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Nitrosoarene−Cu(I) Complexes Are Intermediates in Copper-Catalyzed Allylic Amination

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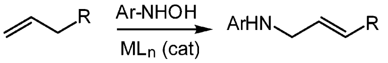
The direct synthesis of organonitrogen compounds from hydrocarbons (nitrogenation) is a practically attractive but chemically challenging goal. Besides the rapidly expanding range of N-functionalization options involving addition to C−C unsaturation,[1] *allylic* nitrogenation of unsaturated hydrocarbons offers a desirable route to polyfunctional amines.[2] We and others have described allylic aminations catalyzed by Mo(VI),[3] Fe(II,III),[4,5] and Cu(I,II)[6,7] salts and complexes, using aryl hydroxylamines as aminating agents (eq 1). More recently, nitroarene-[8] and aminoarene[9]-based, metal-catalyzed allylic aminations have also been developed.

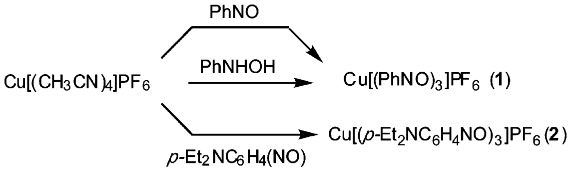


(1)

Mechanistic studies of the hydroxylamine/olefin reactions catalyzed by LMo(VI)O_2,[3b] (phthalocyanine)Fe(II),[5] and hydrated $CuCl_2$[7] revealed the intervention of free PhNO, a proven enophile,[10] as the active aminating agent. However, the aminations catalyzed by Fe(II,III) salts involve a novel iron−azodioxide complex[4b,c] as the active PhN transfer agent. Our preliminary study on the Cu(I)-catalyzed allylic amination[6] excluded the intermediacy of free nitrosoarene and aryl nitrene from trapping experiments, suggesting that a coordinated organonitrogen species could be the active aminating agent. Relatedly, group 10 metal complexes of nitrosoarenes have been proposed as intermediates in enantioselective hetero-Diels−Alder[11] and *O*-nitroso aldol reactions.[12] To explore further the nature of the reactive intermediates in these reactions, we report herein (1) the isolation and structure determination of the first homoleptic nitrosoarene−metal complexes, and (2) evidence that such complexes are intermediates and likely N-transfer agents in Cu(I)-catalyzed allylic aminations.

Seeking to produce copper complexes that could be potential intermediates in Cu(I)-catalyzed allylic aminations, $[Cu(CH_3CN)_4]PF_6$ was treated with 4.2 equiv of PhNO ($CHCl_3$, rt) to produce a dark red, labile complex **1** which is formulated as $[Cu(PhNO)_3]PF_6$ based on its Cu content, the amount of recovered PhNO, and its ^1H NMR spectrum, which shows a 2:1:2 set of aromatic resonances downfield from PhNO (Scheme 1). Unfortunately, the sensitivity and lability of **1** has thus far thwarted its detailed structure determination.[13] A more tractable Cu−ArNO derivative was obtained from the reaction of $[Cu(CH_3CN)_4]PF_6$ with excess *N*,*N′*-diethyl-4-nitrosoaniline (1:4.3, CH_2Cl_2, rt). The resulting greenish−red solid **2** (70% yield) was identified with the aid of IR, NMR, MS (FAB), and X-ray crystallography. As shown in Figure 1, the cation of **2** consists of a distorted trigonal planar, 16-electron $Cu(ArNO)_3^+$ moiety. The copper atom is coordinated to the nitrosoarene ligands through the N-atom with the NO units directed out of the CuN_3 plane. The Cu−N bond lengths (av. 1.933 Å) are markedly varied, ranging from 1.898 to 1.970 Å, as are the N−Cu−N bond angles, which range from 105 to 134°. These distortions from ideal trigonal planarity are among the most severe found in d^{10} ML_3 complexes[14] and are presumed to be sterically derived.[15] The N−O bond lengths, however, are relatively uniform (av. 1.258 Å) and are comparable to those in the free ligand (1.252 Å),[16] suggesting the absence of significant back-bonding from Cu(I) to the nitrosoarene ligand. Compound **2** is the first crystallographically characterized, homoleptic nitrosoarene−metal complex and the first copper complex bearing a simple C-nitroso ligand.[17]

Scheme 1



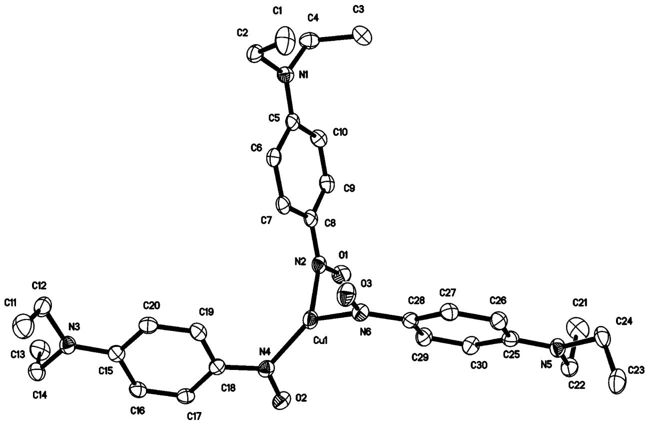


Figure 1. X-ray structure of the cation of **2**. Selected bond lengths (Å) and bond angles (deg): Cu(1)−N(4) 1.8983(15), Cu(1)−N(6) 1.9296(19), Cu(1)−N(2) 1.9701(18), O(1)−N(2) 1.2646(16), N(4)−Cu(1)−N(6) 133.81(6), N(4)−Cu(1)−N(2) 120.96(6), N(6)−Cu(1)−N(2) 104.96(4).

Most importantly, complex **1** is an intermediate, and possibly the active N-transfer agent, in the Cu-catalyzed amination reactions with PhNHOH based on the following observations. First, **1** was isolable (47%) in the reaction of PhNHOH with α-methylstyrene (AMS) in the presence of $[Cu(CH_3CN)_4]PF_6$ (90 °C, dioxane, 3 h; Scheme 1). Second, the reaction of nitrosobenzene complex **1** with excess AMS (90 °C, dioxane, 20 h) produced the corresponding allylamine **3** cleanly (40%, Scheme 2),[18] whereas the more electron-rich nitrosoaniline complex **2**, like its free ligand, was unreactive toward olefins. Third, slow addition of PhNHOH to a mixture of either **1** or **2** (8 mol %) and AMS at 90−95 °C (24 h) produces allylamine **3** (36% from **1** and 15% from **2**), indicating that **1** and

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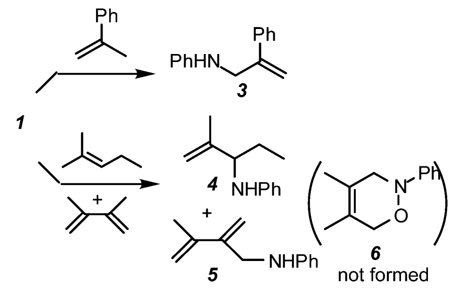
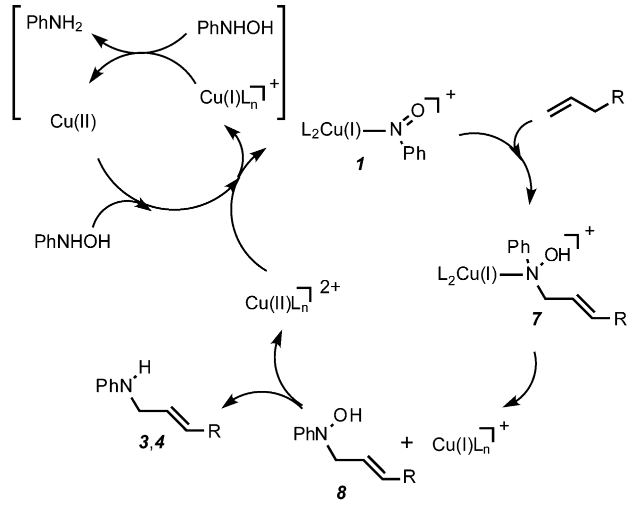
Scheme 2



Scheme 3



L = PhNO, dioxane, alkene

2 are (pre)catalysts for the amination of AMS by PhNHOH. Significantly, the stoichiometric amination by complex **1** does not involve the intermediacy of free PhNO since heating **1** with a 1:1 mixture of 2-methyl-2-pentene and 2,3-dimethylbutadiene (a trapping agent for free PhNO[19]) gave allylic amination products **4** and **5** exclusively (8 and 18%, respectively, based on **1**), rather than the Diels−Alder trapping product **6**, the same result found previously in the Cu(I)-catalyzed aminations with ArNHOH.[6]

The above observations, together with the distinctive regioselectivity of the Cu-catalyzed reactions, lead us to suggest as a plausible reaction pathway the one shown in Scheme 3. Initially, some Cu(II) is likely generated by Cu(I) reduction of ArNHOH (PhNH$_2$ detected).[20] The resulting Cu(II) then oxidizes PhNHOH to PhNO with formation of the C-nitroso complex **1**. This likely electrophilic species could then transfer the activated C-nitroso unit to a free or coordinated olefin by a metal-mediated *ene*-type reaction.[21] Support for the latter pathway is provided by the formation of an adduct between **1** and styrene at room temperature.[13] PM3(TM) MO calculations[22] on **1** find a set of three nearly degenerate LUMOs (Figure SI4) that are primarily centered on the N−O unit (π^*) with much of the positive charge on N (negative on O). Reduction of the resulting allyl hydroxylamine by Cu(I) would produce allylamine and regenerate Cu(II).[20]

We have thus established here the first structurally verified Cu(I) complex of a C-nitroso compound, demonstrated its intermediacy in the Cu(I)-catalyzed allylic amination of olefins, and suggested its role as the active group transfer agent. Further investigations of the synthetic and mechanistic aspects of Cu-catalyzed allylic amination are underway.

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Supporting Information Available: Preparative and characterizational data for **1** and **2**, including the X-ray crystallographic data for **2** and the PM3(TM) computational output for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) The active N-transfer agent **1** could also have L = dioxane and/or olefin. The apparent N-centered, enophilicity of **1** parallels that found in some nitrosoaldol reactions proposed to involve Ag(I)−ArNO complexes but contrasts with the O-based reactivity of others (ref 12) and with the N−O-centered reactivity in Cu(I)-catalyzed hetero-Diels−Alder reactions (ref 11).
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