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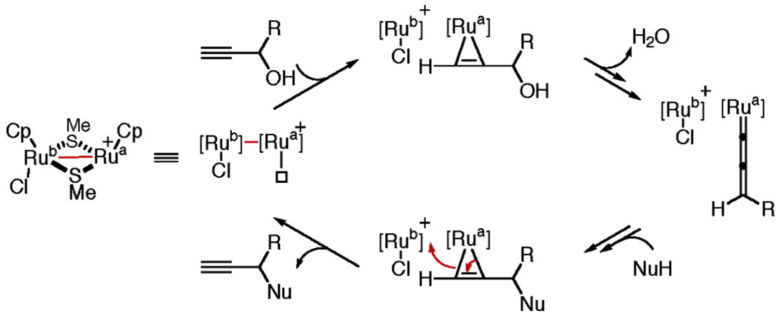

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Synergistic Dimetallic Effects in Propargylic Substitution Reaction Catalyzed by Thiolate-Bridged Diruthenium Complex

Salai Cheettu Ammal,† Naohiko Yoshikai,† Youichi Inada,‡
Yoshiaki Nishibayashi,‡ and Eiichi Nakamura*,†

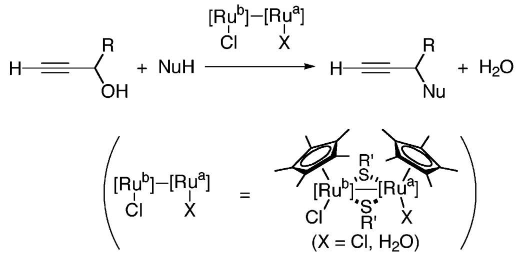
Contribution from the Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan, and Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Received January 17, 2005; E-mail: nakamura@chem.s.u-tokyo.ac.jp

Abstract: The origin of unique catalytic activity of a thiolate-bridged diruthenium complex in nucleophilic substitution reactions of propargylic alcohols, which features a diruthenium−allenylidene complex as a key intermediate, was studied with the aid of density functional calculations (B3LYP). Comparison of mono- and diruthenium systems has shown that the rigid but reasonably flexible Ru−Ru core structure plays a critical role in the catalyst turnover step (i.e., dissociative ligand exchange of the product π-complex with the starting propargyl alcohol that goes through a coordinatively unsaturated Ru complex). In the diruthenium system, the energy loss due to coordinative unsaturation can be compensated by reinforcement of the Ru−Ru bond, while such an effect is unavailable in the monoruthenium counterpart. Weaker back-donation ability of the diruthenium complex is also advantageous for dissociation of the π-complex. Thus, ligand exchange takes place smoothly in the diruthenium system to regenerate the reactive species, while the monoruthenium reaction stops at a dead-end Ru product π-complex. The present studies have also shown the important role of protic molecules (e.g., MeOH) that mediate smooth proton transfer in the propargyl alcohol−allenylidene transformation.

Introduction

Homogeneous catalysis by polynuclear transition metal complexes offers opportunities for chemists to ponder new mechanistic and synthetic possibilities that would be available only through cooperation of multiple transition metal atoms.[1] In addition, it may serve as a bridge between homogeneous and heterogeneous catalysis, the mechanism of the latter not being well understood in most cases.[2] In the multimetallic catalysis, there are a priori a number of modes conceivable for interaction between the catalyst and the substrates. Multiple metals may interact simultaneously with a single substrate or multiple substrates,[3] or a single metal may interact with the substrate(s) while the other metals may remain just as spectators or as indispensable participants in the catalysis. Though numerous reports describe catalysis starting with multimetallic complexes, they seldom guarantee that the multimetallic integrity of the starting complex is maintained throughout the catalytic cycle or that the multimetallic catalyst is superior to the corresponding monometallic catalysts. A series of structurally rigid thiolate-bridged diruthenium complexes, $[Cp^*RuCl(\mu_2\text{-}SR)]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = Me, *n*-Pr, *i*-Pr) and $[Cp^*RuCl(\mu_2\text{-}SMe)_2RuCp^*(OH_2)]OTf$ ($OTf = OSO_2CF_3$), designed by Nishibayashi et al., are notable in this respect.[4] They were designed to act as a multimetallic catalyst, have been shown to maintain the multimetallic structure in catalysis, and carefully compared with the monometallic catalysts. One out of the two ruthenium atoms is considered to offer an active site to effect catalytic substitution reactions of a propargylic alcohol with a variety of heteroatom- and carbon-centered nucleophiles (eq 1), which cannot be catalyzed by common monoruthenium complexes.



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† The University of Tokyo.

‡ Kyoto University.

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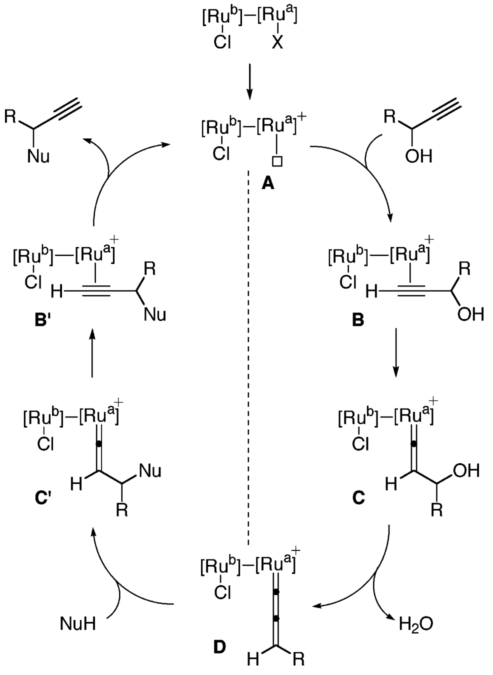
10.1021/ja050298z CCC: $30.25

Scheme 1



A proposed mechanism for the diruthenium-catalyzed transformations of propargylic alcohols is shown in Scheme 1.[4] It must be noted first that the catalytic cycle is essentially symmetric to the broken line in the scheme. The first half concerns the loss of water from the propargylic alcohol to form an allenylidene complex **D**, and the second half the addition of NuH (e.g., MeOH) to regenerate the catalyst. A cationic, coordinatively unsaturated (for Ru^a) diruthenium complex **A** first forms a π-complex **B** with the propargylic alcohol. Then 1,2-migration of the acetylenic proton occurs to generate a γ-hydroxy vinylidene complex **C**. The complex **C** is spontaneously dehydrated to give the allenylidene complex **D** as a key reactive intermediate.[5] In the second half, addition of a nucleophile (alcohol, amine, thiol, etc.) to the allenylidene complex **D** now gives a vinylidene complex **C′**, followed by proton migration affording a product π-complex **B′**. Because the complex **B′** is 18-electron with respect to the Ru^a center, exchange of the product with the substrate (**B′** → **A** → **B**) should take place in a dissociative fashion.[6] Among the proposed species in the catalytic cycle, the allenylidene complex **D** has been identified as an intermediate on the basis of stoichiometric and catalytic reactions. In this proposal, only the Ru^a atom takes part in the reaction,[7] yet the catalysis has thus far never been achieved by any similar monometallic complexes. How then can the second metal Ru^b activate Ru^a, and what is unique in the catalysis by such bimetallic complexes possessing a metal−metal bond in their resting state?

Careful theoretical studies based on our knowledge on the synergy in polymetallic catalysis[7−10] have provided us with a plausible account of the cooperative role of the second metal atom. The key finding is that the metal−metal bond dissociates and re-forms during the catalysis while the whole structure of the catalyst is rigidly maintained by the chalcogen bridges. Having essentially the same electron configuration as the first metal, the second metal acts as a powerful internal ligand that affects much the reactivity of the first metal even with very small change of geometry. The idea of considering the second metal as a key ligand to control the reactivity of the first reactive metal has already proven successful for understanding the catalytic activity of a dirhodium tetracarboxylate complex and is probably an important general principle in the catalysis by multimetallic complexes, clusters, and perhaps solids that possess metal−metal bonds. As demonstrated by the effect of MeOH molecules on the reaction pathways and energetics, participation of hydrogen-bonded protic molecules (used as a solvent or a nucleophile) is essential for the reaction to take a smooth and low-energy pathway in the catalysis.[11,12]

Experimental Background. Cationic metal−allenylidene complexes often serve as an equivalent of a stabilized propargylic cation that is intrinsically unstable.[13] There have been reported a number of reactions, in which a monoruthenium allenylidene complex reacts with a nucleophile that may attack either the C$^\alpha$ or C$^\gamma$ carbon center of the allenylidene ligand to give a new carbene complex or an alkynyl complex, respectively. The regioselectivity of the nucleophilic addition is controlled by the electronic and steric properties of the metallic fragment. Complexes having an electron-rich or a sterically crowded metal center favor the addition to the C$^\gamma$ center.[14]

Despite such intriguing reactivities, it has been difficult to build these elementary reactions into a catalytic cycle. Common monoruthenium complexes such as [CpRuCl(PPh$_3$)$_2$] (Cp = η^5-C$_5$H$_5$), [RuCl$_2$(dppe)$_2$] (dppe = 1,2-bis(diphenylphosphino)ethane), [RuCl$_2$(PPh$_3$)$_3$], and [RuCl$_2$(p-cymene)], which are known to react with propargylic alcohols to produce the corresponding allenylidene complexes,[13] are entirely ineffective for catalytic transformation of these substrates.[15] A few examples of catalytic reactions that go through a metal−allenylidene intermediate have been known to date.[16]

An experimental approach has previously been taken to obtain insight into the role of the two Ru atoms in the catalytic reaction

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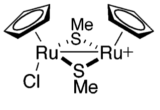
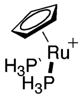
shown in eq 1. A series of calcogenolate (S, Se, and Te)-bridged diruthenium complexes have been synthesized, and their structures, catalytic activities, and electrochemical properties have been studied.[17] These studies suggested the importance of electronic communication between the two metal atoms, which enhances the electrophilicity of the allenylidene ligand (**D** → **C′** in Scheme 1) and/or facilitates the ligand exchange of the product with the substrate (**B′** → **B**). The experimental observations notwithstanding, the origin of the cooperative effect of two Ru atoms has not been established yet at the molecular level.

Models and Methods

Chemical Models. In the present study, we employed [Cp(Cl)Ru(μ_2-SMe)$_2$RuCp]$^+$ (**1a**) as a model of the diruthenium catalyst. While the real catalyst bears a bulky Cp* ligand that is likely to be the origin of γ-selective nucleophilic attack to the corresponding allenylidene complex,[4] it was replaced by a Cp ligand in the interest of computational time (and since we can computationally preclude nucleophilic attack to the α-position). For comparison with the diruthenium catalysis, we also examined the reaction of [CpRu(PH$_3$)$_2$]$^+$ (**1b**), a PPh$_3$ version of which reacts stoichiometrically with propargyl alcohol to give an allenylidene complex.[13]

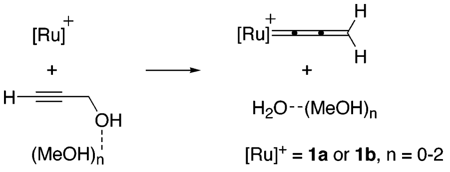


1a



1b

The catalytic cycle being quasi-symmetric (Scheme 1), we mainly focus on the reaction between these model catalysts and propargyl alcohol leading to Ru−allenylidene complexes (eq 2). Since the second half is a “mirror image” of the former, the former reaction must consist of fast equilibrium through smooth and low-energy potential surface. To mimic the reaction conditions for MeOH substition where MeOH is used as a solvent, we employed zero to two MeOH molecules that are hydrogen-bonded to each other as well as to the propargyl alcohol. The results will be described with an increasing number of the MeOH molecules. Throughout this article, the symbol [Ru] will be commonly employed to indicate either the monoruthenium fragment [CpRu(PH$_3$)$_2$] or the diruthenium fragment [[Cp(Cl)Ru(μ_2-SMe)$_2$RuCp]. For discussions on the di-Ru reaction, the symbols [Ru^a] and [Ru^b] will be used to identify the “active site” Ru center and the “spectator” Ru center, respectively.



(2)

Computational Methods. All calculations were performed with the Gaussian 98 and Gaussian 03 packages.[18] The density functional theory (DFT) method was employed using the B3LYP hybrid functional.[19] Geometry optimization was performed with a basis set (denoted as 631LAN) consisting of the LANL2DZ basis set including a double-ζ valence basis set with the Hay and Wadt effective core potential (ECP) for Ru[20] and 6-31G(d) basis set for C, H, O, P, and S.[21] The B3LYP/631LAN-optimized structure of [Cp*RuCl(μ_2-SMe)]$_2$ showed good agreement with the X-ray crystallographic data.[22,23] Each stationary point was adequately characterized by normal coordinate analysis. The intrinsic reaction coordinate (IRC) analysis[24] was carried out to confirm that stationary points are smoothly connected to each other. However, owing to the flatness of the potential energy surface, some of the stationary points could not be fully connected computationally, whereas they are, by all means, chemically connected to each other. Some of the important intermediate structures were also optimized by adding diffuse functions (6-31+G(d) instead of 6-31G(d)) or by changing the hybrid functional (BPW91 instead of B3LYP).[25] These calculations gave similar structures and energetic trend as the B3LYP/631LAN results (see Supporting Information). Thus, the B3LYP/631LAN results including natural population analysis/natural bond orbital (NBO) analysis will be presented throughout this article.[26] The energetics of the reaction pathways will be discussed on the basis of Gibbs free energy calculated at 298 K,[27] while electronic energy data are given in the Supporting Information and discussed when necessary.[28]

Results and Discussion

Reaction Pathways of Ru−Allenylidene Complex Formation. (a) Without MeOH Molecules. We first examined the reaction pathway for the Ru−allenylidene complex formation without any additional MeOH molecules (Scheme 2 and Figure 1). First, complexation of coordinatively unsaturated complex **1** with the C−C triple bond of propargyl alcohol gives a π-complex **2** with energy changes of +2.2 and −14.6 kcal/mol for the di- and mono-Ru systems, respectively. Relocation of the metal atom in **2b** takes place via TS **3b** ($\Delta G^{\ddagger} = +10.7$ kcal/mol) to afford an unstable C−H σ-complex **4b** (less stable than **2b** by +10.1 kcal/mol). For the di-Ru complex **2a**, corresponding TS and σ-complex could not be located. As has been well-documented for transition metal-mediated vinylidene formation,[29,30] subsequent 1,2-migration of the acetylenic proton (TS **5**) gives a vinylidene complex **6**. Net activation barriers for this process are +12.3 (from **1a**) and +16.3 kcal/mol (from **2b**) for the di-Ru and mono-Ru systems, respectively. The γ-hydroxy vinylidene complex **6** needs to undergo high activation energy dehydration via a four-centered TS **7** ($\Delta G^{\ddagger} = +39.8$ and +43.5 kcal/mol for di- and mono-Ru) to give an allenylidene

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(27) Gibbs free energy here stands for $E_{\mathrm{elec}} + \mathrm{ZPE} + E_{\mathrm{vib}} + E_{\mathrm{rot}} + E_{\mathrm{trans}} + RT - TS$ (E_{elec}: electronic energy, ZPE: zero-point energy, E_{vib}: vibrational energy, E_{rot}: rotational energy, E_{trans}: translational energy, S: sum of vibrational, rotational and translational entropy). The temperature (T) of 298 K was employed for the calculation.

(28) A complete set of data including electronic energies and various corrections to them is given in Supporting Information.

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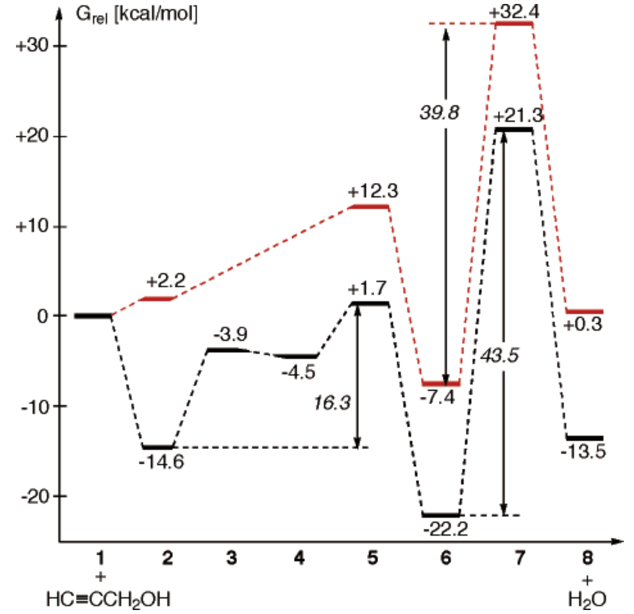
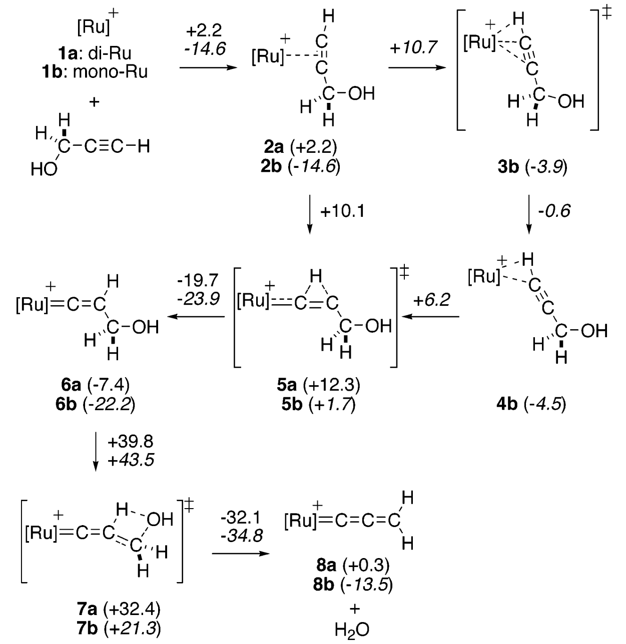


Figure 1. Free energy diagram (kcal/mol) for the reaction of **1** with propargyl alcohol. Di-Ru (red) and mono-Ru reactions (black) are color-coded throughout this article.

complex **8**. While the reaction proceeds with moderate activation energies from **1** to the vinylidene complex **6**, the dehydration process requires unreasonably high activation energies. Thus, we expected that there should be solvent assistance in this step as discussed in the following sections.

The 3-D structures of the stationary points in the di-Ru and mono-Ru reactions are shown in Figures 2 and 3, respectively. The Ru^a−Ru^b distance is elongated significantly upon π-complexation (2.684 → 2.855 Å). While the distance changes less significantly (i.e., ranges from 2.814 to 2.855 Å, as the structure of the complex is rigidly held by the sulfur bridge) in the following process, it becomes longer when the Ru^a center donates an electron to the substrate as in the π-complex and vinylidene/allenylidene complexes (this occurs irrespective of the absence or presence of solvent molecules). The structures around the reactive site are not significantly different between the di- and mono-Ru systems.

Scheme 2. Reaction Pathway for Mono- and Di-Ruthenium Allenylidene Complex Formation from **1** and Propargyl Alcohol[a]



[a] [Ru]$^+$ refers to **1a** ([Cp(Cl)Ru(μ_2-SMe)$_2$RuCp]$^+$) or **1b** ([CpRu(PH$_3$)$_2$]$^+$). Free energies (kcal/mol) are relative to [**1** + HCCCH$_2$OH] (diruthenium in roman and monoruthenium in italic). Energy changes are shown above arrows.

From an energetic point of view, it must be pointed out that the energies of the π-complex (**2a**), vinylidene complex (**6a**), and allenylidene complex (**8a**) relative to that of **1a** are much higher than those of the corresponding mono-Ru complexes (**2b**, **6b**, and **8b**) relative to that of **1b** (Figure 1). To obtain an insight into the origin of the difference, complexes **2** and **8** were separated into two fragments and their deformation energies and interaction energies were calculated according to Schemes 3 and 4.

The weaker complexation energies (ΔE) in the di-Ru system were found to originate from the larger deformation energy of the [Ru] fragment (DEF$_{Ru}$) and from the smaller interaction energy between the [Ru] fragment and the acetylene or

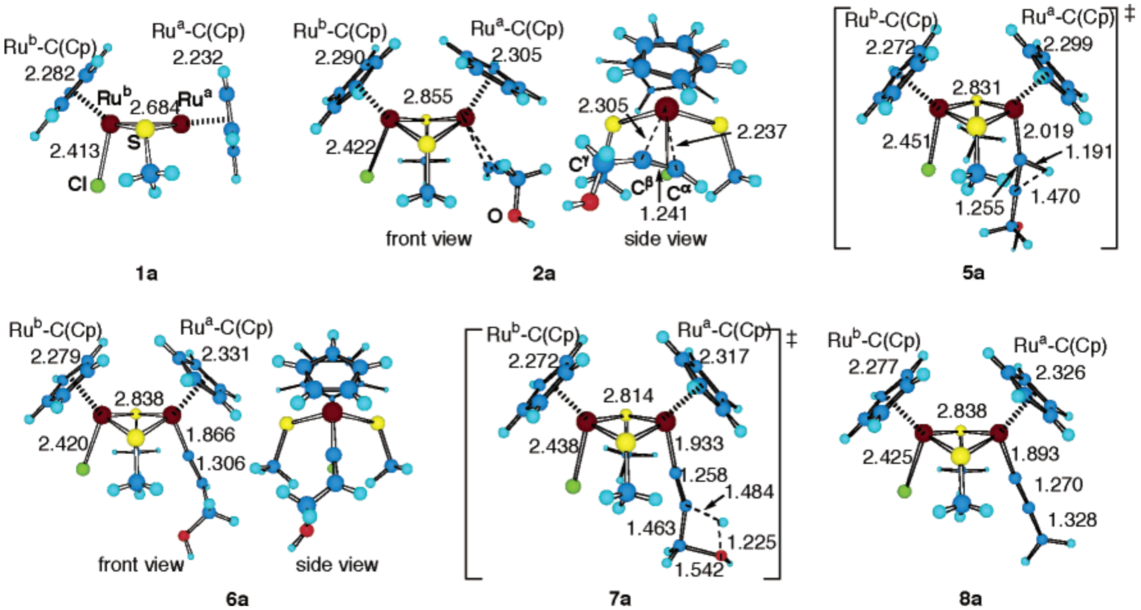


Figure 2. Structures of stationary points in the reaction of **1a** with propargyl alcohol. Numbers refer to distances (Å).

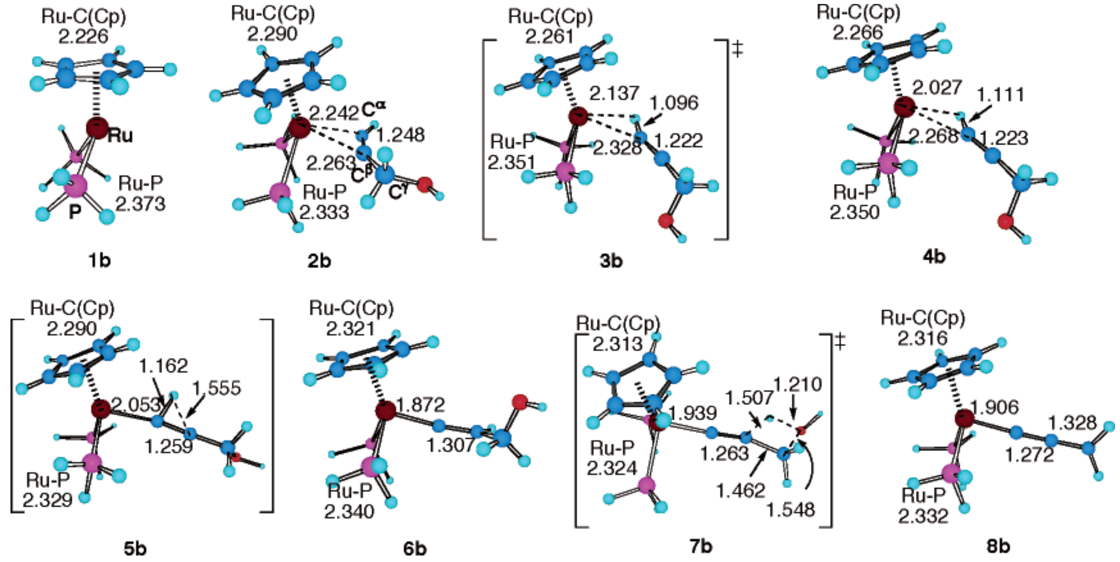
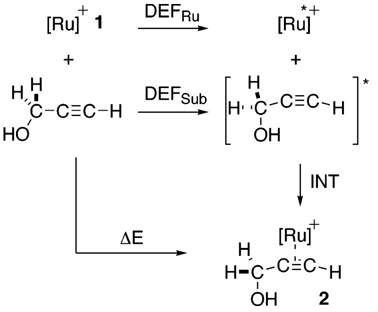


Figure 3. Structures of stationary points in the reaction of **1b** with propargyl alcohol. Numbers refer to distances (Å).

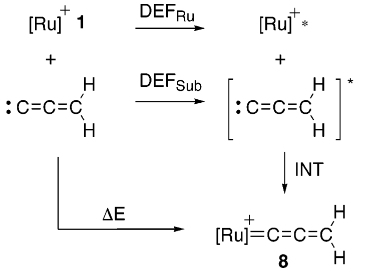
Scheme 3. Fragment Analysis of Ru/Propargyl Alcohol π-Complex **2**[a]



	a	b
DEF_{Ru}	+16.8	+4.9
DEF_{Sub}	+9.3	+12.8
INT	-39.4	-46.1
ΔE	-13.3	-28.4

[a] Formulas with asterisks refer to the parts taken from complex **2**. Numbers (kcal/mol) are based on the electronic energies.

Scheme 4. Fragment Analysis of Ru−Allenylidene Complex **8**[a]



	a	b
DEF_{Ru}	+14.8	+6.4
DEF_{Sub}	+0.4	+0.3
INT	-83.5	-88.1
ΔE	-68.3	-81.4

[a] Formulas with asterisks refer to the parts taken from complex **8**. Numbers (kcal/mol) are based on electronic energies.

allenylidene ligands (INT). The former feature is due to the much stronger Ru^a−Ru^b bonding in **1a** than that in **2a** and **8a** (Figure 2), which stabilizes the coordinatively unsaturated Ru^a center.

The second feature originates from the difference of the back-donation ability of the [Ru] fragments between the di- and mono-Ru systems. For the π-complexes **2a** and **2b**, the C^{α}−C^{β} bond length (**2a**: 1.241 Å, **2b**: 1.248 Å) and the C^{β}−C^{α}−H (**2a**: 155.8°, **2b**: 154.7°) and C^{α}−C^{β}−C^{γ} (**2a**: 161.3°, **2b**: 154.6°) bond angles indicate weaker back-donation in the di-Ru system (Figures 2 and 3). Natural charge of the propargyl alcohol (**2a**: +0.15, **2b**: +0.07) also supports this conjecture. For the vinylidene and allenylidene complexes (**6**, **8**), weaker back-donation in the di-Ru system is indicated by natural charges at the C^{α} atom (**6a**: +0.24, **6b**: +0.18; **8a**: +0.11, **8b**: +0.05) and (in the case of allenylidene complex) the $C^{\gamma}H_2$ moiety (**7a**: +0.27, **7b**: +0.25). (Note, however, that the geometry of the Ru−C^{α}−C^{β}−C^{γ} moiety is similar for the di-Ru and mono-Ru systems.) As discussed later, the stability of a coordinatively unsaturated species **1a** and the weaker back-donation in the di-Ru system are critical factors in the dimetallic catalysis.

(b) Solvation with One MeOH Molecule. Next, the chemical model including one MeOH molecule was studied. A propargyl alcohol, hydrogen-bonded with one MeOH molecule, was allowed to react with the di- and mono-Ru complexes (Scheme 5 and Figure 4). In this case, π-complexation (**1** → **9**), π-bond to σ-bond slippage (**9** → **11**), and 1,2-proton migration (**11** → **13**) proceeded in essentially the same way as the MeOH-free model (Scheme 2). However, the presence of a MeOH molecule opened up a low-energy six-centered path for dehydration of the vinylidene complex **13** (instead of the four-centered path without methanol). The activity of protons at the β-position of vinylidene complexes being well-documented,[29] **13** is easily deprotonated by MeOH via TS **14** (activation free energies are 14.0 and 17.5 kcal/mol for the di-Ru and mono-Ru complexes, respectively). The resulting Ru−alkynyl complex **15**, with a very small barrier, loses its propargylic hydroxy group as protonated by $MeOH_2^+$ to afford the allenylidene complex **17** (or **8**).

The structures of stationary points from **1** to **13** are very similar to their counterparts in the solvent-free reaction pathway (Figures 2 and 3) and hence not shown here, but the TSs and intermediates after **13** are shown in Figures 5 and 6. Upon deprotonation of the β-position of the Ru−vinylidene complex (**13** → **14** → **15**), the Ru−C^{α} bond becomes longer (di-Ru: 1.869 → 1.976 → 1.998 Å, mono-Ru: 1.878 → 1.992 → 2.015 Å), which indicates decrease of back-donation in this process.[31] To the contrary, during γ-dehyroxylation of the resulting Ru-alkynyl complex (**15** → **16** → **17**), it becomes shorter again (di-Ru: 1.998 → 1.953 → 1.914 Å, mono-Ru: 2.015 → 1.975 → 1.917 Å), reflecting the increase of back-donation.

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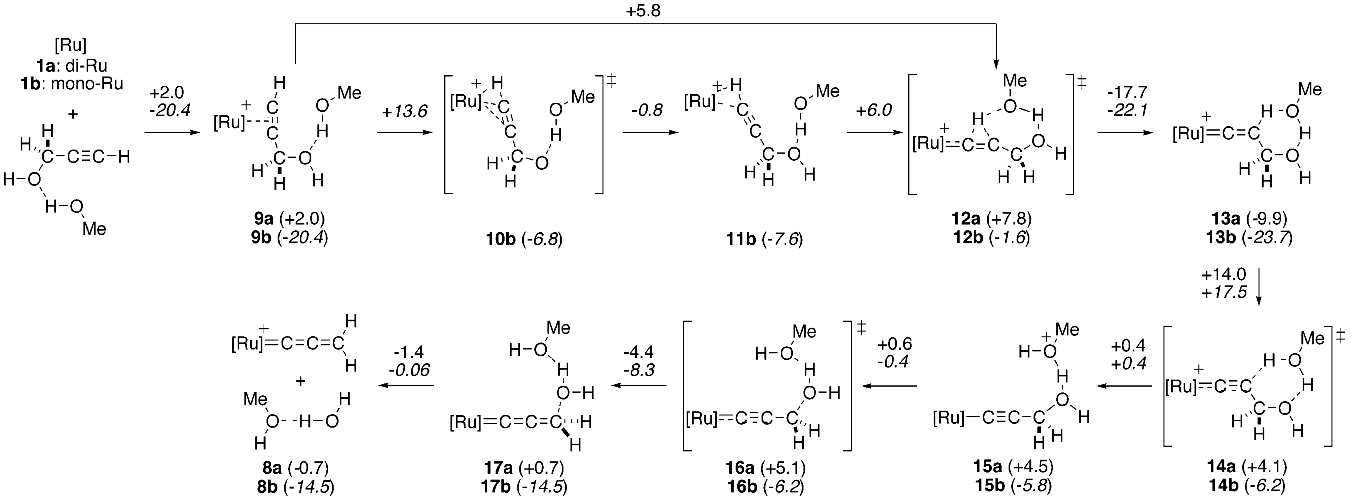
(31) For back-donation in metal−acetylide complexes, see: (a) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276−3285. (b) McGrady, J. E.; Lovell, T.; Stranger, R.; Humphrey, M. G. *Organometallics* **1997**, *16*, 4004−4011. (c) Bruce, M. I.; Low, P. J.; Costuas, K.; Halet, J. F.; Best, S. P.; Heath, G. A. *J. Am. Chem. Soc.* **2000**,

Scheme 5. Reaction Pathway for Di- and Mono-Ruthenium Allenylidene Complex Formation from **1** and Propargyl Alcohol in the Presence of One MeOH Molecule[a]



[a] Free energies (kcal/mol) are relative to [**1** + HCCCH$_2$OH−MeOH] (diruthenium in roman and monoruthenium in italic). Energy changes are shown above arrows.

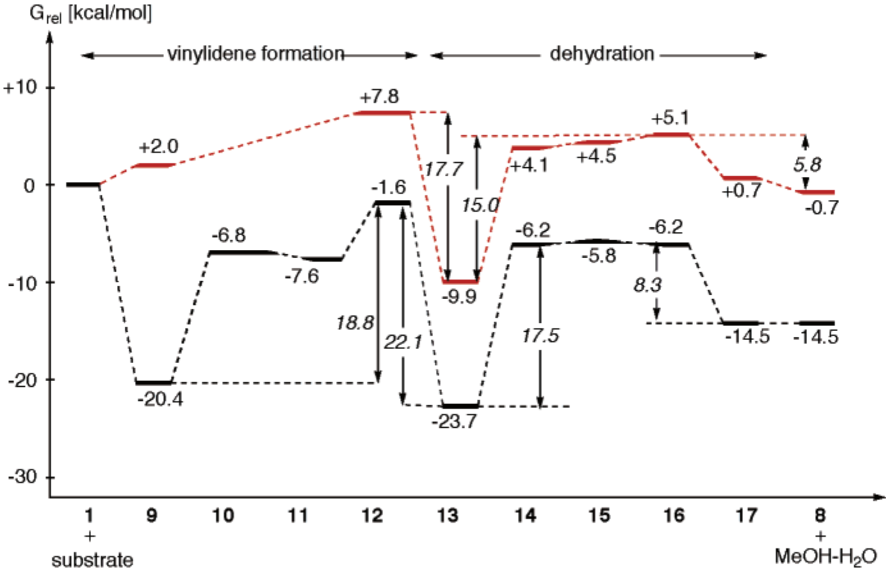


Figure 4. Free energy profile (kcal/mol) for the reaction of **1** with propargyl alcohol in the presence of one MeOH molecule. Di-Ru (red) and mono-Ru reactions (black) are color-coded.

In Figure 4, one can see that the activation free energies for vinylidene formation (di-Ru: +7.8 kcal/mol (**1a** → **12a**); mono-Ru: +18.8 kcal/mol (**9b** → **12b**)) and subsequent dehydration (di-Ru: +15.0 kcal/mol (**13a** → **16a**); mono-Ru: +17.5 kcal/mol (**13b** → **15b**)) are lower in the di-Ru system than in the mono-Ru system. This is also the case for their reverse reactions, that is, water addition to the allenylidene complex (di-Ru: +5.8 kcal/mol (**8a** → **16a**); mono-Ru: +8.3 kcal/mol (**8b** → **16b**)) and hydrogen migration of the vinylidene complex (di-Ru: +17.7 kcal/mol (**13a** → **12a**); mono-Ru: +22.1 kcal/mol (**13b** → **12b**)).

We consider that the lower activation barriers in the di-Ru reaction are due to the lower back-donation ability of the di-Ru fragment (vide supra). All of the aforementioned processes involve loss (or weakening) of back-donation on the way from the reactant to the transition state. For example, in the vinylidene formation step (**9** → **13**), the TS **12** does not involve back-donation either to the C$^{\alpha}$−C$^{\beta}$ π^* orbital (as in **9**) or to the C$^{\alpha}$ vacant 2p orbital (as in **13**). In addition, in the vinylidene−allenylidene transformation (**13** → **8**), the C$^{\alpha}$ atom of the intermediary Ru−alkynyl moiety in **14**−**16** does not accept considerable back-donation from the Ru center, judging from much longer Ru−C$^{\alpha}$ bond lengths in **14**−**16** than in **8** and **13** (and natural population analysis; see below). Thus, only less activation energy is required to disturb the back-donation in the di-Ru system, where the back-donation ability of the reactive site is lower.

Analysis of natural charges along the reaction pathways also supports the above discussion (Figure 7). In the mono-Ru reaction (Figure 7b), the charges of the Ru atom, the Cp, and PH$_3$ ligands (shown by blue, pink, and green lines, respectively) change in a parallel way except for the first π-complexation (this is also the case for the di-Ru reaction). Thus, the total charge of the CpRu(PH$_3$)$_2$ fragment (denoted as [Ru]) serves

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122, 1949−1962. (d) Low, P. J.; Rousseau, R.; Lam, P.; Udachin, K. A.; Enright, G. D.; Tse, J. S.; Wayner, D. D. M.; Carty, A. J. *Organometallics* **1998**, *18*, 3885−3897. (e) Koentjoro, O. F.; Rousseau, R.; Low, P. J. *Organometallics* **2001**, *20*, 4502−4509.

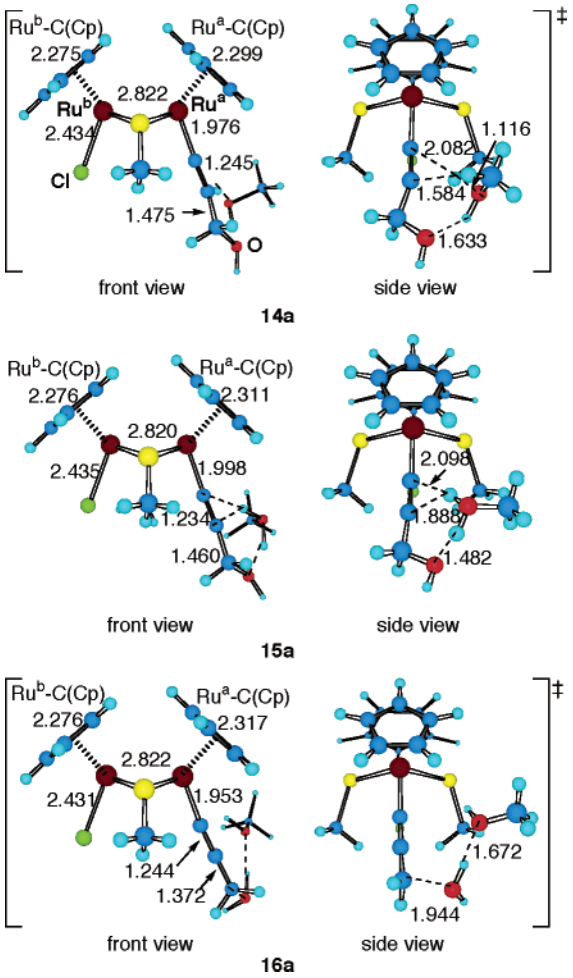


Figure 5. Structures of stationary points in the dehydration of di-Ru vinylidene complex **13a**. Numbers refer to distances (Å).

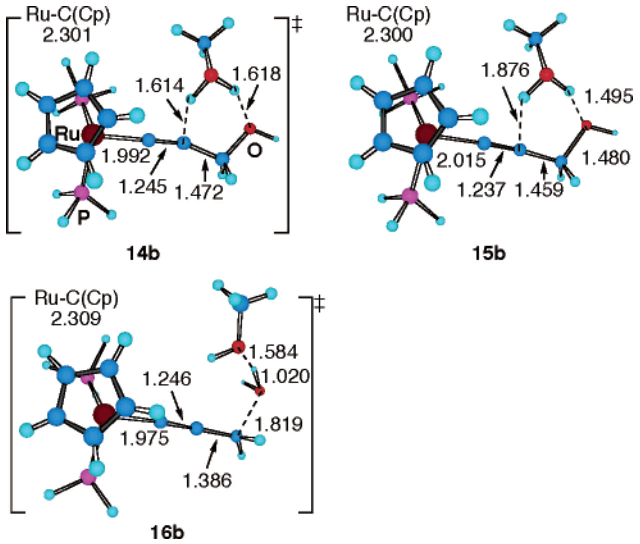


Figure 6. Structures of stationary points in the dehydration of mono-Ru vinylidene complex **13b**. Numbers refer to distances (Å).

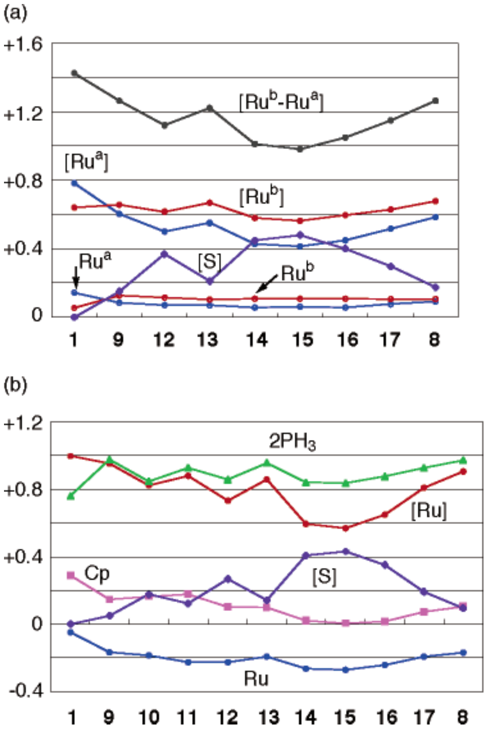
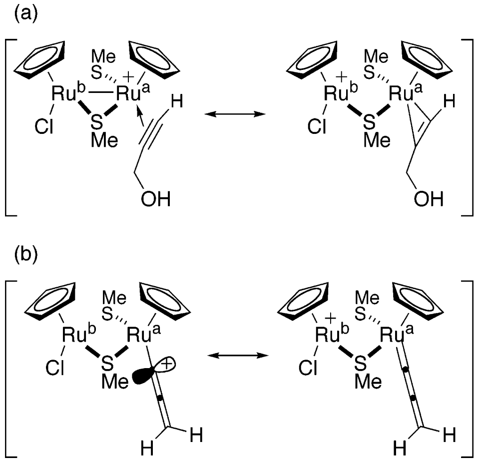


Figure 7. Changes of natural charges through the reaction of **1** with propargyl alcohol in the presence of one MeOH molecule. (a) Di-Ru system. Ru^i, [Ru^i], and [S] refer to the Ru^i atom, the CpRu^i(SMe) fragment (SMe means half of the sum of two SMe charges), and [propargyl alcohol + MeOH], respectively. [Ru^b−Ru^a] refers to {[Ru^a] + [Ru^b]}. (b) Mono-Ru system. Ru, [Ru], and [S] refer to the Ru atom itself, the CpRu(PH$_3$)$_2$ fragment, and [propargyl alcohol + MeOH], respectively.

Chart 1



as a good indicator of the Ru oxidation state. The positive charge of [Ru] is large at the π-complex **9**, vinylidene complex **13**, and allenylidene complex **8** and becomes smaller between them, reflecting the extent of back-donation.

Figure 7a shows how the natural charges of two Ru atoms change in a complementary way. The interaction of two Ru centers is demonstrated clearly by the parallel change of the charges of the [Ru^a] and [Ru^b] fragments (note that [Ru^i] refers to CpRu^i(SMe)). Interestingly, the [Ru^a] fragment is less positive than the [Ru^b] fragment throughout the reaction pathway (except for the initial complex **1a**), while the valence formalism in Scheme 1 indicates a positive charge at the [Ru^a] moiety. This suggests that the Ru−Ru moiety can be formally represented by two resonance structures, as shown in Chart 1.

To obtain further information on the bonding changes along the reaction pathways, we carried out the Wyberg bond index (WBI) analysis (Figure 8).[32] One can see that the bond indices

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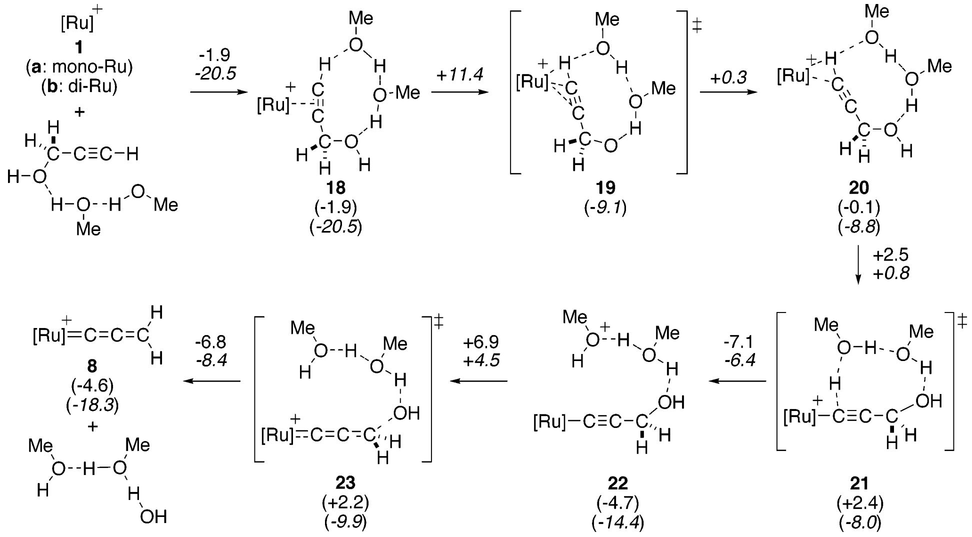
(32) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083−1096.

Scheme 6. Reaction Pathway for Allenylidene Complex Formation from **1** and Propargyl Alcohol in the Presence of Two MeOH Molecules[a]



[a] Free energies (kcal/mol) are relative to [**1** + $HCCCH_2OH-(MeOH)_2$] (diruthenium in roman and monoruthenium in italic). Energy changes are shown above arrows.

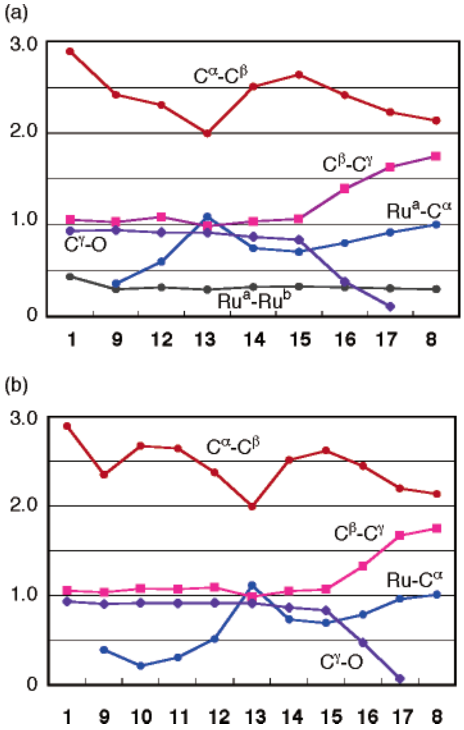


Figure 8. Changes of the Wiberg bond indices through the reaction of **1** with propargyl alcohol in the presence of one MeOH molecule. (a) Di-Ru system. (b) Mono-Ru system.

for the $C^{\alpha}-C^{\beta}$, $C^{\beta}-C^{\gamma}$, and $C^{\gamma}-O$ bonds are parallel with the mechanism illustrated in Scheme 5 for both the di- and mono-Ru systems. For example, the $C^{\alpha}-C^{\beta}$ triple bond (WBI: 2.89) of the propargyl alcohol weakens (WBI: 2.42 (di-Ru), 2.35 (mono-Ru)) upon π-complexation (**9**) and becomes a normal double bond (WBI: 2.00) in the vinylidene complex (**13**). It once again becomes stronger (WBI: 2.64 (di-Ru), 2.62 (mono-Ru)) in the Ru−alkynyl complex (**15**), and finally becomes a normal double bond (WBI: 2.14) again along with formation of the allenylidene complex (**8**).

The WBIs for the $Ru-C^{\alpha}$ and Ru−Ru bonds are also in line with the present mechanistic scheme. The former index becomes larger when the Ru and C^{α} atoms form a formal double bond in the vinylidene and allenylidene complexes (**13** and **15**). While the change of the latter index is very subtle (0.29−0.32, except for **1** (0.434)), it becomes smaller in the π-complex, vinylidene complex, and allenylidene complexes. This indicates that the Ru^a-Ru^b bond becomes weaker when there is back-donation from the Ru^a atom, which rationalizes the schematic representations in Chart 1.

(c) Solvation with Two MeOH Molecules. In the previous model, one MeOH molecule plays two roles in the dehydration steps (Scheme 5). It deprotonates the β-position of the vinylidene complex **13** as a base, and the resulting conjugate acid promotes subsequent dehydroxylation of the alkynyl complex **15**. In the actual experiment performed in MeOH, however, it looks more likely that more than one MeOH molecule is involved in these two different reactions. Therefore, we included two MeOH molecules in the next stage.

The two-MeOH reaction pathway and energetics are shown in Scheme 6 and Figure 9, respectively. First, the Ru complex **1** forms a π-complex (**18**) with an alcohol trimer [propargyl alcohol−2MeOH]. Through an unstable σ-complex **20**, deprotonation of the acetylenic hydrogen takes place via TS **21** to give a Ru−alkynyl complex **22** *in a single step* without forming a vinylidene intermediate (cf. Scheme 5). As shown in Figure 10, while one of the two MeOH molecules deprotonates the acetylenic C−H bond through TS **21** of linear C−H−O geometry, the other MeOH concurrently forms stronger hydrogen bonding with the propargylic hydroxy group (changes of the distance between the propargylic oxygen and the MeOH proton are: 1.976 → 1.842 Å (di-Ru), 1.908 → 1.835 Å (mono-Ru)).

The activation barrier for the deprotonation step is much lower in the di-Ru system (4.3 kcal/mol) than that in the mono-Ru system (12.5 kcal/mol). We ascribe this again to the weaker back-donation in the di-Ru system (vide infra). Note that these activation barriers are much lower than those in the 1,2-proton migration mode in the one-MeOH models (Figure 4). The resulting Ru−alkynyl complex **22** undergoes dehydroxylation ($\Delta G^{\ddagger} = 6.9$ kcal/mol for di-Ru, 4.5 kcal/mol for mono-Ru) to

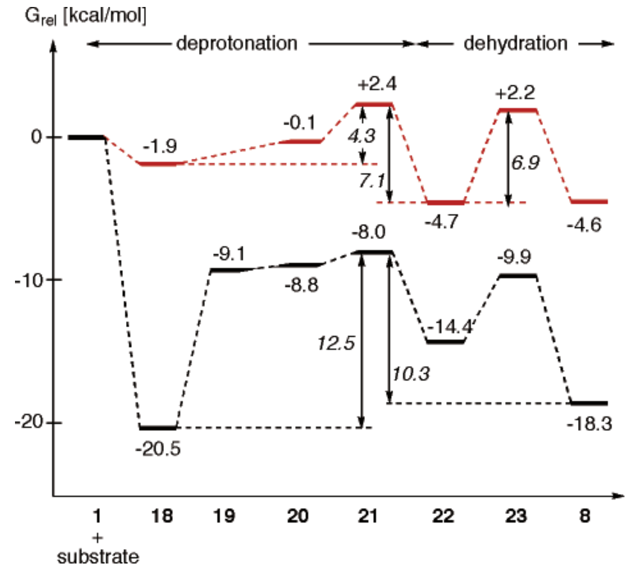


Figure 9. Free energy profile (kcal/mol) for the allenylidene complex formation from **1** and propargyl alcohol in the presence of two MeOH molecules. Di-Ru (red) and mono-Ru reactions (black) are color-coded.

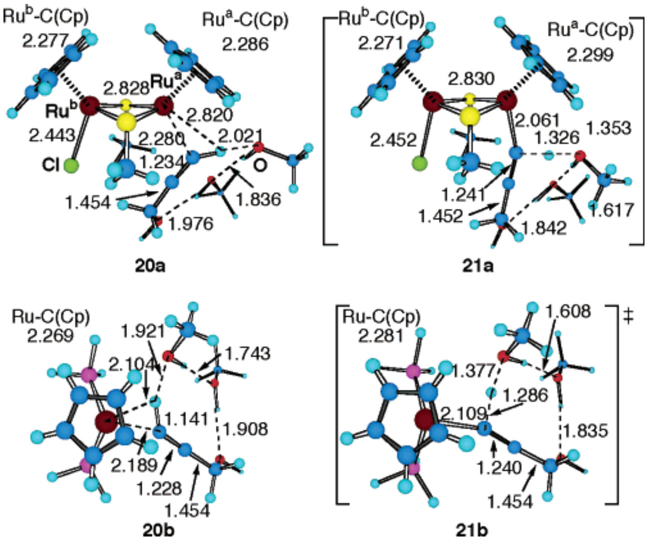
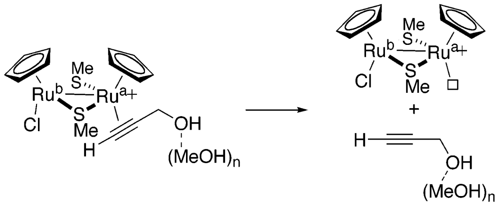


Figure 10. Structures of σ-complex **20** and deprotonation TS **21**. Numbers refer to distances (Å).

give the final product. Being similar to the one-MeOH models, the free energy diagram shows that both forward and reverse reactions of the di-Ru complex are more favorable than those of the mono-Ru complex (Figure 9).

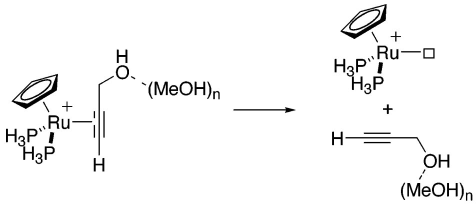
Catalyst Turnover Step. In addition to the energetic argument of the one-way process, one must also consider the catalyst turnover step (i.e., dissociative exchange of the product with the substrate; see Scheme 1) to assess the feasibility of the *catalytic* process. The free energy changes for the dissociation of the di-Ru π-complexes **2a**, **9a**, and **18a** are very small (eq 3), which indicates that product−substrate exchange (and vice versa) can readily take place in the di-Ru system. Considering this and the flat energy diagram (Figure 9), it looks like all intermediates in the di-Ru reaction may equilibrate with each other. However, the catalytic cycle should work because the thermodynamics of the net reaction (propargyl alcohol + methanol → methyl propargyl ether + water) favors the product side.



(3)

ΔG = -2.2 (n = 0)
-2.0 (n = 1)
+1.9 (n = 2)

On the other hand, in the case of the mono-Ru complexes **2b**, **9b**, and **18b**, dissociation of the propargyl alcohol requires free energy barriers as much as 15−20 kcal/mol (eq 4), which indicates that smooth exchange of the product with the substrate (and vice versa) on the mono-Ru center is difficult. Such a situation does not satisfy a prerequisite for a catalytic reaction, that is, no intermediate or TS should be too stable or too unstable compared with others. Thus, the mono-Ru complex has difficulty in working as a catalyst.[33]

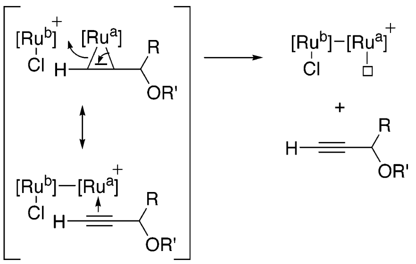


(4)

ΔG = +14.6 (n = 0)
+20.4 (n = 1)
+20.5 (n = 2)

The easier catalyst turnover in the di-Ru system originates from its weaker back-donation ability as well as the stability of the coordinatively unsaturated species **1a**, which benefit from much stronger Ru−Ru bond (2.684 Å) than other intermediates (>2.8 Å) (vide supra). In light of the resonance description of the Ru−Ru bond in Chart 1, this concept can be illustrated as in Scheme 7. Thus, in the ligand dissociation step, the Ru^b center accepts electrons from the Ru^a center, which have been offered for the back-donation in the π-complex.

Scheme 7. Schematic Representation of Dissociation of C−C Triple Bond from Diruthenium Complex



Comparison of the present reaction with the previously studied dirhodium-catalyzed C−H insertion between a diazo compound and an alkane in terms of the bimetallic effects is intriguing.[9] The roles of the spectator metal centers in these catalytic reactions are opposite. In the Ru catalysis, the spectator

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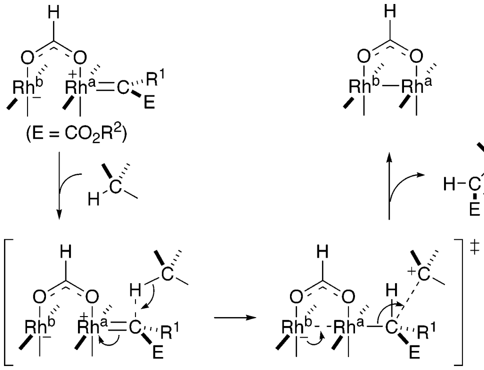
(33) For an example of a metal-catalyzed reaction where product/substrate exchange is the turnover-limiting step, see: Brunkan, N. M.; White, P. S.; Gagné, M. R. *Organometallics* **2002**, *21*, 1565−1575.

Scheme 8. C−H Insertion of Alkane with Dirhodium Carbene Complex



Ru^b atom acts as an electron *acceptor* for the Ru^a atom in the critical ligand exchange step. On the other hand, in the Rh catalysis, the Rh^b atom acts as an electron *donor* to the Rh^a atom, which facilitates the Rh^a−carbene σ-bond cleavage in the C−H insertion step (Scheme 8).

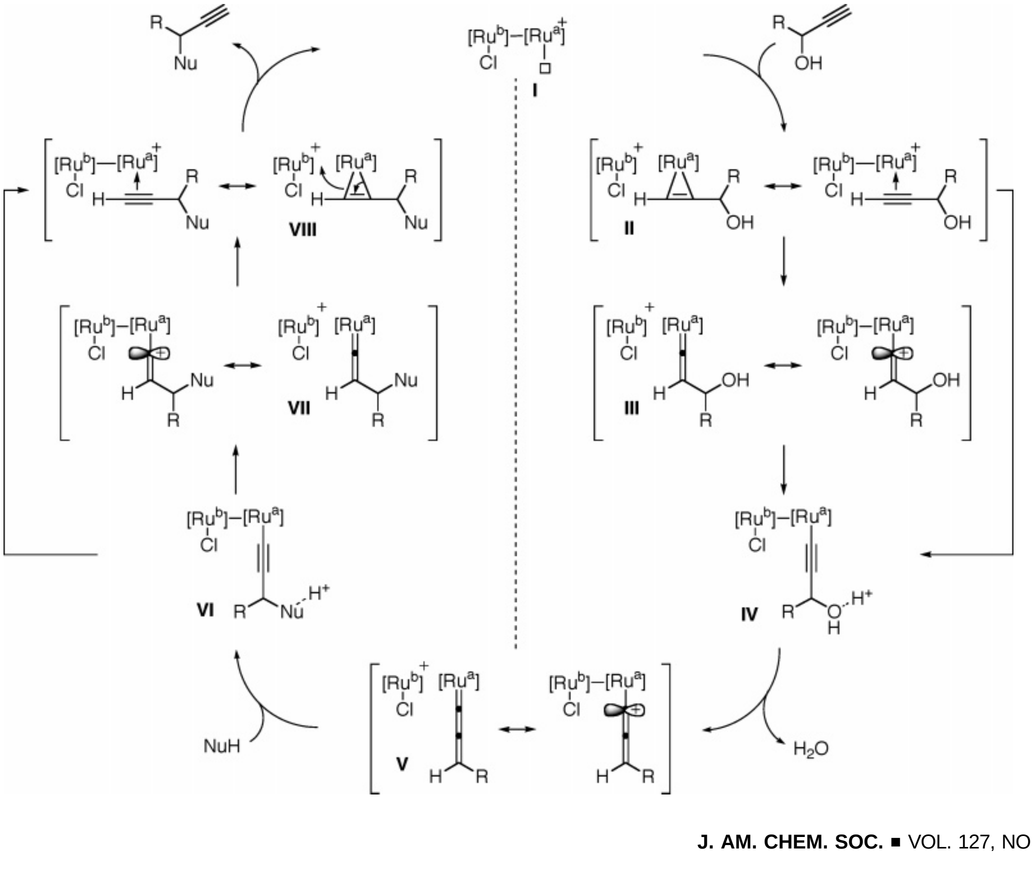
Conclusions

The present theoretical study has revealed the pathway of the nucleophilic substitution of a propargyl alcohol catalyzed by a thiolate-bridged diruthenium complex that features a cationic Ru−allenylidene complex as a key intermediate (Scheme 9). It was found that a solvent molecule(s) plays important roles as a base and an acid to facilitate proton transfer during the transformation of the substrate on the metal center. A generally proposed mechanism for metal−allenylidene complex formation from a propargyl alcohol involves a metal−γ-hydroxyvinylidene complex, which forms via well-established 1,2-proton migration of the acetylenic moiety (**II** → **III** → **IV** → **V**). On the other hand, the new mechanism goes through direct deprotonation of the acetylenic proton (**II** → **IV** → **V**). We consider that the latter mechanism is very feasible in protic media, while the mechanism for the reaction with aprotic carbon nucleophiles is debatable.[4c,e]

A concrete answer to the essential question on the uniqueness of the diruthenium system is now given. There are two critical factors: First, the high stability of the coordinatively unsaturated Ru complex **I** enables smooth catalyst turnover (i.e., dissociative exchange of the product (in **VIII**) with the substrate that regenerates **II**). Upon product dissociation from **VIII** to **I**, the energy loss due to the coordinative unsaturation can be compensated by the stronger Ru−Ru interaction, while such an effect is unavailable in the mono-Ru system. Second, the weaker back-donation ability of the di-Ru system that is inherent to the Ru^{III} (Ru^{II} in the mono-Ru system) center facilitates transformations of the substrate into the product (**II** → **VIII**). Because each of these processes involves a decrease of back-donation from the reactant to the transition state, the di-Ru system that has less back-donation ability than the mono-Ru system goes through lower activation barriers.

The dimetallic effects in the diruthenium catalysis and in the previously studied dirhodium catalysis point to the importance of the "spectator" metal center as an electron reservoir for the "reactive site" metal center. Essential for the achievement of such effects are stable but reasonably flexible metal−metal core structures, which are supported by the thiolate and carboxylate ligands in the diruthenium and dirhodium systems, respectively. These findings suggest that the design of the metal−metal bond(s) as to the distance and flexibility is essential in multimetallic

Scheme 9. Bimetallic Mechanism of Propargylic Substitution Reaction that Is Near Symmetric to the Broken Line in the Center



catalysis as has been known widely that the design of the metal–ligand bonding is essential in monometallic catalysis.

Acknowledgment. The present research was supported by a Grant-in-Aid for Scientific Research (Specially Promoted Research) and The 21st Century COE Programs in Fundamental Chemistry. Generous allotment of computational time from Research Center for Computational Science, Okazaki National Institutes, and Intelligent Modeling Laboratory, The University of Tokyo, is gratefully acknowledged. N.Y. thanks JSPS for a predoctoral fellowship.

Supporting Information Available: Energies and Cartesian coordinates of stationary points and full citations of the Gaussian packages. This material is available free of charge via the Internet at http://pubs.acs.org.

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