Ruthenium Complex-catalysed Selective Redistribution Reaction of Aryltrihydrosilanes and Desilanative Polymerization of Bis(trihydrosilyl)benzenes

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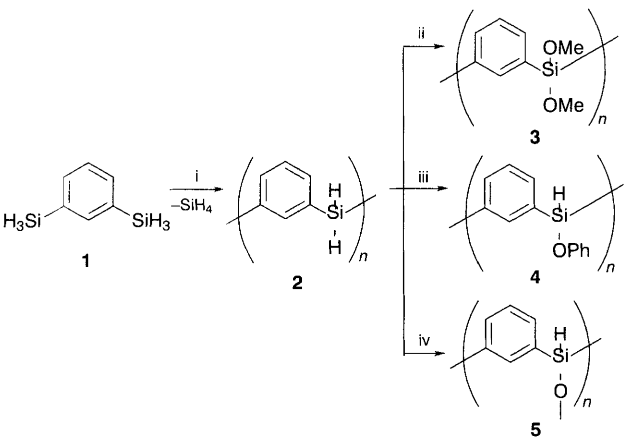
Ruthenium complexes catalyse desilanative condensation of bis(trihydrosilyl)benzenes to give poly[(dihydrosilylene)(phenylene)]s, a new class of organic–inorganic hybrid polymers that allow numerous transformations.

Organic–inorganic hybrid polymers that combine the advantages of organic and inorganic polymers such as light weight, easy fabrication, and flexibility coming from organic polymers, and mechanical strength and thermo-oxidative stability of inorganic polymers, are attracting much attention.[1–4] Among various organic–inorganic hybrids, of particular interests are the polymers with a backbone containing metal/metalloid atoms and functional side groups that allow modification of structures and cross-linking to control the properties. Polyphosphazenes represent such polymers and are attracting widespread attention. Here we report the synthesis of another class of versatile organic–inorganic hybrid polymers, poly[(dihydrosilylene)(phenylene)]s, based on a new and highly selective redistribution reaction of aryltrihydrosilanes.† Redistribution reaction of silanes, *i.e.* transposition of substituents between silicon atoms, has been long known,[5] but very little is reported for organotrihydrosilanes.[6]

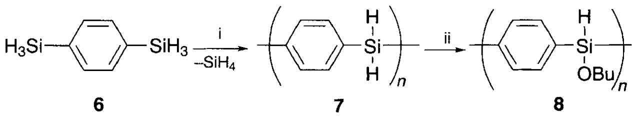
When trihydrophenylsilane was treated with [RuCl$_2${P(C$_6$H$_4$Me-*p*)$_3$}$_3$] (0.35 mol%) in benzene at room temperature for 0.5 h, silane gas was liberated and dihydrodiphenylsilane was formed in the mixture as nearly a sole non-volatile product.‡,§ Despite patent applications claiming ruthenium-catalysed synthesis of poly(hydrophenylsilylene),[7] we were unable to reconfirm the results therein. Trihydro(*p*-tolyl)silane reacted similarly to give only SiH$_4$ and dihydrodi(*p*-tolyl)silane. Other isomeric dihyroditolylsilanes (*m*- and *o*-isomers) were not detected at all. Triarylhydrosilane was not substantially formed either, but could be the major product when the reaction was run without the use of the solvent in the presence of a relatively large amount of Ru (6 mol%). The reaction of *n*-hexyltrihydrosilane also took place, albeit much slower.

Since the foregoing redistribution reaction is highly selective, it can be successfully applied to the synthesis of poly[(dihydrosilylene)(phenylene)]s. Thus, the reaction of 1,3-bis(trihydrosilyl)benzene at room temperature afforded a soluble colourless polymer **2** with M_w ranging from 4000 to 20000 (Scheme 1).¶ Spectral data of the polymer were consistent with the expected structure depicted in Scheme 1.|| Neither isomeric phenylene rings nor trisubstituted silicon units (triphenylsilane-type Si–H) were observed in the polymer chain. 1,4-Bis(trihydrosilyl)benzene also polymerized at room temperature (Scheme 2). The resulting polymer **7**, however, precipitated out from the reaction mixture as an insoluble white powder and only a low molecular mass polymer ($M_w \approx 1000$) was tractable.

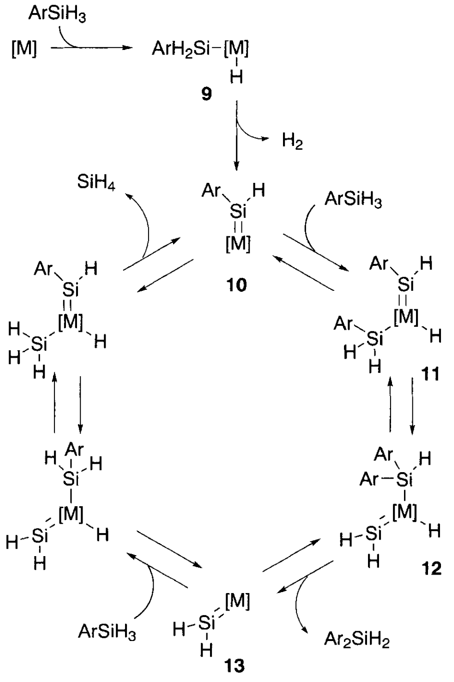
The desilanative condensation is best explained by the mechanism outlined in Scheme 3. Based on the very recent paper by Corriu *et al.*,[8] the (aryldihydrosilyl)hydridoruthenium complex **9** formed by oxidative addition of aryltrihydrosilane is envisioned to be transformed into the (arylhydrosilylene)ruthenium species **10** with extrusion of a hydrogen molecule. Oxidative addition of another aryltrihydrosilane molecule to **10** is likely to take place to generate a hydrido(silyl)(silylene)ruthenium intermediate **11**, which presumably undergoes 1,3-migration of the aryl group to generate another hydrido(silyl)(silylene)ruthenium complex **12**. The 1,3-migration in (silyl)(silylene)metal systems has been well documented for the last several years.[9] Reductive elimination from **12** gives diaryldihydrosilane and (dihydrosilylene)ruthenium species **13**. Repetition of similar oxidative addition, 1,3-migration of a hydrogen atom, and reductive elimination leads to the formation of SiH$_4$ and **10** is regenerated.



Scheme 1 *Reagents and conditions*: i, cat. RuCl$_2$[P(C$_6$H$_4$Me-*p*)$_3$]$_3$; ii, 2.3 equiv. of MeOH, cat. RuCl$_2$[P(C$_6$H$_4$Me-*p*)$_3$]$_3$; iii, 1 equiv. of PhOH, cat. RuCl$_2$[P(C$_6$H$_4$Me-*p*)$_3$]$_3$; iv, 200 °C under air



Scheme 2 *Reagents and conditions*: i, cat. RuCl$_2$[P(C$_6$H$_4$Me-*p*)$_3$]$_3$; ii, 1 equiv. of Bu^{n}OH, cat. RuCl$_2$[P(C$_6$H$_4$Me-*p*)$_3$]$_3$



Scheme 3 Ar = aryl

The principal advantage of poly(phenylenesilylene)s is their *versatile* reactivity for structure modification; obviously, a wide range of transformations such as hydrosilation, alcoholysis, aminolysis, oxidation, chlorination and alkylation would be possible at the reactive Si–H bonds. Indeed, preliminary results demonstrate this merit as follows. The insoluble poly[(dihydrosilylene)(1,4-phenylene)] **7** was solubilized by selective monoalkoxylation onto silicon with butanol in the presence of a ruthenium catalyst.[10] Similarly, treatment of **2** with phenol or methanol resulted in selective mono- or di-substitution at the silylene unit (Scheme 1). Cross-linking of **2** with bisphenol-A resulted in gelation. Oxidation of **2** at 200 °C with air also resulted in cross-linking to yield colourless transparent material **5** that was hard, insoluble, and thermally stable; 5% weight loss temperature of thermogravimetric analysis was 700 °C (heating rate 10 °C min^{-1}, under He). A strong broad IR absorption around 1100 cm^{-1} and a shift of ^{29}Si NMR signals to lower fields are in agreement with a cross-linked structure through Si–O–Si bond. On the other hand, thermal treatment of **2** under inert atmosphere up to 900 °C gave a black solid in 85% yield. TG–MS analysis revealed major weight loss taking place at 200–400 °C and generation of fragments with m/z 30 and 31 in this temperature range. Accordingly, the weight loss is presumably due to silylene extrusion from the polymer and the resulting black solid is likely to contain poly(phenylene) blocks.

In conclusion, we have reported highly selective redistribution of aryltrihydrosilanes, the synthesis of poly[(dihydrosilylene)(phenylene)]s, and their structure modification. Synthesis and property evaluation of various derivatives, and mechanistic studies on the new polymerization are now under way.

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Footnotes

† A part of this work was presented at the 65th Spring Annual Meeting of Japan Chemical Society, Abstract 3F335, Tokyo, 1993.

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§ **CAUTION**: SiH_4 is pyrophoric!

¶ A typical example of the polymerization: to a toluene solution (2 ml) of $[RuCl_2\{P(C_6H_4Me\text{-}p)_3\}_3]$ (0.007 mmol) was added 1,3-bis(trihydrosilyl)benzene **1** (4.2 mmol) at room temp. The mixture was stirred overnight under nitrogen. The resulting polymer was purified by Florisil column chromatography or preparative GPC (70% yield) $(C_6H_6Si)_n$. Poly[(dihydrosilylene)(phenylene)]s (**2** and **7**) should be stored as a solution to avoid insolubilization during storage.

‖ *Spectral data* for polymers: NMR was recorded in C_6D_6 unless otherwise stated. **2**: colourless gum. ^{1}H NMR (300 MHz) δ 4.16 (s, 0.10H, SiH_3), 4.99 (s, 2H, SiH_2), 7.03 (t, *J* 7.4 Hz, 1H), 7.46 (dd, *J* 7.4 and 1.1 Hz, 2H), 7.98 (s, 1H); ^{13}C NMR (75.5 MHz) δ 128.4, 131.6, 137.5, 143.3; ^{29}Si NMR (59.6 MHz) δ −66.6 (SiH_3), −40.1 (SiH_2); IR (film, $\tilde{\nu}/\text{cm}^{-1}$) 2138 (SiH). **3**: colourless gum. ^{1}H NMR δ 3.41 (s, 6H, MeO), 3.43 (s, 1.1H, MeO), 7.17 (t, *J* 7.4 Hz, 1H), 7.79 (dd, *J* 7.4 and 1.0 Hz, 2H), 8.53 (s, 1H); ^{13}C NMR δ 50.6, 127.9, 132.6, 137.3, 141.8. **4**: colourless gum. ^{1}H NMR δ 5.56 (s, 0.06H, Si–H), 5.84 (s, 1H, Si–H), 6.7–7.2 (m, 6H), 7.62 (d, *J* 7.3, 2H), 8.35 (s, 1H); ^{13}C NMR δ 119.7, 122.3, 130.0, 133.2, 137.3, 141.4, 155.7; ^{29}Si NMR ($CDCl_3$) δ −36.7, −14.3; IR (film, $\tilde{\nu}/\text{cm}^{-1}$) 2146 (Si–H). **5**: colourless solid. ^{13}C NMR (solid) δ 127.8, 136.4; ^{29}Si NMR (solid) δ −36.4, −20.6; IR (KBr, $\tilde{\nu}/\text{cm}^{-1}$) 2138 (Si–H). **7**: colourless gum. ^{1}H NMR δ 4.20 (s, 0.74H, SiH_3), 5.03 (s, 2H, SiH_2), 7.5 (m, 4H); IR (film, $\tilde{\nu}/\text{cm}^{-1}$) 2152 (Si–H). **8**: colourless gum. ^{1}H NMR δ 0.8 (m, 3H), 1.32 (m, 2H), 1.50 (m, 2H), 3.69 and 3.77 (t, *J* 6.0 Hz, 2H), 5.24 (s, 0.14 H, Si–H), 5.66 (s, 1H, Si–H), 7.73 (m, 4H); ^{29}Si δ −30.3, −12.1; IR (film, $\tilde{\nu}/\text{cm}^{-1}$) 2122 (Si–H).

References

1 H. R. Allcock, *Adv. Mater.*, 1994, **6**, 106.

2 B. M. Novak, *Adv. Mater.*, 1993, **5**, 422.

3 L. J. Henderson and T. M. Keller, *Macromolecules*, 1994, **27**, 1660.

4 Y. Chujo, N. Takizawa and T. Sakurai, *J. Chem. Soc., Chem. Commun.*, 1994, 227.

5 M. D. Curtis and P. S. Epstein, *Adv. Organomet. Chem.*, 1981, **19**, 213.

6 J. L. Speier and R. E. Zimmerman, *J. Am. Chem. Soc.*, 1955, **77**, 6395.

7 Y. Yagihashi, K. Takatsuna, Y. Okumura, T. Nakano and H. Matsumoto, the 58th Spring Annual Meeting of Japan Chemical Society, Abstract 1 IIA 31, Kyoto, 1989; K. Yokoyama, K. Taniguchi and Y. Kiso, *Jap. Pat. Appl.*, 88/251,577; *Chem. Abstr.*, 1990, **112**, 8036t; Y. Yagihashi, K. Takatsuna and Y. Okumura, *Jap. Pat. Appl.*, 89/3,907; *Chem. Abstr.*, 1991, **114**, 7467p.

8 R. J. P. Corriu, G. F. Lanneau and B. P. S. Chauhan, *Organometallics*, 1993, **12**, 2001.

9 H. Tobita, K. Ueno, M. Shimoi and H. Ogino, *J. Am. Chem. Soc.*, 1990, **112**, 3415; K. H. Pannell, M.-C. Brun, H. Sharma, K. Jones and S. Sharma, *Organometallics*, 1994, **13**, 1075; Y. Tanaka, H. Yamashita and M. Tanaka, *Organometallics*, in the press.

10 R. J. P. Corriu and J. J. E. Moreau, *J. Chem. Soc., Chem. Commun.*, 1973, 38.