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Published on Web 11/16/2007

Mechanistic Studies of Copper(I)-Catalyzed Allylic Amination

Radhey S. Srivastava,*,† Nathan R. Tarver,† and Kenneth M. Nicholas‡

Contribution from the Department of Chemistry, University of Louisiana at Lafayette, Louisiana 70504, and Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73109

Received July 10, 2007; E-mail: rss1805@louisiana.edu

Abstract: The reactions of nitrosobenzene and *N,N*′-diethyl-4-nitrosoaniline with $[Cu(CH_3CN)_4]PF_6$ provide novel Cu(I) complexes, $[Cu(PhNO)_3]PF_6$ (**1**) and $[Cu(Et_2NPhNO)_3]PF_6$ (**2**); in **2** the copper atom is *N*-coordinated to the nitrosoarenes in a distorted trigonal planar geometry. Complex **1** is strongly implicated as a reactive intermediate in the Cu(I)-catalyzed allylic amination of olefins based on (i) its isolation from the catalytic reaction, (ii) its stoichiometric regioselective allylic amination of α-methyl styrene (AMS), (iii) the non-involvement of free PhNO in its amination of AMS, and (iv) its function as a catalyst for the amination of alkenes from phenylhydroxylamine. The reaction between AMS and **1** (80 °C, dioxane) is first order in both alkene and **1**. Relative rate studies of the reaction of **1** with para substituted AMS derivatives gives a Hammett ρ value of −0.035. Alkene adducts isolated from the reaction of **1** with styrene and α-methylstyrene are formulated as $[(PhNO)_3Cu(\eta^2\text{-alkene})]PF_6$ (**7**,**8**) on the basis of spectroscopic characterization and thermolysis. PM3 and DFT MO calculations support the role of $[(alkene)Cu(RNO)_3]^+$ and (η^1- or η^3-allyl)$Cu(RNO)_2(RNHOH)^+$ complexes as probable catalytic intermediates and address the origin of the distinctive reaction regioselectivity. A mechanistic scheme is proposed which is consistent with the accumulated experimental and computational results.

Introduction

Catalytic reactions that transfer an -NR group with C−H insertion can convert hydrocarbons into valuable amines. The development of new catalytic reactions for the efficient synthesis of allyl amines from inexpensive feedstocks, remains an enticing goal in both industry and in the laboratory, owing to the importance of these amines as intermediates in organic synthesis and as useful end-products.[1−5] Convenient methods for direct allylic amination have been sought, including alkene reactions with S/Se-imido reagents[6,7] and *ene*-reactions with azo-,[8] *N*-carboalkoxynitroso-,[9] and *N*-sulfinylcarbamate derivatives.[10]

Transition-metal-promoted allylic amination of unsaturated hydrocarbons presents an attractive alternative means to functionalize olefins via C−N bond formation.[11,12] We and others contributed to the early development of Mo(VI)[13] and Fe(II,-III)[14,15]-catalyzed allylic amination of alkenes by aryl hydroxylamines (Scheme 1). Nitroarene-[16] and aminoarene-based,[17] metal-catalyzed allylic aminations have also been developed by us and the Cenini/Ragaini group. More recently, we[18] and a Chinese group[19] independently found that the Cu-catalyzed reactions of olefins with aryl hydroxylamines produce moderate

† University of Louisiana at Lafayette.
‡ University of Oklahoma.

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10.1021/ja0751072 CCC: $37.00

yields of allyl amines regioselectively, with *N*-functionalization at the less substituted of the original olefinic carbons. Additionally, Cu(II) salts catalyze the α-amination of saturated ketones.[19] Our initial mechanistic probes of allylic amination catalyzed by Cu(I) suggested the involvement of coordinated organonitrogen species as the ArN-transfer agent.[18]

In our preliminary report on the copper species involved in allylic amination we described the first homoleptic nitrosoarene−Cu(I) complexes, $[Cu(PhNO)_3]PF_6$ (**1**) and $[Cu(Et_2NPhNO)_3]PF_6$ (**2**), and implicated **1** as an intermediate in amination on the basis of its ability to stoichiometrically aminate alkenes.[20] Other group 10 metal complexes of nitrosoarenes have also been proposed as intermediates in enantioselective hetero-Diels−Alder[21] and *O*-nitroso aldol reactions.[22] Further synthetic development of the allylic amination and related reactions would be aided by a better understanding of the reaction mechanism. We report here the full details of our preliminary synthetic and mechanistic studies along with new kinetic and reactivity investigations of **1** and **2**, both experimental and computational, including the isolation of an alkene adduct **7** of a type that appears to be on the catalytic pathway as well.

Experimental Section

General Methods and Materials. All reactions were performed in an atmosphere of argon using standard Schlenk tube or drybox techniques. Reagent grade solvents were dried, distilled, and stored over activated (250 °C) 4 Å molecular sieves in a Schlenk flask under argon. Phenylhydroxylamine[23] and α-methylstyrene-d_3[24] were prepared following literature methods. FT-IR spectra were obtained as KBr pellets. ^{1}H NMR spectra (FT) were acquired in $CDCl_3$ and CD_2Cl_2 solutions at 270, 300, or 400 MHz; mass spectra were obtained by direct insertion (70 eV) or FAB; UV−vis spectra were recorded on a diode array spectrophotometer. Analytical GC was carried out using a 3-foot column packed with 3% OV 101 or a 30-meter SE-30 capillary column with naphthalene as internal standard and flame ionization detection. Yields of volatile products were obtained by GC analysis with sensitivity factors determined from authentic samples relative to napthalene. GC−MS (70 eV) analyses were obtained using packed SPB-5 (30 m) and SE-30 (30 m) capillary columns. Copper was analyzed by ICP (Perkin-Elmer emission spectrometer).

Typical Procedure for Catalytic Amination of Olefins Catalyzed by $[Cu(CH_3CN)_4]PF_6$ or 1. A 1,4-dioxane (2 mL) solution of olefin (7.0 mmol) and $[Cu(CH_3CN)_4]PF_6$ or **1** (0.08 g, 0.15 mmol) was heated to 80−100 °C. A phenyl hydroxylamine (0.164 g, 1.5 mmol) solution in 1,4-dioxane (8 mL) was delivered with a syringe pump over a period of 5−6 h to the heated solution. After cooling, the volatiles were removed in vacuum, and the residue was dissolved in diethyl ether. Column chromatography was carried out on silica gel using dichloromethane/petroleum ether as eluant to afford the allylamine (Table 1). The IR, MS, and NMR spectra of the allyl amines were compared with the pure samples prepared as described previously for qualitative analysis.[14,15]

Synthesis of $[Cu(PhNO)_3]PF_6$ (1). To a solution of $[Cu(CH_3CN)_4]PF_6$ (0.22 g, 0.58 mmol) in chloroform (15 mL), solid nitrosobenzene (0.26 g, 2.5 mmol) was added, producing a red color immediately. After being stirred at room temperature for 3−4 days, the dark-red solution was filtered, and the solvent was removed under vacuum. The resulting dark-red solid was triturated with diethyl ether (2 × 10 mL), and then dried under vacuum. ^{1}H NMR (CD_2Cl_2, δ): 8.0 (d, J = 8 Hz, 2H), 7.8 (t, J = 8 Hz, 1H), 7.6 (t, J = 8 Hz, 2H). IR (KBr, cm^{-1}): 1600, 1437, 1398, 1326. Visible spectrum (CD_2Cl_2): 420 nm (ϵ 19542 L·mol^{-1}·cm^{-1}). Attempts to obtain a mass spectrum of **1** (EI, ESI, FAB) failed to provide interpretable fragments as did efforts to obtain suitable crystals of labile **1** for X-ray diffraction. ICP analysis of **1** digested in 1 mL of concentrated HCl had a Cu content of 11.7%; Cu calcd for $[Cu(PhNO)_3]PF_6$ = 12.0%. The C,H,N-microanalyses of samples of **1** by commercial providers were unsatisfactory. When the above synthetic procedure was employed with $[Cu(CH_3CN)_4]PF_6$ (0.24 g, 0.64 mmol) and PhNO (0.30 g, 2.8 mmol), trituration of the reaction residue with Et_2O recovered 0.083 g (0.78 mmol) of unreacted PhNO (containing a small amount of azoxybenzene detected by GC). Assuming complete conversion of $[Cu(CH_3CN)_4]PF_6$ the Cu:PhNO ratio in the product complex is calculated to be 1:3.1.

Synthesis of $[Cu(Et_2NPhNO)_3]PF_6$ (2). $[Cu(CH_3CN)_4]PF_6$ (0.22 g, 0.59 mmol) was dissolved in dichloromethane (50 mL) and then solid *N*,*N*′-diethyl-4-nitrosoaniline (0.45 g, 2.5 mmol) was added. The initially colorless solution changed to dark red-green immediately. After stirring 24 h the dark red-green solution was filtered, and the solvent was removed from the filtrate in vacuum. The solid residue was triturated with diethyl ether (30 mL × 3) and vacuum-dried to obtain **2** as a dark red-green solid (70% based on $[Cu(Et_2NPhNO)_3]PF_6$). Recrystallization from CH_2Cl_2/diethyl ether at −20 °C provided greenish crystals suitable for X-ray diffraction. IR (KBr, cm^{-1}): 1600, 1420, 1375, 1330. MS (FAB): 419 $[(Et_2NPhNO)_2{}^{63}Cu]^+$, 421$[(Et_2NPhNO)_2{}^{65}Cu]^+$. UV−vis (nm, CH_2Cl_2): 421 (ϵ 22426 L·mol^{-1}·cm^{-1}). ^{1}H NMR (CD_2Cl_2) 8.6 (bs, 1H), 7.2 (bs, 1H), 6.8 (bs, 2H), 3.55 (q, 4H), 1.28 (t, 6H).

X-ray Structure Determination of 2. The data were collected at 120(2) K on a Bruker Apex (CCD) diffractometer using Mo Kα (λ = 0.71073 Å) radiation. Intensity data, which approximately covered the full sphere of the reciprocal space, were measured as a series of ω oscillation frames each 0.3 for 25 s/frame. The detector was operated in 512 × 512 mode and was positioned 6.12 cm from the crystal. Coverage of unique data was 97.1% complete to 55.4° (2θ). Cell parameters were determined from a nonlinear least-squares fit of 3322 reflections in the range of $2.6 < \theta < 26.7°$. A total of 31514 reflections were measured. The structure was solved by the direct method using SHELXTL system 22, and refined by full-matrix least-squares on F2 using all reflections. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were included with idealized parameters. Crystals were twined and required SHELXTL twin refinement with HKLF 5 type data containing 2 components of 70% and 30% ratio. Crystal data and structure refinement information for **2** are summarized in Table 2. Tables of atomic coordinates and complete X-ray data tables were provided as Supporting Information for the preliminary report (ref 20).

Reaction of 1 with α-Methylstyrene (AMS). AMS (0.10 mL, 0.77 mmol), 6.2 mg (0.048 mmol) of naphthalene (GC internal reference), and 27 mg (0.051 mmol) of **1** were dissolved in 4 mL of 1,4-dioxane and heated at 90−100 °C for 20 h. Analysis of the mixture by GC and GC−MS indicated that 40% (0.010 mmol) of the allyl amine (**4**) had formed; the calculated yield is based on a stoichiometry of 2Cu(I) + PhNO + AMS → allyl amine.

Reaction of 2 with 2-Methyl-2-pentene. A Schlenk flask was charged with complex **2** (0.010 g, 0.013 mmol) in dry 1,4-dioxane (5 mL), and 2-methyl-2-pentene (0.10 mL, 0.82 mmol) was added. The reaction mixture was heated for 24 h at 100 °C. GC analysis detected only free 4-diethylamino-nitrosobenzene, but no product derived from reaction of **2** and the olefin.

Reaction of 1 with a Mixture of 2-Methyl-2-pentene and 2,3-Dimethyl-1,3-butadiene. A dioxane solution (5 mL) containing 2-methyl-2-pentene (10 μL, 0.081 mmol), 2,3-dimethyl-1,3-butadiene (8.5 μL, 0.0.081 mmol), and **1** (0.032 g, 0.06 mmol) was heated at 80−90 °C for 24 h. GC and GC−MS analysis of an aliquot was found

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to contain allyl amines from the alkene (**4**, *m*/*e* 175; 0.005 mmol, 8%) and diene (**5**, *m*/*e* 173; 0.011 mmol, 18%), respectively. None of the hetero-Diels−Alder adduct **6** was detected. (Scheme 2)

Stability of Diels−Alder Adduct 6. A mixture of 0.10 g (0.54 mmol) of **6**, 2-methyl-2-pentene, (70 μL, 0.57 mmol), and 0.20 g (0.55 mmol) of $[Cu(CH_3CN)_4]PF_6$ in 5 mL of dioxane was heated to 100 °C for 5 h. GC analysis detected only the starting adduct **6**; no allyl amine derived from 2-methyl-2-pentene was detected.

Catalytic Amination of AMS by Phenyl Hydroxylamine and 1. A mixture of **1** (0.058 g, 0.11 mmol), naphthalene (0.030 g, 0.23 mmol) as GC internal standard, and AMS (0.6 mL, 4.6 mmol) was heated in 1,4-dioxane (2 mL) at 90−95 °C. Phenyl hydroxylamine (1.37 mmol) dissolved in 8 mL of dioxane was added over a period of 5−6 h with a syringe pump. Aniline (0.07 mmol, 5%), azobenzene (0.04 mmol, 6%), azoxybenzene (0.15 mmol, 22%), and the *N*-phenyl allylamine **3** (0.49 mmol, 36%) were detected by GC and GC−MS after 24 h. A second run with a lower loading of **1** was also carried out. To a dioxane solution (2 mL) of **1** (0.023 g, 0.043 mmol), naphthalene (0.019 g, 0.15 mmol), and AMS (0.4 mL, 3.1 mmol) at 100 °C, phenyl hydroxylamine (0.82 g, 0.75 mmol in 8 mL of dioxane) was slowly added over a period of 5 h with a syringe pump. The amine **3** (0.26 mmol, 34%) was detected by GC and GC−MS after 24 h.

Catalytic Amination of AMS by Phenyl Hydroxylamine and 2. To a 1,4-dioxane solution (2 mL) of **2** (0.025 g, 0.03 mmol), naphthalene (0.019 g, 0.15 mmol) as GC internal standard, and AMS (0.40 mL, 3.1 mmol) at 100 °C was added phenyl hydroxylamine (0.30 mmol in 5 mL of dioxane) over a period of 4−5 h with a syringe pump. The *N*-phenyl allylamine **3** (0.042 mmol, 15%) and *N*,*N*-diethyl-4-nitrosoaniline were detected by GC and GC−MS after 24 h.

Detection of 1 in the Reaction of $[Cu(CH_3CN)_4]PF_6$, AMS and Phenyl Hydroxylamine. PhNHOH (1.6 mmol) in dioxane (4 mL) was added slowly over a period of 2.5 h to a solution of $[Cu(CH_3CN)_4]PF_6$ (0.15 g, 0.40 mmol) and AMS (0.53 mL, 3.8 mmol) in dioxane (10 mL) at 90 °C and allowed to stir for an additional 0.5 h at the same temperature. The solution was cooled, and the solvent was removed under reduced pressure on a warm water bath. The resulting dark-red residual mass (0.10 g, 0.19 mmol, 47%) was recrystallized from CH_2Cl_2/diethyl ether. The IR spectrum (KBr) of the product was indistinguishable from that of **1**.

Styrene Adduct 7. A solution of **1** (0.126 g, 0.24 mmol) in dry dichloromethane (20 mL) was treated with styrene (0.03 mL, 0.26 mmol), and the mixture was stirred at room temperature for 25 h. The solvent was removed at reduced pressure, and the residue was triturated with hexane (3 × 5 mL). GC analysis of the extract showed the presence of PhNO. The resulting dark-red solid was dried under vacuum for 2 days. The visible spectrum of the product (CH_2Cl_2) exhibited peaks at 348 (ϵ 7174 L·mol^{-1}·cm^{-1}) and 455 nm (ϵ 2210 L·mol^{-1}·cm^{-1}). The ^{1}H NMR spectrum of **7** (CH_2Cl_2) had peaks at 7.20−8.30 (m, 20H), 6.45 (dd, J = 15, 10 Hz, 0.8H), 5.35 (d, J = 15 Hz, 0.8H, overlapped w/$CHDCl_2$), 4.85 (d, J = 10 Hz, 0.8H). Solid **7** was thermolyzed in an evacuated, sealed flask for 1 h at >250 °C. After cooling, the residue was dissolved in CH_2Cl_2; GC−MS analysis of the solution showed the presence of styrene, azobenzene, and azoxybenzene.

α-Methylstyrene Adduct 8. A solution of **1** (0.12 g, 0.23 mmol) and α-methystyrene (0.040 mL, 0.37 mmol) in dry dichloromethane (15 mL) was stirred for 23 h at room temperature; the solvent was then removed under vacuum to leave a red-brown residue. Alternatively, to a solution of $[Cu(CH_3CN)_4]PF_6$ (0.11 g, 0.28 mmol) in CH_2Cl_2 (20 mL), solid PhNO (0.13 g, 1.2 mmol) and AMS (0.50 mL, 3.8 mmol) were added. The red solution was stirred at room temp for 24 h; the solvent and excess AMS were removed at reduced pressure. The residue from either reaction was washed with hexane (3 × 5 mL) and vacuum-dried. A red solid (0.136 g, 74%) was obtained. ^{1}H NMR ($CDCl_3$, δ): 6.7−8.29 (br m, 20H), 4.99 (broad s, 1H), 5.25(broad s, 1H), 2.14 (s, 3.4 H); the shift of the -CH_2 and -CH_3 resonances from free AMS is 0.15−0.25 ppm. IR (KBr, cm^{-1}): 1626 (w, C═C). UV−vis (2.9 × 10^{-5} M in CH_2Cl_2, nm): 230 (ϵ 27182 L·mol^{-1}·cm^{-1}), 282 (ϵ 10831 L·mol^{-1}·cm^{-1}), 310 (ϵ 6281 L·mol^{-1}·cm^{-1}) and 350 nm (ϵ 1735 L·mol^{-1}·cm^{-1}). Separate solutions of **1** and AMS were prepared in dry CH_2Cl_2; these solutions were mixed in varied proportion to systematically change the concentration of AMS while keeping the concentration of **1** constant (2.32×10^{-6} M). The UV−vis spectra of these mixtures (ratios of **1** and AMS: 1:0, 1:1, 1:2, 1:5, 1:10, 1:20, 1:40) were measured at room temp and were largely unchanged from that of **1**.

On thermolysis in refluxing dioxane, the corresponding *N*-phenyl allylamine, 5% and azoxybenzene, 9% were detected by GC.

Kinetic Studies. Kinetic data were obtained from reactions conducted in a three-necked round-bottom flask fitted with a condenser, argon inlet, and a silicone septum stopper. Complex **1** (0.010 g, 0.019 mmol), AMS (25 μL, 0.23 mmol), and naphthalene (0.0050 g, 0.039 mmol) were dissolved in dioxane (5 mL). The flask was placed in a thermostated oil bath at 80 °C. Aliquots were withdrawn periodically and cooled in ice immediately. GC was used to analyze the samples for the allyl amine. Initial rates were determined from a plot of concentration of allyl amine vs time during the first 10−15% conversion. The concentration of each reacting component was systematically varied, while holding the others constant. The rate constants for the reaction of **1** with AMS at 70, 80, 100, and 120 °C were determined and a plot of ln k vs 1/T according to the Erying equation was used to calculate the activation parameters.

The determination of rates of reaction of **1** with para-substituted α-methylstyrenes was carried out analogously at 80 °C.

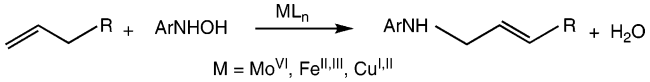
Kinetic D-Isotope Effect. Complex **1** (0.19 g, 0.36 mmol) was dissolved in 10 mL of 1,4-dioxane. To this solution α-methylstyrene (150 μL, 0.115 mmol) and α-(trideuteriomethyl) styrene (150 μL, 0.115 mmol, 90% D_3) were added. The solution was heated to 80 °C for 20 h. After vacuum removal of the volatiles, the allyl amine was isolated by chromatography on silica gel using petroleum ether and ethyl acetate (95:5) as eluant. The ratio of protio to deuterio products was determined by ^{1}H NMR integration of the allylic CH_2 and ═CH_2 groups. Correcting for the % D in the α-(tridueteriomethyl)styrene a 2.2 ratio of protio/deuterio allylamines (=k_H/k_D) was calculated.

Computational Studies. PM3 and DFT computations were carried out using the Spartan 04 software suite (Wavefunction, inc.). The energetically minimized structures (shown) were determined in the semiempirical PM3 mode, followed by single energy point calculations with the DFT method (B3LYP with 6-31G basis set) to provide final calculated energies for comparison. A summary of the Cartesian coordinates, calculated energies, and electrostatic charges for structures **A**−**E** is provided in the Supporting information.

Results and Discussion

Synthetic and General Catalytic Reactivity Studies. Slow addition of phenyl hydroxylamine to a heated solution of the alkene (in excess) and $[Cu(CH_3CN)_4]PF_6$ (10 mol %) in 1,4-dioxane provides the corresponding *N*-aryl-*N*-allylamines in fair to good yield after 8 h (Table 1, Scheme 1). Aniline, azo-, and

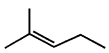
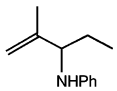
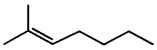
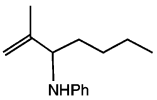
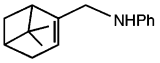
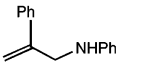
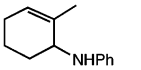
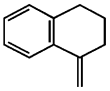
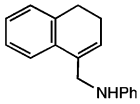
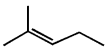
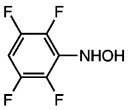
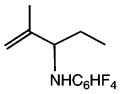
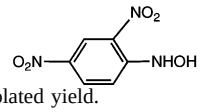
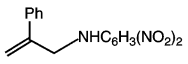
Scheme 1



azoxybenzenes are the major byproducts, derived from competing phenyl hydroxylamine side reactions. The amination reactions, like the aryl hydroxylamine reactions catalyzed by Mo−[13] and Fe− salts and complexes,[14,15] and those involving metal-catalyzed nitroarene reduction by CO,[16] proceed highly regioselectively, with nitrogenation occurring at the less substituted carbon of the original unsaturated unit. Other important

features of the reactions include (1) trisubstituted and 1,1-disubstituted alkenes give the best yield and (2) no other alkene-derived products are observed. The distinctive regioselectivity and alkene reactivity behavior are typical of ene-type reactions.[25] This selectivity complements and is superior to that observed in stoichiometric aminations by $(RN)_2X$ (X = S, Se),[6,7] which favor preservation of the double bond position but with variable selectivity. Furthermore, the catalysts used in the present system are commercially available and inexpensive.

Table 1. Cu(I)-Catalyzed Allylic Amination of Alkenes

Alkene	Hydroxylamine	Allyl Amine	Yield (%)[a]
	PhNHOH		38
	PhNHOH		45
	PhNHOH		15
	PhNHOH		30
	PhNHOH		10
	PhNHOH		60
			38
			38

[a] GC yield. [b] Isolated yield.

Trapping Studies: The Non-involvement of PhNO. Two general catalytic pathways for metal-promoted allylic amination have been postulated. A coordinated organonitrogen species as the ArN-transfer agent has been implicated in the $FeCl_2/_3$-catalyzed reactions,[14] whereas those catalyzed by $LMoO_2$[13] and (phthal)Fe[15] involve the intermediacy of free PhNO, a proven enophile,[26] as the aminating agent. We have investigated whether ArNO is the active aminating agent in Cu(I)-catalyzed amination reactions. The hetero-Diels−Alder reaction of PhNO with 2,3-dimethyl-1,3-butadiene (DMB) was used as a trapping reaction for PhNO.[27] Initially, the effective Diels−Alder trapping of PhNO by DMB at 80 °C (dioxane) in the presence of α-methylstyrene was established. When the Cu(I)-catalyzed reaction (5 mol % $[Cu(CH_3CN)_4]PF_6$) of PhNHOH with 2-methyl-2-pentene was carried out in the presence of DMB (1:1, 80 °C, dioxane), the allyl amines derived from the alkene **4** (*m*/*e* 175; 8%) and the diene **5** (*m*/*e* 173; 18%) were formed exclusively, with none of the PhNO-derived Diels−Alder adduct **6** being detected (Scheme 2). A control experiment established that **6** is stable under the amination conditions. These results rule out the intermediacy of free nitrosobenzene in the Cu(I)-catalyzed reactions and is consistent with (but does not prove) the involvement of a Cu(I)-coordinated species in the transfer of an RN- or RNO-group to the alkene.

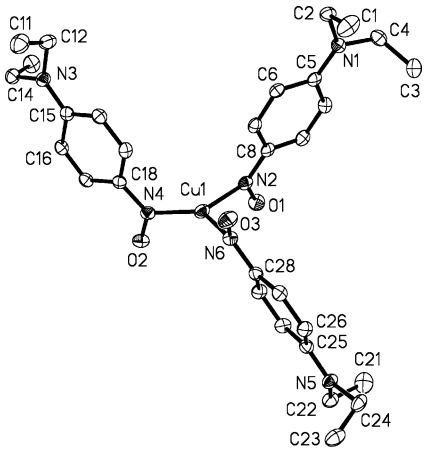
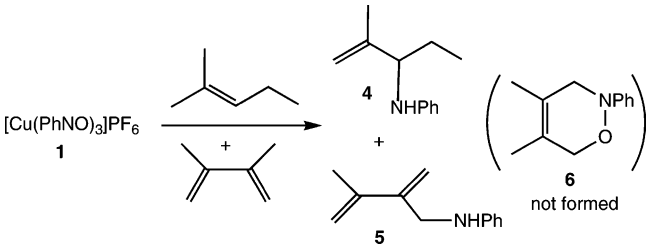


Figure 1. X-ray structure of the cation of **2**.

Preparation of Catalytically Relevant Copper Complexes. Seeking to prepare potential intermediate complexes in the Cu-mediated allylic aminations, $[Cu(CH_3CN)_4]PF_6$ was treated with 4.2 equiv of PhNO in $CHCl_3$ at room temperature (Scheme 3). A dark-red (λ 420 nm), labile complex **1** was isolated that was formulated as $[Cu(PhNO)_3]PF_6$ on the basis of spectroscopic evidence and its metal content. The ^{1}H NMR spectrum of **1** showed a 2:1:2 (d,t,t) set of aromatic resonances downfield from PhNO itself. Unfortunately, our efforts to determine the detailed structure of **1** were frustrated by its sensitivity and lability. A more stable Cu−ArNO derivative was prepared from the reaction of $[Cu(CH_3CN)_4]PF_6$ with excess *N*,*N*′-diethyl-4-nitrosoaniline in CH_2Cl_2 at room temperature. The greenish-red product **2** (70% yield) was identified with the aid of IR, NMR, MS (FAB), and X-ray crystallography (Figure 1); bond lengths and angles for **2** are given in Table 3. Complex **2** consists of distorted trigonal planar, 16 electron $Cu(ArNO)_3^+$ and

Scheme 2



Scheme 3

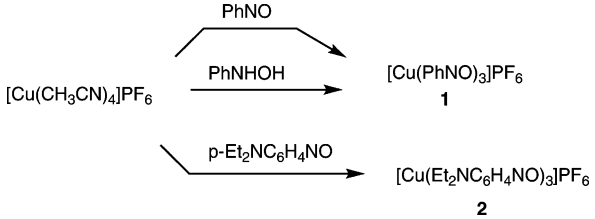


Table 2. Crystal Data and Structure Refinement for **2**

empirical formula	$C_{31}H_{44}Cl_2Cu\ F_6N_6O_3P$
molecular weight	828.13
temperature	120(2) K
wavelength	0.71073 Å
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimensions	$a = 8.396(7)$ Å, $\alpha = 68.477(7)°$ $b = 14.281(11)$Å, $\beta = 84.072(7)°$ $c = 16.138(13)$Å, $\gamma = 86.267(7)°$
vol, Z	1790(2)Å^3, 2
density (calculated)	1.537 Mg/m^3
absorption coefficient	0.878 mm^{-1}
F(000)	856
crystal size	0.28 × 0.12 × 0.10 mm^3
θ range for data collection	2.39 to 27.69°
index ranges	$-10 < h < 10$, $-17 < k < 18$, $-20 < 1 < 20$
reflection collected	31514
independent reflections	31518 [R(int) = 0.0000]
completeness of $\theta = 25.00°$	99.4%
absorption correction	semiempirical from equivalents
max. and min. transmission	0.9174 and 0.7912
refinement method	full-matrix least-squares on F^2
data/ restraints/parameters	31518/0/460
GOF on f^2	1.027
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0531, wR2 = 0.1369
R indices (all data)	R1 = 0.0701, wR2 = 0.1445
Largest diff. Peak and hole	0.906 and −0.978 e. Å^{-3}

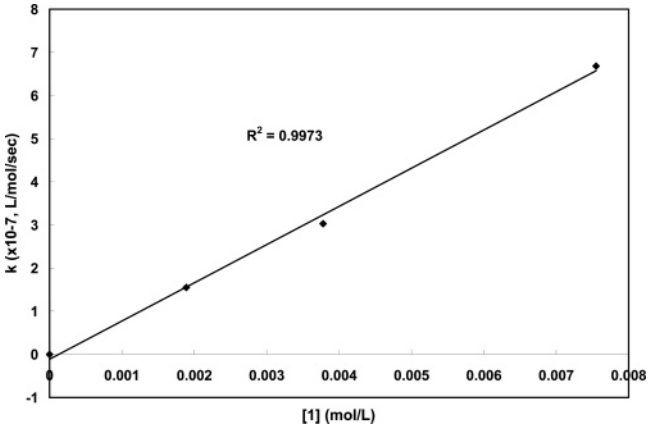
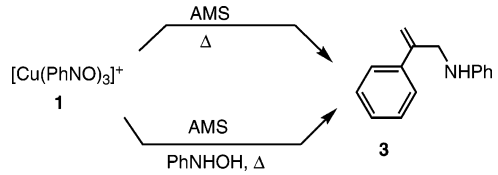


Figure 2. Effect of [**1**] on k_{obs} for the reaction of **1** with α-methylstyrene at 80 °C.

Scheme 4



octahedral PF_6^-. 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[28] and are probably derived from steric and/or crystal packing effects.[29] The N−O bond lengths, however, are relatively uniform (av. 1.258 Å) and are comparable to those in free *N*,*N*′-diethyl-4-nitrosoaniline (1.252 Å),[30] suggesting the absence of appreciable backbonding from Cu(I) to the nitrosoarene ligand. Compound **2** constitutes the first crystallographically characterized, homoleptic nitrosoarene−metal complex and the first copper complex bearing a simple *C*-nitroso ligand.[31]

Reactivity Studies of 1: Role in the Catalytic Amination of Alkenes. Once the three-coordinate copper complex **1** was identified, we sought to determine its relevance to the copper-catalyzed allylic amination reactions; that is, is **1** on the product forming catalytic pathway or is it a dead end? Initially, treatment of **1** with α-methylstyrene (1:15) in dioxane (100 °C) resulted in its conversion to the corresponding allyl amine **3** (40%, Scheme 4). Likewise, as found in the Cu(I)-catalyzed amination reaction, **1** reacts with alkenes without the intervention of free PhNO. Thus, when **1** was heated with an equimolar mixture of α-methylstyrene and 2,3-dimethyl-1,3-butadiene (DMB), the allylic amination products **4**, **5** were produced exclusively (1:13). None of the Diels−Alder adduct **6**[27] was detected (Scheme 2). Finally, **1** also was found to catalyze the allylic amination of α-methylstyrene by PhNHOH (100 °C, 24 h) at an initial rate comparable to (or somewhat faster than) that of the Cu-catalyzed reaction (Scheme 4). These observations, coupled with the isolation of **1** in Cu-catalyzed reactions, strongly indicate that complex **1** is on the amination catalytic pathway.

Kinetics of the Reactions of $[(PhNO)_3Cu]PF_6$ with Alkenes. To gain further insight into the mechanism of the amination reaction we performed kinetic studies on the reaction of α-methylstyrene (excess) with **1**. Kinetic information gained from the direct reaction of **1** was deemed likely to be more informative than from the catalytic reaction because (1) the former system would probe steps closer to the critical C−N, C−C, and C−H transforming steps (rather than the formation of **1** from ArNHOH) and (2) acquisition of meaningful kinetic data for the catalytic reaction would be complicated by the inefficiency of the batch process (all reactants together) and the need for slow addition of the hydroxylamine. The reactions were conducted in dioxane at 80 °C and initial rates were determined by GC monitoring the allylamine formation at low conversion (0−15%). On varying the concentration of **1** (9.44×10^{-6} to 3.77×10^{-5} M) at constant α-methylstyrene concentration, the appearance of allylamine is first order in the copper complex (Figure 2). Likewise, at a constant concentration of **1** (1.88×10^{-5} M) the rate of reaction is also first order in alkene over the concentration range 9.6×10^{-5} to 3.84×10^{-4} M (Figure 3). Overall, these results reveal the involvement of the alkene

(25) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476. Hoffman, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. Snider, B. *Acc. Chem. Res.* **1980**, *13*, 426.
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(28) Most $Cu(I)L_3$ complexes display nearly ideal trigonal planar geometries: Kappenstein, C.; Hugel, R. P. *Inorg. Chem.* **1978**, *17*, 1945. Eller, P. G.; Corfield, P. W. R. *Chem. Commun.* **1971**, 105. Gruf, E. S.; Koch, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 1245. A few examples with significant distortions towards Y- or T-shapes have been reported: Coucouvanis, D.; Murphy, C. N.; Kanodia, S. K. *Inorg. Chem.* **1980**, *19*, 2993. Gruf, E. S.; Koch, S. A. *J. Am. Chem. Soc.* **1989**, *111*, 8762. Lewin, A. H.; Michl, R. J. *Chem. Commun.* **1972**, 661.
(29) Riehl, J. F.; El-Idrissi, R.; Jean, Y.; Pelissier, M. *New J. Chem.* **1991**, *15*, 239.
(30) Talberg, H. J. *Acta Chem. Scand. A* **1977**, *31*, 743.
(31) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889. Doyle, G.; Eriksen, K. A.; Engen Van, D. *Organometallics*, **1985**, *4*, 830.

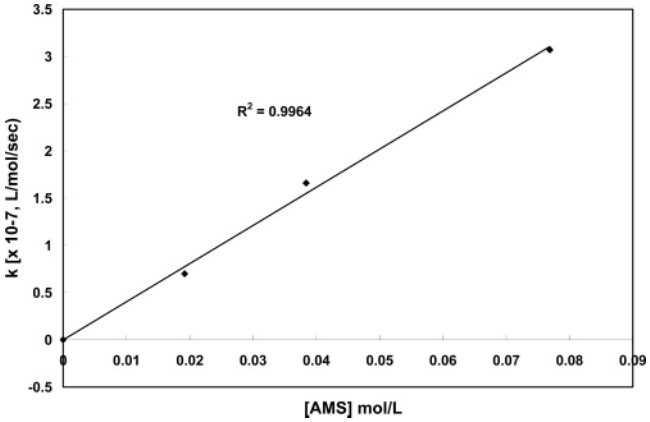


Figure 3. Effect of [AMS] on k_{obs} for the reaction of **1** with α-methylstyrene at 80 °C.

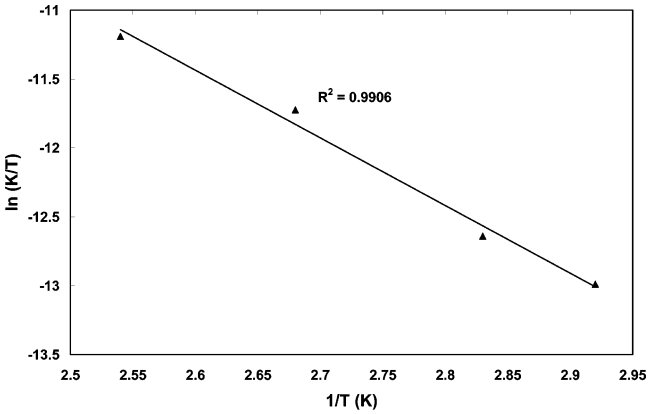


Figure 4. Temperature dependence of k_{obs} for the reaction of **1** with α-methylstyrene.

before or in the rate-determining step and suggest that alkene coordination or at least association is involved.

Temperature-dependent rate studies of the reaction of **1** with α-methylstyrene between 70 and 120 °C afforded rate constants which were subjected to Eyring analysis (Figure 4), yielding the activation parameters $\Delta H_{(act)} = 9.9$ kcal/mol and $\Delta S_{(act)} = -44$ eu. These results, especially the large negative entropy of activation, point to an associative, highly ordered rate-determining step.

The electronic character of the transition state was also probed. The rate constants were determined for the reaction of **1** with a small set of para substituted α-methylstyrenes at 80 °C (Figure 5). A small Hammett ρ value of −0.035 indicates a negligible effect of either electron withdrawing or electron donating groups on the allylic amination of **1** with α-methylstyrene and suggests that there is little charge development in the transition state for the reaction.

Since the amination reaction requires transfer of an allylic hydrogen from the alkene substrate, it was of interest to determine if allylic C−H bond-breaking is involved in the rate-limiting step. This issue was addressed by determination of the kinetic isotope effect (k_H/k_D) from a competitive reaction of AMS and α-CD_3-AMS with **1** (80 °C, dioxane, Scheme 5). NMR analysis of the isolated allylic amine revealed a 2.2 ($^{\pm}$0.1): 1.0 ratio of protio- to deuterio-allyl amines, hence a $k_H/k_D = 2.2$ (ignoring secondary effects). This moderate sized primary isotope effect indicates a significant degree of C−H bond-breaking in the transition state for the RLS.

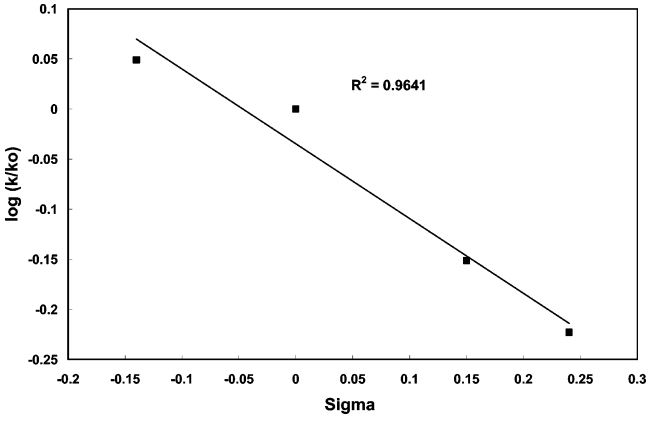


Figure 5. Hammett plot for the reaction of **1** with para substituted α-methylstyrenes.

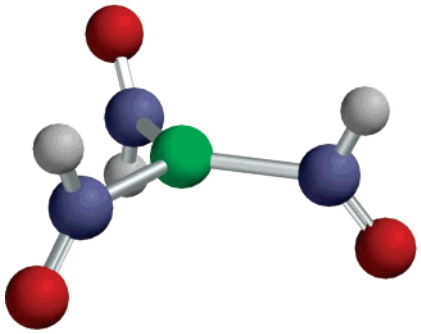
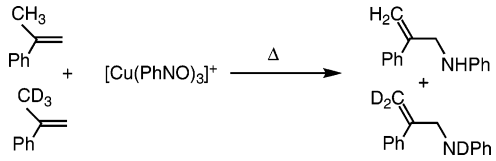
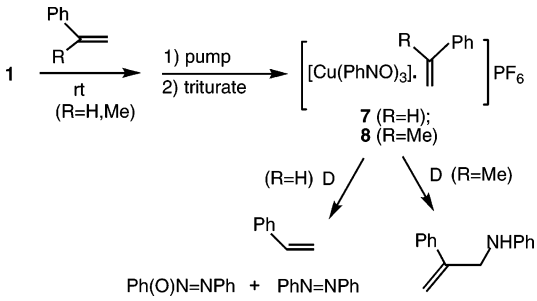


Figure 6. Calculated structure of $[Cu(HNO)_3]^+$ (**A**).

Scheme 5



Scheme 6

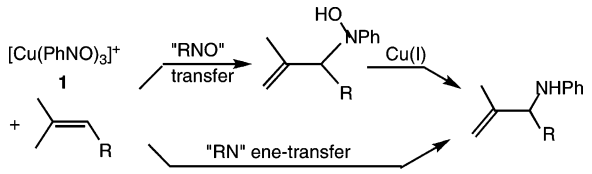


Olefin Adducts 7, 8. The above kinetics and trapping results suggest that the alkene substrate may be coordinated during the ArN-group transfer step. To test this hypothesis the room-temperature reactions of **1** with excess styrene (which lacks allylic hydrogens) and AMS were examined (Scheme 6) to determine if adducts could be detected or isolated. After solvent evaporation and trituration to remove residual alkene, spectroscopic analysis indicated the formation of new compounds **7**, **8** whose ^{1}H NMR spectra exhibited resonances in both the aromatic and vinylic regions, shifted ca. 0.2 ppm from those of the free alkene, but with the same patterns. Such modest

Table 3. Bond Lengths [Å] and Angles [deg] for **2**

Cu(1)−N(4)	1.8983(15)	C(15)−C(20)	1.422(2)	O(1)−N(2)−C(8)	118.11(11)	C(9)−C(10)−C(5)	121.27(12)
Cu(1)−N(6)	1.9296(19)	C(15)−C(16)	1.424(2)	O(1)−N(2)−Cu(1)	113.50(9)	N(3)−C(12)−C(11)	111.60(13)
Cu(1)−N(2)	1.9701(18)	C(16)−C(17)	1.349(2)	C(8)−N(2)−Cu(1)	127.30(10)	N(3)−C(14)−C(13)	112.29(12)
O(1)−N(2)	1.2646(16)	C(17)−C(18)	1.4081(19)	C(15)−N(3)−C(12)	122.28(12)	N(3)−C(15)−C(20)	121.00(13)
O(2)−N(4)	1.2517(16)	C(18)−C(19)	1.388(2)	C(15)−N(3)−C(14)	121.68(12)	N(3)−C(15)−C(16)	121.40(12)
O(3)−N(6)	1.2582(16)	C(19)−C(20)	1.359(2)	C(12)−N(3)−C(14)	116.02(11)	C(20)−C(15)−C(16)	117.61(12)
N(1)−C(5)	1.3297(19)	C(21)−C(22)	1.511(2)	O(2)−N(4)−C(18)	117.80(12)	C(17)−C(16)−C(15)	121.33(13)
N(1)−C(2)	1.471(2)	C(23)−C(24)	1.509(2)	O(2)−N(4)−Cu(1)	117.11(9)	C(16)−C(17)−C(18)	120.10(13)
N(1)−C(4)	1.4730(18)	C(25)−C(30)	1.422(2)	C(18)−N(4)−Cu(1)	124.31(10)	N(4)−C(18)−C(19)	118.15(12)
N(2)−C(8)	1.358(2)	C(25)−C(26)	1.430(2)	C(25)−N(5)−C(22)	123.07(12)	N(4)−C(18)−C(17)	122.57(13)
N(3)−C(15)	1.3455(18)	C(26)−C(27)	1.342(2)	C(25)−N(5)−C(24)	122.04(12)	C(19)−C(18)−C(17)	119.25(12)
N(3)−C(12)	1.455(2)	C(27)−C(28)	1.414(2)	C(22)−N(5)−C(24)	114.88(11)	C(20)−C(19)−C(18)	121.48(13)
C(5)−C(6)	1.4236(19)	C(28)−C(29)	1.400(2)	O(3)−N(6)−C(28)	117.92(12)	C(19)−C(20)−C(15)	119.98(13)
C(5)−C(10)	1.434(2)	C(29)−C(30)	1.359(2)	O(3)−N(6)−Cu(1)	116.40(9)	N(5)−C(22)−C(21)	112.56(13)
C(6)−C(7)	1.351(2)	Cl(2)-C(31)	1.756(2)	C(28)−N(6)−Cu(1)	125.43(9)	N(5)−C(24)−C(23)	112.74(12)
C(7)−C(8)	1.404(2)	Cl(1)-C(31)	1.734(2)	N(1)−C(2)−C(1)	112.82(11)	N(5)−C(25)−C(30)	121.94(12)
C(8)−C(9)	1.411(2)	N(3)−C(14)	1.4703(19)	N(1)−C(4)−C(3)	113.56(11)	N(5)−C(25)−C(26)	120.36(13)
C(1)−C(2)	1.513(2)	N(4)−C(18)	1.3784(18)	N(1)−C(5)−C(6)	122.26(13)	C(30)−C(25)−C(26)	117.70(12)
C(3)−C(4)	1.520(2)	N(5)−C(25)	1.3347(18)	N(1)−C(5)−C(10)	120.61(12)	C(27)−C(26)−C(25)	121.38(13)
N(6)−C(28)	1.3671(18)	N(5)−C(22)	1.465(2)	C(6)−C(5)−C(10)	117.13(12)	C(26)−C(27)−C(28)	120.54(13)
N(5)−C(24)	1.468(2)	N(4)−Cu(1)−N(6)	133.81(6)	C(7)−C(6)−C(5)	120.65(13)	N(6)−C(28)−C(29)	118.66(12)
C(9)−C(10)	1.343(2)	N(4)−Cu(1)−N(2)	120.96(6)	C(6)−C(7)−C(8)	121.65(12)	N(6)−C(28)−C(27)	122.59(12)
C(11)−C(12)	1.509(2)	N(6)−Cu(1)−N(2)	104.96(4)	N(2)−C(8)−C(7)	118.40(12)	C(29)−C(28)−C(27)	118.75(12)
C(13)−C(14)	1.518(2)	C(5)−N(1)−C(2)	122.30(11)	N(2)−C(8)−C(9)	123.31(13)	C(30)−C(29)−C(28)	121.56(13)
		C(5)−N(1)−C(4)	121.13(12)	C(7)−C(8)−C(9)	118.29(13)	C(29)−C(30)−C(25)	120.06(13)
		C(2)−N(1)−C(4)	116.39(11)	C(10)−C(9)−C(8)	120.96(13)	Cl(1)−C(31)−Cl(2)	112.11(10)

Scheme 7



coordination shifts are common for Cu(I)−olefin complexes[31] in which there is rapid exchange on the NMR time scale between free and coordinated olefin. The electronic spectra of these adducts **7**, **8** (5.7×10^{-4} to 2.94×10^{-5} M in CH_2Cl_2) exhibit peaks at 348 and 455 nm for **7** (and 230, 282, and 310 nm for **8**), which are quite different from **1**. Although the adducts **7**, **8** were isolable from very concentrated solutions, in dilute solutions (ca. 10^{-6} M) their electronic spectra were similar to that of $[Cu(PhNO)_3]^+$ (**1**) and the spectrum of **1** in dilute solution was little changed by the addition of excess (2−20 equiv) of these alkenes. These observations indicate that alkene coordination is reversible and at lower concentrations the equilibrium is shifted toward **1** and the free alkene.

The thermolysis of **7** produced styrene, azobenzene, and azoxybenzene while heating **8** gave the *N*-phenyl allyl amine and the azo and azoxy compounds in moderate yield. Overall, the spectroscopic features of **7** and **8** and the thermolysis results indicate the formation of 1:1 adducts that we formulate as $[(PhNO)_3Cu(\eta^2\text{-alkene})]PF_6$. The isolation of these adducts lends additional support to the hypothesis that a complex having the alkene and ArNO simultaneously coordinated is an intermediate in the amination process.

RN or RNO Group Transfer? An important mechanistic issue is whether the product allyl amine is formed via an arylimido (RN)-group insertion into the alkene directly from **1** or whether an arylnitroso (RNO) unit is initially transferred, giving an intermediate allyl hydroxylamine that is subsequently reduced to the amine (Scheme 7). Evidence supporting the viability of the RNO-transfer route was provided indirectly by the fact that Cu(I) is effective for reducing PhNHOH to $PhNH_2$[32] and suggests that Cu(I) complexes present in the catalytic reactions would be capable of reducing an intermediate allyl hydroxylamine.

Computational Studies. Semiempirical (PM3[33]) and density functional calculations were conducted on several potential reaction intermediates to evaluate their viability, structures, and reactivity. To economize computational time the RNO ligand and alkene were modeled by HNO and 1-butene, respectively. The structure of $Cu(HNO)_3^+$ (**A**) at the PM3 level minimized to trigonal planar as defined by the copper and the nitrogen atoms of the HNO ligands (Figure 6). The oxygen atoms are out of the CuN_3-plane as observed in solid state (X-ray), but the distorted Y-geometry seen in the X-ray structure was not reproduced. As noted earlier (op cit) this distortion is most likely not electronic in origin.

The association of 1-butene with **A** was probed by computations on $[(Cu(HNO)_3(1\text{-butene})]^+$ (**B**, Figure 7). Complex **B** is an 18 e^- species and minimizes in an expected pyramidal geometry. The DFT-calculated enthalpy of **B** (−2188.76292 hartrees; 1 H = 627.5 kcal) is lower (−8.0 kcal/mol) than the sum of those of **A** (−2031.53252 H) and free 1-butene (−157.21775 H). While this comparison ignores the entropy penalty accompanying alkene association with **1**, it does suggest that formation of a $[Cu(RNO)_3(alkene)]^+$ species is an energetically viable step. This is also in line with the isolability of $[(styrene)Cu(PhNO)_3]PF_6$, the first-order kinetic dependence on the alkene concentration, and the large ΔS_{act} value that would accompany olefin association in or before the rate-limiting step. For energy comparisons with other prospective intermediate complexes the relative energy of **B** was set to zero kcal/mol.

We envision two alternative pathways for the allylic-H

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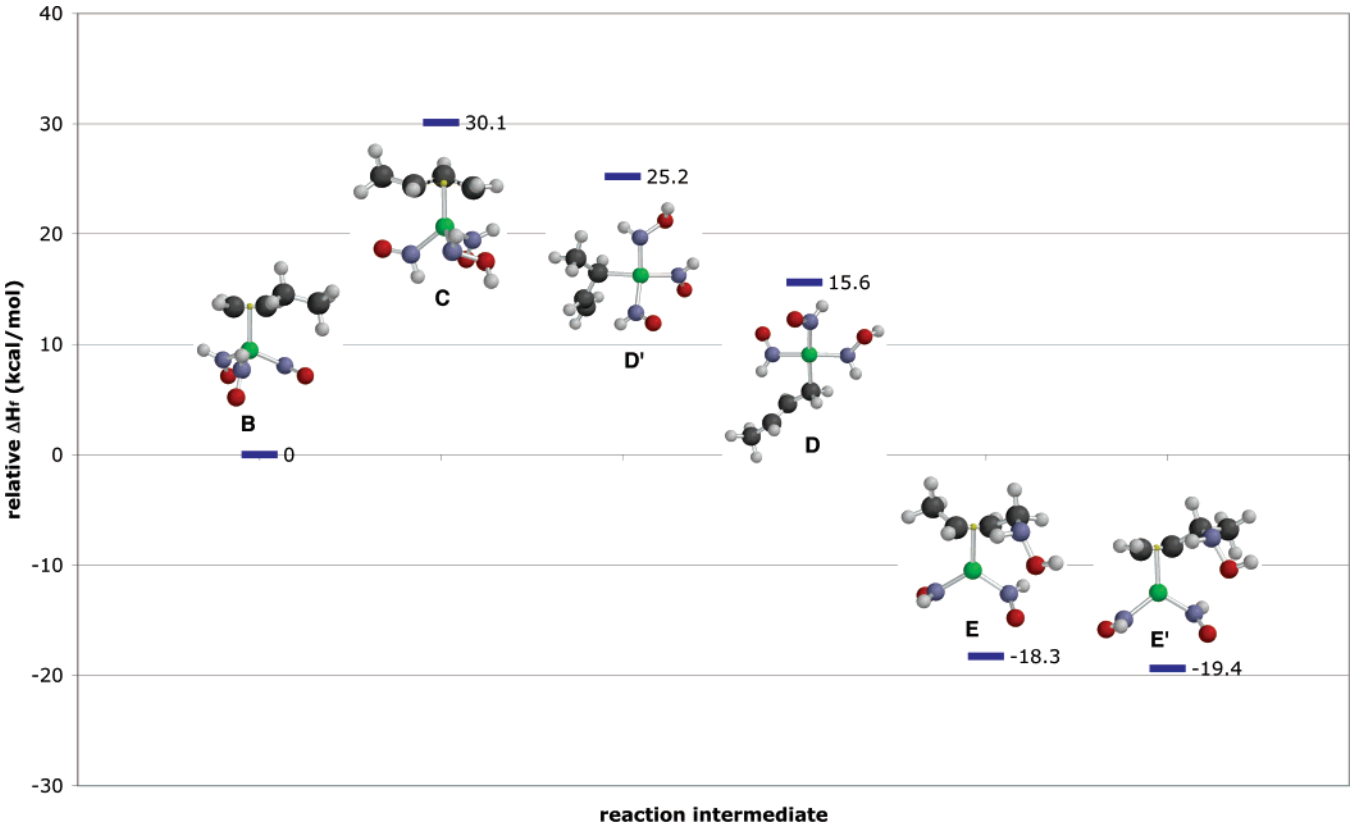

Figure 7. Computed structures and energies of potential reaction intermediates in Cu-catalyzed allylic amination.

transfer to coordinated RNO from intermediate $[Cu(RNO)_3(alkene)]^+$ (**B**). In the first of these H-transfer is accompanied by an η^2 to η^3 shift in Cu bonding, giving $[(\eta^3\text{-1-methallyl})Cu(HNO)_2(NHOH)]^+$ (**C**). Such an 18 e^- species is calculated to have a pyramidal geometry with a ΔH_{form} substantially higher than the η^2-alkene adduct (+30 kcal/mol). Alternatively, allylic H-transfer in **B** could occur together with an η^2- to η^1-Cu shift to produce $[(\eta^1\text{-methallyl})Cu(HNO)_2(NHOH)]$ (**D**). Complex **D** and its isomer **D′** could also be generated from the η3-allyl species **C** since facile η^1/η^3 equilibria are likely for Cu−allyl complexes.[34] The η^1-allyl derivative **D** is calculated to be substantially lower in energy ($\Delta\Delta H$ 14.5 kcal) than the η3-isomer **C** and is predicted to have nearly a square planar geometry, as expected for a d^8-four coordinate species. The isomeric, branched η^1-allyl species, **D′**, is calculated to be substantially less stable than the terminal isomer ($\Delta\Delta H$ 9.6 kcal), probably the result of a weaker Cu−(2°)−C bond, greater steric crowding, and the higher energy, terminal C═C. The calculated greater stability of the η^1-allyl complexes **D**, **D′** relative to **C** contrasts with recent DFT calculations on the reductive elimination of $(allyl)CuMe_2$ complexes which found the η^3-allyl derivatives to be lower in energy.[34d] The origin of this difference could lie in the differing charges, total electron count, and auxiliary ligands in the two systems. In any event the H-transfer conversion from alkene-complex **B** to either of these high energy intermediates **C**, **D**, or **D′** is likely the rate-limiting step in the allylic amination. This would account for the experimentally observed D-isotope effect, the olefin rate dependency, and the negative ΔS_{act}. With the crude assumption that the activation energies to form **C**, **D**, or **D′** from η^2-alkene complex **B** parallel the energies of the intermediates, the η^1-intermediate **D** appears to be the most energetically accessible.

C−N bond formation to form an allyl hydroxylamine derivative, for example, η^2-complexes **E**, **E′**, could proceed from any of the allyl-Cu complexes **C**, **D** by reductive elimination. This step would determine the product regiochemistry. Its highly exothermic nature (30−45 kcal calculated) would likely make it fast and essentially irreversible. Little energy difference is calculated between the isomeric η^2-allyl hydroxylamine complexes **E**, **E′**, so their relative stability (thermodynamic control) would not appear to be the origin of the high reaction regioselectivity. Reductive elimination from the most stable of the allyl complexes, **D** to **E**, would produce the allyl hydroxylamine (and eventually the allyl amine) derived from *N*-functionalization of the original, less substituted olefinic carbon, as observed experimentally. RE (internal NHOH-transfer) from the η3-methallyl complex **C** could also produce **E** or **E′**, depending on to which carbon (C5 vs C6) the −NHOH unit is delivered. We have not addressed this possibility in depth computationally but the calculated structure of **C** does show significant asymmetry of the Cu-allyl unit, Cu−C1 (2.15 Å) versus Cu−C3 (2.03 Å), C1−C2 (1.42 Å) versus C2−C3 (1.46 Å), and electrostatic charges, C1 (+0.18) versus C3 (−0.33), which suggests a predisposition to form the allyl hydroxylamine isomer that is observed experimentally.

Plausible Catalytic Mechanism. The above observations, together with the distinctive regioselectivity of the Cu-catalyzed reactions, lead us to suggest as a plausible reaction pathway

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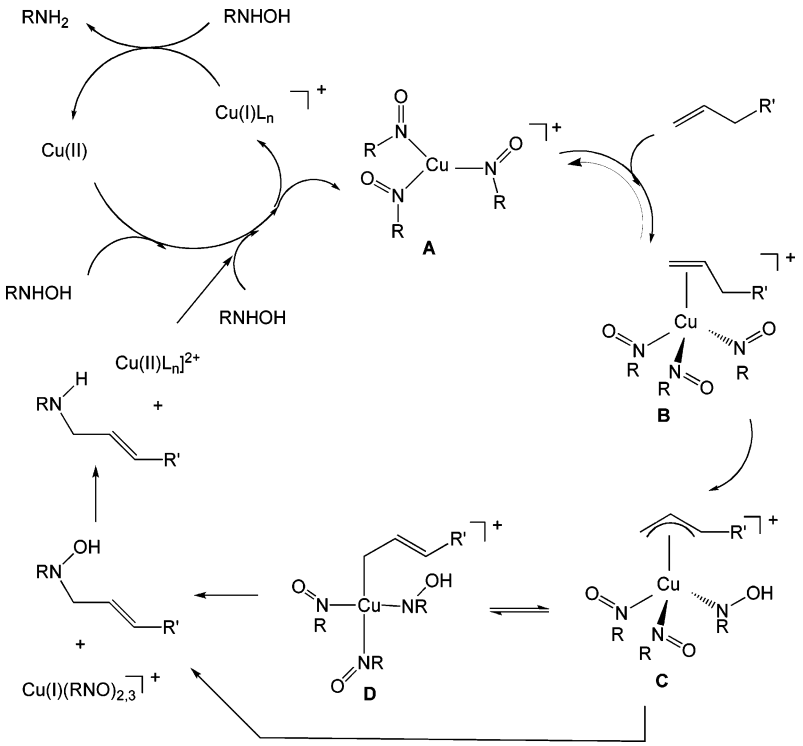
Scheme 8



the one shown in Scheme 8. Initially, some Cu(II) is likely generated by Cu(I) reduction of ArNHOH ($PhNH_2$ is detected); the available Cu(II) then oxidizes PhNHOH to PhNO with formation of the *C*-nitroso complex **A**. Alkene association with **A** produces the (η^2-alkene)$Cu(RNO)_3]^+$ species (**B**) which can be converted by allyl-H transfer and Cu-haptotropic shift, to an allyl-Cu complex, most likely the η^1-allyl species **D**. Reductive elimination from **D** could produce an allyl hydroxylamine derivative, either coordinated (as in **E**) or free. Reduction of the hydroxylamine by Cu(I) would give the allyl amine and regenerate Cu(II) for return into the catalytic cycle.

Conclusions

The Cu(I)-catalyzed amination of alkenes with aryl hydroxylamines constitutes a useful and regioselective method for the direct preparation of *N*-aryl-*N*-allylamines. We have established the first structurally verified copper complex of a C-nitroso compound. The involvement of **1** as the aminating agent in $[Cu(CH_3CN)_4]PF_6$-catalyzed allylic amination also has been implicated on the basis of kinetics and isolation reactions with alkenes. The mechanism of the copper-catalyzed allylic amination has been further elucidated with trapping experiments, isotope and substituent effects, and computational studies which point to the involvement of $[(allyl)Cu(RNO)_2(NHOH)]^+$ as important reaction intermediates. Efforts are underway to expand the synthetic scope and generality of this reaction and to develop enantioselective variants.

Acknowledgment. We thank Dr. Masood Khan (O.U. Analytical Services) for determination of the X-ray structure of **2** and Dr. R. D. Braun (UL-L, Chemistry Department) for ICP measurements. Financial support provided by the National Science Foundation (to K.M.N.) and the Research Corporation (Cottrell College Science Award, CC6234 to R.S.S.) is greatly appreciated.

Supporting Information Available: The DFT calculational output (Cartesian coordinates, calculated energies, and electrostatic charges for structures **A**−**E**). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0751072