Phenylethenyl-substituted silicones via Heck coupling reaction

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ABSTRACT

Systematic studies of several palladium complexes (Pd(OAc)$_2$, [PdCl$_2$(cod)], [Pd$_2$(dba)$_3$], [Pd(PPh3)4], [PdCl(SnCl$_3$)(P{p-Tol}$_3$)$_2$], [Pd$_2$Cl$_2$(SnCl$_3$)$_2$(P{p-Tol}$_3$)$_2$]) as potential catalytic systems for arylation of vinylsiloxanes via Heck coupling reactions are described. Catalytic activity and selectivity were studied for a model reaction of trimethylvinylsilane with PhBr and m-ClC$_6$H$_6$Br and then the most effective systems were applied for functionalisation of tetramethyltetravinylcyclotetrasiloxane and poly(dimethylsiloxane-co-methylvinylsiloxane), leading to the silicone fluids having high refractive index (1.5–1.6).

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1. Introduction

Carbon–carbon double bond formation is one of the essential aims of organic and polymer chemistry, leading, e.g. to fine organics, pharmaceuticals, monomers and specialty materials. Palladium catalysed coupling of aryl halides and olefins (Heck reaction), is widely recognised as a powerful tool for synthesis of substituted olefins, dienes and a variety of unsaturated compounds, including processes run on industrial scale [1–5]. This is also a useful route yielding conjugated polymer systems and nanocomposite materials [6,7], applied in optoelectronics. Currently, organosilicon polymers and oligomers incorporating arylethenyl moieties in the main or side chains have received considerable attention [8]. Their potential applications, as materials in personal care as gloss ingredients [8], polymers for non-linear optics and light emitting devices [6,9], result from the presence of π-conjugated moieties. In the synthesis of main chain conjugated oligo(phenylenevinylenes)s, the Heck reaction was found to be an effective, alternate route to cross-metathesis [10,11], where unsaturated carbon–carbon bonds are rearranged in the presence of metal carbene complexes.

On the other hand, structurally related oligo(phenylenesilylene-vinylene)s were made by silylative coupling [12] in the presence of non-carbene transition metal complexes [13].

Our interest, for some time now, has focused on high refractive index (closed to human hair RI) siloxane fluids, bearing phenylethenyl moieties as side chain pendants. Such materials are important components of haircare products. For the first time, they were ob-

tained by hydrosilylation of phenyl- and diphenylacetylene with linear poly(dimethylsiloxane-co-methylhydridosiloxane)s and tetramethylcyclotetrasiloxane (Scheme 1A) [8,14]. Recently, we presented alternative routes involving cross-metathesis (Scheme 1B and C) and silylative coupling of vinylsilicones and styrenes, in the presence of ruthenium and molybdenum complexes [15]. All three pathways, i.e. hydrosilylation, metathesis and silylative coupling are limited, from technological point of view, due to a rather elevated catalyst cost. In the case of silylative coupling, which was earlier also described for reaction of styrene with six and eight-membered cyclosiloxanes [16], the method requires higher concentrations of transition metal complexes (1–2×10^{-2} mol/per 1 mol of Vi moieties), compared to the ones applied in Heck coupling. Additionally, we have detected a rather serious disadvantageous side process, both in silylative coupling and metathesis. Due to the use of excess styrene as a substrate in both methods, free radical polymerisation of styrene takes place. Formation of polystyrene was reported, independently, by Marciniec et al. [16]. The extent of this undesired polyreaction and formation of polystyrene can be limited or eliminated either by the use of free radical scavengers or applying α-methylstyrene as a substrate [15].

2. Results and discussion

The aim of the present work was to select the most effective palladium complexes and to determine reaction conditions, which would ensure high yields of phenylethenyl-modified linear and cyclic siloxanes, leading to silicone fluids with high refractive indices. The fourth pathway (Scheme 1D), via Heck type coupling
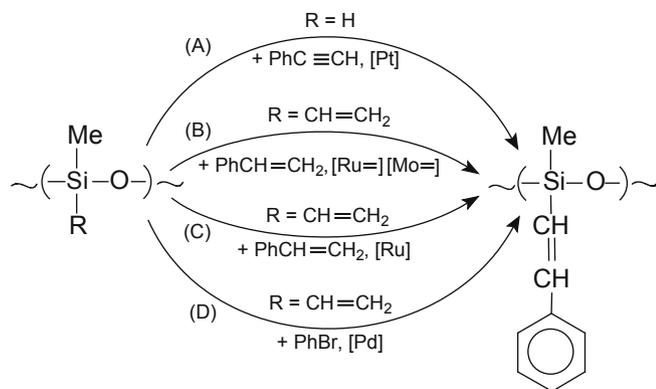
Scheme 1. Alternative routes to phenylethenyl substituted silicones: (A) hydrosilylation, [Pt] = PTDD; (B) metathesis, [Ru=], [Mo=] = Grubbs and Schrock type catalysts; (C) silylative coupling, [Ru] = e.g. [RuH(Cl)(CO)(PPh$_3$)$_3$]; (D) Heck reaction, [Pd] = e.g. [PdCl$_2$(cod)].

offers, the use of less expensive catalysts, at lower concentration and elimination of the undesired formation of polystyrene (metathesis, silylative coupling). Although, there are a number of patents referring, in general, also to vinylsilicones as substrates in the Heck reaction [17,18], one cannot find any reliable comparison of the real effectiveness of various palladium complexes for such reactants. Dependence of coupling yield on reaction conditions has not been given and most of all refraction indices, important from the point of view of application of the materials, were not reported. In a number of patent applications, describing processes designed for synthesis of a wide range of structures [19–24], the reactions were carried out in solution [25–28], which does not make the process technologically attractive.

Below, we present results from systematic studies of several palladium complexes as catalytic systems for arylation of vinylsiloxanes in bulk. Apart from typical palladium complexes and Pd(OAc)$_2$ two novel compounds with −SnCl$_3$ ligands ([PdCl(SnCl$_3$)(P{p-Tol}$_3$)$_2$], [Pd$_2$Cl$_2$(SnCl$_3$)$_2$(P{p-Tol}$_3$)$_2$]) were also applied. They are known to facilitate reduction of Pd(II) to in situ generated catalytically active Pd(0) species [29,30].

As a preliminary step, we chose to the evaluate effectiveness of palladium catalysts, known to be effective in Heck coupling, basing on a low molecular weight model system. It involved coupling trimethylvinylsilane with PhBr and m-ClC$_6$H$_4$Br (Table 1). Evaluation of conversion of vinyl groups into phenylethenyl ones was, in this work, based on ^{1}H NMR analysis (Fig. 1) and integration of unreacted vinyl groups at siloxy monomeric units and the formed phenylethenyl substituents. The range of 5.80–6.10 ppm (3H, −MeSiViO−, unreacted) and 6.15–6.45 ppm (1H, MeSiCH = CHPh) was taken into account as the resonances corresponding

Table 1
Heck reaction of aryl bromides with trimethylvinylsilane (molar ratio 1:1) in toluene (50% by volume); reaction conditions: 80 °C, 24 h, PR$_3$ (R = o-Tol[a], R = Ph[b]), NEt$_3$; molar ratios: [Me$_3$SiVi]:[ArBr]:[NEt$_3$] = 1:1:1, [Pd]:[PR$_3$]:[Me$_3$SiVi] = 1:2:3700.

Entry	Aryl bromide	Catalyst	Yield [±0.5%]
1	PhBr	[Pd(cod)Cl$_2$]	70.0[a]
2	m-ClC$_6$H$_4$Br	[Pd(cod)Cl$_2$]	77.5[a]
3	m-ClC$_6$H$_4$Br	[Pd(cod)Cl$_2$]	77.0[b]
4	PhBr	Pd(OAc)$_2$	78.0[a]
5	m-ClC$_6$H$_4$Br	Pd(OAc)$_2$	82.5[a]
6	m-ClC$_6$H$_4$Br	Pd(OAc)$_2$	65.0[b]
7	PhBr	[Pd$_2$(dba)$_3$]	72.5[a]
8	m-ClC$_6$H$_4$Br	[Pd$_2$(dba)$_3$]	82.5[a]
9	m-ClC$_6$H$_4$Br	[Pd$_2$(dba)$_3$]	64.5[b]
10	PhBr	[Pd(PPh$_3$)$_4$]	26.0[a]
11	PhBr	[Pd$_2$Cl$_2$(SnCl$_3$)$_2$(P{p-Tol}$_3$)$_2$]	21.0[a]
12	PhBr	[PdCl(SnCl$_3$)(P{p-Tol}$_3$)$_2$]	16.5[a]

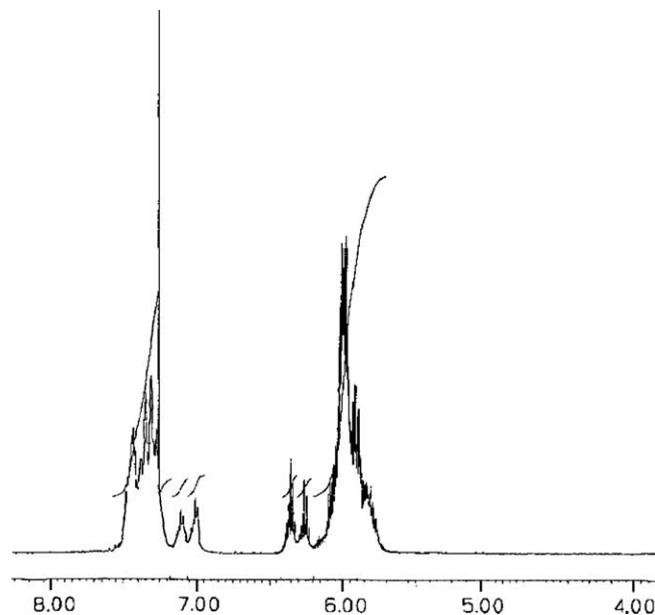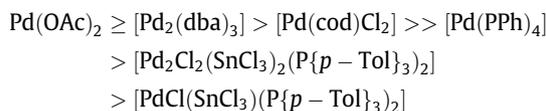**Fig. 1.** ^{1}H NMR spectrum of reaction mixture in the Heck coupling of tetramethyltetravinylcyclotetrasiloxane and bromobenzene at 27% conversion.

to the other vinylene proton at 6.95–7.15 ppm (1H, MeSiCH = CHPh) slightly overlap with aromatic protons. Apart from −SnCl$_3$ ligand bearing complexes, other catalysts used in this work were claimed to be efficient in Heck reaction of organic substrates [2]. Among the palladium catalysts both Pd$_2$(dba)$_3$ and Pd(OAc)$_2$ led to formation of arylethenyltrimethylsilanes with high yield (82.5% yield, entries 5 and 9) for the reaction with m-ClC$_6$H$_4$Br and 72.5–78% (entries 4 and 7) with PhBr as the aryl substrate. For (1,5-cyclooctadiene)dichloropalladium the respective yields were 78% and 70%. It was confirmed, that the use of sterically demanding tri-ortho-tolyl phosphine generates higher conversions, compared to triphenyl phosphine. On the other hand the catalyst, frequently used in Heck and Suzuki coupling reactions – tetrakis(triphenylphosphine)palladium(0) (entry 10) gave low efficiencies (26% yield) in the model process. The yield of phenylethenyltrimethylsilane was even lower in the presence of −SnCl$_3$ ligand containing palladium complexes (21% and 16.5% respectively for entries 11 and 12), used as catalyst precursors. Thus, the simple model reaction allowed for choosing the most effective palladium catalytic systems, which were subsequently applied in studies of Heck coupling, involving oligomeric and polymeric siloxanes. The above preliminary evaluation have shown the following general order of catalytic activity:

$$\text{Pd(OAc)}_2 \geq [\text{Pd}_2(\text{dba})_3] > [\text{Pd(cod)Cl}_2] >> [\text{Pd(PPh}_3)_4]$$
$$> [\text{Pd}_2\text{Cl}_2(\text{SnCl}_3)_2(\text{P}\{p-\text{Tol}\}_3)_2]$$
$$> [\text{PdCl(SnCl}_3)(\text{P}\{p-\text{Tol}\}_3)_2]$$

The three most effective catalysts – Pd(OAc)$_2$, [Pd$_2$(dba)$_3$], [Pd(cod)Cl$_2$] were subsequently used in reaction of organosilicon substrates – tetramethyltetravinylcyclotetrasiloxane (I) (D$_4^{Me,Vi}$) and poly(dimethylsiloxane-co-methylvinylsiloxane), containing 65% of ∼MeViSiO∼ monomeric units (M_n = 3200; M_w/M_n = 1.1) (II), and aryl compounds. The arylhalides used in the Heck coupling reaction included bromo- and chlorobenzene, bromotoluenes and m-bromochlorobenzene. For reactions with PhBr and (I) the highest conversion rate (97%) was obtained with Pd(OAc)$_2$ as a catalyst (Table 2, entry 12). Under the same reaction conditions, [PdCl$_2$(cod)] and [Pd$_2$(dba)$_3$] gave 93 and 95% conversion, respectively (entries 5 and 10). Once chlorobenzene was applied as a substrate (entry 6)

Table 2
Heck coupling of silicone vinyl bearing fluids with aryl halides.

Entry	Siloxane[a]	ArX[b]	Catalyst[b]	[Pd][b]	Temp (°C)	React. time (h)	Conversion (%)	Product RI
1	I	C_6H_5Br	$[PdCl_2(cod)]$[c]	$5.0\ 10^{-4}$	100	24	95	1.582
2	I	C_6H_5Br	$[PdCl_2(cod)]$	$1.4\ 10^{-4}$	100	12	65	1.453
3	I	C_6H_5Br	$[PdCl_2(cod)]$	$1.4\ 10^{-4}$	80	96	59	1.441
4	I	C_6H_5Br	$[PdCl_2(cod)]$	$5.0\ 10^{-3}$	100	12	90	1.575
5	I	C_6H_5Br	$[PdCl_2(cod)]$	$1.4\ 10^{-3}$	100	24	93	1.58
6	I	C_6H_5Cl[d]	$[PdCl_2(cod)]$	$1.4\ 10^{-3}$	100	96	56	1.442
7	I	m-MeC$_6$H$_4$Br	$[PdCl_2(cod)]$	$1.4\ 10^{-3}$	100	24	53	1.59
8	I	m-MeC$_6$H$_4$Br	$[PdCl_2(cod)]$	$1.4\ 10^{-3}$	80	24	47	1.581
9	I	p-MeC$_6$H$_4$Br	$[PdCl_2(cod)]$	$1.4\ 10^{-3}$	100	24	53	1.565
10	I	C_6H_5Br	$[Pd_2(dba)_3]$[e]	$1.4\ 10^{-3}$	100	24	95	1.583
11	I	m-MeC$_6$H$_4$Br	$[Pd_2(dba)_3]$	$1.4\ 10^{-3}$	100	24	52	1.589
12	I	C_6H_5Br	$Pd(OAc)_2$[f]	$1.4\ 10^{-3}$	100	24	97	1.591
13	I	m-MeC$_6$H$_4$Br	$Pd(OAc)_2$	$1.4\ 10^{-3}$	100	24	53	1.591
14	I	m-ClC$_6$H$_4$Br	$Pd(OAc)_2$	$1.4\ 10^{-3}$	100	24	52	1.595
15	II	C_6H_5Br	$[Pd_2(dba)_3]$	$1.4\ 10^{-3}$	100	12	73	1.477
16	II	C_6H_5Br	$[Pd_2(dba)_3]$	$1.4\ 10^{-3}$	100	24	80	1.496
17	II	C_6H_5Br	$[Pd_2(dba)_3]$	$5.0\ 10^{-3}$	100	24	83	1.504

[a] I – tetramethyltetravinylcyclotetrasiloxane ($D_4M^{e,Vi}$), II – poly(dimethylsiloxane-co-methylvinylsiloxane) (65% MeViSiO m.u., M_n = 3200).
[b] [–MeViSiO–]:[ArX]:[Et$_3$N] = 1:1:1, [Pd]:[P(o-Tol)$_3$]:[–MeSiViO–] = 1:2:3700 = 1:2.
[c] [PdCl$_2$(cod)] = (1,5-cyclooctadienedichloropalladium (II).
[d] In the presence of CuI.
[e] [Pd$_2$(dba)$_3$] – tris(dibenzylideneacetone)dipalladium(0).
[f] Pd(OAc) – palladium (II) acetate.

the coupling yield was low (56%) even after extended reaction time (96 h) and in the presence of 2 mol% of CuI as a co-catalyst [31].

There is also a clear effect of reaction temperature and concentration of the palladium catalyst. Lowering both, the temperature (entries 2, 3 and 7, 8) and the catalyst concentration (entries 1, 5 and 16, 17) leads to decreases in reaction rates. In such cases, the reaction times must be prolonged to obtain higher conversions. Once m-MeC$_6$H$_4$Br, p-MeC$_6$H$_4$Br or m-ClC$_6$H$_4$Br were used, the catalytic effectiveness of the three palladium catalytic systems was almost the same (52–53% conversion, entries 7, 11, 13). The coupling yield did not depend on the electron-withdrawing or electron-donating character of substituents and one could expect that steric factor dominated for the processes involving cyclic siloxane system. On close examination of the published results [32–34], what seems to be a general picture and once substituted aryl halides are used, higher coupling yields are assured by longer reaction time. Such substituents, changing electron density, can affect the relative strength of the C–X and Pd–C, and Pd–X bonds in a transition state of oxidative addition to palladium. GC/MS analysis of the siloxane products, run for the reaction between $D_4^{Me,Vi}$ and PhBr, revealed that the resultant silicone fluid contains mono-, di- and tri-phenylethenyl substituted cyclosiloxane isomers (see Experimental and Supplementary material). Under experimental conditions, tetra-substituted cyclosiloxane isomers could not be detected due to long retention times.

One additional factor concerning the Heck process under solvent-less conditions should be mentioned. The process carried out in bulk involving equimolar amounts of PhBr and Me$_3$SiVi with Pd(OAc)$_2$ as a catalyst, ($k = 3.5\ 10^{-5}$ l mol^{-1}s^{-1}) is ~8 times faster than the one run in toluene (50% by volume) ($k = 4.4\ 10^{-6}$ l mol^{-1}s^{-1}) (Fig. 2).

At the end it is important to underline the applied aspect of the above results as the Heck coupling leads to organosilicon products, both oligomers and polymers, that consist potential hair care additives. In the case of materials obtained from co-polysiloxane (II), having both [–MeViSiO–] and [–Me$_2$SiO–] monomeric units, due to relative "dilution" of phenylethenyl moieties, the respective RI values are rather low (1.47–1.50, entries 15–17). For the oligomeric cyclotetrasiloxane without [–Me$_2$SiO–] units, the RI values of the coupling products are much higher and in general, they depend on conversion and the structure of aryl bromide, falling in the range of 1.58–1.59, which is even higher than human hair RI
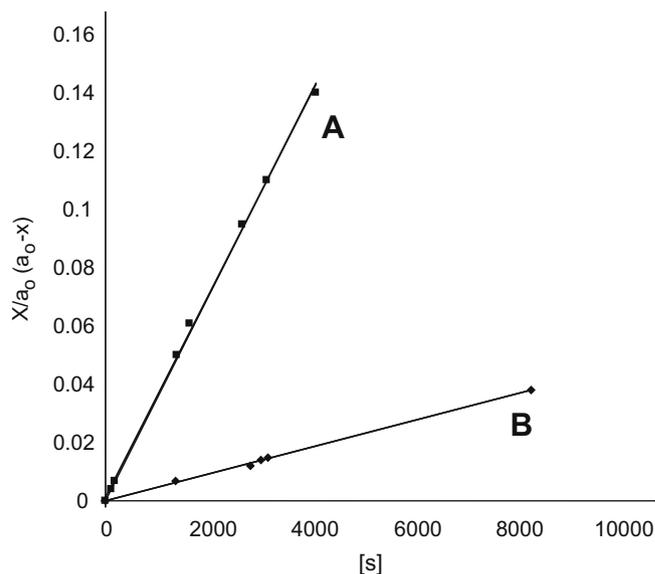

Fig. 2. A second order dependence for the Heck coupling in bulk (A) and in toluene (B). ([Me$_3$SiVi] = [PhBr], 100 °C).

(1.548) [36]. Thus, such materials shall have excellent "shine" properties, once applied in hair care products. Although in the case of substituted aryl bromides the Heck coupling proceeds slower than for bromobenzene, as a substrate, the refraction indices reach relatively high values (m-ClC$_6$H$_4$Br) as a result of higher RI of the substituted aryl bromides themselves (e.g. RI for C_6H_5Br = 1.559, RI for m-ClC$_6$H$_4$Br = 1.576).

3. Conclusions

We have developed an efficient and convenient catalytic pathway leading to high RI siloxane fluids in the course of the Heck coupling of aryl bromides with vinyl substituted cyclic and linear siloxanes. Although similar processes are described in the literature [35], including ionic liquids [33,37] or in water-organic solvent mixtures [27,34]. In this work we have evaluated effectiveness of

a series of palladium catalysts in a reaction involving model organosilicon substrate – trimethylvinylsilane and aryl bromides as: $Pd(OAc)_2 \geqslant [Pd_2(dba)_3] > [Pd(cod)Cl_2] \gg [Pd(PPh_3)_4] > [Pd_2Cl_2(SnCl_3)_2(P\{p\text{-}Tol\}_3)_2] > [PdCl(SnCl_3)(P\{p\text{-}Tol\}_3)_2]$. The three most effective catalysts have been successfully used in several Heck coupling reactions under solvent-less conditions, providing an useful method leading to high refraction index silicone fluids (from RI of 1.430 (II) and 1.433 (I) to even 1.590). It has been also shown that reactions carried out without solvent proceed faster than the ones performed in solution.

4. Experimental

4.1. General

Poly(dimethylsiloxane-*co*-methylvinylsiloxane) was made by ring-opening cationic polymerisation of octamethylcycloterasiloxane (D$_4$) with teramethyltetravinylcyclotetra-siloxane (D$_4^{\text{Vi,Me}}$) using decamethyltetrasiloxane (MD$_2$M) as chain terminator [15]. D$_4^{\text{Vi,Me}}$ (Aldrich), [Pd(dba)$_3$], [Pd(PPh$_3$)$_4$], Pd(OAc)$_2$, [PdCl$_2$(cod)], [PdCl$_2$(P{*o*-Tol}$_3$)$_2$] (all from Strem) were used as supplied. [PdCl(SnCl$_3$)(P{*p*-Tol}$_3$)$_2$] and [Pd$_2$Cl$_2$(SnCl$_3$)$_2$(P{*p*-Tol}$_3$)$_2$] were prepared as described in [29]. Triethylamine (Fluka) was purified using standard method [38]. The ^{1}H and ^{29}Si NMR spectra were recorded using a Bruker MSL 200 MHz and a Bruker DRX 500 MHz spectrometers in CDCl$_3$ solutions. GC–MS (EI) analyses were run on a Thermo-Quest apparatus using 30 m DB-1 column (the temperature was programmed as follows: 50 °C (2 min), then a linear increase at the rate of 10 °C/min up to isotherm of 250 °C (10 min). All experiments were carried out in inert atmosphere (Ar). RI measurements were performed with Carl Zeiss Refractometer, equipped with Haake DC-10 Thermostat at 20 °C.

Progress of the coupling reaction was followed by proton NMR.

4.2. Heck coupling of D$_4^{Me,Vi}$ with bromobenzene, a representative procedure

Bromobenzene (12.6 g, 0.08 mol) and D$_4^{\text{Vi,Me}}$ (6.9 g, 0.02 mol) were stirred under argon in a 50 ml round bottom flask, equipped with magnetic stirrer, reflux condenser and thermometer. The flask was purged with argon for 15 min. at room temperature and then triethylamine (7.88 g, 0.08 mol), dichloro(1,5-cyclooctadiene)palladium(II) (38.5 mg, 0.14 mmol) and tri(*o*-tolyl)phosphine (82 mg, 0.28 mmol) were added. The reaction mixture was stirred at 80 °C for 96 h. After cooling to room temperature, hexane (50 ml) was added, the mixture was washed with water, the layers were separated and the organic one was filtered through Celite. The solvent was evaporated and the product was dried on vacuum line connected to mercury pump (10^{-3} mmHg) at room temperature for 24 h, yielding 8.62 g of yellowish oil containing 59% phenylethenylated oligomer.

^{1}H NMR: δ (CDCl$_3$): 0.10–0.25 (m, 3H, *Me*SiViO, unreacted); 0.25–0.50 (m, 3H, *Me*SiCH = CHPh); 5.80–6.10 (m, 3H, MeSi*Vi*O, unreacted); 6.15–6.45 (d, 1H, MeSi*CH* = CHPh, J$_{\text{CH=CH}}$ = 18.9 Hz); 6.95–7.15 (m, 1H, MeSiCH = *CH*Ph, J$_{\text{CH=CH}}$ = 18.9 Hz); 7.15–7.55 (m, Ph). Proportions of monomeric units based on ^{1}H NMR: 59% of –[MeSi(CH=CHPh)O]– and 41% of –[MeSiViO]–; ^{29}Si NMR: δ (CDCl$_3$, Cr(acac)$_3$): −18.6 (Me*Si*ViO); −17.6 (MeSi(CH=CHPh)O); EI GC/MS (*m/z*): [Si(Me)(Vi)O]$_3$[Si(Me)(CH=CHPh)O] 420 (M$^+$), 405 (M$^+$−Me), 392 (M$^+$−CH$_2$=CH$_2$), 378 (M$^+$−Me−Vi), 290 (M$^+$−CH=CHPh−Vi,), 275 (M$^+$−Me−Vi−CH=CHPh); [Si(Me)(Vi)O]$_2$[Si(Me)(CH=CHPh)O]$_2$ 496 (M$^+$), 392 (M$^+$−CH$_2$=CHPh), 365 (M$^+$−CH$_2$=CH$_2$−CH=CHPh), 351 (M$^+$−Me−Vi−CH=CHPh), 325 (M$^+$−Me−2C$_6$H$_6$), 288 (M$^+$−2 CH$_2$=CHPh), 275 (M$^+$−Me−2 CH=CHPh), 251 (M$^+$−CH$_2$=CH$_2$−Vi−Si(Me)(CH=CHPh)O); [Si(Me)-(Vi)O][Si(Me)(CH=CHPh)O]$_3$ 572 (M$^+$), 366 (M$^+$−2 CH=CHPh), Conditions for all other coupling reactions are given in Tables 1 and 2.

4.3. Comparative rate measurements for reactions of PhBr with Me$_3$SiVi in bulk and in toluene

Reactions were carried out as described above, using Me$_3$SiVi (1.50 g, 0.015 mol), PhBr (2.36 g, 0.015 mol), Et$_3$N (1.53 g, 0.015 mol), PPh$_3$ (0.012 g, 4.4 10^{-5} mol) and Pd(OAc)$_2$ (0.005 g, 2.2 10^{-5} mol). In a solution experiment the reaction mixture was diluted with toluene (1:1). Reaction mixtures were heated at 100 °C for 1 h (bulk experiment) or over 2 h (solution experiment). At time intervals small samples (0.2 ml) were withdrawn, extracted with hexane, dried and analysed (^{1}H NMR). The results are shown in Fig. 2.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.07.001.

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