

A Dicopper(I)-Dimesoionic Carbene Complex as a Click Catalyst: Mechanistic Implications

Julia Beerhues,^a Kevin Fauché,^b Federico Cisnetti,^b Biprajit Sarkar,^{*a} Arnaud Gautier^{*b}

Abstract:

A dimesoionic carbene and acetate-bridged dicopper(I) complex is synthesized and fully characterized. This complex is a potent pre-catalyst for the azide-alkyne cycloaddition reaction. A full kinetic investigation shows a first order in azide and a catalyst order inferior to one due to an equilibrated dimerization of the catalyst.

Table of contents.

Experimental Section.....	2
NMR Spectra.....	3
Single-Crystal X-Ray Diffraction Data & Crystal Structure.	5
Catalysis.....	9
Substrate Scope & Screening.	9
Rate low.....	11
Re-calculation of the kinetics curves using calculated k and Ke values.....	12

Experimental Section

NMR Spectra.

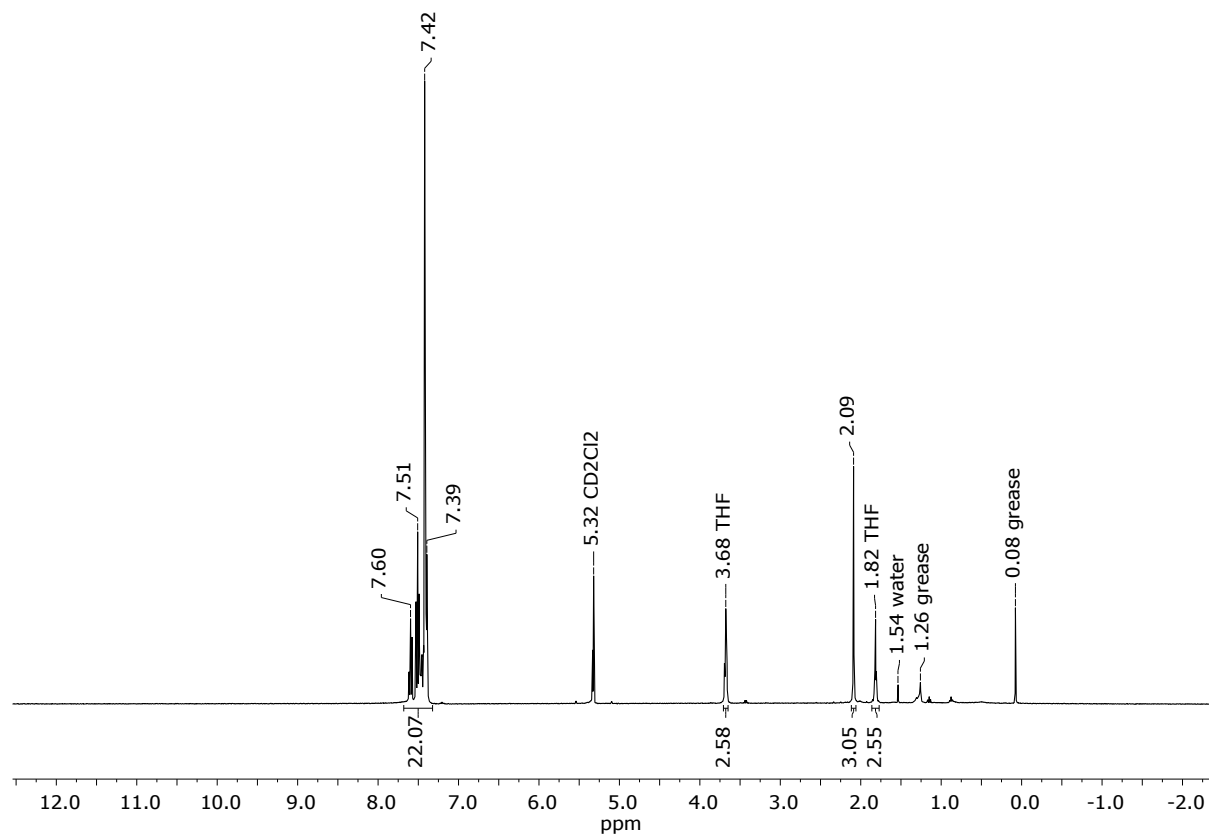


Figure S3: ¹H NMR spectrum of [1]OTf in CD₂Cl₂.

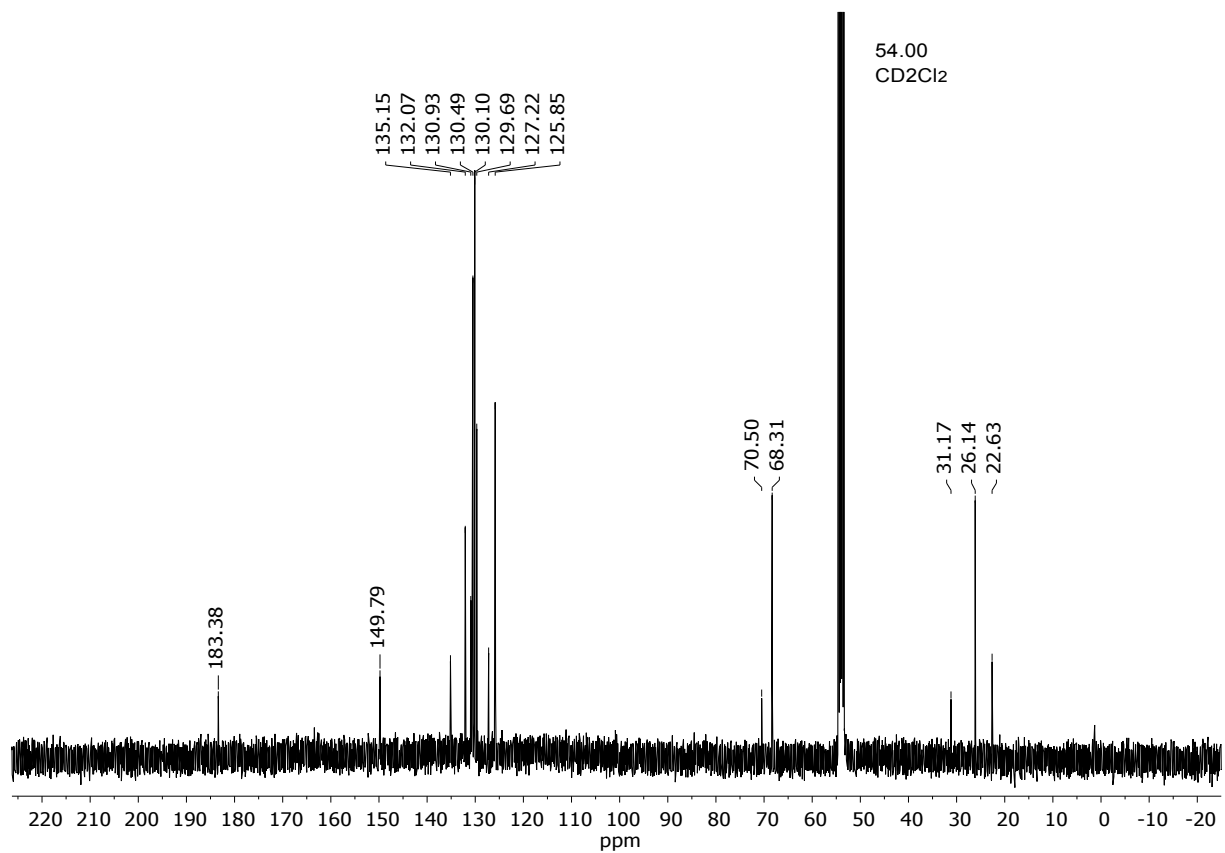


Figure S4: ¹³C NMR spectrum of [1]OTf in CD₂Cl₂.

Single-Crystal X-Ray Diffraction Data & Crystal Structure.

Table S5: Crystallographic details for [1]OTf.

	[[1]OTf · 0.5 CH ₂ Cl ₂ , Pentane]
Chemical formula	C32.50 H26 Cl Cu2 F3 N6 O5 S
<i>Mr</i>	832.18
Crystal system	Orthorhombic, Pca2 ₁
Space group	
<i>a</i> (Å)	19.1009(15)
<i>b</i> (Å)	18.6389(13)
<i>c</i> (Å)	20.5642(15)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	7321.3(9)
<i>Z</i>	8
Density (g cm ⁻³)	1.510
<i>F</i> (000)	3368
Radiation Type	Mo K α
μ (mm ⁻¹)	1.354
Crystal size	0.50 x 0.01 x 0.01
Meas. Refl.	83594
Indep. Refl.	13047
Obsvd. [<i>I</i> > 2 σ (<i>I</i>)] refl.	11969
<i>R</i> _{int}	0.0340
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.0349, 0.0992, 1.033
$\Delta\rho$ _{max} , $\Delta\rho$ _{min} (e Å ⁻³)	0.682, -0.715

Table S6: Selected bond lengths (Å) and angles (°) for [1]OTf.

Atoms	[1 · 0.5 CH ₂ Cl ₂ , Pentane]
Bond lengths	
Cu1-Cu2	2.7608(8)
Cu1-C1	1.867(4)
Cu2-C16	1.871(5)
Cu1-O1	1.865(3)
Cu2-O2	1.871(3)
O1-C30	1.263(6)
O2-C30	1.272(6)
Angles	
C1-Cu1-O1	172.59(17)
O2-Cu2-C16	172.25(17)
N1-C15-N4	109.7(4)

Figure S7: ORTEP plot of [1]OTf. Hydrogen atoms, solvent molecules and counter ions are omitted for clarity. Thermal ellipsoids are shown at a probability level of 50%.

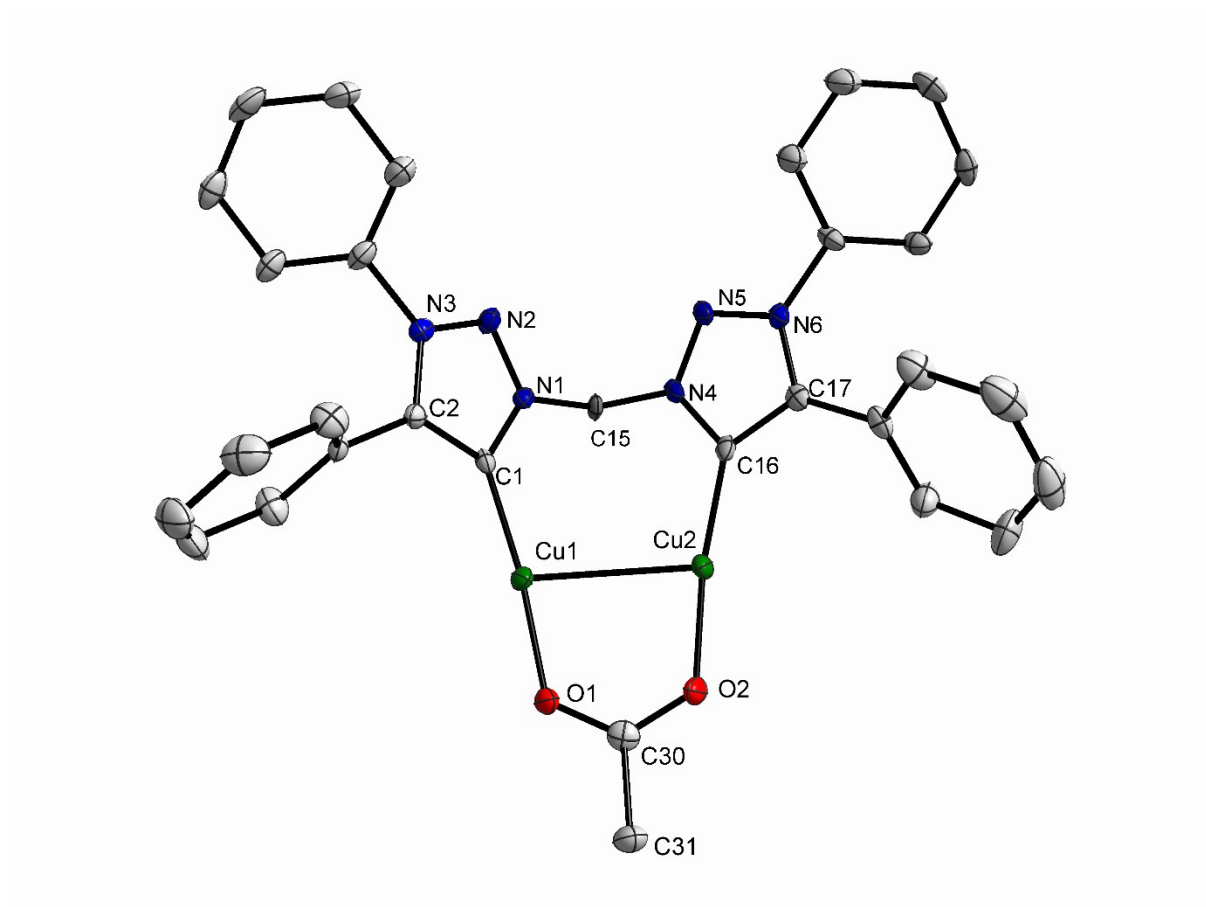
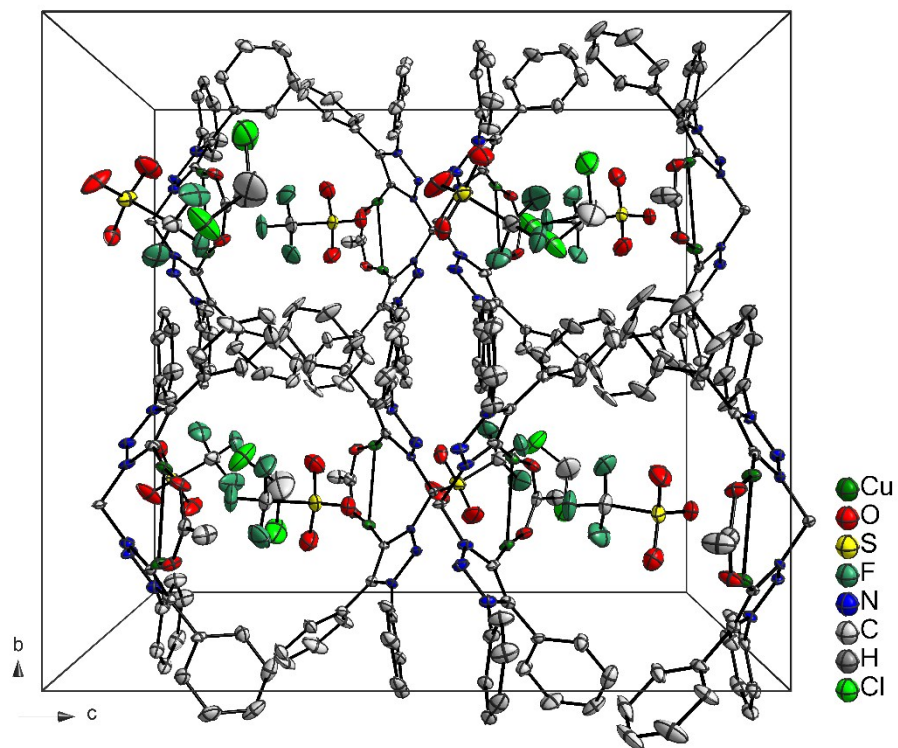


Figure S8: ORTEP representation of the unit cell of [1]OTf (view along a axis). Hydrogen atoms are omitted for clarity.



Catalysis.

Substrate Scope & Screening.

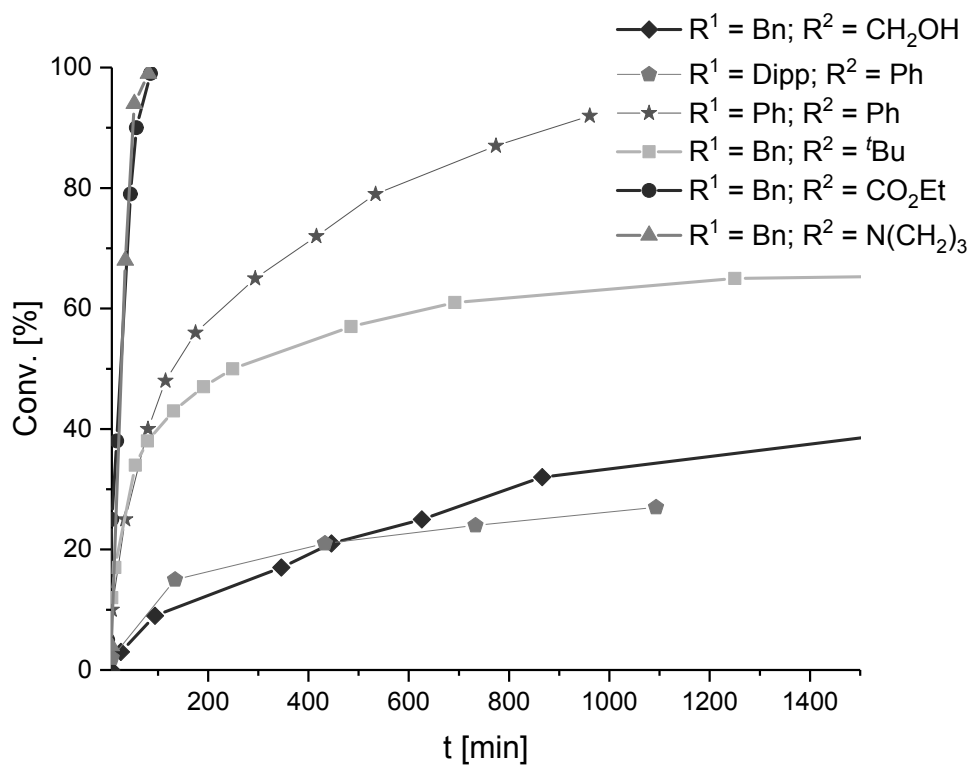


Figure S9: Conversion of the reaction vs. time.

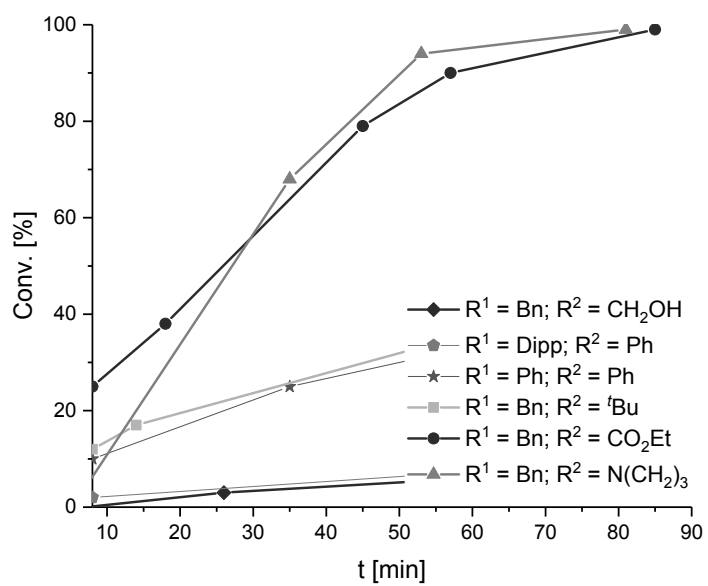
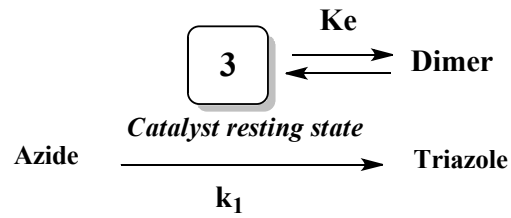


Figure S10: Conversion of the reaction vs. time (zoom).

Rate low.



Equilibrium constant:

$$k_e = \frac{[Dimer]}{[3]^2}; [Dimer] = Ke.[3]^2$$

Conservation of the catalyst (C_0 is the total amount of catalyst added in the reaction vessel):

$$C_0 = [3] + 2.[Dimer]$$

Thus:

$$2.Ke.[3]^2 + [3] - C_0 = 0$$

$$[3] = \frac{-1 + \sqrt{1 + 8.KeC_0}}{4.Ke}$$

The rate is:

$$v = -\frac{\partial[Azide]}{\partial t} = k_{obs}[Azide] = k.[3].[Azide] = k \cdot \frac{-1 + \sqrt{1 + 8.KeC_0}}{4.Ke} \cdot [Azide]$$

$$\frac{\partial[Azide]}{[Azide]} = -k \cdot \frac{-1 + \sqrt{1 + 8.KeC_0}}{4.Ke} \cdot \partial t$$

$$[Azide]_t = [Azide]_0 \cdot e^{-\left(k \cdot \frac{-1 + \sqrt{1 + 8.KeC_0}}{4.Ke}\right) \cdot t}$$

$$\text{With } k_{obs} = k \cdot \frac{-1 + \sqrt{1 + 8.KeC_0}}{4.Ke}$$

Remarks:

1– When K_e dominates:

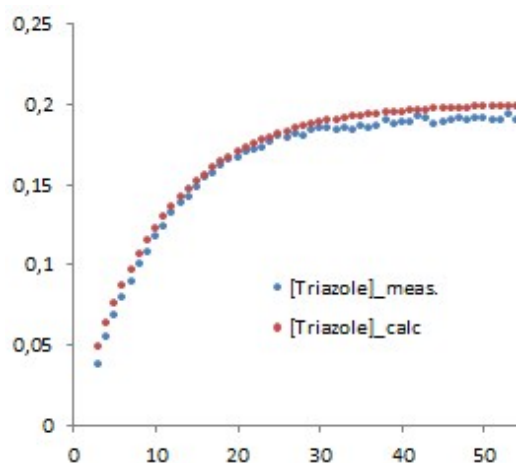
$$v = k \cdot \frac{2 \cdot \sqrt{2 \cdot K_e C_0}}{4 \cdot K_e} \cdot [Azide] = k \cdot \frac{\sqrt{C_0}}{\sqrt{2 \cdot K_e}} \cdot [Azide] : \text{The catalyst order is 0.5.}$$

2– When K_e is small, using Taylor's formula ($\sqrt{1+x} \approx 1 + x/2$):

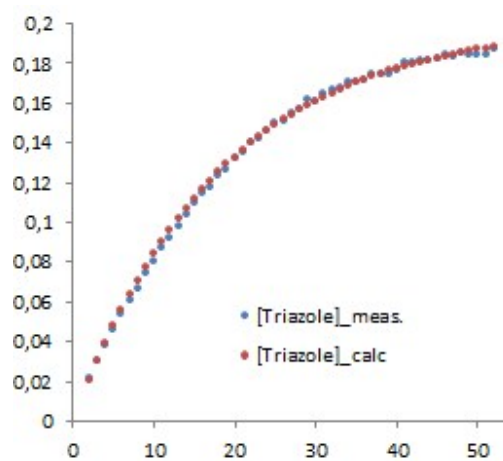
$$v = k \cdot \frac{-1 + 1 + 4 \cdot K_e C_0}{4 \cdot K_e} \cdot [Azide] = k \cdot C_0 \cdot [Azide] : \text{The catalyst order is 1.}$$

Re-calculation of the kinetics curves using calculated k and Ke values.

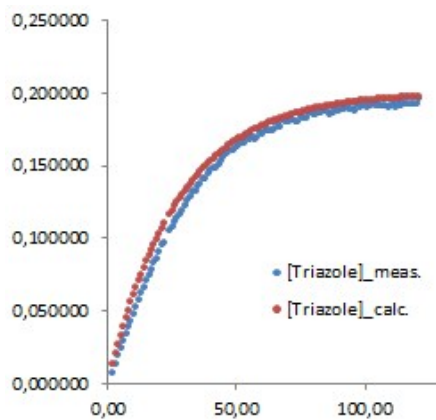
$[1]_0 = 1 \text{ mol-\%}$



$[1]_0 = 0.5 \text{ mol-\%}$



$[1]_0 = 0.31 \text{ mol-\%}$



$[1]_0 = 0.15 \text{ mol-\%}$

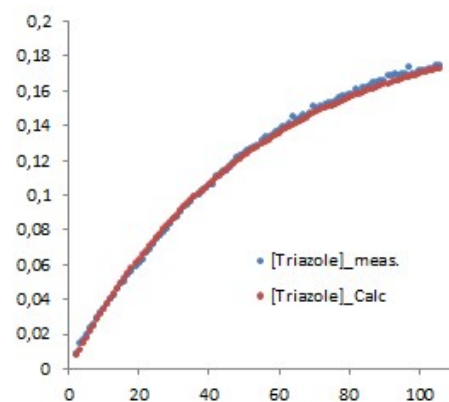


Figure S13: Comparison of calculated and measured values.