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Reactions of Ruthenabenzene with Propynols Involving Hydrogen-Bonding-Induced [2 + 2] Cycloaddition

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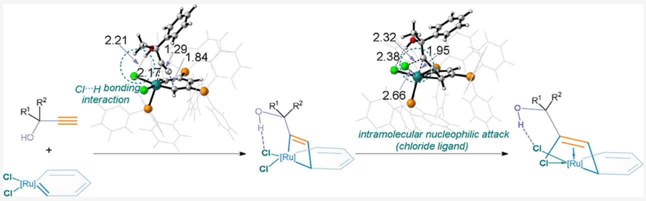
ABSTRACT: Enyne metathesis reactions involving metallacyclobutene intermediates have been comprehensively studied and utilized in numerous synthetic processes and catalytic transformations. We describe here our initial results toward the utilization of metalla-aromatic in classical [2 + 2] cycloaddition that η^3-allyl structures are formed stoichiometrically through hydrogen-bonding-induced [2 + 2] cycloaddition between several propynol and a ruthenabenzene complex. The effect of the intramolecular hydrogen bonding interaction was analyzed by experimental and computational studies.

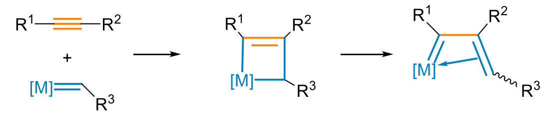


INTRODUCTION

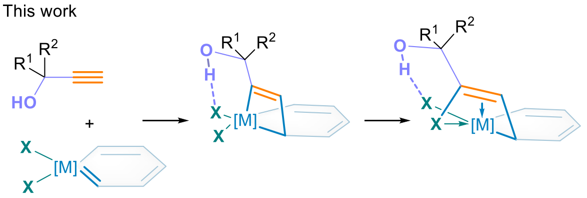
Transition metal carbene complexes are excellent catalysts or important reaction intermediates for a diverse range of synthetic transformations, including X−H (X = C, Si, O, S, N, etc.) insertion reactions, cycloaddition reactions, cyclopropanations, ylide formation followed by rearrangement, 1,2-migrations, etc.[1−14] Due to their diverse and controllable reactivity, they can be used to initiate cascade sequences, leading to the generation of complex structural motifs of enduring interest. One of the most well-studied chemistries of metal-carbene complexes is metathesis reactions.[15−24] The synthetically very important transformations usually react through elementary [2 + 2] cycloaddition steps that involve metallacyclobutene intermediates (Scheme 1a). The stability of metallacyclobutene is sensitively dependent on the electronic and steric properties of the ligands on the metal center and substituents of alkynes and thus greatly influence the following transformation processes.

Scheme 1. Reactions of Metal Carbene Complexes with Alkynes

a) [2+2] cycloaddition and ring opening reaction



b) This work



Up to date, a number of metal carbene complexes with aromaticity, known as metalla-aromatics,[25−30] have been demonstrated to undergo stoichiometric[31−36] or catalytic metathesis reactions.[37,38] We have been studying metalla-aromatics with group VIII transition metals, which display characteristic reactivities of aromatics and transition metal carbenes.[29,39−42] We now examine their ability to stabilize the intermediates in chemical bond activation processes, which can be potentially useful for our understanding of the effects of supporting ligands in transition-metal reactivity and catalysis. Herein, we report the [2 + 2] reactivity of ruthenabenzene with propynols (Scheme 1b), in which the hydrogen-bond-acceptor properties of the [Ru−Cl] unit and the polycyclic structural rigidity account for the conversions of metallacyclobutenes, thereby facilitating the following nucleophilic addition reactions of the resulting metallacyclobutenes to give η^3-allyl structures.

RESULTS AND DISCUSSION

As summarized in Scheme 2, we started our investigation by examining the substituted propynols (see the SI for its synthesis). Reaction of ruthenabenzene **1**[43] with excess 2-methyl-3-butyn-2-ol in dichloromethane at room temperature provided **2** in 85% yield. Either increasing the reaction temperature or reducing the loading of propynols led to decreased yields, which may be due to the decomposition of the starting material **1**. Three additional analogues **3**−**5** were

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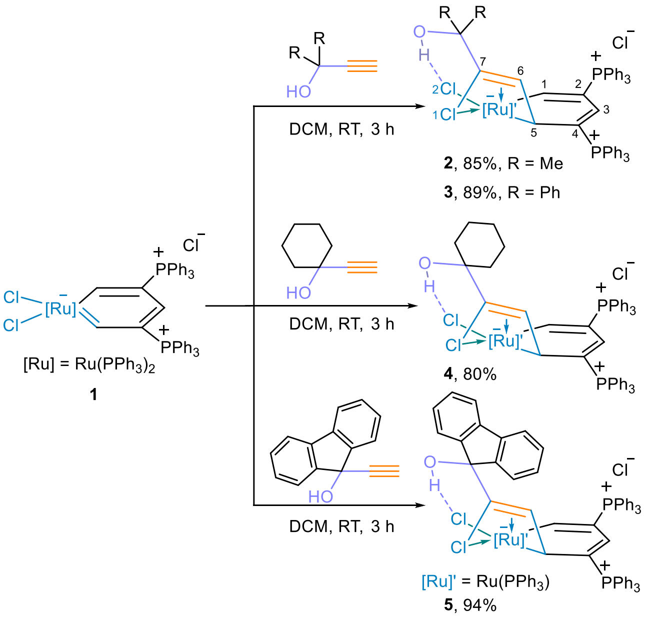
Scheme 2. Reactions of 1 with $HC{\equiv}CC(OH)R_2$



synthesized under identical reaction conditions in high yields. All new compounds prepared in this study were characterized by a combination of NMR spectroscopy (Figures S1−S21 of the Supporting Information), elemental analysis, and high-resolution mass spectrometry.

The broken aromaticity of the metallacycles is evidenced in the ^{1}H NMR and ^{13}C NMR spectra that the peaks shift to high field (take **2** for example, ^{1}H: 13.8 ppm; ^{13}C: 238.9 ppm) attributable to H1 and C1, relative to those observed for the ruthenabenzene **1**[43] (^{1}H: 17.5 ppm, H1; ^{13}C: 284.3 ppm, C1). The H5 (3.8 ppm) chemical shift lies within the typical range of Ru-C$_{sp3}$H species and is also high-frequency-shifted compared to that of **1** (8.2 ppm, H5). The OH proton resonate is observed at low field (δ = 5.2 ppm). The product **4** was characterized by single-crystal X-ray diffraction, and their molecular structures are shown in Figure 1 with refinement data summarized in Figure S22 of the Supporting Information. Single-crystal X-ray analyses reveal that a six-coordinated metal center bearing the C6=C7 fragment in a distorted-octahedral geometry, which retains the six-membered metallacycle. The bond distance of C6−C7 (1.395(3) Å) lies within the range observed in those reported coordinated allyl complexes.[44,45] Interestingly, the structure in the solid state revealed a clear intramolecular association between the hydroxyl and the [Ru−Cl] unit, where the O−H group is engaged in a hydrogen-bonding interaction with the chloride ligand (O1−H···Cl2 bond distance is 2.344 Å). The O1−H−Cl2 angle (163.5°) falls into the typical range for hydrogen bonding with a metal halide unit.[46−48] The Ru−Cl1 bond in **4** (2.7129(5) Å) is obviously longer than that in the precursor ruthenabenzene **1**[43] (2.5196(13) Å), while the bond distance of Ru−Cl2 (2.4530(4) Å) is comparable to that of **1**. This suggests that the chloride ligand Cl1 changes from X-type ligands to L-type ligands. The new C7−Cl1 bond formation, meanwhile, can be inferred from by the bond distance of 1.7956(19) Å.

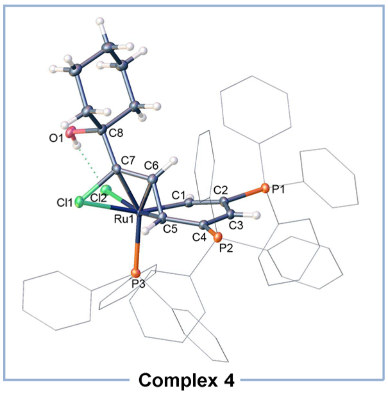
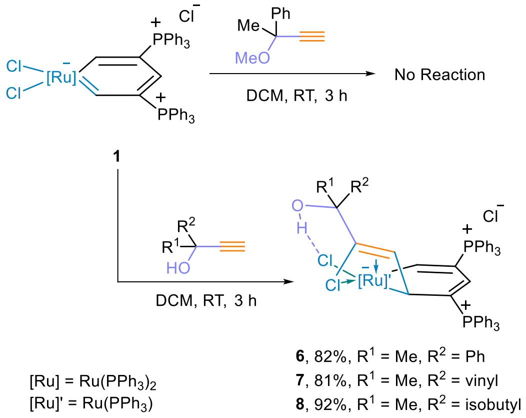


Figure 1. X-ray molecular structure for the cation of complex **4** drawn with 50% probability level. The hydrogen atoms on the phenyl group are omitted for clarity. Selected bond lengths [Å]. Ru1−C5 2.1879(18), Ru1−C6 2.1395(18), Ru1−C7 2.1376(19), Ru−Cl1 2.7129(5), Ru−Cl2 2.4530(4), C5−C6 1.444(3), C6−C7 1.395(3), and C7−Cl1 1.7956(19).

We propose that the reaction is facilitated by the hydrogen bonding between the hydroxyl proton of the incoming propynol substrate and a chloride ligand of the metal center. When ruthenabenzene **1** is treated with alkyne of a non-hydroxyl group (Scheme 3), no reaction was detected after 3 h at room temperature (Figure S25 of the Supporting Information). The reactivity of **1** toward the propynol substrates with two different groups are also investigated. As shown in Scheme 3, the propynol substrates with phenyl, vinyl, and even the sterically demanding isobutyl are feasible in the reactions. Following X-ray crystallography studies, the product **6** was established (Figure S23 of the Supporting Information). As shown in Figure 2, an intramolecular hydrogen bonding interaction was observed between the chlorine of the metal center and the hydroxyl in **6** (O1−H···Cl2 bond distance is 2.319 Å), similar to the reaction with the propynol substrates containing identical geminal substituents. As suggested by in situ NMR, secondary and primary alcohols can also react with **1** to form the similar products (Figure S27 of the Supporting Information). However, it is difficult to separate them since the products of related reactions are very labile in solution. We speculate that the instability of the products might be attributed to the decreasing protecting effect by the reducing number of bulky substituents.

Scheme 3. Reactions of 1 with $HC{\equiv}CC(OMe)(R^1R^2)$ or $HC{\equiv}CC(OH)(R^1R^2)$



Based on our observations, a plausible mechanism has been proposed (Figure 3a). Initially, the substrate coordination to the ruthenium center could afford intermediate **A**. Sub-

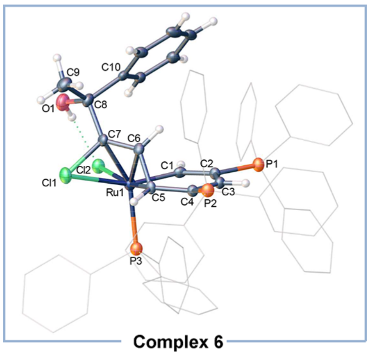


Figure 2. X-ray molecular structure for the cation of complex **6** drawn with 50% probability level. The hydrogen atoms on the phenyl group of PPh_3 are omitted for clarity. Selected bond lengths [Å]. Ru1−C5 2.170(3), Ru1−C6 2.126(3), Ru1−C7 2.138(4), Ru−Cl1 2.6789(9), Ru−Cl2 2.4832(9), C5−C6 1.437(5), C6−C7 1.407(5), C7−Cl1 1.814(4).

sequently, the classical [2 + 2] cycloaddition may occur, producing metallacyclobutene intermediate **B**. Finally, intramolecular nucleophilic attack of metallacyclobutene unit by the chloride ligand affords the η^3-allyl unit. The transformation of intermediate **B** to product **6** can be regarded as a formal reductive elimination process, resulting in a decreased oxidation state of the metal center. To shed light on the reaction mechanism, DFT calculations were performed at the B3LYP-D3[49−51]/def2-TZVP[52]/PCM(DCM)// B3LYP/6-31G(d) (SDD for Ru)[53] level of theory. Geometry optimization is in satisfactory agreement with the reported crystallographic data of **1**[43] and **6** (see Figures S31 for further details). As shown in Figure 3b, the substrate coordination to form intermediate **A** is endergonic by 2.1 kcal/mol with concomitant release of PPh_3. The ruthenacyclobutene intermediate **B** is formed via transition state **TS1** with an activation free energy of 15.6 kcal/mol. Alternatively, in the model reaction without the effect of hydrogen-bonding (Figure 3c, purple line), the calculated activation free energy for the [2 + 2] cycloaddition step via transition state **TS3** is 22.5 kcal/mol, which is 6.9 kcal/mol higher than that via **TS1**. Furthermore, both of the non-hydrogen-bonding intermediates **C** and **E** are relatively more unstable than **A** (the energy differences are 11.7 and 8.3 kcal/mol). In addition, the [2 + 2] cycloaddition barrier of the methoxyl substituted alkyne was found to be 21.2 kcal/mol (Figure 3c, green line), affording a more unstable intermediate **F**, which is in good agreement with the experiment result shown in Scheme 3. Therefore, the intramolecular hydrogen bonds can significantly increase the stability of the transition state structures and the intermediates, which may affect the reactivity of the metal carbene complexes. Further experiments show that the additional chloride cannot accelerate the rate of reaction, and the reaction of non-hydroxyl-substituted alkyne is not run in the presence of added ethanol. When the reaction temperature raised to 45 °C, only a trace of the product was obtained (see Figures S28−S30 for further details).

The calculated activation free energy for the final intramolecular nucleophilic attack is 19.0 kcal/mol, which indicates that the conversion of ruthenacyclobutene **B** to **6** can be achieved under the reaction conditions. We hypothesized that the formation of congested metallacyclobutene intermediates

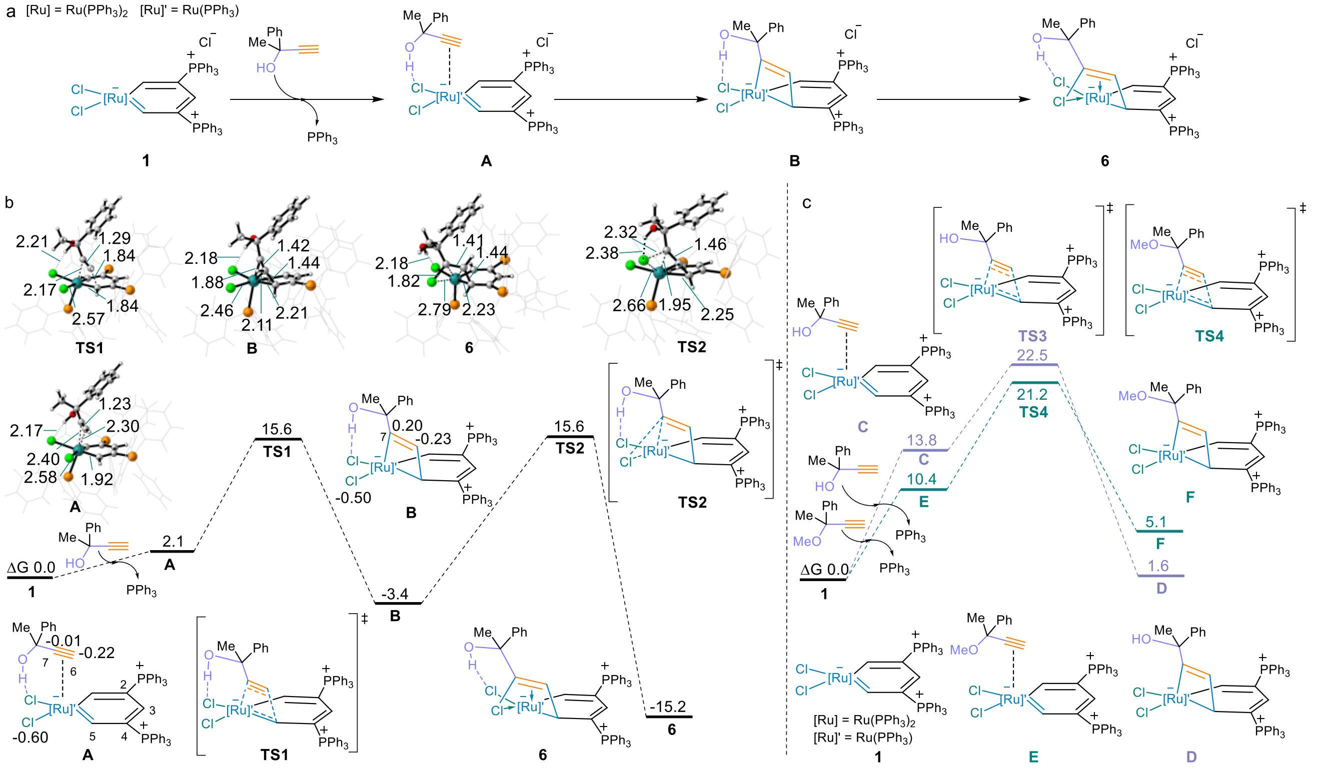


Figure 3. (a) Proposed mechanisms for the formation of **6**. DFT-computed Gibbs free energy profile for TSs and products. (b) Reaction between **1** and 2-phenyl-3-butyn-2-ol (with chlorine-hydrogen), including the charge values. (c) Reaction between **1** and 2-phenyl-3-butyn-2-ol (without chlorine-hydrogen) and reaction between **1** and (2-methoxybut-3-yn-2-yl)benzene. All energies were computed at the level B3LYP-D3/def2-TZVP/PCM(DCM)//B3LYP/6-31G(d)(SDD for Ru) and are given in kcal/mol.

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may facilitate the subsequent intramolecular nucleophilic attack step. Additionally, the intramolecular hydrogen bonding may also contribute to the conversion. As expected, natural bond orbital (NBO) analysis suggests the increased electrophilic reactivity of internal carbon atom C7, which has more positive natural population analysis (NPA) charges (**A**: −0.01; **B**: 0.20). This is in line with the experimental observation that the η^3-allyl structures were obtained instead of metallacyclobutene structures. Metallacyclobutenes, η^3-vinylcarbene complexes, η^1-vinylcarbene complexes, and η^3-allyl complexes have been extensively speculated as key intermediates in the literature (Figure 4).[54,55] We now demonstrate that hydrogen bonding, together with the polycyclic structural rigidity, can be utilized to manipulate the equilibration in the reaction of ruthenabenzene and alkynes. This reactivity pattern may be especially promising for the development of new strategies in metallaaromatic-catalyzed metathesis.

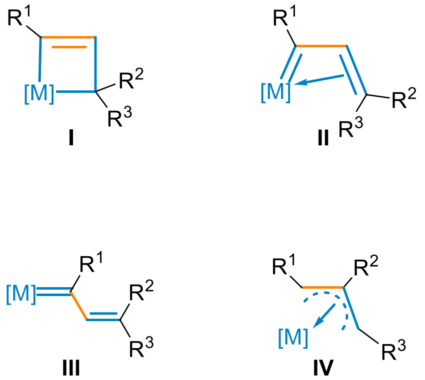

Figure 4. Key intermediates proposed for the metathesis reactions: metallacyclobutenes (**I**), η^3-vinylcarbene (**II**), η^1-vinylcarbene (**III**), and η^3-allyl (**IV**) complexes.

CONCLUSIONS

We have demonstrated that ruthenabenzene, with chlorine and sterically hindered phosphine ligands, can act as metal carbene to react with propynols. The NMR spectroscopic analysis and single crystal X-ray diffraction crystallography support the existence of an intramolecular hydrogen bonding interaction between the hydroxyl and the chlorine ligand. DFT calculations have demonstrated that this interaction stabilizes the corresponding transition-state structures and metallacyclobutene intermediates and also increases the electrophilic reactivity of internal carbon atom of initial propynols to yield product containing a η^3-allyl moiety. Considering the widely utilized metallacyclobutenes in organic synthesis, it could be useful for developing novel catalytic transformation based on their reactivities. Extending the metallaaromatic family to develop new metal carbene catalysts is ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.3c00179.

Crystallographic data for complexes **4** and **6** and copies of ^1H, ^{31}P, and ^{13}C NMR spectra of all new products (PDF)

Cartesian coordinates of the structures (XYZ)

Accession Codes

CCDC 2242731−2242732 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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