Organometallics **2003,** *22,* 5054−5062

Exploring Two Reactions of Ketones with $Ge[CH(SiMe_3)_2]_2$: CH and OH Insertion

Ryan D. Sweeder, Karla A. Miller, Fern A. Edwards, Jia Wang,
Mark M. Banaszak Holl,* and Jeff W. Kampf

Chemistry Department, University of Michigan, Ann Arbor, Michigan 48109-1055

Received April 28, 2003

Herein we report the CH insertion of a stable germylene, $Ge[CH(SiMe_3)_2]_2$, into the α-CH bonds of the acetyl-containing ketones acetone, butanone, and cyclopropyl methyl ketone. This CH insertion reaction requires the presence of $MgCl_2$, yet the reaction can be successfully carried out in hydrocarbon, aromatic, and ethereal solvents. In the absence of $MgCl_2$, these acetyl-containing ketones do not undergo CH insertion but instead undergo an OH insertion to give a germyl vinyl ether. A number of other ketones, including the acetyl-containing pinacolone, have been observed to only undergo insertion into the OH bond even in the presence of $MgCl_2$.

Introduction

The functionalization of CH bonds has been a goal of both industry and academia for many years.[1,2] Recently, a number of different methods involving divalent germanium species, germylenes, have been reported. These approaches include selective intermolecular insertion into primary or secondary CH bonds α to a nitrile group,[3] intramolecular CH insertion,[4−7] and intermolecular CH activation mediated by a GeR_2/PhX (X = Cl, Br, I) complex.[8] The germylene used in this study, $Ge[CH(SiMe_3)_2]_2$ (**1**), combines both weak Lewis acidic and basic sites on the same atom.[9] This reagent is fairly reactive and must be stored and used under inert atmosphere conditions; however under these conditions it is stable.

In previous studies of the reaction between ketones and germylenes, six major modes of reactivity were reported. The reaction of $GeCl_2$·dioxane or $GeBr_2$ with ketones such as acetophenone and acetone leads to crotonic condensation.[10] The condensation of cyclohexanone to form dimers and trimers has also been observed when using $(GeCl_2)_x$ or $GeBr_2$.[11] Germylenes also react with α,β-unsaturated ketones to undergo 2 + 4 cycloaddition reactions,[12] to form polymers,[13] or with phenones to give a conjugated triene.[14] Some diketone reactivities have also been reported in the literature. α-Diketones have been reported to react through a 2 + 4 cyclization reaction with germylenes,[12,15] although *para* quinones give polymers when reacted with germylenes.[16]

We wish to report two new reactivity modes of germylenes with ketones. For ketones containing acetyl groups, facile intermolecular CH insertion chemistry has been observed. Unlike the previously reported CH insertions into organic nitriles, no examples of secondary CH bonds were found to undergo the CH insertion chemistry. Similar to the previously reported nitrile work, these reactions are found to be dependent upon the addition of $MgCl_2$. In the absence of $MgCl_2$, a reaction equivalent to the insertion of the germylene into the OH bond of the enol tautomer of the ketone is observed to form a germyl vinyl ether. The presence of a 2-fold excess of $MgCl_2$ during the reaction results in the formation $[(Me_3Si)_2CH]_2GeHCl$.

Experimental Section

All manipulations were performed using air-free techniques and dry, deoxygenated solvents.[17] Tetrahydrofuran (THF), THF-d_8, hexanes, diethyl ether, toluene, benzene, and benzene-d_6 were degassed and dried over sodium benzophenone ketyl. Acetone was dried and degassed over $CaSO_4$. All other liquid ketones (Aldrich Chemical) were degassed and dried over 4 Å molecular sieves. Butyryl ferrocene (Aldrich Chemical) was degassed in vacuo and stored under dinitrogen in a drybox. $Ge[CH(SiMe_3)_2]_2$ (**1**) was prepared via previously reported

---

[1] Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879−2932.

[2] Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987−1007.

[3] Miller, K. A.; Watson, T. W.; Bender, J. E.; Banaszak Holl, M. M.; Kampf, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 982−983.

[4] Lei, D. Q.; Lee, M. E.; Gaspar, P. P. *Tetrahedron* **1997**, *53*, 10179−10196.

[5] Gehrhus, B.; Hitchcock, P.; Lappert, M. *Angew. Chem., Int. Ed.* **1997**, *36*, 2514−2516.

[6] Jutzi, P.; Schmidt, H.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 741−746.

[7] Lange, L.; Meyer, B.; Mont, W.-W. d. *J. Organomet. Chem.* **1987**, *329*, C17−C20.

[8] Miller, K. A.; Bartolin, J. M.; O'Neill, R. M.; Sweeder, R. D.; Owens, T. M.; Kampf, J. W.; Banaszak Holl, M. M.; Wells, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 8986−8987.

[9] Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551−1556.

[10] Mironov, V. F.; Feoktistov, A. E.; Viktorov, N. A. *Z. Obshchei Khim.* **1986**, *56*, 966−967.

[11] Satgé, J.; Massol, M.; Rivière, P. *J. Organomet. Chem.* **1973**, *56*, 1−39.

[12] Michels, E.; Neumann, W. P. *Tetrahedron Lett.* **1986**, *27*, 2455−2458.

[13] Kobayashi, S.; Iwata, S.; Yajima, K.; Yagi, K.; Shoda, S. *J. Am. Chem. Soc.* **1992**, *114*, 4929−4931.

[14] Sweeder, R. D.; Edwards, F. A.; Miller, K. A.; Banaszak Holl, M. M.; Kampf, J. W. *Organometallics* **2002**, *21*, 457−459.

[15] Litz, K. E.; Bender, J. E.; Sweeder, R. D.; Banaszak-Holl, M. M.; Kampf, J. W. *Organometallics* **2000**, *19*, 1186−1189.

[16] Kobayashi, S.; Iwata, S.; Hiraishi, M. *J. Am. Chem. Soc.* **1994**, *116*, 6047−6048.

[17] Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*, 3rd ed.; Wiley: New York, 1986.

10.1021/om030308+ CCC: $25.00
Publication on Web 10/28/2003

literature methods.[9] Additional purification steps employed included Soxhlet extraction using hexane and recrystallization from hexane. $MgCl_2$-free **1** was critical when performing reactions to make pure enol insertion products. For CH-insertion reactions to which $MgCl_2$ was added, **1** known to contain traces of $MgCl_2$ could be employed. Dry $MgCl_2$ used was obtained from the reaction used to make **1**. $MgCl_2$ was also purchased as anhydrous beads from Aldrich and ground before use. Both sources gave identical reactivity. ^{1}H NMR spectra were recorded at 400 MHz on a Varian Inova 400 spectrometer and referenced to the residual protons in C_6D_6 at 7.15 ppm and in THF-d_8 at 3.58 ppm. ^{13}C NMR spectra were recorded at 100.581 MHz and referenced to the natural abundance of ^{13}C in C_6D_6 or THF-d_8 at 128.00 and 67.57 ppm, respectively. IR spectra were obtained as thin films of the products formed by evaporation from solution on NaCl plates on a Perkin-Elmer Spectrum BX. High-resolution mass spectra were collected on a VG 70-250-S mass spectrometer using electron impact (70 eV) or chemical ionization with methane (for **3** only) for ionization.

All reactions reported give quantitative yields of the products described as determined via ^{1}H NMR spectroscopy. Isolation of analytically pure material typically resulted in substantially lower yields due to the high degree of solubility of these compounds.

Bis[bis(trimethylsilyl)methyl]-2-ketopropylgermane (2). A glass bomb was charged with **1** (100 mg, 0.26 mmol) and $MgCl_2$ (24 mg, 0.25 mmol) in benzene (5 mL). Acetone (21 μL, 0.29 mmol) was added via syringe, and the reaction was stirred for 48 h. The volatiles were removed in vacuo to leave a white residue. The residue was dissolved in hexane (2 mL) and filtered through a Whatman 0.02 μm syringe top filter to give a colorless filtrate. The solvent was evaporated from the filtrate, leaving a colorless oil of **2** (75 mg, 65% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 4.68 (tt, $^3J_{HH} = 2.8$ Hz, $^3J_{HH} = 2.4$ Hz, 1 H, Ge*H*), 2.40 (d, $^3J_{HH} = 2.8$ Hz, 2 H, CH_2), 1.94 (s, 3 H, CH_3), 0.20 (s, 18 H, Si(CH_3)$_3$, 0.19 (s, 18 H, Si(CH_3)$_3$), -0.32 (d, $^3J_{HH} = 2.4$ Hz, 2 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C_6D_6): δ 204.68 (*C*═O); 36.85 (*C*H$_3$) , 30.55 (*C*H$_2$); 8.90 (Ge*C*HSi); 3.50 and 2.72 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): 2010 ν(Ge−H), 1696 ν(C═O). EI/MS *m*/*z*: M$^+$ = 450.1683 amu. Anal. Calcd for $C_{17}H_{44}GeOSi_4$: C, 45.43; H, 9.87. Found: C, 45.04; H, 9.56.

Bis[bis(trimethylsilyl)methyl]-2-ketobutylgermane (3). Butanone (70 μL, 0.78 mmol) was added to a solution of **1** (300 mg, 0.767 mmol) in toluene (40 mL) with added $MgCl_2$ (70 mg, 0.74 mmol). The solution was stirred for 36 h, changing from an orange to a yellow color. An aliquot was removed and the solvent evaporated. ^{1}H NMR of the residual oil indicated that the reaction had completed, although the solution was not yet colorless. The toluene was then removed in vacuo to give a pale yellow oil. Pentane was added (5 mL), and the solution was filtered at −78 °C, removing a white solid. The collected filtrate was stripped of solvent, yielding a pale yellow oil. This oil was distilled under vacuum (10^{-5} Torr) at 100 °C to give **3** (163 mg, 51.5% yield) as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): C−H insertion: δ 4.67 (tt, $^3J_{HH} = 2.4$ Hz, $^3J_{HH} = 2.4$ Hz, 1 H, Ge*H*), 2.39 (d, $^3J_{HH} = 2.4$ Hz, 2 H, CH_2), 2.26 (q, $^3J_{HH} = 7.2$ Hz, 2 H, CH_2), 1.02 (t, $^3J_{HH} = 7.2$ Hz, 3 H, CH_3), 0.21 (s, 18 H, Si(CH_3)$_3$), 0.19 (s, 18 H, Si(CH_3)$_3$), -0.31 (d, $^3J_{HH} = 2.4$ Hz, 2 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C_6D_6): δ 207.84 (*C*═O); 36.46 (*C*H$_2$), 35.48 (CH$_3$), 30.21 (*C*H$_2$), 8.15 (Ge*C*HSi), 3.52 and 2.74 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): 2010 ν(Ge−H), 1695 ν(C═O). CI/MS *m*/*z*: [M − H]$^+$ = 463.1751 amu. Anal. Calcd for $C_{18}H_{46}GeOSi_4$: C, 46.64; H, 10.00. Found: C, 46.26; H, 10.37.

Bis[bis(trimethylsilyl)methyl]-(2-cyclopropyl-2-ketoethyl)germane (4). A glass bomb was charged with **1** (300 mg, 0.767 mmol) and $MgCl_2$ (72 mg, 0.77 mmol) in toluene (20 mL). Cyclopropyl methyl ketone (75 μL, 0.80 mmol) was added via syringe and the reaction stirred for 18 h. During this time the solution faded from the germylene orange color to a pale yellow color. The ^{1}H NMR spectrum of a small aliquot indicated that the reaction had completed. The volatiles were removed in vacuo to leave a tan oil. The oil was dissolved in pentane (5 mL) and cold (−78 °C) filtered through a glass frit. The collected filtrate was stripped of solvent to give a pale yellow oil. The oil was distilled under vacuum (10^{-5} Torr) at 120 °C to give **4** as a colorless oil (85 mg, 23% yield.) ^{1}H NMR (400 MHz, C_6D_6): δ 4.83 (tt, $^3J_{HH} = 3.2$ Hz, $^3J_{HH} = 2.5$ Hz, 1 H, Ge*H*), 2.62 (d, $^3J_{HH} = 3.2$ Hz, 2 H, CH_2), 1.73 (m, 1 H, C*H*), 1.60 (m, 2 H, CH_2), 0.53 (m, 2 H, CH_2), 0.23 (s, 18 H, Si(CH_3)$_3$), 0.22 (s, 18 H, Si(CH_3)$_3$), 0.05 (d, $^3J_{HH} = 2.5$ Hz, 2 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C_6D_6): δ 208.6 (*C*═O); 37.09 (*C*H$_2$), 21.33 (*C*H), 10.82 (Ge*C*HSi), 4.88 (*C*H$_2$), 3.57 and 2.77 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): 2010 ν(Ge−H), 1680 ν(C═O). EI/MS *m*/*z*: [M − CH$_3$]$^+$ = 461.1604 amu. Anal. Calcd for $C_{19}H_{46}GeOSi_4$: C, 47.99; H, 9.75. Found: C, 47.97; H, 9.91.

Bis[bis(trimethylsilyl)methyl]isopropenoxygermane (5). Acetone (80 μL, 1.1 mmol) was added to **1** (400 mg, 1.02 mmol) in THF (8 mL). The solution was stirred for 66 h. Over this time the solution faded from orange to yellow to colorless, indicating the consumption of the germylene. The solvent was removed in vacuo to give a colorless oil. This oil was pure **5** by ^{1}H NMR spectroscopy. Analytically pure **5** was isolated by trituration with toluene (3 × 8 mL) to ensure all the THF was removed. The oil was dissolved in pentane and filtered before the pentane was removed in vacuo. The resultant oil was distilled via a short path distillation at 80 °C to give 271 mg (59% isolated yield) of analytically pure **5**. ^{1}H NMR (400 MHz, C_6D_6): δ 6.21 (t, $^3J_{HH} = 2.3$ Hz, 1 H, Ge*H*), 4.11 (s, 1 H, C═C*H*), 4.08 (s, 1 H, C═C*H*), 1.84 (s, 3 H, CH_3), 0.29 (s, 18 H, Si(CH_3)$_3$), 0.18 (s, 18 H, Si(CH_3)$_3$), -0.14 (d, $^3J_{HH} = 2.3$ Hz, 2 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C_6D_6): δ not observed (*C*−O); 86.30 (C═*C*); 23.90 (*C*H$_3$); 9.33 (Ge*C*HSi); 3.11 and 2.46 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): 2036 ν(Ge−H). EI/MS *m*/*z*: [M − CH$_3$]$^+$ = 435.1453 amu. Anal. Calcd for $C_{17}H_{44}GeOSi_4$: C, 45.43; H, 9.87. Found: C, 45.55; H, 10.12.

Bis[bis(trimethylsilyl)methyl]-(1-methyl-1-propenoxy)germane (6a) and Bis[bis(trimethylsilyl)methyl]-(1-ethylethenoxy)germane (6b). Butanone (150 μL, 1.67 mmol) was added to a solution of **1** (400 mg, 1.02 mmol) in THF (15 mL). The solution was stirred for 66 h, during which time the color progressed from orange to yellow to colorless. The volatiles were removed in vacuo, leaving a colorless oil. The oil was triturated with toluene (4 × 8 mL) to ensure all THF was removed. Pentane (5 mL) was then distilled into the dissolved oil and the solution filtered. The pentane was removed in vacuo to give a colorless oil of a mixture of **6a** and **6b**, pure by ^{1}H NMR spectroscopy (426 mg, 90% yield). Analytically pure material distilled from the oil at 80 °C via a short path distillation to yield 30 mg (6.3%) of a mixture of **6a** and **6b** in a 2:1 ratio as measured via ^{1}H NMR spectroscopy. **6a** ^{1}H NMR (400 MHz, C_6D_6): δ 6.23 (t, $^3J_{HH} = 2.0$ Hz, 1 H, Ge*H*), 4.14 (s, 1 H, C═C*H*), 4.09 (s, 1 H, C═C*H*), 2.16 (q, $^3J_{HH} = 7.5$ Hz, 2 H, CH_2), 1.10 (t, $^3J_{HH} = 7.5$ Hz, 3 H, CH_3) 0.29 (s, 18 H, Si(CH_3)$_3$), 0.19 (s, 18 H, Si(CH_3)$_3$) and -0.14 (d, $^3J_{HH} = 2.0$ Hz, 2 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C_6D_6): δ 151.43 (*C*-O); 84.61 (C═*C*); 30.73 (*C*H$_2$), 12.09 (*C*H$_3$); 9.34 (Ge*C*HSi); 3.18 and 2.49 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): 2045 ν(GeH), 1664 ν(C═C). **6b** ^{1}H NMR (400 MHz, C_6D_6): δ 6.18 (t, $^3J_{HH} = 2.4$ Hz, 1 H, Ge*H*), 4.59 (q, $^3J_{HH} = 6.8$ Hz, 1 H, C═C*H*), 1.81 (s, 3 H, CH_3), 1.60 (d, $^3J_{HH} = 6.8$ Hz, 3 H, CH_3), 0.29 (s, 18 H, Si(CH_3)$_3$), 0.19 (s, 18 H, Si(CH_3)$_3$) and -0.01 (d, $^3J_{HH} = 2.4$ Hz, 2 H, GeC*H*Si$_2$). ^{13}C NMR (100.5 MHz, C_6D_6): δ 152.76 (*C*-O); 95.79 (C═*C*); 18.41, 12.40 (*C*H$_3$); 9.24 (Ge*C*HSi); 3.16 and 2.49 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): 2038 ν(Ge−H). Anal. Calcd for $C_{18}H_{46}GeOSi_4$ (mixture of **6a** and **6b**): C, 46.64; H, 10.00. Found: C, 46.54; H, 9.93. Only one isomer is formed for **6b**; however the data do not allow a definitive assignment of the *Z* or *E* isomer.

Bis[bis(trimethylsilyl)methyl]-(1-cyclopropyethenoxy)germane (7). A glass bomb was charged with **1** (400 mg, 1.02 mmol) in benzene (14 mL). Cyclopropyl methyl ketone

(205 μL, 2.18 mmol) was added via syringe and the reaction stirred for 11 days, until the solution had faded to colorless. The volatiles were removed in vacuo to leave an oil of **7** that was pure by ^{1}H NMR spectroscopy. The oil was triturated with toluene (4 × 8 mL) before dissolving in pentane (6 mL) and filtered. The pentane was removed in vacuo to yield a colorless oil. The oil was distilled via short path distillation. At 95 °C 21 mg (4.3% yield) of **7** was collected. Continued heating to 120 °C provided 235 mg (48.3%) of isolated **7**. Although no impurities were identifiable via ^{1}H NMR spectroscopy, a satisfactory elemental analysis could not be obtained. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 6.23 (t, $^3J_{\mathrm{HH}} = 2.4$ Hz, 1 H, GeH), 4.15 (s, 1 H, C=CH), 4.05 (s, 1 H, C=CH), 1.41 (m, 1 H, CH), 0.77 (m, 2 H, CH_2), 0.49 (m, 2 H, CH_2), 0.29 (s, 18 H, Si(CH_3)$_3$), 0.19 (s, 18 H, Si(CH_3)$_3$), −0.01 (d, $^3J_{\mathrm{HH}} = 2.4$ Hz, 2 H, GeCHSi). ^{13}C NMR (100.5 MHz, $\mathrm{C_6D_6}$): δ 152.76 (C−O); 83.48 (C=C); 20.80 (CH), 9.30 (GeCHSi); 5.63 (CH$_2$); 3.19 and 2.51 (Si(CH$_3$)$_3$). IR (cm^{-1}): 2039 ν(Ge−H). EI/MS m/z: $[\mathrm{M} - \mathrm{CH_3}]^+ = 461.1597$ amu.

Bis[bis(trimethylsilyl)methyl]chlorogermane (8). A glass bomb was charged with **1** (400 mg, 1.02 mmol) and $\mathrm{MgCl_2}$ (160 mg, 1.68 mmol) in THF (20 mL). Butanone (110 μL, 1.228 mmol) was added via syringe and the reaction stirred for 11 h, until the solution had faded to colorless. The volatiles were removed in vacuo to leave an oil that was triturated with toluene (3 × 10 mL) until the residue became a white solid. The solid was dissolved in pentane (6 mL) and filtered. The pentane was reduced to 3 mL and cooled to −78 °C. The resulting white crystalline solid was isolated via filtration at −78 °C from the residual pentane to yield 187 mg of pure **8** (44% yield). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 6.03 (t, $^3J_{\mathrm{HH}} = 2.8$ Hz, 1 H, GeH), 0.30 (s, 18 H, Si(CH_3)$_3$), 0.16 (s, 18 H, Si(CH_3)$_3$), 0.05 (d, $^3J_{\mathrm{HH}} = 2.8$ Hz, 2 H, GeCHSi). ^{1}H NMR ($\mathrm{C_4D_8O}$): δ 5.91 (t, $_3J_{\mathrm{HH}} = 2.8$ Hz, 1 H, GeH), 0.25 (s, 18 H, Si(CH_3)$_3$), 0.21 (s, 18 H, Si(CH_3)$_3$), 0.13 (d, $^3J_{\mathrm{HH}} = 2.8$ Hz, 2 H, GeCHSi). ^{13}C NMR (100.5 MHz, $\mathrm{C_6D_6}$): δ 10.82 (GeCHSi), 3.18 and 2.23 (Si(CH$_3$)$_3$). ^{13}C NMR (100.5 MHz, $\mathrm{C_4D_8O}$): δ 11.45 (GeCHSi), 3.22 and 2.30 (Si(CH$_3$)$_3$). IR (cm^{-1}): 2049 ν(Ge−H). EI/MS m/z: $[\mathrm{M} - \mathrm{CH_3}]^+ = 413.0783$ amu. Anal. Calcd for $\mathrm{C_{14}H_{39}GeClOSi_4}$: C, 39.30; H, 9.19. Found: C, 38.90; H, 9.28.

Structural Determination of 8. Colorless blocks of **8** were grown from a pentane solution at 0 °C. Crystal data for **8** ($\mathrm{C_{14}H_{39}GeClOSi_4}$): $M = 427.85$, $T = 118(2)$ K, monoclinic, space group $P2_1/n$, $a = 11.7422(4)$ Å, $b = 12.3432(4)$ Å, $c = 17.3674(7)$ Å, $\alpha = 90°$, $\beta = 108.655(2)°$, $\gamma = 90°$, $V = 2384.92(15)$ Å^3, $Z = 4$, calcd = 1.192 g cm^{-3}, $\mu = 1.591$ mm^{-1}, $\lambda = 0.71073$ Å, $2\theta_{\max} = 56.70°$, 32 627 measured reflections, 5928 independent reflections, 4702 reflections greater than $2\sigma(I)$, 196 refined parameters, GOF = 1.023, $R_1 = 0.0285$, $wR_2 = 0.0650$ ($I > 2\sigma(I)$), $R_1 = 0.0463$, $wR_2 = 0.0718$ (for all data), largest difference peak and hole 0.483 and −0.529 e Å^{-3}. A crystal of dimensions 0.08 × 0.48 × 0.52 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low-temperature device and normal focus Mo-target X-ray tube operated at 2000 W power (50 kV, 40 mA). The detector was placed at a distance 4.950 cm from the crystal. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS[18] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL software package[19] by full-matrix least-squares procedures on F^2 for all reflections. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Additional crystallographic information can be found in the Supporting Information.

Bis[bis(trimethylsilyl)methyl]-(1-*tert*-butylethenoxy)-germane (9). A glass bomb was charged with **1** (100 mg, 0.256 mmol) in benzene (6 mL). Pinacolone (106 mg, 1.06 mmol) was added via syringe and the reaction stirred for 96 h, over which time the solution became colorless. The volatiles were removed in vacuo to leave a white residue. The residue was dissolved in hexane (2 mL) and filtered through a Whatman 0.02 μm syringe top filter to give a colorless filtrate. The solvent was evaporated from the filtrate, leaving a colorless oil of **9** (88 mg, 70% yield). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 6.22 (t, $^3J_{\mathrm{HH}} = 2.0$ Hz, 1 H, GeH), 4.27 (d, $^2J_{\mathrm{HH}} = 2.1$ Hz, 1 H, C=CH), 4.02 (d, $^2J_{\mathrm{HH}} = 2.1$ Hz, 1 H, C=CH), 1.24 (s, 9 H, CH$_3$), 0.30 (s, 18 H, Si(CH_3)$_3$), 0.20 (s, 18 H, Si(CH_3)$_3$), −0.11 (d, $^3J_{\mathrm{HH}} = 2.0$ Hz, 2 H, GeCHSi). ^{13}C NMR (100.5 MHz, $\mathrm{C_6D_6}$): δ 171.07 (C-O), 83.47 (C=C), 37.03 (CMe$_3$), 29.45 (CH$_3$) 9.28 (GeCHSi), 3.40 and 2.63 (Si-(CH$_3$)$_3$). IR (cm^{-1}): 2047 ν(Ge−H). EI/MS m/z: $[\mathrm{M} - \mathrm{CH_3}]^+ = 477.1901$ amu.

Bis[bis(trimethylsilyl)methyl]-1-cyclopentenoxygermane (10). A glass bomb was charged with **1** (100 mg, 0.256 mmol) in benzene (6 mL). Cyclopentanone (24 μL, 0.27 mmol) was added via syringe and the reaction stirred for 16 h. The volatiles were removed in vacuo to leave a white residue. The residue was dissolved in hexane (2 mL) and filtered through a Whatman 0.02 μm syringe top filter to give a colorless filtrate. The solvent was evaporated from the filtrate, leaving a colorless oil of **10** (85 mg, 70% yield). ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 6.18 (t, $^3J_{\mathrm{HH}} = 2.4$ Hz, 1 H, GeH), 4.61 (s, 1 H, C=CH), 2.39 (m, 4H, CH_2), 1.81 (m, 2 H, CH_2), 0.29 (s, 18 H, Si-(CH_3)$_3$), 0.18 (s, 18 H, Si(CH_3)$_3$), and −0.12 (d, $^3J_{\mathrm{HH}} = 2.4$ Hz, 2 H, GeCHSi). ^{13}C NMR (100.5 MHz, $\mathrm{C_6D_6}$): δ 160.15 (C-O), 97.18 (C=CH), 34.88, 29.33, 21.90 (CH$_2$), 9.74 (GeCHSi), 3.14 and 2.47 (Si(CH$_3$)$_3$). IR (cm^{-1}): 2044 ν(Ge−H), 1633 ν(C=C). Anal. Calcd for $\mathrm{C_{19}H_{46}GeOSi_4}$: C, 47.99; H, 9.75. Found: C, 47.67; H, 9.70.

Bis[bis(trimethylsilyl)methyl]-(2-indenyl-1-oxy)germane (11). A glass bomb was charged with **1** (100 mg, 0.256 mmol) and 1-indanone (32 mg, 0.24 mmol). Benzene (7 mL) was added and the reaction stirred for 72 h. The volatiles were removed in vacuo to leave a pale yellow solid. The residue was dissolved in hexane (2 mL) and filtered through a Whatman 0.02 μm syringe top filter to give a colorless filtrate. The solvent was evaporated from the filtrate, leaving a white solid of **11** (80 mg, 60% yield). ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 7.55 (d, $^3J_{\mathrm{HH}} = 7.6$ Hz, 1 H, ArH), 7.29 (dd, $^3J_{\mathrm{HH}} = 7.6$ Hz, $^3J_{\mathrm{HH}} = 7.4$ Hz, 1 H, ArH), 7.22 (d, $^3J_{\mathrm{HH}} = 7.2$ Hz, 1 H, ArH), 7.12 (dd, $^3J_{\mathrm{HH}} = 7.4$ Hz, $^3J_{\mathrm{HH}} = 7.2$ Hz, 1 H, ArH), 6.42 (t, $^3J_{\mathrm{HH}} = 2.8$ Hz, 1 H, GeH), 5.33 (t, $^3J_{\mathrm{HH}} = 2.4$ Hz, 1H, C=CH), 3.19 (d, $^3J_{\mathrm{HH}} = 2.4$ Hz, 2 H, CH_2), 0.29 (s, 18 H, Si(CH_3)$_3$), 0.17 (s, 18 H, Si(CH_3)$_3$), and −0.01 (d, $^3J_{\mathrm{HH}} = 2.8$ Hz, 2 H, GeCHSi). ^{13}C NMR (100.5 MHz, $\mathrm{C_6D_6}$): δ 158.22 (C−O); 142.45 143.14, 126.34, 125.42, 124.42, 119.06 (Ar); 101.41 (C=C); 34.10 (CH$_2$); 9.78 (GeCHSi); 3.21 and 2.46 (Si(CH$_3$)$_3$). IR (cm^{-1}): 2043 ν-(Ge−H). Anal. Calcd for $\mathrm{C_{23}H_{46}GeOSi_4}$: C, 52.76; H, 8.86. Found: C, 52.57; H, 8.56.

Bis[bis(trimethylsilyl)methyl]-(1-ferrocenyl-1-butenoxy)germane (12). A glass bomb was charged with **1** (100 mg, 0.256 mmol) and butyrylferrocene (65 mg, 0.25 mmol). Benzene (7 mL) was added and the reaction stirred for 96 h. The volatiles were removed from the still orange solution in vacuo to leave a bright orange solid. The residue was dissolved in hexane (2 mL) and filtered through a Whatman 0.02 μm syringe top filter to give an orange filtrate. The solvent was evaporated from the filtrate, leaving an orange solid of **12** (60 mg, 26% yield). Washing of the filter with 3 mL of benzene followed by recrystallization from hexane afforded an orange solution, which contained another 35 mg of **12** (15%, 41% total yield). ^{1}H NMR: δ 6.29 (t, $^3J_{\mathrm{HH}} = 2.2$ Hz, 1 H, GeH), 4.88 (t, $^3J_{\mathrm{HH}} = 7.2$ Hz, 1 H, C=CH), 4.58 (pseudo t, $^3J_{\mathrm{HH}} = 2.4$ Hz, 2 H, CpH), 4.04 (pseudo t, $^3J_{\mathrm{HH}} = 2.4$ Hz, 2 H, CpH), 3.91 (s, 5 H, Cp ring), 2.54 (qd, $^3J_{\mathrm{HH}} = 7.6$ Hz, $^3J_{\mathrm{HH}} = 7.2$ Hz, 2 H, CH_2), 1.17 (t, $^3J_{\mathrm{HH}} = 7.6$ Hz, 3 H, CH_3) 0.32 (s, 18 H, Si(CH_3)$_3$), 0.20 (s, 18 H, Si(CH_3)$_3$), −0.08 (d, $^3J_{\mathrm{HH}} = 2.2$ Hz, 2 H, GeCHSi). ^{13}C NMR (100.5 MHz, $\mathrm{C_6D_6}$): δ 151.91 (C−O); 106.78 (C=C);

---

[18] Sheldrick, G. M. *SADABS*, Program for Empirical Absorption correction of Area Detector Data; University of Göttingen: Göttingen, Germany, 1996.

[19] Sheldrick, G. M. *SHELXTL*; Bruker Analytical X-ray: Madison, WI, 1997.

70.50, 69.62, 69.34, 67.99 (Cp); 21.17 (CH$_2$); 16.06 (*C*H$_3$); 9.42 (Ge*C*HSi); 3.31 and 2.56 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): 2038 ν(Ge−H). EI/MS *m*/*z*: M$^+$ = 648.1821 amu.

1,1-Bis[bis(trimethylsilyl)methyl]-3-methyl-1,7a-dihydrobenzo[*c*][1,2]oxagermole (13). Acetophenone (9.6 μL, 0.082 mmol) was added to **1** (30 mg, 0.077 mmol) in benzene (3 mL) in a glass bomb. The solution was stirred for 48 h as the color changed from orange to pale yellow. The volatiles were removed in vacuo to give a pale yellow residue. A mixture of products (39 mg, 97% yield) was obtained of the aromatic activation and OH insertion products with 87% and 13% yields, respectively. Pure **13** has not been isolable due to similar solubilities and the slow conversion to **17**. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 6.38 (d, $^3J_{\mathrm{HH}}$ = 8.8 Hz, 1 H, C*H*), 5.99 (m, 1 H, C*H*), 5.90 (d, $^3J_{\mathrm{HH}}$ = 8.8 Hz, 1 H, C*H*), 5.62 (m, 1 H, C*H*), 3.75 (broad s, 1 H, C*H*Ge), 1.84 (d, $^5J_{\mathrm{HH}}$ = 3.6 Hz, 3 H, C*H*$_3$), 0.27 (s, 18 H, Si(C*H*$_3$)$_3$), 0.22 (s, 9 H, Si(C*H*$_3$)$_3$), 0.19 (s, 1 H, GeC*H*Si), 0.12 (s, 9 H, Si(C*H*$_3$)$_3$), and 0.04 (s, 1 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C$_6$D$_6$): δ 154.48 (*C*−O); 128.41, 126.13, 126.03, 124.24, 117.90 (C=*C*); 37.51 (*C*HGe); 15.95 (*C*H$_3$); 13.30 and 11.62 (Ge*C*HSi); 3.69, 3.47, 3.34, and 2.99 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): No Ge−H or C=O. ^{1}H-COSY NMR indicates that the methyl group appearing as a doublet at δ = 1.84 is coupled to the CHGe functionality at δ = 3.75.

1,1-Bis[bis(trimethylsilyl)methyl]-3-ethyl-1,7a-dihydrobenzo[*c*][1,2]oxagermole (14). Propiophenone (10.7 μL, 0.0805 mmol) was added to **1** (30 mg, 0.077 mmol) in THF (3 mL). A bright yellow solution was immediately formed. The solution was stirred for 15 min until the color had vanished, and the volatiles were removed in vacuo. The residue contained the product along with the excess propiophenone. Slow evaporation of **14** from benzene produced crystals of **14** (6 mg, 14% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 6.42 (d, $^3J_{\mathrm{HH}}$ = 9.6 Hz, 1 H, C*H*), 5.98 (m, 1 H, C*H*), 5.91 (d, $^3J_{\mathrm{HH}}$ = 9.3 Hz, 1 H, C*H*), 5.62 (m, 1 H, C*H*), 3.78 (s, 1 H, C*H*Ge), 2.36 (m, 1 H, C*H*$_2$CO), 2.14 (m, 1 H, C*H*$_2$CO), 1.12 (pseudo t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 3 H, C*H*$_3$), 0.27 (s, 18 H, Si(C*H*$_3$)$_3$), 0.21 (s, 9 H, Si(C*H*$_3$)$_3$), 0.12 (s, 1 H, GeC*H*Si), 0.12 (s, 9 H, Si(C*H*$_3$)$_3$), and 0.05 (s, 1 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C$_6$D$_6$): δ 159.21 (*C*−O); 125.99, 125.87, 124.26, 117.92 and 107.97 (C=C); 37.53 (*C*HGe); 23.17 (*C*H$_2$); 13.33 (*C*H$_3$); 12.39 and 11.63 (Ge*C*HSi); 3.75, 3.55, 3.35, and 2.96 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): No Ge−H or C=O.

1,1-Bis[bis(trimethylsilyl)methyl]-3,4,5,8a-tetrahydronaphtho[*c*,*d*][1,2]oxagermole (15). α-Tetralone (67 μL, 0.050 mmol) was added to **1** (200 mg, 0.511 mmol) in hexane (10 mL). After stirring for 4 h, the solution lost the orange color, indicating consumption of the germylene. Removal of the volatiles in vacuo led to the isolation of 220 mg (80% yield) of a material that was 95% **15** and 5% **19** via ^{1}H NMR spectroscopy. Isolation of pure **15** was prevented due to the facile formation of **19**. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 5.97 (dd, $^3J_{\mathrm{HH}}$ = 9.4 Hz, $^3J_{\mathrm{HH}}$ = 5.6 Hz, 1 H, C=C*H*), 5.79 (dd, $^3J_{\mathrm{HH}}$ = 9.4 Hz, $^3J_{\mathrm{HH}}$ = 3.0 Hz, 1 H, C=C*H*), 5.36 (d, $^3J_{\mathrm{HH}}$ = 5.6 Hz, 1 H, C=C*H*), 3.77 (br s, 1 H, Ge−C*H*) 2.28 (m, 4 H, C*H*$_2$) 1.63 (m, 2 H, C*H*$_2$), 0.29 (s, 9 H, Si(C*H*$_3$)$_3$), 0.28 (s, 9 H, Si(C*H*$_3$)$_3$), 0.24 (s, 9 H, Si(C*H*$_3$)$_3$), 0.14 (s, 9 H, Si(C*H*$_3$)$_3$), 0.12 (s, 1 H, Ge*C*HSi), and 0.09 (s, 1 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C$_6$D$_6$): δ 157.84 (*C*−O); 138.42, 126.58, 121.09, 111.69, and 101.41 (C=*C*); 37.03 (*C*HGe), 29.08, 24.41, and 22.98 (*C*H$_2$); 13.88 and 11.75 (Ge*C*HSi); 3.65, 3.42, 3.33, and 2.99 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): no ν(Ge−H) or ν(C=O). EI/MS *m*/*z*: [M]$^+$ = 536.1825 amu.

1,1-Bis[bis(trimethylsilyl)methyl]-7,10a-dihydroanthraceno[*c*,*d*][1,2]oxagermole (16). Anthrone (100 mg, 0.515 mmol) was added to **1** (200 mg, 0.511 mmol) and dissolved in hexane (10 mL). The solution was stirred for 16 h before the volatiles were removed in vacuo. The pale yellow residue (288 mg, 96% yield) contained **16** with **20** as a 2% impurity (by ^{1}H NMR spectroscopy.) This same level of impurity was still observed for shorter reaction times. Attempted purification of **16** by recrystallization led to the exclusive isolation of **20**. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.86 (d, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1 H, Ar*H*), 7.10 (dd, $^3J_{\mathrm{HH}}$ = 7.6 Hz, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 1 H, Ar*H*), 6.94 (dd, $^3J_{\mathrm{HH}}$ = 7.6 Hz, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 1 H, Ar*H*) 6.81 (d, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1 H, Ar*H*) 6.01 (m, $^3J_{\mathrm{HH}}$ = 12.0 Hz, 1 H, C=C*H*), 5.81 (d, $^3J_{\mathrm{HH}}$ = 12.0 Hz, 1H, C=C*H*), 5.40 (s, 1 H, C=C*H*), 4.06 (s, 1 H, C*H*Ge), 3.86 (d, $^2J_{\mathrm{HH}}$ = 20.6 Hz, 1 H, C*H*$_2$), 3.40 (d, $^2J_{\mathrm{HH}}$ = 20.6 Hz, 1 H, C*H*$_2$), 0.32 (s, 9 H, Si(C*H*$_3$)$_3$), 0.26 (s, 9 H, Si(C*H*$_3$)$_3$), 0.20 (s, 9 H, Si(C*H*$_3$)$_3$), 0.19 (s, 1 H, GeC*H*Si), 0.16 (s, 1 H, GeC*H*Si) and 0.14 (s, 9 H, Si(C*H*$_3$)$_3$). ^{13}C NMR (100.5 MHz, C$_6$D$_6$): δ 153.67 (*C*−O); 136.83, 135.94, 131.44, 127.51, 126.57, 126.33, 125.07, 122.28, and 121.83, (Ar, C=*C*); 114.14 (*C*=C−O), 37.82 (*C*HGe); 34.64 (*C*H$_2$) 14.55 and 12.46 (Ge*C*HSi); 3.57, 3.52, 3.37, and 3.05 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): No Ge−H or C=O. EI/MS *m*/*z*: [M − CH$_3$]$^+$ = 584.1854 amu.

Bis[bis(trimethylsilyl)methyl]-(1-phenylethenoxy)germane (17). Acetophenone (4.7 μL, 0.040 mmol) was added to **1** (15 mg, 0.038 mmol) in benzene-*d*$_6$ (0.6 mL) in a sealable NMR tube. Monitoring the solution by ^{1}H NMR spectroscopy indicated that after 20 days the solution contained 66% **17** and 34% **13**. Heating this mixture at 60 °C for 48 h drove the reaction to completion. The volatiles were removed in vacuo to give an oily residue. This material was dissolved in pentane and filtered. Slow evaporation of the solvent yielded 9 mg (45% yield) of pure **17** as a colorless oil. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.80 (d, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 2 H, Ar*H*), 7.19 (dd, $^3J_{\mathrm{HH}}$ = 7.4 Hz, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 2 H, Ar*H*), 7.09 (t, $^3J_{\mathrm{HH}}$ = 7.4 Hz, 1 H, Ar*H*), 6.38 (t, $^3J_{\mathrm{HH}}$ = 2.4 Hz, 1 H, Ge*H*) 4.93 (d, $^2J_{\mathrm{HH}}$ = 2.0 Hz, 1 H, C*H*$_2$), 4.47 (d, $^2J_{\mathrm{HH}}$ = 2.0 Hz, 1 H, C*H*$_2$), 0.27 (s, 18 H, Si(C*H*$_3$)$_3$), 0.18 (s, 18 H, Si(C*H*$_3$)$_3$), and −0.03 (d, $^3J_{\mathrm{HH}}$ = 2.4 Hz, 2 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C$_6$D$_6$): δ 160.29 (*C*−O); 139.65, 128.16, 126.26, and 124.22 (Ar); 87.27 (*C*=C); 9.57 (Ge*C*HSi); 3.15 and 2.50 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): 2044 ν(Ge−H). Anal. Calcd for C$_{22}$H$_{46}$GeOSi$_4$: C, 51.65; H, 9.06. Found: C, 51.87; H, 9.32.

Bis[bis(trimethylsilyl)methyl]-(1-phenyl-1-propoxy)germane (18). Propiophenone (125 mg, 0.932 mmol) was added to **1** (300 mg, 0.767 mmol) in toluene (20 mL). The solution was refluxed under an argon atmosphere for 16 h. The volatiles were removed in vacuo, leaving 384 mg of an oily pale yellow residue of **18** that solidified over a 12 h period (95% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.57 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 2 H, Ar*H*), 7.21 (dd, $^3J_{\mathrm{HH}}$ = 7.2 Hz, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 2 H, Ar*H*), 7.07 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 1 H, Ar*H*), 6.27 (s, 1 H, Ge*H*), 4.98 (q, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 1 H, C=C*H*), 1.73 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 3 H, C*H*$_3$), 0.25 (s, 18 H, Si(C*H*$_3$)$_3$), 0.20 (s, 18 H, Si(C*H*$_3$)$_3$), and −0.09 (s, 2 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C$_6$D$_6$): δ 155.02 (*C*−O); 129.16, 129.09, 127.88, and 127.54 (Ar); 99.33 (C=*C*); 13.52 (*C*H$_3$); 9.58 (Ge*C*HSi); 3.16 and 2.45 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): 2040 ν(Ge−H). Anal. Calcd for C$_{23}$H$_{48}$GeOSi$_4$: C, 52.56; H 9.21. Found: C, 52.26; H, 9.38. The formation of **18** was also observed if samples of **14** were heated.

After sitting for 9 months in a dinitrogen atmosphere, 40% of **18** had converted to a second isomer through what appeared to be an *E*/*Z* isomerization. Second OH insertion isomer: ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.57 (d, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 2 H, Ar*H*), 7.21 (dd, $^3J_{\mathrm{HH}}$ = 7.2 Hz, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 2 H, Ar*H*), 7.04 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 1 H, Ar*H*), 6.15 (s, 1 H, Ge*H*), 5.18 (q, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 1 H, C=C*H*), 1.90 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 3 H, C*H*$_3$), 0.26 (s, 18 H, Si(C*H*$_3$)$_3$), 0.16 (s, 18 H, Si(C*H*$_3$)$_3$), and 0.05 (s, 2 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C$_6$D$_6$): δ 155.95 (*C*−O); 129.11, 127.91, 127.57 and 126.91 (Ar); 105.36 (C=*C*); 12.69 (*C*H$_3$); 7.63 (Ge*C*HSi); 3.34 and 2.82 (Si(*C*H$_3$)$_3$). IR (cm^{-1}): 2040 ν(Ge−H).

2,2-Bis(bis(trimethylsilanyl)methyl)-2a,6,7,8-tetrahydro-2*H*-1-oxa-2-germa-acenaphthylene (19). α-Tetralone (67 μL, 0.050 mmol) was added to **1** (200 mg, 0.511 mmol) in hexane (10 mL). After stirring for 4 h, the solution lost the orange color, indicating consumption of the germylene. Continued stirring for 1 week followed by removal of the volatiles in vacuo led to the quantitative isolation of **19**. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.94 (d, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1 H, Ar*H*), 7.23 (dd,

$^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.4 Hz, 1 H, Ar*H*), 7.05 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, Ar*H*), 6.98 (d, $^3J_{HH}$ = 6.8 Hz, 1 H, Ar*H*), 6.37 (t, $^3J_{HH}$ = 2.7 Hz, 1 H, Ge*H*), 5.21 (t, $^3J_{HH}$ = 4.8 Hz, 1 H, C=C*H*), 2.66 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2), 2.27 (m, 2 H, CH_2), 0.28 (s, 18 H, Si(CH_3)$_3$), 0.19 (s, 18 H, Si(CH_3)$_3$), −0.02 (d, $^3J_{HH}$ = 2.7 Hz, 2 H, GeC*H*Si). ^{13}C NMR (100.5 MHz, C_6D_6): δ 152.28 (*C*−O); 137.71, 134.42, 127.42, 127.29, 126.35, 123.10 (Ar); 100.61 (C=*C*); 29.03, 22.68 (*C*H_2); 9.47 (Ge*C*HSi); 3.21 and 2.52 (Si(*C*H_3)$_3$). IR (cm^{-1}): 2039 ν(Ge−H). EI/MS *m*/*z*: [M]$^+$ = 538.1980 amu.

Bis[bis(trimethylsilyl)methyl]-9-anthrenoxygermane (20). Crude compound **16** (350 mg, 0.561 mmol) was dissolved in pentane. The pentane was removed in vacuo and acetonitrile vacuum distilled into the flask. This solution was stirred for 90 min in order to dissolve any excess anthrone as well as a portion of the desired product, then filtered, leaving a yellow solid of analytically pure **20** (45 mg, 11% yield). Another 300 mg (86%) of **20** and a small amount (3%) of anthrone were isolated in the filtrate. ^{1}H NMR (400 MHz, C_6D_6): δ 8.65 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, Ar*H*), 7.90 (s, 1 H, Ar*H*), 7.82 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, Ar*H*), 7.33 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.2 Hz, 2 H, Ar*H*), 7.24 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.2 Hz, 2 H, Ar*H*), 6.68 (t, $^3J_{HH}$ = 2.0 Hz, 1 H, Ge*H*), 0.26 (s, 18 H, Si(CH_3)$_3$), 0.16 (d, $^3J_{HH}$ = 2.0 Hz, 2 H, GeC*H*Si), −0.01 (s, 18 H, Si(CH_3)$_3$). ^{13}C NMR (100.5 MHz, C_6D_6): δ 152.42 (*C*-O); 133.33, 128.71, 125.58, 125.25, 124.53, 123.72, and 119.12 (Ar); 8.36 (Ge*C*HSi); 3.08 and 2.93 (Si(*C*H_3)$_3$). IR (cm^{-1}): 2040 ν-(Ge−H). Anal. Calcd for $C_{28}H_{48}GeOSi_4$: C, 57.43; H, 8.26. Found: C, 57.71; H, 8.30.

Effects of Salt. Reactions similar to those describe for compounds **2**−**4** were performed replacing the $MgCl_2$ with either LiCl or $CaCl_2$. Reactions containing less than 1 equiv of $MgCl_2$ were also examined. One such example is described. Butanone (7.4 μL, 0.083 mmol) was added to **1** (30 mg, 0.077 mmol) and $MgCl_2$ (1 mg, 0.01 mmol) in THF-d_8 (0.8 mL) in a sealable NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy. After 72 h, all of the germylene had been consumed, resulting in the disappearance of the yellow color. The ^{1}H NMR spectrum showed that the composition of products was 40% **3**, 40% **6a**, and 20% **6b**.

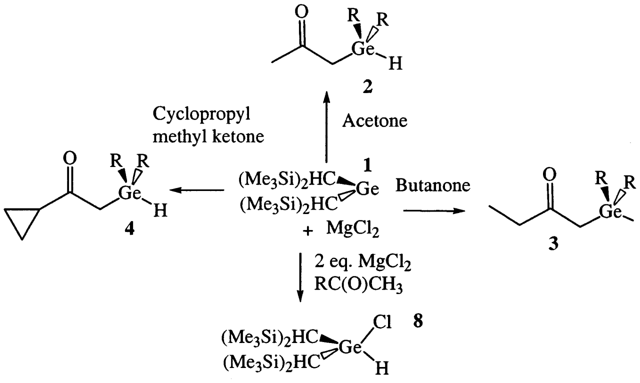
Attempted Benzil Trapping Experiments. A sample benzil trapping experiment is described. Benzil (16.5 mg, 0.079 mmol) was added to **2** (30 mg, 0.067 mmol) in benzene-d_6 (0.7 mL). The solution was monitored via ^{1}H NMR spectroscopy. After 24 h, no visible change was observed in the NMR spectrum. The solution was then placed in a 55 °C oil bath for 24 h. Still no reaction was observed via ^{1}H NMR spectroscopy; only the starting reagents were detected.

Benzil Trapping of Reversible α-Tetralone Product. α-Tetralone (10.3 μL, 0.0774 mmol) was added to a solution of **1** (30 mg, 0.077 mmol) in benzene-d_6 (1.4 mL). The solution was stirred for 2 min to ensure reaction. The solution was divided evenly (based on volume) into two sealable NMR tubes. Benzil (6 mg, 0.3 mmol) was added to one of the two tubes, 4 min after the initial addition of α-tetralone. Ninety percent of the **15** was consumed (as determined by NMR spectroscopy) after 45 min. Complete consumption of **15** had occurred within 1 h and 45 min to give the benzil-trapped germylene. The tube without benzil added had only converted 4% of **15** to **19** in this same time period. Complete conversion of **15** to **19** occurred between 23 and 26 h after the initial addition of α-tetralone.

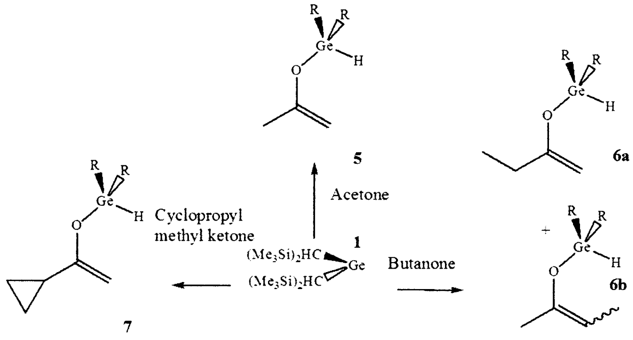
Results and Discussion

Ge[CH(SiMe_3)$_2$]$_2$ (**1**) reacts with ketones in one of four manners: CH insertion (in the presence of $MgCl_2$); formal OH insertion into the enol tautomer; in the case of phenone moieties a [2 + 4] cyclization to give a five-membered ring, containing the germanium and C−O bond, and the formation of a conjugated triene;[14] and formal oxidative addition of HCl insertion (in the presence of $MgCl_2$). The product obtained is dependent upon the presence of an acetyl or phenone moiety; however, these are only necessary and not sufficient conditions to obtain CH insertion and cyclization products, respectively. The steric bulk of the selected ketone and the presence of $MgCl_2$ also play a large role. Although the presence of $MgCl_2$ can lead to CH insertion, the presence of a 2-fold or greater excess leads primarily to the formation of [(Me_3Si)$_2$CH]$_2$GeHCl (**8**).

Scheme 1. Insertion of 1 into CH Bonds in the Presence of MgCl₂



Scheme 2. Insertion of 1 into OH Bonds in the Absence of MgCl₂



CH Insertion Reactions. Reaction of **1** with 1 equiv of acetone in either THF, benzene, or toluene solvent at 20 °C in the presence of 1 equiv of $MgCl_2$ leads to the formation of the CH insertion product $CH_3C(O)CH_2$-GeH[CH(SiMe_3)$_2$]$_2$ (**2**). Butanone and cycylopropyl methyl ketone have also shown similar reactivity, giving CH insertion at the position α to the carbonyl (Scheme 1). In the case of butanone, CH insertion has only been observed on the methyl group α to the ketone not on the methylene. Likewise, cyclopropyl methyl ketone has only shown activation of the CH bond on the primary carbon, not on the tertiary carbon α to the ketone. Both butanone and cyclopropyl methyl ketone also require the presence of $MgCl_2$ for CH insertion chemistry and give 100% CH insertion products **3** and **4**, respectively, when ~1 equiv of $MgCl_2$ is added. In the absence of added $MgCl_2$, the relative amounts of CH insertion product and OH insertion product vary as a function of germylene batch, as $MgCl_2$ is a typical impurity present in Ge[CH(SiMe_3)$_2$]$_2$ (**1**); exclusive formation of the OH insertion products (**5**−**7**, Scheme 2) has been observed for all these reactants when **1** is scrupulously purified to remove traces of $MgCl_2$.

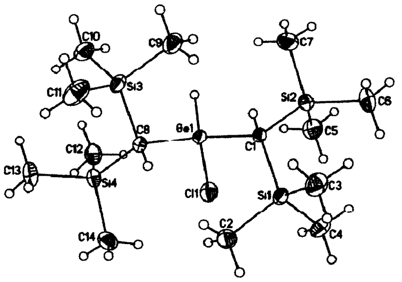


Figure 1. ORTEP of **8** with selected bond lengths (Å) and angles (deg): Ge(1)−Cl(1) 2.1944(5), Ge(1)−C(1) 1.9397(17), C(1)−Ge(1)−Cl(1) 104.74(5), C(1)−Ge(1)−C(9) 115.83(8).

The CH insertion products have a number of distinctive spectroscopic characteristics. The Ge−H peak was observed between 4.5 and 5.0 ppm and 2008−2012 cm^{-1} in the ^{1}H NMR and IR spectra, respectively. As a comparison, the reported ν(Ge−H) for the CH insertion product α to a nitrile appears consistently near 2020 cm^{-1}.[3] The presence of a ν(C═O) was also an important observation for all CH insertion products.

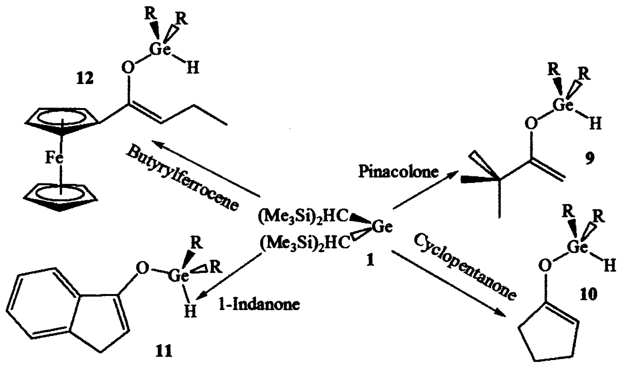
Acetone is a unique ketone in that it theoretically could afford the opportunity for the insertion of two molecules of **1**. Reaction of acetone with 2 equiv of **1** in the presence of added $MgCl_2$ resulted in the formation of **2** with 1 equiv of **1** remaining unreacted. Similar results were achieved with butanone.

Effects of Salts. The reactions of **1** with equimolar amounts of acetone, butanone, or cyclopropyl methyl ketone in benzene or THF were examined in the presence of 1 equiv of $MgCl_2$, LiCl, or $CaCl_2$. The presence of $MgCl_2$ led to the formation of the CH insertion products **2**−**4**. Reaction with LiCl or $CaCl_2$ on the other hand has no effect on the constitution of the product, giving **5**−**7**, the same OH insertion observed as when no salt is added. Substoichiometric amounts of $MgCl_2$ added to reactions of butanone or acetone and **1** showed a mixture of the CH and OH insertion products. The use of other common Lewis acidic salts such as $CdCl_2$ and $ZnCl_2$ shows direct reaction of **1** with the salt, both in the presence and in the absence of a ketone.

The effect of solvent on the CH insertion reactions appears to be minimal on its own. Rather the solvent simply allows for magnification of the effect of the salt, likely by affecting the solubility of the salt in solution. Although THF, toluene, and benzene all allow for complete CH activation of butanone when 1 equiv of $MgCl_2$ is added to 30 mg of **1** in 5 mL of solvent, the same amount of salt in hexane affords only a 30% yield of CH activation. Similar effects (40% yield of CH activation) can be accomplished by decreasing the volume of the solvent to 0.6 mL of benzene per 30 mg of germylene.

The presence of $MgCl_2$ in the reaction also has the possibility of leading to the formation of **8** (Scheme 1). This product can be intentionally formed through the addition of two or more equivalents of $MgCl_2$ to the typical CH activation reactions described above. The composition of this product was identified both through the comparison of the product to the direct reaction of the germylene with HCl and through single-crystal X-ray crystallography (Figure 1).

Scheme 3. OH Insertion of 1 with Ketones



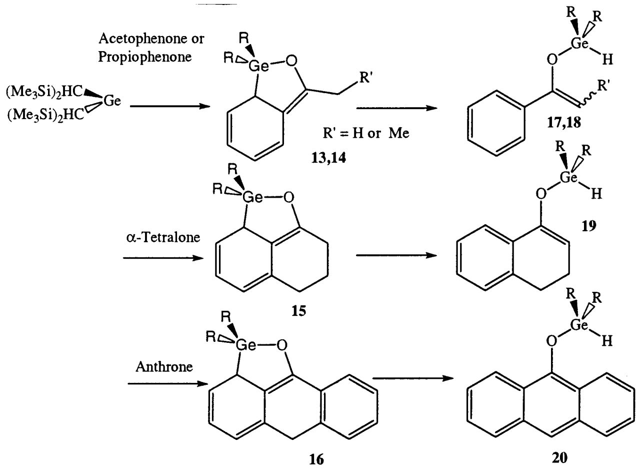
Compound **8** is formed through a pathway that is competitive to CH insertion, requiring similar conditions. Germylene **1** does not react directly with $MgCl_2$ in THF, benzene, or hexane: it is not until a ketone is added that the formation of **8** proceeds. The proton observed in **8** is derived directly from the added ketone. Reaction of acetone-d_6 or 1,1,1,3,3-butanone-d_5 and 2.5 equiv of $MgCl_2$ with **1** in THF led to the formation of **8** with a deuterium on the germanium. Similarly, protic acetone or butanone and deuterated solvent in the presence of $MgCl_2$ and **1** leads to protic **8**. The addition of **8** to a typical reaction of **1** and ketone does not change the distribution of product formation, nor does it get consumed during the reaction. **1** does not react with a mixture of **3** and **8** in the presence or absence of $MgCl_2$. On the basis of these observations, **8** is not an intermediate in the formation of **3**. We have also tested to see if the CH insertion products are intermediates in the formation of **8**. **3** is inert in the presence of excess $MgCl_2$ and/or butanone in THF or benzene and under the reaction conditions employed does not convert to **8**.

OH Insertion Reactions. The reaction of **1** with the ketones pinacolone, cyclopentanone, 1-indanone, and butyrylferrocene resulted in products equivalent to OH insertion chemistry into the enol tautomers (Scheme 3) yielding **9**−**12**, respectively. For these substrates, no CH insertion has been observed. These germyl vinyl ether products have a distinct set of spectroscopic characteristics. The chemical shift of the Ge−H moiety appears in the ^{1}H NMR spectrum at 6.0−6.6 ppm with the downfield shift due to the presence of the Ge−O bond. The ^{1}H NMR spectrum also shows a distinct vinylic hydrogen peak with a position between 4.0 and 6.0 ppm depending on the level of conjugation present. The ^{13}C NMR spectrum exhibits a set of peaks that are consistent with a vinyl ether, with one C appearing between 153 and 163 ppm and another located between 85 and 105 ppm. In addition, the IR spectrum has a strong band between 2035 and 2044 cm^{-1} corresponding to ν(Ge−H).

Acetone, butanone, and cyclopropyl methyl ketone also form O−H bond insertion products if $MgCl_2$ is absent in the reaction mixture to give products **5**−**7** (Scheme 2). It is interesting to note that butanone gives two different OH insertion products (**6a** and **6b**), one containing the external double bond and one containing the more thermodynamically stable internal double bond in an approximately 2:1 ratio.

Substrates containing the phenone moiety, acetophenone, propiophenone, α-tetralone, and anthrone, have

Scheme 4. Reactions of 1 to Activate Aromatic Rings, Followed by OH Insertion

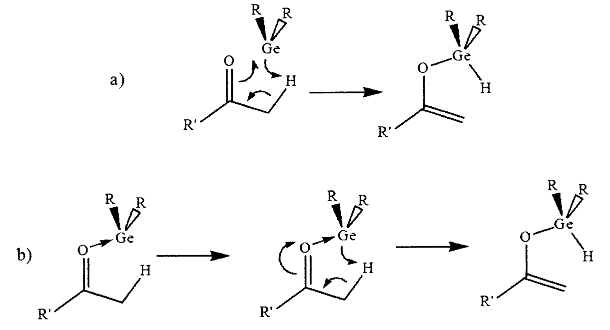


been observed to undergo an apparent [4 + 2] cycloaddition reaction resulting in the formation of a conjugated triene (Scheme 4).[14] Each of these substrates initially forms the conjugated triene characteristic of the phenone activation, compounds **13**−**16**, respectively, but over time converts into the OH insertion product, compounds **17**−**20**. These aromatic activation reactions are not a surprising observation since they are kinetically favorable, though the reversibility eventually leads to the more thermodynamically favorable and irreversibly formed products.

These reactions offer a profoundly simple manner to access a whole host of germyl vinyl ether compounds.[20] Some ketones with the acetyl group (pinacolone and acetophenone) and all other ketones with secondary C−H bonds in the α position tested (Schemes 3 and 4) give the OH insertion as the main thermodynamic product. Unlike previously reported OH insertions,[21] **1** gives a product equivalent to insertion into the enol tautomer as opposed to an alcohol or carboxylic acid.

Cyclopentanone, 1-indanone, and butyrylferrocene do not contain the acetyl group and show exclusively OH insertion chemistry. This suggests that the secondary CH bonds are not active toward CH insertion either due to steric bulk or due to the greater extent of enol tautomerization observed with these reagents (vida infra). For pinacolone and acetophenone, reagents where the requisite acetyl group is present, the lack of CH insertion in the presence of $MgCl_2$ may be rationalized by invoking the increase in steric bulk of the reagents.

Scheme 5. (a) Concerted, Single-Step Insertion; (b) Oxygen Coordination Prior to Concerted Insertion



Mechanistic Considerations. The intermolecular α-CH insertion observed for acetone, butanone, and cyclopropyl methyl ketone initially appears related to that observed for nitriles.[3] In both cases, a functional group consisting of two atoms is present adjacent to the reactive CH bond. Furthermore, the functional group contains lone pairs capable of donating into the empty germanium p orbital. Despite these apparent similarities, a number of striking differences suggest the mechanisms for the insertion could be different. Although both the reactions with nitriles and ketones exhibit a salt dependence, the nitrile reactions are catalyzed by a number of salts including LiCl, LiBr, and $MgCl_2$.[3] In contrast, the ketones demonstrate CH insertion only in the presence of $MgCl_2$. This difference could be attributed simply to the fact that a second reaction pathway (OH insertion) is present in the case of the ketones, whereas the nitriles show no alternative reaction. Another major difference is that no activations of secondary CH bonds have been observed for ketones; instead exclusively OH insertion products are observed with secondary ketones such as cyclopentanone, indanone, butyrylferrocene, and propiophenone.

A variety of concerted, electron transfer, and acid/base mechanisms have been proposed for related germylene chemistry.[22−26] For the OH insertion reactions, a single-step concerted mechanism or dative coordination of the oxygen to germylene followed by a proton shift to get the observed products is probable (Scheme 5). This mechanistic scheme is consistent with the inactivity of $Ge[N(SiMe_3)_2]_2$ toward this chemistry and the formation of both **6a** and **6b**.

The oxygen coordination to the germylene is critical in explaining why **1** will undergo OH insertion, but the structurally similar germylene, $Ge[N(SiMe_3)_2]_2$ (**21**),[27] does not show reactivity with acetone, butanone, or cyclopentanone. The lower Lewis acidity of the germanium center of **21** due to the electron donation by the nitrogen atoms would result in the lack of reactivity by **21** toward ketones that **1** shows. Direct insertion of **1** into the enol tautomer of the ketones does not satisfactorily explain the ratio of **6a** to **6b** observed. By comparing the percentage of enolization of acetone and butanone (0.00015% and 0.012%, respectively),[28] we can get an estimation of the preference with which the internal enolization should be formed, a factor of 80. The acetone, which can form only an external double bond, shows 2 orders of magnitude less enolization than the butanone, which may form the internal double bond. A similar difference would be anticipated between the two

---

(20) Miura, K.; Taniguchi, M.; Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 6391−6394.

(21) Klein, B.; Neumann, W. P.; Weisbeck, M. P.; Wienken, S. *J. Organomet. Chem.* **1993**, *446*, 149−159.

(22) Satgé, J. *J. Organomet. Chem.* **1990**, *400*, 121−147.

(23) Shoda, S.; Iwata, S.; Yajima, K.; Yagi, K.; Ohnishi, Y.; Kobayashi, S. *Tetrahedron* **1997**, *53*, 15281−15295.

(24) Georgoul, C.; Gross, B.; Ziegler, J. C.; Prevost, C. *C. R. Acad. Sci., Paris, Ser. C* **1968**, *266*, 1465−1467.

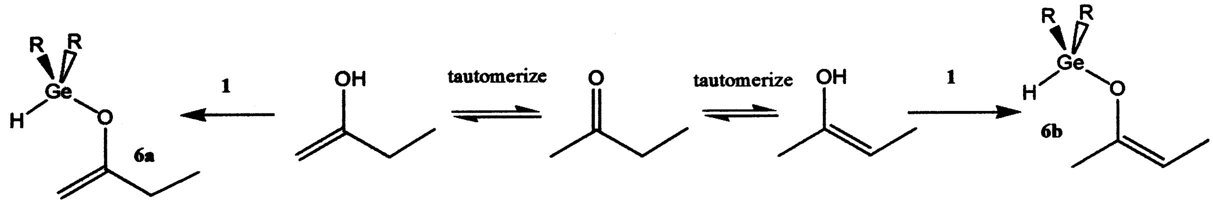
(25) Su, M. D.; Chu, S. Y. *J. Am. Chem. Soc.* **1999**, *121*, 4229−4237.

(26) Valentin, B.; Castel, A.; Riviere, P.; Mauzac, M.; Onyszchuk, M.; Lebuis, A. M. *Heteroatom. Chem.* **1999**, *10*, 125−132.

(27) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Riviere, P.; Riviere-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004−2009.

(28) Gero, A. *J. Org. Chem.* **1954**, *19*, 1960−1970.

Scheme 6. Tautomerization and Reaction of Butanone with 1

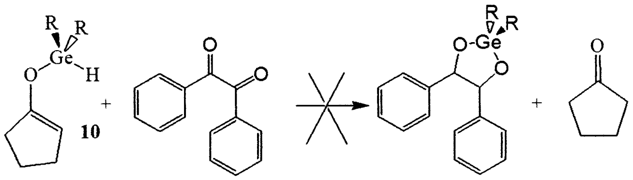


different enolic isomers possible from the butanone (Scheme 6). The anticipated difference in concentration of the two isomers is inconsistent with the nearly equal ratios of the two OH regioisomers observed in the reaction, thus refuting the hypothesis of direct insertion into the enol. A simple acid–base deprotonation of the ketone and recombination of the ions to give the observed OH insertion product is inconsistent with the fact that **1** was observed not to deprotonate fluorene or pentamethylcyclopentadiene (pK_a 23 and 26, respectively), which have pK_a values similar to acetone (26).[29]

Radical mechanisms and mechanisms that develop significant charge on the oxygen can be eliminated on the basis of the reaction with cyclopropyl methyl ketone. This reagent has been observed to undergo OH insertion, but opening of the cyclopropyl ring has never been observed; the cyclopropyl ring will open in the presence of an adjacent radical[30] or significant charge on the oxygen.[31] Direct testing for the radical mechanism via radical traps such as TEMPO is not possible due to reaction between **1** and TEMPO or other common radical traps. However, **8** would be expected to be an effective radical trap because of the presence of the Ge–H bond, which should be readily abstracted by an acetyl radical. As stated earlier, the presence of added **8** has no effect upon the reaction. Recent theoretical calculations by Su and Chu indicate a concerted insertion for germylenes with electropositive substituents into CH bonds,[25] although their calculations do not include MgCl$_2$. The increased steric bulk around secondary CH bonds is consistent with observing exclusively primary CH insertions.

A concerted style mechanism may occur through a magnesium-containing cluster. The cluster could also contain either the germylene or the ketone, as the order of addition does not effect the product composition, indicating that any cluster formation occurs faster than the insertion reaction. The solvent effects of CH insertion in hexane further support this conclusion. The lower solubility of a polar MgCl$_2$-containing cluster would lead to a slower reaction rate for CH insertion. Meanwhile, the OH insertion products could continue to form since it would not be dependent on a semisoluble cluster. This same hypothesis would also explain the results of a decrease in equivalents in MgCl$_2$ added. In the case of the addition of only 0.13 equiv of MgCl$_2$ to a reaction of **1** and butanone, 40% CH insertion and 60% OH insertion occurred. This indicates that the salt can act in a catalytic fashion with the germylene. Unfortunately, in situations with substoichiometric quantities of salt, the second mechanistic pathway of OH insertion is highly competitive.

Scheme 7. Reaction of 10 with Benzil



To understand why some reagents are unable to undergo CH insertion with MgCl$_2$, one can use the extent of tautomerization as a means for trying to identify the differing reactivities between reagents. Since extent of tautomerization simply indicates the ability of a molecule to undergo a simple hydrogen shift, it may be a measure to judge how readily a shift to the added germanium center will occur. In general, one may expect that moieties that more readily tautomerize will also more readily shift a hydrogen onto a datively coordinated germanium. Thus one would predict that the OH insertion product should be the dominant reaction for any ketones with a higher affinity to tautomerize. This prediction holds true in that the reagents that were observed to undergo CH insertion had the lowest percent enol in the pure liquid, although those observed to undergo only OH insertion had a higher tendency to tautomerize into the enol. Acetone has the smallest tendency to tautomerize to form the enol out of any of the reagents examined, reported at 0.00015% as the pure liquid.[28] Butanone, acetophenone, and cyclopentanone are reported to have percentages of 0.012, 0.035, and 0.088 enol in the pure liquid.[28] On the other hand, the low level of enol for the CH active reagents may simply be reflecting the requisite acetyl functionality.

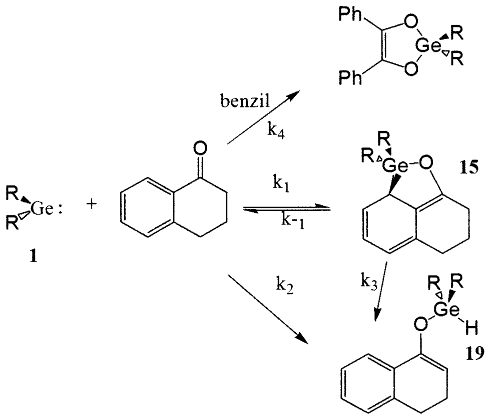
Examination of Reversibility of Reactions. Since the triene formation for the phenones is known to be reversible,[14] the other reactions reported in this paper were examined for reversibility. The stability of the products was examined by attempting to trap any free germylene with the known germylene trap, benzil.[15] Compound **10** remained stable in the presence of 4 equiv of benzil at 60 °C for 6 days (Scheme 7), showing no benzil-trapped product. This suggests that the reaction to form **10** is a nonreversible process. Compound **2** showed no reactivity with 1 equiv of benzil under similar heating conditions, indicating that the CH insertion reaction is also a nonreversible process.

The triene formation observed with acetophenone, propiophenone, anthrone, and α-tetralone is known to occur via a reversible step (Scheme 8).[14] To determine if the OH insertion product was formed directly through the triene (k_3) or via simple direct reaction of the germylene with the enol tautomer of the ketone, benzil was added to **15**. Typically, the reaction between **1** and α-tetralone occurs within 5 min at 20 °C to give **15**. This

---

(29) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.
(30) Tanko, J. M.; Phillips, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 6078–6079.
(31) Dieter, R. K.; Pounds, S. *J. Org. Chem.* **1982**, *47*, 3174–3177.

Scheme 8. Reactions of 1 with Tetralone and the Addition of Benzil



triene species slowly decreases over 48 h as assessed by ^{1}H NMR spectroscopy until exclusively **19** is present. One equivalent of benzil added to **15** efficiently trapped the germylene in 2 h, and no trace of **19** was observed for a 0.015 M solution by ^{1}H NMR spectroscopy. The complete trapping of the germylene from **15** occurred more rapidly than the conversion to **19** takes. Based on this result, we have demonstrated that $k_{-1} > k_3$. Combining this fact with the knowledge that $k_{-1}k_2$ is a viable mechanism for the formation of **19** from **15** suggests the OH insertion occurs through $k_{-1}k_2$.

Conclusions

We have demonstrated that germylene **1** will react with ketones in a number of different manners, including both CH insertion and OH insertion that lead to either an α-germyl ketone or a germyl vinyl ether. For many reagents containing the acetyl moiety, the presence or absence of $MgCl_2$ governs the production of CH insertion products versus the OH insertion products. A 2-fold excess or greater of $MgCl_2$ in the reaction mixtures will lead to the formation of $[((CH_3)_3Si)_2CH]_2GeHCl$. Other salts including LiCl and $CaCl_2$ do not lead to CH insertion products and do not result in the formation of $[((CH_3)_3Si)_2CH]_2GeHCl$. For ketones lacking the acetyl moiety we have not observed CH activation.

Acknowledgment. Support for this work from the Petroleum Research Fund and from the Research Corporation is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic data for compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from the CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K. (fax, +44 1223 336033; e-mail, deposit@cam.ac.uk or http://www.ccdc.cam.ac.uk).

OM030308+