SYNTHESES AND METAL-CATALYZED C–H BOND ACTIVATION OF ALKYNE π COMPLEXES OF COPPER(I) TRIFLUOROMETHANESULFONATE

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(Received June 24th, 1983)

Summary

The copper(I) trifluoromethanesulfonate π complexes of 1,8-cyclotetradecadiyne and 1,7-octadiyne have been synthesized. For a series of terminal alkyne (CuO_3SCF_3) π complexes, vibrational spectra show weakening of both C≡C and C_{sp}–H bonds upon copper(I) coordination. NMR analysis shows less Cu(I) caused deshielding of C(1) than C(2) of the alkyne and increased C_{sp}–H coupling. Copper(I) π coordination to terminal alkynes increases the rate of exchange of protium on C(1) for deuterium from CD_3COOD. Copper enhances the rate of exchange by a factor of 1.2×10^5 with 1,7-octadiyne. The exchange is catalytic in copper(I) and is faster than the rate of copper alkynide formation in the absence of deuterium donor. Copper(I) catalyzes deuterium exchange for protium at C(1) between 1,7-octadiyne and 1-hexyne-1-d_1.

Introduction

The chemistry of terminal alkynecopper(I) π complexes has remained virtually unexplored. To date the only complexes isolated have been of the type $(RCCH)CuAlCl_4$ (R = C_6H_5, H, t-C_4H_9) from reaction of the corresponding alkyne with $L_2CuAlCl_4$ (L = C_6H_6, $CH_3C_6H_5$) at −10°C [1]. Heating of the π complexes liberated the free alkynes, and addition of water led to copper alkynide σ complexes.

Syntheses of these complexes have been limited by two factors. First, copper alkynide σ complexes are more stable than the corresponding π complexes so that attempted π complex synthesis often leads to contaminated products. Second, copper(I) is prone to redox disproportionation to copper(0) and copper(II). Salomon and Kochi have shown in synthesis of a series of monoene and polyene π complexes that the latter problem can be reduced by use of the poorly coordinating trifluoromethanesulfonate (triflate, OTf) anion [2,3]. Ginnebaugh et al. have used silver(I) triflate to prepare the first reported silver π complexes of terminal monoynes and diynes [4].

An NMR investigation of the ethyne/HCl/H$_2$O/CuCl system has been reported [5]. The report mentions in passing that D$_2$O was not used as a solvent because chemical exchange between the protons leads to diminishment of ethyne proton NMR resonance. No further mention was made of the ethyne C$_{sp}$–H bond activation.

In this paper we report the synthesis and characterization of terminal and internal alkyne π complexes of copper triflate. Also reported is the enhanced activation of the alkyne C$_{sp}$–H bond toward deuterium exchange catalyzed by copper(I). Studies designed to elucidate mechanistic possibilities for this exchange are described.

Experimental

General

All samples were transferred in a dry bag or dry box under an atmosphere of dried and purified nitrogen. Syntheses were carried out in standard airlessware apparatus. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Melting points were measured in sealed, evacuated capillaries and are uncorrected. Reagents were purified before use by standard methods, and liquids were further dried over activated 4A molecular sieves. Benzene(CuO$_3$SCF$_3$)$_2$ was prepared as described by Salomon and Kochi [3]. Terminal alkynes-1-d_1 were prepared as described previously [6].

Instrumental analyses

NMR spectra were obtained from a JEOL FX-90Q spectrometer operating at 90 or 22.5 MHz. Chemical shifts were reported in parts per million from internal Me$_4$Si. NMR samples of complexes were prepared from mixtures of benzene(CuO$_3$SCF$_3$)$_2$ and alkyne in benzene-d_6 such that the concentrations of alkyne and copper(I) were 8.10 $\pm$ 0.15 mole percent. Reference spectra without copper were of the same concentrations.

Mass spectra were obtained on a Hewlett–Packard 5995A GC-MS system operating at 70 eV.

Infrared spectra were recorded as described previously [4].

Preparation of 1,8-cyclotetradecadiyne(CuO$_3$SCF$_3$)$_2$

To C$_6$H$_6$(CuO$_3$SCF$_3$)$_2$ (1.23 g, 2.44 mmol) was added 1,8-cyclotetradecadiyne (0.56 g, 2.98 mmol) dissolved in benzene (10 ml). The mixture was stirred vigorously and heated to 80°C for 15 min to afford a dark purple suspension. The suspension was filtered, and white crystals were collected on the frit. They were washed with pentane and dried in vacuo (0.95 g, 63%), m.p. with decomposition at 213.5–214°C. (Found: C, 31.58; H, 3.50. C$_{16}$H$_{20}$Cu$_2$F$_6$O$_6$S$_2$ calcd.: C, 31.70; H, 3.32%). The complex was air stable but hygroscopic. Upon exposure to moist air, the complex absorbed water to form the hydrate, 1,8-cyclotetradecadiyne(CuO$_3$SCF$_3$)$_2$ · 4H$_2$O. (Found: C, 28.04; H, 4.08. C$_{16}$H$_{28}$Cu$_2$F$_6$O$_{10}$S$_2$ calcd.: C, 28.35; H, 4.16%). Heating of the hydrate at 110°C in an evacuated vessel resulted in loss of water with regeneration of the original complex.

Preparation of 1,7-octadiyne(Cu$_2$O$_3$SCF$_3$)$_2$

To C$_6$H$_6$(CuO$_3$SCF$_3$)$_2$ (1.23 g, 2.44 mmol) was added 2-butanone (1.5 ml) to give

a colorless solution. After addition of 1,7-octadiyne (0.45 ml, 2.8 mmol), the solution became dark red during 20 min of vigorous stirring. Nitromethane (1.0 ml) was added, and the solution was cooled to 5°C. Upon addition of pentane (7 ml), a white solid precipitated. The mixture was filtered, the white crystalline solid was washed with two portions of nitromethane (10 ml each), and it was dried in vacuo (1.26 g, 97%), m.p. with decomposition at 157–161°C. (Found: C, 22.82; H, 1.99. $C_{10}H_{10}Cu_2F_6O_6S_2$ calcd.: C, 22.60; H, 1.90%). The complex was air sensitive and hygroscopic.

Deuterium exchange of terminal alkynecopper trifluoromethanesulfonate π complexes with CD_3COOD

To benzene$(CuO_3SCF_3)_2$ (0.221 g, 0.440 mmol) in an NMR tube was added CD_3NO_2 (0.676 ml) and enough terminal alkyne to give a 1/1 ratio of copper ion to triple bond. Dichloromethane (8 to 10 μl) was added as an internal standard. A proton NMR spectrum with integration was obtained. Acetic acid-d_4 was added so that the ratio of copper ion/triple bond/CD_3COOD was 1/1/1, and the solution was 0.8 M in each. The reaction was followed by repeated integration of the terminal and α-methylene proton NMR resonances of the alkyne. The terminal proton resonance decreased in area with time, while the area of the α-methylene resonance remained constant. Integrations were made every 25 sec for 10.5 min, then at periodic intervals up to 1 h, when a final spectrum was obtained.

The reactions without copper were identical to those above except benzene $(CuO_3SCF_3)_2$ was omitted.

Copper alkynide formation

The same procedure was used as for deuterium exchange except (a) acetic acid-d_4 was omitted and (b) the proton NMR spectra were integrated over a period of days rather than hours. The copper alkynides formed were soluble in the reaction solution.

Catalytic efficiency of deuterium exchange

A stock solution was prepared which contained 1,7-octadiyne (4.30 g, 40.5 mmol) and benzene$(CuO_3SCF_3)_2$ (20.4 mg, 4.05×10^{-2} mmol) in CH_3NO_2. To this solution was added enough acetic acid-d_4 (5.19 g, 81.0 mmol) to afford a solution 0.4 M in alkyne.

At various intervals, a 10 ml aliquot was transferred to a separatory funnel containing 10 ml of water saturated with $NaHCO_3$ to terminate copper(I) π coordination [7]. The aqueous solution was extracted with pentane, and the layers were separated. The pentane layer was washed with water, dried over Na_2SO_4, and filtered. The pentane was removed in vacuo. The alkyne residue was analyzed for deuterium incorporation by IR as a thin film between NaCl plates.

Deuterium exchange between 1,7-octadiyne$(CuO_3SCF_3)_2$ and 1-hexyne-1-d_1

To benzene$(CuO_3SCF_3)_2$ (152 mg, 0.302 mmol) was added CD_3NO_2 (1.40 ml). A 1/1 mole ratio of C≡C–D to C≡C–H and a 4/1 mole ratio of triple bond to copper ion were obtained by addition of 1,7-octadiyne (64.1 mg, 0.604 mmol) and 1-hexyne-1-d_1 (100.6 mg, 1.21 mmol). At intervals of 1 and 24 h reaction time, 300 μl aliquots of the solution were transferred to a distilling bulb. The liquid was flash evaporated

(24°C, 10 mmHg pressure) into a receiver cooled to −196°C. The colorless condensate was analyzed by GC-mass spectrometry. The amounts of 1,7-octadiyne-d_0, 1,7-octadiyne-1-d_1, and 1,7-octadiyne-1,8-d_2 were determined.

Results and discussion

Syntheses of alkyne(CuO₃SCF₃)₂ complexes

The complexes 1,8-cyclotetradecadiyne(CuO₃SCF₃)₂ and 1,7-octadiyne(CuO₃-SCF₃)₂ were prepared by reaction of the diyne with benzene(CuO₃SCF₃)₂. Benzene (CuO₃SCF₃)₂ had been prepared by the method of Salomon and Kochi [3]. The diyne complexes could be generated in a variety of solvents (benzene, 2-butanone, 2-butanol); however, in many cases workup led to insoluble green solids or the desired white, crystalline product contaminated with them. As the procedures in the experimental section indicate, we have found no single procedure that is suitable for all alkynes.

When the diyne complexes were exposed to moisture during their syntheses hydrated complexes were obtained. The 1,8-cyclotetradecadiyne π complex upon exposure to water yielded a hydrated complex as evidenced by elemental analysis and broad absorption at 3000–3500 cm^{-1} in the IR. Elemental analysis indicated a reproducible stoichiometry of 1,8-cyclotetradecadiyne(CuO₃SCF₃)₂ · 4H₂O. The analogous anhydrous complex could be generated by heating of the hydrate at reduced pressure. None of the volatile 1,8-cyclotetradecadiyne ligand was lost in the process.

Similarly, the copper(I) π complex of 1,7-octadiyne may be obtained as the hydrate. We did not determine the stoichiometry of this hydrate, but found that it too could be converted to the anhydrous π complex as described for the 1,8-cyclo-tetradecadiyne complex.

Analysis of vibrational spectra

The effect of π coordination of copper(I) to terminal alkynes is apparent from the IR spectra. They were obtained from solutions of benzene(CuO₃SCF₃)₂ dissolved in a minimum amount of terminal alkyne. Since there exists an equilibrium between free and complexed alkyne, the IR spectra exhibited absorptions from both species. However, with nearly saturated solutions free alkyne absorptions were very weak. IR stretching frequencies are recorded in Table 1.

The absorptions from terminal C_{sp}–H bond stretching were clearly present and were of similar intensity for both the free and coordinated alkyne. Thus, copper alkynide σ complexes were not formed in solution. Upon copper(I) π coordination the C_{sp}–H absorptions decreased in frequency (68–107 cm^{-1}) and were significantly broadened. While the effect of copper(I) π coordination upon C_{sp}–H stretching frequencies has not been reported previously, the decrease in stretching frequencies seen here is similar to those reported for terminal alkynecopper(II) adsorbed in Na–Y zeolite (99–165 cm^{-1}) [8]. It is important for prediction of C_{sp}–H bond activation by transition metals (vide infra) that this bond is apparently weakened by π coordination.

The C≡C stretching frequencies are decreased also (81–173 cm^{-1}) upon copper(I) π coordination, consistent with the Dewar–Chatt–Duncanson model [9]. The termi-nal diynes exhibit two absorptions in the coordinated triple bond region; the

TABLE 1

INFRARED STRETCHING FREQUENCIES (cm^{-1}) FOR UNCOORDINATED AND COPPER(I) COORDINATED ALKYNES

Alkyne	C_{sp}–H stretch		C≡C stretch	
	Uncoordinated alkyne	Coordinated alkyne	Uncoordinated alkyne	Coordinated alkyne
1-Hexyne	3317	3210	2120	1960
3-Methyl-1-pentyne	3310	3210	2113	1949
3,3-Dimethyl-1-butyne	3305	3211	2112	1951
1,5-Hexadiyne	3293	3225	2125	2044,1952
1,7-Octadiyne	3295	3214	2130	2036, 2011

monoynes exhibit one. For the diynes this is consistent with a dimer–monomer equilibrium of species with 1/1 ratio of C≡C to copper(I) or a mixture of complexes with varying ratio of C≡C to copper(I). There is precedent for variable coordination number of copper(I) in the 1,5-cyclooctadiene(CuO$_2$CCF$_3$)$_2$ and 1,5-cyclooctadiene(CuO$_2$CCF$_3$) complexes reported by Dines [10].

Analysis of NMR spectra

In Table 2 are presented the NMR chemical shifts and coupling constants of selected nuclei of terminal alkynes both with and without one equivalent of copper(I). In both cases the solvent was C$_6$D$_6$.

Comparison of NMR spectral parameters among different alkyne CuOTf complexes if difficult because exchange between free and complexed alkyne is rapid on the NMR timescale. Only a time average of species in solution is seen even with addition of excess alkyne. Values of spectral data are a function of complex stability constants.

TABLE 2

PROTON AND CARBON NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF ALKYNE π COMPLEXES OF COPPER(I)

Compound	Chemical shift (δ, ppm)			Coupling constant (Hz), terminal H–C(1)
	Terminal H	C(1)	C(2)	
1-Hexyne	2.01	68.12	83.78	246.59
1-Hexyne [a]	3.50	69.15	90.55	251.46
3-Methyl-1-pentyne	2.15	68.29	88.01	246.58
3-Methyl-1-pentyne [a]	4.00	68.99	98.08	251.46
3,3-Dimethyl-1-butyne	1.94	66.77	92.07	246.58
3,3-Dimethyl-1-butyne [a]	3.60	68.50	102.25	250.24
1,5-Hexadiyne	1.96	69.32	81.99	247.81
1,5-Hexadiyne [a]	3.36	71.48	87.85	256.96

[a] Alkyne/Cu (1/1) in C$_6$D$_6$ (8.1 mole percent).

The NMR work of Vestin et al. with ethyne/HCl/H_2O/CuCl reported ethyne proton deshielded by δ 2.65 ppm and ethyne carbon shielded by δ 1.1 ppm compared to the system without CuCl [5]. In our studies copper(I) π coordination deshields not only proton on C(1), but also C(1) and C(2). The variation is not surprising in light of the work by Salomon and Kochi with copper(I) where olefinic proton shielding or deshielding was dependent upon coordination geometry [11]. Our observations differ from those of terminal alkyne complexes of AgOTf where C(2) and the proton on C(1) are deshielded, but the C(1) resonance undergoes a silver(I) induced movement to higher magnetic field strength [12]. The silver(I) coordination effects were interpreted as evidence for C_{sp}–H bond polarization (I), leading to enhanced reactivity toward electrophilic substitution.

$$\overset{\delta-}{-C} \equiv \overset{\delta+}{C} - H$$
$$\underset{Ag^+}{\big|}$$
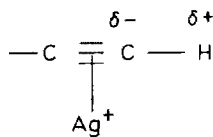
(I)

Although C(1) is deshielded in our copper(I) π complexes, copper(I) induced C_{sp}–H bond polarization as for silver(I) is still possible. The deshielding of C(1) results from electron withdrawal by copper(I). With a relatively high charge/size ratio, copper(I) is so poor at back donation into the vacant $\pi^\star$ orbital of the triple bond that net deshielding of both sp carbons occurs. However, deshielding of C(1) (δ < 2.2 ppm deshielding) is much less than that of C(2) (δ 6–10 ppm deshielding). Thus, C(1) deshielding may be reduced by copper(I) enhanced polarization of the C_{sp}–H bond.

A reason for C_{sp}–H bond polarization would be enhanced s character of C(1) upon copper(I) π coordination. The increase in C(1) s character is supported by the increase in ^{13}C–H coupling constant at the terminal carbon in every alkyne with copper(I) coordination (Table 2).

Lowered values of ^{13}C–H$_\alpha$ coupling constants have been found in electron deficient alkylidene complexes (Ta(CHPh)(PMe$_3$)$_2$Cl$_3$) [13]. The lowering was attributed to increased p character in the C–H$_\alpha$ bond from a direct interaction with Ta [14]. While our system is certainly different and it is not clear how generally valid the correlation of ^{13}C–H coupling constant with metal interaction is, there is no evidence in our NMR data to support bonding interaction between copper(I) and the C_{sp}–H bond in the ground state. However, on the basis of C_{sp}–H bond weakening (IR evidence) and C_{sp}–H bond polarization (NMR evidence), it is possible that copper(I) π coordination will lead to selective and enhanced reactivity of the alkyne terminal C–H bond.

Enhancement of terminal C–H bond reactivity by copper(I)

To determine whether C_{sp}–H bond activation would be facilitated by copper(I) π coordination, the exchange of D for H at the terminal carbon was measured as a function of time (eq. 1).

$$\underset{Cu^+}{RC \equiv CH} + CD_3COOD \xrightleftharpoons{CD_3NO_2} \underset{Cu^+}{RC \equiv CD} + CD_3COOH \qquad (1)$$
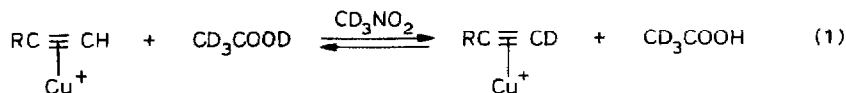
The alkyne used was 1,7-octadiyne and the deuterium source was acetic acid-d_4. The reaction was monitored by proton NMR spectroscopy. Area decrease of the resonance from the H on sp carbon relative to the constant areas for resonances of H on sp^2 carbon and CH_2Cl_2 (the internal standard) was measured by repeated integration. No D incorporation was observed at other than the sp carbon. The solvent CD_3NO_2 was not seen to incorporate H, and a resonance appeared at δ 11–12 ppm from the formation of CD_3COOH. The only H for D exchange observable was that shown in eq. 1. Any loss of 1,7-octadiyne occurring from polymerization would have been observable by proton NMR spectroscopy; no polymerization products were seen.

Fig. 1. Proton NMR spectra of 1,7-octadiyne(CuO$_3$SCF$_3$)$_2$: a = CH$_2$Cl$_2$, b = CD$_3$NO$_2$(CD$_2$HNO$_2$), c = proton on C(1), d = proton on C(3), e = proton on C(4); (above) before addition of CD$_3$COOD, (below) 20 min after addition of one equivalent of CD$_3$COOD.

In 0.4 M solutions of 1,7-octadiyne(CuO$_3$SCF$_3$)$_2$ in CD$_3$NO$_2$ with CD$_3$COOD (1 Cu/1 C≡CH/1 CD$_3$COOD) rapid decrease in area of the terminal H resonance was observed (Fig. 1 and 2). After 20 min, equilibrium between 1,7-octadiyne, 1,7-octadiyne-1-d_1, 1,7-octadiyne-1,8-d_2, CD$_3$COOD, and CD$_3$COOH was reached with 37% D incorporation at the terminal carbon.

In the absence of CuOTf, the exchange occurs but at a much slower rate. With 1,7-octadiyne, 17% exchange occurs in 764 days. Copper(I) causes D exchange to occur a minimum of 1.2×10^5 times faster than without copper(I).

We have observed the same copper(I) caused C_{sp}–H bond activation for the alkynes 3,3-dimethyl-1-butyne and 1,5-hexadiyne. In both cases D exchange reached equilibrium in less than 20 min. Because of the very long reaction times without copper(I), we have measured the extended time rate of D exchange without copper(I) for 1,7-octadiyne only. Short reaction times (1 week) for 3,3-dimethyl-1-butyne and 1,5-hexadiyne without copper(I) give negligible D exchange. So, activation of the C_{sp}–H bond toward electrophilic substitution appears general for terminal alkynes when π coordinated to copper(I). In this property, they parallel the chemistry found in the presence of silver(I) salts [4,6].

In order to elucidate the mechanism of this marked C_{sp}–H bond activation, the effect of variables such as copper(I) concentration, D donor strength and concentration, and alkyne concentration needs study. Unfortunately, a complete kinetic analysis is not feasible at this stage. Figure 3 illustrates the change in proton NMR chemical shift of terminal H with changing Cu^I/C≡C ratio for 1,7-octadiyne. With silver salts it has been shown that a sharp breakpoint and leveling of the plot is indicative of the complex stoichiometry (i.e. the major species in solution) [4,15]. With 1,7-octadiyne, there is no clearly discernable breakpoint, and leveling does not occur until an excess of copper(I) is present. Thus, more than one complex stoichiometry and/or a significant amount of uncoordinated alkyne exists in solu-
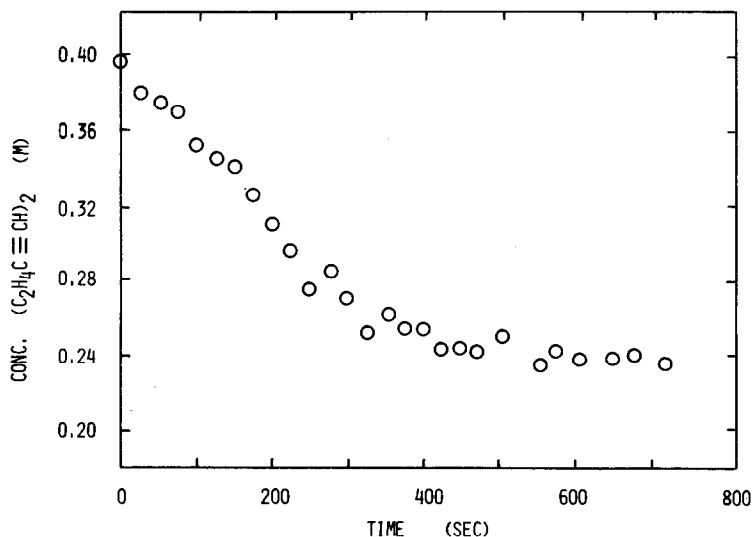

Fig. 2. Change in concentration of 1,7-octadiyne-d_0 versus time for the deuterium exchange reaction (eq. 1).
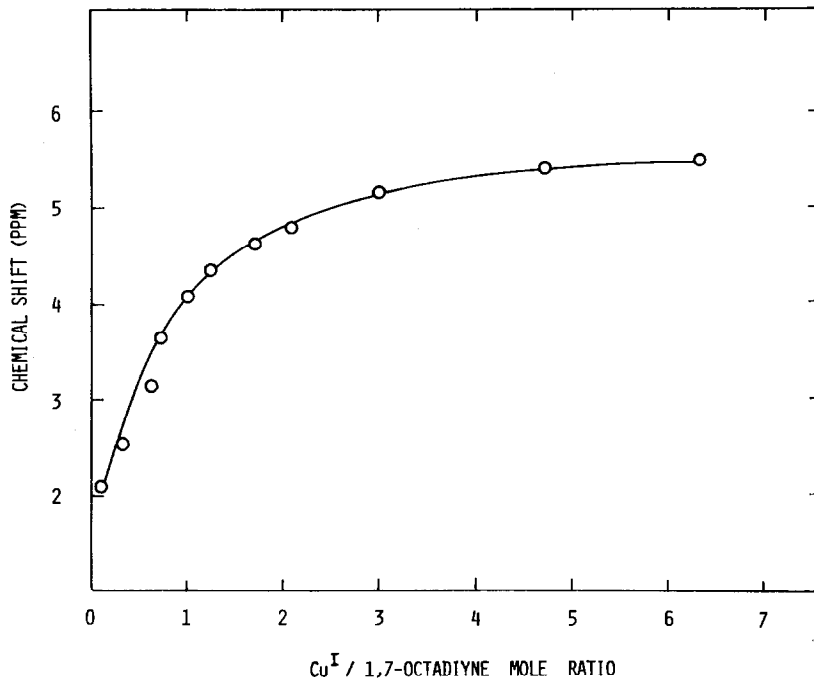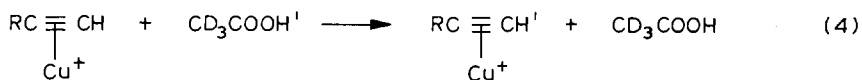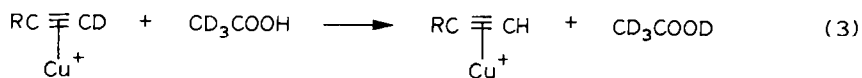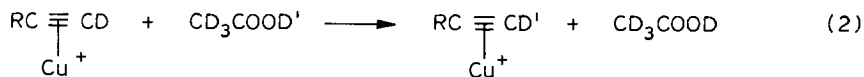
Fig. 3. Plot of Cu^I/1,7-octadiyne mole ratio versus chemical shift of proton on C(1).

tion. This type of plot is found for 1-hexyne also. Without a knowledge of complex stoichiometry in solution useful kinetic analysis is impossible.

Catalysis of terminal C–H bond activation

Without a rigorous kinetic analysis it is still possible to clarify some of the mechanistic features of C_{sp}–H bond activation. To determine if copper(I) is playing a stoichiometric or catalytic role, solutions of 1,7-octadiyne (0.4 M) in CH_3NO_2 containing benzene$(CuO_3SCF_3)_2$ and CD_3COOD were prepared. The mole ratios of $C≡C/CD_3COOD/Cu^I$ were 100/100/1. Progress of the D exchange reaction could not be monitored by proton NMR spectroscopy because of overlap of H on *sp* carbon resonance with other resonances. Analysis by IR was possible because the C_{sp}–D stretching frequency (2585 cm^{-1}) is 710 cm^{-1} less than the C_{sp}–H stretching frequency (3295 cm^{-1}), allowing quantitative measurement of D exchange. Decrease in C_{sp}–H band intensity and increase in C_{sp}–D band intensity was measured as a function of time relative to the unchanging C–H bending band at 1440 cm^{-1}. The extinction coefficient of the 1440 cm^{-1} band is identical for both 1,7-octadiyne-d_0 and 1,7-octadiyne-1,8-d_2. The D exchange values are found in Table 3. For the reactants described above, D exchange occurred more slowly than with the 1/1/1 ratio of $C≡C/CD_3COOD/Cu^I$. From the time required to reach 17% exchange, the reaction with the 100/100/1 ratio occurred approximately 500 times slower. After ~ 15 days, 43% D incorporation into the alkyne has occurred. The minimum number of turnovers seen at these concentrations is 43 C_{sp}–H per copper(I) ion. The real turnover number is much higher because of nonproductive exchanges (eq. 2–4).

$$RC \equiv CD \quad + \quad CD_3COOD' \quad \longrightarrow \quad RC \equiv CD' \quad + \quad CD_3COOD \qquad (2)$$
$$\underset{Cu^+}{|}$$

$$RC \equiv CD \quad + \quad CD_3COOH \quad \longrightarrow \quad RC \equiv CH \quad + \quad CD_3COOD \qquad (3)$$

$$RC \equiv CH \quad + \quad CD_3COOH' \quad \longrightarrow \quad RC \equiv CH' \quad + \quad CD_3COOH \qquad (4)$$

In an identical experiment with a $C\equiv C/CD_3COOD/Cu^I$ ratio of 1000/1000/1 over ~ 40 days, the minimum number of turnovers for D exchange was 497 C_{sp}–H per copper(I) ion. Thus, activation of the C_{sp}–H bond is truly catalytic in copper(I).

Mechanistic role of copper alkynides

Because of the known ability of Group IB metals to form metal alkynides from terminal alkynes (eq. 5) [16], the intermediacy of copper alkynides could be pro-

$$RC\equiv CH + M^+ \rightarrow RC\equiv CM + H^+ \qquad (5)$$
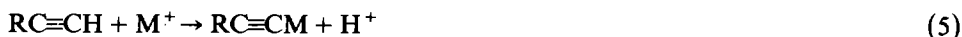
posed in the D exchange reaction. If the reaction in eq. 5 occurred before or as the rate-determining step, the rate of D exchange (eq. 1) should be no faster than the rate of copper alkynide formation.

We have measured the rate of alkynide formation with 1,7-octadiyne at the same concentrations as in the D exchange reaction except that no CD_3COOD was present. Analysis by proton NMR spectroscopy showed that the resonance from H on the *sp* carbon compared to the unchanging α-methylene resonance decreased in area by 14% over 18 days. Since no polymer formation or loss of 1,7-octadiyne from solution was seen, this corresponds to 14% copper alkynide formation requiring 18 days. Since (a) copper alkynide formation requires days while at the same concentrations D exchange requires less than 20 min and (b) alkynide formation occurs to a

TABLE 3

CATALYSIS BY COPPER(I) OF DEUTERIUM EXCHANGE BETWEEN 1,7-OCTADIYNE AND CD_3COOD

Time $(min \times 10^{-3})$ [a]	% exchange	Time $(min \times 10^{-3})$ [b]	% exchange
0	0	0	0
0.81	13.3	1.32	0.8
1.41	16.0	2.04	2.2
1.89	17.2	2.79	3.0
2.28	22.6	4.65	5.3
2.91	25.7	7.50	6.6
4.71	27.2	21.96	18.8
7.59	42.9	47.70	45.6
22.05	43.1	57.60	49.7

[a] 100 $C\equiv C$/100 CD_3COOD/1 Cu^I. [b] 1000 $C\equiv C$/1000 CD_3COOD/1 Cu^I.

TABLE 4

OBSERVED ION INTENSITIES IN THE MOLECULAR ION REGION OF 1,7-OCTADIYNE

m/e	Peak	Intensity (%)
105	$(M-1)^+$	100
106	$(M)^+$	8.8
107	$(M+1)^+$	–

significant extent in 18 days, D exchange cannot take place via copper alkynide intermediates.

Deuterium exchange between alkynes

The above work describes copper(I) catalyzed activation of terminal alkynes evidenced by deuterium exchange from CD_3COOD. The question remains as to whether D incorporation in the alkyne must necessarily come from a carboxylic acid and whether carboxylic acid must play a mechanistic role in copper(I) catalysis.

We have allowed 1,7-octadiyne to react with 1-hexyne-1-d_1 in the presence of benzene(CuOTf)$_2$. The ratio of 1,7-octadiyne/1-hexyne-1-d_1/Cu^I was 1.0/2.0/1.0 in CH_3NO_2. The appearance of protium in 1-hexyne and deuterium in 1,7-octadiyne could not be monitored by proton NMR because of overlap of resonances from protium on C(1) of both alkynes. Consequently, analysis was done by mass spectrometry. The solution was sampled at 1 and 24 hour reaction times.

The observed ion intensities in the molecular ion region of 1,7-octadiyne (MW 106.17) are given in Table 4. The $(M-1)^+$ fragment at m/e 105 has been adjusted to 100%. The observed molecular ion intensities for terminal alkynes are negligible [17]. Therefore, the intensity of the m/e 106 ion can be attributed almost totally to the ^{13}C and ^2H natural abundance in the 1,7-octadiyne $(M-1)^+$ fragment. Before using ion intensities to evaluate deuterium incorporation, the ^{13}C and ^2H contributions were subtracted. The theoretical isotopic contributions of the $(M-1)^+$ fragment to the $(M)^+$ and $(M+1)^+$ peaks of 1,7-octadiyne are 8.8 and 0.34% respectively [18].

Another consideration is the isotope effect in cleavage of ˙H and ˙D. Gross and Aerni have reported that in the mass spectral fragmentation of 1,5-hexadiyne-1,6-d_2, a deuterium isotope effect (k_H/k_D) of 2.3 is observed, following complete scrambling [19]. Dolejsek et al. have reported that deuterium is mostly retained in terminally labelled alkynes [20]. With 1-octyne-1-d_1, 82% of the deuterium was retained in the $(M-1)^+$ fragment.

TABLE 5

PRODUCT DISTRIBUTION FROM REACTION OF 1-HEXYNE-1-d_1 AND 1,7-OCTADIYNE-d_0 IN THE PRESENCE OF COPPER(I)

	% composition			
	after 1 h		after 24 h	
	Set 1	Set 2	Set 1	Set 2
1,7-Octadiyne-d_0	99.6	99.5	79.3	74.6
1,7-Octadiyne-1-d_1	0.4	0.5	19.1	23.4
1,7-Octadiyne-1,8-d_2	–	–	1.6	2.0

Using the above information, two calculations of ion intensities have been made (Table 5). In Set 1, the assumption is made that in partially deuterated 1,7-octadiyne ˙H is always fragmented. In the event of ˙D cleavage, deuterated products will contribute to several ion intensities in the molecular ion region, while with no ˙D cleavage each deuterated product will contribute to only one ion intensity. In Set 2, a k_H/k_D value of 4.0 is assumed based on the work of Dolejsek et al. [20]. Using either assumption the data in Table 5 show that slow exchange of D between 1-hexyne-1-d_1 and 1,7-octadiyne can occur. Both 1,7-octadiyne-1-d_1 and 1,7-octadiyne-1,8-d_2 were observed by mass spectrometry. Thus, it is possible for Cu(I) to activate the C_{sp}–H bond of a terminal alkyne without the mechanistic intervention of a carboxylic acid. This would make unlikely D exchange occurring by addition of the deuterium bearing reagent across the triple bond followed by elimination.

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