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Copper(I) Complexes with Bis(trimethylsilyl)acetylene: Role of Ancillary Ligands in Determining π Back-Bonding Interactions

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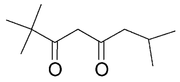
Summary: We present syntheses and structures of Cu(I) complexes with bis(trimethylsilyl)acetylene (BTMSA) that demonstrate the role of the ancillary ligands in the copper coordination sphere. The bonding interaction between the Cu(I) ion and the coordinated alkyne is influenced by the ancillary ligand. The ligands in this study are the bidentate ligands **1** *and* **2***, which form monomeric, trigonal planar Cu(I) complexes with olefins and alkynes. In these complexes, the ancillary ligands vary from a hard β-diketone* **1** *to a softer β-diketimine* **2***. Earlier studies of Cu(I)−acetylene complexes have shown the Cu(I) ion to be a poor π back-bonding ion, but the results here demonstrate that the degree of back-bonding is strongly influenced by the ancillary ligands. Although ligands* **1** *and* **2** *provide very similar geometries about the Cu(I) ion, the interaction with the coordinated BTMSA is considerably different. The degree of π back-bonding for the complex with the β-diketimine ligand is indicated by the spectroscopic properties of the coordinated triple bond.*

We present in this communication the syntheses and structures of Cu(I) complexes with bis(trimethylsilyl)acetylene (BTMSA) that demonstrate the role of the ancillary ligands in determining the bonding interaction of the Cu(I) ion with the coordinated alkyne. The bidentate β-diketone ligand **1** and β-diketimine **2** were studied. Both ligands form monomeric, trigonal planar complexes with olefins and alkynes.[1] The need for new materials and processes to facilitate future applications of microelectronics has created a challenging opportunity for the design of new Cu(I) complexes. In this regard, we have developed chemical precursors specifically for deposition of copper metal based on this family of ligands.[1] In the complexes reported here, the coordinated atoms from the ligands vary from oxygen to nitrogen, from two hard donor atoms to two softer ones.



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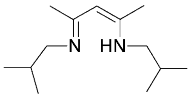

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Many studies in the literature have established η^2-bonding for Cu(I) complexes with alkynes.[2,3] Typically trigonal planar Cu(I) complexes with a side-bound acetylene are obtained; dimeric structures with η^2-bonding of the acetylene to two Cu(I) ions are also common with persistence of the trigonal planar geometry about the Cu(I) ion.[2,3] The bonding in these complexes is described as predominately σ bonding from alkyne to the copper atom, with little or no π back-bonding from the metal ion.[2,3] Compared with the isoelectronic Ni(0) complexes, the Cu(I) ion is considered to be a poor π back-bonding metal.[4] The stretching frequencies of alkynes coordinated to Cu(I) ions show only small shifts compared with the free molecule. For example, the stretching frequency for a side-bound acetylene molecule was observed at 1795 cm^{-1} versus 1974 cm^{-1} for free acetylene in [Cu(2,2′-dipyridylamine)(acetylene)]ClO$_4$.[3a,b] This shift of −179 cm^{-1} is indicative of weak π bonding.[5] This weak π back-bonding interaction is also observed with olefin and carbonyl complexes.[2,3]

Cu(I) complexes with BTMSA have been prepared with only a small group of ancillary ligands: halides and oxygen-donating ligands such as hexafluoroacetylacetonate.[2,3c,d] The spectroscopic properties of these complexes tabulated in Table 1 are consistent with a weak π back-bonding interaction. However, Strauss has shown that the extent of π back-bonding to Cu(I)−carbonyl complexes is determined by the basicity of the ancillary ligand.[6] Increased electron density on the Cu(I) ion from ancillary ligands leads to greater π back-bonding, as shown by changes in the spectroscopic and structural parameters. The complexes reported here demonstrate a similar phenomenon with BTMSA: the ancillary ligand greatly influences the bonding interactions with the unsaturated molecules. Our conclusions on the bonding interactions are based on the differences observed in spectroscopic features, such as stretching frequencies and ^{13}C NMR data for the coordinated alkyne carbon atoms as well as C−C−Si bond angles of the coordinated BTMSA molecule. There are some significant differences in the bonding interactions of Cu(I) ion and the unsaturated molecule in the complex with **2** reported here compared with those previously reported.[2,3] Although there is an extensive literature of Cu(I) complexes with β-diketonates and aryl-substituted β-diketimines,[7] Cu(I) complexes with **2** have only recently been reported.[1] Ligands **1**

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Table 1. Spectroscopic Data and Bond Angles for CuL(BTMSA) Complexes

compound	stretching frequency (cm^{-1})	^{13}C NMR (ppm)	Si−C−C bond angles (deg)	ref
free BTMSA	2107	113.8	179.2(8)	13
$Cu_2Cl_2(BTMSA)_2$	1949	115.2	164.2(3); 166.3(3)	2
Cu(hfac)(BTMSA)	1941	113.2	171(3); 157(3)	3d
$(Cu(BTMSA))_2$(oxalate)	1935	114.2	170.5(2), 163.2(2)	3c
Cu(O2)(BTMSA), **3**	1926 (1918)[a]	114.6	170.0(6), 168.8(6)	this work
Cu(N2)(BTMSA), **4**	1854 (1862)[a]	125.0	151.2(2), 150.1(3)	this work

[a] Theoretical values.

and **2** differ in basicity. These range from values typical of many Cu(I) ligands to extremely basic. We estimate that the pK_a of **2** is >16, whereas the β-diketonate has a pK_a of approximately 11.[8]

Copper complexes **3** and **4** are synthesized in a straightforward manner. The ligands are prepared by literature methods.[9,10] The complex Cu(O2)(BTMSA), **3**, with the β-diketonate ligand, is prepared from CuCl,[11] whereas the complex Cu(N2)(BTMSA), **4**, is prepared with tetrakis(acetonitrile)copper(I) trifluoromethanesulfonate salt to obtain a significantly better yield of desired product; disproportionation of the Cu(I) complex is observed when starting with CuCl.[12] Both compounds **3** and **4** are low-melting, colorless solids at room temperature. The β-diketiminate complex is sensitive to both oxygen and water, whereas the β-diketonate complex tolerates low levels of moisture.

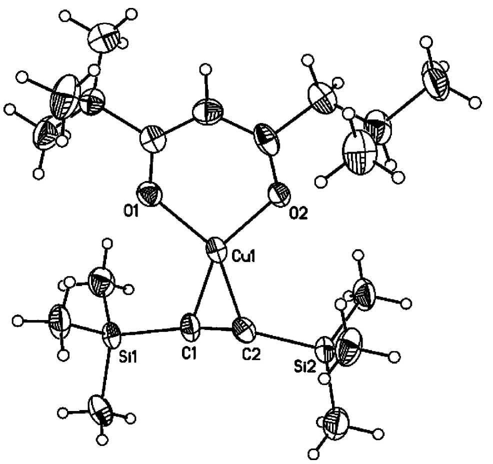

Figure 1. Structure of Cu(O2)(BTMSA), **3**. Distances: Cu(1)−O(1), 1.931(4); Cu(1)−O(2), 1.920(4);); Cu(1)−C(1), 1.974(7); Cu(1)−C(2), 1.969(6); C(1)−C(2), 1.225(8). Angles: O(2)−Cu(1)−O(1), 96.75(18); O(1)−Cu(1)−C(1), 111.4(2); O(2)−Cu(1)−C(2), 115.7(2); C(2)−Cu(1)−C(1), 36.2(2).

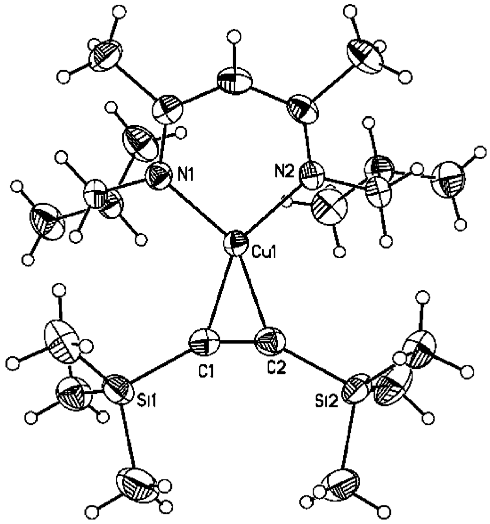

Figure 2. Structure of Cu(N2)(BTMSA), **4**. Distances: Cu(1)−N(1), 1.949(2); Cu(1)−N(2), 1.937(2); Cu(1)−C(1), 1.973(3); Cu(1)−C(2) 1.975(3); C(1)−C(2), 1.243(4). Angles: N(2)−Cu(1)−N(1), 97.04(10); N(1)−Cu(1)−C(1), 113.49(12); N(2)−Cu(1)−C(2), 112.43(12); C(1)−Cu(1)−C(2), 36.70(13).

The overall structures of **3** and **4** are shown in Figures 1 and 2, respectively. Both complexes have similarities such as a trigonal planar geometry about the Cu(I) cation. The Cu(I) bond distances to nitrogen, oxygen, and acetylenic carbon atoms are typical of this type of complex.[2,3] The Cu−C distances (1.969−1.974 Å) are similar to Cu(I) complexes with BTMSA and acetylenes in general.[2,3] The C−C bonding distance for the coordinated BTMSA molecule of 1.225(8) Å in **3** is typical of oxygen-donating ligands and halides. This value is slightly longer than the free molecule value of 1.208(3) Å.[13] The value for **4** at 1.243(4) Å is significantly longer than the values typically observed. This longer bond suggests greater π back-donation from Cu(I) ion to the coordinated BTMSA molecule compared with most other ligand systems, owing to the increased basicity of the ligand. However, C−C bond distance is in most cases not a very helpful way to determine the bonding interaction in alkyne complexes.[14]

The bending of the C−C−Si bond angle of the coordinated BTMSA molecule is another indication of the delocalization

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[11] All manipulations were performed in a drybox under nitrogen atmosphere. Cuprous chloride (1.5 g, 15.153 mmol) was mixed with BTMSA (2.582 g, 15.153 mmol) in ether (30 mL), and the resultant mixture was stirred at room temperature for 0.5 h. At the same time 2,2,7-trimethyloctane-3,5-dione (H(tod), 2.792 g, 15.153 mmol) was mixed with NaH (60%, 0.606 g, 15.153 mmol) in ether (30 mL), and the mixture was also stirred at room temperature for 0.5 h. The latter mixture was added to the former mixture, and the reaction mixture was stirred at room temperature overnight. The solvent was stripped under reduced pressure. The resultant residue was treated with hexane (40 mL) and filtered. The filtrate was concentrated under reduced pressure to afford 6.02 g of crude product (95%) as a white solid. This solid was recrystallized in hexane at −30 °C to give 3 g of pure product with a melting point of 79−80 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ 5.45 (s, 1H), 2.09−2.04 (m, 3H), 1.13 (s, 9H), 0.92 (d, $J = 6.2$ Hz, 6H), 0.31 (s, 18H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 199.4, 193.9, 114.6, 94.9, 51.8, 41.4, 28.9, 27.0, 23.1, −0.01. Anal. Calcd for $C_{19}H_{37}CuO_2Si_2$: C, 54.70; H, 8.94. Found: C, 54.80; H, 8.76.

[12] In the drybox, a 100 mL round-bottom flask was charged with $[Cu(CH_3CN)_4]SO_3CF_3$ (1.0 g, 2.6 mmol), bistrimethylsilylacetylene (1.5 g, 8.8 mmol), and diethyl ether (20 mL). In a separate 100 mL round-bottom flask, 1.5 M *tert*-butyllithium (1.7 mL, 2.6 mmol) was added to a solution of *N,N′*-diisobutyl-2,4-pentanediketimine (0.550 g, 2.6 mmol). After 0.5 h, the solutions were combined. The combined solution changed from a cloudy white suspension to a dark brown solution after the uptake of all solids. After 2 h, the solution was concentrated to a pasty solid, extracted with pentane (3 × 15 mL), filtered, and concentrated to give a brown solid (0.680 g, 59% yield). A single crystal suitable for X-ray analysis was grown from a pentane solution at −32 °C. ^1H NMR δ (500 MHz, C_6D_6): 0.26 (s, 18H), 0.99 (d, 16H, $J = 6.77$ Hz), 1.83 (m, 2H) 1.94 (s, 6H), 3.46 (d, 4H, $J = 6.93$ Hz), 4.57 (s, 1H). ^{13}CNMR δ (125 MHz, C_6D_6): 162.25, 125.29, 96.17, 62.12, 32.07, 20.99, 19.89, −0.92.

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of electron density from the Cu(I) ion to the coordinated ligand. Table 1 lists values for **3** and **4** as well as examples from the literature. The Si−C−C bond angles for **4** are significantly distorted (30°) from the 180° linear geometry of the free molecule. The analogous complexes with Hfac and the β-diketonate do not show this degree of bending of the trimethylsilyl substituents, although the angles are significantly smaller than that of the free molecule in all cases. The planarity of the copper coordination sphere and the trimethylsilyl groups suggests an alignment of the π orbitals of the alkyne with the d orbitals on the Si atom.

The acetylene C−C stretching frequencies of these complexes show the differences between these two ligands. Values for **3** and **4** as well as examples from the literature are shown in Table 1. Depending on the ancillary ligands in the copper coordination sphere, a range of stretching frequencies is observed. IR data reveal a significant lowering of acetylene stretch for **4**, whereas the complex **3** has a stretching frequency more typical of Cu(I) complexes, which show a lowering of the C−C of ca. -150 cm^{-1}.[1,2,4] However, the considerably more basic β-diketiminate ligand shows a significantly larger shift in stretching frequency, indicative of greater donation of electron density to acetylene from the Cu(I)−N2 group. The observed stretching frequency at 1854 cm^{-1} is the lowest stretching frequency reported for an η^2-BTMSA-Cu(I) complex, having a shift of -253 cm^{-1} relative to free BTMSA. The observed values for **3** and **4** are consistent with values calculated using density functional theory (DFT)[15] at the BP86/DZVP level of theory[16] (see Table 1). The molecular structures were first optimized at this level of theory and then used in the subsequent analytic vibrational frequency computations. The theoretical values are in good agreement with the experimental data. The vibrational analysis is within 8 cm^{-1} of the recorded stretching frequencies.

The ^{13}C NMR data are consistent with the observed change in bonding for the coordinated BTMSA. The ^{13}C NMR resonance of the coordinated alkyne in **4** is shifted 11 ppm downfield relative to **3**. The coordinated alkyne of compound **4** has a chemical shift of 125.6 ppm. This value is more typical of a sp^2-hybridized carbon and indicates a greater degree of double-bond character, consistent with the infrared and X-ray data.

The perturbations of the BTMSA molecule coordinated to a Cu(I) in **4** approach more closely the values found for a Ni(0) complex with BTMSA. The Dewar−Chatt−Duncanson model can be used to describe the bonding interaction between metal and BTMSA, based on the spectroscopic and structural features.[17] The C−C bond distance of the coordinated alkyne in $Ni(P(C_6H_5)_3)(BTMSA)$ is 1.256(2) Å.[18] The C−C−Si bond angle is 143°. The C−C stretching frequency of the coordinated BTMSA at 1737 cm^{-1}, a shift of -370 cm^{-1}, approaches a value expected for a C−C double bond.[5] These properties suggest delocalization of electron density onto the BTMSA molecule from the electron-rich Ni(0)−triphenylphosphine moiety. The spectroscopic parameters for **4** approach those of the isoelectronic Ni(0) complexes more closely than any other Cu(I) complex with BTMSA reported to date; the ligand **2** is basic enough to cause delocalization of electron density from the Cu(I) ion onto the coordinated BTMSA molecule.

In summary, the BTMSA complexes prepared with ligands **1** and **2** demonstrate the role of ancillary ligand on the interaction between Cu(I) ion and coordinated alkyne. The Cu(I) ion has been shown to be a poor π back-bonding ion, but the results here show that the degree of back-bonding is strongly influenced by the ancillary ligands in alkyne complexes. Although ligands **1** and **2** provide very similar geometries about the Cu(I) ion, the interaction with the coordinated BTMSA changes on going from a β-diketonate to the β-diketiminate ligand because of the greater basicity of the β-diketiminate ligand. The degree of π back-bonding is indicated by the decrease of the C−C−Si bond angle of the coordinated BTMSA molecule, the decreased stretching frequency of the coordinated triple bond, and the downfield shift of the ^{13}C NMR resonance. The role of ancillary ligands in determining the bonding interaction of alkynes with other transition metals is well established.[19] The work shows a similar trend for Cu(I)−BTMSA complexes.

Supporting Information Available: Details of experimental procedures, computations, X-ray crystal structure cif files, and ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Gaussian 03 was employed for computations. See Supporting Information for full reference.

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