ELSEVIER

Journal of Organometallic Chemistry 553 (1998) 493–496

Journal of Organometallic Chemistry

Preliminary communication

Palladium-catalyzed metathesis of phenylalkyl- or chloroalkyldigermanes with allylic chlorides at room temperature

Taichi Nakano [a,*], Tatsuki Enokido [a], Sigeyuki Noda [a], Nao-aki A-ihara [a], Masanori Kosugi [b], Toshihiko Migita [a,1]

[a] *Department of Material Science and Technology, School of High-Technology for Human Welfare, Tokai University, 317 Nishino, Numazu, Shizuoka 410-03, Japan*

[b] *Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan*

Received 1 July 1997; received in revised form 1 September 1997

Abstract

Metathesis of phenylalkyldigermanes (1,2-diphenyltetraethyl-, 1,2-diphenyltetramethyl-, phenylpentaethyl- or phenylpentamethyldigermane) or chloroalkyldigermanes (1,2-dichlorotetraethyl- or 1,2-dichlorotetramethyldigermane) with allylic chlorides proceeds smoothly even at room temperature in the presence of tris(dibenzylideneacetone)dipalladium(0) to afford the corresponding 2-alkenylgermanes in good to high yields. © 1998 Elsevier Science S.A.

Keywords: Germanium; Digermane; Palladium-catalysis; Metathesis; Allylgermanes

---

1. Introduction

Palladium-catalyzed metathesis of group 14 bimetallic compounds with allylic halides or esters is one of the important methods [2] to prepare allylated 14 metallic compounds. In fact, disilanes have been reported to undergo the metathesis with allylic chlorides or esters in the presence of $Pd(PPh_3)_4$ [5] or $Pd(P(OPh)_3)_4$ [6]. Tsuji et al. [7] have recently reported that the use of $Pd(dba)_2$–LiCl combination catalyst made the conditions in the metathesis of hexamethyldisilane with allylic acetates much milder than those of previously reported. Quite recently, they also reported that when allylic trifluoroacetates were used instead of allylic acetates, the reaction proceeded at room temperature in the presence of $Pd(dba)_2$ to give allylsilanes in good yields [8]. On the other hand, little attention has been paid to the reaction of digermanes with allylic halides except for our recent report [9], although the reactions of bromobenzene [10,11], benzyl chloride [11] or styryl bromide [11] in the presence of $Pd(PPh_3)_4$ have been published. In 1996, we reported that $Pd_2(dba)_3$ effected the metathesis of hexaethyl-digermane with allylic halides to produce allylgermanes with a good regioselectivity [9]. However, it required vigorous reaction conditions (170°C) to ensure the reaction. Therefore, it is desirable to search for the milder reaction conditions. Thus, we tried to enhance the reactivity of the digermane by selecting substituent(s) on germanium. After several trials, we have found that, quite interestingly, the germanium–germanium bond of digermanes such as 1,2-diphenyltetraethyldigermane **1**, 1,2-diphenyltetramethyldigermane **2**, phenylpentaethyldigermane **3**, phenylpentamethyldigermane **4**, 1,2-dichlorotetraethyldigermane **5** and 1,2-dichlorotetramethyl-digermane **6** was easily cleaved without heating or additive such as LiCl in the presence of a catalytic amount of $Pd_2(dba)_3$ and reacted with allylic chlorides to give corresponding allylgermanes in good yields. To our knowledge, there is no reports that palladium-catalyzed reaction of digermanes with organic halides proceeds even at room temperature.

---

[*] Corresponding author.

[1] Retired, March 31, 1997.

[2] For allylgermanes: see Refs. [1–4]

2. Results and discussion

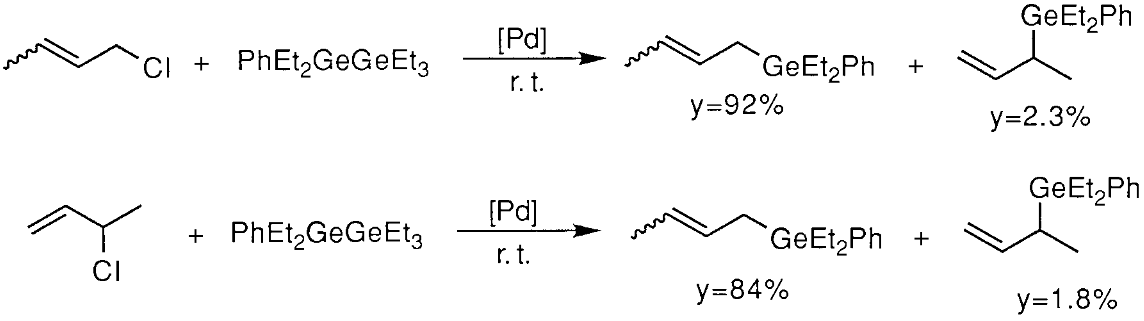
The reaction of **2** with *trans*-cinnamyl chloride in the presence of 1 mol% of tris(dibenzylideneacetone)dipalladium(0) in benzene proceeded smoothly at room temperature to produce *trans*- and *cis*-cinnamyldimethylphenylgermane in 96% and 3% yields based on the digermane consumed, respectively, while no reaction took place without the palladium catalyst. The formation of another expected product, (1-phenylprop-2-enyl)dimethylphenylgermane, was not observed by GLC analysis. The results encouraged us to examine the reaction of other digermanes such as **1**, **3**, **4**, **5** and **6**. These digermanes reacted with various allylic chlorides such as crotyl chloride, 3-chlorobut-1-ene, prenyl chloride or methallyl chloride as well as cinnamyl chloride at room temperature to give the corresponding allylgermanes in good yields. Results are summarized in Table 1.

As shown in Table 1, the palladium-catalyzed reaction of **1** with crotyl chloride (entry 1) gave a mixture of crotyldiethylphenylgermane (78%) and (1-methylprop-2-enyl)diethylphenylgermane (10%) and with 3-chlorobut-1-ene (entry 2) the same products were also produced in 82% and 16% based on the digermane consumed, respectively. It suggests that the reactions seem to proceed through a similar intermediate. On the other hand, digermane **1** reacted with prenyl chloride to give only prenyldiethylphenylgermane in 80% yield. The metathesis of **1** with *trans*-cinnamyl chloride similarly proceeded to give *trans*- and *cis*-cinnamyldiethylphenylgermane in 90% and 10% yields based on the digermane consumed. In these reactions, high regioselectivity was observed.

Table 1
Palladium-catalyzed reaction of digermanes (XR_2GeGeR_2X') with allylic chlorides[a]

Entry	R	X	X′	Halide	Time/h[b]	Solvent	Conversion/%[c]	Product/%[d]
1	Et	Ph	Ph	$CH_3CH=CHCH_2Cl$[e]	15	PhH	96	*trans*- and *cis*-$CH_3CH=CHCH_2GeEt_2Ph$ (78) $CH_2=CHCH(GeEt_2Ph)CH_3$ (10)
2	Et	Ph	Ph	$CH_2=CHCHClCH_3$	25	PhH	93	*trans*- and *cis*-$CH_3CH=CHCH_2GeEt_2Ph$ (82) $CH_2=CHCH(GeEt_2Ph)CH_3$ (16)
3	Et	Ph	Ph	$(CH_3)_2C=CHCH_2Cl$	17	none	100	$(CH_3)_2C=CHCH_2GeEt_2Ph$ (80)
4	Et	Ph	Ph	*trans*-$PhCH=CHCH_2Cl$	15	PhH	93	*trans*-$PhCH=CHCH_2GeEt_2Ph$ (90) *cis*-$PhCH=CHCH_2GeEt_2Ph$ (10)
5	Me	Ph	Ph	$CH_2=CHCHClCH_3$	4	PhH	100	*trans*- and *cis*-$CH_3CH=CHCH_2GeMe_2Ph$ (70) $CH_2=CHCH(GeMe_2Ph)CH_3$ (9)
6	Me	Ph	Ph	$(CH_3)_2C=CHCH_2Cl$	15	none	100	$(CH_3)_2C=CHCH_2GeMe_2Ph$ (61)
7	Me	Ph	Ph	*trans*-$PhCH=CHCH_2Cl$	1	PhH	94	*trans*-$PhCH=CHCH_2GeMe_2Ph$ (96) *cis*-$PhCH=CHCH_2GeMe_2Ph$ (3)
8	Et	Ph	Et	$CH_3CH=CHCH_2Cl$[e]	17	PhH	72	*trans*- and *cis*-$CH_3CH=CHCH_2GeEt_2Ph$ (92) $CH_2=CHCH(GeEt_2Ph)CH_3$ (2.3)
9	Et	Ph	Et	$CH_2=CHCHClCH_3$	16	PhH	77	*trans*- and *cis*-$CH_3CH=CHCH_2GeEt_2Ph$ (84) $CH_2=CHCH(GeEt_2Ph)CH_3$ (1.8)
10	Et	Ph	Et	$(CH_3)_2C=CHCH_2Cl$	18	none	100	$(CH_3)_2C=CHCH_2GeEt_2Ph$ (68)
11	Me	Ph	Me	$CH_3CH=CHCH_2Cl$[e]	17	PhH	86	*trans*- and *cis*-$CH_3CH=CHCH_2GeMe_2Ph$ (55)
12	Me	Ph	Me	$CH_2=CHCHClCH_3$	16	PhH	95	*trans*- and *cis*-$CH_3CH=CHCH_2GeMe_2Ph$ (40)
13[f]	Me	Ph	Me	*trans*-$PhCH=CHCH_2Cl$	16	PhH	96	*trans*-$PhCH=CHCH_2GeMe_2Ph$ (86) *cis*-$PhCH=CHCH_2GeMe_2Ph$ (14)
14	Et	Cl	Cl	$CH_3CH=CHCH_2Cl$[e]	17	none	100	*trans*- and *cis*-$CH_3CH=CHCH_2GeEt_2Cl$ (46)
15	Et	Cl	Cl	$CH_2=CHCHClCH_3$	16	none	100	*trans*- and *cis*-$CH_3CH=CHCH_2GeEt_2Cl$ (65)
16	Et	Cl	Cl	*trans*-$PhCH=CHCH_2Cl$	62	PhH	100	*trans*-$PhCH=CHCH_2GeEt_2Cl$ (80) *cis*-$PhCH=CHCH_2GeEt_2Cl$ (1.8) $PhCH(GeEt_2Cl)CH=CH_2$ (4)
17	Me	Cl	Cl	$CH_3CH=CHCH_2Cl$[e]	11	PhH	90	*trans*- and *cis*-$CH_3CH=CHCH_2GeMe_2Cl$ (75)
18	Me	Cl	Cl	$CH_2=CHCHClCH_3$	11	PhH	100	*trans*- and *cis*-$CH_3CH=CHCH_2GeMe_2Cl$ (55)
19	Me	Cl	Cl	$(CH_3)_2C=CHCH_2Cl$	14	PhH	98	$(CH_3)_2C=CHCH_2GeMe_2Cl$ (80)
20	Me	Cl	Cl	$CH_2=C(CH_3)CH_2Cl$	16	PhH	100	$CH_2=C(CH_3)CH_2GeMe_2Cl$ (quant.)
21	Me	Cl	Cl	*trans*-$PhCH=CHCH_2Cl$	7	PhH	100	*trans*-$PhCH=CHCH_2GeMe_2Cl$ (70) *cis*-$PhCH=CHCH_2GeMe_2Cl$ (2) $PhCH(GeMe_2Cl)CH=CH_2$ (1.8)

[a] Conditions: digermane (0.5 mmol), allylic chloride (1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.005 mmol) and solvent (1 ml), at room temperature.
[b] Reaction time was not optimized.
[c] Conversion of the digermane.
[d] GLC yields based on the digermane consumed.
[e] *trans*- and *cis*-isomeric mixture.
[f] Conditions: digermane (0.5 mmol), allylic chloride (0.5 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.01 mmol) and PhH (1 ml).



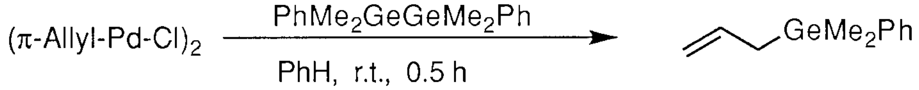
Scheme 1.

It should be noted that the metathesis occurred at room temperature even in the reaction of monophenylated digermanes. Entries 8 through 13 show the results for the reactions of phenylpentaalkyldigermanes **3** and **4**. In these cases, there are two possible products expected; one of which is the allylated phenyldialkylgermane, and the other is allylated trialkylgermane. In these reactions, 2-alkenyldialkylphenylgermane was a predominant product. Actually, the reaction of **3** with crotyl chloride smoothly proceeded to afford crotyldiethylphenylgermane and (1-methylprop-2-enyl)diethylphenylgermane in 92% and 2.3% yields, respectively (entry 8), as shown in Scheme 1.

A similar reaction with 3-chlorobut-1-ene also gave the same products in 84% and 1.8% yields, respectively (entry 9, Scheme 1). Phenylpentamethyldigermane reacted with cinnamyl chloride to produce *trans*- and *cis*-cinnamyldimethylphenylgermane in 86% and 14% yields based on the digermane consumed, respectively (entry 13). The results for the selective formation of 2-alkenyldialkylphenylgermanes are well consistent with those reported for the metathesis of phenylpentamethyldisilane with allylic acetates [8].

1,2-Dichlorinated digermanes were also subject to the metathesis with allylic chlorides at room temperature. Entries 14 through 21 show the results for the reaction of digermanes **5** and **6**. The metathesis of **5** or **6** with crotyl chloride or 3-chlorobut-1-ene gave regioselectively the corresponding crotylchlorodiethylgermane(s) or crotylchlorodimethylgermane(s) (entries 14 and 17), while the reactions of phenyldigermanes **1** and **3** were accompanied by the formation of (1-methylprop-2-enyl)germanes (entries 1 and 8). The reason is not clear yet. Metallylchlorodimethylgermane was formed in the reaction of **6** with methallyl chloride in quantitative yield (entry 20). Digermane **5** also entered into the reaction with cinnamyl chloride to form *trans*- (80%) and *cis*-cinnamylchlorodiethylgermane (1.8%) and (1-phenyl-prop-2-enyl)chlorodiethylgermane (4%) based on the digermane consumed (entry 16). A similar reaction of **6** gave the corresponding products in 70%, 2% and 1.8% yields, respectively (entry 21). High regioselectivities were also observed for these reactions.

From the results of Scheme 2, it is easy to assume the formation of the same π-allylpalladium chloride intermediate which derived from the reaction of $Pd_2(dba)_3$ with crotyl chloride or 3-chlorobut-1-ene at room temperature [12]. So we examined the reaction of (π-allylchloropalladium)dimer with 1,2-diphenyltetramethyldigermane in benzene at room temperature and found the reaction reached to completion for 30 min giving allylphenyldimethylgermane in quantitative yield (Scheme 2). In addition, the reaction of $Pd_2(dba)_3$ with the digermane **2** was extremely slow at room temperature compared to that of the Pd-dibenzylideneacetone complex with an allylic chloride. Thus, stirring a benzene solution of equimolecular amounts of $Pd_2(dba)_3$ and **2** for 10 h did not cause any reaction, although 16% of **2** was consumed after 72 h. Consequently, the mechanism for the reactions seems to be interpreted by the well-known oxidative addition and reductive elimination processes (Fig. 1). In addition, it should be emphasized that the metathesis of the digermane bearing phenyl or chloro substituent(s) proceeds smoothly even at room temperature, although the activating effect of phenyl or chloro substituent(s) to a metal–metal bond in group 14



Scheme 2.

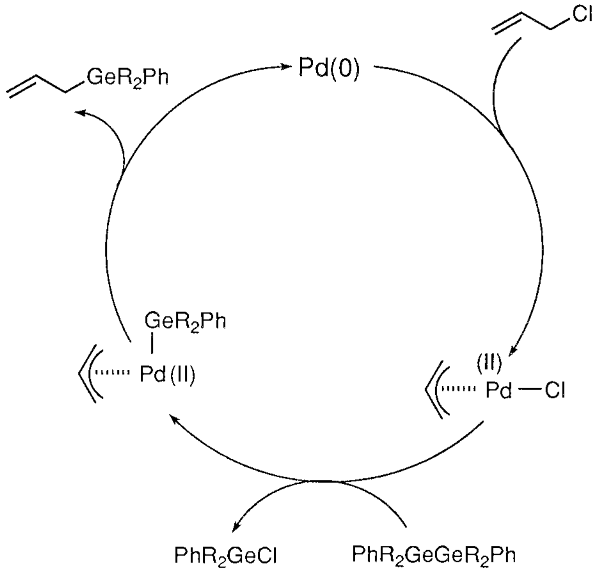


Fig. 1. A plausible mechanism in the formation of allylgermanes.

bimetallics such as disilanes has been reported [5,8,13]. Further studies including applications and limitation of the present reaction are now in progress.

3. Experimental

A benzene (1 ml) solution of 1,2-diphenyltetramethyldigermane (0.5 mmol), *trans*-cinnamyl chloride (1 mmol) and $Pd_2(dba)_3$. $CHCl_3$ (0.005 mmol) was stirred at room temperature. The reaction was traced with a gas chromatograph. After 1 h, a 94% of the digermane was consumed and *trans*-cinnamyldiethylphenylgermane and its *cis*-isomer were formed in 96% and 3% yields based on the digermane consumed, respectively. However, ^1H NMR analysis of a mixture of the products collected with GLC (column; silicone KF-96, 10% on celite 545 AW) disclosed that the products consisted of *trans*-isomer (88%), *cis*-isomer (11%) and (1-phenylprop-2-enyl)dimethylphenylgermane (1%). A similar product distribution was also observed in GLC analysis of the collected sample. Spectral data for the sample are as follows: IR (neat): 3050, 3005, 2970, 2900, 1640, 1595, 1495, 1425, 1235, 1135, 1095, 960, 800, 745, 730, 695 cm^{-1}. ^1H NMR($CDCl_3$, 400 MHz): δ 0.41 and 0.43 (s, s, 6H), 2.03 and 2.04 (dd, 1.78 H, $J = 4.8$, 2.8 Hz,), 2.19–2.21 (dd, 0.27 H, $J = 9.2$, 1.2 Hz), 2.63 (m, 0.01 H), 5.04–5.09 (m, 0.02 H), 5.71–5.79 (dt, 0.11H, $J = 11.6$, 9.2 Hz), 6.25–6.28 (m, 1.86H), 7.15–7.49 (m, 10H). EIMS: 298 (M^+), 181 ($[M - {}^{\cdot}CH_2CH{=}CHPh]^+$, base peak).

Acknowledgements

We thank Asai Germanium Research Institute for supplying tetrachlorogermane.

References

[1] R.M.G. Robert, F. El Kaissi, J. Organomet. Chem. 12 (1968) 79.
[2] J. Yamaguchi, Y. Tamada, T. Takeda, Bull. Chem. Soc. Jpn. 66 (1993) 607.
[3] R.H. Fish, H.G. Kuivila, J. Org. Chem. 31 (1966) 2445.
[4] Y. Ichinose, K. Ohshima, K. Utimoto, Bull. Chem. Soc. Jpn. 61 (1988) 2693.
[5] H. Matsumoto, T. Yako, S. Nagashima, T. Motegi, Y. Nagai, J. Organomet. Chem. 148 (1978) 97.
[6] H. Urata, H. Suzuki, Y. Moro-oka, T. Ikawa, Bull. Chem. Soc. Jpn. 57 (1984) 607.
[7] Y. Tsuji, S. Kajita, S. Isobe, M. Funato, J. Org. Chem. 58 (1993) 3607.
[8] Y. Tsuji, M. Funato, M. Ozawa, H. Ogiyama, S. Kajita, T. Kawamura, J. Org. Chem. 61 (1996) 5779.
[9] T. Nakano, H. Yamashita, T. Enokido, K. Ono, T. Migita, Main Group Chem. 1 (1996) 179.
[10] D. Azarian, S.S. Dua, C. Eaborn, D.R.M. Walton, J. Organomet. Chem. 117 (1976) C55.
[11] N.P. Reddy, T. Hayashi, M. Tanaka, Chem. Lett. 1 (1991) 677.
[12] T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet, J.A. Ibers, J. Organomet. Chem. 65 (1974) 253.
[13] Y. Tsuji, R.M. Lago, S. Tomohiro, H. Tsuneishi, Organometallics 11 (1992) 2352.