Supporting information for the manuscript

Must *N*-Heterocyclic Carbene be a Terminal Ligand?

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General Considerations. Except the *N*-allylbenzothiazolium iodide preparation, all experiments were performed under inert Ar atmosphere using a Labmate glove box or by Schlenk techniques. THF and diethyl ether were distilled over benzophenone sodium-ketyl and kept under Ar. Benzothiazole was purchased from Sigma–Aldrich and distilled prior to use. Allyl iodide, NaOtBu and CuCl were purchased from Sigma–Aldrich and used as received. *N*-allylbenzothiazolium iodide and CuOtBu were prepared according to literature methods.¹ ¹H- and ¹³C-NMR spectra were

recorded on Bruker AMX 500 spectrometers using Me₄Si as an internal standard. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

Preparation of $[Cu_2(\mu-I)_2(AllBzThzylid)_3]$ (1). А suspension of N-allylbenzothiazolium iodide (152 mg, 0.5 mmol) in THF (8 ml) was added to the solution of CuOtBu (68 mg, 0.5 mmol) in THF (2 ml). The suspension turned to a clear solution after a few minutes, followed by yellow precipitation. It was then stirred for 1 h, and filtered. The yellow precipitate collected was washed with Et₂O to give **1**. Yield: 81 mg (0.089 mmol, 54%). ¹H-NMR (500 MHz, CD₂Cl₂): δ 7.82 (d, 3H, J = 7.6 Hz, Aryl-H), 7.65 (d, 3H, J = 8.2 Hz, Aryl-H), 7.50 (m, 3H, Aryl-H), 7.43 (m, 3H, Aryl-H), 6.10 (m, 3H, CH), 5.52 (m, 6H, CH=CH₂), 5.24 (m, 6H, CH2). ¹³C-{¹H} NMR: δ 219.4 (NCS), 143.9 (s, Aryl-C), 135.0 (s, Aryl-C), 131.6 (s, CH=CH2), 126.6 (s, Aryl-C), 124.9 (s, Aryl-C), 122.4 (s, Aryl-C), 118.9 (s, CH=CH₂), 114.8 (s, Aryl-C), 56.7 (s, CH2). Anal. Calcd for 1, C₃₀H₂₇Cu₂I₂N₃S₃: C, 39.74; H, 3.00; N, 4.63. Found: C, 39.89; H, 3.01; N, 4.56.

Crystal Structure Analyses. $C_{30}H_{27}Cu_2I_2N_3S_3$, Mr = 906.61, triclinic, *P-1*, a = 8.9141(5) Å, b = 19.3304(12) Å, c = 19.5110(12) Å, a = 98.9550(10)^{\circ}, $\beta = 102.7300(10)^{\circ}$, $\gamma = 97.0770(10)^{\circ}$, V = 3195.8(3) Å³, Z = 4, $\rho = 1.884$ Mg/m³, $\mu = 3.484$ mm⁻¹, T = 100(2) K, F(000) = 1760, $2\theta_{max} = 50.00^{\circ}$, 18542 reflections measured, 11155 unique reflections [Rint = 0.0269], GOF = 1.145, R [*I*>2 σ *I*]: R1 = 0.0524, wR2

= 0.1320, λ (MoKa) = 0.71073 Å, crystal dimensions: 0.42 x 0.06 x 0.05 mm³. CCDC-761797 contains the supplementary crystallographic data of this paper. These data can be obtained free of charge from the Cambridge Crystallographic

Calculation Details. All the DFT calculations have been performed with the SIESTA package.² The utilized exchange-correlation functional was at the level of the Perdew-Burke-Ernzerf (PBE) flavor of the generalized-gradient approximation (GGA).³ The interaction between atomic cores and valence electrons was described by Troullier-Martins norm-conserving pseudopotentials.⁴ A numerical atomic orbital basis set of the double- ξ plus polarization was utilized, with a radii confinement of the orbitals equivalent to an energy shift of 0.01 eV.⁵ The kinetic energy cutoff for the real-space mesh employed to represent the density was specified to be 200 Ry. Geometry optimization was implemented with the L-BFGS method until all the remaining forces acting on each relaxed coordinate were below 0.01 eV/Å. Transition states (TSs) of all the catalytic reactions were searched with our recently developed constrained-Broyden-minimization method.⁶ Vibrational frequencies were computed by diagonalizing the Hessian matrix which was constructed numerically using the finite difference method with the step size of ± 0.02 Å along each Cartesian coordinate. Convergence of reported reaction energies and barriers was verified with regard to the basis set, energy shift and kinetic energy cutoff.



S-Figure: Charge density difference contour plot before and after the NHC ligand bonding with $[Cu_2(\mu-I)_2(AllBzThzylid)_2]$. The isosurface is +/- 0.01 e/A³. Red: electron accumulation region; Yellow: electron depletion region.

Distance / angle	DFT	Expt.
Cu(1)-Cu(2)	2.440	2.412(2)
C(21)-Cu	1.995(Cu1), 2.223(Cu2)	1.978(9), 2.285(9)
I(1)-Cu(1)	2.745	2.752 (1)
I(1)-Cu(2)	2.989	2.926(1)
C(1)-Cu(1)	1.905	1.901(9)
C(11)-Cu(2)	1.920	1.926(9)
C(21)-Cu(1)-Cu(2)	59.157	61.8(3)
Cu(3)-Cu(4)	2.704	2.753(2)
C(51)-Cu(4)	1.932	1.921(9)
C(51)-Cu(3)	3.206	3.220
I(3)-Cu(4)	2.888	2.881(1)
I(4)-Cu(4)	2.871	2.798(1)
C(41)-Cu(4)	1.930	1.928(9)
C(31)-Cu(3)	1.905	1.935(9)
C(51)- $Cu(4)$ - $Cu(3)$	85.765	85.1(3)

 Table 1 Comparison between the calculated structures from DFT and those from experiment

References

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