

Communication

Non-Selective Dimerization of Vinyl Silanes by the Putative (Phenanthroline)PdMe Cation to 1,4-Bis(trialkoxysilyl)butenes

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Abstract: Activation of the dialkylpalladium complex (phen)Pd(CH₃)₂ (phen = 1,10-phenanthroline) with B(C₆F₅)₃ affords a competent catalyst for the dimerization of vinyl silanes. All organic products of the catalytic dimerization of trialkoxyvinylsilanes were characterized by in situ NMR spectroscopy and GC–MS. The putative palladium cation was characterized by NMR spectroscopy. Upon activation, the palladium complex generated products in moderate yield (60–70%) and selectivity (~60:40, dimer:disproportionation products).

Keywords: vinyl silane; palladium; coupling; dimerization; phenanthroline

1. Introduction

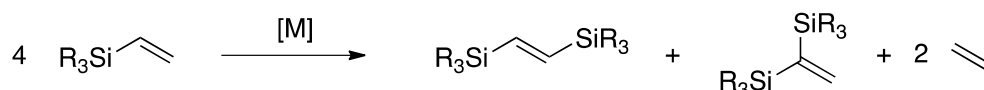
Transformations of chemical feedstocks, small molecules such as ethylene and styrene, are of interest in the area of organometallic chemistry [1–5]. Of particular interest are the products of homocoupling reactions of unsaturated substances; such processes attract attention because they function as model systems for both oligomerization and polymerization reactions of alkenes [6,7]. A wide variety of homocoupling reactions of unsaturated substrates are known [8–20]; however, only a few exist that involve vinyl silanes [21–29].

Trialkoxyvinylsilanes are attractive substrates to target as they are used extensively in materials and surface science [30–38], nanotechnology [39,40] for various applications including modification of surfaces [31,37], formation of sol–gel [36,37], and organogelators [32,34,35], to obtain novel organic–inorganic hybrid materials [33], preparation of nanocomposites [39], and several hybrid [38] and supported catalysts. In most of these applications, the nature of the precursor trialkoxysilane has a profound effect on the properties of the final product [1–20]. Therefore, the availability of a diverse pool of trialkoxysilane precursors would enable incorporation of unprecedented properties to those end products [30–41]. In organic syntheses, trialkoxyvinylsilanes are reaction partners in numerous transformations including Heck reactions [42,43], Friedel–Crafts alkylations [44,45], Diels–Alder reactions [46,47], and 1,3-dipolar additions [48,49].

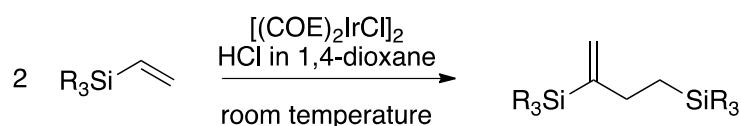
Similarly, bis(trialkoxysilanes) containing unsaturated double bonds would be even more important reagents in building molecular complexity via aforementioned transformations since they may contain two similar or dissimilar alkoxy silane groups [50]. Surprisingly, bis(trialkoxysilanes) containing unsaturated double bonds, such as 1,4-bis(trimethoxysilyl)butenes, are very rarely used in organic syntheses or materials science [50]. Synthetic methods for their preparation are scarce [51,52]. For example, Khvostenko et al. reported the formation of (*E*)-1,4-bis(trimethoxysilyl)-1-butene in 80% yield with 49% conversion of starting trimethoxy(vinyl)silane in the presence of a complex Ti(OBu)₄:Ph₃P:Et₃Al (1:1:6) catalytic system [51]. Keller and Matusiak observed that, in the

presence of alkylidenedinitrosylmolybdenum complexes ($\text{Mo}(\text{NO})_2(\text{CHMe})(\text{OR})_2(\text{AlCl}_2)(\text{EtAlCl}_2)$ ($\text{R} = \text{Et}, \text{O-}i\text{-Pr}$)), self-metathesis and dimerization of trimethyl(vinyl)silane takes place, resulting in formation of 1,2-bis(trimethylsilyl)ethene (yield = 20%) and 1,4-bis(trimethylsilyl)but-2-ene (yield = 30%) as major reaction products, respectively [52]. A number of transition-metal complexes are known to mediate homocoupling of (vinyl)silanes via disproportionation leading to 1,2- or 1,1-diylbis(trialkoxo/alkylsilyl)ethene derivatives (Scheme 1) [53]. We were intrigued by the recent report of Jun and coworkers that a simple iridium catalyst could affect vinyl silane dimerization in a regioselective manner (Scheme 1) [29].

Disproportionation



Regioselective Dimerization

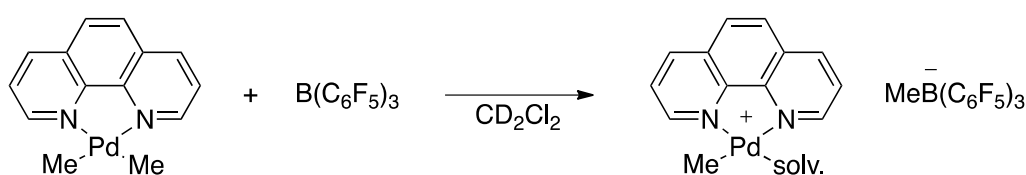


Scheme 1. Homocoupling of vinyl silanes via disproportionation or dimerization.

Pd-complexes are not typically employed in catalyzing the disproportionation of (vinyl)silanes, although they do mediate other reactions, which include dehydrogenative silylation, hydrosilylation, and self- and *co*-polymerizations of various (vinyl)silyl compounds with olefins [54–57]. For example, cationic Pd(II) complexes, $[(\text{phen})\text{Pd}(\text{CH}_3)\text{L}]^+[\text{BAR}'_4]^-$ ($\text{phen} = 1,10\text{-phenanthroline}$; $\text{L} = \text{Et}_2\text{O}, \text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$; $\text{Ar}' = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) are known to catalyze dehydrogenative silylation and hydrosilylation of (vinyl)silanes [54]. Additionally, (α -Diimine)PdMe⁺ complexes (α -diimine = (2,6-*i*Pr₂-C₆H₃)N=C(Me)C(Me)=N(2,6-*i*Pr₂-C₆H₃)) copolymerize (vinylsilyl)ethers with olefins forming OSiR₃-containing polyolefins [55]. Moreover, the aforementioned complexes are able to polymerize (vinyl)ethers [56]. The palladium complex $[(\alpha\text{-diimine})\text{Pd}(\mu\text{-Cl})_2]^+$ dimerizes (vinyl)ethers, including (vinylsilyl)ether, to the corresponding acetals [57]. In this brief communication, we report on the capability of the in situ generated cationic system (Phen)PdMe to dimerize (vinyl)silanes to 1,4-bis(trialkoxysilyl)butenes. Products were characterized using a combination of GC–MS and multi-nuclear NMR analysis.

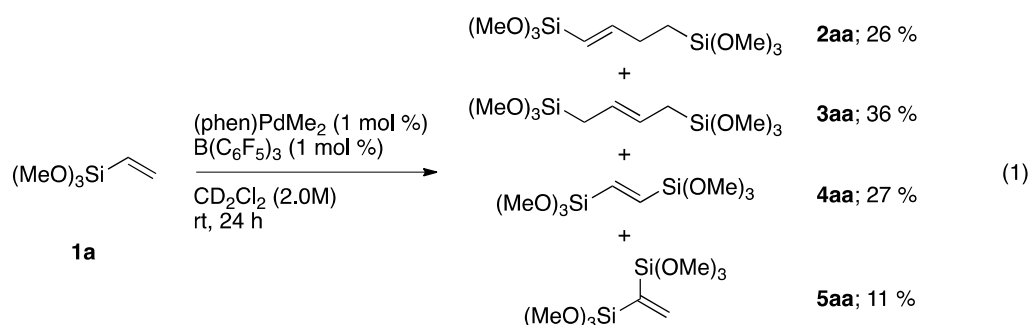
2. Results and Discussion

The cationic system (Phen)PdMe is readily prepared by mixing the known dimethyl precursor, (Phen)PdMe₂ [58], with one equivalent of B(C₆F₅)₃ (Scheme 2). Upon mixing, the newly formed compound is readily soluble in methylene chloride. When carried out in CD₂Cl₂ at room temperature, formation of a new ionic complex is clear from NMR analysis; the ¹¹B NMR of the reaction mixture shows a new sharp peak at –16 ppm, while, in the ¹H NMR of the same mixture, a new singlet shows up at 0.2 ppm. These new NMR signals represent the tetra-coordinated anionic boron species $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ [59,60]. From these observations, the formation of the ionic species $[(\text{Phen})\text{PdMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ is proposed.



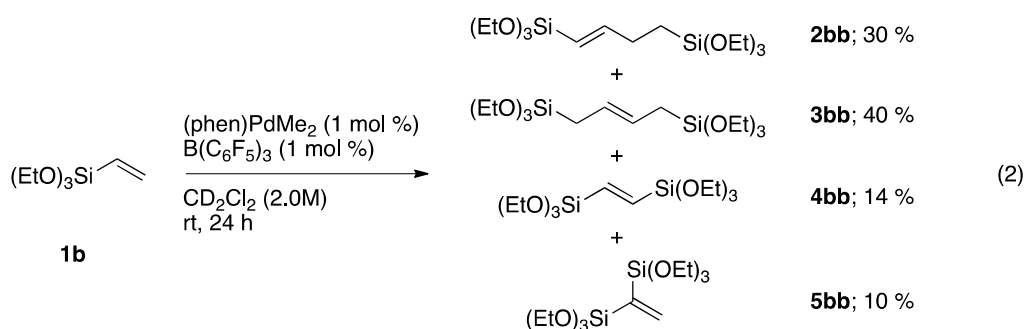
Scheme 2. Synthesis of the putative Pd cation (phen)Pd(Me)(solv.).

Subsequently, we applied this complex as the catalyst (1 mol %) in the homodimerization of trimethoxy(vinyl)silane (**1a**) to furnish 1,4-bis(trimethoxysilyl)butene isomers (**2aa** and **3aa**), 1,2-bis(triethoxy(silane))ethylene (**4aa**), and 1,1'-bis(trimethoxysilylmethyl)ethylene (**5aa**) (Scheme 3). Organic reaction products were identified based upon GC–MS and NMR analysis (see Supplementary Materials). There is moderate selectivity for homodimers **2aa** and **3aa** over disproportionation products **4aa** and **5aa**. Notably, control experiments that employed (Phen)PdMe₂ or B(C₆F₅)₃ alone, under otherwise identical conditions, did not affect the dimerization reaction. We believe this strongly implicates the cationic, coordinatively unsaturated [(Phen)PdMe]⁺ to be responsible for catalytic activity.



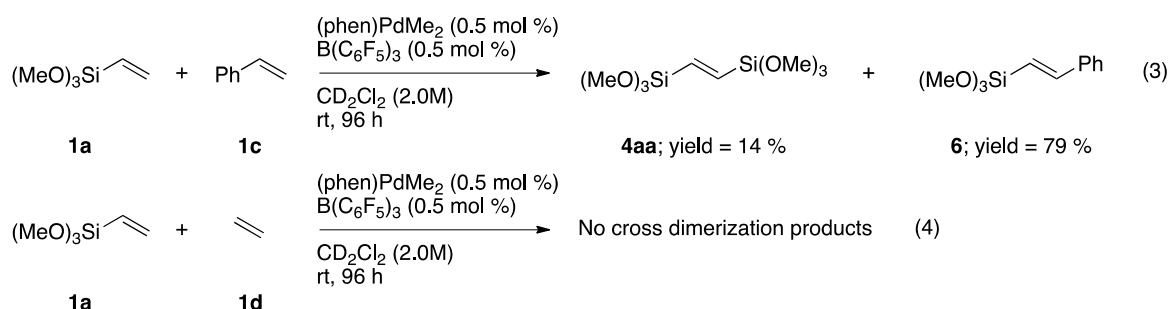
Scheme 3. NMR-scale homodimerization studies of **1a** catalyzed by (phen)Pd(Me)(solv.).

Under these non-optimized reaction conditions triethoxy(vinyl)silane also dimerizes to form the corresponding dimers with 70% combined yield as a mixture of isomers (Scheme 4). Disproportionation of (vinyl)silanes was somewhat minimized in the reaction of the bulkier substrate **1b** compared to **1a**; 1,2- and 1,1-bis(trialkoxysilyl)ethene isomers produced in combined yields of 38% (**4aa** and **5aa**, Scheme 4) and 24% (**4bb** and **5bb**, Scheme 4) with trimethoxy- and triethoxy(vinyl)silane, respectively.

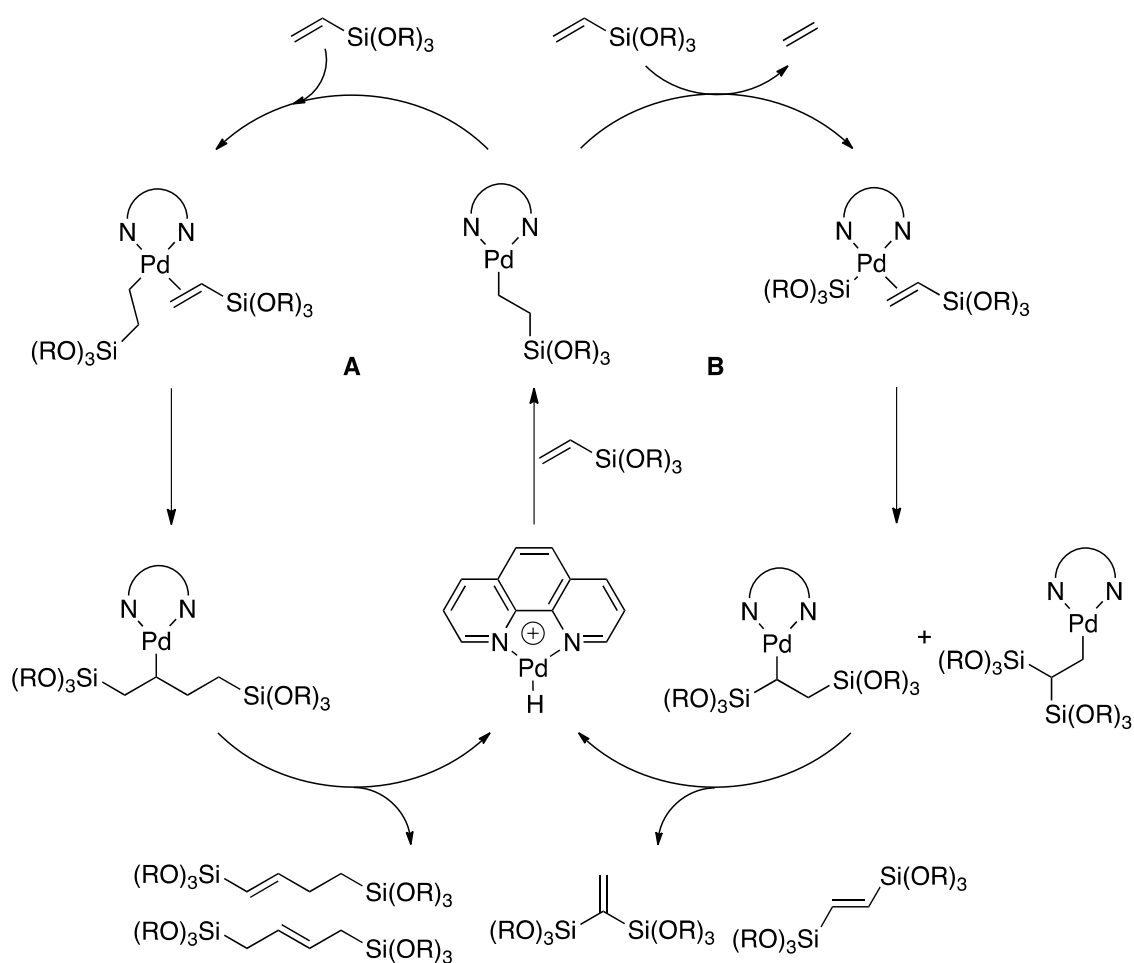


Scheme 4. NMR-scale homodimerization studies of **1b** catalyzed by (phen)Pd(Me)(solv.).

In competing reactions of **1a** with styrene (**1c**), under similar reaction conditions, the cross-dimer product **6** was obtained as the major product after a 96-h reaction period (Scheme 5, top). At 96 h, the conversion of trimethoxy(vinyl)silane was only 76%. Homodimerization and disproportionation of trimethoxy(vinyl)silane also took place, forming corresponding products in trace amounts (as evidenced by GC–MS). In a similar competition experiment between trimethoxy(vinyl)silane and ethylene (**1d**), no cross-dimer product between alkene monomers or homodimerization product of trimethoxy(vinyl)silane was observed (Scheme 5, bottom). Taken together, our results lead us to propose the catalytic cycle shown in Scheme 6. Of particular significance, the work of Elsyby and Johnson, in closely related C–H silylation chemistry employing a nickel catalyst, lends support to our proposed mechanism [61].



Scheme 5. NMR-scale cross-dimerization studies of **1a** with **1c** (top) or **1d** (bottom) catalyzed by (phen)Pd(Me)(solv.).



Scheme 6. Proposed mechanism of dimerization and disproportionation to account for product distribution.

3. Conclusions

In summary, we disclosed a (vinyl)silane dimerization reaction leading to a mixture of 1,4-bis(trimethylsilyl)but-2-ene and 1,4-bis(trimethylsilyl)but-1-ene as major products. This reaction is believed to be mediated by the [(Phen)PdMe]⁺[MeB(C₆F₅)₃]⁻ complex generated in situ at a 1 mol % catalyst loading. The substrate scope of the reaction over various (vinyl)silanes and more detailed mechanistic studies are underway in our laboratories to elaborate on this preliminary communication.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2304-6740/6/4/102/s1>: General remarks; typical procedure for catalytic dimerization reactions; NMR data of catalytic reactions. Reference [54] is cited in the supplementary materials.

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Conflicts of Interest: The authors declare no conflicts of interest.

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