



Efficient synthesis of *E*-1,2-bis(silyl)ethenes via ruthenium-catalyzed homocoupling of vinylsilanes carried out in ionic liquids

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ABSTRACT

A series of ruthenium complexes ($\text{RuCl}_3 \times 3\text{H}_2\text{O}$, $[\text{C}_5\text{H}_5\text{Ru}(\text{CH}_3\text{CN})_3]^+[\text{PF}_6]^-$, $[\text{RuCl}_2(\text{PPh}_3)_3]$, $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$, $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$) immobilized in $[\text{bmim}][\text{Tf}_2\text{N}]$ were tested in homocoupling of vinylsilanes ($\text{H}_2\text{C}=\text{CHSi}(\text{OEt})_3$, $\text{H}_2\text{C}=\text{CHSi}(\text{O}^i\text{Pr})_3$, $\text{H}_2\text{C}=\text{CHSi}(\text{OSiMe}_3)_3$, $\text{H}_2\text{C}=\text{CHSiMe}(\text{OSiMe}_3)_2$, and $\text{H}_2\text{C}=\text{CHSiPh}(\text{OSiMe}_3)_2$) performed in a biphasic system. The highest catalytic activity and selectivity of homocoupling product was observed for $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$. The complex $[\text{RuHCl}(\text{CO})(\text{PCy}_3)_2]$ immobilized in a variety ionic liquids ($[\text{bmim}][\text{PF}_6]$, $[\text{bmim}][\text{BF}_4]$, $[\text{bmim}][\text{Tf}_2\text{N}]$, $[\text{bmim}][\text{TfO}]$, $[\text{bmim}][\text{HSO}_4]$, $[\text{bmim}][\text{Cl}]$, $[\text{trimim}][\text{MeSO}_4]$, $[\text{NBu}_3\text{Me}][\text{MeSO}_4]$, $[\text{PBu}_4][\text{Cl}]$, $[\text{bpy}][\text{PF}_6]$, $[\text{bpy}][\text{BF}_4]$, $[\text{bpy}][\text{Cl}]$) exhibits high catalytic activity in homocoupling of $\text{H}_2\text{C}=\text{CHSiMe}_2\text{Ph}$, $\text{H}_2\text{C}=\text{CHSi}(\text{OEt})_3$ and $\text{H}_2\text{C}=\text{CHSiMe}(\text{OSiMe}_3)_2$ and enables high-yield stereoselective synthesis of the corresponding *E*-1,2-bis(silyl)ethenes. The immobilized complex can be easily recycled up to 12 times in the homocoupling of $\text{H}_2\text{C}=\text{CHSiMe}_2\text{Ph}$ and up to 10 times in the homocoupling of $\text{H}_2\text{C}=\text{CHSiMe}(\text{OSiMe}_3)_2$ without a significant drop in activity and selectivity. Results of a split test indicate that the source of catalytic activity is the catalyst immobilized in ionic liquid phase.

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1. Introduction

Vinyl-substituted silanes and siloxanes constitute a class of unsaturated organosilicon compounds of prospective wide applicability in organic synthesis [1–4]. In particular, Pd-catalyzed cross-coupling reactions (Hiyama coupling) of vinylsilanes with various halide partners seem to be processes of high usefulness in organic synthesis especially as a reliable alternative to Suzuki, Stille and Negishi couplings [5–13]. Bis-silyl olefins, particularly bis(silyl)ethenes, are well-known coupling partners [14–22]. Moreover, *E*-1,2-bis(triethoxysilyl)ethene was found to be a good starting compound for the preparation of mesoporous organosilicas [23–26]. The main catalytic routes to bis(silyl)ethenes involve hydrosilylation of silylacetylenes with hydrosilanes [17,27–30], dehydrogenative silylation of vinylsilanes [31–34], bis-silylation of acetylenes [35–39], homometathesis [40–42] and homocoupling of vinylsilanes [32,40–42]. However, most of these methods led to mixtures of isomers or, as it is in the case of metathesis, they are

limited to a specific group of reactants [42,43]. From among the known methods of synthesis, homocoupling seems to be particularly interesting [44,21]. Silylative coupling occurs via cleavage of the C–H bond of the olefin and the C–Si bond of vinylsilanes, and is catalyzed by complexes containing or generating hydride or silyl ligands. It proceeds according to a mechanism that involves insertion of a vinylsilane molecule into the M–H bond, β -Si transfer to the metal with elimination of ethylene and generation of M–Si species, followed by insertion of a second molecule of vinylsilane into the M–Si bond, and finally a β -H transfer leading to regeneration of the hydride complex and elimination of products [45–47].

This study was aimed at finding systems and conditions that would enable ruthenium catalyzed homocoupling of vinylsilanes with high yield and high selectivity, while using ionic liquids as the reaction media. We present effective procedures for syntheses and isolation of 1,2-bis(silyl)ethenes as well as procedures for catalyst recycling and reusing. There are numerous examples of highly efficient applications of transition metal-catalyzed reactions in ionic liquids (organic salts usually defined as compounds with the melting points below 100 °C) [48–55]. Reactions proceeding in ionic liquids catalyzed by ruthenium hydride complexes (or systems in which hydride complexes are generated) are mainly hydrogenation reactions [48–55] including asymmetric hydrogenation [56].

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