DOI: 10.1021/om100733n

ORGANOMETALLICS
Article

A Versatile Cuprous Synthon: [Cu(IPr)(OH)] (IPr = 1,3 bis(diisopropylphenyl)imidazol-2-ylidene)

George C. Fortman, Alexandra M. Z. Slawin, and Steven P. Nolan*

EastCHEM School of Chemisty, University of St Andrews, St Andrews, KY16 9ST, U.K.

Received July 26, 2010

The novel *1,3*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (hydroxy) copper ([Cu(IPr)(OH)]) exhibits a versatile capacity to activate numerous X−H bonds including all major hybridizations of C−H (i.e., sp, sp^2, sp^3), N−H, P−H, O−H, S−H, and one example of M−H (M = Mo) bonds. This reactivity also includes the cleavage of the Si−N and Si−C bonds to form unprecedented Cu-centered complexes.

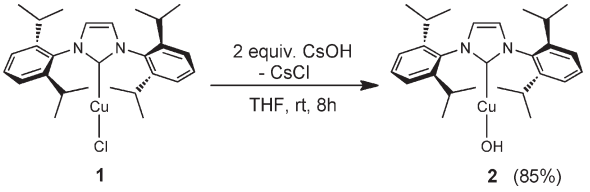
Introduction

The ever-increasing number of applications involving organocopper complexes in organic synthesis has led to the discovery of a plethora of innovative transformations.[1] In the past decade, this has been particularly true of dicoordinate $14e^-$ [Cu(NHC)X] complexes (NHC = N-heterocyclic carbenes). The use of Cu-NHC with alkoxide ligands has greatly enhanced the potential reaches of this chemistry. A most interesting accomplishment was reported by Sadighi, who, by using [Cu(NHC)(O^{t}Bu)], generated [Cu(NHC)(Bpin)] (pin = pinacolato) *in situ*. This complex was identified as an active catalyst for the reduction of CO_2 to CO.[2] Additionally, [Cu(NHC)(alkoxide)] have previously been shown to catalytically enable the formation of boryl aldehydes[3] and carboxylate boronic esters[4] and aid in the synthesis of novel complexes.[5] Gunnoe et al. employed [Cu(IPr)Me] to activate a limited number of X−H bonds (X = N, O, and C).[6] [Cu(SIPr)(CF_3)] has proven an efficient trifluoromethylating agent, while [Cu(IPr)F], in reactions with Ar−Si(OR)$_3$ (R = CH_3 and CH_2CH_3), has permitted the isolation of several Cu(I)-Ar derivatives.[5a] With these diverse reactivities and potential for more, we reasoned that the design and synthesis of a versatile, stable Cu(I) synthon would be highly desirable.

Although, a number of copper-hydroxide complexes have been reported, these have been bimetallic or Cu(II) derivatives.[7] To our knowledge, no example of 14-electron dicoordinate [Cu(L)OH] (L = two-electron donor) complex has been reported to date.[8] Our working hypothesis hoped for a versatile reactivity of a Cu-OH moiety associated with the stabilizing properties of an NHC ancillary ligand. Prospective applications included, at the early stage, the use of such a species as a synthon and as a probe for mechanistic studies. Herein, we disclose the optimized synthesis of such a versatile copper(I) synthon and its use as a key entryway into a myriad of novel organocopper complexes.

Results and Discussion

The reaction of [Cu(IPr)Cl] (**1**) with 2 equiv of anhydrous CsOH in THF led to the formation of [Cu(IPr)(OH] (**2**) in very good yield (eq 1).[9]



1 **2** (85%) (1)

Formation of **2** was somewhat difficult to detect by ^{1}H NMR due to the strikingly similar NMR spectra. For example, the carbene backbone protons of the hydroxide are shifted upfield by only 0.02 ppm in CD_2Cl_2 with respect to **1** (CH-imide **1** δ 7.17 ppm; **2** δ 7.19 ppm in CD_2Cl_2). To unequivocally determine the atom connectivity in **2**, single crystals suitable for X-ray diffraction (XRD) were grown by slow diffusion of pentane into a THF-saturated

*To whom correspondence should be addressed. E-mail: snolan@st-andrews.ac.uk.

(1) (a) Alexakis, A.; Bäckvall, J. E.; Krause, N.; Pámies, O.; Diéguez, M. *Chem. Rev.* **2008**, *108*, 2796. (b) Breit, B.; Schmidt, Y. *Chem. Rev.* **2008**, *108*, 2928. (c) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074. (d) Deutsch, C.; Krause, N.; Lipshutz, B. H. *Chem. Rev.* **2008**, *108*, 2916. (e) Díaz-Requejo, M. M.; Pérez, P. J. *Chem. Rev.* **2008**, *108*, 3379. (f) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054. (g) Gschwind, R. M. *Chem. Rev.* **2008**, *108*, 3029. (h) Harutyunyan, S. R.; den Hartog, T.; Geurts, K.; Minnaard, A. J.; Feringa, B. L. *Chem. Rev.* **2008**, *108*, 2824. (i) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561. (j) Matsuo, Y.; Nakamura, E. *Chem. Rev.* **2008**, *108*, 3016. (k) Meldal, M.; Tornøe, C. W. *Chem. Rev.* **2008**, *108*, 2952. (l) Monnier, F.; Taillefer, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 6954. (m) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395. (n) Poulsen, T. B.; Jørgensen, K. A. *Chem. Rev.* **2008**, *108*, 2903. (o) Shibasaki, M.; Kanai, M. *Chem. Rev.* **2008**, *108*, 2853. (p) Stanley, L. M.; Sibi, M. P. *Chem. Rev.* **2008**, *108*, 2887. (q) Struthers, H.; Mindt, T. L.; Schibli, R. *Dalton Trans.* **2010**, *39*, 675. (r) Yamada, K.-i.; Tomioka, K. *Chem. Rev.* **2008**, *108*, 2874.

(2) Laitar, D. S.; Müller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 17196.

(3) Bonet, A.; Lillo, V.; Ramírez, J.; Díaz-Requejo, M. M.; Fernández, E. *Org. Biomol. Chem.* **2009**, *7*, 1533.

(4) Ohishi, T.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 5792.

(5) (a) Herron, J. R.; Ball, Z. T. *J. Am. Chem. Soc.* **2008**, *130*, 16486. (b) Díez-González, S.; Stevens, E. D.; Scott, N. M.; Petersen, J. L.; Nolan, S. P. *Chem.—Eur. J.* **2008**, *14*, 158. (c) Bhattacharyya, K. X.; Akana, J. A.; Laitar, D. S.; Berlin, J. M.; Sadighi, J. P. *Organometallics* **2008**, *27*, 2682.

(6) Goj, L. A.; Blue, E. D.; Munro-Leighton, C.; Gunnoe, T. B.; Petersen, J. L. *Inorg. Chem.* **2005**, *44*, 8647.

 Published on Web 08/10/2010

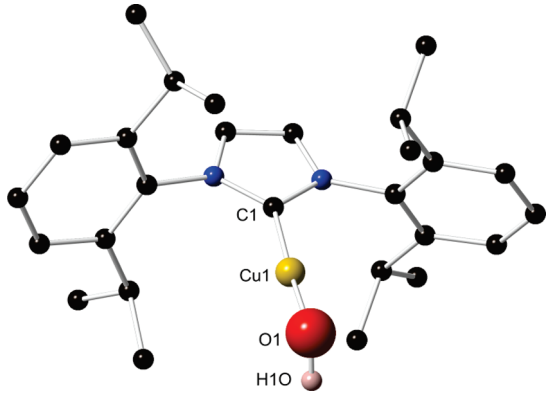


Figure 1. Molecular representation of [Cu(IPr)OH] (**2**). All hydrogens are omitted with the exception of H10. Cu1−O1 1.804(2) Å, Cu1−C1 1.867(3) Å, O1−Cu1−C1 177.13(11)°.

solution of **2**. Figure 1 shows a molecular representation of [Cu(IPr)(OH)].

Noteworthy, among metrical parameters, is the shorter Cu1−O1 bond (1.804(2) Å) observed in **2** compared to most Cu(II) complexes with Cu−O bond lengths of >1.9 Å.[7c−h] Presumably, the shorter bond length is not due to the difference in charge but to the fact that the central copper atom in **2** is only two-coordinate. When compared to [Au(IPr)(OH)],[10] **2** possesses a much shorter M−O bond length (Au−O = 2.078(6) Å; Cu−O 1.804(2) Å).

The reactivity of **2** toward H−X activation was examined next and expected to be very similar to that of the gold derivative [Au(IPr)(OH)].[10,11] For the gold congener, synthetic feasibility of complexes was rationalized by simple Brønsted−Lowry acid/base theory.[12] Investigations into C−H activation were guided by the pK_a hypothesis. Gratifyingly, activations of sp^3, sp^2, and sp C−H bonds were all successfully achieved. The reaction of **2** with nitromethane resulted in the production of [Cu(IPr)(CH_2NO_2)] (**3**). The reaction occurred upon addition of nitromethane to a solution of **2** in toluene at room temperature. This represents a formal C−H bond activation reaction. Moreover, the reaction of **2** with dimethylmalonate in toluene proceeded instantaneously to form [Cu(IPr)($CH(COOMe)_2$)] (**4**). The presence of an acidic C−H is suspected to favor the Cu−C bond forming reaction. [Cu(NHC)(alkyl)] complexes are relatively rare; for example the route to [Cu(IPr)(CH_3)] involved treatment of [Cu(IPr)(OAc)] with dimethylaluminum ethoxide generated *in situ*.[13] [Cu(IPr)(Et)] was prepared by a similar method.[6] Use of [Cu(IPr)(OH)] as a synthon enables efficient and clean Cu−alkyl bond formation at room temperature without the necessity of additional reagents. The C−H bond is required to be acidic, and at this stage we estimate the C−H pK_a requirement to be on the order of 27−30 pK_a units. To support the hypothesis of reactions proceeding predominately *via* a protonolysis mechanism, NMR experiments were carried out in which a radical trap was present. Reactions of **2** with CH_3NO_3 in C_6D_6 in the presence of 2 equiv of TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) proceeded cleanly to produce **3**. The absence of side products formed with TEMPO present is in line with a mechanism involving proton and not radical transfer.

Activation of the CH_2 moiety of cyclopentadiene (CpH) resulted in the formation of the half-sandwich complex [Cu(IPr)(η^5-Cp)] (**5**). π-Coordination of the Cp unit was confirmed by both ^{1}H and ^{13}C NMR spectroscopy. Wang et al. reported the synthesis of a series of [Cu(NHC)(η^5-Cp)] complexes using LiCp and [Cu(NHC)Cl].[14] The reaction was reported to require several hours, whereas the reaction of **1** with C_5H_6 was observed to reach completion within minutes.

Activation of an aromatic sp^2 C−H bond was exemplified with 1,2,4,5-tetrafluorobenzene. The reaction was observed to reach completion within minutes. Ball et al. have synthesized several Cu−aryl compounds but were required to resort to transmetalation with organosilanes.[5a] The workups in these reactions are further complicated by the presence of silanol byproduct and led to difficult isolation of the target compounds. Formation of Cu−aryl bonds *without* the use of silanes is therefore desirable and demonstrated here to generate the targeted product and water as sole byproduct.

As compared to gold, very few studies have focused on (NHC)Cu-acetylide complexes.[6,7h,15] Reaction of **2** with 1,3,5-triethynylbenzene in toluene proved to easily produce the trisubstituted 1,3,5-(IPrCu-C≡C)C_6H_3 (**7**). The reaction was observed to reach completion in as little as 14 h, while the synthesis of [Cu(IPr)(C≡CPh)] from phenylacetylene and [Cu(IPr)Me] reportedly requires 22 h.[6] Two discrete principles were confirmed by the synthesis of complex **7**. First, addition of the (IPr)Cu moiety to acetylene derivatives in a sterically demanding environment was achieved. This could in principle be extended to the modification of polymers (or other large repetitive structures) with (NHC)Cu moieties. Second, the compound was observed to be luminescent when placed under UV radiation. While the photoluminescent properties of gold acetylide complexes have been extensively studied,[11,16] few data have been reported for NHC copper complexes.[17]

(7) (a) Liu, B.; Liu, B.; Zhou, Y.; Chen, W. *Organometallics* **2010**, *29*, 1457. (b) Yamaguchi, K.; Oishi, T.; Katayama, T.; Mizuno, N. *Chem.—Eur. J.* **2009**, *15*, 10464. (c) Shahid, M.; Mazhar, M.; Brien, P. O.; Malik, M. A.; Raftery, J. *Polyhedron* **2009**, *28*, 807. (d) Balboa, S.; Carballo, R.; Castiñeiras, A.; González-Pérez, J. M.; Niclós-Gutiérrez, J. *Polyhedron* **2008**, *27*, 2921. (e) Padhi, S. K.; Manivannan, V. *Inorg. Chem.* **2006**, *45*, 7994. (f) Price, J. R.; Fainerman-Melnikova, M.; Fenton, R. R.; Gloe, K.; Lindoy, L. F.; Rambusch, T.; Skelton, B. W.; Turner, P.; White, A. H.; Wichmann, K. *Dalton Trans.* **2004**, 3715. (g) Tubbs, K. J.; Fuller, A. L.; Bennett, B.; Arif, A. M.; Berreau, L. M. *Inorg. Chem.* **2003**, *42*, 4790. (h) Fujisawa, K.; Kobayashi, T.; Fujita, K.; Kitajima, N.; Moro-oka, Y.; Miyashita, Y.; Yamada, Y.; Okamoto, K.-i. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1797.

(8) Complex **2** was recently shown to be active in C−H bond functionalization reactions : Boogeart, I. F. F.; Fortman, G. C.; Furst, M.R. L.; Cazin C. S. J; Nolan, S. P., manuscript submitted.

(9) Unlike its gold congener[10] synthetic attempts using NaOH and KOH proved unsuccessful, yet once isolated, solid-state samples of **2** left in the air for more than 1 month showed no visible decomposition as monitored by NMR spectroscopy.

(10) Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 2742.

(11) Fortman, G. C.; Poater, A.; Levell, J. W.; Gaillard, S.; Slawin, A. M. Z.; Samuel, I. D. W.; Cavallo, L.; Nolan, S. P. *Dalton Trans.* **2010**, *39*, DOI: 10.1039/c0dt00276c.

(12) Potentiometric titration data in DMSO revealed a pK_a = 30.4(2) for [Au(IPr)(OH)] (Boogaerts, I. I. F.; Slawin, A. M. Z.; Nolan, S. P. *J. Am. Chem. Soc.* **2010**, *132*, 8858–8859). A lower pK_a of 2 is suspected as a result of the the higher electronegativity of Cu(I) compared to Au(I). This greater electronegativity would decrease the electron density about the oxygen atom and thus lower its nucleophilicity.

(13) (a) Mankad, N. P.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 1191. (b) Kaur, H.; Kauer, F.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2004**, *23*, 1157.

(14) Ren, H.; Zhao, X.; Xu, S.; Song, H.; Wang, B. *J. Organomet. Chem.* **2006**, *691*, 4109.

(15) Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8881.

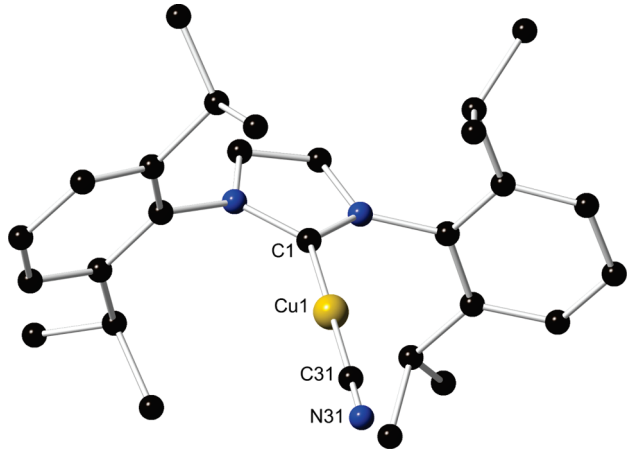
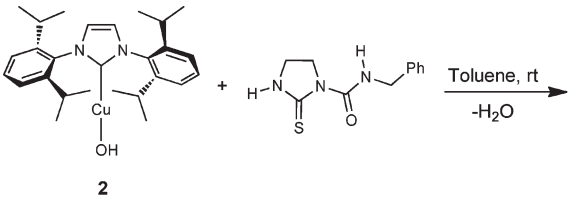


Figure 2. Molecular representation of [Cu(IPr)(CN)] (**8**). Hydrogens are omitted for clarity. Cu1−C31 1.862(5) Å, Cu1−C1 1.900(4) Å, C31−N31 1.139(6) Å, C1−Cu1−C31 177.5(3)°, Cu1−C31−N31 177.9(7)°.

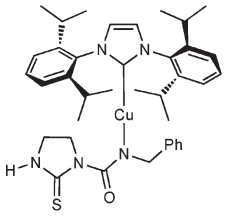
The [Cu(IPr)(CN)] (**8**) species was not accessed by C−H activation, but rather via the reaction of **2** with trimethylsilyl cyanide. Unfortunately, the reaction with TMS-CN led to simultaneous formation of a salt formed in ∼15% yield.[18] This salt was later identified by single-crystal XRD (Figure S1) and ^{1}H NMR spectroscopy to be [IPrH][Cu(CN)$_2$]. X-ray structures of several Cu-CN compounds have been previously published; however most are polymeric in nature.[19] To our knowledge [Cu(IPr)(CN)] is the first isolated example of a 14-electron, dicoordinate Cu(I) complex. Single crystals suitable for XRD analysis were obtained from vapor diffusion of pentane into a saturated solution of **8** in THF. A graphical representation of **8** is shown in Figure 2. Bond lengths and angles for **8** are similar to those of other more electron rich Cu(I)−CN complexes.[19c,f]

Attempted formation of Cu−Si bonds through Si−H activation failed, as formation of Si−OH is more favorable than H−OH formation by more than 20 kcal/mol.[20] Formation of a Cu−Si bond was however successfully accomplished through reaction of **2** with Me$_2$N-SiMe$_3$ to produce [Cu(IPr)(SiMe$_3$)] (**9**). Relatively few examples of neutral Cu−Si complexes have been reported.[21] None are however 14-electron dicoordinate linear complexes.

N−H bonds were also readily activated. Two such complexes were prepared as proof-of-concept examples. First, the reaction of **2** with a thiocarbonylamide (eq 2) selectively led to activation of the amide N−H bond. The product was isolated as a white solid in 79% yield. This demonstrates the regioselectivity of **2** for activation of the most acidic proton of the substrate.[22]

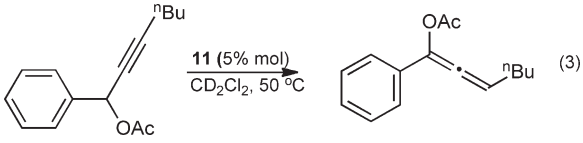


2



10 (2)

The second example of N−H activation was inspired from a gold analogue. [Cu(IPr)(NTf$_2$)] (**11**) was successfully prepared in 86% yield from **2** and HNTf$_2$ (Tf = SO$_2$CF$_3$). The gold analogue, also known as a Gagosz-type complex,[23] has been utilized in the functionalization of bicycloheptanes,[24] [4+1] cyclization of propargyl tosylates with *N*-tosylaldimines,[25] and rearrangement of 3-cyclopropyl propargylic acetates.[26] Indeed, initial catalytic screenings in our laboratory have shown the ability of **11** to transform phenylpropargyl acetates into the corresponding allenes as shown in eq 3.[27]



(3)

Single crystals of **11** were grown from vapor diffusion of pentane into a saturated solution of **11** in benzene. A graphical representation of **11** is presented in Figure 3. Similar metrical comparisons between the Cu and Au complexes are found and are in line with those found for the [M(IPr)OH] (M = Cu and Au) complexes. Both the M−C and M−N bonds are shorter in the copper case (M−C Au: 1.969(2), Cu 1.859(5) Å; M−N Au: 2.091(2), Cu 1.911(4) Å).[23]

Activation of the P−H bond of diphenylphosphine was seemingly instantaneous, producing the yellow [Cu(IPr)(PPh$_2$)] (**11**). Fortunately, the phosphine appears to be somewhat resistant to electrophilic attack by water, which is the

(16) (a) Feilchenfeld, H.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 4276. (b) Fluegge, S.; Anoop, A.; Goddard, R.; Thiel, W.; Fürstner, A. *Chem.—Eur. J.* **2009**, *15*, 8558. (c) Hunks, W. J.; MacDonald, M.-A.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 5063. (d) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11.

(17) Fujimura, O.; Fukunaga, K.; Honma, T.; Machida, T. *JP* 2007297347, Japan, 2007.

(18) See Supporting Information for details. X-ray diffraction data for this complex can be found in the SI.

(19) (a) Pike, R. D.; deKrafft, K. E.; Ley, A. N.; Tronic, T. A. *Chem. Commun.* **2007**, 3732. (b) Saravanabharathi, D.; Nethaji, M.; Venugopalan, P.; Samuelson, A. G. *Polyhedron* **2002**, *21*, 2433. (c) Coles, M. P.; Hitchcock, P. B. *Polyhedron* **2001**, *20*, 3027. (d) Chesnut, D. J.; Plewak, D.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2001**, 2567. (e) Chesnut, D. J.; Kusnetzow, A.; Birge, R.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2001**, 2581. (f) Ellermann, J.; Knoch, F. A.; Meier, K. J.; Moll, M. *J. Organomet. Chem.* **1992**, *428*, C44. (g) Anderson, O. P.; Packard, A. B. *Inorg. Chem.* **1980**, *19*, 2941.

(20) *Comprehensive Handbook of Chemical Bond Energies*; Luo, Y.-R., Ed.; CRC Press: Boca Raton, FL, 2007; 462 and 255.

(21) (a) Avent, A. G.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Maciejewski, H. *J. Organomet. Chem.* **2003**, *686*, 321. (b) Klett, J.; Klinkhammer, K. W.; Niemeyer, M. *Chem.—Eur. J.* **1999**, *5*, 2531. (c) Schubert, U.; Mayer, B. C. *Russ. Chem. Ber.* **1994**, *127*, 2189. (d) Cowley, A. H.; Elkins, T. M.; Jones, R. A.; Nunn, C. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1349.

(22) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

(23) Ricard, L.; Gagosz, F. *Organometallics* **2007**, *26*, 4704.

(24) Li, G.; Huang, X.; Zhang, L. *J. Am. Chem. Soc.* **2008**, *130*, 6944.

(25) Suarez-Pantiga, S.; Rubio, E.; Alvarez-Rua, C.; Gonzalez, J. M. *Org. Lett.* **2009**, *11*, 13.

(26) Garayalde, D.; Gomez-Bengoa, E.; Huang, X.; Goeke, A.; Nevado, C. *J. Am. Chem. Soc.* **2010**, *132*, 4720.

(27) 1-Acetate-1-hexyn-1-ylbenzenemethanol was observed to be converted to 3-acetate-1-phenyl-1,2-heptadien-3-ol in 91% yield as determined by ^{1}H NMR spectroscopy.

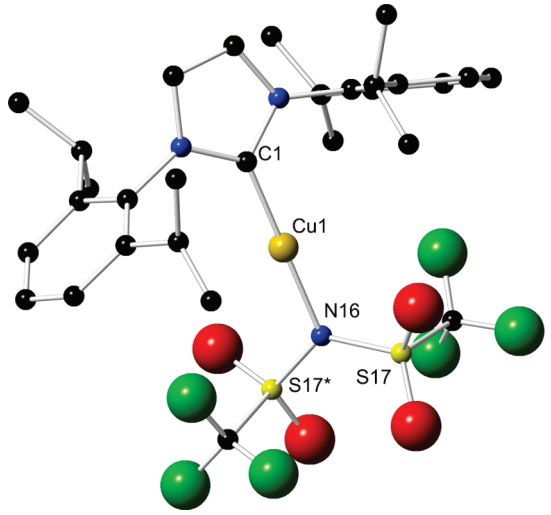


Figure 3. Molecular representation of [Cu(IPr)(NTf_2)] (Tf = trifluoromethanesulfonate) (**11**). Hydrogens are omitted for clarity. Cu−C1 1.859(5) Å, Cu1−N16 1.911(4) Å, C10−Cu1−N16 180.00°.

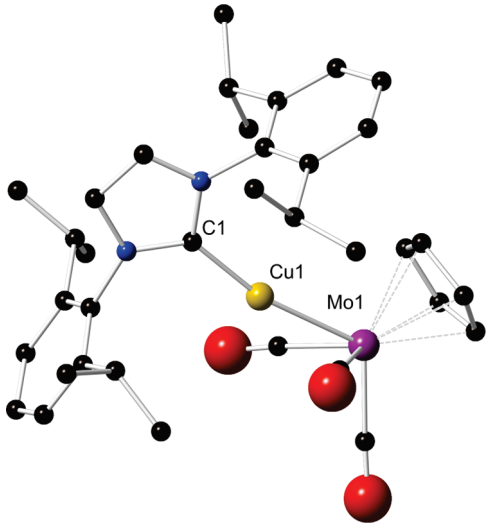


Figure 4. Molecular representation of [(IPr)Cu-Mo($CO)_3$Cp] (**16**). Hydrogens are omitted for clarity. Cu1−C1 1.916(5) Å, Cu1−Mo1 2.5600(8) Å, C1−Cu1−Mo1 167.28(15)°.

byproduct in this reaction. The proton-coupled ^{31}P NMR spectrum of **11** in C_6D_6 displayed a single resonance at δ −26.0 ppm [for comparison: $HPPh_2$ (δ −41.4 ppm) and PPh_3 (δ −5.5 ppm)]. Caulton et al. have reported the synthesis of the sole other example of this type, [Cu(PPh_3)(PPh_2)], which exhibits a ^{31}P NMR resonance at δ −32.2 ppm.[28] The downfield shift of the NHC derivative compared with the triphenylphosphane complex can be explained by the greater σ-donating ability of the NHC.[29]

Alcohols were also activated using **2**. Stirring [Cu(IPr)(OH)] in MeOH overnight resulted in formation of the Cu-methoxide complex [Cu(IPr)(OMe)] (**13**) in high yield, 91%. Additionally reaction of **2** with *tert*-butanol resulted in high yields of [Cu(IPr)(O^{t}Bu)] (**14**), 93%. Stoichiometric reactions in C_6D_6 resulted in similarly high yields, as confirmed by ^{1}H NMR spectroscopy. Although the synthesis of these complexes[2,5b,14] and their use in catalysis[2−4,5c,6] have previously been reported, the simple fact that they can be synthesized directly from [Cu(IPr)(OH)] suggests that **2** is a more reactive and consequently more versatile synthon.

Access to the formation of Cu−S bonds through S−H was also accomplished. Protonation of **2** with *para*-thiocresol resulted in formation of [Cu(IPr)(S-*p*-tol)] (**15**) in 88% yield. Thiocopper species have been know for several centuries.[30] Preparation of these complexes was accomplished with the use of alkyl copper complexes, and they have been proposed as catalytic intermediates in the hydrothiolation of vinylarenes[31] and olefins.[32]

In addition to reactions with H−A bonds commonly found in organic chemistry, examination of reactions with a metal hydride to form bimetallic complexes was also examined.[33] The combination of the intrinsic basicity of **2** with the abundance of metal hydrides provides a perfect route to form just such a novel complex. The reaction of [Cu(IPr)(OH)] with [$HMo(CO)_3(\eta^5$-$C_5H_5)$] led to the formation of a Cu−Mo bond. A graphical representation as determined by XRD of **16** is shown in Figure 4. Of particular note is the large deviation from linearity of the Mo1−Cu−C1 bond angle (167.28(15)°) presumably caused by steric repulsion between the pendant ^{i}Pr groups and the carbonyls. Analysis of the ν_{CO} stretching frequencies in CH_2Cl_2 revealed three major stretches (1925.8, 1821.9, and 1798.6 cm^{-1}), which are characteristic of a [(L)M-M′($CO)_3$Cp] (L = two-electron donor; M = Au, Cu; M′ = Cr, Mo, W) tightly bound ion pair.[34]

Conclusion

In summary, the synthesis of **2** has been achieved and its chemical versatility as a key synthon has been demonstrated (see Figure 5) in reactions involving numerous X−H bond activation including C−H bonds (i.e., sp, sp^2, sp^3) as well as N−H, P−H, O−H, and S−H bonds. The cleavage of Si−N and Si−C bonds has also been shown as a viable synthetic route leading to unprecedented copper complexes. Additionally, we have demonstrated that the use of **2** with a metal hydride can serve as a simplistic strategy for the synthesis of heterobimetallic complexes. Further work in our laboratory is aimed at exploring the use of **2** as a synthon and as a (pre)catalyst.

Experimental Section

General Considerations. Unless stated otherwise all reactions were carried out inside an MBraun glovebox under inert conditions. Solvents were distilled and dried as required. Nitromethane and 1,2,4,5-tetraflourobenzene were purchased from Alfa-Aesar. Dimethyl malonate, dicyclopentadiene, trimethylsilane

(28) Lemmen, T. H.; Goeden, G. V.; Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3680.
(29) (a) For a monograph on NHC in synthesis see: *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2006. (b) For a review on NHC in late transition metal catalysis see: Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612.
(30) (a) Bridges, A. J.; Ross, R. J. *Tetrahedron Lett.* **1983**, *24*, 4797. (b) Kubota, M.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3622.
(31) Munro-Leighton, C.; Delp, S. A.; Alsop, N. M.; Blue, E. D.; Gunnoe, T. B. *Chem. Commun.* **2008**, 111.
(32) Delp, S. A.; Munro-Leighton, C.; Goj, L. A.; Ramirez, M. A.; Gunnoe, T. B.; Petersen, J. L.; Boyle, P. D. *Inorg. Chem.* **2007**, *46*, 2365.
(33) Hetero-bimetallic complexes have led to some interesting chemistry; see for example: Ruiz, J.; Perandones, B. F. *J. Am. Chem. Soc.* **2007**, *129*, 9298.
(34) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc., A* **1968**, 46.

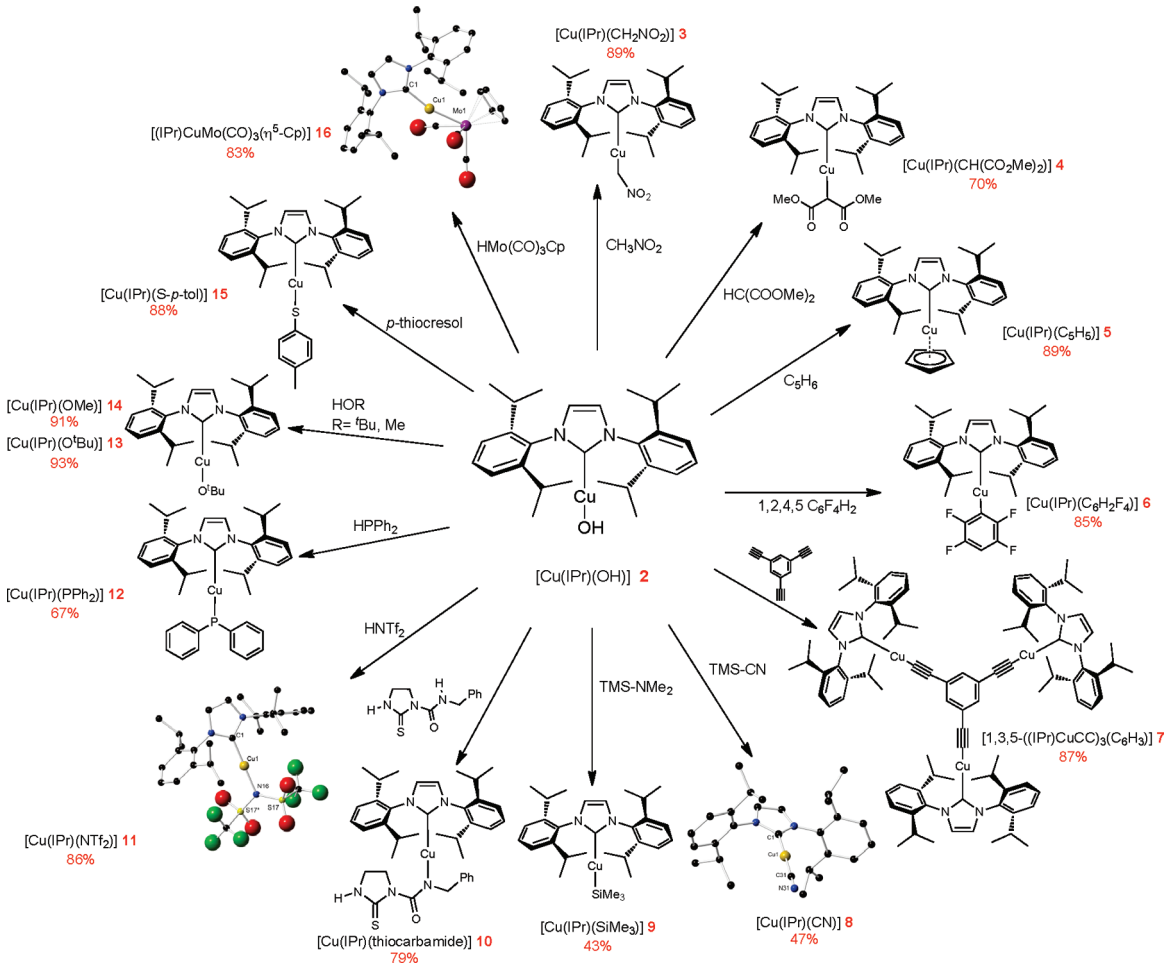


Figure 5. Summary of complexes synthesized using [Cu(IPr)(OH)] (**2**).

cyanide, dimethyltrimethysilane amine, triflimide, diphenylphosphane, *tert*-butanol, methanol, and *para*- and thiocresol were purchased from Sigma-Aldrich and used as received. 1,3,5-Triethynylbenzene was purchased from ABCR. [Cu(IPr)Cl],[35] [$HMo(CO)_3Cp$],[36] and *N*-phenyl-2-thioxo-1-imidazolidinecarboxamide[36] were prepared according to literature procedures. ^1H and ^{13}C NMR were recorded on either a Burker 400 MHz or a Bruker 300 MHz NMR spectrometer. Spectra were referenced to CD_2Cl_2 at δ 5.32 (^{13}C, δ 54.0), C_6D_6 at δ 7.16 (^{13}C δ 128.4), $CDCl_3$ at δ 7.26 (δ ^{13}C 77.2), or THF-d_8 at δ 3.58 (δ ^{13}C 67.6) ppm. Elemental analyses were performed at the University of St Andrews.

Synthesis of [Cu(OH)(IPr)] (2). In the glovebox a 20 mL scintillation vial was charged with 100 mg (0.205 mmol) of [Cu(IPr)Cl] and 2 equiv of anhydrous CsOH. The solids were then dissolved in 4.0 mL of dry, degassed THF. The solution was stirred at rt for 8 h. The resulting clear light yellow solution was filtered through a plug of Celite, and the solution was concentrated *in vacuo* until a white precipitate formed (ca. 1 mL remaining). Slow addition of pentane (ca. 8 mL) was then used to precipitate the remaining product. The white microcrystalline product was collected on a glass frit, then dried *in vacuo* to yield 82 mg of **2** (85% yield). Single crystals for XRD were grown from a saturated solution of THF and pentane at −40 °C. CD_2Cl_2 used to take NMR was first passed through basic alumina to remove HCl traces. ^1H NMR (CD_2Cl_2, 300 MHz, δ ppm): 7.56 (t, 2H, ^2J_H = 7.8 Hz, Ar-CH), 7.35 (d, 4H, ^2J_H = 7.8 Hz Ar-CH), 7.17 (s, 2H, imid-CH), 2.60 (sept, 4H, ^2J_H = 6.9 Hz, ^{i}Pr-CH), 1.32 (d, 12H, ^2J_H = 7.0 Hz, ^{i}Pr-CH_3), 1.24 (d, 12H, ^2J_H = 7.0 Hz, ^{i}Pr-CH_3), OH proton not observed. ^{13}C NMR (CD_2Cl_2, 75.5 MHz, δ ppm): 182.3 (s, carbene C), 146.3 (s, Ar-C), 135.5 (s, Ar-C), 130.7 (s, imid-C), 124.6 (s, Ar-C), 123.6 (s, Ar-C), 29.2 (s, ^{i}Pr-C), 25.0 (s, ^{i}Pr-C), 24.1 (s, ^{i}Pr-C). Anal. Calcd for $C_{27}H_{37}CuN_2O$ (MW 469.14): C, 69.12; H, 7.95; N, 5.97. Found: C, 68.84; H, 7.95; N, 5.99.

Synthesis of [Cu(IPr)(R)] Utilizing R−H Bond Activation. Typically 100 mg (0.213 mmol) of [Cu(IPr)OH] (**2**) was placed with 2 mL of toluene. One molar equivalent of H−R was added to the white suspension. Generally, dissolution of the complex occurred within minutes, at which point the reaction was stirred for an additional 1 h. The solvent was subsequently stripped *in vacuo* to approximately 0.75 mL, at which point the product was precipitated from solution with the addition of pentane. The products were filtered from the solution, washed with pentane (3 × 3 mL), and dried under reduced pressure.

[Cu(IPr)($CH_2(NO_2)$)] (3): white microcrystals, 89% yield, unstable in DCM. ^1H NMR (C_6D_6, 300 MHz, δ ppm): 7.18 (t, 2H, ^2J_H = 7.8 Hz, Ar-CH), 7.07 (d, 4H, ^2J_H = 7.6 Hz Ar-CH), 6.32 (s, 2H, imid-CH), 5.35 (s, 1H, Cu-$CH_2(NO_2)$), 3.28 (s, 6H, OCH_3), 2.63 (sept, 4H, ^2J_H = 6.9 Hz, ^{i}Pr-CH), 1.44 (d, 12H, ^2J_H = 6.8 Hz, ^{i}Pr-CH_3), 1.08 (d, 12H, ^2J_H = 6.9 Hz, ^{i}Pr-CH_3). ^{13}C NMR (C_6D_6, 75 MHz, δ ppm): 185.0 (s, carbene C), 174.0 (s, C=O), 146.8 (s, Ar-C), 136.2 (s, Ar-C), 130.4 (s, imid-C), 124.4 (s, Ar-C), 122.7 (s, Ar-C), 63.2 (s, Cu-CH), 50.2 (s, OCH_3), 29.2 (s, ^{i}Pr-C), 24.35 (s, ^{i}Pr-C), 24.31 (s, ^{i}Pr-C). Anal. Calcd for $C_{28}H_{38}CuN_3O_2$ (MW 512.17): C, 65.66; H, 7.48; N, 8.20. Found: C, 65.77; H, 7.32; N, 8.12.

(35) Citadelle, C. A.; LeNouy, E.; Bisaro, F.; Slawin, A. M. Z.; Cazin, C. S. J. *Dalton Trans.* **2010**, 4489.
(36) Burchell, R. P. L.; Sirsch, P.; Decken, A.; McGrady, G. S. *Dalton Trans.* **2009**, 5851.

[Cu(IPr)(CH(COOMe)$_2$)] (4): 70% yield. ^{1}H NMR (CD_2Cl_2, 300 MHz, δ ppm): 7.49 (t, 2H, ^2J_H = 7.8 Hz, Ar-CH), 7.32 (d, 4H, ^2J_H = 7.7 Hz Ar-CH), 7.11 (s, 2H, imid-CH), 3.80 (s, 1H, Cu-CH), 3.28 (s, 6H, OCH_3), 2.71 (sept, 4H, ^2J_H = 6.9 Hz, ^{i}Pr-CH), 1.31 (d, 12H, ^2J_H = 6.7 Hz, ^{i}Pr-CH_3), 1.23 (d, 12H, ^2J_H = 7.0 Hz, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2, 75 MHz, δ ppm): 184.1 (s, carbene C), 146.3 (s, Ar-C), 135.7 (s, Ar-C), 130.9 (s, imid-C), 124.6 (s, Ar-C), 122.7 (s, Ar-C), 96.8 (s, Cu-$CH_2(NO_2)$), 29.4 (s, ^{i}Pr-C), 25.2 (s, ^{i}Pr-C), 24.2 (s, ^{i}Pr-C). Anal. Calcd for $C_{32}H_{43}CuN_2O_4$ (MW 583.25): C, 65.90; H, 7.43; N, 4.80. Found: C, 65.97; H, 7.44; N, 4.86.

[Cu(IPr)Cp] (5): light yellow powder, 89% yield. Compound identity was confirmed with literature ^{1}H NMR.[37] ^{13}C NMR was not included in original publication. ^{13}C NMR (CD_2Cl_2, 100 MHz, δ ppm): 188.3 (s, carbene C), 146.5 (s, Ar-C), 136.7 (s, Ar-C), 130.1 (s, imid-C), 124.2 (s, Ar-C), 123.0 (s, Ar-C), 95.1 (s, Cp), 29.1 (s, ^{i}Pr-C), 24.6 (s, ^{i}Pr-C), 24.1 (s, ^{i}Pr-C).

[Cu(IPr)(C_6F_4H)] (6): white powder, 85% yield. ^{1}H NMR (CD_2Cl_2, 300 MHz, δ ppm): 7.53 (t, 2H, ^2J_H = 7.8 Hz, Ar-CH), 7.35 (d, 4H, ^2J_H = 7.8 Hz Ar-CH), 7.23 (s, 2H, imid-CH), 6.50 (m, 1H, C_6F_4H), 3.28 (s, 6H, OCH_3), 2.67 (sept, 4H, ^2J_H = 6.8 Hz, ^{i}Pr-CH), 1.34 (d, 12H, ^2J_H = 6.8 Hz, ^{i}Pr-CH_3), 1.27 (d, 12H, ^2J_H = 6.9 Hz, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2, 75 MHz, δ ppm): 183.0 (s, carbene C), 174.0 (s, C=O), 151.7, 148.7, 146.6, 143.4 (m, CF), 146.5 (s, Ar-C), 135.2 (s, Ar-C), 130.8 (s, imid-C), 124.5 (s, Ar-C), 123.7 (s, Ar-C), 102.4 (t, ^3J_F = 23 Hz Cu-C), 29.4 (s, ^{i}Pr-C), 25.0 (s, ^{i}Pr-C), 24.2 (s, ^{i}Pr-C). Anal. Calcd for $C_{33}H_{37}CuF_4N_2$ (MW 601.20): C, 65.90; H, 7.43; N, 4.80. Found: C, 65.74; H, 7.87; N, 4.98.

[1,3,5-((IPr)-Cu-CC)$_3$C$_6$H$_3$] (7): reaction left stirring for 14 h, 87% yield. ^{1}H NMR (CD_2Cl_2, 300 MHz, δ): 7.53 (t, 6H, ^2J_H = 7.8 Hz, Ar-CH), 7.34 (d, 12H, ^2J_H = 7.3 Hz Ar-CH), 7.13 (s, 6H, imid-CH), 6.60 (s, 3H, benzene-CH), 2.59 (sept, 12H, ^2J_H = 7.0 Hz, ^{i}Pr-CH), 1.32 (d, 36H, ^2J_H = 6.8 Hz, ^{i}Pr-CH_3), 1.22 (d, 36H, ^2J_H = 6.9 Hz, ^{i}Pr-CH_3). ^{13}C NMR (CH_2Cl_2, 75 MHz, δ ppm): 183.2 (s, carbene C), 146.3 (s, Ar-C), 135.2 (s, Ar-C), 132.3 (s, benzene-C), 130.8 (s, imid-C), 126.9 (s, benzene-C), 124.6 (s, Ar-C), 123.5 (s, Ar-C), 121.0 (s, alkyne) 105.0 (s, alkyne), 29.3 (s, ^{i}Pr-C), 24.8 (s, ^{i}Pr-C), 24.3 (s, ^{i}Pr-C). Anal. Calcd for $C_{93}H_{111}Cu_3N_6$ (MW 1503.55): C, 74.29; H, 7.44; N, 5.59. Found: C, 74.56; H, 7.64; N, 5.88.

[Cu(IPr)(CN)] (8). The product obtained was recrystallized from a minimal amount of THF to remove the side product [HIPr][Cu(CN)$_2$]. XRD of **8** and Cu salt were grown from a saturated solution of pentane and THF at −40 °C. Colorless crystals, 47% yield. ^{1}H NMR (CD_2Cl_2, 300 MHz, δ ppm): 7.55 (t, 2H, ^2J_H = 7.7 Hz, Ar-CH), 7.35 (d, 4H, ^2J_H = 7.8 Hz Ar-CH), 7.20 (s, 2H, imid-CH), 2.53 (sept, 4H, ^2J_H = 7.0 Hz, ^{i}Pr-CH), 1.28 (d, 12H, ^2J_H = 6.9 Hz, ^{i}Pr-CH_3), 1.23 (d, 12H, ^2J_H = 6.8 Hz, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2, 75 MHz, δ ppm): 180.7 (s, carbene C), 146.2 (s, Ar-C), 142.4 (s, CN), 134.6 (s, Ar-C), 131.2 (s, imid-C), 124.7 (s, Ar-C), 124.1 (s, Ar-C), 29.3 (s, ^{i}Pr-C), 25.2 (s, ^{i}Pr-C), 24.1 (s, ^{i}Pr-C). Anal. Calcd for $C_{28}H_{36}CuN_3$ (MW 478.15): C, 70.33; H, 7.59; N, 8.79. Found: C, 70.53; H, 7.40; N, 8.96.

[Cu(IPr)(SiMe$_3$)] (9): product isolated from a saturated solution of THF and pentane at −40 °C, colorless crystals, 43% yield. ^{1}H NMR (CD_2Cl_2, 400 MHz, δ ppm): 7.51 (t, 2H, ^2J_H = 7.8 Hz, Ar-CH), 7.32 (d, 4H, ^2J_H = 7.8 Hz Ar-CH), 7.14 (s, 2H, imid-CH), 2.58 (sept, 4H, ^2J_H = 6.9 Hz, ^{i}Pr-CH), 1.30 (d, 12H, ^2J_H = 6.8 Hz, ^{i}Pr-CH_3), 1.22 (d, 12H, ^2J_H = 6.8 Hz, ^{i}Pr-CH_3), −0.45 (s, 9H, $SiMe_3$). ^{13}C NMR (CD_2Cl_2, 100 MHz, δ ppm): 182.5 (s, carbene C), 146.3 (s, Ar-C), 135.5 (s, Ar-C), 130.7 (s, imid-C), 124.6 (s, Ar-C), 123.6 (s, Ar-C), 29.2 (s, ^{i}Pr-C), 25.0 (s, ^{i}Pr-C), 24.2 (s, ^{i}Pr-C), 4.2 (s, $SiMe_3$). Anal. Calcd for $C_{30}H_{45}CuN_2Si$ (MW 525.32): C, 68.59; H, 8.63; N, 5.33. Found: C, 68.31; H, 8.39; N, 5.02.

[Cu(IPr)(thiocarbonylamide)] (10): white powder, 79% yield. ^{1}H NMR (CD_2Cl_2, 400 MHz, δ ppm): 12.42 (s, 1H, NH), 7.54 (t, 2H, ^2J_H = 7.8 Hz, Ar-CH), 7.45 (d, 2H,, ^2J_H = 8.2 Hz, CH-Ph), 7.36 (d, 4H, ^2J_H = 7.9 Hz, Ar-CH), 7.21 (s and t overlapping, 2H and 2H, imid-CH and CH-Ph), 6.95 (t, 1H, ^2J_H = 7.5 Hz, CH-Ph), 3.83 (t, 2H, ^2J_H = 8.8 Hz, CH_2), 3.00 (t, 2H, ^2J_H = 8.3 Hz, CH_2), 2.63 (sept, 4H, ^2J_H = 6.8 Hz, ^{i}Pr-CH), 1.34 (d, 12H, ^2J_H = 6.9 Hz, ^{i}Pr-CH_3), 1.25 (d, 12H, ^2J_H = 7.0 Hz, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz, δ ppm): 181.7 (s, carbene C), 179.0 (s, C=S), 152.2 (s, C=O) 146.4 (s, Ar-C), 139.9 (s, Ph-C), 135.3 (s, Ar-C), 130.8 (s, imid-C), 129.1 (s, Ph-C), 124.6 (s, Ar-C), 123.6 (s, Ar-C), 122.8 (s, Ph-C), 119.6 (s, Ph-C), 48.6 (s, C-imidazole), 48.0 (s, C-imidizole), 29.3 (s, ^{i}Pr-C), 25.0 (s, ^{i}Pr-C), 24.3 (s, ^{i}Pr-C). Anal. Calcd for $C_{38}H_{48}CuN_5OS$ (MW 686.43): C, 66.49; H, 7.05; N, 10.20. Found: C, 66.11; H, 6.85; N, 10.03.

[Cu(IPr)(NTf$_2$)] (11) (Tf = SO$_2$CF$_3$): white powder, XRD crystals grown from slow vapor diffusion of pentane into a saturated solution of benzene, 86% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.51 (t, 2H, ^2J_H = 7.8 Hz, Ar-CH), 7.31 (d, 4H, ^2J_H = 8.0 Hz Ar-CH), 7.32 (s, 2H, imid-CH), 2.53 (sept, 4H, ^2J_H = 6.8 Hz, ^{i}Pr-CH), 1.26 (d, 12H, ^2J_H = 6.9 Hz, ^{i}Pr-CH_3), 1.22 (d, 12H, ^2J_H = 6.9 Hz, ^{i}Pr-CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 178.7 (s, carbene C), 145.7 (s, Ar-C), 134.2 (s, Ar-C), 130.9 (s, imid-C), 124.4 (s, Ar-C), 123.9 (s, Ar-C), 119.1 (q, ^1J_F = 322 Hz, CF_3), 29.0 (s, ^{i}Pr-C), 24.5 (s, ^{i}Pr-C), 24.2 (s, ^{i}Pr-C). ^{19}F NMR ($CDCl_3$, 282.4 MHz, δ ppm): −77.15 (s, CF_3). Anal. Calcd for $C_{29}H_{36}CuF_6N_3O_4S_2$ (MW 732.28): C, 47.57; H, 4.96; N, 5.74. Found: C, 47.62; H, 5.05; N, 5.83.

[Cu(IPr)(PPh$_2$)] (12): synthesis performed in benzene, yellow powder, 67% yield, decomposition observed in CD_2Cl_2. ^{1}H NMR (C_6D_6, 300 MHz, δ ppm): 7.36 (m, 4H, PPh), 7.27 (t, 2H, ^2J_H = 7.5 Hz, Ar-CH), 7.07 (d, 4H, ^2J_H = 7.6 Hz Ar-CH), 7.00−6.94 (m, 6H, PPh), 6.24 (s, 2H, imid-CH), 2.50 (sept, 4H, ^2J_H = 6.5 Hz, ^{i}Pr-CH), 1.20 (d, 12H, ^2J_H = 6.9 Hz, ^{i}Pr-CH_3), 1.04 (d, 12H, ^2J_H = 7.0 Hz, ^{i}Pr-CH_3). ^{13}C NMR (THF-d_8, 75 MHz, δ ppm): 183.5 (s, carbene C), 148.4 (d, ^1J_P = 27 Hz, C-P), 146.7 (s, Ar-C), 136.2 (s, Ar-C), 134.1 (d, ^2J_P = 17 Hz, C-Ph), 131.1 (s, imid-C), 127.8 (d, ^2J_P = 5.2 Hz, C-Ph), 125.0 (s, Ar-C), 124.4 (s, Ar-C), 123.3 (s, C-Ph), 29.8 (s, ^{i}Pr-C), 25.2 (s, ^{i}Pr-C, overlapping solvent), 24.2 (s, ^{i}Pr-C). ^{31}P NMR (C_6D_6, 121.5 MHz, δ ppm): −27.8 (s, CF_3). Anal. Calcd for $C_{39}H_{46}CuN_2P$ (MW 637.32): C, 73.50; H, 7.28; N, 4.40. Found: C, 73.68; H, 7.56; N, 4.59.

[Cu(IPr)(OMe)] (13): reaction left to stir for 14 h, white powder, 91% yield. Identity was confirmed by ^{1}H NMR of previously reported preparation.[38]

[Cu(IPr)(O^{t}Bu)] (14): reaction left to stir for 14 h, white powder, 93% yield. Identity was confirmed by ^{1}H NMR of previously reported preparation.[39]

[Cu(IPr)(S-*p*-tol)] (15): white microcrystalline powder, 88% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.52 (t, 2H, ^2J_H = 7.8 Hz, Ar-CH), 7.30 (d, 4H, ^2J_H = 7.8 Hz Ar-CH), 7.14 (s, 2H, imid-CH), 6.5 (m, 4H, cresol-CH) 2.61 (sept, 4H, ^2J_H = 7.0 Hz, ^{i}Pr-CH), 2.14 (s, 3H, CH_3) 1.28 (d, 12H, ^2J_H = 6.9 Hz, ^{i}Pr-CH_3), 1.23 (d, 12H, ^2J_H = 6.9 Hz, ^{i}Pr-CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 181.6 (s, carbene C), 145.7 (s, Ar-C), 139.5 (s, C-S), 134.5 (s, Ar-C), 132.5 (s, CH-cresol), 130.4 (s, imid-C), 128.2 (s, CH-cresol), 124.7 (s, CH-cresol), 124.2 (s, Ar-C), 122.8 (s, Ar-C), 28.7 (s, ^{i}Pr-C), 24.7 (s, ^{i}Pr-C), 23.8 (s, ^{i}Pr-C), 20.7 (s, CH_3-cresol). Anal. Calcd for $C_{34}H_{43}CuN_2S$ (MW 575.24): C, 70.98; H, 7.53; N, 4.87. Found: C, 71.13; H, 7.86; N, 4.95.

[(IPr)Cu-Mo(CO)$_3$Cp] (16): yellow powder, 83% yield. ^{1}H NMR (CD_2Cl_2, 300 MHz, δ ppm): 7.52 (t, 2H, ^2J_H = 7.8 Hz, Ar-CH), 7.36 (d, 4H, ^2J_H = 7.9 Hz Ar-CH), 7.18 (s, 2H, imid-CH), 4.82 (s, 5H, Cp), 2.70 (sept, 4H, ^2J_H = 7.2 Hz, ^{i}Pr-CH),

(37) Pilling, G. M.; Johnson, R. E. *Tetrahedron Lett*. **1990**, *31*, 6763.

(38) Ren, H.; Zhao, X.; Xu, S.; Song, H.; Wang, B. *J. Organomet. Chem*. **2006**, *691*, 4109.

(39) Bonet, A.; Lillo, V.; Ramírez, J.; Díaz-Requejo, M. M.; Fernández, E. *Org. Biomol. Chem*. **2009**, *7*, 1533.

1.31 (d, 12H, ^2J_H = 6.8 Hz, ^{i}Pr-CH_3), 1.21 (d, 12H, ^2J_H = 7.0 Hz, ^{i}Pr-CH_3). ^{13}C NMR (CD_2Cl_2, 75 MHz, δ ppm): 230.0 (s, CO) 181.5 (s, carbene C), 146.5 (s, Ar-C), 135.5 (s, Ar-C), 130.8 (s, imid-C), 124.5 (s, Ar-C), 123.7 (s, Ar-C), 87.7 (s, Cp), 29.3 (s, ^{i}Pr-C), 24.8 (s, ^{i}Pr-C), 24.1 (s, ^{i}Pr-C). FTIR (CH_2Cl_2, cm^{-1}): 1925.8, 1821.9, 1798.6. Anal. Calcd for $C_{36}H_{47}CuMoN_2O_3$ (MW 715.26): C, 60.45; H, 6.62; N, 3.92. Found: C, 60.54; H, 6.82; N, 4.01.

Reaction of [Cu(IPr)(OH)] with Nitromethane in the Presence of TEMPO (TEMPO = 2,2,5,5-tetramethylpiperidin-1-oxyl). In the glovebox a J-Young tube was charged with 10.0 mg (2.13×10^{-2} mmol) of [Cu(IPr)(OH)] and 2 equiv (6.6 mg) of TEMPO. The solids were dissolved in 0.7 mL of C_6D_6, after which 1 equiv (1.1 μL) of nitromethane was injected to the solution with stirring. The contents were examined by ^{1}H NMR and confirmed to be [Cu(IPr)(CH_2NO_3)] with the aid of a separately prepared sample.

Reaction of [Cu(IPr)(OH)] with Quantitative Amounts of ROH (R = ^{t}Bu, Me). In a glovebox a 2.5 mL vial was charged with 10.0 mg (2.13×10^{-2} mmol) of [Cu(IPr)(OH)], which was dissolved in 0.7 mL of C_6D_6. The solution was then injected with 1 equiv of ROH (R = ^{t}Bu, Me) and stirred for 14 h. The contents were examined by ^{1}H NMR and confirmed to be [Cu(IPr)(OR)] (R = ^{t}Bu, Me) with the aid of a separately prepared sample.

(40) Marion, N.; Díez-González, S.; Frémont, P. d.; Noble, A. R.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3647.

Catalytic Conversion of Phenylpropargyl Acetate to Allene with [Cu(IPr)(NTf_2)]. In the glovebox a J-Young tube was charged with 0.2 mmol (46.1 mg) of phenylpropargyl acetate and 0.01 mmol (7.3 mg) of [Cu(IPr)(NTf_2)]. CD_2Cl_2 (0.7 mL) was added to the tube, which was subsequently sealed and removed from the glovebox. A blank experiment containing the exact amount of the phenylpropargyl acetates and CD_2Cl_2 but without the catalyst was also prepared. An initial ^{1}H NMR was taken of both NMR solutions. The tubes were kept at a constant temperature of 50 °C, and spectra were run over the course of 4 days. No conversion of the blank was observed. Production of the allene was monitored by the characteristic allenic proton at δ 6.58 ppm.[40] A 91% conversion was reached in 4 days at 50 °C, as determined by ^{1}H NMR using CH_2Cl_2 as an internal standard.

Acknowledgment. The authors would like to thank Drs. Ine I. F. Boogaerts and Sylvain Gaillard for fruitful discussions. The authors would also like to thank Christopher Britton for his artisanship. S.P.N. acknowledges the EPSRC and the ERC (Advanced Researcher Grant-FUNCAT) for support. S.P.N. is a Royal Society–Wolfson Research Merit Award holder.

Supporting Information Available: Supporting Information for this manuscript including XRD and spectroscopic data can be found free of charge via the Internet at http://pubs.acs.org.