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Double Germylation of Unsaturated Carbon Compounds with Digermanes in the Presence of Palladium and Platinum Catalysts

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Double germylation of acetylenes, isoprene, and ethylene with 1,2-dichloro-1,1,2,2-tetramethyldigermane proceeds in the presence of palladium- and platinum-phosphorus ligand complexes to afford α,ω-bis(chlorodimethylgermyl) compounds in moderate to good yields.

Stimulated by the vigorous growth of organosilicon chemistry,1) organogermanium chemistry is also emerging to be developed for broad applications such as electric conduction, nonlinear optics, photoresist, and thermochromism.2) However, the development is hampered because synthetic methods available for organogermanium compounds are very much limited as compared with organosilicon compounds. For instance, double silylation of unsaturated carbon compounds with disilanes has been long known, and provides a unique way leading to α,ω-bis(silyl) compounds.3) On the other hand, double germylation with digermanes has not been documented except for the reaction of acetylenes with strained digermiranes.4) We now report that strain-free linear digermanes react with a variety of unsaturated carbon compounds, and that tuning of the nature of palladium catalysts allows us to synthesize α,ω-bis(germyl) compounds in good yields.

When a toluene (2 cm^3) solution of 1,2-dichloro-1,1,2,2-tetramethyldigermane (**1a**, 1 mmol), phenylacetylene (2 mmol), and $Pd(PPh_3)_4$ (0.05 mmol) was heated at 120 °C for 3 h, the digermane was completely consumed. GC analysis revealed that α,β-bis(chlorodimethylgermyl)styrene (**2a**) was formed in 88% yield (*Z*/*E* = 92/8). A small amount of 2,2,5,5-tetramethyl-3-phenyl-1,2,5-oxadigermolene (**3**) was also detected in the reaction mixture (4%), presumably owing to incidental contamination with moisture. The reaction mixture was distilled (Kugelrohr) to afford fairly pure (*Z*)-**2a** (66% isolated yield; *Z*/*E* = 94/6) which showed satisfactory spectral data.5) The geometry was confirmed by the fact that the *Z* isomer was transformed into the cyclic digermoxane (**3**)6) upon hydrolysis at room temperature.

$$\mathrm{PhC{\equiv}CH + XMe_2GeGeMe_2X \longrightarrow XMe_2GeC(Ph){=}CHGeMe_2X}$$

1a: X = Cl	**2a**: X = Cl, 88% (3 h)
1b: X = Me	**2b**: X = Me, 1.3% (3 h)

A similar reaction of hexamethyldigermane (**1b**, 1 mmol) with phenylacetylene (5 mmol) gave only 1.3% yield of α,β-bis(trimethylgermyl)styrene (**2b**). Under the same conditions, hexamethyldisilane reacted with phenylacetylene to form α,β-bis(trimethylsilyl)styrene in 5.1% yield, suggesting low reactivity of the digermane as compared with the disilane.

Unsubstituted acetylene of atmospheric pressure also reacted with **1a** at 100 °C. The outcome of the reactions very much depended on the catalyst. The reaction carried out in the presence of $\mathrm{Pd(PPh_3)_4}$ for 24 h formed (*E*)-1,2-bis(chlorodimethylgermyl)ethylene ((*E*)-**4**) in 45% yield.[7) As previously observed for double silylation,[8) $\mathrm{Pd(dba)_2\text{-}P(OCH_2)_3CEt}$ (P/Pd = 2) proved to be a more active catalyst which afforded 72% yield of (*E*)-**4** in 4 h. On the other hand, the use of $\mathrm{Pt(PPh_3)_4}$ resulted in selective formation of (*Z*)-**4** in 20% yield (*Z*/*E* = 99/1).[9) Hydrolysis of (*Z*)-**4** afforded 2,2,5,5-tetramethyl-1,2,5-oxadigermolene (**5**),[10) confirming the geometry. The selective (*E*)-**4** formation in palladium-catalyzed reactions was apparently in contrast with the predominant *Z* isomer formation observed in the corresponding double silylation.[11) The *E* selectivity does not seem to be due to intrinsic nature of the reaction, but suggests *Z* to *E* isomerization having taken place subsequently after the initial formation of the (*Z*)-**4**. As a matter of fact, separately prepared *Z* isomer nearly quantitatively isomerized to the *E* isomer upon heating at 100 °C for 15 h in the presence of $\mathrm{Pd(PPh_3)_4}$ and **1a**. Another support came from the lower *E* selectivity (*Z*/*E* = 17/83) observed in a separate $\mathrm{Pd(PPh_3)_4}$-catalyzed reaction interrupted at 12 h reaction time.

$$\mathrm{HC{\equiv}CH\ +\ \mathbf{1a} \longrightarrow ClMe_2GeCH{=}CHGeMe_2Cl}$$

Catalyst:	**4**
$\mathrm{Pd(PPh_3)_4}$	33% (12 h, *Z*/*E* = 17/83)
$\mathrm{Pd(PPh_3)_4}$	45% (24 h, *Z*/*E* = 0/100)
$\mathrm{Pd(dba)_2\text{-}2P(OCH_2)_3CEt}$	72% (4 h, *Z*/*E* = 0/100)
$\mathrm{Pt(PPh_3)_4}$	20% (12 h, *Z*/*E* = 99/1)

Isoprene also reacted with **1a** to give the (*E*)-1,4-adduct (**6**).[12) Lack of the formation of seven membered cyclic digermoxane upon alkaline hydrolysis supports the *E* geometry. With $\mathrm{PdCl_2L_2}$ complexes used as catalyst at 120 °C, performance decreased as follows; L (yield/% at 12 h reaction time): $\mathrm{PMe_3}$ (28.2) > $\mathrm{PEt_3}$ (12.9) >

PPh_3 (5.1) > P^iBu_3 (≈0). As was in the reaction of unsubstituted acetylene, much better yield could be obtained with $Pd(dba)_2$ combined with $P(OCH_2)_3CEt$ (P/Pd = 2).

$$CH_2{=}C(CH_3)CH{=}CH_2 + \mathbf{1a} \longrightarrow ClMe_2GeCH_2C(CH_3){=}CHCH_2GeMe_2Cl$$

Catalyst:	**6**
$Pd(dba)_2$-$2P(OCH_2)_3CEt$	77% (3 h)

We reported previously that double silylation of ethylene with disilanes occurred with platinum but not with palladium complex used as the catalyst. However, palladium complexes proved to be capable of double germylation of ethylene (50 kg/cm^2 at room temperature) with **1a** at 120 °C in 45 h to give 1,2-bis(chlorodimethylgermyl)ethane (**7**).13) Trimethylphosphine or $P(OCH_2)_3CEt$ was found to be the ligand of choice. Note that, in platinum-catalyzed reaction of ethylene with 1,2-diphenyl-1,1,2,2-tetramethyldisilane, the use of PMe_3 as an auxiliary ligand resulted in extensive formation of a vinylsilane via dehydrogenative single silylation.14) On the other hand, formation of a vinylgermane was not observed at all in the present reaction.

$$CH_2{=}CH_2 + \mathbf{1a} \longrightarrow ClMe_2GeCH_2CH_2GeMe_2Cl$$

Catalyst:	**7**
$Pd(PPh_3)_4$	15%
$PdCl_2(PMe_3)_2$	77%
$Pd(dba)_2$-$2P(OCH_2)_3CEt$	≈100%

In summary, the first successful double germylation with 1,2-dichlorodigermane allows us to synthesize various α,ω-bis(chlorogermyl) compounds. Intriguing properties of polymers obtained through dechlorinative condensation with sodium of these compounds will be uncovered separately.

References

1) "Silicon-Based Polymer Science," ed by J. M. Zeigler and F. W. G. Fearon, Adv. Chem. Ser., **224**, American Chemical Society, Washington DC (1990); "Silicon Chemistry," ed by J. Y. Corey , E. R. Corey, and P. P. Gaspar, Ellis Horwood, Chichester (1988).

2) R. D. Miller and R. Sooriyakumaran, *J. Polym. Sci., Polym. Chem.*, **25**, 111 (1987); J. C. Baumert, G. C. Bjorklund, D. H. Jundt, M. C. Jurich, H. Looser, R. D. Miller, J. Rabolt, R. Sooriyakumaran, J. D.

Swalen, and R. J. Twieg, *Appl. Phys. Lett.*, **53**, 1147 (1988); H. Ban, K. Deguchi, and A. Tanaka, *J. Appl. Polym. Sci.*, **37**, 1589 (1989).

3) T. Hayashi, T. -a. Kobayashi, A. M. Kawamoto, H. Yamashita, and M. Tanaka, *Organometallics*, **9**, 280 (1990), and references cited therein.

4) T. Tsumuraya and W. Ando, *Organometallics*, **8**, 2286 (1989).

5) Compound (*Z*)-**2a**: bp 105-120 °C/1.0 Torr; ^{1}H-NMR ($CDCl_3$, TMS) δ 0.82 (s, 6H, CH_3), 1.04 (s, 6H, CH_3), 6.94 (s, 1H, CH=), 7.05-7.40 ppm (m, 5H, C_6H_5); IR (neat) 815 cm^{-1} (=CH). Anal. Found: C, 38.04; H, 4.82%. Calcd for $C_{12}H_{18}Cl_2Ge_2$: C, 38.09; H, 4.80%.

6) Compound **3**: ^{1}H NMR ($CDCl_3$, TMS) δ 0.54 (s, 6H, CH_3), 0.63 (s, 6H, CH_3), 7.35 (s, 5H, C_6H_5), 7.50 ppm (s, 1H, CH=); MS (high resolution) found: m/z 325.9861, calcd for $C_{12}H_{18}Ge_2O$: M, 325.9781.

7) Compound (*E*)-**4**: bp 80-90 °C/8 Torr; ^{1}H NMR ($CDCl_3$, TMS) δ 0.80 (s, 12H, CH_3), 6.90 ppm (s, 2H, CH=); IR (neat) 965 cm^{-1} (CH=CH). Anal. Found: C, 23.89; H, 4.69%. Calcd for $C_6H_{14}Cl_2Ge_2$: C, 23.84; H, 4.67.

8) H. Yamashita, M. Catellani, and M. Tanaka, preceding paper.

9) Compound (*Z*)-**4**: bp 70-80 °C/9 Torr; ^{1}H NMR ($CDCl_3$, TMS) δ 0.90 (s, 12H, CH_3), 7.03 ppm (s, 2H, CH=).

10) Coumpound **5**: MS (high resolution) found: m/z 249.9515; calcd for $C_6H_{14}Ge_2O$: M, 249.9468.

11) H. Matsumoto, I. Matsubara, T. Kato, K. Shono, H. Watanabe, and Y. Nagai, *J. Organomet. Chem.*, **199**, 43 (1980).

12) Compound (*E*)-**6**: ^{1}H NMR ($CDCl_3$, TMS) δ 0.69 (s, 6H, CH_3), 0.73 (s, 6H, CH_3), 1.77 (s, 3H, CH_3C), 2.01 (d, *J* = 8.5 Hz, 2H, $GeC\underline{H}_2CH=$), 2.14 (s, 2H, $GeC\underline{H}_2C(CH_3)=$), 5.24 ppm (t, *J* = 8.5 Hz, 1H, $GeCH_2C\underline{H}=$); MS (high resolution) found: m/z 345.9345, calcd for $C_9H_{20}Cl_2Ge_2$: M, 345.9325.

13) C. Couret, J.Satge, J. Escudie, and J. D. Andriamizaka, *J. Organomet. Chem.*, **132**, C5 (1977).

14) T. Hayashi, A. M. Kawamoto, T. -a. Kobayashi, and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1990**, 563.

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