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Ligand-Controlled Cross-Dimerization and -Trimerization of Alkynes under Nickel Catalysis

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Abstract: The cross-dimerization of diphenylacetylene with trimethylsilylacetylene *via* C–H bond cleavage in the presence of a catalytic amount of bis(cyclooctadiene)nickel [$Ni(cod)_2$] together with a pyridine-based ligand efficiently proceeds to give the corresponding enyne compound with good yield. In contrast, their 1:2 cross-trimerization leading to a dienyne derivative takes place selectively using a triarylphosphine ligand. The regioselective cross-dimerization of some unsymmetrical internal arylalkynes with terminal silylacetylenes is also accomplished using the pyridine ligand.

Keywords: alkynes; cross-dimerization; cross-trimerization; ligand effects; nickel

Introduction

Alkyne coupling reactions under transition metal catalysis are of genuine synthetic utility in preparing π-conjugated compounds such as enynes which are versatile building blocks in organic synthesis.[1] Thus, the homo-dimerization of terminal alkynes as a straightforward and practical method leading to enynes has been extensively studied to selectively synthesize one of the three possible (*E*)-, (*Z*)-, and geminal-enyne isomers. In contrast, the selective cross-dimerization of two different alkynes is, in general, difficult due to the fact that the formation of cross- and homo-dimerized regio- and stereoisomers is possible and, thus, has been a major challenge.[2–6] Among the early leading examples is the palladium-catalyzed reaction with internal alkynes having an electron-withdrawing group as acetylene acceptors.[2] Such reactions have also been achieved by using other transition metal catalysts including Ru, Rh, and Ir.[3] Recently, some selective cross-dimerization reactions of terminal silylacetylenes as acetylene donors with unactivated internal and terminal alkynes have been disclosed.[4] On the other hand, formation of linear cross-trimerization products in a 1:2 or 2:1 manner together with 1:1 cross-dimerization products has been reported in some reactions such as those of 1-phenylsulfonyl-1-propyne with phenylacetylene or propargyl alcohol, diphenylacetylene with silylacetylenes, and *tert*-butylacetylene with trimethylsilylacetylene in the presence of $Pd(OAc)_2$/TDMPP [TDMPP = tris(2,6-dimethoxyphenyl)phosphine],[2b] $Ni(PEt_3)_4$,[5] and $Cp^*_2UMe_2$[6] as catalysts, respectively. Thus, the selective linear trimerization leading to dienynes is a relatively more difficult, but also interesting, target in constructing π-conjugated systems.[7] In the course of our study of regio- and stereoselective alkyne cross-couplings using silylacetylenes,[4c,e,8] we have examined the reactions *via* C(*sp*)–H bond cleavage using Ni, since such reactions with this metal have been less explored.[5,9] It has been found that the combination of $Ni(cod)_2$ together with a pyridine-based ligand such as 4-(*N,N*-dimethylamino)pyridine effectively catalyzes the cross-dimerization of diphenylacetylene with trimethylsilylacetylene. In contrast, the 1:2 cross-trimerization of the substrates takes place selectively using a triarylphosphine ligand in place of the pyridine. The regioselective cross-dimerization of a number of unsymmetrical internal arylalkynes with terminal silylacetylenes has also been achieved using the pyridine ligand. These new findings are reported herein.

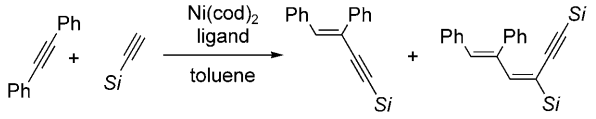
Results and Discussion

When diphenylacetylene (**1a**) (0.25 mmol) was treated with trimethylsilylacetylene (**2a**) (0.75 mmol) in the presence of $Ni(cod)_2$ (2.5 mol%) in pyridine at 100 °C,

the 1:1 cross-dimerization product **3aa** was formed in 94% yield with an *E*/*Z* ratio of 94:6 together with a small amount of the 1:2 cross-trimerization product **4aa** with 1*Z*,3*E*-configuration (Table 1, entry 1). The reaction in toluene with use of 4-(dimethylamino)pyridine (DMAP) (30 mol%) as ligand proceeded efficiently at 50 °C to allow the selective formation of **3aa** (entry 2), whereas the conversion of **1a** was very low (less than 5%) in the absence of DMAP. A bidentate nitrogen ligand, 2,2′-bipyridine, was far less effective (entry 3). In contrast to the nitrogen-based ligand DMAP, the use of triarylphosphines (2.5 mol%) significantly promoted the formation of cross-trimer **4aa** (entries 4–7). Among the phosphines examined, P(4-$CF_3C_6H_4)_3$ was most effective for the trimerization, giving an 83% yield of **4aa** along with only a small amount of **3aa**. The use of bidentate phosphines, dppb and Xantphos, resulted in high selectivity for **3aa** with the *E*-configuration, albeit the yield was moderate to low (entries 8 and 9). The reaction of **1a** with *tert*-butyldimethylsilylacetylene (**2b**) in place of **2a** in the presence of $Ni(cod)_2$ with DMAP or P(4-$CF_3C_6H_4)_3$ selectively gave the corresponding enyne **3ab** or dienyne **4ab** in good yields (entries 10 and 11). It should be mentioned that the formation of a mixture of **3ab** and **4ab** in a ratio of *ca.* 1:3 from **1a** and **2b** using Ni($PEt_3)_4$ as catalyst was previously reported by Ishikawa and co-workers.[5] Thus, the product distribution is a marked function of steric and electric properties of ligands as in the case using **2a**. The use of a further bulky terminal alkyne, triisopropylsilylacetylene (**2c**) in the presence of P(4-$CF_3C_6H_4)_3$ resulted in a considerable increase in the ratio of enyne **3ac** to dienyne **4ac** (entry 13), while **3ac** was exclusively formed on using DMAP (entry 12). We also examined the reactions of **1a** with phenylacetylene and *tert*-butylacetylene under the conditions used for entries 2 and 7. With use of these terminal alkynes in the presence of DMAP as ligand, formation of the expected 1:1 cross-dimerization products was detected by GC-MS, but the yields were only around 25%. The reactions using P(4-$CF_3C_6H_4)_3$ were not successful, giving complex mixtures.

Next, we carried out the co-dimerization reactions of 3-phenyl-2-propyn-1-ol (**5a**) and its derivatives **5b–e** with silylacetylene **2b** for the sake of comparison with our previous study using a rhodium catalyst; we reported that the reactions of propargyl alcohols **5a**, **5c**, and **5e** with **2b** using $[Rh(OH)(cod)]_2$/dppb as catalyst proceed regio- and stereoselectively to give the corresponding enynes **6ab**, **6cb**, and **6eb**.[4c] While the reaction of **5a** with **2a** in the presence of $Ni(cod)_2$/DMAP was sluggish (Table 2, entry 1), the enyne **6ab** was selectively formed using Xantphos as ligand (entry 2). This regioselectivity is in harmony with the rhodium catalysis[4c,d] as well as the related palladium-catalyzed reactions.[2c] The co-dimerization of methyl ether **5b** with **2b** proceeded using 2,6-lutidine as well as DMAP and Xantphos as ligands (entries 3–5). Interestingly, the product regioselectivity was highly dependent on the identity of ligands; the pyridine ligands afforded unexpectedly and preferably **7bb**, while **6bb** was selectively formed in the case of Xantphos. The reactions of **5c–e** with **2b** using 2,6-lutidine as ligand also showed unusual regioselectivity to give **7cb**, **7db**, and **7eb** selectively (entries 6, 8, 10). The use of Xantphos in the reaction of **5c** unexpectedly led not to **6cb**, but to **7cb** with almost complete *E*-selectivity (entry 7). The bidentate ligand was, however, not effective for the reactions of **5d** and **5e** (entries 9 and 11).

Table 1. Nickel-catalyzed reaction of diphenylacetylene (**1a**) with silylacetylenes **2a–c**.[a]

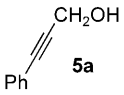
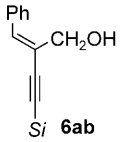
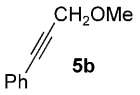
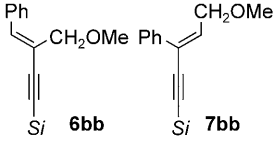
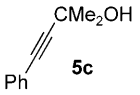
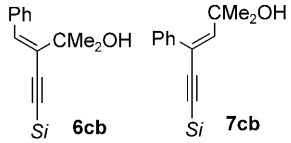
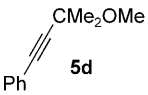
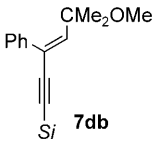
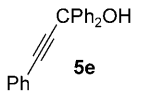
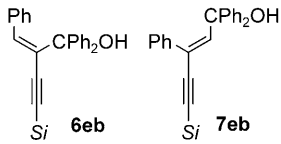


1a **2a:** *Si* = $SiMe_3$ **3aa:** *Si* = $SiMe_3$ **4aa:** *Si* = $SiMe_3$
2b: *Si* = Si(*t*-Bu)Me_2 **3ab:** *Si* = Si(*t*-Bu)Me_2 **4ab:** *Si* = Si(*t*-Bu)Me_2
2c: *Si* = Si(*i*-Pr)$_3$ **3ac:** *Si* = Si(*i*-Pr)$_3$ **4ac:** *Si* = Si(*i*-Pr)$_3$

Entry	2	Ligand	Temp. [°C]	Time [h]	% Yield[b] 3	% Yield[b] 4
1	**2a**[c]	pyridine	100	9	94 [94/6][d]	6
2	**2a**	DMAP[e]	50	9	97 (82) [88/12][d]	trace
3	**2a**	bpy[f]	120	6	5	4
4	**2a**	P(4-$MeOC_6H_4)_3$	50	9	7	63
5	**2a**	PPh_3	50	6	5	60
6	**2a**	P(4-$FC_6H_4)_3$	50	3	5	79
7	**2a**	P(4-$CF_3C_6H_4)_3$	50	3	3	83 (82)
8	**2a**	dppb[g]	120	6	25	trace
9	**2a**	Xantphos[h]	120	6	55	trace
10	**2b**	DMAP[e]	50	6	(78) [85/15][d]	trace
11	**2b**	P(4-$CF_3C_6H_4)_3$	50	3	5	83 (79)
12	**2c**	DMAP[e]	50	9	(74) [80/20][d]	0
13	**2c**	P(4-$CF_3C_6H_4)_3$	50	3	20	28

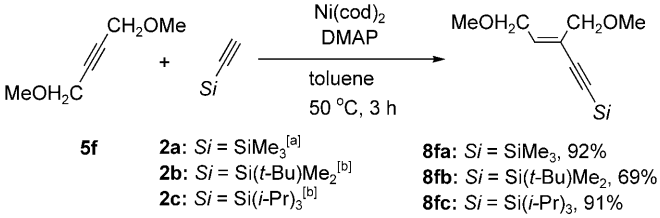
[a] *Reaction conditions:* $[Ni(cod)_2]$:[Ligand]:[**1a**]:[**2**] = 0.00625:0.00625:0.25:0.75 (in mmol) in toluene (2.5 mL) under N_2.
[b] GC yield based on the amount of **1a** used. Value in parentheses indicates isolated yield.
[c] Pyridine (2.5 mL) was used as solvent.
[d] *E*/*Z* ratio of **3a**, determined by GC or ^{1}H NMR.
[e] DMAP [4-(*N*,*N*-dimethylamino)pyridine, 0.0375 mmol] was used.
[f] bpy = 2,2′-bipyridine.
[g] dppb = $Ph_2P(CH_2)_4PPh_2$.
[h] Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

Table 2. Cross-dimerization of arylalkynes **5a–e** with silylacetylene **2b**.[a]

Entry	5	Ligand	Temp. [°C]	Time [h]	% Yield[b] of enynes **6** and/or **7** (*E*/*Z*)
	 **5a**				 **6ab**
1		DMAP[c]	50	3	–[g]
2		Xantphos[d]	120	1	72
	 **5b**				 **6bb** **7bb**
3		DMAP[c]	50	3	81 (**6bb:7bb** = 21:79)
4		2,6-lutidine[e]	50	3	99 (**6bb:7bb** = 18:82)
5		Xantphos[d]	120	1	91 (**6bb:7bb** = 88:12)
	 **5c**				 **6cb** **7cb**
6		2,6-lutidine[e]	100	1	n.d. 64 [55/45]
7		Xantphos[d]	120	1	n.d. 67
	 **5d**				 **7db**
8[f]		2,6-lutidine[e]	50	3	76
9		Xantphos[d]	120	1	–[h]
	 **5e**				 **6eb** **7eb**
10[f]		2,6-lutidine[e]	50	3	n.d. 99 [92/8]
11		Xantphos[d]	120	1	n.d. –[i]

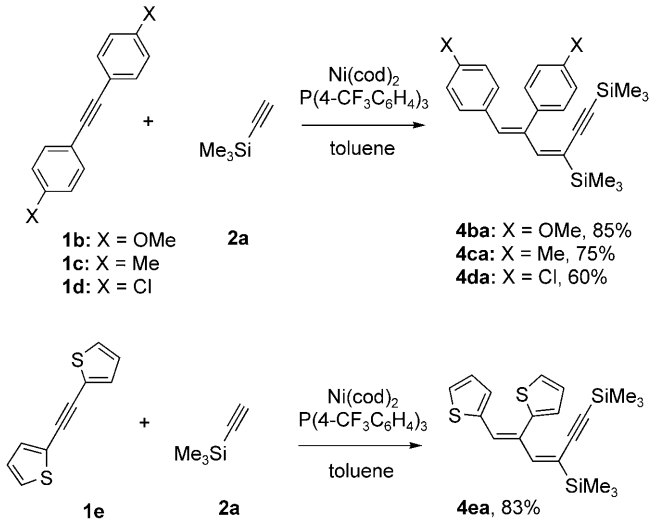
[a] *Reaction conditions:* [Ni(cod)$_2$]:[**2b**]:[**5**] = 0.0125:0.75:0.25 (in mmol) in toluene (2.5 mL) under N_2. *Si* = $SiMe_2Bu$-*t* (**2b**).
[b] Isolated yield based on the amount of **5** used. Product ratio was determined by ^{1}H NMR. Unless the *E*/*Z* ratio is noted, *E* > 98%.
[c] 30 mol% of ligand was used.
[d] 5 mol% of ligand was used.
[e] 2,6-Lutidine (0.1 mL) was used.
[f] Toluene (1.4 mL) was used.
[g] Less than 10% yield.
[h] Complex mixture.
[i] No reaction.

The reactions of some symmetrical internal alkynes including 4-octyne, 2-butyne-1,4-diol, 1,4-dimethoxy-2-butyne, and dimethyl acetylenedicarboxylate with **2a** were also examined using Ni(cod)$_2$/DMAP. Among the alkynes, 1,4-dimethoxy-2-butyne (**5f**) smoothly reacted with **2a** to give the corresponding enyne **8fa** with a good yield (Scheme 1), although the reactions of the other internal alkynes did not proceed. The alkyne **5f** was also coupled with silylacetylenes **2b** and **2c**. The reaction of **5f** with **2a** using Xantphos as ligand also took place stereoselectively, albeit the yield of **8fa** (35%) was moderate.



Scheme 1. Reaction of 1,4-dimethoxy-2-butyne (**5f**) with silylacetylenes **2a–c**. *Reaction conditions:* [a] [Ni(cod)$_2$]:[Ligand]:[**5f**]:[**2**] = 0.025:0.15:0.5:1.5 (in mmol). [b] [Ni(cod)$_2$]:[Ligand]:[**5f**]:[**2**] = 0.075:0.0125:0.25:0.75 (in mmol).

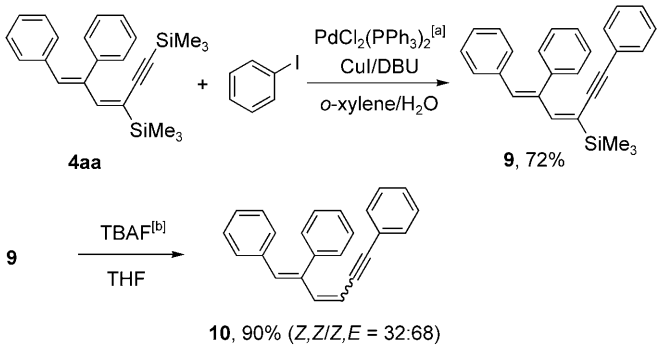
Since the selective 1:2 cross-trimerization of alkynes such as that of **1a** with **2a** is an attractive, straightforward way to construct a π-conjugated dienyne system, the reactions of a number of diarylacetylenes with **2a** were examined under the conditions used for entry 7 in Table 1 using P(4-$CF_3C_6H_4$)$_3$ as ligand. As depicted in Scheme 2, the diarylacetylenes



Scheme 2. Reaction of diarylacetylenes **1b–e** with silylacetylene **2a** to give dienynes **4**. *Reaction conditions:* [Ni(cod)$_2$]:[P(4-$CF_3C_6H_4$)$_3$]:[**1**]:[**2a**] = 0.00625:0.00625:0.25:0.75 (in mmol).

having electron-donating **1b,c** and -withdrawing substituents **1d** as well as bis(2-thienyl)acetylene (**1e**) effectively reacted with **2a** to produce 1:2 cross-trimers **4ba**–**4ea** with good isolated yields. Treatment of the unsymmetrical acetylene **5b** with **2a** under the same conditions, however, gave a complex mixture containing trimerized products, which was confirmed by GC-MS.

The silyl groups in compounds **4** may be expected to undergo certain desilylative transformation reactions. As an example, the terminal silyl moiety of **4aa** was selectively substituted by desilylative Sonogashira coupling[10] with iodobenzene to afford 1,2,6-triphenyl-4-trimethylsilyl-(1*Z*,3*E*)-1,3-hexadien-5-yne (**9**) in 72% yield. The subsequent protodesilylation by treatment with Bu_4NF also proceeded to form of 1,2,6-triphenyl-1,3-hexa-5-yne (**10**) (Scheme 3). It is worth noting that compound **10** was previously used as a substrate for electrocyclization after partial hydrogenation.[11]



Scheme 3. Sonogashira coupling and desilylation of **4aa**. *Reaction conditions:* [a] [**4aa**]:[Pd]:[CuI]:[DBU] = 0.25:0.015:0.25:1.5 (in mmol) in *o*-xylene-H_2O (1.0 mL, 95:5 v/v), 100 °C, 9 h. [b] **10** (0.25 mmol), 0 °C, 30 min.

As for the first step of the nickel-catalyzed reactions of terminal silylacetylenes *via* C(*sp*)–H bond cleavage, oxidative addition of the acetylenes to nickel(0) species to give $(R_3SiCC)(H)Ni(II)$ complexes is usually postulated.[5,9] It may be reasonable to consider that the subsequent insertion of the internal acetylene or successive double insertion of internal and terminal acetylenes to the Ni–C or Ni–H bonds of the key intermediates and reductive elimination afford enynes and dienynes. It was confirmed that enyne **3aa** did not react with **2a** under the conditions used for entry 7 in Table 1. This suggests that a stepwise route to **4** through **3** does not participate. The striking effects of pyridine- or phosphine-based ligands on the selectivity of di- and trimerizations could be caused by the different ease of reductive elimination after the first insertion. However, further studies are required to establish this as well as to understand the observed ligand effects on regioselectivity in the insertion steps. Also, participation of an alternative mechanism that involves a nickelacycle as intermediate, especially for the cross-trimerization, cannot be excluded.

Conclusions

We have described remarkable ligand effects on the nickel-catalyzed cross-oligomerization of alkynes. The cross-dimer of diphenylacetylene and trimethylsilylacetylene is selectively formed in the presence of $Ni(cod)_2$/DMAP, while their 1:2 cross-trimerization takes place with use of $P(4\text{-}CF_3C_6H_4)_3$ as ligand in place of DMAP. The cross-dimerization of internal arylalkynes having an oxygen function at the propargyl position in place of diphenylacetylene also proceeds effectively to give the corresponding enynes with unusual regioselectivity in some cases.

Experimental Section

General Remarks

^1H and ^{13}C NMR spectra were measured at 400 MHz and 100 MHz, respectively, for $CDCl_3$ solutions. The configurations of the products were determined with the aid of NOE, HMBC, and HMQC measurements. MS data were obtained in the EI mode unless otherwise noted. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m) or a CBP-1 capillary column (i.d. 0.5 mm × 25 m). GC-MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m).

Diarylacetylenes **1b**–**1e** were prepared by the Sonogashira coupling of trimethylsilylacetylene (**2a**) with aryl iodides according to the published method.[10]

The following experimental procedures may be regarded as typical in methodology and scale. Other product data are given in the Supporting Information.

Nickel-Catalyzed Cross-Dimerization of Diphenylacetylene (1a) with Trimethylsilylacetylene (2a) (Table 1, entry 2)

A mixture of $Ni(cod)_2$ (0.00625 mmol, 1.70 mg = 0.125 mL of 0.05 M toluene solution), DMAP (0.0375 mmol, 4.5 mg), **1a** (0.25 mmol, 45 mg), **2a** (0.75 mmol, 74 mg), and hexamethylbenzene (*ca.* 50 mg) as internal standard in toluene (2.5 mL) was stirred in a Schlenk tube at 50 °C for 9 h under an N_2 atmosphere. The solvent was evaporated, and then the residue was purified by column chromatography on silica gel using hexane as eluent to afford **3aa** as a white solid; yield: 57.5 mg (82%). The ^1H and ^{13}C NMR spectra matched with those reported previously.[8c] The *E*/*Z* ratio of **3aa** estimated by ^1H NMR was 88:12. Recrystallization with hexane gave (*E*)-**3aa**; mp 87 °C; ^1H NMR: $\delta = 0.24$ (s, 9H), 7.04–7.07 (m, 2H), 7.10 (s, 1H), 7.14–7.16 (m, 3H), 7.26–7.30 (m, 3H), 7.36–7.38 (m, 2H); ^{13}C NMR: $\delta = -0.01$, 94.46, 107.60,

124.19, 127.66, 127.80, 128.08, 128.40, 129.08, 129.33, 135.99, 137.33, 137.36; HR-MS: $m/z =$ 276.1338, calcd. for $C_{19}H_{20}Si$: 276.1334; anal. calcd. for $C_{19}H_{20}Si$: C 82.55, H 7.29; found: C 82.52, H 7.31.

Nickel-Catalyzed 1:2 Cross-Trimerization of Diphenylacetylene (1a) with Trimethylsilylacetylene (2a) (entry 7 in Table 1)

A mixture of $Ni(cod)_2$ (0.00625 mmol, 1.70 mg = 0.125 mL of 0.05 M toluene solution), $(4\text{-}CF_3C_6H_4)_3P$ (0.00625 mmol, 2.9 mg), **1a** (0.25 mmol, 45 mg), **2a** (0.75 mmol, 74 mg), and hexamethylbenzene (*ca.* 50 mg) as internal standard in toluene (2.5 mL) was stirred in a Schlenk tube at 50 °C for 3 h under N_2 atmosphere. The solvent was evaporated, and then the residue was purified by column chromatography on silica gel using hexane as eluent to afford **4aa** as a white solid; yield: 72 mg (82%); mp 90 °C (from methanol); ^{1}H NMR: $\delta = 0.05$ (s, 9H), 0.20 (s, 9H), 6.62 (s, 1H), 6.93–6.96 (m, 2H), 7.08–7.10 (m, 3H), 7.22–7.24 (m, 2H), 7.26 (s, 1H), 7.32–7.33 (m, 3H); ^{13}C NMR: $\delta = -1.92$, 0.10, 104.47, 109.04, 125.11, 127.19, 127.47, 127.92, 128.53, 129.69 (overlapped), 133.46, 136.72, 139.59, 140.90, 147.64; HR-MS: $m/z = 374.1884$, calcd. for $C_{24}H_{30}Si_2$: 374.1886; anal. calcd. for $C_{24}H_{30}Si_2$: C 76.94, H 8.07; found: C 76.72, H 8.02.

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