Fulvene Synthesis

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Catalytic [2+2+1] Cross-Cyclotrimerization of Silylacetylenes and Two Alkynyl Esters To Produce Substituted Silylfulvenes[**]

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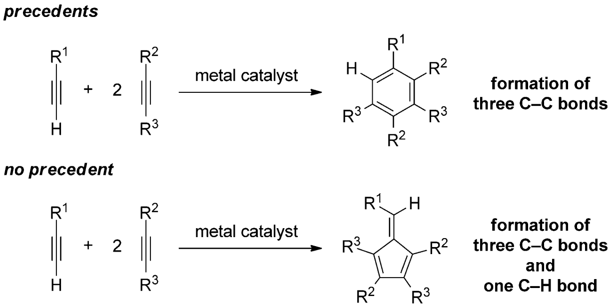
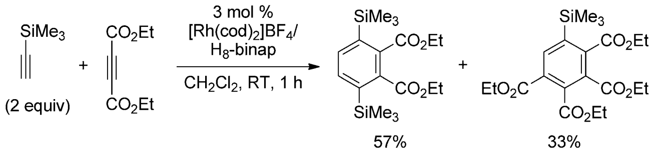
The transition-metal-catalyzed [2+2+2] cross-cyclotrimerization of two or three different alkynes,[1] a transformation in which three C−C bonds form simultaneously, is a useful method for the synthesis of substituted benzenes. A number of successful examples have been reported (Scheme 1).[2] In sharp contrast, the synthesis of substituted fulvenes by a transition-metal-catalyzed [2+2+1] cross-cyclotrimerization of two different alkynes, a transformation in which one C−H bond as well as three C−C bonds form simultaneously, has not been reported (Scheme 1). There have been only a few reported examples of the transition-metal-catalyzed [2+2+1] homo-cyclotrimerization of alkynes.[3–7] Rothwell and co-workers reported the titanium(IV)-catalyzed homo-cyclotrimerization of *tert*-butylacetylene, leading to a 1,3,6-substituted fulvene.[3] Yamamoto and co-workers reported the palladium(II)-catalyzed homo-cyclotrimerization of terminal alkynes, leading to 1,2,4-substituted fulvenes.[4,5] Herein, we disclose the first catalytic [2+2+1] cross-cyclotrimerization of two different alkynes to produce substituted silylfulvenes.[8]



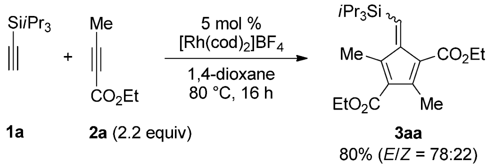
Scheme 1. Transition-metal-catalyzed cross-cyclotrimerizations.

Our research group previously reported that a cationic rhodium(I)/H_8-binap (2,2′-bis(diphenylphosphino)-5,5′,6,6′,-7,7′,8,8′-octahydro-1,1′-binaphthyl) complex is a highly effective catalyst for the [2+2+2] cross-cyclotrimerization of electron-rich terminal alkynes and electron-deficient alkynyl esters.[2a,b] In this catalyst system, the use of trimethylsilylacetylene and diethyl acetylenedicarboxylate furnished 2:1 and 1:2 cross-cyclotrimerization products in high combined yield (Scheme 2).[2a,b]



Scheme 2. Rhodium-catalyzed [2+2+2] cross-cyclotrimerization. cod = 1,5-cyclooctadiene.

We examined different combinations of electron-rich terminal alkynes, electron-deficient internal alkynes, and rhodium(I) catalysts in detail. As a result, we were pleased to find that the [2+2+1] cross-cyclotrimerization of triisopropylsilylacetylene (**1a**) and two alkynyl esters **2a** proceeded at 80 °C and gave substituted silylfulvene **3aa** in high yield using $[Rh(cod)_2]BF_4$ (5 mol%) as the catalyst and 1,4-dioxane as the solvent (Scheme 3).[9]



Scheme 3. Rhodium-catalyzed [2+2+1] cross-cyclotrimerization of **1a** and **2a**.

In this rhodium(I)-catalyzed silylfulvene synthesis, the choice of catalyst and solvent is important. The effect of the catalyst and solvent is summarized in Table 1, starting with the best catalyst and solvent combination with a higher catalyst loading (10 mol%) and at a lower temperature (60 °C; entry 1) than used in the initial reaction conditions shown in Scheme 3. With regard to the catalyst, $[Rh(cod)OAc]_2$ (entry 2) and an in situ generated cationic rhodium(I)/cod complex (entry 3) catalyzed the fulvene formation. However, the use of a cationic rhodium(I)/nbd complex (entry 4), a neutral rhodium(I)/cod complex (entry 5), and a cationic rhodium(I)/binap (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) complex (entry 6) led to poor substrate conversions. The use of a rhodium catalyst is

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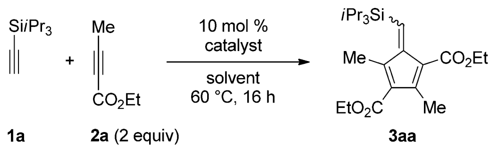
Table 1: Effect of catalysts and solvents.[a]

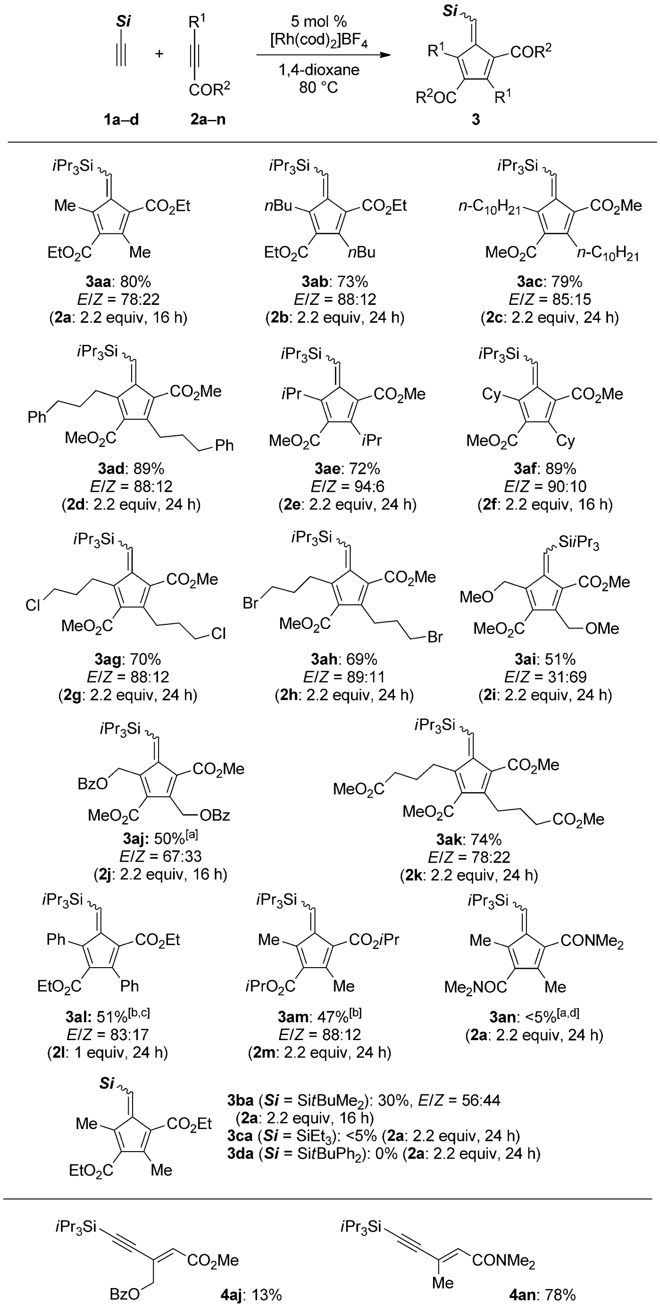


Entry	Catalyst	Solvent	Yield[b][%]	E/Z
1	$[Rh(cod)_2]BF_4$	1,4-dioxane	86	59:41
2	$[\{RhOAc(cod)\}_2]$	1,4-dioxane	67	80:20
3	$[\{RhCl(cod)\}_2]/2AgBF_4$	1,4-dioxane	40	95:5
4	$[Rh(nbd)_2]BF_4$	1,4-dioxane	<5	–
5	$[\{RhCl(cod)\}_2]$	1,4-dioxane	<5	–
6	$[Rh(cod)_2]BF_4$/*rac*-binap	1,4-dioxane	0	–
7	$[\{IrCl(cod)\}_2]/2AgBF_4$	1,4-dioxane	0	–
8	$Pd(OAc)_2$	1,4-dioxane	0	–
9	$[Rh(cod)_2]BF_4$	DME	71	77:23
10	$[Rh(cod)_2]BF_4$	THF	67	79:21
11	$[Rh(cod)_2]BF_4$	acetone	39	60:40
12	$[Rh(cod)_2]BF_4$	toluene	23	82:18
13	$[Rh(cod)_2]BF_4$	CH_3CN	<5	–
14	$[Rh(cod)_2]BF_4$	CH_2Cl_2	0	–

[a] Catalyst (0.010 mmol), **1a** (0.10 mmol), **2a** (0.20 mmol), and solvent (1.0 mL) were used. [b] Determined by ^1H NMR spectroscopy. DME = 1,2-dimethoxyethane, nbd = norbornadiene, THF = tetrahydrofuran.

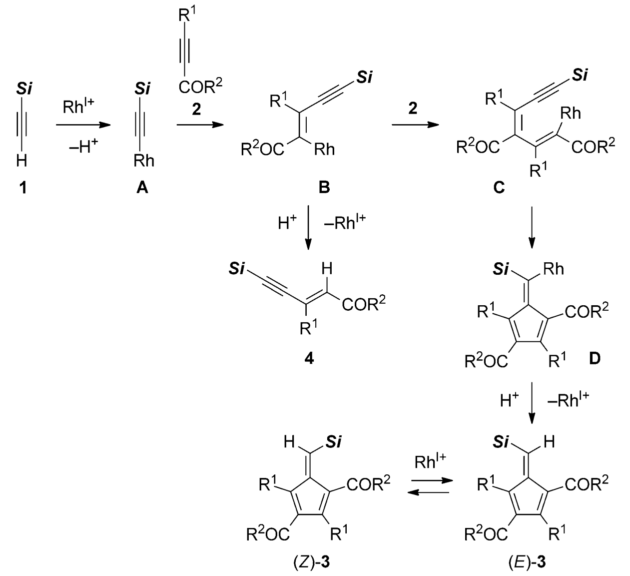
essential to promote this reaction; both a cationic iridium(I)/cod complex (entry 7) and $Pd(OAc)_2$ (entry 8) failed to catalyze the fulvene formation. With regard to the solvent, the fulvene formation proceeded in moderately coordinating solvents (entries 9–12). However, the use of a highly coordinating solvent (entry 13) and a less-coordinating solvent (entry 14) led to poor substrate conversions.

The scope of this rhodium(I)-catalyzed silylfulvene synthesis is shown in Scheme 4. With respect to the alkynyl ester, not only the methyl-substituted alkynyl ester **2a** but also a variety of primary and secondary alkyl-substituted esters (**2b–f**) reacted with **1a** to give the corresponding silylfulvenes in high yields. The reactions of **1a** and haloalkyl-substituted alkynyl esters **2g** and **2h** also proceeded to give the corresponding silylfulvenes in good yields. Alkynyl esters **2i–k**, which have oxygen-containing functional groups (R^1), could also participate in this reaction, although the product yields from propargyl alcohol derivatives **2i** and **2j** were moderate owing to their partial decomposition during isolation by chromatography on silica gel. Phenyl-substituted alkynyl ester **2l** and isopropyl 2-butynoate (**2m**) could be employed, although high catalyst loadings were required. Unfortunately, the reaction of **1a** and alkynyl amide **2n** furnished the corresponding silylfulvene **3an** in $<5\%$ yield.[10] Importantly, when alkynyl ester **2j** and alkynyl amide **2n** were used, cross-dimerization products **4aj** and **4an** were generated in 13% and 78% yields, respectively;[11] the reason for this result is not clear. The scope of the silylacetylenes was also examined. The reactions of various bulky silylacetylenes **1b–d** with **2a** were attempted, but (*tert*-butyldimethylsilyl)acetylene (**1b**) was the only silylacetylene that could be employed for this reaction.[12]



Scheme 4. Scope of silylacetylenes and alkynyl esters (amide). $[Rh(cod)_2]BF_4$ (0.015 mmol), **1** (0.30 mmol), **2** (0.66 or 0.30 mmol), and 1,4-dioxane (3.0 mL) were used. The cited yields are of the isolated products. [a] Cross-dimerization product **4aj** or **4an** was also isolated. [b] 10 mol% of catalyst. [c] Yield is based on **2l**. [d] 20 mol% of catalyst.

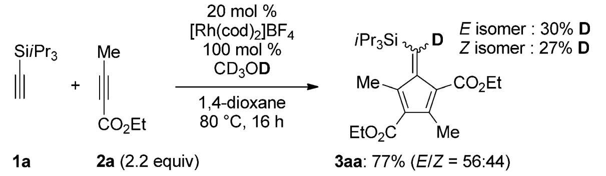
A mechanistic proposal for this rhodium(I)-catalyzed fulvene synthesis is shown in Scheme 5.[13] Carborhodation of alkynyl ester **2** with rhodium acetylide **A**, which was generated through the reaction of silylacetylene **1**[11b–e] and the cationic rhodium(I) complex, affords (alkenyl)rhodium **B** and this compound reacts with another **2** to generate (dienyl)rhodium **C**. Subsequent intramolecular carborhodation to the silyl-bound triple bond affords (fulvenyl)rhodium



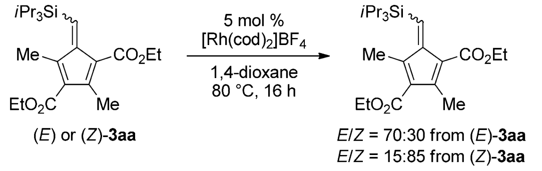
Scheme 5. A mechanistic proposal for the formation of fulvenes **3**.

D. Protonation of intermediate **D** affords the cross-trimerization product (*E*)-**3** and regenerates the rhodium(I) catalyst. As the cationic rhodium(I) complexes are effective catalysts for the *E*/*Z* isomerization of conjugated carbonyl compounds,[14] the isomerization of the initially formed (*E*)-**3** would furnish (*Z*)-**3**. Alternatively, protonation of intermediate **B** affords cross-dimerization product **4**.

Consistent with the above pathway, partially deuterated **3aa** was generated in the presence of an external deuterium source (CD_3OD, Scheme 6), and the *E*/*Z* isomerization of the isolated (*E*)- and (*Z*)-**3** proceeded under the same reaction conditions as described in Scheme 3 (Scheme 7).

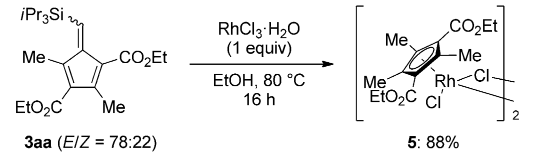


Scheme 6. Rhodium-catalyzed [2+2+1] cross-cyclotrimerization of **1a** and **2a** in the presence of CD_3OD.



Scheme 7. Rhodium-catalyzed *E*/*Z* isomerization of (*E*)- and (*Z*)-**3aa**.

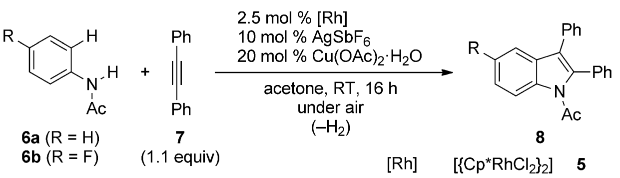
The *E*/*Z* mixture of silylfulvene **3aa** can serve as a useful precursor for the preparation of a η^5-cyclopentadienyl rhodium(III) complex as shown in Scheme 8. The direct



Scheme 8. Reductive complexation of **3aa** with $RhCl_3$.

reductive complexation[15,16] of **3aa** with $RhCl_3$ smoothly proceeded in EtOH at 80°C to give the corresponding dinuclear electron-deficient cyclopentadienyl rhodium(III) **5** in high yield.[6e,f,17,18]

A dicationic rhodium(III)/Cp* complex, derived from $[\{Cp^*RhCl_2\}_2]$, is known to be a highly effective catalyst for a number of C–H bond activation reactions.[19] To improve the selectivity and reactivity, sterically tuned cyclopentadienyl ligands have been investigated recently,[20,21] but an electronically tuned cyclopentadienyl ligand has not been investigated. We anticipated that an in situ generated dicationic complex of **5**, bearing the electron-deficient cyclopentadienyl ligand, would show higher catalytic activity than that of $[\{Cp^*RhCl_2\}_2]$ in the electrophilic C–H bond activation reaction. Indeed, the dicationic complex derived from **5** had significantly higher activity and selectivity than the complex derived from the commonly employed $[\{Cp^*RhCl_2\}_2]$, in the oxidative coupling of both electron-rich and electron-deficient acetanilides, **6a** and **6b**, respectively, with alkyne **7**, thus complete substrate conversion and quantitative product yields were achieved at room temperature (Scheme 9).[22]



	[Rh]	$[\{Cp^*RhCl_2\}_2]$	**5**
8a (R = H)		28%	quant.
8b (R = F)		25%	quant.

Scheme 9. Comparison of catalytic activity between two cationic rhodium(III) complexes, generated in situ from $[\{Cp^*RhCl_2\}_2]$ and **5**.

In conclusion, we have developed the [2+2+1] cross-cyclotrimerization of silylacetylenes and two alkynyl esters catalyzed by the cationic rhodium(I)/cod complex to produce substituted silylfulvenes. The unprecedented reductive complexation of the silylfulvene product with $RhCl_3$ in EtOH furnished the corresponding dinuclear electron-deficient cyclopentadienyl rhodium(III) complex. This rhodium(III) complex is a highly active and selective precatalyst for the oxidative coupling of acetanilides and alkynes. Future work will focus on further utilization of the novel electron-deficient cyclopentadienyl rhodium(III) complexes in various electrophilic C–H bond activation reactions.

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Keywords: [2+2+1] cross-cyclotrimerization · alkynes · cyclopentadienyl complexes · fulvenes · rhodium

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[13] The formation of fulvene derivatives via metalacyclopentadiene intermediates (Ref. [6h–j,8g]) or metal vinylidene intermediates (Ref. [6c,f,g]) has been proposed for the stoichiometric reactions, but the mechanism shown in Scheme 4 is more plausible because of the formation of cross-dimerization products **4**.

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