Inorganic Chemistry

Communication

Cleavage of X–H Bonds (X = N, O, or C) by Copper(I) Alkyl Complexes To Form Monomeric Two-Coordinate Copper(I) Systems

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The monomeric copper(I) alkyl complexes (IPr)Cu(R) [R = Me or Et; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] react with substrates that possess N–H, O–H, and acidic C–H bonds to form monomeric systems of the type (IPr)Cu(X) (X = anilido, phenoxide, ethoxide, phenylacetylide, or *N*-pyrrolyl) and methane or ethane. Solid-state X-ray crystal structures of the anilido, ethoxide, and phenoxide complexes confirm that they are monomeric systems. Experimental studies on the reaction of (IPr)Cu(Me) and aniline to produce (IPr)Cu(NHPh) suggest that a likely reaction pathway is coordination of aniline to Cu(I) followed by proton transfer to produce methane and the copper(I) anilido complex.

Controlled activation of small molecules by transition metals provides the foundation for homogeneous catalytic cycles. Among the transition series, copper is an attractive metal because of its relatively low expense and utility in a variety of important synthetic methods.[1−6] However, the use of well-defined and tunable [i.e., by variation of ancillary ligand(s)] copper-based systems for transformations that involve metal-mediated bond cleavage is relatively limited.[7−9] Two challenges for the development of such systems are

avoiding bond homolysis reactions that generate free radicals, which are relatively common for first-row transition metals, and accessing copper systems that remain monomeric throughout a series of transformations. The latter issue is especially problematic for nondative heteroaromatic ligands (e.g., amido, alkoxide, etc.). For example, despite increased interest in late-transition-metal complexes with nondative ligands in the past decade,[10−19] the isolation of monomeric copper(I) amido complexes is extremely rare.[20] Although more common than amido systems, structurally characterized monomeric copper(I) alkoxides are also limited.[21−24] Herein, we report on the cleavage of N−H, O−H, and acidic C−H bonds by copper(I) alkyl complexes to produce *monomeric* copper(I) anilido, ethoxide, phenoxide, phenylacetylide, and *N*-pyrrolyl systems.

Copper alkyl reagents have been utilized extensively in organic synthesis; however, the preparation of well-defined systems is limited.[25] Sadighi et al. have previously reported

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**Scheme 1.** Reactions of (IPr)Cu(Me) (**1**) {[Cu] = (IPr)Cu}
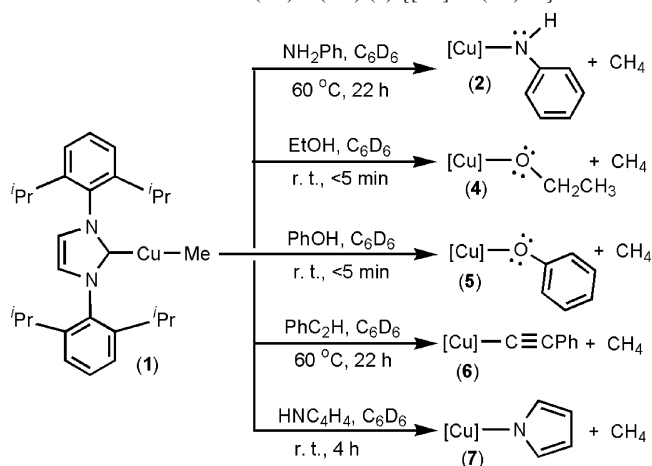
**Scheme 2.** Preparation of **3** and Reaction with Aniline To Produce **2** and Ethane
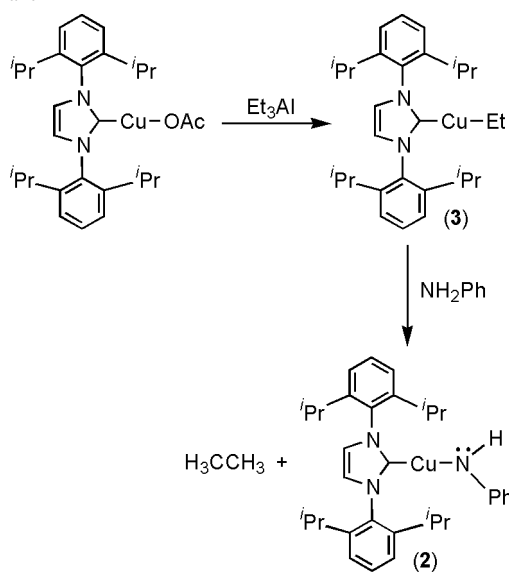
and fully characterized the copper(I) methyl complex (IPr)-Cu(Me) [**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene].[26] Heating (60 °C) **1** in C_6D_6 with 1 equiv of aniline for 22 h leads to the quantitative (^1H NMR) formation of (IPr)Cu(NHPh) (**2**, 70% isolated yield; Scheme 1). Consistent with an independent ^1H NMR spectrum of CH_4 in C_6D_6, the observation of a singlet at 0.16 ppm (^1H NMR) from the reaction of **1** with NH_2Ph is likely due to the formation of CH_4. To confirm that CH_4 is formed from the methyl ligand of **1**, we prepared (IPr)Cu(Et) (**3**; Scheme 2). The reaction of **3** with aniline in a sealed NMR tube produces **2** and a resonance (0.8 ppm, ^1H NMR) that is consistent with formation of ethane without observation of the resonance due to CH_4. The monomeric nature of **2** has been confirmed by a single-crystal X-ray diffraction (XRD) study (Figure 1). To our knowledge, the formally 14-electron complex **2** is the second example of a structurally characterized monomeric copper(I) amido system, with the other example being the 16-electron, three-coordinate complex (dtbpe)Cu(NHPh)

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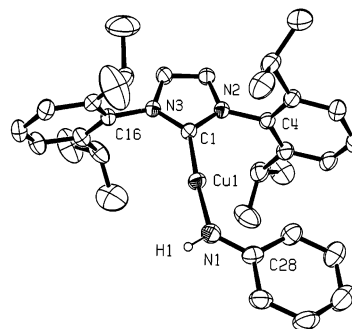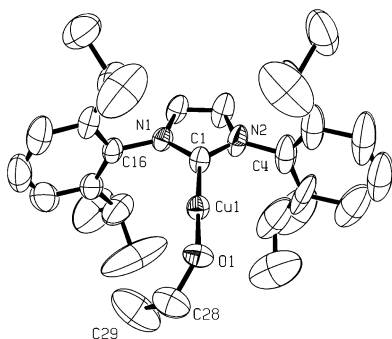
Figure 1. ORTEP of (IPr)Cu(NHPh) (**2**; 20% probability). Selected bond distances (Å): N3−C1, 1.353(3); N2−C1, 1.359(3); Cu1−C1, 1.875(3); Cu1−N1, 1.841(2); N1−C28, 1.351(4). Selected bond angles (deg): N2−C1−Cu1, 124.0(2); C1−Cu1−N1, 174.8(1); Cu1−N1−C28, 127.4(2).
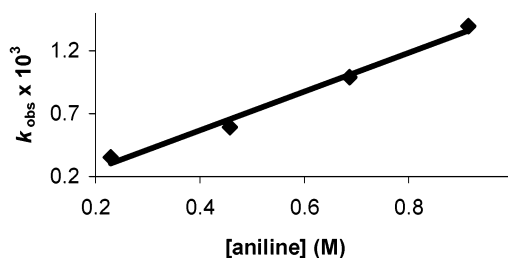

Figure 2. Plot of k_{obs} versus concentration of aniline for the conversion of complex **1** and aniline to complex **2**.

[dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane].[20] The Cu−N bond length of **2** is 1.841(2) Å, consistent with the anticipated bond length for a Cu−N single bond (see the Supporting Information), and is similar to the Cu−N bond distance [1.890(6) Å] of (dtbpe)Cu(NHPh). As expected for a two-coordinate d^{10} system, the C−Cu−N linkage is nearly linear at 174.8(1)°.

We have considered two likely pathways for the formation of **2**. Bond homolysis of the Cu−Me linkage of **1** could lead to the formation of a methyl radical with subsequent hydrogen atom abstraction from aniline to produce methane and complex **2**. Alternatively, **1** could coordinate aniline and activate it toward proton transfer to the methyl ligand of **1** to form **2** and CH_4. The latter pathway provides greater opportunity for incorporation into selective catalytic sequences. In the presence of either 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 1,4-cyclohexadiene, the reaction of **1** with aniline forms **2** and CH_4 without observation of additional organic compounds that would result from trapping of the methyl radical by TEMPO or 1,4-cyclohexadiene. The conversion of **1** and aniline to **2** in toluene-d_8, which possesses a relatively weak benzylic C−H(D) bond, yields observations identical with those of reactions performed in C_6D_6. These experiments suggest that Cu−C bond homolysis is an unlikely reaction pathway. In addition to this point, complex **1** has only been found to react with relatively acidic bonds and has failed to produce clean transformations with substrates that possess pK_a's (in DMSO) > ∼31 (e.g., ammonia, furan, and benzene). Finally, the rate of conversion of **1** and aniline to **2** increases with increasing concentration of aniline (Figure 2), a result which is inconsistent with a rate-limiting Cu−C bond homolysis.

Figure 3. ORTEP of (IPr)Cu(OEt) (**4**; 20% probability). Selected bond distances (Å): N1−C1, 1.363(6); N2−C1, 1.347(6); Cu1−C1, 1.863(5); Cu1−O1, 1.799(3); O1−C28, 1.366(8). Selected bond angles (deg): N1−C1−Cu1, 128.1(4); N2−C1−Cu1, 129.1(4); C1−Cu1−O1, 176.9(2); Cu1−O1−C28, 128.1(4).
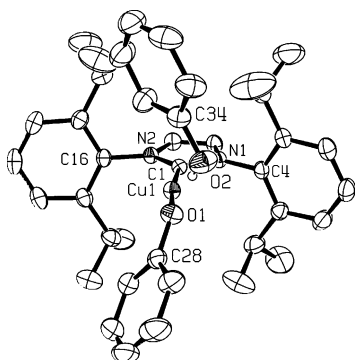

Figure 4. ORTEP of (IPr)Cu(OPh)−(HOPh) (**5**−HOPh; 20% probability). Selected bond distances (Å): N1−C1, 1.356(2); N2−C1, 1.357(2); Cu1−C1, 1.868(2); Cu1−O1, 1.839(2); O1−C28, 1.339(3). Selected bond angles (deg): N1−C1−Cu1, 122.7(1); N2−C1−Cu1, 133.5(1); C1−Cu1−O1, 173.0(1); Cu1−O1−C28, 124.0(1).

The reaction of **1** in benzene at room temperature with ethanol or phenol immediately releases CH_4 and forms the copper complexes (IPr)Cu(OEt) (**4**) and (IPr)Cu(OPh) (**5**) in 72% and 75% isolated yields, respectively (Scheme 1). The ethoxide complex **4** shows no evidence of β-hydride elimination after several hours at room temperature in C_6D_6. XRD studies reveal that **4** and **5** crystallize as monomeric copper systems (Figures 3 and 4). The Cu−O bond length of **5** is 1.839(2) Å and is consistent with a Cu−O single bond. The corresponding bond length of **4** is shorter at 1.799-(3) Å and is intermediate between the anticipated bond length for a single and double bond. Sadighi et al. have reported the solid-state structure of (IPr)Cu(O^{t}Bu), for which the Cu−O bond distance is 1.8104(13) Å.[21] The Cu1−O1−C28 [128.1(4)°] and C1−Cu1−O1 [176.9(2)°] bond angles of **4** are similar to the analogous angles [122.85(12)° and 179.05-(7)°] of (IPr)Cu(O^{t}Bu). Crystals of complex **5** were grown from a reaction with excess PhOH, and **5** crystallized with 1 equiv of PhOH, which forms a hydrogen bond with the phenoxide ligand of **5** (Figure 4). The reaction of **1** with 1 equiv of PhOH also forms **5** with no evidence of free PhOH in the final purified product.

The combination of **1** and phenylacetylene in C_6D_6 for 22 h at 60 °C leads to the formation of (IPr)Cu(C≡CPh) (**6**)

in quantitative yield (as determined by ^{1}H NMR spectroscopy) as well as the production of CH_4 (Scheme 1). Complex **6** is characterized by resonances at 105.5 and 101.0 ppm in the ^{13}C NMR spectrum that are assigned as the acetylide carbons. Thus, apparently complex **1** can mediate the cleavage of weakly acidic C−H bonds. The reaction of **6** with HCl in C_6D_6 cleanly produces the previously reported complex (IPr)Cu(Cl) and free phenylacetylene (eq 1).[8]
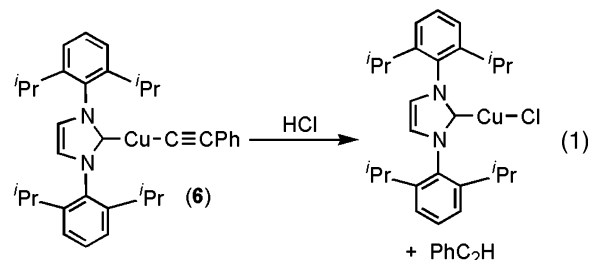
Complex **1** can also initiate the cleavage of the N−H bond of pyrrole. After 4 h at room temperature, a solution of **1** and pyrrole converts to (IPr)Cu(N-pyrrolyl) (**7**). The ^{1}H NMR spectrum of **7** reveals resonances due to symmetry-equivalent α- and β-hydrogens of the pyrrolyl fragment at 6.88 and 6.71 ppm, respectively.

Two-coordinate copper(I) alkyl complexes of the type (IPr)Cu(R) can be used to mediate the cleavage of X−H (X = N, O, or C) bonds. Such transformations could be integral to the development of catalytic cycles if metal-mediated bond-forming reactions are accessible with these and related Cu systems. On the basis of preliminary results, the acidity of the X−H bond appears to be a key factor, albeit not likely the sole factor, for kinetic accessibility to these reactions. Thus, it may be feasible to break less activated bonds (e.g., arenes, alkanes) with closely related Cu systems that are more electrophilic. We are currently exploring the incorporation of these systems into catalytic cycles as well as the preparation of Cu complexes with increased reactivity.

Supporting Information Available: Complete data from XRD studies of complexes **2**, **4**, and **5**, details of synthesis and characterization, kinetic plots, and bond distance estimates. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0517624