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

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Reaction of the known germylene $Ge[N(SiMe_3)_2]_2$ and a new heterocyclic variant $Ge[(NMes)_2(CH)_2]$ with $[L^{Me2}Cu]_2$ (L^{Me2} = the β-diketiminate derived from 2-(2,6-dimethylphenyl)amino-4-(2,6-dimethylphenyl)imino-2-pentene) yielded novel Cu(I)–Ge(II) complexes $L^{Me2}Cu–Ge[(NMes)_2(CH)_2]$ (**1a**) and $L^{Me2}Cu–Ge[N(SiMe_3)_2]_2$ (**1b**), which were characterized by spectroscopy and X-ray crystallography. The lability of the Cu(I)–Ge(II) bond in **1a** and **b** was probed by studies of their reactivity with benzil, PPh_3, and a N-heterocyclic carbene (NHC). Notably, both complexes are cleaved rapidly by PPh_3 and the NHC to yield stable Cu(I) adducts (characterized by X-ray diffraction) and the free germylene. In addition, the complexes are highly reactive with O_2 and exhibit chemistry which depends on the bound germylene. Thus, oxygenation of **1a** results in scission and formation of thermally unstable $L^{Me2}CuO_2$, which subsequently decays to $[(L^{Me2}Cu)_2(\mu\text{-}O)_2]$, while **1b** yields $L^{Me2}Cu(\mu\text{-}O)_2Ge[N(SiMe_3)_2]_2$, a novel heterobimetallic intermediate having a $[Cu^{III}(\mu\text{-}O)_2Ge^{IV}]^{3+}$ core. The isolation of the latter species by direct oxygenation of a Cu(I)–Ge(II) precursor represents a new route to heterobimetallic oxidants comprising copper.

Efforts to understand the mechanisms of oxidation catalysis[1] are aided by studies aimed at isolating and characterizing metal−oxygen intermediates in proteins[2] and synthetic systems.[3] Such intermediates are often derived from reactions of reduced metal sites with the versatile and abundant reagent O_2, and particular attention has been placed on those species that incorporate a single type of metal ion. For instance, extensive examination of the reactions of O_2 with Cu(I) complexes has led to the identification of a variety of binding motifs and activation pathways of relevance to important biological processes.[4] Mixed-metal systems that operate synergistically to activate O_2 also are of interest, as they are implicated in some synthetically and biologically useful catalytic reactions. Notable examples that involve Cu include Cu−Pd species in Wacker-type oxidations[5] and Cu−Fe intermediates in cytochrome *c* oxidase.[3d,6]

Examples of well-characterized heterobimetallic oxygen intermediates derived from O_2 are rare, however, due in part to the challenges associated with preventing formation of products arising from oxygenation of only one of the two types of metal ions provided in the starting material(s). Nonetheless, mixed heme−Fe/nonheme−Cu species with

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(1) Recent reviews: (a) Punniyamurthy, T.; Velusamy, S.; Iqbal, J. *Chem. Rev.* **2005**, *105*, 2329. (b) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400. (c) *Advances in Catalytic Activation of Dioxygen by Metal Complexes*; Simándi, L. I., Ed.; Kluwer Academic Publishers: Dordrecht, 2003.

(2) Selected reviews, for M = Cu: (a) Solomon, E. I.; Chen, P.; Metz, M.; Lee, S.-K.; Palmer, A. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 4570. (b) Klinman, J. P. *Chem. Rev.* **1996**, *96*, 2541. (c) Solomon, E. I.; Sundaram, U. M.; Machonkin, T. E. *Chem. Rev.* **1996**, *96*, 2563. For M = Fe: (d) Que, L., Jr.; Ho, R. Y. N. *Chem. Rev.* **1996**, *96*, 2607. (e) Wallar, B. J.; Lipscomb, J. D. *Chem. Rev.* **1996**, *96*, 2625. (f) Merkx, M.; Kopp, D. A.; Sazinsky, M. H.; Blazyk, J. L.; Müller, J.; Lippard, S. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2782.

(3) Selected illustrative reviews, for M = Fe: (a) Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L., Jr. *Chem. Rev.* **2005**, *104*, 939. (b) Bois, J. D.; Mizoguchi, T. J.; Lippard, S. J. *Coord. Chem. Rev.* **2000**, *200−202*, 443. (c) McLain, J. L.; Lee, J.; Groves, J. T., In *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Meunier, B., Ed.; Imperial College Press: London, 2000; pp 91−169. (d) Collman, J. P.; Boulatov, R.; Sunderland, C. J.; Fu, L. *Chem. Rev.* **2004**, *104*, 561.

(4) Recent reviews: (a) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, *104*, 1013. (b) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, *104*, 1047. (c) Hatcher, L.; Karlin, K. D. *J. Biol. Inorg. Chem.* **2004**, *9*, 669. (d) Itoh, S. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Amsterdam, 2004; Vol. 8, pp 369−393. (e) Halcrow, M. A. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Amsterdam, 2004; Vol. 8, pp 395−436.

(5) (a) Hosokawa, T.; Takano, M.; Murahashi, S. *J. Am. Chem. Soc.* **1996**, *118*, 399. (b) Hosokawa, T.; Nomura, T.; Murahashi, S. *J. Organomet. Chem.* **1998**, *551*, 387.

(6) (a) Michel, H.; Behr, J.; Harrenga, A.; Kannt, A. *Annu. Rev. Biophys. Biomol. Struct.* **1998**, *27*, 329. (b) Kim, E.; Chufan, E. E.; Kamaraj, K.; Karlin, K. D. *Chem. Rev.* **2004**, *104*, 1077.

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peroxo and oxo bridges have been isolated from reactions of Fe(II)−Cu(I) precursors.[6] In addition, heterobimetallic bis(μ-oxo)CuNi or −CuPd species have been generated by reacting isolable 1:1 Cu/O_2 species[7] or $(PPh_3)_2PdO_2$ with a mononuclear complex of a reduced metal (e.g., Ni(I) or Cu(I), respectively).[8] While this "stepwise" approach toward the synthesis of heterobimetallic oxygen intermediates is attractive, we were intrigued by the reported[9] discoveries that the two metal ions in $(PR_3)_2M{-}Ge[N(SiMe_3)_2]_2$ (M = Pd, Pt) acted together to activate O_2 to afford mixed-metal peroxo and bis(μ-oxo)MGe complexes despite the capability of the M-Ge precursors to cleave to reactive monomeric fragments (e.g., the trappable germylene $Ge[N(SiMe_3)_2]_2$). Reasoning by analogy, we hypothesized that related Cu(I)−Ge(II) compounds might be prepared and that they might react similarly with O_2 to yield novel Cu−Ge oxygen intermediates.

Herein we report the synthesis and structural characterization of Cu(I)−Ge(II) complexes that contain bonds between these metal centers. Studies of the reactivity of these complexes with a variety of reagents show that the nature of the germylene fragment (i.e., the supporting ligands on Ge) is critical for determining whether monomeric fragments are produced or the heterobimetallic nature of the Cu−Ge compound is retained. Notably, we report the characterization of a novel bis(μ-oxo)Cu(III)Ge(IV) species derived from oxygenation of a Cu(I)−Ge(II) precursor, thus demonstrating the feasibility of a new type of direct route to heterobimetallic oxygen intermediates comprising copper.

Experimental Section

All solvents and reagents were obtained from commercial sources and used as received unless noted otherwise. The solvents tetrahydrofuran (THF), toluene, pentane, diethyl ether (Et_2O), and acetonitrile (MeCN) were degassed and passed through solvent purification columns (Glass Contour, Laguna, CA or MBraun) prior to use. The NMR solvents C_6D_6 and THF-d_8 were dried over CaH_2 or Na/benzophenone and distilled under a nitrogen atmosphere. All metal complexes were prepared and stored in a Vacuum Atmospheres inert atmosphere glovebox under a dry nitrogen atmosphere or were manipulated under argon using standard Schlenk line techniques. NMR spectra were recorded on a Varian VXR-300 or VI-300 spectrometer. Chemical shifts (δ) for ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were referenced to residual nuclei in the deuterated solvent. Chemical shifts (δ) for $^{31}P\{^1H\}$ (121 MHz) NMR spectra were referenced to an external standard (85% H_3PO_4). UV−vis spectra were recorded on a HP8453 (190−1100 nm) diode-array spectrophotometer equipped with a Unisoku low-temperature cryostat. Resonance Raman spectra were recorded on an Acton 506 spectrometer using a Princeton Instruments LN/CCD-11100-PB/UVAR detector and ST-1385 controller interfaced with Winspec software. The spectra were obtained at −196 °C using a backscattering geometry. Excitation at 457.9 and 488 nm was provided by a Spectra Physics BeamLok 2065-7S Ar Laser. Samples were frozen in a copper cup attached to a coldfinger Dewar filled with liquid N_2. Raman shifts were externally referenced to liquid indene. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA) and Robertson Microlit (Madison, NJ). $GeCl_2\cdot$dioxane and benzil were purchased from Aldrich Chemical Corp. and used as received. The complexes L^{R2}Cu (MeCN) (R = Me, Et, ^{i}Pr; L^{R2} = β-diketiminate derived from respective 2-(2,6-di-R-phenyl)amino-4-(2,6-dimethylphenyl)imino-2-pentene),[10] $[L^{Me2}Cu]_2$,[10] $L^{iPr2}CuO_2$,[7a] 1,3-dimesitylimidazol-2-ylidene (NHC^{Mes2}),[11] *N,N′*-dimesitylethanediimine,[12] and $Ge[N(SiMe_3)_2]_2$[13] were synthesized according to literature procedures.

1,3-Dimesityl-1,3,2-diazagermol-2-ylidene ($Ge[(NMes)_2(CH)_2]$). Solid yellow *N,N′*-dimesitylethanediimine (496 mg, 1.7 mmol) was placed in a 50 mL Schlenk flask with lithium metal (30 mg, 4.3 mmol) under argon, and THF (15 mL) was added via cannula transfer. The mixture immediately turned deep red and was stirred overnight. The resulting red-brown solution was filtered through Celite, and to the filtrate was added $GeCl_2\cdot$dioxane (393 mg, 1.7 mmol) in 5 mL of THF. The solution was stirred for 2 h, after which the solvent was removed under reduced pressure to give an orange-brown solid. The solid was extracted with pentane (15 mL) and filtered through Celite to give a light orange solution. Removal of the pentane gave $Ge[(NMes)_2(CH)_2]$ as an orange powder. Recrystallization from pentane (4 mL) at −20 °C yielded analytically pure orange crystals (425 mg, 69%). ^1H NMR (C_6D_6): 6.87 (s, 4H), 6.58 (s, 2H), 2.23 (s, 12H), 2.19 (S, 6H) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8): 142.0, 134.7, 133.3, 128.4, 125.0, 19.8, 17.2 ppm. Anal. Calcd for $C_{20}H_{24}N_2Ge$: C, 65.80; H, 6.63; N, 7.67. Found: C, 65.53; H, 6.48; N, 7.61.

$L^{Me2}Cu{-}Ge[(NMes)_2(CH)_2]$ (1a). To a solution of $[L^{Me2}Cu]_2$ (54 mg, 0.073 mmol) in THF (4 mL) was added a solution of $Ge[(NMes)_2(CH)_2]$ (53 mg, 0.15 mmol) in THF (4 mL). An immediate color change from very pale yellow to bright lemon yellow was observed, and the reaction was stirred for 30 min. The solution was filtered through Celite, and removal of the solvent from the filtrate under reduced pressure resulted in the isolation of **1a** as a bright yellow powder. Recrystallization from Et_2O (10 mL) at −20 °C yielded analytically pure yellow crystals (83 mg, 78%). X-ray-quality crystals were grown from a concentrated pentane solution at −20 °C. ^1H NMR (C_6D_6): 6.95 (m, 6H) 6.82 (s, 4H), 6.21 (s, 2H), 4.88 (s, 1H), 2.22 (s, 6H), 1.99 (s, 12H), 1.91 (s, 12H), 1.61 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8): 161.5, 152.4, 139.9, 135.2, 133.7, 129.1, 128.4, 127.4, 123.5, 122.0, 93.4, 21.1, 19.9, 17.6, 16.9 ppm. Anal. Calcd for $C_{41}H_{49}N_4CuGe$: C, 67.09; H, 6.73; N, 7.63. Found: C, 66.66; H, 6.76; N, 7.57.

$L^{Me2}Cu{-}Ge[N(SiMe_3)_2]_2$ (1b). $Ge[N(SiMe_3)_2]_2$ (71 mg, 0.18 mmol) in THF (4 mL) was added to a solution of $[L^{Me2}Cu]_2$ (67 mg, 0.09 mmol) in THF (4 mL), which immediately turned deep orange. The reaction was stirred for 30 min, filtered through Celite, and the solvent removed from the filtrate under reduced pressure to give **1b** as an orange solid in approximately quantitative yield

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(7) (a) Aboelella, N. W.; Kryatov, S. V.; Gherman, B. F.; Brennessel, W. W.; Young, Victor G., Jr.; Sarangi, R.; Rybak-Akimova, E. V.; Hodgson, K. O.; Hedman, B.; Solomon, E. I.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2004**, *126*, 16896. (b) Reynolds, A. M.; Gherman, B. F.; Cramer, C. J.; Tolman, W. B. *Inorg. Chem.* **2005**, *44*, 6989.

(8) Aboelella, N. W.; York, J. T.; Reynolds, A. M.; Fujita, K.; Kinsinger, C. R.; Cramer, C. J.; Riordan, C. G.; Tolman, W. B. *Chem. Commun.* **2004**, 1716.

(9) (a) Litz, K. E.; Banaszak Holl, M. M.; Kampf, J. W.; Carpenter, G. B. *Inorg. Chem.* **1998**, *37*, 6461. (b) Cygan, Z. T.; Bender, J. E.; Litz, K. E.; Banaszak Holl, M. M. *Organometallics* **2002**, *21*, 5373.

(10) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Pape, L. L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307.

(11) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(12) Abrams, M. B.; Scott, B. L.; Baker, R. T. *Organometallics* **2000**, *19*, 4944.

(13) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Riviere, P.; Riviere-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

(135 mg). X-ray-quality crystals were grown from a concentrated MeCN/Et_2O solution at −20 °C. ^{1}H NMR (C_6D_6): 6.98 (m, 6H), 4.95 (s, 1H), 2.33 (s, 12H), 1.66 (s, 6H), 0.14 (s, 36H) ppm. ^{13}C{^{1}H} NMR (THF-d_8): 162.7, 152.3, 130.0, 127.9, 122.5, 94.0, 21.8, 19.0, 4.5 ppm. Anal. Calcd for $C_{33}H_{61}N_4Si_4CuGe$: C, 51.99; H, 8.06; N, 7.35. Found: C, 49.50; H, 7.51; N, 6.68. Repeated attempts to obtain satisfactory elemental analysis were unsuccessful due to small amounts of impurities present, as evidenced by ^{1}H NMR spectroscopy (see text).

Benzil Trapping Experiments. **1b** (5 mg, 0.0066 mmol) was mixed with 4 equiv of benzil (5.5 mg, 0.026 mmol) in C_6D_6 (0.5 mL), and the solution was transferred to a screwcap NMR tube. ^{1}H NMR spectra were monitored over the course of 6 h, and the conversion to trapped germylene was followed by the growth of a resonance at 0.36 ppm for the Me_3Si hydrogens of the germanium(IV) species **2**. The extent of the conversion to **2** was determined by comparing the integration of the peak at 0.14 ppm for **1b** and that at 0.36 ppm for **2**.

$L^{Me2}Cu(PPh_3)$ (3). Independent Synthesis. A solution of PPh_3 (36 mg, 0.14 mmol) in Et_2O (4 mL) was added to a suspension of $[L^{Me2}Cu]_2$ (50 mg, 0.068 mmol) in Et_2O (5 mL). The solution was stirred for 30 min, filtered through Celite, and the solvent was removed from the filtrate under reduced pressure to yield **3** as a tan powder (82 mg, 95%). X-ray-quality crystals were grown from a concentrated pentane solution at −20 °C. ^{1}H NMR (C_6D_6): 6.88 (m, 21H), 5.05 (s, 1H), 2.12 (s, 12H), 1.73 (S, 6H) ppm. ^{13}C{^{1}H} NMR (THF-d_8): 161.7, 152.3, 133.5, 133.0, 132.9, 132.7, 129.9, 128.9, 128.1, 127.9, 127.7, 122.0, 93.5, 21.6, 17.8 ppm. ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): 5.45 ppm. Anal. Calcd for $C_{39}H_{40}N_2PCu$: C, 74.20; H, 6.39; N, 4.44. Found: C, 74.06; H, 6.57; N, 4.36.

From 1a. To a solution of **1a** (10 mg, 0.014 mmol) in 0.5 mL C_6D_6 was added 1 equiv of PPh_3 (3.6 mg). The solution immediately changed from a bright to a pale yellow. ^{1}H NMR spectroscopy revealed quantitative formation of **3** and the free germylene Ge[$(NMes)_2(CH)_2$].

From 1b. To a solution of **1b** (10 mg, 0.013 mmol) in 0.5 mL C_6D_6 was added 1 equiv of PPh_3 (3.4 mg). The solution immediately changed from deep orange to pale yellow. ^{1}H NMR spectroscopy revealed quantitative formation of **3** and free germylene Ge[$N(SiMe_3)_2]_2$.

$L^{Me2}Cu(NHC^{Mes2})$ (4). Independent Synthesis. A solution of NHC^{Mes2} (50 mg, 0.16 mmol) in THF (4 mL) was added to a solution of $[L^{Me2}Cu]_2$ (60 mg, 0.08 mmol) in THF (5 mL). The solution was stirred for 30 min, filtered through Celite, and the solvent was removed from the filtrate under reduced pressure to yield **4** as a tan powder (100 mg, 91%). X-ray-quality crystals were grown from a concentrated pentane solution at −20 °C. ^{1}H NMR (C_6D_6): 7.01 (m, 6H), 6.77 (s, 4H), 5.78 (s, 2H), 4.81 (s, 1H), 2.18 (S, 6H), 1.96 (s, 12H), 1.63 (s, 12H), 1.53 (s, 6H) ppm.^{13}C{^{1}H} NMR (THF-d_8): 185.3, 160.0, 153.7, 137.7, 136.9, 135.6, 130.3, 128.5, 127.2, 121.1, 120.9, 92.3, 21.4, 20.1, 18.7, 17.5 ppm. Anal. Calcd for $C_{42}H_{49}N_4Cu$: C, 74.91; H, 7.33; N, 8.32. Found: C, 75.17; H, 6.95; N, 8.27.

From 1a. To a solution of **1a** (10 mg, 0.014 mmol) in 0.5 mL C_6D_6 was added 1 equiv of NHC^{Mes2} (4.3 mg). The solution immediately changed from bright to pale yellow. ^{1}H NMR spectroscopy revealed quantitative formation of **4** and the free germylene Ge[$(NMes)_2(CH)_2$].

From 1b. To a solution of **1b** (10 mg, 0.013 mmol) in 0.5 mL C_6D_6 was added 1 equiv of NHC^{Mes2} (4.0 mg). The solution immediately changed from deep orange to pale yellow. ^{1}H NMR spectroscopy revealed quantitative formation of **4** and the free germylene Ge[$N(SiMe_3)_2]_2$.

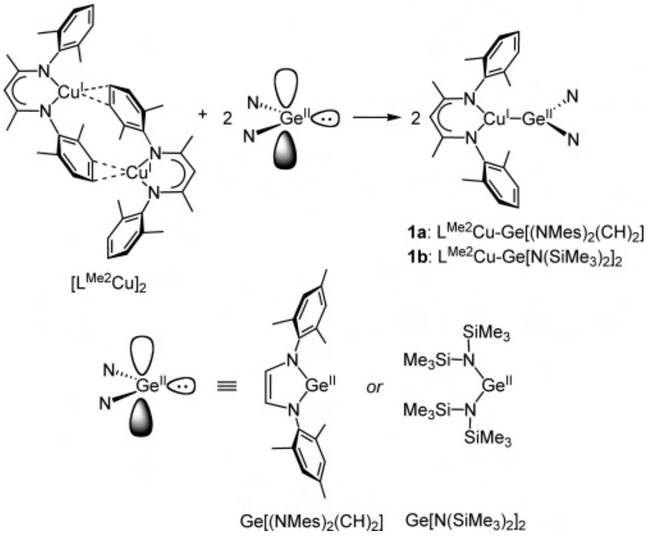
Oxygenation of 1b to Form $L^{Me2}Cu(\mu\text{-}O)_2Ge[N(SiMe_3)_2]_2$. A solution of **1b** (20 mg, 0.026 mmol) in toluene (1.2 mL) was cooled to −80 °C in a MeOH/liquid N_2 bath. Dry O_2 was bubbled through the cold solution for 10 min, during which time very little change was observed. The solution was stirred at −80 °C for 4 h, during which time the color became deep orange-brown. The UV−vis spectrum was measured by transfer of a known volume of the oxygenated solution using a precooled gastight syringe to a UV−vis cuvette filled with a known volume of toluene at −80 °C ($\lambda_{max} \approx 440$ nm, $\epsilon \approx 4400$ M^{-1} cm^{-1}, as approximated from the initial concentration of **1b**). To prepare the ^{18}O-isotopomer, the solution of **1b** was frozen by immersion in liquid N_2, the headspace was evacuated, and $^{18}O_2$ gas was transferred from a glass bulb. The solution was allowed to warm to −80 °C, and it was stirred for 4 h, during which time the solution turned deep orange-brown. Resonance Raman spectra were obtained by micropipet transfer of the solution to a copper cup on a coldfinger and frozen with liquid N_2.

Reaction of $L^{iPr2}CuO_2$ with $Ge[N(SiMe_3)_2]_2$ to Form $L^{iPr2}Cu(\mu\text{-}O)_2Ge[N(SiMe_3)_2]_2$. Dry O_2 was passed through solution of L^{iPr2}Cu(MeCN) (10 mg, 0.019 mmol) in toluene (1.0 mL) at −80 °C for 10 min to form $L^{iPr2}CuO_2$. The solution was freeze−pump−thaw degassed and purged with argon to remove excess O_2. One equivalent of $Ge[N(SiMe_3)_2]_2$ (7.4 mg, 0.019 mmol) was added in 0.2 mL of toluene by syringe, upon which time the solution immediately turned deep orange-brown. The ^{18}O-isotopomer was prepared similarly, except the solution of L^{iPr2}Cu(MeCN) (10 mg, 0.019 mmol) in toluene (1.0 mL) was frozen in a 10 mL Schlenk flask by immersion in liquid N_2, the headspace was evacuated, $^{18}O_2$ gas was transferred from a glass bulb, and the solution was allowed to thaw to −80 °C and stirred for 30 min. The solution was freeze−pump−thaw degassed and purged with argon to remove excess O_2. One equivalent of $Ge[N(SiMe_3)_2]_2$ (7.4 mg, 0.019 mmol) was added in 0.2 mL of toluene by syringe, resulting in an immediate color change to deep orange-brown. Resonance Raman spectra were obtained by transfer of the solutions to a copper cup on a coldfinger and frozen with liquid N_2. The UV−vis spectrum was measured by addition of 1 equiv of $Ge[N(SiMe_3)_2]_2$ in toluene by syringe to a toluene solution of degassed $L^{iPr2}CuO_2$ in a UV−vis cuvette at −80 °C ($\lambda_{max} \approx 463$ nm, $\epsilon \approx 4100$ M^{-1} cm^{-1}, as approximated from the initial concentration of L^{iPr2}Cu(MeCN)).

Oxygenation of 1a to Form $L^{Me2}CuO_2$. A 0.1 mM solution of L^{Me2}Cu−Ge[$(NMes)_2(CH)_2$] (**1a**) in THF was cooled to −80 °C in a UV−vis cuvette, and dry O_2 was bubbled for ~10 s. The addition of O_2 was followed by the immediate disappearance of the 402 nm band in the UV−vis spectrum and the growth of a new shoulder at 390 nm ($\epsilon \approx 2400$ M^{-1} cm^{-1}, approximated on the basis of the initial concentration of **1a**) over ~10 min. Warming the solution to −65 °C resulted in the growth of a new feature at 422 nm. Likewise, addition of O_2 to more concentrated solutions of **1a** in THF at −80 °C (5−20 mM) resulted in the rapid formation of a dark yellow-brown intermediate with a UV−vis feature at 422 nm. Resonance Raman experiments on the concentrated solutions (λ_{ex} = 457.9 nm) revealed a strong peak at 608 cm^{-1}, consistent with the formation of $[(L^{Me2}Cu)_2(\mu\text{-}O)_2]$ and the observed UV−vis spectrum.

Addition of $Ge[N(SiMe_3)_2]_2$ to $L^{Me2}CuO_2$ to Form $L^{Me2}Cu(\mu\text{-}O)_2Ge[N(SiMe_3)_2]_2$. A 0.1 mM solution of **1a** in THF was cooled to −80 °C in a UV−vis cuvette, and dry O_2 was bubbled for ~10 s. The addition of O_2 was followed by the immediate disappearance of the 402 nm band in the UV−vis spectrum and the growth of a

Scheme 1



new shoulder at 390 nm over ∼10 min. The solution was purged with argon for 30 min to remove excess O_2, and 1 equiv of Ge[N$(SiMe_3)_2$]$_2$ in 0.1 mL THF was added by syringe. The rapid formation of an absorption feature was observed ($\lambda_{max} \approx 440$ nm, $\epsilon \approx 4000$ M^{-1} cm^{-1}, approximated on the basis of the initial concentration of **1a**), consistent with that observed previously for L^{Me2}Cu(μ-O)$_2$Ge[N$(SiMe_3)_2$]$_2$ obtained upon oxygenation of L^{Me2}Cu−Ge[N$(SiMe_3)_2$]$_2$.

X-ray Crystallography. Data were collected on either a Bruker or Siemens SMART Platform CCD diffractometer at 173(2) K. Data collections were carried out using Mo Kα radiation (graphite monochoromator) at a distance of 4.9 cm. The intensity data were integrated using SAINT[14] and were corrected for absorption and decay using SADABS.[15] The structures were solved by direct methods using SHELXL-97[16] software. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. X-ray crystallographic data and tables (Table S1) with pertinent details for each structure are located in the Supporting Information.

Results and Discussion

Synthesis and Characterization of Cu(I)−Ge(II) Complexes. We chose as starting material a β-diketiminate complex of Cu(I) previously described by Warren and coworkers,[17] [L^{Me2}Cu]$_2$ (Scheme 1), which we prepared in a slightly different fashion by vacuum-drying of L^{Me2}Cu(MeCN)[10] and recrystallization from pentane. An X-ray crystallographic analysis (Figure S1) revealed a dimeric structure similar to that which was reported, although variations in the crystal system and slight differences in some bond distances were observed. Two germylenes were selected for reaction with the Cu(I) reagent, the known compound Ge[N$(SiMe_3)_2$]$_2$[13] and a previously unreported heterocyclic germylene Ge[$(NMes)_2(CH)_2$]. The latter compound was synthesized by the reductive dimetalation of the α-diimine *N*,*N*′-dimesitylethanediimine[12] with Li metal followed by metathesis with $GeCl_2$•dioxane, a procedure similar to that used previously to synthesize related heterocyclic stannylenes[18] and germylenes.[19] Studies of the reactivity and stability of related heterocyclic germylenes[19,20] suggested that Ge[$(NMes)_2(CH)_2$] would exhibit different electronic properties than Ge[N$(SiMe_3)_2$]$_2$, which we hypothesized might be manifested in reactivity differences for the targeted Cu(I)−Ge(II) complexes.

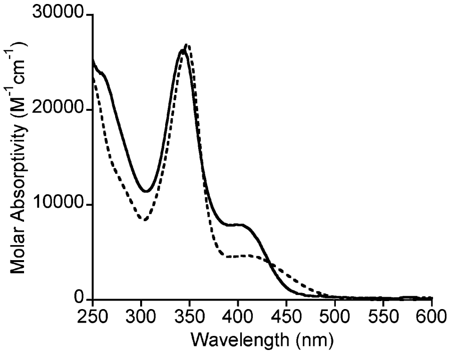


Figure 1. UV−vis spectra of L^{Me2}Cu−Ge[$(NMes)_2(CH)_2$] (**1a**, solid line) and L^{Me2}Cu−Ge[N$(SiMe_3)_2$]$_2$ (**1b**, dashed line) in THF at 25 °C.

Addition of 1 equiv (per copper) of Ge[N$(SiMe_3)_2$]$_2$ or Ge[$(NMes)_2(CH)_2$] to a pale yellow THF solution of [L^{Me2}Cu]$_2$ resulted in the instantaneous formation of deep orange or bright lemon-yellow solutions, respectively. In the case of the reaction with Ge[$(NMes)_2(CH)_2$], the product was isolated analytically pure upon filtration and crystallization from Et_2O and identified on the basis of UV−vis and ^{1}H NMR spectroscopy and X-ray crystallography as L^{Me2}Cu−Ge[$(NMes)_2(CH)_2$] (**1a**, Scheme 1). For the reaction with Ge[N$(SiMe_3)_2$]$_2$, the exceedingly high solubility of the product (**1b**) in common organic solvents hindered the isolation of an analytically pure sample, and ^{1}H NMR spectra in both C_6D_6 and THF-d_8 revealed a small amount of free Cu(I) complex in all batches synthesized (∼2−3% relative to **1b**). Nevertheless, we were able to obtain X-ray-quality crystals of **1b** from a concentrated acetonitrile/Et_2O solution at −20 °C that enabled determination of its structure.

The UV−vis spectra of **1a** and **1b** in THF exhibit an intense band at 342 or 345 nm ($\epsilon \approx 27000$ M^{-1} cm^{-1}) and a weaker shoulder at 402 or 409 nm ($\epsilon \approx 7700$ or 4700 M^{-1} cm^{-1}), respectively (Figure 1). On the basis of analogy to spectra previously reported for L^{R2}Cu(NCR′) complexes,[7a,10] the former intense features may be assigned as β-diketiminate-based $\pi \rightarrow \pi^*$ transitions and the latter shoulders as Cu → Ge[N$(SiMe_3)_2$]$_2$/Ge[$(NMes)_2(CH)_2$] charge transfer

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(14) *SAINT V6.45A*; Bruker Analytical X-ray Systems: Madison, WI, 2001.

(15) An empirical correction for absorption anisotropy: Blessing, R. *Acta Crystallogr. A* **1995**, *51*, 33.

(16) *SHELXTL V6.12*; Bruker Analytical X-ray Systems: Madison, WI, 2000.

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

(18) Gans-Eichler, T.; Gudat, D.; Nieger, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1888.

(19) (a) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F. R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31* 1485. (b) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 11162. (c) Kuhl, O.; Lonnecke, P.; Heinicke, J. *Polyhedron* **2001**, *20*, 2215.

(20) (a) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039. (b) Lehmann, J. F.; Urquhart, S. G.; Ennis, L. E.; Hitchcock, A. P.; Hatano, K.; Gupta, S.; Denk, M. K. *Organometallics* **1999**, *18*, 1862. (c) Leites, L. A.; Bukalov, S. S.; Zabula, A. V.; Garbuzova, I. A.; Moser, D. F.; West, R. *J. Am. Chem. Soc.* **2004**, *126*, 4114.

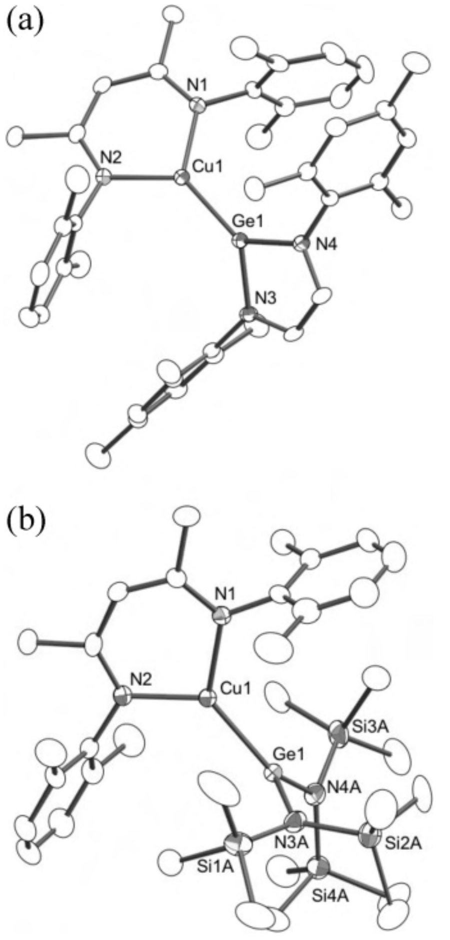
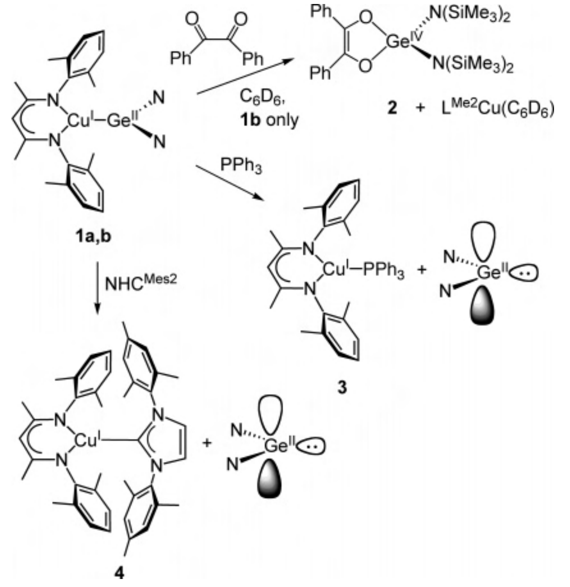


Figure 2. Molecular structures of (a) **1a** and (b) **1b** with heteroatoms labeled, all atoms as 50% thermal ellipsoids, and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): (a) Cu1−N1, 1.9194(17); Cu1−N2, 1.9153(17); Cu1−Ge1, 2.2138(4); N1−Cu1−N2/N3−Ge1−N4, 44.03(7). (b) Cu1−N1, 1.956(3); Cu1−N2, 1.938(3); Cu1−Ge1, 2.2492(4); N1−Cu1−N2/N3A-Ge1−N4A, 88.15(21). For **1b**, only one conformation of the disordered $N(SiMe_3)_2$ groups is shown.

(MLCT) transitions. Both complexes exhibit sharp ^1H NMR spectra that are shifted relative to the starting materials. Thus, for example, the ^1H NMR spectrum of **1a** in C_6D_6 shows the β-diketiminate backbone hydrogen peak at 4.88 ppm, downfield from the value of 4.75 ppm for the Cu(I) starting material, and the olefinic hydrogens of the germylene ligand at 6.21 ppm shifted upfield relative to their position in free $Ge[(NMes)_2(CH)_2]$ (6.58 ppm). Resonances for the germylene olefin and the 2,6-methyl groups of the mesitylene ring for **1a** are somewhat broadened, suggestive of a fluxional process in solution that we have yet to define.

The X-ray structures of **1a** and **1b** (Figure 2) confirm their formulations and are consistent with the presence of direct Cu(I)−Ge(II) bonds, with Cu−Ge distances of 2.2138(4) and 2.2492(4) Å, respectively. In the structure of **1b**, the $N(SiMe_3)_2$ groups were found to be disordered over two positions (Supporting Information). Only a few other complexes with Cu−Ge bonds are known,[21] and these feature Ge(IV) centers with longer Cu−Ge distances in the range 2.33−2.38 Å. While the Cu(I)−Ge(II) distances in **1a** and **1b** are similar to each other, the relative orientation of the N−M−N planes in the two complexes differ significantly. In **1a**, the N1−Cu1−N2 plane forms an angle of 44° relative to the N3−Ge1−N4 plane, whereas in **1b**, these respective planes are nearly perpendicular. The latter arrangement would maximize back-bonding interaction between the filled copper d_{xy} orbital and the empty germanium p_y orbital, where the x axis is defined by the Cu−Ge vector. Due to its involvement in the heterocyclic aromatic system, this p orbital may be less available for this interaction in **1a** than in **1b**,[22] helping to rationalize the observed conformational preferences. Similar back-bonding has been invoked in related Cu(I)−carbene[23] and other metal−germylene complexes,[24] but given the relatively poor back-bonding capabilities of Cu(I) and the steric differences between the supporting ligands, other influences such as crystal packing could also be important.

Scheme 2



Reactivity with Benzil, PPh_3, and a N-Heterocyclic Carbene. To probe the propensity of the Cu(I)−Ge(II) bond in **1a** and **1b** to dissociate we explored reactions of these compounds with reagents that are known to trap germylenes (benzil) or Cu(I) (PPh_3 and N-heterocyclic carbenes). The results are summarized in Scheme 2.

Benzil is known to be reduced rapidly by $Ge[N(SiMe_3)_2]_2$ to yield the Ge(IV)-enediolate $(Ph_2C_2O_2)Ge[N(SiMe_3)_2]_2$, so it has been used as a trapping agent to assess the degree of germylene dissociation from $(PR_3)_2M{-}Ge[N(SiMe_3)_2]_2$ complexes, where M = Ni, Pd, and Pt.[9b,25] We envisioned similar use of benzil to probe germylene dissociation from **1a** and **1b**. However, addition of excess benzil to a C_6D_6 solution of $Ge[(NMes)_2(CH)_2]$ resulted only in slow decom-

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(21) (a) Orlov, N. A.; Bochkarev, L. N.; Nikitinsky, A. V.; Zhiitsov, S. F.; Zakharov, L. N.; Fukin, G. K.; Ya. Khorshev, S. *J. Organomet. Chem.* **1997**, *547*, 65. (b) Orlov, N. A.; Bochkarev, L. N.; Nikitinsky, A. V.; Kropotova, V. Y.; Zakharov, N. L.; Fukin, G. K.; Khorshev, S. Y. *J. Organomet. Chem.* **1998**, *560*, 21. (c) Glocking, F.; Hooton, K. A. *J. Chem. Soc.* **1962**, 2658.

(22) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801.

(23) (a) Dai, X.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 10085. (b) Badiei, Y. M.; Warren, T. H. *J. Organomet. Chem.* **2005**, *690*, 5989.

(24) Kuhl, O.; Lonnecke, P.; Heinicke, J. *Inorg. Chem*. **2003**, *42*, 2836.

(25) Litz, K. E.; Bender, J. E.; Sweeder, R. D.; Banaszak Holl, M. M.; Kampf, J. W. *Organometallics* **2000**, *19*, 1186.

position and no isolable Ge(IV) product. Thus, only the reaction of benzil with **1b** was explored. Addition of 4 equiv of benzil to a C_6D_6 solution of **1b** and monitoring by ^1H NMR spectroscopy revealed the slow formation of $(Ph_2C_2O_2)Ge[N(SiMe_3)_2]_2$ and $L^{Me2}Cu(C_6D_6)$[17] to the extent of ~90% conversion after 5 h ($t_{1/2} \approx 70$ min). In comparison, the complexes $(PR_3)_2M{-}Ge[N(SiMe_3)_2]_2$ were reported to generate the same Ge(IV) product within 1 min for M = Ni, and to reach ~90% conversion after 4 and 94 h for M = Pd and Pt, respectively.[9b] Thus, by this crude measure, the Cu(I)−Ge(II) bond in **1b** is less prone to dissociation than the Ni(I)−Ge(II) compound, is similarly labile compared to the Pd(II)−Ge(II) bond, and is more reactive than the Pt(II)−Ge(II) case.

In contrast to the slow benzil trapping of free germylene observed for **1b**, complexes **1a** and **1b** both react instantaneously at room temperature and at −100 °C with PPh_3 and the N-heterocyclic carbene NHC^{Mes2},[11] with concurrent bleaching of the solution color and disappearance of the ~400 nm absorption feature in the UV−vis spectra. ^1H NMR spectra revealed the quantitative formation of the respective free germylene and the Cu(I) adducts **3** and **4**, each of which was synthesized independently from $[L^{Me2}Cu]_2$ and PPh_3 or NHC^{Mes2}, respectively, and characterized structurally by X-ray crystallography (Figure S2). Overall, the structures resemble those of related molecules reported previously.[23,26,27] Notably, in **4**, the N3−C−N4 plane of the carbene is nearly perpendicular to the N1−Cu−N2 plane, most likely due to steric interactions as N-heterocyclic carbenes are known to be weak π-acceptor ligands for Cu(I).[22]

The findings that benzil traps $Ge[N(SiMe_3)_2]_2$ from **1b** only slowly and the reactions of **1a** and **1b** with PPh_3 and NHC^{Mes2} proceed essentially instantaneously suggest that the latter reactions proceed through associative pathways. This hypothesis is consistent with the previously described associative pathway for the oxygenation of $L^{iPr2}Cu(NCR)$ to yield $L^{iPr2}CuO_2$,[7] as well as for the displacement of O_2 from this product by phosphines.[27] Although detailed kinetic studies would be required to more definitively show that associative mechanisms are operative, the data nonetheless suggest that **1a** and **b** might react with O_2 in a similar manner such that substrate and germylene are bound *simultaneously* to the copper, with the nature of the bound germylene possibly playing a role in the intermediates observed.

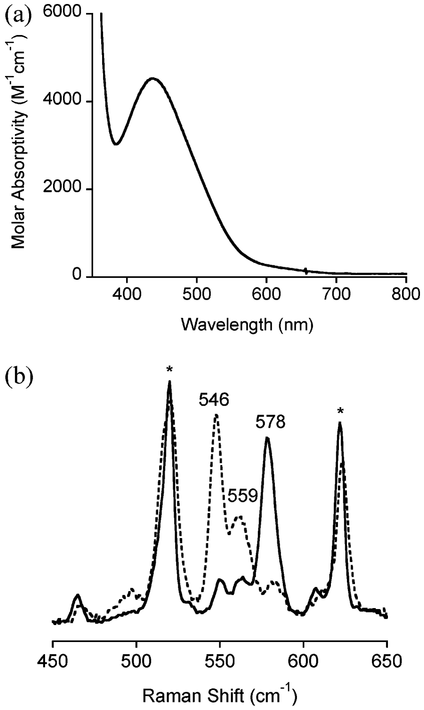
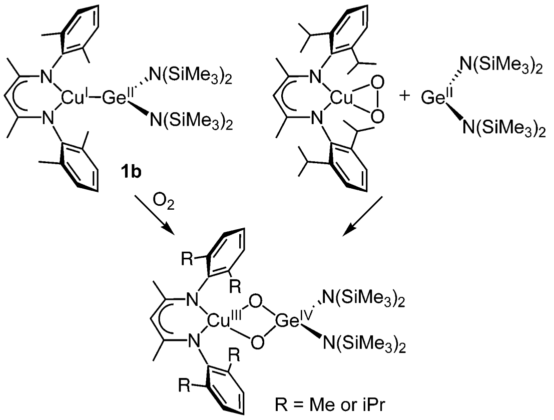


Figure 3. (a) UV−vis spectrum of $L^{Me2}Cu{-}Ge[N(SiMe_3)_2]_2$ (**1b**) + O_2 in toluene at −80 °C. (b) Resonance Raman spectra (λ_{ex} = 488 nm) of frozen toluene solutions (77K) of $L^{Me}Cu(\mu{-}O)_2Ge[N(SiMe_3)_2]_2$ (solid line for $^{16}O_2$, dashed line for $^{18}O_2$, * denotes solvent peaks).

Scheme 3



Reactivity with Dioxygen. Both **1a** and **1b** dissolved in THF or toluene reacted with O_2 at low temperature (−80 °C), but the course of the reactions differ significantly. Considering first **1b**, oxygenation in toluene resulted in development of a deep orange-brown color accompanied by a feature at λ_{max} = 440 nm ($\epsilon \approx 4400\ M^{-1}\ cm^{-1}$) in the UV−vis spectrum which degraded upon warming of the sample. Resonance Raman experiments using 488 nm laser excitation[28] revealed a single strong peak at 578 cm^{-1} that shifted to two peaks when the sample was prepared with $^{18}O_2$ (Figure 3). The magnitude of the isotopic shift to the average of the two $^{18}O_2$ peaks is $\Delta_{avg} = 26\ cm^{-1}$, consistent with attribution of the 578 cm^{-1} feature to a bis(μ-oxo)-dimetal core vibration that is split into a Fermi doublet upon O-isotope substitution.[8,29] The λ_{max} and $\nu(M_2O_2)$ values (440 nm, 578 cm^{-1}) differ significantly from those of $[(L^{Me2}Cu)_2(\mu{-}O)_2]$ (422 nm, 608 cm^{-1}),[10] thus arguing against dissociation of **1b** into germylene and $L^{Me2}Cu(I)$ fragments that individually oxygenate. Instead, the data indicate formation

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(26) (a) Tulloch, A. A. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, *20*, 2027. (b) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340. (c) Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755.

(27) Reynolds, A. M.; Lewis, E. L.; Aboelella, N. W.; Tolman, W. B. *Chem. Commun.* **2005**, 2014.

(28) Rapid photobleaching of the sample was observed when 457.9 nm laser excitation was used.

(29) (a) Holland, P. L.; Cramer, C. J.; Wilkinson, E. C.; Mahapatra, S.; Rodgers, K. R.; Itoh, S.; Taki, M.; Fukuzumi, S.; L. Que, J.; Tolman, W. B. *J. Am. Chem. Soc.* **2000**, *122*, 792. (b) Henson, M. J.; Mukherjee, P.; Root, D. E.; Stack, T. D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **1999**, *121*, 10332.

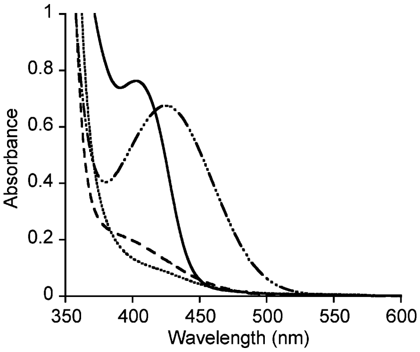


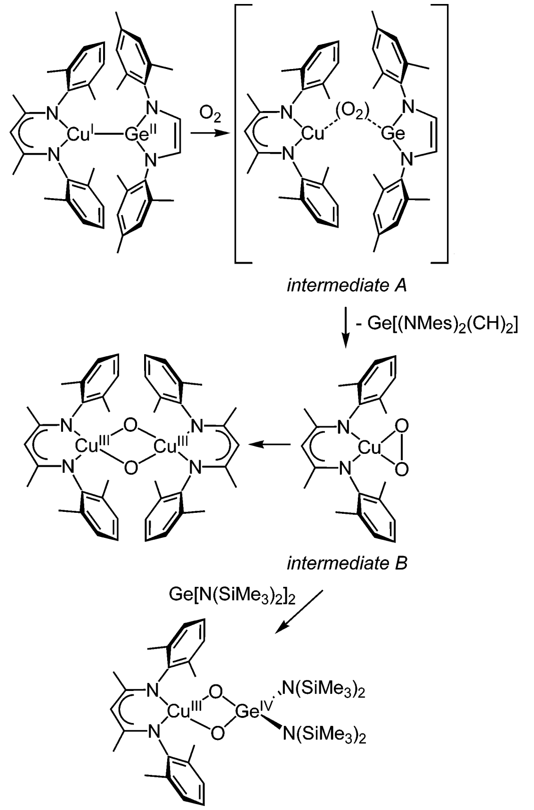
Figure 4. UV−vis spectra of $L^{Me2}Cu-Ge[(NMes)_2(CH)_2]$ (**1a**) in THF (0.1 mM) at −80 °C (solid line), the immediate product of oxygenation (intermediate A, Scheme 4, dotted line), the species resulting after allowing intermediate A to stand for 10 min (intermediate B, dashed line), and the product resulting from warming of intermediate B to −65 °C (dot−dash line).

of the heterobimetallic bis(μ-oxo)copper(III)germanium(IV) complex $L^{Me2}Cu(\mu\text{-}O)_2Ge[N(SiMe_3)_2]_2$ (Scheme 3). Similar results were reported for the oxygenations of $(PR_3)_2M-Ge[N(SiMe_3)_2]_2$ (M = Pd, Pt) that yield $[M^{II}(\mu\text{-}O)_2Ge^{IV}]^{2+}$ cores,[9] but the generation of a heterobimetallic bis(μ-oxo) complex via oxygenation of a reduced heterobimetallic precursor comprising Cu(I) is unprecedented.

A similar $[Cu^{III}(\mu\text{-}O)_2Ge^{IV}]^{3+}$ core is also accessible via a stepwise approach (Scheme 3). Thus, addition of 1 equiv of $Ge[N(SiMe_3)_2]_2$ to a deoxygenated solution of $L^{iPr2}CuO_2$ in toluene at −80 °C resulted in the immediate development of a deep orange-brown color, a UV−vis band at $\lambda_{max} = 463$ nm ($\epsilon \approx 4100$), and a peak at 578 cm^{-1} in the resonance Raman spectrum ($\lambda_{ex} = 488$ nm) that shifted to a doublet when $L^{iPr2}Cu^{18}O_2$ was used ($\Delta_{avg} = 27$ cm^{-1}) (Figure S3). These data clearly support formation of $L^{iPr2}Cu(\mu\text{-}O)_2Ge[N(SiMe_3)_2]_2$ via a reaction akin to previously reported syntheses involving such a stepwise method[8] and provide further confirmation of the similar nature of the product from the direct oxygenation of **1b**.

In contrast to the O_2 reaction with **1b**, oxygenation of **1a** in THF (0.1 mM) at −80 °C resulted in instantaneous disappearance of the 402 nm Cu → $Ge[(NMes)_2(CH)_2]$ MLCT feature in the UV−vis spectrum (intermediate A, Figure 4), followed by the gradual (∼10 min) development of a new absorption feature at 390 nm ($\epsilon \approx 2400$) and a shift of the $\pi \rightarrow \pi^*$ bands from 345 to 326 nm (intermediate B). These new features remain unperturbed at −80 °C, even upon purging with argon, but convert further upon warming to −65 °C or when the reaction is performed at higher concentrations (∼5−15 mM) at temperatures less than −90 °C to the spectrum previously reported for $[(L^{Me2}Cu)_2(\mu\text{-}O)_2]$ (Figure S4). The formation of this species was confirmed by resonance Raman spectroscopy ($\nu(Cu_2O_2) = 608$ cm^{-1}). On the basis of analogy to the UV−vis spectrum for $L^{iPr2}CuO_2$, we assign intermediate B as the previously unobserved, relatively sterically unhindered variant $L^{Me2}CuO_2$. Unfortunately, the rapidity of the decay of intermediate B to $[(L^{Me2}Cu)_2(\mu\text{-}O)_2]$ at the higher concentrations required to obtain resonance Raman spectra prevented direct confirmation of its structural assignment via this method. Consistent with it being $L^{Me2}CuO_2$, however, was our finding that addition of 1 equiv of $Ge[N(SiMe_3)_2]_2$ to a deoxygenated solution yielded the spectral features for $L^{Me2}Cu(\mu\text{-}O)_2Ge[N(SiMe_3)_2]_2$. Identification of intermediate A is more difficult, as it is metastable and lacks diagnostic spectroscopic features. Thus, we can only speculate that it is some sort of O_2 adduct of **1a** that decays to $L^{Me2}CuO_2$ and a germanium species, such as the germylene $Ge[(NMes)_2(CH)_2]$, which unlike $Ge[N(SiMe_3)_2]_2$,[30] appears not to react cleanly with available O_2 under ambient conditions to yield a $[Ge^{IV}_2(\mu\text{-}O)_2]^{4+}$ core.

Scheme 4



In summary, on the basis of the available evidence, we propose that the sequence of reactions shown in Scheme 4 occurs upon oxygenation of **1a**. In contrast to **1b**, which yields a stable heterobimetallic $[Cu^{III}(\mu\text{-}O)_2Ge^{IV}]^{3+}$ complex, **1a** cleaves to yield $L^{Me2}CuO_2$ and, presumably, $Ge[(NMes)_2(CH)_2]$. The relatively unhindered (compared to $L^{iPr2}CuO_2$)[7] $L^{Me2}CuO_2$ decays to $[(L^{Me2}Cu)_2(\mu\text{-}O)_2]$ via a process facilitated by warming or when high concentrations of **1a** are used. Differences in the nature of the germylene fragment are clearly responsible for the divergent O_2 reactivity of **1a** and **1b**, with the greater intrinsic stability of the heterocyclic $Ge[(NMes)_2(CH)_2]$ possibly underlying its ejection rather than formation of a heterobimetallic $[Cu^{III}(\mu\text{-}O)_2Ge^{IV}]^{3+}$ core.

Conclusions

A pair of novel Cu(I)−Ge(II) complexes, **1a** and **1b**, that differ with respect to the nature of the germylene fragment

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[30] Ellis, D.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton. Trans.* **1992**, 3397.

have been synthesized and characterized by spectroscopic and X-ray crystallographic methods. Studies of their reactivity with benzil, PPh_3, and a N-heterocyclic carbene (NHC) showed that (a) the lability of the Cu(I)−Ge(II) bond in **1b** with respect to trapping of the germylene with benzil is similar to that of a previously reported Pd(II)−Ge(II) analogue and (b) both complexes are cleaved rapidly by PPh_3 and an NHC to yield stable Cu(I) adducts and the free germylene, presumably by associative processes. In addition, the complexes are highly reactive with O_2 and exhibit unique chemistry which depends on the bound germylene. In one case (**1a**), oxygenation results in the generation of a new 1:1 Cu/O_2 adduct supported by a relatively sterically unhindered β-diketiminate ligand, whereas in another (**1b**), a heterobimetallic intermediate having a $[Cu^{III}(\mu\text{-}O)_2Ge^{IV}]^{3+}$ core forms. The isolation of the latter species by direct oxygenation of a Cu(I)−Ge(II) precursor represents a new route to heterobimetallic oxidants comprising copper, the reactivity of which will be of great interest in future work aimed at understanding O_2 activation and catalysis by mixed-metal systems.

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Supporting Information Available: X-ray crystallographic details (PDF, CIF); depictions of the X-ray structures of $[L^{Me2}Cu]_2$, $L^{Me2}Cu(PPh_3)$, and $L^{Me2}Cu(NHC^{Mes2})$ (PDF); and additional spectroscopic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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