A Facile Synthesis of 2,2,6,6-Tetramethyl-2-germa-3,5-heptandione: The Preparation and Characterization of the First Germa-β-diketonate Copper(II) Complex

Kulbinder K. Banger, Claudia Birringer, Rolf U. Claessen, Poay Lim, Paul J. Toscano,* and John T. Welch*

Department of Chemistry and NYS Center for Advanced Thin Film Technology, The University at Albany, State University of New York, Albany, New York 12222

Received June 5, 2001

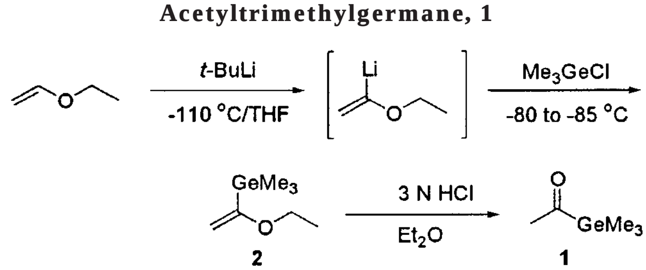
*Summary: High-yield synthesis of acetyltrimethylgermane (**1**) facilitated the synthesis of the first germa-β-diketone, 2,2,6,6-tetramethyl-2-germa-3,5-heptanedione (tmghdH; **3**), and its Cu(II) complex, Cu(tmghd)$_2$ (**4**). Cu(tmghd)$_2$ was found to be more volatile than Cu(tmhd)$_2$ (tmhdH = 2,2,6,6-tetramethyl-3,5-heptanedione) by thermogravimetric analysis. X-ray diffraction studies of Cu(tmghd)$_2$ showed it to have essentially square planar geometry, with the Cu atom situated on a center of symmetry.*

Introduction

The unique chemical and spectral properties of group 14 acyl organometalloids, (R′C(O)ER$_3$, E = Si, Ge) have generated considerable interest in the study of these substances. A number of excellent reviews and articles, with a primary focus on synthetic approaches to silicon derivatives, have been reported.[1−5] However, only a few preparative routes to the less accessible α-germyl ketones have been reported,[5−9] and those often require novel techniques.[9]

Previously, the metalation of alkyl vinyl ethers[5,6,10] has been successfully used for the preparation of acylsilanes,[5,6,11] as well as a small number of acylgermanes.[5−8] The known acylgermanes generally have limited synthetic utility as building blocks for metal-ion ligands, as both R and R′ are either long chain alkyl or aromatic derivatives. We now report an extended and modified procedure for the preparation of acetyltrimethylgermane **1** in good yield. Further, we have developed a method to convert **1** into the first germa-β-diketone, which we have utilized to prepare a novel volatile, homoleptic copper(II) germa-β-diketonate complex with potential utility as a metal organic chemical vapor deposition (MOCVD) precursor.

Scheme 1. Preparation of Acetyltrimethylgermane, 1



Results and Discussion

The preparation of **1** requires the metalation of ethyl vinyl ether in a key step (Scheme 1).[12−14] Addition of chlorotrimethylgermane smoothly provides 1-(trimethylgermyl)-1-(ethoxy)ethene, **2**, which is readily hydrolyzed to **1** under acidic conditions. We have found that the yield of the hydrolysis of **2** to **1** is somewhat dependent on the scale of hydrolysis. On a 0.010 mol scale, acidic hydrolysis of **2** gave **1** in greater than 90% yields. However, on a larger scale (0.14 mol), even with vigorous mechanical stirring, only 82% conversion was obtained.

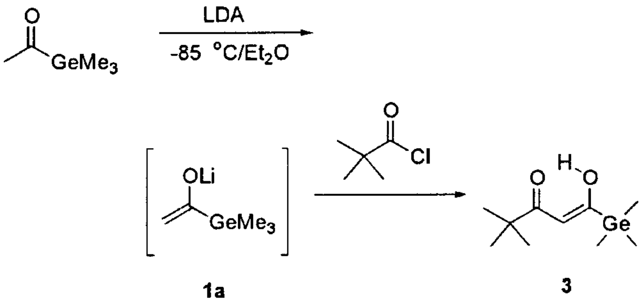
The exploration of the chemistry of acylgermanes has been very limited; therefore, we investigated the preparation of 2,2,6,6-tetramethyl-2-germa-3,5-heptanedione, tmghdH (**3**), and its application in the preparation of a metal complex as a potential MOCVD precursor. Previously, silicon-containing β-diketones have been used as ligands in the synthesis of complexes for MOCVD.[15] These complexes exhibited remarkable volatility and

* To whom correspondence should be addressed. Fax: (518) 442-3462. E-mail: ptoscano@csc.albany.edu; jwelch@uamail.albany.edu.

(1) (a) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 95. (b) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431.
(2) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647.
(3) Bulman Page, P. C.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, 147.
(4) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434.
(5) Soderquist, J. A.; Castro-Rosario, L. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; J. Wiley and Sons: London, UK, 1995; Vol. 5, p 3408.
(6) Soderquist, J. A.; Hassner, A. *Tetrahedron Lett.* **1988**, *29*, 1899.
(7) Soderquist, J. A.; Hassner, A. *J. Org. Chem.* **1980**, *45*, 541.
(8) Soderquist, J. A.; Hassner, A. *J. Am. Chem. Soc.* **1980**, *102*, 1577.
(9) Kazankova, M. A.; Lutsenko, I. F.. *J. Gen. Chem. USSR (Engl. Transl.)* **1969**, *39*, 891; *Zh. Obshch. Khim.* **1969**, *39*, 926.
(10) (a) Baldwin, J. E.; Hofle, G. A.; Lever, O. W. *J. Am. Chem. Soc.* **1974**, *96*, 7125−7127. (b) Schollkopf, U.; Hanssle, P. *Justus Liebigs Ann. Chem.* **1972**, *763*, 208.
(11) (a) Cunico, R. F.; Kuan, C. *J. Org. Chem.* **1985**, *50*, 5410. (b) Soderquist, J. A.; Rivera, I.; Negron, A. *J. Org. Chem.* **1989**, *54*, 4051.
(12) Soderquist, J. A.; Hsu, G. *Organometallics* **1982**, *1*, 830.
(13) Settle, F. A.; Haggerty, M.; Eastham, J. F. *J. Am. Chem. Soc.* **1964**, *86*, 2076.
(14) We note that **1** has been previously prepared starting from methyl vinyl ether in different solvents, though no experimental details were provided (refs 5 and 6).
(15) Claessen, R. U.; Welch, J. T.; Toscano, P. J.; Banger, K. K.; Kornilov, A. M.; Eisenbraun, E.T.; Kaloyeros A. E. *Mater. Res. Soc. Symp. Proc.* **2001**, *612*, D6.8.1.

10.1021/om010479j CCC: $20.00
Publication on Web 09/26/2001

Scheme 2. Preparation of 2,2,6,6-Tetramethyl-2-germa-3,5-heptanedione, tmghdH, 3.



unique spectrochemical properties, an indication of the influence of the organometalloid on bonding. The lithium enolate **1a** was formed by the reaction of **1** with freshly prepared LDA in dry diethyl ether. Addition of trimethylacetyl chloride at low temperature afforded **3** in good yield (Scheme 2).

The ^{13}C NMR spectrum of **3** has resonances attributed to the enolic carbon and the carbonyl carbon at 199.2 and 207.8 ppm, respectively. Importantly, there is no low-field resonance at ca. 240 ppm, which would be expected for a carbonyl carbon adjacent to a metalloid atom such as germanium or silicon. For example, the ^{13}C resonance assigned to the carbonyl carbon of **1** and for the corresponding acylsilane appear at δ 240 ppm, while a chemical shift of 244 ppm was observed for the carbonyl carbon adjacent to silicon in the only sila-β-diketone, which is known to exist as an enolic tautomer *away* from silicon.[16] The ^{13}C NMR data for **3** strongly suggest that enolization *toward* germanium (Figure 1) is highly favored. The low-field ^{1}H resonance at 15 ppm is also consistent with the assignment of the enolic proton in the corresponding sila-β-diketone.[15]

The electronic absorption spectrum of **1**, recorded in hexane (Table 1), falls within the expected hypsochromic and hyperchromic trends for group 14 acyl compounds;[1,17] i.e., $MeC(O)GeMe_3 > MeC(O)SiMe_3 > MeC(O)CMe_3$. In addition, the fine structure observed for the germanium and silicon derivatives was only previously observed in more polar solvents.[1] On the other hand, comparison of the electronic spectrum of **3** with those of 2,2,6,6-tetramethyl-2-sila-3,5-heptanedione (tmshdH) and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) indicates that each diketone has an absorption maximum at ca. 276 nm, without electronic fine structure but with the hypochromic trend tmghdH < tmshdH < tmhdH (Table 1). Importantly, both tmghdH and tmshdH do not display the expected bathochromic shift or hyperchromic effect expected with acylgermanes or silanes. These observations lend further evidence for the predominance of the enolic tautomer toward germanium for **3** (Figure 1), discussed above with regard to the NMR spectra of **3**.

The copper(II) complex $Cu(tmghd)_2$, **4**, was prepared by modification of standard methods[18] and was purified

(16) Apeloig, Y.; Zharov, I.; Bravo-Zhivotovskii, D.; Ovchinnikov, Y.; Struchkov, Y. *J. Organomet. Chem.* **1995**, *499*, 73.
(17) Ramsey, R. G.; Brook, A.; Bassindale, A. R.; Bock, H. *J. Organomet. Chem.* **1974**, *74*, C41.
(18) Toscano, P. J.; Dettelbacher, C.; Waechter, J.;. Pavri, N.; Hunt, D. H.; Eisenbraun, E. T.; Zheng, B.; Kaloyeros, A. E. *J. Coord. Chem.* **1996**, *38*, 319.

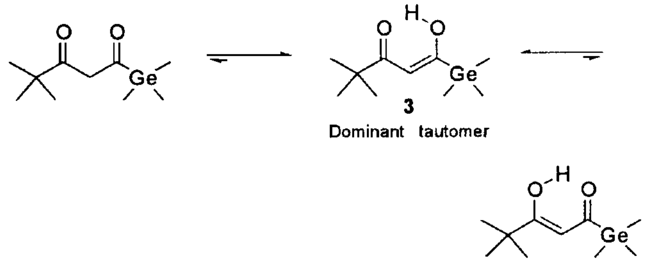


Figure 1. Preferred enol-stabilized tautomer for tmghdH, **3**.

via sublimation. The UV/vis spectrum of **4** in hexane has transitions very similar to $Cu(tmshd)_2$.[15] Five absorption maxima in the region associated with charge transfer were detected for **4**, whereas $Cu(tmhd)_2$ has only three maxima. Both $Cu(tmghd)_2$ and $Cu(tmshd)_2$ have only one distinct d−d transition (a second absorption being masked by a more intense charge transfer transition), in contrast with the two transitions detected with $Cu(tmhd)_2$. As in the case of $Cu(tmshd)_2$,[15] the distinct green color of **4** can be attributed to the moderately strong absorption at 370 nm, which tails into the blue region of the visible, masking the higher energy d−d transition.

Crystals of $Cu(tmghd)_2$ suitable for single-crystal X-ray diffraction studies, obtained by controlled growth from pentane at 5 °C over 7 days, led to the first determination of the structure of a metal germa-β-diketonate (Figure 2; bond lengths and angles within the coordination sphere are unexceptional and are provided in the caption). The complex is square planar with the copper atom located on a center of symmetry. Site disorder associated with occupancy of the peripheral *tert*-butyl and trimethylgermyl positions (see Experimental Section), as well as rotational disorder at the position predominantly occupied by Ge (only the predominant rotamer at 60% occupation is shown in Figure 2), necessarily limits the discussion of the structure. The dihedral angle between the plane defined by the O(1), O(2), C(1), C(2), and C(3) atoms of the ligand (planar to within ±0.010 Å) and the plane defined by Cu(1), O(1), O(2), O(1a), and O(2a) (planarity enforced by symmetry) is 3.2°. The $Ge-CH_3$ bond distances in the disordered trimethylgermyl substituents for $Cu(tmghd)_2$ are ca. 0.15 Å longer than for the $Si-CH_3$ bonds in the isomorphous $Cu(tmshd)_2$,[15] as expected based on the larger covalent radius for Ge.[19] There are few intermolecular contacts in the solid state less than 4.0 Å for **4**, which may explain its good volatility (vide infra).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) facilitated evaluation of the volatility and thermal stability of **4**, relative to $Cu(tmshd)_2$ and $Cu(tmhd)_2$. Following drying in vacuo (60 °C, 0.5 mmHg), the complexes were analyzed in a dynamic dinitrogen atmosphere at ambient pressure. A comparison of the thermal profile of **4** with $Cu(tmshd)_2$ and $Cu(tmhd)_2$ is shown in Figure 3. The sublimation of **4** has an onset of 89 °C, with less than 1% residue. Calculation of the derivative weight loss (%/°C) reveals

(19) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and* Reactivity, 4th ed.; HarperCollins: New York, 1993.

Table 1. UV Spectra for Group IV Acylketones Recorded in Distilled Hexane

1,3-diketones/nm (ϵ)			MeC(O)ER$_3$/nm (ϵ)		
tmhdH	tmshdH	tmghdH	C	Si	Ge
274 (11 500)	276 (10 300)	276 (9300)	278 (15)	230 (20)	230 (60)
				356 (110)	348 (110)
				370 (140)	360 (140)
				386 (100)	376 (120)

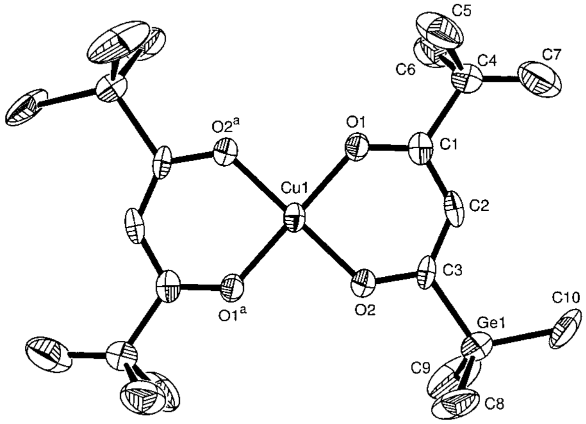


Figure 2. Molecular structure and atom-numbering scheme for Cu(tmghd)$_2$, **4**. The view is perpendicular to the square plane defined by the copper and oxygen atoms. Selected bond lengths (Å) and angles (deg): Cu(1)−O(1) 1.892(10), Cu(1)−O(2) 1.917(7), C(1)−O(1) 1.276(15), C(1)−C(2) 1.382(16), C(2)−C(3) 1.386(20), C(3)−O(2) 1.268(15), O(1)−Cu(1)−O(2) 92.8(3), O(1)−Cu(1)−O(1a) 180.0(1), O(1)−Cu(1)−O(2a) 87.2(3).

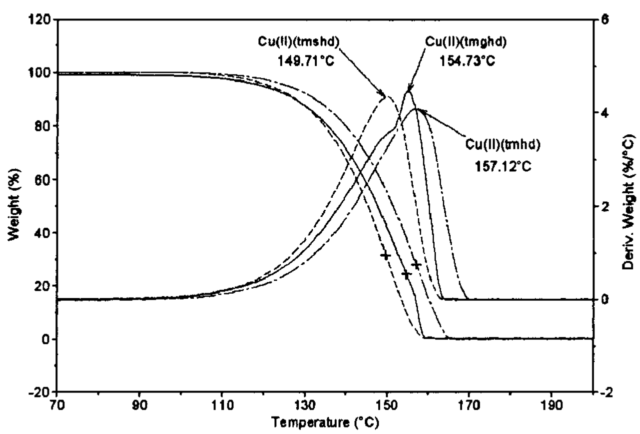


Figure 3. TGA overlay for Cu(tmghd)$_2$, Cu(tmshd)$_2$, and Cu(tmhd)$_2$.

the maximum rate of weight loss to occur at 155 °C. Remarkably, **4** is more volatile than Cu(tmhd)$_2$, even though **4** has a 28% higher molecular mass. DSC analysis of a hermetically sealed sample of **4** has a phase change attributed to melting at 148 °C, with complete decomposition occurring after 200 °C is reached as compared to 172 °C for Cu(tmshd)$_2$. Although **4** displays apparently lower volatility than Cu(tmshd)$_2$, Cu(tmghd)$_2$ has a much higher decomposition temperature. Presenting a larger window between sublimation and decomposition, Cu(tmghd)$_2$ possesses significant potential as a versatile precursor for MOCVD processes.

Experimental Section

General Remarks. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Gemini 300 spectrometer at 300 and 75.4 MHz, respectively, in CDCl$_3$ solution. Electronic spectra were determined on dilute *n*-hexane (Aldrich, spectrophotometric grade) solutions in a quartz cell (1 cm) vs air using a Hewlett-Packard HP8452A diode array spectrophotometer at ambient temperature (resolution: ±2 nm). Background from solvent absorption was subtracted utilizing a spectrum of pure *n*-hexane vs air. Molar absorptivity coefficients are reported in mol^{-1} dm^3 cm^{-1}. DSC measurements were obtained using a TA Instruments DSC 2920 differential scanning calorimeter on ~2.5 mg of sample hermetically sealed in an aluminum pan (N$_2$ flow rate = 8 cm^3/min, 1 atm pressure) at a heating rate of 10 °C/min up to 500 °C and referenced relative to indium. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA 2050 thermogravimetric analyzer on ~0.7 mg of sample at ambient pressure. Heating rates were 1 °C/min under a nitrogen purge (100 cm^3/min).

Table 2. UV/Vis Spectra Recorded for CuL$_2$ in Distilled Hexane

	copper(II) complexes/nm (ϵ)		
	tmhd	tmshd	tmghd
n → σ*	204 (12 600)	198 (13 500)	196 (15 400)
n → σ*	250 (17 800)	228 (10 600)	226 (10 800)
n → σ*		254 (20 300)	254 (21 700)
n → π*	300 (21 000)	312 (17 500)	308 (17 500)
		362 (8700)	370 (8700)
d−d	532 (42)	sh	sh
	656 (47)	656 (101)	658 (117)

Preparation of Acetyltrimethylgermane (1) via 1-(Trimethylgermyl)-1-(ethoxy)ethene (2). Under dry N$_2$, *tert*-butyllithium (0.163 mol, 96.0 mL of a 1.7 M solution in THF) was added dropwise to a solution of distilled ethyl vinyl ether (11.7 g, 0.163 mol) in dry THF (43.5 mL) at −110 °C. A highly exothermic reaction ensued, with the internal temperature rising to −78 °C and concomitant formation of a yellow precipitate. On completion of the addition, the yellow solid dissolved and the temperature of the reaction was maintained at −25 °C for 30 min. The solution was cooled to −85 °C, and chlorotrimethylgermane (25.0 g, 0.163 mol) was added dropwise so that the reaction temperature did not exceed −80 °C. After stirring at −80 °C for 4 h, the reaction mixture was warmed to room temperature and opened to air; quenching slowly with saturated NaHCO$_3$ solution, extraction with pentane (2 × 150 mL), drying over Na$_2$SO$_4$, and concentration in vacuo provided 26.8 g (0.142 mol, 87.2%) of crude **2** as a sweet-smelling, colorless, transparent liquid. For **2**: ^{1}H NMR (CDCl$_3$): δ 4.49 (d, *J* = 1.78 Hz 1H, =C*H*$_2$), 4.41 (d, *J* = 1.78 Hz 1H, =C*H*$_2$), 3.68 (q, *J* = 7.01 Hz, 2H, OC*H*$_2$), 1.26 (t, *J* = 7.01 Hz, 3H, CH$_2$-C*H*$_3$), 0.23 (s, 9H, Ge-C*H*$_3$). ^{13}C NMR (CDCl$_3$): 171.84 (*C*-OEt), 91.38 (=*C*H$_2$), 62.20 (O-*C*H$_2$CH$_3$) 14.49 (O-CH$_2$*C*H$_3$), −2.48 (Ge-*C*H$_3$).

The crude **2** was of sufficient purity to be carried over for hydrolysis to **1**. Thus, a solution of **2** (26.8 g, 0.142 mol) in diethyl ether (50 mL) was treated with 3 M HCl (47.3 mL, 0.142 mol HCl) under vigorous stirring. The hydrolysis was monitored via TLC (10:1, hexane/ethyl acetate) to ascertain complete conversion of **2** to the ketone **1** (For **1**, R_f = 0.4−0.5; **2**, R_f = 0.6−0.7). When the reaction was complete, diethyl ether (30 mL) was added and the ethereal layer was separated, washed with water (3 × 30 mL), and dried over Na$_2$SO$_4$. The solvent was removed at ambient temperature using a rotary evaporator; short path flash distillation of the residue at 62

°C and 40 mmHg gave 18.7 g (0.116 mol, 81.7%) of **1** as a sweet-smelling, yellow liquid. For **1**: ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H, C*H*$_3$-CO), 0.35 (s, 9H, (Ge-C*H*$_3$). ^{13}C NMR ($CDCl_3$): 244.92 (C═O), 36.37 (*C*H$_3$-CO), −3.10 (Ge-*C*H$_3$). Anal. Calcd for $C_5H_{12}GeO$: C, 37.36; H, 7.52. Found: C, 37.47; H, 7.76.

2,2,6,6-Tetramethyl-2-germa-3,5-heptanedione (tmghdH, 3). Under dry N_2 at 0 °C, a solution of MeLi (8.9 mL of a 1.4 M solution in diethyl ether; 12.5 mmol) was added by syringe to a stirred solution of diisopropylamine (1.26 g, 12.5 mmol) in anhydrous diethyl ether (40 mL). After the addition was complete, the reaction was stirred for 1 h at 0 °C. The temperature was then lowered to −85 °C, and **1** (2.00 g, 12.5 mmol) was slowly added to the mixture. A smooth, exothermic reaction ensued, which resulted in the formation of the corresponding lithium enolate. A solution of trimethylacetyl chloride (1.50 g, 12.5 mmol) in anhydrous diethyl ether (40 mL) was prepared and held at −110 °C. After 10 min, the solution of the lithium enolate was transferred via cannula to the second flask, the temperature of which was maintained between −110 and −75 °C. After 1 h, the reaction was essentially complete and was quenched with saturated NH_4Cl solution. The ethereal layer was separated and the solvent removed in vacuo to give 2.20 g (9.00 mmol, 72.0%) of crude **3**. Further purification of **3** was effected via flash chromatography on silica gel (40 μm) using hexane as eluant. ^{1}H NMR ($CDCl_3$): δ 15.17 (s, 1H, O*H*), 5.84 (s, 1H, ═C*H*), 1.14 (s, 9H, ^{t}Bu-C*H*$_3$), −0.33 (s, 9H, Ge-C*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 207.80 (*C*═O), 199.17 (*C*-OH), 103.60 (═*C*H), 41.27 (*C*(CH$_3$)$_3$), 27.02 (^{t}Bu-*C*H$_3$), −3.10 (Ge-*C*H$_3$).

Bis(2,2,6,6-tetramethyl-2-germa-3,5-heptanedionato)copper(II) (Cu(tmghd)$_2$; 4). To a stirred solution of crude **3** (0.34 g, 1.4 mmol) in diethyl ether (10 mL) was added a slurry of excess copper(II) acetate monohydrate (0.28 g, 1.4 mmol) in water (10 mL). A deep green solution formed upon vigorous stirring. *n*-Pentane (10 mL) was added and the organic layer separated and washed with water (10 mL). Drying over Na_2SO_4 and removal of the solvent in vacuo gave 0.19 g (3.45 mmol; 48% yield based on ligand) of **4** as an olive-green powder. Analytically pure metal complex was obtained via sublimation (0.1 mmHg, 98 °C); mp 148 °C. Anal. Calcd for $C_{20}H_{38}CuGe_2O_4$: C, 43.57; H, 6.95. Found: C, 43.80; H, 7.48.

X-ray Structure Determination. Crystal data for Cu(tmghd)$_2$, $C_{20}H_{38}CuGe_2O_4$: monoclinic, $P2_1/n$, $a = 10.233(5)$ Å, $b = 12.283(8)$ Å, $c = 11.685(5)$ Å, $\beta = 110.50(3)°$, $V = 1376(1)$ Å^3, $T = 296$ K, $Z = 2$. Data were collected on a Bruker *R*3*m* diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), μ(Mo Kα) = 9.0 cm^{-1}. The structure was solved by direct methods using the SHELXTL Plus package of programs. The trimethylgermyl and *tert*-butyl groups were disordered about the inversion center on which the copper atom is situated. The position labeled Ge(1) was modeled as 70% Ge, 30% C occupancy, while the position labeled C(4) was modeled with 30% Ge, 70% C occupancy (see Figure 1). Further, the methyl substituents on the position labeled Ge(1) were rotationally disordered; two rotamers were identified and modeled with 60% and 40% occupancy, respectively. Full-matrix least-squares refinement of the structure on $|F^2|$, based on 1582 unique reflections ($2\theta_{max} = 43°$, ω scans) of which 1012 reflections were considered observed ($F > 4\sigma(F)$) gave final $R = 0.0736$, $R_w = 0.0836$.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for Cu(tmghd)$_2$, **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010479J