PAPER

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Vinylidene rearrangements of internal borylalkynes *via* 1,2-boryl migration†

Takahiro Iwamoto, [ID] *[a,b] Takuya Mitsubo,[a] Kosuke Sakajiri[a] and Youichi Ishii [ID] *[a]

Vinylidene rearrangement of alkynes is a well-established and powerful method for alkyne transformations, while use of borylalkynes has remained largely unexplored. This paper describes vinylidene rearrangements of internal borylalkynes using a cationic ruthenium complex. This rearrangement is applicable to alkynes with both tri-(B(pin), B(dan)) and tetracoordinate (B(mida)) boryl groups, and the reaction rate is dramatically affected by the Lewis acidity of the boryl group. Mechanistic study revealed that the rearrangement proceeds *via* 1,2-boryl migration regardless of the coordination number of the boron center. The migration mode was elucidated by theoretical calculations to indicate that the migration of the tricoordinate boryl groups is an electrophilic process in contrast to the previous vinylidene rearrangements of internal alkynes with two carbon substituents.

Introduction

Since organoboron compounds are versatile synthetic intermediates in organic chemistry,[1,2] substantial efforts have been devoted to the development of synthetic methods to expand their availability and diversity. Recently, significant advances have been made in the chemistry of boryl migrations, and various types of rearrangement reactions have been achieved by nucleophilic,[3–13] electrophilic,[14–17] and radical[18–24] boryl migrations.[25] These transformations provide useful synthetic tools to access organoboron compounds, which are complementary to the conventional approaches.

Transition-metal mediated vinylidene rearrangement from an η²-alkyne ligand to the corresponding vinylidene species represents a powerful method for alkyne transformations.[26–31] The most common is vinylidene rearrangement of terminal alkynes because of the high migration ability of a hydrogen atom.[32] Over the last few decades, the substrate scope has been expanded to internal alkynes to demonstrate that a variety of carbon and heteroatom groups can participate in this rearrangement as a migrating group (Fig. 1a).[33–48] However, vinylidene rearrangement of borylalkynes has been largely unexplored; the successful vinylidene rearrangements

are limited to just a few examples (Fig. 1b).[49,50] Hill and co-workers reported the vinylidene rearrangement of HC≡CB (mida) (mida = *N*-methyliminodiacetato) (Fig. 1b, top).[49b] Subsequently, the first instance of vinylidene rearrangement of internal borylalkyne, *p*-C₆H₄MeC≡CB(pin) (pin = pinacolato), was reported by Ozerov and coworkers.[49c] Braunschweig also described an equilibrium between rhodium-borylvinylidene and -(hydrido)(borylalkynyl) complexes, the latter of which was derived from a terminal borylalkyne.[49a] However, although Hill
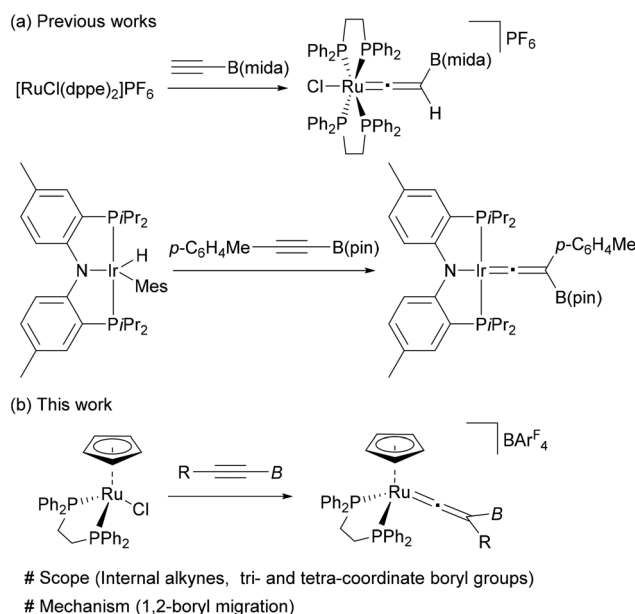

Fig. 1 Vinylidene rearrangements of borylalkynes.

[a]Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan.
E-mail: iwamoto@kc.chuo-u.ac.jp, yo-ishii@kc.chuo-u.ac.jp
[b]Faculty of Molecular Chemistry and Engineering, Kyoto Institute of Technology, Goshokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.
E-mail: tiwamoto@kit.ac.jp
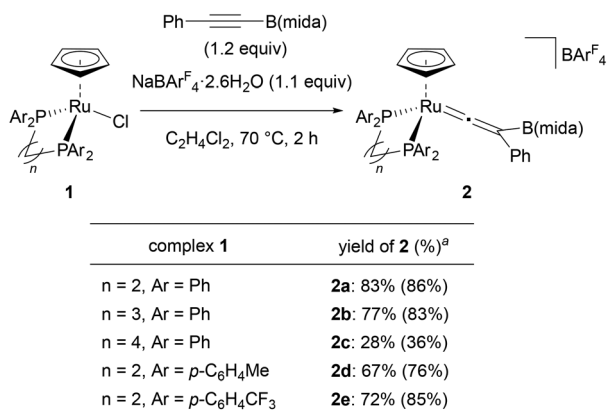† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4dt01042f

proposed that the boryl group would serve as a 1,2-migration group, no mechanistic information on the 1,2-migration process of η^2-borylalkyne is provided in these reports.

In this paper, we have investigated vinylidene rearrangements of internal borylalkynes by using [Ru(dppe)Cp]$^+$, in which both tetra- and tricoordinate boryl groups are applicable (Fig. 1b, bottom). Isotopic labelling experiments provided the first experimental evidence showing that the boryl groups serve as a migrating group. Theoretical studies on a migration mode of the boryl group (*i.e.*, either nucleophilic or electrophilic processes) is also reported. These results not only expand the scope of the vinylidene rearrangements but also add a new entry to the boryl group migration chemistry.
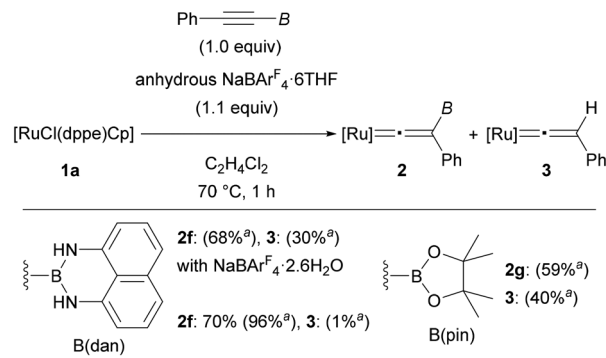
Results and discussion

We selected PhC≡CB(mida) as a standard substrate and started our investigation with a ligand screening in a reaction of this internal boryl alkyne with [Ru(L)Cp]BAr$^F_4$ (L = bidentate phosphine ligand) generated *in situ* (Fig. 2). When ruthenium complex [RuCl(dppe)Cp] (**1**) was treated with PhC≡CB(mida) in the presence of NaBAr$^F_4$·2.6H$_2$O (Ar^F = 3,5-bis(trifluoromethyl)phenyl) at 70 °C, vinylidene complex **2a** was obtained in 87% yield after 1 h. Sterically more demanding ligands obviously diminished the yields (**2a** *versus* **2b**, **2c**) indicating that the present rearrangement is sensitive to the steric effect. The coordination of a bulky internal boryl alkyne prior to the rearrangement may be hampered by dppb with a large bite angle. Electronically differentiated ligands provided the corresponding vinylidene complex, yet the yields were slightly low (**2d** and **2e**).

By using [RuCl(dppe)Cp] (**1a**) as the optimal precursor, we next conducted reactions of tricoordinate borylalkynes (Fig. 3). Treating PhC≡CB(dan) (dan = naphthalene-1,8-diaminato) under the same reaction conditions resulted in the complete consumption of **1a**. However, a mixture of complex **2f** and protodeboronated complex **3** was obtained in 68 and 30% yields,

Fig. 3 Vinylidene rearrangements of tricoordinate borylalkynes ([Ru] = [Ru(dppe)Cp]$^+$).

respectively. Through careful screening of the reagents and the reaction conditions, we found that use of anhydrous NaBAr$^F_4$·6THF was effective to produce complex **2f** in 70% isolated yield (96% NMR yield) along with formation of a small amount of **3**. The susceptibility to the protodeboronation was more serious in the case of internal alkynes with B(pin). Treatment of PhC≡CB(pin) with [RuCl(dppe)Cp] in the presence of anhydrous NaBAr$^F_4$·6THF provided a mixture of **2g** and **3** in 59 and 40% NMR yield, respectively, and the high susceptibility toward H$_2$O hampered isolation of complex **2g**. Consequently, characterization of **2g** was performed solely by NMR analyses, while several NMR signals characteristic of vinylidene complexes provided reliable information on the formation of vinylidene complex **2g** (see the ESI†).

To gain insight into the formation of **3**, we conducted brief studies on the protodeboronation. When a solution of PhC≡CB(dan) in C$_2$H$_4$Cl$_2$ was treated with H$_2$O (2.5 equiv.) at 70 °C for 1 h, PhC≡CH (**4**) was not formed, and the starting alkyne was fully recovered (Fig. 4a, up). In contrast, complex **2f** underwent protodeboronation under similar conditions to give complex **3** in 89% yield. Protodeboronation of complex **2g** proceeded much rapidly even at room temperature to afford **3** in 82% (Fig. 4a, bottom). Note that vinylidene complex **2a** is stable under these reaction conditions. These results implied that the formation of complex **3** observed in the vinylidene rearrangements (Fig. 3) is derived from the protodeboronation of vinylidene complex **2**, but not from the vinylidene rearrangement of terminal alkyne **4** (Fig. 4b). The remarkable susceptibility of vinylidene complex **2f** and **2g** to the protodeboronation likely results from their unique structure associated with the cationic vinylidene and the β-boryl functionalities.

Common organoboronate compounds are moderately stable toward hydrolysis. The high reactivity of **2f** and **2g** toward protodeboronation may be accounted for by two possible mechanisms: (1) addition of water at the boron atom followed by deprotonation and B–C bond cleavage, or (2) electrophilic addition of H$_2$O to the vinylidene α-carbon followed by B–OH elimination like bora-Wittig-type reactions (Fig. 4b, bottom).[51] Although a common protodeboronation mecha-

Fig. 2 Ligand screening.

complex **1**	yield of **2** (%)[a]
n = 2, Ar = Ph	**2a**: 83% (86%)
n = 3, Ar = Ph	**2b**: 77% (83%)
n = 4, Ar = Ph	**2c**: 28% (36%)
n = 2, Ar = p-C$_6$H$_4$Me	**2d**: 67% (76%)
n = 2, Ar = p-C$_6$H$_4$CF$_3$	**2e**: 72% (85%)

[a] NMR yields are shown in parentheses.

(a) protodeboronations

Ph———B(dan) → $\xrightarrow[\substack{C_2H_4Cl_2 \\ 70\,^\circ C,\ 1\ h}]{H_2O\ (2.5\ equiv)}$ → Ph———H **4** (N.D.)

2f [Ru]=•= (B(dan), Ph) $\xrightarrow[\substack{C_2H_4Cl_2 \\ 70\,^\circ C,\ 1\ h}]{H_2O\ (2.3\ equiv)}$ [Ru]=•= (H, Ph) **3** (89%)

2g [Ru]=•= (B(pin), Ph) $\xrightarrow[\substack{CDCl_3 \\ r.t.,\ 10\ mins}]{H_2O\ (2.1\ equiv)}$ [Ru]=•= (H, Ph) **3** (82%)

(b) Plausible mechanism

Ph———B $\xrightarrow[\text{slow}]{H_2O}$ **4** → **3**

Ph———B → **2f** or **2g** $\xrightarrow[\text{fast}]{H_2O}$ **3**

$\xrightarrow[\substack{-H^+}]{H_2O}$ [Ru]=•= (B–OH, Ph) **2** → [Ru]===Ph (HO—B) → H⁺ → **3**
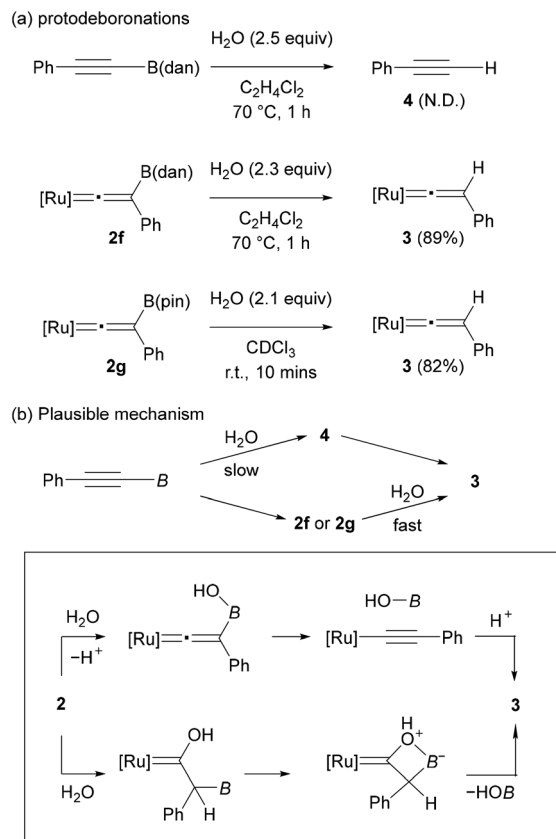
[Ru]=•= → [Ru]= (OH, ...B, Ph H) → [Ru]= (O⁺ H ... B⁻, Ph H) → **3**, $-HOB$

Fig. 4 (a) Control experiments and (b) a proposed reaction mechanism for the protodeboronation ([Ru] = [Ru(dppe)Cp]⁺).

nism (1) cannot be excluded, we assume that the latter mechanism (2) may be operative considering that the electron-deficient nature of the α-carbon in the cationic vinylidene complex **2** should be strongly enhanced by the Lewis acidic boryl group at the β-carbon.[52] In any event, both mechanisms are in accordance with the actual reactivity order that the more Lewis acidic boryl group accelerates the protodeboronation.

To further assess the vinylidene rearrangements, we performed time course studies monitoring the formation of the vinylidene complexes by using ¹H NMR analyses (Fig. 5). The
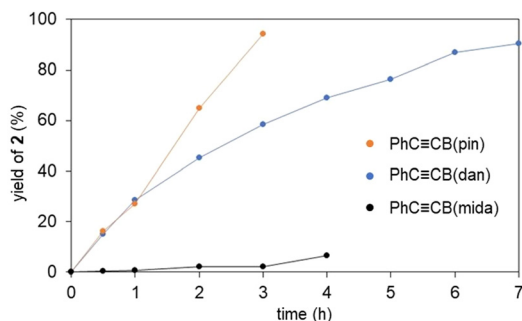

Fig. 5 Time course studies on the formation of vinylidene complexes. Reactions were performed at room temperature in CDCl₃ using an NMR tube. Yields of complexes **2** were determined by ¹H NMR spectroscopy.

vinylidene formation from PhC≡CB(pin) and **1a** was found to proceed rapidly even at room temperature, and the vinylidene complex was formed almost quantitatively after 3 h. PhC≡CB(dan) also showed high activity, while the reaction rate was slightly lower compared with PhC≡CB(pin). In contrast, the reaction with PhC≡CB(mida) was sluggish at room temperature. Thus, the reaction rates of the vinylidene rearrangements are dramatically affected by the boryl groups and likely correlated with the Lewis acidity of the boryl groups (B(pin) > B(dan) > B(mida)).

To clarify the migrating group, ¹³C-labeling experiments were performed using 25% ¹³C-enriched alkyne, PhC≡¹³CB(mida) (Fig. 6). After a reaction under the optimal conditions, vinylidene complex **2–¹³C$_\alpha$** was obtained as the major product (**2–¹³C$_\alpha$** : **2–¹³C$_\beta$** = 22.6 : 1), and the migration ratio of B(mida) and Ph was calculated to be 99:<1 on the basis of the product ratio **2–¹³C$_\alpha$** : **2–¹³C$_\beta$** determined by ¹³C{¹H} NMR. In the case of an alkyne bearing B(dan) (19.5% enriched), the isomer ratio was determined after protodeboronation of the vinylidene complex because of a partial overlap of ¹³C NMR signals of the boryl vinylidene complex. Again, B(dan) group was found to serve as the migrating group with >99% selectivity. These results represent the first observations of 1,2-boryl migration in vinylidene rearrangement.

Our previous mechanistic studies on the vinylidene rearrangements of internal alkynes with two carbon substituents revealed that the rearrangement proceeds via nucleophilic migration pathway to highlight the importance of nucleophilicity of a migration group.[34,36] However, the observation of the rapid rearrangements of less nucleophilic B(pin) and B(dan) over B(mida) is contradiction to this mechanistic scenario. Thus, we performed validation of the migration mode. In the previous nucleophilic vinylidene rearrangements, the rate of the rearrangement was revealed to be remarkably dependent on the electron-donating ability of a non-migrating group (Fig. 7).[36] Thus we compared the reactivities of alkynes with an electronically different non-migrating group. In reactions of p-RC₆H₄C≡CB(mida), the rearrangement of (p-C₆H₄OMe)

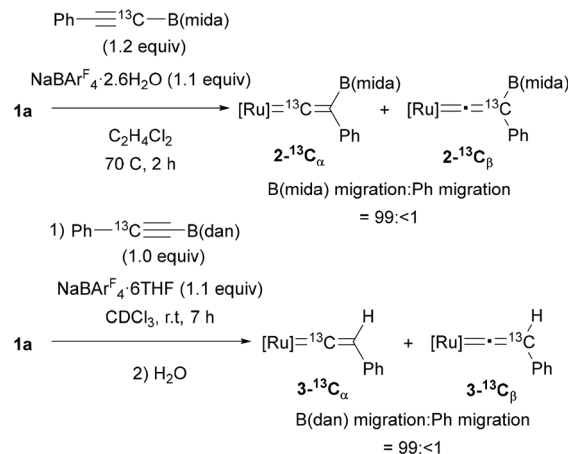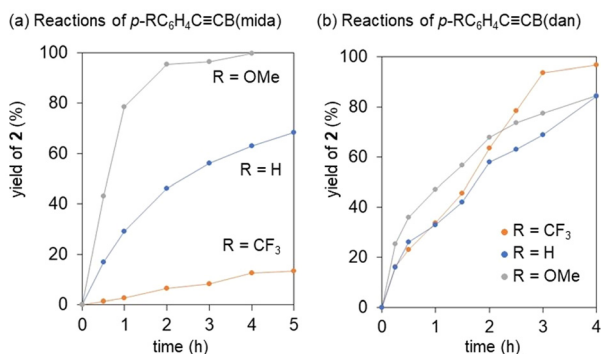**Fig. 6** Isotopic labeling experiments ([Ru] = Ru(dppe)Cp⁺).

Fig. 7 Vinylidene rearrangements of borylalkynes with an electronically differentiated aryl group. Reactions were performed at 50 °C for B(mida) group and at room temperature for B(dan) group. Yields of **2** were determined by ^{1}H NMR spectroscopy.

C≡CB(mida) with an electron donating aryl group was faster than that of PhC≡CB(mida), while electron withdrawing p-C$_6$H$_4$CF$_3$ group retarded the reaction significantly (Fig. 7a). The observed electronic effects were entirely identical with our previous observations in nucleophilic vinylidene rearrangements.[36] On the other hand, in reactions of p-RC$_6$H$_4$C≡CB (dan), no obvious migration preference depending on the electronic character of the non-migrating group was observed (Fig. 7b). This different structure-reactivity relationship is indicative of the distinct migration mode with the tricoordinate borylalkynes.[53]

To further obtain an insight into the migration mode, the boryl migrations of B(dan) and B(mida) group were evaluated by DFT calculations at B3LYP/6-311G(d) + SDD (Fig. 8). Both process from η^2-alkyne to the corresponding vinylidene species is endothermic with a ΔG value of 10.1 kcal mol^{-1}. An activation barriers of B(dan) migration is significantly lower than that of B(mida) migration. These results are consistent with the experimental observation that the vinylidene rearrangement of B(dan) proceeds smoothly at room temperature, while that of B(mida) needs a higher reaction temperature. At the transition state (**TS**) for the B(dan) migration, the C1–B bond length (1.703 Å) is obviously shorter than C2–B bond length (1.929 Å), which corresponds to the nearly generating C–B bond. A linear alignment of C1, C2, and C3 atoms (177°) and a nearly orthogonal conformation of the non-migrating phenyl group toward the C1–B bond (100°) indicates that π-orbitals of the non-migrating phenyl group can effectively interact with the C1–C2 π bond, which should be directly involved in the boryl migration. Of interest, this TS structure is similar with that in 1,3-boryl migration of a (boryl)(alkynyl)osmium complex.[50a] In the **TS** of B(mida) migration, C1–B bond (1.911 Å) is shorter than C2–B bond (2.067 Å), while the difference in these bond lengths is smaller than that in the B(dan) migration. Furthermore, in contrast to the B(dan) migration, the angle of C1–C2–C3 is slightly bent (167°). Note that, in the B(mida) migration, a dative B–N bond remains during the whole calculated processes from **A** to **B** (N–B = 1.711–1.717 Å).
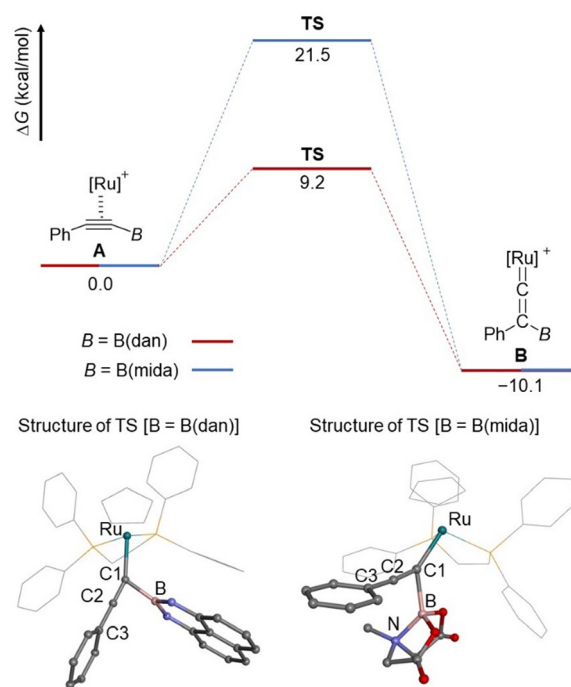

Fig. 8 DFT calculations at the B3LYP/SDD (Ru) and 6-311G(d) (other atoms) level of theory ([Ru] = Ru(dppe)Cp). In the structures of TS, dppe and Cp ligands are shown by wireframe representations for clarity. Color code: grey, C; pink, B; green, Ru; purple, N; red, O; yellow, P.

NBO analyzes were performed at HF/6-311G(d)+SDD for **A**, **TS**, and **B**. In the **TS** of B(dan) migration, a definite interaction is estimated between the C1–C2 π bond as a donor and the p orbital of the boron center as an acceptor (Fig. 9a). The donor acceptor interaction supports the electrophilic migration mode of B(dan) group. On the other hand, B(mida) migration hardly

(a) donor/acceptor interaction at TS [B = B(dan)]

π_{C1-C2} orbital   p*$_B$ orbital

$\pi_{C1-C2} \rightarrow$ p*$_B$: 38.53 kcal/mol

(b) NBO charges

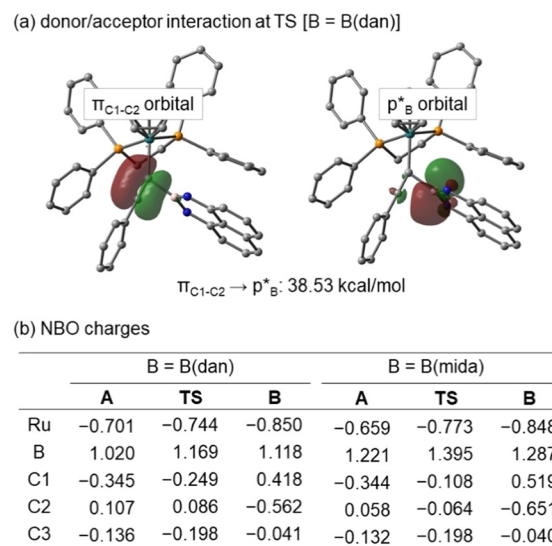|	B = B(dan)			B = B(mida)		
	A	**TS**	**B**	**A**	**TS**	**B**
Ru	−0.701	−0.744	−0.850	−0.659	−0.773	−0.848
B	1.020	1.169	1.118	1.221	1.395	1.287
C1	−0.345	−0.249	0.418	−0.344	−0.108	0.519
C2	0.107	0.086	−0.562	0.058	−0.064	−0.651
C3	−0.136	−0.198	−0.041	−0.132	−0.198	−0.040

Fig. 9 (a) NBO charges and (b) donor/acceptor interactions in TS of B(dan).

includes the same type of interaction, because the corresponding p orbital of the boron center participates in the dative bond formation with the nitrogen atom. Fig. 9b shows NBO charges of **A**, **TS**, and **B**. In B(dan) migration, a positive charge of the boron atom increases from intermediate **A** (1.020) to **TS** (1.169). Although C2 has a positive charge in **A** and **TS**, the value decreases from **A** to **TS** by 0.021. These changes of the charge distributions are completely different with our previous results for the nucleophilic vinylidene rearrangements,[36] yet consistent with the other theoretical calculations of electrophilic vinylidene rearrangements.[54] Similar electron flows are calculated in the case of the B(mida) migration. Although we cannot conclude either electrophilic or nucleophilic migration mode of B(mida) group based on the present experimental and theoretical studies,[55] these calculations suggest the B(dan) migration proceeds *via* the electrophilic mode. We believe that the migration of a tricoordinate boryl group, B(pin), also follows the mechanistic scenario similar to that of B(dan). This conclusion is consistent with the high migration aptitude of Lewis acidic boryl groups.

We finally examined substrate scope by using $RC\equiv CB$ (mida) (Fig. 10). Reactions of p-$RC_6H_4C\equiv CB$(mida) (R = Me and F) proceeded smoothly to provide the corresponding vinylidene complexes in 70 and 71% yield, respectively. Boryl alkynes with an aryl group substituted at o- and m-positions also provided vinylidene complexes in good yields, while a sterically hindered substrate with an o-methyl group diminished the yield. As indicated by the ligand screening, the present rearrangement is rather sensitive toward the steric hindrance. Reactions of alkynes bearing biphenyl and naphthyl proceeded in moderate yields. Electron-rich heteroaromatic groups were applicable to afford the corresponding vinylidene complexes in moderate yields. Unfortunately, a reaction with alkylalkyne was found to be sluggish.
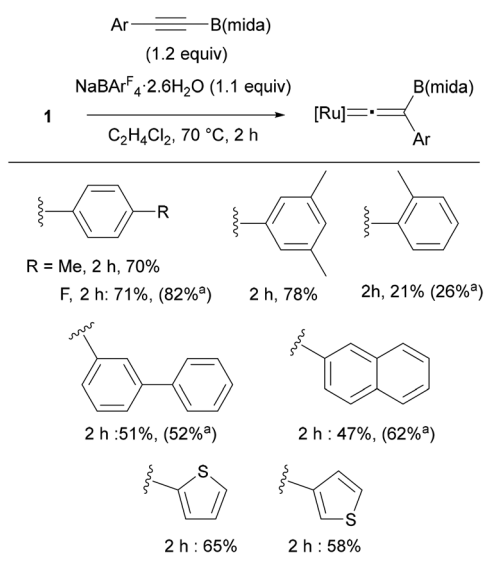
Fig. 10 Substrate scope ([Ru] = [Ru(dppe)Cp]$^+$).

Conclusions

In conclusion, we have developed the vinylidene rearrangements of internal borylalkynes with tri- and tetra-coordinate boryl groups. Mechanistic studies revealed the selective migration of the boryl group regardless of the coordination number of the boron center, and that the migration rate was dramatically enhanced by the Lewis acidic tricoordinate boryl group. Theoretical calculation implied that the migration mode is an electrophilic process at least in the case of B(dan) group, which is completely different from the previous rearrangements of diarylalkynes. Therefore, vinylidene rearrangements can proceed through either nucleophilic or electrophilic migration modes depending on the migration groups. This allows for the utilization of various groups, including nucleophilic group 16 elements (S and Se) and electrophilic group 13 element (B) as well as electronically neutral groups (*e.g.*, group 14 elements like C, Si and Sn). Note that the resulting vinylidene complexes with the tricoordinate boryl group are remarkably susceptible toward hydrolysis. We assumed that the observed rapid hydrolysis results from the high electrophilicity of the α-carbon of the vinylidene unit. This reactivity would be beneficial for their application to catalytic processes.

Experimental

General

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques unless otherwise noted. 1,2-Dichloroethane was distilled over P_4O_{10}, degassed, and stored under an argon atmosphere. [RuCl(dppe)Cp], analogous ruthenium complexes,[34] $NaBAr^F_4·2.6H_2O$,[56] $NaBAr^F_4·6THF$,[56] and alkynes[57–60] are synthesized according to the literature procedures. ^1H (495 MHz), $^{13}C\{^1H\}$ (125 MHz), and $^{31}P\{^1H\}$ (200 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer, except for those of complex **2g**, which were recorded by Varian-400 spectrometer [^1H (400 MHz) and $^{13}C\{^1H\}$ NMR (100 MHz)]. Chemical shifts are reported in δ and referenced to residual ^1H and ^{13}C signals of deuterated solvents as internal standards. Note that several signals assignable to the $Ru=C=C$ could not be found, probably because it is overlapped with other signals and the quadrupolar boron is likely to further complicate its identification (*vide infra*). High-resolution mass spectra were measured on a JEOL JMS-T100LC AccuTOF spectrometer. Elemental analyses were performed on a PerkinElmer 2400 series II HCN analyzer. Procedures and data for other complexes mentioned in the text are given in the ESI.†

Procedure for vinylidene rearrangements of alkynes with B(mida)

A mixture of [RuCl(L)Cp] (1.0 equiv.), $PhC\equiv CB$(mida) (1.2 equiv.), and $NaBAr^F_4·2.6H_2O$ (1.1 equiv.) in 1,2-dichloroethane (2 mL) was heated at 70 °C for 2 h. The resulting orange suspension was filtered through a short pad of Celite and rinsed

with 1,2-dichloroethane (*ca.* 1 mL). The filtrate was dried *in vacuo*, and the residue was purified by column chromatography on silica gel (dichloromethane). The eluate was further purified by recrystallization from dichloromethane/hexane to afford the vinylidene complex as yellow crystals. The NMR yields were determined by using tetrachloroethane as an internal standard.

Synthesis of [Ru(=C=C(Ph){B(mida)})(dppe)Cp][BAr$^F_4$] (2a)

Complex **2a** was obtained as yellow crystals (71.6 mg, 0.0425 mmol, 83% yield) by the reaction of [CpRuCl(dppe)] (30.7 mg, 0.0512 mmol), PhC≡CB(mida) (15.6 mg, 0.0607 mmol), and NaBAr$^F_4$·2.6H$_2$O (51.1 mg, 0.0548 mmol).

^{1}H NMR (acetone-d_6): δ 7.79 (s, 8H, *o*-H of BAr$^F_4$), 7.75 (m, 4H, *o*-H of Ph in dppe), 7.67 (s, 4H, *p*-H of BAr$^F_4$), 7.45 (m, 4H, *p*-H of Ph in dppe × 2), 7.35 (m, 8H, *m*-H of Ph in dppe × 2), 7.24 (m, 4H, *o*-H of Ph in dppe), 7.01 (m, 3H, *m*- and *p*-H of Ru=C=CPh), 6.88 (m, 2H, *o*-H of Ru=C=CPh), 5.67 (s, 5H, Cp), 3.99 (d, 2H, $^2J_{HH}$ = 17.3 Hz, CH$_2$ of mida), 3.39 (m, 2H, CH$_2$ of dppe), 3.24 (d, 2H, $^2J_{HH}$ = 16.8 Hz, CH$_2$ of mida), 3.03 (m, 2H, CH$_2$ of dppe), 2.72 (s, 3H, CH$_3$ of mida). ^{31}P{^{1}H} NMR (acetone-d_6): δ 79.5 (s, dppe). ^{13}C{^{1}H} NMR (acetone-d_6): δ 339.2 (t, $^2J_{CP}$ = 15.4 Hz, Ru=*C*=C), 167.7 (s, CO of mida), 162.6 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr$^F_4$), 138.0 (m, *ipso*-C of Ph in dppe), 135.5 (br, *o*-C of BAr$^F_4$), 134.9 (m, *ipso*-C of Ph in dppe), 133.9 (virtual t, *o*-C of Ph in dppe), 132.0 (m, *o*- and *p*-C of Ph in dppe), 131.5 (s, *p*-C of Ph in dppe), 130.8 (s, *o*-C of Ru=C=C*C*$_6$H$_5$), 130.0 (brq, $^2J_{CF}$ = 34.4 Hz, *m*-C of BAr$^F_4$), 129.7 (m, *m*-C of Ph in dppe × 2 and *m*-C of Ru=C=C*C*$_6$H$_5$), 128.8 (s, *ipso*-C of Ru=C=C*C*$_6$H$_5$), 127.3 (s, *p*-C of Ru=C=C*C*$_6$H$_5$), 125.4 (q, $^1J_{CF}$ = 272.9 Hz, CF$_3$ of BAr$^F_4$), 118.4 (m, *p*-C of BAr$^F_4$), 92.0 (s, Cp), 62.8 (s, CH$_2$ of mida), 47.2 (s, CH$_3$ of mida), 28.5 (m, P*C*H$_2$). The signal assignable to the Ru=C=*C* could not be found, probably because it is overlapped with other signals. Elemental analysis calcd for C$_{76}$H$_{53}$O$_4$B$_2$F$_{24}$P$_2$NRu·0.5CH$_2$Cl$_2$: C, 53.19; H, 3.09; N, 0.81. Found: C, 53.13; H, 3.06; N, 0.80.

Procedures for vinylidene rearrangements of tricoordinate borylalkynes

A reaction of PhC≡CB(dan) with NaBAr$^F_4$·2.6H$_2$O. A mixture of [RuCl(dppe)Cp] (30.1 mg, 0.0502 mmol), PhC≡CB(dan) (13.7 mg, 0.0511 mmol), and NaBAr$^F_4$·2.6H$_2$O (50.9 mg, 0.0546 mmol) in 1,2-dichloroethane (2 mL) was heated at 70 °C for 1 h. The resulting brown suspension was filtered through a short pad of Celite and rinsed with 1,2-dichloroethane (*ca.* 1 mL). The NMR yields were determined by using tetrachloroethane as an internal standard.

A reaction of PhC≡CB(dan) with anhydrous NaBAr$^F_4$·6THF. A reaction of PhC≡CB(dan) with anhydrous NaBArF$_4$·6THF was performed according to the same procedure by using [RuCl(dppe)Cp] (29.9 mg, 0.0498 mmol), PhC≡CB(dan) (13.8 mg, 0.0515 mmol), and NaBAr$^F_4$·6THF (81.1 mg, 0.0615 mmol). The NMR yield was determined by ^{1}H NMR spectrum of the crude product (96% NMR yield). The combined filtrate was purified by recrystallization from dichlor-

oethane/hexane to afford a vinylidene complex **2f** as yellow crystals in 70% yield.

^{1}H NMR (CDCl$_3$, see ESI† for the atom numbering): δ 7.74 (s, 8H, *o*-H of BAr$^F_4$), 7.52 (s, 4H, *p*-H of BAr$^F_4$), 7.38 (m, 12H, *p*- ×2, *m*- and *o*-H of Ph in dppe), 7.02 (m, 15H, *o*- and *m*-H of Ph in dppe and H3, H4, H6, H7), 6.62 (d, 2H, $^3J_{HH}$ = 6.9 Hz, H2), 5.90 (br, 2H, H5), 5.43 (s, 5H, Cp), 4.73 (br, 2H, NH of dan), 3.05 (m, 2H, CH$_2$ of dppe), 2.87 (m, 2H, CH$_2$ of dppe). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 78.0 (s, dppe). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 335.6 (t, $^2J_{CP}$ = 14.8 Hz, Ru=*C*=C), 161.8 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr$^F_4$), 140.0 (s, C10), 136.2 (br, C8), 135.0 (m, *o*-C of BAr$^F_4$ and *ipso*-C of Ph in dppe), 133.1 (m, *ipso*-C of Ph in dppe), 132.0 (m, *p*- × 2 and *o*-C of Ph in dppe), 131.4 (m, *o*-C of Ph in dppe), 129.0 (m, *m*-C × 2 of Ph in dppe, and C2, C3, and *m*-C of BAr$^F_4$), 127.3 (s, C6), 127.0 (s, C4), 125.8 (s, C1), 124.7 (q, $^1J_{CF}$ = 273.6 Hz, CF$_3$ of BAr$^F_4$), 119.6 (s, C9), 118.4 (s, C7), 117.6 (s, *p*-C of BAr$^F_4$), 117.1 (br, Ru=C=*C*), 106.5 (s, C5), 91.3 (s, Cp), 27.8 (m, P*C*H$_2$). High resolution mass measurement and elemental analysis have failed due to the high susceptibility toward hydrolysis.

A reaction of PhC≡CB(pin) with anhydrous NaBAr$^F_4$·6THF. A mixture of [RuCl(dppe)Cp] (29.9 mg, 0.0498 mmol), PhC≡CB(pin) (11.6 mg, 0.0509), and NaBAr$^F_4$·6THF (81.8 mg, 0.0620 mmol) in 1,2-dichloroethane (2 mL) was heated at 70 °C for 1 h. The resulting dark orange suspension was filtered through a short pad of Celite and rinsed with 1,2-dichloroethane (*ca.* 1 mL). The combined filtrate was dried *in vacuo*. The NMR yield was determined by using 1,3,5-trimethoxybenzene as an internal standard. Isolation of the corresponding vinylidene complex cannot be performed due to the instability toward hydrolysis. However, the efficient formation of the vinylidene complex **2g** in a reaction using NMR tube provided reliable information on the formation of the vinylidene complex (for the procedure of the reaction using NMR tube, see the section of time course studies shown below).

^{1}H NMR (CDCl$_3$): δ 7.74 (s, 8H, *o*-H of BAr$^F_4$), 7.53 (s, 4H, *p*-H of BAr$^F_4$), 7.48–7.28 (m, 12H, *p*- ×2, *m*- and *o*-H of Ph in dppe), 7.24 (m, 4H, *m*-H of Ph in dppe), 7.10 (m, 7H, *o*-H of Ph in dppe and *m*- and *p*-H of Ru=C=CPh), 6.69 (m, 2H, *o*-H of Ru=C=CPh), 5.22 (s, 5H, Cp), 2.98 (m, 4H, CH$_2$ of dppe × 2), 0.93 (s, 12H, CH$_3$ of pin). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 78.3 (s, dppe). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 347.4 (t, $^2J_{CP}$ = 15.4 Hz, Ru=*C*=C), 161.8 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr$^F_4$), 136.1 (m, *ipso*-C of Ph in dppe), 134.9 (br s, *o*-C of BAr$^F_4$), 132.8 (m, *o*-C of Ph in dppe), 132.7 (m, *ipso*-C of Ph in dppe), 131.8 (s, *p*-C of Ph in dppe), 131.6 (s, *p*-C of Ph in dppe), 131.0 (m, *o*-C of Ph in dppe), 129.2 (m, *m*-C of Ph in dppe), 129.0 (brq, $^2J_{CF}$ = 29.7 Hz, *m*-C of BAr$^F_4$), 128.9 (m, *m*-C of Ph in dppe and *m*- and *o*-C of Ru=C=C*C*$_6$H$_5$), 126.7 (s, *p*-C of Ru=C=C*C*$_6$H$_5$), 124.6 (q, $^1J_{CF}$ = 271.0 Hz, CF$_3$ of BAr$^F_4$), 117.5 (s, *p*-C of BAr$^F_4$), 91.5 (s, Cp), 84.0 (s, CO of pin), 28.9 (m, P*C*H$_2$), 24.4 (s, CH$_3$ of pin). The signal assignable to the Ru=C=*C* and *ipso*-C of Ru=C=C*C*$_6$H$_5$ could not be found, probably because it is overlapped with other signals. High resolution mass measurement and elemental analysis have failed due to the high susceptibility toward hydrolysis.

Procedures for the protodeboronation

A 20 ml Schlenk was charged with PhC≡CB(dan) (13.9 mg, 0.0518 mmol) and H_2O (2.3 mmol, 0.1276 mg) in 1,2-dichloroethane (2 ml) under an argon atmosphere. The mixture was heated 70 °C for 1 h. The brown solution was dried *in vacuo* and analyzed by ^{1}H NMR. The NMR yield was determined by using 1,3,5-trimethoxybenzene as an internal standard.

A J Young NMR tube was charged with [RuCl(dppe)Cp] (30.0 mg, 0.0500 mmol), PhC≡CB(dan) (13.6 mg, 0.0507 mmol), and $NaBAr^F_4$·6THF (81.7 mg, 0.0619 mmol) in $CDCl_3$ (0.5 mL). After 7 h at room temperature, vinylidene complex **2f** was formed in 94% NMR yield. After solvent was removed under reduced pressure, H_2O (1.8 mg, 0.10 mmol) and 1,2-dichloroethane (0.5 ml) were added. The mixture was heated 70 °C for 1 h. The black solution was dried *in vacuo* and analyzed by ^{1}H NMR spectrum. The NMR yield was determined by using 1,3,5-trimethoxybenzene as an internal standard. The same procedure was used for the protodeboronation of vinylidene complex **2g**.

Syntheses of the byproduct 3 formed by protodeboronation

To characterize byproducts in the vinylidene rearrangements, we performed synthesis of the protodeboronated complex **3** as follows; A mixture of [RuCl(dppe)Cp] (60.3 mg, 0.1005 mmol), PhC≡CH (10.4 mg, 0.1018 mmol), and $NaBAr^F_4$·2.6H_2O (102.1 mg, 0.1094 mmol) in 1,2-dichloroethane (2 mL) was heated at 70 °C for 1 h. The resulting brown suspension was filtered through a short pad of Celite and rinsed with 1,2-dichloroethane (*ca*. 1 mL). The filtrate was dried *in vacuo*, and the residue was purified by column chromatography on silica gel (dichloromethane/hexane = 1:1). Complex **3** was obtained as a red oil (124.2 mg, 0.08812 mmol).

^{1}H NMR ($CDCl_3$): δ 7.76 (s, 8H, *o*-H of BAr^F_4), 7.53 (s, 4H, *p*-H of BAr^F_4), 7.40 (m, 16H, *p*- ×2, *m*- ×2 and *o*-H of Ph in dppe), 7.15 (m, 4H, *o*-H of Ph in dppe), 6.92 (m, 1H, *p*-H of Ru=C=CPh), 6.86 (m, 2H, *m*-H of Ru=C=CPh), 6.23 (m, 2H, *o*-H of Ru=C=CPh), 5.52 (s, 5H, Cp), 4.68 (s, 1H, Ru=C=CH), 3.00 (m, 2H, CH_2 of dppe), 2.71 (m, 2H, CH_2 of dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 77.3 (s, dppe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 354.1 (t, $^2J_{CP}$ = 16.1 Hz, Ru=C=C), 161.9 (q, $^1J_{CB}$ = 50.0 Hz, *ipso*-C of BAr^F_4), 135.0 (br, *o*-C of BAr^F_4), 134.7 (m, *ipso*-C of Ph in dppe), 133.6 (m, *ipso*-C of Ph in dppe), 132.1 (m, *p*- ×2 and *o*-C of Ph in dppe), 131.4 (virtual t, *o*-C of Ph in dppe), 129.4 (m, *m*-C of Ph in dppe × 2), 129.0 (brq, $^2J_{CF}$ = 34.0 Hz, *m*-C of BAr^F_4), 128.8 (s, *m*-C of Ru=C=CC_6H_5), 126.9 (s, *p*-C of Ru=C=CC_6H_5), 125.8 (s, *o*-C of Ru=C=CC_6H_5), 125.1 (s, *ipso*-C of Ru=C=CC_6H_5), 124.7 (q, $^1J_{CF}$ = 273.5 Hz, CF_3 of BAr^F_4), 117.9 (s, Ru=C=C), 117.6 (m, *p*-C of BAr^F_4), 92.0 (s, Cp), 27.2 (m, PCH_2). HRMS *m/z*: [M + Na]$^+$ calcd for $RuP_2C_{39}H_{35}{}^+$: 667.12575; found 667.12595.

Procedure for time course studies

A J Young NMR tube was charged with [RuCl(dppe)Cp] (1.0 equiv.), PhC≡C*B* (1.0 equiv.), and $NaBAr^F_4$·6THF (1.1 equiv.) in $CDCl_3$ (0.5 mL). The reaction was monitored by means of ^{1}H NMR analysis, and the NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard.

Conflicts of interest

There are no conflicts to declare.

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