Cycloaddition

Rhodium-Catalyzed [2+2+2] Cycloaddition of Diynes with Carbodiimides and Carbon Dioxide under Ambient Conditions

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Abstract: It has been established that a cationic rhodium(I)/H₈-binap complex is able to catalyze the [2+2+2]cycloaddition of diynes with carbodiimides and carbon dioxide under ambient conditions. Enantio- and/or regioselective variants of these reactions are also disclosed.

The transition-metal-catalyzed [2+2+2] cycloadditions involving heterocumulenes have been extensively explored for the efficient synthesis of heterocycles because of their atom economical and convergent nature.^[1] In particular, the [2+2+2] cycloaddition involving isocyanates is an efficient method for the synthesis of nitrogen heterocycles.^[2-10] For example, a number of the efficient transition-metal-catalyzed [2+2+2] cycloadditions of two alkynes including diynes with isocyanates to form substituted 2-pyridones have been achieved under mild reaction conditions by using cobalt,^[2] nickel,^[3] ruthenium,^[4] iridium,^[5] and rhodium^[6-8] catalysts. On the contrary, the transitionmetal-catalyzed [2+2+2] cycloadditions of two alkynes with carbodiimides and carbon dioxide^[11] require harsh reaction conditions.^[2b,e, 10a, 12-17] Cobalt(I)-cyclopentadiene complexes are able to catalyze the [2+2+2] cycloaddition of diynes or two monoynes with carbodiimides, however, microwave irradiation and/or high reaction temperature are necessary (Scheme 1).^[2b,e,12] Very recently, it was reported that [RhCl(PPh₃)₃] is able to catalyze the complete intramolecular [2+2+2] cycloaddition of bis(propargylphenyl)carbodiimides under toluene reflux, whereas the intermolecular reaction was not included.^[13a] Cobalt,^[2e] nickel^[15] and rhodium^[16] complexes are able to catalyze the [2+2+2] cycloaddition of diynes or two monoynes with carbon dioxide at RT-130°C, however, these reactions suffer from low product yields and/or employment of extremely high pressure carbon dioxide. The use of nickel(0)-Nheterocyclic carbene complexes allows the employment atmospheric pressure carbon dioxide in the [2+2+2] cycloaddition with internal diynes, whereas elevated reaction tempera-

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Scheme 1. Transition-metal-catalyzed [2+2+2] cycloadditions of diynes with carbodiimides and carbon dioxide.

ture (60 °C) is still required (Scheme 1).^[17] On the other hand, our research group previously reported that cationic rhodium(I)/biaryl bisphosphine complexes are able to catalyze the [2+2+2] cycloaddition of diynes or two monoynes with isocyanates at room temperature.^[6b,c,f-h] Herein, we have achieved the [2+2+2] cycloadditions of diynes with carbodiimides and atmospheric pressure carbon dioxide at room temperature using the cationic rhodium(I)/biaryl bisphosphine complexes as catalysts.

We first examined the reactions of malonate-linked terminal 1,6-diyne 1a with diaryl carbodiimide 2a (1.1 equiv) in the presence of a cationic rhodium(I)/bisphosphine catalysts (10 mol%) at room temperature (Table 1, entries 1-9). In this catalyst screening, a (CH₂Cl)₂ solution of 1 a and 2 a was added to a (CH₂Cl)₂ solution of the rhodium catalyst at room temperature. Pleasingly, all the bisphosphine complexes examined were able to catalyze the room temperature [2+2+2] cycloaddition of 1a with 2a to give the expected cycloadduct 3aa. Among them, H₈-binap (entry 1) and dppe (entry 8) were found to be the most effective ligands (Figure 1). In order to improve the yield of 3aa, increasing the amount of 2a (2 equiv) was tested. Although the identical yield of 3 aa was observed by using dppe as a ligand (entry 10), the significantly improved yield of 3aa was observed by using H₈-binap as ligand (entry 11). Further improved yield of 3aa was achieved when a (CH₂Cl)₂ solution of 1 a was added dropwise over 5 min to a (CH₂Cl)₂ solution of **2a** and the rhodium catalyst (entry 12), whereas prolonged addition time over 30 min decreased the yield of 3 aa. This operation effectively suppressed the undesired homo-[2+2+2] cycloaddition of 1a. Unfortunately, decreasing the catalyst loading to 5 mol % lowered the yield of 3 aa (entry 13).

Thus, we explored the scope of this process under the above-optimized reaction conditions (Scheme 2). With respect

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Table 1. Optimization of reaction conditions for rhodium-catalyzed $[2+2+2]$ cycloaddition of 1 a with 2 a. ^[a] $[2+2+2]$ cycloaddition of 1 a with 2 a. ^[a] MeO_2C					
Entry	Ligand	Catalyst [mol %]	2 a [equiv]	Yield [%] ^[b]	
1	H ₈ -binap	10	1.1	43	
2	binap	10	1.1	42	
3	segphos	10	1.1	36	
4	biphep	10	1.1	35	
5	dppf	10	1.1	27	
6	dppb	10	1.1	28	
7 ^[c]	dppp	10	1.1	28	
8 ^[c]	dppe	10	1.1	54	
9 ^[c]	dppm	10	1.1	34	
10	dppe	10	2.0	54	
11	H ₈ -binap	10	2.0	69	
12 ^[d]	H ₈ -binap	10	2.0	77	
13 ^[d,e]	H ₈ -binap	5	2.0	59	

[a] [Rh(cod)₂]BF₄ (0.010 mmol), ligand (0.010 mmol), **1a** (0.10 mmol), **2a** (0.11–0.20 mmol), and (CH₂Cl)₂ (2.0 mL) were used. A (CH₂Cl)₂ solution of **1a** and **2a** was added to a (CH₂Cl)₂ solution of the Rh catalyst; [b] isolated yield; [c] [Rh(nbd)₂]BF₄ was used; [d] **1a** was added dropwise to a (CH₂Cl)₂ solution of **2a** and the Rh catalyst over 5 min; [e] **1a** (0.20 mmol), **2a** (0.40 mmol), and (CH₂Cl)₂ (4.0 mL) were used.



Figure 1. Structures of bisphosphine ligands.

to diynes, malonate- and dimethoxypropane-linked terminal 1,6-diynes 1a-c treated with 2a gave the corresponding cycloadducts 3aa-ca in high yields. However, the use of tosylamide-linked terminal 1,6-diyne 1d lowered the cycloadduct yield (3 da) due to the rapid homo-[2+2+2] cycloaddition of 1d. Importantly, methylene-linked terminal 1,6-diyne 1e smoothly reacted with 2a to give cycloadduct 3ea in high yield despite the absence of the Thorpe-Ingold effect.^[18] Not only 1,6-diynes, but also 1,7-diynes 1 f,g could be employed. In the reactions of internal 1,6-diynes 1h-l, the use of 1.1 equiv of 2a was optimum and the slow addition of substrates were not required due to low reactivity of internal 1,6-diynes towards the homo-[2+2+2] cycloaddition. With respect to carbodiimides, not only diaryl carbodiimide 2a but also dialkyl carbodiimide **2b** could be employed.^[19] Next, the regioselective [2+2+2] cycloadditions using unsymmetrical 1,6-diynes were examined. The reaction of unsymmetrical 1,6-diyne 1m, pos-



Scheme 2. Rhodium-catalyzed [2+2+2] cycloadditions of diynes 1 with carbodiimides 2. $[Rh(cod)_2]BF_4$ (0.010 mmol), H_8 -binap (0.010 mmol), 1 (0.10 mmol), 2 (0.11–0.20 mmol), and $(CH_2CI)_2$ (2.0 mL) were used. A $(CH_2CI)_2$ solution of 1 was added dropwise to a $(CH_2CI)_2$ solution of 2 and the Rh catalyst over 5 min. The cited yields are of the isolated products. [a] A $(CH_2CI)_2$ solution of 1 and 2 was added to a $(CH_2CI)_2$ solution of the Rh catalyst.

sessing hydrogen and a methyl group at each alkyne terminus, with 2a furnished 3ma with high regioselectivity along with minor regioisomer 3ma'. On the other hand, lower regioselectivity was observed in the reaction of methyl- and phenyl-substituted unsymmetrical 1,6-diyne 1n with 2a.

The regio- and enantioselective [2+2+2] cycloaddition of unsymmetrical 1,6-diynes, possessing hydrogen and an *ortho*substituted phenyl group at each alkyne terminus, with **2a** was also examined (Scheme 3).^[20,21] Pleasingly, methylenelinked 1,6-diyne **1o**, possessing the 2-chloro-substituted phenyl group, reacted with **2a** in the presence of the cationic rhodium(I)/(S)-H₈-binap catalyst at room temperature to give axially chiral heterobiaryl **3oa**^[22] as a single regioisomer with good yield and *ee* values. The use of (*R*)-DTBM-segphos as a ligand significantly increased the *ee* value, although the

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Scheme 3. Rhodium-catalyzed regio- and enantioselective [2+2+2] cycloaddition of unsymmetrical diynes $1 \circ -q$ with carbodiimide 2 a.

product yield decreased. Malonate-linked 1,6-diyne **1p** also reacted with **2a** to give heterobiaryl **3pa** with high *ee* value. Although the product yield decreased, 1,6-diyne **1q**, possessing the methoxycarbonyl-substituted phenyl group, also reacted with **2a** to give heterobiaryl **3qa** with high *ee* value.

The successful cationic rhodium(I)/H₈-binap complex-catalyzed [2+2+2] cycloaddition of diynes with carbodiimides prompted our investigation into the use of carbon dioxide in place of the carbodiimide. Pleasingly, after prestirring a (CH₂Cl)₂ solution of the cationic rhodium(I)/H₈-binap complex (20 mol%) under atmospheric pressure carbon dioxide, a (CH₂Cl)₂ solution of malonate-linked internal 1,6-diyne **1h** was added dropwise over 10 min at room temperature and the resulting solution was stirred for 16 h to give the corresponding bicyclic 2-pyrone 4h in moderate yield (Table 2, entry 1). Effect of solvents (entries 1-5) and ligands (entries 6-13) were then examined, which revealed that the use of (CH₂Cl)₂ as a solvent and H₈-binap as a ligand is the best combination (entry 1). Decreasing the catalyst loading to 5 mol% significantly lowered the yield of 4h due to the formation of the homo-[2+2+2] cycloaddition product of 1h (entry 14). In order to suppress the undesired homo-[2+2+2] cycloaddition, the slow addition of 1h was examined. Gratifyingly, the addition of 1h over 30 min significantly improved the yield of 4h (entry 15). Prolonged addition time (120 min) further improved the yield of 4h (entry 16). The effect of prestirring time of the catalyst solution under carbon dioxide was also examined (5-60 min, entries 16-18). Interestingly, short stirring time (5 min) significantly increased the yield of **4h** as a result of the suppression of the homo-[2+2+2] cycloaddition of 1h (entry 18).^[23] This reaction was found to be very rapid and was completed after only 1 h (entry 19). The reaction under reduced carbon dioxide pressure (0.5 atm) significantly decreased the yield of 4h (entry 20). Finally, the use of inexpensive binap instead of H₈-binap was tested under the best conditions shown in entry 19, but the yield of 3aa decreased (entry 21).

Thus, we explored the scope of this process under the above-optimized reaction conditions (Scheme 4). With respect to diynes, malonate- (1 h,i), 1,3-diketone- (1 r,s), and 1,3-dialkox-ypropane-linked internal 1,6-diynes (1 t,u) reacted with atmospheric pressure carbon dioxide to give the corresponding bicyclic 2-pyrones 4 in good to excellent yields. 1,6-Diyne 1 v, pos-

Table 2. Optimization of reaction conditions for rhodium-catalyzed $[2+2+2]$ cycloadditions of 1 h with CO ₂ . ^[a] 5-20 mol % MeO ₂ C Me Me Ne MeO ₂ C Me Me Ne MeO ₂ C Me Me Ne Me Ne Ne Ne						
	1h (1 atm) 4h ^{Me}					
Entry	Ligand	Catalyst [mol %]	Solvent	Prestirring time [min]	Addition time [min]	Yield [%] ^[b]
1	H ₈ -binap	20	(CH ₂ Cl) ₂	30	10	48
2	H ₈ -binap	20	CH_2CI_2	30	10	19
3	H ₈ -binap	20	C₀H₅CI	30	10	35
4	H ₈ -binap	20	toluene	30	10	< 5
5	H ₈ -binap	20	THF	30	10	< 5
6	binap	20	$(CH_2CI)_2$	30	10	41
7	segphos	20	$(CH_2CI)_2$	30	10	19
8	biphep	20	$(CH_2CI)_2$	30	10	9
9	dppf	20	$(CH_2CI)_2$	30	10	25
10	dppb	20	$(CH_2CI)_2$	30	10	0
11 ^[c]	dppp	20	$(CH_2CI)_2$	30	10	0
12 ^[c]	dppe	20	$(CH_2CI)_2$	30	10	0
13 ^[c]	dppm	20	$(CH_2CI)_2$	30	10	0
14	H ₈ -binap	5	$(CH_2CI)_2$	30	10	18
15	H ₈ -binap	5	$(CH_2CI)_2$	30	30	59
16	H ₈ -binap	5	$(CH_2CI)_2$	30	120	78
17	H ₈ -binap	5	$(CH_2CI)_2$	60	120	77
18	H ₈ -binap	5	$(CH_2CI)_2$	5	120	94
19 ^[d]	H ₈ -binap	5	$(CH_2CI)_2$	5	120	90
20 ^[d,e]	H ₈ -binap	5	$(CH_2CI)_2$	5	120	42
21 ^[d]	binap	5	$(CH_2CI)_2$	5	120	79
[a] $[Rh(cod)_2]BF_4$ (0.010-0.040 mmol), ligand (0.010-0.040 mmol), 1h (0.20 mmol), CO ₂ (1 atm), and solvent (5.0 mL) were used. A solution of 1h was added to a solution of the Rh catalyst at RT over 10-120 min; [b] isolated yield; [c] $[Rh(nbd)_2]BF_4$ was used; [d] reaction time: 1 h; [e] CO ₂ (0.5 atm) and N ₂ (0.5 atm).						

sessing free hydroxyl groups, also reacted with carbon dioxide to give the corresponding diol 4v in moderate yield. Heteroatom-linked internal 1,6-diynes 1j,k could be employed, but the product yields were low. Sterically demanding diethyl-substituted internal 1,6-diyne 1w smoothly reacted with carbon dioxide to give the corresponding bicyclic 2-pyrone 4w in high yield. However, malonate-linked terminal 1,6-diyne 1a and methylene-linked internal 1,6-diyne 11 failed to react with atmospheric pressure carbon dioxide due to the rapid homo-[2+2+2] cycloaddition of diynes. Next, the regioselective [2+2+2] cycloadditions using unsymmetrical 1,6-diynes were examined. Although unsymmetrical 1,6-diynes 1 m,n employed in Table 2 failed to react with atmospheric pressure carbon dioxide, the reaction of ethyl- and methyl-substituted unsymmetrical 1,6-diyne 1x proceeded to give 4xa (major) and 4xa' (minor) with moderate regioselectivity. The reaction of isopropyl- and methyl-substituted unsymmetrical 1,6-diyne 1y with carbon dioxide also proceeded to give 4ya (major) and 4 ya' (minor) with high regioselectivity.

As the reactions of diynes with atmospheric pressure carbon dioxide proceeded more smoothly than those with carbodiimides, a large-scale reaction was attempted at low-catalyst loading. Pleasingly, the reaction of **1h** (236 mg) with atmospheric pressure carbon dioxide proceeded at room tempera-

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Scheme 4. Rhodium-catalyzed [2+2+2] cycloaddition of diynes 1 with CO₂. [Rh(cod)₂]BF₄ (0.010 mmol), H₈-binap (0.010 mmol), 1 (0.20 mmol), CO₂ (1 atm), and (CH₂Cl)₂ (5.0 mL) were used. After stirring a (CH₂Cl)₂ solution of the Rh catalyst at RT under CO₂ (1 atm) for 5 min, a (CH₂Cl)₂ solution of 1 was added to this solution over 120 min. The cited yields are of the isolated products.

ture for 1 h by using 1 mol% of the Rh catalyst, although bicyclic 2-pyrones **4h** was obtained in somewhat lower yield due to the formation of the homo-[2+2+2] cycloaddition product of **1h** (Scheme 5).



Scheme 5. [2+2+2] Cycloaddition of 1,6-diyne 1 h with CO₂ using 1 mol% of the rhodium catalyst.

Possible mechanisms for the regioselective [2+2+2] cycloadditions are shown in Scheme 6. Oxidative coupling of two alkyne moieties of diyne 1 furnishes rhodacyclopentadiene **A**. Regioselective insertion of carbodiimide **2** or carbon dioxide between the sterically less demanding Rh–C bond furnishes rhodacycle **B**. Reductive elimination affords cycloadduct **3** or **4**, respectively, as a major product and regenerates the rhodium



Scheme 6. Possible reaction mechanism (R^1 = large substituent, R^2 = small substituent).

catalyst. Alternatively, oxidative coupling of the sterically less demanding alkyne moiety of diyne 1 and carbodiimide 2 or carbon dioxide furnishes heterorhodacyclopentene C. Insertion of another alkyne moiety of 1 would also furnish the same rho-dacycle B.

In order to determine the reaction pathway, the enantioselective desymmetrization reactions of phenylacetate-derived 1,6-diynes 1α and 1β were examined. If the reaction of proceeds via rhodacycle A an almost racemic cycloadduct would be generated due to the absence of the interaction between a quaternary chiral center and a chiral ligand. On the contrary, if the reaction proceeds via rhodacycle C, an enantioenriched cycloadduct would be generated due to the presence of such interaction. In our previous report, the rhodium(I)/(R)-binap complex-catalyzed [2+2+2] cycloaddition of 1α with phenyl isothiocyanate proceeded to give enantioenriched cycloadduct with 61% ee presumably via the corresponding azarhodacyclopentene intermediate.^[24] The cationic $rhodium(I)/(S)-H_8$ -binap complex-catalyzed [2+2+2] cycloadditions between $1\alpha,\beta$ and 2a proceeded to give cycloadducts $3\alpha a$ and $3\beta a$ with low ee values (Scheme 7). On the other hand, the corresponding cy-



Scheme 7. Rhodium-catalyzed enantioselective desymmetrization of 1,6diynes 1α , β with carbodiimide 2a.

cloadditions using (*R*)-DTBM-segphos as ligand gave $3\alpha a$ and $3\beta a$ with 33 and 23% *ee*, respectively. These results would suggest that in addition to rhodacycle **A**, rhodacycle **C** contributes, at least in part, to the formation of $3\alpha a$ and $3\beta a$.

The cationic rhodium(I)/(S)-H₈-binap complex-catalyzed [2+2+2] cycloadditions between 1β and carbon dioxide also proceeded to give cycloadduct 4β with 20% *ee*, although no reaction was observed when using (*R*)-DTBM-segphos as a ligand (Scheme 8). This result would also suggest the contribution of rhodacycle **C**, at least in part, to the formation of bicyclic 2-pyrone 4β .

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Scheme 8. Rhodium-catalyzed enantioselective desymmetrization of 1,6-diyne $1\,\beta$ with CO_2.

In conclusion, we have established that a cationic rhodium(I)/H₈-binap complex is able to catalyze the [2+2+2] cycloaddition of diynes with carbodiimides and carbon dioxide under ambient conditions. Enantio- and/or regioselective variants of these reactions were also disclosed. Mechanistic studies implied that in addition to a rhodacyclopentadiene intermediate, a heterorhodacyclopentene intermediate contributes, at least in part, to the [2+2+2] cycloaddition reactions of diynes with carbodiimides and carbon dioxide. Future work will focus on further utilization of the cationic rhodium(I)/biaryl bisphosphine complexes for the [2+2+2] cycloaddition involving heterocummulenes.

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