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

Cory A. Jaska, Alexandra Bartole-Scott and Ian Manners *

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6. E-mail: imanners@chem.utoronto.ca

This Perspective discusses the application of transition metal-catalyzed reactions to the formation of rings, oligomeric chains and macromolecules based on p-block and d-block elements. For example, the catalytic dehydrocoupling of Group 13–Group 15 Lewis acid–Lewis base adducts (*e.g*. 1° or 2° phosphine–boranes or amine–boranes) has been shown to yield high molecular weight polyphosphinoboranes, cyclic aminoborane species or borazines. The metal-catalyzed ring-opening polymerization (ROP) of silicon-bridged [1]ferrocenophanes allows molecular weight control through the use of silane capping agents, and permits the synthesis of block copolymers *via* the use of reactive polymer end-groups.

1. Introduction

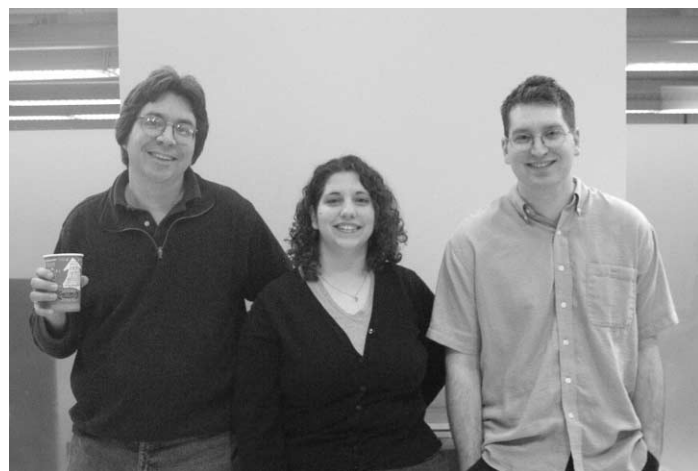Transition metal catalysis plays a profound role in organic synthesis, allowing for the controlled formation of C–C, C–N and C–O bonds, in addition to many other useful transformations. In contrast, the development of analogous methods for the formation of homonuclear or heteronuclear bonds between inorganic 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 1980's, and is now well-developed and represents an important 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 use of late transition metal catalysts for the ROP of silaheterocycles was first

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Left to right: Ian Manners, Alexandra Bartole-Scott and Cory Jaska

Ian Manners was born in London, England, in 1961 and received his B.Sc. and Ph.D. degrees at the University of Bristol in the UK. After postdoctoral work in Germany and the US he joined the faculty at the University of Toronto, Canada as an Assistant Professor in 1990. He was promoted to Associate Professor in 1994, to Full Professor in 1995, and since 2001 has held a Canada Research Chair in Inorganic and Polymer chemistry. Manners' research interests focus on the synthesis, properties and applications of inorganic molecules, macromolecules, and supramolecular materials. He has received a range of awards and these include a Corday-Morgan Medal from the UK (1997), an Alfred P. Sloan Fellowship from the USA (1994–1998), and the Steacie Prize from Canada (2000). He is the author or co-author of over 300 publications and holds or co-holds 10 patents.

Alexandra Bartole-Scott was born in Toronto, Ontario in 1977. She graduated from the University of Toronto with an Honours B.Sc. degree in Chemistry. She joined Prof. Ian Manners' group as an M.Sc. student in September 2000. Her Ph.D. thesis has focused on applications of polyferrocenylsilanes in material science, telechelic polyferrocenylsilanes and the synthesis and polymerization of novel strained metal-containing rings. She has received two University of Toronto Fellowships (2001–2003). Her main scientific interests include the study of metal-containing polymers in materials chemistry and the development of new monomers.

Cory Jaska was born in Brandon, Manitoba, Canada in 1976. He graduated from the University of Calgary in 1999 with B.Sc. degrees in both Chemistry and Physics, while working with Prof. Tris Chivers in the area of tellurium–nitrogen chemistry. Since joining Prof. Ian Manners' group in 1999, his Ph.D. thesis has focused on the development of new catalytic dehydrocoupling routes to rings and polymers involving elements from Groups 13 and 15. He has received an Ontario Graduate Scholarship in Science and Technology (2001–2002) and a Natural Science and Engineering Research Council (NSERC) of Canada postgraduate fellowship (2002–2004). His scientific interests involve the incorporation of main group elements into polymers.

discovered in the 1960's, 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 work directed at the development of new catalytic routes to inorganic rings, chains, and macromolecules is discussed.

2. Catalytic dehydrocoupling of Group 13–Group 15 Lewis acid–Lewis base adducts

The preparation of polymers with backbones of alternating phosphorus and boron atoms attracted significant attention in the 1950's and early 1960's as a consequence of their anticipated high thermal stability and resistance to oxidation and hydrolysis. The main synthetic route explored at that time involved thermally-induced dehydrocoupling of phosphine–borane adducts at 180–200 °C, to afford predominantly six-membered rings. Only negligible yields of low molecular weight, partially characterized polymers were claimed, mainly in patents.[15] More recently we have shown that the dehydrocoupling process can be catalyzed by late transition metal complexes.[16,17] This has permitted the formation of six- and eight-membered phosphinoborane rings under more facile conditions, novel linear oligomeric chains, and high molecular weight polyphosphinoboranes.

Catalytic dehydrocoupling of secondary phosphine–borane adducts

The uncatalyzed dehydrocoupling of the secondary phosphine–borane adduct $Ph_2PH \cdot BH_3$ at 170 °C gives a mixture of the cyclic trimer $[Ph_2P–BH_2]_3$ (1) and tetramer $[Ph_2P–BH_2]_4$ (2) in an 8 : 1 ratio. However, upon heating $Ph_2PH \cdot BH_3$ in the presence of $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ or $[Rh(1,5\text{-}cod)_2][OTf]$ (0.5–1 mol% Rh) at 120 °C, 1 and 2 are formed in a 2 : 1 ratio (Scheme 1). Upon lowering the temperature to 90 °C, the novel linear compound $Ph_2PH–BH_2–PPh_2–BH_3$ (3) was formed as the exclusive product (Scheme 1; Fig. 1).[16,17] In the absence of catalyst at 90 °C, no conversion of $Ph_2PH \cdot BH_3$ was observed; 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]
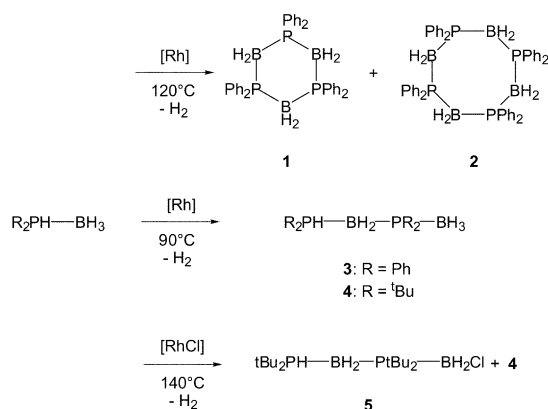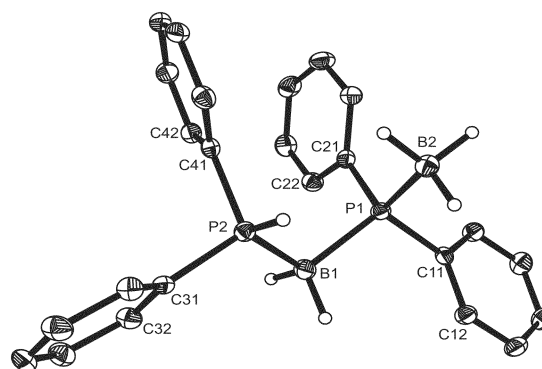

Fig. 1 Molecular structure of 3 by X-ray diffraction. Reproduced from ref. 16 with permission.

Heating of the sterically encumbered adduct $^tBu_2PH \cdot BH_3$ in the presence of $[Rh(1,5\text{-}cod)_2][OTf]$ or $Rh_6(CO)_{16}$ at 140 °C also resulted in dehydrocoupling to form the linear compound $^tBu_2PH–BH_2–P^tBu_2–BH_3$ (4). The use of the chlorinated catalysts $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ or $RhCl_3 \cdot 3H_2O$ at 160 °C was found to give an inseparable mixture of 4 and the chlorinated compound $^tBu_2PH–BH_2–P^tBu_2–BH_2Cl$ (5) (Scheme 1).[18]

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

In the early 1960's, the uncatalyzed pyrolysis of the primary phosphine–borane adduct $PhPH_2 \cdot BH_3$ at 150–250 °C for 13 h was reported to give a benzene-soluble polymer $[PhPH–BH_2]_n$ with a molecular weight (M_n) of 2,150. 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 $M_n = 2,630$).[19] We found that heating of a toluene solution of $PhPH_2 \cdot BH_3$ at reflux (110 °C) in the presence of $[Rh(1,5\text{-}cod)_2][OTf]$ (0.5–1 mol% Rh) for 15 h led to dehydrogenative coupling to afford poly(phenylphosphinoborane) $[PhPH–BH_2]_n$ (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 with $M_w = 5,600$. However, dehydrocoupling in the absence of solvent and modification of the reaction temperatures led to higher molecular weight polymer. Thus, neat $PhPH_2 \cdot BH_3$ in the presence of $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ or $RhCl_3 \cdot 3H_2O$ (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 $M_w = 33,300$.
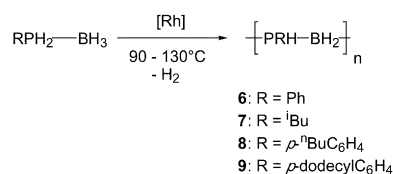
Scheme 2

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 crosslinked through additional interchain 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 $PhPH_2 \cdot BH_3$ proceeds very slowly and forms only low molecular weight, poorly defined materials.[17]

[Rh] = Rhodium Catalyst
[RhCl] = Chlorine containing Rh Catalyst

Scheme 1

Several other primary phosphine–borane adducts have been shown to undergo metal-catalyzed dehydrocoupling to form polyphosphinoboranes (**7**: R = iBu; **8**: p-nBuC6H4; **9**: p-dodecyl-C6H4; Scheme 2). The alkyl substituted adduct iBuPH2·BH3 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 Pt(PEt3)3 with PhRPH·BH3 results in insertion of the Pt center into the P–H bond of the adduct to afford the *trans* hydride complexes [PtH(PPhR·BH3)(PEt3)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.

PEt3
|
H—Pt—PPhR—BH3
|
PEt3

10: R = H
11: R = Ph
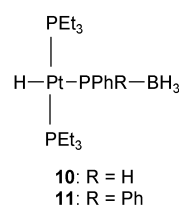
Metal-catalyzed dehydrocoupling routes to aminoboranes

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 aminoboranes [H2B–NRR′]x (x = 2 or 3) and borazine

derivatives [HB–NR]3.[24] For example, Me2NH·BH3 thermally eliminates hydrogen at or above 130 °C in the condensed phase to form the cyclic aminoborane dimer [Me2N–BH2]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 polymers and ceramic materials.

Catalytic dehydrocoupling of secondary amine–borane adducts

Treatment of the secondary amine–borane adduct Me2NH·BH3 with a catalytic amount of [Rh(μ-Cl)(1,5-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 [Me2N–BH2]2 (**12**) in high yields (Scheme 3; Fig. 2).[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 [RR′N–BH2]2 (**13**: R = R′ = 1,4-C4H8; **14**: R = CH2Ph, R′ = Me) under similar mild conditions of 25–45 °C (Scheme 3).[27]

R′RNH—BH3 —[Rh]/–H2→ ½

12: R = R′ = Me
13: R = R′ = (1,4-C4H8)
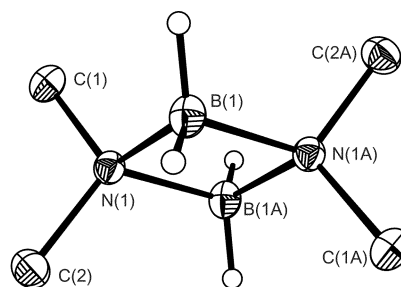**14**: R = PhCH2, R′ = Me
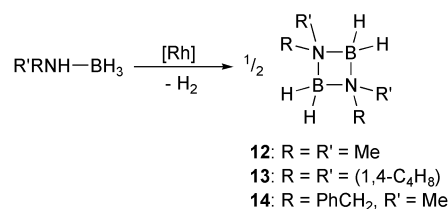
Scheme 3

Fig. 2 Molecular structure of **12** by X-ray diffraction.

One of the proposed intermediates in the catalytic cycle is the linear compound R2NH–BH2–NR2–BH3 (**15**: R = Me; **16**: R = 1,4-C4H8), 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]

R2NH—BH2—NR2—BH3 —[Rh]/–H2→

15: R = Me
16: R = 1,4-C4H8

12: R = Me
13: R = 1,4-C4H8
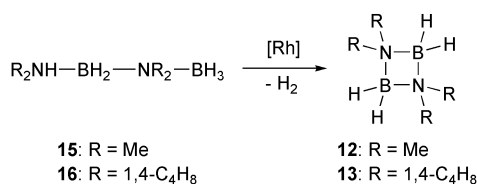
Scheme 4

### Catalytic dehydrocoupling of primary amine–borane adducts and NH3·BH3

The uncatalyzed formation of borazine directly from NH3·BH3 typically requires high temperature forcing conditions (> 150 °C).[28] However, treatment of a glyme solution of NH3·BH3 with a catalytic amount of [Rh(μ-Cl)(1,5-cod)]2 (1.5 mol%

Rh) was found to result in the formation of borazine [HB–NH]$_3$ (**17**) after *ca.* 48–84 h at 45 °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 non-volatile coupled species. The primary adducts RNH$_2$·BH$_3$ were also found to undergo similar mild catalytic dehydrocoupling reactions to afford the substituted borazines [HB–NR]$_3$ (**18**: R = Me; **19**: R = Ph) in reasonable isolated yields (40–60%) (Scheme 5). In the case of the methyl derivative **18**, the intermediate cyclic trimer [H$_2$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 MeNH$_2$·BH$_3$ is also reflected in the uncatalyzed thermal route to **18**. Initial pyrolysis at 100 °C gives the intermediate trimer [H$_2$B–HNMe]$_3$, which then has to be heated to 200 °C in order to eliminate the second equivalent of hydrogen to yield **18**.[29]
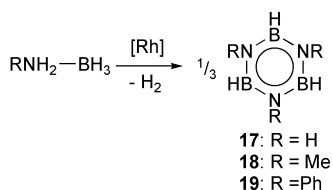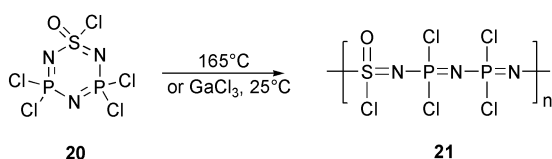

Scheme 5

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 is unclear, the rapid discolouration of solutions of amine–borane adducts in the presence of Rh precatalysts to afford black, opaque media suggested that a heterogeneous process involving Rh(0) colloids may be involved.[27] Future work in the area of catalytic dehydrocoupling of Group 13/15 adducts will involve the extension of this methodology to heavier element analogues such as amine–alanes, R$_2$NH·AlR′$_2$H, *etc.* with the intention of developing new facile routes to rings, clusters, and polymers.

3. Catalytic ROP of cyclic thionylphosphazenes

Our group has also been interested in the possibility of creating new macromolecular chains based on main group elements using ROP processes. We have found, for example, that the cyclic thionylphosphazene (**20**) thermally polymerizes at 165 °C to yield poly(pentachlorothionylphosphazene) (**21**) (Scheme 6), which undergoes halide substitution in a manner similar to poly(dichlorophosphazene) (*e.g.* with amines) to form hydrolytically stable sulfur–nitrogen–phosphorus polymers.[31,32] Mechanistic studies of the process suggested a cationic, chain growth ROP mechanism. We have found that the ROP can be performed at room temperature by using halide-accepting, Lewis acids as catalysts (*e.g.* GaCl$_3$).[33] Interestingly, the polymerization shows a dramatic dependence on monomer concentration, with no polymer formed below a concentration of 0.15 M. This is characteristic of a weakly exothermic polymerization which indicates that the monomer **20** is virtually
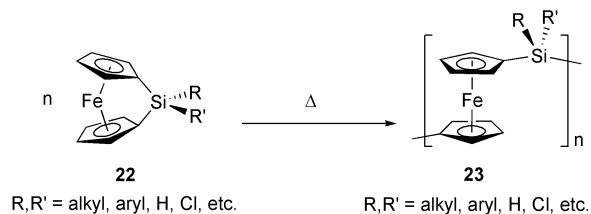

Scheme 6

unstrained.[33] The mechanism for the catalytic ROP is currently under study. Abstraction of the Cl substituent at the sulfur(VI) center to generate a thionylphosphazene cation may well be involved.[33]

Polythionylphosphazenes represent an interesting class of main group polymers with tunable properties. The backbone is stable to hydrolysis and even water soluble derivatives have been made. The high gas permeability of some of these materials has led to interest in their use as matrices for luminescent, oxygen sensors.[34]

4. 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 favourable. Among the species studied were silicon-bridged [1]ferrocenophanes **22** ([1]silaferrocenophanes), the first examples of which were prepared by Osborne and co-workers in England in the mid 1970's.[35] These strained molecules are readily available on a substantial (> 100 g) scale from the reaction of dilithioferrocene–tetramethylethylenediamine (fcLi$_2$-TMEDA) with dichloroorganosilanes RR′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 **23** (Scheme 7).[36]

R,R′ = alkyl, aryl, H, Cl, etc.   R,R′ = alkyl, aryl, H, Cl, etc.

Scheme 7

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 (Ge, P, Sn, S, *etc.*), two-atom bridges (C–C, C–P, C–S, *etc.*) and transition metals (*e.g.* Ru, Cr) and/or different π-hydrocarbon rings (arenes).[37,38] 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 nano-structures, liquid crystalline materials, charge dissipative coatings, and variable refractive-index sensing materials, are currently under study.[39,40]

Thermal ROP provides an excellent method for preparing high molecular weight polymetallocenes but the polydispersities are broad (PDI = 1.5–2.5) and no control of molecular weight has been possible to date.[36,37] Subsequently, living anionic ROP routes to polymetallocenes using initiators such as [n]BuLi at ambient or subambient temperatures have been developed.[41,42] These methods have permitted unprecedented control of main chain metal-containing polymer architectures. In particular, the first block copolymers with metals in the main chain have been prepared, providing access to materials with controlled molecular weights and narrow molecular weight distributions. 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 polymetallocenes *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 Pt(II), Pt(0), Rh(I), and Pd(II) precatalysts.[43,44] Transition metal-catalyzed ROP is a mild method which 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 polymetallocene architectures is possible.[45,46] For example, [1]silaferrocenophanes with different cyclopentadienyl rings can undergo regioregular transition metal-catalyzed ROP, whereas thermal ROP affords a regioirregular PFS material.[46] In the presence of Si–H containing species, such as Et_3SiH, the transition metal-catalyzed ROP of silicon-bridged [1]ferrocenophanes allows the formation of PFS **24** (Scheme 8) with a molecular weight control dictated by the initial ratio of monomer to silane (Fig. 3). However, unlike the case of anionically ring-opened materials, the polydispersities are appreciable (typically *ca.* 1.4–1.5 *versus* < 1.1).[45,46]
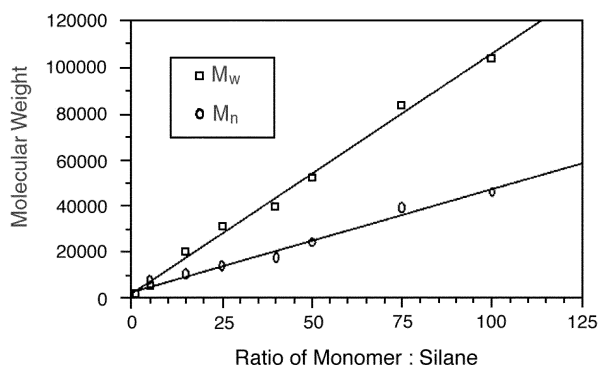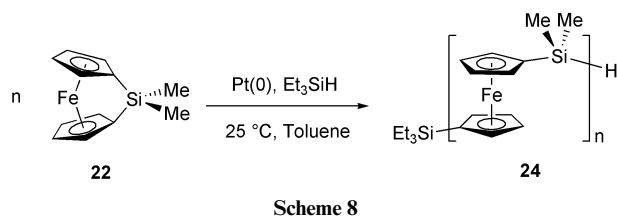
Scheme 8

Fig. 3 Plot of the M_w and M_n values of the mole ratio of monomer : silane for the synthesis of polyferrocenylsilane **24**. Reproduced from ref. 46 with permission.

This transition metal-catalyzed ROP methodology has been extended towards the formation of comb and star copolymers with the appropriate Si–H source.[46] Block copolymers can be formed *via* the addition of macromonomers with Si–H end groups.[46] 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.[47] The use of polysiloxane macromonomers with two Si–H termini yields novel PFS-*b*-PDMS-*b*-PFS triblock copolymers.[46] It should be noted that, unlike anionic polymerization, the transition metal-catalyzed ROP route 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 have been prepared *via* transition metal-catalyzed ROP of **22** (R = R′ = 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 terminal Si–Cl bond with poly(ethylene glycol)methyl ether, which yielded poly(ethylene oxide-*b*-ferrocenylsilane) diblock copolymers (Scheme 9).[48]

The mechanism of the platinum-catalyzed ROP of [1]silaferrocenophanes is of intense interest in our research group. The ROP is proposed to proceed through initial formation of a [2]platinasilaferrocenophane *via* oxidative addition of the platinum center.[49] Colloidal platinum is proposed to subsequently form, and oxidative addition and reductive elimination reactions at the colloid surface are then believed to allow formation of the polymer. End group analysis experiments, and the discovery that mercury inhibits ROP support this proposition.[49]

Scheme 9
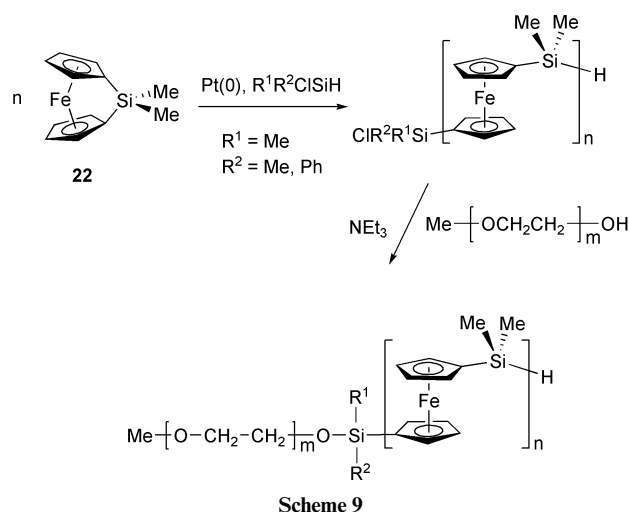
However, even in the presence of mercury, a small amount of polymer is formed very slowly. Therefore, the overall mechanism for the transition metal-catalyzed ROP of [1]silaferrocenophanes may be more complex and could involve both homogeneous and heterogeneous mechanisms.[49]

A typical platinum-catalyzed ROP of a [1]silaferrocenophane achieves very high conversion in 24 h.[50] Remarkably, catalytic amounts of cationic rhodium(I) complexes [Rh(1,5-cod)₂]A (A = OTf, PF₆) have been found to initiate the ROP of [1]silaferrocenophanes with quantitative conversion within 2 minutes.[50] Prolonged exposure of the high molecular weight polymers to the catalyst solution, however, led to gradual cleavage of the polymer backbone. In addition, [Rh(1,5-cod)(dmpe)]OTf (dmpe = bis-(dimethylphosphino)methane) 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 **22** (R = R′ = Me). Moreover, no subsequent cleavage of the resulting polyferrocenylsilane chains was detected in this case.[50] It is probable that colloidal Rh generated from [Rh(1,5-cod)₂]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 prepare 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 material science applications and the extension of this method to 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.[51] In addition, elucidation of the mechanism of the ROP of [1]silaferrocenophanes by transition metals is a continued area of focus in our research group.

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 and with interesting architectures, such as block copolymers. These materials offer unique opportunities for the creation of novel supramolecular materials *via* self-assembly processes.[14]

Acknowledgements

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