

Reaction of alkynylsilanes with CuCl in polar solvents leading to alkynyl group transfer from Si to Cu

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Received 8 September 2000; received in revised form 16 October 2000; accepted 18 October 2000

Abstract

The reaction of 1-phenyl-2-trimethylsilylethyne with CuCl at 80–100°C in *N,N*-dimethylformamide (DMF) or *N,N*-dimethylimidazolidinone (DMI) yielded the alkynylcopper species $[\text{Cu}_2\text{Cl}(\text{C}\equiv\text{CPh})]_n$ (**1**) in 56–63% yields. Heating **1** at 80°C under aerobic conditions gave 1,4-diphenyl-1,3-butadiyne in 82% yield via an oxidative coupling of the phenylethynyl ligands. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkynylsilane; Transmetalation; Copper salt; Oxidative coupling; Diyne

1. Introduction

Recently Hosomi and his coworkers and our group independently found cross-coupling reactions of $\text{PhC}\equiv\text{CSiMe}_3$ with acyl chlorides catalyzed by CuCl [1] and with aryl triflates catalyzed by CuCl–Pd(PPh₃)₄ [2] (Scheme 1).

The latter reaction is a modified version of the Sonogashira–Takahashi–Hagihara coupling of terminal alkynes with aryl halides [3] and takes advantage of the use of $\text{PhC}\equiv\text{CSiMe}_3$ rather than $\text{PhC}\equiv\text{CH}$ as a source of the phenylethynyl part. Both reactions probably involve CuCl promoted Si–C(*sp*) bond cleavage of the alkynylsilane to form an alkynylcopper species with high reactivity toward coupling with the electrophiles and transmetalation giving an alkynylpalladium species leads to the smooth catalytic reactions shown in Scheme 1.

Although oxidative addition of alkynylsilane to Pt(0) [4], Rh(I) [5] and Ru(0) [6] complexes was reported to cause formation of metal–C(*sp*) and/or metal–Si bonds, activation of Si–C(*sp*) bond promoted by Cu(I) compound has attracted much less attention. Hosomi et al. suggested that the reaction of $\text{PhC}\equiv\text{CSiMe}_3$ with CuCl in *N,N*-dimethylimidazolidinone (DMI) gave $[\text{Cu}(\text{C}\equiv\text{CPh})]_n$ after ultrasonication of the product in

NH₃ aq. [7]. In this paper we report results of the study on the reaction in DMF to give another type of Cu compound with alkynyl ligands.

2. Experimental

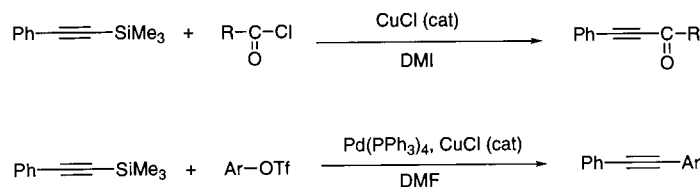
All reactions were carried out under an argon atmosphere using standard Schlenk tube techniques. *N,N*-dimethylformamide (DMF) and DMI were distilled over CaSO₄ and stored over MS-4A under an argon atmosphere. Copper(I) chloride was purified by reprecipitation of a solution in conc. HCl with water. The ²⁹Si{¹H}-NMR spectra were obtained on a JEOL EX-400 (79.6 MHz) using tetramethylsilane (Me₄Si) as the reference (0 ppm). The IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer in KBr. Elemental analyses were carried out by Yanaco MT-5 CHN autocorder. XRD patterns were measured with Rigaku X-ray diffractometer RINT Ultima + /PC.

2.1. Reaction of 1-phenyl-2-trimethylsilylethyne with CuCl in DMF

To a suspension of CuCl (4.0 g, 40 mmol) in DMF (40 ml) placed in a 50 ml of Schlenk tube equipped with a magnetic stirring bar was added 1-phenyl-2-trimethylsilylethyne (3.9 ml, 20 mmol) at room temper-

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Scheme 1. CuCl catalyzed cross-coupling reactions of alkynylsilane.

ature (r.t.). The reaction mixture was heated to 80°C and stirred for 3 h. The solution was transferred to a 100 ml of round-bottom flask under Ar atmosphere and was subjected to distillation giving Me₃SiCl (bp 58°C) in 75% yield. The residual bright yellow precipitates in the Schlenk were collected and washed successively with 50 ml of acetonitrile and 50 ml of diethyl ether. Bright yellow powders were dried under vacuum to give [Cu₂Cl(C≡CPh)]_n (**1**) (2.95 g, 11.2 mmol, 56%). Anal. Calc. for C₈H₅ClCu₂; C, 36.44; Cl, 13.44; H, 1.91. Found: C, 36.30; Cl, 13.50; H, 1.74%.

2.2. Reaction of 1-phenyl-2-trimethylsilylethyne with CuCl in DMI

To a solution of 1-phenyl-2-trimethylsilylethyne (590 μl, 3.0 mmol) in 30 ml of DMI placed in a 50 ml of Schlenk tube equipped with a magnetic stirring bar was added CuCl (600 mg, 6.0 mmol) at r.t. The reaction mixture was heated to 100°C and stirred for 48 h. The formed bright canary yellow precipitates were collected by filtration and washed successively with 50 ml of acetonitrile and 50 ml of diethyl ether. Bright yellow powders were dried under vacuum to give [Cu₂Cl(C≡CPh)]_n (**1**) (498 mg, 1.9 mmol, 63%). Anal. Calc. for C₈H₅ClCu₂; C, 36.44; Cl, 13.44; H, 1.91. Found: C, 35.42; Cl, 13.46; H, 1.91%.

2.3. Reaction of [Cu(C≡CPh)]_n with CuCl

To a suspension of [Cu(C≡CPh)]_n [**8**] (165 mg, 1.0 mmol) in 20 ml of DMI was added CuCl (200 mg, 2.0 mmol) at r.t. The reaction mixture was heated to 100°C for 48 h. The resulting yellow solid was collected by filtration and washed with 50 ml of acetonitrile and 50 ml of diethyl ether. The complete removal of the volatiles gave [Cu₂Cl(C≡CPh)]_n (**1**) as bright yellow powders in 91% yield. Anal. Calc. for C₈H₅ClCu₂; C, 36.44; Cl, 13.44; H, 1.91. Found: C, 36.95; Cl, 13.40; H, 1.87%.

2.4. Treatment of [Cu₂Cl(C≡CPh)]_n (**1**) with ultrasonication in NH₃ aq.

To [Cu₂Cl(C≡CPh)]_n (**1**) (1.0 g, 3.9 mmol) placed in 200 ml of Erlenmeyer flask was poured 50 ml of

ammonia solution. The resulting mixture was treated with ultrasonication for 5 min at r.t. The resulting yellow solid was collected by filtration and the above procedure was repeated until the color of solution became colorless. The obtained yellow solid was washed with water (50 ml), ethanol (50 ml), and diethyl ether (50 ml) and the complete removal of the volatiles gave [Cu(C≡CPh)]_n (469 mg, 2.9 mmol) in 73% yield. Anal. Calc. for C₈H₅Cu; C, 58.35; Cl, 0.00; H, 3.06. Found: C, 57.64; Cl, 0.00; H, 3.33%.

2.5. Homocoupling reaction of [Cu₂Cl(C≡CPh)]_n (**1**)

To a DMF (25 ml) suspension of [Cu₂Cl(C≡CPh)]_n (**1**) (1.3 g, 5.0 mmol) placed in a reaction tube equipped with a magnetic stirring bar. The reaction mixture was stirred for 72 h at 80°C under exposure to an atmospheric air and quenched with 3 M hydrochloric acid. The aqueous layer was separated and extracted with 30 ml of diethyl ether. The combined ethereal layer was washed with brine and dried over anhydrous MgSO₄. Bulb to bulb distillation (220–230°C/7 Torr) gave 1,4-diphenyl-1,3-butadiyne [**9**] (415 mg, 2.1 mmol) in 82% yield as a white solid.

2.6. Cross-coupling reaction of [Cu₂Cl(C≡CPh)]_n (**1**) with an aryl triflate

To a suspension of [Cu₂Cl(C≡CPh)]_n (**1**) (1.58 g, 6.0 mmol) in DMF (50 ml) placed in a Schlenk tube equipped with a magnetic stirring bar were added tetrakis(triphenylphosphine)palladium (290 mg, 0.25 mmol, 5 mol%) and 4-acetylphenyl trifluoromethanesulfonate (945 μl, 5.0 mmol) at r.t. The reaction mixture was stirred for 72 h at 80°C under an argon atmosphere, and quenched with 3 M HCl. The aqueous layer was separated and extracted with diethyl ether (25 ml × 4). The combined ethereal layers were washed with NaHCO₃ aq., brine and dried over MgSO₄. Filtration and evaporation afforded a brown oil. Bulb to bulb distillation (240–250°C/7 Torr) and column chromatography (silica gel, hexane–diethyl ether = 1: 1, R_f = 0.56) gave 1-[4-(phenylethynyl)phenyl]ethanone [**10**] (191 mg, 0.86 mmol) in 17% yield as a white solid, along with 1,4-diphenyl-1,3-butadiyne (312 mg, 1.54 mmol) in 51% yield.

Table 1
Synthesis of **1** and the results of elemental analysis

Run	Alkynylsilane:CuCl	Solvent	Temperature (°C)	Time (H)	Yield (%)	Analyses (%) ^a		
						C	H	Cl
1	1:1	DMF	r.t.	12	19	36.45	1.78	12.99
2	1:1	DMF	80	6	8	35.88	1.67	12.81
3	1:1	DMF	80	24	32	36.22	1.71	12.52
4	1:2	DMF	r.t.	22	42	36.45	1.92	13.52
5	1:2	DMF	80	3	56	36.30	1.74	13.53
6	1:1	DMI	60	6	35	36.01	1.93	13.57
7	1:2	DMI	100	48	63	35.42	1.93	13.46

^a Anal. Calc. for **1** (C₈H₅ClCu₂): C, 36.44; H, 1.91; Cl, 13.44%. Anal. Calc. for [Cu(C≡CPh)]_n (C₈H₅Cu): C, 58.35; H, 3.06; Cl, 0.00%.

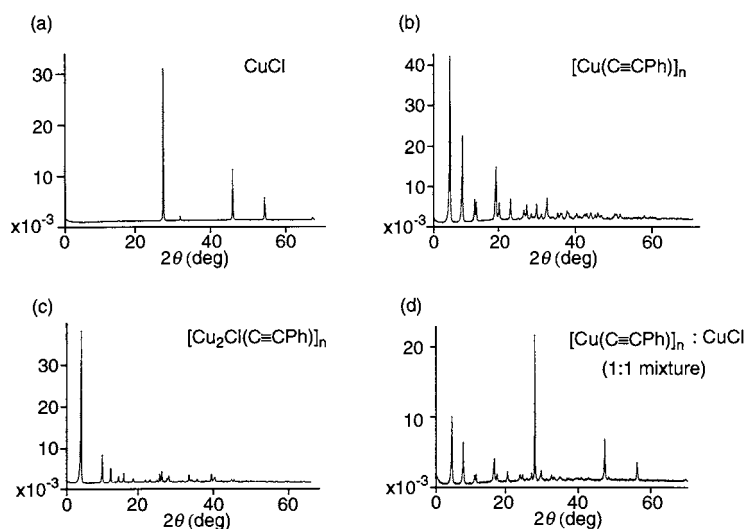


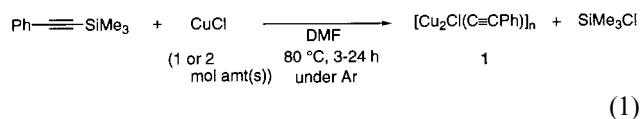
Fig. 1. X-ray diffraction of (a) CuCl; (b) [Cu(C≡CPh)]_n; (c) [Cu₂Cl(C≡CPh)]_n (**1**); and (d) 1:1 mixture of [Cu(C≡CPh)]_n and CuCl.

2.7. XRD analysis

CuCl, [Cu(C≡CPh)]_n, [Cu₂Cl(C≡CPh)]_n, and 1:1 mixture of [Cu(C≡CPh)]_n and CuCl were subjected to a glass plate for XRD analysis and set in the diffractometer.

3. Results and discussion

The reaction of PhC≡CSiMe₃ with CuCl in 1:1 and 1:2 molar ratios in DMF proceeded at 80°C to give [Cu₂Cl(C≡CPh)]_n (**1**) in 32 and 56% yields, respectively, based on the alkynylsilane (Eq. (1)).

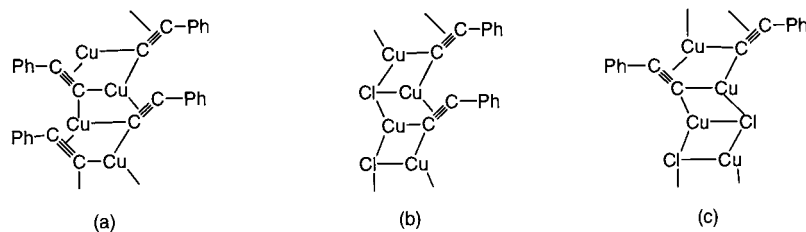


Complex **1** was isolated as a bright yellow solid by washing the solid product with acetonitrile to remove a soluble fraction containing CuCl. Elemental analyses (C, H, and Cl) of the product agree with the calculated

values from the proposed formulae (Table 1)¹. Although the poor solubility of **1** in organic solvents, such as THF, DMF, Et₂O, and hexane, prevented a detailed NMR characterization, the IR spectrum of **1** in a KBr disk demonstrated that the ν(C≡C) vibration (1950 (w), 1935 (w) cm⁻¹) is similar to that of [Cu(C≡CPh)]_n (1950 (sh), 1930 (w) cm⁻¹) [8].

Fig. 1 shows the wide angle X-ray diffraction pattern of **1** with angles and relative intensities quite different from both CuCl and [Cu(C≡CPh)]_n. All these data indicate that complex **1** has a unique structure of [Cu₂Cl(C≡CPh)]_n and is not a physical mixture of CuCl and [Cu(C≡CPh)]_n. Complex **1** appears to have an infinite crystal structure with Cu centers bonded both to Cl and C≡CPh ligands. By comparison with the reported structure of [Cu(C≡CPh)]_n (Scheme 2(a)) [11], two possible arrays of the Cu₂Cl(C≡CPh) units are shown in Scheme 2(b) and (c).

¹ Incomplete combustion of the complex **1**, probably due to the polymeric material, led to large deviations from the calculated value. For instance, the observed values for the same complex **1** (Table 1, run 1) were as follows: C, 36.45; H, 1.78 and C, 37.14; H, 2.00.

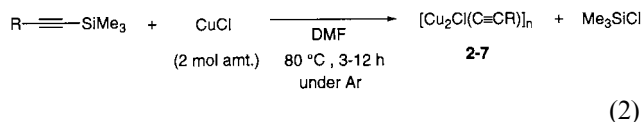
Scheme 2. (a) Crystal structure of $[\text{Cu}(\text{C}\equiv\text{CPh})]_n$, (b), (c) Possible structures of **1**.Table 2
Synthesis of **2–7** and the results of elemental analyses and IR

R	Yield (%)	Color	Found (Calc.)			IR (cm^{-1}) ($\nu_{\text{C}\equiv\text{C}}$)
			C	H	Cl	
4-MeCO-C ₆ H ₄ - (2)	58	Orange	39.56 (39.29)	2.17 (2.31)	11.49 (11.60)	1923
4-MeO-C ₆ H ₄ - (3)	67	Yellow	36.80 (36.81)	2.48 (2.40)	11.93 (12.07)	1877
2-Thienyl (4)	49	Brown	26.62 (26.72)	1.18 (1.12)	13.04 (13.15)	1863
4-Cl-C ₆ H ₄ - (5)	40	Pale yellow	31.67 (32.23)	1.57 (1.35)	22.93 (23.78)	1898
4-C ₈ H ₁₇ -C ₆ H ₄ - (6)	41	Yellow	51.17 (51.13)	5.37 (5.63)	9.46 (9.43)	1902
C ₆ H ₁₃ - (7)	52	Pale yellow	34.61 (35.61)	4.65 (4.82)	13.21 (13.05)	1927

The organic product of reaction (1) was collected by distillation and identified as Me_3SiCl by its boiling point and a comparison of the $^{29}\text{Si}\{^1\text{H}\}$ -NMR peak position (31.8 ppm) from tetramethylsilane (Me_4Si) with an authentic sample.

The equimolar reaction of $\text{PhC}\equiv\text{CSiMe}_3$ with CuCl in DMI followed by treatment with NH_3 aq. was reported to give $[\text{Cu}(\text{C}\equiv\text{CPh})]_n$ rather than **1** [7]. We conducted several related reactions and elucidated detailed aspects of the reaction. Heating a mixture of $\text{PhC}\equiv\text{CSiMe}_3$ and CuCl in DMF and in DMI followed by washing the insoluble bright yellow product with acetonitrile gave **1** as a sole product. Further treatment of **1** with ultrasonication in NH_3 aq. led to $[\text{Cu}(\text{C}\equiv\text{CPh})]_n$ in 73% yield accompanied by removal of CuCl . On the other hand, heating a mixture of $[\text{Cu}(\text{C}\equiv\text{CPh})]_n$ and CuCl at 100°C in DMI gave **1** in 91% yield.

The reactions of other $\text{RC}\equiv\text{CSiMe}_3$ with CuCl in DMF also led to formation of $[\text{Cu}_2\text{Cl}(\text{C}\equiv\text{CR})]_n$ **2–7** as shown in Eq. (2). The results of elemental analyses and IR data for **2–7** in Table 2 are consistent with the proposed structure, $[\text{Cu}_2\text{Cl}(\text{C}\equiv\text{CR})]_n$.



The occurrence of $\text{Si}-\text{C}(\text{sp})$ bond cleavage promoted by CuCl is evidenced by direct homocoupling and cross-coupling reactions of the alkynyl group in alkynylsilanes [2,10]. In order to show that **1** is the real intermediate in the above reactions, we heated isolated **1** in DMF under aerobic conditions and found that the

homocoupled product, $\text{PhC}\equiv\text{C}-\text{C}\equiv\text{CPh}$ was formed in 82% yield [12]. The cross-coupling reaction with an aryl triflate using a stoichiometric amount of **1** produced 1-[4-(phenylethynyl)phenyl]ethanone in 17% yield, along with 1,4-diphenyl-1,3-butadiyne in 51% yield².

DMF performs as an efficient medium in these $\text{Si}-\text{C}(\text{sp})$ bond activation promoted by CuCl , whereas other polar solvents such as Et_2O , THF and MeCN are not suitable as the reaction solvent [1,2]. Kobayashi et al. reported a significant shift of the $^{29}\text{Si}\{^1\text{H}\}$ -NMR signal of crotyltrichlorosilane in DMF (ca. -170 ppm) to low frequency, suggesting stable coordination of the solvent molecule to the Si center giving a reactive penta- or hexa-coordinated silyl compound [13]. $\text{PhC}\equiv\text{CSiMe}_3$, however, did not show a solvent dependent shift of the $^{29}\text{Si}\{^1\text{H}\}$ -NMR signal³. Thus, the role of DMF in the reactions (1) and (2) may be coordination to Cu and activation of the $\text{Si}-\text{C}$ bond rather than coordination to the Si center.

4. Conclusions

The simple reaction system, CuCl -DMF (or DMI), activates the $\text{Si}-\text{C}(\text{sp})$ bond of alkynylsilanes under

² High concentration of an alkynylcopper species in the cross-coupling reaction with an aryl triflate leads to the formation of 1,4-diphenyl-1,3-butadiyne even under an argon atmosphere; see Ref. [2].

³ The $^{29}\text{Si}\{^1\text{H}\}$ -NMR of $\text{PhC}\equiv\text{CSiMe}_3$ appeared as a singlet in all cases at -17.78 ppm (CDCl_3), -17.78 ppm (C_6D_6), -18.19 ppm (CD_3CN), -16.39 ppm ($\text{THF}-d_8$), and -17.85 ppm ($\text{DMF}-d_7$), respectively.

mild conditions. The resulting species containing a Cu–C(*sp*) bond are probably involved in the cross-coupling reactions of alkynylsilane with acyl chlorides and aryl triflates reported recently and in the oxidative homo-coupling of $\text{RC}\equiv\text{CSiMe}_3$ giving conjugated diynes.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (A) no. 07405042 from the Ministry of Education, Science, Sports, and Culture, Japan.

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