Dehydrocoupling: A General Route to Bonds Between P-Block Elements

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Abstract

Dehydrocoupling is a unique reaction to p-block elements that allows for the formation of bonds between these main group elements with loss of hydrogen. The transformation is highly atom economical, and hydrogen is a relatively benign byproduct that also provides the thermodynamic driving force for the reaction. For these reactions, couplings between most of the p-block elements are known. In the instance when bonds between the same elements are formed, then this reaction primarily applies to elements in the third period (3p) and heavier. For reactions between different elements, most any combination of p-block elements is possible. These reactions are known to make small molecules and polymers. Catalysts for this reaction include metal compounds (i.e., organometallic catalysts), Lewis acids, and frustrated Lewis pairs, and the mechanisms of dehydrocoupling are highly varied, representing much of the spectrum of catalysis.

Keywords: Dehydrocoupling, catalysis, main group, p-block, hydrogen, mechanism

Dedication: This review is dedicated to the memory of Ian Manners, a leader catalysis for main group chemistry whose creativity in chemistry was only exceeded by his enthusiasm for it.

Introduction

Heavier main group elements, particularly those in the p-block or groups 13–18, suffer from a less well articulated synthetic chemistry than carbon and related second period (2p) elements. In some comparisons to synthetic organic chemistry, these elements (3p and heavier) primarily lean on S_N2 and E1 and not much else. This is, of course, not true. As the 21st century has continued to reveal, p-block chemistry is a fertile ground for fundamental chemical discovery and greater chemical utility.[1]

One of the transformations unique to the heavier p-block elements is dehydrocoupling,[2] and like all reactions in an ideal universe, it is named for what it does. A dehydrocoupling reaction loses hydrogen (“dehydro”) to form a new element–element bond (“coupling”) per equation 1 for the general element “E.” For most elements in the third period (3p elements) or heavier, this reaction has been realized, and for some of the heaviest p-block elements, this reaction is spontaneous. In most cases, however, dehydrocoupling requires a catalyst.

A side note on catalysis is merited. Catalysts are compounds that are added to reactions and remain unchanged over the course of the reaction. They work by effectively reducing the activation energy required for the uncatalyzed reaction. The word “effectively” is not semantic, but the simpler statement “catalysts reduce activation energy” is sometimes said casually. That simpler statement is incorrect because a catalyst avails an *alternative* lower-energy path for a possible reaction. The key point, though, is that dehydrocoupling illustrates a greater reason for catalysis than just improved efficiency. In the uncatalyzed effort to form a new element–element bond with loss of hydrogen, the system would proceed by a $2\sigma+2\sigma$ cycloaddition (Figure 1, left), which is a symmetry-forbidden transformation. It is this symmetry-forbidden transition state that prohibits spontaneous dehydrocoupling for most systems. The catalyst does not make $2\sigma+2\sigma$ cycloaddition allowed, rather a new pathway becomes available that is not only symmetry allowed, but at lower energy than that without the catalysts (Figure 1, right). The new, catalytic path is necessarily different than the uncatalyzed reaction, despite making the same product. This is a crucial point in catalysis that is well illustrated with dehydrocoupling, where many reactions would not proceed in the absence of a catalyst.

Fundamental reactions involving of main group compounds with E–H bonds accelerated in the 1960s, though examples of dehydrocoupling reactions are known before that time. Other reactions that afford E–E bonds in the p block had been known for much longer, often achieved by reduction of E–Cl compounds, reactions generally known as Würtz couplings or reactions. A more deliberate effort to explore metal-catalyzed dehydrocoupling emerged in the 1980s, initially led by Sneddon's work on B–B products.[3] A strong interest in the synthesis of polysilanes, or polymers with a silicon-only backbone, drove many advances in the dehydrocoupling of group 15 elements. Interest in dehydrocoupling grew again in the early 2000s with exploration of ammonia borane and related derivatives as potential medium for chemical storage of hydrogen.[4-8] This and related *hetero*dehydrocoupling reactions, or dehydrocoupling reactions between different elements, continue today with popular combinations being between groups 13 and 15 as well as between group 14 and group 15 or 16 elements with these various combinations yielding unique polymers or precursors for ceramics and other electronics-relevant materials.[9-14]

Thermodynamics of dehydrocoupling

Catalyzed or not, a reaction must have a driving force to proceed. A crude thermodynamic analysis explains why these dehydrocoupling reactions are viable. For much of the p-block, element–hydrogen bonds are relatively weak. The word "relative" needs a scale of some type, and the strength of 3p element–hydrogen bonds compared to carbon analogs provides a good benchmark for the relative strength. For example, the C–H bond of methane is 103 kcal mol^{-1}, but that of phosphine (PH_3) is closer to 78 kcal mol^{-1}, which gives a good sense of 'relatively' weak. This disparity is general around the p-block regardless of the degree of covalency or whether the E–H bond is hydridic like a silane or acidic like a thiol. The consequence of 'relatively' weak chemical bonds is higher reactivity, and E–H bonds in the p-block are easy to break with a variety of reagents. The resultant E–E bonds of the products are not typically strong either (e.g., P–P σ-only bond = 61 kcal mol^{-1}).[15] The set of modest bond dissociation energies for many E–E and E–E' mean that the bond formation component (the "coupling" of dehydrocoupling) is not the driving force for the reaction. The hydrogen gas produced is the strongest purely σ bond known at 104 kcal mol^{-1}, and it is invariably a gas. Thus, the production of hydrogen provides the enthalpic and entropic benefits that make possible a reaction in which weak bonds are broken to make weak(er) bonds.

Production of hydrogen is the thermodynamic driver of this reaction, but it is a benefit in other ways. Reactions that lose only H_2 exhibit very good atom economy, which is one of the 12 Principles of Green Chemistry, and catalysis is another.[16] The loss of hydrogen as a byproduct is a synthetic boon because it is a gas with low reactivity to many compounds and poor solubility in most solvents. This makes hydrogen easy to separate from many reactions. Furthermore, hydrogen is invisible in the infrared, and its low mass allows it to float out of the atmosphere. It is an easy to dispose of byproduct with virtually no environmental impact. Despite these perks, hydrogen is quite flammable, and gas evolution presents unique risks in performing a chemical reaction. Appropriate caution and protocols in these reactions are required.

For the 2p elements, like carbon, these thermodynamic considerations are no longer favorable where strong C–H bonds are broken to form weaker C–C bonds. However, there is tremendous economic value to converting methane, which is abundant and underutilized as a chemical feedstock, to higher alkanes and other organic products. Therefore, the idea of dehydrocoupling methane and other alkanes has been explored. In fact, the initial identification of σ-bond metathesis is attributed to Watson during exploration of this kind of reactivity.[17] These studies did not yield a dehydrocoupling process of methane, but significant discoveries about the reactivity of C–H bonds and d^0 metal compounds were made. Such an outcome is a good reminder that the products of good science are not always the original intention of an investigation.

Substrates and mechanisms

There are two broad categories of dehydrocoupling reactions, those that form homoatomic bonds and those between different elements (E–E vs. E–E'). Both categories have copious examples in the literature. Initial interest in dehydrocoupling stemmed from "homodehydrcoupling" reactions, like the early borane dehydrocoupling reactions reported by Sneddon as noted above.[3] The evolution to silane dehydrocoupling reactions and efforts for silane dehydropolymerization, dehydrocoupling reactions that result in a polymer, happened thereafter and was a tremendous growth point in this catalysis (eq 2). Silane dehydrocoupling was primarily led by three investigators, Corey, Harrod, and Tilley, who had different strategies and aims.[18-20] The major common goal of these studies was to arrive at long-chain polysilanes via dehydrocoupling. This was intended to be a safer strategy to these materials in comparison to a reductive (Würtz coupling) strategy, which uses alkali metals and necessarily produces copious metal-halide waste. The intense interest in these products derived from a property of polysilanes, and heavier group 14 derivatives, known as σ conjugation, meaning they conduct through an extended array of σ bonds. This behavior stands in contrast to carbon-based σ-bonded materials, like polyethylene, that are typically insulators.

Through investigation of silane substrates and related group 14 compounds like germanes and stannanes,[21] several normative mechanisms were observed.[22] For d^0 metal compounds, like group 4 or lanthanide metallocene compounds, the reactions largely appeared to proceed via σ-bond metathesis (Figure 1, right).[17,23] Late transition-metal compounds typically proceed through sequences of oxidative addition and reductive elimination.[24] These mechanistic steps have been identified for other substrates, like phosphines (R_xPH_{3-x}) that can be dehydrocoupled to diphosphine (RR'P–PRR') or cyclophosphine (P_nR_n, $n = 4$, 5, or 6, commonly) products.[15]

Some substrates have revealed mechanisms that are unique. For example, metal-ligand multiply bonded compounds have been implicated in the dehydrocoupling of phosphines as reported by Stephan.[25] In those reactions, cyclophosphines were prepared by dehydrocoupling of primary phosphines at a zirconocene catalysts. This catalyst relied on a phosphinidene (M=P bonded) intermediate that activated the P–H bonds of the substrate via 1,2-addition across the Zr–P bond (Scheme 1), a reaction type that is well documented for metal–nitrogen multiple bonds.[26]

Germanium–germanium bond formation using ruthenium compounds as catalysts was observed to take a significant detour from these archetypal organometallic mechanistic steps. Berry and coworkers found that trimethyl germane was polymerized via loss of methane equivalents ("demethylcoupling," perhaps?). That reaction relied on the migration of methyl substituents from germanium and subsequent addition to the resultant ruthenium germylene intermediates (Scheme 2).[27] This step may seem unusual but there is ample precedence for such migrations with metal silyl compounds that has been extended to heavier elements as well.[28]

Low valent fragments can be effectively ejected from a metal compound in some dehydrocoupling reactions, a transformation that was termed α elimination by Neale and Tilley, who first identified this step in stannane dehydropolymerization reactions.[29] This kind of transformation has been extended to other elements, like antimony, arsenic, and even lighter elements like silicon and phosphorus.[22,30,31] The extrusion of a low valent fragment means that the new element-element bond forming step will be off the metal compound. For these fragments, like stannylenes that are formally tin(II) compounds, they were already known to insert into Sn–H bonds. It is likely that an off-metal E–H bond insertion step is how many of these α elimination based dehydrocoupling reactions proceed.

Heterodehydrocoupling reactions often proceed with very different mechanisms from those between the same elements. A potential reason for this disparity is that the electronegativities between the various p-block elements and hydrogen can vary significantly. Elements like boron and silicon, with electronegativities significantly less than hydrogen, have hydridic (H^- like) E–H bonds, while elements like phosphorus and sulfur, with greater electronegativities than hydrogen, have relatively acidic (H^+ like) E–H bonds. Because hydride is an excellent Brønste~~a~~d base, ~~a~~ the hydridic and acidic compounds can react to form E–E' bonds with spontaneous loss of hydrogen. This reactivity has been known for amine boranes (RR'$NHBH_3$) for decades.[6] Compounds like the parent ammonia borane, NH_3BH_3, have moderate thermal stability in the solid state and will more rapidly decompose to a variety of products including borazine, $N_3B_3H_6$, a six-membered ring akin to benzene.[6] Similar reactions are known for other elements in the p-block.

Manners started and led intense interest on catalyzed amine-borane and, to a lesser extent, phosphine-borane dehydrocoupling reactions.[32] The initial interest in these substrates was focused on efforts to prepare new materials, polymers with E–E' backbones. This aim was realized relatively quickly with phosphine boranes as precursors to poly(phosphinoboranes), but the realization of long-chain poly(aminoboranes) was a longer effort.[6,33] Both categories of materials are interesting in their own right and part of larger efforts in developing polymers containing p-block elements in the main chain.[34] After the initial investigations of polymers of these elements, investigators became keenly interested in using ammonia borane as a chemical storage agent for hydrogen because it has a high percent of hydrogen by mass (~19%) and its lower reactivity than H_2 gas.[7] Mechanistic studies of the wide range of catalysts for amine borane dehydrocoupling has been a fertile ground for discovery, as has been well illustrated and described by Weller.[35] The key factors are that the activation of E–H bonds by catalysts dehydrocoupling these substrates is variable, and the steps that yield polymers are also variable. For example, an imidoborane, like $Me_2N{=}BH_2$ (eq 3), is unstable but can condense with other imidoborane equivalents to form oligomers or polymers. However, imidoboranes can be formed by several potential pathways. Thus, it is very useful to conceptualize the activity of catalysts as activating substrates and think separately about the catalyst reactivity with respect to the polymerization reaction.[33]

Other heterodehydrocoupling reactions engage in yet different mechanisms. Despite the difference in E–H bond polarity, couplings between nitrogen and silicon are not spontaneous. However, the relative electronegativity differences of these elements avail effective catalytic preparation of N–Si bonds via dehydrocoupling. For example, the electrophilicity of the silane substrate can be enhanced by a highly Lewis acidic phosphonium salt $[(C_6F_5)_3PF][B(C_6F_5)_4]$ to facilitate direct attack by a nucleophilic amine substrate.[36] In that particular study, the hydrogen evolved is transferred to an alkene substrate in a concurrent hydrogenation reaction.

This idea of nucleophilic/electrophilic reactivity in heterodehydrocoupling reactions is long standing. The first highly detailed kinetic and mechanistic study of a amine/silane dehydrocoupling catalysis reported by Sadow indicated that the amine is deprotonated to enhance its nucleophilicity as the magnesium amide.[37] This amide nucleophile then attacks silane and promotes greater hydricity of the Si–H bond, leading to hydrogen loss and N–Si bond formation (Scheme 4). This nucleophilic mechanism has also been seen for other combinations like Si–O bond formation, which is well explored.[12] Other mechanisms that are non-nucleophilic are also known for these reactions.[38]

Traditional organometallic steps are also routine for these heterodehydrocoupling reactions, and this kind of catalysis may more useful for system where the relative electronegative of substrates are more similar. Han and Tilley, for example, leveraged a sequence of oxidative addition and reductive elimination steps in the dehydrocoupling of phosphines and thiols.[39] In those reactions, the rhodium catalyst favors formation of rhodium–sulfur σ bonds, and subsequent oxidative addition of a phosphorus–hydrogen bond affords a presumed rhodium(III) intermediate that can reductively eliminate product thiophosphine (Scheme 5). Interestingly, other investigators have taken advantage of the a metal catalyst's affinity for one substrate versus another, which is often predicted by hard-soft acid-base arguments, to afford high selectivity in heterodehydrocoupling reactions.[22]

Concluding remarks

This review, while far from authoritative, includes mention of homocouplings (B–B, Si–Si, Ge–Ge, Sn–Sn, P–P, As–As, and Sb–Sb) as well as heterocouplings (N–B, P–B, Si–N, Si–O, and P–S), though there are far more examples than these. As with many established transformations, it can seem like there might be little left to do with dehydrocoupling. Regardless of the number of reactions known, the continued use of products from dehydrocoupling reactions as materials or materials precursors stands in contrast to this notion and therefore demonstrates utility for this transformation in consumer goods and energy applications.[9] There are still even basic discoveries to be made, and at time of this report, there are many examples of main group bonds that have not yet been prepared by this strategy as well as open questions about how many catalysts work. Thus, this reaction has ample room for growth and increasing utilization.

Acknowledgements

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(1) Rather than a limited set of articles to prove this point, two particular efforts are noted here: *Chemical Reviews* published a special edition titled "Frontiers in Main Group Chemistry" in 2019 (issue 14) and *Chemical Society Reviews* developed a theme collection "Modern Main Group Chemistry" in 2016.

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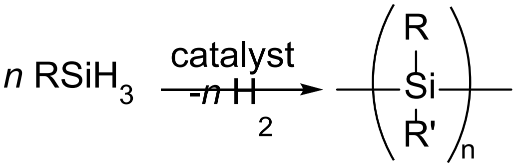
Equations

Equation 1

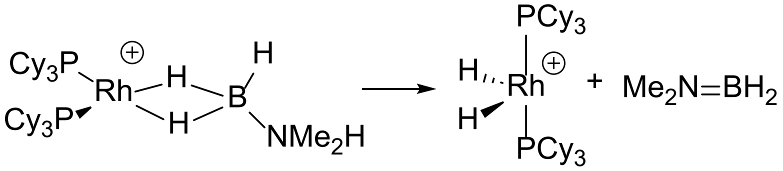
$$2\ \mathrm{R}_n\mathrm{E{-}H} \xrightarrow{\mathrm{L}_n\mathrm{M}} \mathrm{R}_n\mathrm{E{-}ER}_n + \mathrm{H_2}$$

Equation 2



$$n\ \mathrm{RSiH_3} \xrightarrow[-n\,\mathrm{H_2}]{\text{catalyst}} \left(\overset{\mathrm{R}}{\underset{\mathrm{R'}}{\mathrm{Si}}}\right)_n$$

Equation 3



Figures

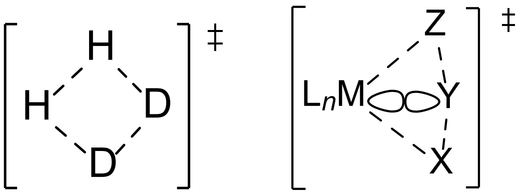
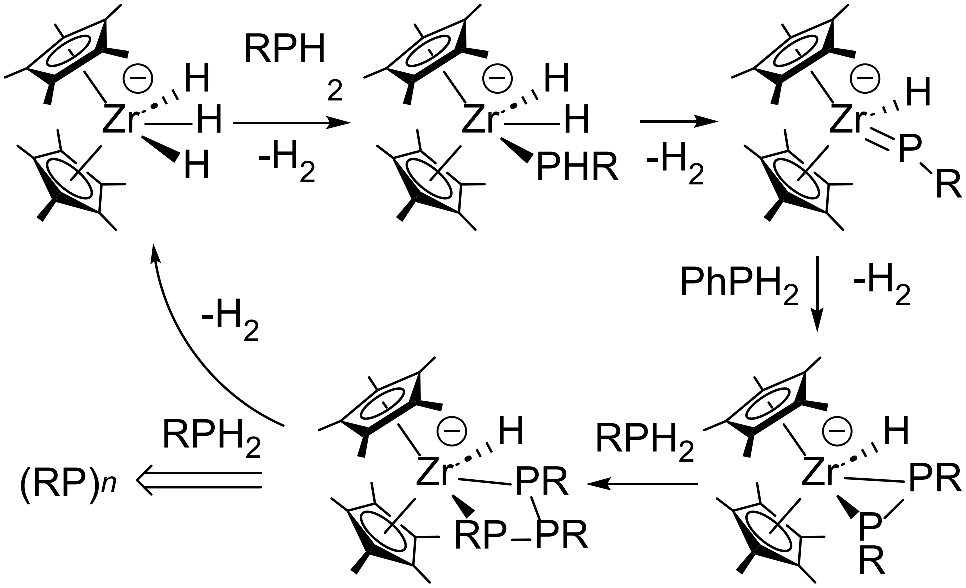
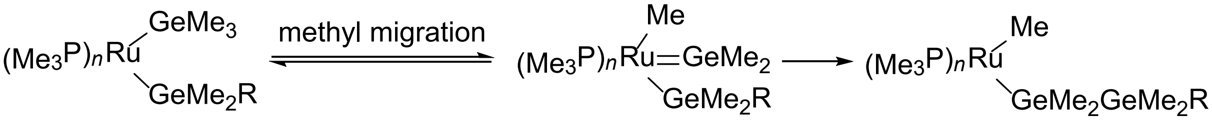


Figure 1 Left: A purely $2\sigma+2\sigma$ cycloaddition transition state, which is symmetry forbidden. This prohibition ceases spontaneous dehydrocoupling but also explains why, for example, mixtures of hydrogen (H_2) and deuterium (D_2) would not spontaneously form HD. Right: One example of a catalyst overcoming this symmetry prohibition. For formally d^0 metal compounds, the kite-like transition state of a σ-bond metathesis reaction relaxes the symmetry of this transition state through orbital overlap of a vacant metal orbital with an orbital of the distal element in the transition state.

Schemes

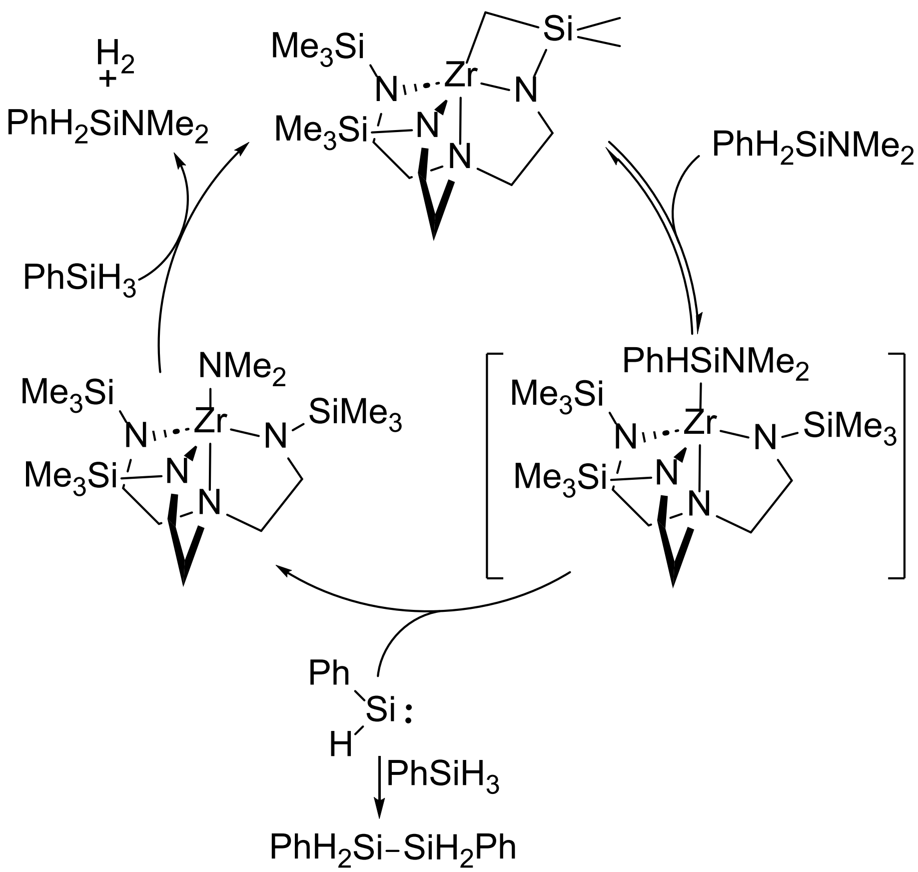


Scheme 1 Proposed catalytic cycle for the dehydrocoupling of phosphines leveraging a zirconium phosphinidene intermediate.

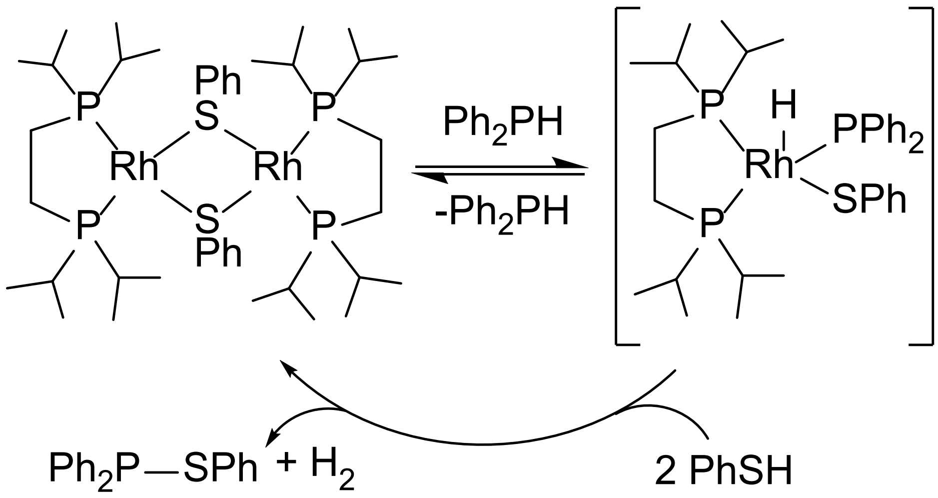


$(Me_3P)_nRu(GeMe_3)(GeMe_2R) \rightleftharpoons (Me_3P)_nRu(Me)(=GeMe_2)(GeMe_2R) \longrightarrow (Me_3P)_nRu(Me)(GeMe_2GeMe_2R)$

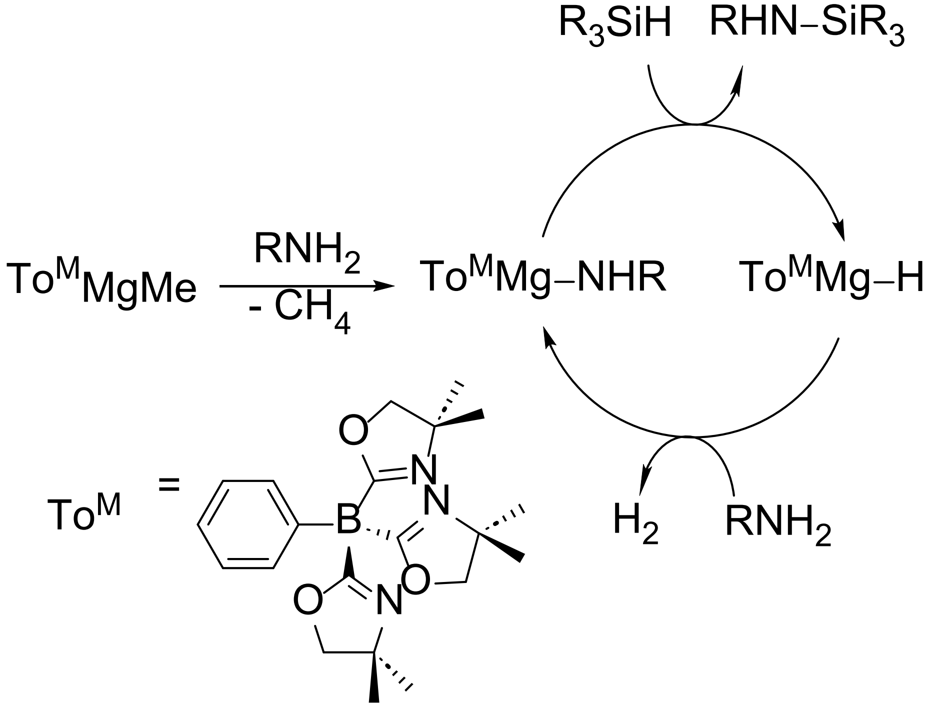
Scheme 2 Poly(methylgermanes) prepared by methyl migration in ruthenium-catalyzed dehydrocoupling of Me_3GeH.



Scheme 3 A dehydrocoupling process of organosilanes that relies on the elimination of α silylene, or low-valent silicon fragment.



Scheme 5 Rhodium-catalyzed dehydrocoupling of phosphines and thiols that relies on traditional oxidative addition and reductive elimination steps.



Scheme 4 N–Si dehydrocoupling affected by the enhanced nucleophilicity of an amine through deprotonation.