(Z)-Selective cross-dimerization of arylacetylenes with silylacetylenes catalyzed by vinylideneruthenium complexes^{\dagger}

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The vinylideneruthenium(II) complexes bearing bulky and basic tertiary phosphine ligands, RuCl₂(=C=CHPh)L₂ (L = PPrⁱ₃, PCy₃), serves as a good catalyst precursor for (*Z*)-selective cross-dimerization between arylacetylenes and silylacetylenes in the presence of *N*-methylpyrrolidine.

Catalytic dimerization of alkynes is one of the simplest methods for synthesizing conjugated enynes, which are useful building blocks in organic synthesis.¹ Enyne structures are also present as active components in conducting and light-emitting polymers.² Accordingly, a number of studies have been carried out for dimerization of alkynes, and some transition metal complexes have proven to be highly selective catalysts.³ However, most studies have been concerned with homo-dimerization, and crossdimerization of two different alkynes has remained almost unexamined. Trost et al. showed that a variety of terminal alkynes, RC=CH (R = alkyl, aryl, silyl), are selectively coupled with electron-deficient internal alkynes, R'C=CEWG (R' = alkyl, silyl; EWG = CO_2Me , COMe, SO_2Ph), in the presence of $Pd(OAc)_2$ and tris(2,6-dimethoxyphenyl)phosphine.⁴ Cu/Pd-catalyzed version of this reaction was recently reported by Li et al.5 As for the cross-dimerization between two kinds of terminal alkynes, to the best of our knowledge, there have been only two reports on gem-selective catalysis. Nakamura et al. demonstrated that Cp*2TiCl2/Pr'MgBr efficiently catalyzes the cross-dimerization between RC=CH (R = 1-cyclohexenyl, Ph) and $R'C \equiv CH$ (R' = alkyl, silyl) into $RC \equiv CHC(R') = CH_2$ in 63–99% selectivities.⁶ Eisen et al. reported the reaction catalyzed by a cationic uranium complex [U(NEt₂)₃][BPh₄].⁷ On the other hand, in this study it was found that arylacetylenes (2) are coupled with silvlacetylenes (3) to form (Z)-1-aryl-4-silvl-1-buten-3-ynes ((Z)-4) in high selectivities using RuCl₂(=C=CHPh)(PPrⁱ₃)₂ (1-Prⁱ) as a catalyst precursor (Scheme 1).

Catalytic dimerization of terminal alkynes generally forms three isomers of butenynes: *i.e.*, (*Z*), (*E*), and geminal (*gem*) isomers (Scheme 2). It is widely accepted that the (*Z*)-isomer is afforded by intramolecular addition of an alkynyl ligand onto the α -carbon of the vinylidene ligand (path A).⁸ On the other hand, (*E*)- and *gem*isomers are produced by insertion of an alkyne into the metal– alkynyl bond in the opposite regiochemical course with each other (paths B and C, respectively). Therefore it was considered that



Scheme 1 Cross-dimerization of arylacetylenes with silylacetylenes catalyzed by vinylideneruthenium complexes.



Scheme 2 Alkyne-dimerization pathways.

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(Z)-selective cross-dimerization may be possible by the combination of two types of alkynes that possess significantly different properties, toward the tautomerization between alkyne and vinylidene ligands. Thus, the nature of several types of alkynes was examined in homo-dimerization systems.

The results are listed in Table 1. All reactions were performed in CH₂Cl₂ at room temperature in the presence of catalytic amounts of **1**-Pr^{*i*} and *N*-methylpyrrolidine, the latter of which was added to generate a catalytically active alkynylruthenium species [RuCl(C=CPh)(PPr^{*i*}₃)₂] by abstracting HCl from **1**-Pr^{*i*}.⁹ Although alkylacetylenes and *p*-MeO₂CC₆H₄C=CH, having an electron-withdrawing substituent, were poorly reactive (runs 7–9), electron-rich arylacetylenes (**2a**–**f**) underwent highly (*Z*)-selective dimerization to yield (*Z*)-ArCH=CH–C=CAr (**5**) in 90–97% selectivities. On the other hand, (trimethylsilyl)acetylene (**3m**) yielded a 15 : 85 mixture of (*E*)- and *gem*-dimerization products (**6m**); no trace of the (*Z*)-dimer was detected in the system using GC-MS analysis. The product selectivity thus observed may be

 Table 1
 Homo-dimerization of terminal alkynes catalyzed by 1-Pr^{ia}

Run	Alkyne	Time/h	Yield $(\%)^b$	(Z) : (E) : gem^b
1	Me	9	>99	92:0:8
2 ^{<i>c</i>}	(2b)	3	>99	96:1:3
3	Me (2c)	5	>99	93:0:7
4	MeO-(2d)	5	96	91:1:8
5	(2e)	6	82	97:0:3
6 ^{<i>c</i>}	(2f)	2	99	90:0:10
7	<i>n</i> -C ₆ H ₁₃	24	0	
8	<i>t</i> -C ₄ H ₉ -===	24	0	
9	MeO ₂ C	24	0	
10	Me ₃ Si (3m)	48	54	0:15:85

^{*a*} Reaction conditions: alkyne (1.0 mmol), 1-Pr^{*i*} (0.010 mmol (runs 1 and 2), 0.050 mmol (runs 3–10)), *N*-methylpyrrolidine (0.20 mmol), CH₂Cl₂ (1.0 mL), room temperature. ^{*b*} Determined by GLC. ^{*c*} The data were taken from ref. 2a.

rationalized by the effect of substituents on the formation of vinylidene ligand: arylacetylenes, especially those bearing electrondonating substituents, facilitate the alkyne-to-vinylidene tautomerization on ruthenium(II) coordinated with bulky and basic phosphine ligands.¹⁰

The cross-dimerization between two strikingly different types of acetylenes, aryl- and silyl-acetylenes, was next examined. The optimal reaction conditions were investigated using 2a as a substrate (Table 2). Treatment of a 1 : 1 mixture of 2a and 3m with 1-Prⁱ (5 mol%) and N-methylpyrrolidine (20 mol%) in CH₂Cl₂ at room temperature formed the cross-dimer 4am with 86% (Z)-content in 38% yield, together with homo-dimers 5a [(Z) : (E): gem = 92: 0: 8 and **6m** [(Z): (E): gem = 0: 15: 85] (run 1). On the other hand, the cross-dimer 7, with the opposite substitution pattern, was not detected in the system using GLC analysis. Increasing the amount of 3m effectively reduced the amount of 5a (run 2). Using a 10 molar excess of 3m, the crossdimer 4am [(Z): (E): gem = 90: 1: 9] was obtained in 93% yield (run 3). The homo-dimer 5a and 6m were successfully separated by silica gel column chromatography, yielding (Z)-4am with 93% isomeric purity in 78% yield after isolation.

N-Methylpyrrolidine was the base of choice, while DBU gave a comparable result (run 4). On the other hand, the less basic pyridine, bulky amines such as Pr_2^iNH and proton sponge, and potassium carbonate as an inorganic base were less effective (runs 5–7). PCy₃-coordinated 1-Cy exhibited catalytic ability similar to 1-Pr^{*i*} (run 8). 1-Ph, having PPh₃ ligands, was poorly reactive (run 9). Although other dimerization catalysts such as Cp*RuCl(PPh₃)₂,¹¹ TpRuCl(PPh₃)₂,¹² RhCl(PPh₃)₃,¹³ and Pd(OAc)₂/SIMes·HCl/Cs₂CO₃ (SIMes·HCl = 1,3-dimesitylimida-zolinium chloride)³⁶ were also tested, complex mixtures of homo-and cross-dimerization products were formed in all cases.

The cross-dimerization with **3m** was also successful for nonsubstituted and substituted phenylacetylenes (**2b-d**), and 2-thienyland 2-fluorenyl-acetylenes (**2e**, **2f**) (Table 3). All reactions afforded (*Z*)-**4** in over 90% selectivity (runs 1–5). (Phenyldimethylsilyl)- and (triisopropylsilyl)-acetylenes (**3n**, **3o**) also served as good coupling partners with almost perfect (*Z*)-selectivities; however, their

Table 2 Cross-dimerization of 4-ethynyltoluene (2a) with (trimethyl-silyl)acetylene $(3m)^{\it a}$

		Cross-dimer 4am		Homo-dimer	
\mathbf{m}^b Base ^c	Time/ h	$\frac{\text{Yield}}{(\%)^d}$	$(Z):(E):gem^e$	5a ^d	6m ^{<i>f</i>}
C ₄ H ₈ NMe	3	38	86:0:14	56	25
C ₄ H ₈ NMe	5	86	91:0:9	13	28
C ₄ H ₈ NMe	16	93	90:1:9	5	24
		(78)	93:0:7		
DBU	16	82	88:4:8	10	20
Pyridine	16	40	89:0:11	< 1	8
Pr ⁱ ₂ NH	16	12	88:0:12	0	1
K_2CO_3	16	< 1			
C ₄ H ₈ NMe	16	89	90:1:9	4	20
C ₄ H ₈ NMe	24	6	82:17:1	<1	4
	\mathbf{m}^{b} Base ^c C_4H_8NMe C_4H_8NMe DBU Pyridine Pr_2^iNH K_2CO_3 C_4H_8NMe C_4H_8NMe	$\begin{array}{c c} & Time/\\ m^b & Base^c & h \end{array} \\ \hline \\ \hline \\ C_4H_8NMe & 5 \\ C_4H_8NMe & 16 \\ \hline \\ DBU & 16 \\ Pyridine & 16 \\ Pyridine & 16 \\ Pr'_2NH & 16 \\ K_2CO_3 & 16 \\ C_4H_8NMe & 16 \\ C_4H_8NMe & 24 \\ \hline \end{array}$	$ \begin{array}{c} {\begin{tabular}{lllllllllllllllllllllllllllllllllll$	$ \begin{array}{c} \mbox{Cross-dimer 4am} \\ \hline \mbox{Time/} & \hline \mbox{Yield} \\ \hline \mbox{Well} & (\%)^{d} & (Z): (E): gem^e \\ \hline \mbox{C}_{4}H_8NMe & 3 & 38 & 86: 0: 14 \\ \hline \mbox{C}_{4}H_8NMe & 5 & 86 & 91: 0: 9 \\ \hline \mbox{C}_{4}H_8NMe & 16 & 93 & 90: 1: 9 \\ \hline \mbox{(78)} & 93: 0: 7 \\ \hline \mbox{DBU} & 16 & 82 & 88: 4: 8 \\ \hline \mbox{Pyridine} & 16 & 40 & 89: 0: 11 \\ \hline \mbox{Pr}_2NH & 16 & 12 & 88: 0: 12 \\ \hline \mbox{K}_2CO_3 & 16 & <1 \\ \hline \mbox{C}_{4}H_8NMe & 16 & 89 & 90: 1: 9 \\ \hline \mbox{C}_{4}H_8NMe & 24 & 6 & 82: 17: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 17: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 17: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 17: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 17: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 17: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 17: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 17: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 17: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 17: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 11: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 11: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 11: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 11: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 11: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 11: 1 \\ \hline \mbox{C}_{4}H_8NE & 24 & 6 & 82: 11: 1 \\ \hline \mbox{C}_{4}H_8N$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

^{*a*} Reaction conditions: **2a** (1.0 mmol), **1**-Pr^{*i*} (0.050 mmol), base (0.20 mmol), CH₂Cl₂ (1.0 mL), room temperature. ^{*b*} Molar ratio. ^{*c*} C₄H₈NMe = *N*-methylpyrrolidine. ^{*d*} GLC yield based on the amount of **2a** employed. Isolated yield is in parentheses. ^{*e*} Determined by GLC. ^{*f*} GLC yield based on the amount of **3m** employed. ^{*g*} **1**-Cy was used in place of **1**-Pr^{*i*}. ^{*h*} **1**-Ph was used in place of **1**-Pr^{*i*}.



^{*a*} Reaction conditions: **2** (1.0 mmol), **1**-Pr^{*i*} (0.050 mmol), *N*-methylpyrrolidine (0.20 mmol), CH₂Cl₂ (1.0 mL), room temperature, 16–24 h. ^{*b*} GLC yield based on the amount of **2** employed. Isolated yield is in parentheses. ^{*c*} Isomer ratio of isolated product. Determined by ¹H NMR. ^{*d*} Reaction time = 80 h. ^{*e*} Reaction time = 5 h. ^{*f*} Determined by GLC.

reactivities were lower than that of 3m (runs 6 and 7). The products (*Z*)-4 were easily desilylated by treatment with K₂CO₃ in

MeOH, so that the overall process provides a new entry for the synthesis of terminal alkenylacetylenes (ArCH=CH–C=CH (7)) with (Z)-configurations.¹⁴

In conclusion, it has been discovered that cross-dimerization between arylacetylenes (**2a–f**) and (trimethylsilyl)acetylene (**3m**) proceeds in high (*Z*)-selectivity using vinylideneruthenium $1-Pr^{i}$ as a catalyst precursor. The reaction provides complementary regioand stereo-selectivities to Nakamura's titanium-catalyzed system yielding ArC=C-C(SiMe_3)=CH_2.

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