

Metal-catalyzed routes to rings, chains, and macromolecules based on inorganic elements*

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Abstract: In this perspective article, some of our recent work directed at the development of new catalytic routes to rings, chains, and macromolecules based on main group and transition elements will be discussed.

Keywords: Catalytic dehydrocoupling; inorganic polymers; Lewis acid–Lewis base adducts; ring-opening polymerization; polyferrocenes.

INTRODUCTION

Transition-metal catalysis has revolutionized the synthesis of organic molecules and polymers. In contrast, the development of analogous methods for the formation of homonuclear or heteronuclear bonds between inorganic elements is relatively unexplored. Nevertheless, the discovery of new synthetic methods, which can complement the classical reactions used in inorganic chemistry such as salt eliminations, is likely to be of key future importance for the general development of molecular and macromolecular inorganic chemistry.

The catalytic dehydropolymerization of silanes, germanes, and stannanes originated through key discoveries in the mid-1980s, and is now well developed and represents a key advance [1–5]. More recently, homodehydrocoupling chemistry has been extended to include P–P bond formation [6], and catalytic heterodehydrocoupling reactions to form, for example, B–Si [7], Si–P [8], and Si–O bonds [9,10] have also been reported. The use of metal complexes to catalyze ring-opening polymerization (ROP) reactions also represents a highly promising methodology to prepare macrocycles and polymers containing inorganic elements. For example, the discovery of late transition-metal catalysts for the ROP of silaheterocycles was first discovered in the 1960s, with the advantage that polymers such as polycarbosilanes can be formed under relatively mild conditions [11,12].

Our group has a fundamental interest in the development of new routes to rings, chains, and macromolecules based on main group and transition elements. Polymers containing inorganic elements are of particular importance as a result of their promise as functional macromolecular [13] and supramolecular [14] materials. In this perspective article, some of our recent efforts in the area of new catalytic routes to inorganic rings, chains, and macromolecules are discussed.

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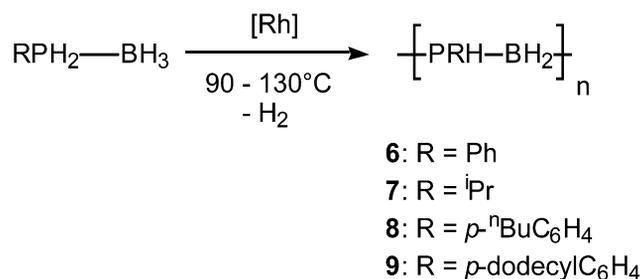
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served; at 120 °C, no cyclic products and only a minor amount (<5 %) of **3** was observed. The catalytic activity of other transition-metal complexes (e.g., Ti, Ru, Rh, Ir, Pd, Pt) for the formation of **3** was also demonstrated. In general, Rh(I) and Rh(III) complexes were found to possess the highest catalytic dehydrocoupling activities [17].

Heating of the sterically encumbered adduct $t\text{Bu}_2\text{PH}\cdot\text{BH}_3$ in the presence of $[\text{Rh}(1,5\text{-cod})_2][\text{OTf}]$ or $\text{Rh}_6(\text{CO})_{16}$ at 140 °C also results in dehydrocoupling to form the linear compound $t\text{Bu}_2\text{PH}-\text{BH}_2-\text{P}'\text{Bu}_2-\text{BH}_3$ (**4**). The use of the chlorinated catalysts $[\text{Rh}(\mu\text{-Cl})(1,5\text{-cod})]_2$ or $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ at 160 °C was found to give an inseparable mixture of **4** and the chlorinated compound $t\text{Bu}_2\text{PH}-\text{BH}_2-\text{P}'\text{Bu}_2-\text{BH}_2\text{Cl}$ (**5**) (Scheme 1) [18].

Catalytic dehydrocoupling of primary phosphine–borane adducts; synthesis of polyphosphinoboranes

In the early 1960s, the uncatalyzed pyrolysis of the primary phosphine–borane adduct $\text{PhPH}_2\cdot\text{BH}_3$ at 100–150 °C for 13 h was reported to give a benzene-soluble polymer $[\text{PhPH}-\text{BH}_2]_n$ with a molecular weight (M_n) of 2150. Prolonged heating at elevated temperatures (250 °C) led to the formation of insoluble material, without significant molecular weight increase of the benzene-soluble fraction (maximum $M_n = 2630$) [19]. We found that heating of a toluene solution of $\text{PhPH}_2\cdot\text{BH}_3$ at reflux (110 °C) in the presence of $[\text{Rh}(1,5\text{-cod})_2][\text{OTf}]$ (0.5–1 mol % Rh) for 15 h led to dehydrogenative coupling to afford poly(phenylphosphinoborane) $[\text{PhPH}-\text{BH}_2]_n$ (**6**) as an off-white powder (Scheme 2) [16,17]. Static light scattering (SLS) of **6** in THF showed the material to be of relatively low molecular weight of $M_w = 5600$. However, dehydrocoupling in the absence of solvent and modification of the reaction temperatures led to higher-molecular-weight polymer. Thus, neat $\text{PhPH}_2\cdot\text{BH}_3$ in the presence of $[\text{Rh}(\mu\text{-Cl})(1,5\text{-cod})]_2$ or $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ (0.6 mol % Rh) was heated at 90 °C for 3 h, and then at 130 °C for 3 h. The reaction mixture gradually became viscous during the heating stage at 90 °C and completely solidified after 3 h at 130 °C. The polymer obtained was spectroscopically identical to the material prepared in toluene, but SLS confirmed a higher molecular weight of $M_w = 33\,300$.



Scheme 2

Prolonged heating of **6** at 130 °C in the presence of catalyst afforded insoluble products that were found to swell significantly in THF or CH_2Cl_2 . As branching positions could not be detected in the ^{31}P and ^{11}B NMR spectra, the polymers may either become lightly cross-linked through additional inter-chain P–B coupling, or may increase in molecular weight above the solubility limit. We confirmed that in the absence of a transition-metal catalyst, the thermally induced dehydrocoupling of $\text{PhPH}_2\cdot\text{BH}_3$ proceeds very slowly and forms only low-molecular-weight materials [17].

Several other primary phosphine–borane adducts have been shown to undergo metal-catalyzed dehydrocoupling to form polyphosphinoboranes (**7**: R = *i*Bu; **8**: *p*-ⁿBuC₆H₄; **9**: *p*-dodecyl-C₆H₄; Scheme 2). The alkyl-substituted adduct $t\text{BuPH}_2\cdot\text{BH}_3$ was found to require more forcing dehydrocoupling conditions (15 h at 120 °C) in order to form **7** [17,20]. This is likely due to the decreased polarity of the P–H bond as a result of the strong (+)-inductive effect of the alkyl group. SLS studies of **7** in

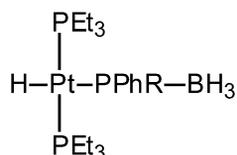
THF gave molecular weight values of $M_w = 13\,100$. In contrast to **6** and **7**, molecular weight analysis of **8** and **9** by GPC gave M_w values of ca. 19 000 and 168 000 (relative to polystyrene standards), respectively.

Wide-angle X-ray scattering of solution cast films of **6** and **8** indicated that the polymers were essentially amorphous [20]. This was expected, as the dehydropolymerization process should not provide any stereochemical control, and thus atactic polymers would result. Glass-transition temperatures (T_g) below that of room temperature were found for polymers **7–9**, which may be attributed to the high degree of torsional flexibility in the polymer main chains. This may be a result of the long B–P bonds (1.9–2.0 Å), which would reduce the steric interference between the side groups, facilitating polymer motion and thereby lowering T_g . Thermogravimetric analysis of **6** indicated the onset of decomposition at 160 °C with a ceramic yield of 75–80 % upon heating to 1000 °C [20]. Lower onset temperatures of 120 °C were found for both **7** and **8**. Substantial weight loss was observed upon heating to 1000 °C, resulting in moderate ceramic yields of 40–45 % and 35–40 % for **7** and **8**, respectively. The high ceramic yield of **6** suggests that it may function as a useful preceramic polymer for BP-based materials [20]. Indeed, preliminary pyrolysis studies of **6** at 1000 °C under nitrogen show the formation of boron phosphide as the major crystalline component by powder X-ray diffraction.

Mechanistic studies of catalytic dehydrocoupling of phosphine–borane adducts

An understanding of the dehydropolymerization mechanism is of considerable interest, and could allow for the development of more efficient catalysts in order to access higher-molecular-weight polymers [21]. Initial reactions involving insertion of the metal center into either P–H or B–H bonds, followed by subsequent σ -bond metathesis and/or oxidative addition/reductive elimination steps may define the catalytic cycle.

We found that the reaction of $\text{Pt}(\text{PEt}_3)_3$ with $\text{PhRPH}\cdot\text{BH}_3$ results in insertion of the Pt center into the P–H bond of the adduct to afford the *trans* hydride complexes $[\text{PtH}(\text{PPhR}\cdot\text{BH}_3)(\text{PEt}_3)_2]$ (**10**: R = H; **11**: R = Ph) [22,23]. However, subsequent B–P bond formation at the Pt center was not observed. This lack of reactivity may imply that metal–boryl complexes may be a key intermediate in the catalytic cycle, or that the bond-forming processes involve more complicated reaction sequences. In addition, a heterogeneous process involving metal colloids has not been ruled out.



10: R = H

11: R = Ph

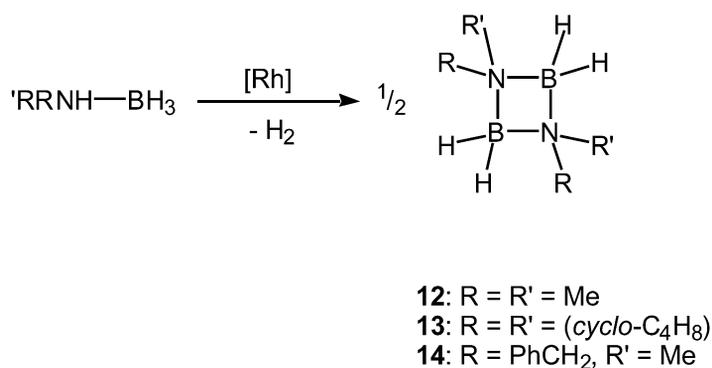
Metal-catalyzed dehydrocoupling routes to aminoboranes

The generalization of this catalytic dehydrocoupling methodology to other group 13/15 systems was of particular interest to our group. It is well known that primary and secondary amine–borane adducts undergo thermally induced dehydrocoupling at elevated temperatures (>100 °C) to yield cyclic amino-borane $[\text{H}_2\text{B}-\text{NRR}']_x$ ($x = 2$ or 3) and borazine derivatives $[\text{HB}-\text{NR}]_3$ [24]. For example, $\text{Me}_2\text{NH}\cdot\text{BH}_3$ thermally eliminates hydrogen at or above 130 °C in the condensed phase to form the cyclic amino-borane dimer $[\text{Me}_2\text{N}-\text{BH}_2]_2$ (**12**) [25]. We anticipated that the use of a transition-metal catalyst might allow the dehydrocoupling to be achieved under milder conditions. This would result in improved

routes to boron–nitrogen rings and chains, which could serve as useful precursors to boron–nitrogen-based materials.

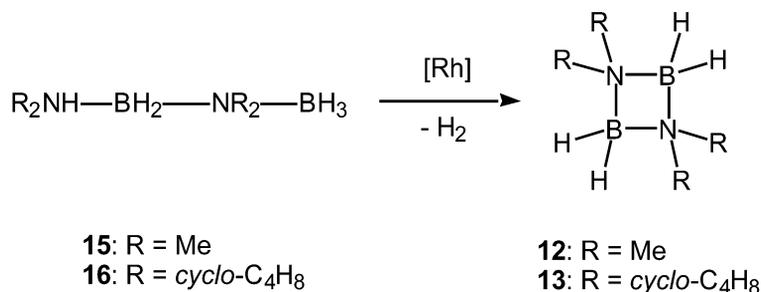
Catalytic dehydrocoupling of secondary amine–borane adducts

Treatment of the secondary amine–borane adduct $\text{Me}_2\text{NH}\cdot\text{BH}_3$ with a catalytic amount of $[\text{Rh}(\mu\text{-Cl})(1,5\text{-cod})_2]$ (0.5 mol % Rh), either in the melt at 45 °C, or in solution at 25 °C, was found to result in the formation of the cyclic dimer $[\text{Me}_2\text{N}-\text{BH}_2]_2$ (**12**) in high yields (Scheme 3) [26,27]. This method represents a significant improvement over the uncatalyzed route to **12**, which requires temperatures of up to 130 °C [25]. The catalytic activity of other transition-metal complexes (e.g., Ti, Ru, Rh, Ir, Pd) for the formation of **12** was also demonstrated. It was found that treatment of cyclic and unsymmetrically substituted adducts with a Rh precatalyst also gave the cyclic dimers $[\text{RR}'\text{N}-\text{BH}_2]$ (**13**: $\text{R} = \text{R}' = \text{cyclo-C}_4\text{H}_8$; **14**: $\text{R} = \text{Me}$, $\text{R}' = \text{CH}_2\text{Ph}$) under similar mild conditions of 25–45 °C (Scheme 3) [27].



Scheme 3

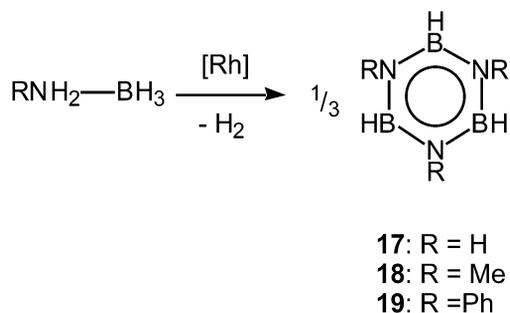
One of the proposed intermediates in the catalytic cycle is the linear compound $\text{R}_2\text{NH}-\text{BH}_2-\text{NR}_2-\text{BH}_3$ (**15**: $\text{R} = \text{Me}$; **16**: $\text{R} = \text{cyclo-C}_4\text{H}_8$), which would result from a single intermolecular dehydrocoupling reaction between two adduct species. Treatment of **15** and **16** with a Rh precatalyst was found to result in the formation of **12** and **13** (Scheme 4), most likely via an intramolecular dehydrocoupling reaction that gives the cyclic dimer [27].



Scheme 4

Catalytic dehydrocoupling of primary amine–borane adducts and $\text{NH}_3 \cdot \text{BH}_3$

The uncatalyzed formation of borazine directly from $\text{NH}_3 \cdot \text{BH}_3$ typically requires high-temperature forcing conditions ($>150\text{ }^\circ\text{C}$) [28]. However, treatment of a glyme solution of $\text{NH}_3 \cdot \text{BH}_3$ with a catalytic amount of $[\text{Rh}(\mu\text{-Cl})(1,5\text{-cod})_2]$ (1.5 mol % Rh) was found to result in the formation of borazine $[\text{HB-NH}]_3$ (**17**) after ca. 48–84 h at $45\text{ }^\circ\text{C}$ (Scheme 5) [26,27]. Complete conversion to **17** was confirmed by the ^{11}B NMR spectrum of the reaction mixture. However, isolation by vacuum fractionation routinely yielded only small quantities (ca. 10 %) of pure **17**. This was attributed to undesirable intermolecular dehydrocoupling reactions of the intermediates or the product itself to give nonvolatile coupled species. The primary adducts $\text{RNH}_2 \cdot \text{BH}_3$ were also found to undergo similar mild catalytic dehydrocoupling reactions to afford the substituted borazines $[\text{HB-NR}]_3$ (**18**: R = Me; **19**: R = Ph) (Scheme 5). In the case of the methyl derivative **18**, the intermediate cyclic trimer $[\text{H}_2\text{B-HNMe}]_3$ was initially formed in solution after 4–6 h, and slowly converted to **18** by subsequent dehydrocoupling reactions over 48–72 h. This difference in the dehydrocoupling rates for the step-wise loss of hydrogen from $\text{MeNH}_2 \cdot \text{BH}_3$ is also reflected in the uncatalyzed thermal route to **18**. Initial pyrolysis at $100\text{ }^\circ\text{C}$ gives the intermediate trimer $[\text{H}_2\text{B-HNMe}]_3$, which then has to be heated to $200\text{ }^\circ\text{C}$ in order to eliminate the second equivalent of hydrogen to yield **18** [29].



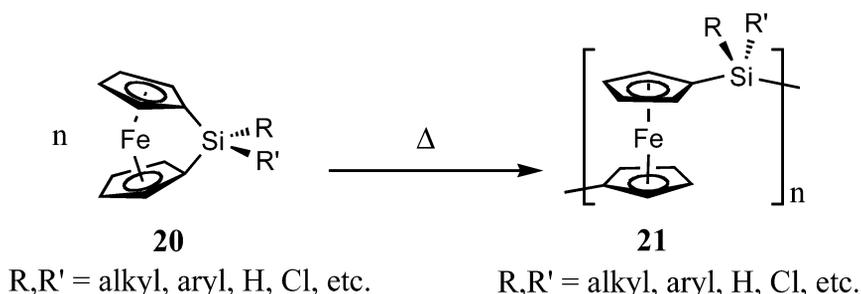
Scheme 5

This new mild route to boron–nitrogen rings may be of significant importance, as borazine derivatives have been shown to function as useful precursors to cyclo-linear polymers and boron nitride ceramics [30]. Although the mechanism of the dehydrocoupling reactions are unclear, the rapid discoloration of solutions of amine–borane adducts in the presence of Rh precatalysts to black, opaque media suggested that a heterogeneous process involving Rh(0) colloids may be involved. Recent work has allowed us to obtain convincing evidence that the catalytic dehydrocoupling of amine–borane adducts is indeed heterogeneous, whereas the process is homogeneous of phosphine–borane analogs [27]. Future work in the area of catalytic dehydrocoupling of group 13/15 adducts will involve the extension of this methodology to heavier element analogs such as phosphine–gallanes, $\text{R}_2\text{PH} \cdot \text{GaH}_3$, etc. with the intention of developing new facile routes to rings, clusters, and polymers. Possible applications of the dehydrocoupling chemistry in organic synthesis—such as catalytic transfer hydrogenations [31]—will also be explored.

CATALYTIC ROP OF [1]FERROCENOPHANES

We initiated studies on ROP routes to metal-containing polymers approximately a decade ago. We targeted potential monomers with strained structures so that ROP would be thermodynamically favorable. Among the species studied were silicon-bridged [1]ferrocenophanes **20** ([1]silaferrocenophanes), the first examples of which were prepared by Osborne and coworkers in England in the mid-1970s [32]. These strained molecules are readily available on a substantial ($>100\text{ g}$) scale from the reaction of

dilithioferrocene.tetramethylethylenediamine ($\text{fcLi}_2\cdot\text{TMEDA}$) with dichloroorganosilanes $\text{RR}'\text{SiCl}_2$. We found that these species polymerized when heated in the melt in sealed evacuated tubes at 120–150 °C to afford high-molecular-weight ($M_n > 10^5$) polyferrocenylsilanes **21** (Scheme 6) [33].



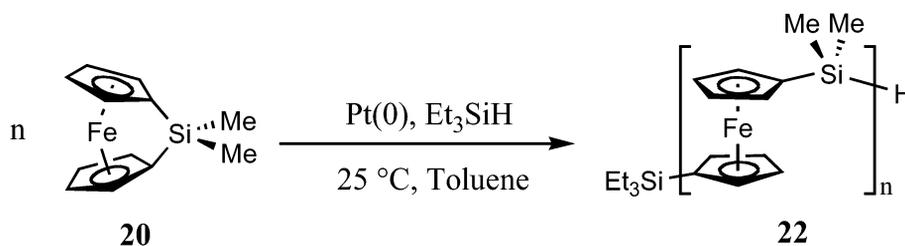
Scheme 6

Since the initial ROP discovery, we and others have expanded this ROP methodology to a range of analogous strained monomers which contain other single-atom bridges ($\text{E} = \text{Ge}, \text{P}, \text{Sn}, \text{S}, \text{etc.}$), two-atom bridges ($\text{E} = \text{C}-\text{C}, \text{C}-\text{P}, \text{C}-\text{S}, \text{etc.}$) and transition metals (e.g., Ru, Cr) and/or different π -hydrocarbon rings (arenes) [34,35]. The potential applications of many of these polymers as, for example, redox-active materials with uses in colloidal crystal photonic devices, thermal precursors to magnetic films, micro- and nanostructures, liquid-crystalline materials, charge-dissipative coatings, and variable refractive-index sensing materials are currently under study [36,37].

Thermal ROP provides an excellent method for preparing high-molecular-weight polymetalloenes, but the polydispersities are broad (polydispersities, PDIs, = 1.5–2.5) and no control of molecular weight has been possible to date [33,34]. Subsequently, living anionic ROP routes to polymetalloenes using initiators such as $n\text{BuLi}$ at ambient or subambient temperatures have been developed [38,39]. These methods have permitted unprecedented control of main chain metal-containing polymer architectures. In particular, materials with controlled molecular weights and narrow molecular weight distributions and access provided to the first block copolymers with metals in the main chain have been prepared. This has created unique opportunities for the generation of self-assembled, supramolecular materials. However, stringent experimental requirements need to be met for anionic ROP to be successful. Due to the low concentration of highly reactive anionic chain propagating sites, impurity levels need to be extremely low. This led to interest in similarly mild, but more convenient methods for preparing polymetalloenes via ROP.

Transition-metal-catalyzed ROP of silicon-bridged [1]ferrocenophanes was reported in 1995 and occurs in solution at room temperature in the presence of $\text{Pt}^{\text{II}}, \text{Pt}^0, \text{Rh}^{\text{I}}$, and Pd^{II} precatalysts [40,41]. Transition-metal-catalyzed ROP is a mild method which, significantly, has the key advantage over anionic methods in that extensive monomer and solvent purification is unnecessary. This route has now been developed to the stage where considerable control over polymetalloene architectures is possible [42,43]. For example, [1]silaferrocenophanes with different cyclopentadienyl rings can undergo regio-regular transition-metal-catalyzed ROP, whereas thermal ROP affords a regioirregular polyferrocenylsilane (PFS) material [43].

Transition-metal-catalyzed ROP of silicon-bridged [1]ferrocenophanes in the presence of Si–H containing species such as Et_3SiH allows the formation of PFSs **22** (Scheme 7) with a molecular weight control dictated by the initial ratio of monomer to silane (Fig. 1). However, unlike the case of anionically ring-opened materials, the polydispersities are appreciable (typically ca. 1.4–1.5 vs. <1.1) [42,43].



Scheme 7

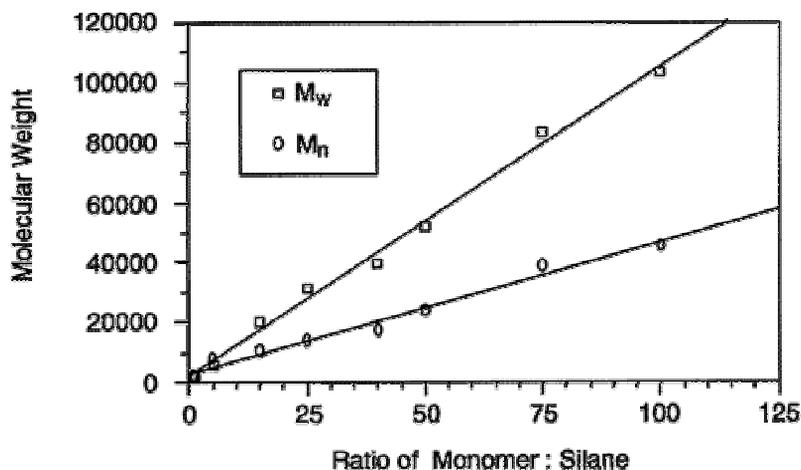
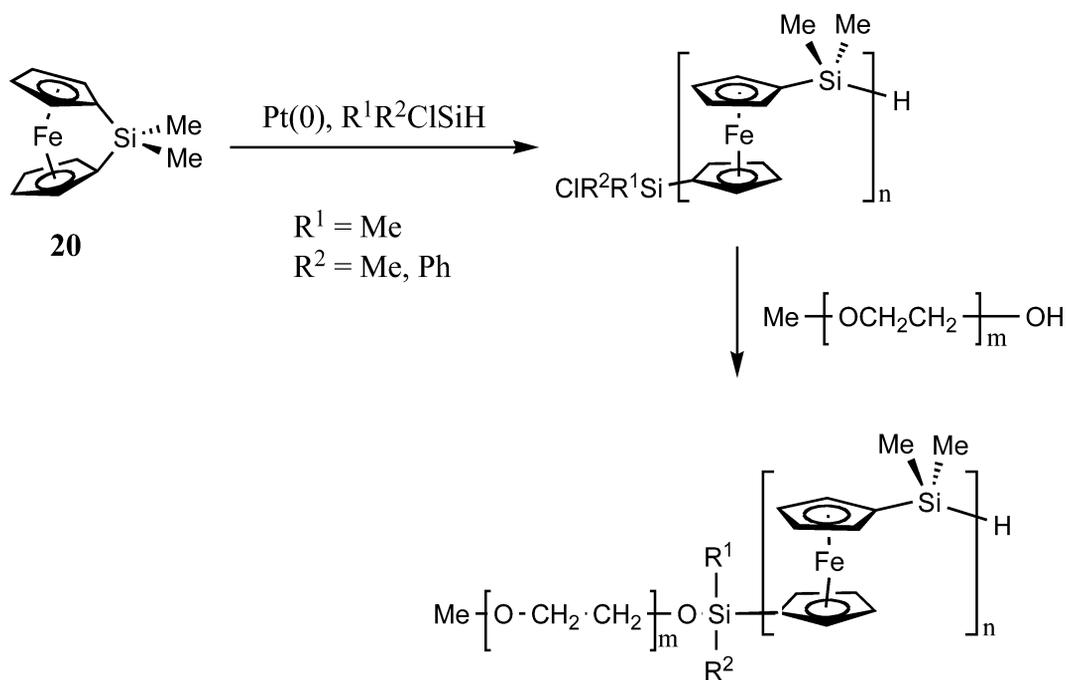


Fig. 1 Plot of the M_w and M_n values of the mole ratio of monomer:silane for the synthesis of polyferrocenylsilane, **22**. Reproduced from ref. [43] with permission.

This transition-metal-catalyzed ROP methodology has been extended toward the formation of comb and star copolymers with the appropriate Si–H source [43]. Block copolymers can be formed via the addition of macromonomers with Si–H end groups [43]. For example, a PFS diblock copolymer with a poly(ethylene oxide) (PEO) block has been prepared which is soluble in water provided the organic block is sufficiently long [44]. The use of polysiloxane macromonomers with two Si–H termini yields novel PFS-*b*-polydimethylsiloxane-*b*-PFS triblock copolymers [43]. It should be noted that, unlike anionic polymerization, the transition-metal-catalyzed ROP route also provides block copolymers with appreciable polydispersities (ca. 1.4) and subsequent fractionation is necessary to access narrow PDI samples.

In addition, telechelic polyferrocenylsilanes with Si–Cl and Si–H end-functionalities were prepared via transition-metal-catalyzed ROP of **20** ($R = R' = \text{Me}$) using chlorosilanes as the terminating agents. Chlorosilanes were found to be much more effective terminating agents than Et_3SiH for the “capping” of polyferrocenylsilane chains. Further functionalization was achieved by reaction of the Si–Cl bond with poly(ethyleneglycol)methyl ether, which yielded poly(ethylene oxide-*b*-ferrocenylsilane) diblock copolymers (Scheme 8) [45].

The mechanism of the platinum-catalyzed ROP of [1]silaferrocenophanes is of interest in our research group. The ROP is proposed to proceed through initial formation of a [2]platinasiliferrocenophane via oxidative-addition to the platinum center [46]. Colloidal platinum is proposed to subsequently form, and oxidative-addition and reductive-elimination of the [1]silaferrocenophane at the colloid surface is believed to allow growth of the polymer. End-group analysis experiments, and the discovery that mercury inhibits ROP, support this proposition [46]. However, even in the presence of mercury, a small amount of polymer is formed very slowly, therefore, the overall mechanism of the transition-metal-cat-



Scheme 8

alyzed ROP of [1]silaferrocenophanes may be more complex and could involve both homogeneous and heterogeneous mechanisms [46].

A typical platinum-catalyzed ROP of a [1]silaferrocenophane achieves very high conversion in 24 h [47]. Remarkably, catalytic amounts of cationic rhodium(I) complexes $[\text{Rh}(\text{1,5-cod})_2]\text{A}$ ($\text{A} = \text{OTf}$, PF_6) have been found to initiate the ROP of [1]silaferrocenophanes with quantitative conversion within 2 min [47]. Prolonged exposure of the high-molecular-weight polymers to the catalyst solution, however, led to gradual cleavage of the polymer backbone. In addition, $[\text{Rh}(\text{1,5-cod})(\text{dmpe})]\text{OTf}$ [$\text{dmpe} = \text{bis}(\text{dimethylphosphinomethane})$] was also explored as a catalyst, and although this complex was significantly less active, it represents the first phosphine-ligated transition-metal species to be catalytically active toward the ROP of **20** ($\text{R} = \text{R}' = \text{Me}$). Moreover, no subsequent cleavage of the resulting polyferrocenylsilane chains was detected in this case [48]. It appears probable that colloidal Rh generated from $[\text{Rh}(\text{1,5-cod})_2]\text{A}$ complexes is a highly active ROP catalyst and the subsequent cleavage reactions may be associated with oxidation of the ferrocene centers.

Transition-metal-catalyzed ROP of ferrocenophanes represents a facile and effective method to form high-molecular-weight polyferrocenes. Future work in this area includes the continued use of this approach to prepare polyferrocenylsilanes of controlled molecular weight for a variety of materials science applications and the use of platinum-catalyzed methods for the ring-opening of other strained monomers. For example, Pt-catalyzed methods have been successfully used to prepare polyferrocenylsilane microspheres using a precipitation polymerization methodology [48]. In addition, recently redox-active vesicles have been accessed via the aqueous self-assembly of a PFS block copolymer with a hydrophilic PFS block [49].

SUMMARY

Metal-catalyzed processes appear to show exceptional potential for the creation of new macromolecules based on inorganic elements. Further studies of the mechanism of these reactions are critical to allow

more efficient and general catalysts to be developed. Of particular significance is the potential to generate polymers with controlled molecular weights or morphologies, or with interesting architectures such as block copolymers. The latter materials offer exceptional opportunities for the creation of novel supramolecular materials via self-assembly processes [14].

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