(*Z*)-Selective cross-dimerization of arylacetylenes with silylacetylenes catalyzed by vinylideneruthenium complexes†

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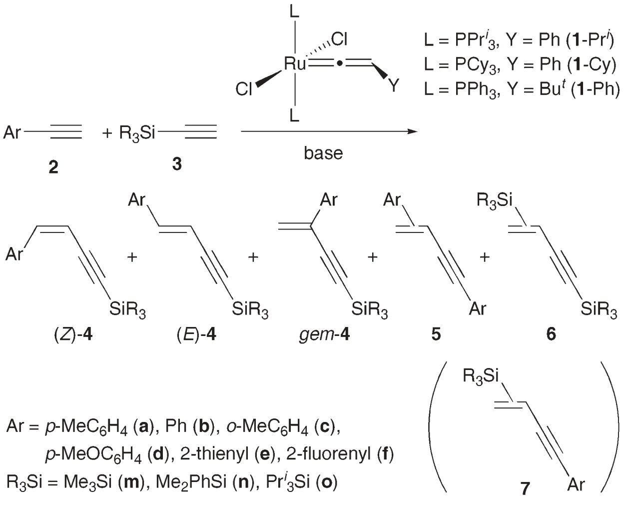
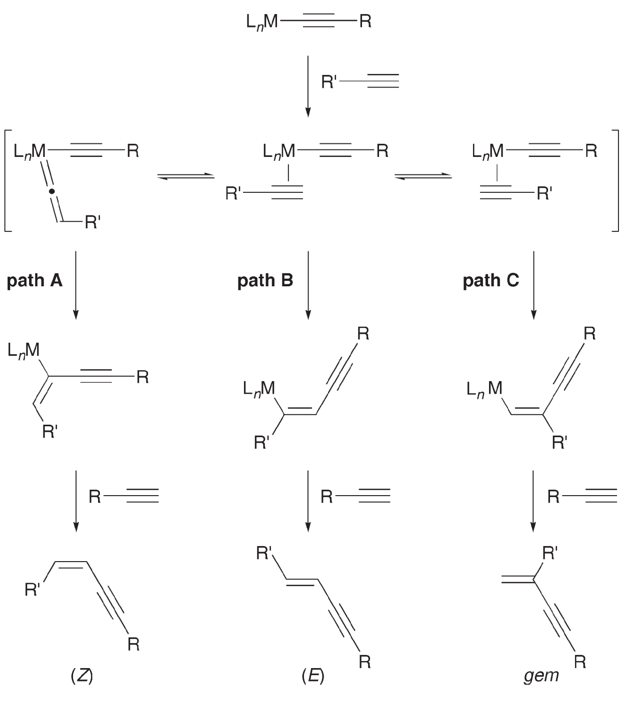
The vinylideneruthenium(II) complexes bearing bulky and basic tertiary phosphine ligands, $RuCl_2(=C=CHPh)L_2$ (L = PPr^i_3, PCy_3), serves as a good catalyst precursor for (*Z*)-selective cross-dimerization between arylacetylenes and silylacetylenes in the presence of *N*-methylpyrrolidine.

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 cross-dimerization 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] The 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 $Cp^*_2TiCl_2/Pr^iMgBr$ efficiently catalyzes the cross-dimerization between RC≡CH (R = 1-cyclohexenyl, Ph) and R′C≡CH (R′ = alkyl, silyl) into $RC≡CHC(R')=CH_2$ in 63–99% selectivities.[6] Eisen *et al.* reported the reaction catalyzed by a cationic uranium complex $[U(NEt_2)_3][BPh_4]$.[7] On the other hand, in this study it was found that arylacetylenes (**2**) are coupled with silylacetylenes (**3**) to form (*Z*)-1-aryl-4-silyl-1-buten-3-ynes ((*Z*)-**4**) in high selectivities using $RuCl_2(=C=CHPh)(PPr^i_3)_2$ (**1**-Pr^i) 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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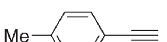
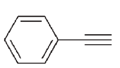
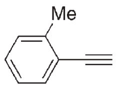
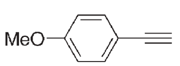
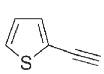
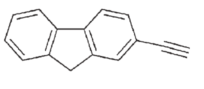
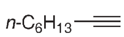
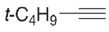
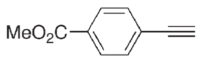
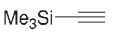
(*Z*)-selective cross-dimerization may be possible by the combination of two types of alkynes that possess significantly different properties, toward the tautomerization between alkyne and vinylidene ligands. Thus, the nature of several types of alkynes was examined in homo-dimerization systems.

The results are listed in Table 1. All reactions were performed in CH_2Cl_2 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 $[RuCl(C{\equiv}CPh)(PPr^i_3)_2]$ by abstracting HCl from **1**-Pr^i.[9] Although alkylacetylenes and *p*-$MeO_2CC_6H_4C{\equiv}CH$, 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 rationalized by the effect of substituents on the formation of vinylidene ligand: arylacetylenes, especially those bearing electron-donating substituents, facilitate the alkyne-to-vinylidene tautomerization on ruthenium(II) coordinated with bulky and basic phosphine ligands.[10]

Table 1 Homo-dimerization of terminal alkynes catalyzed by **1**-Pr$^{i\,a}$

Run	Alkyne	Time/h	Yield (%)^b	(*Z*) : (*E*) : *gem*^{b}
1	 **(2a)**	9	>99	92 : 0 : 8
2^c	 **(2b)**	3	>99	96 : 1 : 3
3	 **(2c)**	5	>99	93 : 0 : 7
4	 **(2d)**	5	96	91 : 1 : 8
5	 **(2e)**	6	82	97 : 0 : 3
6^c	 **(2f)**	2	99	90 : 0 : 10
7		24	0	
8		24	0	
9		24	0	
10	 **(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), CH_2Cl_2 (1.0 mL), room temperature. ^{b} Determined by GLC. ^{c} The data were taken from ref. 2a.

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**-Pr^i (5 mol%) and *N*-methylpyrrolidine (20 mol%) in CH_2Cl_2 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 cross-dimer **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^i_2NH and proton sponge, and potassium carbonate as an inorganic base were less effective (runs 5–7). PCy_3-coordinated **1**-Cy exhibited catalytic ability similar to **1**-Pr^i (run 8). **1**-Ph, having PPh_3 ligands, was poorly reactive (run 9). Although other dimerization catalysts such as $Cp^*RuCl(PPh_3)_2$,[11] $TpRuCl(PPh_3)_2$,[12] $RhCl(PPh_3)_3$,[13] and $Pd(OAc)_2$/SIMes·HCl/Cs_2CO_3 (SIMes·HCl = 1,3-dimesitylimidazolinium chloride)[3b] were also tested, complex mixtures of homo- and cross-dimerization products were formed in all cases.

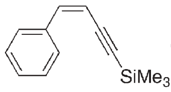
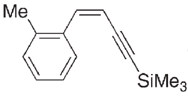
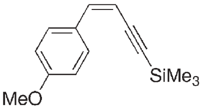
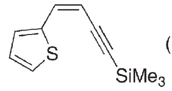
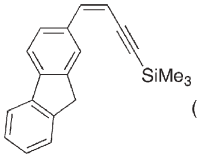
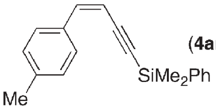
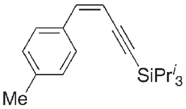
The cross-dimerization with **3m** was also successful for non-substituted and substituted phenylacetylenes (**2b–d**), and 2-thienyl- and 2-fluorenyl-acetylenes (**2e**, **2f**) (Table 3). All reactions afforded (*Z*)-**4** in over 90% selectivity (runs 1–5). (Phenyldimethylsilyl)- and (triisopropylsilyl)-acetylenes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

Table 2 Cross-dimerization of 4-ethynyltoluene (**2a**) with (trimethylsilyl)acetylene (**3m**)^a

				Cross-dimer **4am**		Homo-dimer	
Run	**2a** : **3m**^{b}	Base^c	Time/h	Yield (%)^d	(*Z*) : (*E*) : *gem*^{e}	**5a**^{d}	**6m**^{f}
1	1 : 1	C_4H_8NMe	3	38	86 : 0 : 14	56	25
2	1 : 5	C_4H_8NMe	5	86	91 : 0 : 9	13	28
3	1 : 10	C_4H_8NMe	16	93	90 : 1 : 9	5	24
				(78)	93 : 0 : 7		
4	1 : 10	DBU	16	82	88 : 4 : 8	10	20
5	1 : 10	Pyridine	16	40	89 : 0 : 11	<1	8
6	1 : 10	Pr^i_2NH	16	12	88 : 0 : 12	0	1
7	1 : 10	K_2CO_3	16	<1			
8^g	1 : 10	C_4H_8NMe	16	89	90 : 1 : 9	4	20
9^h	1 : 10	C_4H_8NMe	24	6	82 : 17 : 1	<1	4

^{a} Reaction conditions: **2a** (1.0 mmol), **1**-Pr^i (0.050 mmol), base (0.20 mmol), CH_2Cl_2 (1.0 mL), room temperature. ^{b} Molar ratio. ^{c} C_4H_8NMe = *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.

Table 3 Cross-dimerization of arylacetylene **2** with silylacetylene **3**[a]

Run	Alkynes (molar ratio)	Product	Yield (%)[b] [(*Z*) : (*E*) : *gem*][c]
1	**2b** : **3m** (1 : 20)	 **(4bm)**	83 (79) [95 : 5 : 0]
2[d]	**2c** : **3m** (1 : 5)	 **(4cm)**	72 (65) [90 : 5 : 5]
3[e]	**2d** : **3m** (1 : 5)	 **(4bm)**	85 (76) [93 : 7 : 0]
4	**2e** : **3m** (1 : 10)	 **(4em)**	81 (76) [93 : 7 : 0]
5	**2f** : **3m** (1 : 10)	 **(4fm)**	95 (90) [93 : 0 : 7]
6	**2a** : **3n** (1 : 10)	 **(4an)**	74 [100 : 0 : 0[f]]
7	**2a** : **3o** (1 : 10)	 **(4ao)**	45 (38) [100 : 0 : 0]

[a] Reaction conditions: **2** (1.0 mmol), **1**-Pr^i (0.050 mmol), *N*-methylpyrrolidine (0.20 mmol), CH_2Cl_2 (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 K_2CO_3 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 regio- and stereo-selectivities to Nakamura's titanium-catalyzed system yielding ArC≡C–C($SiMe_3$)=CH_2.

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