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Article

Rh-Catalyzed [4 + 1] Reaction of Cyclopropyl-Capped Dienes (but not Common Dienes) and Carbon Monoxide: Reaction Development and Mechanistic Study

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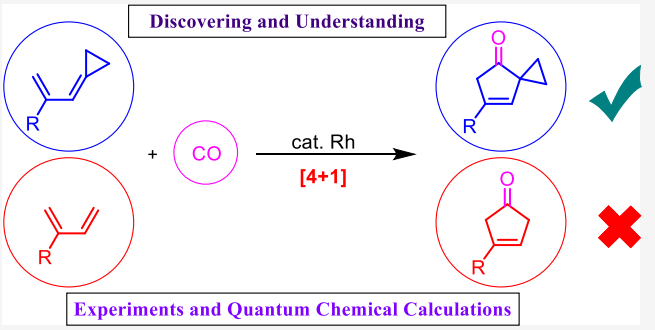
ABSTRACT: Transition-metal-catalyzed [4 + 1] reaction of dienes and carbon monoxide (CO) is the most straightforward and easily envisioned cyclization for the synthesis of five-membered carbocycles, which are ubiquitously found in natural products and functional molecules. Unfortunately, no test of this reaction was reported, and consequently, chemists do not know whether such kind of reaction works or not. Herein, we report that the [4 + 1] reaction of common dienes and CO cannot work, at least under the catalysis of $[Rh(cod)Cl]_2$. However, using cyclopropyl-capped dienes (also named allylidenecyclopropanes) as substrates, the corresponding [4 + 1] reaction with CO proceeds smoothly in the presence of $[Rh(cod)Cl]_2$. This [4 + 1] reaction, with a broad scope, provides efficient access to five-membered carbocyclic compounds of spiro[2.4]hept-6-en-4-ones. The [4 + 1] cycloadducts can be further transformed into other molecules by using the unique chemistry of cyclopropyl groups present in these molecules. The mechanism of this [4 + 1] reaction has been investigated by quantum chemical calculations, uncovering that cyclopropyl-capped dienes are strained dienes and the oxidative cyclization step in the [4 + 1] catalytic cycle can release this (angular) strain both kinetically and thermodynamically. The strain release in this step then propagates to all followed CO coordination/CO insertion/reductive elimination steps in the [4 + 1] catalytic cycle, helping the realization of this cycloaddition reaction. In contrast, common dienes (including cyclobutyl-capped dienes) do not have such advantages and their [4 + 1] reaction suffers from energy penalty in all steps involved in the [4 + 1] catalytic cycle. The reactivity of ene-allenes for the [4 + 1] reaction with CO is also discussed.



INTRODUCTION

Transition-metal-catalyzed cycloadditions have been becoming powerful tools in the synthesis of various carbocyclic compounds.[1] Among them, the most impactful cycloaddition reaction is the Pauson−Khand reaction, which is a formal [2 + 2 + 1] cycloaddition of alkynes, alkenes, and CO. This reaction has been widely used in the synthesis of five-membered carbocycles (FMCs),[2] which are the most ubiquitous cyclic structure motifs in natural products and many other functional molecules. Despite this, chemists have also been spending great efforts to discover and develop other cycloadditions to supplement or complement the original Pauson−Khand reactions for constructing FMCs with various substitutions and stereochemistries. The newly developed cycloaddition reactions could then become tools for the step-economic synthesis of FMC-embedded target molecules. For example, chemists have so far developed many [3 + 2] reactions for the synthesis of FMCs.[3] Several [4 + 1] cycloadditions of ene-allenes and CO for accessing FMCs have also been invented for the same reasons (Scheme 1a).[4−6] Interestingly, asymmetric versions of Rh- and Pt-catalyzed [4 + 1] reactions of ene-allenes have also been developed, and some of these reactions have been studied mechanistically.[4g]

We thought that the allene moieties in the above-mentioned [4 + 1] reactions of ene-allenes and CO are very critical[4,5] (see the discussion part of this paper). Otherwise, a straightforward and easily envisioned [4 + 1] reaction of common dienes with CO should have been invented and used considering that there are many ways to synthesize conjugated dienes. To the best of our knowledge, no transition-metal-catalyzed [4 + 1] cycloaddition using common dienes and CO has been reported in the literature. One possible reason for this is that chemists had tested this idea, but all of these attempts failed. Consequently, they did not report their experiments. Another possible reason is that nobody had tested this before. No matter what the

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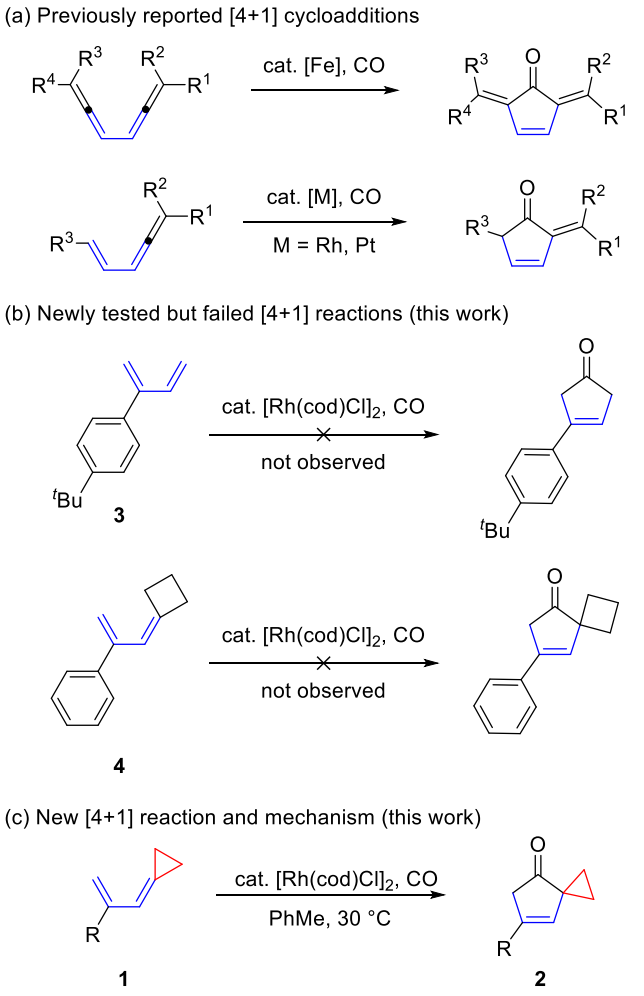
Scheme 1. [4 + 1] Reaction of Butadiene Derivatives and CO



reason this is, we wanted to answer this important scientific question. On the other hand, if this reaction really works, then a new way to synthesize FMCs can be realized. Here, we give an answer to this question: such a type of [4 + 1] reaction does not work under the catalysis of $[Rh(cod)Cl]_2$ (see Scheme 1b). We do not know whether the [4 + 1] reaction of common dienes and CO could be catalyzed by other metal catalysts, which is an open question to the synthetic community in the future. Of the same importance, we carried out quantum chemical calculations to answer why this reaction did not work under rhodium catalysis, which is presented in the current paper.

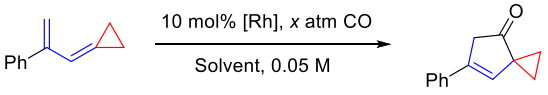
In addition, we report that using allylidenecyclopropanes, which are hereafter renamed as CP-capped dienes to emphasize their identity as a 4-carbon synthon, the corresponding [4 + 1] reaction with CO proceeds smoothly under the catalysis of $[Rh(cod)Cl]_2$. This [4 + 1] reaction provides an efficient way to synthesize FMCs with two functional groups, namely, carbonyl and cyclopropyl (CP) groups. The CP group in the [4 + 1] cycloadducts is of high recommendation. One reason is that CP is an important pharmacophore and the [4 + 1] cycloadducts in this report could be useful in the future in medicinal chemistry and related fields.[7] Another reason is that CP is an advanced intermediate group with rich chemistry, implying that various molecules could be synthesized by using CP chemistry starting from the [4 + 1] cycloadducts. We also carried out *ab initio* calculations to understand why the [4 + 1] reaction of CP-capped dienes and CO can succeed, showing that strain release of the methylenecyclopropane (MCP) moiety in CP-capped dienes is the key.

In what follows, we first report our discovery of the [4 + 1] reaction of CP-capped dienes and CO and its reaction scope as well as further transformation of [4 + 1] cycloadducts to other functionalized molecules. Then, we deliver quantum chemical calculation results to answer why CP-capped dienes, common dienes, and ene-allenes have different reactivities in the [4 + 1] reactions.

RESULTS AND DISCUSSION

Rhodium-Catalyzed [4 + 1] Reaction of CP-Capped Dienes and CO. We serendipitously found the [4 + 1] reaction in our study of the three-component [4 + 2 + 1] reaction of **1a**, alkyne and CO, catalyzed by $[Rh(CO)_2Cl]_2$.[8] Unexpectedly, only **1a** and CO reacted (the used alkyne, 4-

Table 1. Optimization of Rh-Catalyzed [4 + 1] Cycloaddition[a]



1a 2a

entry	Rh catalyst	x	solvent	T/°C	t/h	yield[b]
1	$[Rh(CO)_2Cl]_2$	1	PhMe	60	36	51%
2	$[Rh(CO)_2Cl]_2$	1	PhMe	30	24	84%
3	$[Rh(CO)_2Cl]_2$	0.2	PhMe	30	36	56%
4	**$[Rh(cod)Cl]_2$**	**1**	**PhMe**	**30**	**18**	**92% (86%[c])**
5	$[Rh(coe)_2Cl]_2$	1	PhMe	30	36	59%
6	$Rh(PPh_3)_3Cl$	1	PhMe	30	36	N. R.
7	$Rh(CO)(PPh_3)_2Cl/AgSbF_6$	1	PhMe	30	36	N. R.
8	$[Rh(cod)Cl]_2$	1	DCE	30	18	87%
9	$[Rh(cod)Cl]_2$	1	1,4-Dioxane	30	19	77%
10	$[Rh(cod)Cl]_2$	1	THF	30	18	42%
11	$[Rh(cod)Cl]_2$	1	$PhCF_3$	30	19	57%

[a]Reaction conditions: 0.20 mmol of **1a**, 10 mol % [Rh], in 4 mL of solvent, stirred under x atm of CO at T °C for t h. cod = 1,5-cyclooctadiene; coe = cyclooctene; DCE = 1,2-dichloroethane;. [b]NMR yield, 1,3,5-dimethoxybenzene as the internal standard. N. R., no reaction;. [c]Isolated yield.

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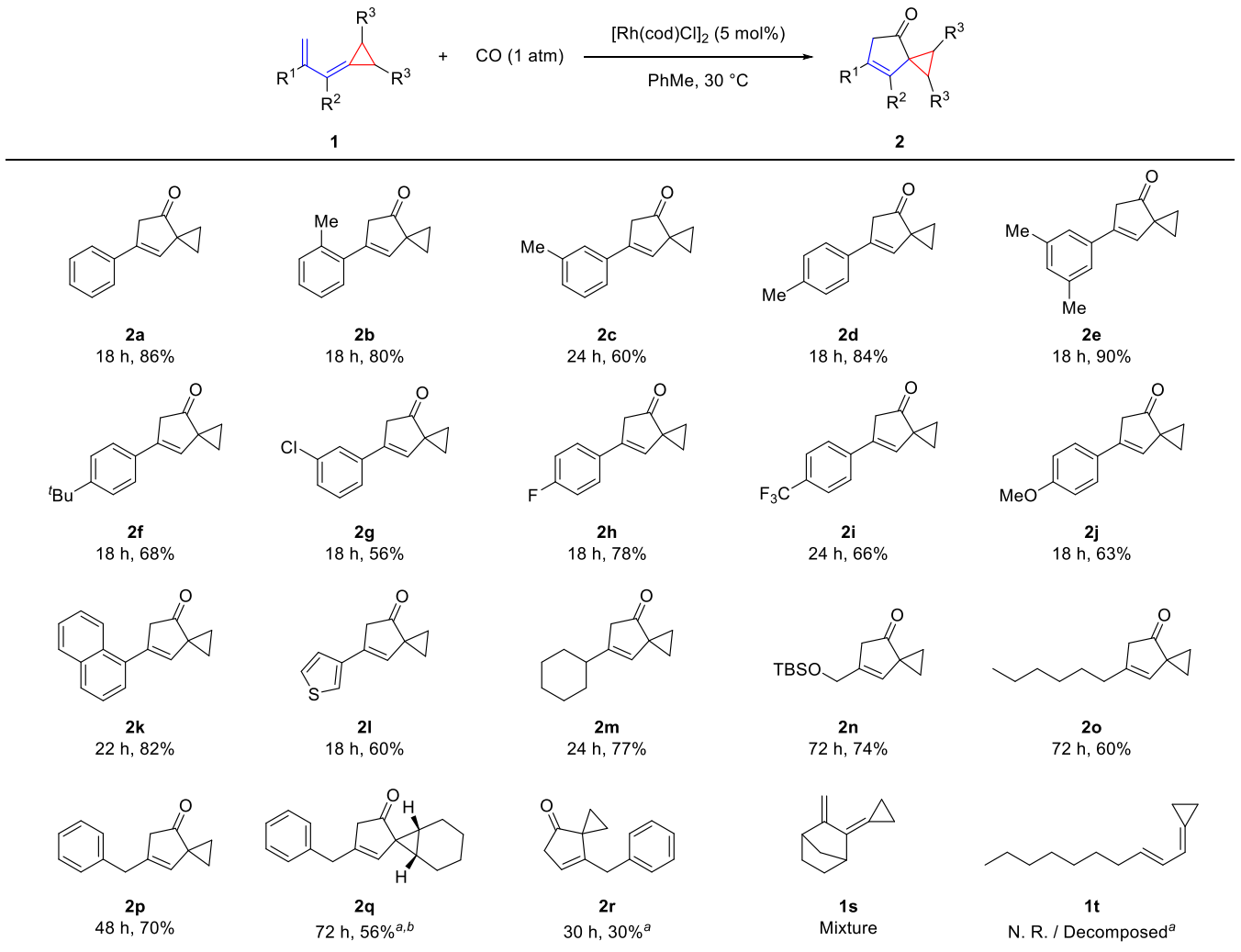

Figure 1. Reaction scope of [4 + 1] cycloaddition. Reaction conditions: 0.2 mmol of **1**, 5 mol % $[Rh(cod)Cl]_2$, 4 mL of PhMe (0.05 M), 30 °C, 1 atm CO. The yields shown here are the average of two runs. [a] 60 °C; [b] at a 0.13 mmol scale.

octyne, was left untouched in the reaction system) to give the [4 + 1] product **2a** (Table 1). We then used substrate **1a** for reaction optimization (Table 1). In the presence of $[Rh(CO)_2Cl]_2$ (5 mol %), 1 atm CO in toluene at 60 °C, the [4 + 1] cycloaddition product **2a** was obtained in 51% NMR yield (Table 1, entry 1). We then lowered the reaction temperature to 30 °C and obtained product **2a** in 84% NMR yield (Table 1, entry 2). We attempted to reduce the CO pressure from 1 to 0.2 atm, finding that the reaction yield decreased to 56% (Table 1, entry 3). To our delight, switching the catalyst from $[Rh(CO)_2Cl]_2$ to $[Rh(cod)Cl]_2$ helped the [4 + 1] reaction: product **2a** was obtained in 92% NMR yield (the separation yield was 86%, Table 1, entry 4). Using $[Rh(coe)_2Cl]_2$ as the catalyst gave only 59% yield of the target product (Table 1, entry 5). The [4 + 1] reaction of **1a** failed to occur using either $Rh(PPh_3)_3Cl$ with a phosphine ligand or $Rh(CO)(PPh_3)_2Cl/AgSbF_6$ as the catalyst (Table 1, entries 6−7). Several other solvents such as 1,2-dichloroethane, 1,4-dioxane, tetrahydrofuran, and trifluorotoluene had been tested for the [4 + 1] reaction, but all of them gave decreased reaction yields (Table 1, entries 8−11).

Based on the above results, we chose the conditions shown in entry 4 of Table 1 (1 atm CO and 5 mol % $[Rh(cod)Cl]_2$ in toluene at 30 °C) as the optimal conditions to study the scope of the [4 + 1] reaction (Figure 1). For substrates **1b−d** with *ortho*, *meta*, or *para*-methylphenyl groups, their [4 + 1] reactions gave their corresponding cycloadducts in 80, 60, and 84% yields, respectively. When the R^1 substituent in the substrate is 3,5-dimethylphenyl, the corresponding [4 + 1] reaction gave **2e** in 90% yield. For substrate **1f** with a bulky R^1 group (R^1 = 4-*tert*-butylphenyl), the [4 + 1] reaction could still take place, giving **2f** in 68% yield. For substrates **1g** and **1h** with the R^1 substituent containing a halogen atom, either Cl or F, their [4 + 1] reactions proceeded smoothly (**2g**, 56% yield; **2h**, 78% yield). Strong electron-withdrawing or electron-donating substituents on the aromatic ring are also tolerated, as illustrated by the moderate to good yields, respectively, for products **2i** (66%) and **2j** (63%). The [4 + 1] reaction could still occur when the R^1 substituent in the substrate is naphthyl (82% yield, **2k**). In contrast, the yield of the [4 + 1] reaction decreased when the R^1 substituent in the substrate is thienyl (60% yield, **2l**). It was noticed that the [4 + 1] reaction could still take place smoothly when the R^1 substituent is a cyclohexyl group (**2m**). However, when R^1 is a primary alkyl group, the [4 + 1] reactions became relatively sluggish and required 2-fold to 4-fold elongation of the reaction time for achieving complete conversions (**2n−p**). Nevertheless, these products could still be obtained in moderate to good yields. To

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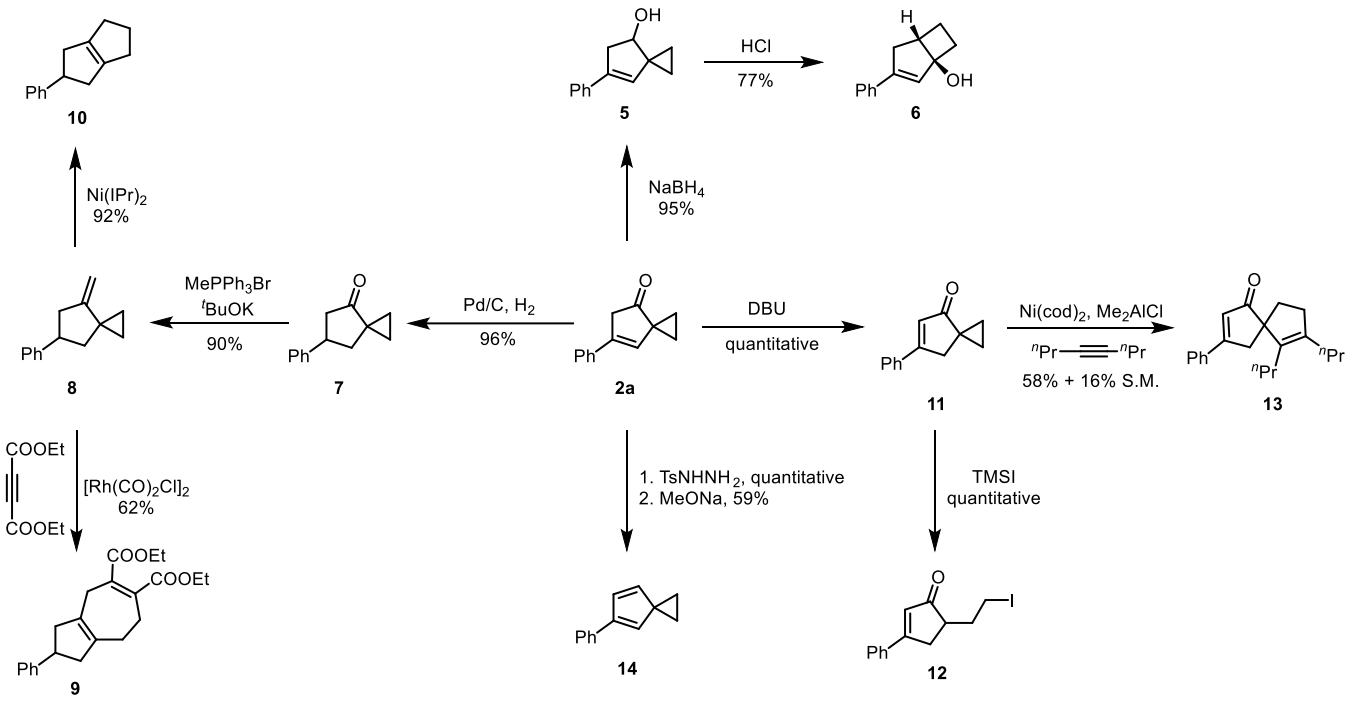

Figure 2. Further transformations of the [4 + 1] cycloadduct **2a**. All yields are average of two runs.

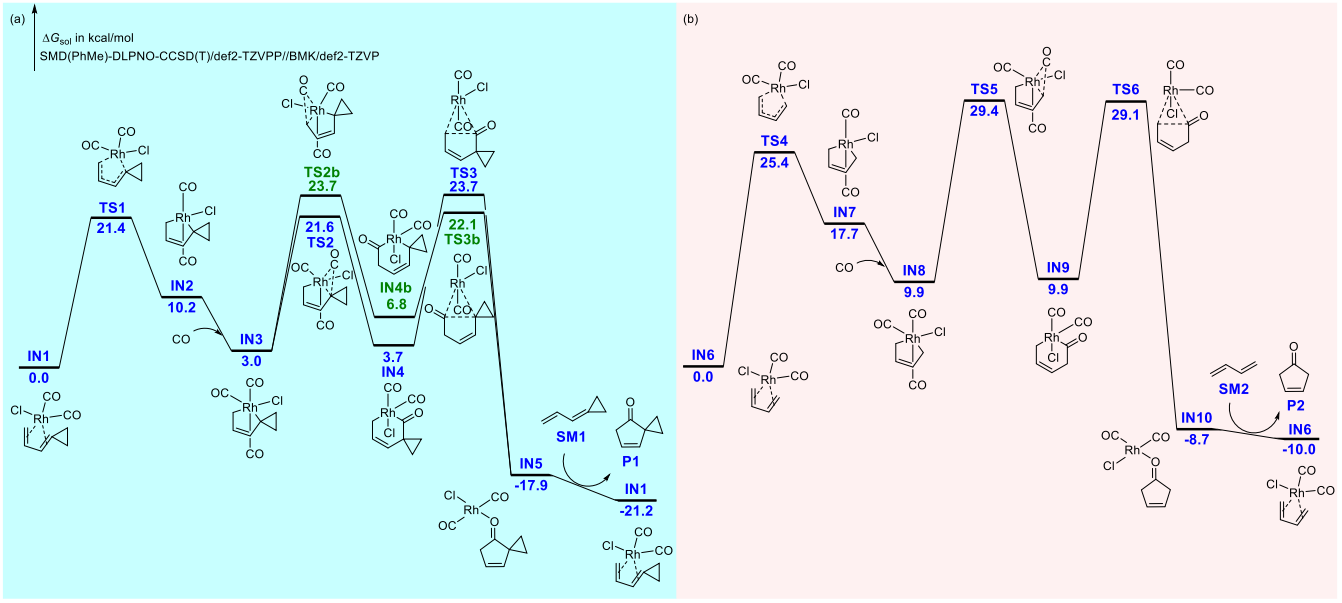

Figure 3. (a) Gibbs energy profile for [4 + 1] cycloaddition of CP-capped diene and CO. (b) Gibbs energy profile for [4 + 1] cycloaddition of 1,3-butadiene and CO. All computations were performed at the DLPNO-CCSD(T)-SMD(PhMe)/def2-TZVPP//BMK/def2-TZVP level.

our delight, the [4 + 1] reaction could still happen when the cyclopropyl group of the substrate had a fused-ring structure. In this case, the temperature of the reaction had to be increased to 60 °C so that **2q** could be obtained in 56% yield. Substitution at the R^2 position is still tolerated (**2r**), although in this case, the substrate itself is extremely susceptible to decomposition: the [4 + 1] product can only be isolated in 30% yield even after several attempts to optimize the reaction condition. For the R^1,R^2-disubstituted substrate **1s** with a norbornane backbone, the reaction gave a complex mixture, while the terminally substituted substrate **1t** was completely inert toward [4 + 1] cycloaddition (see the Supporting Information for computational understanding). We determined the structure of the [4 + 1] cycloadduct **2i** by X-ray diffraction (XRD), indicating that the product of the [4 + 1] cycloaddition did not undergo a double-bond isomerization (see the Supporting Information).

Further Transformations of the [4 + 1] Cycloadduct. With the above results, we then carried out some transformation reactions of **2a** to demonstrate that the products of the [4 + 1] cycloaddition can, in principle, be used for synthesizing other functionalized FMCs (Figure 2). The carbonyl group of **2a** can be reduced by $NaBH_4$ to give **5** in 95% yield, which, upon treatment with HCl, rearranged[9] to a

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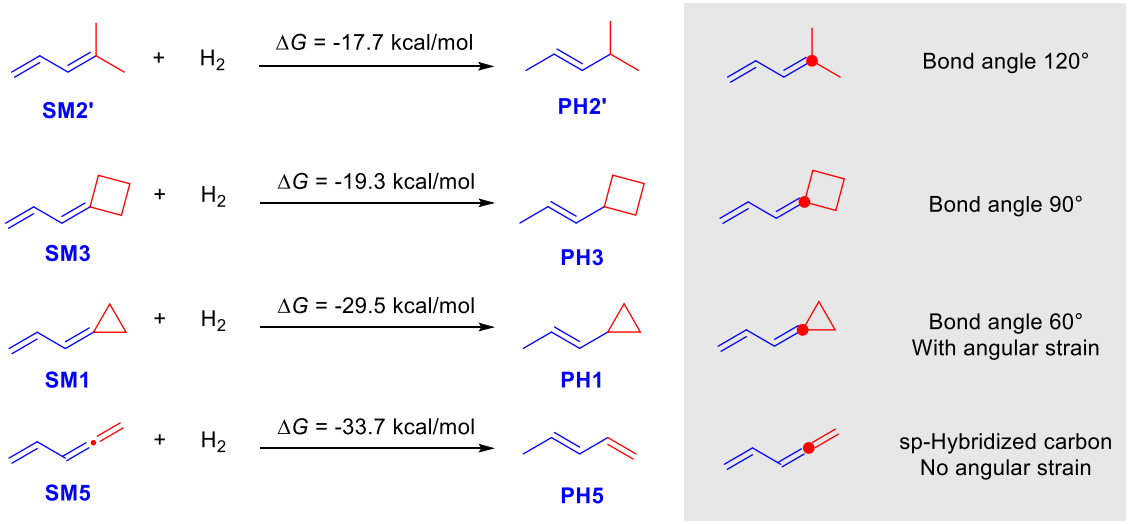
Scheme 2. Thermodynamics for the Hydrogenation of Common Diene, Cyclobutyl-Capped Diene, CP-Capped Diene, and Vinylallene in the Gas Phase, Computed at the DLPNO-CCSD(T)/def2-TZVPP//BMK/def2-TZVP Level



bridgehead tertiary alcohol **6** with a 5/4 fused-ring skeleton in 77% yield. In addition, the alkene moiety of **2a** can be reduced by catalytic hydrogenation to give **7** in 96% yield. This compound can be further converted into **8** in 90% yield via a Wittig reaction. From **8**, several typical reactions of vinylcyclopropanes can be carried out, such as Wender's Rh-catalyzed [5 + 2] cycloaddition[10] (to **9**, 62% yield) and Louie's Ni-catalyzed cycloisomerization[11] (to **10**, 92% yield). It should be noted that the [4 + 1] cycloadduct readily isomerizes to a more stable conjugated enone under basic or acidic conditions. Shown here is the basic isomerization of **2a** in the presence of DBU, which gave **11** quantitatively. Starting from **11**, typical transformations of cyclopropyl ketones can be realized, such as the ring-opening reaction of the cyclopropyl group by trimethyliodosilane (to **12**, in quantitative yield). Considering that spiral molecules are useful, we then carried out a [3 + 2] reaction[12] of **11** with alkyne. To our delight, the 5/5 spiro compound **13** was obtained in 58% yield, using $Ni(cod)_2$ as the catalyst and Me_2AlCl as the additive, at 50 °C in tetrahydrofuran, together with 16% of **11** recovered in the reaction. In addition, ketone **2a** could also be converted into a tosylhydrazone, which then gave compound **14** via a Bamford−Stevens olefination (59% yield). We found that the [5 + 1] reaction[13] of **8** failed: the starting material was fully recovered when treated with [Rh(dppp)]OTf / 0.2 atm CO at 85 °C in DCE.

Computational Study on the Mechanisms of [4 + 1] Reactions of both CP-Capped Dienes and Common Dienes with CO. We computed the Gibbs free energy profiles of two model [4 + 1] reactions shown in Figure 3 to understand how the reaction of CP-capped diene and CO (model reaction 1) occurs and why the reaction of common diene and CO (model reaction 2) fails. We proposed that the catalytic species of this reaction is a monomer $[Rh(CO)_2Cl]$, which is formed from $[Rh(cod)Cl]_2$ and CO.[14] Actually, we monitored the reaction using $[Rh(cod)Cl]_2$ as a catalyst, finding that its reaction progress was similar to that using $[Rh(CO)_2Cl]_2$ (see the Supporting Information).

Let us first discuss the model reaction 1 (Figure 3a). This [4 + 1] reaction starts from forming complex **IN1** from the dimeric catalyst of $[Rh(cod)Cl]_2$ and the substrate, based on our previous study of [5 + 2 + 1] and [4 + 2 + 1] reactions.[15] **IN1** can then undergo oxidative cyclization, generating intermediate **IN2** via **TS1**. The activation free energy of this step is 21.4 kcal/mol. Intermediate **IN2** is then coordinated by CO to form a more stable intermediate, **IN3**. From **IN3**, there are two possible pathways for CO migratory insertion and reductive elimination: **TS2**→**IN4**→**TS3** and **TS2b**→**IN4b**→**TS3b**. The former pathway, in which CO insertion takes place between rhodium and the cyclopropyl moiety, has a lower activation free energy (18.6 kcal/mol in the former vs. 20.7 kcal/mol in the latter, both from **IN3**) for the migratory insertion step as it releases the steric repulsion of CP with ligands on Rh. However, its subsequent reductive elimination step (**TS3**) is more difficult than that in the latter pathway (**TS3b**). As a result, the overall activation free energies for both pathways are almost the same (23.7 kcal/mol from **IN1**). Both pathways here can occur and lead to **IN5**, which can then undergo a ligand exchange to release the product **P1** and enter the next catalytic cycle.

Figure 3b is the computed free energy profile for the model reaction 2 of 1,3-butadiene and CO. A similar process from the monomer Rh-complex **IN6** to the final [4 + 1] product was computed for this reaction, compared to that in model reaction 1. The rate-determining step in this model reaction is migratory insertion, and the overall activation free energy is 29.4 kcal/mol.

The oxidative cyclization step in model reaction 2 is disfavored both kinetically (by ca. 4 kcal/mol) and thermodynamically (more endergonic by 7.5 kcal/mol) compared to the same process in model reaction 1. We attributed this to the strain release of the MCP group in the CP-capped diene, converting the MCP group in the substrate to a CP. MCP has a strained C−C double bond with a bond angle of 60°, while the general alkene bond is 120°. This strain (which is actually called angular strain) can be estimated to be around 12 kcal/mol by comparing the reaction thermodynamics for the hydrogenation of CP-capped diene and common diene shown in Scheme 2.[8]

A comparison of Gibbs free energy profiles of model reactions 1 and 2 shows that the CO coordination, CO insertion, and reductive elimination steps are very similar. For

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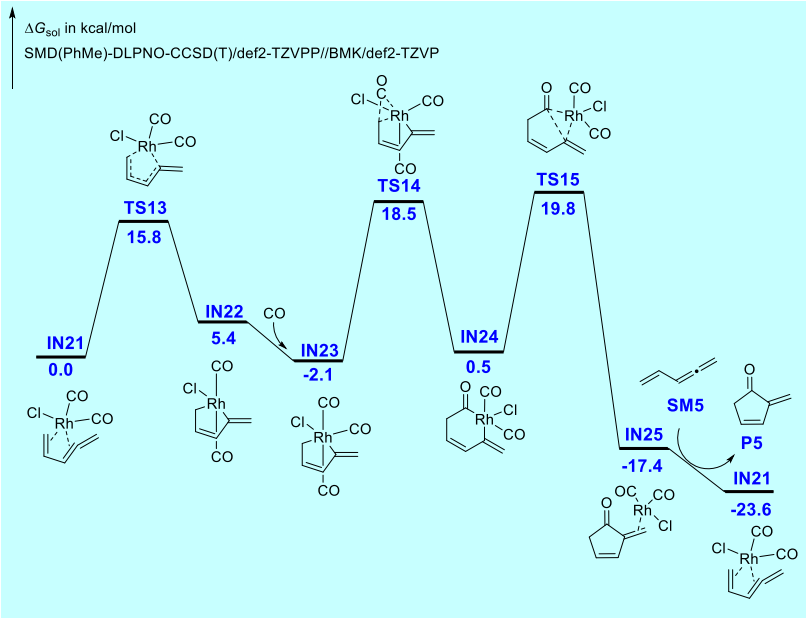

Figure 4. Gibbs energy profile for [4 + 1] cycloaddition of vinylallene and CO, computed at the DLPNO-CCSD(T)-SMD(PhMe)/def2-TZVPP//BMK/def2-TZVP level.

example, CO coordination steps are exergonic by 7 kcal/mol (**IN2** to **IN3**, and **IN7** to **IN8**); CO insertion steps require activation free energies of about 20 kcal/mol (**IN3** to **TS2b**, and **IN8** to **TS5**); and reductive elimination steps need about 20 kcal/mol (**IN4** to **TS3**, and **IN9** to **TS6**). Therefore, the effect of strain release, about 7.5 kcal/mol in terms of thermodynamics, in the first step of oxidative cyclization in model reaction 1, propagates to the followed CO coordination / CO insertion / reductive elimination. Consequently, the activation free energy of the model reaction 2 (29.4 kcal/mol) is higher than that of model reaction 1 (23.7 kcal/mol). This difference of activation free energy of about 5.7 kcal/mol partially reflects the thermodynamic difference of 12 kcal/mol in Scheme 2. Therefore, we conclude that strain release is the key to making the [4 + 1] reaction of CP-capped dienes and CO happen compared to the failed [4 + 1] reaction of common dienes and CO. This conclusion can also be kept if one considers the pathway of **TS2b→IN4b→TS3b** for model reaction 1 because the strain release makes **TS2b** easier. Similar reactions driven by strain release from MCPs include Cope rearrangement of CP-capped 1,5-dienes by Tantillo and Gagné,[16] the Diels–Alder reaction of CP-capped dienes with alkenes,[17] and our recent [4 + 2 + 1] reaction of CP-capped diene-ynes/diene-enes and CO.[8]

Here, we want to mention that, since we do not know the resting state of the [4 + 1] reactions, the activation free energy for model reaction 2 could be higher than 29.4 kcal/mol and the reaction would become more difficult. That is why reaction b in Scheme 1 failed. Model reaction 1, on the other hand, requires 23.7 kcal/mol or a little bit higher if considering the existence of an unknown resting state. This is reasonable for explaining why this [4 + 1] reaction can usually occur at room temperature.

With the above understanding, we then predicted that cyclobutyl-capped dienes are not suitable for the Rh-catalyzed [4 + 1] reaction because there is almost no strain release, revealed by the similar thermodynamic values of hydrogenation of common diene and cyclobutyl-capped diene, −17.7 kcal/mol vs −19.3 kcal/mol (Scheme 2). We verified this by carrying out the [4 + 1] reaction of **4** with CO, finding that only the starting material was recovered at 30 or 80 °C (Scheme 1b). Quantum chemical calculations show that the [4 + 1] reaction of cyclobutyl-capped diene and CO has an activation free energy of 31.1 kcal/mol (see the Supporting Information), well explaining why the [4 + 1] reaction using **4** was not successful.

Why Ene-Allenes Can Undergo the [4 + 1] Reaction. Ene-allenes can undergo [4 + 1] cycloaddition with CO in the presence of either cationic[4b] or neutral[5] Rh species. For comparison, we computed the Gibbs energy profile for the [4 + 1] cycloaddition between vinylallene and CO catalyzed by $[Rh(CO)_2Cl]_2$ (see Figure 4). A similar process was calculated previously,[5d] but here we just used simple vinylallene to compute this reaction to know the intrinsic reactivity of ene-allenes compared to common dienes and CP-capped dienes (Figure 4). Calculations show that the first step of oxidative cyclization is easy (with an activation free energy of 15.8 kcal/mol) and endergonic (by 5.4 kcal/mol). Then, CO coordination gives **IN23**, from which migratory insertion into the nonallenic Rh–C bond occurs with an activation free energy of 20.6 kcal/mol (via **TS14**). The product of this step, **IN24**, then undergoes reductive elimination to afford the complex of the [4 + 1] cycloadduct and Rh. It is important to point out that the CO insertion and reductive elimination in Figure 4 are similar to those in Figure 3a,b in terms of reaction kinetics and thermodynamics.

The oxidative cyclization in the [4 + 1] reaction of vinylallene is much easier than those of CP-capped diene and common diene (the computed activation free energies are 15.8, 21.4, and 25.4 kcal/mol, respectively). In addition, this step is less endergonic than those of CP-capped diene and common diene (the computed Gibbs reaction energies are 5.4, 10.2, and 17.7 kcal/mol, respectively). This thermodynamic preference in vinylallene is propagated to the followed CO insertion step and the reductive elimination step (rate-determining). The overall activation free energy is only 21.9

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kcal/mol (from **IN23** to **TS15**). Consequently, the [4 + 1] reaction is easy for vinylallene. The thermodynamic preference of oxidative cyclization of vinylallene is due to the inherent instability of cumulated double bonds,[18] as can be appreciated by the hydrogenation reaction of vinylallene shown in Scheme 2.

CONCLUSIONS

In conclusion, we report that the straightforward and easily envisioned [4 + 1] reaction of common dienes and CO cannot work under the catalysis of $[Rh(cod)Cl]_2$. However, using CP-capped dienes as substrates, the corresponding [4 + 1] reaction with CO catalyzed also by $[Rh(cod)Cl]_2$ can be realized. This [4 + 1] reaction has a broad scope and provides efficient access to five-membered carbocyclic compounds of spiro[2.4]hept-6-en-4-ones. These cycloadducts have two functional groups, namely, carbonyl and cyclopropyl groups, and will have great potential application in synthesis, as demonstrated by several transformations shown in Figure 2. The mechanisms of [4 + 1] reactions of cyclopropyl-capped dienes and common dienes with CO have been studied by *ab initio* calculations, showing that these reactions start from diene oxidative cyclization, CO coordination, CO insertion, and reductive elimination (rate-determining step). The success of the [4 + 1] reaction of CP-capped dienes and CO is due to the strain release in the oxidative cyclization step, where the strained MCP moiety in the CP-capped dienes can release this (angular) strain both kinetically and thermodynamically. This strain release then propagates to all followed steps in the [4 + 1] catalytic cycle, which consequently helps the realization of the [4 + 1] reaction. However, the common dienes do not have such advantages and their [4 + 1] reaction suffers from energy penalty in all steps involved in the catalytic cycle. The reason for the easy [4 + 1] reaction of ene-allenes with CO is due to the high reactivity of allene, which is also present in the paper for comparing reactivities of ene-allenes, common dienes, and CP-capped dienes in cycloadditions.

COMPUTATIONAL METHODS

DFT calculations were performed by Gaussian 09 E.01.[19] DLPNO-CCSD(T)[20] single-point energy calculations were performed by ORCA 4.2.1.[21] Pruned integration grids with 99 radial shells and 590 angular points per shell were used in DFT calculations (int = ultrafine). Geometry optimizations of all of the minima and transition states were carried out with the BMK functional[22] in the gas phase, and the def2-TZVP[23] basis set was used for all atoms. The BMK functional performed well in our previously reported [4 + 2 + 1] cycloaddition of cyclopropyl-capped diene-ynes/diene-enes with CO[8] and was used in this study as well. Enthalpy and Gibbs free energy corrections were obtained through frequency analyses at 298 K. Solvent effects were considered based on gas-phase-optimized structures using the same basis set and functional. Solvation energies in toluene were evaluated by a self-consistent reaction field employing the SMD model.[24] Based on the optimized structures, single-point energy refinements were performed at the DLPNO-CCSD(T)/def2-TZVPP[23] level (def2-TZVPP/C auxiliary basis set) with TightSCF and TightPNO keywords. In this paper, all discussed energies are Gibbs free energies in the solution phase (ΔG_{sol} 298 K) unless otherwise specified. We have searched for all possible conformers for all intermediates and transition states, and the discussed ones in this paper are the most stable. The standard state for CO is its solubility in toluene at 30 °C (7.5 mM),[25] and other species have standard states of 1.0 M.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c03047.

Experimental procedures, characterization data, copies of NMR spectra, and computational details (PDF)

Accession Codes

CCDC 2250702 contains 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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