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Cationic Rhodium(I)/H_8-binap Complex Catalyzed [2+2+2] Cycloadditions of 1,6- and 1,7-Diynes with Carbonyl Compounds

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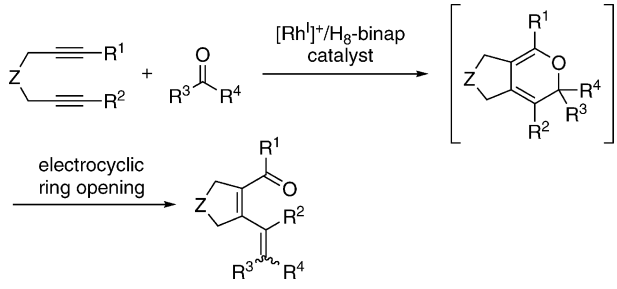
We have established that a cationic rhodium(I)/H_8-binap complex catalyzes [2+2+2] cycloadditions of a variety of 1,6- and 1,7-diynes with both electron-deficient and electron-rich carbonyl compounds, leading to dienones in high yield under mild reaction conditions. In the reactions with acyl phosphonates, the reactivity of 1,6- and 1,7-diynes was highly dependent on their own structures. The addition of chelating diethyl oxalate effectively promoted the [2+2+2] cycloadditions involving acyl phosphonates, presumably due to the equilibrium formation of the desired 1:1 rhodium complex of the diyne and the acyl phosphonate by facile ligand exchange between the diyne and weakly coordinated diethyl oxalate. In the reactions involving bifunctional carbonyl compounds or unsymmetrical 1,6-diynes, high chemo- or regioselectivities were observed.

Introduction

Transition-metal-catalyzed [2+2+2] cycloadditions of diynes with C_{sp}–heteroatom multiple bonds such as nitriles and heterocumulenes are valuable methods to construct various heterocycles in a highly atom economical manner.[1] Although a number of transition-metal complexes can catalyze or mediate these reactions, analogous [2+2+2] cycloadditions involving C_{sp^2}–heteroatom multiple bonds such as aldehydes and ketones have been reported in a limited number of examples.[2–11] The pioneering work for such a catalytic [2+2+2] cycloaddition was reported in nickel(0)/monophosphane complex catalyzed reactions of 1,6- and 1,7-diynes with aldehydes.[2] After this report, Cp*Ru(cod)Cl-catalyzed reactions involving electron-deficient ketones (diethyl ketomalonate and indanetrione)[3,4] and nickel(0)/imidazolylidene complex catalyzed reactions involving electron-rich aldehydes and ketones were reported.[5,6] Other than these catalytic reactions, the reactions using stoichiometric transition-metal complexes were also reported in cobalt-mediated reactions involving electron-rich aldehydes and ketones[7] and zirconium-mediated reactions involving diethyl ketomalonate.[8] For the rhodium-catalyzed reactions, [2+2+2+1] cycloadditions of diynals with CO by using a neutral rhodium(I) complex, $[Rh(cod)Cl]_2$, as a catalyst furnished intramolecular [2+2+2] cycloaddition products as byproducts.[9] Carbonyl insertion into a cationic rhodacyclopentadiene was reported in cationic rhodium(I)/biphep complex catalyzed carbonyl *Z*-dienylations through multicomponent reductive coupling of aldehydes and α-keto esters mediated by hydrogen in the presence of a catalytic amount of triphenylacetic acid, but this example is not the straightforward [2+2+2] cycloaddition of alkynes with carbonyl compounds.[10] Thus, a study concerning the [2+2+2] cycloaddition of diynes with carbonyl compounds by using a rhodium(I) complex as a catalyst has not been reported. Furthermore, a catalyst that can be used in [2+2+2] cycloaddition reactions of diynes with both electron-deficient and electron-rich carbonyl compounds has not been developed.

In contrast, our research group reported cationic rhodium(I)/biaryl bisphosphane complex catalyzed [2+2+2] cycloadditions of diynes with both electron-deficient and electron-rich C_{sp}–heteroatom multiple bonds under mild reaction conditions,[11,12] which prompted our investigation into cationic rhodium(I)/biaryl bisphosphane complex catalyzed [2+2+2] cycloadditions of diynes with both electron-de-



Scheme 1. Cationic rhodium(I)/H_8-binap complex catalyzed [2+2+2] cycloadditions of diynes with carbonyl compounds.

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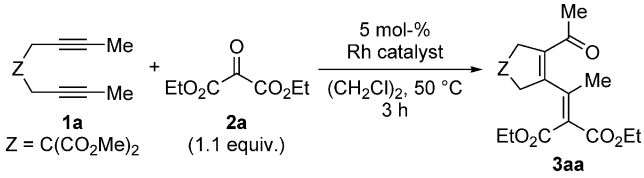
ficient and electron-rich carbonyl compounds. In this paper, we describe our study concerning [2+2+2] cycloadditions of 1,6- and 1,7-diynes with various carbonyl compounds, leading to dienones through thermal electrocyclic ring opening of fused α-pyrans,[13] catalyzed by a cationic rhodium(I)/H_8-binap complex under mild reaction conditions (Scheme 1).[14–16]

Results and Discussion

Cationic Rhodium(I)/H_8-binap Complex Catalyzed [2+2+2] Cycloadditions of 1,6- and 1,7-Diynes with Carbonyl Compounds

We first investigated the reaction of malonate-linked 1,6-diyne **1a** with an electron-deficient carbonyl compound [diethyl ketomalonate (**2a**)] in the presence of various [Rh(cod)$_2$]-BF_4/bisphosphane complexes (5 mol-%) as shown in Table 1. After screening the bisphosphane ligands (Figure 1; Table 1, Entries 1–6), we were pleased to find that the use of H_8-binap showed the highest catalytic activity and selectivity, and dienone **3aa** was obtained in excellent yield (Table 1, Entry 3). Removal of the cod ligand by hydrogenation and the use of the cationic rhodium(I) complex and not the neutral one are essential for this transformation (Table 1, Entries 7 and 8).

Table 1. Screening of rhodium catalysts for [2+2+2] cycloaddition of 1,6-diyne **1a** with diethyl ketomalonate (**2a**).[a]



Entry	Rh catalyst	Yield [%][b]
1	[Rh(cod)$_2$]BF_4/binap	64
2	[Rh(cod)$_2$]BF_4/segphos	21
3	[Rh(cod)$_2$]BF_4/H_8-binap	98
4	[Rh(cod)$_2$]BF_4/biphep	79
5	[Rh(cod)$_2$]BF_4/dppb	75
6	[Rh(cod)$_2$]BF_4/dppf	63
7[c]	[Rh(cod)$_2$]BF_4/H_8-binap	32
8	[Rh(cod)Cl]$_2$/2H_8-binap	0

[a] Rh complex (0.0075 mmol of Rh), bisphosphane (0.075 mmol), **1a** (0.15 mmol), **2a** (0.165 mmol), and (CH_2Cl)$_2$ (1.5 mL) were used. The active catalyst was generated in situ by hydrogenation (H_2: 1 atm, r.t., 0.5 h). [b] Determined by ^{1}H NMR spectroscopy. [c] Without hydrogenation.

Thus, we explored the scope of this process with respect to electron-deficient acyclic carbonyl compounds as shown in Table 2. Not only 1,2,3-tricarbonyl compounds [diethyl ketomalonate (**2a**; Table 2, Entry 1)] but also a variety of 1,2-dicarbonyl compounds [α-keto esters (**2b**–**e**; Table 2, Entries 2–5) and 1,2-diketones (**2f** and **2g**; Table 2, Entries 6 and 7)] reacted with 1,6-diyne **1a** to give the corresponding dienones or α-pyrans in excellent yields under mild conditions.

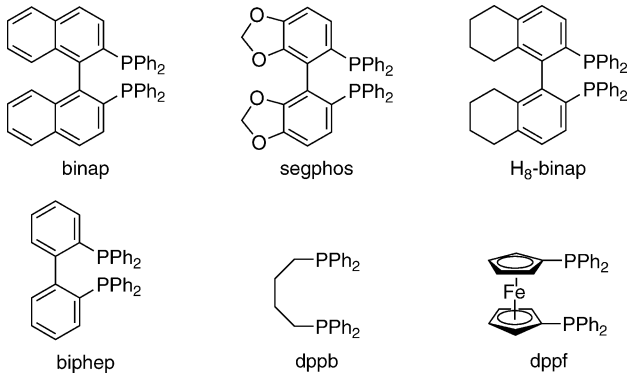
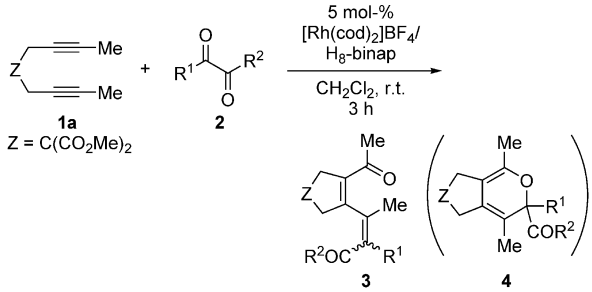


Figure 1. Structures of the bisphosphane ligands.

Table 2. Scope of acyclic tri- and dicarbonyl compounds **2a**–**g** in the reactions with 1,6-diyne **1a**.[a]

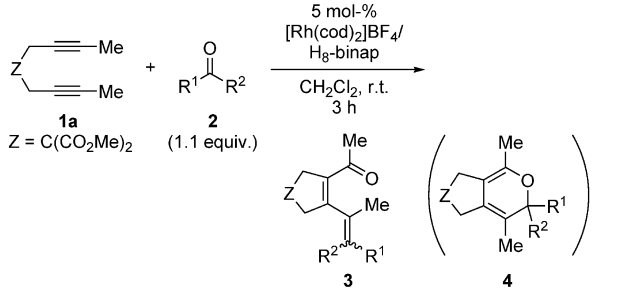


Entry	**2** (R^1, R^2)	**2** [equiv.]	**3**/**4**	% Yield (*E*/*Z*)[b]
1[c]	**2a** (CO_2Et, OEt)	1.1	**3aa**	95
2	**2b** (Me, OEt)	1.5	**3ab**	99 (14:86)
3	**2c** (*i*Pr, OEt)	1.1	**3ac**/**4ac**	87 (**3ac**/**4ac**, 5:>95)[d]
4	**2d** (CF_3, OEt)	1.1	**3ad**/**4ad**	88 (**3ad**/**4ad**, 5:>95)[d]
5	**2e** (Ph, OEt)	1.1	**3ae**	98 (29:71)
6	**2f** (Me, Me)	2.0	**3af**	90 (5:>95)
7	**2g** (Ph, Ph)	1.1	**3ag**	99 (25:75)

[a] [Rh(cod)$_2$]BF_4 (0.015 mmol), H_8-binap (0.015 mmol), **1a** (0.30 mmol), **2** (0.33–0.60 mmol), and CH_2Cl_2 (2.0 mL) were used. [b] Isolated yield. Products were isolated as a mixture of *E*/*Z* isomers. [c] At 50 °C in (CH_2Cl)$_2$. [d] Products were isolated as a mixture of dienone **3** and α-pyran **4**.

The successful [2+2+2] cycloadditions of 1,6-diyne **1a** with electron-deficient acyclic carbonyl compounds prompted our investigation into the reactions of 1,6-diyne **1a** with electron-rich acyclic carbonyl compounds as shown in Table 3. Pleasingly, a variety of aromatic (**2h**–**l**; Table 3, Entries 1–5) and aliphatic aldehydes (**2m**–**o**; Table 3, Entries 6–8) could participate in this reaction to give the corresponding dienones in excellent yields at room temperature. Not only aldehydes but also an electron-rich ketone [acetone (**2p**)] could react with **1a** at 50 °C, although a large excess of **2p** was required (Table 3, Entry 9).[17]

Table 3. Scope of acyclic monocarbonyl compounds **2h**–**p** in the reactions with 1,6-diyne **1a**.[a]



Entry	2 (R^1, R^2)	2 [equiv.]	3/4	% Yield (*E*/*Z*)[b]
1	**2h** (Ph, H)	1.1	**3ah**	97 (90:10)
2	**2i** (4-MeOC$_6$H$_4$, H)	1.1	**3ai**	94 (89:11)
3	**2j** (4-F$_3$CC$_6$H$_4$, H)	1.1	**3aj**	96 (95:5)
4	**2k** (2-MeC$_6$H$_4$, H)	1.1	**3ak**	81 (>95:5)
5	**2l** (2-furyl, H)	1.1	**3al**	>99 (>95:5)
6	**2m** (PhCH$_2$CH$_2$, H)	1.1	**3am**	93 (>95:5)
7	**2n** (Cy, H)	1.1	**3an**	99 (>95:5)
8	**2o** (*t*Bu, H)	1.1	**3ao**	82 (60:40)
9[c]	**2p** (Me, Me)	solvent	**3ap**/**4ap**	51 (**3ap**/**4ap**, 74:26)[d]

[a] [Rh(cod)$_2$]BF$_4$ (0.015 mmol), H_8-binap (0.015 mmol), **1a** (0.30 mmol), **2** (0.33 mmol), and CH_2Cl_2 (2.0 mL) were used. In Entry 9, **2p** was used as the solvent. [b] Isolated yield. Products were isolated as a mixture of *E*/*Z* isomers. [c] Ligand: tol-binap. At 50 °C. [d] Product was isolated as a mixture of dienone **3ap** and α-pyran **4ap**.

The reactions of 1,6-diynes with cyclic carbonyl compounds **2q**–**v** were also examined as shown in Table 4. Five-membered 1,2-dicarbonyl compounds **2q**–**s** reacted with 1,6-diyne **1a** or **1b** at room temperature to give the corresponding dienones in excellent yields (Table 4, Entries 1–3).[18] However, six-membered 1,2-dicarbonyl compound **2t** failed to react with **1a** even at elevated temperatures (80 °C), and the starting materials were recovered (Table 4, Entry 4). Five-membered monocarbonyl compound [cyclopentanone (**2u**)] failed to react with **1a** due to the rapid homo-[2+2+2] cycloaddition of **1a** (Table 4, Entry 5), but six-membered monocarbonyl compound [cyclohexanone (**2v**)] was able to react with **1a** at 50 °C to give a mixture of dienone **3av** and α-pyran **4av** in good yield (Table 4, Entry 6).

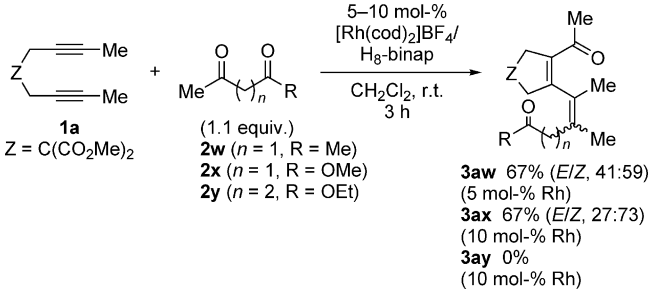
As shown in Tables 2–4, 1,2-dicarbonyl compounds show high reactivity, whereas monocarbonyl compounds show low reactivity in the present [2+2+2] cycloaddition. Therefore, the reactions of 1,6-diyne **1a** with 1,3- and 1,4-dicarbonyl compounds **2w**–**y** (1.1 equiv.) were also examined as shown in Scheme 2. 1,3-Dicarbonyl compounds **2w** and **2x** reacted with **1a** at room temperature to give the corresponding dienones **3aw** and **3ax**, respectively, in good yields, whereas 1,4-dicarbonyl compound **2y** failed to react with **1a** due to the rapid homo-[2+2+2] cycloaddition of **1a**.

Next, the scope of diyne substrates was investigated as shown in Table 5. With respect to 1,6-diynes, not only malonate-linked internal 1,6-diyne **1a** (Table 5, Entries 1 and 2) but also tosylamide-, ether-, and 1,3-dimethoxypropane-linked internal 1,6-diynes **1b**–**e** could be employed for this reaction (Table 5, Entries 3–7). Furthermore, internal 1,7-

Table 4. Scope of cyclic carbonyl compounds **2q**–**v** in the reactions with 1,6-diyne **1a** or **1b**.[a]

Entry	1	2 (equiv.)	3 % Yield (*E*/*Z*)[b]
1	**1b**	**2q** (1.1)	**3bq** >99 (16:84)
2	**1a**	**2r** (1.1)	**3ar** >99 (5:>95)
3[c]	**1a**	**2s** (1.1)	**3as** 93 (5:>95)
4[d]	**1a**	**2t** (1.1)	**3at** <5[e]
5	**1a**	**2u** (solvent)	**3au** 0[f]
6[g]	**1a**	**2v** (solvent)	70 (**3av**/**4av**, 70:30)[h]

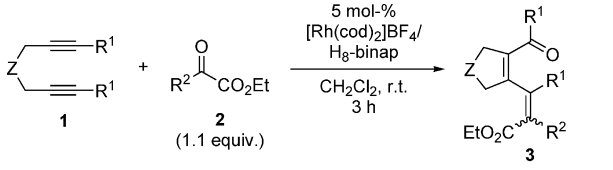
[a] Reactions were conducted by using [Rh(cod)$_2$]BF$_4$ (0.015 mmol), H_8-binap (0.015 mmol), **1** (0.30 mmol), **2** (0.33 mmol), and CH_2Cl_2 (1.5 mL) at r.t. for 3 h. In Entries 5 and 6, ketones **2u** and **2v** were used as the solvent. [b] Isolated yield. Products were isolated as a mixture of *E*/*Z* isomers. [c] $(CH_2Cl)_2$ (3.0 mL) was used. [d] At 80 °C. [e] Diyne **1a** remained unchanged. [f] Homo-[2+2+2] cycloaddition of **1a** proceeded. [g] At 50 °C. [h] Product was isolated as a mixture of dienone **3av** and α-pyran **4av**.



Scheme 2. [2+2+2] Cycloadditions of 1,6-diyne **1a** with 1,3- and 1,4-dicarbonyl compounds **2w**–**y**.

diyne **1f** could also participate in this reaction (Table 5, Entry 8). Although terminal 1,6-diyne **1g** failed to react with keto ester **2e** due to the rapid homo-[2+2+2] cycloaddition of **1g** (Table 5, Entry 9), terminal 1,7-diyne **1h**, which shows low reactivity toward the homo-[2+2+2] cycloaddition, could react with **2e** to give the corresponding dienyl aldehyde **3he** in moderate yield (Table 5, Entry 10).

Table 5. Scope of 1,6- and 1,7-diynes **1a**–**h** in the reactions with **2a** or **2e**.[a]

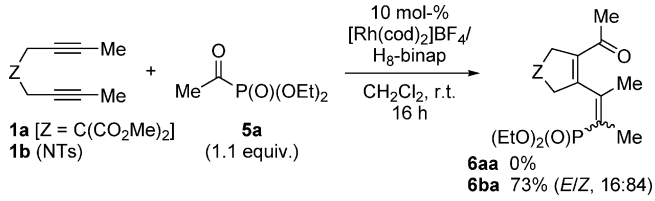


Entry	**1** (Z, R^1)	**2** (R^2)	**3**	% Yield (*E*/*Z*)[b]
1[c]	**1a** [$C(CO_2Me)_2$, Me]	**2a** (CO_2Et)	**3aa**	95
2	**1a** [$C(CO_2Me)_2$, Me]	**2e** (Ph)	**3ae**	98 (29:71)
3	**1b** (NTs, Me)	**2a** (CO_2Et)	**3ba**	88
4	**1b** (NTs, Me)	**2e** (Ph)	**3be**	98 (23:77)
5	**1c** (O, Et)	**2a** (CO_2Et)	**3ca**	84
6	**1d** (O, Me)	**2e** (Ph)	**3de**	94 (24:76)
7	**1e** [$C(CH_2OMe)_2$, Me]	**2e** (Ph)	**3ee**	96 (26:74)
8	**1f** (CH_2CH_2, Me)	**2e** (Ph)	**3fe**	84 (13:87)
9	**1g** (NTs, H)	**2e** (Ph)	**3ge**	0[d]
10	**1h** (CH_2CH_2, H)	**2e** (Ph)	**3he**	55 (36:64)

[a] $[Rh(cod)_2]BF_4$ (0.015 mmol), H_8-binap (0.015 mmol), **1** (0.30 mmol), **2** (0.33 mmol), and CH_2Cl_2 (1.5 mL) were used. [b] Isolated yield. Products were isolated as a mixture of *E*/*Z* isomers. [c] At 50 °C in $(CH_2Cl)_2$. [d] Homo-[2+2+2] cycloaddition of **1g** proceeded.

Cationic Rhodium(I)/H_8-binap Complex Catalyzed [2+2+2] Cycloadditions of 1,6- and 1,7-Diynes with Acyl Phosphonates

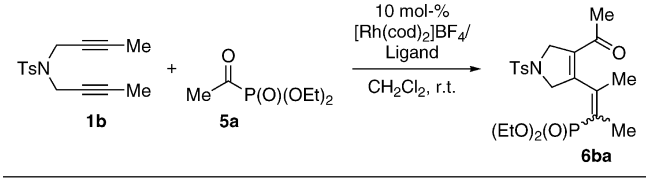
We have recently found that alkynylphosphonates are suitable substrates for cationic rhodium(I)/H_8-binap complex catalyzed [2+2+2] cycloadditions.[19] Therefore, we anticipated that acyl phosphonates, which are useful building blocks for the synthesis of functionalized phosphorus compounds through alkylation[20] or olefination,[21] would show high reactivity in cationic rhodium(I)/H_8-binap complex catalyzed [2+2+2] cycloadditions.[22] Unfortunately, acetyl phosphonates **5a** failed to react with malonate-linked 1,6-diyne **1a**, which was recovered unchanged (Scheme 3). Surprisingly, **5a** smoothly reacted with tosylamide-linked 1,6-diyne **1b** at room temperature to give desired dienone **6ba** in good yield by using 10 mol-% of the $[Rh(cod)_2]BF_4/H_8$-binap complex (Scheme 3).



Scheme 3. Reactions of 1,6-diynes **1a** and **1b** with acetyl phosphonate **5a**.

Reaction conditions for the [2+2+2] cycloaddition of **1b** with **5a** were then optimized as shown in Table 6. Like the cycloadditions with tricarbonyl compound **2a**, H_8-binap was the best ligand for this reaction (Table 6, Entries 1–4). The use of 2 equiv. of **5a** further improved the yield of **6ba**, and the reaction could be completed within 1 h (Table 6, Entry 5). Unfortunately, decreasing the catalyst loading to 5 mol-% dramatically lowered the yield of **6ba** (Table 6, Entry 6).

Table 6. Optimization of reaction conditions for the rhodium-catalyzed [2+2+2] cycloaddition of 1,6-diyne **1b** with acetyl phosphonate **5a**.[a]



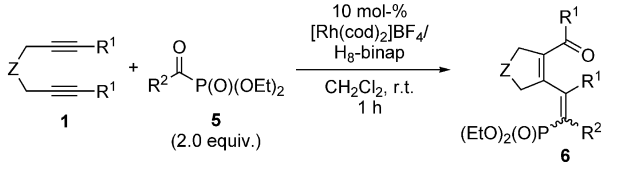
Entry	Ligand	**5a** [equiv.]	Catalyst [%]	Time [h]	Yield [%][b]
1	H_8-binap	1.1	10	16	73
2	binap	1.1	10	16	55
3	segphos	1.1	10	16	67
4	dppb	1.1	10	16	13
5	H_8-binap	2.0	10	1	84
6	H_8-binap	2.0	5	72	30

[a] $[Rh(cod)_2]BF_4$ (0.0050–0.010 mmol), ligand (0.0050–0.010 mmol), **1b** (0.10 mmol), **5a** (0.11–0.20 mmol), and CH_2Cl_2 (1.5 mL) were used. [b] Isolated yield.

The scope of this process was then examined with respect to both the acyl phosphonates and the diynes as shown in Table 7. Not only acetyl phosphonate (**5a**; Table 7, Entry 1) but also benzoyl phosphonate (**5b**; Table 7, Entry 2) could participate in this reaction. In contrast, the reactivity of diynes was highly dependent on their own structures. Tosylamide- and ether-linked internal 1,6-diynes **1b** and **1d** could react with **5b** (Table 7, Entries 2 and 3), whereas malonate- and dimethoxypropane-linked internal 1,6-diynes **1a** and **1e** and internal 1,7-diyne **1f** failed to react with **5b**, and they remained unchanged (Table 7, Entries 4–6). In the case of terminal diynes, although 1,6-diyne **1g** failed to react with **5b** due to the rapid homo-[2+2+2] cycloaddition of **1g** (Table 7, Entry 7), 1,7-diyne **1h** could react with acyl phos-

phonates **5a** and **5b** to give the corresponding dienyl aldehydes **6ha** and **6hb**, respectively, in good yields (Table 7, Entries 8 and 9).

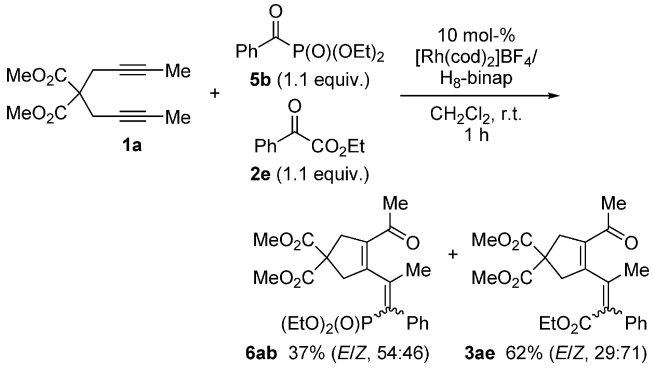
Table 7. Scope of 1,6- and 1,7-diynes **1** in the reactions with **5a** or **5b**.[a]



Entry	**1** (Z, R^1)	**5** (R^2)	**6**	Yield [%][b] *E* isomer	*Z* isomer
1	**1b** (NTs, Me)	**5a** (Me)	**6ba**	84 (*E*/*Z*, 12:88)[c]	
2	**1b** (NTs, Me)	**5b** (Ph)	**6bb**	36	54
3	**1d** (O, Me)	**5b** (Ph)	**6db**	ca 13[d]	ca 20[d]
4	**1a** [$C(CO_2Me)_2$, Me]	**5b** (Ph)	**6ab**	0[e]	0[e]
5	**1e** [$C(CH_2OMe)_2$, Me]	**5b** (Ph)	**6eb**	0[e]	0[e]
6	**1f** (CH_2CH_2, Me)	**5b** (Ph)	**6fb**	0[e]	0[e]
7	**1g** (NTs, H)	**5b** (Ph)	**6gb**	0[f]	0[f]
8	**1h** (CH_2CH_2, H)	**5a** (Me)	**6ha**	42	28
9	**1h** (CH_2CH_2, H)	**5b** (Ph)	**6hb**	48	28

[a] $[Rh(cod)_2]BF_4$ (0.020 mmol), H_8-binap (0.020 mmol), **1** (0.20 mmol), **5** (0.40 mmol), and CH_2Cl_2 (1.5 mL) were used. [b] Isolated yield. [c] Product was isolated as a mixture of *E*/*Z* isomers. [d] The product could not be isolated in a pure form. [e] Diyne **1** remained unchanged. [f] Homo-[2+2+2] cycloaddition of **1g** proceeded.

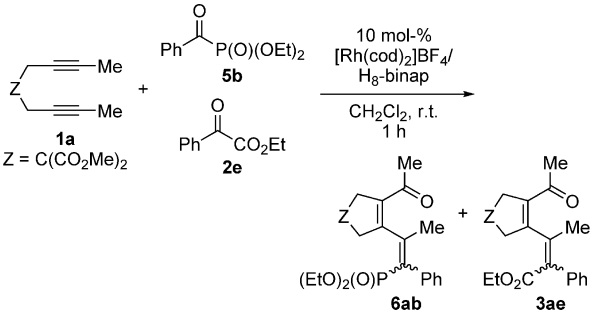
As α-keto ester **2e** is a highly reactive coupling partner for the cationic rhodium(I)/H_8-binap catalyzed [2+2+2] cycloaddition with 1,6-diyne **1a** (Table 2, Entry 5), it would be interesting to investigate a competitive [2+2+2] cycloaddition of **1a** with acyl phosphonate **5b** and α-keto ester **2e**. We anticipated that **1a** would selectively react with **2e**, leading to ester-substituted dienone **3ae**. Contrary to our expectation, **1a** reacted with both **5b** and **2e** (Scheme 4).



Scheme 4. Competitive [2+2+2] cycloaddition of 1,6-diyne **1a** with carbonyl compounds **5b** and **2e**.

As α-keto ester **2e** plays an important role in the present catalysis, the amount of **2e** was examined as shown in Table 8. Decreasing the amount of **2e** decreased the yield of dienone **3ae** and increased the yield of dienone **6ab** (Table 8, Entries 3–5).

Table 8. [2+2+2] Cycloadditions of 1,6-diyne **1a** with benzoyl phosphonate **5b** in the presence of ethyl phenylglyoxylate (**2e**).[a]

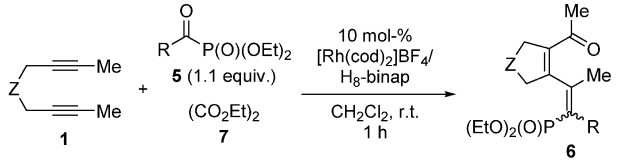


Entry	**5b** [equiv.]	**2e** [equiv.]	**6ab** % Yield (*E*/*Z*)[b]	**3ae** % Yield (*E*/*Z*)[c]
1	–	1.1	–	96 (26:74)
2	1.1	–	0[d]	–
3	1.1	2.0	5 (45:55)	76 (29:71)
4	1.1	1.1	37 (52:48)	62 (29:71)
5	1.1	0.2	74 (52:48)	19 (29:71)

[a] $[Rh(cod)_2]BF_4$ (0.020 mmol), H_8-binap (0.020 mmol), **1a** (0.20 mmol), **5b** (0–0.22 mmol), **2e** (0–0.40 mmol), and CH_2Cl_2 (1.5 mL) were used. [b] Isolated yield. *E*/*Z* isomers were isolated separately. [c] Isolated yield. Products were isolated as a mixture of *E*/*Z* isomers. [d] Diyne **1a** remained unchanged.

We assumed that bidentate coordination of α-keto ester **2e** to rhodium might promote the formation of the desired 1:1 rhodium complex of 1,6-diyne **1a** and benzoyl phosphonate **5b**, which will be discussed in the section of the reaction mechanism. Therefore, the reaction of **1a** and **5b** in the presence of chelating diethyl oxalate (**7**), which cannot react with **1a**, was examined as shown in Table 9.[23] We were pleased to find that desired product **6ab** was obtained in excellent yield in the presence of 1.1 equiv. of **7** (Table 9,

Table 9. [2+2+2] cycloadditions of 1,6- and 1,7-diynes **1** with acyl phosphonates **5** in the presence of diethyl oxalate (**7**).[a]



Entry	**1** (Z)	**5** (R)	**7** [equiv.]	**6**	Yield [%][b] *E* isomer	*Z* isomer
1	**1a** [Z = $C(CO_2Me)_2$]	**5b** (Ph)	1.1	**6ab**	49	45
2	**1a** [Z = $C(CO_2Me)_2$]	**5b** (Ph)	0.2	**6ab**	49	47
3	**1a** [Z = $C(CO_2Me)_2$]	**5a** (Me)	0.2	**6aa**	9	81
4	**1d** (Z = O)	**5b** (Ph)	0.2	**6db**	ca 30[c]	51
5	**1d** (Z = O)	**5a** (Me)	0.2	**6da**	74 (*E*/*Z*, 12:88)[d]	
6	**1e** [Z = $C(CH_2OMe)_2$]	**5b** (Ph)	0.2	**6eb**	41	41
7	**1e** [Z = $C(CH_2OMe)_2$]	**5a** (Me)	0.2	**6ea**	12	88
8	**1f** (Z = CH_2CH_2)	**5b** (Ph)	0.2	**6fb**	0[e]	0[e]

[a] $[Rh(cod)_2]BF_4$ (0.020 mmol), H_8-binap (0.020 mmol), **1** (0.20 mmol), **5** (0.22 mmol), **7** (0.040–0.22 mmol), and CH_2Cl_2 (1.5 mL) were used. [b] Isolated yield. [c] The product could not be isolated in a pure form. [d] Product was isolated as a mixture of *E*/*Z* isomers. [e] Diyne **1f** remained unchanged.

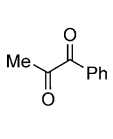
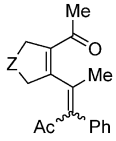
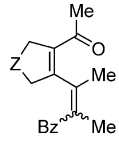
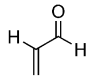
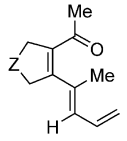
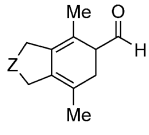
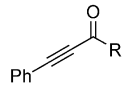
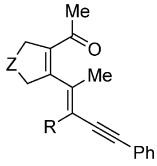
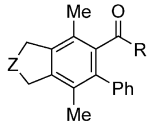
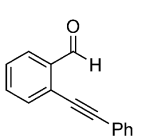
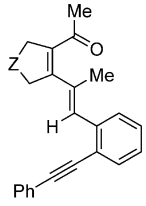
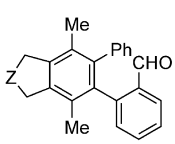
Entry 1). The amount of **7** could be reduced to a catalytic amount (Table 9, Entry 2). Under these optimized reaction conditions, the reactions of both benzoyl and acetyl phosphonates **5b** and **5a** with malonate-, ether-, and dimethoxypropane-linked 1,6-diynes **1a**, **1d**, and **1e**, respectively, proceeded in high yields (Table 9, Entries 2–7). However, 1,7-diyne **1f** failed to react with **5b** even in the presence of **7** (Table 9, Entry 8).

Cationic Rhodium(I)/H_8-binap Complex Catalyzed Chemo- or Regioselective [2+2+2] Cycloadditions of 1,6-Diynes with Carbonyl Compounds

Chemoselective [2+2+2] cycloadditions of 1,6-diyne **1a** with bifunctional carbonyl compounds **8** were examined, as shown in Table 10. As both dimethyl and diphenyl-substituted symmetrical 1,2-diketones **2f** and **2g** reacted with 1,6-diyne **1a** to give the corresponding dienones **3af** and **3ag**, respectively, in high yields (Table 2, Entries 6 and 7), a chemoselective cycloaddition between acetyl and benzoyl groups is of interest. The study revealed that the benzoyl group of unsymmetrical 1,2-diketone **8a** was more reactive than its acetyl group to give dienone **9aa** as a major product (Table 10, Entry 1). As the cationic rhodium(I)/H_8-binap complex is a highly effective catalyst for [2+2+2] cycloadditions of 1,6-diynes with alkenes[24] and alkynes,[18,25] chemoselective cycloadditions involving alkenyl and alkynyl carbonyl compounds were also examined. In the case of acrolein (**8b**), the carbonyl group of **8b** exclusively reacted with **1a** (Table 10, Entry 2).[26] Like acrolein (**8b**), the carbonyl groups of alkynyl aldehyde **8c** and alkynyl keto ester **8e** exclusively reacted with **1a** (Table 10, Entries 3 and 5), but the alkyne moiety exclusively reacted with **1a** in the case of alkynyl ketone **8d** to furnish hexasubstituted benzene **10ad** in excellent yield (Table 10, Entry 4).[27] Furthermore, the carbonyl group of 2-alkynylbenzaldehyde **8f** exclusively reacted with **1a** (Table 10, Entry 6).

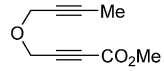
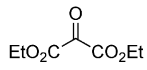
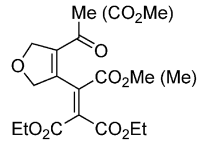
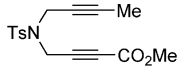
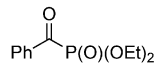
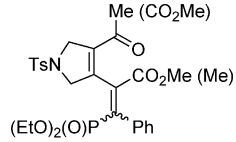
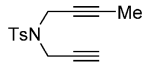
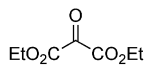
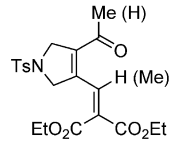
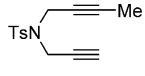
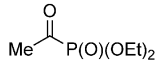
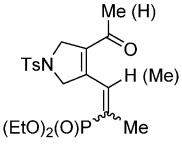
Next, regioselective [2+2+2] cycloadditions of unsymmetrical 1,6-diynes **1i**–**k** with carbonyl compounds were also examined, as shown in Table 11. The reaction of un-

Table 10. Chemoselective [2+2+2] cycloadditions of bifunctional carbonyl compounds **8a**–**f** with 1,6-diyne **1a** [Z = $C(CO_2Me)_2$].[a]

Entry	**8** (equiv.)	**9**/**10** % Yield[b]	
1	 **8a** (1.1)	 **9aa** (*E*/*Z*, 12:88)	 **10aa** (*E*/*Z*, 13:87)
		91% (**9aa**/**10aa**, 70:30)	
2[c]	 **8b** (5.0)	 **9ab** 55% (*E*/*Z*, >95:5)	 **10ab** 0%
3	 **8c** (R = H, 1.1)	 **9ac** 90% (*E*/*Z*, >95:5)	 **10ac** 0%
4	**8d** (R = Me, 1.1)	**9ad** 0%	**10ad** 99%
5	**8e** (R = CO_2Et, 1.1)	**9ae** 96% (*E*/*Z*, 5:>95)	**10ae** 0%
6	 **8f** (1.1)	 **9af** 95% (*E*/*Z*, >95:5)	 **10af** 0%

[a] Reactions were conducted by using $[Rh(cod)_2]BF_4$ (0.015 mmol), H_8-binap (0.015 mmol), **1a** (0.30 mmol), **8** (0.33–1.50 mmol), and CH_2Cl_2 (1.5 mL) at r.t. for 3 h. [b] Isolated yield. Products were isolated as a mixture of *E*/*Z* isomers. [c] For 8 h.

Table 11. Regioselective [2+2+2] cycloadditions of unsymmetrical 1,6-diynes **1i**–**k** with carbonyl compounds **2a**, **5a**, and **5b**.

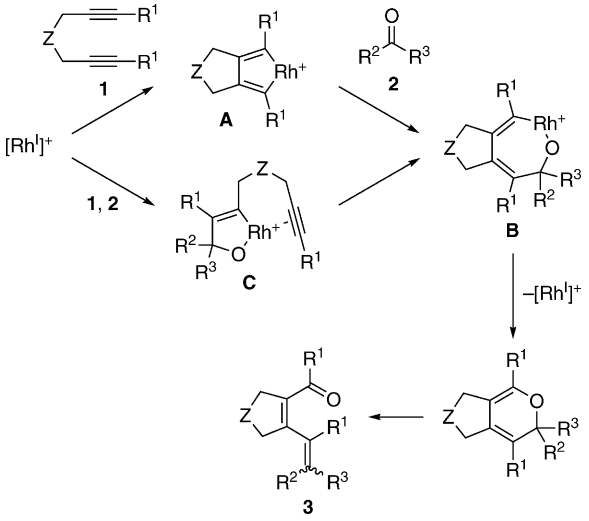
Entry	**1**	**2** or **5** (equiv.)	**3** (**11**) or **6** (**12**) % Yield[a] (**3**/**11** or **6**/**12**)
1[b]	 **1i**	 **2a** (1.1)	 **3ia** (**11ia**) 77% (75:25)
2[c]	 **1j**	 **5b** (2.0)	 **6jb** (**12jb**) 71% (>99:1) (*E*/*Z*, 59:41)
3[b]	 **1k**	 **2a** (1.1)	 **3ka** (**11ka**) <10%[d]
4[c]	 **1k**	 **5a** (2.0)	 **6ka** (**12ka**) 78% (>99:1) (*E*)-**6ka** 31% (*Z*)-**6ka** 47%

[a] Isolated yield. [b] Reactions were conducted with the use of $[Rh(cod)_2]BF_4$ (0.015 mmol), H_8-binap (0.015 mmol), **1** (0.30 mmol), and **2a** (0.33 mmol) at 80 °C in $(CH_2Cl)_2$ (1.5 mL) (Entry 1) or at r.t. (Entry 3) in CH_2Cl_2 (1.5 mL) for 3 h. [c] Reactions were conducted with the use of $[Rh(cod)_2]BF_4$ (0.020 mmol), H_8-binap (0.020 mmol), **1** (0.20 mmol), **5** (0.40 mmol), and CH_2Cl_2 (1.5 mL) at r.t. for 1 h. [d] Homo-[2+2+2] cycloaddition of **1k** proceeded.

symmetrical 1,6-diyne **1i**, possessing a methyl group and a methoxycarbonyl group at each alkyne terminus, with diethyl ketomalonate (**2a**) furnished the corresponding dienones **3ia** and **11ia** with moderate regioselectivity (Table 11, Entry 1). On the contrary, the reaction of 1,6-diyne **1j** with benzoyl phosphonate **5b** furnished the corresponding dienone **6jb** with complete regioselectivity (Table 11, Entry 2). Although **2a** reacted with unsymmetrical 1,6-diyne **1k**, possessing a methyl group at an alkyne terminus, in very low yield due to the rapid homo-[2+2+2] cycloaddition of **1k** (Table 11, Entry 3), acetyl phosphonate **5a** smoothly reacted with **1k** to give the corresponding dienone **6ka** in good yield with complete regioselectivity (Table 11, Entry 4).

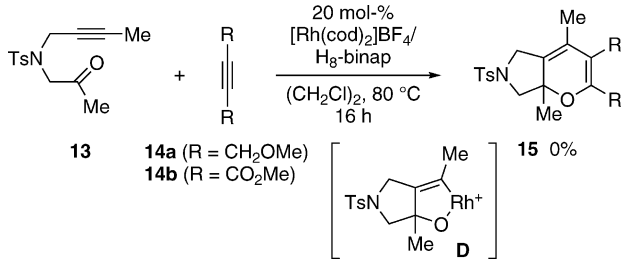
Mechanistic Consideration Regarding Cationic Rhodium(I)/H_8-binap Complex Catalyzed [2+2+2] Cycloadditions of 1,6- and 1,7-Diynes with Carbonyl Compounds

Scheme 5 depicts a possible mechanism for the cationic rhodium(I)/H_8-binap complex catalyzed [2+2+2] cycloaddition of diyne **1** with carbonyl compound **2**. Diyne **1** reacts with rhodium to generate rhodacyclopentadiene intermediate **A**. Insertion of carbonyl compound **2** into intermediate **A** generates intermediate **B**.[28] Reductive elimination of rhodium followed by electrocyclic ring opening furnishes dienone **3**. Alternatively, diyne **1** and carbonyl compound **2** react with rhodium to generate oxarhodacyclopentene intermediate **C**. Insertion of another alkyne moiety of **1** into intermediate **C** also can generate the same intermediate **B**.



Scheme 5. Two possible pathways for the cationic rhodium(I)/H_8-binap complex catalyzed [2+2+2] cycloaddition of diyne **1** with carbonyl compound **2**.

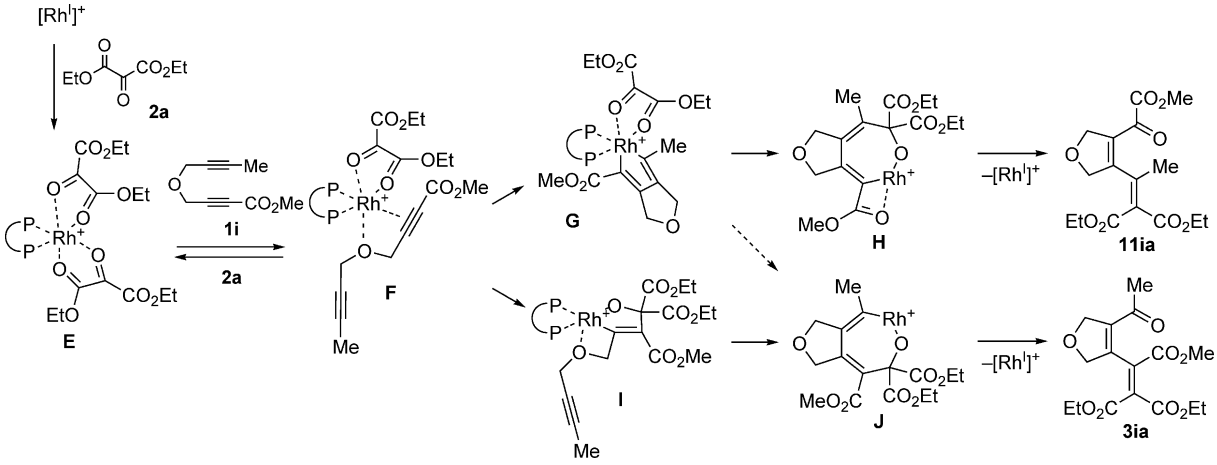
In the reactions of diynes with aldehydes, homo-[2+2+2] cycloaddition of diynes proceeded in very low yields. Oxarhodacyclopentene intermediate **C** could not furnish the homo-[2+2+2] cycloaddition products of diynes, which suggests that oxarhodacyclopentene **C** might be the major intermediate. In contrast, homo-[2+2+2] cycloaddition of diynes proceeded in high yields in the reactions of diynes with electron-rich ketones [acetone (**2p**) and cyclohexanone (**2v**)]. Therefore, the formation of rhodacyclopentadiene intermediate **A** is more likely. Indeed, the reactions of alkynyl ketone **13**, which would generate bicyclic oxarhodacyclopentene intermediate **D**, with monoynes **14** did not furnish the corresponding cycloadducts **15**, and **12** was recovered unchanged even at the elevated temperature (Scheme 6).[29]



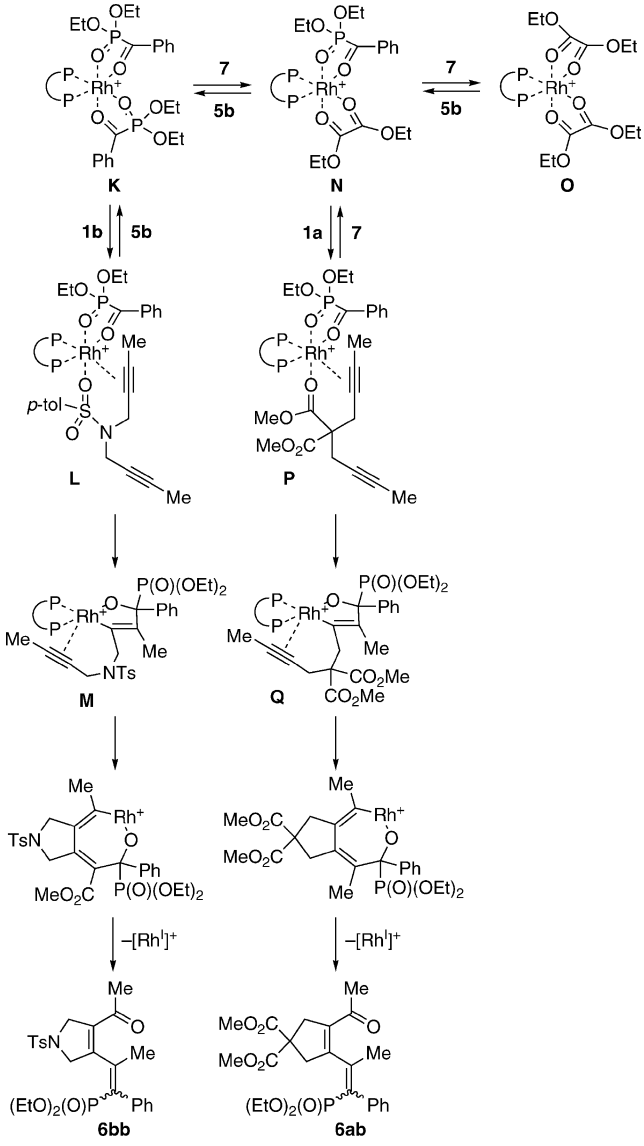
Scheme 6. Reactions of alkynyl ketone **13** and monoynes **14**.

A possible mechanism for the regioselective [2+2+2] cycloaddition of unsymmetrical 1,6-diyne **1i** with tricarbonyl compound **2a** is shown in Scheme 7. The reaction of **1i** and **2a** with rhodium generates an equilibrium mixture of intermediates **E** and **F** through the bidentate coordination of **2a** and **1i**. Oxidative coupling of two alkyne moieties of **1i** furnishes rhodacyclopentadiene intermediate **G**. Insertion of the carbonyl group of **2a** would furnish intermediate **H** and/or intermediate **J**. However, the regioselective formation of intermediate **H** might be predominant due to the steric bulk of the methoxycarbonyl group of intermediate **G** and the stabilization of intermediate **H** through the coordination of the carbonyl oxygen atom to the cationic rhodium. Reductive elimination of rhodium from intermediate **H** followed by electrocyclic ring opening furnishes dienone **11ia**. Alternatively, oxidative coupling of the highly reactive electron-deficient alkyne moiety[25] of **1i** and the carbonyl group of **2a** would furnish oxarhodacyclopentene intermediate **I**. Insertion of another alkyne moiety of **1i** furnishes intermediate **J**. Reductive elimination of rhodium followed by electrocyclic ring opening furnishes regioisomeric dienone **3ia**. The reaction of **1i** and **2a** might proceed preferably through oxarhodacyclopentene **I**, which results in the formation of dienone **3ia** as a major product. According to this consideration and the low yields of homo-[2+2+2] cycloaddition byproducts of diynes, oxarhodacyclopentene **C** (Scheme 5) would be a major intermediate in the reactions of diynes with tri- and dicarbonyl compounds.

A possible explanation for the significant acceleration of the [2+2+2] cycloadditions with acyl phosphonates **5b** by employing tosylamide-linked 1,6-diyne **1b** as a coupling partner or adding diethyl oxalate (**7**) to malonate-linked 1,6-diyne **1a** is shown in Scheme 8. The reaction of tosylamide-linked 1,6-diyne **1b** and acyl phosphonate **5b** with rhodium generates an equilibrium mixture of intermediates **K** and **L** through the bidentate coordination of both **1b** and **5b** to rhodium. Intermediate **L** subsequently undergoes oxidative coupling, leading to oxarhodacyclopentene intermediate **M**. Insertion of another alkyne moiety of **1b** followed



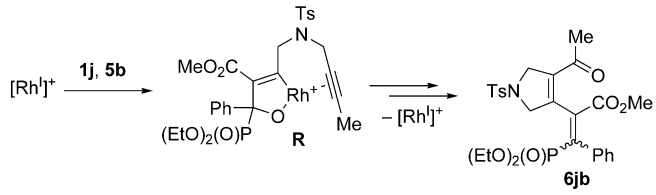
Scheme 7. Possible mechanism for the regioselective [2+2+2] cycloaddition of unsymmetrical 1,6-diyne **1i** with 1,2,3-tricarbonyl compound **2a**.



Scheme 8. Possible mechanism for rhodium-catalyzed [2+2+2] cycloadditions of tosylamide-linked 1,6-diyne **1b** with benzoyl phosphonate **5b** and malonate-linked 1,6-diyne **1a** with **5b** in the presence of diethyl oxalate (**7**).

by reductive elimination of rhodium and electrocyclic ring opening furnishes dienone **6bb**. The absence of homo-[2+2+2] cycloaddition product of **1b** through the rhodacyclopentadiene intermediate would support this mechanism. In the reaction of malonate-linked 1,6-diyne **1a**, acyl phosphonate **5b**, and rhodium, two molecules of **5b** coordinate to rhodium in a bidentate fashion to generate intermediate **K** as a result of the higher coordination ability of **5b** than that of **1a**, which results in no conversion of **1a**. In contrast, an equilibrium mixture of intermediates **K**, **N**, and **O** would be generated in the presence of diethyl oxalate (**7**). Subsequent ligand exchange between **1a** and weakly coordinated **7** generates the desired 1:1 rhodium complex **P** of **1a** and **5b**, which furnishes dienone **6ab** through oxarhodacyclopentene intermediate **Q**.[30] Successful [2+2+2] cycloadditions of dimethoxypropane-linked 1,6-diyne **1e** with acyl phosphonates **5** in the presence of diethyl oxalate (**7**) could reasonably be explained by the same mechanism. Ligand exchange between 1,7-diyne **1f** bearing no heteroatom in the tether and **7** would be difficult to proceed, which results in no conversion of **1f**.

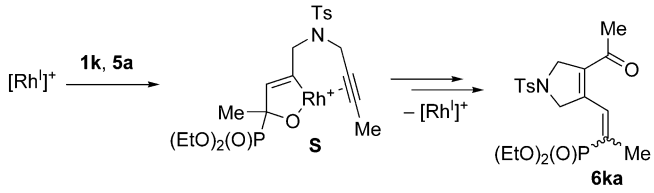
The exclusive formation of dienone **6jb** from unsymmetrical 1,6-diyne **1j** and benzoyl phosphonate **5b** might be explained by the mechanism shown in Scheme 9. Oxidative coupling of the highly reactive terminal alkyne moiety of **1j** and the carbonyl group of **5b** furnishes oxarhodacyclopentene intermediate **R**, which provides dienone **6jb**.



Scheme 9. Possible mechanism for the regioselective [2+2+2] cycloaddition of unsymmetrical 1,6-diyne **1j** with benzoyl phosphonate **5b**.

Like the formation of **6jb**, the exclusive formation of dienone **6ka** from unsymmetrical 1,6-diyne **1k** and acetyl phosphonate **5a** might be explained by oxidative coupling

of the highly reactive terminal alkyne moiety[25] of **1k** and the carbonyl group of **5a**, leading to oxarhodacyclopentene intermediate **S** (Scheme 10).[31]



Scheme 10. Possible mechanism for the regioselective [2+2+2] cycloaddition of unsymmetrical 1,6-diyne **1k** with acetyl phosphonate **5a**.

Finally, complete intermolecular [2+2+2] cycloadditions of two terminal monoynes with activated carbonyl compounds were investigated at room temperature in the presence of the [Rh(cod)$_2$]BF$_4$/H_8-binap complex (5 mol-%). Methyl propargyl ether (**16a**, Figure 2) failed to react with diethyl ketomalonate (**2a**) as a result of the rapid homo-cyclotrimerization, leading to trisubstituted benzenes **17** (Figure 2). Under the same reaction conditions, no conversion of 1-dodecyne (**16b**, Figure 2) was observed. Similarly, the homo-cyclotrimerization of **16a** and no conversion of **16b** were observed in the reactions with benzoyl phosphonate **5b**. Thus, the use of chelating diynes is necessary to promote the desired [2+2+2] cycloaddition of two alkyne units with carbonyl compounds.

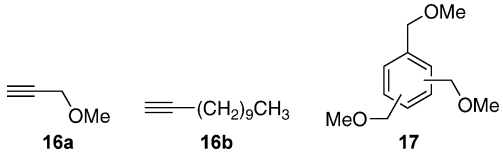


Figure 2. Terminal monoynes **16** and homo-cyclotrimerization product **17**.

Conclusions

In conclusion, we have established that a cationic rhodium(I)/H_8-binap complex catalyzes [2+2+2] cycloadditions of a variety of 1,6- and 1,7-diynes with both electron-deficient and electron-rich carbonyl compounds, leading to dienones in high yields under mild reaction conditions. The reactions of diynes with carbonyl compounds might proceed via an oxarhodacyclopentene intermediate and/or a rhodacyclopentadiene intermediate depending on the structures of the carbonyl compounds. In the reactions with acyl phosphonates, the reactivity of 1,6- and 1,7-diynes was highly dependent on their own structures. The addition of chelating diethyl oxalate effectively promoted the [2+2+2] cycloadditions presumably as a result of the equilibrium formation of the desired 1:1 rhodium complex of the diyne and the acyl phosphonate by facile ligand exchange between the diyne and weakly coordinated diethyl oxalate. In the reactions involving bifunctional carbonyl compounds or unsymmetrical 1,6-diynes, high chemo- or regioselectivities were observed.

Experimental Section

General Methods: ^{1}H NMR spectra were recorded at 300 MHz (JEOL AL 300). ^{13}C NMR spectra were obtained with complete proton decoupling at 75 MHz (JEOL AL 300). HRMS data were obtained with a Bruker micrOTOF Focus II and a JEOL JMS-700 instrument. Infrared spectra were obtained with a JASCO FT/IR-4100. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

Starting Materials: Diynes **1a**,[32] **1b**,[11c] **1c**,[25g] **1d**,[33] **1e**,[32] **1g**,[34] **1i**,[35] **1j**,[35] and **1k**[3] and carbonyl compounds **2e**,[36] **8c**,[37] **8e**,[38] and **8f**[18] were prepared according to literature procedures. Anhydrous CH_2Cl_2 (No. 27099-7) and anhydrous $(CH_2Cl)_2$ (No. 28450-5) were obtained from Aldrich and used as received. The H_8-binap and segphos ligands were obtained from Takasago International Corporation. Rhodium complexes were obtained from Umicore. All other reagents were obtained from commercial sources and used as received.

Typical Procedure for the [2+2+2] Cycloaddition of Diynes with Carbonyl Compounds: The H_8-binap ligand (9.5 mg, 0.015 mmol) and [Rh(cod)$_2$]BF$_4$ (6.1 mg, 0.015 mmol) were dissolved in CH_2Cl_2 (2.0 mL), and the mixture was stirred at room temperature for 5 min. H_2 was introduced into the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness and dissolved in CH_2Cl_2 (0.5 mL). To this solution was added dropwise a solution of **1a** (70.9 mg, 0.300 mmol) and **2e** (58.8 mg, 0.330 mmol) in CH_2Cl_2 (1.5 mL) at room temperature. The mixture was stirred at room temperature for 3 h. The resulting solution was concentrated and purified by preparative TLC (hexane/ethyl acetate, 3:1), which furnished **3ae** (121.4 mg, 0.293 mmol, 98% yield; Table 2, Entry 5) as a pale-yellow oil. *E*/*Z*, 29:71. IR (neat): $\tilde{\nu}$ = 2954, 1738, 1660, 1268, 732 cm^{-1}. Data for the *Z* isomer: ^{1}H NMR ($CDCl_3$): δ = 7.42–7.30 (m, 3H), 7.29–7.23 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 6H), 3.47 (t, *J* = 1.5 Hz, 2H), 3.38 (t, *J* = 1.5 Hz, 2H), 2.33 (s, 3H), 1.87 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm. Data for the *E* isomer: ^{1}H NMR ($CDCl_3$): δ = 7.29–7.23 (m, 3 H), 7.16–7.10 (m, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 3.65 (s, 6 H), 3.16 (t, *J* = 1.5 Hz, 2 H), 3.09 (t, *J* = 1.5 Hz, 2 H), 2.23 (s, 3 H), 2.19 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 195.6, 171.5, 171.2, 167.8, 166.8, 152.7, 150.6, 141.9, 140.5, 136.2, 135.8, 135.2, 133.4, 132.2, 132.1, 129.0, 128.29, 128.25, 128.0, 127.7, 127.6, 60.9, 57.0, 56.6, 53.0, 45.7, 45.1, 41.1, 28.7, 28.6, 20.2, 19.8, 14.1, 13.9 ppm. HRMS (EI): calcd. for $C_{23}H_{26}O_7$ 414.1679 [M]$^+$; found 414.1733.

Typical Procedure for the [2+2+2] Cycloaddition of Diynes with Acyl Phosphonates in the Presence of Diethyl Oxalate: The H_8-binap ligand (12.6 mg, 0.020 mmol) and [Rh(cod)$_2$]BF$_4$ (8.1 mg, 0.020 mmol) were dissolved in CH_2Cl_2 (2.0 mL), and the mixture was stirred at room temperature for 5 min. H_2 was introduced into the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness and dissolved in CH_2Cl_2 (0.5 mL). To this solution was added dropwise a solution of **1a** (47.3 mg, 0.200 mmol), **7** (5.8 mg, 0.040 mmol), and **5b** (53.3 mg, 0.220 mmol) in CH_2Cl_2 (1.0 mL) at room temperature. The mixture was stirred at room temperature for 1 h. The resulting solution was concentrated and purified by preparative TLC (hexane/ethyl acetate/triethylamine, 5:3:1), which furnished (*E*)-**6ab** (46.7 mg, 0.0976 mmol, 49% yield) as a pale-yellow oil and (*Z*)-**6ab** (44.6 mg, 0.0932 mmol, 47% yield; Table 9, Entry 2) as a pale-yellow oil. Data for (*E*)-**6ab**: IR (neat): $\tilde{\nu}$ = 2984, 2955, 2909, 1738, 1685, 1238, 1024, 703 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.25–7.15 (m, 3 H), 7.07–6.97 (m, 2 H), 4.12–3.91 (m, 4 H), 3.60 (s, 6 H), 3.10–3.02 (m, 2 H), 2.95 (s, 2 H), 2.35 (d, *J* = 3.3 Hz,

3 H), 2.18 (s, 3 H), 1.20 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 195.4, 171.0, 152.0, 151.7, 151.6, 151.4, 137.4, 137.3, 133.8, 129.8, 128.8, 128.7, 127.8, 127.5, 127.3, 61.9, 61.8, 56.8, 53.0, 44.9, 40.8, 29.0, 20.2, 20.1, 16.2, 16.1 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 15.6 ppm. HRMS (ESI): calcd. for $C_{24}H_{31}NaO_8P$ 501.1654 [M + Na]$^+$; found 501.1648. Data for (*Z*)-**6ab**: IR (neat): $\tilde{\nu}$ = 2984, 2951, 2905, 1737, 1659, 1254, 1022, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.40–7.28 (m, 3 H), 7.22–7.16 (m, 2 H), 3.96–3.70 (m, 4 H), 3.74 (s, 6 H), 3.70–3.30 (m, 4 H), 2.33 (s, 3 H), 1.79 (d, J = 2.4 Hz, 3 H), 1.10 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 195.8 152.4, 152.2, 150.1, 150.0, 136.8, 136.6, 133.9, 130.5, 129.11, 129.05, 128.4, 128.0, 127.5, 127.4, 61.9, 61.8, 57.3, 53.0, 45.6, 41.0, 28.9, 21.1, 20.9, 16.1, 16.0 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 14.7 ppm. HRMS (ESI): calcd. for $C_{24}H_{31}NaO_8P$ 501.1654 [M + Na]$^+$; found 501.1642.

Supporting Information (see footnote on the first page of this article): Characterization data for all new compounds including ^{1}H and ^{13}C NMR spectra and synthesis of compound **13**.

Acknowledgments

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[1] For reviews on transition-metal-catalyzed [2+2+2] cycloadditions, see: a) K. Tanaka, *Chem. Asian J.*, DOI: 10.1002/asia.200800378; b) J. A. Varela, C. Saá, *Synlett* **2008**, 2571–2578; c) T. Shibata, K. Tsuchikama, *Org. Biomol. Chem.* **2008**, *6*, 1317–1323; d) B. Heller, M. Hapke, *Chem. Soc. Rev.* **2007**, *36*, 1085–1094; e) N. Agenet, O. Buisine, F. Slowinski, V. Gandon, C. Aubert, M. Malacria in *Organic Reactions* (Ed.: L. E. Overman), Wiley, Hoboken, **2007**, vol. 68, pp. 1–302; f) P. R. Chopade, J. Louie, *Adv. Synth. Catal.* **2006**, *348*, 2307–2327; g) V. Gandon, C. Aubert, M. Malacria, *Chem. Commun.* **2006**, 2209–2217; h) S. Kotha, E. Brahmachary, K. Lahiri, *Eur. J. Org. Chem.* **2005**, 4741–4767; i) V. Gandon, C. Aubert, M. Malacria, *Curr. Org. Chem.* **2005**, *9*, 1699–1712; j) Y. Yamamoto, *Curr. Org. Chem.* **2005**, *9*, 503; k) J. A. Varela, C. Saá, *Chem. Rev.* **2003**, *103*, 3787–3801; l) M. Malacria, C. Aubert, J. L. Renaud in *Science of Synthesis*: *Houben-Weyl Methods for Molecular Transformations* (Eds.: M. Lautens, B. M. Trost), Thieme, New York, **2001**, vol. 1, pp. 439–530; m) S. Saito, Y. Yamamoto, *Chem. Rev.* **2000**, *100*, 2901–2915; n) D. B. Grotjahn in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson, L. Hegedus), Pergamon Press, Oxford, **1995**, vol. 12, pp. 741–770; o) R. Boese, A. P. V. Sickle, K. P. C. Vollhardt, *Synthesis* **1994**, 1374; p) N. E. Schore in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, vol. 5, pp. 1129–1162; q) K. P. C. Vollhardt, *Angew. Chem.* **1984**, *96*, 525–541; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539–556.

[2] T. Tsuda, T. Kiyoi, T. Miyane, T. Saegusa, *J. Am. Chem. Soc.* **1988**, *110*, 8570–8572.

[3] Y. Yamamoto, H. Takagishi, K. Itoh, *J. Am. Chem. Soc.* **2002**, *124*, 6844–6845.

[4] Ruthenium(II)-catalyzed hydrative cyclizations and [4+2] cycloadditions of yne-enones were reported; see: B. M. Trost, R. E. Brown, F. D. Toste, *J. Am. Chem. Soc.* **2000**, *122*, 5877–5878.

[5] a) T. N. Tekevac, J. Louie, *Org. Lett.* **2005**, *7*, 4037–4039; b) T. N. Tekevac, J. Louie, *J. Org. Chem.* **2008**, *73*, 2641–2648.

[6] Nickel-catalyzed [4+2+2] cycloadditions of 1,6-diynes with cyclobutanones were reported; see: M. Murakami, S. Ashida, T. Matsuda, *J. Am. Chem. Soc.* **2006**, *128*, 2166–2167.

[7] a) D. F. Harvey, B. M. Johnson, C. S. Ung, K. P. C. Vollhardt, *Synlett* **1989**, 15–18; b) R. Gleiter, V. Schehlmann, *Tetrahedron Lett.* **1989**, *30*, 2893–2896.

[8] T. Takahashi, Y. Li, T. Ito, F. Xu, K. Nakajima, Y. Liu, *J. Am. Chem. Soc.* **2002**, *124*, 1144–1145.

[9] B. Bennacer, M. Fujiwara, S.-Y. Lee, I. Ojima, *J. Am. Chem. Soc.* **2005**, *127*, 17756–17767.

[10] J. R. Kong, M. J. Krische, *J. Am. Chem. Soc.* **2006**, *128*, 16040–16041.

[11] a) K. Tanaka, A. Wada, K. Noguchi, *Org. Lett.* **2005**, *7*, 4737–4739; b) K. Tanaka, A. Wada, K. Noguchi, *Org. Lett.* **2006**, *8*, 907–909; c) K. Tanaka, N. Suzuki, G. Nishida, *Eur. J. Org. Chem.* **2006**, 3917–3922; d) A. Wada, K. Noguchi, M. Hirano, K. Tanaka, *Org. Lett.* **2007**, *9*, 1295–1298; e) H. Hara, M. Hirano, K. Tanaka, *Org. Lett.* **2008**, *10*, 2537–2540.

[12] For our accounts, see: a) K. Tanaka, *Synlett* **2007**, 1977–1993; b) K. Tanaka, G. Nishida, T. Suda, *J. Synth. Org. Chem. Jpn.* **2007**, *65*, 862–873.

[13] The thermal electrocyclic ring opening of fused α-pyrans has been reported; see: a) E. N. Marvell, G. Caple, T. A. Gosink, G. Zimmer, *J. Am. Chem. Soc.* **1966**, *88*, 619–620; b) E. N. Marvell, T. Chadwick, G. Caple, T. Gosink, G. Zimmer, *J. Org. Chem.* **1972**, *37*, 2992–2997; c) A. F. Kluge, C. P. Lillya, *J. Org. Chem.* **1971**, *36*, 1977–1988; d) B. M. Trost, M. T. Rudd, M. G. Costa, P. I. Lee, A. E. Pomerantz, *Org. Lett.* **2004**, *6*, 4235–4238.

[14] A part of this work was previously communicated; see: a) K. Tanaka, Y. Otake, A. Wada, K. Noguchi, M. Hirano, *Org. Lett.* **2007**, *9*, 2203–2206; b) K. Tanaka, R. Tanaka, G. Nishida, M. Hirano, *Synlett* **2008**, 2017–2022.

[15] After our publication (ref.[14a]), another research group published a similar reaction; see: K. Tsuchikama, Y. Yoshinami, T. Shibata, *Synlett* **2007**, 1395–1398.

[16] For cationic rhodium(I)/H_8-binap complex catalyzed regio-, diastereo-, and enantioselective [2+2+2] cycloadditions of 1,6-enynes with electron-deficient carbonyl compounds, see: K. Tanaka, Y. Otake, H. Sagae, K. Noguchi, M. Hirano, *Angew. Chem.* **2008**, *120*, 1332–1336; *Angew. Chem. Int. Ed.* **2008**, *47*, 1312–1316.

[17] The reactions of internal 1,6-diynes and aryl ketones furnished *ortho*-dienylated aryl ketones, not [2+2+2] cycloaddition products; see ref.[14a,16]

[18] For rhodium-catalyzed enantioselective [4+2] annulations of 2-alkynylbenzaldehydes with cyclic dicarbonyl compounds, see: D. Hojo, K. Noguchi, M. Hirano, K. Tanaka, *Angew. Chem.* **2008**, *120*, 5904–5906; *Angew. Chem. Int. Ed.* **2008**, *47*, 5820–5822.

[19] a) G. Nishida, K. Noguchi, M. Hirano, K. Tanaka, *Angew. Chem.* **2007**, *119*, 4025–4028; *Angew. Chem. Int. Ed.* **2007**, *46*, 3951–3954; b) G. Nishida, K. Noguchi, M. Hirano, K. Tanaka, *Angew. Chem.* **2008**, *120*, 3458–3461; *Angew. Chem. Int. Ed.* **2008**, *47*, 3410–3413; c) G. Nishida, S. Ogaki, Y. Yusa, T. Yokozawa, K. Noguchi, K. Tanaka, *Org. Lett.* **2008**, *10*, 2849–2852.

[20] For selected recent examples, see: a) T. Mandal, S. Samanta, C.-G. Zhao, *Org. Lett.* **2007**, *9*, 943–945; b) S. Samanta, C.-G. Zhao, *J. Am. Chem. Soc.* **2006**, *128*, 7442–7443; c) A. S. Demir, O. Reis, M. Kayalar, S. Eymur, B. Reis, *Synlett* **2006**, 3329–3333; d) D. Y. Kim, D. F. Wiemer, *Tetrahedron Lett.* **2003**, *44*, 2803–2805.

[21] For examples, see: a) M. Yamashita, M. Kojima, H. Yoshida, T. Ogata, S. Inokawa, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1625–1628; b) M. Kojima, M. Yamashita, H. Yoshida, T. Ogata, *Synthesis* **1979**, 147–148.

[22] To the best of our knowledge, only two examples of a cycloaddition reaction using acyl phosphonates as a coupling partner have been reported. For a photochemical cycloaddition with aziridines, see: a) N. Gakis, H. Heimgartner, H. Schmid, *Helv.*

Chim. Acta **1975**, *58*, 748–760. For hetero-Diels–Alder reactions involving α,β-unsaturated acyl phosphonates, see: b) D. A. Evans, J. S. Johnson, E. J. Olhava, *J. Am. Chem. Soc.* **2000**, *122*, 1635–1649.

[23] We deeply appreciate one of the referees of our previous paper (ref.[14b]) for this valuable suggestion.

[24] For examples of the cationic rhodium(I)/biaryl bisphosphane complex catalyzed [2+2+2] cycloadditions of α,ω-diynes with alkenes, see: a) K. Tanaka, G. Nishida, H. Sagae, M. Hirano, *Synlett* **2007**, 1426–1430; b) Y. Shibata, K. Noguchi, M. Hirano, K. Tanaka, *Org. Lett.* **2008**, *10*, 2825–2828; c) K. Tanaka, M. Takahashi, H. Imase, T. Osaka, K. Noguchi, M. Hirano, *Tetrahedron* **2008**, *64*, 6289–6293; d) K. Tsuchikama, Y. Kuwata, T. Shibata, *J. Am. Chem. Soc.* **2006**, *128*, 13686–13687; e) T. Shibata, A. Kawachi, M. Ogawa, Y. Kuwata, K. Tsuchikama, K. Endo, *Tetrahedron* **2007**, *63*, 12853–12859.

[25] For selected examples of the cationic rhodium(I)/biaryl bisphosphane complex catalyzed [2+2+2] cycloadditions of α,ω-diynes with alkynes other than alkynylphosphonates, see: a) K. Tanaka, K. Shirasaka, *Org. Lett.* **2003**, *5*, 4697–4699; b) K. Tanaka, G. Nishida, A. Wada, K. Noguchi, *Angew. Chem.* **2004**, *116*, 6672–6674; *Angew. Chem. Int. Ed.* **2004**, *43*, 6510–6512; c) K. Tanaka, K. Toyoda, A. Wada, K. Shirasaka, M. Hirano, *Chem. Eur. J.* **2005**, *11*, 1145–1156; d) K. Tanaka, K. Takeishi, K. Noguchi, *J. Am. Chem. Soc.* **2006**, *128*, 4586–4587; e) K. Tanaka, H. Sagae, K. Toyoda, K. Noguchi, M. Hirano, *J. Am. Chem. Soc.* **2007**, *129*, 1522–1523; f) K. Tanaka, A. Kamisawa, T. Suda, K. Noguchi, M. Hirano, *J. Am. Chem. Soc.* **2007**, *129*, 12078–12079; g) T. Suda, K. Noguchi, M. Hirano, K. Tanaka, *Chem. Eur. J.* **2008**, *14*, 6593–6596 and references cited therein.

[26] The same chemoselectivity was observed in a cobalt-catalyzed [2+2+2] cycloaddition of tolane and acrolein; see: a) H. Bonnemann, X. Chen. *Proc. Swiss Chem. Soc. Autumn Meet*., Bern, **1987**, p. 39. On the contrary, the double bond of acrolein exclusively reacted with terminal 1,6-diynes in ruthenium-catalyzed [2+2+2] cycloadditions; see: b) J. A. Varela, S. G. Rubín, C. González-Rodríguez, L. Castedo, C. Saá, *J. Am. Chem. Soc.* **2006**, *128*, 9262–9263.

[27] The cyano group exclusively reacted with **1a** in the case of acetyl and benzoyl cyanides; see: ref.[11c]

[28] For examples of carbonyl insertion into a Rh–C bond, see: a) C. Krug, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 1674–1679; b) T. Fujii, T. Koike, A. Mori, K. Osakada, *Synlett* **2002**, 298–300.

[29] 5-Alkynals spontaneously cyclized to generate intramolecular hydroacylation products (cylopentanones) in the presence of the cationic rhodium(I)/biaryl bisphosphane catalyst at room temperature; see: K. Takeishi, K. Sugishima, K. Sasaki, K. Tanaka, *Chem. Eur. J.* **2004**, *10*, 5681–5688.

[30] Equilibrium coordination of the ester carbonyl oxygen atom versus the alkyne moiety of a malonate-linked 1,6-diyne is proposed in the ruthenium-catalyzed [2+2+2] cycloaddition of alkynes; see: Y. Yamamoto, T. Arakawa, R. Ogawa, K. Itoh, *J. Am. Chem. Soc.* **2003**, *125*, 12143–12160.

[31] A similar regioselectivity to this was observed in the ruthenium-catalyzed [2+2+2] cycloadditions of 1,6-diynes, possessing a methyl group at the alkyne terminus, with diethyl ketomalonate; see: ref.[3]

[32] H. A. Duong, M. J. Cross, J. Louie, *J. Am. Chem. Soc.* **2004**, *126*, 11438–11439.

[33] T. N. Tekevac, G. Zuo, K. Simon, J. Louie, *J. Org. Chem.* **2006**, *71*, 5834–5836.

[34] K. Tanaka, H. Hara, G. Nshida, M. Hirano, *Org. Lett.* **2007**, *9*, 1907–1910.

[35] K. Tanaka, T. Osaka, K. Noguchi, M. Hirano, *Org. Lett.* **2007**, *9*, 1307–1310.

[36] X. Creary, *J. Org. Chem.* **1987**, *52*, 5026–5030.

[37] M. Journet, D. Cai, L. M. DiMichele, R. D. Larsen, *Tetrahedron Lett.* **1998**, *39*, 6427–6428.

[38] M. Guo, D. Li, Z. Zhang, *J. Org. Chem.* **2003**, *68*, 10172–10174.

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