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Dehydrogenative Bond-Forming Catalysis Involving Phosphines

Rory Waterman*

Department of Chemistry, University of Vermont, Cook Physical Science Building, 82 University Place, Burlington, Vermont, 054055, USA

Abstract: This review presents developments in the young field of dehydrogenative coupling reactions of phosphines. Catalytic phosphorus–element bond formation via dehydrocoupling has rapidly expanded since the first discoveries in the mid 1990s. A survey of the available catalysts, P–P and P–E products, and mechanistic understanding is presented with emphasis on the emerging synthetic applications of this reaction.

INTRODUCTION

Catalytic methods for generating bonds to phosphorus are still limited despite the well-developed stoichiometric chemistry associated with phosphorus-containing molecules [1-5]. In recent years however, there has been an increased demand for reactions that catalytically form phosphorus–element bonds in biology [6-8] and organic synthesis [9-15], with a particular eye on preparation of chiral phosphines for ligands [16]. There has also been a surge in the demand for phosphorus-containing materials with π-conjugation [17-21]. These needs have prompted investigation of new catalytic methods to generate bonds to phosphorus.

Historically, synthesis of P–P bonds has been achieved through Würtz-type reductions of R_mPX_n (X = halide; $m = 1, 2$; $n = 3 - m$) reagents [1, 22] or dehydrohalogenation of R_mPX_n and R_mPH_n reagents [5]. These reactions have been tremendously effective in the stoichiometric preparation of P–P bonds. However, these methodologies are limited by the lack of selectivity, use of strong reducing agents such as alkali or alkaline earth metals, generation of mineral acids, and/or the need for both phosphine halide and phosphine reagents.

A major synthetic leap in element–element (E–E) bond formation was achieved through the development of dehydrocoupling catalysis. In dehydrocoupling, two molecules with element–hydrogen bonds undergo a net metathesis forming the E–E bond and H_2. Spontaneous dehydrocoupling is all but unknown except for the heaviest elements of the main group, such as lead [23]. In some cases however, forcing conditions of high temperatures or photolysis are known to induce dehydrocoupling reactions [24, 25]. A number of organometallic complexes are now known to catalyze this reaction (eq. 1). The principal benefit of metal catalysis is the greatly increased scope of main-group hydrides that undergo dehydrocoupling [26-32].

$$2\ R_nE{-}H \xrightarrow{L_nM} R_nE{-}ER_n + H_2 \qquad (1)$$

Utilization of dehydrocoupling catalysis offers three major advantages: (i) Safety. Dehydrocoupling catalysis circumvents the potential hazards of using strong reducing agents in Würtz-type reductions of halogenated main-group species, which is a mainstay method of forming E–E bonds [22]. (ii) Selectivity. Dehydrocoupling catalysis selects for reactions at E–H bonds. Strong reducing agents, such as those employed in Würtz-type reductions, are known to cleave other bonds such as the P–C bonds of aryl phosphines [22]. Further, dehydrocoupling catalysts can select for single or multiple E–H bonds. (iii) "Green" synthesis. Dehydrocoupling catalysis produces only one byproduct, hydrogen—a desirable commodity. In reductive E–E bond-forming reactions, the byproduct is an inorganic salt, a considerably more voluminous and potentially hazardous waste [28, 30]. Similarly, dehydrohalogenation, which is a more selective process than Würtz-type reductions, necessarily produces an equivalent of mineral acid per P–P bond formed and is best run in the presence of stoichiometric base.

Application of dehydrocoupling in E–E bond-forming catalysis has been known for some time. This reactivity was first investigated by Sneddon and coworkers for the formation of B–B bonds [33, 34], but since that time, this catalysis has focused largely on formation of Si–Si bonds [27, 28, 31]. Dehydrocoupling catalysis has allowed for improved synthesis of σ-conjugated polysilanes, and it has also been extended to the synthesis of polystannanes [29]. One of the rapid-growth areas in dehydrocoupling catalysis has been the development of heterodehydrocoupling, the dehydrogenative coupling of two different elements or the same element with different substitution patterns—a reaction that has dramatically increased the synthetic versatility of E–E bond-forming catalysis [30].

Recently, there has been a piqued interest is the application of heterodehydrocoupling toward hydrogen storage. Chemical storage of hydrogen may present unique advantages over liquefaction, pressurization, and physisorption [35]. Ammonia borane ($H_3N{\cdot}BH_3$) is emerging as a potentially valuable chemical storage medium for hydrogen [36], and there are several catalysts that are known to affect hydrogen liberation from ammonia-borane [37-41].

One of the major problems associated with developing catalysis based on P–H bond activation is the potential of the

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*Address correspondence to this author at the Department of Chemistry, University of Vermont, Cook Physical Science Building, 82 University Place, Burlington, Vermont, 05405-0125, USA;
E-mail: rory.waterman@uvm.edu

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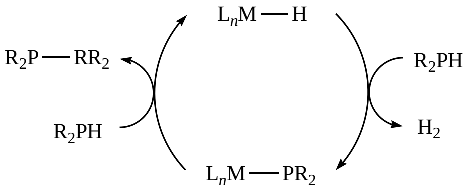
π-basic lone pair at phosphorus to act as a ligand [1]. Any activation step would presumably require some degree of unsaturation at the metal catalyst, and competitive binding of a hydrophosphine ligand may occur. Thus, phosphine dehydrocoupling catalysis is potentially hampered by strong phosphorus-to-metal dative bonding.

However, reaction of phosphines by dehydrocoupling remains attractive (Scheme **1**). The relatively low phosphorus–hydrogen bond dissociation energy of ca. 78 kcal/mol favors catalytic strategies involving P–H bond activation. A simple tabulation of the bond dissociation enthalpies (BDEs) of phosphine (78 kcal/mol), diphosphine (P–P, 47 kcal/mol), and hydrogen (104 kcal/mol) suggests a reaction enthalpy for the dehydrocoupling of phosphine (Scheme **1**, E = P, R = H) to be mildly exothermic at –5 kcal/mol [1]. In similar analyses of the dehydrocoupling of a variety of main-group elements, Harrod and coworkers found that many of those reactions were approximately thermoneutral. They suggested that some caution should be made in extrapolating the energetics of the parent systems to the substituted species used in the laboratory because of the substantial difference in E–H BDEs that are possible [28]. Similarly for phosphorus, the BDEs of substituted phosphines may be significantly different from that of phosphine. The key observation to be made from these data is that the driving force is based primarily on the entropic benefit of H_2 formation rather than the strength of the resultant P–P bond.



Scheme 1. General strategy for metal-catalyzed phosphine dehydrocoupling.

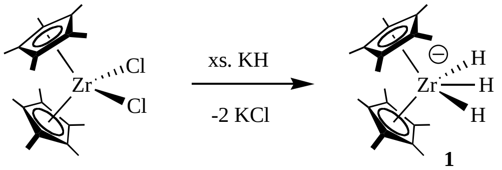
Additionally, commercial syntheses of many primary alkyl phosphines utilize phosphine (PH_3), which provides ready access to P–H bonds at relatively low cost [42-45]. Some typical methods of preparing phosphine in the patent literature involve the hydrolysis of calcium- or aluminum phosphide or the reduction of elemental phosphorus [46-49]. Numerous methods to more specialized phosphines have been reported, making primary and secondary phosphines ubiquitous reagents [50, 51]. Aryl phosphines, most commonly $PhPH_2$, are prepared by reduction of aryl phosphine dihalides [52, 53].

1. DEHYDROCOUPLING OF PHOSPHINES

In a little over a decade, a number of catalysts have been developed for the dehydrogenative coupling of phosphines. Many of these catalysts effect P–P bond formation with unique reactivity patterns. Additionally, this class of catalysis is beginning to see wider application in the synthesis of materials, particularly through heterodehydrocoupling or the formation of P–E bonds. The isolation of a number of potential intermediate complexes and mechanistic analysis has provided much insight into these bond-forming reactions, but it is clear that a greater understanding is necessary as this reaction increases in scope and application.

1a. Catalysts

Catalytic dehydrocoupling of phosphines was first reported by Fermin and Stephan in 1995. A simple catalyst precursor, $[Cp^*_2ZrH_3]^-$ (**1**), was prepared via KH reduction of $Cp^*_2ZrCl_2$ and structurally characterized (eq 2) [54, 55]. In this initial report, the potassium or lithium salt of complex **1** was demonstrated to catalytically oligomerize $PhPH_2$, $CyPH_2$, and $MesPH_2$ with the predominant product in all three cases being the cyclic pentamer $(PR)_5$ (eq. 3, Anionic trihydride complexes are typically introduced as the "ate" precursors $[Cp^*_2Zr(\mu\text{-}H)_3Li]_3$ or $Cp^*_2Zr(\mu\text{-}H)_3K(THF)_4$.) [54]. The anionic charge or coordinative saturation at zirconium appear to be important features for this catalysis as related neutral zirconocene derivatives have not been reported to perform this catalysis.



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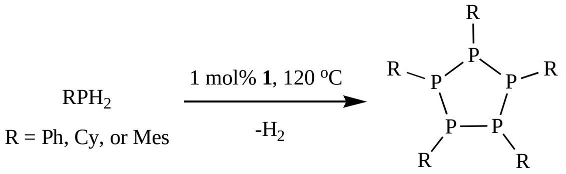

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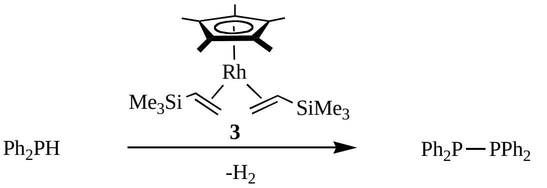
In 1997, Harrod, Samuel, and coworkers reported titanocene complexes including $[(EBTHI)TiH]_2$ (**2**) [56] as a photo-activated catalysts for the dehydrocoupling of $PhPH_2$ to $(PhPH)_2$ and $(PPh)_6$ (eq. 4) [57]. The observation of phosphine dehydrocoupling was made while attempting dehydrogenative P–Si bond formation. A series of reactions with cyclohexylphosphine were undertaken, but no dehydrocoupling catalysis was noted.

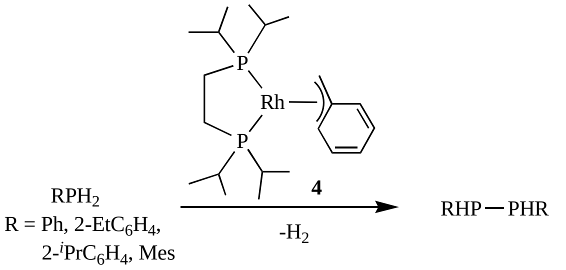
$$PhPH_2 \xrightarrow[-H_2]{[(EBTHI)TiH]_2\ (\mathbf{2})} PhHP\text{—}PHPh \ + \ (PPh)_6 \qquad (4)$$

Böhm and Brookhart reported the first late transition-metal catalyst for phosphine dehydrocoupling, Cp*Rh $(CH_2{=}CHSiMe_3)_2$ (**3**) [58]. Unlike the early metal catalysts, this rhodium complex displayed limited activity in the dehydrocoupling of primary phosphines. However, complex **3** was very successful in the dimerization of secondary phosphines and, notably, was the first reported complex to dehydrocouple secondary phosphines (eq. 5). This rhodium system does liberate hydrogen, but it was also found that catalysis could be affected at lower temperatures in the presence of a hydrogen acceptor such as trimethylsilylethylene [58].



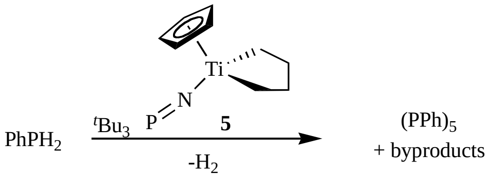
(5)

A second kind of rhodium catalyst, (dippe)Rh(η^2-CH_2Ph) (**4**), was reported by Han and Tilley in 2006 [59]. Complex **4** was much more effective at the dehydrocoupling of primary phosphines than **3** and provides the diphosphine products with high selectivity over the cyclic polyphosphine oligomers (eq. 6). The yield in dehydrocoupling of $PhPH_2$ was limited (maximum ~ 51%), but yields for more sterically encumbered phosphines were higher, up to 80% for 2-$^iPrC_6H_4PH_2$. Complex **4**, like complex **3**, was also effective at the dimerization of Ph_2PH [59].



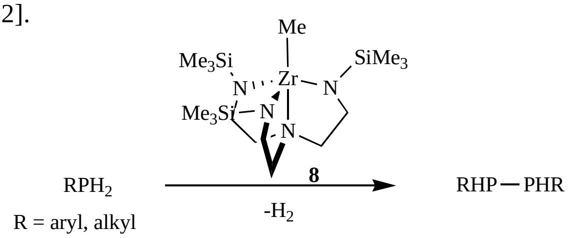
(6)

Since their initial report, Stephan and coworkers have developed a family of neutral titanium and zirconium catalysts $CpTi(NP^tBu_3)(CH_2)_4$ (**5**) and $Cp^*M(NP^tBu_3)(CH_2)_4$ (**6**, M = Ti; **7**, M = Zr) [60]. For example, reaction of $PhPH_2$ with 1 mol% **5** gave $(PPh)_5$ in 41% yield (eq. 7). Unfortunately, this reaction required nine days versus three days when catalyzed by complex **1** under the same conditions. Furthermore, several byproducts including $(PhPH)_2$, $(PPh)_4$, and $(PPh)_6$ were observed in dehydrocoupling catalyzed by **5**. The use of a phosphinimide ligand to support the metal is based on the hypothesis that these ligands provide a monoanionic charge and steric bulk slightly remote from the metal which is complementary to cyclopentadienyl-derived ligands [61]. These phosphinimide complexes, however, appear to dehydrocouple primary phosphines at a qualitatively slower rates than the anionic zirconocene hydride derivatives [60].



(7)

Recently, Waterman reported that triamidoamine-supported zirconium complexes of the general type $(N_3N)ZrX$ (X = Me, **8**; X = PHR, R = Ph, **9**; R = Cy, **10**) are effective in the dehydrocoupling of primary alkyl and aryl phosphines (eq. 8). Interestingly, these catalysts gave exclusively the diphosphine products at lower temperatures and a mixture of cyclic polyphosphines at elevated temperatures [62].



(8)

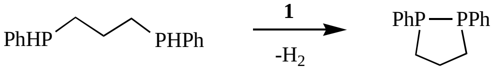
These catalysts each present various advantages and disadvantages from cost to relative rates and selectivity for a single product. All of the reported catalysts are air sensitive. No effort has yet been made to develop air-stable catalyst precursors most likely because of the inherent air-instability of the phosphine substrates and products.

1b. Synthesis Involving Phosphine Dehydrocoupling

Current efforts have focused on developing catalysts capable of overcoming the difficulties associated with dehydrogenative coupling of phosphines. However, some interesting molecular architectures have already emerged as a result of this catalysis.

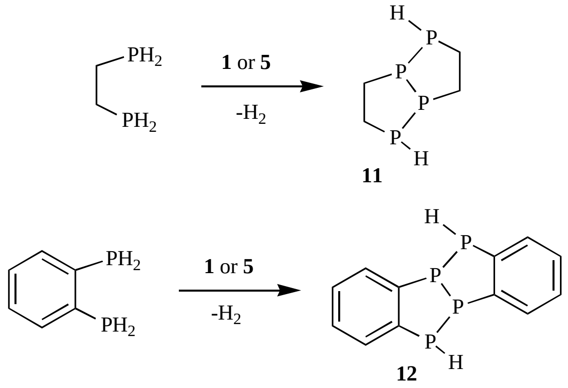
The selectivity of these catalysts in the dehydrocoupling of primary hydrophosphines is an interesting feature. Rhodium complex **4** produced aryl diphosphines with high selectivity [59]. The zirconium catalyst **8** produced both alkyl and aryl diphosphines with equally high selectivity [62]. Alternatively, anionic zirconocene hydride complex **1** selects for the cyclic pentaphosphine $(PPh)_5$ [54]. Other catalysts often give mixtures of the diphosphine and cyclic oligomeric products. These cyclophosphines can exist in a variety of isomeric forms as evidenced by the four known polymorphs of empirical structure $(PPh)_6$ [5]. In these catalytic reactions, ^{31}P NMR spectroscopy has been a mainstay method in characterizing products, but little effort has been make to identify specific isomers that may be present except in cases where assignement by NMR spectroscopy is explicit such as for the racemic and mesomeric isomers of $(PhPH)_2$ [57].

The greatest development of phosphine dehydrocoupling in the preparation of unique molecular structures has come from the application of complex **1** to a variety of phosphines by Stephan and coworkers. Complex **1** catalyzes the dehydrogenative ring closure of 1,3-bis(phenylphosphino) propane to give the five-membered cyclic product (eq. 9) [60]. The product formed appeared to be an enantiomeric mixture of a single diastereomer by ^{31}P NMR spectroscopy.



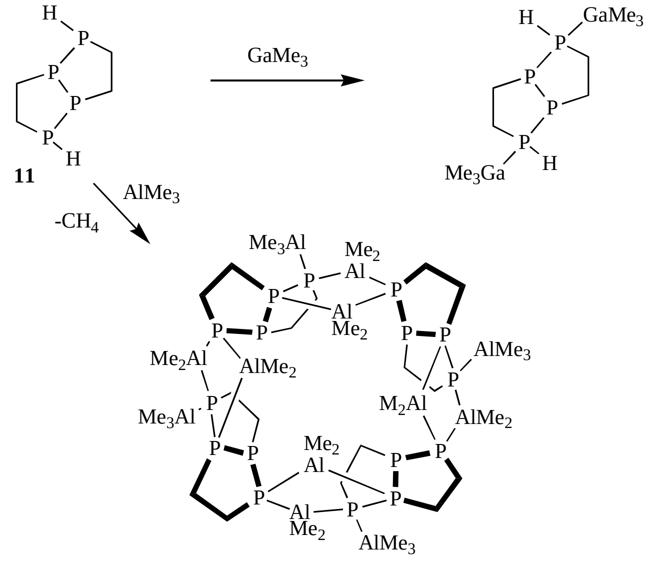
(9)

Further structures has become available by dehydrocoupling of 1,2-bisphosphines. Reaction of **1** or **5** with 1,2-bis (phenylphosphino)ethane or 1,2-bis(phenylphosphino)benzene gave bicyclic complexes $(PCH_2CH_2PH)_2$ (**11**) and $(PC_6H_4PH)_2$ (**12**) with intercalated phosphorus atoms (Scheme **2**) [60, 63, 64].



Scheme 2. Dimerization of 1,2-bisphosphines.

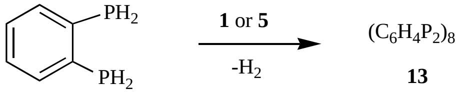
These two dimers are each precursors to more complex structures. Bicycle **11** reacted with Lewis acid $GaMe_3$ to give a meta-stable 2:1 adduct $(PCH_2CH_2PH)_2(GaMe_3)_2$, which was characterized by NMR spectroscopy (Scheme **3**). The



Scheme 3. Reactions of dimer **11** with Lewis acids.

reaction of **11** and $AlMe_3$ was slow, but gave a tetrameric product linked by $AlMe_2$ groups, $[(CH_2CH_2P_2AlMe_2)_2]_4{\cdot}4AlMe_3$, which was structurally characterized [63].

Further dehydrocoupling of 1,2-bis(phenylphosphino) benzene with anionic zirconocene hydride **1** afforded a unique 16-member phosphacycle $(C_6H_4P_2)_8$ (**13**), which was structurally characterized (eq. 10) [64]. In the synthesis of this unprecedented phosphorus complex, it was hypothesized that dimer **12** is an intermediate in the formation of **13**. Later studies using the titanium catalyst **5** in the dehydrocoupling of 1,2-bis(phenylphosphino)benzene also afforded X-ray quality crystals of **13** (Fig. (**1**)), but this product was not uniformly crystalline as evidenced by powder diffraction studies. It was suggested that incomplete dehydrocoupling of the substrate by **5** gave rise to the non-uniformity in the product macrocycle **13** [60].



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These phosphorus macrocycles have features that may make them interesting for applications in material science. In the solid sate structure of **13**, a "double crown" structure was found consistent with ^{31}P NMR spectroscopic data [64]. The cavity created by the 16-member ring has a diameter of approximately 5.10 Å, which would allow for binding interactions in up to two sites. Interestingly, the macrocyclic rings are aligned in the solid state creating cavities or channels that could also be applied to ion binding [64]. One limiting feature of the potential utility of this molecule is its poor solubility in common solvents. In an effort to over come this problem, $Me_2C_6H_2(PH_2)_2$ was dehydrocoupled by complex **5** to give the dimer $(Me_2C_6H_2(P)PH)_2$, which is highly related to dimer **12**. Attempts to further dehydrocouple $Me_2C_6H_2(PH_2)_2$ gave $(Me_2C_6H_2P_2)_2]_2(\mu\text{-}Me_2C_6H_2P_2)$ as the exclusive product (eq. 11) [60].

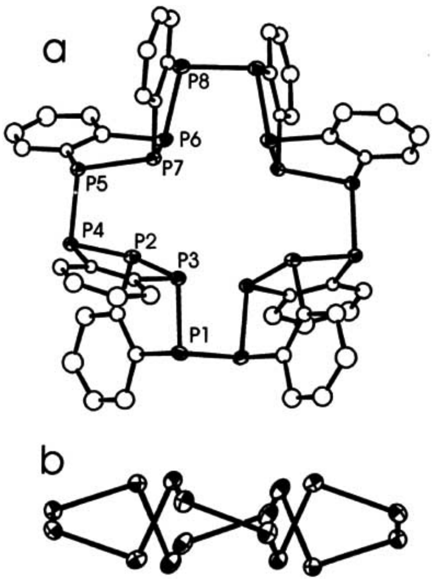
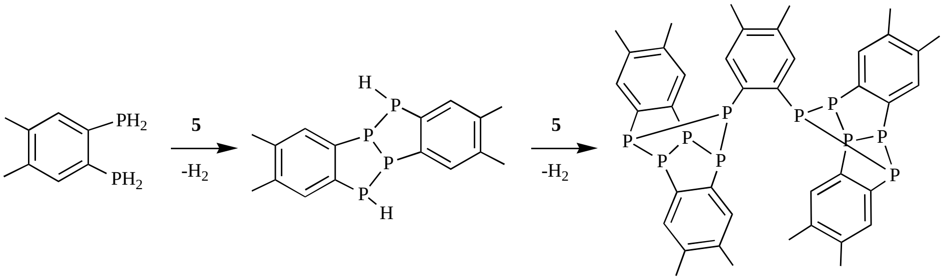


Fig. (1). (a) Molecular structure of $(C_6H_4P_2)_8$ (**13**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been removed for clarity. (b) Profile view of the P_{16} core of **13**. Reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc.*, **1997**, *119*, 2954-2955.

The isolation of these phosphacycles and the preparation of small rings $(RP)_n$ (n = 4, 5, 6) highlights the current inability of these catalysts to generate long polyphosphines chains. Though a rich reaction chemistry associated with cyclophosphines has been discovered [5, 22]. While there is limited precedent for catenated structures involving substituted phosphorus [65], it is a desirable target given the observation in recent years of π-conjugation through the phosphorus lone pair [17, 66, 67]. Similar difficulties were seen in the early development of dehydrocoupling catalysis of hydrosilanes. Discovery of group 4 metallocene catalysts for these dehydrogenative polymerizations was a key advance in moving from short (10–20 Si atoms) to long chain polymers [27, 28, 31]. Such an analogy suggests that new catalyst types might yield new polyphosphine architectures.

The reverse reaction, hydrogenation of a P–P bond, has only recently appeared. Geirer and Stephan have reported that β-diketiminate-supported rhodium complexes catalyze the hydrogenation of tetraphenyldiphosphine [68].



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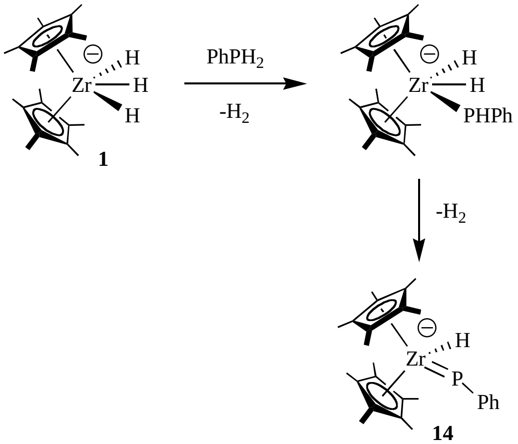
2. MECHANISTIC CONSIDERATIONS

Detailed mechanistic study on the dehydrocoupling of phosphines has been limited, though valuable observations have been made. These studies have predominantly focused on the early metal catalysts, but there is also information about the late-transition metal catalysts that highlights the unique features of each type of catalyst.

2a. Early Metal Catalysts

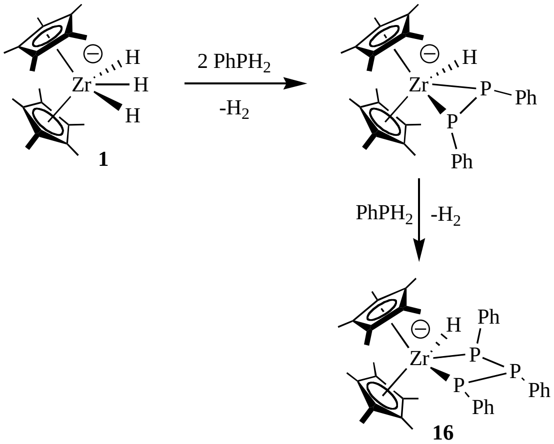
Stephan and coworkers were first to propose mechanistic steps associated with the dehydrocoupling of phosphines. It was suggested that a key complex in the dehydrocoupling of phenylphosphine might be an anionic zirconium phenylphosphinidene complex, $[Cp^*_2Zr(H)=PPh]^-$ (**14**) [54]. Such a complex could be formed by H_2 elimination from an anionic phosphido intermediate (Scheme **4**). Complex **14** was identified during the catalysis through observation by ^{31}P NMR spectroscopy, and an assignment was made based on comparison to the previously reported supermesityl derivative $[Cp_2Zr(H)=PMes^*]^-$ [54]. Related neutral phosphinidene complexes of zirconium, $Cp_2Zr(PMe_3)=PMes^*$ (**15**) [69, 70] and $Cp_2Zr(PMe_3)=Pdmp$ [71], have been prepared and fully characterized. Complex **15** and related species have exhibited substantial reaction chemistry including cycloaddition, insertion, and phospha-Wittig reactivity [72], which makes involvement of metal phosphinidene complexes in catalysis very attractive. However, the only other instance of a catalytic process associated with a terminal phosphinidene ligand is a report by Mindiola and coworkers of titanium-catalyzed hydrophosphination of alkynes [73]. In this catalysis, hydrophosphination appeared to proceed via [2+2]-cycloaddition of alkyne to the Ti=P bond. This hydrophosphination mechanism can be considered similar to the hydroamination mechanism first proposed by Bergman and coworkers for zirconocene catalysts [74].



Scheme 4. Formation of an anionic zirconium phosphinidene complex.

There has been a dramatically increased number of isolated transition-metal complexes with terminal phosphinidene ligands [75]. With this plethora of new complexes, a rich variety of stoichiometric reaction chemistry of the M=P bond has emerged [72, 73, 75-81]. This new chemistry is also suggestive of the potential for new catalysis associated with the phosphinidene moiety. Transient phosphinidene complexes have been responsible for making numerous otherwise difficult to prepare organophosphorus species synthetically accessible through stoichiometric transformations [2, 75, 77]. Such well-developed chemistry associated with transient phosphinidene complexes is further suggestive of the potential for novel catalytic chemistry.

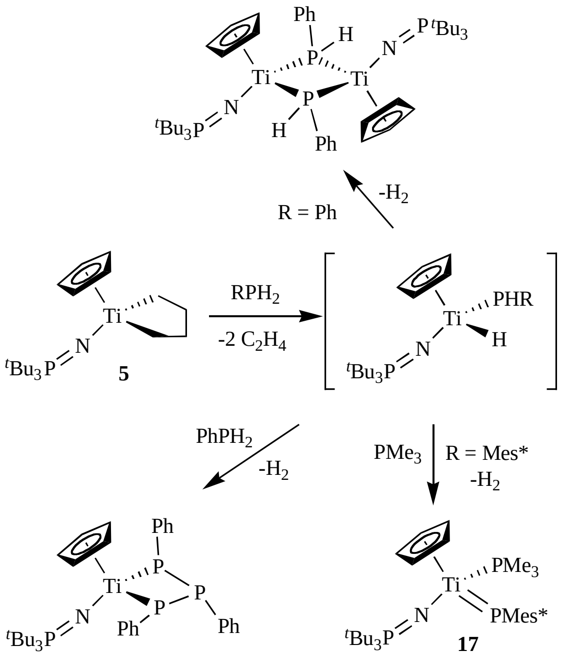
Despite the uncertain role of a phosphinidene ligand in this catalysis, valuable mechanistic information has been obtained on these early transition-metal catalysts. Careful stoichiometric chemistry established that di- and triphosphinato complexes $[Cp^*_2ZrH(PPh)_2]^-$ and $[Cp^*_2ZrH(PPh)_3]^-$ (**16**) are present in solution and that the triphosphinato derivative **16** appears to be the catalyst resting state (Scheme 5) [54]. The triphosphinato complex has been fully characterized, but X-ray diffraction data remains elusive. However, highly related di- and triphosphinato complexes $[Cp_2ZrBr(PPh)_2]^-$ [82], $Cp_2Zr(PPh)_3$ [82], $Cp_2Zr(PCy)_3$ [82], $Cp^*_2Zr(PPh)_3$ [83], and hafnium derivatives $Cp_2Hf(PR)_2$ and $Cp_2Hf(PR)_3$ [84] are known and several of these have been structurally characterized. Interestingly, di- and triphosphinato ligands are somewhat ubiquitous among early transition metal phosphido complexes, but isolated yields of complexes bearing these ligands are frequently low.



Scheme 5. Formation of di- and triphosphinato complexes from **1**.

Similar behavior is seen with titanium catalysts such as $CpTi(NP^tBu_3)(CH_2)_4$ (**5**). The phosphinimide ligand was chosen as an alternative to a cyclopentadienyl with similar, though somewhat remote, steric properties and strong N–M bonding [61, 85]. This complex was an active precatalyst in the dehydrocoupling of $PhPH_2$, and true to the similarities of the phosphinimide ligand to cyclopentadienyl, a triphosphinato derivative, $CpTi(NPtBu_3)(PPh)_3$, was isolated [60]. Furthermore, evidence for generating a transient titanium phosphinidene complex of the type $Cp(^tBuPN)Ti=PPh$ was accrued by isolation of the trimethyphosphine-stabilized supermesityl derivative $Cp(^tBuPN)Ti(PMe_3)=PMes^*$ (**17**). It was also observed that the putative phosphido intermediate resulting from P–H oxidative addition to a formally Ti(II) center, $Cp(^tBuPN)Ti(H)PHPh$ undergoes dimerization to give $[Cp(^tBuPN)Ti(\mu\text{-}PHPh)]_2$ (Scheme **6**) [60].

One of the central difficulties in establishing that a phosphinidene ligand may play a role in the catalytic cycle is that multiple reasonable mechanisms can be drawn for the



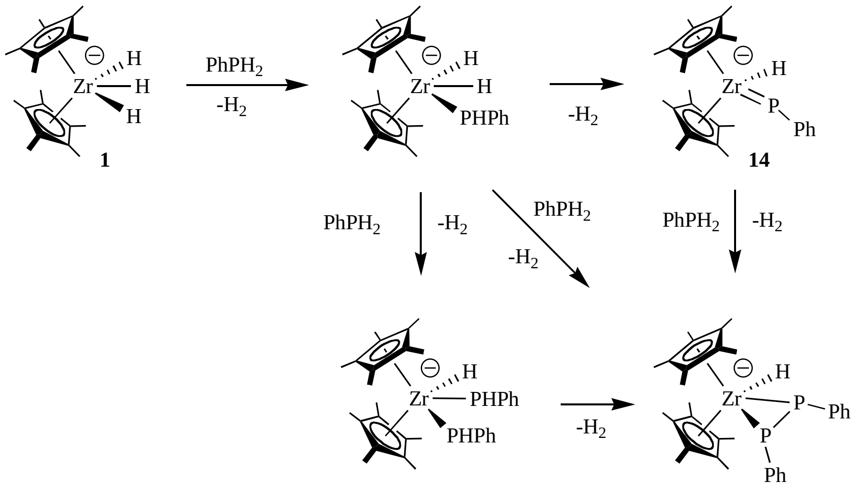
Scheme 6. Triphosphinato and phosphinidene complexes derived from **5**.

formation of $[Cp^*_2ZrH(PR)_2]^-$, one invoking a phosphinidene complex and others not (Scheme **7**). The observation of a phosphinidene complex is not unusual. In the preparation of neutral phosphinidene complexes, elimination of phosphine or methane is an effective synthetic procedure [72, 75, 77]. The likelihood that such a complex is present in the reaction is high, but it is uncertain if that phosphinidene species is catalytically active or simply a spectator in the catalysis. Clearly, further study is need to understand this exact series of transformations and to establish whether or not a phosphinidene ligand plays an active role in the catalysis.

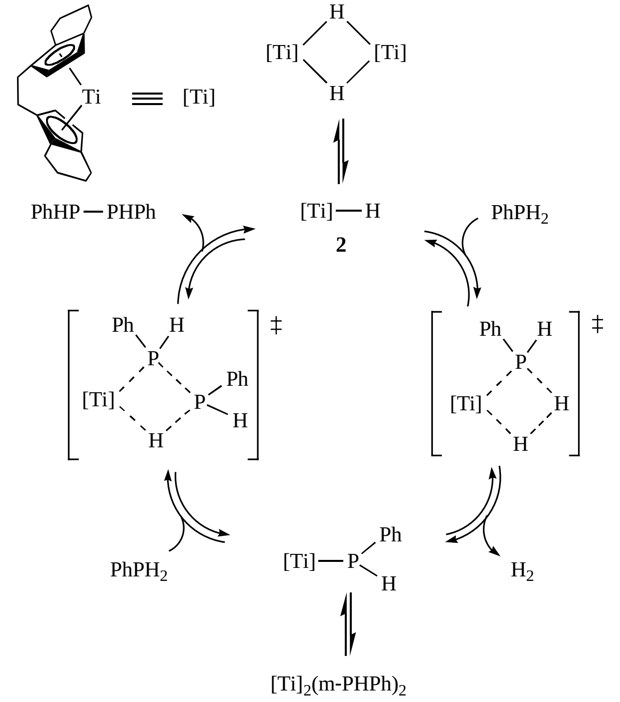
Related *ansa*-titanocene catalysts also dehydrocouple phenylphosphine, but a different mechanism was proposed in these reactions [57]. A key difference between these mechanisms is the ability of titanocene complexes to access a Ti(III) oxidation state. It was proposed that the active catalyst in these reactions is a dimeric Ti(III) hydride complex, $[(EBTHI)_2Ti(\mu\text{-}H)]_2$ (**2**), that can dissociate in solution. The monomeric titanium hydride can then undergo σ-bond metathesis to form a phosphido derivative with loss of hydrogen. This hypothesis was supported by the isolation of $[Cp_2Ti(\mu\text{-}PHCy)]_2$ upon reaction of Cp_2TiMe_2 with $CyPH_2$ [86,87]. Confirmation of the dimeric structure came in part by a single crystal X-ray diffraction study. Though the data was disordered, the study provided evidence for connectivity. Further evidence for a dimeric structure came via a derivatization reaction with PMe_3 that gave $Cp_2Ti(PHCy)(PMe_3)$, where the secondary phosphido derivative $Cp_2Ti(PPh_2)(PMe_3)$ has been structurally characterized [87]. An additional σ-bond metathesis reaction of the Ti(III) phosphido complex with phenylphosphine then would give the diphosphine product, $(PhPH)_2$, and restore the titanium hydride catalyst or **2** (Scheme **8**) [57].

Unidentified ^{31}P NMR resonances in the reaction mixture were hypothesized to be higher oligomers of phenylphosphine, molecules that are known to be unstable [88]. It was suggested that these products arise from further σ-bond metathesis reaction steps of a Ti(III) phosphido complex and the diphosphine [57]. This reaction pathway bears high similarity to that proposed for the dehydrocoupling of silanes to high molecular weight polysilanes with group 4 metallocene catalysts [26-28, 31].

While this mechanism adequately explains the observation of $(PhPH)_2$ and the possibility of linear polyphosphines [65], it does not account for some of the titanium products observed in stoichiometric reactions. For instance, a diphosphinato complex $(EBTHI)_2Ti(PPh)_2$ (**18**) was isolated upon reaction of **2** with $PhPH_2$. Similarly, reaction of Cy_2PH and Cp_2TiMe_2 gave $[Cp_2Ti]_2(\mu\text{-}H)(\mu\text{-}PCy_2)$, which was structurally characterized (Fig. (**2**)) [57]. These complexes and the $(PPh)_6$ product in the dehydrocoupling of $PhPH_2$ did not appear accessible by the mechanism presented. It was hypothesized that the titanium hydride dimer was susceptible to disproportionation to $(EBTHI)_2Ti(H)_2$ and a formal equivalent of Ti(II). The Ti(II) complex could then oxida-



Scheme 7. Possible mechanisms to form diphosphinato complex $Cp^*_2ZrH(PPH)_2]^-$.



Scheme 8. Proposed catalytic cycle for the dehydrocoupling of $PhPH_2$ by **2**.

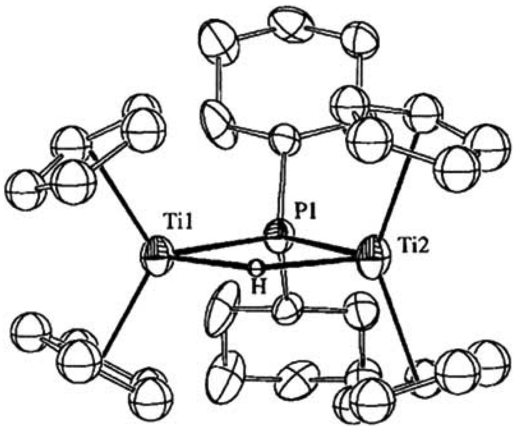
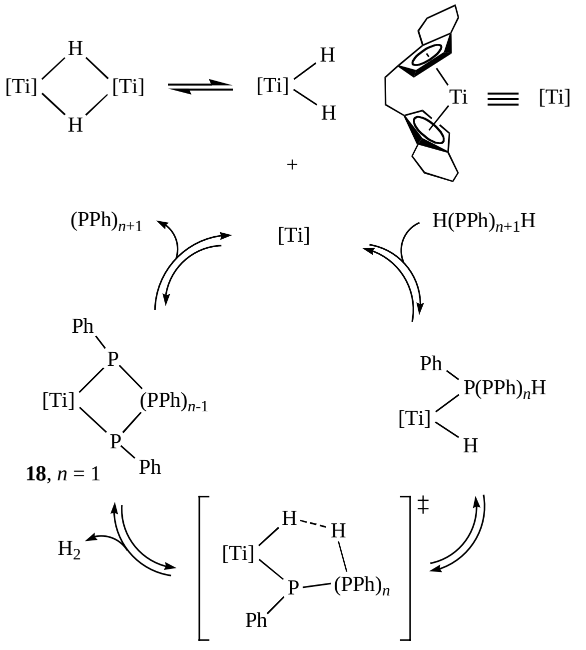


Fig. (2). Molecular structure of $[Cp_2Ti]_2(\mu\text{-H})(\mu\text{-PCy}_2)$ with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms except the bridging hydride have been removed for clarity. Reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc.*, **1997**, *119*, 5307-5313.

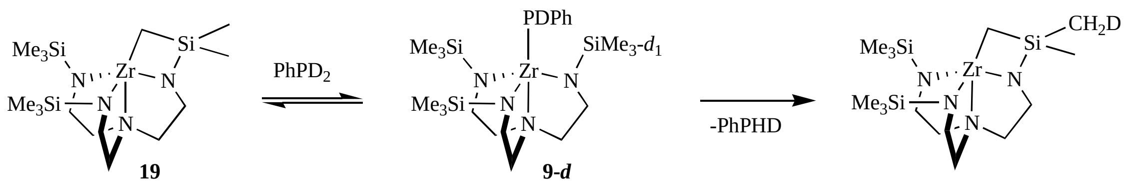
tively add P–H bonds to give products such as $Cp_2TiH(PHR)$. Through reaction with phenylphosphine and elimination of hydrogen the diphosphinato complex **18** could be formed. Complex **18** might be an intermediate in the formation of the observed $(PPh)_6$ product (Scheme **9**) [57].



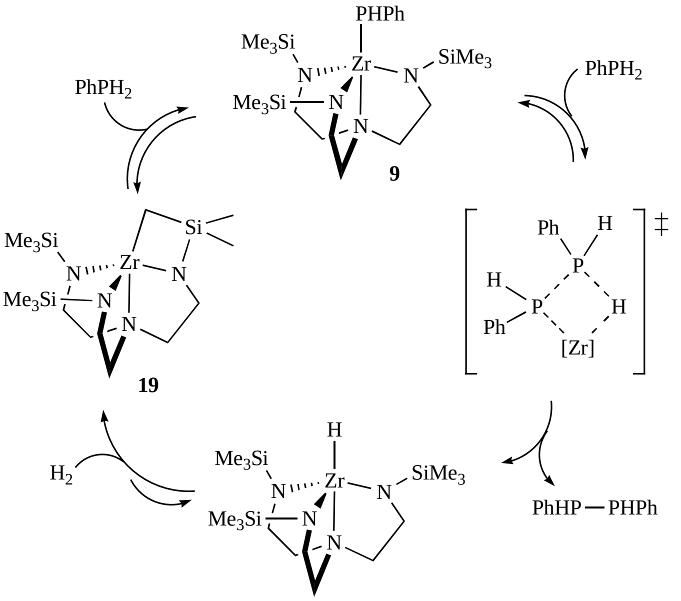
Scheme 9. Proposed mechanism of formation of **18** and cyclic phosphines in the dehydrocoupling of $PhPH_2$ by **2**.

The dehydrocoupling of primary phosphines by triamidoamine-supported zirconium complexes was investigated through kinetic measurements and isotopic labeling by Waterman. In this system, a kinetic isotope effect was obtained in an internal competition experiment by reaction of $(N_3N)ZrPHPh$ (**9**) with PhPHD. This method was chosen because of the ability of phosphines to undergo H/D exchange with the trimethylsilyl groups of the triamidoamine ligand by a mechanism shown in Scheme 10. Reaction of **9** with PhPHD gives two potential products PhHP–PDPh and $(PhPH)_2$ based on P–H and P–D bond activation, respectively. In these experiments, a kinetic isotope effect $k_H/k_D = 3.1(5)$ was obtained [62].

It is important to note that H/D exchange still occurs in the reaction with PhPHD. Two exchange reactions are possible. First the deuterated phosphido complex $(N_3N)ZrPDPh$ (**9-*d***) could be formed. Reaction of complex **9-*d*** with PhPHD would give the same products PhHP–PDPh and $(PhPD)_2$, but formation of these products would be based on P–D and P–H bond activation steps, respectively. Observation of $(PhPD)_2$ in the reaction mixture supported this hypothesis. This reaction pathway would artificially lower the observed KIE by forming PhHP–PDPh with P–D bond activation. In the H/D exchange process, deuterium could be lost into the triami-



Scheme 10. Mechanism of phosphine H/D exchange with triamidoamine ligand.



Scheme 11. Proposed mechanism of phosphine dehydrocoupling by triamidoamine-supported zirconium complexes.

doamine ligand resulting in additional $PhPH_2$ in solution. Reaction of free $PhPH_2$ with **9** gives only $(PhPH)_2$ resulting in an artificially increased KIE. A small amount of free $PhPH_2$ was observed in the reaction mixture. A copious excess of PhPHD was used to attempt to minimize the ability of any free $PhPH_2$ to react [62].

From an Eyring analysis, a large negative entropy of activation $\Delta S^\ddagger = -35.7(2)$ eu was obtained. This data, in concert with kinetic analysis and order of reactants, led to a catalytic cycle based on σ-bond metathesis steps (Scheme **11**). The proposed catalytic cycle explains the low-temperature dimerization of phosphines but does not account for the cyclic oligomers $(PR)_n$ (n = 4, 5, or 6) observed upon performing the catalysis at higher temperatures [62]. No effort was made to address the formation of those products. However, it is known that $(PhPH)_2$ and $(PPh)_5$ enter into a thermal equilibrium at elevated temperatures [22]. Interestingly, this study appears to be the only instance where mechanistic data to support σ-bond metathesis reactivity of pnictogen-hydrogen bonds has been reported.

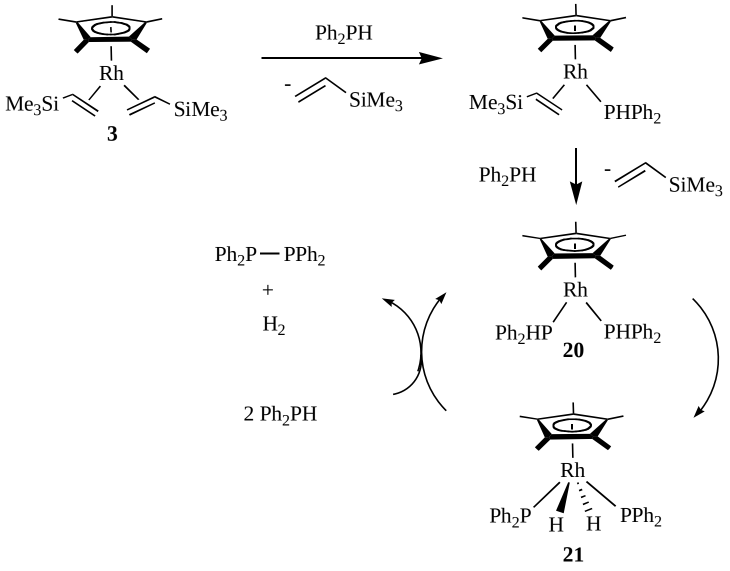
As expected from the proposed mechanism, the catalysis was inhibited by hydrogen. The presence of the metalated complex, $[\kappa^5\text{-}N,N,N,N,C\text{-}(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr$ (**19**), in the catalytic cycle rather than in a side step was supported by the inability to observe a hydride complex $(N_3N)ZrH$ when exposing **19** to H_2 pressure. That the equilibrium at elevated H_2 pressure favors **19** over a hydride complex suggests that H_2 elimination from any zirconium hydride intermediate would be faster than reaction with phosphine. Complex **19** was independently prepared by hydrogenation or thermolysis of methyl complex **8** and fully characterized [62].

2b. Late Metal Catalysts

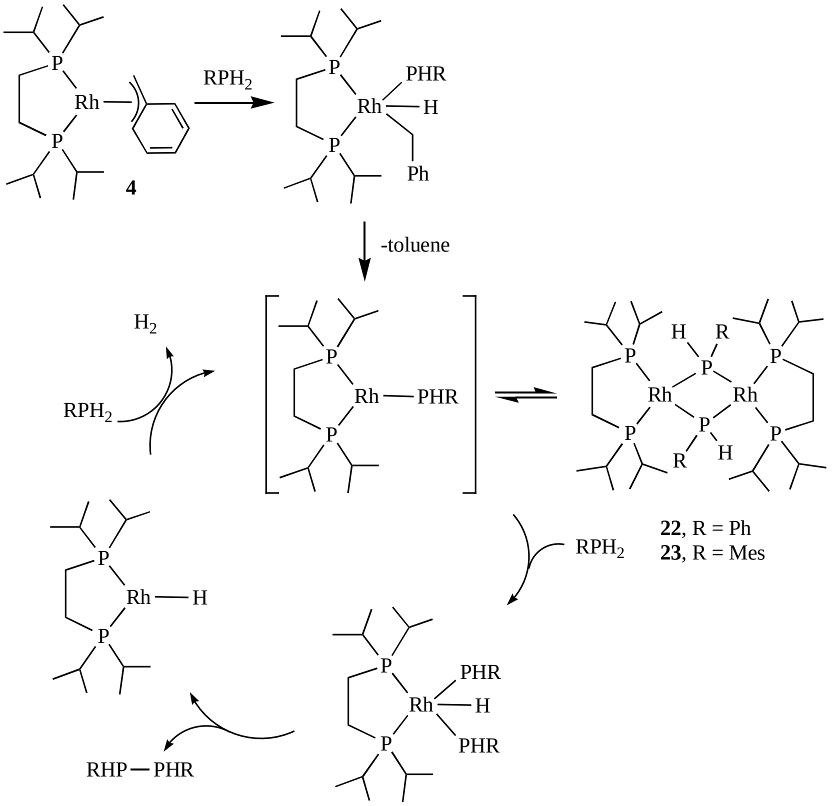
The two different rhodium dehydrocoupling catalysts appear to exhibit different dehydrocoupling mechanisms. The rhodium half-sandwich precursor, **3**, was converted to the bisphosphine complex, $Cp^*Rh(PHPh_2)_2$ (**20**), via stepwise loss of alkene ligands (Scheme **12**) [58]. This complex, which appeared to be the catalyst resting state, is hypothesized to undergo two P–H oxidative addition events to form a Rh(V) bisphosphido dihydride complex, $Cp^*Rh(H)_2(PPh_2)_2$ (**21**). There is precedent in the literature for organometallic complexes that posses a formally Rh(V) center [89-95], and complexes of Cp*-supported rhodium complexes with a diphenylphosphido ligand are well known [96-99]. The Rh(V) intermediate would then reductively eliminate tetraphenyldiphosphine and hydrogen to then be trapped with two equivalents of Ph_2PH to restore **20**. Presumably these steps would be related rather than generating a Cp*Rh fragment. Increased steric bulk at phosphorus was cited as a potentially stabilizing feature for the putative Rh(V) intermediate and may be the reason for the selective dehydrocoupling of secondary over primary hydrophosphines. The increased steric bulk may also favor reductive elimination from Rh(V) [58].

For this catalysis, the importance of P–H activation was further demonstrated by the formation of minor amounts of Ph_2PD in mixtures of **3** and Ph_2PH in deuterated solvents. Interestingly, the typical H/D exchange between the alkene ligands of **3** and deuterated solvent was not observed in the presence of diphenylphosphine. It was hypothesized that this exchange was inhibited by displacement of alkene from the rhodium complex and strong coordination of the phosphine ligands [58].

For dippe-supported rhodium complex **4**, a different mechanism is likely to be operant. It was observed that the benzyl complex reacted rapidly with primary phosphines to give the P–H oxidative addition product (dippe)$RhH(CH_2Ph)(PHAr)$ (Ar = Ph, Mes) [59]. These complexes were further observed to reductively eliminate toluene and dimerize to give $[(dippe)Rh(\mu\text{-}PHAr)]_2$ (Ar = Ph, **22**; Ar = Mes, **23**). Complexes **22** and **23** were active catalysts for the dehydrocoupling of primary phosphines. It was noted, however, that yields of diphosphine product increased with steric bulk of the aryl substituent (for phosphines RPH_2, yield increases R = Ph < Mes ~ 2,4,6-^{i}$Pr_3C_6H_4$ < 2-EtC_6H_4 < 2-



Scheme 12. Proposed mechanism of Ph_2PH dehydrocoupling by complex **3**.



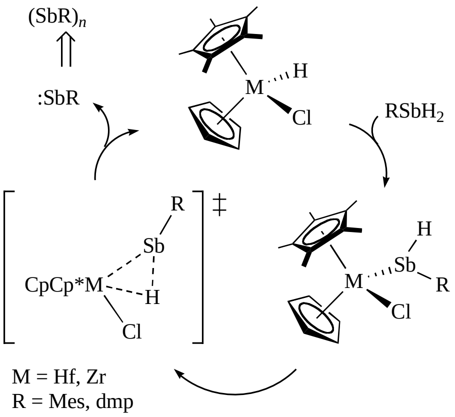
Scheme 13. Proposed mechanism for the dehydrocoupling of primary phosphines by dippe-supported rhodium catalysts.

${}^{i}PrC_6H_4$) [59]. This feature implies that dissociation of dimeric complexes such as **22** and **23** was necessary for the catalysis to occur.

Complex **4** reacted uniquely with Ph_2PH to give (dippe)$RhPPh_2(PHPh_2)$ (**24**) with elimination of toluene. Though an intermediate was not observed, sequential P–H oxidative addition followed by reductive elimination of toluene is likely based on the reactivity of the primary phosphines to give complexes **22** and **23**. Complex **24** slowly decomposed to $[(dippe)Rh(\mu\text{-}PPh_2)]_2$ (**25**) with loss of Ph_2PH. Interestingly, only complex **24** and not **25** catalyzed the dehydrocoupling of Ph_2PH [59], further suggesting that a monomeric metal complex is required for the dehydrocoupling catalysis. A mechanism incorporating these features and based on the observation of Rh(I)/Rh(III) oxidative addition/reductive elimination reactivity can be drawn (Scheme **13**).

3. HEAVIER PNICTOGEN DEHYDROCOUPLING

Examples of metal-catalyzed dehydrocoupling for group 15 elements other than phosphorus are rare. Like phosphorus, reduction of dihalostibines gives small rings [100]. Hydrostibines have long been known to decompose to small rings, but this process is often induced by stoichiometric hydrogen acceptors or alkyl lithium reagents [101, 102]. In the only reported instance of catalytic dehydrocoupling of stibines, it was found that mixed ring zirconocene and hafnocene catalysts promoted α-stibinidene elimination (Scheme **14**) [103]. A mechanism based on α-stibinidene elimination was supported by isolation of stibido complexes CpCp*HfSbHR (R = Mes, dmp) and observation of thermally induced α elimination. Key data to support α-stibinidene elimination included a first-order dependence on the stibido complex in the decomposition, negative entropy of activation, and large primary kinetic isotope effect [103]. These features were very similar to those observed for α-stannylene elimination from highly related stannyl complexes [104-106].



Scheme 14. Catalytic stibine dehydrocoupling via α-stibinidene elimination.

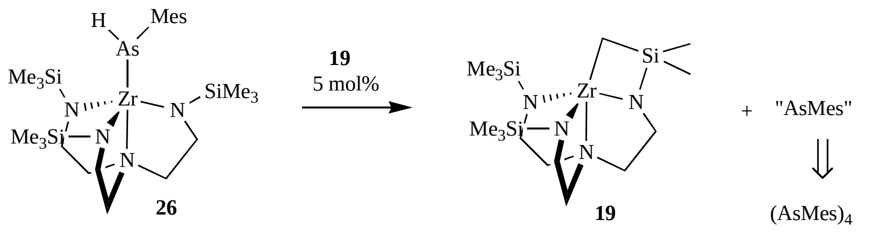
Recently, Waterman and coworkers have investigated the dehydrocoupling of arsines by triamidoamine-supported zirconium complexes. For these complexes, two mechanism have been identified [107]. In the dehydrocoupling of Ph_2AsH to $(Ph_2As)_2$, kinetic data supported As–As bond formation via σ-bond metathesis similar to the dehydrocoupling of phosphines by related catalysts [62]. An intermediate in the catalysis, $(N_3N)ZrAsPh_2$, was identified, and this complex was independently prepared and structurally characterized. However, for primary arsines with sterically encumbered aryl substituents $RAsH_2$ (R = Mes, dmp), evidence supported an α-arsinidene elimination pathway. Decomposition of the primary arsenido complexes was complicated by an equilibrium between free arsine, the metalated complex **19**, and the arsenido derivatives. However, in the presence of a small quantity of **19**, the equilibrium favors complex $(N_3N)ZrAsHMes$ (**26**) and the decomposition of **26** to $(AsMes)_4$ and **19** obeys first-order kinetics, consistent with α elimination (eq. 12) [107].

In the dehydrocoupling of phosphines, there has not yet been evidence to support α-phosphinidene elimination in any of the known catalysts. Indeed, the same group 4 mixed-ring metallocene derivatives that engage in α-stibinidene elimination did not appear to undergo α-phosphinidene elimination and favored bimolecular ligand exchange and α-phosphine elimination instead. These bisphosphido complexes thermally eliminated phosphine to form phosphinidene species (eq. 13) [108]. Notably, these complexes were *not* active dehydrocoupling catalysts. Similar α-phosphine elimination reactivity was observed by Stephan and coworkers in the preparation of zirconocene phosphinidene complexes [72].

It would be highly desirable to discover metal complexes that engage in α-phosphinidene elimination. There is extensive and valuable synthetic chemistry associated with transient metal phosphinidene species [2, 75, 77], yet despite recent improvements, molecular precursors [109] to these phosphinidene complexes are still more difficult to access synthetically than primary phosphines, many of which are commercially available.

4. HETERODEHYDROCOUPLING

Many of the same catalysts that are effective at the dehydrocoupling of phosphines are also able to affect catalytic P–E bond formation. Investigations into heterodehydrocoupling have revealed methodologies for phosphorus-group 13, 14, 15, and 16 bond-forming catalysis. In some instances, unique materials have been discovered and in others cases new routes to otherwise difficult to synthetically access molecules have been found. The discovery of polymers with main-group elements, particularly phosphorus, in the back bone has been a significant and active area of research in recent years [17, 30, 110]. Heterodehydrocoupling reactions



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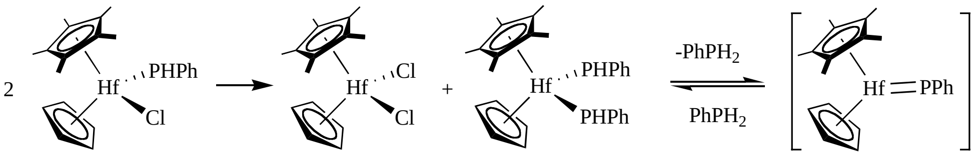


(13)

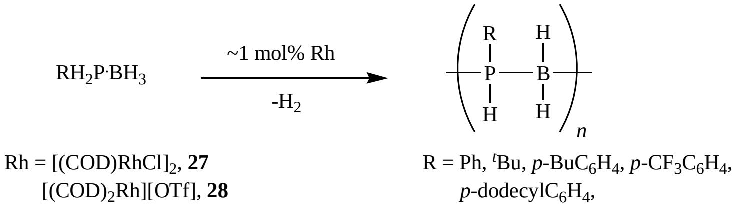
involving phosphines already appear to be playing a significant role in this field.

4a. P–B Bond Formation

It has been known since the 1950s that phosphine-borane adducts thermally dehydrocouple to form small rings [24, 25, 111]. A great deal of speculation has surrounded the properties of the linear polymers (RR'P–BH$_2$)$_n$, which were thought to be most similar in thermal and oxidative stability to silicones. Thus, an effort was made to prepare these polymers, and despite several patents [42, 112], long-chain polyphosphinoboranes failed to emerge as materials.

The dehydrocoupling of these reagents was reinvestigated by Manners and coworkers over the last several years. It was discovered that (PhHP–BH$_2$)$_n$, with M_w = 2150 produced by the thermolysis of PhPH$_2$·BH$_3$, is an ill-defined mixture of oligomers. Since that time, Manners and coworkers have applied transition-metal catalysis to the dehydrocoupling of phosphine-borane adducts [30]. Two remarkable advances have accompanied the metal-catalyzed heterodehydrocoupling process: (i) improved efficiency leading to lower reaction temperatures and (ii) control of product morphology.

Simple rhodium derivatives, such as [(COD)Rh(μ-Cl)]$_2$ (**27**) or [Rh(COD)$_2$][OTf] (**28**), reacted readily with phosphine-borane adducts to form P–B bonds with liberation of hydrogen [113, 114]. These reactions occurred at lower temperatures than the uncatalyzed dehydrocoupling. Refluxing toluene solutions of PhPH$_2$·BH$_3$ in the presence of catalytic **28** gave (PhHP–BH$_2$)$_n$, with M_w = 5600 as an off-white solid (eq. 14). Heating the reaction further provides an even higher molecular weight product M_w = 33,300. At yet higher reaction temperatures, cross-linked polymers were obtained [113, 114].



(14)

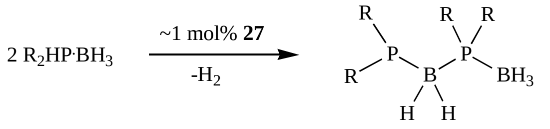
Additional polymers can be prepared by heterodehydrocoupling of different phosphine-borane adducts (eq. 14) [115]. Dehydrocoupling of ^{t}BuPH$_2$·BH$_3$ by **27** gave polymers with M_w = 20,000. Higher molecular weights were be obtained with *para*-substituted aryl phosphine-borane adducts. Dehydrocoupling of the respective phosphine-borane precursors gave polymers [(BuC$_6$H$_4$)HP–BH$_2$)]$_n$ with M_w = 80,000 (M_n ~ 10,000) and [(dodecylC$_6$H$_4$)HP–BH$_2$)]$_n$ with M_w = 168,000 (M_n ~ 12,000). Molecular weights were determined most commonly by dynamic light scattering, but in some cases, gel-permeation chromatography analysis was used as confirmation. Wide angle X-ray scatting data indicated amorphous polymers demonstrating little stereo control from the rhodium catalyst. Glass transition temperatures (T$_g$) were below ambient temperature. This feature was suggested to arise from the flexibility of the P–B bonds, which are quite long (1.9–2.0 Å) compared to the backbone of hydrocarbon polymers [115].

These polymers may have application in the preparation of boron-phosphide ceramics. Decomposition of (PhHP–BH$_2$)$_n$ began at 160 °C according to thermogravimetric analysis, and upon heating to 1000 °C, ceramic yields in the range of 75–80% were found. Thermolysis of this polymer under nitrogen indeed gave boron phosphide as the major crystalline product by powder X-ray diffraction studies [115].

Fine control of this catalysis can be achieved at lower temperatures. Heating secondary phosphine-borane adducts R$_2$PH·BH$_3$ (R = Ph, p-CF$_3$C$_6$H$_4$) with catalytic **27** afforded the unique linear dimer R$_2$HP–BH–PR$_2$–BH$_3$ (**29**) as colorless crystals in 85% isolated yield (eq 15) [113, 114]. This dimer was observed in only trace quantities in the uncatalyzed thermolysis of the phosphine-borane adducts.

At slightly higher temperatures, small P-B cycles were formed in the dehydrocoupling. Reaction of R$_2$PH·BH$_3$ (R = Ph, p-CF$_3$C$_6$H$_4$) with catalytic **27** gave a mixture of (R$_2$P–BH$_2$)$_3$ and (R$_2$P–BH$_2$)$_4$ in an approximately 2:1 ratio (eq. 16). In the uncatalyzed thermolysis of Ph$_2$PH·BH$_3$, a mixture of the same two products was obtained. However, the cyclic trimer was the favored product by approximately 8:1. It was hypothesized that dimer **29** is an intermediate in the formation of the cyclic trimer and tetramer as well as the formation of higher oligomers and polymers [113, 114, 116].

Rhodium complexes have been the mainstay catalysts in P–B dehydrocoupling. Complexes of metals including Pt, Ir, Ru, and Ti have been sampled as catalysts. These other metals have demonstrated some activity in the heterodehydrocoupling of these phosphine-borane adducts, but those catalytic reactions were not as efficient as with rhodium [114].



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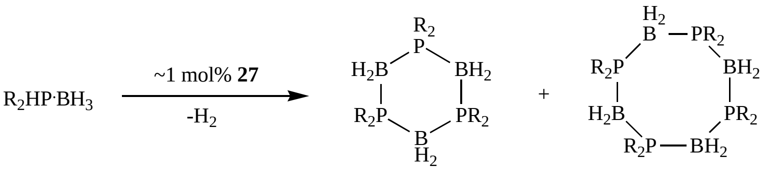
29, R = Ph, p-CF$_3$C$_6$H$_4$,



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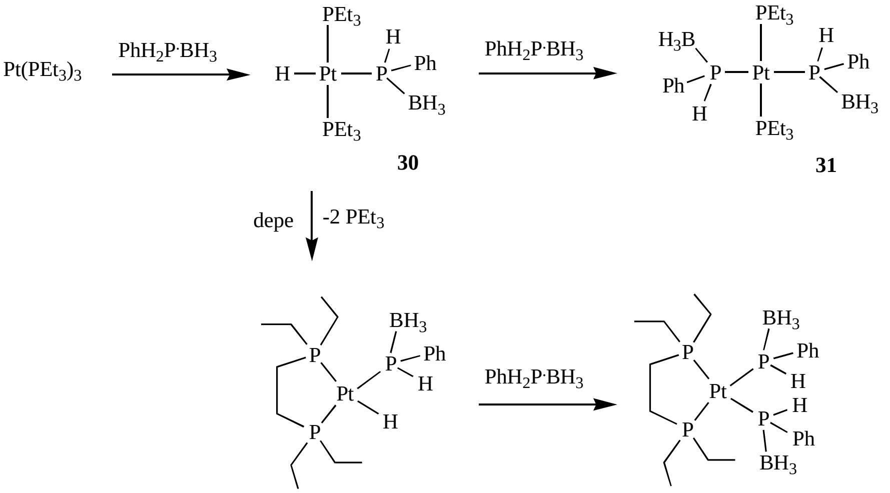
R = Ph, p-CF$_3$C$_6$H$_4$,



Scheme 15. Stoichiometric reactivity of platinum complexes with phosphine-borane adducts.

Platinum(0) sources react with phosphine-borane adducts via oxidative addition of a P–H bond [117, 118]. Thus, reaction of $Pt(PEt_3)_3$ with $Ph_2HP{\cdot}BH_3$ gave *trans*-$(PEt_3)_2PtH(PPh_2BH_3)$ (**30**, Scheme **15**). Complex **30** underwent ligand exchange with $PhH_2P{\cdot}BH_3$ resulting in the formation of *trans*-$(PEt_3)_2Pt(PHPhBH_3)_2$ (**31**), which can be independently prepared. Although a P–H bond activation event was observed in the formation of $(depe)Pt(PHPhBH_3)_2$, none of these platinum complexes underwent any observable P–B bond-forming catalysis. This lack of reactivity suggests that complexes featuring M–P σ-bonds may not be important in the catalysis [117, 118].

In mechanistic studies of the catalysis, one key finding has been that the rhodium-catalyzed heterodehydrocoupling appears to be homogenous [119]. Filtration of the reaction mixture and addition of mercury did not adversely effect rate of reaction. Moreover, monitoring the catalysis by ^{11}B NMR spectroscopy showed no induction period and nearly linear conversion to product. These observations stand in contrast to the dehydrocoupling of amine-borane adducts by the same rhodium complexes, which appeared to be a heterogeneous process. It has been suggested that amine-borane adducts are sufficiently reducing to convert rhodium(I) to rhodium metal. The B–H bonds of phosphine-borane adducts are less hydridic than amine boranes, a feature that explains the observation that the rhodium catalysts are not reduced. Furthermore, phosphine ligation may keep the active catalyst soluble [119]. It is noteworthy that free boranes and derivatives have the potential to poison late transition-metal catalysts [120].

The electronic nature of the phosphorus substituent has a dramatic effect on the rate of dehydrocoupling. Electron withdrawing substituents on phosphorus have increased rates of heterodehydrocoupling [116]. Reaction of p-$CF_3C_6H_4PH_2{\cdot}BH_3$ with catalytic **27** gave $[(p\text{-}CF_3C_6H_4)HP\text{–}BH_2)]_n$ at 60 °C (**32**, $M_w = 56{,}170$; eq. 14), a considerable reduction in temperature over the dehydrocoupling of $PhPH_2{\cdot}BH_3$. Interestingly, polymer **32** demonstrated favorable properties as an electron beam resist in lithography. Using the direct-write methods, micron-scale bars of **32** were printed, and thin films of **32** were demonstrated to acted as a negative-tone resist [116].

These materials appear to be dependent on the initial Lewis acid-base interaction of the phosphine and borane. The antithesis of this interaction has been explored by Stephan and coworkers through design of so-called frustrated Lewis acid-base pairs, sterically encumbered phosphines and boranes that engage in little to no bonding. These frustrated Lewis pairs engage in a wide range of chemical reactivity from hydrogen activation to catalysis [121-125].

4b. P–Ga Bond Formation

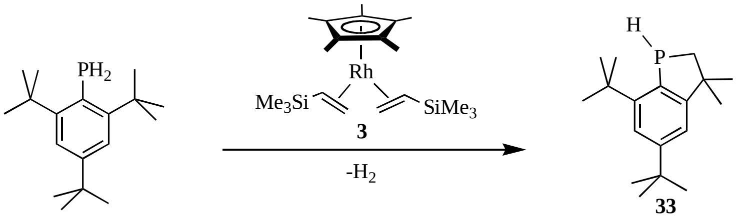
Attempts to engage in catalytic P–Ga bond formation via heterodehydrocoupling have also taken place [126]. Reaction of secondary phosphine-gallane adducts with catalytic amounts of **27** resulted in formation of gallium metal and liberation of phosphine and hydrogen (eq. 17). Interestingly, this reduction process deactivated **27** from further heterodehydrocoupling reactions, including those with phosphine-borane adducts [126]. This observation is consistent with earlier hypothesis that the dehydrocoupling of phosphine-borane adducts occurs via homogenous catalysis. Further attempts to catalyze the dehydrocoupling of phosphine-gallane adducts have not been reported.

$$\mathrm{Cy_2HPGaH_3} \xrightarrow[\mathrm{-H_2}]{5\text{ mol\% }\mathbf{27}} \mathrm{Ga^0} + \mathrm{Cy_2PH} + \mathrm{Rh^0} \tag{17}$$

4c. P–C Bond Formation

Catalytic functionalization of hydrocarbons with phosphines is an area of active research. While efforts have largely focused on hydrophosphination [9, 10, 12] other catalysis such as hydrophosphinylation [6-9, 127, 128] and phosphination [14, 15] or cross-coupling, are actively being pursued. Early findings suggest that heterodehydrocoupling may become a complementary reaction to these efforts.

Observation of catalytic P–C bond formation via dehydrocoupling came first from Böhm and Brookhart. As part of their studies on $Cp^*Rh(CH_2{=}CHSiMe_3)_2$ (**3**), it was noted that attempts to dehydrocouple Mes*PH_2 gave 5,7-di-*tert*butyl-2,3-dihydro-3,3-dimethyl-1*H*-phosphindole (**33**) in high isolated yields (eq. 18) [58].



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(18)

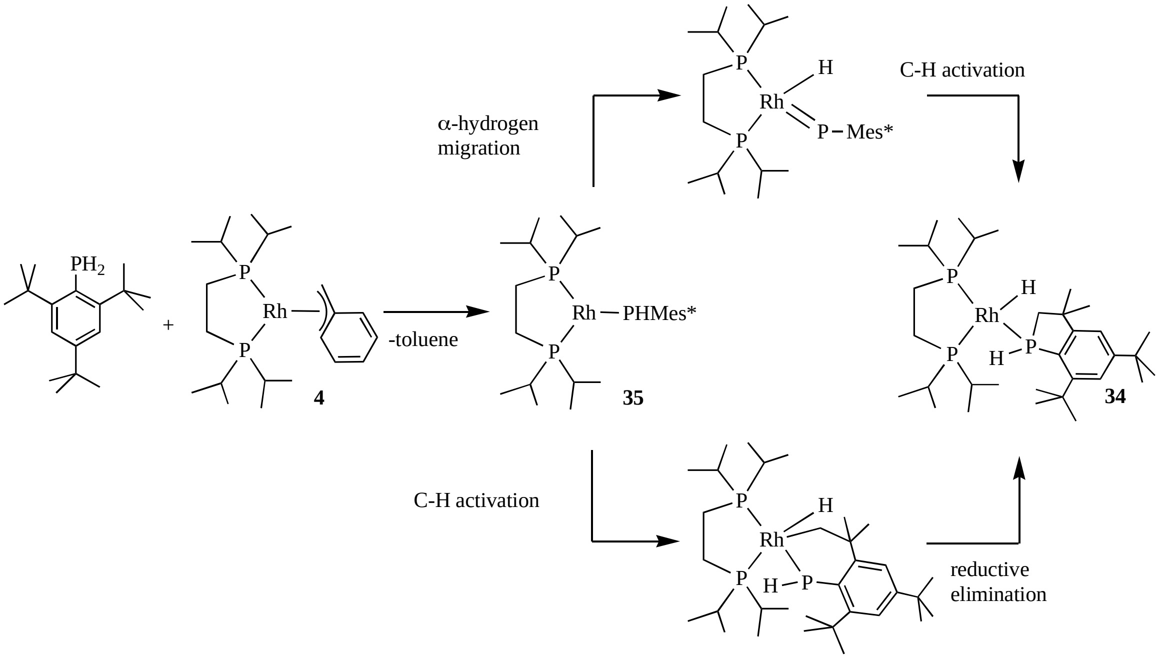
Phosphine **33** is well known and has been prepared in stoichiometric reactions involving intramolecular insertion of a supermesitylphosphinidene (Mes*P:) into the C–H bond of a *tert*-butyl substituent. Frequently the free phosphinidene has been generated by reduction or photolysis [129-137]. However, Glueck and coworkers have reported rhodium-mediated isomerization of phosphacumulenes that form **33** [138, 139].

Tilley and coworkers demonstrated that (dippe)Rh(η^2-CH_2Ph) (**4**) is effective at the intermolecular heterodehydrocoupling of Mes*PH_2 as well [140]. Reaction of **4** with Mes*PH_2 gave toluene and a rhodium phosphindole complex, (dippe)RhH(η^1-**33**) (**34**, Scheme 16). Notably, an iron complex of **33** has been reported by Champion and Cowley by reaction of $Fe_2(CO)_9$ with Mes*P=C=O. In that study, it was proposed that the phosphaketene was cleaved to give $(CO)_4$Fe=PMes* followed by intramolecular insertion of the phosphinidene into the C–H bond [141]. Cleavage of phosphaketene P=C bonds to form phosphinidene ligands has been documented [142]. However, in the case of complex **4**, a rhodium phosphinidene complex was not observed. Reaction of **4** with Mes*PD_2 gave evidence for rapid C–H bond activation of the isopropyl methyl groups of the dippe ligand by formation of Mes*PHD and Mes*PD_2 with deuterium incorporation into the isopropyl substituents of the dippe ligand [140].

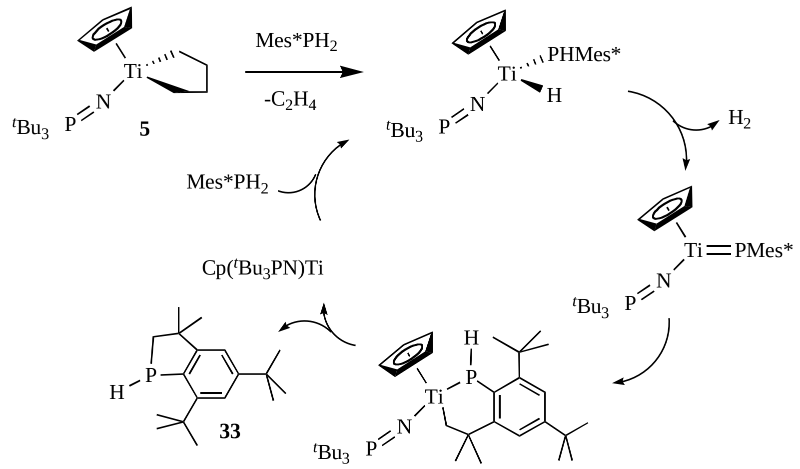
Heating Mes*PH_2 in the presence of 10 mol% of **4** gave **33** in 90% conversion with no detectable byproducts [140]. The authors note two mechanistic possibilities. The first is based on the formation of **33** via a rhodium phosphinidene complex (vida supra). A rhodium phosphido complex (dippe)RhPHMes* (**35**), formed by reaction of **4** with Mes*PH_2 and elimination of toluene, could undergo an α-hydrogen migration to form a phosphinidene hydride complex (dippe)Rh(H)=PMes* (Scheme **16**). The phosphinidene ligand could then be subject to intermolecular C–H activation across the Rh=P bond. A second mechanistic possibility is that the unobserved intermediate **35** could undergo C–H bond oxidative addition at the rhodium center followed by P–C and H_2 reductive elimination processes. The propensity with which these rhodium complexes activate the C–H bonds of the dippe ligand suggests that the latter mechanism may be more appropriate [140].

Interestingly, complex **4** appears to only catalyze the dehydrocoupling of (^{i}Pr$_3$C$_6$H$_2$)PH_2 without competitive intermolecular P–C bond formation [59]. Clearly, the increased steric bulk of Mes*PH_2 is important for P–C bond formation.

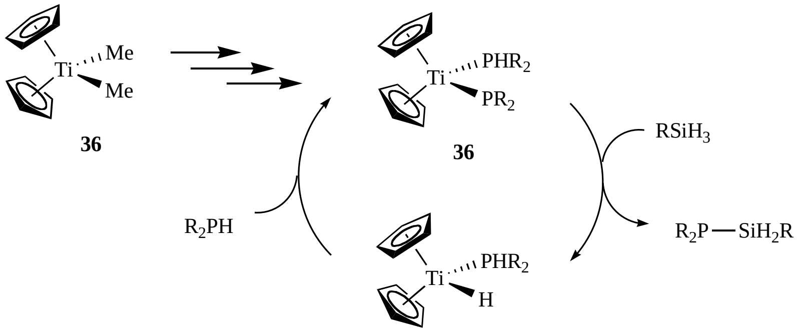
Conversion of Mes*PH_2 to **33** has also been demonstrated by CpTi(NPtBu$_3$)$(CH_2)_4$ (**5**) [60]. Reaction of Mes*PH_2 with 5 mol% of complex **5** at 120 °C gave **33**



Scheme 16. Possible mechanisms for the formation of complex **34**.



Scheme 17. Proposed catalytic cycle for the formation of **33** by **5**.



Scheme 18. Simplified proposed mechanism of heterodehydrocoupling of silanes and phosphines by complex **36**.

quantitatively in 2 h (Scheme **17**). Preparation of Cp(NPtBu$_3$)Ti(PMe$_3$)=PMes* (**17**) via a stoichiometric reaction of **5** with Mes*PH$_2$ in the presence of PMe$_3$ indicated a phosphinidene complex may play a role (Scheme **6**), and a catalytic cycle based on P–H activation of Ti followed by C–H activation across the Ti=P bond has been proposed [60].

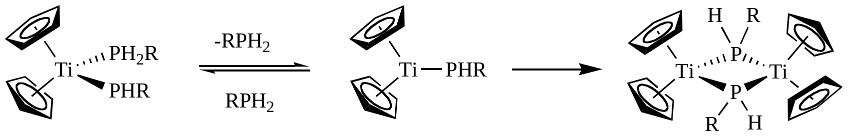
4d. P–Si Bond Formation

Harrod and coworkers reported the heterodehydrocoupling of secondary phosphines with primary and secondary silanes using Cp$_2$TiMe$_2$ (**36**) as the precatalyst [143]. These reactions are high-yielding and relatively rapid, producing no competitive phosphine or silane dehydrocoupling products. This catalyst was also able to heterodehydrocouple CyPH$_2$ with primary silanes. However, these reactions were significantly slower and gave much lower yields [143].

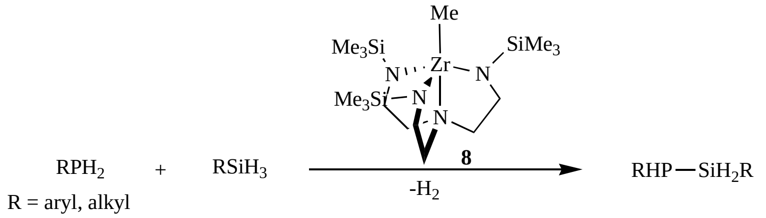
Careful stoichiometric chemistry and use of PMe$_3$ as a trapping ligand allowed for the identification of potential intermediates and models of intermediate complexes. It was found that P–Si bond formation could take place from either a titanium silyl or phosphido complex, and it was presumed that these bond-forming steps were occurring by σ-bond metathesis. The bond forming step would afford a titanium hydride, Cp$_2$TiH(PHR$_2$), that could restore a silyl or phosphido complex by Si–H or P–H activation, respectively. A general catalytic cycle based on the reaction of a titanium phosphido complex with organosilane is depicted (Scheme **18**) [143].

Complex **36** was proposed to decompose to a formally Ti(II) complex that could be trapped with two phosphine ligands. Further reaction, namely P–H bond activation at Ti(II), would afford a Ti(IV) phosphido hydride Cp$_2$TiH (PRR'). Studies of Cp$_2$Ti(PMe$_3$)$_2$ as a model complex demonstrated that comproportionation of the Ti(IV) and Ti(II) complexes is facile and would give Ti(III) hydride and Ti(III) phosphido complexes, each of which could be catalytically active [143].

It was suggested that the sluggish reactivity of primary phosphines in the heterodehydrocoupling was, in part, due to the formation of Cp$_2$Ti(PHR)(PH$_2$R) complexes that are very stable. Furthermore, dissociation of the primary phosphine ligand from these species led to dimeric species, [Cp$_2$Ti(μ-PHR)]$_2$, that are poorly soluble and crystallize under the reaction conditions (eq 19) [143].

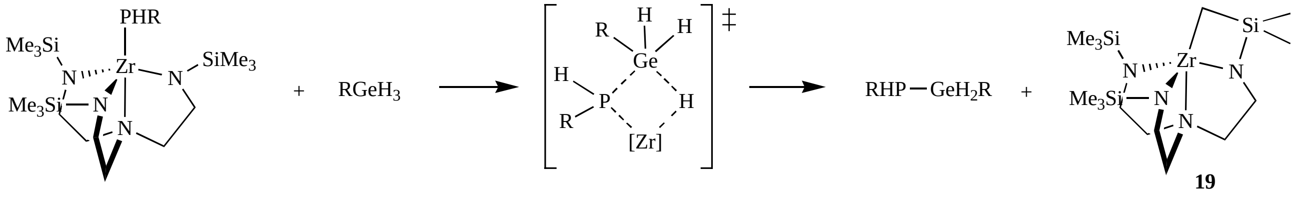


(19)



(20)

Catalytic heterodehydrocoupling of primary phosphines with primary and secondary silanes was reported by Waterman and coworkers [144]. In these reactions, triamidoamine-supported zirconium phosphido complexes, such as **8**, were found to catalyze the reaction of phosphines with silanes to give the silylphosphine product (eq. 20). This catalysis gave exclusively the P–Si product, a feature attributed to the greater propensity of silicon to assume the β-position in a σ-bond metathesis transition state. A catalytic cycle based on that determined for the dehydrocoupling of phosphines (Scheme **11**) by the same catalysts was proposed [144].



Scheme 19. Proposed P–Ge bond-forming step in zirconium-catalyzed heterodehydrocoupling of phosphines and germanes.

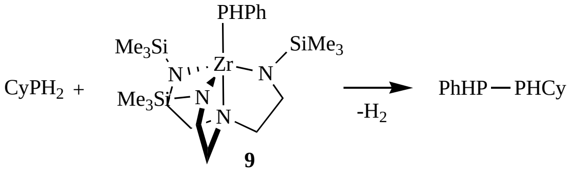
These two catalysts provide a complementary set of P–Si products and do so in fewer steps than conventional stoichiometric synthesis of silylphosphines [145-147]. An alternative route to these molecules, catalytic silylation of a diphosphine, has recently been reported [68].

4e. P–Ge Bond Formation

Triamidoamine-supported zirconium complexes were also demonstrated to catalyze the heterodehydrocoupling of primary phosphines with primary and secondary germanes [144]. In these reactions, the phosphido complexes $(N_3N)ZrPHR$ (R = Ph, **9**; Cy, **10**) were the only observed zirconium species in solution and presumed to be the catalyst resting state. It was further hypothesized that the P–Ge bond-forming event occurs by reaction of germane with the phosphido complex. In these reactions, like those for the P–Si heterodehydrocoupling, exclusive formation of the P–Ge product was attributed to the greater propensity of germanium over phosphorus to assume the β-position in a σ-bond metathesis transition state (Scheme **19**). Additionally, the germylphosphine was the only observed product, suggesting that competitive P–P or Ge–Ge bond formation did not occur. The fact that coupling of $PhPH_2$ with Ph_2GeH_2 is qualitatively slower than dehydrocoupling of $PhPH_2$ under the same conditions implies that the selectivity in these reactions may not merely be kinetic [144].

4f. P–P Bond Formation

In the only instance of phosphine *hetero*dehydrocoupling, $CyPH_2$ and $PhPH_2$ were reacted with catalytic methyl complex **8** to form a non-statistical excess of CyHP–PHPh (eq 21) [62]. There was $(PhPH)_2$ produced in the catalysis as well. However, no $(CyPH)_2$ or $(CyP)_4$ was observed until all $PhPH_2$ was consumed. It was found that the methyl complex reacts selectively with an equivalent excess of $CyPH_2$ and $PhPH_2$ to exclusively form $(N_3N)ZrPHPh$ (**9**), which was structurally characterized [144]. The cyclohexyl derivative, $(N_3N)ZrPHCy$, is known [62] but was not observed within the limits of detection. During the catalysis, only complex **9** was observed until all $PhPH_2$ was consumed. It was hypothesized that $CyPH_2$ reacts with **9** in the P–P bond forming step of the catalysis [62].



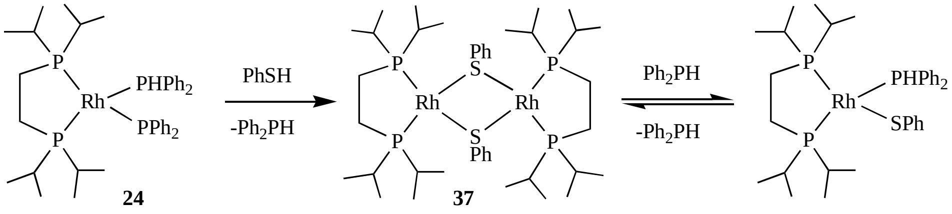
(21)

While this reaction exhibits limited selectivity for the desired product, it does present an alterative route to stoichiometric preparation of differentially substituted diphosphines, which have most recently shown utility in the preparation of unsymmetrical diphosphinoethene ligands [148, 149].

4g. P–S Bond Formation

Recently, Han and Tilley have demonstrated that dippe-supported rhodium complexes catalyzed the heterodehydrocoupling of PhSH and Ph_2PH (eq. 22) [59]. Not unexpectedly, in stoichiometric reactions, a thiolate ligand was favored and phosphido complexes of rhodium reacted rapidly to form $[(dippe)Rh(\mu\text{-}SPh)]_2$ (**37**). Upon heating **37** in the presence of phosphine, monomeric rhodium complexes $(dippe)RhSPh(PHR_2)$ (PHR_2 = $MesPH_2$ or Ph_2PH) were formed. In reactions with Ph_2PH, a monomeric complex $(dippe)RhSPh(PHPh_2)$ was isolable (eq 23), but for $MesPH_2$, a mixture of **37** and $(dippe)RhSPh(PH_2Mes)$ was observed [59].

$$Ph_2PH \quad + \quad PhSH \xrightarrow[-H_2]{\mathbf{4}} Ph_2P\text{—}SHPh \qquad (22)$$



(23)

CONCLUDING REMARKS

Dehydrocoupling of phosphines, a reaction first reported in 1995, has become a general route to P–P bond formation. Several catalysts are now known from across the transition metals, and a good deal of information has been accrued regarding the mechanisms of this catalysis. Catalysts reported to date are known to selectively dimerize phosphines and produce cyclic phosphines including complex macrocycles.

Similarly, heterodehydrocoupling catalysis has allowed the use of phosphines in synthetic schemes to access phosphorus–element bonds. These reactions, beside producing small molecules often difficult to prepare by other means, have given long chain P–B polymers and related materials.

Mechanistic understanding of these dehydrogenative bond-forming process has led to significant advances, but there is yet more to learn and new directions in this catalysis are possible. For instance, no example of asymmetric dehydrocoupling catalysis [150] has appeared despite the possibility and importance of generating *P*-stereogenic molecules [15]. However, it is clear from the examples in this review that this reaction has demonstrated great promise in small molecule synthesis and in the preparation of materials. While there have been some initial advances in both areas, these avenues have yet to be significantly developed. Indeed, many exciting discoveries have yet to be made in this field of catalysis.

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ABBREVIATIONS

Bu = *n*-butyl
COD = 1,5-cyclooctadiene
Cp = cyclopentadienyl, $C_5H_5^-$
Cp* = pentamethylcyclopentadienyl, $C_5Me_5^-$
Cy = cyclohexyl
depe = bis(diethylphosphino)ethane
dippe = bis(diisopropylphosphino)ethane
dmp = 2,6-dimesityphenyl
EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)
E = element
Et = ethyl
Mes = mesityl, 2,4,6-$C_6H_2Me_3$
N_3N = $N(CH_2CH_2NSiMe_3)_3^{3-}$
OTf = $^{-}O_3SCF_3$
Ph = phenyl
^{i}Pr = isopropyl
THF = tetrahydrofuran

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