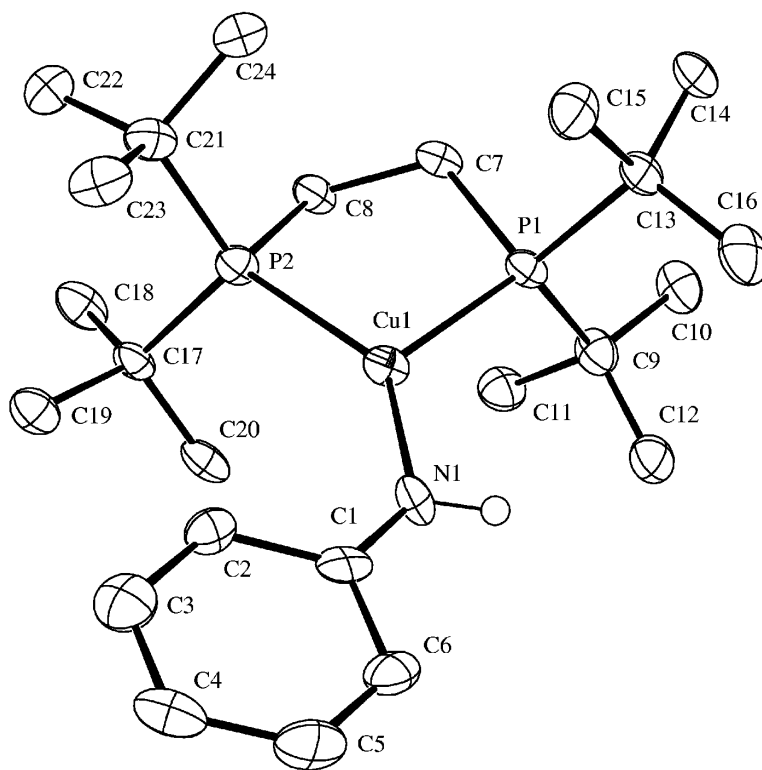


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Synthesis, Solid-State Crystal Structure, and Reactivity of a Monomeric Copper(I) Anilido Complex

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Abstract: Synthesis and isolation of the Cu(I) amido complex (dtbpe)Cu(NHPh) (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane) is accomplished upon reaction of [(dtbpe)Cu(μ -Cl)]₂ with LiNHPh. The anilido complex has been fully characterized by IR spectroscopy and multinuclear NMR spectroscopy as well as by single-crystal X-ray diffraction study. Salient features of the solid-state structure include an amido orientation that allows π -interaction of the nitrogen-based lone pair with both the empty copper p-orbital and the π^* -system of the phenyl substituent. A solid-state X-ray diffraction study of [(dtbpe)Cu(NH₂Ph)]-[BF₄] has allowed a direct comparison of the structural features upon conversion of the amine ligand to an amido. The reactivity of the amido ligand of (dtbpe)Cu(NHPh) is consistent with nucleophilic character. For example, the formation of Ph₃CNHPH is observed upon treatment with [Ph₃C][BF₄], and reaction at room temperature with EtX (X = Br or I) yields *N*-ethylaniline. The reactivity of (dtbpe)Cu(NHPh) is compared to that of the octahedral and d⁶ complex TpRu(PMe₃)₂(NHPh) (Tp = hydridotris(pyrazolyl)borate).

Introduction

Late transition metal complexes that possess nondative heteroatomic ligands (e.g., amido, oxide, imido, and oxo) exhibit diverse patterns of reactivity.^{1–3} For example, amide and oxide complexes have been implicated in a variety of metal-mediated transformations including hydroamination and C–N/C–O coupling reactions.^{4–7} The parent amido complexes *trans*-(DMPE)Ru(H)(NH₂) (DMPE = 1,2-bisdimethylphosphinoethane), TpRu(L)(L')(NH₂) (Tp = hydridotris(pyrazolyl)borate), and *cis*-(PMe₃)₄Ru(H)(NH₂) deprotonate weakly acidic C–H bonds, and *cis*-(PMe₃)₄Ru(H)(NH₂) undergoes an array of reactivity that demonstrates a highly nucleophilic amido ligand.^{8–13} The reactivity of other octahedral and d⁶ complexes that possess

amido ligands has been reported.^{2,8,10,11,14–22} Remarkably, the Os(IV) anilido complex TpOsCl₂(NHPh) is unreactive with HCl, and [TpOsCl₂(NH₂Ph)][OTf] is deprotonated by chloride anion.²³ In contrast to the even-electron reactions of the octahedral Ru(II) and Os(IV) amido systems discussed above, octahedral Fe(III) hydroxide and methoxide complexes undergo odd-electron hydrogen atom abstraction reactions with compounds that possess relatively weak C–H bonds.^{24,25} The disparate nature of these amido and oxide ligands reveals a significant scope of reactivity for nondative ligands bound to closely related group 8 octahedral metal centers.

Understanding the factors that control ligand-based reactivity of late transition metal amido and related complexes requires access to a variety of coordination environments including variable ligand sets, metal identities, and oxidation states. The

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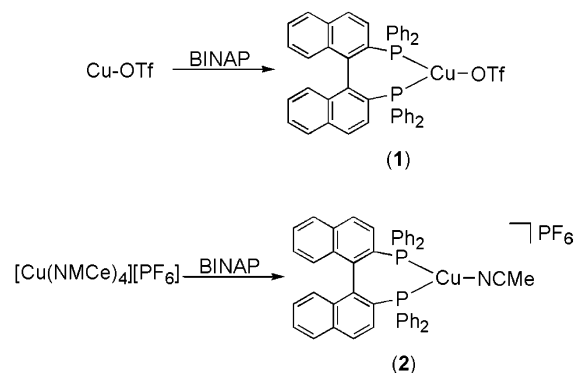
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chemistry of well-defined late transition metal amido complexes is primarily dominated by systems of the Fe, Co, and Ni triads.^{2,3,8,10–12,14–22,26–35} In contrast, the chemistry of copper complexes that possess nondative heteroatomic ligands is limited in scope. Copper complexes possessing aryloxo or bridging oxo ligands have been prepared and studied.^{36–43} Although an isolable copper nitrene complex has not been reported, copper nitrene systems have been implicated as intermediates in olefin aziridination reactions.^{44–50} The chemistry of copper amido complexes is limited to bridging amido ligands and amido moieties that are incorporated into chelating ligands as well as the reactivity of poorly defined copper amido complexes.^{51–57} Although the isolation and reactivity of well-defined monomeric copper amido complexes have not been described, recent reports of catalytic reactions that involve C–N bond forming steps underscore the potential importance of such substrates.^{58–64} We report herein the isolation and full characterization of a

Scheme 1. Preparation of (BINAP)Cu-OTf (**1**) and [(BINAP)Cu(NCMe)][PF₆] (**2**)



monomeric Cu(I) anilido complex as well as initial reactivity studies of this system.

Results and Discussion

Synthesis and Characterization of Cu(I) Anilino and Anilido Complexes. Our strategy to isolate a Cu(I) amido system was to incorporate a bis-chelating phosphine into the copper coordination sphere along with a ligand capable of facile displacement. Along these lines, (BINAP)Cu(OTf) (**1**) and [(BINAP)Cu(N≡CMe)][PF₆] (**2**) (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl); OTf = trifluoromethanesulfonate) can be prepared by reaction of Cu(I) triflate with BINAP or [Cu(NCMe)₄][PF₆] with BINAP, respectively (Scheme 1). Unfortunately, all efforts to convert the BINAP-copper complexes **1** or **2** to corresponding Cu(I) amido complexes failed. Reactions of **1** or **2** with (1) lithium or sodium amides, (2) amines followed by strong bases, or (3) mixtures of amines and lithium or sodium amide bases resulted in the formation of free BINAP.

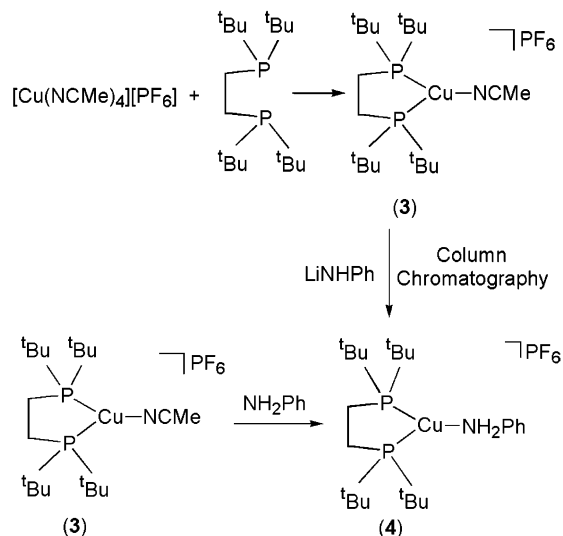
Assuming that reduction of Cu(I) was problematic, efforts to prepare systems with more reducing phosphine ligands were made. The combination of [Cu(NCMe)₄][PF₆] and the bisphosphine 1,2-bis(di-*tert*-butylphosphino)ethane (dtbpe) yields [(dtbpe)Cu(NCMe)][PF₆] (**3**) in 95% yield after workup (Scheme 2). Complex **3** is characterized by a singlet at 2.33 ppm in the ¹H NMR spectrum and resonances at 119.2 and 2.5 ppm in the ¹³C NMR spectrum due to the coordinated acetonitrile. In addition, IR spectroscopy reveals $\nu_{\text{CN}} = 2276 \text{ cm}^{-1}$, and the cyclic voltammogram of complex **3** exhibits a reversible oxidation at 1.3 V (vs NHE).

The reaction of complex **3** with LiNPh followed by chromatography on silica gel yields the Cu(I) amine complex [(dtbpe)Cu(NH₂Ph)][PF₆] (**4**) (Scheme 2). Complex **4** is characterized by a singlet at 29.8 ppm and a septet at -143.7 ppm (¹J_{PF} = 714 Hz) in the ³¹P NMR spectrum. A broad singlet at 5.46 ppm in the ¹H NMR is assigned as the resonance due to the amine protons. The IR spectrum of **4** exhibits two high-energy absorptions corresponding to symmetric and asymmetric ν_{NH} at 3345 and 3295 cm⁻¹. A chemically irreversible oxidation of the amine complex **4** is observed at 1.3 V (vs NHE). Attempts to deprotonate the amine complex **4** or to isolate the putative Cu(I) anilido complex from the reaction of **3** and LiNPh (prior to column chromatography) resulted in decomposition. The

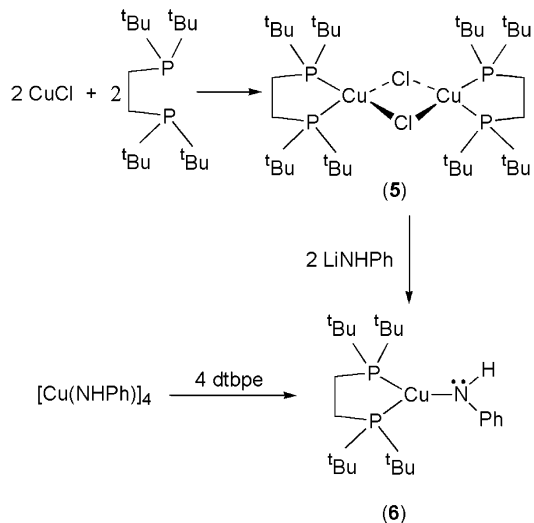
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Scheme 2. Preparation of [(dtbpe)Cu(NCMe)][PF₆] (**3**) and [(dtbpe)Cu(NH₂Ph)][PF₆] (**4**).



Scheme 3. Preparation of [(dtbpe)Cu(μ -Cl)]₂ (**5**) and (dtbpe)Cu(NHPh) (**6**).



amine complex **4** can also be made by reacting [(dtbpe)Cu(NCMe)][PF₆] (**3**) with aniline (Scheme 2).

Reaction of dtbpe and CuCl in methylene chloride yields [(dtbpe)Cu(μ -Cl)]₂ (**5**). In the solid state complex **5** is binuclear (see below). The cyclic voltammogram of complex **5** reveals two oxidations at $E_{1/2} = 0.55$ V (vs NHE, quasi-reversible if the return scan is made before the second oxidation) and $E_{p,a} = 0.88$ V. The reaction of the chloride complex **5** with LiNHPh yields the Cu(I) amido complex (dtbpe)Cu(NHPh) (**6**) as a pale yellow solid after workup (Scheme 3). Complex **6** can also be prepared by reaction of the previously reported [Cu(NHPh)]₄ with dtbpe (Scheme 3).⁵⁶ A solid-state X-ray diffraction study of the anilido complex **6** reveals a monomeric structure (see below). The amido proton resonates as a broad singlet at 4.70 ppm in the ¹H NMR spectrum (C₆D₆), and the ³¹P NMR spectrum displays a resonance at 30.2 ppm. The cyclic voltammogram of the amido complex **6** reveals a chemically irreversible oxidation at 0.10 V (vs NHE). Thus, the shift in oxidation potential upon deprotonation of the amine complex **4** is approximately 1.2 V (both oxidations are chemically irreversible). It is possible that the observed oxidation of

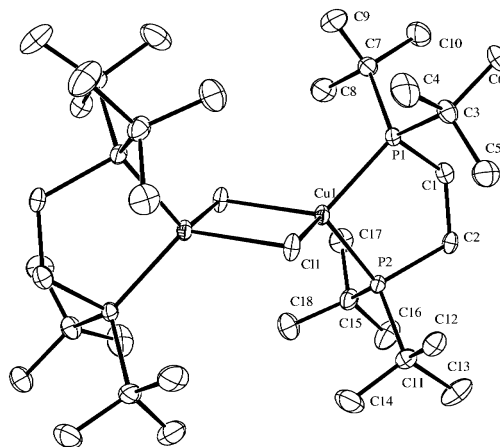


Figure 1. ORTEP diagram (50% probability) of [(dtbpe)Cu(μ -Cl)]₂ (**5**) (hydrogen atoms omitted for clarity).

(dtbpe)Cu(NHPh) (**6**) is a ligand-centered oxidation. In contrast, conversion of octahedral Ru(II) amine complexes to corresponding amido systems results in a change in oxidation potential of approximately 2.0 V.¹⁵ The two phosphine moieties are symmetry inequivalent if the amido C_{ipso}-N_{amido}-H plane is aligned approximately parallel with the P-Cu-P plane (this geometry is observed in the solid state, see below), and hindered Cu-N_{amido} rotation should be detected by variable-temperature ³¹P NMR spectroscopy. However, no evidence of decoalescence of the single phosphine resonance is observed down to -80 °C in toluene-*d*₈. Thus, either the ΔG^\ddagger for Cu-N_{amido} bond rotation is small or the amido ligand prefers an alignment in solution that is approximately perpendicular to the solid-state orientation (see below). Espinet et al. have attributed Pt-N bond rotational barriers primarily to steric effects for square-planar d⁸ arylamido complexes.²⁹ The Cu(I) amido complex **6** is highly air-sensitive and decomposes within minutes upon exposure to air in either the solid state or solution. Under a dinitrogen atmosphere, complex **6** is persistent in the solid state for at least 1 day at room temperature and several days at low temperature. In methylene chloride, **6** decomposes to uncharacterized products after approximately 2 h at room temperature.

Solid-State Structures. An X-ray diffraction study of [(dtbpe)Cu(μ -Cl)]₂ (**5**) revealed a binuclear species with bridging chloride ligands (Figure 1). Table 1 presents crystal data, and Table 2 displays selected bond distances and angles for complex **5**. The Cu-Cl (~2.38 Å) and Cu-P bond distances (~2.28 Å) are typical of related Cu(I) systems.⁶⁵⁻⁷⁰

A solid-state X-ray diffraction study of the Cu(I) amine complex [(dtbpe)Cu(NH₂Ph)][BF₄] reveals a three-coordinate monomeric cation with tetrafluoroborate anion (Figure 2). Selected crystal data and bond distances and angles are depicted in Tables 1 and 2, respectively. The coordination geometry is distorted trigonal planar around Cu with a small P(1)-Cu-

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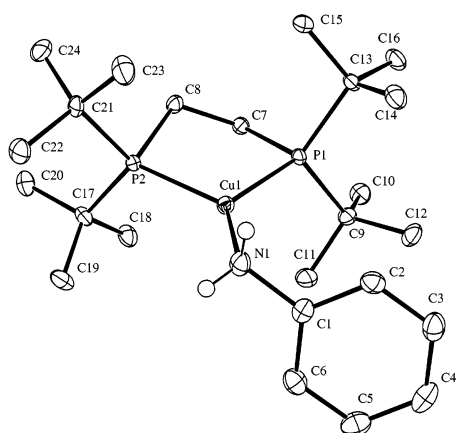
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Table 1. Selected Crystallographic Data for [(dtbpe)Cu(NH₂Ph)][BF₄] (**4**), [(dtbpe)Cu(μ -Cl)]₂ (**5**), and (dtbpe)Cu(NHPh) (**6**)

	4	5	6
formula	C ₂₄ H ₄₇ BCuF ₄ NP ₂	C ₁₈ H ₄₀ ClCuP ₂	C ₂₉ H ₅₆ CuNP ₂ O _{0.5}
mol wt	561.93	417.46	552.26
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	11.199(3)	11.3260(7)	19.486(4)
<i>b</i> , Å	16.080(3)	15.3216(9)	14.682(3)
<i>c</i> , Å	15.882(3)	13.7667(9)	21.649(8)
β , deg	97.36(3)	112.7524(18)	99.58(3)
<i>V</i> , Å ³	2836.5(11)	2203.1(2)	6107(3)
<i>Z</i>	4	4	8
<i>D</i> _{calcd} , g cm ⁻³	1.316	1.259	1.201
total no. of reflns	6765	15 186	10 641
no. of unique reflns	6765	5254	10641
<i>R</i>	0.041	0.051	0.067
<i>R</i> _w	0.042	0.060	0.068
temp (°C)	-100	-125	-125

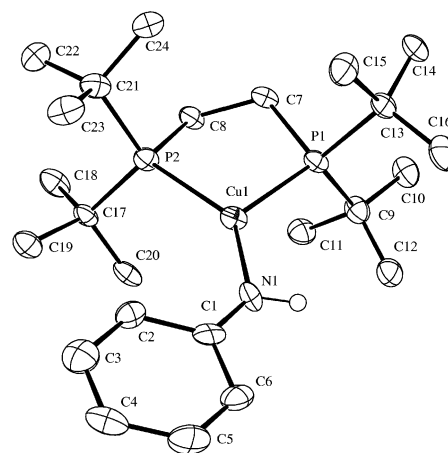
Table 2. Selected Bond Distances (Å) and Angles (deg) for [(dtbpe)Cu(NH₂Ph)][BF₄] (**4**), [(dtbpe)Cu(μ -Cl)]₂ (**5**), and (dtbpe)Cu(NHPh) (**6**)

	4	5	6
Bond Distances			
Cu1–Cl1		2.3844(9)	2.298(2)
Cu1–P1	2.2719(10)	2.2863(8)	2.298(2)
Cu1–P2	2.2637(9)	2.2832(9)	2.261(2)
Cu1–N1	2.010(2)		1.890(6)
N1–C1	1.444(4)		1.354(9)
C1–C2	1.390(4)		1.421(10)
C2–C3	1.385(4)		1.382(11)
C3–C4	1.378(5)		1.380(12)
C4–C5	1.383(5)		1.381(12)
C5–C6	1.386(4)		1.370(11)
C1–C6	1.385(4)		1.415(11)
Bond Angles			
Cl1–Cu–Cl1a		95.73(3)	
Cl1–Cu–P1		118.71(3)	
Cl1–Cu–P2		115.23(3)	
P1–Cu–P2	95.95(3)	94.40(3)	93.19(8)
Cu1–Cl1a–Cu1a		84.27(3)	
N1–Cu–P1	131.33(8)		125.63(16)
N1–Cu–P2	132.36(8)		141.00(16)
Cu–N1–C1	114.28(18)		134.5(5)

**Figure 2.** ORTEP diagram (50% probability) of [(dtbpe)Cu(NH₂Ph)][BF₄] (**4**) (counterion and most hydrogen atoms omitted for clarity).

P(2) bond angle of 95.95(3)°. The Cu(1)–N(1) bond distance is 2.010(2) Å, and the N(1)–C(1) bond distance {1.444(4) Å} is slightly longer than that of free aniline (1.398 Å).⁷¹

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**Figure 3.** ORTEP diagram (50% probability) of (dtbpe)Cu(NHPh) (**6**) (most hydrogen atoms omitted for clarity).

The amido complex **6** crystallizes as a monomeric complex from a solution of THF and cyclohexane. Crystal data and selected bond distances and angles are depicted in Tables 1 and 2, and the structure of complex **6** is displayed in Figure 3. Two independent molecules were observed; however, the structural details are similar (see Supporting Information). The Cu–N(1) bond distance of complex **6** (1.890(6) Å) is shorter than that of complex **4** by approximately 0.12 Å. The shorter Cu–N bond distance of **6** compared to **4** could be due to Coulombic interactions between the positively charged metal center and negatively charged amido ligand, amido to copper π -donation (see below), or a combination of these two effects. Parkins et al. have reported a binuclear Cu(II) complex that possesses *p*-tolylmethylamido ligands with Cu–N bond distances of 1.993(4) Å, while tetranuclear copper complexes with bridging amido groups display shorter Cu–N bond distances of approximately 1.88–1.99 Å.^{51,52,54,72} The P(2)–Cu(1)–N(1)–C(1) torsional angle of the amido complex **6** is approximately 13° (Figure 4). Thus, the amido ligand is oriented for π -donation (orientation for maximum orbital overlap would result in an approximate torsional angle of 0°) into the empty p-orbital of the Cu(I) system that is perpendicular to the P–Cu–P plane (Scheme 4). The amido orientation is approximately perpendicular to that observed by Hillhouse and Mindiola for Ni(I)

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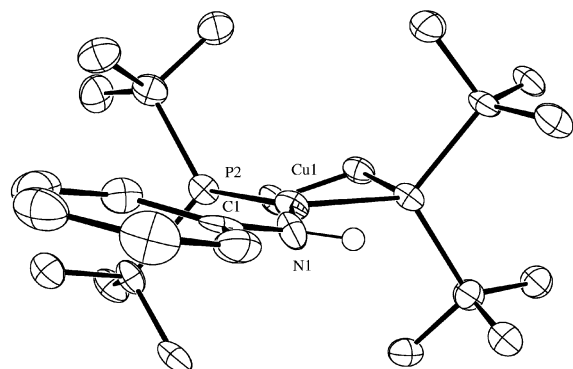
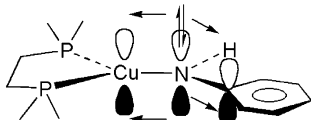
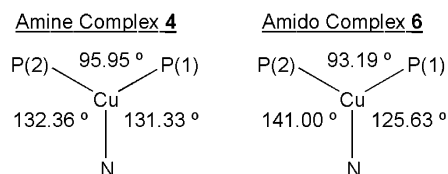


Figure 4. Structure of (dtbpe)Cu(NHPh) (**6**) showing amido orientation.

Scheme 4. Orientation of Amido Ligand Allows Interaction of Amido Lone Pair with Cu p-Orbital and Phenyl π^*



Scheme 5. Comparison of Bond Angles around Copper for Complexes **4** and **6**

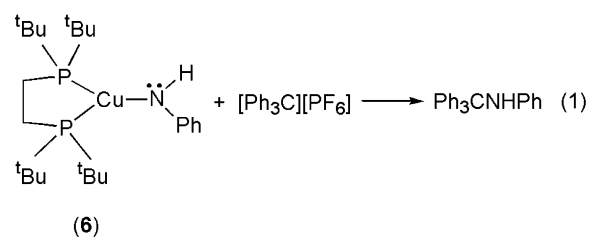


(dtbpe)Ni(NH(2,6-CHMe₂)₂C₆H₃).⁷³ The bond angles around the amido nitrogen sum to 359.1(9)°; however, the amido hydrogen was placed at an idealized position. Structural similarities between the amine complex **4** and the amido complex **6** include three-coordinate copper with one small and two large bond angles around the central copper atom (Scheme 5). However, the P(1)–Cu–N(1) and P(2)–Cu–N(1) bond angles for the amine complex **4** are nearly identical (the bond angle difference is approximately 1°), while the P(1)–Cu–N(1) bond angle of the amido complex **6** is approximately 15° smaller than the P(2)–Cu–N(1) bond angle. The amido ligand seemingly exhibits an electronic predilection toward an orientation that maximizes overlap of the amido lone pair with the empty Cu p-orbital as well as the π^* -system of the phenyl substituent. The amine complex lacks this electronic influence, and the plane of the phenyl ring for complex **4** is oriented approximately perpendicular to that of complex **6** (see Figures 2–4). The amido nitrogen to phenyl ipso carbon bond distance of complex **6** {1.354(9) Å} is shorter than a N–C single bond (~1.54 Å) and the corresponding bond of the amine complex **4** {1.444(4) Å}. To our knowledge, this is the first example of a structurally characterized monomeric copper complex that possesses a simple nonchelating amido ligand.

Reactivity of (dtbpe)Cu(NHPh) (6**).** Highly basic amido complexes coordinated to octahedral and d⁶ complexes have been reported.^{2,8,10,11,14–22} The reactivity of such complexes is likely derived from the combination of filled d π manifolds (i.e., amido to metal π -donation is disrupted) and highly ionic M–N

bonds.^{1,74–76} Even though Cu(I) is a high d-electron count metal center, the three-coordinate copper anilido complex **6** has a vacant p-orbital available for π -bonding with the amido ligand (Scheme 4), and the solid-state structure of **6** indicates that the orientation of the amido ligand is correct for π -overlap (see above). It might be anticipated that the empty metal p-orbital could serve to attenuate amido-based reactivity; however, the extent to which transition metal p-orbitals can engage in π -bonding with electron-donating ligands is unclear. In addition to the empty p-orbital, the higher electronegativity of copper compared with earlier transition metal centers could serve to mitigate amido-based reactivity due to increased covalency of the Cu–N bond. Thus, we sought to explore the reactivity of complex **6**.

The combination of (dtbpe)Cu(NHPh) (**6**) with [Ph₃C][PF₆] results in an immediate reaction at room temperature. Analysis by ¹H NMR spectroscopy indicates the formation of the free organic amine Ph₃CNHPh (eq 1).⁷⁷ No evidence of electron



transfer to form trityl radical or net hydride abstraction to yield triphenylmethane and a Cu nitrene complex is observed. The II/I potential of (dtbpe)Cu(NHPh) (**6**) ($E_{p,a} = 0.1$ V vs NHE) does not preclude single-electron transfer chemistry since trityl cation is reduced at approximately 0.44 V (vs NHE in methylene chloride).⁷⁸ Thus, the high nucleophilicity of the anilido ligand likely renders N–C bond formation kinetically competitive with single-electron oxidation. In contrast, upon combination with single-electron oxidants, octahedral ruthenium(II) anilido complexes of the type TpRu(L)(L')(NHPh) (L = L' = PMe₃ or P(OMe)₃ or L = CO and L' = PPh₃) undergo aryl–aryl coupling reactions.⁷⁹ The Ru(III/II) oxidation potentials of the TpRuL₂(NHPh) (L = P(OMe)₃ or PMe₃) complexes (–0.28 and –0.25 V; chemically reversible) indicate that single-electron oxidation is more facile than for (dtbpe)Cu(NHPh) ($E_{p,a} = 0.10$ V).¹⁵ Thus, the difference in reactivity between TpRuL₂(NHPh) and (dtbpe)Cu(NHPh) might be explained by the relative oxidation potentials. However, TpRu(CO)(PPh₃)(NHPh) undergoes analogous reactivity {i.e., similar to TpRuL₂(NHPh)}, and its Ru(III/II) potential ($E_{p,a} = 0.11$ V) is virtually identical to the copper amido complex (dtbpe)Cu(NHPh) (**6**).⁸⁰ Thus, redox potential does not explain the dissimilar reactivity of the TpRu anilido complexes and (dtbpe)Cu(NHPh).

The anilido complex (dtbpe)Cu(NHPh) (**6**) reacts with ethylbromide to yield *N*-ethylaniline and a copper product whose

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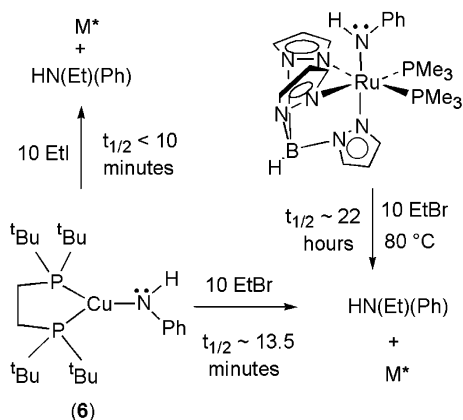
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Scheme 6. Reaction of Copper and Ruthenium Amido Complexes with EtBr or EtI Results in Nucleophilic Substitution^a

^a *Resonances consistent with the formation of [(dtbpe)Cu(μ -X)]₂ (X = Br or I) are observed for the reaction of **6** with EtBr and EtI.

NMR spectra are consistent with [(dtbpe)Cu(μ -Br)]₂ (Scheme 6). At room temperature, TpRu(PMe₃)₂(NHPh) does not react with ethylbromide after 24 h; however, at 80 °C a slow conversion ($t_{1/2} \approx 22$ h) to TpRu(PMe₃)₂(Br) and *N*-ethylaniline is observed (Scheme 6). This reaction is consistent with observations made for *cis*-(PMe₃)₄Ru(H)(NH₂).¹¹ The copper amido complex **6** also reacts with ethyl iodide to yield *N*-ethylaniline and a copper complex whose spectroscopic features are consistent with [(dtbpe)Cu(μ -I)]₂. Monitoring the reactions of the Ru and Cu anilido complexes with 10 equiv of EtX (X = Br or I) reveals substantial differences. For example, the conversion of **6** and EtI is complete within 10 min at room temperature, while the reaction between **6** and approximately 10 equiv of EtBr occurs with a $t_{1/2}$ of approximately 13.5 min at room temperature ($k_{\text{obs}} = 8.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$; Scheme 6). These results are consistent with a simple nucleophilic S_N2 type reaction. The reaction of TpRu(PMe₃)₂(NHPh) with EtBr is slower than the reaction of the copper anilido complex **6**. The half-life for the reaction of the ruthenium complex is approximately 22 h at 80 °C ($k_{\text{obs}} = 8.6 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$; Scheme 6).

Summary and Conclusions

The synthesis, isolation, and full characterization of a monomeric Cu(I) anilido system has been accessed using a bulky bisphosphine ligand to stabilize the amido complex. Even though the *tert*-butyl groups of the bisphosphine ligand result in a sterically crowded coordination sphere, the amido ligand of (dtbpe)Cu(NHPh) has been demonstrated to undergo nucleophilic reactivity, and reactions with ethylbromide suggest that complex **6** is *more reactive* than a corresponding octahedral and d⁶ ruthenium anilido system. These results suggest that while the anilido ligand of **6** may interact with the empty metal p-orbital, its reactivity is not significantly attenuated. In addition, the increased electronegativity of Cu(I) versus Ru(II) does not seemingly decrease amido-based nucleophilicity.

Experimental Section

General Methods. All reactions and procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and monitored by an oxygen analyzer {O₂(g) < 15 ppm for all reactions}. Hexanes and methylene chloride were

purified by passage through a column of activated alumina. THF and benzene were dried by distillation over sodium/benzophenone. Acetonitrile was distilled over calcium hydride. Benzene-*d*₆ was purified by distillation from CaH₂, degassed, and stored over 4 Å sieves. CDCl₃ and CD₂Cl₂ were degassed via three freeze-pump-thaw cycles and stored over 4 Å sieves. ¹H and ¹³C NMR spectra were obtained on a Varian Mercury 300 or 400 MHz. All ¹H and ¹³C NMR spectra were referenced against tetramethylsilane using residual proton signals (¹H NMR) or the ¹³C resonances of the deuterated solvent (¹³C NMR). ³¹P NMR spectra were obtained on a Varian 300 or 400 MHz spectrometer and referenced against external 85% H₃PO₄. Variable-temperature NMR experiments were performed on a Varian Mercury 300 MHz spectrometer. IR spectra were obtained on a Mattson Genesis II spectrometer either as thin films on a KBr plate or in solution using a KBr solution cell. Electrochemical experiments were performed under a nitrogen atmosphere using a BAS Epsilon Potentiostat. Cyclic voltammograms were recorded in a standard three-electrode cell from -2.00 V to +2.00 V with a glassy carbon working electrode and tetrabutylammonium hexafluorophosphate as electrolyte. Tetrabutylammonium hexafluorophosphate was dried under dynamic vacuum at 140 °C for 48 h prior to use. All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate as an internal standard. Elemental analyses were performed by Atlantic Microlabs, Inc. LiNHPh was generated by reaction of aniline with 1 equiv of *n*-BuLi in benzene followed by vacuum filtration to collect the resulting white precipitate. Tetrakis(acetonitrile)copper(I) hexafluorophosphate, TpRu(PMe₃)₂(NHPh), and bis(*di-tert*-butyl)phosphinoethane (dtbpe) were prepared according to reported procedures.^{15,81,82} [Cu(NHPh)]₄ was prepared according to a previously reported procedure.⁵⁶ All other reagents were used as purchased from commercial sources.

(BINAP)CuOTf (1). BINAP (0.775 g, 1.25 mmol) was dissolved in 5 mL of CH₃CN and was slowly added to a solution of CuOTf-benzene (0.402 g, 1.24 mmol) in 30 mL of CH₂Cl₂. The resulting solution was stirred for 3 h at room temperature, and the solvent was removed in vacuo. A yellow solid was recrystallized from CH₂Cl₂ and hexanes (0.863 g, 83% yield). ¹H NMR (CD₂Cl₂, δ): 7.84 (4H, m), 7.61 (4H, m), 7.50 (6H, m), 7.34 (2H, t, $J = 7$ Hz), 7.27 (2H, m), 7.10 (6H, m), 6.79 (2H, t, $J = 7$ Hz), 6.74 (2H, d, $J = 9$ Hz), 6.64 (4H, t, $J = 7$ Hz). ¹³C{¹H} NMR (CD₂Cl₂, δ): 135.3 (t, $J = 9$ Hz), 133.7 (m), 131.5 (t, $J = 10$ Hz), 128.6 (s), 128.1 (m), 127.8 (d, $J = 25$ Hz), 127.1 (s). ³¹P{¹H} NMR (CD₂Cl₂, δ): -0.8 (s, BINAP). Anal. Calc for C₄₄H₃₂CuF₃O₃P₂S₁: C, 64.71; H, 3.86; N, 5.75. Found: C, 64.78; H, 3.90; N, 5.66.

[(BINAP)Cu(NCMe)]PF₆ (2). A solution of [Cu(NCMe)₄][PF₆]₂ (0.195 g, 0.52 mmol) in 5 mL of THF was added to a THF solution of 35 mL with BINAP {(±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene} (0.327 g, 0.53 mmol). The solution was allowed to stir for 3 h, and the solvent was reduced in vacuo to 15 mL. Approximately 20 mL of hexanes was added to precipitate a white solid. The resulting solid was collected by vacuum filtration and dried under reduced pressure (0.417 g, 91% yield). ¹H NMR (CD₂Cl₂, δ): 7.80 (4H, m), 7.60 (10H, m), 7.35 (2H, t, $J = 7$ Hz), 7.17 (2H, m), 7.05 (6H, m), 6.78 (2H, t, $J = 7$ Hz), 6.72 (2H, d, $J = 8$ Hz), 6.60 (4H, t, $J = 7.2$ Hz), 2.47 (3H, s, CH₃CN). ¹³C{¹H} NMR (CD₂Cl₂, δ): 139.7 (bs, CH₃CN), 135.3 (t, $J_{\text{PC}} = 9$ Hz), 133.9 (s), 133.6 (t, $J = 9$ Hz), 132.1 (s), 130.5 (s), 130.2 (t, $J = 5$ Hz), 129.8 (s), 128.6 (s), 128.2 (t, $J = 6$ Hz), 127.7 (s), 127.5 (s), 127.3 (s), 3.6 (s, CH₃CN). ³¹P{¹H} NMR (CD₂Cl₂, δ): 2.5 (s, BINAP), -144.2 (septet, $^1J_{\text{PF}} = 710$ Hz, PF₆). Anal. Calc for C₄₆H₃₅CuF₆N₁P₃: C, 63.34; H, 4.04; N, 1.61. Found: C, 63.20; H, 4.11; N, 1.70.

[(dtbpe)Cu(NCMe)]PF₆ (3). The bisphosphine dtbpe (0.213 g, 0.67 mmol) was dissolved in approximately 50 mL of CH₂Cl₂, and [Cu(NCMe)₄][PF₆]₂ (0.249 g, 0.67 mmol) was added to the solution.

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The solution was stirred at room temperature for 2 h, and the solvent was removed in vacuo. A light yellow solid was isolated (0.362 g, 95% yield). Complex **3** can be further purified by dissolution in methylene chloride followed by precipitation with hexanes. ^1H NMR (CDCl_3 , δ): 2.33 (3H, s, NCCH_3), 1.88 (4H, s, methylene), 1.27 (36H, vt, $N = 14$ Hz, *t*-Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 119.2 (s, NCMe), 33.8 (vt, $N = 15$ Hz, quat *t*-Bu), 29.7 (s, methyl), 20.7 (vt, $N = 25$ Hz, methylene), 2.5 (s, NCCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 31.8 (bs, dtbpe), -143.7 (septet, $^1J_{\text{PF}} = 710$ Hz, PF_6). IR (CCL_4): $\nu_{\text{CN}} = 2276$ cm^{-1} . CV (CH_2Cl_2 , TBAH, 100 mV/s): $E_{1/2} = 1.28$ V (II/I). Anal. Calc for $\text{C}_{20}\text{H}_{43}\text{Cu}_1\text{F}_6\text{N}_1\text{P}_3$: C, 42.29; H, 7.63; N, 2.47. Found: C, 42.06; H, 7.64; N, 2.23.

[(dtbpe)Cu(NH₂Ph)][PF₆] (4). Method A. To a stirred THF solution (50 mL) of [(dtbpe)CuNCMe][PF₆] (0.6265 g, 1.1 mmol) was added LiNHPPh (0.1085 g, 1.1 mmol). The resulting solution was stirred for 2 h at room temperature; then the solvent was removed in vacuo. The nonvolatiles were dissolved in approximately 10 mL of CH_3CN and applied to a silica column, which was eluted with approximately 50 mL of CH_3CN . The solvent was removed in vacuo, and the resulting white powder was dissolved in CH_2Cl_2 . The product was precipitated upon addition of hexanes and filtered to isolate a white powder (0.3824 g, 78% yield). Prior to the solid-state X-ray diffraction study, a counterion metathesis reaction to yield [(dtbpe)Cu(NH₂Ph)][BF₄] was performed. Crystals suitable for a solid-state X-ray diffraction study were grown at room temperature by layering a THF solution of **4** with cyclohexane. ^1H NMR (CDCl_3 , δ): 7.28 (2H, t, $^3J_{\text{HH}} = 7$ Hz, *m*-phenyl), 7.14 (2H, d, $^3J_{\text{HH}} = 7$ Hz, *o*-phenyl), 7.05 (1H, t, $^3J_{\text{HH}} = 7$ Hz, *p*-phenyl), 5.46 (2H, bs, NH_2), 1.88 (4H, s, methylene), 1.17 (36H, vt, $N = 14$, *tert*-butyl). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 142.5 (bs, ipso-Ph), 129.8, 123.6 and 119.2 (all s, phenyl *o*, *m*, and *p*), 33.9 (vt, $N = 12$ Hz, quat *t*-Bu), 30.4 (vt, $N = 8$ Hz, methyl), 20.9 (vt, $N = 25$ Hz, methylene). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 29.8 (s, dtbpe), -143.7 (septet, $^1J_{\text{PF}} = 714$ Hz, PF_6). IR (CH_2Cl_2): $\nu_{\text{NH}} = 3345, 3295$ cm^{-1} . CV (CH_2Cl_2 , TBAH, 100 mV/s): $E_{\text{p,a}} = 1.31$ V (II/I). Anal. Calc for $\text{C}_{24}\text{H}_{47}\text{Cu}_1\text{F}_6\text{N}_1\text{P}_3$: C, 46.48; H, 7.64; N, 2.26. Found: C, 46.23; H, 7.50; N, 2.59.

Method B. To a stirred THF solution (30 mL) of [(dtbpe)Cu(NCMe)]-[PF₆] (**3**) (0.2367 g, 0.42 mmol) was added aniline (38 μL , 0.42 mmol). The resulting solution was stirred for 1 h at room temperature, and the solvent was removed in vacuo. The resulting pale yellow solid (0.228 g, 97% yield) was vacuum-dried overnight. ^1H NMR spectroscopy revealed clean formation of complex **4**.

[(dtbpe)Cu(μ -Cl)]₂ (5). The white solid dtbpe (bis(*di-tert*-butyl)-phosphino ethane; 0.5455 g, 1.71 mmol) was dissolved in approximately 30 mL of methylene chloride. CuCl (0.1672 g, 1.69 mmol) was added to the dtbpe solution and allowed to stir until all of the CuCl dissolved (approximately 2 h). The solvent was then removed under reduced pressure, and the resulting white solid product was isolated (0.6342 g, 90% yield). Complex **5** can be further purified by dissolution in methylene chloride followed by precipitation with hexanes. Crystals suitable for a solid-state X-ray diffraction study were grown at room temperature by layering a methylene chloride solution of **5** with cyclohexane. ^1H NMR (CD_2Cl_2 , δ): 1.86 (4H, br s, methylene), 1.25 (36H, vt, $N = 13$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 33.9 (vt, $N = 9$ Hz, quat *t*-Bu), 30.4 (vt, $N = 9$ Hz, methyl), 20.8 (vt, $N = 25$ Hz, methylene). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , δ): 25.6 (s). CV (CH_2Cl_2 , TBAH, 100 mV/s): $E_{1/2} = 0.55$ V (II/I, quasi-reversible), $E_{\text{p,a}} = 0.88$ V (II/I). Anal. Calc for $\text{C}_{36}\text{H}_{80}\text{Cl}_2\text{Cu}_2\text{P}_4$: C, 51.79; H, 9.66. Found: C, 51.64; H, 9.74.

(dtbpe)Cu(NHPh) (6). Method A. The white powder [(dtbpe)Cu(μ -Cl)]₂ was weighed out (0.257 g, 0.62 mmol) and dissolved in approximately 40 mL of benzene. LiNHPPh (0.063 g, 0.64 mmol) was

added to the solution and allowed to stir for 1 h. The pale yellow solution was filtered through a fine-porosity frit to remove the LiCl. The filtrate was dried in vacuo, and the product was isolated as a yellow powder (0.2176 g, 75% yield). Crystals suitable for a solid-state X-ray diffraction study were grown at room temperature by layering a THF solution of **6** with cyclohexane. ^1H NMR (C_6D_6 , δ): 7.34 (2H, t, $^3J_{\text{HH}} = 7$ Hz, *m*-Ph), 7.23 (2H, d, $^3J_{\text{HH}} = 7$ Hz, *o*-Ph), 6.67 (1H, t, $^3J_{\text{HH}} = 7$ Hz, *p*-Ph), 4.70 (1H, bs, NH), 1.37 (4H, bs, methylene), 1.06 (36H, vt, $N = 12$ Hz, *t*-Bu). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , δ): 162.3 (bs, ipso Ph), 129.6, 117.0, and 110.9 (all s, phenyl *o*, *m*, and *p*), 33.6 (br s, quat *t*-Bu), 30.5 (vt, $N = 10$ Hz, methyl), 21.3 (vt, $N = 24$ Hz, methylene). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , δ): 30.2 (s). IR (C_6H_6): $\nu_{\text{NH}} = 3332$ cm^{-1} . CV (THF, TBAH, 100 mV/s): $E_{\text{p,a}} = 0.10$ V (II/I). Satisfactory elemental analysis was not obtained due to the air-sensitive nature of the material.

Method B. The copper complex [Cu(NHPh)]₄ (0.056 g, 0.36 mmol) was added to a benzene (30 mL) solution of dtbpe (0.114 g, 0.358 mmol). The solution immediately turned yellow and was allowed to stir at room temperature for 20 min. The volatiles were removed under reduced pressure to yield a yellow powder (0.167 g, 98% yield). ^1H and ^{31}P NMR spectra of the isolated yellow solid are consistent with the quantitative formation of (dtbpe)Cu(NHPh) (**6**).

Reactions with Ethylbromide or Ethyliodide. The general procedures for all reactions with ethylbromide or ethyliodide were similar. A representative procedure is provided: In a screw cap NMR tube, TpRu(PMe₃)₂(NHPh) (0.0140 g, 0.0251 mmol) was dissolved in 0.82 g of C_6D_6 . A small amount of Cp_2Fe was added as an internal standard. Bromoethane (18.0 μL , 0.243 mmol) was added using a microsyringe. The resulting solution was heated to 80 °C and monitored at regular time intervals by ^1H NMR. The formation of *N*-ethylaniline was confirmed by addition of pure *N*-ethylaniline to the final reaction products. In addition, analysis using gas chromatography confirmed the formation of *N*-ethylaniline. The formation of TpRu(PMe₃)₂(Br) was based upon the close relationship of the final TpRu complex to TpRu(PMe₃)₂(Cl). The formation of [(dtbpe)Cu(μ -X)]₂ (X = I or Br) complexes was ascertained by similarities of the ^1H NMR spectra to that of [(dtbpe)Cu(μ -Cl)]₂; however, these complexes have not been isolated.

Solid-State X-ray Diffraction Studies of [(dtbpe)Cu(μ -Cl)]₂ (5), [(dtbpe)Cu(NH₂Ph)][BF₄] (4), and (dtbpe)Cu(NHPh) (6). For details of X-ray data collection and analysis see Supporting Information.

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Supporting Information Available: Complete tables of crystal data, collection and refinement data, atomic coordinates, bond distances and angles, and anisotropic displacement coefficients for [(dtbpe)Cu(NH₂Ph)][BF₄] (**4**), [(dtbpe)Cu(μ -Cl)]₂ (**5**), and (dtbpe)Cu(NHPh) (**6**). Kinetic plots for the reactions of (dtbpe)Cu(NHPh) (**6**) or TpRu(PMe₃)₂(NHPh) with EtBr. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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