

# Palladium-Catalyzed Cross-Coupling Reactions of Allyl, Phenyl, Alkenyl, and Alkynyl Germatranes with Aryl Iodides

J. W. Faller\* and Roman G. Kultyshev

Department of Chemistry, Yale University, New Haven, Connecticut 06520

Received July 19, 2002

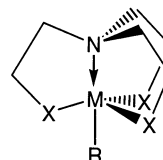
The potential of using organogermatranes in palladium-catalyzed cross-coupling with aryl iodides has been investigated. We have found that organogermatranes are less reactive in this analogue of Stille coupling than trialkylorganostannanes; nevertheless activation by fluoride promotes the reaction. The hypervalent germanium species produced from the germatranes provide a more efficient and more easily handled reagent than trialkoxygermanium analogues.

## Introduction

In the past decade the palladium-catalyzed cross-coupling reactions between organic electrophiles and various organometallic reagents became a standard tool for construction of carbon–carbon bonds. Among them the reaction of trialkylorganostannanes (the Stille–Migita–Kosugi reaction) is of great importance owing to the high reactivity and availability of the tin reagents as well as their stability toward air and moisture.<sup>1</sup> Nevertheless, a serious drawback of the Stille reaction, that is, the toxicity of the starting materials and byproducts, has prompted many research groups to search for alternative reagents. In particular, silicon reagents have received significant attention. This area of research was pioneered by Hiyama, who found that silanes could be activated toward transmetalation in the presence of a fluoride-ion source via formation of hypervalent silicates.<sup>2</sup> Later Shibata<sup>3</sup> and DeShong<sup>4</sup> reported on the palladium-catalyzed cross-coupling of aryl siloxanes with aryl halides in the presence of tetrabutylammonium fluoride (TBAF). In some cases, the presence of a phosphine was necessary to achieve high yields. *N*-Heterocyclic carbene ligands instead of phosphines have also been used in similar systems.<sup>5</sup> Reactions of aryl bromides with alkynylsilanes can also be catalyzed by a palladium/imidazolium salt system that could potentially involve carbene intermediates. Denmark and co-workers<sup>6a</sup> demonstrated the validity of vinylpolysiloxanes as cross-coupling partners in reactions with aryl iodides and noted the beneficial effect

of triphenylarsine as a ligand in reactions with slower reacting aryl iodides. Their intramolecular variant of alkenyl iodide–alkenyl siloxane coupling resulted in an effective synthesis of medium-sized rings with an internal 1,3-*cis-cis* diene unit.<sup>6b</sup> They also demonstrated mild cross-coupling conditions for a number of silyl compounds that employed tetrabutylammonium fluoride as the activator.<sup>6c</sup> These studies led to the development of fluoride-free cross-couplings using organosilanols.<sup>6d,e</sup>

Organogermanes, however, received much less attention as possible replacements for organostannanes, presumably owing to their higher cost, lower reactivity, and less developed chemistry. Kosugi et al.<sup>7</sup> reported that 1-aza-5-germa-5-organobicyclo[3.3.3]undecanes (carbagermatranes, **1**) are much more reactive in the cross-coupling reaction with aryl bromides than tetracoordinated germanes owing to the internal coordination of nitrogen to germanium. A similar observation for the internally coordinated carbastannatranes N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>SnR (**2**) has been previously made by Vedejs et al.<sup>8a</sup> This intramolecular nucleophilic assistance allowed alkyl group transfer, which does not usually occur in the case of tetracoordinated stannanes, to aryl halides<sup>8a</sup> and alkenyl triflates.<sup>8b</sup>



1, M = Ge, X = CH<sub>2</sub>

2, M = Sn, X = CH<sub>2</sub>

3, M = Ge, X = O

In our hands, however, an attempted synthesis of N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>GeCl, a precursor necessary for the

(1) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1997**, *50*, 1.

(2) (a) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471–1478. (b) Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; Chapter 10.

(3) Shibata, K.; Miyazawa, K.; Goto, Y. *Chem. Commun.* **1997**, 1309–1310.

(4) (a) Mowery, M.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 1684–1688. (b) Mowery, M.; DeShong, P. *J. Org. Lett.* **1999**, *1*, 2137–2140. (c) DeShong, P.; Handy, C. J.; Mowery, M. E. *Pure Appl. Chem.* **2000**, *72*, 1655–1658. (d) Manoso, A. S.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7449–7455.

(5) (a) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2000**, *2*, 2053–2055. (b) Yang, C. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 1020–1022.

(6) (a) Denmark, S. E.; Wang, Z. *J. Organomet. Chem.* **2001**, *624*, 372–375. (b) Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 2102–2103. (c) Denmark, S. E.; Pan, W. T. *Org. Lett.* **2001**, *3*, 61–64, and references therein. (d) Denmark, S. E.; Sweis, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 6439–6440. (e) Denmark, S. E.; Pan, W. T. *J. Organomet. Chem.* **2002**, *653*, 98–104.

(7) Kosugi, M.; Tanji, T.; Tanaka, Y.; Yoshida, A.; Fugami, K.; Kameyama, M.; Migita, T. *J. Organomet. Chem.* **1996**, *508*, 255–257.

(8) (a) Vedejs, E.; Haight, A. R.; Moss, W. O. *J. Am. Chem. Soc.* **1992**, *114*, 6556–6558. (b) Jensen, M. S.; Yang, C.; Hsiao, Y.; Rivera, N.; Wells, K. M.; Chung, J. Y. L.; Yasuda, N.; Hughes, D. L.; Reider, P. J. *Org. Lett.* **2000**, *2*, 1081–1084.

synthesis of organocarbagermatranes, met with only very limited success. Consequently, we decided to look for a similar class of molecules with internal coordination, which would allow more facile synthesis. Germatranes (**3**) appeared to be good candidates owing to the ease of their preparation in good yields from organotrihalogermanes and triethanolamine.<sup>9</sup> In this report we present our findings with respect to the behavior of this class of compounds in palladium-catalyzed cross-coupling reactions with aryl iodides.

## Results and Discussion.

**Preliminary Studies with Allyl, Phenyl, and Phenylethynyl Germatranes.** Our attempts to repeat the results of Kosugi et al.<sup>7</sup> for the cross-coupling between **1** (R = allyl, phenyl) and aryl bromides using analogous germatranes (R = allyl, **3a**; R = phenyl, **3b**) were unsuccessful. Only a trace amount of allylbenzene was detected after the reaction of **3a** with PhBr in THF in the presence of Pd<sub>2</sub>(dba)<sub>3</sub>CHCl<sub>3</sub> (1 mol %)-PPh<sub>3</sub> (4 mol %) for 45 h at 115 °C in a sealed glass ampule. Moreover, phenyl germatrane was found to be completely inert to phenyl group transfer upon Kosugi's conditions or heating at 120 °C for 24 h in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (3 mol %). In further experiments 4-iodotoluene (**4a**) was used as a substrate with a catalyst obtained in situ from Pd(dba)<sub>2</sub> and a ligand. Under "ligandless" conditions, formation of small amounts of 4-allyltoluene was observed. Surprisingly, in a similar experiment in the presence of PPh<sub>3</sub> (20 mol %) no coupling product could be detected. Although replacing PPh<sub>3</sub> with bulkier phosphines, such as P(*o*-tol)<sub>3</sub> and 2-(dicyclohexylphosphino)biphenyl, resulted in low conversions to 4-allyltoluene, addition of AsPh<sub>3</sub> as a ligand (1:1) was more effective, resulting in 27% conversion to 4-allyltoluene. In all of these experiments a second, minor coupling product was also detected. It was identified as  $\alpha$ , $p$ -dimethylstyrene by comparison with the <sup>1</sup>H NMR data reported in the literature.<sup>10</sup> Similarly, formation of  $\alpha$ -methylstyrene was observed in a stoichiometric reaction between allyl germatrane and (PPh<sub>3</sub>)<sub>2</sub>Pd(Ph)-(I)<sup>11</sup> in toluene at 100 °C.

Despite the limited success with allyl germatrane, phenyl and phenylethynyl germatranes were inert in attempted coupling reactions with **4a** in the presence of Pd(dba)<sub>2</sub>/AsPh<sub>3</sub>. The observed reactivity of germatranes bearing different apical substituents clearly contradicted the order established for the Stille reaction, that is, ethynyl > alkenyl > aryl > allyl.<sup>12</sup> In addition, formation of the internally arylated product in the allyl germatrane case cannot be explained by a Stille-like mechanism. If we assume that allyl germatrane reacts with 4-iodotoluene in a Heck-type reaction by virtue of the double bond present, then it becomes clear why phenyl and phenylethynyl ger-

matranes are unreactive. On the other hand, an addition-elimination or Heck-type mechanism (Scheme 1) can explain the formation of the internally arylated product,  $\alpha$ , $p$ -methylstyrene. In the Heck reaction, aryl palladation of a double bond is followed by  $\beta$ -hydrogen elimination. In the case of allyl germatrane elimination of *GeO<sub>3</sub>N* is probably more favorable since we do not observe any arylated germatranes among the products. Addition of the aryl group to the double bond can occur either terminally or internally (pathways "a" and "b", respectively). In pathway "a" *GeO<sub>3</sub>N* is attached to the  $\beta$ -carbon and can be eliminated, yielding the terminally arylated product that is also expected from a Stille reaction pathway. In pathway "b" *GeO<sub>3</sub>N* is attached to the  $\gamma$ -carbon; therefore  $\beta$ -hydrogen elimination takes place, resulting in an internally arylated germatrane  $\pi$ -bound to LPd(H)(I). Insertion of this olefin into the Pd-H bond can lead to the  $\sigma$ -alkyl complex from which a *GeO<sub>3</sub>N* group can be eliminated to yield  $\alpha$ , $p$ -dimethylstyrene.

Although we found no examples of a similar Heck reaction featuring allyl germanes in the literature, similar allylsilane systems have been studied. Thus Karabelas et al.<sup>13a</sup> observed the formation of silylated, as well as desilylated, products in the reaction of iodobenzene with allyltrimethylsilane. Olofsson et al.<sup>13b</sup> showed that internally arylated allyltrimethylsilanes can be obtained preferentially from allyltrimethylsilanes and aryltriflates if the chelating ligand DPPF is used with Pd(OAc)<sub>2</sub>. Jeffery demonstrated<sup>13c</sup> recently that the direction of the palladium-catalyzed arylation of allyltrimethylsilane toward the formation of either silylated or desilylated product can be controlled by choice of the base used in the reaction. Allylsilanes have been also used as terminating moieties in the asymmetric intramolecular Heck reaction leading to the stereoselective construction of sp<sup>3</sup> carbon centers bearing a vinyl substituent.<sup>13d</sup> There are a few examples of Heck reaction of vinylgermanes and vinylsilanes. Thus, Kosugi et al.<sup>7</sup> reported that vinyltributylgermane afforded *p*-methylstyrene in 60% yield upon reaction with *p*-bromotoluene. Ikenaga et al.<sup>14a</sup> published the first example of aryldegermylation of styryltrimethylgermanes by arenediazonium tetrafluoroborates leading to both  $\alpha$ - and  $\beta$ -arylated styrenes. Reaction of a hypervalent alkenyl silicon reagent with aryl iodides has also been reported to produce both  $\alpha$ - and  $\beta$ -styrene derivatives.<sup>14b</sup>

In agreement with a Heck-type mechanism, addition of 1 and 2 equiv of triethylamine as a base improved the conversion of **4a** to 4-allyltoluene to 44 and 51%, respectively. Similarly, upon reaction of 3-butenylgermatrane with 4-iodotoluene under the conditions that gave maximum conversion in the case of allyl germatrane, the major product was 1-(4-tolyl)-2-butene (33%), with one of the minor products being identified as 2-(4-tolyl)-2-butene (ratio 2.4:1).

(9) Gar, T. K.; Khromova, N. Yu.; Sonina, N. V.; Nikitin, V. S.; Polyakova, M. V.; Mironov, V. F. *Zh. Obshch. Khim.* **1979**, *49*, 1516–1522.

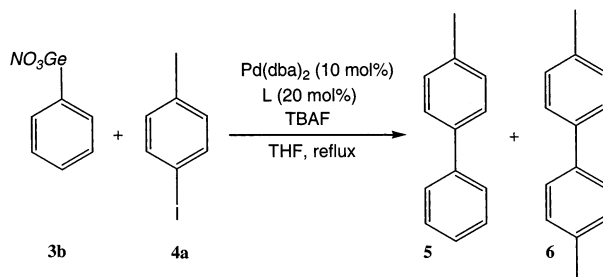
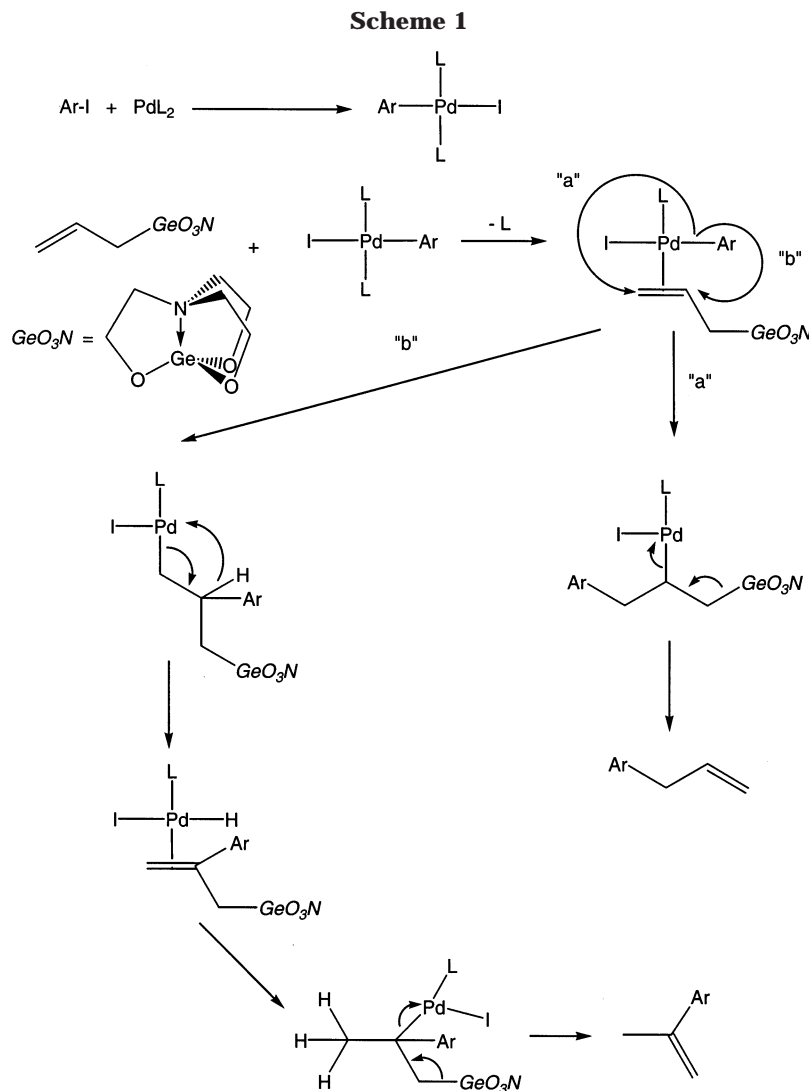
(10) Barton, D. H. R.; Parekh, S. I. *Synth. Commun.* **1989**, *19*, 3353–3361.

(11) Fitton, P.; Johnson, M. P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 6–7.

(12) (a) Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice Hall: Upper Saddle River, NJ, 1996; p 422. (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508–523.

(13) (a) Karabelas, K.; Westerlund, C.; Hallberg, A. *J. Org. Chem.* **1985**, *50*, 3896–3900. (b) Olofsson, K.; Larhed, M.; Hallberg, A. *J. Org. Chem.* **1998**, *63*, 5076–5079. (c) Jeffery, T. *Tetrahedron Lett.* **2000**, *41*, 8445–8449. (d) Tietze, L. F.; Raschke, T. *Synlett.* **1995**, *6*, 597–598.

(14) (a) Ikenaga, K.; Matsumoto, S.; Kikukawa, K.; Matsuda, T. *Chem. Lett.* **1990**, 185–188. (b) Hojo, M.; Murakami, C.; Aihara, H.; Komori, E.; Kohra, S.; Tominaga, Y.; Hosomi, A. *Bull. Soc. Chem. Fr.* **1995**, *132*, 499–508.

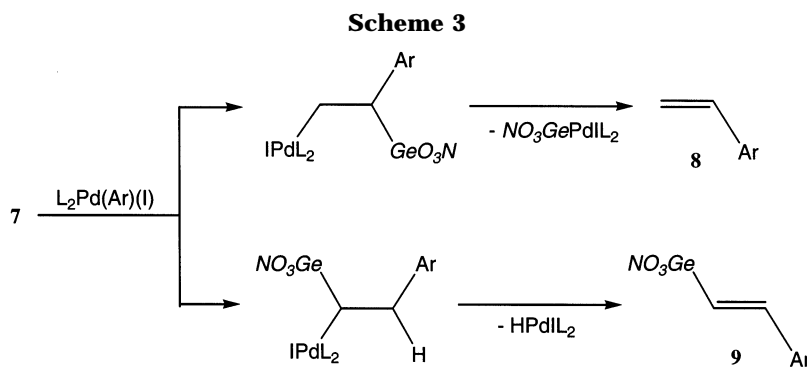
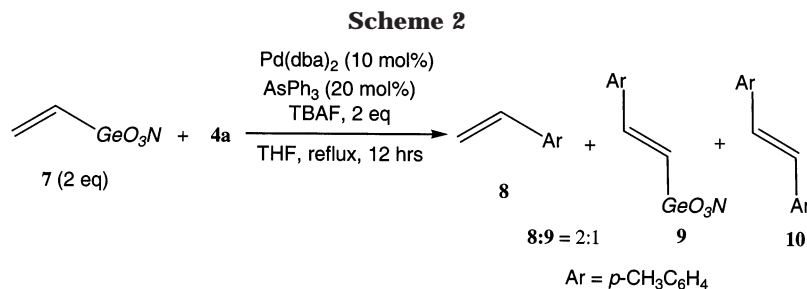
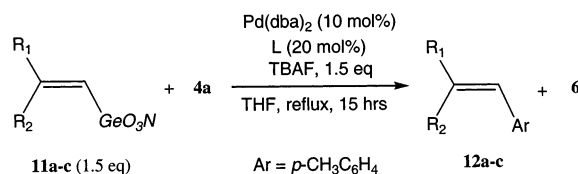


entry	<b>3b</b> , equiv	L	TBAF, equiv	time, h	yield of <b>5</b> , %	conversion of <b>4a</b> to <b>6</b> , %
1	1	AsPh <sub>3</sub>	1	16	28 <sup>a</sup>	32 <sup>a</sup>
2	0	AsPh <sub>3</sub>	1	20		42 <sup>a</sup>
3	1		1	20	18 <sup>a</sup>	28 <sup>a</sup>
4	2	AsPh <sub>3</sub>	2	16	43 <sup>b</sup> /38 <sup>c</sup>	34 <sup>b</sup>
5	2	2-P( <i>t</i> -Bu) <sub>2</sub> -biphenyl	2	12	31 <sup>a</sup>	14 <sup>a</sup>
6	2	2-PCy <sub>2</sub> -biphenyl	2	12	31 <sup>a</sup>	13 <sup>a</sup>
7	2	(2-furyl) <sub>3</sub> P	2	12	36 <sup>a</sup>	24 <sup>a</sup>
8	2	AsPh <sub>3</sub>	4	15	22 <sup>b</sup>	60 <sup>b</sup>

<sup>a</sup> Determined by integration of *p*-CH<sub>3</sub> signals of **5**, **6**, and **4a** in the <sup>1</sup>H NMR spectra of crude products. <sup>b</sup> Determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup> Isolated yield.

**Reactions of Phenyl Germatrane (3b) in the Presence of TBAF.** To avoid possible complications from a Heck reaction pathway in the case of germatranes containing isolated double bonds, we exam-

ined the activation of **3b** toward transmetalation using TBAF (Table 1). The reaction of **4a** with phenylgermatrane (1:1) in THF in the presence of Pd(dba)<sub>2</sub>, AsPh<sub>3</sub>, and 1 equiv of TBAF (entry 1) resulted in 28% conver-

**Table 2. Cross-Coupling of Alkenyl Germatranes with 4a**

entry	alkenyl germatrane	R <sub>1</sub>	R <sub>2</sub>	L	yield of <b>12</b> , %	yield of <b>6</b> , %
1	<i>E</i> - <b>11a</b>	Ph	H	2- <i>P</i> ( <i>t</i> -Bu) <sub>2</sub> -biphenyl	53 <sup>a</sup>	21 <sup>a</sup>
2	<i>E</i> - <b>11a</b>	Ph	H	AsPh <sub>3</sub>	64 <sup>a</sup>	16 <sup>a</sup>
3	<i>Z</i> - <b>11a</b> ( <i>E</i> / <i>Z</i> = 1:3.5) <sup>c</sup>	H	Ph	AsPh <sub>3</sub>	73 <sup>b</sup>	15 <sup>b</sup>
4	<i>Z</i> - <b>11b</b> ( <i>E</i> / <i>Z</i> = 1:7.5) <sup>c</sup>	H	<i>p</i> -Tol	AsPh <sub>3</sub>	71 <sup>a</sup>	16 <sup>a</sup>
5	<i>Z</i> - <b>11c</b> ( <i>E</i> / <i>Z</i> = 1:5.5) <sup>c</sup>	H	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	AsPh <sub>3</sub>	73 <sup>b</sup>	12 <sup>b</sup>
					<i>E</i> / <i>Z</i> = 1:3.4 <sup>d</sup>	

<sup>a</sup> Determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>b</sup> Determined by <sup>1</sup>H NMR using 1,2-diphenoxyethane as a standard. <sup>c</sup> Determined by integration of olefinic hydrogens. <sup>d</sup> Determined by integration of methyl hydrogens.

sion of the starting iodide to **5** and 32% conversion to **6**. This was encouraging since no coupling could be detected in the absence of TBAF. The homocoupling product was also obtained in the absence of phenyl germatrane (entry 2), in agreement with data of Mowery and DeShong<sup>4a</sup> obtained under "ligandless" conditions. Our attempt to use Pd(dba)<sub>2</sub> without added ligand resulted in lower conversions of the iodide to both hetero- and homocoupled products compared to the experiment with triphenylarsine (entry 3). Increasing the germatrane-to-iodide ratio to 2:1 significantly improved the conversion to 4-phenyltoluene (entry 4). Both 2-*P*(*t*-Bu)<sub>2</sub>-biphenyl and 2-PCy<sub>2</sub>-biphenyl were less effective than AsPh<sub>3</sub>, resulting in 31% conversion to the cross-coupling product (entries 5, 6). Tris(2-furyl)phosphine (entry 7) was also less effective than triphenylarsine. Increasing the ratio of TBAF to **4a** to 4:1 resulted in promoting the homocoupling of **4a** rather than the cross-coupling reaction.

**Reactions of Alkenyl Germatranes in the Presence of TBAF.** Vinyl germatrane (**7**) was prepared from vinylgermanium trichloride obtained by the procedure

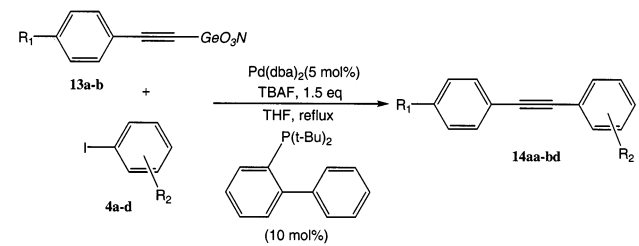
of Guillemin and co-workers.<sup>15</sup> Attempted cross-coupling between vinyl germatrane and **4a** in the presence of TBAF and Pd(dba)<sub>2</sub>/AsPh<sub>3</sub> (1:2) led to a mixture of products, one of them being the desired 4-methylstyrene (Scheme 2). Two more products have been identified, one as (*E*)-β-(4-methyl)styrylgermatrane and another as (*E*)-4,4'-dimethylstilbene. Although product **8** may be interpreted as a Stille product, both **8** and **9** could result from a Heck reaction. In the last step of this reaction either a β-germatranyl moiety or a β-hydrogen is eliminated from two possible regioisomers of the σ-alkylpalladium intermediate (Scheme 3). The stilbene product **10** could form as a result of (1) a Heck reaction between **8** and **4a**; (2) a cross-coupling reaction between **9** and **4a**; or (3) a combination of both pathways.

As shown in Table 2, β-aryl-substituted ethenyl germatranes prepared by rhodium-catalyzed hydrogermylation of arylacetylenes by HGe(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>N<sup>16</sup> were found to form stilbenes upon reaction with **4a** in THF.

(15) Guillemin, J.-C.; Lassalle, L.; Janati, T. *Planet. Space Sci.* **1995**, *43*, 75–81.

(16) Faller, J. W.; Kultyshev, R. G. Submitted to *Organometallics*.



**Table 3. Cross-Coupling of Alkynyl Germatranes with Aryl Iodides**

entry	germatrane	R <sub>1</sub>	iodide	R <sub>2</sub>	acetylene product	yield, %
1	<b>13a</b>	H	<b>4a</b>	<i>p</i> -CH <sub>3</sub>	<b>14aa</b>	91 <sup>a</sup>
2	<b>13a</b>	H	<b>4b</b>	<i>o</i> -CH <sub>3</sub>	<b>14ab</b>	85 <sup>a</sup>
3	<b>13a</b>	H	<b>4c</b>	<i>p</i> -CH <sub>3</sub> O	<b>14ac</b>	68 <sup>b</sup>
4	<b>13b</b>	CH <sub>3</sub>	<b>4a</b>	<i>p</i> -CH <sub>3</sub>	<b>14ba</b>	89 <sup>a</sup>
5	<b>13b</b>	CH <sub>3</sub>	<b>4b</b>	<i>o</i> -CH <sub>3</sub>	<b>14bb</b>	72 <sup>a</sup>
6	<b>13b</b>	CH <sub>3</sub>	<b>4c</b>	<i>p</i> -CH <sub>3</sub> O	<b>14bc</b>	72 <sup>b</sup>
7	<b>13b</b>	CH <sub>3</sub>	<b>4d</b>	<i>p</i> -Cl	<b>14bd</b>	56 <sup>a,c</sup>

<sup>a</sup> Isolated yield. <sup>b</sup> Determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup> Lower yield partially due to the formation of 1,4-bis(*p*-tolylethynyl)benzene as a second cross-coupling product.

Thus, (*E*)- $\beta$ -styrylgermatrane (**11a**) resulted in 53% conversion of the iodide to 4-methylstilbene (**12a**) with 2-P(*t*-Bu)<sub>2</sub>-biphenyl as a ligand and 64% with triphenylarsine (Table 2, entries 1, 2). Interestingly, introduction of an aryl substituent into  $\beta$ -position completely shuts down the pathway that would lead to a  $\beta,\beta$ -biaryl ethenyl germatrane, as only the cross-coupled and homocoupled products are observed in these reactions. The nature of a substituent on the phenyl ring does not appear to significantly affect the yield of the cross-coupling product. Thus, the yields were almost identical for electron-releasing methyl, electron-neutral hydrogen, and electron-withdrawing chloro substituents in *para*-position (entries 3–5). In general, when germatranes containing mostly *Z*-isomer were used as the cross-coupling partners, the *E/Z* ratios of stilbenes obtained were higher than the corresponding ratios in the starting germatranes (entries 3–5).

**Reactions of Alkynyl Germatranes in the Presence of TBAF.** Alkynyl germatranes are readily accessible from the corresponding alkynyl germanium trichlorides, which in turn can be prepared via the method of Lutsenko and co-workers.<sup>17</sup> Preliminary experiments with **4a**, phenylethynyl germatrane, and 10 mol % Pd(dba)<sub>2</sub> demonstrated that in the presence of TBAF transfer of the phenylethynyl group occurs readily, and no homocoupled product is observed with either AsPh<sub>3</sub> or 2-P(*t*-Bu)<sub>2</sub>-biphenyl (20 mol %). However, in the case of arsine formation of diphenylacetylene was detected by GLC (ratio 1:16, yield of *p*-tolylphenylacetylene was 92% from <sup>1</sup>H NMR). No such scrambling of groups was observed when the 2-P(*t*-Bu)<sub>2</sub>-biphenyl ligand was used. For this reason the latter was chosen for the further experiments shown in Table 3. The yield of the cross-coupling product was not affected when the amounts of both Pd(dba)<sub>2</sub> and ligand were reduced to 5 and 10 mol %, respectively.

The results obtained with different germatranes and aryl iodides are summarized in Table 3. Very good yields

of diarylacetylenes were obtained with **4a** as a substrate (entries 1 and 4), while 2-iodotoluene (**4b**) (entries 2 and 5) and 4-iodoanisole (**4c**) (entries 3 and 6) gave lower yields of cross-coupling products. When 4-chloro-1-iodotoluene (**4d**) was used as a substrate, the expected cross-coupling product **14bd** was isolated only in moderate yield (entry 7). This was due to the presence of a second product, which was identified as 1,4-bis(*p*-tolylethynyl)benzene<sup>22</sup> by its <sup>1</sup>H NMR spectrum and mass spectroscopy. This result suggests that aryl chlorides and bromides could also be activated under the reaction conditions.

The fluoride could be involved in several steps in catalysis, the most important of which would seem to be the production of a more active hypervalent germanium complex. Evidence shedding light onto the fate of the germatranyl group was found upon careful examination of products formed after reaction of **13b** with **4c** and **4d**. In both cases addition of dichloromethane to the reaction mixture after removal of THF caused precipitation of white crystalline material, which was identified as fluorogermatrane by comparison of its <sup>1</sup>H and <sup>19</sup>F NMR ( $\delta = -75.5$  vs CHF<sub>2</sub>Cl) spectra with those of the authentic compound prepared by the method of Lukevics et al.<sup>18</sup> Iodogermatrane formation was not detected by <sup>1</sup>H NMR. Instead, the presence of free iodide was confirmed by treatment of aqueous ethanol solution of the residue left after removal of diarylacetylene and fluorogermatrane with aqueous AgNO<sub>3</sub>. This does not necessarily imply the absence of a reductive elimination from palladium forming a Ge–I bond, as one would expect a preference of germanium for fluoride. That is, iodide might be lost after any germanium–palladium interaction.

**Reaction of *E,Z*- $\beta$ -Methylcrotylgermatrane (*E,Z*-**15**) in the Presence of TBAF.** This compound was prepared from *E,Z*- $\beta$ -methylcrotylgermanium trichloride and triethanolamine.<sup>19</sup> This substrate with a trisubstituted double bond was chosen to minimize a possible Heck reaction pathway. Several ligands were used (Table 4); among them 2-P(*t*-Bu)<sub>2</sub>-biphenyl gave the highest conversion to the cross-coupling products. Increase of catalyst loading from 5 to 10 mol % led only to increased conversion of the iodide to the product of homocoupling. Although the starting germatrane contained only a small amount of the 3-(2-methyl)butenyl isomer (11:1), the corresponding ratio of cross-coupling products **16a:16b** was significantly lower (6:1). This result indicates that allylic rearrangement occurred, similar to the observations of others in the Stille reaction.<sup>20</sup>

**Trialkoxygermanes vs Germatranes in TBAF-Assisted Cross-Coupling Reactions.** From our re-

(18) Lukevics, E.; Belyakov, S.; Arsenyan, P.; Popelis, J. *J. Organomet. Chem.* **1997**, *549*, 163–165.

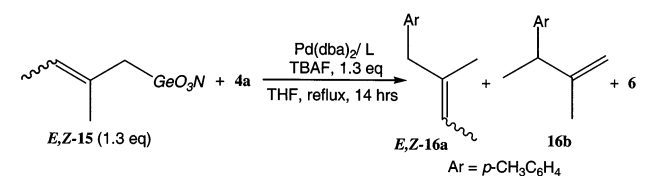
(19) Faller, J. W.; Kultyshev, R. G. To be submitted to *Organometallics*.

(20) (a) Godschalk, J.; Stille, J. K. *Tetrahedron Lett.* **1980**, *21*, 2599–2602. (b) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2595–2598. (c) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478–5486. (d) Labadie, S. S. *J. Org. Chem.* **1989**, *54*, 2496–2498. (e) Obora, Y.; Tsuji, Y.; Kobayashi, M.; Kawamura, T. *J. Org. Chem.* **1995**, *60*, 4647–4649.

(21) Zaitseva, G. S.; Karlov, S. S.; Churakov, A. V.; Howard, J. A. K.; Avtomonov, E. V.; Lorberth, J. Z. *Anorg. Allg. Chem.* **1997**, *623*, 1144–1150.

(22) Nguyen, P.; Yuan, Z.; Agocs, L.; Lesley, G.; Marder, T. B. *Inorg. Chim. Acta* **1994**, *220*, 289–296.

(17) Efimova, I. V.; Kalganov, B. E.; Kazankova, M. A.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1984**, *54*, 459–460.

**Table 4. Cross-Coupling of *E,Z*- $\beta$ -Methylcrotyl Germatrane with **4a****

entry	L, mol %	Pd(dba) <sub>2</sub> , mol %	yield of <i>E,Z</i> - <b>16a</b> + <b>16b</b> , % <sup>a</sup>	conversion of <b>4a</b> to <b>6</b> , % <sup>a</sup>
1	2-P( <i>t</i> -Bu) <sub>2</sub> -biphenyl, 10	5	41	31
2	2-P( <i>t</i> -Bu) <sub>2</sub> -biphenyl, 20	10	40	44
3	P( <i>t</i> -Bu) <sub>3</sub> , 10	5	26	15
4	AsPh <sub>3</sub> , 10	5	28	49

<sup>a</sup> Determined by integration of *p*-CH<sub>3</sub> signals of *E,Z*-**16a** + **16b**, **6**, and **4a** in the <sup>1</sup>H NMR spectra of crude products.

sults it appears that germatranes are unable to participate in cross-coupling reactions without activation with TBAF. Since aryl and vinyl siloxanes have been reported in cross-coupling reactions in the presence of fluoride-ion source, it was of interest to look at the similar reactions of trialkoxygermanes and compare the results with those obtained for germatranes. Preliminary study showed that under the "ligandless" conditions reported by DeShong and Mowery,<sup>4a</sup> PhGe(OEt)<sub>3</sub> (**17a**) did not produce any 4-phenyltoluene when treated with 4-iodotoluene, **4a**, in DMF. Nevertheless, addition of tri(2-furyl)phosphine resulted in formation of the cross-coupled product in 29% yield, which is slightly lower than with phenyl germatrane, **3b**. Table 5 summarizes the results. With triphenylarsine as a ligand, phenyl germatrane also produced a higher yield of **5** compared to the reaction with phenyl triethoxygermane (entries 1 and 2, Table 5). Phenylethynyl triethoxygermane (**17b**) was inferior to the corresponding germatrane **13a** when reacted with 2-iodotoluene, **4b**, under similar conditions (entries 3 and 4).

## Conclusion

We have found that organogermatranes are less reactive in this analogue of Stille coupling than trialkyl-organostannanes; nevertheless activation by fluoride promotes the reaction. In comparison of germatranes and triethoxygermanes it appears that germatranes are more efficient in the cross-coupling reaction with aryl iodides and furthermore they also have the advantage of being easier to handle and purify.

## Experimental Section

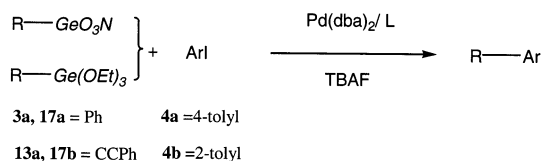
**General Data.** Most synthetic manipulations were carried out using standard Schlenk techniques under an inert atmosphere. Anhydrous solvents were used unless noted otherwise. <sup>1</sup>H NMR spectra were recorded on either a Bruker 500 MHz or a Bruker 400 MHz spectrometer, and chemical shifts are in ppm relative to residual solvent resonances (<sup>1</sup>H). <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on either a Bruker 500 MHz or a Bruker 400 MHz spectrometer operating at 125.8 and 100.6 MHz, respectively, and referenced to the deuterated solvent signals. <sup>19</sup>F NMR spectra were recorded on a Bruker spectrometer operating at 376.3 MHz, and chemical shifts are measured in ppm relative to external CHF<sub>2</sub>Cl. Gas chroma-

tography was performed on a Hewlett-Packard 5890 GC. Melting points were determined in open capillaries and are uncorrected.

**Vinylgermanium Trichloride.** A 50 mL solv-seal flask equipped with a stirbar was charged with 0.0313 g of AIBN and 2.21 g of 97% vinyltributylstannane (6.76 mmol), cooled to -78 °C, and evacuated. The flask was transferred to a glovebox, and 0.77 mL of GeCl<sub>4</sub> (6.75 mmol) was added. The reaction mixture was heated at 90 °C for 3 h, during which time the mixture became light brown. Pure CH<sub>2</sub>=CHGeCl<sub>3</sub> (1.24 g, 89%) was obtained by vacuum distillation. The <sup>1</sup>H NMR agreed with that reported by Guillemin and co-workers.<sup>15</sup>

**Vinyl Germatrane (7).** A 100 mL Schlenk flask equipped with a stirbar was charged under nitrogen with 1.52 g of CH<sub>2</sub>=CHGeCl<sub>3</sub> (7.38 mmol) and 20 mL of anhydrous toluene. EtOH (1.30 mL, 22.2 mmol) and triethylamine (3.09 mL, 22.2 mmol) were added. After stirring for 1 h the white precipitate was filtered in the glovebox and washed with an additional amount of anhydrous toluene (90 mL). The filtrate combined with washings was added to a 250 mL round-bottom flask containing 1.115 g of 98% triethanolamine (7.324 mmol) in 5 mL of toluene. The resulting mixture was stirred under nitrogen at 110 °C for 5.5 h. After cooling to room temperature the resulting solution was filtered and the toluene removed under reduced pressure. Compound **7** was obtained as a fluffy white solid (1.67 g, 92%) melting at 164–165 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 6.14–6.05 (m, 1H, CH=), 5.99–5.92 (m, 2H, CH<sub>2</sub>=), 3.81 (t, 6H, *J* = 5.6, CH<sub>2</sub>O), 2.85 (t, 6H, *J* = 5.6, CH<sub>2</sub>N). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 135.7, 132.4, 56.8, 51.9. Anal. Calcd for C<sub>8</sub>H<sub>15</sub>O<sub>3</sub>NGe: C, 39.09; H, 6.15, N, 5.70. Found: C, 38.96; H, 6.08, N, 5.75. The structure was verified by X-ray crystallography (see Supporting Information). Crystal data for **7**: monoclinic, space group *P*2<sub>1</sub>/*n* (No. 14) *a* = 6.7543(5) Å, *b* = 9.4464(7) Å, *c* = 15.430(2) Å, β = 95.152(5)°, *V* = 980.53(12) Å<sup>3</sup>, *Z* = 4, *T* = 183.2 K; full matrix least squares refinement of *F* (118 parameters)

**Preparation of Arylethynyl Germatranes (13a,b).** Phenylethynyl- and *p*-tolylethynylgermanium trichlorides were obtained via the procedure of Lutsenko and co-workers.<sup>17</sup> Without distillation these trichlorides were converted into the corresponding germatranes using the two-step procedure involving alkoxylation with ethanol followed by transalkoxylation with triethanolamine.<sup>9</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **13a** obtained in 95% yield (based on the trichloride) were identical to those previously reported.<sup>21</sup> A representative procedure for the synthesis of *p*-tolylethynyl germatrane (**13b**) is described. A 50 mL solv-seal flask equipped with a stirring bar was charged under nitrogen with 0.78 mL of 97% 4-ethynyltoluene (5.97 mmol), 10 mL of toluene, 0.70 mL of germanium tetrachloride (6.14 mmol), and triethylamine (6.17 mmol). The flask was sealed, cooled, evacuated, and then placed in an oil bath preheated to 100 °C. After 21 h the white precipitate was filtered off and washed with 20 mL of toluene. The filtrate and washings were combined in a 100 mL Schlenk flask equipped with a stirring bar and a rubber septum followed by addition of 1.05 mL of absolute EtOH (17.9 mmol) and 2.50 mL of Et<sub>3</sub>N (17.9 mmol) and stirring at room temperature for 50 min. The white precipitate was filtered and washed with 50 mL of toluene, and the filtrate and washings were added to a 250 mL round-bottomed flask containing 0.890 g of 98% triethanolamine (5.85 mmol) and a stirbar. A condenser was attached, and the reaction mixture was heated at 100 °C for 6 h. After cooling to room temperature the precipitate was filtered and washed with pentane and 60 mL of dichloromethane. After dichloromethane removal in vacuo **13b** was obtained as a white solid (1.786 g, 87% yield based on GeCl<sub>4</sub>) melting at 263 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.40 (d, 2H, *J* = 8.1, C<sub>6</sub>H<sub>4</sub>), 7.03 (d, 2H, *J* = 8.1, C<sub>6</sub>H<sub>4</sub>), 3.87 (t, 6H, *J* = 5.6, CH<sub>2</sub>O), 2.89 (t, 6H, *J* = 5.6, CH<sub>2</sub>N), 2.29 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125.8 MHz): δ 138.5, 132.5, 128.8, 120.1, 99.8, 89.9, 56.9, 51.6, 21.7. Anal. Calcd for C<sub>15</sub>H<sub>19</sub>O<sub>3</sub>-

**Table 5. Comparison of Germoxanes vs Germatranes as Cross-Coupling Partners**

entry	germanium compound	iodide	Pd(dba) <sub>2</sub> , mol %	ligand, mol %	yield of cross-coupling product, %
1	<b>3b</b>	<b>4a</b>	10	AsPh <sub>3</sub> , 20	43 <sup>a</sup>
2	<b>17a</b>	<b>4a</b>	10	AsPh <sub>3</sub> , 20	25 <sup>a</sup>
3	<b>13a</b>	<b>4b</b>	5	2-P( <i>t</i> -Bu) <sub>2</sub> -biphenyl, 10	85 <sup>b</sup>
4	<b>17b</b>	<b>4b</b>	5	2-P( <i>t</i> -Bu) <sub>2</sub> -biphenyl, 10	30 <sup>b</sup>

<sup>a</sup> Determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>b</sup> Isolated yield.

NGe: C, 53.95; H, 5.74, N, 4.19. Found: C, 53.45; H, 5.77, N, 4.19 (six separate analyses gave acceptable H and N, but consistently gave slightly low values for carbon).

**General Procedure for Cross-Coupling Reactions.** A 25 mL round-bottom three-neck flask equipped with a stirring bar, rubber septum, and stopper was charged with an aryl iodide, Pd(dba)<sub>2</sub>, ligand, and organogermatranes (1.2–2 equiv). A condenser was attached, and the flask evacuated and refilled with nitrogen. Anhydrous THF (10–12 mL) was added followed by a 1 M solution of TBAF in THF (ratio germatrane/TBAF = 1:1). The flask was placed in an oil bath and heated to approximately 75 °C when reflux began. After 12–18 h the solution was filtered through a pad of Celite. The pad was washed with three portions of dichloromethane (15 mL), and the filtrate and washings were combined and volatile materials removed with a rotary evaporator. The cross-coupling product was extracted with petroleum ether (bp 35–60 °C) and purified by column chromatography using petroleum ether as an eluent. To determine yields by <sup>1</sup>H NMR, 25–55 mg of 1,3,5-trimethoxybenzene or 1,2-diphenoxyethane was added to a residue followed by CDCl<sub>3</sub> (2–3 mL). Integrals of methoxy and methylene hydrogens, respectively, of these compounds were used in yield calculations. The representative procedure for the synthesis of 4-chloro-4'-methylbiphenylacetylene (**14bd**) and isolation of fluorogermatranes is as follows. A 25 mL round-bottom three-neck flask equipped with a stirring bar, rubber septum, and stopper was charged with 0.1875 g of 99% **4d** (0.778 mmol), 0.0224 g of Pd(dba)<sub>2</sub> (0.039 mmol, 5 mol %), 0.0233 g of 2-P(*t*-Bu)<sub>2</sub>-biphenyl (0.077 mmol, 10 mol %), and 0.3357 g of **13b** (1.005 mmol, 1.3 equiv). After attaching to a condenser, the flask was evacuated and refilled with nitrogen, and THF (10 mL) was added followed by 1.0 mL of a 1 M solution of TBAF in THF (1.0 mmol). The flask was placed in an oil bath and heated to approximately 75 °C. Twelve hours after the start of reflux the solution was filtered through a pad of Celite. The pad was washed with three portions of dichloromethane (15 mL), and the filtrate and washings were combined and volatile materials were removed with a rotary evaporator. Upon addition of CH<sub>2</sub>Cl<sub>2</sub> to the residue, fluorogermatranes precipitated as a white solid, mp >300 °C. <sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO, 400 MHz): δ 3.70 (td, 6H, *J* = 5.7; 1.5, FGEOCH<sub>2</sub>), 2.95 (t, 6H, *J* = 5.7, CH<sub>2</sub>N). <sup>19</sup>F{<sup>1</sup>H} NMR (*d*<sub>6</sub>-DMSO, 376.3 MHz): δ -75.5. The supernatant liquid was carefully decanted, and the precipitate was washed with an additional portion of CH<sub>2</sub>Cl<sub>2</sub>. Dichloromethane solutions were combined, the solvent was removed in vacuo, and the residue was extracted with petroleum ether. The extract was chromatographed on a silica gel column using petroleum ether as an eluent. From earlier fractions compound **14bd** was obtained as a white solid in 56% yield (0.098 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.46–7.40 (m, 4H, *p*-ClC<sub>6</sub>H<sub>4</sub> and *p*-MeC<sub>6</sub>H<sub>4</sub>), 7.33–7.29 (m, 2H, *p*-ClC<sub>6</sub>H<sub>4</sub>), 7.16 (d, 2H, *J* = 7.9), 2.37 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 138.9, 134.2, 132.9, 131.7, 129.4, 128.9, 122.2, 120.0, 90.7, 87.8, 21.8. Anal. Calcd for C<sub>15</sub>H<sub>11</sub>Cl: C, 79.47; H,

4.89. Found: C, 79.44; H, 4.90. Later fractions contained both **14bd** and 1,4-bis(*p*-tolylethynyl)benzene.<sup>22</sup>

The following coupling products have been identified by comparison with the previously reported <sup>1</sup>H NMR spectra: 4-methylbiphenyl (**5**),<sup>4a</sup> phenyl-*p*-tolylacetylene (**14aa**),<sup>23</sup> phenyl-*o*-tolylacetylene (**14ab**),<sup>23</sup> 4-methoxydiphenylacetylene (**14ac**),<sup>23</sup> bis(4-methylphenyl)acetylene (**14ba**),<sup>24</sup> 4-methoxyphenyl-*p*-tolylacetylene (**14bc**),<sup>25</sup> (*E*)-4-methylstilbene (**E-12a**),<sup>26a,c,d</sup> (*Z*)-4-methylstilbene (**Z-12a**),<sup>26d</sup> (*E*)-4,4'-dimethylstilbene (**E-12b**),<sup>26a-c</sup> (*Z*)-4,4'-dimethylstilbene (**Z-12b**),<sup>26b</sup> and (*E*)-4-chloro-4'-methylstilbene (**E-12c**).<sup>26c</sup> In addition, **5**, **6**, and **14aa** have been identified by comparison of their GC retention times to those of the samples of authentic compounds purchased from Aldrich or synthesized via previously published procedures (**14aa**).<sup>27</sup>

**(Z)-4-Chloro-4'-methylstilbene (E-12c):** colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.19–7.03 (m, 8H, *p*-ClC<sub>6</sub>H<sub>4</sub> and *p*-MeC<sub>6</sub>H<sub>4</sub>), 6.58 (d, 1H, *J* = 12.2, =CH), 6.48 (d, 1H, *J* = 12.2, =CH), 2.32 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 137.3, 136.1, 134.1, 132.8, 131.1, 130.4, 129.2, 128.9, 128.6, 128.4, 21.5.

**(p-Tolyl)(o-tolyl)acetylene (14bb):** white solid (72% yield) melting at 43 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.50 (d, 1H, *J* = 7.5), 7.44 (d, 2H, *J* = 8.0), 7.24–7.16 (m, 5H), 2.52 (s, 3H, *o*-CH<sub>3</sub>), 2.38 (s, 3H, *p*-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125.8 MHz): δ 140.3, 138.5, 132.0, 131.6, 129.6, 129.3, 128.3, 125.8, 123.5, 120.7, 93.7, 87.9, 21.7, 21.0. Anal. Calcd for C<sub>16</sub>H<sub>14</sub>: C, 93.16; H, 6.84. Found: C, 92.91; H, 6.83.

**(E,Z)-4-(4'-Methylphenyl)-3-methyl-2-butene (E,Z-16a) and 3-(4'-methylphenyl)-2-methyl-1-butene (16b):** colorless oil. <sup>1</sup>H NMR of *E,Z*-**16a** (CDCl<sub>3</sub>, 400 MHz): δ 7.12–7.06 (m, 4H, *p*-MeC<sub>6</sub>H<sub>4</sub>), 5.42–5.35 and 5.34–5.27 (2m, 1H, CH=), 3.34 and 3.25 (2s, 2H, CH<sub>2</sub>Ar), 2.33 (s, 3H, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 1.73 and 1.62 (2d, 3H, CH<sub>3</sub>CH=C(Me)CH<sub>2</sub>), 1.61 and 1.55 (2s, 3H, =C(CH<sub>3</sub>)CH<sub>2</sub>). <sup>1</sup>H NMR of **16b** (CDCl<sub>3</sub>, 400 MHz): δ 7.12–7.06 (m, 4H, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 4.89 (br s, 1H, =CH), 4.85 (br s, 1H, =CH), 3.36 (q, 1H, *J* = 7.1, CH<sub>3</sub>CHAr), 2.33 (s, 3H, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 1.61 (s, 3H, CH<sub>3</sub>C=CH<sub>2</sub>), 1.37 (d, 3H, *J* = 7.1, CH<sub>3</sub>CHAr).

**Structure Determination and Refinement of 7.** Crystals suitable for crystallography were obtained by slow diffusion of ethylcyclohexane into a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound. Data were collected on a Nonius KappaCCD (Mo Kα radiation) and corrected for absorption. The structures were solved by direct methods and refined on *F* for all reflections.

(23) Gujadhur, R. K.; Bates, C. G.; Venkataraman, D. *Org. Lett.* **2001**, *3*, 4315–4317.

(24) Kabalka, G. W.; Wang, L.; Pagni, R. M. *Tetrahedron* **2001**, *57*, 8017–8028.

(25) Al-Hassan, M. I. *J. Organomet. Chem.* **1990**, *395*, 227–229.

(26) (a) Katritzky, A. R.; Tymoshenko, D. O.; Belyakov, S. A. *J. Org. Chem.* **1999**, *64*, 3332–3334. (b) Shi, M.; Xu, B. *J. Org. Chem.* **2002**, *67*, 294–297. (c) Warner, P.; Sutherland, R. *J. Org. Chem.* **1992**, *57*, 6294–6300. (d) Ward, W. J., Jr.; McEwen, W. E. *J. Org. Chem.* **1990**, *55*, 493–500.

(27) Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729–1731.



Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions.

**Crystal Data for Vinylgermatrane (7):** monoclinic, space group  $P2_1/n$  (No. 14)  $a = 6.7543(5)$  Å,  $b = 9.4464(7)$  Å,  $c = 15.430(2)$  Å,  $\beta = 95.152(5)^\circ$ ,  $V = 980.53(12)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 183.2$  K; full matrix least squares refinement of  $F$  (118 parameters) was based on 1863 observed reflections ( $I > 3.00\sigma(I)$ ) and converged to  $R = 0.038$ ,  $R_w = 0.054$ . See Supporting Information for details.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE0092222) for support of this research.

**Supporting Information Available:** An ORTEP drawing of vinyl germatrane, **7**, and a CIF file giving crystallographic data for **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020578C