

only ca. 10 h. This reaction is relatively clean (by ^1H NMR in benzene- d_6), and pure 2 can be isolated in ca. 50% yield as yellow crystals from pentane.¹² In the absence of light no product is formed after 5 days, indicating that insertion requires photochemical activation of $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$. The UV-vis spectrum of $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ exhibits an absorption at 461 nm ($\epsilon = 500 \text{ L mol}^{-1} \text{ cm}^{-1}$), and use of cutoff filters has determined that the corresponding electronic transition gives rise to the observed photochemistry. The quantum yield for this reaction ($\lambda = 380\text{--}470 \text{ nm}$, benzene- d_6) in the presence of excess ethylene is 2.5, suggesting a radical chain mechanism initiated by homolytic cleavage of a M-Si bond.¹³

Compound 1 is remarkably stable for an alkyl complex with β -hydrogens, very little decomposition being observed after 3 days at 80 °C (by ^1H NMR in benzene- d_6). Future work will involve further development and study of this insertion chemistry. Preliminary experiments show that $\text{Cp}^*\text{Cl}_2\text{ZrSi}(\text{SiMe}_3)_3$ is unreactive toward styrene, propene, and $\text{Me}_3\text{SiCH}=\text{CH}_2$ and that $\text{Cp}^*\text{Cl}_2\text{HfSi}(\text{SiMe}_3)_3$ is inert toward diphenylacetylene and 1-hexene.

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Supplementary Material Available: A listing of crystal, data collection, and refinement parameters and tables of positional and thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for 1a (9 pages); a table of observed and calculated structure factors for 1a (21 pages). Ordering information is given on any current masthead page.

(12) For 2: Anal. C, H. ^1H NMR (benzene- d_6 , 22 °C, 300 MHz): δ 0.34 (s, 27 H, SiMe_3), 1.08 (m, 2 H, CH_2Si), 1.40 (m, 2 H, ZrCH_2), 1.71 (s, 15 H, Cp^*), 5.90 (s, 5 H, Cp). UV-vis (pentane, nm): 225 ($\epsilon = 6000 \text{ M}^{-1} \text{ cm}^{-1}$), 329 ($\epsilon = 1000 \text{ M}^{-1} \text{ cm}^{-1}$).

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A Palladadigermetane: Palladium-Catalyzed Insertion Reactions of Digermiranes

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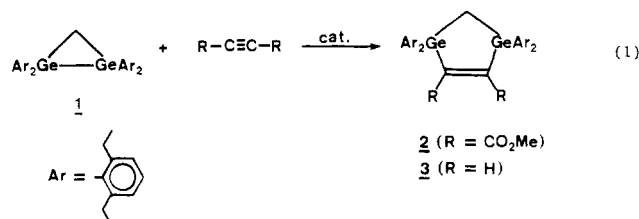
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Summary: The palladium-catalyzed reactions of digermirane 1 with dimethyl acetylenedicarboxylate and acetylene give the ring expansion products 2 and 3. Reaction

with methyl acrylate gives the rearranged product 4. In the stoichiometric reaction of 1 with $\text{Pd}(\text{PPh}_3)_4$, palladadigermetane 6 is isolated as a stable compound. 6 reacts with dimethyl acetylenedicarboxylate, acetylene, and methyl acrylate to yield 2, 3, and 4, respectively. The similar palladium-catalyzed reactions of thia- and selenadigermiranes 9 and 10 with acetylene give the ring expansion products 11 and 12, respectively.

One of the most interesting reactions of the Si-Si bond of the reactive disilanes is the transition-metal-catalyzed insertion of unsaturated hydrocarbons, and numerous papers have been published so far.¹⁻⁷ In spite of these studies, no interest has been shown in the transition-metal-catalyzed insertion of unsaturated compounds into the Ge-Ge bond.⁸ Recently, we reported the preparation and chemical properties of a digermirane and its heterocyclic analogues.^{9,10} We report here the novel palladium-catalyzed ring-expansion reactions of a digermirane and thia- and selenadigermiranes. We also report the stoichiometric reaction of the digermirane with $\text{Pd}(\text{PPh}_3)_4$ to yield a palladadigermetane as stable red crystals.

When a benzene solution of digermirane 1,^{9c} dimethyl acetylenedicarboxylate, and $\text{Pd}(\text{PPh}_3)_4$ (10 mol %) was heated to reflux for 45 h under an argon atmosphere, a crystalline product identified as digermacyclopentene 2,¹¹ a insertion product of the acetylene into the Ge-Ge bond, was obtained in 51% yield (eq 1). It was also found that



$\text{Pd}(\text{II})$ complexes such as $\text{PdCl}_2(\text{PPh}_3)_2$ and $\text{PdCl}_2(\text{PhCN})_2$ and $\text{NiCl}_2(\text{PPh}_3)_2$ catalyzed the insertion of the acetylene into the Ge-Ge bond of the digermirane 1 equally, giving the adduct 2. Unsubstituted acetylene also reacted with

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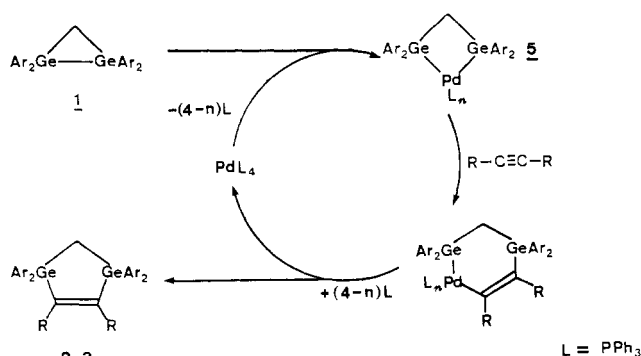
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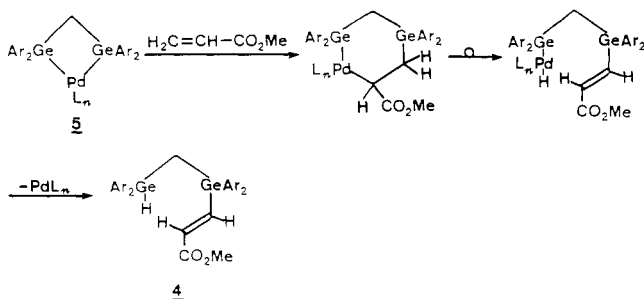
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(11) Compound 2: colorless crystals; mp 173-174 °C; ^1H NMR (60 MHz, CDCl_3) δ 0.87 (t, $J = 7 \text{ Hz}$, 24 H, CH_3), 1.30 (s, 2 H, GeCH_2Ge), 2.50 (q, $J = 7 \text{ Hz}$, 16 H, CH_2), 3.53 (s, 6 H, OMe), 6.9-7.4 (m, 12 H, Ar); ^{13}C NMR (25 MHz, CDCl_3) δ 11.5 (t, GeCH_2Ge), 15.1 (q, CH_3), 30.3 (t, CH_2), 51.8 (q, OMe), 125.9 (d, Ar), 128.8 (d, Ar), 141.2 (s, Ar), 147.8 (s, Ar), 157.9 (s, Ar), 169.9 (s, $\text{C}=\text{C}$).

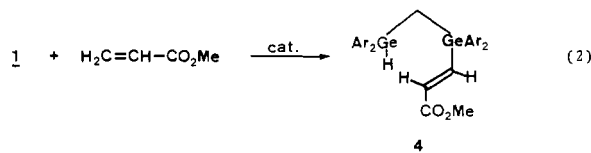
Scheme I



Scheme II



1 to yield an adduct, 3,¹² in 20–25% yield when acetylene was bubbled into a toluene solution of 1 in the presence of a Pd(0) or Pd(II) catalyst at 80 °C (eq 1). The reaction of 1 with methyl acrylate under similar conditions (refluxed in benzene for 18 h) gave a ring-opened type product, 4,¹³ in 20% yield (eq 2).



A reasonable pathway for the formation of the products obtained is shown in Scheme I. We propose that a palladadigermetane intermediate 5 is involved in the formation of compounds 2 and 3. The formation of 4 may be explained by the participation of the same intermediate followed by β -elimination (Scheme II).

To confirm the mechanism, we next tried to isolate a palladadigermetane in a stoichiometric reaction. When a toluene solution of 1 and Pd(PPh₃)₄ was heated at 90 °C for 20 h, palladadigermetane 6 was obtained as a red crystalline solid in 45% yield (eq 3).¹⁴ The fact that the

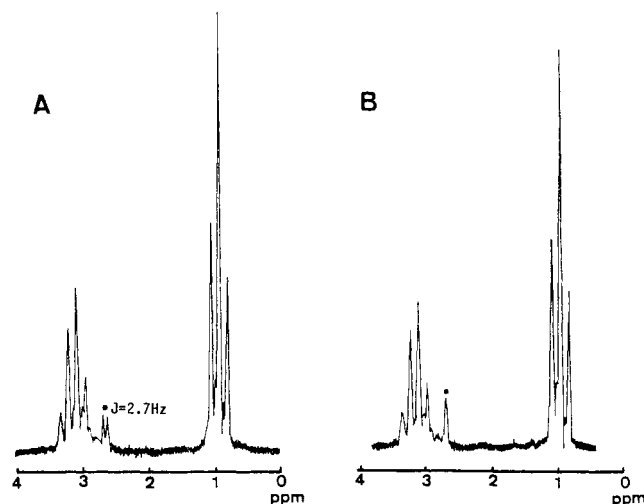
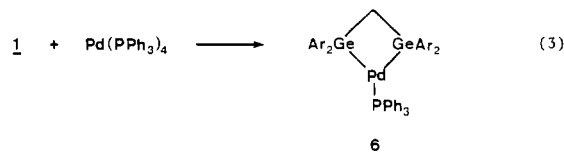
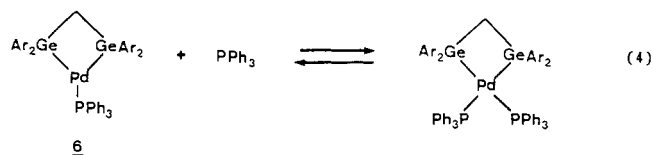


Figure 1. (A) ¹H NMR spectrum of compound 6 in C₆D₆ (60 MHz). (B) After the addition of PPh₃ to a C₆D₆ solution of compound 6 (60 MHz). Asterisks indicate the resonances assigned to methylene protons of the palladadigermetane.



¹H-decoupled ¹³C NMR spectrum of 6 shows a doublet at δ 30.0 ppm ($J_{C-P} = 16.8$ Hz) clearly indicates this resonance can be assigned to the ring carbon atom of palladadigermetane 6 and that only one molecule of PPh₃ is coordinated to palladium. In the ¹H NMR spectrum one doublet was observed at δ 2.68 ppm ($J_{P-H} = 2.7$ Hz) which was assigned to methylene protons in the ring. The crystals of palladadigermetane 6 are air-sensitive, but much less than in solution, and can be handled in air for a short time (mp 182–185 °C dec).¹⁵

When PPh₃ was added to the benzene-*d*₆ solution of 6, a doublet at δ 2.68 ppm in the ¹H NMR spectrum was changed to a singlet at δ 2.68 ppm as shown in Figure 1.¹⁶ The changes can be interpreted in terms of the rapid equilibrium between the mono(triphenylphosphine)palladium complex and the bis(triphenylphosphine)palladium complex (eq 4).



Compound 6 reacted with dimethyl acetylenedicarboxylate, acetylene, and methyl acrylate to form the corresponding addition products 2, 3, and 4 in 100%, 96%, and 45% yields, respectively (Scheme III).¹⁷ These results indicate that the four-membered palladacycle is involved in the catalytic reactions of 1.¹⁸

(15) We attempted an X-ray structure analysis of compound 6, but, because of the decomposition in the X-ray beam, sufficient data could not be obtained. Preliminary results indicate that the four-membered ring system in compound 6 is almost planar.

(16) Also, in the ¹H-decoupled ¹³C NMR spectrum a doublet at δ 30.0 ppm was changed to a singlet, and in the ³¹P NMR spectrum a singlet at δ 7.8 ppm was shifted to δ -4.2 ppm (br). The changes in the spectra were observed even when 6 was treated with a small amount of PPh₃.

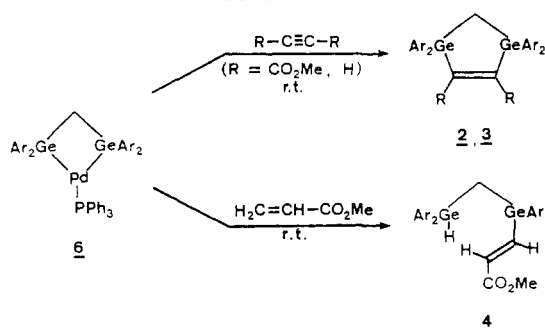
(17) In the presence of PPh₃ 6 reacted with the unsaturated compounds similarly.

(12) Compound 3: colorless crystals; mp 124–125 °C; ¹H NMR (60 MHz, CDCl₃) δ 0.80 (t, $J = 7$ Hz, 24 H, CH₃), 1.20 (s, 2 H, GeCH₂Ge), 2.55 (q, $J = 7$ Hz, 16 H, CH₂), 6.8–7.2 (m, 12 H, Ar), 7.63 (s, 2 H, CH=CH); ¹³C NMR (125 MHz, CDCl₃) δ 8.6 (t, GeCH₂Ge), 15.4 (q, CH₃), 29.9 (t, CH₂), 125.9 (d, Ar), 128.5 (d, Ar), 141.2 (s, Ar), 148.5 (s, Ar), 150.4 (d, C=C).

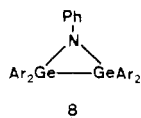
(13) Only one of the two possible isomers was isolated and was identified as trans isomer. Compound 4: colorless crystals; mp 76–81 °C; ¹H NMR (100 MHz, CDCl₃) δ 0.86 (t, $J = 7$ Hz, 12 H, CH₃), 0.96 (t, $J = 7$ Hz, 12 H, CH₃), 1.59 (d, $J = 4$ Hz, 2 H, GeCH₂Ge), 2.53 (q, $J = 7$ Hz, 8 H, CH₂), 2.60 (q, $J = 7$ Hz, 8 H, CH₂), 3.61 (s, 3 H, OMe), 5.42 (t, $J = 4$ Hz, 1 H, GeH), 6.88 (AB, $J_{AB} = 18$ Hz, $\Delta\nu_{AB} = 189$ Hz, 2 H, CH=CH), 6.9–7.3 (m, 12 H, Ar); ¹³C NMR (22.5 MHz, CDCl₃) δ 11.0 (t, GeCH₂Ge), 15.3 (q, CH₃), 29.6 (t, CH₂), 30.0 (t, CH₂), 51.5 (q, OMe), 125.7 (d, Ar), 126.2 (d, Ar), 128.9 (d, Ar), 129.0 (d, Ar), 132.6 (d, C=C), 138.1 (s, Ar), 138.2 (s, Ar), 148.8 (s, Ar), 149.1 (s, Ar), 152.7 (d, C=C).

(14) Compound 6: ¹H NMR (500 MHz, C₆D₆) δ 0.93 (t, $J = 7.4$ Hz, 24 H, CH₃), 2.68 (d, $J_{P-H} = 2.7$ Hz, 2 H, GeCH₂Ge), 3.11 (dq, $J = 7.4$, 14.8 Hz, 8 H, CH₂), 3.21 (dq, $J = 7.4$, 14.8 Hz, 8 H, CH₂), 7.0–7.4 (m, 27 H, Ar); ¹³C NMR (125 MHz, C₆D₆, ¹H-decoupled) δ 15.6 (s, CH₃), 30.0 (d, $J_{P-C} = 16.8$ Hz, GeCH₂Ge), 32.1 (s, CH₂), 125.8–148.9 (aromatic C); ³¹P NMR (C₆D₆, 85% phosphoric acid as external standard) δ 7.8 (s).

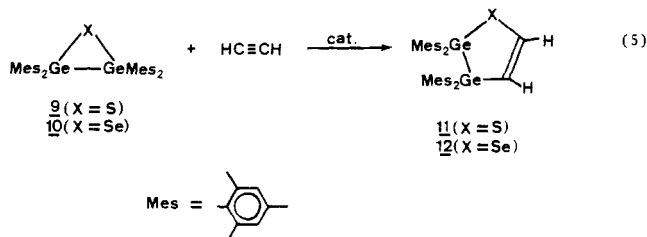
Scheme III



Under similar conditions azadigermiridine **8^{9c}** did not react with dimethyl acetylenedicarboxylate or acetylene in the presence of Pd(PPh₃)₄ or PdCl₂(PPh₃)₂. But,



thiadigermirane **9^{9a,b}** reacted with acetylene in the presence of a catalytic amount of Pd(PPh₃)₄ or PdCl₂(PPh₃)₂ at 80 °C cleanly to produce the adduct **11¹⁹** in 44–54% yield (eq 5). In contrast to the reactions of digermirane **1** the adduct **11** obtained is the insertion product of acetylene into the Ge–S bond. No products of the insertion into the Ge–Ge bond were obtained. The reaction of selenadigermirane **10^{9a,b}** with acetylene under similar conditions gave the corresponding addition product **12** (eq 5).²⁰ A simple



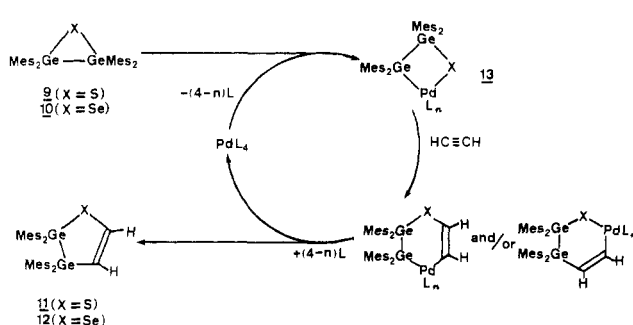
catalytic scheme can be proposed for the formation of adducts **11** and **12** (Scheme IV). We tried to proof the intervention of an intermediate such as **13**. However, attempts to isolate Pd-containing intermediates in stoichiometric reactions were not successful, so the chemistry in Scheme IV is only a suggestion.

(18) The mechanism of the palladium(II)-catalyzed insertions of acetylenes into the Ge–Ge bond of **1** is of some interest. As reported earlier (see ref 5) there is the possibility that a Pd(II) compound is reduced to a Pd(0) species. An experiment in which **1** was treated with a stoichiometric amount of PdCl₂(PPh₃)₂ confirmed that this was the case. The reaction produced two products, palladadigermetane and ClAr₂Ge–C–H₂–GeAr₂Cl (**7**), in about a 1:1 ratio. It would appear that an initial reaction of **1** with PdCl₂(PPh₃)₂ reduces the latter to Pd(PPh₃)₂ and forms **7**. The coordinatively unsaturated Pd(PPh₃)₂ then inserts into the Ge–Ge bond of **1**. Compound **7**: colorless crystals, mp 119–121 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.92 (t, *J* = 7.4 Hz, 24 H, CH₃), 2.51 (dq, *J* = 7.4, 14.8 Hz, 8 H, CH₂), 2.56 (s, 2 H, GeCH₂Ge), 2.77 (dq, *J* = 7.4, 14.8 Hz, 8 H, CH₂), 6.97 (d, *J* = 7.7 Hz, 8 H, Ar), 7.22 (t, *J* = 7.7 Hz, 4 H, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 15.2 (q, CH₃), 28.0 (t, GeCH₂Ge), 29.1 (t, CH₂), 126.7 (d, Ar), 129.8 (d, Ar), 139.4 (s, Ar), 148.1 (s, Ar).

(19) Compound **11**: colorless crystals; mp 174–175 °C; ¹H NMR (60 MHz, CDCl₃) δ 2.10 (s, 12 H, CH₃), 2.21 (br s, 24 H, CH₃), 6.62 (br s, 8 H, Mes), 6.95 (AB, *J*_{AB} = 8.4 Hz, Δ*ν*_{AB} = 30 Hz, 2 H, HC=CH); ¹³C NMR (125 MHz, CDCl₃) δ 20.8 (q, CH₃), 25.1 (q, CH₃), 25.2 (q, CH₃), 128.8 (d, Mes), 128.9 (d, Mes), 129.2 (d, C=C), 135.8 (s, Mes), 138.0 (s, Mes), 138.2 (s, Mes), 140.2 (d, C=C), 143.3 (s, Mes), 143.9 (s, Mes).

(20) Compound **12**: colorless crystals, mp 114–120 °C; ¹H NMR (60 MHz, CDCl₃) δ 2.13 (s, 12 H, CH₃), 2.21 (s, 24 H, CH₃), 6.63 (br s, 8 H, Mes), 7.41 (AB, *J*_{AB} = 10.2 Hz, Δ*ν*_{AB} = 25.0 Hz, 2 H, CH=CH); ¹³C NMR (125 MHz, CDCl₃) δ 20.8 (q, CH₃), 20.9 (q, CH₃), 25.3 (q, CH₃), 25.5 (q, CH₃), 128.8 (d, Mes), 128.9 (d, Mes), 134.3 (d, C=C), 136.1 (s, Mes), 136.2 (d, C=C), 137.9 (s, Mes), 138.2 (s, Mes), 143.2 (s, Mes), 143.8 (s, Mes).

Scheme IV



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Supplementary Material Available: Detailed information concerning IR, MS, and analytical data of new compounds (3 pages). Ordering information is given on any current masthead page.

Inversion of Stereochemistry at the Carbon Bound to Iron in Cyclopropane Formation from *threo*-C₅H₅(CO)₂FeCHDCHDCH₂S(CH₃)C₆H₅⁺

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Summary: Upon heating at 65 °C, *threo*-C₅H₅-(CO)₂FeCHDCHDCH₂S(CH₃)C₆H₅⁺CF₃SO₃[−] is converted to *cis*-1,2-dideuteriocyclopropane with inversion of stereochemistry at the carbon bound to iron.

The reaction of electrophilic carbene complexes with alkenes leads to the formation of cyclopropanes¹ with complete retention of alkene stereochemistry.² Since electron-rich alkenes have enhanced reactivity, electrophilic addition of the carbene carbon to the least substituted alkene carbon has been proposed to lead to a transition state with substantial positive charge at the carbon γ to the metal center. Cyclopropane formation can then be completed by carbon–carbon bond formation between C_α and C_γ by one of two stereochemically differentiated modes of ring closure (Scheme I). Net retention of stereochemistry at C_α could occur by nucleophilic attack of iron at the electrophilic γ-carbon to produce a cationic metallacyclobutane which then reductively eliminates cyclopropane.³ Net inversion of stereochemistry at C_α could occur via a W-shaped transition state in which the electrophilic γ-carbon attacks the backside of the C_α–Fe bond.

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