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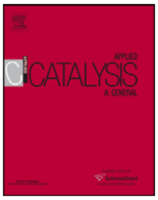

Efficient synthesis of *E*-1,2-bis(silyl)ethenes via ruthenium-catalyzed homocoupling of vinylsilanes carried out in ionic liquids

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ABSTRACT

A series of ruthenium complexes ($RuCl_3 \times 3H_2O$, $[C_5H_5Ru(CH_3CN)_3]^+[PF_6]^-$, $[RuCl_2(PPh_3)_3]$, $[RuHCl(CO)(PPh_3)_3]$, $[RuHCl(CO)(PCy_3)_2]$) immobilized in [bmim][Tf_2N] were tested in homocoupling of vinylsilanes ($H_2C{=}CHSi(OEt)_3$, $H_2C{=}CHSi(O^iPr)_3$, $H_2C{=}CHSi(OSiMe_3)_3$, $H_2C{=}CHSiMe(OSiMe_3)_2$, and $H_2C{=}CHSiPh(OSiMe_3)_2$) performed in a biphasic system. The highest catalytic activity and selectivity of homocoupling product was observed for $[RuHCl(CO)(PCy_3)_2]$. The complex $[RuHCl(CO)(PCy_3)_2]$ immobilized in a variety ionic liquids ([bmim][PF_6], [bmim][BF_4], [bmim][Tf_2N], [bmim][TfO], [bmim][HSO_4], [bmim][Cl], [trimim][$MeSO_4$], [NBu_3Me][$MeSO_4$], [PBu_4][Cl], [bpy][PF_6], [bpy][BF_4], [bpy][Cl]) exhibits high catalytic activity in homocoupling of $H_2C{=}CHSiMe_2Ph$, $H_2C{=}CHSi(OEt)_3$ and $H_2C{=}CHSiMe(OSiMe_3)_2$ 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 $H_2C{=}CHSiMe_2Ph$ and up to 10 times in the homocoupling of $H_2C{=}CHSiMe(OSiMe_3)_2$ 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.

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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The ruthenium-based complexes employed for olefin hydrogenation performed in ionic liquids involve mainly unmodified classical catalyst precursors, e.g. [$RuCl_2(PPh_3)_3$], including a few hydride complexes [48–55]. For instance [$RuHCl(CO)(PCy_3)_2$] was used in hydrogenation of acrylonitrile butadiene rubber [57,58] and a number of ruthenium clusters in hydrogenation of arenes [59–61].

2. Experimental

2.1. Chemicals

Trimethylimidazolium methylsulphate and tributylmethylammonium methylsulphate were purchased from Fluka. Other ionic liquids were obtained from Ionic Liquid Technologies, GmbH. All ionic liquids tested were used as received. $RuCl_3 \times 3H_2O$, $[C_5H_5Ru(CH_3CN)_3]^+[PF_6]^-$, $H_2C{=}CHSi(OEt)_3$, $H_2C{=}CHSi(O^iPr)_3$, $H_2C{=}CHSi(OSiMe_3)_3$, $H_2C{=}CHSiMe(OSiMe_3)_2$ and xylene were purchased from Aldrich. $H_2C{=}CHSiPh(OSiMe_3)_2$ was synthesized according to procedure reported in the literature [62].

2.2. Catalyst preparation

2.2.1. Preparation of catalyst precursors

[$RuCl_2(PPh_3)_3$] [63], [$RuHCl(CO)(PCy_3)_2$] [64] and [$RuHCl(CO)(PPh_3)_3$] [65] were prepared according to the procedures reported in the literature.

2.2.2. Representative procedure of catalyst immobilization

A 2 mL glass vial equipped with a magnetic stirring bar was charged under argon with 0.2 g of ionic liquid and 0.02 g (2.74×10^{-5} mol) of [$RuHCl(CO)(PCy_3)_2$] complex, placed in an oil bath, preheated to 130 °C and stirred for 15 min.

2.3. Catalyst characterization

^1H and ^{13}C NMR spectra were recorded on a Varian VNMR-S at 400 and 100 MHz, respectively, or a Varian Gemini at 300 and 75 MHz. IR spectra were recorded on an FTIR spectrometer Bruker Tensor 27 equipped with SPECAC Golden Gate diamond ATR accessory. In situ FT-IR measurements were performed on a Mettler Toledo ReactIR 15 instrument equipped with a DS 9.5 mm AgX DiComp Fiber Probe (1.5 m) with a diamond sensor and a Mercury Cadmium Telluride (MCT) detector. For all the spectra 256 scans were recorded with the resolution of 1 cm^{-1}. HRMS (ESI) was measured on a Waters Synapt GS-2 (acetonitrile was used as a solvent). Elemental analysis was carried out on a Vario EL III analyzer (Elementar GmbH).

2.4. Catalytic tests

2.4.1. General procedure

All manipulations were carried out under argon using standard Schlenk techniques. Mixture of vinylsilane (1.37×10^{-3} mol) and 0.05 mL of dodecane (internal standard) was added by a syringe to a 2 mL glass vial containing (2.74×10^{-5} mol) of ruthenium complex immobilized in 0.2 g of ionic liquid and preheated to 130 °C. The mixture was vigorously stirred at 130 °C for 5 h. Reactions were monitored by gas chromatography and GC–MS. GC–MS analyses were carried out on a Bruker 450-GC gas chromatograph (DB-5, 30 m capillary column) equipped with a Bruker 320-MS Triple Quad mass spectrometer. GC analyses were performed on a Varian CP-3800 or an HP 5890 Series II gas chromatographs (DB-1, 0.53 mm, 30 m megabore column) equipped with TCD detectors. Ethylene was identified by using HP 5890 Series II gas chromatograph equipped with a packed column (6 ft × 1/8 in., Porapak Q) and a FID.

2.4.2. Representative procedure for recycling experiment

A 2 mL glass vial equipped with a magnetic stirring bar was charged under argon with 0.2 g of ionic liquid and 0.02 g (2.74×10^{-5} mol) of [$RuHCl(CO)(PCy_3)_2$] complex, placed in an oil bath, preheated to 130 °C and stirred for 15 min. Then the mixture of 0.4 mL (1.37×10^{-3} mol) of methylbis(trimethylsilyloxy)vinylsilane and 0.05 mL of dodecane (internal standard) was added under argon. The mixture was vigorously stirred and heated for 5 h. After that time, conversion of the substrate was determined by GC analysis. After each reaction run, the upper layer was decanted under argon and ionic liquid phase was reused in a subsequent run.

2.4.3. Split test (a test for heterogeneously catalyzed reaction)

A 2 mL glass vial containing catalyst [$RuHCl(CO)(PCy_3)_2$] immobilized in **IL 3** was charged under argon with the mixture of 0.4 mL (1.37×10^{-3} mol) of methylbis(trimethylsilyloxy)vinylsilane and 0.05 mL of internal standard (dodecane). The reaction mixture was heated and stirred for 1 h. Then, the conversion of vinylsilane was measured by GC and half of the volume of the upper layer (0.15 mL) was transferred under argon to another vial. Both vials were placed in the same oil bath and heating was continued for additional 4 h. Conversion of the substrate was determined by GC analysis.

3. Results and discussion

3.1. Catalytic tests

While searching for the conditions for effective coupling of vinylsilanes in ionic liquids a number of catalytic tests was carried out with the use of (i) vinylsilanes differing in stereoelectronic properties of silyl group, (ii) several complexes and salts of ruthenium, and (iii) several commercially available ionic liquids. Vinylsilanes employed in the study were $H_2C{=}CHSiMe_2Ph$ (**1a**), $H_2C{=}CHSi(OEt)_3$ (**1b**), $H_2C{=}CHSi(O^iPr)_3$ (**1c**), $H_2C{=}CHSi(OSiMe_3)_3$ (**1d**), $H_2C{=}CHSiMe(OSiMe_3)_2$ (**1e**), and $H_2C{=}CHSiPh(OSiMe_3)_2$ (**1f**). Reactions were conducted in the presence of ruthenium chloride $RuCl_3 \times 3H_2O$ (**2**), tris(acetonitrile)cyclopentadienylruthenium (II) hexafluorophosphate $[C_5H_5Ru(CH_3CN)_3]^+[PF_6]^-$ (**3**), selected ruthenium complexes reported to be active for homocoupling of vinylsilanes and complexes applied to hydrogenation of olefins in ionic liquids, i.e., [$RuCl_2(PPh_3)_3$] (**4**), [$RuHCl(CO)(PPh_3)_3$] (**5**) and [$RuHCl(CO)(PCy_3)_2$] (**6**). The catalysts were immobilized using several imidazolium, pyridinium, phosphonium and ammonium ionic liquids (Fig. 1).

At the first stage of the study, a number of tests was carried out in order to find the most active and the most selective catalysts as well as ionic liquids enabling effective conduction of reactions under biphasic conditions. Salts and complexes of ruthenium at the used concentrations were fully soluble in ionic liquids tested. For each test reaction, the components of the reaction system formed liquid–liquid biphasic systems. Under the reaction conditions (typically 130 °C), the substrates and products were partially miscible with the ionic liquids, whereas they were practically immiscible at room temperature. When vinylsilane (in a mixture with internal standard) was added under argon to preheated solution of a catalyst **3**, **5** or **6** immobilized in ionic liquid phase, a slow evolution of a gas (identified by GC as ethylene) was discerned. Monitoring of the reaction by gas chromatography and GC–MS revealed gradual formation of two products, one of which is formed in a considerably greater quantity. Mass spectrum points to the formation of two bis(silyl)ethene isomers. The analysis of the post-reaction mixture by ^1H and ^{13}C NMR indicates formation of *E*-1,2-bis(silyl)ethenes in a mixture with traces of 1,1-bis(silyl)ethene which leads to a conclusion that vinylsilane homocoupling proceeds in the reaction

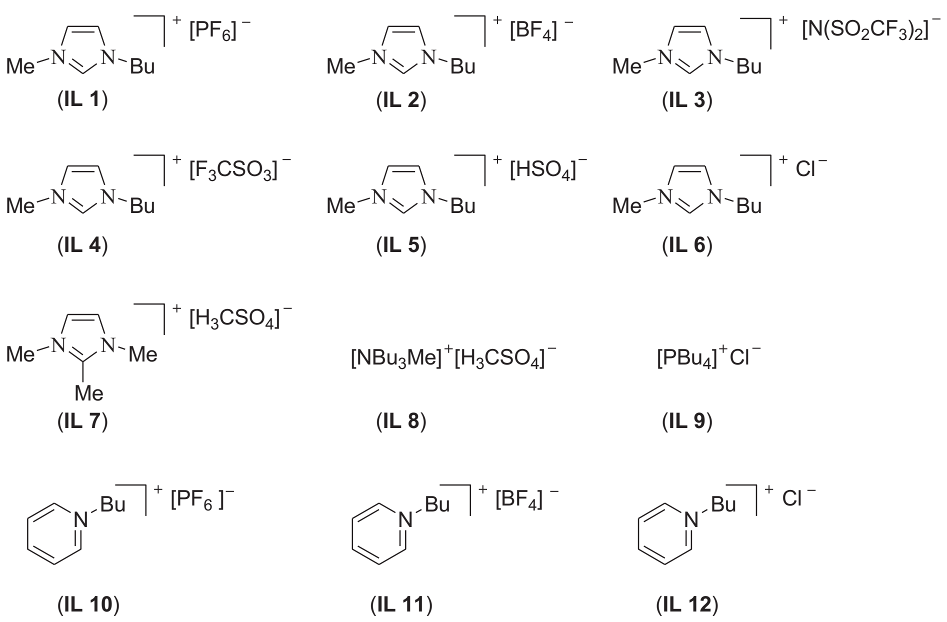
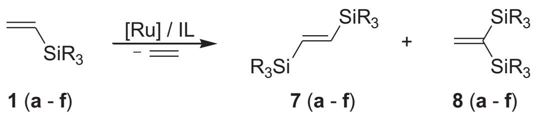


Fig. 1. Ionic liquids used for immobilization of catalysts.

system (Eq. (1)). Identification of both isomers was performed by comparing ^{1}H and ^{13}C NMR spectra with the literature data.



SiR_3 = $SiMe_2Ph$ (**a**), $Si(OEt)_3$ (**b**), $Si(O^iPr)_3$ (**c**), $Si(OSiMe_3)_3$ (**d**), $SiMe(OSiMe_3)_2$ (**e**), $SiPh(OSiMe_3)_2$ (**f**) (1)

Homocoupling of vinylsilanes

Comparative investigation performed for catalysts (**2**–**6**) immobilized in selected ionic liquid (**IL 3**) enabled identification of the most efficient catalytic systems under the reaction conditions tested. Selected results were collected in Table 1.

The highest catalytic activity was observed in the case of the hydride complex $[RuHCl(CO)(PCy_3)_2]$ (**6**) The above complex makes it possible to obtain almost quantitative conversion of all vinylsilanes tested and to form *E*-1,2-bis(silyl)ethene with a very high selectivity. High yields, but lower selectivities, were obtained in the presence of $[RuHCl(CO)(PPh_3)_3]$ (**5**). Other complexes showed both poor activity and selectivity. To perform further optimization of catalytic system, the activity of the complex $[RuHCl(CO)(PCy_3)_2]$ (**6**) immobilized in a large variety of ionic liquids was investigated. Three vinylsilanes, differing in the character of substituents at silicon, were chosen for homocoupling tests. For the sake of comparison, tests were also performed in a homogeneous system using a small volume of xylene (comparable with the volume of ionic liquid used) as a catalyst solvent. The results were summarized in Fig. 2a–c.

On the basis of experiments performed, it has been established that the reaction in the presence of catalyst **6** proceeds effectively while maintaining oxygen-free atmosphere. Moreover, since the reaction proceeded in each case in a biphasic system and phases were only partially miscible at temperatures applied, it was necessary to stir the reaction mixture vigorously. Inadequate stirring or the lack of stirring can lead to considerably lower yields and/or the irreproducibility of results.

The results obtained while using most of ionic liquids were comparable to those observed in homogeneous systems. However, in the case of homocoupling of triethoxyvinylsilane (**1b**) the reaction performed in ionic liquid led to higher selectivities. The isomer ratio [**7b**]:[**8b**] for the reaction performed in xylene was equal to 18:1, while for the reactions proceeding in the presence of ionic liquid-immobilized catalyst the isomer ratio ranged between 21:1 and 45:1. In the presence of ionic liquids **IL 6** and **IL 8** the reaction proceeds fully selectively and exclusive formation **7b** was observed.

Table 1
Catalytic activity of ruthenium complexes (**2**–**6**) immobilized in **IL 3** in homocoupling of vinylsilanes (**1a**–**f**).

Vinylsilane SiR_3=	Catalyst	Conv. of **1** [%]	Yield of **7** [%]	Yield of **8** [%]	By-products [%]
$SiMe_2Ph$	**2**	25 (51)[a]	Traces	–	30[b]
$SiMe_2Ph$	**3**	15 (19)[a]	12 (15)[a]	2 (3)[a]	–
$SiMe_2Ph$	**4**	13 (15)[a]	Traces	–	8[b]
$SiMe_2Ph$	**5**	86 (93)[a]	69 (74)[a]	14 (15)[a]	–
$SiMe_2Ph$	**6**	97	95	2	–
$Si(OEt)_3$	**6**	96	92	5	–
$Si(O^iPr)_3$	**6**	93	92	1	–
$Si(OSiMe_3)_3$	**6**	90	90	0	–
$SiMe(OSiMe_3)_2$	**6**	96	92	5	–
$SiPh(OSiMe_3)_2$	**6**	90	87	3	–

Reaction conditions: $[RuHCl(CO)(PCy_3)_2]$ (2.74×10^{-5} mol), ionic liquid (0.2 g), vinylsilane (1.37×10^{-3} mol), dodecane (internal standard) (0.05 mL), 130 °C, 5 h, vigorous stirring, argon.

[a] 24 h.

[b] $PhMe_2SiOSiMe_2Ph$ and traces of higher siloxanes.

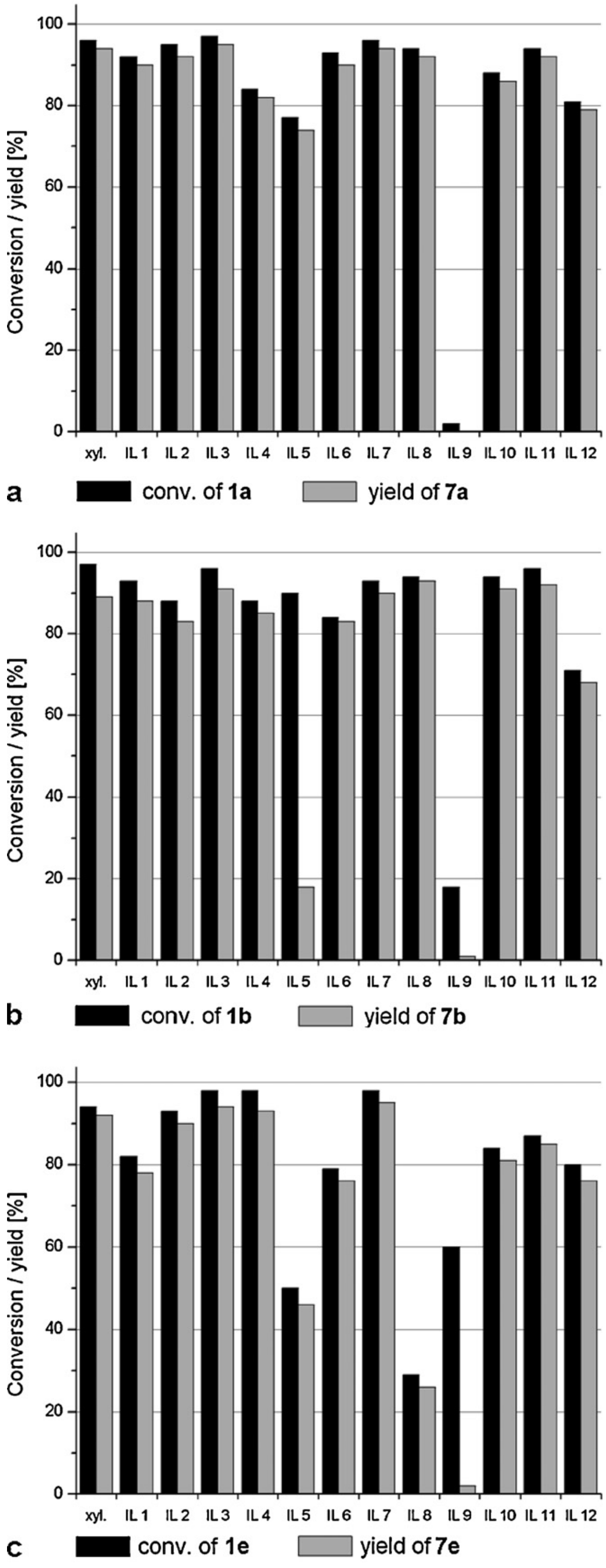


Fig. 2. Conversion of vinylsilane and yields of products 7 in homocoupling of $H_2C{=}CHSiMe_2Ph$ (**1a**) (Fig. 2a), $H_2C{=}CHSi(OEt)_3$ (**1b**) (Fig. 2b) and $H_2C{=}CHSiMe(OSiMe_3)_2$ (**1e**) (Fig. 2c) catalyzed by complex **6** dissolved in xylene or immobilized in ionic liquids **IL 1**–**IL 12**. Reaction conditions: $[RuHCl(CO)(PCy_3)_2]$ (2.74×10^{-5} mol), IL (0.2 g), vinylsilane (1.37×10^{-3} mol), dodecane (internal standard) (0.05 mL), 130 °C, 5 h, argon.

The literature on ionic liquids points to essential importance of their purity as it substantially affects the course of catalytic reactions [54,66–68]. Ionic liquids used in our study were not subjected to additional purification. It has been found that the presence from 100 ppm to 1% of water (which is the limit of water content declared by the manufacturer) does not affect the stability of ruthenium hydride complex. Ionic liquids **IL 1**–**IL 8** and **IL 10**–**IL 12** used for immobilization of hydride complex **6** make it possible to obtain the product of phenyldimethylvinylsilane homocoupling with high yields and high selectivities.

Homocoupling of silane **1a** proceeds with exclusive formation of bis(silyl)ethenes. No other organosilicon compounds were detected. It was therefore concluded that the Si—Me i Si—Ph bonds are stable in the presence of catalyst **6** and all ionic liquid tested. In most of ionic liquids used, homocoupling of $H_2C{=}CHSi(OEt)_3$ (**1b**) and $H_2C{=}CHSiMe(OSiMe_3)_2$ (**1e**) proceeded stereoselectively and lead to high yields of expected products. However, the vinylsilanes containing Si—O—C (**1b**,**c**) or Si—O—Si (**1d**,**e**,**f**) bonds in the presence of ionic liquid **IL 9** and silanes **1b** and **1c** in the presence of ionic liquid **IL 5** are unstable under the reaction conditions (130 °C) and undergo undesirable processes of condensation with the formation of di-, tri- and traces of higher siloxanes. The effectiveness of condensation depends on water content in ionic liquid. Moreover, $[PBu_4]Cl$ (**IL 9**) can play the role of phase transfer catalyst in condensation of alkoxysilanes [69] and very likely also in condensation of vinylsiloxane **1e**, as this side-reaction does not occur in the absence of phosphonium salt. When the ionic liquid **IL 9** was subjected to drying by heating at 80 °C under dynamic vacuum (1 mmHg) for 72 h, the yield of condensation of **1e** (conditions as indicated in Fig. 2c) considerably decreased from 60% (without drying) to 21%.

To understand the differences in the effectiveness of homocoupling in the systems containing different ionic liquids, the process of immobilization of complex **6** in selected ionic liquids has been investigated. The experiments were carried out using IR spectroscopy, because the complex contains carbonyl ligand that is characterized by a high intensity of $\nu_{C{=}O}$ stretching vibrations as well as by the known dependence of the frequency of the carbonyl peaks on the electron density on the metal [70]. We expected that putative changes in the coordination sphere of catalyst **6** during its immobilization would result in a frequency shift of the carbonyl peak. The investigation was conducted using ionic liquids that enabled effective performance of the process (**IL 3**, **IL 7**) and ionic liquid that permitted obtaining moderate yields (e.g., **IL 11**). Moreover, ionic liquid **IL 9** was selected, in the presence of which no reaction products were formed. The IR (ATR) spectra of complex **6**, complex **6** immobilized in 0.2 g of selected ionic liquid and complex **6** immobilized in the mentioned ionic liquid and heated at 130 °C for 3 h were recorded at room temperature in the absence of vinylsilane. The obtained data indicate no changes in the band at 1904 cm^{-1} assigned to $\nu_{(C{=}O)}$ in the complex **6** and complex **6** immobilized in **IL 3** (Fig. 3), **IL 7** and **IL 11** (supplementary data). The absence of a shift in the band at 1904 cm^{-1} observed for the complex **6** immobilized in ionic liquids **IL 3**, **IL 7** and **IL 11** indicates that the coordination sphere did not undergo modification. Therefore, it can be concluded that ionic liquids play only the role of catalyst solvents in the systems studied.

Measurements carried out using hydride complex (**6**) immobilized in **IL 9** revealed 51% conversion of $[RuHCl(CO)(PCy_3)_2]$ ($\nu_{(C{=}O)} = 1904\ cm^{-1}$) and the appearance of a new complex characterized by the absorption band at $\nu_{(C{=}O)} = 1935\ cm^{-1}$ (Fig. 4) which suggested the formation of $[RuCl_2(CO)(PCy_3)_2]$ (**9**) [71].

The immobilization of complex **6** in **IL 9** was also studied in similar equimolar experiment performed in DMF and monitored by ^1H and ^{31}P NMR. The disappearance of signals at $\delta = -20.76$ ppm (^1H NMR) and $\delta = 40.4$ ppm (^{31}P NMR) was observed, which indicates a complete decomposition of **6** after 1 h heating at 130 °C in the

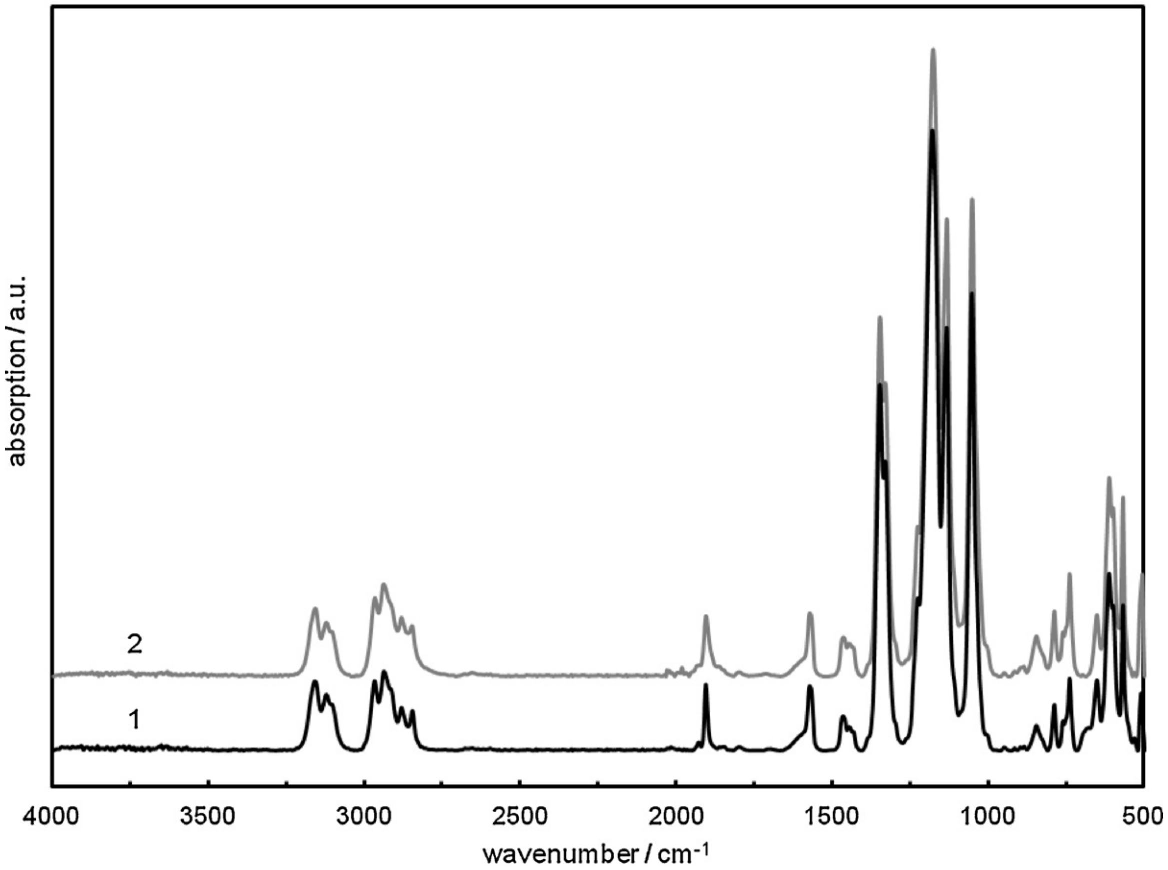


Fig. 3. IR (ATR) spectra. (1) Complex **6** immobilized in **IL 3**; (2) Complex **6** immobilized in **IL 3** and heated at 130 °C for 3 h. Conditions: [RuHCl(CO)(PCy$_3$)$_2$] (2.74 × 10^{-5} mol), **IL 3** (0.2 g), 130 °C, argon.

presence of 20 eq. of **IL 9**. The formation of complex **9** was confirmed by the appearance of a new signal at $\delta = 37.9$ ppm in the ^{31}P NMR spectrum. The above experiments clearly explain why no effective homocoupling of any reactant used was observed in the presence of the catalyst **6** immobilized in **IL 9**.

A significant factor capable of causing differences in the effectiveness of homocoupling carried out in the biphasic system is the solubility of vinylsilanes in ionic liquid. Therefore, the solubility of vinylsilanes **1a 1b** and **1e** in the selected ionic liquids was investigated. Solubility measurement was performed for **IL 3** and **IL 7** for which the process proceeded effectively as well for **IL 5** and **IL 8** for which differences in the process effectiveness were observed depending on the reactant employed. The solubility was measured according to the method described in the literature [66]. The obtained results are presented in Fig. 5.

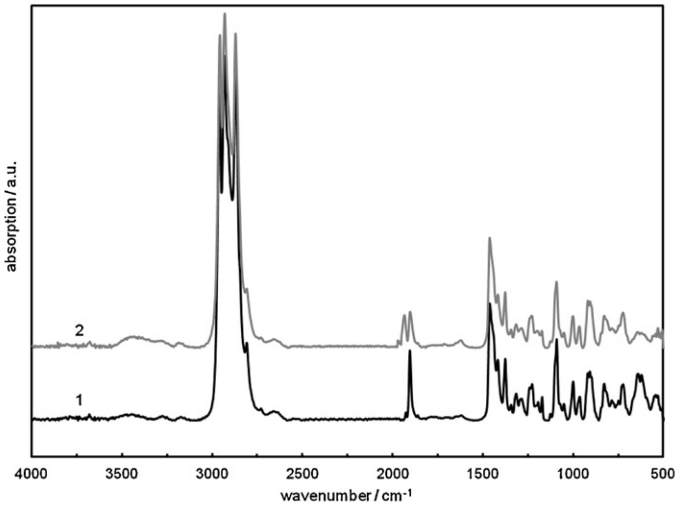


Fig. 4. IR (ATR) spectra. (1) Complex **6** immobilized in **IL 9**; (2) complex **6** immobilized in **IL 9** and heated at 130 °C for 3 h. Conditions: [RuHCl(CO)(PCy$_3$)$_2$] (2.74 × 10^{-5} mol), **IL 9** (0.2 g), 130 °C, argon.

Results of the measurements point to considerable differences in the solubility of particular vinylsilanes in different ionic liquids and in the solubilities of different vinylsilanes in a particular ionic liquid. Moreover, they show that solubility is not the only factor

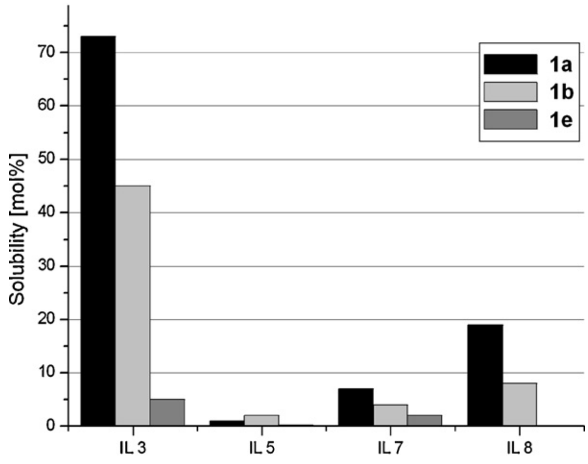


Fig. 5. Solubility of **1a**, **1b** and **1e** in **IL 3**, **IL 5**, **IL 7** and **IL 8** at 130 °C.

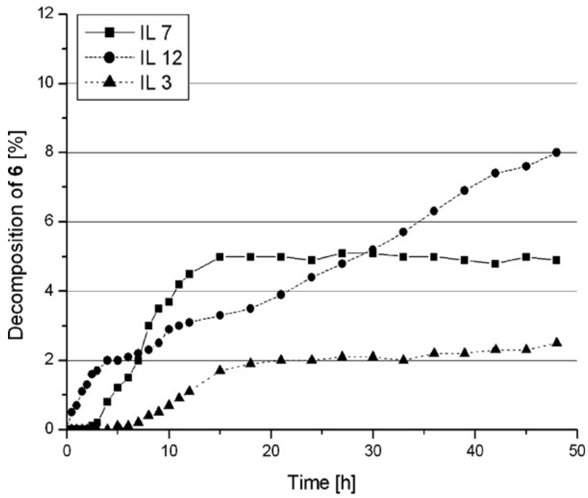


Fig. 6. Stability of complex **6** immobilized in **IL 3**, **IL 7** and **IL 12** under heating at 130 °C.

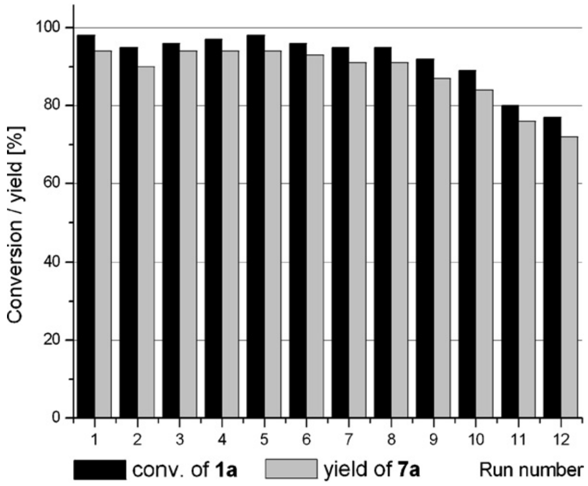


Fig. 7. Homocoupling of phenyldimethylvinylsilane (**1a**). Recycling of **6** immobilized in **IL 3**. Conditions: [RuHCl(CO)(PCy$_3$)$_2$] (2.74 × 10^{-5} mol), **IL 3** (0.2 g), 1a (1.37 × 10^{-3} mol), dodecane (internal standard) (0.05 mL), 130 °C, 5 h, argon.

that decides on the process effectiveness. Despite significant differences in the solubility of vinylsilanes in ionic liquids **IL 3** and **IL 7**, the process proceeds effectively in the presence of both ionic liquids (see Fig. 2a–c). On the other hand, a very poor solubility of vinylsilane **1e** in **IL 5** (0.2 mol%) and in **IL 8** (0.1 mol%) can contribute to the low effectiveness of homocoupling of vinylsilane **1e** in the presence of the above ionic liquids.

To learn more on the stability of catalytic systems used, the decrease in the catalyst concentration under the reaction conditions (however, in absence of vinylsilanes) was determined for selected systems. The catalyst concentration was monitored by observing changes in the intensity of $\nu_{C=O}$ band in IR spectra. Results shown in Fig. 6 prove a high stability of complex **6** immobilized in ionic liquids **IL 3**, **IL 7** and **IL 12**. A particularly high stability was observed in the presence of **IL 3**.

3.2. *Recyclability of the immobilized catalyst*

Representative studies on stability of the most active catalytic system (complex **6** immobilized in **IL 3** and **IL 7**) were performed in a recycling experiment involving the homocoupling of dimethylphenylvinylsilane. Conversions obtained after 5 h of the reaction are given in Fig. 7. The values of conversion decrease slightly in subsequent reaction runs. Conversions obtained after 5 h of the reaction show that the catalyst **6** can be effectively recycled up to 12 times without a substantial decrease in the yield of the reaction product *E*-1,2-bis(silyl)ethene. The experiment demonstrated effective recycling of [RuHCl(CO)(PCy$_3$)$_2$] and the total TON was 554. For catalyst **6** immobilized in **IL 7**, the total TON was 531 (see supplementary data). For the sake of comparison, the homocoupling of **1a** was carried out under homogeneous conditions (in xylene) using 0.17 mol% of complex **6** (i.e. at the concentration 12 times lower than that used in the recycling test). After 24 h *E*-1,2-bis(dimethylphenylsilyl)ethene (**7a**) was observed as the exclusive product with the yield of 65%, that gives TON equal to 390. Recycling experiment carried out for the homocoupling of methylbis(trimethylsiloxy)vinylsilane demonstrated effective recycling of the immobilized catalyst up to 10 times and TON reaching 456 for **IL 3** (Fig. 8) and 435 for **IL 7** (see supplementary data).

It is important and worth of emphasizing that in the case of both reactions for which reproducibility was investigated, i.e. homocoupling of phenyldimethylvinylsilane and homocoupling of methylbis(trimethylsiloxy)vinylsilane, the isomer ratio was similar in subsequent repetitions, which means that that the catalyst selectivity did not decrease with time on stream.

To evaluate leaching of the catalyst, post-reaction mixtures were collected and total content of the metal leached from ionic liquid phase after 10 reaction runs was determined by ICP-MS. The obtained results show that percentages of ruthenium remaining in the ionic liquid phase after 10 runs of homocoupling of **1a** and **1e** were 87% and 82%, respectively. Therefore, both catalyst leaching and partial deactivation of the catalyst contribute to the decrease in the yield.

3.3. *Split test*

In order to make sure that the catalytic activity originates from the immobilized catalyst and not from some active species leached from the ionic liquid, we performed a split test [72]. The reaction chosen was homocoupling of methylbis(trimethylsiloxy)vinylsilane in the presence of **6** immobilized in **IL 3**. One hour after the start of the reaction, half of the upper layer was decanted under argon (at the conversion of 58%) and transferred to another reactor. Both reactions were monitored for 5 h by GC. After 5 h of the reaction, the conversion in the presence of

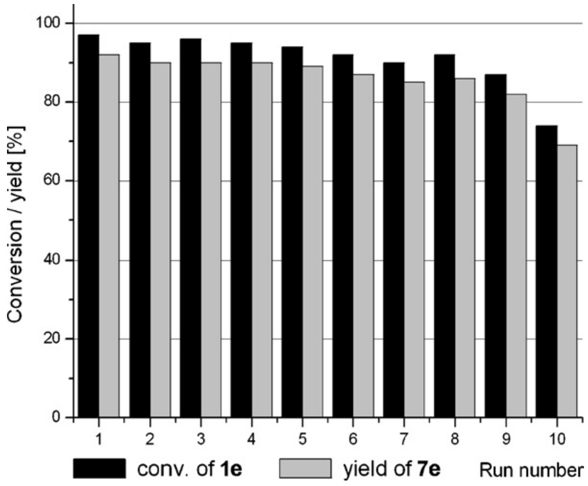


Fig. 8. Homocoupling of methylbis(trimethylsilyloxy)vinylsilane (**1e**). Recycling of **6** immobilized in **IL 3**. Conditions: [RuHCl(CO)(PCy$_3$)$_2$] (2.74 × 10^{-5} mol), **IL 3** (0.2 g), **1e** (1.37 × 10^{-3} mol), of dodecane (internal standard) (0.05 mL), 130 °C, 5 h, argon.

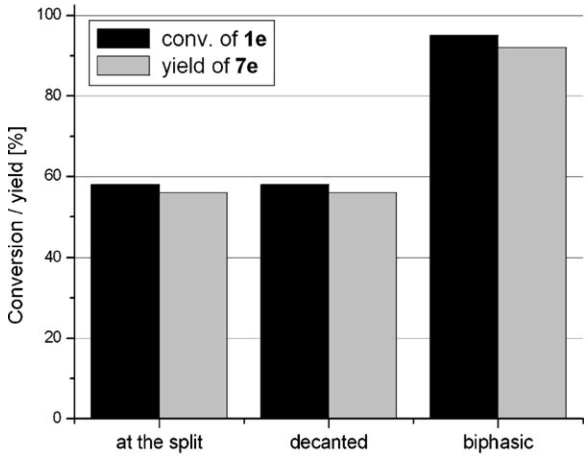


Fig. 9. Split test. Conditions: $[RuHCl(CO)(PCy_3)_2]$ (2.74×10^{-5} mol), **IL 3** (0.2 g), **1e** (1.37×10^{-3} mol), dodecane (internal standard) (0.05 mL), 130 °C, argon.

immobilized complex **6** was 95%, whereas no further progress in conversion took place in the decanted portion of the upper layer (Fig. 9). Results of the experiment suggest that catalytic activity originates from the complex immobilized in ionic liquid.

4. Conclusions

Comprehensive screening of a number of ruthenium complexes and a variety of commercially available ionic liquids enabled determination of the optimum conditions for high yield stereoselective syntheses of *E*-1,2-bis(silyl)ethenes carried out in ionic liquids as reaction media. $[RuHCl(CO)(PCy_3)_2]$ tolerates well ammonium-, pyridinium- and imidazolium-based ionic liquids tested, including chloride derivatives even at 130 °C. $[RuHCl(CO)(PCy_3)_2]$ immobilized in 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide (**IL 3**) and 1,2,3-trimethylimidazolium methylsulphate (**IL 7**) exhibit catalytic activity in regio- and stereoselective homocoupling of vinylsilanes and can be recycled up to 10 times in homocoupling of methylbis(trimethylsilyloxy)vinylsilane and up to 12 times in homocoupling of phenyldimethylvinylsilane without a significant change in catalytic performance. The effectiveness of the catalytic system is determined by several factors including stability of the catalyst and solubility of vinylsilanes in ionic liquids under the reaction conditions. The developed synthesis procedures enables a simple separation of products from ionic liquid by decantation. The source of catalytic activity is the catalyst immobilized in ionic liquid phase as concluded from results of a split test.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2012.08.038.

References

[1] T.H. Chan, I. Fleming, Synthesis (1979) 761–786.
[2] W.P. Weber, Silicon Reagents for Organic Synthesis, Springer, Berlin, 1983.
[3] E.W. Colvin, Silicon Reagents in Organic Synthesis, Academic Press, London, 1988.
[4] T.-Y. Luh, S.-T. Liu, in: Z. Rappoport, Y. Apeloig (Eds.), The Chemistry of Organosilicon Compounds, Wiley, Chichester, 1998.
[5] H.F. Sore, W.R.J.D. Galloway, D.R. Spring, Chem. Soc. Rev. 41 (2012) 1845–1866.
[6] Y. Nakao, T. Hiyama, Chem. Soc. Rev. 40 (2011) 4893–4901.
[7] S.E. Denmark, J.H.-C. Liu, Angew. Chem. Int. Ed. 49 (2010) 2978–2986.
[8] S.E. Denmark, J. Org. Chem. 74 (2009) 2915–2927.
[9] S.E. Denmark, C.S. Regens, Acc. Chem. Res. 41 (2008) 1486–1499.
[10] S.E. Denmark, J.D. Baird, Chem. Eur. J. 12 (2006) 4954–4963.
[11] Y. Nakao, A.K. Sahoo, H. Imanaka, A. Yada, T. Hiyama, Pure Appl. Chem. 78 (2006) 435–440.
[12] S.E. Denmark, R.F. Sweis, in: A. de Meijere, F. Diederich (Eds.), Metal-Catalysed Cross-Coupling Reactions, Wiley-VCH, Weinheim, 2004.
[13] S.E. Denmark, M.H. Ober, Aldrichim. Acta 36 (2003) 75–85.
[14] F. Babudri, G.M. Farinola, V. Fiandanese, L. Mazzone, F. Naso, Tetrahedron 54 (1998) 1085.
[15] S.E. Denmark, S.A. Tymonko, J. Am. Chem. Soc. 127 (2005) 8004–8005.
[16] K. Karabelas, A. Hallberg, Acta Chem. Scand. 44 (1990) 257–261.
[17] C. Thiot, C. Mioskowski, A. Wagner, Eur. J. Org. Chem. 74 (2009) 3219–3227.
[18] Y. Hatanaka, T. Hiyama, J. Org. Chem. 54 (1989) 268–270.
[19] K. Karabelas, A. Hallberg, J. Org. Chem. 54 (1989) 1773–1776.
[20] H.F. Sore, C.M. Boehner, L. Laraia, P. Logoteta, C. Prestinari, M. Scott, K. Williams, W.R.J.D. Galloway, D.R. Spring, Org. Biomol. Chem. 9 (2011) 504–515.
[21] P. Pawluc, G. Hreczycho, J. Szudkowska, A. Franczyk, B. Marciniec, Appl. Organomet. Chem. 24 (2010) 853–857.
[22] E. Hagiwara, K.-I. Gouda, Y. Hatanaka, T. Hiyama, Tetrahedron Lett. 38 (1997) 439–442.
[23] X. Meng, T. Yokoi, D. Lu, T. Tatsumi, Angew. Chem. Int. Ed. 46 (2007) 7796–7798.
[24] C. Vercaemst, M. Ide, B. Allaert, N. Ledoux, F. Verpoort, P. Van Der Voort, Chem. Commun. (2007) 2261–2263.
[25] K. Nakajima, I. Tomita, M. Hara, S. Hayashi, K. Domen, J.N. Kondo, J. Mater. Chem. 15 (2005) 2362–2368.
[26] T. Asefa, M. Kruk, M.J. MacLachlan, N. Coombs, H. Grondey, M. Jaroniec, G.A. Ozin, J. Am. Chem. Soc. 123 (2001) 8520–8530.
[27] B. Marciniec (Ed.), Comprehensive Handbook on Hydrosilylation, Pergamon Press, Oxford, 1992, pp 192–196.
[28] F. Alonso, R. Buitrago, Y. Moglie, J. Ruiz-Martinez, A. Sepulveda-Escribano, M. Yus, J. Organomet. Chem. 696 (2011) 368–372.
[29] A. Sato, H. Kinoshita, H. Shinokubo, K. Oshima, Org. Lett. 6 (2004) 2217–2220.
[30] P. Arsenyan, K. Oberte, K. Rubina, S. Belyakov, Tetrahedron Lett. 46 (2005) 1001–1003.
[31] For review see: B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluc, in: B. Marciniec (Ed.), Hydrosilylation. A Comprehensive Review on Recent Advances, Springer, Berlin, 2009, pp. 3–51.
[32] B. Marciniec, Coord. Chem. Rev. 249 (2005) 2374–2390.
[33] M. Chauhan, B.J. Hauck, L.P. Keller, P. Boudjouk, J. Organomet. Chem. 645 (2002) 1–13.
[34] R.N. Naumov, M. Itazaki, M. Kamitani, H. Nakazawa, J. Am. Chem. Soc. 134 (2012) 804–807.
[35] M. Suginome, Y. Ito, Chem. Rev. 100 (2000) 3221–3256.
[36] I. Beletskaya, C. Moberg, Chem. Rev. 106 (2006) 2320–2354.
[37] M. Suginome, T. Matsuda, T. Ohmura, A. Seki, M. Murakami, in: R. Crabtree, D.M.P. Mingos (Eds.), Comprehensive Organometallic Chemistry III, vol. 10, Elsevier, Oxford, 2007, pp. 725–787.
[38] H.E. Burks, J.P. Morken, Chem. Commun. (2007) 4717–4725.
[39] C. Pubill-Ulldemolins, A. Bonet, C. Bo, H. Gulyas, E. Fernandez, Org. Biomol. Chem. 8 (2010) 2667–2682.
[40] B. Marciniec, C. Pietraszuk, in: R.H. Grubbs (Ed.), Handbook of Metathesis, Wiley-VCH, Weinheim, 2003, pp. 463–490.
[41] B. Marciniec, C. Pietraszuk, Curr. Org. Chem. 7 (2003) 691–735.
[42] C. Pietraszuk, B. Marciniec, S. Rogalski, H. Fischer, J. Mol. Catal. A: Chem. 240 (2005) 67–71.
[43] A. Keller, R. Matusiak, J. Mol. Catal. A: Chem. 104 (1996) 213–219.
[44] M. Majchrzak, B. Marciniec, Y. Itami, Adv. Synth. Catal. 347 (2005) 1285–1294.
[45] Y. Wakatsuki, H. Yamazaki, M. Nakano, Y. Yamamoto, J. Chem. Soc. Chem. Commun. (1991) 703–704.
[46] B. Marciniec, C. Pietraszuk, J. Chem. Soc. Chem. Commun. (1995) 2003–2004.
[47] B. Marciniec, C. Pietraszuk, Organometallics 16 (1997) 4320–4326.
[48] T. Welton, Coord. Chem. Rev. 248 (2004) 2459–2477.
[49] T.J. Geldbach, P.J. Dyson, Metal Catalysed Reactions in Ionic Liquids, Springer, Berlin, 2005.
[50] Z.C. Zhang, Adv. Catal. 49 (2006) 153–238.
[51] R. Giernoth, Top. Curr. Chem. 276 (2007) 1–23.
[52] V.I. Parvulescu, C. Hardacre, Chem. Rev. 107 (2007) 2615–2665.
[53] S. Liu, J. Xiao, J. Mol. Catal. A: Chem. 270 (2007) 1–43.
[54] H. Olivier-Bourbigou, L. Magna, D. Morvan, Appl. Catal. A: Gen. 373 (2010) 1–56.
[55] J.P. Hallett, T. Welton, Chem. Rev. 111 (2011) 3508–3576.
[56] J. Durand, E. Teuma, M. Gomez, C. R. Chim. 10 (2007) 152–177.
[57] L.A. Muller, J. Dupont, R.F. de Souza, Macromol. Rapid Commun. 19 (1998) 409–411.
[58] R.F. de Souza, V. Rech, J. Dupont, Adv. Synth. Catal. 344 (2002) 153–155.
[59] P.J. Dyson, D.J. Ellis, D.G. Parker, T. Welton, Chem. Commun. (1999) 25–26.
[60] P.J. Dyson, D.J. Ellis, W. Henderson, G. Laurenczy, Adv. Synth. Catal. 345 (2003) 216–221.
[61] P.J. Dyson, Appl. Organomet. Chem. 16 (2002) 495–500.

[62] P. Żak, C. Pietraszuk, B. Marciniec, J. Mol. Catal. A: Chem. 289 (2008) 1–8.
[63] P.S. Hallman, T.A. Stephenson, G. Wilkinson, Inorg. Synth. 12 (1970) 237.
[64] C.S. Yi, D.W. Lee, Y. Chen, Organometallics 18 (1999) 2043–2045.
[65] N. Ahmad, J.J. Levinson, S.D. Robinson, M.F. Uttely, Inorg. Synth. 15 (1974) 45–64.
[66] A. Stark, M. Ajam, M. Green, H.G. Raubenheimer, A. Ranwell, B. Ondruschka, Adv. Synth. Catal. 348 (2006) 1934–1941.
[67] Sigma-Aldrich Co., ChemFiles 5 (6) (2005) 8–9.
[68] K.R. Seddon, A. Stark, M.J. Torres, Pure Appl. Chem. 72 (2000) 2275–2287.
[69] H. Wang, Z.J. Duan, S. Raychaudhuri, Yazaki Corporation, US 7,329,716 (2008).
[70] P.S. Braterman, Metal Carbonyl Spectra, Academic Press, New York, 1975.
[71] S.D. Drouin, D. Amoroso, G.P.A. Yap, D.E. Fogg, Organometallics 21 (2002) 1042–1049.
[72] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485–493.