

Supporting Information

For

**Heterobimetallic Activation of Dioxygen: Characterization and Reactivity of Novel
Cu(I)-Ge(II) Complexes**

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X-ray Crystallography. Crystal data and collection parameters are listed in Table S1. Crystals of appropriate size were chosen and placed in oil on the tip of a 0.1 mm diameter glass fiber and mounted on a Bruker or Siemens SMART Platform CCD diffractometer for data collection at 173(2) K. Data collections were carried out using MoK α radiation (graphite monochromator) with a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. Four major sections of frames were collected with 0.30° steps in ω at 4 different ϕ settings and a detector position of -28° in 2θ . The intensity data were corrected for absorption and decay (SADABS).¹ Final cell constants were calculated from the xyz centroids of strong reflections from the actual data collection after integration (SAINT).² Please refer to the CIFs for additional crystal and refinement information.

The structures were solved by direct methods using SHELXL-97³ software. Full-matrix least squares/difference Fourier cycles were performed using SHELXL-97³ software, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Space groups were determined based on systematic absences and intensity statistics. Pertinent details for each structure are noted below; see CIFs for full crystallographic information.

[L^{Me2}Cu]₂. Yellow block crystals suitable for X-ray crystallography were grown from pentane at -20°C . The space group determined by XPREP was $P\bar{1}$, and all non-hydrogen atoms were located during the refinement. Large solvent voids were present in the crystal, and electron density was located consistent with disordered pentane. Attempts to model the solvent disorder were unsuccessful, however, and the SQUEEZE function of PLATON⁴ was used to remove the effects of the disordered solvent. A void space of 415.8 Å³ per unit cell was detected, and 46 electrons per void space were removed, consistent with approximately 0.64 pentane molecules per unit cell. The final solution converged with $R_1 = 0.0301$ and $wR_2 = 0.0876$ (F^2 , all data). A similar structure was obtained by Warren et. al. in which the molecule crystallized in the monoclinic space group $P2(1)/c$.⁵

L^{Me2}Cu-Ge[(NMe)₂(CH)₂] (1a). Large yellow block crystals suitable for X-ray crystallography were grown from pentane at -20°C . Several crystals were mounted and all were determined to be twinned. The chosen crystal was indexed as a two-component non-merohedral twin using both the programs GEMINI⁶ and CELL NOW.⁷ The twin law used to treat the data was a rotation of 180° in direct space around the a-axis. The corrected data was integrated using SAINT² and absorption corrected with TWINABS¹ and subsequently treated with STRIP

¹ An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **1995**, *A51*, 33.

² SAINT V6.45A, Bruker Analytical X-Ray Systems, Madison, WI (2001).

³ SHELXTL V6.12, Bruker Analytical X-Ray Systems, Madison, WI (2000).

⁴ Spek, A. L. (2002). *Platon. A Multipurpose Crystallographic Tool*. Utrecht University, The Netherlands

⁵ Amisial, L. D.; Dai, X.; Kinney, R. A.; Krishnaswamy, A.; Warren, T. H. *Inorg. Chem.* **2004**, *43*, 6537.

⁶ GEMINI, R. A. Sparks, Burker AXS, Madison, WI 2000.

⁷ CELL NOW, G. Shedrick, 2005.

REDUNDANT⁸ to remove redundant reflections from the non-merohedral twinned diffraction data. The space group determined using XPREP was P2(1)/c, and refinement resulted in the location of all non-hydrogen atoms. The structure converged with nearly equal mass twin components (BASF = 0.501) and a final value of R1 = 0.0286 and wR2 = 0.0731 (F², all data).

L^{Me2}Cu-Ge[N(SiMe₃)₂]₂ (1b). Orange blocks suitable for X-ray crystallography were grown by slow evaporation of a concentrated acetonitrile/Et₂O solution at -20 °C. The space group P2(1)/c was determined using XPREP, and all non-hydrogen atoms were located during the refinement. The crystals were determined to consist of a non-merohedral twin, and the twin law [-1 0 0 0 -1 0 0 0 1] was used, with a final BASF of 0.403. The two trimethylsilyl groups of the germylene ligand are disordered over two positions and were modeled over the two positions with occupancy factors of 63:37. The final solution converged to R1 = 0.0288 and wR2 = 0.0723 (F², all data).

L^{Me2}Cu-PPh₃ (3). Large colorless block crystals suitable for X-ray crystallography were grown from pentane at -20 °C. The space group P2(1)/c was determined using XPREP and the final solution converged to R1 = 0.0291 and wR2 = 0.0813 (F², all data).

L^{Me2}Cu-NHC (4). Large colorless block crystals suitable for X-ray crystallography were grown from pentane at -20 °C. The space group P2(1)/n was determined using XPREP and the final solution converged to R1 = 0.0335 and wR2 = 0.0822 (F², all data).

Table S1. Selected crystallographic data and collection parameters.

⁸ STRIP REDUNDANT, W. W. Brennessel and V.G. Young, Jr., 2003, unpublished.

	$[L^{Me_2}Cu]_2$	$L^{Me_2}Cu-Ge[(NMe)_2(CH)_2]$	$L^{Me_2}Cu-Ge[N(SiMe_3)_2]_2$	$L^{Me_2}Cu-PPh_3$	$L^{Me_2}Cu-NHC^{Mes_2}$
formula	$C_{42}H_{50}N_4Cu_2$	$C_{41}H_{50}N_4GeCu$	$C_{32}H_{50}N_4Si_4GeCu$	$C_{39}H_{40}N_2PCu$	$C_{42}H_{49}N_4Cu$
fw	737.94	734.98	762.35	631.24	673.39
cryst syst	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$	$P2(1)/n$
a (Å)	11.0407(10)	11.9187(13)	16.4202(17)	10.488(5)	11.6773(11)
b (Å)	16.4017(15)	12.5273(13)	15.0946(15)	20.258(5)	21.0164(19)
c (Å)	17.3877(16)	15.4357(17)	16.8570(17)	16.272(5)	15.6297(14)
α (deg)	89.331(2)	71.776(2)	90	90	90
β (deg)	78.885(2)	70.134(20)	90.080(2)	104.362(5)	107.941(2)
γ (deg)	88.813(2)	62.922(2)	90	90	90
V (Å ³)	3088.9(5)	1895.3(4)	4178.1(7)	3354(2)	3649.2(6)
Z	3	2	4	4	4
T(K)	173	173	173	173	173
ρ_{calcd} (Mg/m ³)	1.190	1.288	1.212	1.250	1.226
θ range (deg)	1.72 to 25.05	1.97 to 26.38	1.21 to 25.07	1.64 to 25.05	1.68 to 25.05
μ (mm ⁻¹)	1.064	1.387	1.369	0.728	0.633
reflens collcd	30785	37312	39437	32690	35670
unique reflens	10917	7696	7344	5939	6463
params	667	437	517	394	436
R1, wR2 (for $I > 2\sigma(I)$)	0.0301, 0.0852	0.0286, 0.0702	0.0288, 0.0694	0.0291, 0.0719	0.0335, 0.0788
GOF	0.981	1.014	1.036	1.061	1.053
largest peak, hole (e. Å ³)	0.380, -0.329	0.529, -0.445	0.346, -0.227	0.381, -0.255	0.285, -0.330

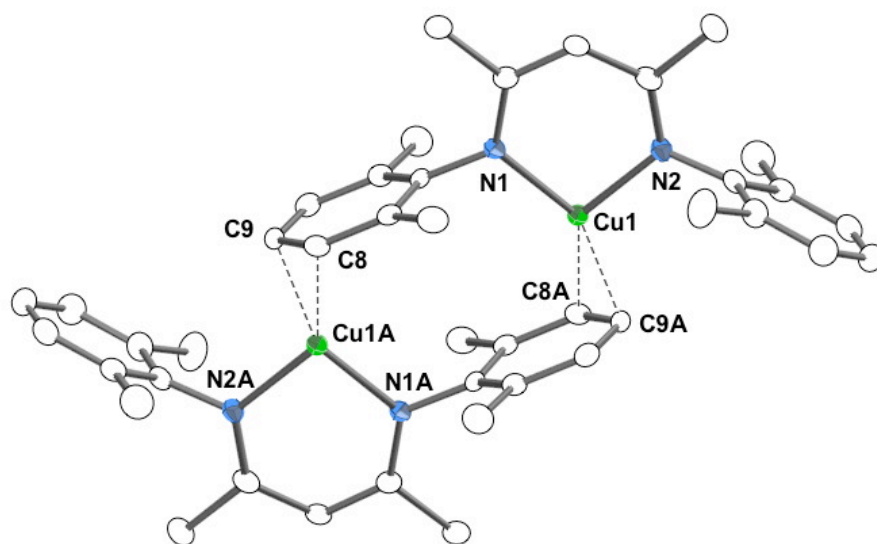
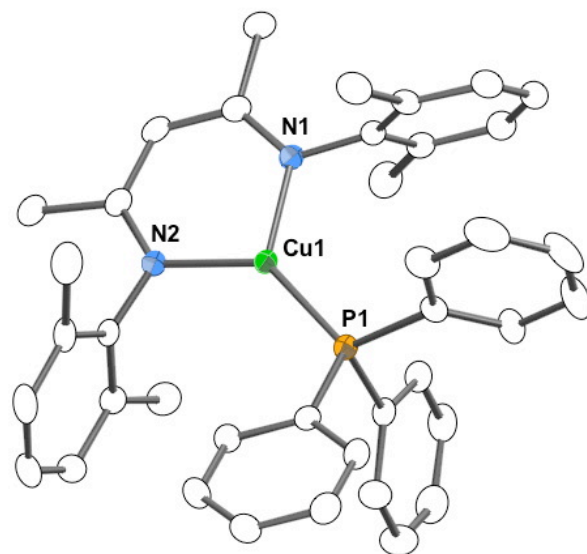
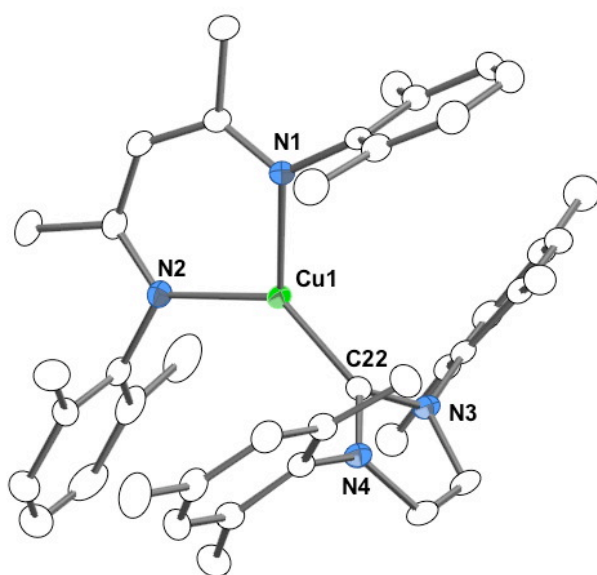


Figure S1. Molecular structure of $[L^{Me_2}Cu]_2$ with heteroatoms labeled, all atoms as 50% ellipsoids, and H-atoms omitted for clarity. Selected bond distances (Å): Cu1-N1, 1.9101(16); Cu1-N2, 1.9629(16); Cu1-C9A, 2.0467(19); Cu1-C8A, 2.247(2); C8A-C9A, 1.395(3).



(a)



(b)

Figure S2. Molecular structures of (a) $L^{\text{Me}_2}\text{Cu}(\text{PPh}_3)$ (**3**) and (b) $L^{\text{Me}_2}\text{Cu}(\text{NHC}^{\text{Mes}_2})$ (**4**) with heteroatoms labeled, all atoms as 50% ellipsoids, and H-atoms omitted for clarity. Selected bond distances (\AA): (a) Cu1-N1, 1.9553(17); Cu1-N2, 1.9465(17); Cu1-P1, 2.1664(8). (b) Cu1-N1, 1.9950(15); Cu1-N2, 2.0022(16); Cu1-C22, 1.9181(19).

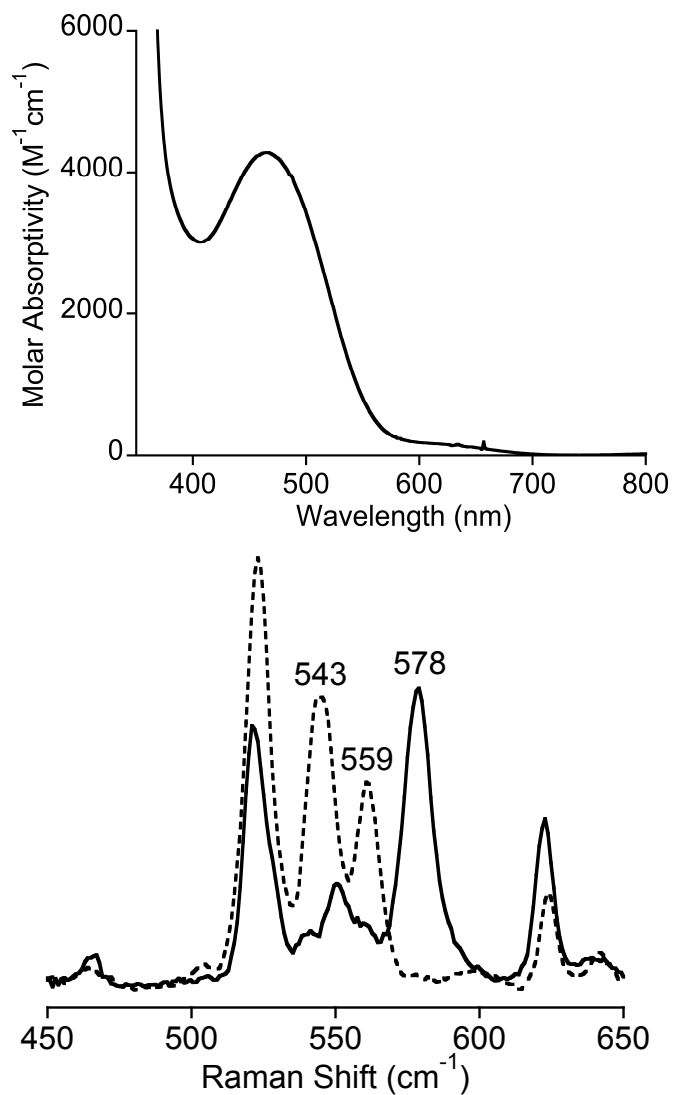


Figure S3. (top) UV-vis spectra of $L^{iPr_2}Cu(\mu-O)_2Ge[N(SiMe_3)_2]_2$ in toluene at $-80\text{ }^\circ\text{C}$. (bottom) Resonance Raman spectra ($\lambda_{ex} = 488\text{ nm}$) of frozen toluene solutions (77K) of $L^{iPr_2}Cu(\mu-O)_2Ge[N(SiMe_3)_2]_2$ (solid line for $^{16}O_2$, dashed line for $^{18}O_2$, * denotes solvent peaks).

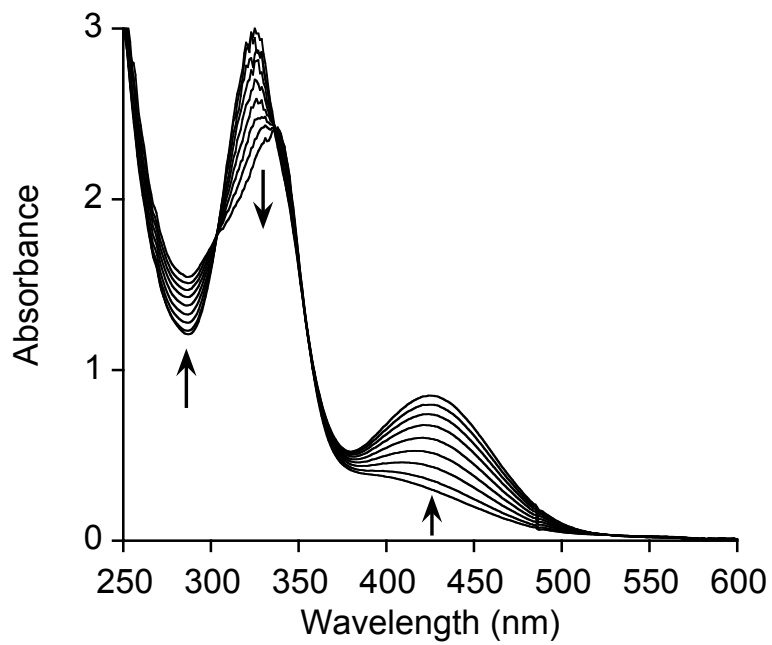


Figure S4. UV-vis spectra showing the conversion of unhindered $L^{\text{Me}_2}\text{CuO}_2$ to $[(L^{\text{Me}_2}\text{Cu})_2(\mu\text{-O})_2]$ in THF at $-65\text{ }^\circ\text{C}$.