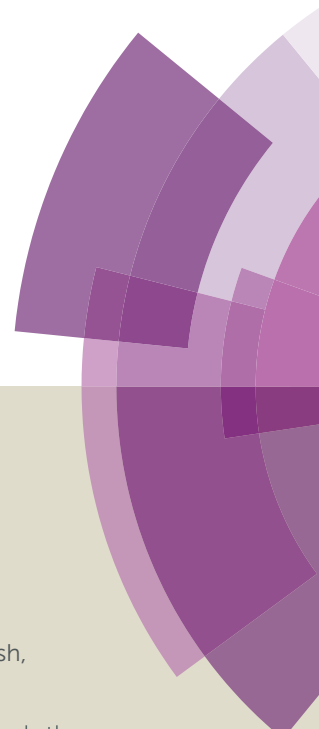


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Reversible [4+2] Cycloaddition Reaction of 1,3,2,5-Diazadiborinine with Ethylene

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Under ambient conditions, a [4+2] cycloaddition reaction of 1,3,2,5-diazadiborinine **1** with ethylene afforded a bicyclo[2.2.2] derivative **2**, which was structurally characterized. The cyclization process was found to be reversible, and thus retro-[4+2] cycloaddition reproduced **1** quantitatively, concomitant with the release of ethylene. Compound **1** reacted regio-selectively and stereo-selectively with styrene derivatives and norbornene, respectively, and these processes were found to be reversible too. Computational studies determined reaction pathways consistent with the regio-selectivity observed in the reaction of styrene, and the reaction was suggested to be essentially concerted but highly asynchronous.

Introduction

Reversible coordination processes between a metal center and olefins are of paramount significance in transition metal catalysis.¹ The labile propensity of metal-olefin interactions can be accounted for by the Dewar-Chatt-Duncanson model,² this model rationalizes, for example, the bonding mode in Zeise's salt [Cl₃Pt(η²-C₂H₄)]K,³ in which donation of π-electrons from ethylene to an unoccupied d-orbital of the metal and π-backdonation of d-electrons from the metal to the π*-orbital of ethylene occur concurrently.⁴ Such simultaneous donor-acceptor interactions confer unique chemical properties on transition metal complexes.

In recent years, it has been amply demonstrated that main group elements can behave as transition metals,⁵ e.g., in unique activation reactions of ethylene⁶ as well as other olefins⁷ where several systems were found to bind to olefins reversibly. In 2009, Power et al. reported a cycloaddition reaction of distannyne **1a** with two equivalents of ethylene, which afforded a bicycle[2.2.0] derivative **1b**.^{8a} Remarkably, **1b** readily released ethylene molecules via thermal retro-cycloaddition under reduced pressure or upon standing at 25 °C, to reproduce **1a**. Kato, Baceiredo, and co-workers

demonstrated that ethylene could be incorporated onto phosphonium sila-ylide, giving rise to silirane **11b**.⁹ The formation of **11b** depended on the ethylene pressure, and indeed, **11b** reverted to **11a** after a decrease in ethylene pressure. Recently, Tuononen and Power et al. reported reversible binding of ethylene to two-coordinate acyclic silylene **111a** under ambient conditions, which generated silirane **111b** with a tetra-coordinate silicon atom.¹⁰ Very recently, Tokitoh and Sasamori et al. have reported that 1,2-digermacyclobutene **IVa** underwent sequestration of two ethylene molecules to furnish **IVb**.¹¹ Retro-conversion of **IVb** to **IVa** was observed by reducing ethylene pressure. In these reactions, formation of the cycloadducts is inferred to involve a [1+2] interaction between the heavier group 14 element center and the C=C bond of ethylene in the initial step. With a group 13 compound, Jordan et al. reported that cationic aluminum β-diketimate derivative **Va** and ethylene underwent a [4+2] cycloaddition reaction, yielding cycloadduct **Vb**, which was characterized only by NMR spectroscopy.¹² Although **Vb** did not release ethylene even under vacuum, addition of N,N-dimethylaniline to a solution of **Vb** allowed ethylene elimination concomitant with the formation of **Vc** at room temperature. Additive-free reversible [4+2] cyclization between a 6π-compound and ethylene still remains highly challenging.¹³

Recently, we have reported the preparation of aromatic 1,3,2,5-diazadiborinine **1**,^{14a} which formally involves a neutral tricoordinate boron center surrounded by eight electrons.^{5a,14b-}

^h Preliminary studies indicated the unique reactivity of **1** toward unsaturated compounds such as carbon dioxide, forming bicyclo[2.2.2] derivatives, which prompted us to investigate the reactions of **1** with ethylene and other non-

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[†] Electronic supplementary information (ESI) available: Experimental and calculation details, and crystallographic information for **2**, **4a**, **4b**, **4d**, **6**. CCDC 1418724, 1418725, 1418726, 1418727, and 1418728. For ESI and crystallographic data in CIF or other electronic format see. See DOI: 10.1039/x0xx00000x



activated olefins in detail. Herein, we report reversible cycloaddition reactions of **1** with various alkenes. We also describe single-crystal X-ray diffraction analysis of the cycloadducts, kinetic experiments, and computational studies.

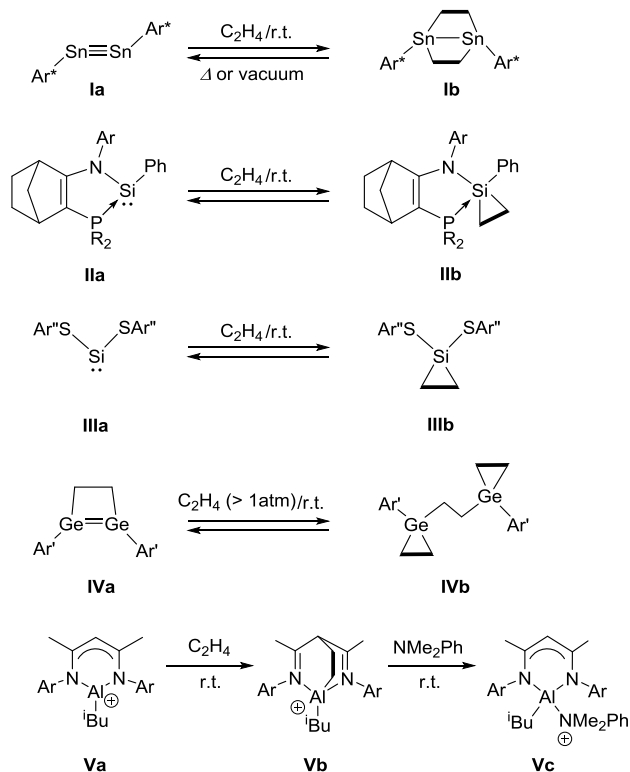


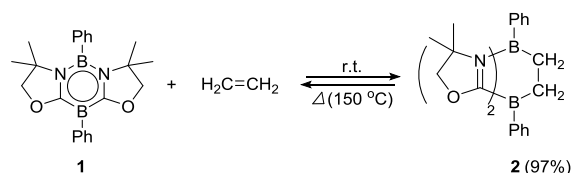
Fig. 1 Examples of reversible cycloaddition reactions between main group compounds and ethylene.

Results and discussion, Experimental

Reaction of **1** with ethylene

Ethylene was introduced into a benzene solution of **1** at 1 bar and the reaction mixture was stirred at ambient temperature for 3 h. After removal of all volatiles in vacuo, compound **2** was obtained as a white powder in 97% yield (Scheme 1). In the ^{11}B NMR spectrum of **2**, two peaks were detected at -16.0 ppm and 1.6 ppm that are shifted upfield with respect to those (7.3 ppm and 24.9 ppm) for the corresponding boron atoms in **1**.¹⁴ Recrystallization from a saturated benzene solution at room temperature afforded single crystals of **2**, and the solid-state structure was confirmed by X-ray diffraction analysis (Figure 2). Both of the boron centers are tetra-coordinated, indicating sp^3 hybridization. The B1–C1 ($1.653(5)$ Å) and B2–C2 ($1.671(5)$ Å) distances are significantly longer than the typical B–C single bond (1.59 Å). The long C1–C2 ($1.550(4)$ Å) distance is an indication of a $\text{C}(sp^3)\text{--C}(sp^3)$ single bond. There is a lengthening of the B1–N1 ($1.588(5)$ Å) and B2–C3 ($1.593(5)$ Å) bonds and a

shortening of the C3–N1 ($1.302(4)$ Å) bond, compared to those of **1**.¹⁴ Compound **2** is stable at room temperature, both in the solid state and in solution. However, upon heating a C_6D_6 solution of **2** at 150°C , a clean ring opening occurred, giving rise to **1** quantitatively. Note that the Diels-Alder reaction between benzene and ethylene as well as the retro Diels-Alder reaction have scarcely described thus far,¹⁵ despite the extensive application of the elementary reactions in organic synthesis.¹⁶



Scheme 1 Reversible [4+2] cycloaddition reaction between **1** and ethylene.

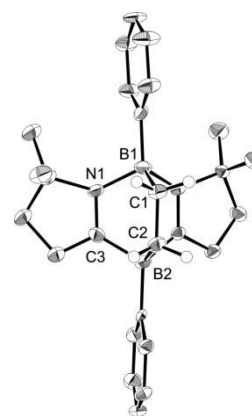
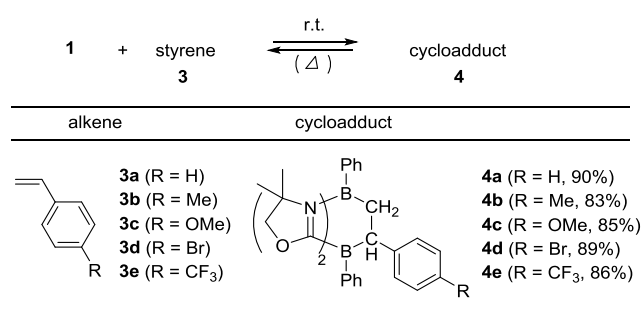


Fig. 2 Solid-state structure of **2**. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms except for those on the C1 and C2 atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–C1 $1.653(5)$, B1–N1 $1.588(5)$, B2–C2 $1.671(5)$, B2–C3 $1.593(5)$, C1–C2 $1.550(4)$, C3–N1 $1.302(4)$; N1–B1–C1 $104.0(3)$, B1–C1–C2 $110.4(3)$, C1–C2–B2 $113.3(3)$, C2–B2–C3 $100.7(3)$.

Reaction of **1** with styrene derivatives

To examine the scope of the cycloaddition reaction, we employed styrene derivatives **3** as alkene substrates (Scheme 2). A slight excess amount (2.0 eq) of styrene **3a** was added to a C_6D_6 solution of **1** in a J-Young NMR tube, and the reaction was monitored by NMR spectroscopy. This reaction was drastically slower than that of ethylene, with full conversion of **1** observed only after 12 h at room temperature. After workup, **4a** was isolated as a white powder in 90% yield. In the ^{11}B NMR spectrum of **4a**, two singlets appeared at -14.3 ppm and 0.8 ppm, which are comparable to those (-16.0 ppm and 1.6 ppm) of **2**. X-ray diffraction analysis revealed the bicyclo[2.2.2]

structure of **4a** and confirmed that the CH₂ and the CHPh carbons of **3a** selectively bind to the boron between two nitrogen atoms and the boron between two carbon atoms in **1**, respectively (Figure 3a). Remarkably, retro [4+2] cycloaddition of **4a** was observed at ambient conditions. Thus, when isolated **4a** was re-dissolved in C₆D₆ and the solution was kept at ambient temperature, partial regeneration of **1** and **3a** was detected in the ¹H NMR spectrum. Meanwhile, a full conversion of **4a** into **1** and **3a** was confirmed upon heating the solution at 110 °C. Cyclization reactions of **1** with *para*-substituted styrene derivatives **3b-e** also proceeded cleanly at room temperature, and the corresponding [4+2] cycloadducts **4b-e** were obtained. Analogous to **4a**, the bicyclo[2.2.2] structures of **4b** and **4d** formed via regio-selective [4+2] cycloaddition were confirmed by X-ray diffraction studies (Figures 3b and 3c). We also confirmed that **4b-e** underwent retro [4+2] cycloaddition reactions at 110-150 °C, to afford **1** and **3b-e** in 80-100% yields (see the Supporting Information).



Scheme 2. Regio-selective [4+2] cycloaddition reactions between **1** and styrenes **3**.

Interestingly, we noted that the cyclization reaction proceeded faster with styrenes bearing an electron-withdrawing group under the same reaction conditions. Thus, while the reactions with **3a-c** required more than 12 h for the full conversion into the cycloadducts **4a-c**, the reactions with **3d** and **3e** completed within 6 h and 3 h, respectively. Indeed, the equilibrium constant for the reversible cycloaddition highly depends on the *para*-substituent of the styrene derivatives (Table 1). To evaluate the substituent effect on the cycloaddition reaction, we checked the Hammett correlation for the reaction of **1** with **3a-e**.¹⁷ The rate constants *k* were measured based on the conversion rate of **1** using its integral values in ¹H NMR spectra (see the Supporting Information). Figure 4 shows a linear correlation between log *k* and substituent constants with ρ of +1.43, which is in line with the sensitivity of the cycloaddition reaction to the inductive effect of the substituents.

Table 1. Equilibrium constants (*K*₄₋₁) at room temperature.

styrene	3a	3b	3c	3d	3e
<i>K</i> ₄₋₁	1.148×10^3	0.601×10^3	0.457×10^3	8.741×10^3	2.011×10^4

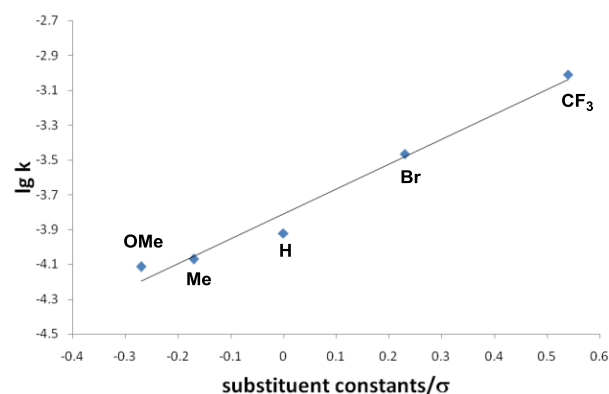


Fig. 4. Hammett plot for the reactions of **1** with *para*-substituted styrenes **3a-e** in THF-d₈ at room temperature.

Computational study on reaction pathway

To gain insight into the reaction mechanism, pathways for the cycloaddition reaction between **1** and styrene **3a** were explored theoretically using DFT calculations at the M06-2X(SCRF, solvent = benzene)/Def2-TZVP//M06-2X/6-31G* level of theory, where the M06-2X functional accounts for dispersion effects.¹⁸ We attempted to obtain pathways for the concerted and stepwise mechanisms. However, only concerted pathways could be determined (Figure 5a), which suggests that the reaction proceeds in a concerted fashion. We could determine two possible pathways for the concerted reaction, namely, a favored pathway (path A) leading to the experimentally observed product and a less favored pathway (path B). Stephan et al. demonstrated a stepwise activation of

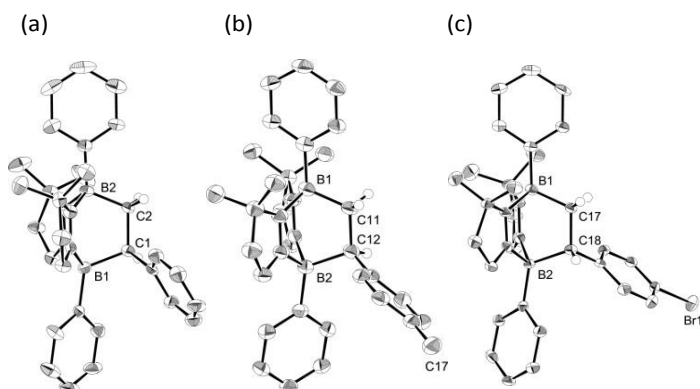


Fig. 3. Solid-state structures of **4a** (a), **4b** (b) and **4d** (c). Thermal ellipsoids are set at the 50% probability level. Most of the hydrogen atoms are omitted for clarity.

olefin with an intermolecular frustrated Lewis pair system.¹⁹ Thus, by employing a Lewis acidic borane tethered to a vinyl group through an alkyl chain, they experimentally confirmed that a unique borane-olefin van der Waals (vdW) complex was formed prior to nucleophilic attack by a Lewis base. In our system, a similar vdW interaction could not be observed at the stage of a reactant complex (RC). An important steric reason appears to be that the phenyl ring attached to the Lewis acidic boron atom in the N-B-N moiety is perpendicular to the diazadiborinine ring, and thus the phenyl ring hinders the full coordination of an olefin onto the boron. Moreover, both Lewis acidic and Lewis basic boron centers are present in **1** and interact with each other in the 6π -system system, which could allow for cooperative activation of olefin.

Consistent with the experimental observation, path A has a lower energy barrier. The computationally estimated activation parameters for the [4+2] cycloaddition process on path A ($\Delta H^\ddagger = 6.6 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -48.9 \text{ e.u.}$, $\Delta G^\ddagger_{(298)} = 21.2 \text{ kcal mol}^{-1}$) agreed reasonably with the experimental values ($\Delta H^\ddagger = 11.6 \pm 0.9 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -37.6 \pm 3.0 \text{ e.u.}$, $\Delta G^\ddagger_{(298)} = 22.8 \pm 1.8 \text{ kcal mol}^{-1}$). The reaction on path A was calculated as slightly exergonic, consistent with the fact that heating is necessary for the retro-conversion (Scheme 2). It is interesting to note that although the reaction is essentially concerted, the transition state (TS) geometries shown in Figure 5b suggest that the reaction is highly asynchronous. On path A, one of the two forming B–C bonds has a distance of 2.18 Å, whereas the other B–C bond is longer (2.69 Å). The same trend was also observed recently by Liu et al.²⁰ The short distance of the former B–C bond reflects an efficient orbital interaction between the LUMO+3 of **1** and the HOMO of styrene **3a** which has large amplitude on the terminal carbon (Figure 6). In addition to the orbital interaction, the effects of exchange and electrostatic interactions should play important roles in determining the regioselectivity. The exchange repulsion between the HOMOs of styrene **3a** and **1** may be reduced in this asynchronous configuration, because the HOMO of **1** has significant amplitude on the C–B–C moiety and the phenyl ring substituted on the boron atom. Furthermore, as shown in Figure S4-2, the boron atoms at the N–B–N and C–B–C moieties in **1** have positive (+0.35) and negative (−0.18) charges, respectively, whereas the terminal carbon (−0.39) in styrene **3a** is more electronegative than the internal carbon (−0.12). Therefore, the TS for path B will feel a larger electrostatic repulsion. In terms of orbital interaction, path B should be more favorable because it can form an efficient HOMO (1)–LUMO (**3a**) interaction (Figure 6). However, the stabilization arising from this orbital interaction is significantly diminished because of the above-mentioned repulsive effects. It is inferred that in addition to the repulsion at the reaction centers, the steric repulsion between the phenyl ring of **3a** and the two dimethyl moiety (−CMe₂−) of **1** in the TS of path B may also contribute to the distinct regio-selectivity in this reaction (Figure 5b).

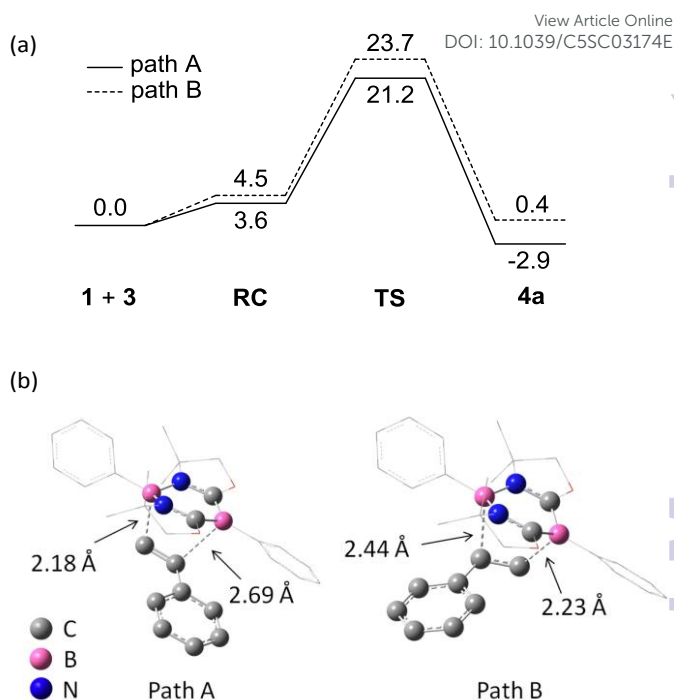


Fig. 5 (a) DFT-calculated free energy profiles (kcal mol^{-1}) for the proposed mechanism of the [4+2] cycloaddition reaction between **1** and ethylene. The optimized structures were obtained at the M06-2X/6-31G* level. The ΔG values in C₆H₆ at 298 K were obtained from the M06-2X/6-31G* gas-phase harmonic frequencies and the energy in C₆H₆ calculated with the Def2-TZVP basis set. (b) Transition-state geometries.

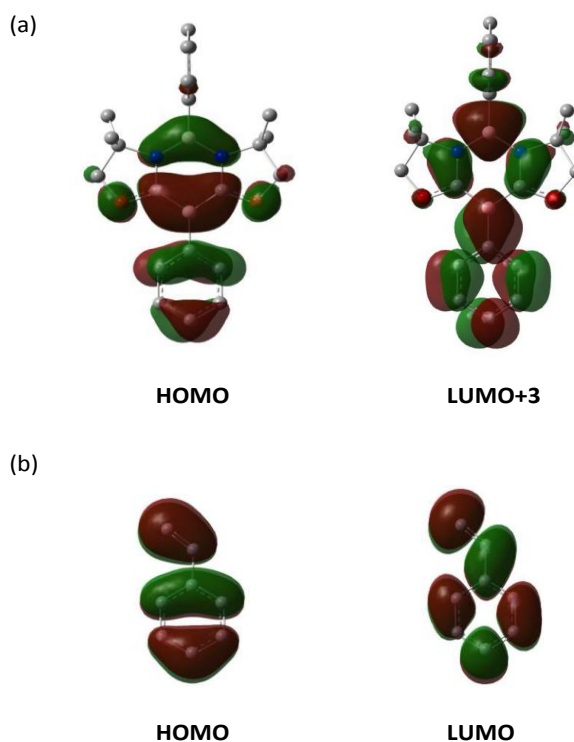
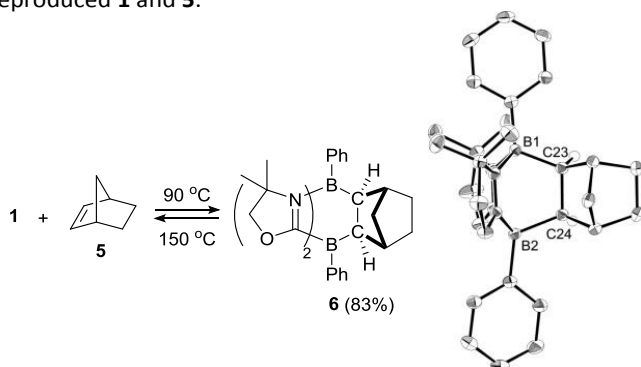


Fig. 6 Key frontier orbitals of **1** (a) and styrene **3a** (b).



Reaction of **1** with norbornene

We also investigated the limitation of the substrate scope. Cyclization reactions of **1** with cyclic and acyclic internal alkenes such as 1,1-bis(trimethylsilyl)ethene, *trans*-diphenylethene, cyclohexene, cyclohexadiene did not proceed even under heating conditions (r.t. ~ 150 °C), presumably because of steric hindrance. By contrast, the reaction of **1** with norbornene **5**, which features a strained bicyclic skeleton, underwent stereo-selective [4+2] cycloaddition at 90 °C, and **6** was obtained as a solo product in 83 % yield (Scheme 3). The stereoselectivity of the reaction originated probably from the fact that the steric hindrance of the CH₂ moiety is smaller than that of the CH₂CH₂ part of **5**. Retro-[4+2] cycloaddition of **6** proceeded thermally by heating at 150 °C, which cleanly reproduced **1** and **5**.



Scheme 3. Stereo-selective [4+2] cycloaddition reaction between **1** and norbornene **5** and its retro-conversion.

Conclusions

In summary, we have demonstrated a [4+2] cycloaddition reaction between **1** and ethylene which afforded bicyclo[2.2.2] compound **2** at room temperature. We also showed regio-selective and stereo-selective [4+2] cycloaddition of **1** with styrene derivatives and norbornene, respectively. All of the cycloadducts underwent retro-[4+2] cycloaddition reactions that reproduced **1** and the corresponding alkenes quantitatively. Computational studies using DFT calculations revealed that the transition state for the cycloaddition is concerted, but highly asynchronous. Studies on reversible cycloaddition of **1** with substrates featuring other unsaturated bonds, and its application²⁰ are currently under investigation in our laboratory.

Acknowledgements

We are grateful to Nanyang Technological University (NTU) and PSF/A*STAR (SERC 1321202066) of Singapore, for financial support. H.H. thanks the High Performance Computing Centre of NTU for computer resources.

Notes and references

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DOI: 10.1039/C5SC03174E

- (a) N. Winterton, G. J. Leigh, *Modern Coordination Chemistry: The Legacy of Joseph Chatt* (RSC, Cambridge, UK, 2002); (b) R. Jones, *Chem. Rev.* 1968, **68**, 785 – 806.
- (a) J. Chatt, L. A. Duncanson, L. M. Venanzi, *J. Chem. Soc.* 1955, 4456 – 4460; (b) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* 1953, 2939 – 2947; (c) M. Dewar, *Bull. Soc. Chim. Fr.* 1951, **18**, C79.
- (a) W. C. Zeise, *Poggendorff's Ann. Phys.* 1837, **40**, 234 – 252; (b) W. C. Zeise, *Poggendorff's Ann. Phys.* 1831, **21**, 497 – 541; (c) W. C. Zeise, *Poggendorff's Ann. Phys.* 1827, **9**, 632 – 633; (d) W. C. Zeise, *Overs. K. Dan. Vidensk. Selsk. Forh.* 1825, 13.
- (a) A. Fürstner, P. W. Davies, *Angew. Chem. Int. Ed.* 2007, **46**, 3410 – 3449; (b) G. Frenking, N. Fröhlich, *Chem. Rev.* 2000, **100**, 717 – 774; (c) A. Dedieu, *Chem. Rev.* 2000, **100**, 543 – 600.
- (a) H. Braunschweig, R. D. Dewhurst, F. Hupp, M. Nutz, K. Radacki, C. W. Tate, A. Vargas, Q. Ye, *Nature* 2015, **522**, 327 – 330; (b) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* 2015, **54**, 6400 – 6441; (c) D. W. Stephan, *Acc. Chem. Res.* 2015, **48**, 306 – 316; (d) S. K. Mandal, H. W. Roesky, *Acc. Chem. Res.* 2012, **45**, 298 – 307; (e) D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* 2011, **2**, 389 – 399; (f) S. Yao, Y. Xiong, M. Driess, *Organometallics* 2011, **30**, 1748 – 1767; (g) P. P. Power, *Acc. Chem. Res.* 2011, **44**, 627 – 637; (h) P. P. Power, *Nature* 2010, **463**, 171 – 177; (i) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* 2010, **49**, 46 – 76.
- (a) T. J. Hadlington, J. Li, M. Hermann, A. Davey, G. Frenking, C. Jones, *Organometallics* 2015, **34**, 3175 – 3185; (b) C. A. Caputo, Z. Zhu, Z. D. Brown, J. C. Fetting, P. P. Power, *Chem. Commun.* 2011, **47**, 7506 – 7508; (c) S. Ishida, T. Iwamoto, M. Kira, *Heteroatom. Chem.* 2011, **22**, 432 – 437; (d) J. S. Han, T. Sasamori, Y. Mizuhata, N. Tokitoh, *J. Am. Chem. Soc.* 2010, **132**, 2546 – 2547; (e) R. Kinjo, M. Ichinohe, A. Sekiguchi, N. Takagi, M. Sumimoto, S. Nagase, *J. Am. Chem. Soc.* 2007, **129**, 7766 – 7767; (f) J. S. J. McCahill, G. C. Welch, D. W. Stephan, *Angew. Chem. Int. Ed.* 2007, **46**, 4968 – 4971; (g) N. Wiberg, S. K. Vasisht, G. Fischer, P. Z. Mayer, *Anorg. Allg. Chem.* 2004, **630**, 1823 – 1828; (h) T. Ohtaki, W. Ando, *Organometallics* 1996, **15**, 3103 – 3105.
- (a) B.-H. Xu, K. Bussmann, R. Fröhlich, C. G. Daniliuc, J. G. Brandenburg, S. Grimme, G. Kehr, G. Erker, *Organometallics* 2013, **32**, 6745 – 6752; (b) S. Schwendemann, S. Oishi, S. Saito, R. Fröhlich, G. Kehr, G. Erker, *Chem. Asian, J.* 2013, **8**, 212 – 217; (c) B.-H. Xu, R. A. A. Yanez, H. Nakatsuka, M. Kitamura, R. Fröhlich, G. Kehr, G. Erker, *Chem. Asian, J.* 2012, **7**, 1347 – 1356; (d) M. A. Dureen, C. C. Brown, D. W. Stephan, *Organometallics* 2010, **29**, 6594 – 6607; (e) T. Voss, C. Chen, G. Kehr, E. Nauha, G. Erker, D. W. Stephan, *Chem. Eur. J.* 2010, **16**, 3005 – 3008; (f) J.-B. Sortaiste, T. Voss, G. Kehr, R. Fröhlich, G. Erker, *Chem. Commun.* 2009, **45**, 7417 – 7418.
- (a) Y. Peng, B. D. Ellis, X. Wang, J. C. Fetting, P. P. Power, *Science* 2009, **325**, 1668 – 1670. For reversible [1+2] cycloaddition between stannylene and alkyne, see: (b) L. R. Sita, R. D. Bickerstaff, *J. Am. Chem. Soc.* 1988, **110**, 5208 – 5209.
- R. Rodriguez, D. Gau, T. Kato, N. Saffon-Merceron, A. D. Cózar, F. P. Cossío, A. Baceiredo, *Angew. Chem. Int. Ed.* 2011, **50**, 10414 – 10416.
- F. Lips, J. C. Fetting, A. Mansikkamäki, H. M. Tuononen, P. P. Power, *J. Am. Chem. Soc.* 2014, **136**, 634 – 637.
- T. Sasamori, T. Sugahara, T. Agou, K. Sugamata, J.-D. Guo, S. Nagase, N. Tokitoh, *Chem. Sci.* 2015, **6**, DOI: 10.1039/C5SC01266J.
- (a) C. E. Radzewich, M. P. Coles, R. F. Jordan, *J. Am. Chem. Soc.* 1998, **120**, 9384 – 9385.

- 13 For recent reports on reversible [4+2] reaction with activated olefins, see (references are therein): (a) R. J. Burford, B. Li, M. Vasiliu, D. A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* 2015, **54**, 7823 – 7827; (b) A. K. H. Hirsch, P. Reutenauer, M. L. Moignan, S. Ulrich, P. J. Boul, J. M. Harrowfield, P. D. Jarowski, J.-M. Lehn, *Chem. Eur. J.* 2014, **20**, 1073 – 1080; (c) S. Kotha, S. Banerjee, *RSC Adv.* 2013, **3**, 7642 – 7666; (d) J. Chen, Z. Bajko, J. W. Kampf, A. J. Ashe, *Organometallics* 2007, **26**, 1563 – 1564.
- 14 (a) D. Wu, L. Kong, Y. Li, R. Ganguly, R. Kinjo, *Nat. Commun.* 2015, **6**, 7340; (b) J. Böhnke, H. Braunschweig, T. Dellermann, W. C. Ewing, T. Kramer, I. Krummenacher, A. Vargas, *Angew. Chem. Int. Ed.* 2015, **54**, 4469 – 4473; (c) L. Kong, R. Ganguly, Y. Li, R. Kinjo, *Chem. Sci.* 2015, **6**, 2893 – 2902; (d) L. Kong, Y. Li, R. Ganguly, D. Vidovic, R. Kinjo, *Angew. Chem. Int. Ed.* 2014, **53**, 9280 – 9283; (e) D. A. Ruiz, M. Melaimi, G. Bertrand, *Chem. Commun.* 2014, **50**, 7837 – 7839; (f) M. A. Celik, R. Sure, S. Klein, R. Kinjo, G. Bertrand, G. Frenking, *Chem. Eur. J.* 2012, **18**, 5676 – 5692; (g) R. Kinjo, B. Donnadiou, M. A. Celik, G. Frenking, G. Bertrand, *Science* 2011, **333**, 610 – 613.
- 15 (a) A. Talbot, D. Devarajan, S. J. Gustafson, I. Fernández, F. M. Bickelhaupt, D. H. Ess, *J. Org. Chem.* 2015, **80**, 548 – 558; (b) J. J. Serrano-Pérez, F. d. Vleeschouwer, F. d. Proft, D. Mendive-Tapia, M. J. Bearpark, M. A. Robb, *J. Org. Chem.* 2013, **78**, 1874 – 1886; (c) U. Streit, C. G. Bochet, *Beilstein J. Org. Chem.* 2011, **7**, 525 – 542; (d) O. D. Lucchi, V. Lucchini, *J. Chem. Soc., Chem. Commun.* 1982, **7**, 1105 – 1106; (e) K. E. Wilzbach, L. Kaplan, *J. Am. Chem. Soc.* 1971, **93**, 2073 – 2074; (f) C. A. Grob, H. Kny, A. Gagneux, *Helv. Chim. Acta.* 1957, **40**, 130 – 140.
- 16 (a) S. Kobayashi, K. A. Jørgensen, *Cycloaddition Reactions in Organic Synthesis* (Wiley-VCH, Weinheim, Germany, 2001); (b) S. Ma, *Handbook of Cyclization Reaction*, vols. 1 and 2 (Wiley-VCH, Weinheim, Germany, 2009); (c) M. Juhl, D. Tanner, *Chem. Soc. Rev.* 2009, **38**, 2983 – 2992; (d) K. Takao, R. Munakata, K. Tadano, *Chem. Rev.* 2005, **105**, 4779 – 4807.
- 17 (a) J. H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, 2nd ed. McGraw-Hill, New York, 1995, 214 – 228; (b) L. P. Hammett, *J. Am. Chem. Soc.* 1937, **59**, 96 – 103; (c) L. P. Hammett, *Chem. Rev.* 1935, **17**, 125 – 136.
- 18 Details of the quantum chemical calculations are given in the Supporting Information.
- 19 (a) X. Zhao, D. W. Stephan, *J. Am. Chem. Soc.* 2011, **133**, 12448 – 12450. See also: (b) Y. Guo, S. Li, *Eur. J. Inorg. Chem.* 2008, **2008**, 2501 – 2505; (c) W. A. B. J. van der Veken, *J. Am. Chem. Soc.* 1997, **119**, 10446 – 10454; (d) P. R. Jones, *J. Org. Chem.* 1972, **37**, 1886 – 1889.
- 20 L. Liu, C. Chan, J. Zhu, C.-H. Cheng, Y. Zhao, *J. Org. Chem.* 2015, **80**, 8790 – 8795.

View Article Online
DOI: 10.1039/C5SC03174E

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