Journal of Molecular Catalysis A: Chemical 396 (2015) 239–244

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Mechanism of co-dimerization of vinylboronates with terminal alkynes catalyzed by ruthenium-hydride complex

Jadwiga Pyziak[a], Jędrzej Walkowiak[b], Marcin Hoffmann[a], Bogdan Marciniec[a,b,*]

[a] Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland
[b] Centre for Advanced Technologies, Adam Mickiewicz University in Poznań, Umultowska 89c, 61-614 Poznań, Poland

ARTICLE INFO

Article history:
Received 3 April 2014
Received in revised form
26 September 2014
Accepted 30 September 2014
Available online 23 October 2014

Keywords:
Silylalkynes
Co-dimerization
Vinylboronates
DFT calculations
Kinetics

ABSTRACT

The co-dimerization reaction of vinylboronates with terminal alkynes, which was discovered in our group, is an efficient method for the synthesis of boryl- and borylsilylsubstituted buta-1,3-dienes. This study is a continuation of our previous and present results concerning the mechanism of this new catalytic reaction in boron chemistry. DFT calculations, as well as kinetic measurements carried out at several different temperatures in the range of 70–100 °C, provided rational grounds for the mechanism proposed previously on basis of stoichiometric reactions monitored by ^{1}H NMR. The activation energy and the rate determining step were also estimated.

1. Introduction

Synthesis of unsaturated compounds functionalized with metalloids from groups 13 and 14 of the periodic table is a very important branch of organometallic chemistry because of the potential applications of these compounds to organic syntheses and catalysis processes. The possibility for easy exchange of metalloids from these compounds and the introduction of various functional groups are very attractive for chemists. Hence, olefins and alkynes substituted with silyl, boryl, germyl or stannyl moieties have found broad application in the formation of specialty and fine chemicals [1–7].

We specialize in syntheses of olefins and alkynes with silyl, germyl and boryl functions on the basis of trans-metallation reactions discovered previously [8,9]. These catalytic transformations are based on the activation of the C—E bond in the vinylmetalloid compound and the C_{sp2}—H bond in an olefin or the C_{sp}—H bond in an alkyne. The reactions are catalyzed by transition metal (TM) complexes that contain or generate in situ the TM—H or TM—E bonds and occur with the simultaneous evolution of ethylene in the course of the reaction (see Fig. 1). The ruthenium hydride complexes $[Ru(CO)ClH(PCy_3)_2]$ or $[Ru(CO)ClH(PPh_3)_3]$ are especially useful.

In trans-metallation of olefins, we are able to obtain selectively products with *trans*, *cis* configuration or a *geminal* product with both functional groups attached to the same atom of a vinyl group, depending on which bond in the olefin is activated. This mode of reactivity is general for olefins when vinylsilanes, vinylgermanes [10,11] or vinylboranes [12,13] are used, while with alkynes the reaction occurs only with vinylmetalloids from the 14th group of the periodic table [14].

The mechanism of silylative and borylative coupling of vinylsilanes and vinylboronates with olefins was proposed on the basis of stoichiometric reactions as well as DFT calculations [15,16]. We have previously reported that the rate-determining step in the catalytic cycle of silylative coupling is an insertion of an alkene into the Ru—Si bond coupled with a silyl moiety migration from Ru to C atoms. The trans-borylation reaction of olefins with vinylboronates was analyzed in detail with the use of DFT calculation by Lin and Marder [16]. Computational results support the mechanism which was proposed on the basis of a stoichiometric reaction monitored by ^{1}H NMR as well as experiments with deuterated styrene, which permitted a distinction between the non-metalcarbene mechanism of trans-borylation and metathesis using a GC–MS analysis of products enriched with deuterium [17].

The reaction of vinylboronates with terminal alkynes took, unexpectedly, a different course, giving borylsubstituted buta-1,3-dienes as products instead of alkynylboranes [18].

---

* Corresponding author at: Adam Mickiewicz University, Centre for Advanced Technologies, Umultowska 89c, 61-614 Poznań, Poland. Tel.: + 48 61 829 19 88; fax: +48 61 829 19 87.
E-mail addresses: Bogdan.Marciniec@amu.edu.pl, marcinb@amu.edu.pl (B. Marciniec).

http://dx.doi.org/10.1016/j.molcata.2014.09.040

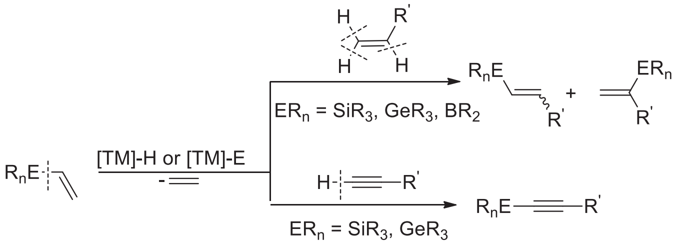

Fig. 1. General scheme of trans-metallation of olefins and alkynes with vinylmetalloids.

Co-dimerization of vinylboronates with terminal alkynes (organic and silylacetylenes) occurs in presence of complexes with a Ru—H bond (Fig. 2.). The best results were obtained for the most active complex $[Ru(CO)ClH(PCy_3)_2]$ [18]. Lower reactivity of vinylboronates in reactions with terminal alkynes in comparison to metalative coupling of alkynes with vinylsilanes and vinylgermanes is responsible for different pathway. The aim of this paper is to present the mechanism of this new catalytic transformation in boron chemistry on the basis of quantum chemical calculations using density functional theory (DFT) as well as kinetic measurements.

2. Experimental

2.1. General methods

All syntheses and manipulations were carried out under argon atmosphere using standard vacuum line techniques. The ^{1}H NMR and ^{31}P NMR spectra were recorded using a Bruker Ultra Shield NMR (600 MHz) in toluene-d_8. Volatile compounds were determined by a GC–MS (Varian Saturn 2100 T equipped with a capillary column, Varian VF-1 Factor Four, 0.26 mm, 30 m). GC analyses were carried out on a Varian 3400 CX series gas chromatograph equipped with a capillary column, Varian VF-5 Factor Four, 30 m and TCD. The chemicals were obtained from the following sources: toluene, triethylethynylsilane from Sigma-Aldrich, trimethylethynylsilane from ABCR, decane, pentane, hexane from POCH Gliwice (Poland). All solvents and liquid reagents used for catalytic as well as stoichiometric experiments were dried with standard procedures and distilled under argon atmosphere prior to use.

2-Vinyl-1,3,2-dioxaborinane was synthesized according to literature procedures with some modifications [19,20]. The ruthenium complex $[Ru(CO)ClH(PCy_3)_2]$ (**I**) was synthesized on the basis of a literature procedure [21].

2.2. DFT calculations

For all of the studied molecules, geometries of the potential energy minima and saddle points were optimized by density functional theory (DFT) calculations using several popular functionals: BLYP [22], B3LYP [23–25], M06 [26]. Basis sets of triple valence and double valence quantity SDD [27,28] and LANL2DZ were checked to see if they provided similar results. Frequency calculations at the same level of theory were also performed to confirm the characteristics of all of the optimized structures as minima or transition states. Thermal corrections to Gibbs free energies calculated at 298 K were included. All computations were carried out with Gaussian09 [29].

2.3. Kinetic examinations

Kinetic measurements were carried out in a reactor (4 mL) equipped with a reflux condenser, an inlet for inert gas and a magnetic stirrer. An oil bath was employed as a heating medium. Appropriate amounts of the catalyst and reagents were placed into the reactor. GC analyses were carried out during the course of the reactions. Conversion of substrates and the yield of products were calculated using the internal standard method.

2.3.1. Kinetic reaction of 2-vinyl-1,3,2-dioxaborinane with triethylethynylsilane: [ethynyltrimethylsilane]:[vinylboronate] = 1:2; (70–100 °C)

A kinetic reactor (Schlenk tube) was loaded with 16 mg (0.022 mmol) of $[Ru\ (CO)ClH(PCy_3)_2]$ complex, 125 mg of ethynyltrimethylsilane (1.13 mmol), 0.38 mL (2.26 mmol) of 2-vinyl-1,3,2-dioxaborinane, 2 mL of toluene and 0.32 mL decane under argon atmosphere. The reactor was placed in an oil bath and heated to the desired temperature. Changes in the reagent and product concentrations were monitored by GC analysis using the internal standard method. Reactions were conducted at five different temperatures: 70, 75, 80, 90 and 100 °C. The samples for GC analysis were frozen in dry ice. Each reaction was repeated four times. The average conversion and reaction kinetics were calculated with four repetitions.

2.4. Stoichiometric reaction of the Ru—H complex with triethylethynylsilane

The complex $[Ru(CO)ClH(PCy_3)_2]$ (66 mg, 0.138 mmol), triethylsilylacetylene (13 mg, 0.138 mmol) and toluene-d_8 (0.6 mL) were placed in an NMR tube under an argon atmosphere. The reaction mixture was heated from room temperature to 80 °C and monitored by ^{1}H NMR and ^{31}P NMR spectroscopy. Free tricyclohexylphoshpine was observed at 10.6 ppm in ^{31}P NMR even at room temperature, therefore it can be confirmed that the dissociation of phosphine and the formation of the 14-electron proper ruthenium catalyst began this catalytic cycle.

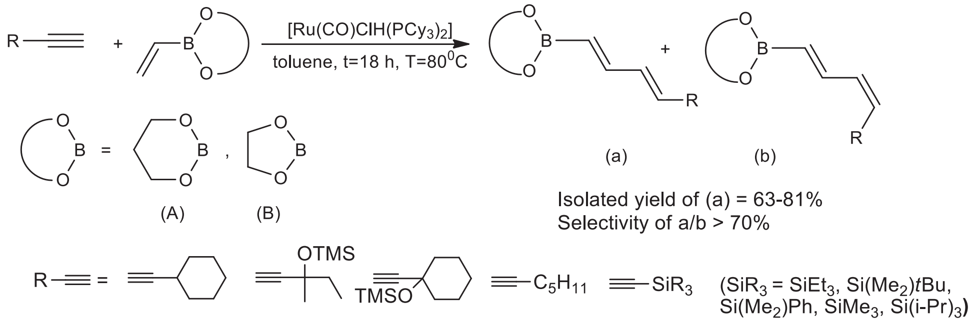

Fig. 2. Co-dimerization of vinylboronates with terminal alkyne.

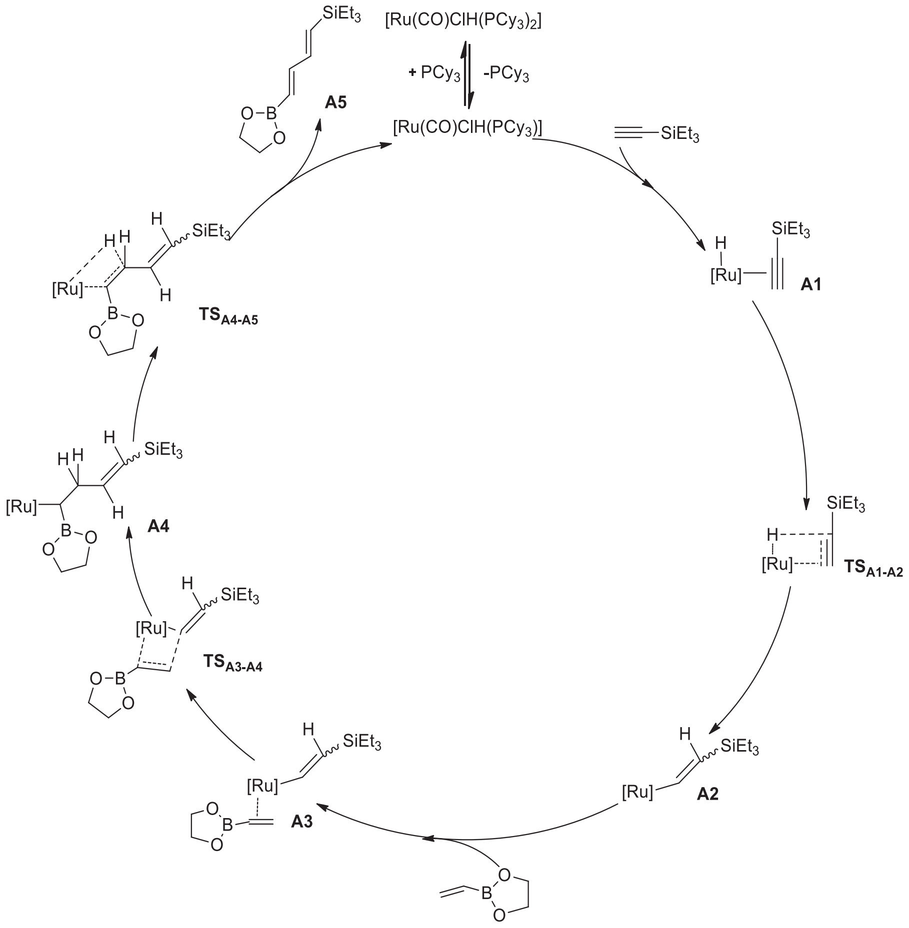

Fig. 3. Catalytic cycle of the co-dimerization of terminal ethynylsilanes with vinylboronates catalyzed by [Ru]—H complexes.

3. Results and discussion

The mechanism proposed in our previous work was based on catalytic and stoichiometric studies (Fig. 3). We were able to verify the presence of **A2**, **A3** and **A4** intermediate steps, but the transition states were to be determined. We could not earlier identify rate determining step of the mechanism of the catalytic cycle.

According to the proposed mechanism [18], the catalytic cycle reported by Lin and Marder [16] starts with the dissociation of tricyclohexylphosphine and the formation of a four-coordinative catalyst as suggested by calculations of the trans-borylation of an olefin with boronates. Such 14-electron complex can easily coordinate a terminal alkyne (**A1**). In our current studies we focused on the detailed mechanism. The freed PCy$_3$ was monitored by its ^{31}P NMR spectrum (δ = 10.6 ppm) in the first stage of the stoichiometric reaction of the [Ru]—H complex with triethylethynylsilane. Insertion of terminal silylacetylene into the [Ru]—H bond with the formation of the vinylene complex (**A2**) is the next step of the catalytic process. ^{31}P as well as ^{1}H NMR spectra showed the formation of a new Ru–vinylene complex.

The generation of a vinylene ruthenium complex by the insertion of an alkyne into the Ru—H bond is known in the catalytic dimerization of acetylene [30] and proceeds very rapidly even at room temperature [31–35]. We have shown that this type of complex is formed as an intermediate in the codimerization reaction of vinylboronates with terminal organic alkynes and ethynylsilanes [18].

A3 complex is formed by the coordination of vinylboroate to metal centre, which then is transformed in complex (**A4**) by its two-step insertion into the [Ru]—C=C bond with formation of a new [Ru]—C—C bond.

β-H elimination of borylsilylsubstituted buta-1,3-diene gives product **A5** with the regeneration of [Ru(CO)ClH(PCy$_3$)] and closes the catalytic cycle.

In our DFT calculations we used the ruthenium catalyst [Ru(CO)ClH(PCy$_3$)] (Cy, cyclohexyl), in which the strong σ-donating PCy$_3$ ligand was replaced with a smaller PH$_3$ group serving as a model catalyst, which is a standard approximation (Fig. 4.) [15,16].

The η^2-ethynylsilane complex [(PH$_3$)RuCl(CO)(η^2-CH$_2$ = CHSi (C$_2$H$_5$)$_3$] **A1**, was formed by binding ethynylsilane to ruthenium. Fig. 5 shows the energy profile for the **A1 A2 A3 A4 A5** process. The relative free energies are given in [kcal/mol]. Structural details of selected intermediates and transition states are shown in Fig. 3.

As shown in Fig. 6, the carbon–carbon triple bond coordinates to the Ru central atom prior to the terminal silylacetylene insertion into the [Ru]—H single bond in **A1**. In the transition state **TS$_{A1-A2}$**, the hydrogen atom migrates from the ruthenium centre to the α-carbon atom of the terminal silylacetylene. The product of this hydrogen atom migration is the formally 16-electron Ru–vinylene

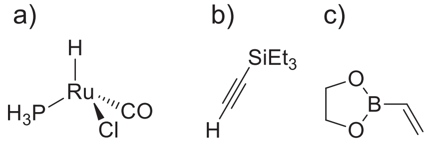

Fig. 4. Ruthenium catalyst [Ru]—H, (a) ethynylsilane (b) and vinylboronate (c) used in DFT calculations.

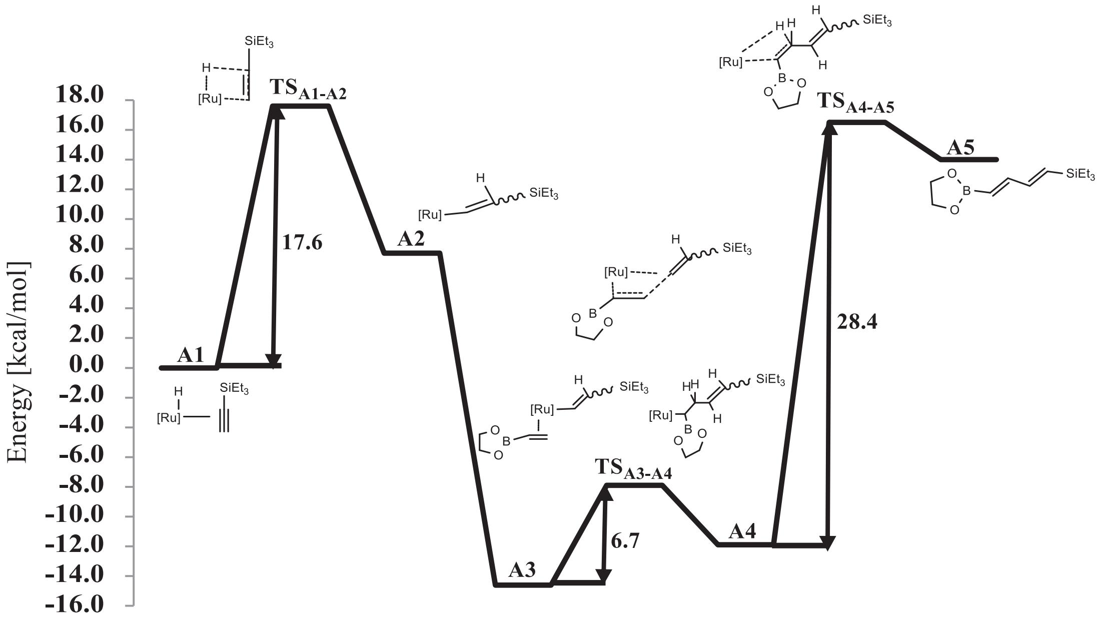

Fig. 5. Energy profile calculated for the proposed pathway of co-dimerization of terminal silylacetylene with vinylboronate. The relative free energies are given in [kcal/mol].

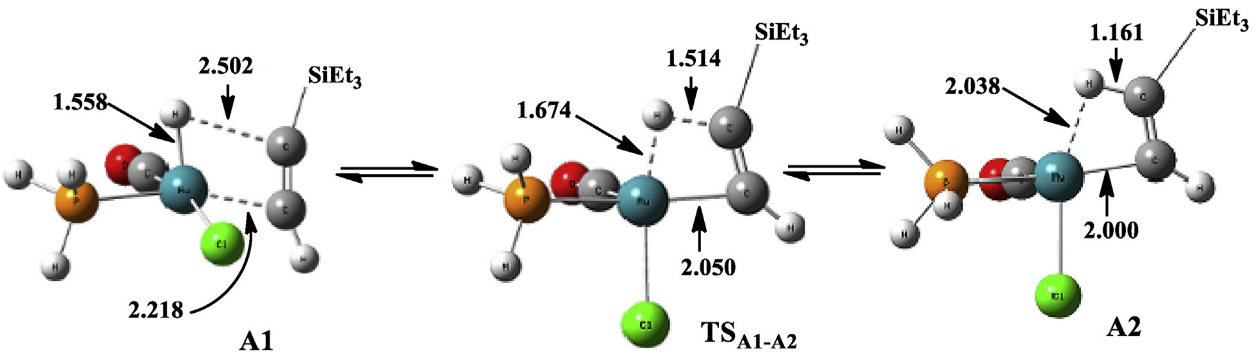

Fig. 6. The first step of co-dimerisation of terminal silylacetylene with vinylboronates: coordinated terminal triethylethynylsilane inserts into [Ru]—H bond. All distances are in Ångstroms.

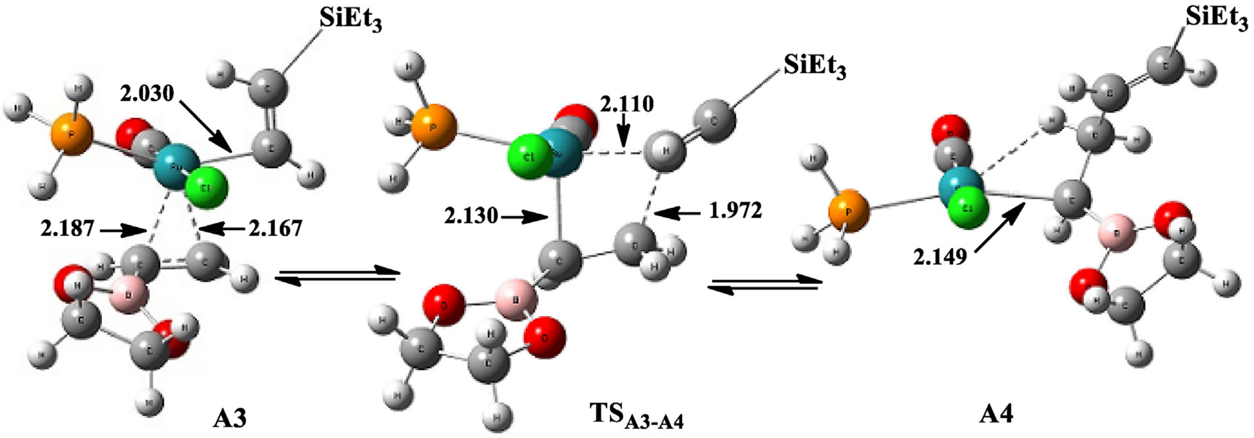

Fig. 7. The coordination of vinylboronate and its insertion into the [Ru]—C=C bond. All distances are in Ångstroms.

complex **A2** (see Fig. 6). In the $\mathbf{TS_{A1-A2}}$ transition state Ru. . .H and H. . .C distances are 1.674 Å and 1.514 Å, respectively. The energy barrier for ethynylsilane insertion is low 17.6 [kcal/mol]. That is in agreement with experimental results on both the co-dimerization reaction as well as the Ru-catalyzed dimerization of acetylenes.

Initial coordination of a carbon–carbon double bond from vinylboronate into the ruthenium atom of complex **A3** leads to formation of the $\mathbf{TS_{A3-A4}}$ transition state. The new carbon–carbon bond between the β-carbon bound to the boron atom in the vinylboronate and the β-C atom bound to the silicon atom in the **A3**

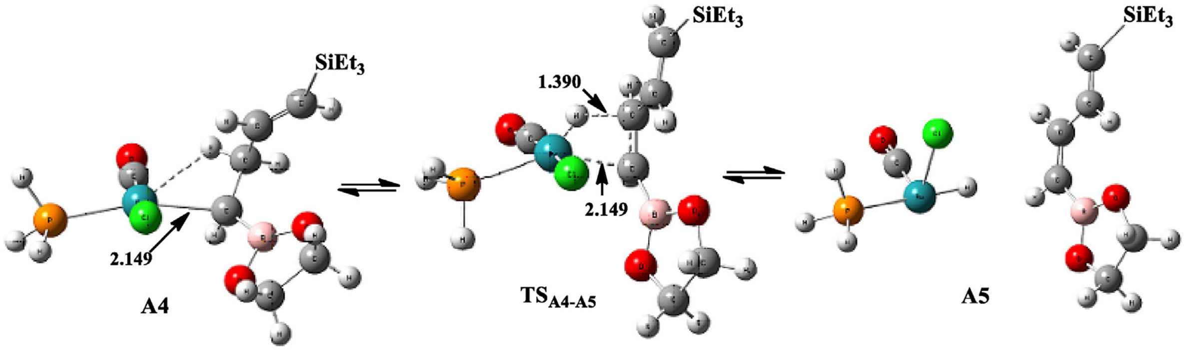

Fig. 8. Structures of molecules involved in the last step of the examined reaction. All distances are in Ångstroms.

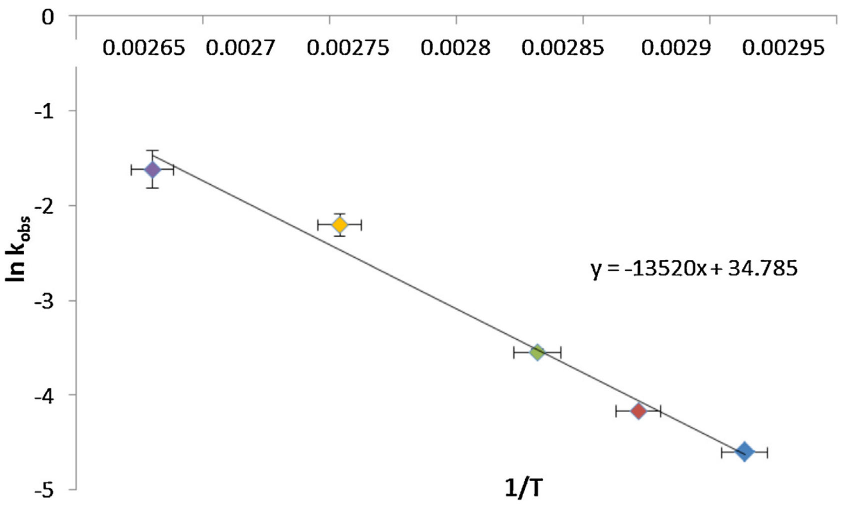

Fig. 9. Arrhenius plot of ln k_{obs} on the 1/T.

complex is formed in this transition state At the same time, the α-C atom of the vinylboronate is getting closer to the central ruthenium atom. The shortening of the distance between the α-carbon atom of the vinylboronate and ruthenium, as well as the lengthening of the bond between Ru and the C atom directly attached to the metal centre in the vinylene complex were observed. As a result of a rearrangement involving the vinylboronate insertions into the [Ru]—C=C bond, the $\mathbf{TS_{A3-A4}}$ transition state is converted into complex **A4**. As shown in Fig. 7, the distances between the Ru. . .C α-carbon of vinylboronate and the Ru. . .C for ethynylsilane are 2.130 Å and 2.110 Å, respectively, in the $\mathbf{TS_{A3-A4}}$ transition state. The energy barrier for this step is very small 6.7 [kcal/mol].

In last step of examined reaction, complex **A4** undergoes β-hydride elimination, which occurs through the $\mathbf{TS_{A4-A5}}$ transition state**.** Finally, the borylsilyl-substituted buta-1,3-diene **A5** and the regenerated [Ru(CO)ClH(PCy$_3$)] are obtained. The relative energies of these species are presented in Fig. 8. This is the rate-determining step in the catalytic cycle of terminal silylacetylene with vinylboronates co-dimerization. The energy barrier for this step is 28.4 [kcal/mol]. This value is so high probably because of the appearance of an additional positive charge on the boron atom, which is already an electron deficient element, and fully supports earlier findings of Z. Lin et al. that the "empty" *p* orbital of B does not participate in the reaction studied.

In order to confirm the results of the DFT studies, a separate series of kinetic measurements were performed using 2-vinyl-1,2,3-dioxaborinane and ethynyltrimethylsilane for co-dimerization in the temperature range of 70–100 °C. The pseudo-first-order rate constants were calculated for the reaction (see Table 1, Fig. 9).

Table 1
Co-dimerization of 2-vinyl-1,3,2-dioxaborinane with ethynyltrimethylsilane at given temperatures.

T (°C)	Time (h)	Conversion of ethynylsilane (%)	k_{obs}
70[a]	11.0	81	0.010 ± 0.001
75	11.0	84	0.015 ± 0.002
80	11.0	87	0.031 ± 0.002
90	11.5	96	0.117 ± 0.014
100	11.0	98	0.198 ± 0.042

$\Delta E_A = 26.9 \pm 1.6$ [kcal/mol].

[a] Reaction conditions unless otherwise stated: [Ru]:[Si]:[B] = 2×10^{-2}:1:2, 24 h, toluene, argon.

These kinetic data were obtained by measurements of the consumption of the substrate (ethynyltrimethylsilane) by gas chromatography using decane as the internal standard. The effect of temperature on the respective k_{obs} gave an activation energy of $E_a = 26.9 \pm 1.6$ [kcal/mol]. This value is in very good agreement with the theoretical calculations.

4. Conclusions

We have studied *in silico* the mechanism of the co-dimerization reaction of 2-vinyl-1,3,2-dioxaborolane and triethylethynylsilane employing three density functional theories (DFT): BLYP, B3LYP and M06 functionals. All of the methods gave comparable results indicating that the β-hydride elimination of borylsilylbuta-1,3-diene with the regeneration of the Ru—H complex is the rate determining step. The energy barrier calculated by the DFT method is in agreement with the kinetic measurements from *in vitro* experiments, which confirms our DFT calculations as well as the stoichiometry of the reactions.

Acknowledgements

This work was supported by the National Science Centre (Poland), grant Maestro no. UMO-2011/02/A/ST5/00472 and as a part of the HOMING PLUS/2012-5/14 grant of the Foundation for Polish Science.

This research was supported in part by PL-Grid Infrastructure.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.09.040.

References

[1] C. Thirsk, A. Whiting, J. Chem. Soc., Perkin Trans. 1 (2002) 999–1023.
[2] P. Knochel, F. Kopp, Introduction, in: Handbook of Functionalized Organometallics, Wiley-VCH Verlag GmbH, Weinheim, Germany, 2008, pp. 1–5.
[3] P. Pawluć, W. Prukala, B. Marciniec, Eur. J. Org. Chem. 2 (2010) 219–229.
[4] J.H. Delcamp, P.E. Gormisky, M.C. White, J. Am. Chem. Soc. 135 (2013) 8460–8463.
[5] H. Fuwa, K. Mizunuma, M. Sasaki, T. Suzuki, H. Kubo, Org. Biomol. Chem. 11 (2013) 3442–3450.
[6] M. Altendorfer, D. Menche, Chem. Commun. (Cambridge, U.K.) 48 (2012) 8267–8269.
[7] R.S. Coleman, M.C. Walczak, Org. Lett. 7 (2005) 2289–2291.
[8] B. Marciniec, Acc. Chem. Res. 40 (2007) 943–952.
[9] B. Marciniec, Coord. Chem. Rev. 249 (2005) 2374–2390.
[10] B. Marciniec, H. Ławicka, M. Majchrzak, M. Kubicki, I. Kownacki, Chem. Eur. J. 12 (2006) 244–250.
[11] B. Marciniec, H. Ławicka, Appl. Organomet. Chem. 22 (2008) 510–515.
[12] B. Marciniec, M. Jankowska, C. Pietraszuk, Chem. Commun. 5 (2005) 663–665.
[13] J. Walkowiak, B. Marciniec, M. Jankowska-Wajda, J. Organomet. Chem. 695 (2010) 1287–1292.
[14] B. Marciniec, B. Dudziec, I. Kownacki, Angew. Chem. Int. Ed. 45 (2006) 8180–8184.
[15] A. Kubas, M. Hoffmann, B. Marciniec, J. Mol. Model. 16 (2010) 395–400.
[16] K.C. Lam, Z. Lin, T.B. Marder, Organometallics 26 (2007) 3149–3156.
[17] M. Jankowska, O. Shuvalova, N. Bespalova, M. Majchrzak, B. Marciniec, J. Organomet. Chem. 690 (2005) 4492–4497.
[18] J. Walkowiak, M. Jankowska-Wajda, B. Marciniec, Chem. Eur. J. 14 (2008) 6679–6686.
[19] F.E. Brinckman, F.G.A. Stone, J. Am. Chem. Soc. 82 (1960) 6218–6223.
[20] H.C. Brown, D. Basavaiah, N.G. Bhat, Organometallics 2 (1983) 1309–1311.
[21] C.S. Yi, D.W. Lee, Y. Chen, Organometallics 18 (1999) 2043–2045.
[22] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B: Condens. Matter 37 (1988) 785–789.
[23] A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.
[24] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270–283.
[25] T.H.D.J.a.P.J. Hay, in: H.F. Schaefer III (Ed.), Modern Theoretical Chemistry, 3, Plenum, New York, NY, 1976, pp. 1–28.
[26] Y. Zhao, D.G. Truhlar, Chem. Phys. Lett. 502 (2011) 1–13.
[27] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, Theor. Chim. Acta 77 (1990) 123–141.
[28] A. Bergner, M. Dolg, W. Küchle, H. Stoll, H. Preuß, Mol. Phys. 80 (1993) 1431–1441.
[29] M. J. Frisch, G.W.Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G., Scalmani, V., Barone, B., Mennucci, G. A. Petersson, H., Nakatsuji, M., Caricato, X., Li, H. P. Hratchian, A. F. Izmaylov, J., Bloino, G., Zheng, J. L. Sonnenberg, M., Hada, M., Ehara, K. Toyota,R. Fukuda, J., Hasegawa, M., Ishida, T., Nakajima, Y., Honda, O., Kitao, H., Nakai, T., Vreven, J. A. Montgomery, Jr., J. E. Peralta, F., Ogliaro, M., Bearpark, J. J. Heyd, E., Brothers, K. N. Kudin, V. N. Staroverov, T., Keith, R., Kobayashi, J., Normand, K., Raghavachari, A., Rendell, J. C. Burant, S. S. Iyengar, J., Tomasi, M., Cossi, N., Rega, J. M. Millam, M., Klene, J. E. Knox, J. B. Cross, V., Bakken, C., Adamo, J., Jaramillo, R., Gomperts, R. E. Stratmann, O., Yazyev, A. J. Austin, R., Cammi, C., Pomelli, J. W. Ochterski, R. L. Martin, K., Morokuma, V. G. Zakrzewski, G. A. Voth, P., Salvador, J. J. Dannenberg, S., Dapprich, A. D. Daniels, O., Farkas, J. B. Foresman, J. V. Ortiz, J., Cioslowski, D. J. Fox, Gaussian 09 (revision C.01. Gaussian Inc. Wallingford CT).
[30] C.S. Yi, N. Liu, Synlett 3 (1999) 281–287.
[31] M.R. Torres, A. Vegas, A. Santos, J. Ros, J. Organomet. Chem. 309 (1986) 169–177.
[32] S.M. Maddock, C.E.F. Rickard, W.R. Roper, L.J. Wright, Organometallics 15 (1996) 1793–1803.
[33] A.V. Marchenko, H. Gerard, O. Eisenstein, K.G. Caulton, New J. Chem. 25 (2001) 1382–1388.
[34] S. Jung, C.D. Brandt, J. Wolf, H. Werner, Dalton Trans. 3 (2004) 375–383.
[35] M. Jimenez-Tenorio, M.C. Puerta, P. Valerga, Organometallics 28 (2009) 2787–2798.