[{Cu(IPr)}$_2$(μ-OH)][BF$_4$]: Synthesis and Halide-Free CuAAC Catalysis.

Houssein Ibrahim[a,b], Régis Guillot[c], Federico Cisnetti*[a,b] and Arnaud Gautier*[a,b]

[a] Clermont Université, Université Blaise Pascal, Institut de Chimie de Clermont-Ferrand, BP 10448, F-63000 Clermont-Ferrand, FRANCE.

[b] CNRS, UMR 6296, ICCF, F-63171 AUBIERE, FRANCE

[c] Institut de Chimie Moléculaire et des Matériaux d'Orsay, Bât. 420, Université Paris-Sud, UMR CNRS 8182, F-91405 ORSAY Cedex, France.

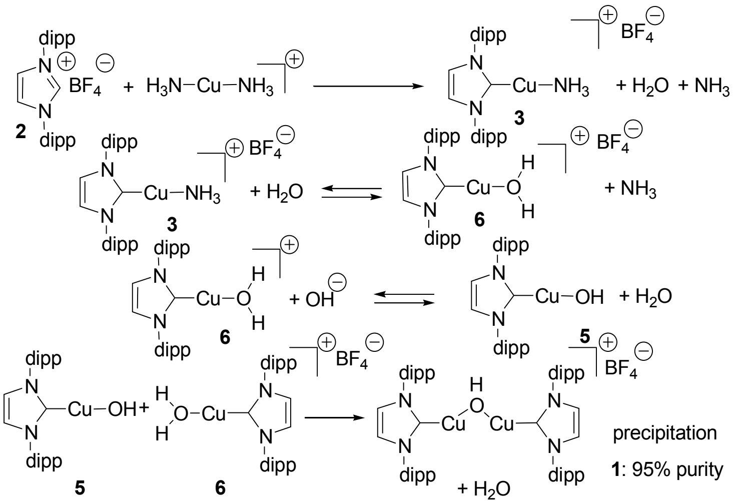
Supporting information

Preparation of 1:

IPr.HBF$_4$ (1 mmol, 476.4 mg, 1.0 eq.) was suspended in 5 mL of 96% ethanol. Copper(I) oxide (78.7 mg, 0.55 mmol, 0.55 eq.) was added, the solution was degassed by bubbling argon for 5 minutes and the flask was stoppered. Then, 0.63 mL of aqueous ammonia (15.7 mol.L^{-1}, 10 eq.) was added with a syringe and the reaction vessel was degassed for 1 more minute. The mixture was stirred vigorously at 40°C overnight then cooled back to room temperature. The resulting almost colorless solution was filtered through a cotton plug onto an erlenmeyer containing 20 mL of water under agitation. A white precipitate formed instantaneously. The mixture was stirred for 15 minutes. Filtration, washing with H_2O and drying under vacuum afforded 408.7 mg (81% yield) of crude **1** (~95% purity) as a white powder. 100 mg of the crude mixture was taken up in 5 mL of dichloromethane, layered with 40 mL of *n*-pentane and crystallization was performed over 18 hours. Large prisms consisting in pure **1** were manually separated from the mixture (46 mg).

^{1}H NMR (400MHz, CD_2Cl_2) δ ppm = 7.50 (t, *J* = 7.9 Hz, 2H); 7.26 (d, *J* = 7.9 Hz, 2H); 7.14 (s, 2H); 2.39 (hept, *J* = 6.9 Hz, 4H); 1.18 (d, *J* = 6.9 Hz, 6H); 1.03 (d, *J* = 6.9 Hz, 6H); OH proton not observed. ^{13}C NMR (100MHz, acetone–d$_6$) δ ppm = 179.3($C_{carbene}$); 146.4(C_{arom}); 135.5(C_{arom}); 131.4(C_{imid}); 125.3(C_{arom}); 125.0(C_{arom}); 29.4 (C_{Ipr}); 25.7(C_{CH3}); 23.9(C_{CH3}) . I.R. (KBr) □(cm^{-1}) = 3380(br); 2964(m); 1644(w); 1465(m); 1051(st, BF_4). Elemental analysis calcd. for $C_{54}H_{75}BCu_2F_4N_4O$ C: 64.21, H: 7.48, N: 5.55; found C: 64.47, H: 7.50, N: 5.57.

Supplementary scheme



Scheme S1. Proposed mechanism for the formation of **1**.

Selected NMR spectra:

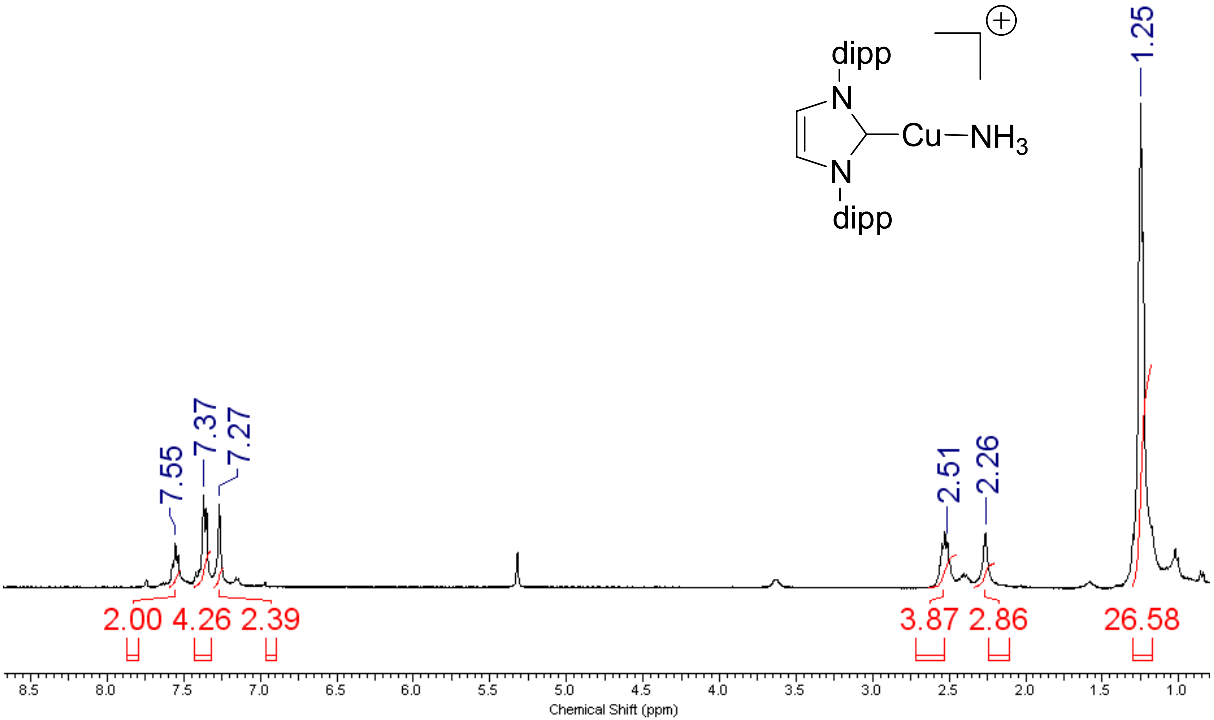


Figure S1. ^{1}H NMR spectrum (CD_2Cl_2) of a quickly evaporated (high vacuum pump) sample of the reaction mixture before aqueous treatment highlighting the formation of a major species **3**.

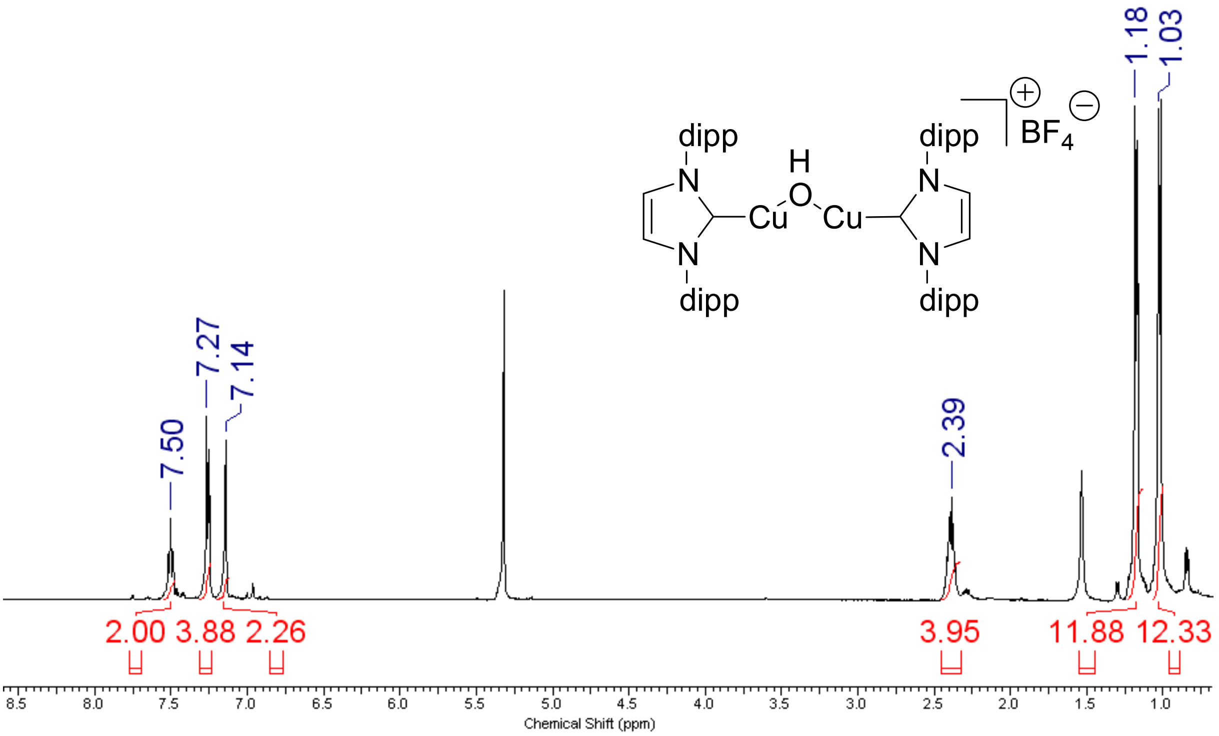


Figure S2. ^{1}H NMR spectrum of crude **1** after aqueous treatment of the solution corresponding to the spectrum displayed in figure S1.

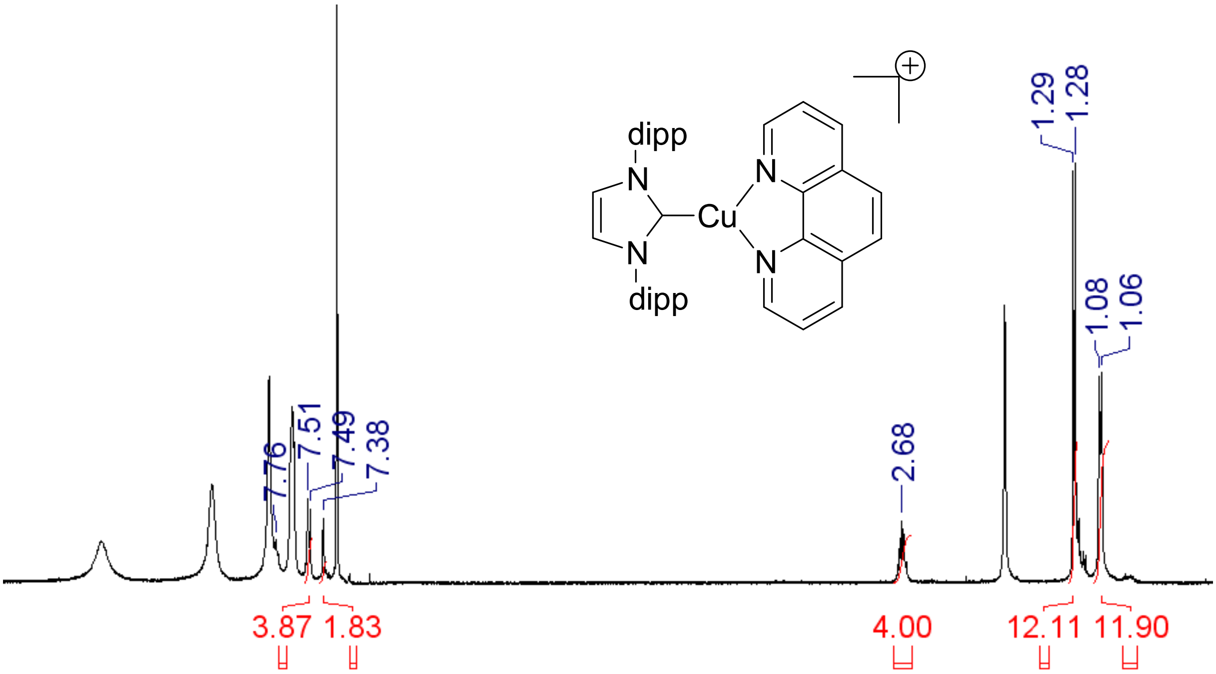


Figure S3. ^{1}H NMR spectrum of **1** after treatment with 10 equiv of phen. Marked peaks correspond to [IPr(Phen)]$^+$. Broad peaks correspond to phen in dynamic equilibrium between bound and free sites.

X-ray cristallography

X-ray diffraction data was collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[1] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[2] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[3]

The crystal data collection and refinement parameters are given in Table S1.

CCDC 989122 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

---

1) Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, **1997**.

2) Sheldrick, G. M. SHELXL-97, Program for the refinement of crystal structures from diffraction data, University of Göttingen, Göttingen, Germany, **1997**.

3) Farrugia, L. J. *J. Appl. Cryst.*, **1999**, *32*, 837.

Table S1. Crystallographic data and structure refinement details for compound **1**.

Compound	**1**
Formula	$C_{54} H_{73} Cu_2 N_4 O; B F_4$
M_r	1008.05
Crystal size, mm^3	0.26 x 0.23 x 0.22
Crystal system	monoclinic
Space group	$P\ 2_1/n$
a, Å	10.5133(6)
b, Å	27.0087(15)
c, Å	18.8062(10)
α, °	90
β, °	93.125(2)
γ, °	90
Cell volume, $Å^3$	5332.1(5)
Z	4
T, K	100(1)
F_{000}	2128
μ, mm^{-1}	0.851
θ range, °	1.32 – 35.07
Reflection collected	93 365
Reflections unique	23 121
R_{int}	0.0363
GOF	1.025
Refl. obs. ($I>2\sigma(I)$)	16 438
Parameters	656
wR_2 (all data)	0.1206
R value ($I>2\sigma(I)$)	0.0444
Largest diff. peak and hole (e-.$Å^{-3}$)	-0.871; 1.083