CHEMISTRY LETTERS, pp. 1635-1638, 1992.

A Useful Palladium Catalyst for Addition of Ge-Ge Bonds to Alkynes

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Germanium-germanium bonds of digermanes, octamethyltrigermane, and decamethyltetragermane add readily to alkynes in the presence of $Pd(dba)_2$-$2P(OCH_2)_3CEt$ (dba = dibenzylideneacetone).

Palladium-catalyzed addition of organometals, particularly those with metal-metal σ bonds, to alkynes is of interest because of their importance as metal-carbon σ bond formation reactions in the last few years. These catalytic studies have been mainly focussed on the silicon-silicon bonds.$^{1)}$ However, there have been few reports on conventional palladium catalysts for addition of sterically hindered germanium-germanium bond$^{2)}$ and chlorine substituted germanium-germanium bond$^{3)}$ to alkynes. The conventional palladium catalysts for insertion of non activated germanium-germanium bond to alkynes are not effective. We herein describe the first insertion of alkynes into simple germanium-germanium bonds of polygermanes (digermanes, octamethyltrigermane, and decamethyltetragermane) in the presence of palladium catalyst, $Pd(dba)_2$-$2P(OCH_2)_3CEt$.

A typical reaction is as follows. A mixture of octamethyltrigermane, Me_8Ge_3 (0.4 mmol) and phenylacetylene (3.6 mmol) in benzene (0.1 cm^3) was heated in the presence of $Pd(dba)_2$ (0.012 mmol) and $P(OCH_2)_3CEt$ (0.024 mmol) in a sealed tube at 120 °C for 20 h. GC, NMR, and GC-MS spectra analyses of products revealed the presence of the single insertion product ($\underline{1}$)$^{4)}$ and the double insertion product ($\underline{2}$)$^{5)}$ in 14% and 86% yields, respectively. Under similar reaction conditions, the use of conventional catalysts such as $Pd(PPh_3)_4$ and $PdCl_2(PPh_3)_2$ resulted in very low yields (4% for $\underline{1}$, and 4% for $\underline{1}$ and 15% for $\underline{2}$, respectively). The yields of insertion products were slightly improved by the use of $Pd(dba)_2$-$2P(OPh)_3$ instead of $Pd(dba)_2$-$2PPh_3$. These results are summarized in Table 1.

As shown in Table 1, $Pd(dba)_2$-$P(OCH_2)_3CEt$ system is a useful catalyst for insertion of phenylacetylene into germanium-germanium bonds of octame-

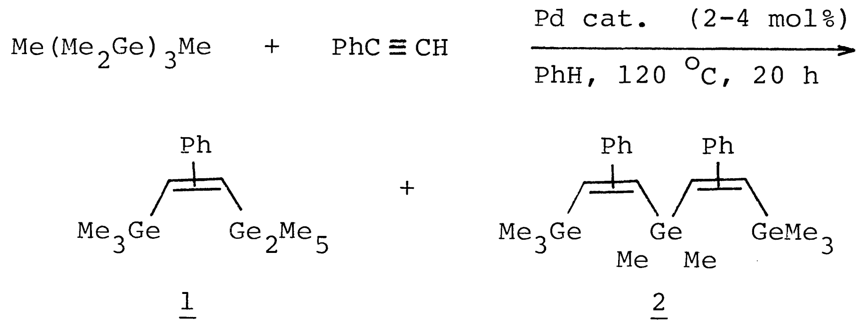


Table 1. Palladium-catalyzed Addition of Octamethyltrigermane to Phenylacetylene

Pd cat.[a)]	Product (Yield/%)[b)]	
	1	2
$Pd(PPh_3)_4$	4	0
$PdCl_2(PPh_3)_2$	4	15
$Pd(dba)_2$ + $2PPh_3$	3	0
$Pd(dba)_2$ + $2P(OPh)_3$	36	4
$Pd(dba)_2$ + $2P(OCH_2)_3CEt$	14	86

a) dab = dibenzylideneacetone. b) Yields of products were calculated on the basis of the amounts of the starting octamethyltrigermane.

thyltrigermane. The effective performance of $P(OCH_2)_3CEt$ seems to be mainly associated with the steric factor and basicity of the ligand.[1c)]

To extend the scope of above reaction, the reaction of several alkynes and trigermanes were examined in the presence of $Pd(dba)_2$-$P(OCH_2)_3CEt$ catalyst. Phenylacetylene easily reacted with germanium-germanium bond of 1,3-diphenylhexamethyltrigermane ($(PhMe_2Ge)_2GeMe_2$) under similar conditions (120 °C for 20 h) to give the single insertion product (8%)[6)] and the double insertion product (61%).[7)] Similarly, the double insertion product[8)] was obtained in good yields by the reaction of dimethyl acetylenedicarboxylate with Me_8Ge_3 at 120 °C for 5 h. With 1-hexyne, Me_8Ge_3 gave only the single insertion product.[9)] Trimethylsilylacetylene and phenylpropyne failed to react with Me_8Ge_3 in the presence of the present palladium complex. With $Pd(dba)_2$-$P(OCH_2)_3CEt$ catalyst at 120 °C, the yield of the double insertion product increased in the reaction of terminal alkynes and electron withdrawing-substituted alkynes with Me_8Ge_3. As was in the reaction of phenylacetylene, better yield could be obtained as follows; $Me_8Ge_3 > (PhMe_2Ge)_2GeMe_2$.

The present catalyst, $Pd(dba)_2$-$P(OCH_2)_3CEt$, was also applied to insertion reaction of phenylacetylene into germanium-germanium bond of decameth-

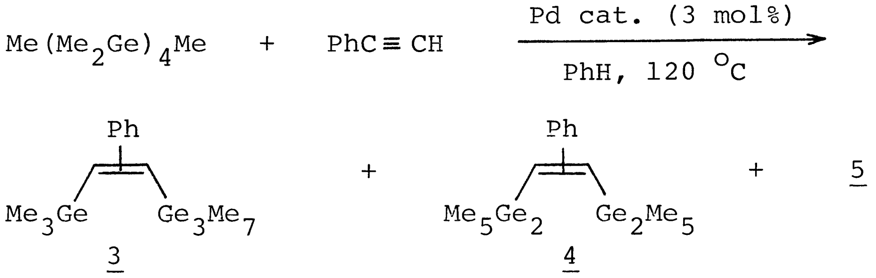
Table 2. Insertion of Alkynes into Ge-Ge Bonds of Octamethyltrigermane in the Presence of $Pd(dba)_2$-$P(OCH_2)_3CEt$

Alkynes	Reaction conditions	Products (Yield/%)[a)] 1	2
$MeO_2CC\equiv CCO_2Me$	120 °C, 5 h	0	54
$PhC\equiv CH$	120 °C, 20 h	14	86
$Me(CH_2)_3C\equiv CH$	120 °C, 20 h	11	0
$Me_3SiC\equiv CH$	120 °C, 20 h	trace	0
$PhC\equiv CMe$	120 °C, 20 h	0	0

a) Yields of products were calculated on the basis of the amounts of Me_8Ge_3 used.

yltetragermane, $Me_{10}Ge_4$, at 120 °C for 5 h. In addition to unidentified high-boiling products, two single insertion products, (3, 31%) and (4, 21%) and the double insertion product, (5, 5%),[10)] were mainly obtained together with small amounts of hexamethyldigermane, 1,2-bis(trimethylgermyl)phenylethene, 1, and 1,1-dimethyl-1-germacyclopentadiene. The minor products formed in this study are ascribed to degradation products of $Me_{10}Ge_4$.

Phenylacetylene inserted equally into the terminal germanium-germanium bond and into the internal germanium-germanium bond of $Me_{10}Ge_4$ at the beginning of the reaction. After 20 h at 120 °C, the product 3 decreased, resulting in inreasing of the product 5.



time/h	5	31%	22%	5%
	20	4%	36%	22%

We reported previously that the double germylation of phenylacetylene with 1,2-dichlorotetramethyldigermane occurred with $Pd(PPh_3)_4$ in high yields.[3)] However, with $Pd(dba)_2$-$P(OCH_2)_3CEt$ system at 120 °C for 5 h, the double germylation product was obtained in only 30% yield.

In conclusion, $Pd(dba)_2$-$P(OCH_2)_3CEt$ system has been demonstrated to be a useful catalyst for insertion of alkynes into germanium-germanium bonds of polygermanes.

The author (K. M.) thank Denka Co. Ltd., for gift of palladium complexes. We also thank Prof Isao Shimizu of Waseda University for measuring NMR spectra of some reaction products. This work was supported in part by the Ministry of Education, Science and Culture (Grant-in-Aid for Scientific Research No. 03215228 for K. M.).

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4) The compound 1 seems to have (Z) geometry on the basis of this ^{1}H NMR; see Ref. 1c. ^{1}H NMR (δ in $CDCl_3$) 0.21 (s, 9H), 0.35 (s, 9H), 0.37 (s, 6H), 6.45 (s, 1H), 7.00-7.30 (m, 5H).

5) The compound 2 was obtained as a mixture of two regio isomers (2a, b) (38:62) which seem to have (Z, Z) geometry; see Ref. 1c. ^{1}H NMR (δ in $CDCl_3$) 2a: 0.31 (s, 18H), 0.53 (s, 6H), 6.53 (s, 2H), 7.01-7.18 (m, 10 H). 2b: 0.16 (s, 9H), 0.25 (s, 9H), 0.34 (s, 6H), 6.44 (s, 2H), 6.72-6.94 (m, 5H), 7.22-7.48 (m, 5H).

6) GC and GC-MS analyses of this product revealed th be the single insertion product. m/z 386 (1), 346 (1), 307 (5), 284 (15), 244 (10), 216 (5), 182 (100), 152 (25), 103 (3), 91 (10), 77 (5).

7) The double insertion product seems to have (Z, Z) geometry on the basis of this ^{1}H NMR. ^{1}H NMR (δ in CCl_4) 0.40 (s, 6H), 0.65 (s, 6H), 0.70 (s, 6H), 5.93 (s, 2H), 6.83-7.73 (m, 20H).

8) The double insertion productseems to have (Z, Z) geometry on the basis of this ^{1}H NMR. ^{1}H NMR (δ in C_6D_6) 0.48 (s, 18H), 0.77 (s, 6H), 3.44 (s, 6H), 3.49 (s, 6H).

9) The single insertion product seems to have (Z) geometry on the basis of this ^{1}H NMR. ^{1}H NMR (δ in CCl_4) 0.23 (s, 18H), 0.34 (s, 6H), 1.73-2.10 (m, 9H), 5.23 (s, 1H).

10) GC and GC-MS analyses revealed that compounds 3 and 4 were the single insertion products and the compound 5 was the double insertion product.

(Received April 30, 1992)