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Modification of (Poly)Siloxanes *via* Hydrosilylation Catalyzed by Rhodium Complex in Ionic Liquids[#]

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Summary. The hydrosilylation of 1-heptene, allyl glycidyl ether and, allyl polyether by heptamethylhydrotrisiloxane and poly(hydro, methyl)(dimethyl)siloxane catalyzed by rhodium(I) complexes (particularly $[\{Rh(\mu{-}OSi\mathit{Me}_3)(\mathit{cod})\}_2]$) in imidazolium ionic liquids (especially $[Tri\mathit{MIM}]\mathit{Me}SO_4$) gives heptyl and glycidyloxy functional (poly)siloxanes and silicone polyethers with high yield and selectivity. The catalytic system based on rhodium siloxide can be easily separated from the product and successfully reused up to five times.

Keywords. TM complexes; Catalysis; (Poly)Siloxanes; Hydrosilylation; Ionic liquids.

Introduction

The chemistry and technology of silicon-based polymers, particularly silicones, is a very broad and still growing research area. The interest in these compounds has aroused owing to their many unique properties such as thermal and oxidative stability, low surface tension, gas permeability, excellent dielectric properties, physiological inertness, and moisture resistance [1–3]. Because of these properties silicones have found a tremendous number of applications [4, 5]. Modifications of polysiloxanes side groups have been extensively explored in order to obtain polymers with special properties or to make them chemically active, thus giving access to new industrial applications [6–9]. The desired properties are achieved thanks to the possibility of introducing a great variety of functional groups in the side chain of polysiloxanes, *e.g.*, epoxy-, polyether-, or alkyl-groups containing silicones [6, 10–13].

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[#] Dedicated to Professor *Ulrich Schubert* on the occasion of his 70th birthday in recognition of his significant contributions to silicon and materials chemistry

The major method used for attachment of an organofunctional group to a siloxane backbone is hydrosilylation catalyzed predominately by platinum complexes [14–17]. Platinum catalysts tolerate a variety of functional groups, however, some impurities may interact with them leading to catalyst poisoning [18]. This problem has stimulated much research aimed at employing other transition metal compounds as potential catalysts.

Our contribution to this field was the synthesis, isolation, and full characterization of a few new rhodium and iridium siloxide complexes, both dimeric [19] and monomeric [20]. Catalytic activity of these Rh(I) siloxide complexes has been demonstrated in some reactions, *i.e.* in the hydrosilylation of alkenes [21] and allyl alkyl ethers [20, 22, 23] as well as in the silylative coupling of vinylsilanes with alkenes [24].

Biphasic catalysis in a liquid–liquid system seems to be an ideal solution allowing a combination of the advantages of both homogeneous and heterogeneous catalysis [25]. The ionic liquids (ILs) generally form the phase in which the catalyst is dissolved and immobilized. The first example of the homogeneous transition metal catalysis in ionic liquids was the platinum catalysed hydroformylation of ethene, described by *Parshal* in 1972 [26], but the use of ionic liquids for biphasic catalysis was reported by *Wilkes* describing the first air and moisture stable imidazolium salts, based on tetrafluoroborate and hexafluorophosphate [27]. This approach has seen explosive growth during the past decade.

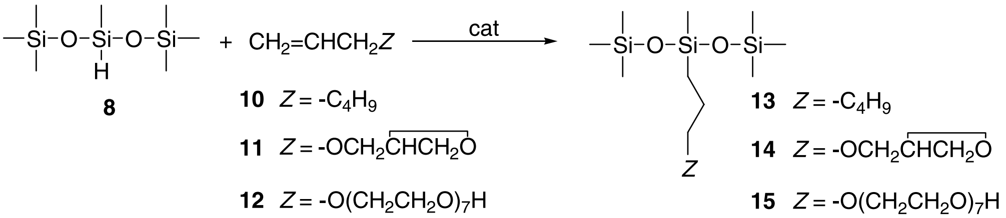
Nowadays, many examples of biphasic reactions employing ionic liquids, *i.e.* hydroformylation, hydrogenation, oxidation, dimerization, coupling reactions are known [25, 28, 29], however, there are only a few examples of hydrosilylation with the use of ILs [30–32]. These reactions were catalysed by platinum complexes.

The aim of this work was to examine the synthesis of organomodified silicones *via* hydrosilylation employing ionic liquids for the immobilization of rhodium (and, for comparison, platinum) complexes as catalysts.

Results and Discussions

Rhodium(I) siloxide complexes have shown high catalytic activity in the hydrosilylation with (poly)hydrosiloxanes [23b, c], even at room temperature (in contrast to platinum catalysts), however, due to the difficulty in separating the homogenously dissolved catalyst from the reaction products (especially from the polymeric product of high viscosity), the recovery and reuse of the catalyst was not possible. Therefore, one of our objectives was to search for suitable ionic liquids, which *via* immobilization of the metal complex would permit easy isolation of the catalyst from the product. Ionic liquids with weakly coordinating, inert anions and inert cations can activate homogenously dissolved TM complexes. They can at the same time play the role of ordinary solvents [29]. Ionic liquids employed in our studies were based on imidazolium derivatives. In order to establish basic conditions for hydrosilylation of olefins by polysiloxanes, some experiments were carried out using the model reaction of Scheme 1 between heptamethylhydrotrisiloxane and olefins.

Contrary to the polymeric system, this model reagents made the GC analysis of the reaction mixture possible. The rhodium complexes $[\{Rh(\mu\text{–}OSi\mathit{Me}_3)(\mathit{cod})\}_2]$



Scheme 1

(**1**), [{Rh(μ-Cl)(*cod*)}$_2$] (**2**), and platinum complex H_2PtCl_6 in cyclohexanone (**3**) were selected as catalysts of the reactions. The results for the different catalytic systems are presented in Table 1. In most reactions only one main product and small amounts of products of olefin isomerization were observed.

We tested also other imidazolium salts, containing various anions *i.e.* Cl^-, Br^-, NO_3^-, *etc.*, however, either because of the catalysts insolubility or the problems with separation of ILs from the product phase they had to be rejected.

The products obtained in most of the reactions examined were easily isolated from the ILs and could be reused. However, the catalytic activity of imidazolium salts containing BF_4^- or $SO_3CF_3^-$ anions in the next cycles decreased. One of the

Table 1. The conversion of substrates and the yield of product obtained in the reaction between heptamethyltrisiloxane and $CH_2{=}CHCH_2Z$ catalyzed by different catalytic systems

Z (*cf.* Scheme 1)	ILs	Catalyst[a]	Conversion of SiH/%[b]	Yield of product/%[b]
$-C_4H_9$	[*MIM*]BF_4	H_2PtCl_6 in cyclohexanone	0	0
		[{Rh(μ-Cl)(*cod*)}$_2$]	89 (87, 29)	86 (81, 29)
		[{Rh(μ–OSi*Me*$_3$)(*cod*)}$_2$]	91 (44, 20)	88 (39, 18)
	[*EMIM*]BF_4	H_2PtCl_6 in cyclohexanone	20 (4)	20 (4)
		[{Rh(μ-Cl)(*cod*)}$_2$]	86 (10)	86 (10)
	[*MIM*]SO_3CF_3	H_2PtCl_6 in cyclohexanone	93 (50, 3)	91 (48, 3)
		[{Rh(μ-Cl)(*cod*)}$_2$]	92 (61, 0)	90 (56, 0)
	[Tri*MIM*]*Me*SO_4	H_2PtCl_6 in cyclohexanone	98 (95, 89, 75)	97 (93, 85, 69)
		[{Rh(μ-Cl)(*cod*)}$_2$]	96 (93, 88, 80, 77)	94 (90, 85, 75, 70)
		[{Rh(μ–OSi*Me*$_3$)(*cod*)}$_2$]	100 (98, 97, 93, 90)	98 (95, 94, 90, 88)
$-OCH_2\overline{CHCH_2O}$	[*EMIM*]BF_4	H_2PtCl_6 in cyclohexanone	10 (0)	7 (0)
		[{Rh(μ-Cl)(*cod*)}$_2$]	0	0
	[Tri*MIM*]*Me*SO_4	H_2PtCl_6 in cyclohexanone	74 (74, 74, 74, 29)	71 (70, 70, 70, 25)
		[{Rh(μ-Cl)(*cod*)}$_2$]	78 (77, 76, 74, 71, 22)	71 (68, 61, 58, 58, 20)
		[{Rh(μ–OSi*Me*$_3$)(*cod*)}$_2$]	92 (86, 83, 80, 80, 78, 64)	86 (81, 78, 77, 75, 69, 56)
$-(OCH_2CH_2)_7OH$	[Tri*MIM*]*Me*SO_4	H_2PtCl_6 in cyclohexanone	97 (75, 38, 5)	90 (68, 25, 2)
		[{Rh(μ-Cl)(*cod*)}$_2$]	90 (82, 71, 35)	85 (77, 65, 26)
		[{Rh(μ–OSi*Me*$_3$)(*cod*)}$_2$]	99 (95, 90, 87, 72)	90 (82, 78, 72, 65)

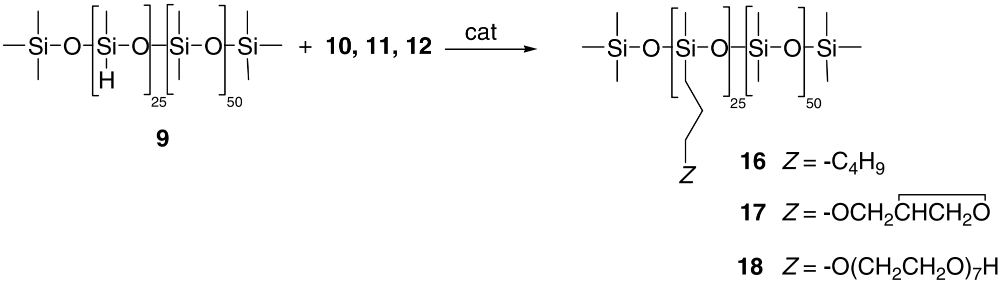
[a] [HSi]:[CH=CH]:[cat] = 1:1.2:10^{-5}, [Ils] = 1% based on total weight of combined substrates, $T = 90$°C, $t = 2$ h; [b] value of the conversion and the yield in next catalytic cycles with the same recovered catalytic system given in parentheses

reasons for this decrease could be the decomposition of ionic liquid's anion (as a result of the contact with moisture) involving liberation of fluoride ions acting as catalyst poison. [Tri*MIM*]*Me*SO_4 (**4**) which was used earlier by *Weyershausen et al.* for immobilisation of platinum catalyst in similar processes [31, 32] seems to be the most suitable also for the reactions catalysed by rhodium complexes.

The results confirmed the high catalytic activity of the siloxy rhodium complex **1** in the reactions. The facility of product separation and the possibility of multiple use of the catalyst depend on the hydrophobicity of the silicones modified as mentioned earlier [31, 32]. Alkyl modified siloxanes are more hydrophobic than epoxy or polyether ones. Therefore, the catalytic activity observed for the former was almost the same after a few times repeated use of the catalytic system (**1** + **4**).

On the basis of the results for the model reactions, the reactions between poly(hydro, methyl)(dimethyl)siloxanes and olefins were carried out in a similar way, according to Scheme 2.

These reactions were carried out in the presence of **3** or **1** immobilized in **4**. After the reaction, the resulting viscous mixture was characterized by IR and NMR methods. In most cases, the pure product without any side products was obtained after 2 hours at 90°C. The results are summarized in Table 2. These data confirmed the high catalytic activity of the rhodium siloxide complex and showed that the catalyst was very well immobilized in **4**.



Scheme 2

Table 2. The conversion of poly(hydro, methyl)(dimethyl)siloxane obtained in the hydrosilylation of $CH_2{=}CHCH_2Z$ catalyzed by Pt and Rh complexes immobilized in [Tri*MIM*]*Me*SO_4

Z	Catalyst[a]	Conversion of HSi/%[b]
$-C_4H_9$	H_2PtCl_6 in cyclohexanone	99 (95, 90, 80, 69)
	$[\{Rh(\mu{-}OSiMe_3)(cod)\}_2]$	100 (96, 94, 87, 80, 78)
$-OCH_2\overline{CHCH_2O}$	H_2PtCl_6 in cyclohexanone	95 (89, 80, 70, 45)
	$[\{Rh(\mu{-}OSiMe_3)(cod)\}_2]$	99 (95, 92, 89, 88, 75)
$-(OCH_2CH_2)_7OH$	H_2PtCl_6 in cyclohexanone	91 (85, 75, 38)
	$[\{Rh(\mu{-}OSiMe_3)(cod)\}_2]$	99 (93, 90, 85, 80, 78)

[a] $[HSi]:[CH{=}CH]:[cat] = 1:1.2:10^{-5}$, $[[TriMIM]MeSO_4] = 1\%$ based on total weight of combined substrates, $T = 90°C$, $t = 2\,h$; [b] value of the conversion in next catalytic cycles with the same recovered catalytic system given in parentheses

Conclusion

The rhodium siloxide complex **1** dissolved in **4** appeared to be a very efficient catalytic system in the hydrosilylation of alkenes, allyl glycidyl ether, and allyl polyether with hydrotrisiloxane and hydro(poly)siloxanes to obtain alkylsiloxanes and silicone waxes, as well as silicone polyethers and epoxyfunctional (poly)siloxanes. Compared to Pt-complex catalyzed reactions, high yields and selectivities were observed even after fivefold usage of rhodium-siloxide-ionic liquid catalytic system.

Experimental

All reagents were dried and purified before use by the usual procedures. Rhodium complexes [{Rh(μ–OSi*Me*$_3$)(*cod*)}$_2$] (**1**), [{Rh(μ-Cl)(*cod*)}$_2$] (**2**), and platinum complex H_2PtCl_6 in cyclohexanone (**3**) were prepared as described in Refs. [19a, 33]. Ionic liquids 1,2,3-trimethylimidazolium methylsulfate [Tri*MIM*]*Me*SO$_4$ (**4**), 1-methylimidazolium tetrafluoroborate [*MIM*]BF$_4$ (**5**), 1-ethyl-3-methylimidazolium tetrafluoroborate [*EMIM*]BF$_4$ (**6**), and 1-methylimidazolium trifluoromethylsulfonate [*MIM*]SO$_3$CF$_3$ (**7**) were purchased from Aldrich. All ILs were dried prior to use under vacuum at 60°C over 8 h. Heptamethyltrisiloxane (**8**) and poly(hydro, methyl)(dimethyl)siloxane (**9**) were purchased from Gelest, olefins and other reagents from Aldrich.

The NMR spectra (^{1}H, ^{13}C, ^{31}P, ^{29}Si) were recorded on a Varian XL 300 spectrometer. C_6D_6 or $CDCl_3$ were used as the solvents; GC–MS analyses were carried out with a Varian 3300 chromatograph (equipped with a DB-1, 30 m capillary column), connected to a Finnigan Mat 700 mass detector. GC analysis was also carried out with a Varian 3800 chromatograph with Megabore column (30 m, DB-1).

General Procedure for Catalytic Test

All manipulations were carried out under Ar using standard *Schlenk* techniques. The Si–H functional siloxane (or polysiloxane) and 1.2 equiv of the olefin (calculated to each Si–H group) were placed into the reaction vessel and heated up to 90°C. Then the appropriate amount of catalyst (in the ratio 10^{-5} mol per mol Si–H) and the ionic liquid (1% based on total weight of combined substrates) were added. After 2 h, the reaction mixture was separated from the phase of catalytic system by decantation. The mixture was analysed by GC method and the formation of desired products was verified by GC–MS and NMR analysis. The recovered catalytic system (catalyst in ionic liquid) was reused in the next reaction cycle.

3-(3-Glycidyloxypropyl)heptamethyltrisiloxane ($C_{13}H_{33}Si_3O_4$)

^{1}H NMR (CDCl$_3$, 298 K, 300 MHz): $\delta = -0.02$ (s, –OSiMeO–), 0.06 (s, –OSiMe$_3$), 0.43 (m, –CH$_2$Si), 1.59 (m, –C*H*$_2$CH$_2$Si), 2.59 (m), 2.76 (t, –CH–C*H*$_2$–O), 3.13 (m, –CH–O), 3.38 (m, –OC*H*$_2$CH$_2$CH$_2$Si, –OC*H*$_2$CH–O), 3.67 (dd, –OC*H*$_2$CH–O) ppm; ^{13}C NMR (CDCl$_3$, 298 K, 75.46 MHz): $\delta = -0.46$ (–OSiMeO–), 1.77 (–OSiMe$_3$), 13.44 (–CH$_2$Si), 23.21 (–*C*H$_2$CH$_2$Si), 44.25 (CH$_2$–O), 50.80 (–O–CH–), 71.34 (–O*C*H$_2$CH$_2$CH$_2$Si), 74.16 (–O*C*H$_2$CH–O–) ppm; ^{29}Si NMR (CDCl$_3$, 298 K, 59.61 MHz): $\delta = -21.01$ (SiMe), 7.88 (–OSiMe$_3$) ppm.

Poly(3-glycidyloxypropyl, methyl)(dimethyl)siloxane ($C_{281}H_{668}Si_{77}O_{126}$)

^{1}H NMR (CDCl$_3$, 298 K, 300 MHz): $\delta = 0.03$, 0.06 (s, –OSiMe$_2$–, –OSiMe$_3$), 0.49 (m, –CH$_2$Si), 1.61 (m, –C*H*$_2$CH$_2$Si), 2.58 (m), 2.77 (t, –CH–C*H*$_2$–O), 3.12 (m, –CH–O), 3.39 (m, –OC*H*$_2$CH$_2$CH$_2$Si, –OC*H*$_2$CH–O), 3.67 (dd, –OC*H*$_2$CH–O) ppm; ^{13}C NMR (CDCl$_3$, 298 K, 75.46 MHz): $\delta = -0.60$, 1.06, 1.75 (–OSiMe$_2$O–, –OSiMe$_3$), 13.34 (–CH$_2$Si), 23.13 (–*C*H$_2$CH$_2$Si), 44.26 (–CH*C*H$_2$–O), 50.80 (–O–CH–), 71.36 (–O*C*H$_2$CH$_2$CH$_2$Si), 74.11 (–O*C*H$_2$CH–O–) ppm; ^{29}Si NMR (CDCl$_3$, 298 K, 59.61 MHz): $\delta = -21.15$, -22.84 (–OSiMe$_2$O–) ppm.

3-Heptylheptamethyltrisiloxane ($C_{14}H_{36}Si_3O_2$)
^{1}H NMR (C_6D_6, 298 K, 300 MHz): $\delta = 0.18$, 0.20 (s, –OSiMeO–, –OSiMe$_3$), 0.65 (m, –CH$_2$Si), 0.93 (t, –CH$_3$), 1.41 (bm, –CH$_2$–) ppm.

Poly(heptyl, methyl)(dimethyl)siloxane ($C_{306}H_{768}Si_{77}O_{76}$)
^{1}H NMR (C_6D_6, 298 K, 300 MHz): $\delta = 0.21$, 0.23, 0.38 (bs, –OSiMeO–, –OSiMe$_2$O–, –OSiMe$_3$), 0.79 (m, –CH$_2$Si), 0.96 (m, –CH$_3$), 1.41 (bm, –CH$_2$–) ppm.

3-Polyetherheptamethyltrisiloxane ($C_{24}H_{56}Si_3O_{10}$)
^{1}H NMR (C_6D_6, 298 K, 300 MHz): $\delta = 0.08$, 0.18, 0.20 (s, –OSiMeO–, –OSiMe$_2$O–, –OSiMe$_3$), 0.60 (m, –CH$_2$–), 1.72 (m, –C*H*$_2$CH$_2$Si), 3.03, 3.26–3.52, 3.65 (m, –OCH$_2$–) ppm.

Silicone polyether ($C_{556}H_{1268}Si_{77}O_{276}$)
^{1}H NMR (C_6D_6, 298 K, 300 MHz): $\delta = 0.08$, 0.18, 0.20 (s, –OSiMeO–, –OSiMe$_2$O–, –OSiMe$_3$), 0.61 (m, –CH$_2$–), 1.76 (m, –CH$_2$CH$_2$Si), 3.03 (m), 3.28–3.56 (m), 3.64 (m, –OCH$_2$–) ppm.

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