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A Mechanistic Study of the Utilization of *arachno*-Diruthenaborane $[(Cp^*RuCO)_2B_2H_6]$ as an Active Alkyne-Cyclotrimerization Catalyst

K. Geetharani,[a] Samat Tussupbayev,[b] Julia Borowka,[b] Max C. Holthausen,*[b] and Sundargopal Ghosh*[a]

Abstract: The reaction of *nido*-[1,2-$(Cp^*RuH)_2B_3H_7$] (**1a**, $Cp^* = \eta^5$-C_5Me_5) with $[Mo(CO)_3(CH_3CN)_3]$ under mild conditions yields the new metallaborane *arachno*-$[(Cp^*RuCO)_2B_2H_6]$ (**2**). Compound **2** catalyzes the cyclotrimerization of a variety of internal- and terminal alkynes to yield mixtures of 1,3,5- and 1,2,4-substituted benzenes. The reactivities of *nido*-**1a** and *arachno*-**2** with alkynes demonstrates that a change in geometry from *nido* to *arachno* drives a change in the reaction from alkyne-insertion to catalytic cyclotrimerization, respectively. Density functional calculations have been used to evaluate the reaction pathways of the cyclotrimerization of alkynes catalyzed by compound **2**. The reaction involves the formation of a ruthenacyclic intermediate and the subsequent alkyne-insertion step is initiated by a [2+2] cycloaddition between this intermediate and an alkyne. The experimental and quantum-chemical results also show that the stability of the metallacyclic intermediate is strongly dependent on the nature of the substituents that are present on the alkyne.

Keywords: boron · cyclotrimerization · density functional calculations · reaction mechanisms · ruthenium

Introduction

The transition-metal-mediated cyclotrimerization of alkynes represents an elegant preparative route to substituted benzenes. Substantial research efforts have been devoted in the past to examine the scope of this reaction and to understand its underlying mechanistic details.[1–3] However, the otherwise-rich chemistry of p-block elements[4,5] has remained largely unexplored in this particular context. Our interest to probe the corresponding catalytic potential of main-group elements was sparked by the fact that boron in particular exhibits a rich organometallic chemistry, with a broad range of useful chemical transformations.[6] In view of the considerable body of knowledge that has been gathered in the field of metallaborane chemistry, it appears rewarding to explore the catalytic potential of this class of compounds for the cyclotrimerization of alkynes.

The chemistry of metallaboranes, which are a class of structures that result from the combination of borane cages and metal clusters, has been studied for some time now.[7,8] The reactions of boranes with alkynes lead to carboranes[9,10] that can further incorporate transition-metal fragments, thereby resulting in the development of metallacarborane chemistry.[11–13] In 1974, Grimes et al. put forward a pioneering report on the generation of *nido*-[1-(η^5-C_5H_5)$CoC_2B_3H_7$] from *nido*-[2-(η^5-C_5H_5)CoB_4H_8][14] and, subsequently, others provided some notable accounts of the reactions of metallaboranes with alkynes.[15–17]

However, by and large, the lack of efficient preparative routes to metallaboranes has encumbered the development of this field. Recent renewed thrust has stemmed from the availability of convenient, high-yielding routes to metallaboranes that replace the older, intricate procedures, which involved long reaction times under pyrolytic conditions. With these new practical routes in hand,[18] metallaboranes that contain Group 4–9 metals have become accessible and a variety of reactions has subsequently been investigated. To the best of our knowledge, only a single catalytic process of metallaboranes has been reported, that is, the catalytic activity of [1,2-$(Cp^*Rh)_2B_3H_7$] (**1b**) with alkynes,[19] which has been a boon for the synthesis of metallaboranes with other transition-metal centers. We have recently reported the reaction of *nido*-[1,2-$(Cp^*RuH)_2B_3H_7$] (**1a**)[20] with $[Mo(CO)_3(CH_3CN)_3]$, which led to *arachno*-$[(Cp^*RuCO)_2B_2H_6]$ (**2**) in high yield.[21] Herein, we report a detailed study of the reactivity of compound **2** with a variety of terminal- and internal alkynes, thereby leading to metallaborane-catalyzed cyclotrimerization reactions. To obtain a detailed mechanistic insight into these reactions, we have evaluated the cyclotrime-

[a] K. Geetharani, Dr. S. Ghosh
Department of Chemistry
Indian Institute of Technology Madras
Chennai 600036 (India)
Fax: (+91) 44-2257-4202
E-mail: sghosh@iitm.ac.in

[b] Dr. S. Tussupbayev, Dr. J. Borowka, Prof. Dr. M. C. Holthausen
Johann Wolfgang Goethe Universität
Institut für Anorganische und Analytische Chemie
Max-von-Laue-Strasse 7, 60438 Frankfurt (Germany)
Fax: (+49) 69-798-29417
E-mail: max.holthausen@chemie.uni-frankfurt.de

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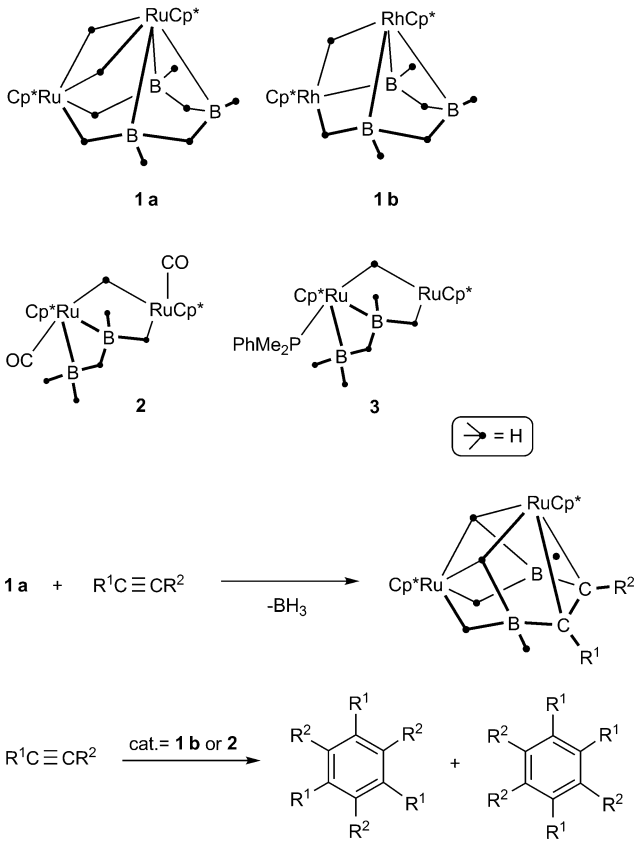
rization reaction that is mediated by the *arachno*-diruthenatetraborane by means of density functional calculations for acetylene and HC≡CCOOEt as a model substrate.

Results and Discussion

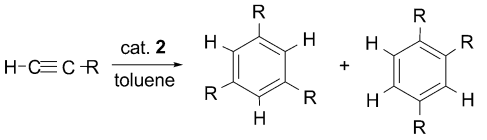
Cyclotrimerization of alkynes mediated by compound 2: A few accounts of metallaborane reactivity with alkynes have been put forward: 1) a facile reaction was observed between compound **1a** and a variety of substituted alkynes,[22,23] 2) the use of $[(Cp^*Ir)_2B_4H_{10}]$[24] yields a range of metallacarborane products, and 3) the reaction of compound **1b** with internal- and terminal alkynes[19] leads to catalytic cyclotrimerization. Owing to the presence of two additional hydride atoms in the ruthenaborane, compounds **1a** and **1b** are isoelectronic with very similar molecular structures (Scheme 1).



Scheme 1. Structures of metallaborane compounds **1a**, **1b**, **2**, and **3** and the reactivity of compounds **1a**, **1b**, and **2** towards alkynes ($Cp^* = \eta^5$-C_5Me_5).

Against this background, we explored the reactivity of compound **2** with various internal- and terminal alkynes, which led to the formation of a mixture of 1,3,5- and 1,2,4-substituted benzenes through catalyzed cyclotrimerization reactions. However, we found that compound **2** was catalytically inactive towards acetylene cyclotrimerization, which was confirmed by thin-layer chromotography (TLC), ^{1}H NMR spectroscopy, and GC analysis. The formation of new metallaboranes or metallacarboranes was not observed. The activities and selectivities for the cyclotrimerization of a variety of terminal and internal alkynes are listed in Table 1 and Table 2, respectively. The activities are higher for terminal alkynes than for internal alkynes and the yields are in the range 20–85% (no attempts were made to optimize the reaction conditions). The ratios of the isomers were determined by ^{1}H NMR spectroscopy on the reaction mixture after removing any unreacted alkyne and solvent or, in the cases where side-reactions were observed, by ^{1}H NMR spectroscopy after thin-layer chromatography. In

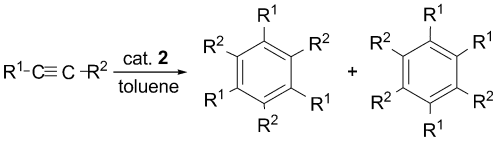
Table 1. Cyclotrimerization of terminal alkynes catalyzed by **2**.[a]



Entry	R	Cat./substrate	t [h]	T [°C]	Yield[b] [%]	Ratio
1	Ph	1:60	36	75	35	1:3
2	*p*-$CH_3C_6H_4$	1:20	30	75	75	1:3
3	*p*-$CF_3C_6H_4$	1:20	72	90	n.c.[c]	–
4	*p*-$NH_2C_6H_4$	1:20	40	75	42	1:1
5	2,4-$F_2C_6H_3$	1:20	60	75	n.c.[c]	–
6	CO_2Et	1:40	24	75	85	1:6
7	CH_2OH	1:24	70	75	n.c.[c]	–
8	$C(CH_3)_2OH$	1:14	60	75	n.c.[c]	–
9	$C_{10}H_7$[d]	1:20	40	75	n.c.[c]	–
10	$SiMe_3$	1:20	36	50	40	1:3

[a] Catalyst to substrate ratio, reaction time, t, reaction temperature, T, total yield, ratio of the 1,3,5- and 1,2,4-trisubstituted benzenes. [b] Yields are given based on product formation as determined by ^{1}H NMR spectroscopy. [c] n.c. = no cyclotrimerization. [d] 1-Naphthyl.

Table 2. Cyclotrimerization of internal alkynes catalyzed by compound **2**.[a]



Entry	R^1	R^2	Cat./substrate	t [h]	T [°C]	Yield[b] [%]	Ratio[c]
1	Ph	Ph	1:20	40	75	51	Hb[d]
2	Me	Ph	1:20	48	75	21	Tpb[e]
3	Me	Me	1:95	70	55	n.c.[f]	–
4	Ph	$SiMe_3$	1:20	48	75	20	Tmsb[g]
5	$SiMe_3$	$SiMe_3$	1:20	60	75	n.c.[f]	–
6	C_4H_9[h]	$SiMe_3$	1:20	60	55	n.c.[f]	–

[a] Catalyst to substrate ratio, reaction time, t, reaction temperature, T, total yield, ratio of the 1,3,5- and 1,2,4-trisubstituted benzenes. [b] Yields are given based on product formation as determined by ^{1}H NMR spectroscopy. [c] A single isomer was isolated. [d] Hb = hexaphenylbenzene. [e] Tpb = 1,2,4-trimethyl-3,5,6-triphenylbenzene. [f] n.c. = no cyclotrimerization. [g] Tmsb = 1,2,4-trimethylsilyl-3,5,6-triphenylbenzene. [h] *n*-butyl.

all cases, the 1,2,4-isomer is predominant, except for *p*-$NH_2C_6H_4C{\equiv}CH$. The reaction of compound **2** with $MeC{\equiv}CPh$ yields 1,2,4-trimethyl-3,5,6-triphenylbenzene as the only isomer that is detectable by ^1H NMR spectroscopy.

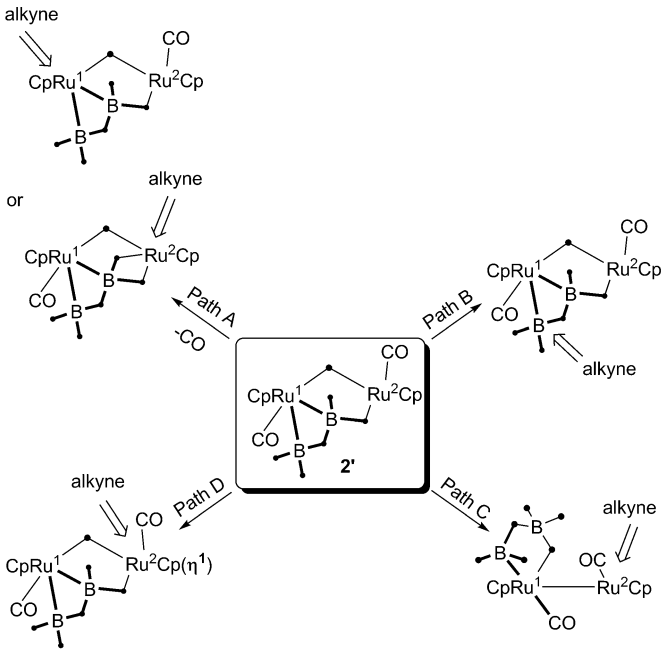
We found that electron-withdrawing substituents generally enhanced the reactivity of an alkyne. For example, with $HC{\equiv}CCO_2Et$, we observed a high yield of the cyclotrimerized product, which was comparable to the results for rhodaborane **1b**. The reactions of $HC{\equiv}CR$ (R = *p*-$CF_3C_6H_4$ or 2,4-$F_2C_6H_3$) gave insoluble materials and no cyclotrimerized products.

To evaluate the scope of this catalytic process, the reaction was also carried out by using the symmetrical alkyne $PhC{\equiv}CPh$, thereby affording the fully substituted arene, hexaphenylbenzene. Notably, rhodaborane **1b**, which catalyzes the cyclotrimerization of a variety of internal alkynes, does not yield the cyclotrimerization product of this alkyne.[19] The decreasing activities of compound **2** for $RC{\equiv}CSiMe_3$ (R = H, Ph, $SiMe_3$, and C_4H_9) imply the presence of a significant steric factor in the reaction mechanism.

There is one striking aspect of these observations with respect to the earlier work of Fehlner and co-workers:[19] in any presumable mechanistic picture, a key requirement for the metal-catalyzed cyclotrimerization is the coordination of the alkyne to the metal center, which, in turn, requires the presence of a vacant metal site or labile ligands. We note that neither compound **2** nor compound **1b** contain vacant metal sites, yet compound **2** contains two potentially labile CO ligands. To establish their role, we tested the cyclotrimerization of alkynes by using $[(Cp^*Ru)(Cp^*RuPMe_2Ph)B_2H_6]$ (**3**),[25] in which the CO ligands were substituted by a more-labile PMe_2Ph ligand. The reaction led to decomposition at room temperature and no sign of the cyclotrimerized product was observed. Up to this point, the catalytic activity remained puzzling and it is still not clear why the presence of the Cp*RuH site in compound **1a** leads to alkyne insertion, the presence of the Cp*RuCO site in compound **2** leads to catalytic cyclotrimerization, and the presence of a Cp*RuP-Me_2Ph fragment in compound **3** offers no reaction (Scheme 1).

Thus, we performed a detailed computational study to establish the mechanism of the cyclotrimerization reaction that is catalyzed by binuclear ruthenaborane compound **2**. Although numerous theoretical papers have focused on the cyclotrimerization of alkynes catalyzed by mononuclear complexes,[26] to the best of our knowledge, only one study has focused on catalysis by binuclear complexes.[27] This latter computational study,[27] which was on the tetramerization of acetylene by a nickel catalyst, revealed that terminally coordinated acetylene ligands insert more-readily into Ni–C bonds than bridging acetylene ligands and, thus, the most-favored dinuclear path strongly resembles the mononuclear pathway.

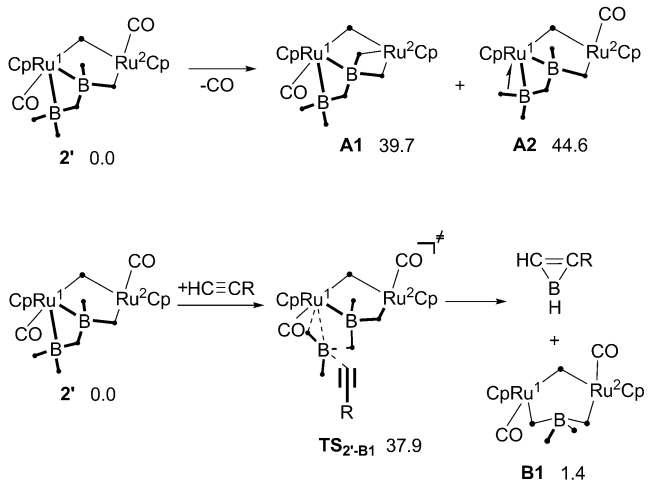
Density functional study on cyclotrimerization pathways: The reaction pathways have been explored by employing $[(CpRuCO)_2B_2H_6]$ (**2′**) as a model catalyst (that is, replacing the Cp* ligands in compound **2** with Cp ligands). Calculations were performed with $HC{\equiv}C{-}COOEt$ as a representative example for the cyclotrimerization reaction. Scheme 2 shows four conceivable pathways that we considered for the initial alkyne interactions with the catalyst. First, a dissociative path (path A) involves the initial release of one of the carbonyl ligands to provide a vacant Ru-coordination site for subsequent alkyne addition. The associative paths (paths B–D) commence with the coordination of the alkyne to three different sites in compound **2′**. Path B starts with the attack of the alkyne on one of the boron atoms of the B_2H_5 group. Alternatively, addition to one of the metal centers involves a concomitant change of the coordination mode of either the B_2H_5 group (from bridging to terminal, path C) or of the adjacent Cp ring (change in hapticity from η^5 to η^1, path D).



Scheme 2. Four pathways that were investigated for the initial interaction between the alkyne and the catalyst.

Path A involves the release of CO from compound **2′**, thereby leading to either structures **A1** or **A2** (Scheme 3). The calculations revealed that this dissociation is highly endothermic ($\Delta_R H_{298} = 39.7$ and 44.6 kcal mol^{-1}, respectively), and, therefore, we did not consider this pathway any further.

Along path B, we examined the potential reactivity of the B_2H_5 group in compound **2′** with respect to alkyne attack. The only transition state that we could locate in extensive potential-energy-surface scans was $\mathbf{TS_{2'-B1}}$, in which the alkyne attacks the terminal boron atom (Scheme 3). In this transition state, one of the Ru–B bonds is broken and a B–C bond is formed synchronously to yield intermediate **B1** and a boracyclopropene, that is, the alkyne abstracts a BH moiety from compound **2′**. However, the calculated energy barrier of this transformation is prohibitively high ($\Delta H^{\neq}_{298} =$



Scheme 3. The calculated reaction steps along paths A and B for the cyclotrimerization reaction of substituted-alkyne HC≡C–COOEt. Enthalpies (ΔH_{298}) are given relative to compound **2′** in kcal mol^{-1}.

37.9 kcal mol^{-1}) and, therefore, this route was also not considered further.

The results of path C are shown in Scheme 4 and Scheme 5. The first sequence of reaction steps leads to the formation of a ruthenacyclopentadiene intermediate (**C8**). This sequence starts with the coordination of the alkyne to compound **2′** to yield structure **C1**. As noted above, this step is associated with a change in the coordination mode of the B_2H_5 moiety from bridging to terminal. We located an isomer of compound **2′** with a terminal B_2H_5 fragment at Ru^1 (**2a′**, not shown in Scheme 4) that was 28.4 kcal mol^{-1} higher in energy than compound **2′**. The isomerization step involves the loss of an agostic Ru^2···H···B interaction that is present in compound **2′**, whereas the Ru-H-Ru bridging bond is retained. This process generates a vacant coordination site at the Ru^2 center and, therefore, a subsequent coordination of the alkyne to compound **2a′** is virtually barrierless. Overall, the coordination of the first alkyne molecule is a slightly endothermic step ($\Delta_R H_{298} = 2.1$ kcal mol^{-1}) with a substantial energy barrier of $\Delta H^{\neq}_{298} = 28.8$ kcal mol^{-1}.

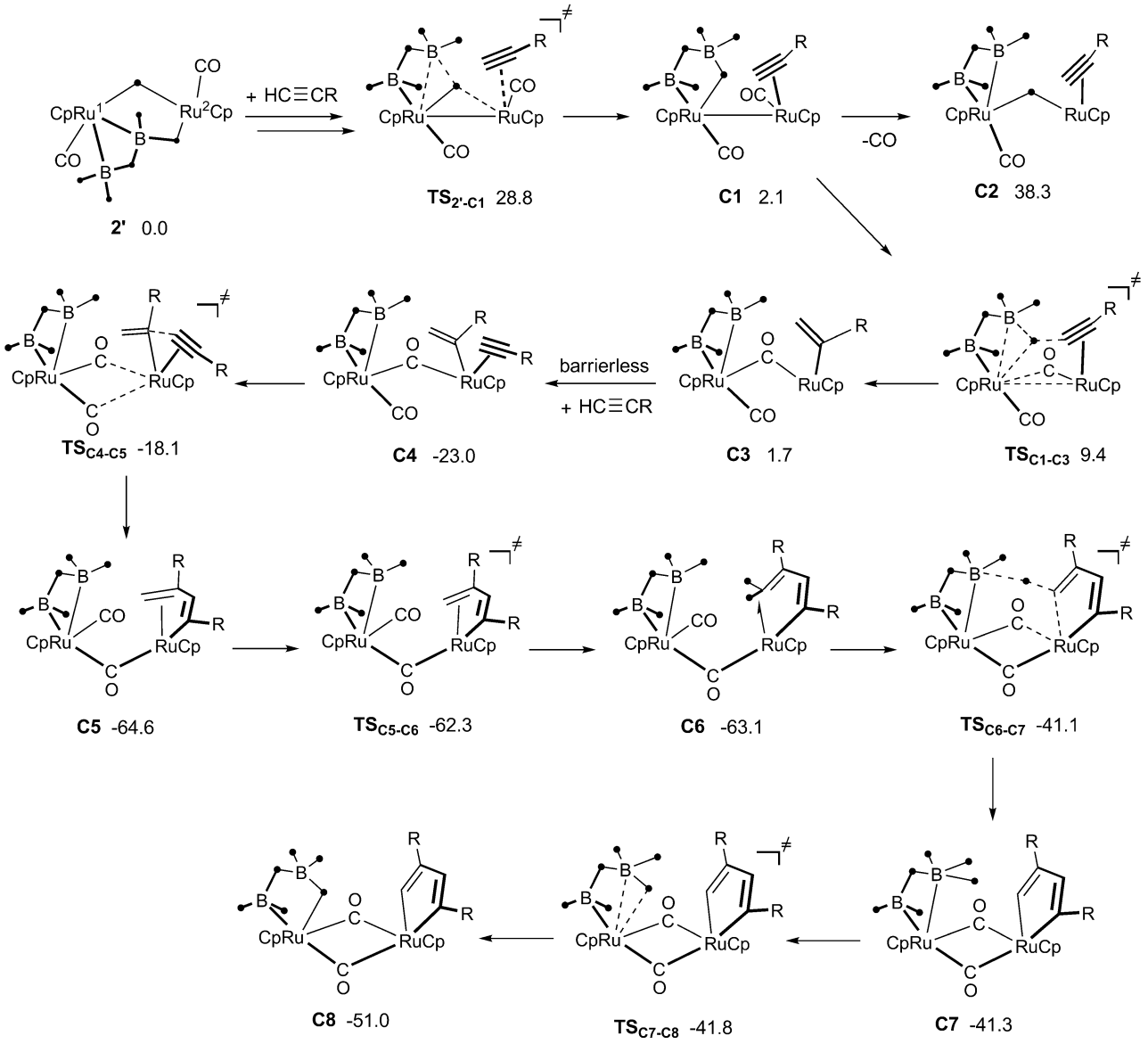
It has been demonstrated previously that the introduction of alkynes into pentacarbonyl complexes accelerates the rate of carbonyl substitution owing to the propensity of alkynes to act as four-electron donors.[28,29] This result led us to examine CO elimination from structure **C1**, but the formation of the resulting complex (**C2**) is prohibitively endothermic ($\Delta_R H_{298} = 36.2$ kcal mol^{-1}). Instead, the transfer of the hydrogen atom, which was formerly involved in the agostic B···H···Ru interaction, from the borane group onto the coordinated alkyne affords vinyl complex **C3** (Scheme 3). This step is essentially thermoneutral ($\Delta_R H_{298} = -0.4$ kcal mol^{-1}) and occurs with a very low energy barrier ($\Delta H^{\neq}_{298} = 7.3$ kcal mol^{-1}). As a result of the hydrogen transfer, the terminal CO ligand that is adjacent to the coordinated alkyne in structure **C1** becomes bridging in structure **C3**, thereby generating a vacant coordination site at the corresponding Ru atom. The coordination of a second alkyne molecule onto structure **C3** to yield structure **C4** proceeds without a barrier in a highly exothermic step ($\Delta_R H_{298} = -24.7$ kcal mol^{-1}).

The next step, which is both facile ($\Delta H^{\neq}_{298} = 4.9$ kcal mol^{-1}) and highly exothermic ($\Delta_R H_{298} = -41.6$ kcal mol^{-1}), is the C–C coupling between the vinyl ligand and the coordinated alkyne in structure **C4** to produce butadienyl complex **C5** (Scheme 3). A subsequent intramolecular rearrangement leads to the loss of the π-interaction between the Ru atom and the butadienyl ligand in structure **C5**; instead, an agostic interaction Ru···H···C$^{\delta}$ is present in structure **C6**. The conversion is slightly endothermic ($\Delta_R H_{298} = 1.5$ kcal mol^{-1}) and essentially barrierless ($\Delta H^{\neq}_{298} = 2.3$ kcal mol^{-1}). Transfer of the hydrogen atom that is involved in the agostic interaction Ru···H···C$^{\delta}$ in structure **C6** onto the B_2H_5 ligand yields structure **C7** and the subsequent formation of structure **C8** is an endothermic process ($\Delta_R H_{298} = 12.1$ kcal mol^{-1}) that proceeds with a considerable energy barrier ($\Delta H^{\neq}_{298} = 22.0$ kcal mol^{-1}).

Coordination of the third alkyne molecule to compound **C8** leads to alkyne–ruthenacyclopentadiene complex **C9** (Scheme 5) in a slightly endothermic step ($\Delta_R H_{298} = 8.1$ kcal mol^{-1}). This transformation occurs with a considerable energy barrier ($\Delta H^{\neq}_{298} = 21.0$ kcal mol^{-1}) and is accompanied by a substantial increase in the Ru–Ru distance.

Subsequent [4+2] cycloaddition via a concerted transition state (**TS_{C9-C10}**) leads directly to benzene complex **C10**. The C–C coupling is facile ($\Delta H^{\neq}_{298} = 8.7$ kcal mol^{-1}) and highly exothermic ($\Delta_R H_{298} = -65.6$ kcal mol^{-1}). Finally, elimination of the η^2-coordinated benzene molecule from compound **C10** generates structure **C11**, which is an isomer of the initial catalyst (**2′**). The elimination step is thermodynamically favorable ($\Delta_R H_{298} = -19.9$ kcal mol^{-1}) and proceeds without a barrier. Intermediate **C11** contains two bridging CO ligands and the B_2H_6 ligand is attached to one of the Ru atoms, whereas the other Ru atom remains coordinatively unsaturated. Therefore, this atom readily coordinates another incoming alkyne molecule to form compound **C12**, thereby closing the catalytic cycle through a facile isomerization ($\Delta H^{\neq}_{298} = 1.7$ kcal mol^{-1}) into compound **C1**.

Another possibility for the generation of a vacant coordination site at the Ru center in compound **2′** is a change in the hapticity of the Cp ring, which is well-known to play an important role in ligand-substitution reactions.[30] We examined this Cp-ring slippage along path D, which was induced by alkyne coordination to compound **2′** to yield structure **D1** (Scheme 6). The calculations reveal a barrier for this step ($\Delta H^{\neq}_{298} = 24.2$ kcal mol^{-1}) that is 4.6 kcal mol^{-1} lower than the initial barrier along path C, but intermediate **D1** ($\Delta_R H_{298} = 13.4$ kcal mol^{-1}) is significantly less-stable than structure **C1**. Furthermore, it is well-known that the presence of electron-donating methyl substituents at the Cp* ligands render ring-slippage processes energetically less favorable.[30a] Therefore, we performed calculations on the real system with Cp* for both paths C and D. As expected, the replacement of Cp with Cp* increases the energy barrier to



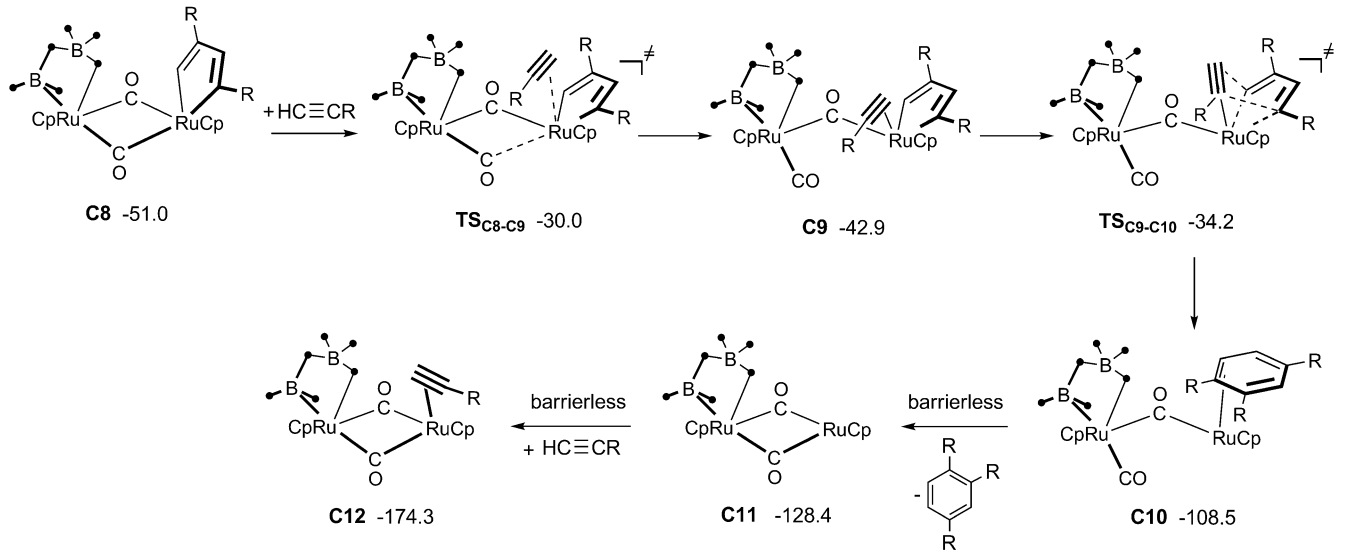
Scheme 4. Reaction sequence along path C (part 1) of the cyclotrimerization reaction of substituted-alkyne HC≡C−COOEt. Enthalpies (ΔH_{298}) are given relative to compound **2′** in kcal mol^{-1}.

29.1 kcal mol^{-1} for the initial step along path D. Moreover, this step becomes even-less thermodynamically favorable ($\Delta_R H_{298} = 20.7$ kcal mol^{-1}) and the energy barrier of the reverse step decreases to only 8.4 kcal mol^{-1}, thus rendering the formation of intermediate **D1** improbable. In contrast, for path C, the replacement of Cp with Cp* results in a noticeable lowering of the energy barrier to 23.3 kcal mol^{-1} and an additional stabilization of intermediate **C1** by 1.9 kcal mol^{-1}. The presence of Cp* also induces changes in the coordination sphere of transition state $\mathbf{TS_{2'-C1}}$ and structure **C1** such that the CO ligands become bridging, which we see as one of the reasons for the additional stabilization.

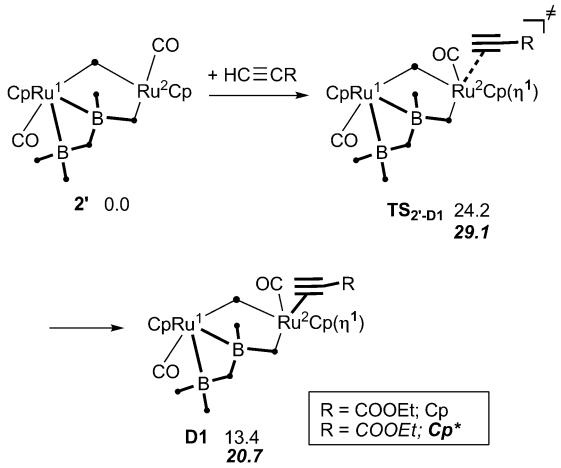
Calculations that were performed with acetylene as a substrate revealed a prohibitively high energy barrier ($\Delta H^{\neq}_{298} = 38.6$ kcal mol^{-1}) for the initial step along path C, that is, acetylene coordination to compound **2′**. This result is in line with the experimental observation that the reaction with acetylene does not lead to the cyclotrimerization product. We identified a significant contribution of the dispersion correction (about 15 kcal mol^{-1}) to the lowering of the relative enthalpy of the transition steps and intermediates when the bulkier C_2H−COOEt molecule was used as a substrate; without the inclusion of these effects, some of the steps have prohibitively high energy barriers.

Conclusion

We have demonstrated the ruthenaborane-catalyzed cyclotrimerization reactions of both internal- and terminal alkynes under mild conditions with wide functional-group compatibility. This reaction is a rare example of this type of



Scheme 5. Reaction sequence along path C (part 2) of the cyclotrimerization reaction of substituted-alkyne HC≡C–COOEt. Enthalpies (ΔH_{298}) are given relative to compound **2′** in kcal mol^{-1}.



Scheme 6. Reaction sequence along path D of the cyclotrimerization reaction of substituted-alkyne HC≡C–COOEt. Enthalpies (ΔH_{298}) are given relative to compound **2′** in kcal mol^{-1}.

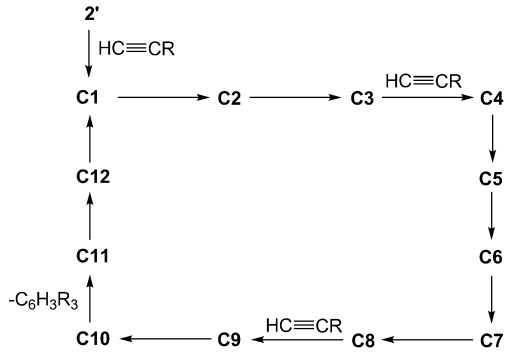
catalytic activity of metallaboranes, which commonly produce metallacarborane complexes upon reaction with alkynes.

The experimental results were complemented and rationalized by means of a computational study on the mechanism of the cyclotrimerization reaction. We considered several different reaction pathways, the most-favorable of which starts with alkyne coordination onto compound **2′**, along with a change in the coordination mode of the B_2H_5 fragment from bridging to terminal, which is preserved along the whole reaction pathway. Both Ru atoms act cooperatively to promote the cyclotrimerization reaction: all of the alkyne-coordination and the C–C-coupling steps take place within the coordination sphere of one of the Ru atoms. The function of the second metal ion is to keep the B_2H_5 fragment in a suitable stereochemical arrangement, from which a hydrogen atom can be readily transferred. Hence, the B_2H_5 ligand plays an important role as a hydrogen-atom buffer. For example, a migration of the bridging hydride in species **2′**, together with the change in the coordination mode of the B_2H_5 fragment in the initial step of path C, opens a vacant coordination site that is suitable for accepting the incoming alkyne. Subsequently, a hydrogen transfer from the B_2H_6 moiety to the coordinated η^2-alkyne molecule in structure **C1** to yield η^1-vinyl ligands in structure **C2** generates a vacant space for the incoming second alkyne molecule. Furthermore, this hydrogen atom shifts back to the B_2H_5 ligand from the butadienyl ligand in structure **C6** to produce ruthenacyclopentadiene complex **C8**.

The dissociation of CO ligands is thermodynamically unfavorable and cyclotrimerization occurs without substitution of the carbonyl ligands in compound **2′**. During the course of the transformations, the CO ligands change their coordination mode within the catalyst from terminal to bridging, thus linking the metal ions together. This finding explains the loss of catalytic activity that is observed for the [(Cp*Ru)(Cp*RuPMe$_2$Ph)B$_2$H$_6$] complex, because the monophosphine PMe$_2$Ph ligand cannot act as a bridging linker.

The rate-determining step of this mechanistic scenario is the initial coordination of the alkyne to the reactant (**2′**), thereby yielding intermediate **C1** with a barrier of $\Delta^{\neq}H_{298}=$ 28.8 kcal mol^{-1}. However, we predict a noticeably lower energy barrier for the real system with Cp* instead of Cp that is used in our molecular model. The calculations also demonstrate the influence of substituents on the alkyne (C_2HR, where R = H or COOEt) on the stability of the intermediates and transition states: the conversion barriers are prohibitively high if acetylene is used as a substrate.

Overall the reaction **2′**+3 C_2HR = **C11**+$C_6H_3R_3$ (R = COOEt) is highly exothermic ($\Delta_R H_{298} = -128.4$ kcal mol^{-1}). The catalyst is regenerated in the form of intermediate **C11**, an isomer of **2′**, which readily coordinates another alkyne molecule to yield product **C12**. The catalytic cycle starts over after the isomerization of alkyne complex **C12** into structure **C1** (Scheme 7).



Scheme 7. The catalytic cycle of the cyclotrimerization reaction of substituted-alkyne HC≡C–COOEt based on the computed path C.

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