are contained in the SHELXTL program library (5.1) (Nicolet Corp., Madison, WI).

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Supplementary Material Available: For complex **5a**, tables of atomic coordinates and isotropic thermal parameters (Table 1S), bond lengths (Table 2S), bond angles (Table 3S), anisotropic thermal parameters (Table 4S), and H atom coordinates and isotropic thermal parameters (Table 5S) (6 pages); a table of observed and calculated structure factors (Table 6S) (20 pages). Ordering information is given on any current masthead page.

(Alkyne)(2,2′-bipyridine)copper(I) Complexes. Controlled Formation of $[Cu(bpy)(alkyne)]^+$ and $\{[Cu(bpy)]_2(alkyne)\}^{2+}$

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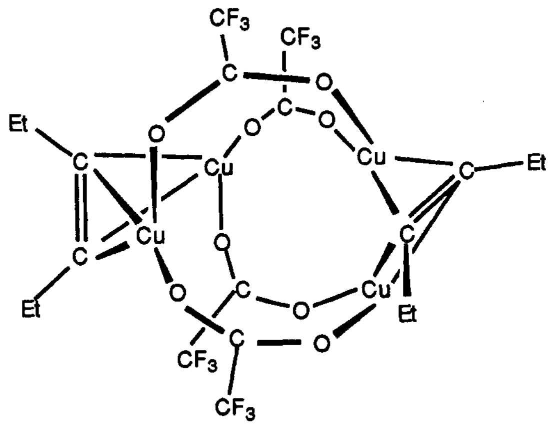
The addition of 1 equiv of 2,2′-bipyridine (bpy) to a solution of $Cu(NCMe)_4X$ ($X = PF_6^-$, SbF_6^-) followed by addition of an excess of alkyne (alkyne = 3-hexyne, 1-pentyne, methyl 2-butynoate, diphenylacetylene, diethyl acetylenedicarboxylate, phenylacetylene) leads to the preparation of [Cu(bpy)(alkyne)]X complexes in good yield. In order to isolate pure products, the alkyne complexes must be precipitated in the presence of excess alkyne. The alkyne ligands are labile in solution, exchanging rapidly on the NMR time scale. Competition studies show that the relative affinities of the alkynes (and ethylene) for copper in this system are $C_2H_4 \sim HC{\equiv}CPr > EtC{\equiv}CEt \sim DEAD > HC{\equiv}CPh > MeC{\equiv}CCO_2Me > PhC{\equiv}CPh$. Repeated precipitation from solutions that initially contain [Cu(bpy)(alkyne)]X (alkyne = diethyl acetylenedicarboxylate, phenylacetylene) complexes in the absence of added alkyne leads to the isolation of $\{[Cu(bpy)]_2(alkyne)\}X_2$, complexes with a 2:1 copper:alkyne stoichiometry.

Introduction

Continuing our interest in the synthesis and reactivity of η^2-alkyne complexes of the transition metals,[1] we have recently reported the preparation and characterization of neutral adducts of copper(I) trifluoroacetate.[2] In addition to the preparation of the expected $[Cu(O_2CCF_3)(alkyne)]_2$ complexes,[3] we reported that tetranuclear complexes with a copper:alkyne ratio of 4:2, $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-alkyne})_2$, can also be prepared. In certain cases, these alkyne-deficient complexes form even in the presence of excess alkyne. In fact, the copper to alkyne stoichiometry (either 4:2 or 2:2) can be controlled by the choice of alkyne or variations in the purification procedures. The solid-state structure of $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-EtC}{\equiv}\text{CEt})_2$ shows that in these unusual tetranuclear complexes each of the alkyne ligands bridge two copper atoms that are not directly bridged by other ligands (structure A). This surprising tendency for the formation of complexes with the $Cu_2(\mu\text{-alkyne})$ bonding arrangement has been noted by others.[4,5]



A

While most transition elements do form stable complexes containing bridging alkynes,[6] the copper subgroup had been a notable exception until these recent studies.

Reported here are the results of studies extending this chemistry to cationic (2,2′-bipyridine)copper(I) derivatives. As observed in the trifluoroacetate system, complexes with both 1:1 and 2:1 copper:alkyne ratios can be prepared. The only similar alkyne complex of copper(I) was reported by Thompson and Whitney.[7] They have prepared and

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characterized in the solid state [Cu(di-2-pyridylamine)-(HC≡CH)]BF_4, but no mention of 2:1 complexes has been made previously.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer using Nujol mulls. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 or AM-500 spectrometer using a 5-mm broad-band probe. Proton and carbon chemical shifts are reported in ppm downfield from TMS using the solvent CD_3COCD_3 (δ_H = 2.04 ppm, δ_C = 29.8, 206.0 ppm) as the internal standard. The reported ^{1}H coupling constants are $^3J_{HH}$ values unless otherwise indicated. All spectra were recorded at room temperature unless otherwise indicated. Elemental analyses were performed by Robertson Laboratories, Inc. FAB mass spectra were run on a VG 70SQ mass spectrometer using a matrix of *m*-nitrobenzyl alcohol. The clusters assigned to specific ions show the appropriate patterns as calculated for the atoms present. $Cu(NCMe)_4PF_6$ and $Cu(NCMe)_4SbF_6$ were prepared by the published methods.[8]

(2,2′-Bipyridine)(3-hexyne)copper(I) Hexafluorophosphate, [Cu(bpy)(3-hexyne)]PF_6. $Cu(NCMe)_4PF_6$ (1.00 g, 2.68 mmol) was dissolved in acetone (100 mL). A solution of 2,2′-bipyridine (bpy) (0.42 g, 2.7 mmol) in acetone (25 mL) was added, and the resulting deep red solution was stirred for 45 min. To the deep red solution was added 3-hexyne (3.04 mL, 2.20 g, 26.8 mmol). The mixture became brown and cloudy and then gained a light greenish tint upon stirring. After stirring for 3 h, the solvent was evaporated under vacuum to half the original volume. Hexane (50 mL) was added to precipitate the product. The solution was filtered away from the powder via filterstick. The product was dried in vacuo overnight (0.938 g, 78%). ^{1}H NMR (δ): 8.91 (2, d, *J* = 5 Hz, bpy), 8.71 (2, d, *J* = 8 Hz, bpy), 8.41 (2, t, *J* = 8 Hz, bpy), 7.92 (2, t, *J* = 5 Hz, bpy), 2.90 (4, q, *J* = 7 Hz, CH_2), 1.40 (6, t, *J* = 7 Hz, CH_3). ^{13}C NMR (δ): 152.9, 151.0, 141.7, 128.0, 123.1 (bpy); 91.7 (C≡); 16.0 (CH_2); 14.8 (CH_3). FABMS (*m*/*e*): 301 (Cu(bpy)(3-hexyne)), 219 (Cu(bpy)). IR (cm^{-1}): 1598, 1602 (m, m, bpy). Anal. Calcd for $CuC_{16}H_{18}N_2PF_6$: C, 43.04; H, 4.06. Found: C, 42.53; H, 3.95.

(2,2′-Bipyridine)(1-pentyne)copper(I) Hexafluorophosphate, [Cu(bpy)(HC≡$CCH_2CH_2CH_3$)]PF_6. A deep red solution of $Cu(NCMe)_4PF_6$ (1.00 g, 2.68 mmol) and bpy (0.42 g, 2.7 mmol) in acetone (125 mL) was prepared as above. Addition of 1-pentyne (2.64 mL, 1.82 g, 26.8 mmol) turned the solution to a clear, light orange color. After stirring for 3 h, the volume was reduced to ca. 20 mL by evaporation of the solvent in vacuo. Hexane (75 mL) was added to precipitate the product. The powder was filtered away from the solution and was dried in vacuo overnight (0.996 g, 86%). ^{1}H NMR (δ): 8.99 (2, d, *J* = 5 Hz, bpy), 8.65 (2, d, *J* = 8 Hz, bpy), 8.38 (2, t, *J* = 8 Hz, bpy), 7.90 (2, t, *J* = 5 Hz, bpy), 5.44 (1, t, ^4J = 2 Hz, HC≡C), 2.94 (2, t of d, ^4J = 2 Hz, ^3J = 7, CH_2C≡), 1.83 (2, sextet, *J* = 7 Hz, CH_2CH_3), 1.10 (3, t, *J* = 7 Hz, CH_3). ^{13}C NMR (−15 °C, δ): 153.0, 151.4, 142.2, 128.3, 123.3 (bpy); 97.5 (-*C*≡CH); 75.9 (HC≡C-); 24.0, 23.4, 13.4 ($CH_2CH_2CH_3$). FABMS (*m*/*e*): 287 (Cu(bpy)(1-pentyne)), 219 (Cu(bpy)). IR (cm^{-1}): 1932 (m, C≡C); 1599, 1608 (s, m, bpy). Anal. Calcd for $CuC_{15}H_{16}N_2PF_6$: C, 41.65; H, 3.73. Found C, 41.61; H, 3.36.

(2,2′-Bipyridine)(methyl 2-butynoate)copper(I) Hexafluorophosphate, [Cu(bpy)(CH_3C≡CCO_2CH_3)]PF_6. A mixture of $Cu(NCMe)_4PF_6$ (1.00 g, 2.68 mmol) and bpy (0.42 g, 2.7 mmol) in acetone (70 mL) was prepared and was stirred for 10 min. To the deep red solution was added methyl 2-butynoate (2.7 mL, 2.6 g, 27 mmol). The color of the solution lightened slightly upon addition of alkyne. After stirring for 1.5 h, the solvent was evaporated under vacuum to ca. 20 mL. Hexane (50 mL) was added to precipitate the product. The solution was filtered away from the solid. The light blue product was washed with hexane (3 × 10 mL) and dried overnight in vacuo (1.19 g, 96%). ^{1}H NMR (δ): 9.05 (2, d, *J* = 5 Hz, bpy), 8.72 (2, d, *J* = 8 Hz, bpy), 8.43 (2, t, *J* = 8 Hz, bpy), 7.95 (2, t, *J* = 5 Hz, bpy), 3.96 (3, s, OCH_3), 2.71 (3, s, CH_3C≡). ^{13}C NMR (δ): 155.35 (C═O); 152.90, 151.29, 142.06, 128.12, 123.22 (bpy); 99.48; 79.34 (C≡C); 55.48 (OCH_3); 7.01 (CH_3). FABMS (*m*/*e*): 317 (Cu(bpy)(MeC≡CCO_2Me)), 219 (Cu(bpy)). IR (cm^{-1}): 2000 (m, C≡C); 1718 (s, C═O); 1609, 1599 (m, m, bpy). Anal. Calcd for $CuC_{15}H_{14}N_2O_2PF_6$: C, 38.95; H, 3.05. Found: C, 38.73; H, 2.93.

(2,2′-Bipyridine)(diphenylacetylene)copper(I) Hexafluorophosphate, [Cu(bpy)(PhC≡CPh)]PF_6. A mixture of $Cu(NCMe)_4PF_6$ (1.00 g, 2.68 mmol) and bpy (0.42 g, 2.7 mmol) in acetone (125 mL) was prepared and was stirred for 30 min. To the deep red solution was added a solution of diphenylacetylene (4.78 g, 26.8 mmol) dissolved in acetone (25 mL). The color of the mixture lightened a little. After stirring for 2 h, the solvent was evaporated under vacuum to ca. 20 mL. The light blue-green product was precipitated with hexane (75 mL), filtered, and washed with hexane (3 × 10 mL). The powder was dried overnight in vacuo (1.37 g, 94%). ^{1}H NMR spectrum (δ): 8.68, 8.36, 8.08 (all 2, br, bpy); 7.79 (6, m, bpy and ortho phenyl protons); 7.59 (6, m, para and meta phenyl protons). ^{13}C NMR (−15 °C, δ): 153.0, 150.0, 142.2, 128.2, 123.6 (bpy); 131.2, 130.4, 130.2 (phenyl); 93.5 (C≡); ipso phenyl carbon atom not observed. FABMS (*m*/*e*): 397 (Cu(bpy)(C_2Ph_2)), 219 (Cu(bpy)). IR (cm^{-1}): 2000 (w, alkyne); 1611, 1602 (m, m, bpy). Anal. Calcd for $CuC_{24}H_{18}N_2PF_6$: C, 53.14; H, 3.34. Found: C, 52.94; H, 3.30.

(2,2′-Bipyridine)(diethyl acetylenedicarboxylate)copper(I) Hexafluorophosphate, [Cu(bpy)($EtCO_2C$≡CCO_2Et)]PF_6. A mixture of $Cu(NCMe)_4PF_6$ (1.00 g, 2.68 mmol) and bpy (0.42 g, 2.7 mmol) in acetone (50 mL) was prepared as above. To this deep red solution was added diethyl acetylenedicarboxylate (DEAD) (5.1 mL, 5.4 g, 32 mmol) via syringe. The color of the solution lightened upon addition of the alkyne. After stirring for 1.5 h, the mixture was filtered and reduced in volume by ca. one-quarter by evaporation of the solvent in vacuo. Hexane (50 mL) was added to precipitate a white powder. The product was isolated via filtration, washed with hexane (3 × 10 mL), and dried overnight in vacuo (1.19 g, 82%). ^{1}H NMR (δ): 9.11 (2, d, *J* = 5 Hz, bpy), 8.73 (2, d, *J* = 8 Hz, bpy), 8.46 (2, t of d, ^4J = 2 Hz, ^3J = 8 Hz, bpy), 8.00 (2, m, ^4J = 2 Hz, ^3J = 8 Hz, bpy), 4.54 (4, q, *J* = 7 Hz, CH_2's), 1.43 (6, t, *J* = 7 Hz, CH_3's). FABMS (*m*/*e*): 389 (Cu(bpy)(DEAD)), 219 (Cu(bpy)). IR (cm^{-1}): 1935 (m, C≡C); 1718 (s, C═O); 1611, 1601 (m, m, bpy). Anal. Calcd for $CuC_{18}H_{18}N_2O_4PF_6$: C, 40.45; H, 3.39. Found: C, 40.63; H, 3.40.

(4,4′-Dimethyl-2,2′-bipyridine)(diethyl acetylenedicarboxylate)copper(I) Hexafluoroantimonate, [Cu(Me_2bpy)($EtCO_2C$≡CCO_2Et)]SbF_6. A mixture of $Cu(NCMe)_4SbF_6$ (0.250 g, 0.539 mmol) and Me_2bpy (0.10 g, 0.54 mmol) in acetone (40 mL) was prepared. To this deep red solution was added DEAD (0.86 mL, 0.92 g, 5.4 mmol) via syringe. The color of the solution disappeared upon addition of the alkyne. After stirring for 1 h, the mixture was filtered and reduced in volume by ca. half by evaporation of the solvent in vacuo. Hexane (30 mL) was added to precipitate a white powder. The product was isolated via filtration, washed with hexane (3 × 10 mL), and dried overnight in vacuo (0.310 g, 88%). ^{1}H NMR (δ): 8.91 (2, d, *J* = 5 Hz, bpy), 8.59 (2, s, bpy), 7.80 (2, d, *J* = 5 Hz, bpy), 4.54 (4, q, *J* = 7 Hz, OCH_2), 2.63 (6, s, $(CH_3)_2$bpy), 1.44 (6, t, *J* = 7 Hz, OCH_2CH_3). Anal. Calcd for $CuC_{20}H_{22}N_2O_4SbF_6$: C, 36.75; H, 3.39. Found: C, 36.56; H, 3.39.

(2,2′-Bipyridine)(phenylacetylene)copper(I) Hexafluoroantimonate, [Cu(bpy)(HC≡CPh)]SbF_6. A solution of bpy (0.34 g, 2.2 mmol in 25 mL of acetone) was added to a solution of $Cu(NCMe)_4SbF_6$ (1.00 g, 2.16 mmol in 25 mL of acetone). To this deep red solution was added phenylacetylene (2.21 g, 21.6 mmol) via syringe. After stirring for ca. 1.5 h, the mixture was filtered and reduced in volume to ca. 15 mL by evaporation of the solvent in vacuo. Hexane (50 mL) was added to precipitate the shiny yellow powder. The product was filtered, washed with hexane (3 × 10 mL) and dried overnight in vacuo (1.20 g, 98%). ^{1}H NMR (δ): 8.71 (2, d, *J* = 8 Hz, bpy), 8.63 (2, d, *J* = 5 Hz, bpy), 8.40 (2, d of t, ^3J = 8 Hz, ^4J = 2 Hz, bpy), 7.86 (2, m, bpy), 7.79 (2, m, Ph), 7.62 (3, m, Ph), 6.34 (1, s, HC≡). Anal. Calcd for $CuC_{18}H_{14}N_2SbF_6$: C, 38.79; H, 2.53. Found: C, 38.49; H, 2.47.

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(2,2′-Bipyridine)(ethylene)copper(I) Hexafluorophosphate, $[Cu(bpy)(C_2H_4)]PF_6$. A mixture of $Cu(NCMe)_4PF_6$ (1.00 g, 2.68 mmol) and bpy (0.42 g, 2.68 mmol) in methanol (25 mL) was prepared. This red solution was stirred under an ethylene atmosphere for 2 h. The mixture was filtered to remove a small amount of insoluble material. After the volume was reduced by ca. 5 mL with an ethylene stream, the product was precipitated with ether (75 mL). The gray powder was isolated via filtration, washed with ether (3 × 10 mL) and dried overnight in N_2 (0.442 g, 42%). The perchlorate salt of this compound has been reported earlier.[7b] ^{1}H NMR spectrum (δ): 8.96 (2, d, J = 5 Hz, bpy), 8.70 (2, d, J = 7 Hz, bpy), 8.40 (2, t, J = 8 Hz, bpy), 7.91 (2, m, bpy), 4.80 (4, s, C_2H_4). FABMS (m/e): 375 ($Cu(bpy)_2$), 219 (Cu(bpy)). IR (cm^{-1}): 1605, 1598 (m, m, bpy). Anal. Calcd for $CuC_{12}H_{12}N_2PF_6$: C, 36.70; H, 3.08. Found: C, 36.63; H, 3.18.

(2,2′-Bipyridine)(acetonitrile)copper(I) Hexafluorophosphate, $[Cu(bpy)(NCMe)]PF_6$. A mixture of $Cu(NCMe)_4PF_6$ (1.00 g, 2.68 mmol) and bpy (0.42 g, 2.7 mmol) in acetone (15 mL) was prepared and was stirred for 30 min. Hexane (50 mL) was added to precipitate the yellow powder. The product was dried in vacuo for 3 h (1.03 g, 94%). ^{1}H NMR (δ): 9.1–7.4 (very br, bpy), 2.37 (s, NCMe). Anal. Calcd for $CuC_{12}H_{11}N_3PF_6$: C, 35.54; H, 2.73. Found: C, 35.62; H, 2.66.

(Diethyl acetylenedicarboxylate)bis[(2,2′-bipyridine)copper(I)] Hexafluorophosphate, $\{[Cu(bpy)]_2(EtCO_2C{\equiv}CCO_2Et)\}(PF_6)_2$. A sample of $[Cu(bpy)(DEAD)]PF_6$ (0.234 g, 0.438 mmol) was dissolved in acetone. Hexane was added to precipitate a white solid, which was isolated by filtration. After two additional reprecipitations, each time with the recovered solid, a white powder was obtained. This powder was isolated, washed with hexane (3 × 10 mL), and dried overnight in vacuo (0.158 g, 80%). ^{1}H NMR (δ): 9.16 (4, d, J = 5 Hz, bpy), 8.68 (4, d, J = 8 Hz, bpy), 8.43 (4, t, J = 8 Hz, bpy), 7.98 (4, t, J = 5 Hz, bpy), 4.68 (4, q, J = 7 Hz, CH_2's), 1.50 (6, t, J = 7 Hz, CH_3's). ^{13}C NMR (δ): 152.9, 151.5, 141.0, 128.4, 123.5 (bpy); 64.7 (OCH_2); 14.0 (CH_3); alkyne carbon atom resonances not located. FABMS (m/e): 389 (Cu(bpy)(DEAD)), 219 (Cu(bpy)). IR (cm^{-1}): 1730 (m, C=O); 1611, 1601 (w, w, bpy). Anal. Calcd for $Cu_2C_{28}H_{26}N_4O_4P_2F_{12}$: C, 37.41; H, 2.91. Found: C, 37.32; H, 2.97.

(Diethyl acetylenedicarboxylate)bis[(4,4′-dimethyl-2,2′-bipyridine)copper(I)] Hexafluoroantimonate, $\{[Cu(Me_2bpy)]_2(EtCO_2C{\equiv}CCO_2Et)\}(SbF_6)_2$. This compound was prepared starting with $[Cu(bpy)(DEAD)]SbF_6$ (0.240 g, 0.367 mmol) as indicated in the above procedure for $\{[Cu(bpy)]_2(EtCO_2C{\equiv}CCO_2Et)\}(PF_6)_2$ to yield a very light blue powder (0.17 g, 81%). ^{1}H NMR (δ): 8.98 (4, br, bpy), 8.56 (4, s, bpy), 7.80 (4, br, bpy), 4.63 (4, q, J = 7 Hz, OCH_2), 2.61 (12, s, $(CH_3)_2$bpy), 1.48 (6, t, J = 7 Hz, OCH_2CH_3). Anal. Calcd for $Cu_2C_{32}H_{34}N_4O_4Sb_2F_{12}$: C, 33.80; H, 3.01. Found: C, 33.83; H, 3.09.

(Phenylacetylene)bis[(2,2′-bipyridine)copper(I)] Hexafluoroantimonate, $\{[Cu(bpy)]_2(HC{\equiv}CC_6H_5)\}(SbF_6)_2$. This compound was prepared starting with $[Cu(bpy)(HC{\equiv}CPh)]SbF_6$ (0.250 g, 0.449 mmol) as indicated in the above procedure for $\{[Cu(bpy)]_2(EtCO_2C{\equiv}CCO_2Et)\}(PF_6)_2$ to yield a very light green powder (0.211 g, 93%). ^{1}H NMR (δ): 8.78 (4, br, bpy), 8.64 (4, br d, bpy), 8.34 (4, br t, bpy), 7.90 (2, m, Ph), 7.80 (4, br t, bpy), 7.66 (3, m, Ph) 6.82 (1, s, HC≡). Anal. Calcd for $Cu_2C_{28}H_{22}N_4Sb_2F_{12}$: C, 33.20; H, 2.19. Found: C, 33.43; H, 2.41.

Results and Discussion

The syntheses of the complexes [Cu(bpy)(alkyne)]X (bpy = 2,2′-bipyridine; X = PF_6^-, SbF_6^-), which have a copper:alkyne ratio of 1:1, are a two-step procedure (eqs 1 and 2). Addition of an acetone solution of 2,2′-bipyridine

$$Cu(NCMe)_4X + bpy \rightarrow [Cu(bpy)(NCMe)_n]X + (4 - n)MeCN \quad (1)$$

$$[Cu(bpy)(NCMe)_n]X + alkyne \rightarrow [Cu(bpy)(alkyne)]X + nMeCN \quad (2)$$

$$X = PF_6^-, SbF_6^-$$

to a solution of $Cu(NCMe)_4X$ yields a deep red solution presumed to contain $Cu(bpy)(NCMe)_nX$. The complex $[Cu(bpy)(NCMe)]PF_6$ can be isolated from this solution by addition of hexane. Addition of an excess of RC≡CR′ (R = R′ = Et; R = R′ = O_2CEt; R = R′ = Ph; R = H, R′ = Pr; R = Me, R′ = O_2CMe; R = H, R′ = Ph) to the acetone solution of $[Cu(bpy)(NCMe)_n]X$ (or to a solution formed by redissolving [Cu(bpy)(NCMe)]X in acetone) leads to the formation of the desired alkyne complexes. The color of the $[Cu(bpy)(NCMe)_n]X$ solution lightens considerably upon addition of the alkyne. The [Cu(bpy)(alkyne)]X products are isolated by precipitation with hexane *in the presence of the excess alkyne*. It is necessary to use an excess of the alkyne to avoid contamination of the product by [Cu(bpy)(NCMe)]X. The isolated powders generally are stable for many months when stored under nitrogen.

These syntheses are similar to that of Munakata's syntheses of $[Cu(bL)(olefin)]^+$ complexes (bL = several bidentate ligands such as bpy and phenanthroline).[9] It is also similar to Thompson's method of preparation of $[Cu(di\text{-}2\text{-}pyridylamine)(HC{\equiv}CH)]BF_4$, except in the preparation of this complex the order of addition of the alkyne and bidentate ligand are reversed.[7]

The only difficulty encountered in these preparations of 1:1 complexes is that the complexes must be precipitated from solutions containing excess alkyne. With low-boiling alkynes, especially 1-pentyne, the product occasionally is contaminated by some of the acetonitrile complex. This problem is easily solved by redissolving the impure sample in a minimal volume of acetone and adding additional 1-pentyne followed by precipitating the pure product with hexane.

The complexes are all very soluble in acetone. They are somewhat less soluble in methylene chloride. Solutions of the compounds are stable at least for several hours under N_2 but decompose in a few minutes upon exposure to air to give green to blue solutions and precipitates.

Alkyne-exchange studies (vide infra) show the alkyne ligands, as expected,[2,10] to be very labile in solution. By exploitation of this property, the less soluble 2:1 complexes, $\{[Cu(bpy)]_2(alkyne)\}X_2$ (alkyne = $EtCO_2C{\equiv}CO_2CEt$, HC≡CPh), and the 4,4′-dimethylbipyridine-substituted complex $\{[Cu(Me_2bpy)]_2(EtCO_2C{\equiv}CCO_2Et)\}(SbF_6)_2$, are prepared by dissolving the parent 1:1 complexes in acetone followed by precipitation of a solid with hexane (eq 3).

$$2[Cu(bpy)(alkyne)]X \rightarrow \{[Cu(bpy)]_2(alkyne)\}X_2 + alkyne \quad (3)$$

Pure 2:1 complexes are obtained by carrying this solid through three cycles of the above procedure. Presumably, in solution some of the copper centers lose an alkyne, and the $[Cu(bpy)(acetone)]^+$ solvate which would form reacts with the triple bond of the coordinated alkyne in $[Cu(bpy)(alkyne)]^+$ to form $\{[Cu(bpy)]_2(alkyne)\}^{2+}$. The lower solubility of these 2:1 complexes allows for their isolation by precipitation.

These 2:1 complexes generally are stable in the solid state for many months when stored under nitrogen. They are less soluble in acetone than their 1:1 counterparts. Solutions of the compounds are stable at least for several hours while under N_2 but decompose in a similar matter to the 1:1 complexes (vide supra) in air.

The structures of the [Cu(bpy)(alkyne)]X complexes are certainly similar to that determined for $[Cu(di\text{-}2\text{-}pyridylamine)(HC{\equiv}CH)]BF_4$, in which the copper atom is in a planar environment of the two pyridine nitrogen

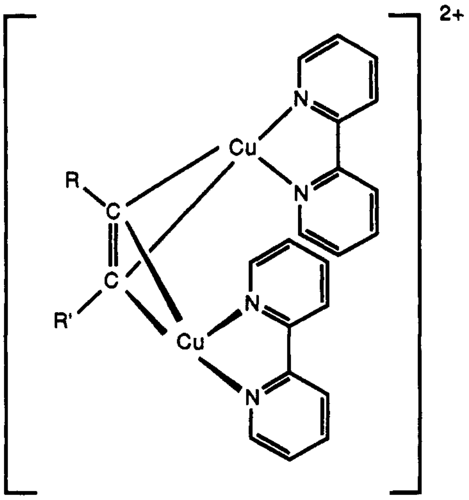
(9) Munakata, M.; Kitagawa, S.; Kosome, S.; Asahara, A. *Inorg. Chem.* **1986**, *25*, 2622.
(10) Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1976**, *113*, 173.

Table I. Electrochemical Data for $[Cu(bpy)(ligand)]PF_6$ Complexes Carried Out in CH_2Cl_2 at −78 °C[a]

ligand	ox. pot., V	red. pot., V
DEAD[b]	0.46	−1.07
DEAD 2:1[c]	0.59	−1.14
3-hexyne	0.65	−1.44
acetonitrile	0.77	−1.00
ethylene	0.80	−0.80

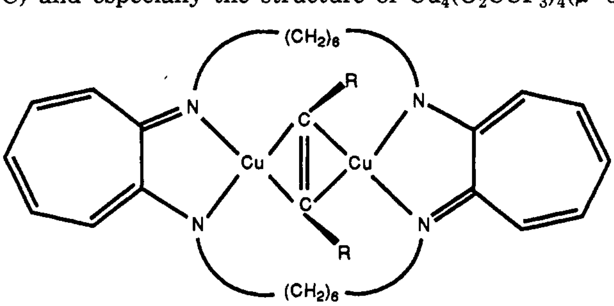
[a] Potentials are given vs Ag/AgCl cell. [b] DEAD = ($EtO_2CC{\equiv}CCO_2Et$). [c] DEAD 2:1 = $\{[Cu(bpy)]_2(DEAD)\}(PF_6)_2$.

donor atoms and the two acetylene carbon atoms.[7] The most reasonable structural arrangement for the $\{[Cu(bpy)]_2(alkyne)\}X_2$ complexes is the alkyne-bridged dimer B.



B

This structure, if correct, is particularly interesting because of the unsupported alkyne bridge between the two copper atoms. This bridging arrangement is quite reasonable in light of Lippard's tropocoronand compounds[5] (C) and especially the structure of $Cu_4(O_2CCF_3)_4(\mu^2$-3-hexyne$)_2$ (A), both of which have an alkyne ligand bridging two copper(I) groups. Also, similar complexes containing an alkyne bridging two nickel(0) groups, unsupported by other ligands, are known.[11]



C

Unfortunately, many attempts at growing crystallographic quality crystals of a 2:1 complex have failed. A variety of alkynes were tried using both PF_6^- and SbF_6^- as the counterions and bpy, 4,4′-Me_2bpy and 4,4′-Ph_2bpy as ancillary ligands. On three occasions data sets were collected on crystals of marginal quality, but in each case the structure could not be solved.

Infrared studies support these bonding assignments. Spectra of the complexes involving unsymmetrical alkynes show a shift of the alkyne stretch by about 100 cm^{-1} to lower wavenumber. For complexes with ester functional groups, the data suggest that the ester oxygen is not bonding with copper, since the ester stretches are very similar to those of the free alkyne.

(11) Porschke, K. R. *J. Am. Chem. Soc.* **1989**, *111*, 5691.

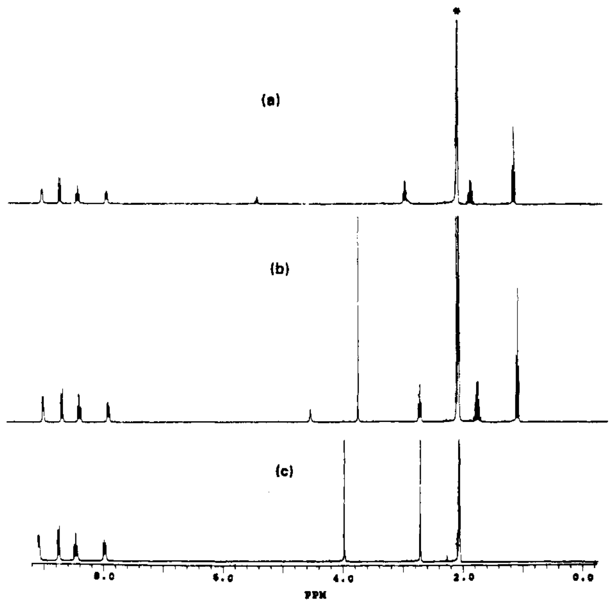


Figure 1. ^1H NMR spectra in acetone-d_6 at room temperature for (a) $[Cu(bpy)(1\text{-pentyne})]PF_6$, (b) a mixture of $[Cu(bpy)(1\text{-pentyne})]PF_6$ and $MeC{\equiv}CCO_2Me$, and (c) $[Cu(bpy)(MeC{\equiv}CCO_2Me)]PF_6$. The asterisk marks the solvent resonance.

Table I summarizes the results of electrochemical studies on several of these complexes. These results have been published elsewhere concerning the impact of ethylene and alkynes on hormonal action in plants[12] and are outlined here for completeness. The data are reported at −78 °C because at this temperature the oxidation waves are quasi-reversible. The reduction waves are irreversible. It has been reported that good π-acceptor ligands shift $E_{1/2}$ anodically, while good σ donors shift $E_{1/2}$ cathodically.[13] Surprisingly, there are no clear correlations of the expected bonding properties of the various ligands with the oxidation or reduction potentials.

NMR Studies

As observed in the alkyne complexes of copper(I) trifluoroacetate,[2] the alkyne ligands in these complexes are labile in solution. Thus, an NMR spectrum of a $[Cu(bpy)(alkyne)]^+$ complex ran in the presence of added alkyne (the same alkyne) shows only one set of alkyne resonances, intermediate in position between the positions of the free and complexed alkyne resonances.

This lability allows a determination of the relative affinities of the alkynes for the copper center in the 1:1 series via exchange studies monitored by ^1H NMR spectroscopy. The basic procedure involved adding via microsyringe a small amount of an alkyne to a solution of a copper complex of a *different* alkyne in an NMR tube. In all cases, the rate of exchange of free and complexed alkyne is fast on the NMR time scale so only one set of resonances is observed for each alkyne present. The results of one experiment of this type of experiment are shown in Figure 1. In this case, $MeC{\equiv}CCO_2Me$ has been added to a

(12) Kovacic, P.; Reger, D. L.; Kiser, P. F.; Huff, M. F.; Feinberg, B. A. *Free Radicals Res. Commun.*, in press.
(13) Addison, A. W.; Carpenter, M.; Lau, L. K.-M.; Wicholas, M. *Inorg. Chem.* **1978**, *17*, 1545.

solution of [Cu(bpy)(1-pentyne)]PF_6 (b) and shown for comparison are the spectra of pure [Cu(bpy)(1-pentyne)]PF_6 (a) and [Cu(bpy)(MeC≡CCO_2Me)]PF_6 (c). The resonance most sensitive to the exchange process is that assigned to the alkynyl hydrogen atom on 1-pentyne, which moves from δ 2.14 in acetone in the free alkyne to δ 5.44 in the complex. Addition of 1 equiv of MeC≡CCO_2Me causes the alkynyl hydrogen atom resonance to move to δ 4.53, still considerably closer to the complexed resonance position than that observed for the free alkyne. In contrast, the resonance for the methyl ester group of MeC≡CCO_2Me in the mixture is at δ 3.74, only 0.04 ppm (δ 3.70) away from the resonance position of the free alkyne and 0.22 ppm (δ 3.96) away from the resonance position of the pure complex. For the alkynyl methyl resonance, it is at δ 2.09 in the mixture compared to δ 2.00 for the free alkyne and δ 2.71 in the spectrum of the pure complex. Although the added MeC≡CCO_2Me has partially displaced the 1-pentyne, clearly 1-pentyne has the greater affinity for the copper center.

In a series of similar experiments, it has been shown that when [Cu(bpy)(1-pentyne)]PF_6 is mixed with any of the other alkynes studied here, the proton chemical shifts of the 1-pentyne resonances in the mixture are close to those observed in solutions of the pure complex. The resonances for the added alkyne in the mixture are close to those observed for the free alkyne. Thus, 1-pentyne has the highest affinity for copper of any of the alkynes investigated. The alkynes, 3-hexyne and diethyl acetylenedicarboxylate (DEAD), have similar affinities, but both compete for coordination to copper less effectively than 1-pentyne. Phenylacetylene has a somewhat lower affinity than either 3-hexyne or diethyl acetylenedicarboxylate and a much lower affinity than 1-pentyne. The affinity of MeC≡CCO_2Me is much less than that of diethyl acetylenedicarboxylate but is higher than that of diphenylacetylene. Also, it was found that ethylene and 1-pentyne compete similarly with each other. The following series for the affinity for alkynes and ethylene bonding to (bpy)copper(I) is then evident from these results:

$$C_2H_4 \sim HC{\equiv}CPr > EtC{\equiv}CEt \sim DEAD > HC{\equiv}CPh > MeC{\equiv}CCO_2Me > PhC{\equiv}CPh$$

The only clear trend along the series is that the least sterically hindered alkyne, HC≡CPr, has the highest affinity for the copper system and the most sterically hindered alkyne, PhC≡CPh, the lowest affinity. It is surprising that MeC≡CCO_2Me is inferior to both EtC≡CEt and DEAD, given that it can be viewed essentially as a hybrid of the latter two alkynes. Possibly, the asymmetry of the π orbitals in MeC≡CCO_2Me lowers its affinity.

Solutions containing both [Cu(bpy)(HC≡CPh)]SbF_6 and {$[Cu(bpy)]_2$(HC≡CPh)}$(SbF_6)_2$ show only a single set of resonances at ambient temperature. At −91 °C, the alkynyl hydrogen resonance and the resonances for the bpy ligand have broadened considerably, but separate sets of resonances for the two complexes could not be observed. This result indicates that the alkyne ligand in these complexes is extremely labile. In our previous copper(I) alkyne paper, it was noted that the exchange of alkyne between the complexes $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-3-hexyne})_2$ and $Cu_2(\mu\text{-}O_2CCF_3)_2(\text{3-hexyne})_2$ could be slowed at low temperatures so as to observe individual spectra at −77 °C. It was not possible to slow the exchange of free alkyne with $Cu_2(\mu\text{-}O_2CCF_3)_2(\text{3-hexyne})_2$. In the trifluoroacetate system, the bonding arrangement in the unusual tetrameric structure of $Cu_4(\mu\text{-}O_2CCF_3)_4(\mu\text{-3-hexyne})_2$ probably lowers the lability of the alkyne so that the exchange can be slowed on the NMR time scale.

Conclusion

This work shows that cationic copper(I) alkyne complexes with a variety of alkynes can be synthesized and are stable in the solid state under an inert atmosphere. The most interesting result is that, with both the neutral copper trifluoroacetate[2] system and the cationic copper bipyridine system that we have studied, two possible sets of complexes with 1:1 and 2:1 copper:alkyne stoichiometries can be prepared, depending on conditions of the syntheses. Clearly, the arrangement of two copper(I) groups bonded to a single alkyne is a favorable arrangement and can form even in the presence of excess alkyne.

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Registry No. DEAD, 762-21-0; [Cu(bpy)(3-hexyne)]PF_6, 137436-65-8; [Cu(bpy)(HC≡$CH_2CH_2CH_3$)]PF_6, 137436-67-0; [Cu(bpy)(CH_3C≡CCO_2CH_3)]PF_6, 137436-69-2; [Cu(bpy)(PhC≡CPh)]PF_6, 137436-71-6; [Cu(bpy)($EtCO_2C$≡CCO_2Et)]PF_6, 137436-73-8; $Cu(NCMe)_4PF_6$, 64443-05-6; CH_3CH_2C≡CCH_2CH_3, 928-49-4; HC≡$CCH_2CH_2CH_3$, 627-19-0; CH_3C≡CCO_2CH_3, 23326-27-4; PhC≡CPh, 501-65-5; [Cu(Me_2bpy)($EtCO_2C$≡CCO_2Et)]SbF_6, 137436-75-0; $Cu(NCMe)_4SbF_6$, 137436-76-1; Me_2bpy, 1134-35-6; [Cu(bpy)(HC≡CPh)]SbF_6, 137436-78-3; Cu(bpy), 137436-86-3; [Cu(bpy)(NCMe)]PF_6, 137436-85-2; {$[Cu(bpy)]_2$($EtCO_2C$≡CCO_2Et)}$(PF_6)_2$, 137436-80-7; {$[Cu(bpy)]_2$(HC≡CC_6H_5)}$(SbF_6)_2$, 137436-83-0; PhC≡CH, 536-74-3; {$[Cu(Me_2bpy)]_2$($EtCO_2C$≡CCO_2Et)}$(SbF_6)_2$, 137436-82-9; C_2H_4, 74-85-1; bpy, 366-18-7.