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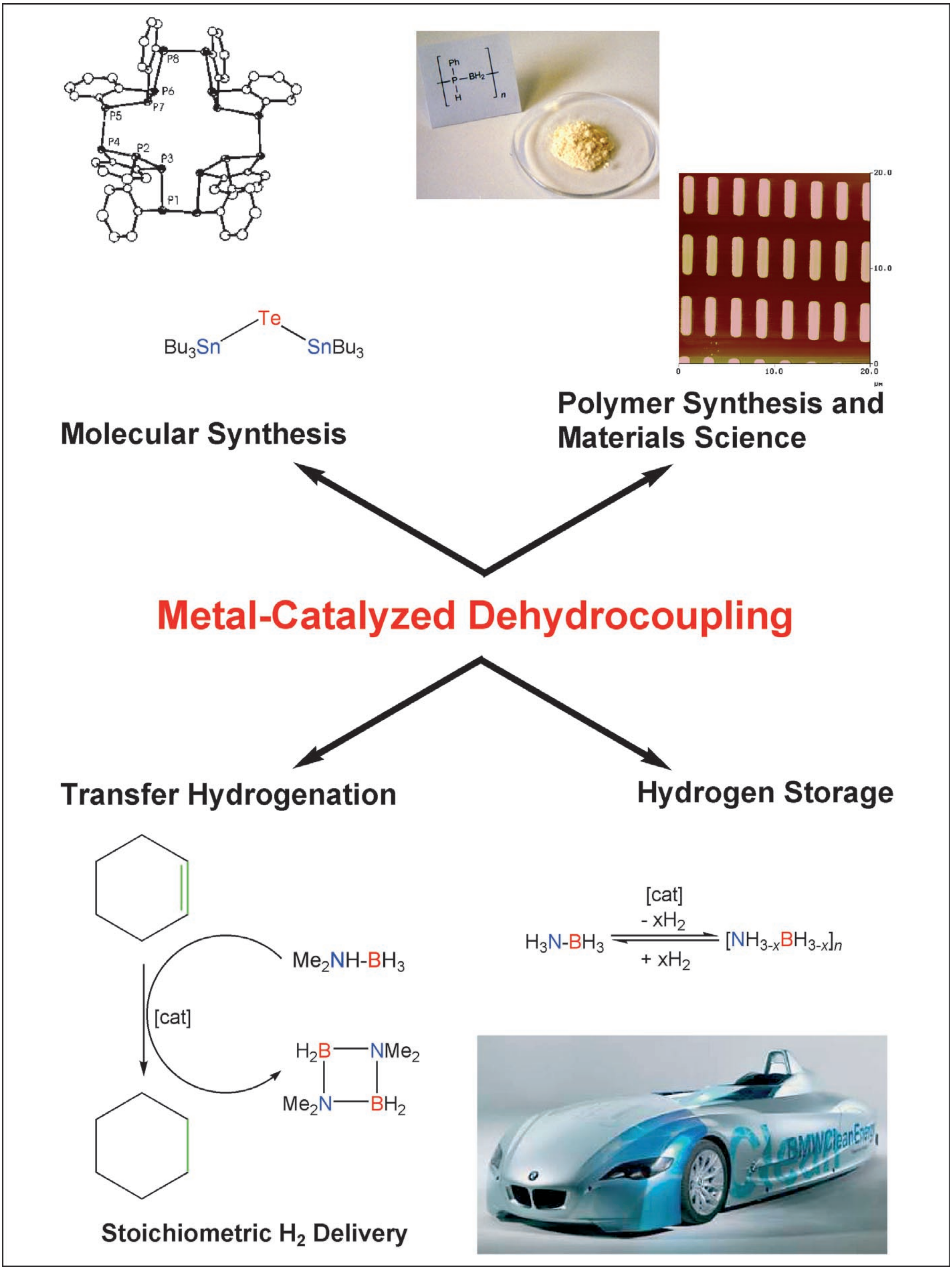

Transition-Metal-Catalyzed Dehydrocoupling: A Convenient Route to Bonds between Main-Group Elements

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Abstract: The development of transition-metal-catalyzed dehydrocoupling reactions as a synthetic method for the formation of main-group element–element bonds provides an increasingly attractive and convenient alternative to traditional routes such as salt metathesis/elimination-type reactions. Since the first reported examples in the early 1980s, there has been a rapid expansion of this field, with extensions to a wide variety of metal-mediated homonuclear and heteronuclear bond-forming processes. Applications of this new chemistry in molecular and polymer synthesis, materials science, hydrogen storage and the transfer hydrogenation of organic substrates are attracting growing attention. An overview of this emerging area is presented in this Concepts article with a focus on recent results.

Keywords: boranes • heterogeneous catalysis • homogeneous catalysis • hydrogen storage • inorganic polymers • phosphorus

Introduction

The development of transition-metal-catalyzed reactions has been of profound importance in the evolution of synthetic organic chemistry since the 1950s. A vast array of homogeneous and heterogeneous catalysts are now available that promote a wide range of bond-forming or bond-breaking reactions involving carbon. Furthermore, these reactions can often be performed under relatively mild conditions with diastereoselectivity and enantioselectivity. In addition to the efficient catalytic synthesis of organic molecules for the pharmaceutical industry, many other large-scale industrial processes are reliant on metal-mediated catalytic routes including Ziegler–Natta polymerization for the commercial production of polyolefins.[1]

In sharp contrast, the development of analogous catalytic routes in preparative inorganic chemistry to form homonuclear or heteronuclear bonds between main-group elements is still in its relative infancy.[2] Traditionally, synthetic methods employed in main-group chemistry are often element-specific and of limited scope and generality. Common procedures are usually confined to salt (e.g. alkali metal halide) elimination reactions. Since the mid 1980s there has been growing interest in the development of catalytic dehydrocoupling routes to form bonds between main-group elements (dehydrocoupling involves the generation of the main-group element–element bond with concomitant elimination of H_2 gas).[3] Such approaches were first discovered in the 1980s for the formation of homonuclear B−B and Si−Si bonds. Subsequently, this type of catalytic reaction has been extended to a wide variety of homonuclear (E−E) and also heteronuclear (E−E′) bonds between main-group elements. Moreover, applications of this new chemistry now exist in molecular and polymer synthesis, materials science, transfer hydrogenation reactions in organic chemistry, and hydrogen storage. An overview of this emerging area is presented in this Concepts article with a particular emphasis on recent results. The survey is divided into separate sections on homonuclear and heteronuclear catalytic bond formation.

Homonuclear Dehydrocoupling Processes

Catalytic formation of B−B bonds: The first reports of metal-mediated dehydrocoupling reactions emerged from the group of Sneddon in the early 1980s. A series of papers were published which dealt with the formation of B−B bonds between borane clusters. It was found that $PtBr_2$

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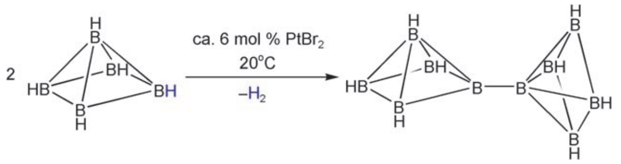
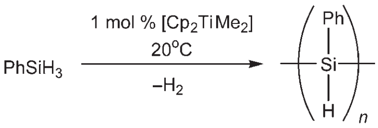
acted as a general dehydrodimerization catalyst for boron hydrides and carboranes leading to the formation of polyhedral cage compounds linked by B–B bonds.[4] The reactions of a variety of small cage systems were explored, and all coupling reactions were found to proceed with high selectivity at moderate temperatures, and gave excellent yields of linked-cage products. For example, treatment of B_5H_9 with catalytic amounts of $PtBr_2$ at room temperature resulted in the evolution of H_2 gas and the linked cage structure $[1,2'-(B_5H_8)_2]$ in 92 % yield (Scheme 1). In a later report, the same catalyst was employed to promote cage growth and dehydrocoupling reactions between diborane and small, polyhedral carboranes and boranes, which yielded either larger single-cage compounds or coupled diborane–carborane/borane complexes.[5]



Scheme 1. Catalytic dehydrocoupling of borane clusters to give linked cages. The bridging H atoms are not shown for clarity.

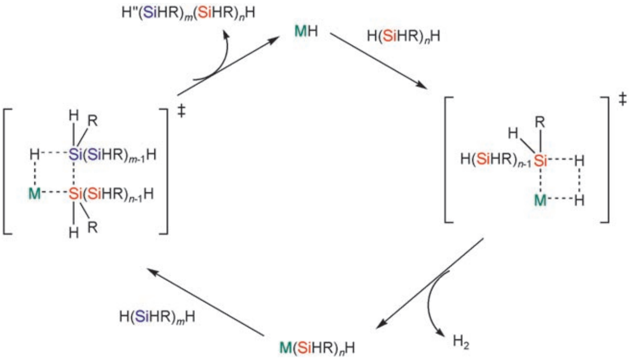
Catalytic formation of Si–Si and Ge–Ge bonds: In 1985, Harrod and co-workers published a seminal report concerning the discovery that Group 4 metallocene complexes such as $[Cp_2TiMe_2]$ (Cp = cyclopentadienyl) catalyzed the dehydrocoupling of primary silanes to afford polysilanes $(SiRH)_n$ (Scheme 2).[6]



Scheme 2.

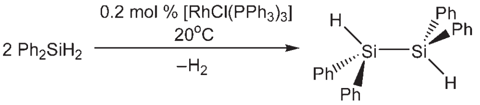
This was a critical breakthrough, not just from the perspective of fundamental science, but because the new method also provided a potentially alternative route to these interesting polymers compared to Wurtz-type polycondensation, which is experimentally dangerous and generally gives very poor yields. Interest in polysilanes (and indeed other polymers consisting of Group 14 elements) derives from their unusual physical properties including σ-electron delocalization along the polymer main chain and the associated relatively small band gap (ca. 4 eV). This has prompted their use as photoconductive materials and near-UV resists.[7] Polysilanes are also of widespread interest as pyrolytic precursors to shaped SiC ceramics and fibers.

Subsequent reports from Harrod and co-workers[8] dealt with their investigations into the mechanism of this intriguing reaction through isolation of key intermediates. It was suggested that the propagation may occur by the repetitive insertion of a silylene moiety into a Ti–Si bond and might involve species with a Ti=Si double bond. However, based on extensive kinetic and synthetic studies, Tilley later postulated a new step-growth coordination polymerization mechanism for zirconocene-catalyzed dehydrocoupling that involved σ-bond metathesis steps, through which σ bonds are broken and formed in a concerted fashion via four-center transition states (Scheme 3).[9] This mechanism is further supported by a lack of isolated and characterized Ti– and Zr–silylene complexes in the literature.[10] Corey and co-workers have successfully prepared oligosilanes through catalytic dehydrocoupling of secondary silanes using Group 4 metallocene catalysts generated in situ by treatment of $[Cp_2MCl_2]$ (M = Ti, Zr, Hf) with *n*BuLi.[11] However, the dehydrocoupling rate was much slower than that of the primary silanes owing to the more sterically encumbered Si center and, as a result, only short-chain products ranging from the disilane to octasilane were isolated. It was proposed that the transient $\{Cp_2M\}$ species that is generated under these conditions subsequently undergoes a rapid reaction with silanes by oxidative addition of Si–H bonds to afford a silyl hydride complex at which point a series of σ-bond metathesis steps of the type indicated in Scheme 3 might occur.



Scheme 3. The σ-bond metathesis mechanism for the catalytic dehydrocoupling of primary silanes.

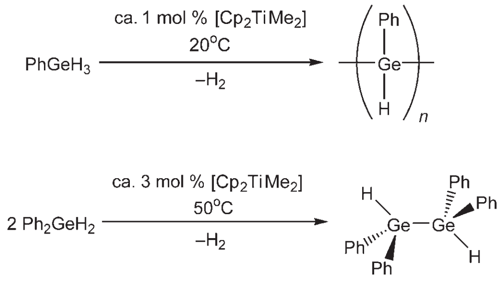
Rosenberg and co-workers have extended the work performed in the area of catalytic Si–Si bond formation employing early-transition-metal catalysts to the preparation of disilanes from secondary organosilanes by using a late-metal complex. For example, Ph_2SiH_2 was reported to dehydrocouple at room temperature using Wilkinson's catalyst to afford $Ph_2HSi–SiHPh_2$ (Scheme 4).[12] These studies indicated experimental factors, some of which are remarkably subtle,



Scheme 4.

have a profound influence on the reaction equilibria that determines whether dehydrocoupling occurs or a redistribution reaction affording $PhSiH_3$ and Ph_3SiH is favoured. These include catalyst loading, presence of solvent and reaction vessel size, along with stir bar size and stirring rate, all of which have a crucial effect on how efficiently the H_2 by-product is removed, and thus generating disilane as the kinetic product.

Given the similarities that exist between the chemistry of Si and Ge, a logical extension of the dehydrocoupling chemistry of silanes was to study the corresponding synthesis of Ge−Ge bonds. Consequently in 1988, Harrod and co-workers reported that phenylgermane, $PhGeH_3$, underwent a reaction with $[Cp_2TiMe_2]$ in a manner analogous to phenylsilane to afford Ge-based oligomers (Scheme 5).[13] However, owing to its greater reactivity, the germane dehydrocoupling reaction occurred much more vigorously than in the case of silanes resulting in considerable cross-linking, yielding an insoluble, three-dimensional gel. Presumably the initially formed linear polymer $(PhGeH)_n$ is able to undergo intermolecular dehydrocoupling to form new Ge−Ge bonds that function as cross-links. A similar catalytic reaction with Ph_2GeH_2 generated tetraphenyldigermane.

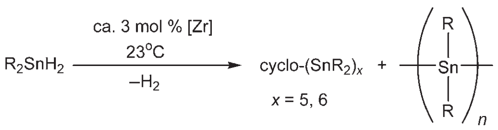


Scheme 5.

A decade later, Tanaka and Choi described the formation of a soluble, high-molecular-weight polyphenylgermane network prepared from the parent monomer by using the same "zirconocene" catalyst previously employed by Corey.[14] It should also be mentioned that Berry and co-workers have successfully synthesized a variety of high-molecular-weight linear poly(arylmethylgermanes) using a catalytic *demethanative* strategy mediated by Ru^{II} complexes.[15]

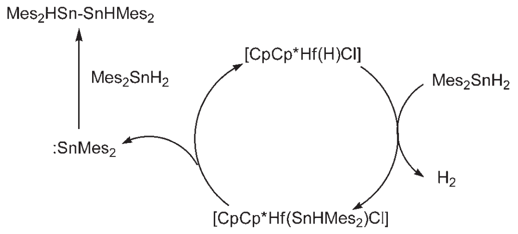
Catalytic formation of Sn−Sn bonds: In a further extension to heavier Group 14 congeners, Tilley and co-workers reported the catalytic dehydropolymerization of secondary stannanes by zirconocenes in the absence of solvent to yield high-molecular-weight polystannanes, $(SnR_2)_n$, as well as cyclic oligomers (predominantly pentamers; Scheme 6).[16]

The polystannanes, which show even more extensive σ-delocalization than polysilanes, were shown to act as excellent precursors to Sn-based semiconductor materials such as SnO_2. Furthermore, they are thermally stable, but rather air- and light-sensitive. For example, exposure of polystannane $(Sn\textit{n}Bu_2)_n$ to fluorescent room lighting for 2 h resulted in degradation to give a mixture of the cyclic pentamer and hexamer. This photosensitivity is not surprising as such behavior has been previously noted for polysilanes and polygermanes, and suggests their potential use as photoresists in patterning applications. Interestingly, Sita and Babcock later showed that by treating $\textit{n}Bu_2SnH_2$ with a catalytic amount of $[RhH(CO)(PPh_3)_3]$ in toluene, the formation of a high-molecular-weight, highly branched polystannane by a novel dehydropolymerization/rearrangement process occurred.[17] Due to the different structural architecture of the polystannane in comparison to the linear material reported by Tilley, the branched analogue was found to be much more robust towards light in solution, and oxidation in the solid state.



Scheme 6.

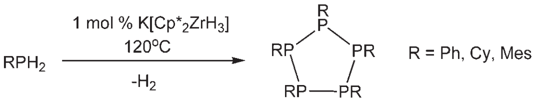
In a further contribution, Tilley and Neale reported the catalytic dehydrocoupling of Mes_2SnH_2 (Mes = mesityl) with $[CpCp^*Hf(H)Cl]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) to produce the distannane $Mes_2HSn{-}SnHMes_2$.[18] However, the focus of this work involved the successful isolation of the d^0 hydrostannyl metal complex $[CpCp^*Hf(SnHMes_2)Cl]$ as an intermediate which allowed mechanistic studies on metal-catalyzed Sn−Sn bond formation to be carried out (Scheme 7). The dehydrocoupling in this system appears to proceed through α-H elimination at the Hf center to produce the free stannylene $:SnMes_2$, which then inserts into a Sn−H bond to yield the distannane product. The experimental data supports the σ-bond metathesis mechanism proposed for other Group 14 bond-forming reactions[9] and there is evidence for coordination of a σ bond in the hydrostannyl intermediate prior to the metathesis step.



Scheme 7.

Catalytic formation of P−P and Sb−Sb bonds: Transition-metal-catalyzed homonuclear bond formation has also been reported for Group 15 elements. The formation of P−P bonds was described by Stephan and co-workers in the mid-1990s. Initially, they described the catalytic dehydrocoupling of primary phosphanes by an anionic zirconocene complex to generate cyclic organophosphane pentamers $(PR)_5$ (Scheme 8).[19]

This was followed by a paper in which a 16-membered ring of contiguous P atoms $(1,2\text{-}C_6H_4P_2)_8$ was constructed by dehydrocoupling the diphosphane $1,2\text{-}C_6H_4(PH_2)_2$ with the same Zr catalyst.[20] The X-ray crystallographic data revealed that the P_{16} macrocycle possesses "double-crown" geometry with the central cavity having a diameter of approximately 5.10 Å (Figure 1). Moreover, the crystal packing is such that the central cavities are aligned, creating channels, which could find use for metal atom complexation and/or intercalation.



Scheme 8.

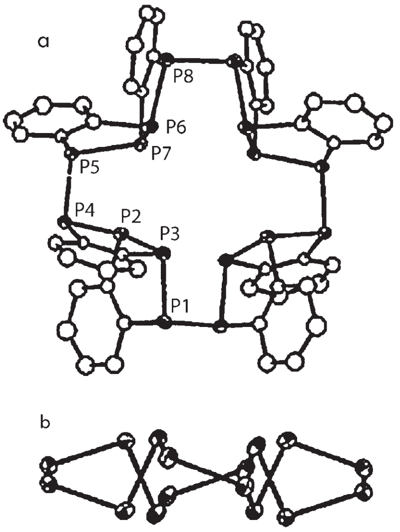
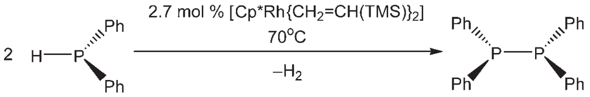


Figure 1. a) Molecular structure of the P_{16} macrocycle $(C_6H_4P_2)_8$ with hydrogen atoms omitted for clarity. b) View of the P_{16} core showing the double-crown geometry. Reproduced by permission of The American Chemical Society from reference [20].

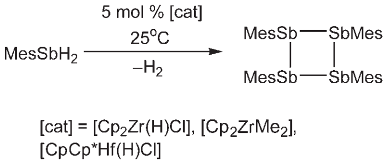
Stephan and Hoskin later employed the same anionic zirconocene catalyst to generate the bicyclic organotetraphosphane $[(PCH_2CH_2PH)_2]$ from the primary bidentate phosphane $PH_2CH_2CH_2PH_2$ at room temperature.[21] The molecule comprises two interlinked five-membered rings, in which one phosphorus atom of each of two diphosphane fragments forms P–P bonds with the two phosphorus atoms of the other diphosphane moiety. Heating this compound with excess $AlMe_3$ afforded the remarkable macrocyclic P_{16}–Al_{12} compound $[\{(PCH_2CH_2PAlMe_2)_2\}_4]\cdot 4\,AlMe_3$ which uses four P_4 chains to link eight aluminum centers forming Al_2P_3 rings that are ultimately bound together by P units.

Shortly thereafter, Brookhart and Böhm reported catalytic P–P bond formation using late-transition-metal precatalysts.[22] Specifically, heating diphenylphosphane with a catalytic amount of the Rh^I complex $[Cp^*Rh\{CH_2{=}CH(SiMe_3)\}_2]$ at 140 °C resulted in the formation of diphosphane Ph_2P–PPh_2 (Scheme 9). Interestingly, the labile olefinic groups on the Rh catalyst are partially hydrogenated by the gaseous H_2 byproduct. The crucial role of the catalyst was verified as diphenylphosphane undergoes no reaction at 140 °C in the absence of Rh^I, while turnover numbers as high as 1300 mol product per mol catalyst were achieved when Rh^I was used.



Scheme 9.

In a report in 2006, Tilley and Waterman extended homonuclear catalytic dehydrocoupling to heavier Group 15 elements, with their observation of Sb–Sb bond formation.[23] It was found that reaction of the primary stibine $MesSbH_2$ with Group 4 metallocene catalysts proceeded effectively to generate the cyclic tetrastibene Sb_4Mes_4 (Scheme 10).

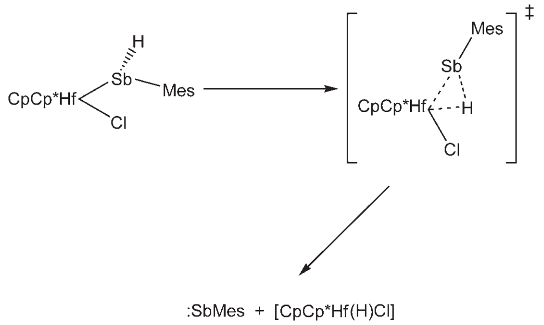


Scheme 10.

A model complex containing a metal-bound stibide ligand, [CpCp*HfCl{Sb(H)Mes}], was formed from a stoichiometric reaction between [CpCp*Hf(H)Cl] and $MesSbH_2$ and was studied together with the deuterated counterpart [CpCp*HfCl{Sb(D)Mes}]. Both compounds were found to be thermally unstable and consequently regenerated the [CpCp*Hf(H/D)Cl] catalyst along with the tetrastibene product. Detailed studies showed a significant kinetic isotope effect for this decomposition pathway, indicating considerable Sb–H/D bond weakening in the transition state. Consequently, an ordered transition state was proposed that leads to α-hydrogen migration and elimination of a stibinidene (RSb:) fragment, which subsequently oligomerizes to form the cyclic tetramer (Scheme 11).

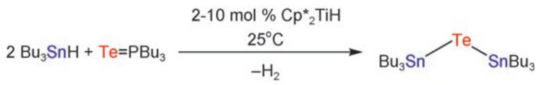
Heteronuclear Dehydrocoupling Processes

Catalytic formation of bonds between Group 14 and Group 16 elements: As noted for polystannanes, the desire to construct frameworks consisting of main-group elements partially resides in their use as single-source precursors to solid-



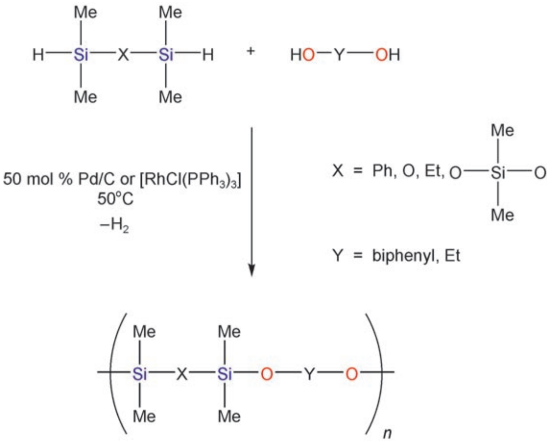
Scheme 11.

state materials with useful properties and applications. In 1998, Piers and co-workers reported the preparation of the bridging tin telluride $[(Bu_3Sn)_2(\mu\text{-}Te)]$ (Scheme 12), a potential single-source precursor to the small band gap semiconductor SnTe, from tributylstannane and tributylphosphane telluride using a titanocene catalyst.[24] A thorough study of a series of stoichiometric reactions and ^{119}Sn NMR analysis provided insight into the possible pathways taken during the course of the catalytic reaction, including conversion of the paramagnetic dimer $[\{(Cp^*Ti)_2(\mu\text{-}Te)\}_2]$ to the intriguing ditelluride $[Cp^*_2Ti(\eta^2\text{-}Te_2)]$.



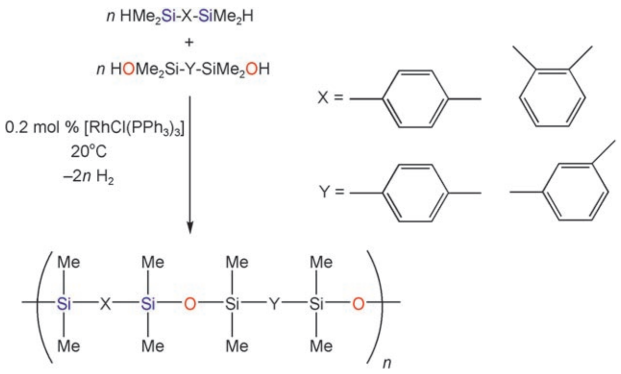
Scheme 12.

In 1999 Kawakami and Li reported a synthetic method for the production of poly(silyl ethers), which have found prominent use as plastics and elastomeric materials. In their preparation, bis(hydrosilane)s were cross-dehydrocoupled with diols in the presence of substoichiometric Pd/C or Wilkinson's catalyst affording high-molecular-weight polymers ($M_n = 6800\text{–}12200$) with Si-O-C backbones (Scheme 13).[25] A variety of functional groups were introduced into the polymer backbone by appropriate choice of linker units within the bis(silane) or the diol which demonstrates the versatility of this protocol.



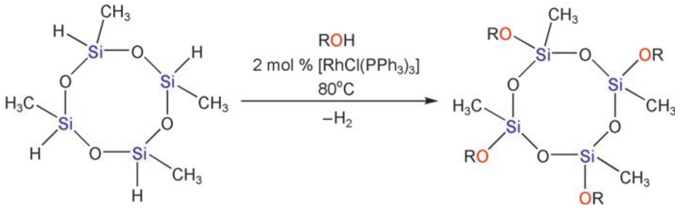
Scheme 13.

In related work, Mark and co-workers described the room-temperature dehydropolymerization of disilanes and disilanols, possessing aromatic linkers, using Wilkinson's catalyst to give a range of high-molecular-weight polysiloxanes (Scheme 14).[26]



Scheme 14.

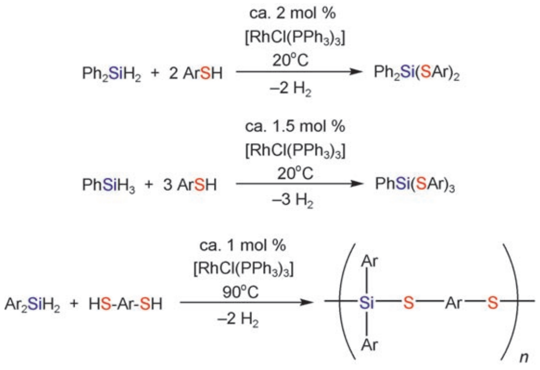
In addition, Boudjouk and co-workers prepared linear and cyclic polysiloxanes with pendant amine groups by means of dehydrogenative alcoholysis (Scheme 15).[27] Again, the addition of Wilkinson's catalyst to a mixture of either a linear or cyclic polysiloxane together with a variety of hydroxyalkylamines resulted in selective alcoholysis of Si–H bonds without degradation of the siloxane backbone.



Scheme 15.

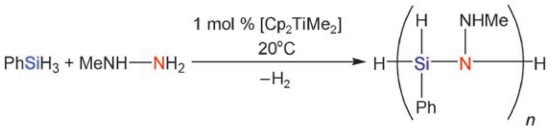
The formation of Si–S bonds by catalytic dehydrocoupling was demonstrated by Osakada and Yamamoto in 1996. Treatment of Ph_2SiH_2 or $PhSiH_3$ with either two or three equivalents of arenethiols (ArSH) was found to afford the corresponding bis- or tris(thiolato)phenylsilanes $Ph_2Si(SAr)_2$ and $PhSi(SAr)_3$, respectively, at room temperature by using Wilkinson's catalyst.[28] Furthermore, this method was extended to the dehydrocoupling of diarylsilanes with benzenedithiols yielding low-molecular-weight polymers ($M_n = 1300\text{–}5400$) (Scheme 16).

Catalytic formation of bonds between Group 14 and Group 15 elements: Employing the same titanocene catalyst $[Cp_2TiMe_2]$ used previously for polysilane formation, Harrod and co-workers found that phenylsilane reacted with



Scheme 16.

hydrazines yielding oligomeric products and gels based on Si–N skeletons (Scheme 17).[29]



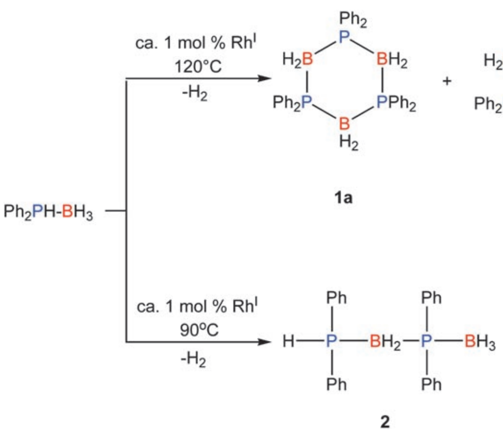
Scheme 17.

The same Ti catalyst has found further use in promoting the formation of Si–P bonds. Specifically, secondary phosphanes were found to catalytically heterodehydrocouple with primary silanes at room temperature to afford phosphasilanes of the type $R_2P\text{-}SiH_2R$.[30] Primary phosphanes were found to be relatively unreactive compared to their more sterically encumbered counterparts; this fact is surprising considering the likelihood of crowding around the Ti center during σ-bond metathesis steps. It was suggested that this may arise from stronger Ti–P bonding in the case of complexes with primary phosphanes, which are likely intermediates during the course of the reaction.

Catalytic dehydrocoupling of Group 13/Group 15 Lewis acid–base adducts

Catalytic formation of B–P bonds: Macromolecules consisting of alternating four-coordinate phosphorus and boron atoms, polyphosphinoboranes $(RR'P\text{-}BH_2)_n$, attracted significant attention as synthetic targets in the 1950s and 1960s as these materials were anticipated to possess useful thermal and oxidative properties which could rival those of the commercially well-developed polysiloxanes (silicones). However, the open literature on phosphinoborane polymers from this period is very limited, with most of the work documented in patents.[31] The main synthetic approach used to attempt to access such materials involved thermally induced dehydrocoupling of phosphane–borane adducts at 150–200 °C. This afforded predominantly cyclic trimers $[(RR'P\text{-}BH_2)_3]$ and very low yields of low-molecular-weight, partially characterized polymers.[32] The considerable stability of the six-membered rings was illustrated by the observation that negligible decomposition was reported even when heated to 300 °C in the presence of HCl.[32] In the late 1990s in an attempt to further develop this promising area, the catalytic dehydrocoupling of secondary and primary phosphane–borane adducts was explored in our research group.

A reinvestigation of the thermal dehydrocoupling of $Ph_2PH{\cdot}BH_3$ at 170 °C yielded a mixture of the cyclic trimer $[\{Ph_2P\text{-}BH_2\}_3]$ **1a** and tetramer $[\{Ph_2P\text{-}BH_2\}_4]$ **1b** in an 8:1 ratio while virtually no reaction occurred at 120 °C. However, upon heating $Ph_2PH{\cdot}BH_3$ in the presence of ≈1 mol % Rh^I precatalysts such as $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ or $[Rh(1,5\text{-}cod)_2][OTf]$ (1,5-cod = 1,5-cyclooctadiene) at 120 °C, the same two cyclic systems are efficiently formed in a 2:1 ratio (Scheme 18).[33] Unlike **1a**,[34] cyclic tetramer **1b** had not been previously structurally characterized, and an X-ray diffraction study showed that the ring adopts a boat–boat conformation.[33]



Scheme 18.

Upon lowering the reaction temperature to 90 °C, the novel linear compound $Ph_2PH\text{-}BH_2\text{-}PPh_2\text{-}BH_3$ **2** was formed as the exclusive product as colorless, air-stable crystals (Scheme 18).[33,35] It seems likely that the cyclic products **1a** and **1b** are generated at 120 °C as a result of chain extension from **2** to form the linear trimer and tetramer followed by back-biting reactions. Interestingly, no evidence for B–B or P–P homodehydrocoupling was detected in any reactions involving $Ph_2PH{\cdot}BH_3$.

In an attempt to obtain polymers rather than cyclic oligomers, the catalytic dehydrocoupling of the sterically less encumbered primary phosphane–borane adduct $PhPH_2{\cdot}BH_3$ (**3a**) was explored. The structure of **3a** determined by X-ray diffraction (Figure 2) showed intermolecular dihydrogen bonds between the protic and basic hydrogens on P and B, respectively. The corrected H···H contacts create a centrosymmetric dimer and possess a separation of 2.375 Å, which is slightly shorter than the sum of the van der Waals radii for two hydrogen atoms (2.4 Å). This suggests the existence of a weak attractive $P\text{–}H^{\delta+}\cdots{}^{\delta-}H\text{–}B$ in-

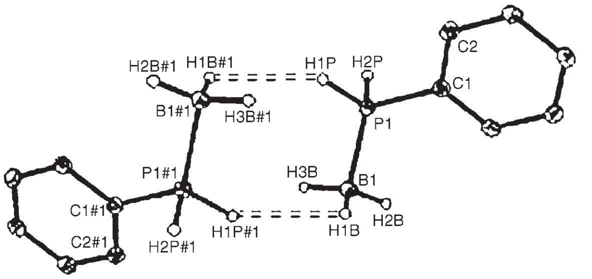
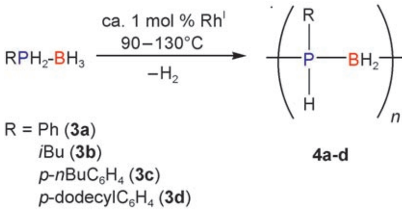


Figure 2. Molecular structure of $PhPH_2{\cdot}BH_3$ and its symmetry-related molecule showing weak intermolecular H···H interactions. Reproduced by permission of The American Chemical Society from reference [33].

teraction as a result of oppositely polarized hydrogen atoms. Furthermore, the P−H···H angle (148(3)°) is more linear relative to the B−H···H angle (111(3)°), which is also observed for most compounds with an $N{-}H^{\delta+}\cdots{}^{\delta-}H{-}B$ arrangement.[36]

In the early 1960s, the uncatalyzed thermolysis of **3a** 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 2150. Prolonged heating at 250 °C led to the formation of an intractable material without any significant molecular weight increase for the benzene-soluble fraction ($M_n = 2630$).[37] A reinvestigation of this chemistry showed that the resulting oligomeric material has a poorly defined structure. In contrast, treatment of $PhPH_2{\cdot}BH_3$ with a catalytic quantity of $[Rh(1,5\text{-}cod)_2][OTf]$ in refluxing toluene (110 °C) was found to give the well-defined poly(phenylphosphinoborane) $[PhPH\text{-}BH_2]_n$ (**4a**) as an off-white powder soluble in polar organic solvents ($M_w = 5600$) (Figure 3, Scheme 19).[33,35] At more elevated temperatures and the absence of solvent in the presence of the same precatalyst higher molecular-weight material was formed ($M_w = 33300$), but thermal treatment for more extended periods yielded polymer samples that swelled but would not dissolve in organic solvents such as THF or CH_2Cl_2 (Figure 3). This is consistent with the presence of cross-linking by interchain P−B coupling by H_2 elimination.



Scheme 19.

Poly(phenylphosphinoborane) is air-stable in the solid state and stable for long periods in solution. The P−B bonds that comprise the polymer backbone are also robust as treatment of **4a** with nucleophilic ligands such as diethylamine and tributylphosphane resulted in no reaction.[38] Intriguingly, as P−B bonds are isoelectronic to C−C single bonds, **4a** can be viewed as an inorganic analogue of polystyrene.

The primary phosphane–borane adducts $RPH_2{\cdot}BH_3$ (R = *i*Bu (**3b**), *p*-*n*BuC_6H_4 (**3c**), *p*-dodecylC_6H_4 (**3d**)) similarly undergo Rh-catalyzed dehydrocoupling to form polyphosphinoboranes **4b**–**d**, respectively.[38] Wide-angle X-ray scattering analysis of polymers **4a** and **4c** indicated they were essentially amorphous as the dehydropolymerization process would not be expected to provide stereochemical control of the side groups arranged along the polymer chain. Glass transition temperatures (T_g) below room temperature were found for polymers **4b**–**d** which may be attributed to the high degree of torsional flexibility in the polymer main chains caused by the long P−B bonds (1.9–2.0 Å). Thermogravimetric analysis of **4a** indicated the onset of decomposition at 160 °C with a ceramic yield of 75–80 % upon heating to 1000 °C. The high ceramic yield of **4a** suggests that it may

Figure 3. Photograph of poly(phenylphosphinoborane) in the solid-state (left) and as a solvent-swellable gel in THF (right).

function as a useful pre-ceramic polymer for BP based materials. Indeed, preliminary pyrolysis studies of **4a** at 1000 °C under nitrogen show the formation of boron phosphide as the major crystalline component by powder X-ray diffraction.[38]

Studies of the catalytic dehydrocoupling of a variety of phosphane–borane adducts suggest that the presence of electron-donating substituents on phosphorus reduces the rate of the reaction. With this in mind, the catalytic dehydrocoupling of fluoroaryl-substituted phosphane–borane adducts $(p\text{-}CF_3C_6H_4)_2PH{\cdot}BH_3$ (**5**) and $(p\text{-}CF_3C_6H_4)PH_2{\cdot}BH_3$ (**6**) was studied with the aim of accessing milder reaction temperatures.[40] This approach was successful, as the Rh-catalyzed dehydrocoupling of **5** at 60 °C in the absence of solvent afforded the linear dimer $R_2PH\text{-}BH_2\text{-}PR_2\text{-}BH_3$ (R = $p\text{-}CF_3C_6H_4$) **7**, while at 100 °C the cyclic species $[\{R_2P\text{-}BH_2\}_3]$ **8a** and $[\{R_2P\text{-}BH_2\}_4]$ (R = $p\text{-}CF_3C_6H_4$) **8b** (Figure 4) were obtained.[40] The temperatures required for all of these transformations are 20–30 °C lower than that of the corresponding dehydrocoupling of $Ph_2PH{\cdot}BH_3$.

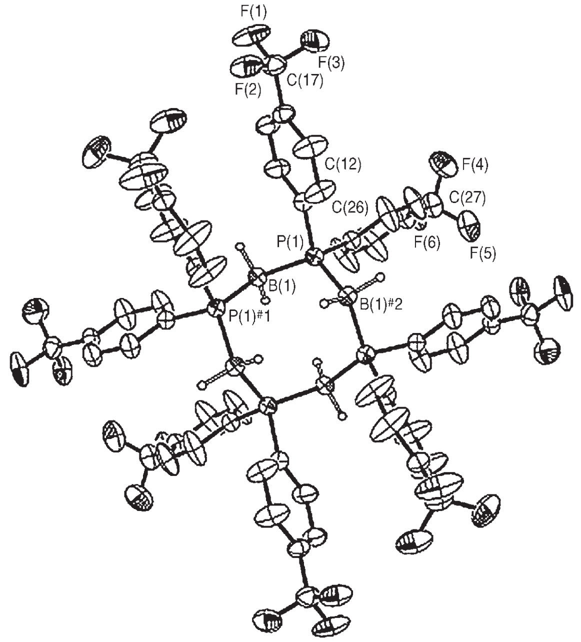


Figure 4. Molecular structure of **8b**.[40]

Moreover, treatment of **6** with a catalytic amount of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ at 60 °C resulted in air- and moisture-stable fluorinated polyphosphinoborane $[RPH\text{-}BH_2]_n$ (R = $p\text{-}CF_3C_6H_4$) **9** ($M_w = 56170$, PDI = 1.67; PDI = polydispersity).[40] Significantly, the catalytic dehydrocoupling temperature of 60 °C for the conversion of **6** to **9** is much lower than that previously reported for the conversions of **3a** to **4a** (90–130 °C for 6 h) and **3b** to **4b** (120 °C for 15 h).[33] This demonstrates the significant influence of changing the substituent at phosphorus in the phosphane–borane adduct on the reaction conditions.

Interestingly, polyphosphinoborane **9** functions as an electron beam resist for lithographic applications.[41] Thin films of **9** were found to act as negative-tone resists, as well-ordered arrays of micron-scale bars were prepared by the direct-write method. Scanning electron microscopy (SEM) revealed that a majority of the bars were well-formed and remained intact, while analysis by atomic force microscopy (AFM) showed they were fairly uniform in shape and size (Figure 5).

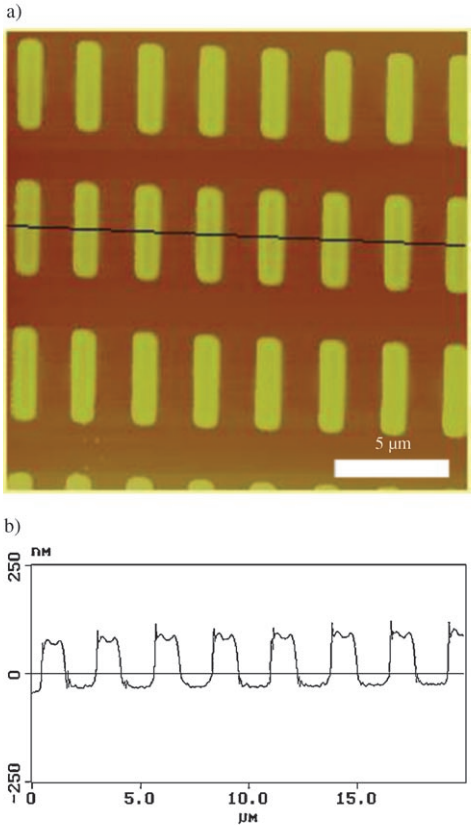
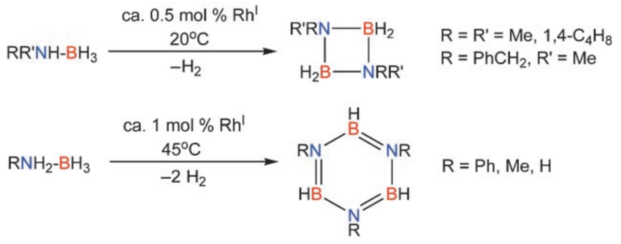


Figure 5. a) Tapping-mode AFM image of lithographically patterned bars of **9** and b) cross-sectional analysis showing high uniformity. Reproduced by permission of Wiley InterScience from reference [40].

Catalytic formation of B–N bonds: Amine–borane adducts[42] have traditionally been used in organic chemistry for reduction and hydroboration reactions[43] and recently, secondary adducts such as $iPr_2NH{\cdot}BH_3$ have been shown to act as reagents for the Pd-catalyzed borylation of aryl halides.[44] Also, amine–boranes are attracting considerable attention as potential hydrogen-storage materials.[45] Primary and secondary amine–borane adducts have previously been thermally dehydrocoupled at elevated temperatures (> 100 °C) to give cyclic aminoboranes $[(R_2B{-}NR'_2)_x]$ ($x = 2$ or 3) and borazine $[(RB{-}NR')_3]$ derivatives.[46–48] Well-characterized transition-metal-catalyzed dehydrocoupling of amine–borane adducts under ambient temperature was first reported in 2001.[49a] Rhodium complexes such as $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ and those of other late transition metals such as Ru, Ir, and Pd were found to catalyze the dehydrocoupling of secondary amine–borane adducts to afford either four-membered rings or, in the cases of sterically demanding substituents on nitrogen, monomeric products. Under similar conditions primary amine–boranes were found to yield borazines (Scheme 20).[49]



Scheme 20.

For example, the dehydrocoupling of $Me_2NH{\cdot}BH_3$ by $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (pre)catalyst (0.5 mol% Rh) either in the melt at 45 °C or in toluene at 25 °C, led to the evolution of H_2 gas and formation of the cyclic dimer $[(Me_2N{-}BH_2)_2]$ (Figure 6) in high yield after 2 or 8 h, respectively. Significantly, no reaction was detected in the absence of the Rh precatalyst. The active catalyst can also be recycled for further reactions.

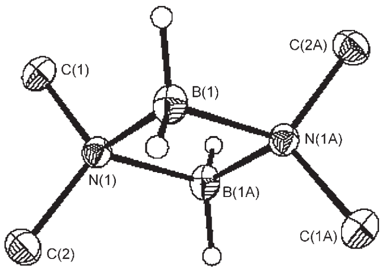
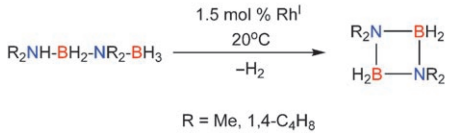


Figure 6. Molecular structure of $[(Me_2N{-}BH_2)_2]$. Reproduced by permission of The American Chemical Society from reference [49b].

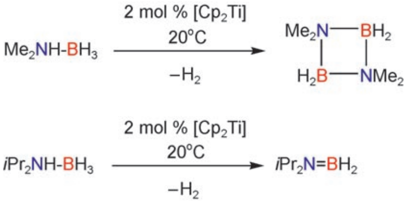
The linear species $R_2NH\text{-}BH_2\text{-}NR_2\text{-}BH_3$ (R = Me; R = cyclo-C_4H_8) was also shown to undergo dehydrocoupling in the presence of a catalytic amount of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ to give $[(R_2N{-}BH_2)_2]$ (Scheme 21).



Scheme 21.

The Rh-catalyzed dehydrocoupling of ammonia–borane ($H_3N{\cdot}BH_3$) and the primary adducts $MeNH_2{\cdot}BH_3$ and $PhNH_2{\cdot}BH_3$ has also been investigated and yields borazines $[(HB{-}NR)_3]$ (R = H, Me, Ph) in diglyme or tetraglyme at 45 °C for the case of R = H, Me or 25 °C for R = Ph.[49]

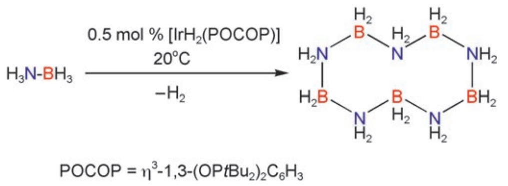
Catalytic dehydrocoupling of amine–borane adducts has been extended to a highly active early-transition-metal catalyst.[50] For example, treatment of $Me_2NH{\cdot}BH_3$ with $[Cp_2Ti]$, generated in situ from $[Cp_2TiCl_2]$ with two equivalents of *n*BuLi, afforded $[(Me_2N{-}BH_2)_2]$ in 4 h at 25 °C (Scheme 22).



Scheme 22.

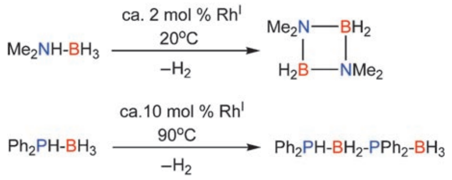
Furthermore, $i\mathrm{Pr}_2NH{\cdot}BH_3$ was found to dehydrocouple using the same catalyst to afford the monomeric aminoborane $i\mathrm{Pr}_2N{=}BH_2$ in just 1 h. Both of these reaction times are considerably less than for the reactions conducted using Rh catalysts, and work is underway to apply this catalyst to the dehydrocoupling of other systems.

Baker has briefly described a homogeneous Cu catalyst for the dehydrocoupling of $Me_2NH{\cdot}BH_3$.[51] Also, Goldberg, Heinekey and co-workers have reported an iridium pincer complex that acts as a highly active catalyst toward the dehydrocoupling of $H_3N{\cdot}BH_3$.[52] It was found that the adduct was converted to a new product after just 14 min at room temperature, and based on IR and XRD characterization, this was assigned as the cyclic pentamer $[(H_2N{-}BH_2)_5]$ (Scheme 23). Significantly, the active catalyst can be regenerated from a dormant species, which forms over time, by reaction with hydrogen gas. The rapid reactivity and clean catalyst regeneration represent an important advance for the development of amine–borane adducts as viable hydrogen storage materials.



Scheme 23.

Mechanistic studies: For the Rh-catalyzed dehydrocoupling of phosphane- and amine–borane adducts, the reaction mixtures are both initially orange, the color of the precatalyst. However, the solutions subsequently display dramatically different appearances; dark red and transparent for the former and black with a black precipitate reminiscent of rhodium metal in the case of the latter.[49,53] This suggested that the mechanisms of the two dehydrocoupling reactions may be different from one another, possibly being homogeneous for phosphane–borane adducts and heterogeneous for the amine–borane analogs. A general approach for distinguishing between true homogeneous catalysis and soluble or insoluble metal-particle heterogeneous catalysis has been carefully developed by Finke through a series of tests involving reaction kinetics, transmission electron microscopy, ligand-poisoning experiments, filtration, catalyst isolation, and so forth.[54] We have recently used this approach to address the nature of the mechanism of the dehydrocoupling of the adducts $Me_2NH{\cdot}BH_3$ and $Ph_2PH{\cdot}BH_3$, with various Rh (pre)catalysts (Scheme 24).[53]



Scheme 24.

When a catalytic amount of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ was added to a solution of $Me_2NH{\cdot}BH_3$ in dry toluene under N_2, a gradual color change from orange to black occurred over approximately 2 h. When the percentage of $[(Me_2N{-}BH_2)_2]$ was monitored by ^{11}B NMR spectroscopy, a sigmoidal-shaped kinetic curve was obtained, reflecting an induction period as the Rh^I was reduced to Rh^0 by the amine–borane adduct (Figure 7).[53] After completion of the reaction, fresh adduct was added and the reaction proceeded without an induction period. Furthermore, no induction period was observed when the Rh^0 source Rh/Al_2O_3 was used for the dehydrocoupling of $Me_2NH{\cdot}BH_3$. When mercury, a well-known poison for heterogeneous metal catalysts, was added to the dehydrocoupling reaction mixture for $Me_2NH{\cdot}BH_3$, the reaction stopped entirely. This was consistent with adsorption to the heterogeneous catalyst surface or amalgam formation.

Filtration of a dehydrocoupling reaction mixture for $Me_2NH{\cdot}BH_3$ through a 0.5 μm filter led to almost complete suppression of the catalytic activity (Figure 8). All of these tests strongly support the operation of an insoluble, heterogeneous catalyst as the main catalytic component for the $Me_2NH{\cdot}BH_3$/Rh system under N_2. Based on a study by Autrey and co-workers who studied the dehydrocoupling of $Me_2NH{\cdot}BH_3$ with $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ under slightly different reaction conditions in which air may be present, a homogeneous catalytic component consisting of Rh_6 clusters may also play a role.[55] Interestingly, the Ti-, Cu- and Ir-catalyzed dehydrocoupling reactions of amine–borane adducts mentioned above appear to operate in a homogeneous manner.[50–52]

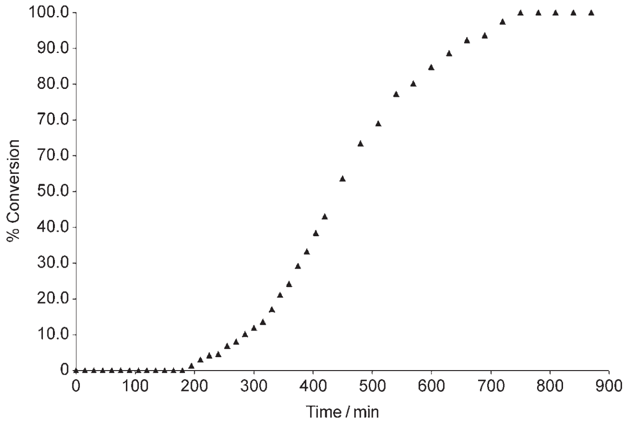


Figure 7. Graph of % conversion of $Me_2NH{\cdot}BH_3$ versus time for the catalytic dehydrocoupling using $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$. Reproduced by permission of The American Chemical Society from reference [53].

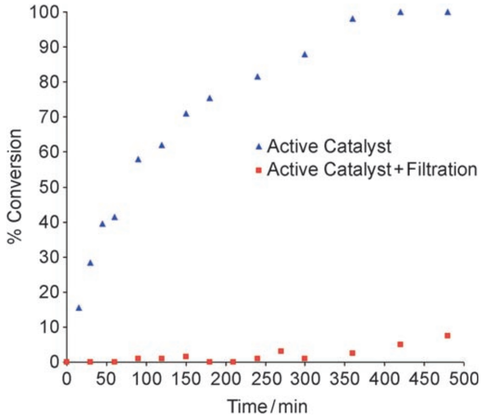
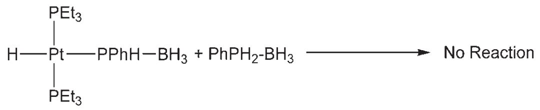


Figure 8. Graph of % conversion of $Me_2NH{\cdot}BH_3$ versus time for the catalytic dehydrocoupling using $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$.

The dehydrocoupling reaction of $Ph_2PH{\cdot}BH_3$ with the precatalyst $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ at 90 °C (which yields **2**, Scheme 18) was also investigated with the same set of tests.[53] The reaction of $Ph_2PH{\cdot}BH_3$ with a catalytic amount of Rh^I precatalyst at 90 °C was monitored by ^{11}B NMR spectroscopy over many repeat trials. An induction period was not observed and a nearly linear, not sigmoidal, conversion with respect to time plot was detected. In addition, the presence of excess mercury was found to have no significant effect on the catalytic dehydrocoupling reaction rate. Moreover, filtration of a catalytically active solution through a 0.5 μm filter followed by the addition of more $Ph_2PH{\cdot}BH_3$ was also found to have little effect on the dehydrocoupling activity. These studies strongly suggest that a soluble, homogeneous Rh species is the active dehydrocoupling catalyst for $Ph_2PH{\cdot}BH_3$. Overall, this work strongly indicates that amine–borane adduct dehydrocoupling under N_2 is a predominantly heterogeneous process, while phosphane–borane dehydrocoupling operates by means of a homogeneous mechanism.

The presence of different mechanisms for the catalytic dehydrocoupling of phosphane–borane adducts appears to be related to three factors: 1) the reducing strength of the adduct, 2) the extent of dissociation of the adduct and 3) phosphane ligation and/or poisoning of the active catalyst.[53] From the perspective of 1), amine–borane adducts are significantly stronger reducing agents than phosphane–borane adducts. This causes the amine–borane adduct to function like a "borohydride-type" reducing agent, which have been widely used for the formation of metal colloids from metal halide precursors. Thus, for $Me_2NH{\cdot}BH_3$ a heterogeneous process is possible as the amine–borane adduct is a strong enough reducing agent for the Rh^I precursors while for $Ph_2PH{\cdot}BH_3$, a homogeneous process is favoured as reduction of Rh^I does not occur because the B−H bond is not sufficiently hydridic.[56] From the perspective of 2) and 3), metal-assisted dissociation of phosphane–borane adducts using colloidal Rh has been demonstrated and both the resulting free phosphane and free borane can effectively bind to the Rh surface to poison the active sites.[57] The detailed mechanisms for the metal-catalyzed dehydrocouplings of phosphane- and amine–borane adducts is currently under investigation, in particular by studies of the reactivity of complexes that model potential intermediates in the catalytic cycle. Such studies may allow for the development of more efficient catalysts, which would be very valuable in the case of P−B bond formation and also for the dehydrocoupling of amine–borane adducts such as $H_3N{\cdot}BH_3$.

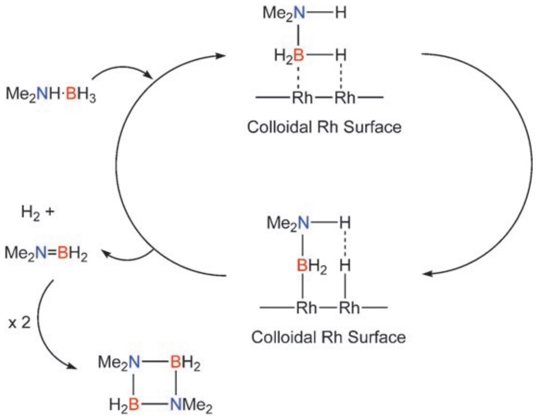
For the catalytic dehydrocoupling of phosphane–borane adducts, initial steps involving insertion of the metal center into either P−H or B−H bonds, followed by subsequent σ-bond metathesis and/or oxidative addition/reductive elimination processes may define the catalytic cycle. Interestingly, stoichiometric treatment of $Pt(PEt_3)_3$ with $PhRPH{\cdot}BH_3$ (R = H, Ph) resulted in P−H bond oxidative addition at the Pt center to afford the *trans* hydride complexes $[PtH(PPhR{\cdot}BH_3)(PEt_3)_2]$.[58] However, when these compounds were treated with a further equivalent of $PhPH_2{\cdot}BH_3$, no subsequent P−B bond formation at the Pt center was observed (Scheme 25). Similarly, reaction of *cis*-$[PtH_2(dcype)]$ (dcype = 1,2-bis(dicyclohexylphosphano)ethane) with $PhRPH{\cdot}BH_3$ (R = H, Ph) was found to exclusively afford the monosubstituted complexes *cis*-$[PtH(PPhR{\cdot}BH_3)(dcype)]$ by means of a dehydrocoupling reaction between Pt-H and P−H bonds.[59] The lack of relevant reactivity may imply that metal-boryl species rather than M−P bonds are the key intermediates in the catalytic cycle.



$$\mathrm{H{-}\overset{PEt_3}{\underset{PEt_3}{Pt}}{-}PPhH{-}BH_3 + PhPH_2\text{-}BH_3} \longrightarrow \text{No Reaction}$$

Scheme 25.

As noted above, amine–borane adduct dehydrocoupling using Rh catalysts appears to mainly be a heterogeneous process; however, the detailed steps involved are not understood. One mechanistic possibility is a concerted process in which hydrogen atoms from B and N are transferred at the same time to form two Rh−H bonds on the catalyst surface. This would afford monomeric $Me_2N{=}BH_2$ species that would cyclodimerize while the Rh colloid surface releases H_2 gas. Another possible mechanism (Scheme 26) involves oxidative addition of a B−H bond to the Rh colloid surface followed by formation of the B=N and H−H bonds to release H_2 and $Me_2N{=}BH_2$.



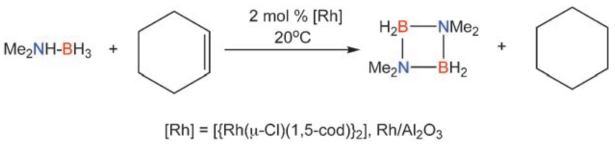
Scheme 26.

Applications in hydrogen storage and transfer hydrogenation: Hydrogen storage materials are desirable as clean energy sources that can potentially replace the petroleum-derived products that currently fuel vehicles.[45,60] Unlike petroleum-fueled vehicles that produce environmentally hazardous wastes such as carbon monoxide, nitrogen oxides and sulfur oxides, hydrogen reacts with oxygen to produce energy with water as the only byproduct. The current challenges include how to store hydrogen efficiently and safely in a vehicle and which catalyst is best for hydrogen release.[60] The volume that hydrogen occupies and the evident hazards associated with the gas have prompted researchers to investigate solid hydrogen-storage materials.[61] The most studied material, $Na[AlH_4]$, eliminates hydrogen at 110 °C when doped with Ti, but this process suffers from drawbacks such as very slow kinetics and low hydrogen-storage densities.[62] The hydrolysis of metal hydrides is also being studied, but regeneration of the spent material is thermodynamically unfavorable, thus hindering practical applications. Carbon-based materials such as graphite particles, fibers and nanotubes show virtually no room-temperature hydrogen sorption (1 wt % or less) and their storage densities are controversial due to reproducibility issues.[63]

Ammonia–borane, $H_3N{\cdot}BH_3$ is attracting considerable interest as it possesses one of the highest densities of hydrogen available (196 grams H_2 per kg), and its release can be thermal or catalytic.[45a,49b] Autrey and co-workers have reported the thermal release of hydrogen from a silica nanoscaffold that contains ammonia–borane.[45a] Ionic liquids can also be used to promote H_2 release from the molecule.[64] Finally, as noted above, Rh and Ir catalysts have been studied for the dehydrogenation of $H_3N{\cdot}BH_3$.[49b,52]

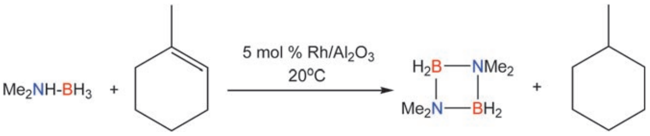
However, although reversibility is a current challenge, catalytic release has advantages over thermal release as it will overcome the obstacle of low rate of hydrogen evolution at relatively low temperatures. In addition, development of a polyaminoborane material may be advantageous over the current pathway, which generates small molecules such as borazines, as handling of the polymeric material is expected to be more facile. Sneddon and co-workers have prepared polyborazylenes using thermal dehydrocoupling and boron nitride ceramic fibers derived from these materials exhibit enhanced oxidation resistance, thermal stability and electrical insulation properties.[65] Boron nitride nanotubes have also been shown to reversibly uptake and store hydrogen at room temperature.[66]

Amine–borane adducts also show promise in transfer hydrogenation of organic substrates. For example, hydrogenation of cyclohexene at 25 °C was observed using $Me_2NH{\cdot}BH_3$, as the hydrogen source with catalytic amount of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (Scheme 27).[67]



Scheme 27.

The scope and selectivity of Rh^0-catalyzed tandem dehydrocoupling–hydrogenation reactions utilizing commercially available $Me_2NH{\cdot}BH_3$ as a stoichiometric H_2 source has been investigated.[68] Use of Rh/Al_2O_3 allows product separation and catalyst recycling. Regioselectivity is exemplified by the hydrogenation of terminal olefin groups in preference to internal C=C bonds in conjugated dienes with one equivalent of $Me_2NH{\cdot}BH_3$. There is a preference for the *E*- over the *Z*-substituted isomer in the hydrogenation of the internal alkyne, 2-hexyne. Interestingly, sterically hindered trisubstituted alkenes such as 1-methyl-1-cyclohexene are readily hydrogenated in 100 % yield with 5 % Rh/Al_2O_3 at 25 °C in 24 h (Scheme 28).



Scheme 28.

Future Outlook

Although the use of metal-mediated dehydrocoupling as a route to the formation of bonds between main-group elements is still in its relative infancy, many significant advances have been made as discussed in this article. The motivations to create catenated structures based on p-block elements are several-fold. Compared to C–C bonds, bonds between main-group elements can be stronger, more oxidatively and thermally stable, and can provide additional conformational flexibility (e.g., Si–O bonds in siloxane-based oligomers and polymers). Chains of p-block elements can also possess unusual delocalization effects (e.g., σ conjugation in the catenated Group 14 systems $(R_2E)_n$, E = Si, Ge, Sn). Novel intermolecular interactions are also made possible. For example, dihydrogen bonds[36] present in dehydrocoupling products derived from Group 13/15 adducts could also find use for stabilizing unique supramolecular architectures.[69]

Catalytic dehydrocoupling has clearly demonstrated significant synthetic potential for the generation of novel rings, polymers and materials based on main-group elements with interesting and useful properties. For example, catalytic dehydrocoupling routes to polysiloxanes, polysilanes and especially polystannanes have already played important roles in the development of these fascinating materials.[8,16,25,26] In recent work, the theoretical structure and properties[70] of polyphosphinoboranes along with the effect of chain substitution[71] have been evaluated by Jacquemin and co-workers providing insight into the chain flexibility and dipole moment. Future studies of the conversion of micro- and nanopatterned arrays of $(p\text{-}CF_3C_6H_4PH{-}BH_2)_n$ and related polyphosphinoboranes into boron phosphide ceramic replicas would be desirable as this could potentially yield nanoscopic patterned semiconductor domains. Extending the dehydrocoupling reaction in an effort to prepare nanomaterials based on main-group elements also shows promise as preliminary work indicates that amine–borane adduct dehydrocoupling can be applied to the synthesis of boron nitride nanotubes.[72] Potentially important future applications for the dehydrocoupling of amine–borane and related adducts also exist in the areas of transfer hydrogenation and hydrogen storage.

Many interesting mechanistic issues need to be considered, as illustrated by the earlier work on silane dehydrocoupling and more recently by the dehydrocoupling of stannanes and phosphane– and amine–borane adducts. The observation that both early and late transition metals can promote the dehydrocoupling of amine–borane adducts is significant, together with the situation that the process can occur through either a homogeneous or heterogeneous mechanism. Detailed mechanistic understanding will be important for the identification of the key factors that will allow catalyst optimization and the potential extension to new substrates. Metal-free, homogeneous catalysis or “organocatalysis” is attracting considerable attention in the organic community as an alternative to the transition-metal-based counterpart due to potential advantages both from an economical and environmental perspective. A preliminary report by Denis and co-workers[39] of $B(C_6F_5)_3$ promoted dehydrocoupling of $PhPH_2{\cdot}BH_3$ is important in this regard and suggests promise for the future.[73]

Considerable scope exists for the further expansion of the catalytic formation of E–E′ bonds to other areas of the p-block elements. In addition, a fascinating new avenue of research would involve the extension of this methodology to transition metals, namely the catalytic dehydrocoupling of $M{-}H^{\delta-}$ and $^{+\delta}H{-}M'$ species to form $M{-}M'$ bonds. Clearly there are substantial future opportunities for exploratory synthetic work, mechanistic insight, and interesting applications in the catalytic dehydrocoupling field.

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[2] The catalytic formation of C–E bonds (E = Main-group element) by processes such as hydrosilation and hydroboration are also well developed but are beyond the scope of this review. For example, see: a) *Comprehensive Handbook on Hydrosilylation* (Ed.: B. Marciniec), Pergamon, New York **1992**; b) H. C. Brown, *Hydroboration*, W. A. Benjamin, New York, **1962**.

[3] Dehydrocoupling reactions between heavy main-group hydrides that proceed without the addition of transition-metal catalysts, but rather by thermal or autocatalytic routes, are known. For example, solutions of R_2BiH ($R = (Me_3Si)_2CH$) are stable below −20 °C; however, warming to room temperature results in the generation of H_2 and dibismuthane $R_2Bi{-}BiR_2$: G. Balázs, H. J. Breunig, E. Lork, *Organometallics* **2002**, *21*, 2584.

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