Supporting Information

First detection of methylgermylene in the gas-phase and time resolved study of some of its reactions

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Experimental

Materials. ^{1}H and ^{13}C spectra were recorded on a Bruker AV200 spectrometer in deuteriochloroform or deuteriobenzene solution at 200 and 50 MHz, respectively, using the solvent signals as reference. Low resolution mass spectra were determined by GC/MS, using a Hewlett-Packard 5890II gas chromatograph equipped with a HP-5971 mass selective detector and a DB-5 fused silica capillary column (30 m x 0.25 mm, Agilent Technologies). Gas chromatographic analyses of materials involved in the synthesis of 3,4-dimethyl-1-germacyclopent-3-ene were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a conventional heated injector, a flame ionization detector, a Hewlett-Packard 3396A integrator, and a DB-5 (25 m × 0.20 mm) column (Chromatographic Specialties).

Tin tetrachloride (Gelest) and methylmagnesium bromide (3.0 M in ether, Sigma-Aldrich) were used as received from the suppliers. Diethyl ether and tetrahydrofuran were distilled under nitrogen from sodium after refluxing for several days. All synthetic manipulations were carried out under an atmosphere of dry nitrogen. 3,4-Dimethyl-1-germacyclopent-3-ene was prepared as described previously.[1]

1-Chloro-3,4-dimethyl-1-germacyclopent-3-ene was prepared by a modification of the procedure of Ushakov and Pritula for the synthesis of 1-chlorosilacyclopent-3-ene.[2] 3,4-Dimethyl-1-germacyclopent-3-ene (2.66 g, 16.8 mmol) was added to anhydrous ether (30 mL) and the solution was cooled to –78 °C with an acetone-dry ice bath. Tin tetrachloride (1.97 mL, 16.8 mmol) was then added with vigorous stirring over 5 min. via disposable syringe. The resulting white suspension was allowed to warm to room temperature, stirred for 12 hr, and then refluxed for 2 hr. The organic layer was decanted off and the remaining precipitate was washed with ether (2 x 15 mL). Hydrolysis of the organic layer with 1M HCl (20 mL) was followed by extraction of the aqueous layer with ether (2 x 50 mL). The combined organic extracts were washed with aqueous brine (15 mL) and water (2 x 15 mL), dried over anhydrous magnesium sulphate, filtered, and the solvent removed by distillation. Vacuum distillation of the resulting liquid afforded a colorless oil (2.16 g, 11.2 mmol, 66%; b.p. 58-59 ºC, 3.0 mmHg), which was identified as 1-chloro-3,4-dimethyl-1-germacyclopent-3-ene on the basis of the following spectroscopic data: ^{1}H NMR ($CDCl_3$) δ 1.76 (s, 6H), 1.95 (bd, 2H, ^2J = -16 Hz), 2.12 (bd, 2H, ^2J = -16 Hz), 6.09 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.7, 28.8, 129.7; EIMS *m/z* (I) = 192 (20, M^+), 157 (11), 109 (52), 83 (100), 67 (45), 55 (80).

The compound from above (2.16 g, 16.8 mmol) was added to anhydrous ether (100 mL) and the solution was cooled to –40 °C with an acetonitrile-dry ice bath. A solution of methylmagnesium bromide (6.7 mL) in ether (10 mL) was added dropwise via an addition funnel over 30 min. with stirring, after which the reaction mixture was allowed to warm to room temperature and stirred for a further 12 hr. The mixture was slowly hydrolysed with saturated aqueous ammonium chloride (25 mL), the layers were separated, and the aqueous layer was extracted with ether (2 x 50 mL). The combined organic extracts were washed with aqueous brine (20 mL) and water (2 x 25 mL), dried over anhydrous magnesium sulphate, filtered and the solvent was removed on the rotary evaporator to yield a yellowish oil, which was distilled under vacuum to afford 1,3,4-trimethylgermacyclopent-3-ene (TMGCP; 85 ºC at 55 mmHg; 0.60 g, 3.5 mmol, 20%) in greater than 95% purity according to GC analysis. The ^{1}H NMR and mass spectra of the compound agreed well with the reported spectra:[3] ^{1}H NMR (C_6D_6) δ 0.23 (d, 3H, ^3J = 3.2 Hz), 1.43 (bd, 2H, ^2J = -16.6 Hz), 1.68 (s, 6H), 1.80 (bd, 2H, ^2J = -16.6 Hz), 4.35 (m, 1H); EIMS *m/z* (I) = 172 (40, M^+), 157 (92), 129 (21), 115 (80), 89 (100), 74 (25), 67 (21), 55 (26).

Commercial samples of reactive substrates used in this work were obtained as follows. C_2H_4, and i-C_4H_8 (isobutene) were from Cambrian gases. C_3H_6 (propene) was from Matheson. C_2H_2 was from BOC and was distilled to remove acetone stabiliser. All hydrocarbons were >99% pure as checked by gas chromatographic (GC). HCl (99+%) and MeOH (Gold label, 99+%) were from Aldrich. SO_2 (99.5%) was from BDH. GeH_4 (no GC detectable impurities) was prepared previously[4] as was Me_2GeH_2 (99.2%).[5] $MeGeH_3$ was prepared by $LiAlH_4$ reduction of $MeGeCl_3$ in dried n-Bu_2O by standard procedures[6a]. $MeGeCl_3$ was made by direct synthesis from Ge and MeCl.[6b] $MeGeH_3$ was purified to 99.3% by low pressure distillation. GC analyses of reactant and product mixtures were carried out using a Perkin-Elmer 8310 chromatograph equipped with a flame ionization detector. A 3m silicone oil (OV101) column operated under temperature programmed conditions was used to analyse most of the reagents investigated and for product analytical checks, although other columns, such as Porapak Q were also used when necessary (for light hydrocarbons and germanes). Retention times and peak sensitivities (GC response factors) were calibrated with authentic samples where possible.

Laser Flash Photolysis. MeGeH was produced by flash photolysis of TMGCP using a Coherent Compex 100 excimer laser operating at 193nm (ArF fill). Photolysis laser pulses (energies ca 50-70 mJ) were fired into a variable temperature quartz reaction vessel with demountable windows, at right angles to its main axis. MeGeH concentrations were monitored in real time by means of a Coherent Innova 90-5 argon ion laser. The monitoring laser beam was multipassed 36 times along the vessel axis, through the reaction zone, to give an effective absorption path length of *ca* 1.5 m. A portion of the monitoring beam was split off before entering the vessel for reference purposes. Light signals were measured by a dual photodiode/differential amplifier combination, and signal decays were stored in a transient recorder (Datalab DL 910) interfaced to a BBC microcomputer. This was used to average the decays of typically 3 photolysis laser shots. The averaged decay traces were processed by fitting the data to an exponential form using a non-linear least-squares package. This analysis provided the initial absorbance values for the transient as well as values of the first-order rate coefficients, k_{obs}, for removal of MeGeH in the presence of known partial pressures of substrate gas.

Gas mixtures for photolysis were made up containing *ca* 40 mTorr of the transient precursor, TMGCP, variable pressures of reactive substrates with total pressures made up to 10 Torr with inert diluent (SF_6). Pressures were measured with capacitance manometers (MKS Baratron). Most measurements were made at room temperature of 299 ± 2 K. All gases used in this work were deoxygenated thoroughly prior to use.

Product characterisation ($MeGeH_2GeHMe_2$). $MeGeH_2GeHMe_2$ was prepared by the technique of mercury (6 $^3P_1$) photosensitisation, known to proceed via X-H bond cleavage[7]. The mechanism for reaction in mixtures of $MeGeH_3$ + Me_2GeH_2 will be as follows:

$$Hg^* + MeGeH_3 \rightarrow MeGeH_2 + H + Hg$$

$$Hg^* + Me_2GeH_2 \rightarrow Me_2GeH + H + Hg$$

$$H + MeGeH_3 \rightarrow MeGeH_2 + H_2$$

$$H + Me_2GeH_2 \rightarrow Me_2GeH + H_2$$

$$2MeGeH_2 \rightarrow MeGeH_2GeH_2Me$$

$$2Me_2GeH \rightarrow Me_2GeHGeHMe_2$$

$$MeGeH_2 + Me_2GeH \rightarrow MeGeH_2GeHMe_2$$

A mixture containing $MeGeH_3$ (1.02 Torr) and Me_2GeH_2 (1.22 Torr) with 100 Torr SF_6 was irradiated in the presence of a drop of Hg using 253.7 nm radiation (Hg resonance lamp) for 3 minutes. When subjected to GC analysis the product mixture contained three new peaks in ca 2-5% yields with retention times of 10.7, 15.5 and 19.2 mins on the temperature programmed silicone (OV101) column. The peaks at 10.7 min. and 19.2 min. were identified as $MeGeH_2GeH_2Me$ and $Me_2GeHGeHMe_2$ respectively in Hg sensitisation experiments with $MeGeH_3$ or Me_2GeH_2 alone. The peak at 15.5 min. was only produced from the mixture and must therefore be that of $MeGeH_2GeHMe_2$. This corresponded exactly to the 15.5 min peak found in the analysis of the product mixture from the 193 nm laser photolysis of TMGCP with Me_2GeH_2. This technique has been used previously to identify Me_3SiGeH_3 as the product of reaction of GeH_2 + Me_3SiH[8].

TD-DFT Calculations. Calculations were performed with the ADF 2004.01 density functional theory package (SCM).[9-11] The calculation of the geometry of MeGeH ($r_{C\text{-}Ge}$ = 2.008 Å; $r_{Ge\text{-}H}$ = 1.615 Å; $\angle_{C\text{-}Ge\text{-}H}$ = 93.0°) was gradient-corrected with the exchange and correlation functionals of Perdew and Wang (PW91);[10] all basis functions were of triple-ζ quality and were composed of uncontracted Slater-type orbitals (STOs), including all core electrons and two auxiliary basis sets of STOs for polarization. Spectroscopic calculations employed the time-dependent extension of density functional theory (TD-DFT) implemented[13-17] in the ADF package. The Adiabatic Local Density Approximation (ALDA) was used for the exchange-correlation kernel[18,19] and the differentiated static LDA expression was used with the

Vosko-Wilk-Nusair parametrization.[20] Zero-order relativistic corrections (ZORA) were applied in all cases. For the exchange-correlation potentials in the zeroth-order KS equations, the first ten excitation energies and oscillator strengths (see Table S1) were obtained using the Davidson iterative diagonalization method.

Table S1. Calculated energies and oscillator strengths (`f`) of the first 10 allowed transitions of MeGeH.

Sym.	ΔE(eV)	λ_{max}(nm)	`f`
1A	2.5459	487	0.0106
2A	3.8348	323	0.0005
3A	5.5203	224	0.0805
4A	6.2722	198	0.1790
5A	6.5963	188	0.0022
6A	6.7095	185	0.0297
7A	6.9545	178	0.0229
8A	7.0880	175	0.0490
9A	7.1121	174	0.1483
10A	7.3081	170	0.0316

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