## ChemComm

Cite this: Chem. Commun., 2011, 47, 7854–7856

## COMMUNICATION

## *Trans*-selective hydrogermylation of alkynes promoted by methyliron and bis(germyl)hydridoiron complexes as a catalyst precursor<sup>†</sup>

Masumi Itazaki, Masahiro Kamitani and Hiroshi Nakazawa\*

Received 30th April 2011, Accepted 24th May 2011 DOI: 10.1039/c1cc12530c

Catalytic *trans*-selective hydrogermylation of terminal and internal alkynes was attained by a methyliron complex,  $CpFe(CO)_2(Me)$ , and a bis(germyl)hydridoiron(IV) complex as a catalyst precursor. The structures of (*Z*)-triphenyl-(2-phenylethenyl)germane and the bis(germyl)hydridoiron(IV) complexes  $CpFe(CO)(H)(GeR_3)_2$  (R = Et, Ph) were confirmed by single crystal X-ray diffraction studies.

Hydrometalation of alkynes is well-established because vinylmetals thus obtained are useful products for the synthetic intermediates in organic chemistry.<sup>1</sup> Especially, organic germanium compounds have attracted considerable attention as alternatives to harmful organic tin compounds.<sup>2</sup> One of the synthetic routes to vinylgermanes is a hydrogermylation reaction of alkynes catalyzed by a transition-metal complex.<sup>3,4</sup> However, regio- and stereo-selectivities of such reactions are not enough. Trans-selective radical hydrogermylation of alkynes has been achieved by Oshima's group,<sup>5a</sup> and Lucarini's group<sup>5b</sup> though only a few examples of the hydrogermylation of alkynes were shown in these methods. In 2005, Gevorgyan and Schwier reported that  $B(C_6F_5)_3$  exhibits catalytic activity for hydrogermylation reaction with trans-addition for simple alkynes and *cis*-addition for propiolate.<sup>6</sup> However the drawback of the catalyst is that it is moisture sensitive and expensive. Very recently Murakami's group reported the trans-selective hydrogermylation of Et<sub>3</sub>GeH with 4-octyne catalyzed by a ruthenium complex.<sup>7</sup> We have reported that a methyliron complex CpFe(CO)<sub>2</sub>(Me) (Cp =  $\eta^5$ -cyclopentadienyl), which is relatively air-stable, is an effective catalyst precursor for the C-CN bond cleavage of organonitriles<sup>8a-c</sup> and for the N-CN bond cleavage of cyanamides.<sup>9</sup> In addition, we found a metathesis reaction between Fe-Me and R<sub>3</sub>Ge-H bonds affording Fe-GeR<sub>3</sub> and Me-H bonds.<sup>10</sup> Creation of catalytic activity of iron complexes instead of rare and expensive metal complexes is important because iron is an inexpensive, a ubiquitous, and an environmentally friendly transition metal. However, the examples of homogeneous iron catalyst for hydrometalation of unsaturated hydrocarbons are quite limited to date.<sup>11</sup> We here report the first *trans*-selective

Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku,

Osaka 558-8585, Japan. E-mail: nakazawa@sci.osaka-cu.ac.jp;

Fax: +81-6-6605-2522; Tel: +81-6-6605-2547

hydrogermylation of alkynes catalyzed by an iron complex. This reaction shows perfect regio- and stereo-selectivity, providing the corresponding (Z)-vinylgermanes.

The mixture of phenylacetylene (0.74 mmol, 82 µL), triethylgermane (0.89 mmol, 144 µL), and CpFe(CO)<sub>2</sub>(Me) (7 mol%, 0.05 mmol, 10 mg) was stirred at 80 °C in a nitrogen atmosphere. After workup, (Z)-triethyl(2-phenylethenyl)-germane 1a was isolated in 78% yield based on phenylacetylene (Table 1, entry 1). The corresponding E-isomer was not observed in the <sup>1</sup>H NMR spectrum. Table 1 presents the results of hydrogermylation of several alkynes. The reactions of phenylacetylene with Ph<sub>3</sub>GeH and "Bu<sub>3</sub>GeH produced 1b and 1c in excellent yields (entries 2 and 3). The yield for the p-F phenylacetylene is similar to that for phenylacetylene (entry 4). The yields of hydrogermylated products slightly decreased when phenylacetylenes having the electron-releasing Me, OMe, NH2 groups in the para position were used (entries 5-7). For alkyl-substituted alkynes, 1-octyne and cyclohexylacetylene reacted smoothly to give the (Z)-vinylgermanes in excellent yields (entries 8 and 9).

 Table 1
 Fe-catalyzed hydrogermylation of alkynes<sup>a</sup>

R <sup>1</sup> 30	GeH +	R <sup>2</sup> ————————————————————————————————————	7 mol% CpFe(Co 80 °C	$\xrightarrow{O)_2(Me)}$ $\xrightarrow{H}$ $\xrightarrow{R^2}$	$= \begin{pmatrix} R^3 \\ & \\ GeR^1_3 \end{pmatrix}$
Entry	$\mathbf{R}^1$	$\mathbb{R}^2$	R <sup>3</sup>	Time/h	$\operatorname{Yield}^{b}(\%)$
1	Et	Ph	Н	18	78 <b>1a</b>
$2^c$	Ph	Ph	Н	6	94 1b
3	<sup>n</sup> Bu	Ph	Н	15	95 1c <sup>d</sup>
4	<sup>n</sup> Bu	Ph-F-p	Н	18	93 1d
5	<sup>n</sup> Bu	Ph-Me-p	Н	15	74 1e
6	<sup>n</sup> Bu	Ph-OMe-p	Н	15	65 1f
7	<sup>n</sup> Bu	$Ph-NH_2-p$	Н	15	64 1g
8	<sup>n</sup> Bu	Hex	Н	15	88 1 <b>h</b>
9	<sup>n</sup> Bu	<sup>c</sup> Hex	Н	15	>99 1i <sup>d</sup>
10	Et	Ph	Me	15	>99 1j
11	<sup>n</sup> Bu	Ph	Me	12	>99 1k
12	Et	Ph	Ph	18	>99 <b>1</b> 1
13	<sup>n</sup> Bu	Ph	Ph	12	>99 1m
14	Et	Pr	Pr	6	43 1n
15	<sup>n</sup> Bu	Pr	Pr	6	55 <b>1o</b>
$16^{c}$	Et	COOMe	COOMe	6	55 1p
$17^{c}$	"Bu	COOMe	COOMe	12	64 <b>1</b> g

<sup>*a*</sup> Reaction conditions: CpFe(CO)<sub>2</sub>(Me) (7 mol%, 0.05 mmol), alkyne (0.74 mmol), hydrogermane (0.89 mmol). <sup>*b*</sup> Isolated yield. <sup>*c*</sup> Using 10 mol% catalyst. <sup>*d*</sup> In this case the *E*-isomer was detected only in a few percent yield.

Department of Chemistry, Graduate School of Science,

<sup>†</sup> Electronic supplementary information (ESI) available. CCDC 815294–815296. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc12530c



**Fig. 1** ORTEP drawing of a Ge1 molecule of **1b** with 50% thermal ellipsoidal plots. Hydrogen atoms except vinyl protons were omitted for simplicity.

Compared with hydrogermylation of terminal alkynes, examples of that of internal alkynes are quite rare.<sup>3i</sup> Our ironcatalyzed system was found to be very effective even for internal alkynes. The reactions of 1-phenyl-1-propyne and diphenylacetylene with Et3GeH and "Bu3GeH proceeded to give the corresponding trans-addition products in quantitative yields (entries 10-13). 4-Octyne and dimethylacetylene-dicarboxylate also could be converted into the desired product in moderate yields (entries 14–17). This is, to the best of our knowledge, the first example of *trans*-addition for the hydrogermylation of the alkyne having the ester group(s) catalyzed by a transition-metal complex. Gevorgyan and Schwier reported that Lewis acid catalyzed hydrogermylation reactions exhibit trans-addition for simple alkynes. However, *cis*-addition products are obtained by using propiolate as an alkyne with the ester group in these reactions.6

The molecular structure of **1b** was determined using single crystal X-ray diffraction (Fig. 1).<sup>‡</sup> The C=C bond apparently possesses a Z configuration. The C=C bond distance for **1b** (1.339(4), 1.335(4) Å) is longer than that for a typical vinyllic  $C_{(sp^2)}=C_{(sp^2)}$  bond (1.299 Å)<sup>12</sup> and the C=C distance found in  $C_2H_4$  (1.3142(3) Å).<sup>13</sup> However, this is quite similar to that previously reported [(Z)- $\beta$ -styrylgermatrane (1.336(4) Å)].<sup>3j</sup>

A proposed catalytic cycle is shown in Scheme 1. A methyl migration in the precursor forms acyl complex CpFe(CO)- $\{C(=O)Me\}$ , which reacts with  $R^{1}_{3}GeH$  to give CpFe(CO)(H)- $\{C(=O)Me\}(GeR^{1}_{3})$ . Reductive elimination of acetoaldehyde produces CpFe(CO)(GeR^{1}\_{3}) (A). The generation of MeCHO was confirmed by the <sup>1</sup>H NMR spectrum. The alkyne coordinates to the iron center of A in an  $\eta^{2}$ -fashion (A  $\rightarrow$  B). This species B undergoes an insertion of the coordinated acetylene into the

Fe-Ge bond ( $\mathbf{B} \rightarrow \mathbf{C}$ ). Then, vinyl isomerization<sup>13</sup> ( $\mathbf{C} \rightarrow \mathbf{E}$ ) takes place through intermediate D or D'. A similar isomerization mechanism has been reported for hydrosilylation of alkynes.<sup>14</sup> Oxidative addition of R<sup>1</sup><sub>3</sub>GeH toward the Fe center gives F. The subsequent reductive elimination of the vinyl and the hydride ligands from F vields the corresponding hydrogermylated product and an intermediate A to complete the catalytic cycle. Although the iron complex A is a very important intermediate in the catalytic cycle, the complex is too reactive to be isolated due to a 16e species. A 16e germyl complex A has a possibility to react with  $R^{1}_{3}$ GeH present in solution to give a bis(germyl)hydridoiron(IV) complex, CpFe(CO)(H)(GeR<sup>1</sup><sub>3</sub>)<sub>2</sub>, through Ge-H oxidative addition. Previously, Akita and co-workers reported that thermal reactions of an alkyl iron complex CpFe(CO)2- $(CH_2CH_2Ph)$  with  $R_3EH$  (E = Si, Sn) afford hydridoiron(IV) complexes having two group 14 element ligands, CpFe(CO)(H)- $(ER_3)_2$ .<sup>15</sup> Therefore, our next efforts were focused on the isolation of a bis(germyl)hydridoiron complex, and we succeeded in isolating bis(germyl)hydridoiron(IV) complex CpFe(CO)(H)- $(GeR_3)_2$  (R = Et: 2, Ph: 3) in the reaction of R<sub>3</sub>GeH with CpFe(CO)<sub>2</sub>(Me) in the 2:1 molar ratio at 60 °C for 12 h (eqn (1)).

$$OC \xrightarrow{Fe}_{C} Me \xrightarrow{2 \text{ eq. } R_3\text{GeH}}_{O} OC, 12 \text{ h} \xrightarrow{R_3\text{Ge}}_{H} C_{O} R = Et: 281\% \text{ Ph: } 367\% \text{ etc.}$$
(1)

The molecular structures of **2** and **3** were determined by single crystal X-ray diffraction studies.<sup>‡</sup> Two independent molecules crystallized in the unsymmetric unit. The ORTEP drawing of a Fe1 molecule is shown in Fig. 2. The Fe center has a typical four-legged piano-stool structure possessing two germyl ligands. The Fe–Ge bond distances (2.4135(6)–2.4237(7) Å for **2** and 2.4102(13)–2.4275(13) Å for **3**) are comparable with previously reported analogous complexes, CpFe(CO)(H)(EEt<sub>3</sub>)(E'Et<sub>3</sub>)



**Fig. 2** ORTEP drawings of Fe1 molecules of (a) **2** and (b) **3** with 50% thermal ellipsoidal plots. Hydrogen atoms except hydrido ligand were omitted for simplicity.



Scheme 1 Proposed catalytic cycle.

 $(E = E' = Si,^{16a} \text{ and } E = Ge, E' = Si, Sn),^{16b} CpFe(CO)(H)-(SnPh_3)_2.^{15a}$  To the best of our knowledge, this is the first report of the X-ray structure of a mononuclear iron complex having two germyl ligands.

We checked the catalytic activity of this bis(germyl)hydrido

Et<sub>3</sub>GeH + Ph 
$$\longrightarrow$$
 H  $\xrightarrow{10 \text{ mol}\% 2}$  70 °C, 6 h  $\xrightarrow{H}$   $\xrightarrow{H}$   $\xrightarrow{H}$   $\xrightarrow{GeEt_3}$  (2)  
1a: 83%

complex 2. Reaction of Et<sub>3</sub>GeH with phenylacetylene in the presence of 10 mol% of 2 at 70 °C yielded the desired (*Z*)-vinylgermane 1a in 83% yield (eqn (2)). It is considered that complex 2 can readily create the active species CpFe(CO)(GeEt<sub>3</sub>) A' by the reductive elimination of Et<sub>3</sub>GeH in solution (eqn (3)).<sup>16b</sup> These results show that the bis(germyl)hydridoiron(iv) complex 2 is the catalyst precursor in our system. Stoichiometric reaction of 2 with phenylacetylene was monitored by the <sup>1</sup>H NMR spectra, but no signal attributable to an intermediate was observed, though the signals due to 1a were observed.



Next, we investigated the hydrogermylation under the similar conditions in entry 1 in Table 1 in the presence of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) as a radical scavenger because *trans*-selective radical hydrogermylation of alkynes with hydrogermane has been reported.<sup>5</sup> The mixture of phenyl-acetylene (1.00 mmol, 106  $\mu$ L), triethylgermane (1.10 mmol, 188 L), TEMPO (0.10 mmol, 16 mg), and CpFe(CO)<sub>2</sub>(Me) (7 mol%, 0.07 mmol, 13 mg) was stirred at 80 °C for 18 h in a nitrogen atmosphere. After workup, (*Z*)-triethyl(2-phenyl-ethenyl)germane **1a** was isolated in 80% yield based on phenylacetylene. The same results were obtained when the reaction took place without TEMPO. These results suggest that our reaction mechanism is not a radical process but an iron-catalyzed process.

In summary, we found effectively *trans*-selective hydrogermylation of alkynes catalyzed by an iron methyl complex. This catalytic system is applicable not only for terminal alkynes but also for internal alkynes and an alkyne having the ester groups as well. The consideration of the catalytic reaction pathway suggests that a germyliron complex is an intermediate.

This work was supported by a Challenging Explorating Research (No. 21655022) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, by Innovation Promotion Program in 2010 from NEDO, and by a Research for Promoting Technological Seeds from JST. M.I. also acknowledges support from the Iketani Science and Technology Foundation (0211033-A).

## Notes and references

‡ Crystal data for **1b**:  $C_{26}H_{22}$ Ge,  $M_w = 407.05$ , colourless, platelet, monoclinic,  $P2_1 \lfloor n$  (No. 14), a = 17.0146(9), b = 8.7374(4), c = 27.2505(15) Å,  $\beta = 93.109(3)^\circ$ , V = 4045.2(4) Å<sup>3</sup>, T = 100(1) K,

Z = 8,  $D_c$  = 1.337 g cm<sup>-3</sup>, 30715 reflections collected, 9118 unique reflections ( $R_{int}$  = 0.062),  $R[I > 2\sigma(I)]$  = 0.0563,  $wR_2$  = 0.0962, GOF = 1.137. CCDC 815294 for **2**: C<sub>18</sub>H<sub>36</sub>OGe<sub>2</sub>Fe,  $M_w$  = 469.50, colourless, prism, triclinic,  $P\overline{1}$  (No. 2), a = 10.4400(12), b = 14.1000(14), c = 16.5000(14) Å,  $\alpha$  = 63.300(5)°,  $\beta$  = 81.670(7)°,  $\gamma$  = 89.180(8)°, V = 2143.4(4) Å<sup>3</sup>, T = 190(2) K, Z = 4,  $D_c$  = 1.455 g cm<sup>-3</sup>, 21116 reflections collected, 9596 unique reflections ( $R_{int}$  = 0.0254),  $R[I > 2\sigma(I)]$  = 0.0477,  $wR_2$  = 0.1009, GOF = 1.000. CCDC 815295 for 3: C4<sub>2</sub>H<sub>36</sub>OGe<sub>2</sub>Fe,  $M_w$  = 757.74, yellow, prism, triclinic,  $P\overline{1}$  (No. 2), a = 12.430(2), c = 19.151(3) Å,  $\alpha$  = 88.061(9)°,  $\beta$  = 87.698(8)°,  $\gamma$  = 74.396(7)°, V = 3431.0(10) Å<sup>3</sup>, T = 200(2) K, Z = 4,  $D_c$  = 1.467 g cm<sup>-3</sup>, 31455 reflections collected, 13765 unique reflections ( $R_{int}$  = 0.0381),  $R[I > 2\sigma(I)]$  = 0.0802,  $wR_2$  = 0.1833, GOF = 1.032. CCDC 815296.

- (a) E. Langkopf and D. Schinzer, *Chem. Rev.*, 1995, **95**, 1375;
   (b) I. P. Beletskaya and V. P. Ananikov, *Chem. Rev.*, 2011, **111**, 1596.
- 2 For example, see: W. N. Aldridge, in *The Organometallic and Coordination Chemistry of Germanium, Tin and Lead*, ed. M. Gielen and P. G. Harrison, Freund: Tel Aviv, Israel, 1978, p. 9.
- 3 (a) R. J. P. Corriu and J. J. E. Moreau, J. Chem. Soc. D, 1971, 812; (b) V. Dirnens, D. I. Barabanov, E. Liepins, L. M. Ignatovich and E. Lukevics, J. Organomet. Chem., 1992, 435, 257; (c) F. Wada, S. Abe, N. Yonemaru, K. Kikukawa and T. Matsuda, Bull. Chem. Soc. Jpn., 1991, 64, 1701; (d) E. Lukevics, D. I. Barabanov and L. M. Ignatovich, Appl. Organomet. Chem., 1991, 5, 379; (e) E. Piers and R. Lemieux, J. Chem. Soc., Perkin Trans. 1, 1995, 3; (f) R. A. Widenhoefer, A. Vadehra and P. K. Cheruvu, Organometallics, 1999, 18, 4614; (g) Y. Ichinose, H. Oda, K. Oshima and K. Utimoto, Bull. Chem. Soc. Jpn., 1987, 60, 3468; (h) M. A. Esteruelas, M. Martín and L. A. Oro, Organometallics, 1999, 18, 2267; (i) H. Kinoshita, T. Nakamura, H. Kakiya, H. Shinokubo, S. Matsubara and K. Oshima, Org. Lett., 2001, 3, 2521; (j) J. W. Faller and R. G. Kultyshev, Organometallics, 2003, 22, 199.
- 4 For a review of hydrogermylation, see: W. Wolfsberger, J. Prakt. Chem., 1992, 334, 453.
- 5 (a) Y. Ichinose, K. Nozaki, K. Wakamatsu, K. Oshima and K. Utimoto, *Tetrahedron Lett.*, 1987, 28, 3709; (b) S. Bernardoni, M. Lucarini, G. F. Pedulli, L. Valgimigli, V. Gevorgyan and C. Chatgilialoglu, *J. Org. Chem.*, 1997, 62, 8009.
- 6 T. Schwier and V. Gevorgyan, Org. Lett., 2005, 7, 5191.
- 7 T. Matsuda, S. Kadowaki, Y. Yamaguchi and M. Murakami, Org. Lett., 2010, 12, 1056.
- 8 (a) H. Nakazawa, K. Kamata and M. Itazaki, *Chem. Commun.*, 2005, 4004; (b) M. Itazaki and H. Nakazawa, *Chem. Lett.*, 2005, 1054; (c) H. Nakazawa, M. Itazaki, K. Kamata and K. Ueda, *Chem.–Asian J.*, 2007, 2, 882.
- 9 K. Fukumoto, T. Oya, M. Itazaki and H. Nakazawa, J. Am. Chem. Soc., 2009, 131, 38.
- 10 M. Itazaki, M. Kamitani, Y. Hashimoto and H. Nakazawa, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2010, 185, 1054.
- 11 For hydrosilylation: (a) S. C. Bart, E. Lobkovsky and P. J. Chirik, J. Am. Chem. Soc., 2004, **126**, 13794; (b) A. M. Archer, M. W. Bouwkamp, M.-P. Cortez, E. Lobkovsky and P. J. Chirik, Organometallics, 2006, **25**, 4269; For hydroboration: (c) J. Y. Wu, B. Moreau and T. Ritter, J. Am. Chem. Soc., 2009, **131**, 12915.
- 12 R. Lide, *Handbook of Chemistry and Physics*, CRC Press, New York, 76th edn, 1995.
- 13 G. J. H. Van Nes and A. Vos, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1979, 35, 2593.
- 14 (a) R. S. Tanke and R. H. Crabtree, J. Am. Chem. Soc., 1990, 112, 7984; (b) C. H. Jun and R. H. Crabtree, J. Organomet. Chem., 1993, 447, 177; (c) I. Ojima, N. Clos, R. J. Donovan and P. Ingallina, Organometallics, 1990, 9, 3127; (d) L. W. Chung, Y.-D. Wu, B. M. Trost and Z. T. Ball, J. Am. Chem. Soc., 2003, 125, 11578; (e) B. M. Trost and Z. T. Ball, J. Am. Chem. Soc., 2005, 127, 17644.
- 15 (a) M. Akita, T. Oku, M. Tanaka and Y. Moro-oka, *Organo-metallics*, 1991, **10**, 3080; (b) M. Akita, T. Oku and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1989, 1790.
- 16 (a) M. Itazaki, K. Ueda and H. Nakazawa, Angew. Chem., Int. Ed., 2009, 48, 3313; M. Itazaki, K. Ueda and H. Nakazawa, Angew. Chem., Int. Ed., 2009, 48, 6938; (b) M. Itazaki, M. Kamitani, K. Ueda and H. Nakazawa, Organometallics, 2009, 28, 3601.