Supporting Information

The Bis(μ–oxo) Dicopper(III) Species of the Simplest Peralkylated Diamine: Enhanced Reactivity towards Exogenous Substrates

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I. Full Gaussian 03 Reference

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.;, *Gaussian 03, Revision C.02*. Gaussian, Inc.: Wallingford, CT, 2004.

II. Titration of the O species with FcCOOH

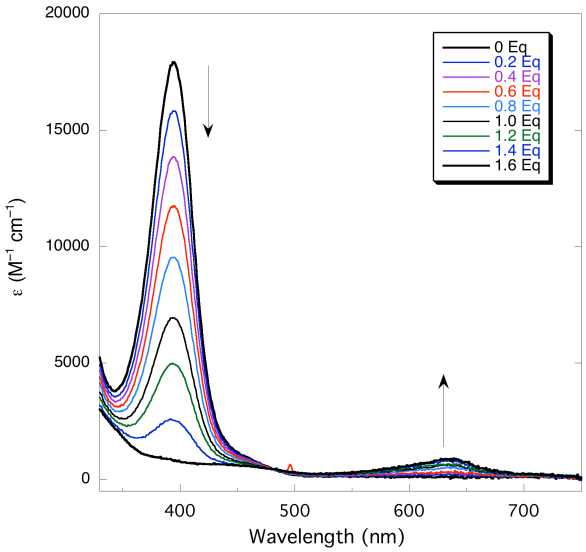

Figure S1. Titration of the TMED **O** species with ferrocene monocarboxylic acid (FcCOOH). Two equivalents of FcCOOH would correspond to the full formation of the **O** species. The feature at ca. 650 nm is due to the ferrocenium carboxylate zwitterion that is formed.

III. X-ray Absorption Spectroscopy

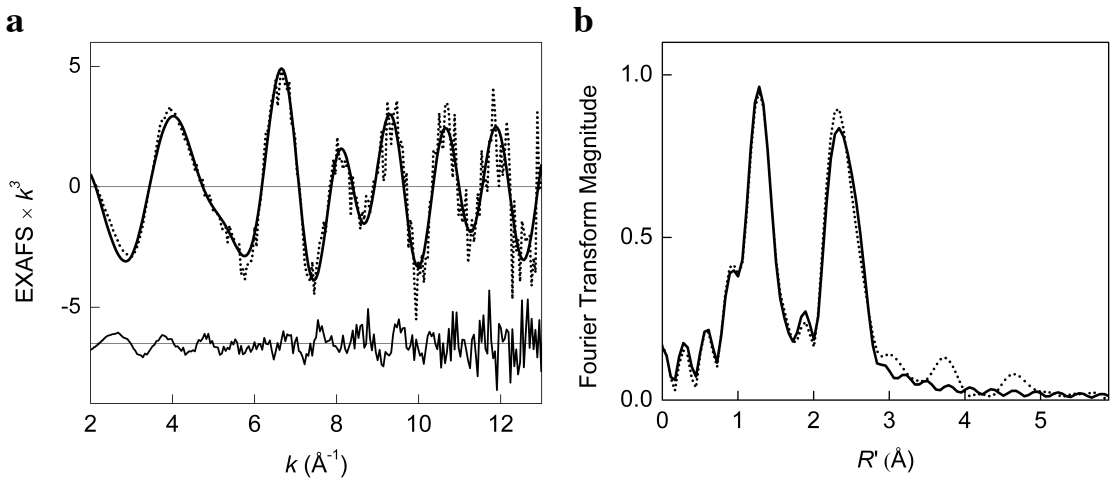

Figure S2. (a) Cu K-edge k^3-weighted EXAFS data for **O**$(CF_3SO_3)_2$ (top) with offset fit residual (bottom) and (b) corresponding nonphase shift corrected Fourier transforms. Data (·····); fit (—).

Table S1. EXAFS Fit Results for **O**$(SbF_6)_2$ and **O**$(CF_3SO_3)_2$.[a]

Sample		R (Å)	σ^2 (Å^2)	ΔE_0 (eV)	F^b
O$(SbF_6)_2$	2 O	1.80	0.0038	-10.6	0.250
	2 N	1.96	0.0041		
	1 Cu	2.74	0.0026		
	6 C	2.77	0.0207		
O$(CF_3SO_3)_2$	2 O	1.80	0.0032	-11.2	0.358
	2 N	1.96	0.0030		

1 Cu	2.75	0.0025
6 C	2.76	0.0217

[a] All fits were performed over the k range of 2-13 Å^{-1}. The estimated uncertainty in R is ± 0.02 Å; the uncertainty in N is ~25%. [b] The goodness of the fit is defined as $F = [\Sigma(k^6(\chi_{exptl} - \chi_{calcd})^2)/(\Sigma k^6 \chi_{exptl}^2)]^{½}$.

IV. Thermal Decomposition Kinetics

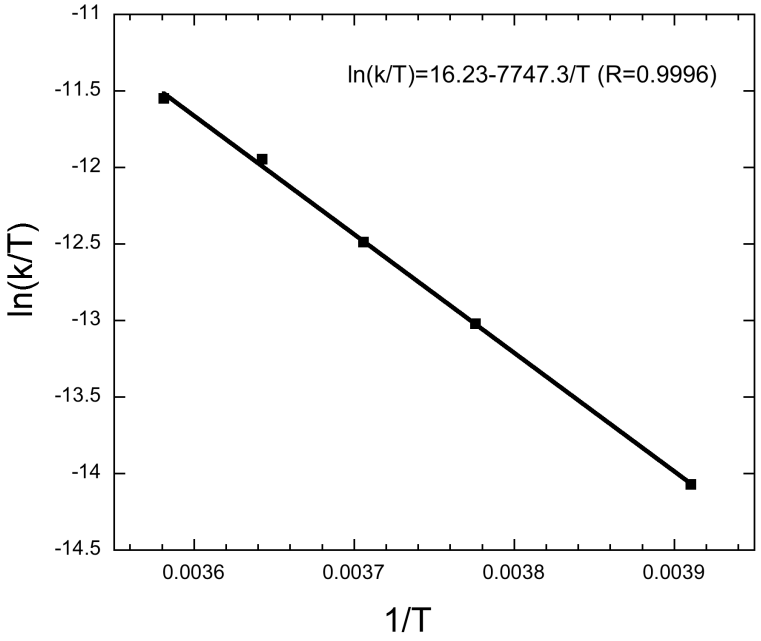

Figure S3. Eyring plot of the decomposition kinetics of the TMED **O** species (acetone, [Cu] = 1mM, $CF_3SO_3^-$).

V. DFT

Table S2. Mulliken population analysis of selected MOs of the TMED **O** species

MO	Energy (eV)	%Cu	%O	%N	%Rest
LUMO+1	-9.74	36	35	23	6
LUMO	-9.88	35	44	16	6
HOMO-1	-13.95	7	40	36	17
HOMO-5	-14.99	11	24	27	38

Table S3. Cartesian coordinates of DFT-optimized D_2 conformation of the **O** species (B3LYP/6-31g(d), gas phase)

Cu	-1.36137400	0.00000000	0.00000000
Cu	1.36137400	0.00000000	0.00000000

O	0.00000000	1.15530200	0.00000000
O	0.00000000	-1.15530200	0.00000000
N	-2.74659700	-1.37297700	0.05291100
N	-2.74659700	1.37297700	-0.05291100
N	2.74659700	1.37297700	0.05291100
N	2.74659700	-1.37297700	-0.05291100
C	-4.04685700	0.70306800	0.28886200
C	-2.46719300	-2.49110600	-0.89356300
C	-2.46719300	2.49110600	0.89356300
C	4.04685700	0.70306800	-0.28886200
C	4.04685700	-0.70306800	0.28886200
C	2.46719300	2.49110600	-0.89356300
C	-2.73953700	-1.89706100	1.45255200
C	-2.73953700	1.89706100	-1.45255200
C	2.46719300	-2.49110600	0.89356300
C	2.73953700	1.89706100	1.45255200
C	2.73953700	-1.89706100	-1.45255200
C	-4.04685700	-0.70306800	-0.28886200
H	-4.13136100	0.68153200	1.37833400
H	-4.88798900	1.29219100	-0.09406300
H	4.88798900	1.29219100	0.09406300
H	4.13136100	0.68153200	-1.37833400
H	4.13136100	-0.68153200	1.37833400
H	4.88798900	-1.29219100	-0.09406300
H	3.48679600	2.69116900	1.55820200
H	1.74704200	2.29430000	1.66878400
H	2.96801900	1.09887500	2.16230900
H	3.48679600	-2.69116900	-1.55820200
H	2.96801900	-1.09887500	-2.16230900
H	1.74704200	-2.29430000	-1.66878400
H	-1.74704200	-2.29430000	1.66878400
H	-3.48679600	-2.69116900	1.55820200
H	-2.96801900	-1.09887500	2.16230900
H	-1.74704200	2.29430000	-1.66878400
H	-2.96801900	1.09887500	-2.16230900
H	-3.48679600	2.69116900	-1.55820200
H	2.44559200	-2.11062200	1.91717700
H	3.25033000	-3.25250700	0.80669900
H	1.49734500	-2.92416900	0.65072000
H	2.44559200	2.11062200	-1.91717700
H	1.49734500	2.92416900	-0.65072000
H	3.25033000	3.25250700	-0.80669900
H	-2.44559200	2.11062200	1.91717700
H	-3.25033000	3.25250700	0.80669900
H	-1.49734500	2.92416900	0.65072000
H	-2.44559200	-2.11062200	-1.91717700
H	-3.25033000	-3.25250700	-0.80669900
H	-1.49734500	-2.92416900	-0.65072000
H	-4.88798900	-1.29219100	0.09406300
H	-4.13136100	-0.68153200	-1.37833400