ORGANIC LETTERS

2012
Vol. 14, No. 6
1468–1471

Ir(I)/HCl Catalyzed Head-to-Tail Homocoupling Reactions of Vinylsilanes

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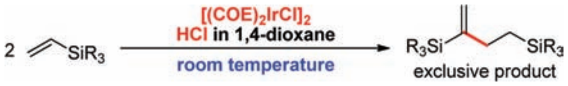
Received January 26, 2012

ABSTRACT



Novel homocoupling reactions of vinylsilanes, catalyzed by a mixture of Ir(I) and HCl, were developed. This process leads to exclusive formation of head-to-tail vinylsilane dimers in high yields at room temperature. Synthetic attributes of transformations of the resulting head-to-tail vinylsilane dimers and polymerization of bis(vinylsilane) were investigated.

Transformations of chemical feedstocks, such as ethylene, styrene, and α-olefins, are of interest in the area of organometallic chemistry.[1] Particularly significant are homocoupling reactions of unsaturated substances, and as a result, these processes have attracted attention because they serve as model systems for oligomerization and polymerization of alkenes and as industrially important processes for the preparation of higher alkenes from simple alkenes.[2] Although a wide variety of homocoupling reactions of unsaturated substances have been reported,[3] only a few exist that involve vinylsilanes.[4,5] These examples show low levels of regio- and chemoselectivity. In the course of recent studies on transition metal/HCl-catalyzed O-silylation reactions of vinylsilanes with alcohols,[6] we observed a new catalytic process in which vinylsilane homocoupling took place under mild conditions (Scheme 1). In this report, we describe an efficient homocoupling reaction of vinylsilane derivatives at ambient temperatures with excellent levels of regioselectivity.

n-Hexyldimethylvinylsilane (**1a**) was chosen as a model substrate to explore various catalytic systems for this homocoupling process (Table 1). Reaction of this substance in the presence of catalyst mixture of [(COE)$_2$IrCl]$_2$ (**2**, COE: cyclooctene) and HCl in 1,4-dioxane (**3**) at room temperature for 30 min led to exclusive formation of the head-to-tail homocoupling product **4a** in 97% yield (determined by GC analysis, Table 1, entry 1).[7] However,

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(1) (a) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610–5618. (b) Pillai, S. M.; Ravindranathan, M.; Sivaram, S. *Chem. Rev.* **1986**, *86*, 353–399. (c) Skupin'ska, J. *Chem. Rev.* **1991**, *91*, 613–648. (d) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74–84. (e) Ho, C.-Y.; Ohmiya, H.; Jamison, T. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 1893–1895.

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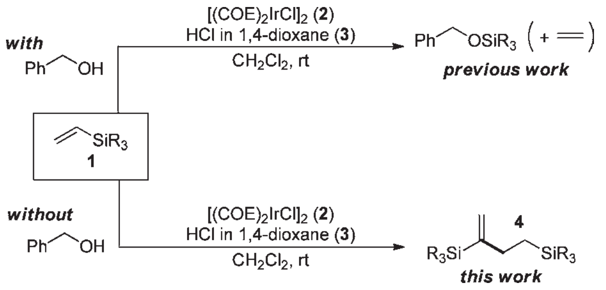
(5) (a) For a reference about desilylative homocoupling reaction, see:Yue, Y.; Yamamoto, H.; Yamane, M. *Synlett* **2009**, 2831–2835. For references about silylative coupling reaction and detailed mechanism, see: (b) Marciniec, B. *Acc. Chem. Res.* **2007**, *40*, 943–952. (c) Marciniec, B.; Walczuk-Guściora, E.; Pietraszuk, C. *Organometallics* **2001**, *20*, 3423–3428. (d) Marciniec, B.; Kownacki, I.; Kubicki, M. *Organometallics* **2002**, *21*, 3263–3270.

(6) Park, J.-W.; Jun, C.-H. *Org. Lett.* **2007**, *9*, 4073–4076.

(7) Other iridium complexes such as [(COD)IrCl]$_2$ (COD: 1,5-cyclooctadiene), (Ph$_3$P)$_2$(CO)IrCl, [Cp*IrCl$_2$]$_2$, and IrCl$_3$·xH$_2$O did not show the catalytic activity of this reaction.

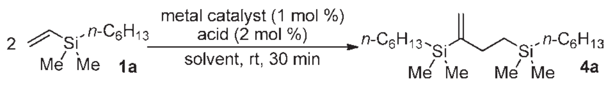
10.1021/ol300203w

Scheme 1. Catalytic Reactions of Vinylsilane **1**



no reaction occurs when either **2** or **3** are not present in the mixture. Interestingly, the reaction promoted by the corresponding rhodium catalytic system $[(COE)_2RhCl]_2/HCl$ is also sluggish (Table 1, entry 3). Hydrogen bromide and trifluoroacetic acid (TFA) can be employed in place of HCl for this process, but formation of **4a** under these conditions takes place more slowly (Table 1, entries 4 and 5). Finally, the homocoupling reaction of **1a** catalyzed by **2**/**3** at room temperature is highly sensitive to solvent. Noncoordinating solvents such as CH_2Cl_2 and toluene are effective for the reaction, while coordinating solvents such as MeCN and DMA are ineffective (Table 1, entries 1, 6–8).

Table 1. Homocoupling Reaction of *n*-Hexyldimethylvinylsilane (**1a**) in the Presence of Various Catalysts



entry	metal catalyst	acid	solvent	yield (%)[a]
1	$[(COE)_2IrCl]_2$ (**2**)	HCl in 1,4-dioxane (**3**)	CH_2Cl_2	97
2	**2**		CH_2Cl_2	0
3	$[(COE)_2RhCl]_2$	**3**	CH_2Cl_2	7
4	**2**	HBr, 48% in H_2O	CH_2Cl_2	82
5	**2**	TFA	CH_2Cl_2	64
6	**2**	**3**	CH_3CN	0
7	**2**	**3**	DMA[b]	0
8	**2**	**3**	toluene	97

[a] GC yield. [b] DMA: *N*,*N*′-dimethylacetamide.

On the basis of the results presented above, we proposed the mechanism displayed in Scheme 2 for the vinylsilane homocoupling reaction.[8] Initially, cyclooctene in the iridium(I) complex **2** undergoes exchange with vinylsilane to generate the corresponding vinylsilane-coordinated iridium(I) complex **5**, which then is protonated by HCl to produce the β-silylethyliridium(III) complex **7** via the intermediacy of hydridoiridium(III) complex **6**.[9] The silylethyl group in **7** undergoes migratory insertion into the vinylsilane ligand through a carbometallation process to give 2,4-disilylbutyliridium(III) complex **8**. β-Hydrogen elimination in **8** then takes place to generate dimer **4** along with regeneration of the hydridoiridium(III) complex **6**.

Scheme 2. Proposed Mechanism for the Homocoupling Process

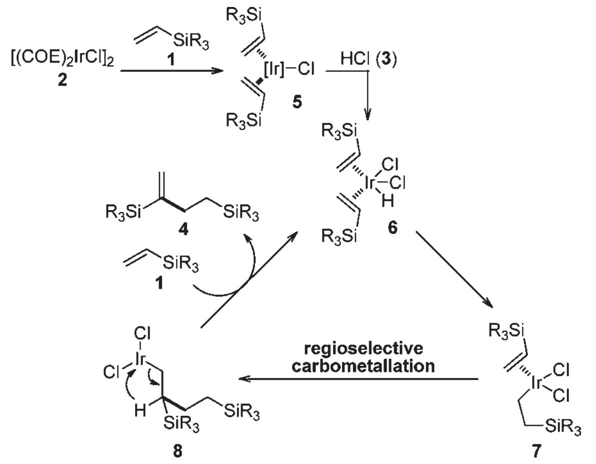
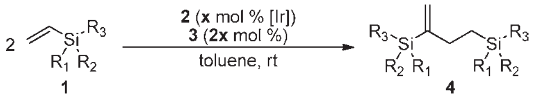
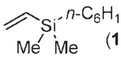
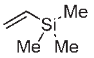
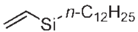
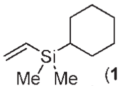
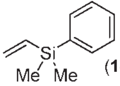
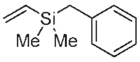
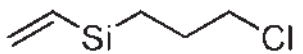
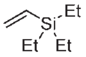
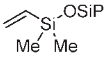


Table 2. Homocoupling Reactions of Vinylsilanes **1** in the Presence of **2** (Ir) and **3** (HCl)



entry	vinylsilane (**1**)	amount of catalyst, x	reaction time (h)	yield (%)[a]
1	 (**1a**)	1	2	**4a**, 97(>99)[b]
2	 (**1b**)	0.5	2	**4b**, 85(>99)[b,c]
3	 (**1c**)	2	2	**4c**, 78(90)[d]
4	 (**1d**)	2	2	**4d**, 91(95)
5	 (**1e**)	2	24	**4e**, 84(85)[e]
6	 (**1f**)	2	2	**4f**, 44(52)
7	 (**1g**)	2	2	**4g**, 74(83)
8	 (**1h**)	2	2	**4h**, 73(80)
9	 (**1i**)	5	2	**4i**, 30

[a] Isolated yield. GC yields are given in parentheses. [b] Reactions were complete within 30 min. [c] CH_2Cl_2 was used as a solvent. [d] Determined by ^1H NMR based on naphthalene as an internal standard. [e] 4% of siloxane was also observed.

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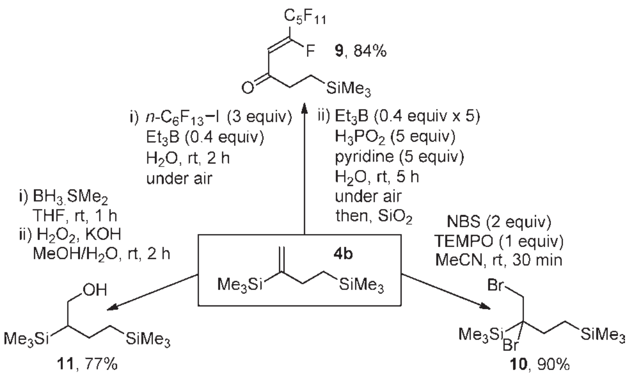
[8] A similar type of heterocoupling reaction mechanism with vinylsilane was explained in ref 4d.

[9] (a) James, B. R.; Morris, R. H. *Can. J. Chem.* **1986**, *64*, 897–903. (b) A heterocoupling reaction with vinylsilane involving hydridoiridium(III) intermediates was reported. See ref 5d.

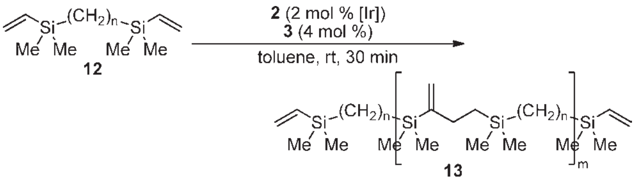
Catalytic homocoupling reactions of vinylsilanes **1** bearing various functional groups were performed to probe the generality of the process (Table 2). In the presence of a mixture of **2** and **3** at room temperature, trimethylvinylsilane (**1b**) is highly reactive, giving the corresponding dimer in > 99% yield (GC), even when 0.5 mol % **2** with 1 mol % **3** are employed (Table 2, entry 2). Vinylsilanes containing common alkyl Si-substituents were found to display similar reactivities (Table 2, entries 2–4, 7, and 8). However, substrates with aromatic substituents on silicon are less reactive than those with aliphatic substituents (Table 2, entries 5–6). The homocoupling reactivity profile indicates that reactivities of vinylsilanes are dependent on steric effects (Table 2, entry 9).

Scheme 3. Synthetic Utilities of Dimer **4b**



To probe the synthetic significance of the homocoupling process, several transformations of the dimer product **4b** were investigated (Scheme 3). Shinokubo and Oshima, et al. have demonstrated earlier that oxidative cleavage of the Si–C bond in vinylsilane moieties occurs to form α-functionalized ketones, indicating that vinylsilanes can be regarded as synthetic equivalents of 2-oxyalkyl radical acceptors.[10] We have observed that dimer **4b** reacts with perfluorohexyl iodide in the presence of BEt_3, followed by treatment with H_3PO_2, pyridine, and BEt_3, to produce the α-perfluorohexyl ketone **9** in a high isolated yield. Interestingly, reaction of **4b** with NBS and an equimolecular amount of TEMPO gives rise to the dibromination product **10**. Hydroboration-oxidation of **4b** takes place to afford the β-silyl alcohol **11** in a 77% yield.

Scheme 4. Polymerization of Bis-vinylsilanes **12**



bis-vinylsilane (12)	polymer (13)	isolated yield of 13 (%)	DP (m)	M_n(PD)
n = 2 (**12a**)	**13a**	86	10.2	2.1 k(1.7)
n = 3 (**12b**)	**13b**	91	15.0	4.0 k(1.8)
n = 5 (**12c**)	**13c**	88	11.9	3.2 k(1.7)

Guided by the results arising in our study of the Ir(I)/HCl-catalyzed homocoupling reactions of vinylsilanes, we attempted to carry out polymerization reactions of bis-vinylsilanes bearing linkers between the two vinylsilyl groups. For this purpose, reaction of 1,2-bis(dimethyl-(vinyl)silyl)ethane (**12a**) was performed using the **2**/**3** co-catalyst system in toluene at room temperature (Scheme 4). This process produced the head-to-tail polymer **13a**. The degree of polymerization was observed to reach 12 within a 30 min period, as determined by a comparison of the intensities of proton resonances in the ^{1}H NMR spectrum associated with the terminal vinyl groups with those of the internal methylene groups. The data obtained by using size-exclusion chromatography were consistent with this assignment (M_n = 2.1 kDa, PD = 1.7). Analyses of the ^{13}C and ^{29}Si NMR spectra of **13a** showed that only head-to-tail type homocoupling had taken place in the polymerization process (Figure 1).

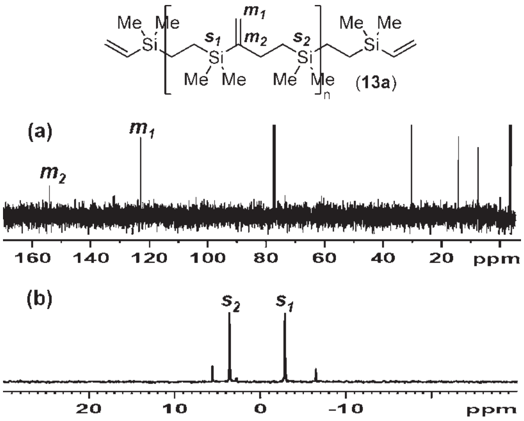


Figure 1. Characteristic peaks of (a) ^{13}C and (b) ^{29}Si NMR spectra of **13a**.

Polymer **13a** (n = 2) was degraded by using perfluorohexyl iodide/BEt_3-promoted iodine atom transfer radical addition followed by atom transfer cleavage with BEt_3/H_3PO_2/pyridine as described above[9] (Scheme 5a). This reaction leads to selective carbon–silicon bond cleavage to give α-perfluoroalkyl ketone **14** and the unstable silanol **15**, which dimerizes to form siloxane **16**. To obtain clear information about the nature of cleavage products **15** and **16**, the product mixture was treated with $BF_3 \cdot OEt_2$ to

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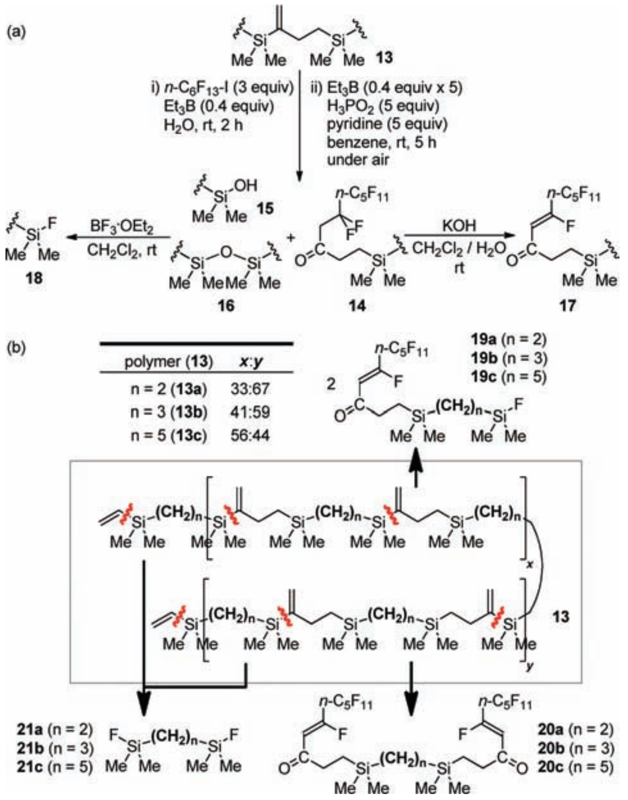
(10) Kondo, J.; Shinokubo, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 825–827.

(11) Compounds **19** were identified by comparison with authentic samples. See the Supporting Information.

(12) The x/y ratio in Scheme 5b was calculated by using the molar ratio of 1/2 (**19a**) and **20a** because the oxidative cleavage reaction in regularly ordered part (x) gives rise to a 2-fold amount of **19a**. Bis(fluorosilane) **21** is disregarded in this calculation because **21** is difficult to isolate because of its high volatility.

(13) It is important to note that this reaction does not occur with dimethyldivinylsilane as the starting material. The reason might be that dimethyldivinylsilane is strongly coordinated to iridium in a bidendate fashion.

Scheme 5. Oxidative Cleavage of Polymers **13**[a]



[a] (a) Overall oxidative cleavage reaction and (b) determination of the *x*/*y* ratios by using oxidative cleavage reactions.

convert the silanol and siloxane groups to fluorosilanes **18**.[11] The oxidative cleavage of **13a** produces three different segments, **19a**, **20a**, and **21a** (Scheme 5b). Fluorosilane **19a** is derived from the regularly ordered part *x*, while diketones **20a** and **21a** are formed from the alternately ordered part *y*. The *x*/*y* ratio was determined to be 33/67 on the basis of the relative amounts of **19a** and **20a** using GC−MS and ^{1}H NMR analysis.[12] Other linked vinylsilanes **12b** (n = 3) and **12c** (n = 5) were transformed to the corresponding polymers **13b** and **13c**, which were produced in respective *x*/*y* ratios of 41/59 and 56/44.[13]

In the studies described above, we have developed a novel homocoupling reaction of vinylsilanes that is promoted by a catalyst mixture comprised of Ir(I) and HCl. This reaction affords exclusive head-to-tail dimers of the vinylsilanes in high yields at room temperature. The synthetic potential of secondary transformations of the head-to-tail dimer derived from vinylsilane was investigated. Further applications of this process to the polymerization of linked bis-vinylsilanes were explored. These reactions generate new head-to-tail polymers, in which the regularity of polymerization is well-defined.

Acknowledgment. This work was supported by a grant from the National Research Foundation of Korea (NRF) (Grant 2011-0016830), WCU (World Class University) program through the Korea Science and Engineering Foundation, the Ministry of Education, Science and Technology (R32-2008-000-10217-0), and CBMH (2011-0001129). J.-W.P. and S.J.P acknowledge fellowships from the BK21 program of the Ministry of Education and Human Resources Development.

Supporting Information Available. Experimental details and ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.