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# Rhodium-Catalyzed [6 + 2] Cycloaddition of Internal Alkynes with Cycloheptatriene: Catalytic Study and DFT Calculations of the Reaction Mechanism

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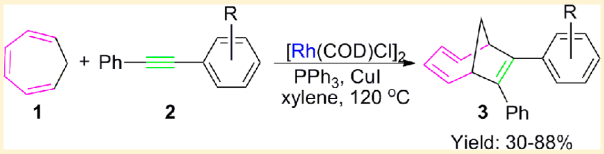
*Supporting Information*

**ABSTRACT:** A rhodium-catalyzed [6 + 2] cycloaddition of internal alkynes with cycloheptatriene is described. A series of substituted alkynes were cycloadded to cycloheptatriene through a [6 + 2] addition to give a variety of substituted bicyclic compounds in excellent yields. The optimal catalytic system for these transformations was a $[Rh(COD)Cl]_2$ (5.0 mol %) catalyst in combination with CuI (10 mol %) and $PPh_3$ (10 mol %). The proposed mechanism for this system includes an initial oxidative coupling reaction between the coordinated cycloheptatriene and the internal alkyne, followed by a [1,3]-shift of the Rh metal center and a reductive elimination from the Rh(III)−allyl complex to give the final product. Calculations using a model Rh(I) catalyst were also carried out to further understand this mechanism.



## ■ INTRODUCTION

In recent years transition-metal catalysts have been widely used in organic synthesis for the efficient preparation of organic compounds.[1] Transition-metal-mediated or -catalyzed higher-order cycloaddition reactions are powerful methods for the construction of a variety of medium-sized ring systems.[2] The [6 + 2] cycloaddition of cyclooctatetraene (COTT) in a tricarbonyl($\eta^4$-COTT)iron(0) complex to internal alkynes to give metal-free adducts under thermal conditions was first reported by Kruerke.[3] Later, Davis et al. demonstrated that the [6 + 2] cycloaddition of 1,3,5-cycloheptatriene (CHT) in a tricarbonyl($\eta^4$-CHT)iron(0) complex to internal alkynes afforded bicyclo[4.2.1]nonatriene adducts under photoinduced reaction conditions.[4] Related chromium(0)-mediated [6 + 2] cycloadditions of tricarbonyl ($\eta^6$-COTT or $\eta^6$-CHT)-chromium(0) to alkynes have also been observed by Fischler et al.,[5] Rigby and co-workers,[6] and Sheridan and co-workers.[7] Tetracyclic adducts were observed when terminal alkynes were replaced with internal alkynes in the chromium-promoted cycloaddition through a stepwise [6 + 2] cycloaddition−homo [6 + 2] cycloaddition sequence.[8]

A variety of stoichiometric [6 + 2] cycloadditions of conjugated cyclic trienes with alkenes, dienes, and alkynes have been intensively investigated, and it has been found that [6 + 2] cycloadditions can be extended to other metal complexes, such as iron,[9] chromium,[10] cobalt,[11] molybdenum,[12] ruthenium,[13] and titanium complexes.[14] A catalytic [6 + 2] cycloaddition reaction using a Ziegler ($TiCl_4/Et_2AlCl$) catalyst was first reported by Mach.[15] A major side reaction, the cyclotrimerization of alkynes, was found to compete with the [6 + 2] cycloaddition reaction in this system.

Rigby and co-workers found that carbonylchromium(0) complexes bearing labile ligands show good catalytic activity for [6 + 2] cycloaddition reactions.[10a−d] Recently, Buono and co-workers demonstrated a cobalt(I)-catalyzed [6 + 2] cycloaddition in which CHT was cyclized with terminal alkynes.[16] Later, this cobalt(I)-catalyzed methodology was extended to [6 + 2] cycloadditions of COTT to internal and terminal alkynes[17] and to [6 + 2] cycloadditions of CHT to substituted allenes.[18] Other groups have also achieved similar accomplishments for [6 + 2] cycloadditions catalyzed by cobalt(I) complexes.[19] These successes have paved the way for using the [6 + 2] cycloaddition as a key reaction for the construction of ring compounds in organic synthesis. In fact, [6 + 2] cycloaddition reactions have also been applied to the synthesis of natural products.[20]

Meanwhile, rhodium complexes have played an increasingly important synthetic role in carbon−carbon bond formation.[21] Rhodium-catalyzed cyclization/cycloaddition reactions, in particular, have proven to be useful for constructing polycyclic carbo- and heterocycles.[22] In recent years many research groups have achieved impressive breakthroughs in this area.[23] Although rhodium complexes exhibit high efficiency in these reported cyclization reactions, there have been only a few reports on the application of rhodium complexes to [6 + 2] cycloadditions.

For example, rhodium(I)-catalyzed [6 + 2] cycloadditions of 2-vinylcyclobutanones and alkenes have been used for the synthesis of eight-membered rings,[24] a $[RhCl(dppp)_2]$-catalyzed intramolecular [6 + 2] cycloisomerization reaction between alkynes and allenylcyclobutane functionalities has been reported for the efficient formation of bicyclo[6.4.0]-dodecatriene frameworks under mild conditions,[25] Rh(I)-catalyzed [6 + 2] cycloadditions of 4-allenals with tethered alkynes have also been reported,[26] and the intermolecular [6 + 2] cycloaddition of 4-allenals with alkynes catalyzed by

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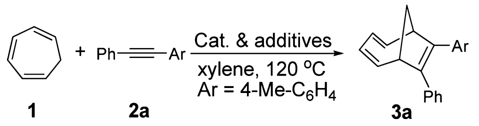
**Table 1. Optimization of Reaction Conditions for the [6 +2] Cycloaddition of CHT (1) to (4-Methylphenyl)phenylacetylene (2a)**



| entry | catalyst | ligand | additive | yield (%)$^a$ |
|---|---|---|---|---|
| 1 | $(PPh_3)_3RhCl$ | | | $0^b$ |
| 2 | $(PPh_3)_3RhCl$ | | | 64 |
| 3 | $(PPh_3)_3RhCl$ | | | $53^c$ |
| 4 | $(PPh_3)_3RhCl$ | | CuI | 75 |
| 5 | $(PPh_3)_3RhCl$ | $PPh_3$ | CuI | 60 |
| 6 | $[Rh(COD)Cl]_2$ | | | 71 |
| 7 | $[Rh(COD)Cl]_2$ | | CuI | 62 |
| 8 | $[Rh(COD)Cl]_2$ | $PPh_3$ | | 80 |
| 9 | $[Rh(COD)Cl]_2$ | $PPh_3$ (5 mol %) | | 69 |
| 10 | $[Rh(COD)Cl]_2$ | $PPh_3$ (2 mol %) | | 64 |
| 11 | $[Rh(COD)Cl]_2$ | $PPh_3$ | CuI | 88 |
| 12 | $[Rh(COD)Cl]_2$ | $PPh_3$ | KI | $63^d$ |
| 13 | $[Rh(COD)Cl]_2$ | $PPh_3$ | n-$Bu_4$NI | $59^d$ |
| 14 | $[Rh(COD)Cl]_2$ | $PPh_3$ | CuCl | 40 |
| 15 | $[Rh(COD)Cl]_2$ | $PPh_3$ | CuBr | 32 |
| 16 | $[Rh(COD)Cl]_2$ | $PPh_3$ | $Cu(OAc)_2$ | 35 |
| 17 | $[Rh(COD)Cl]_2$ | $PPh_3$ | $CuCl_2$ | <5 |
| 18 | | | CuI | 0 |
| 19 | $Pd(OAc)_2$ | $PPh_3$ | CuI | 0 |
| 20 | $(PPh_3)_3RuCl_2$ | $PPh_3$ | CuI | 0 |
| 21 | $Ru(COD)_2Cl_2$ | $PPh_3$ | CuI | 0 |
| 22 | $[RuCl_2(p\text{-cymene})]_2$ | $PPh_3$ | CuI | 0 |

[a] Reaction conditions: **1** (0.10 mmol), **2a** (0.05 mmol), catalyst (5.0 mol % based on **2a**), ligand (10 mol % based on **2a**), additive (10 mol % based on **2a**), xylene (0.5 mL), 120 °C. The isolated yield is based on **2a**. [b] 60 °C. [c] 140 °C. [d] Some unidentified side products were also observed.

rhodium(I) was found to be a good method for the construction of monocyclic eight-membered rings.[27] However, to the best of our knowledge, the direct [6 + 2] cycloaddition of an alkyne to cycloheptatriene catalyzed by a rhodium catalyst has never been reported.

Not only would the development of a rhodium-catalyzed [6 + 2] cycloaddition system expand the cycloaddition methodology but it would also further our understanding of the catalytic behavior of rhodium. With this in mind, rhodium-catalyzed [6 + 2] cycloaddition reactions were explored using cycloheptatriene and different internal alkynes as starting materials. The rhodium-catalyzed [6 + 2] cycloaddition proceeded smoothly to give the corresponding ring products when $[Rh(COD)Cl]_2$ was used in combination with $PPh_3$ and CuI as the catalyst. These results are reported herein.

## ■ RESULTS AND DISCUSSION

In order to explore the possibility of a rhodium-catalyzed [6 + 2] cycloaddition reaction to form an eight-membered ring, CHT (**1**) and (4-methylphenyl)phenylacetylene (**2a**) were initially used as the cycloaddition reaction partners to optimize the reaction conditions. The results are summarized in Table 1. Using $(PPh_3)_3RhCl$ as the catalyst at 60 °C did not result in a reaction between **1** and **2a**, and no [6 + 2] cycloaddition product **3a** was detected (Table 1, entry 1). However, when the reaction temperature was increased to 120 °C, the $(PPh_3)_3RhCl$ exhibited better catalytic activity and gave **3a** in 64% yield (Table 1, entry 2). Further elevating the reaction temperature to 140 °C resulted in a mixture of the desired product and unknown side products, with the isolated yield of **3a** dropping to 53% (Table 1, entry 3).

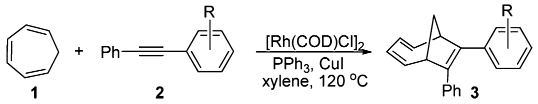
Next, different additives were tested to improve the activity. The addition of CuI (10 mol %), which is a phosphine cleavage reagent,[28] increased the reaction yield to 75% (Table 1, entry 4). However, using both CuI (10 mol %) and $PPh_3$ (10 mol %) with $(PPh_3)_3RhCl$ gave an inferior result with only a 60% yield (Table 1, entry 5).

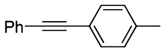
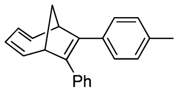
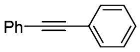
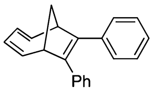
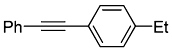
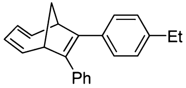
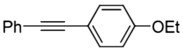
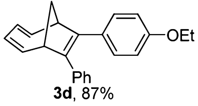
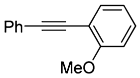
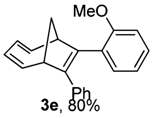
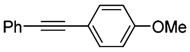
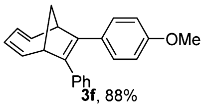
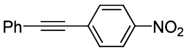
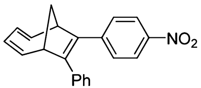
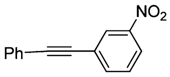
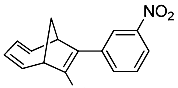
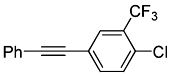
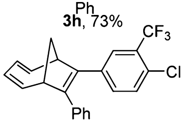
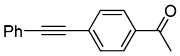
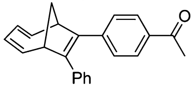
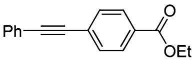
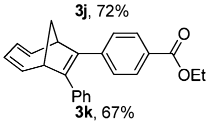
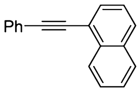
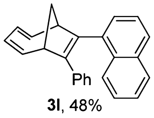
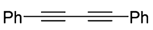
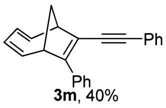
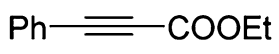
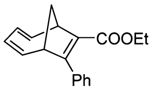
When the catalyst was switched to $[Rh(COD)Cl]_2$, **3a** was obtained in 71% yield (Table 1, entry 6), which is better than that obtained with $(PPh_3)_3RhCl$ (64%). When only CuI (10 mol %) was used as the additive, the yield of **3a** decreased to 62% (Table 1, entry 7). However, the addition of $PPh_3$ (10 mol %) to the $[Rh(COD)Cl]_2$ catalytic system led to a yield of 80% (Table 1, entry 8), which is very different from that for the $(PPh_3)_3RhCl$ system. Reducing the amount of $PPh_3$ additive to 5%, or 2%, gave yields of the desired products of 69% and 64%, respectively (Table 1, entries 9 and 10). To our delight, when $[Rh(COD)Cl]_2$ was used in combination with CuI (10 mol %) and $PPh_3$ (10 mol %), the reaction gave **3a** in 88% yield (Table 1, entry 11). However, when KI or n-$Bu_4$NI was used as the additive instead of CuI, the product yields dropped to 63% and 59%, respectively (Table 1, entries 12 and 13). Some unidentified side products were also observed in the reaction systems, indicating that CuI may play an important role in controlling side reactions by activating the rhodium catalyst.

Other phosphine cleavage reagents, such as CuCl and CuBr, were then tested as additives in combination with $[Rh(COD)Cl]_2$ and $PPh_3$ (10 mol %). In these reactions, **3a** was produced in low yields (Table 1, entries 14 and 15). When $Cu(OAc)_2$ (10 mol %) was used in place of CuI as the additive, the cycloaddition reaction was again suppressed and a yield of only 35% could be isolated after the reaction (Table 1, entry 16). When $CuCl_2$ (10 mol %) was added to the reaction system, the cycloaddition reaction was inhibited, with less than 5% product being obtained (Table 1, entry 17). These results indicate that the effect of the additive depends on the valence state of the copper ion and on the counterion. It should also be noted that the cycloaddition reaction of **1** and **2a** did not take place when CuI was used alone (Table 1, entry 18). The above experimental results indicate that CuI, a known reagent for scavenging and reclaiming phosphines, plays a unique role in accelerating the cycloaddition reaction and controlling the side reactions. However, the specific role of CuI in this reaction is still undetermined, since a reduced amount of $PPh_3$ gave a lower yield and other copper compounds produced different results. Therefore, further investigations are needed to determine exactly how CuI affects the reaction.

Other metal compounds, such as $Pd(OAc)_2$, $(PPh_3)_3RuCl_2$, $Ru(COD)_2Cl_2$, and $[RuCl_2(p\text{-cymene})]_2$, did not exhibit activity for this [6 + 2] cycloaddition reaction (Table 1, entries 19–22) under similar reaction conditions. This indicates that

**Table 2. [6 + 2] Cyclization of Cycloheptatriene and Various Alkynes under the Optimal Conditions**[a,b]



| entry | substrate | product |
|---|---|---|
| 1 |  **2a** |  **3a**, 88% |
| 2 |  **2b** |  **3b**,81% |
| 3 |  **2c** |  **3c**, 85% |
| 4 |  **2d** |  **3d**, 87% |
| 5 |  **2e** |  **3e**, 80% |
| 6 |  **2f** |  **3f**, 88% |
| 7 |  **2g** |  **3g**, 70% |
| 8 |  **2h** |  **3h**, 73% |
| 9 |  **2i** |  **3i**, 70% |
| 10 |  **2j** |  **3j**, 72% |
| 11 |  **2k** |  **3k**, 67% |
| 12 |  **2l** |  **3l**, 48% |
| 13 |  **2m** |  **3m**, 40% |
| 14 |  **2n** |  **3a**, 30% |

[a]Reaction conditions: cycloheptatriene **1** (0.5 mmol), alkynes **2** (0.25 mmol), $[Rh(COD)Cl]_2$ (0.0125 mmol), $PPh_3$ (0.025 mmol), CuI (0.025 mmol), xylene (0.5 mL), 120 °C, 18–24 h. [b]Isolated yield based on **2**.

rhodium metal has a unique reactivity for the formation of C–C bonds. Thus, $[Rh(COD)Cl]_2$ (5 mol %) in combination with CuI (10 mol %) as the additive and $PPh_3$ (10 mol %) as the ligand was selected as the optimal catalytic system for the [6 + 2] cycloaddition reaction of **1** and **2a**.

Under the optimal conditions, a variety of 1,2-diphenylethynes bearing different substituents were investigated for the [6 + 2] cycloaddition reaction with **1**, and the results are shown in Table 2. When **1** was reacted with a diphenylacetylene bearing an electron-donating group such as $-CH_3$ (**2a**), −Et (**2c**), −OEt (**2d**), or −OMe (**2f**) at the *para-* position of the phenyl ring, the corresponding products **3a,c,d,f** were obtained in 88%, 85%, 87%, and 88% yields, respectively (Table 2, entries 1, 3, 4, and 6). When **1** was reacted with diphenylacetylene (**2b**) with no substituent, the product **3b** was obtained in 81% yield (Table 2, entry 2). Diphenylacetylene with −OMe at the *ortho* position of the phenyl ring (**2e**) reacted with **1** to give the product **3e** in 80% yield (Table 2, entry 5). Since this is lower than the yield for **2f**, this indicates that the position of the substituent may affect the product yield.

On the other hand, diphenylacetylenes with an electron-withdrawing group, such as $-NO_2$ (**2g,h**) $-CF_3$ (**2i**), $-COCH_3$ (**2j**), or −COOEt (**2k**), also reacted with **1** to give the corresponding products **3g–k** in 70%, 73%, 70%, 72%, and 67% yields, respectively (Table 2, entries 7–11). The yields of the diphenylacetylenes with electron-withdrawing groups were lower than those with electron-donating groups, indicating that electronic effects play an important role in the [6 + 2] cycloaddition reaction.

When naphthalene-substituted phenylacetylene (**2l**) was subjected to the reaction, the product **3l** was obtained in medium yield (48%) (Table 2, entry 12), which may be due to the strong steric effects in both **2l** and **3l**. This result supports the inference that steric effects exert an important influence on the cycloaddition process. Unfortunately, when phenylacetylenes bearing other groups were used as substrates, the yields of the corresponding products were lower than those for the aromatic group substituted substrates. For example, the reaction of 1,4-diphenylbutadiyne (**2m**) and cycloheptatriene gave **3m** in low yield (40%) (Table 2, entry 13). Ethyl 3-phenylpropiolate, a −COOEt substituted phenylacetylene, displayed low reactivity in the [6 + 2] cycloaddition reaction with **1** (Table 2, entry 14), indicating that the electronic effect has a strong impact on the outcome of the reaction.

In general, the yield of the desired products was influenced by the substituents on the phenylacetylene. Both aromatic groups and aliphatic groups could be introduced as substituents on the phenylacetylene, but the aromatic groups, including both electron-donating and electron-attracting groups, reacted more smoothly with cycloheptatriene to give better yields than the aliphatic groups. It should be noted that the reaction can tolerate many organic functional groups, such as $-NO_2$, $-COCH_3$, −COOEt, and −Cl, which allows for the further expansion of the products if needed.

On the basis of the above results and previous research on cobalt(I)-catalyzed [6 + 2] cycloaddition,[16,17] a plausible catalytic mechanism is shown in Figure 1.

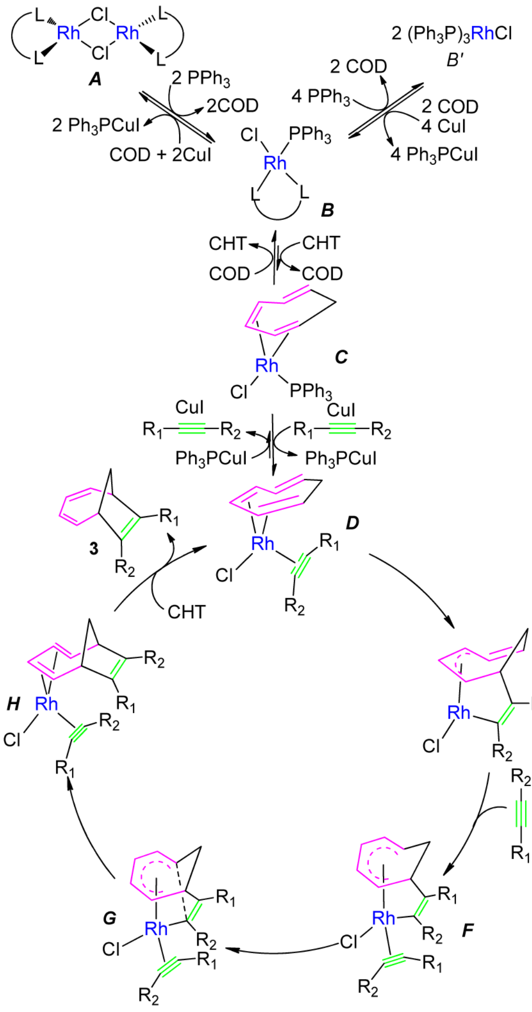


**Figure 1.** Proposed mechanism for the rhodium-catalyzed [6 + 2] cycloaddition of an internal alkyne to cycloheptatriene.

The mechanistic pathway for the formation of **3** involves the following steps: initially, the catalytic precursor [Rh(COD)Cl]$_2$ converts in situ to (Ph$_3$P)Rh(COD)Cl (***B***) after a ligand exchange with a triphenylphosphine in the presence of CuI, a known reagent for scavenging and reclaiming phosphines. The addition of triphenylphosphine and CuI in a mole ratio of 1:1 may also play an important role in controlling the ligand exchange process to give complex ***B***, instead of forming complex ***B'***, a less active species. Subsequently, the exchange of the COD ligand in the rhodium complex ***B*** with CHT gives the rhodium complex **C**, in which a CHT coordinates to the metal center. Next the Ph$_3$P is replaced with the alkyne in the presence of CuI to give intermediate ***D***, a proposed active species in the catalytic cycle. Immediately, intermediate ***D*** converts to rhodacyclopentene ***E***, an $\sigma,\pi$-allyl complex, after intramolecular oxidative cyclometalation. A further addition of an alkyne from the solution gives the $\sigma,\pi$-allyl complex ***F***. Subsequent reductive elimination of ***F*** through the transition state ***G*** produces intermediate ***H***, in which the rhodium atom is bonded with two double bonds, an acetylene, and a chloride. The [6 + 2] cycloaddition product **3** is obtained after a ligand exchange of ***H*** with CHT, regenerating catalytic active complex ***D*** to enter another catalytic cycle.

To gain a better understanding of the catalytic mechanism, DFT calculations were carried out using the M06 functional. The calculated energy profiles are shown in Figure 2. The calculations show that ligand exchange of (Ph$_3$P)Rh(COD)Cl with a CHT to give complex **II** is an endothermic process with an energy increase of 14.1 kcal/mol. The direct addition of an alkyne ligand by **II** without the help of CuI gives the PPh$_3$-coordinated complex **PIII** with an increase in energy of about 10.0 kcal/mol. The subsequent intramolecular cyclization of **PIII** to give the corresponding rhodacyclopentene goes through a transition state with a very high energy barrier (45.4 kcal/mol). Therefore, this reaction pathway is excluded.

Next, other pathways were calculated. The exchange of Ph$_3$P in complex **II** with an alkyne to give complex **III** is also an endergonic process with an energy increase of 12.5 kcal/mol in this stage. However, this process becomes exergonic if the ligand exchange occurs in the presence of CuI, due to the formation of (Ph$_3$P)CuI,[29] and the corresponding energy decreases to −18.9 kcal/mol. Although the specific role of CuI in this reaction is still undetermined, this calculation result is in good agreement with the experimental result that the addition of CuI may significantly accelerate the [6 + 2] cycloaddition reaction.

Complex **III** immediately converts to rhodacyclopentene **IV** after an oxidative cyclometalation through transition state **TSIII-IV** with a barrier of 30.8 kcal/mol. The rhodium metal is complexed with a $\pi$-allyl ligand in intermediate **IV**. A further addition of an alkyne from the reaction solution gives intermediate **V**, and the system energy slightly increases by 3.5 kcal/mol. Next **V** undergoes intermolecular reductive elimination through transition state **TSV-VI** to finally give complex **VI**, in which the rhodium atom is coordinated with the two double bonds of the [6 + 2] cycloaddition product **3**. A ligand exchange of **VI** with another CHT substrate gives the free product **3** and regenerates the catalytically active complex **III** to enter another cycle. The energy decreased by about 0.1 kcal/mol in this regenerated step. The calculated results indicate that the latter pathway is the kinetically and thermodynamically favored reaction. The whole [6 + 2] cycloaddition reaction is an exergonic process by 30.8 kcal/mol, and the overall reaction barrier for the reaction is 29.7 kcal/mol.

Another possibility is that one PPh$_3$ ligand coordinates to **V** instead of one of the alkyne ligands to give **V-P**, and then there is a reductive elimination from **V-P** to give the [6 + 2] cycloaddition product. This possibility was considered, and the profiles are shown in Figure 2. The PPh$_3$ coordinates to the CuI to give a PPh$_3$−CuI complex in this scheme. From **IV**, a transmetalation reaction between **IV** and PPh$_3$−CuI occurs to give intermediate **V-P**. Then, the reaction proceeds to form the final product through a reductive elimination transition state **TSV-VI-P**. This step (**IV** → **TSV-VI-P**) has a higher barrier of 44.8 kcal/mol than the same step (**IV** → **TSV-VI**) in our proposed pathway.

From the calculations, the rate-determining step is **III** → **TSIII-IV** (the oxidative coupling reaction). In this step, the metal center gives two of its electrons to the ligand to form the Me−C bond. Thus, a more electron-rich metal center should facilitate the whole reaction. Additional calculations with substituted 1,2-diphenylethyne models (**III-OMe** and **III-NO$_2$** in Scheme 1) were carried out.

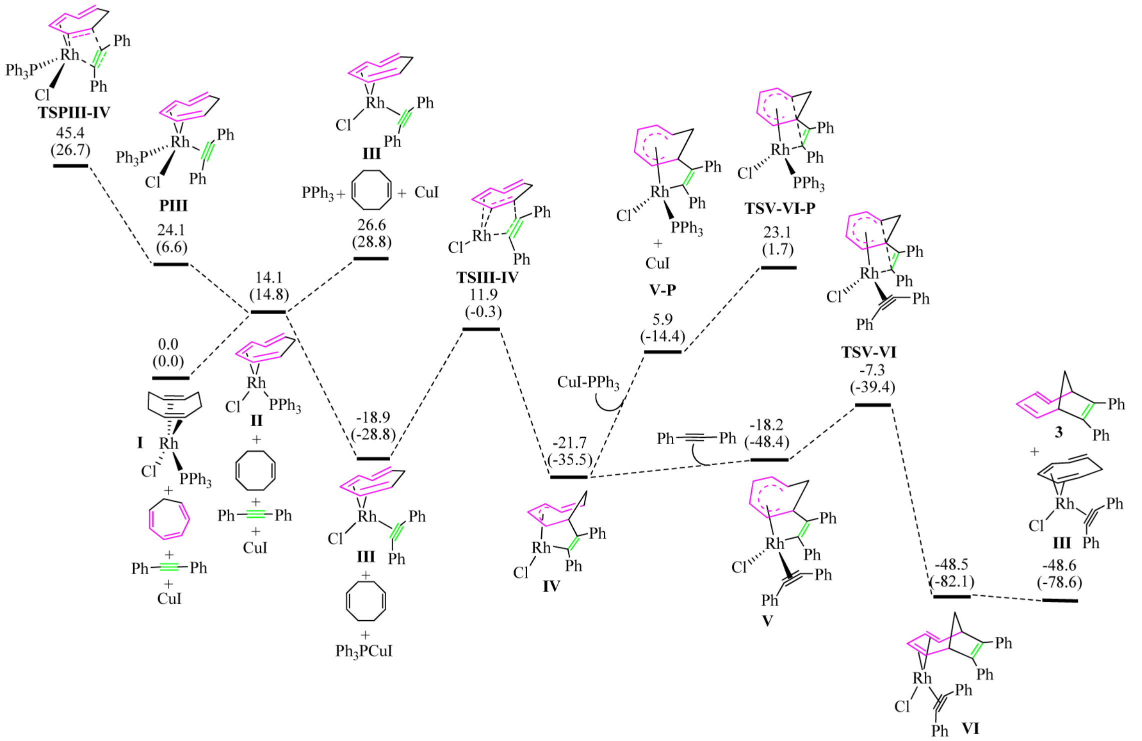
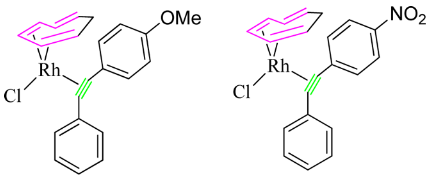


**Figure 2.** Calculated energy profiles for the pathway of the [6 + 2] reaction catalyzed by Rh(I). The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

**Scheme 1. Substituted 1,2-Diphenylethyne Models**



**III-OMe** **III-$NO_2$**

A common description of metal−alkyne bonding interactions is the Dewar−Chatt−Duncanson (DCD) model.[30] This involves the donation of electrons from the C≡C $\pi$ orbital to an empty metal $d_\sigma$ orbital and the back-donation of electrons from a metal $d_\pi$ orbital into the C≡C $\pi$* orbital. The electron richness of the metal center in these metal−alkyne complexes is modulated by the donation and back-donation properties of the coordinated alkynes.[31] The total charge of the alkynes determines how many electrons can be donated or accepted from the alkyne ligands to the metal center.

A second-order perturbation theory analysis on the basis of NBOs[32] suggests that there is a significant donor−acceptor interaction between these two moieties. For **III-OMe**, the stabilization energy $E(2)$ for the "doubly-occupied" Rh d orbitals to the "vacant" $\pi$*(C≡C) orbitals is estimated to be 21.8 kcal/mol and the stabilization energy $E(2)$ for the "doubly-occupied" $\pi$(C≡C) orbitals to the "vacant" Rh d orbitals is estimated to be 42.1 kcal/mol. For **III-$NO_2$**, the relative stabilization energies $E(2)$ are 22.5 and 37.9 kcal/mol, respectively. These results show that the (4-methoxyphenyl)-phenylacetylene ligand in **III-OMe** is a better $\sigma$ donor and a poorer $\pi$ acceptor in comparison with the (4-nitrophenyl)-phenylacetylene ligand in **III-$NO_2$**. Thus, the (4-methoxyphenyl)phenylacetylene ligand can donate more electrons to the metal center than the (4-nitrophenyl)-phenylacetylene ligand. Analysis of the NBO charges that are distributed over the alkyne ligands led to a similar conclusion. The NBO analysis shows that the total charge in the alkyne ligand of **III-OMe** is 0.077 and the total charge in the alkyne ligand of **III-$NO_2$** is 0.044. The calculated reaction barriers proved our assumptions (28.3 kcal/mol for **TSIII-IV$_{OMe}$** and 31.0 kcal/mol for **TSIII-IV$_{NO2}$**). The calculations explain why the diphenylacetylene bearing an electron-donating group has a higher yield and the diphenylacetylene bearing an electron-withdrawing group has a lower yield.

## ■ CONCLUSIONS

An efficient $[Rh(COD)Cl]_2/PPh_3/CuI$ catalytic system for the [6 + 2] cycloaddition of alkynes with cycloheptatriene has been developed. A combination of $PPh_3$ and CuI was the most efficient additive in the $[Rh(COD)Cl]_2$ catalysis system. High yields were obtained for the cycloaddition of a series of substituted alkynes with cycloheptriene. An electronic effect was observed for substituted diphenylacetylenes, and this reaction is tolerant to many organic functional groups, which makes this method valuable for preparing a wide variety of bicyclic compounds. A reaction mechanism including the oxidative coupling between the coordinated cycloheptatriene and the internal alkyne, followed by an intramolecular migration of the C($sp^3$)−Rh bond and reductive elimination from the Rh(III)−pentadienyl complex to give the product, was proposed. DFT calculations using a model Rh(I) catalyst were carried out to verify the proposed reaction mechanism. The strong additive effect observed for the CuI in these reactions was also supported by the DFT calculations.

## EXPERIMENTAL SECTION

**General Information.** All reactions were carried out under $N_2$ and monitored by analytical thin-layer chromatography on 0.20 mm silica gel plates; spots were detected by UV absorption. Silica gel (200−300 mesh) was used for column chromatography. $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker AV 400 and 600 MHz spectrometers with $CDCl_3$ as the solvent. The chemical shifts are reported in ppm relative to $CHCl_3$ ($\delta$ 7.26) for $^1H$ NMR and relative to the central $CDCl_3$ resonance ($\delta$ 77.0) for $^{13}C$ NMR. The NMR data of the known compounds were in agreement with literature values. Coupling constants ($J$) are quoted in Hz for $^1H$. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m).

**Materials and Methods.** Unless otherwise noted, all reactions were performed under an atmosphere of dry $N_2$ with oven-dried glassware. Reactions were monitored by analytical thin-layer chromatography on 0.20 mm Anhui Liangchen silica gel plates, and spots were detected by UV absorption. Silica gel (200−300 mesh) (from Anhui Liangchen Chemical Co., Ltd.) was used for flash chromatography. All substrates were synthesized using methods reported in the literature.[33] Other chemicals or reagents were obtained from commercial sources.

**General Procedure for the Rh-Catalyzed Cycloaddition Reactions.** A Schlenk tube equipped with a magnetic stir bar was charged with an alkyne (0.25 mmol), cycloheptatriene (46 mg, 0.5 mmol), $[Rh(COD)Cl]_2$ (6.2 mg, 0.0125 mmol), CuI (4.8 mg, 0.025 mmol), $PPh_3$ (6.6 mg, 0.025 mol), and xylene (0.5 mL). The tube was kept under an $N_2$ balloon and stirred at 120 °C for the required time. The reactor was then cooled to room temperature, and the crude mixture (typically a brown slurry) was filtered through a short plug of $SiO_2$ using EtOAc as the eluent to remove the rhodium residue. After further purification by $SiO_2$ column chromatography, the products were analyzed by NMR.

**Computational Details.** Molecular geometries of the model complexes were optimized without constraints via DFT calculations using the M06 functional,[34] as implemented in the Gaussian 09 suite of programs.[35] The effective core potentials (ECPs) of Hay and Wadt with a double-$\zeta$ valence basis set (LanL2DZ)[36] were used in describing Rh and I, whereas the 6-31G* basis set[37] was used for all other atoms. Polarization functions were added for Rh ($\zeta_f$ = 1.350) and I ($\zeta_d$ = 0.340).[38] Frequency calculations at the same level of theory were also performed to identify all of the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency) and to provide free energies at 298.15 K which include entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration. Transition states were located using the Berny algorithm. Intrinsic reaction coordinates (IRC)[39] were calculated for the transition states to confirm that such structures connected the two relevant minima. Charge analysis was done with a stand-alone NBO 5.9 program.[32]

To examine the basis set dependence, a larger basis set, i.e., the triple-$\zeta$ basis set of def2-TZVP for Rh and I[40] and the TZVP basis set for all other atoms,[41] was also employed to carry out single-point calculations for the intermediates and the transition states shown in Figure 2. The additional calculations show that the dependence of the basis set is insignificant. For instance, using the smaller basis set, the relative electronic energy barrier heights of **III** → **TSIII-IV**, **V** → **TSV-VI**, and **PIII** → **TSPIII-IV** were 28.4, 9.0, and 20.1 kcal/mol, respectively. Using the larger basis set, the barrier heights were 30.5, 11.2, and 21.6 kcal/mol, respectively.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

Text, figures, and tables giving experimental details and characterization data, $^1H$ NMR and $^{13}C$ NMR spectra of all new compounds, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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