluster model. Energies (ΔE , unit in kcal/mol) relative to the isolated reactants and the $\langle S^2 \rangle$ values for the wave functions of these stationary points are also presented.

π -conjugated molecules, such as 1,3-butadiene, benzene, and thiophene, prefer the [4+2] cycloaddition-like chemisorptions over the [2+2] cycloaddition-like chemisorptions on a rest atom–adatom pair of the Si(111)-7×7 surface, whereas simple alkene (ethylene) and alkyne (acetylene) undergo [2+2] cycloaddition-like adsorptions without inducing severe substrate reconstruction. The stepwise, diradical mechanism for the cycloaddition of π -conjugated molecules on the Si(111) surface differs remarkably from the concerted pathway for their [4+2] cycloaddition on the Si(100) surface, and from the concerted pathway for the prototype [4+2] cycloaddition reactions prevalent in organic chemistry. Experimental evidence of the diradical mechanism for the attachment of π -conjugated molecules on the Si(111) surface can be sought in a recent report on the adsorption of furan on the Si(111)-7×7 surface.³⁴ In addition

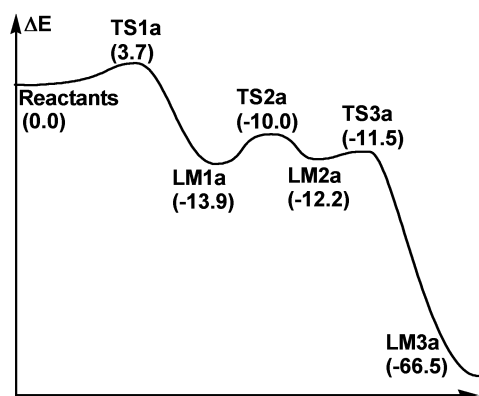


Figure 8. Profile of the energy surface (unit in kcal/mol) for the attachment of acetylene on the $\text{Si}_{16}\text{H}_{18}$ cluster model.

to the [4+2] cycloaddition-like adspecies, adspecies formed by dangling bond mediated dimerization of furan molecules on the $\text{Si}(111)\text{-}7\times 7$ surface were disclosed by HREELS at low temperature.³⁴ Such dimeric adspecies can be attributed to recombination of pairs of radical-like, mono- σ -bonded intermediates³⁴ (similar to **LMIS** in the thiophene case), which is short-lived, but might have substantial stability at low temperature to afford dimerization. It is interesting to note that no such kind of dangling bond mediated dimerization has been found experimentally for the adsorption of benzene and thiophene on the $\text{Si}(111)\text{-}7\times 7$ surface. This can be ascribed to the lower stability of the mono- σ -bonded intermediates formed in these two systems as compared to that of the furan case. The stability of the mono- σ -bonded intermediates depends on the barrier height between the mono- σ -bonded intermediates and the corresponding [4+2] cycloaddition-like products. The higher such a barrier is, the longer is the lifetime of the mono- σ -bonded intermediate and the higher is the probability for the neighboring intermediates to afford dimerization. Note that the barrier

between the mono- σ -bonded intermediates and the [4+2] cycloaddition-like products increases from *cis*-1,3-butadiene, benzene to thiophene with the increase of distance between the 1,4 C-ends of the conjugated dienes (3.10 Å for 1,3-butadiene, 2.80 Å for benzene, and 2.49 Å for thiophene). The distance in furan is 2.20 Å, much shorter than that of thiophene and benzene. Hence, a higher barrier between the intermediate and [4+2]-like product could be expected for furan than that of thiophene and benzene.

Among the above theoretical results, the most interesting is the prediction that *s-trans*-1,3-butadiene can undergo barrierlessly [4+2] cycloaddition-like chemisorption on the $\text{Si}(111)$ surface with the retention of stereochemistry. It is the unique electronic and geometric structures of the $\text{Si}(111)\text{-}7\times 7$ surface that facilitate such stereoselective cycloaddition of a *trans*-diene. This finding stimulates the exploration of further stereoselective reactions on the $\text{Si}(111)\text{-}7\times 7$ surface. Indeed, our preliminary density functional cluster model calculations showed that similar [4+2] cycloaddition-like chemisorption occurs readily for *trans*-1,2-dicarbonyls, such as *trans*-glyoxal and *trans*-biacetyl, on the $\text{Si}(111)\text{-}7\times 7$ surface with the stereochemistry of the *trans*-1,2-dicarbonyls being retained. Moreover, the intriguing mechanisms for the cycloaddition of unsaturated hydrocarbons and the allied heteroaromatics on the $\text{Si}(111)\text{-}7\times 7$ surface reported herein would be of great help in designing and constructing organics-silicon hybrid materials.

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(34) Cao, Y.; Wang, Z. H.; Deng, J. F.; Xu, G. Q. *Angew. Chem., Int. Ed.* **2000**, *39*, 2740.