ARTICLE

Recent Advances in Catalytic Pnictogen Bond Forming Reactions via Dehydrocoupling and Hydrofunctionalization

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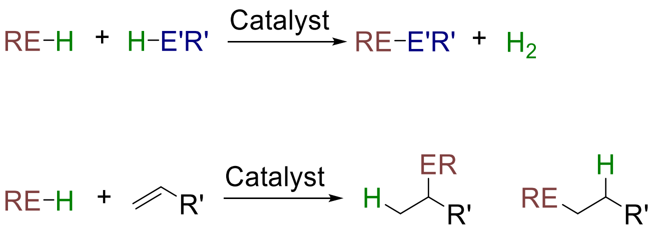
An examination of several catalytic reactions among the group 15 elements is presented. The connections between the chemistry of the pnictogens can sometimes be challenging, but aspects of metal–pnictogen reactivity are the key. The connecting reactivity comes from metal-catalyzed transformations such as dehydrocoupling and hydrofunctionalization. Pivotal mechanistic insights from E–N heterodehydrocoupling have informed the development of highly active catalysts for these reactions. Metal–amido nucleophilicity is often at the core of this reactivity, which diverges from phosphine and arsine dehydrocoupling. Nucleophilicity connects to the earliest understanding of hydrophosphination catalysis, but more recent catalysts are leveraging enhanced insertion activity through photolysis. This photocatalysis extends to hydroarsination, which may also have more metal–arsenido nucleophilicity than anticipated. However, metal-catalyzed arsinidene chemistry foreshadowed related phosphinidene chemistry by years. This examination shows the potential for greater influence of individual discoveries and understanding to leverage new advances between these elements, and it also suggests that the chemistry of heavier elements may have more influence on what is possible with lighter elements.

Introduction

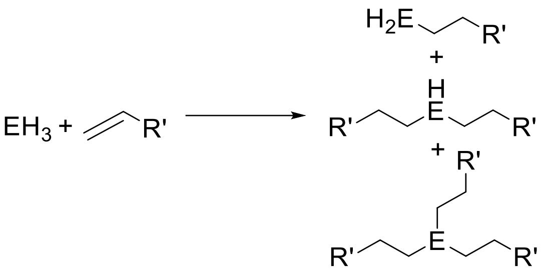
Traditional stoichiometric main group bond formation is being aggressively challenged. Decades ago, Manners identified the limited library of main group small molecules and polymers,[1] which partly ushered in a renaissance in main group chemistry enriched by catalysis.[2] Despite the tremendous advances in synthetic main group chemistry, main group reactivity, and related catalysis, stoichiometric transformations have fundamentally limited the scope of available precursors to main group small molecules and materials. This search for more efficient transformations also coincided with the outlining of green chemistry principles.[3] Notably, the use of catalysts, often with metals, improves efficiency and can leverage more atom economical syntheses,[4] which have empirically opened new pathways to form main group bonds. For the pnictogens (Pn = group 15 elements), catalysis has been transforming synthetic possibilities in the main group. Central to these developments is the rich chemistry of the metal–pnictogen bond.



Scheme 1. General reactions for catalytic dehydrocoupling (top) and hydrofunctionalization (bottom).

Several important reactions in this evolution have either emerged or grown, including dehydrocoupling and hydrofunctionalization, which are versatile routes to form Pn–E bonds through catalysis. Dehydrocoupling forms E–E bonds by the reaction of main group E–H precursors with concomitant loss of H_2 , often requiring a catalyst (Scheme 1, *top*).[5] The liberation of H_2 provides an excellent thermodynamic driving force, which is buttressed by the reactivity of many main group E–H bonds. Moreover, the straightforward removal of H_2 significantly simplifies purification of these products. It should be noted that reactions evolving H_2 present safety hazards, but that is balanced by the ease of disposal and the environmentally benign nature of H_2. Hydrofunctionalization involves adding E–H bonds across unsaturated substrates by a variety of mechanisms, some of which are catalysed by metals (Scheme 1, *bottom*). Hydrofunctionalization reactions are, of course, 100% atom economical, and despite the depiction of an alkene in Scheme 1, any unsaturated substrate may be used in principle. In general, each method has fundamentally expanded the synthetic toolbox for chemists.

Despite the promise of these transformations, challenges remain. For instance, dehydrocoupling is fundamentally limited by the activity and selectivity of the catalyst, which ultimately impacts substrate scope and the availability of products by design. Catalyst activity limitations are shared by hydrofunctionalization reactions that have limited substrate scope,[6, 7] and this is further exacerbated by potential challenges in affording chemo-, regio-, stereo- and enantioselectivity (Scheme 2), despite some gains in these areas. The limited examples of heavier pnictogen-based hydrofunctionalization reactions is also an area for work, which pale in comparison to the diverse and expansive fields of lighter congeners such as hydrophosphination and, more so, hydroamination.



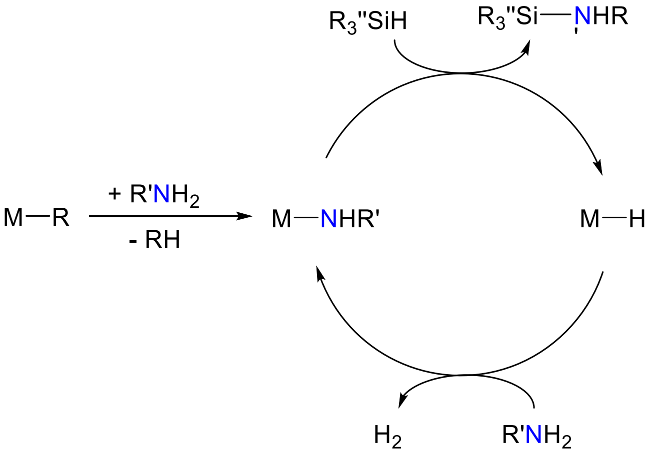
Scheme 2. Issues in selectivity illustrated by the potential mixture of single, double, and triple activation of unsaturated substrates in additions of EH_3 compounds.

The goal of this Feature is to discuss selected recent examples that illustrate either trends or high points related to pnictogen-centred dehydrocoupling and hydrofunctionalization with intermediary M–Pn complexes. While this is an area rife for deeper investigation, even this Feature must be selective and omit examples that are known. Hydroamination, amination, and related C–N bond forming catalysis are well-described and driven by different needs. The continued pressing need for versatility and variety in C–N bond formation for next generation medicines (among other needs) is self-evident. However, relegation of main group chemistry to basic or niche science, particularly the synthetic efficiency in main group chemistry, has left us ill-prepared to manage our increasingly endangered elements. In part, the focus on bond formation among both the heavier pnictogens and that between nitrogen and other p-block elements is meant to highlight the development necessary to combat increasing elemental scarcity. This is most evident with phosphorus, as its dwindling supply is contrasted by the ever growing need for phosphorus-based fertilizers for food production (i.e., “peak phosphorus”),[8, 9] but many other main group elements have been under increasing strain as their use in modern materials and electronics has increased. Nevertheless, despite the frightening concept of elemental scarcity, this is a positive story, one in which global efforts have led to new discoveries and understanding in bond formation catalysis with pnictogens, particularly leveraging the unique chemistry of M–Pn bonds.

Metal–Amido Bonds

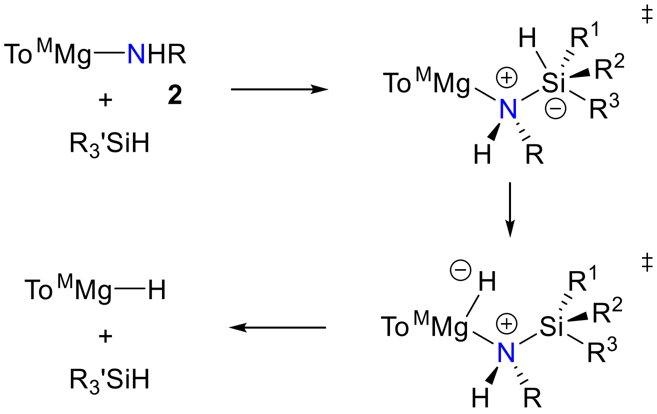
Silicon–Nitrogen Heterodehydrocoupling

The heterodehydrocoupling of silanes has emerged as a powerful method to form Si–N bonds through catalysis.[10-12] Around the turn of the century, homogeneous catalysts started to play a significant role in this transformation,[13, 14] with patterns in fundamental mechanistic understanding also emerging.[15-17] For example, Harder reported on the azametallacyclopropane compound (hmpa)$_3$Ca(η^2-Ph$_2$CNPh) as a precatalyst that coupled ^{n}PeNH$_2$, ^{n}BuMeNH, EtMe$_2$(C)NH, and PhNH$_2$ with Ph$_3$SiH.[18] A heteroleptic calcium–amido compound was proposed as the aminosilane bond-forming intermediate, which was similarly proposed for the ytterbium variant for this transformation.[13] The formation of metal–amido compounds is often invoked as the bond-forming intermediate in this catalysis (Scheme 3).



Scheme 3. General catalytic cycle related to Si–N heterodehydrocoupling.

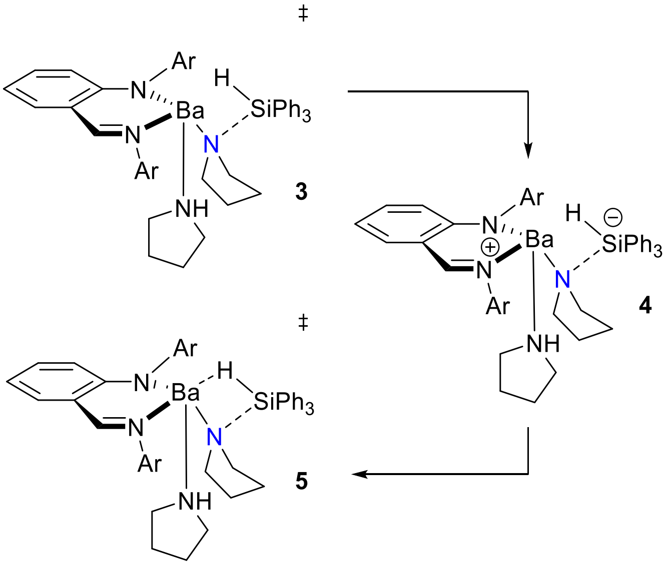
In a seminal 2011 report, Sadow provided critical evidence for a nucleophilic magnesium–amido intermediate through mechanistic study of (To^M)Mg–Me (**1**) [To^M = tris(4,4-dimethyl-2-oxazolinyl)phenylborate].[19] For instance, stoichiometric reactions between (To^M)Mg–NH^{t}Bu (**2**) and PhMeSiH$_2$ produced the desired aminosilane PhMeSiH(NH^{t}Bu). Zeroth-order amine dependence in this reaction may seem surprising but indicates the importance on **2** attacking silane as the turnover-limiting step. Hammett analysis provided a positive slope with rate acceleration for electron-withdrawing silanes, which is consistent with negative charge build up at silicon. Activation parameters and kinetic isotope effect (KIE) were consistent with σ-bond metathesis,[20] although high concentrations of coordinating amine did not affect the reaction.[21, 22] Finally, electron-rich amines showed accelerated rates. The sum of these results is a strong argument for a nucleophilic attack on silane from **2** and the formation of a hypervalent silicon as the turnover-limiting step (Scheme 4). This “Sadow mechanism” has been invoked for other magnesium systems,[23] but more importantly, it has given the field a baseline for comparing other catalysts such that simple mechanistic assumptions can be made using more limited data.



Scheme 4. Nucleophilic attack on silane by (To^M)MgNR$_2$.[19]

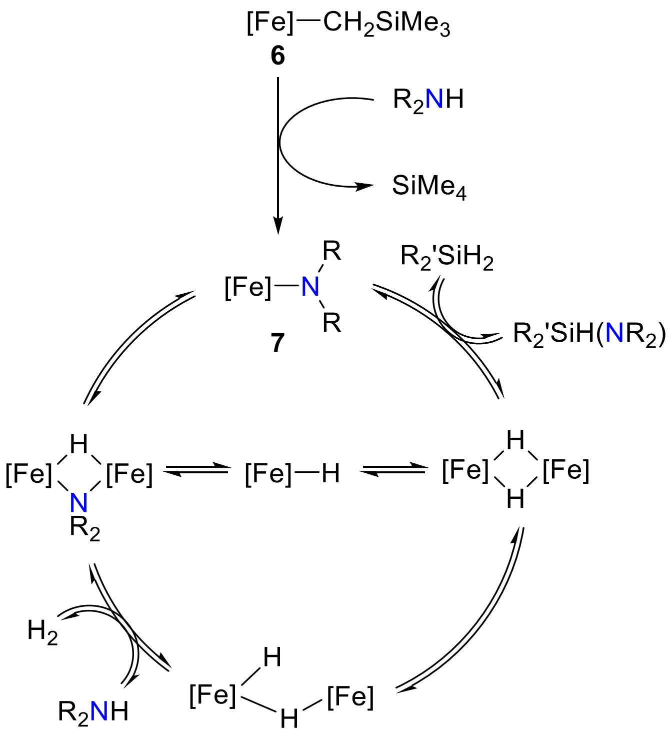
Hill and co-workers examined a series of alkaline earth compounds, Ae[N(SiMe$_3$)$_2$]$_2$ (Ae = Mg, Ca, Sr), that were shown to efficiently couple an array of primary and secondary amines to PhSiH$_3$, Ph$_2$SiH$_2$, and Ph$_3$SiH at modest heating or ambient temperature.[24] In contrast to Sadow's system, a first-order dependence on both the metal (Ca or Mg) and the amine was found. This suggested that amine activation was turnover limiting. Strontium, however, was found to obey second-order kinetics with first-order dependences on both amine and silane. This evidence suggested that the rate limiting step involved the formation of a metal–hydride formed via σ-bond metathesis.[20] Ultimately, this work demonstrated that the mechanism for catalysis differs among alkaline earth elements, with factors such as ligand coordination and polarizability playing a significant role in the nature and reactivity of these catalysts.

A collaboration among the groups of Carpentier, Tobisch, and Sarazin examined several classes of compounds bearing heavy alkaline earth elements (Ae = Mg, Ca, Sr, Ba).[25] The compounds examined included amido and imido complexes, as well as barium–alkyl compounds. Apart from magnesium, all compounds effected the formation of Si–N products. The most catalytically active compounds were (thf)$_2$Ba[N(SiMe$_3$)$_2$]$_2$ and (thf)$_3$Ba[CH(SiMe$_3$)$_2$]$_2$ which afforded high conversions of aminosilanes from uncommon substrates such as disilanes and diamines at mild temperatures, in addition to coupling more routine primary and secondary amines with tertiary silanes. A zeroth-order dependence on amine was deduced from kinetic studies and Hammett analysis indicated a build-up of negative charge in the rate-limiting step, which is consistent with the Sadow-type mechansim.[19] However, a high primary isotope effect in the reaction of Ph$_3$SiD and (*cyclo*-C$_4$H$_8$)NH indicated silane activation, but that value is large enough to indicate that this step is complex. Such complexity may indicate why DFT calculations failed to successfully identify a transition state consistent with σ-bond metathesis.[19] These results are initially consistent with nucleophilic attack on silane from a barium–amido (**3**) forming a hypervalent silicon intermediate (**4**), and it was suggested that proton-transfer from silane to form a barium–hydride (**5**) is turnover limiting for catalysis (Scheme 5).



Scheme 5. Rate-limiting steps in barium-catalysed Si–N heterodehydrocoupling.[25]

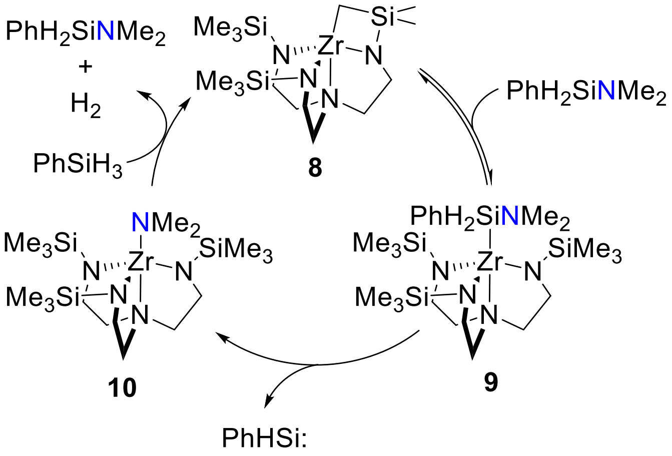
Recently, Webster and co-workers utilized an alkyl iron *β*-diketiminate (**6**) for rapid heterodehydrocoupling.[26] First- and zeroth order dependences were found for amine and silane, respectively. Isolated examples of iron–amido (**7**) were found to overcome the induction period observed with **6**, which is consistent with isolated metal–amido examples.[19, 24, 25] Reactions between silane and PhND$_2$ resulted in a sizable KIE, indicative of highly organized proton-transfer in the transition state. The final feature that strongly impacts this catalysis is dimerization kinetics of a key iron–hydride intermediate as illustrated in the proposed mechanism (Scheme 6).



Scheme 6. Mechanism for Si–N heterodehydrocoupling catalysed by iron β-diketiminate.[26]

The high activity of metal–amido compounds and their importance in this catalysis has somewhat overshadowed metal–silyl intermediates, and these provide an interesting contrast in reactivity. Indeed, only a handful of systems have implicated the presence of these intermediates, originating in the 1990s with Harrod's reports on Cp$_2$TiMe$_2$ (Cp = C$_5$H$_5^-$).[27, 28] The potential for π-bonding and relative electronegativities of many of the most studied catalysts would argue for amido derivatives. In Harrod's reports, the strength of a titanium–silyl bond is doubtlessly a contributor to the importance of that reaction.

The counter to strong metal–nitrogen bonding is that it can over stabilize the amido compound. For triamidoamine-supported zirconium (**8**) compounds with terminal amido ligands, the strong Zr–N bond and tight steric control around zirconium leads to relatively inert amido derivatives.[29] One consequence of this inertness is that metal–silyl reactivity can take over. Interestingly, (N$_3$N)ZrSiR$_3$ (**9**) [N$_3$N = N(CH$_2$CH$_2$NSiMe$_3$)$_3^{3-}$] compounds are unstable with respect to cyclometallation of the ancillary ligand, but evidence to demonstrate formation was accrued, in part, through H/D exchange reactions of PhSiD$_3$ with the trimethylsilyl substituents of the triamidoamine ligand. Thus, (N$_3$N)ZrNMe$_2$ (**10**) is a precatalyst for the heterodehydrocoupling of PhSiH$_3$ with Me$_2$NH but through **9**.[30] As an aside, extrusion of a silylene fragment from **9** was one route to form **10** when the reactivity was tuned for silane dehydrocoupling (Scheme 7). Again, the stability of **10** was a key factor in reactivity and using Si–N bond formation as a method to promote silane dehydrocoupling.



Scheme 7. Silylene extrusion from $(N_3N)Zr$ by Waterman and co-workers.[30]

In an effort to continue to leverage metal–silyl reactivity, the commercially available iron dimer $Cp_2(CO)_4Fe_2$ (**11**) was used as a visible-light activated catalyst.[31] The formation of a $Fe–SiR_3$ species was confirmed via ^1H NMR spectroscopy, yet isolated derivatives were found to be incompetent under both stoichiometric and catalytic conditions. These results are consistent with the limited role that metal–silyl intermediates play in Si–N heterodehydrocoupling, in contrast to amido intermediates. However, they indicate room for growth as well as possible strategies for catalyst design.

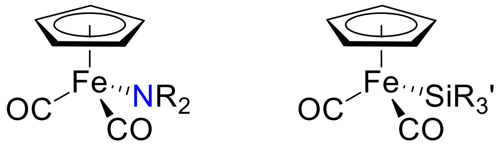
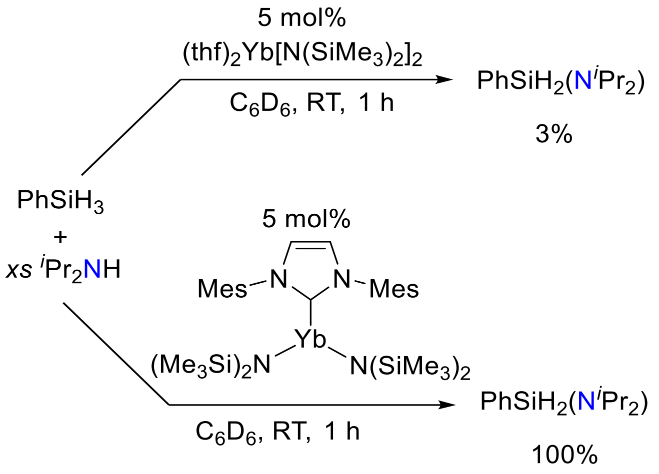


Figure 1. Piano-stool iron compounds formed in iron-catalysed Si–N heterodehydrocoupling.[31]

Beyond mechanistically relevant intermediates, a handful of reports have highlighted the success of precatalysts with reactive amido ligands. These amido substituents generally overcome potentially long activation steps through a more facile protonolysis by the desired amine substrate. As a result, active catalysis is observed under ambient or otherwise mild conditions. For instance, Panda and Carpentier reported on group I $MN(SiMe_3)_2$ compounds as efficient precatalysts to couple electron-rich amines with $PhSiH_3$, Ph_2SiH_2, and Ph_3SiH under mild conditions.[32] Trifonov also demonstrated the efficacy of the $^-N(SiMe_3)_2$ ligand in Si–N heterodehydrocoupling, utilizing a class of calcium compounds bearing Schiff base ligands.[33] Nembenna further reported on $(IMes)(Ar)MgN(SiMe_3)_2$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene, Ar = 2,6-Me-C_6H_3 or 2,4,6-Me-C_6H_2) as a mediator for this transformation.[34] Cui and co-workers reported on two examples of ytterbium complexes bearing *N*-heterocyclic carbene (NHC) ligands, which was a notable example of enhanced Si–N coupling with these compounds (Scheme 8).[35]



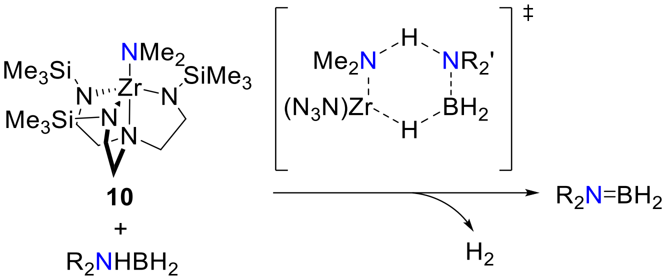
Scheme 8. Catalytic enhancement with ytterbium.[35]

A recent study demonstrated that low catalyst loadings of $(thf)_2La[N(SiMe_3)_2]_3$ afforded a variety of aminosilanes by coupling simple primary and secondary amines to $PhSiH_3$, $PhMeSiH_2$, Ph_2SiH_2, $PhMe_2SiH$, and Ph_3SiH.[36] Regardless of temperatures or amine concentrations, chemoselectivity was often retained. Additionally, it appeared that $(thf)_2La[N(SiMe_3)_2]_3$ was the most active lanthanide compound for Si–N heterodehydrocoupling reported to date despite the excellent activities in reports from Cui and Sadow.[35, 37] The additional amido ligand and Lewis acidity of lanthanum(III) were argued as the primary factors for this activity. Beyond lanthanides, an actinide–amido complex reported by Eisen and co-workers is a precatalyst for the coupling of silanes with simple amines.[14] Finally, Wright and co-workers reported on the aluminium compound $Al(NEt_2)_3$ as a precatalyst as well,[38] consistent with the increasing interest in p-block catalysts.[39]

Boron–Nitrogen Heterodehydrocoupling

The dehydrocoupling of amine–boranes became tremendously popular when those molecules were identified as potential hydrogen storing materials.[40] Such reactions were originally reported by Manners using a rhodium catalyst under the aim to prepare poly(aminoboranes), which were realized later with an iridium catalyst yielding an intriguing new class of materials.[41, 42] In the time since, the field has broadened to encompass a range of elements as catalysts. What is interesting in this reactivity is differences with respect to Si–N heterodehydrocoupling that may inform both areas as well as others. For many early metal compounds, the formation of an amido intermediate is indeed important. Unlike Si–N dehydrocoupling, the B–N bond is pre-formed in the substrate such that different classical organometallic reactivity, like β-hydrogen elimination, can take over that then allows off-metal coupling. Interestingly, this reactivity has been frequently identified to occur from the metal–boron versus metal–amido compounds to afford a net β-hydrogen elimination.[43, 44]

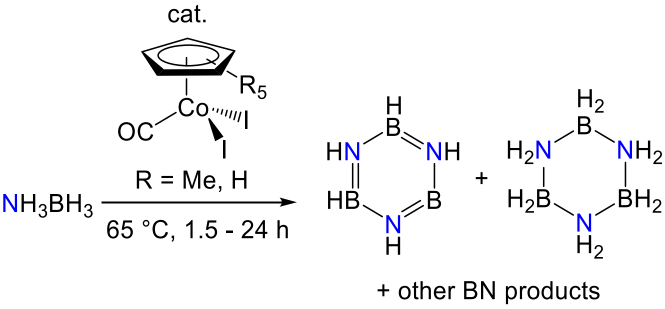
The middle ground in which the metal–element (nitrogen or boron) bond is not the sole driver of reactivity is also known, and this is perhaps most interesting in circumstances where one might anticipate strong metal–element bonding. For example, triamidoamine-supported zirconium compounds are effective dehydrocoupling precatalysts for amine–boranes as well as transfer hydrogenation reactions (Scheme 9).[45] Reactions with a range of $(N_3N)ZrX$ derivatives (X = NMe_2, Cl, O^tBu) afforded comparable conversions, suggesting formation of uniform intermediates, despite how relative inert the Zr–N bond has been.



Scheme 9. Ligand cooperativity in H_2-transfer as demonstrated in zirconium-catalysed B–N heterodehydrocoupling.[45]

Unlike classical amine–boranes dehydrocoupling reactions, $(N_3N)ZrX$ compounds are not prone to β-hydride elimination reactions, with the authors suggesting an alternative reaction involving an outer-sphere hydrogen transfer mechanism. These kinds of reactions continue to be seen and metal-ligand cooperativity has potential for greater involvement in main group bond forming catalysis.

A relatively recent example of transfer-hydrogenation with a 3d metal (i.e., earth abundant) was reported by von Wangelin and Wolf, which illustrates the viability of this concept in metal catalysis.[46] Cobalt catalysis have been a potentially exciting avenue for this catalysis because piano-stool cobalt compounds $Cp(CO)CoI_2$ and $Cp^*(CO)CoI_2$ ($Cp^* = C_5Me_5$) were found to exhibit good activity under aerobic conditions (Scheme 10).[47]



Scheme 10. Amine–borane dehydrocoupling catalysed by a piano-stool cobalt compound to afford saturated and unsaturated products.[47]

The expansion to more earth abundant catalysis is indeed important, but the ability to employ bench-stable precursors without penalty in activity or lag time for activation is an important vista in catalysis, generally speaking.[48]

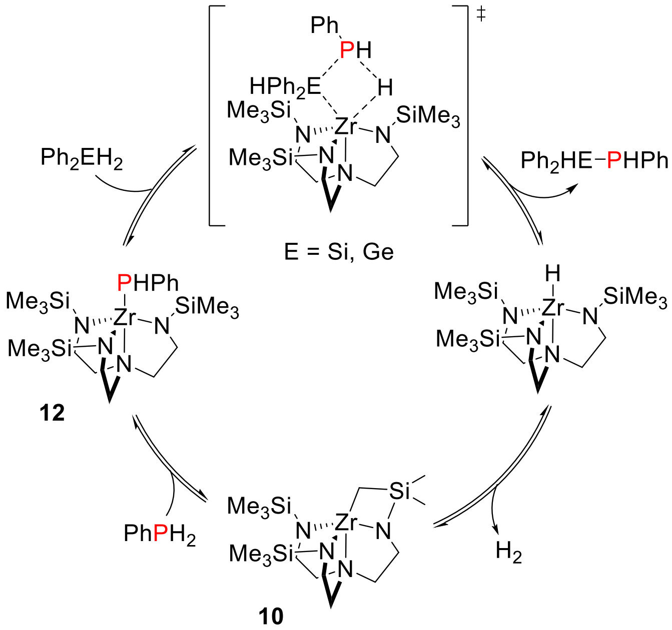
Of course, the idea of transfer hydrogenation from ammonia borane is far from new, but its utilization with main group elements has been an exciting development as initially demonstrated by Radosovich and continued by several others.[49-52] Elements in the p-block are indeed attractive as catalysts (vide supra). Returning to the theme of metals as catalysts, tin compounds have seen application in this reactivity. Use of both Sn(II) and Sn(IV) compounds as precatalysts for group 13-15 E–E' bond formation has been observed. Prior reports of Sn–Pn bond-formation catalysis shows dependence on oxidation state, as seen by the work of Wright[53] and Waterman,[54] exemplified in the dehydrocoupling of phosphines. However, the success that exists in tin-catalysed amine–boranes dehydrocoupling processes are dependent on the scope of substrate used and observe moderate to high conversion with both Sn(II) and Sn(IV) compounds such as Ph_2SnCl_2, $Cp^*_2SnCl_2$, and $SnCl_2$.[55] The authors draw on steric effects as a strong influencer on the activity for a given tin compound, but these and prior studies also indicate that oxidation state may be a significant factor and area for future investigation. Chain growth is speculated for this transformation, and overall reactivity was thought to emulate elimination pathways where off-metal coupling is important. The lack of valid intermediates does mean that metal–nitrogen bonding as a driver in p-block metal catalysis remains an open question.

Metal–Phosphido Bonds

Phosphine Dehydrocoupling

Phosphine dehydrocoupling processes demonstrate modest catalytic turnover in the presence of known p-block and s-block catalysts. The broadest challenge for all systems studied is limited activity. This appears to arise from two specific issues. The first is the fundamental challenge that phosphine substrates are sufficiently Lewis basic to coordinate to and therefore occupy vacant orbitals needed to activate P–H bonds. The second challenge relates to the modest thermodynamics of the reaction, which is marginally favourable in simple calculations. The process of dehydrocoupling is reversible, and dehydrocoupling catalysts quickly cleave P–P bonds in the presence of H_2.[56] Thus, the reactions are frequently limited by the mass transfer of the hydrogen byproduct.

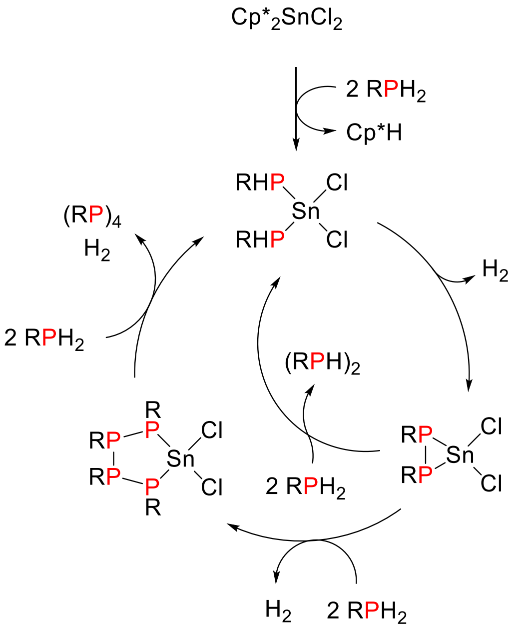
Group 4 metals have dominated this area since the initial discovery of this transformation by Fermin and Stephan.[57] These zirconocene catalysts were viable for the preparation of a variety of oligophosphines at elevated temperatures.[58, 59] These compounds were based on a trihydride precatalyst, that was proposed to operate via a phosphinidene (Zr=PR) intermediate, though terminal phosphido ligands were also available for the metal. Triamidoamine-supported zirconium compounds showed good activity for this transformation.[60] Arguably the innovation of these systems was the high selectivity for both diphosphine products as well as in heterodehydrocoupling reactions, particularly those with silanes or germanes.[61] Selectivity appeared to arise from the relative stability of the phosphido intermediate (**12**) (vs. silyl or germyl), which allowed for the group 14 reagent to assume the β-position of the bond-forming σ-bond metathesis transition state (Scheme 11). Experimental evidence for phosphorus participation in σ-bond metathesis was presented shortly before that study.[20] This feature, the importance of the M–P bond in establishing selectivity, is an idea that is arguably underdeveloped, but instances of selective phosphination catalysis are an excellent example of the further utilization of this idea.[62]



Scheme 11. Zirconium-catalysed heterodehydrocoupling, illustrating how the Zr–PR₂ imparts selectivity on the reaction.

As with nitrogen–element bond formation, main group catalysts are an underexplored area with respect to phosphine dehydrocoupling. Early in such explorations, Stephan demonstrated that Lewis acids are viable catalysts for phosphine dehydrocoupling.[63] Metals in the s-block have demonstrated catalytic utility towards the generation of phosphorus-containing oligomers. Alkali metal salts of strong bases, like KOtBu, are known to facilitate dehydrocoupling of phosphines.[64] Though the mechanism is markedly dependent on the base's ability to deprotonate the phosphine, there is a more rich chemistry here, some of which involving radical generation, than many be initially apparent. Greater generality and much greater reactivity was observed with lithium carbeniods, albeit those transformations were stoichiometric.[65]

Elements of the p-block metals remain promising. Early reports with tin-catalysed dehydrocoupling, suggest mechanistic features similar to that reported by Stephan for zirconocene catalysis (Scheme 12).[54, 57] These studies primarily focused on Sn(IV) compounds, and the activity that was observed was modest in comparison to conventional catalysts at that time, and catalyst activation appeared to be the driving factor for improving relative rate. Bismuth dehydrocoupling catalysis has recently appeared, and these compounds are highly active.[66] These systems operate by radical generation, which has become a more prominent and interesting route to reactivity but is outside the scope of this Feature. It is noteworthy how active and selective these catalysts are, however, and the ability to engage in both heavy and light group 15 dehydrocoupling is unique.



Scheme 12. Proposed catalytic cycle of dehydrocoupling primary phosphine substrates by Sn(IV) catalysts.[54]

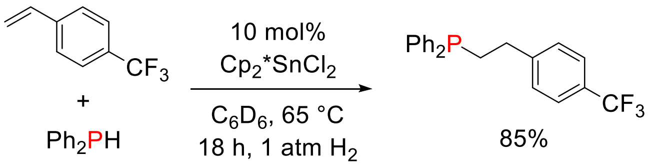
Discrete metal–phosphido compounds have been important to dehydrocoupling catalysis involving phosphines as substrates. While the relative acidity of the P–H bond is certainly a factor in some cases and a potential indicator of reactivity as noted before and in the original reports, metals have the unique ability to activate a range of P–H substrates regardless of the substrates Brønstead acidity. Thus, continued development of metal–phosphido chemistry is key for this area.

Hydrophosphination

There have been several major developments in hydrophosphination catalysis over the last 20 years. The biggest and best of these has been the large group of excellent global researchers engaged in this work. This development alone is responsible for all others. The field itself has been reviewed in parts and now in whole.[67] In this period of increased interest, access to substrates has improved, more abundant catalysts are being used, and new and high selectivity is seen; however, challenges remain in all three of these domains.[6, 7]

The most critical to all challenges is catalytic activity, and the activity of catalysts has increased substantially overall. While there is much more room for growth, the gains in activity, in many ways, appear to be attributable to formation of metal–phosphido intermediates. Naturally, such compounds have rich reactivity, and indeed, several mechanistic possibilities for hydrophosphination have been summarized thus far.[68] Hydrophosphination is a reaction that can occur spontaneously and has been promoted or catalysed by bases, radicals, and irradiation. Molecular catalysts have particular value in this reaction to avail inaccessible substrates as well as affording selectivity, of which there are many kinds for this transformation.[67] In our experience, the importance of a discrete metal–phosphido compound in catalysis is somewhat empirical and related to observations of literature compounds and reactions. These start with limited catalytic activity, and at the risk of shaming others, we note only our own examples of poor catalytic activity in support of this burgeoning hypothesis.

In 2016, a report demonstrated the use of Ph_2SnCl_2 and $Cp^*{}_2SnCl_2$ as precatalysts for the hydrophosphination of alkenes appeared (Scheme 13).[69] This followed Wright's reports of phosphine dehydrocoupling catalysis with the same compound (*vide supra*) and an initial report of hydrophosphination catalysis with tin compounds.[53, 54] For purposes of completeness, these reports also demonstrated Lewis acid catalysed hydrophosphination, but this reactivity was limited. The catalysis with tin across those two reports showed good substrate scope for that time and modest activity compared to both contemporary and more recent catalysts.



Scheme 13. Hydrophosphination of *p*-substituted styrene substrates with Ph_2PH mediated by Sn(IV) catalyst.[54]

The bigger challenge for this system was not identifying catalysts, but viable intermediates with Sn–P bonds. Those studies failed to provide isolable tin–phosphido compounds. Competitive dehydrocoupling was problematic for this catalysis, a problem that was mitigated under an H_2 atmosphere. However, attempts to synthesize desired Sn–P bonds gave P–P and sometimes Sn–Sn bonds instead. The propensity for rapid, apparent redox chemistry was surprising despite productive catalysis. Nevertheless, these observations started to fuel the hypothesis that at least a metastable phosphido compound is needed for more active reactions.

Since then, Webster reported a germanium precatalyst for hydrophosphination (Figure 2, *left*).[70] The germanium system enjoys a greater substrate scope and selectivity than tin. Under classic organometallic arguments, one might surmise that the heavier element is forming more covalent bonds (Sn–P vs. Ge–P) than the lighter element, leading to lower activity of the former. For p-block catalysts, this is an unexplored phenomenon, and one of broader interest (i.e., relative covalency versus activity). Such a phenomenon may be a factor in the lack of catalytic turnover in Coles's report of bismuth hydrophosphination-like reactivity.[71] That said, such a comparison is impossible between these systems because the tin compounds failed to afford phosphido derivatives, whereas Webster and co-workers were successful in identifying germanium–phosphido compounds in their reaction mixtures.[70]

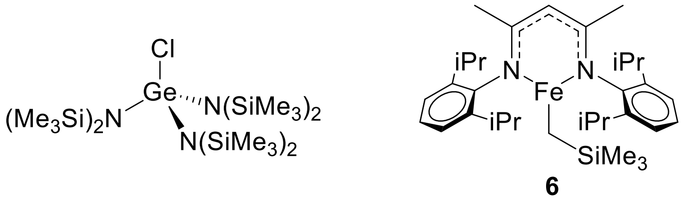


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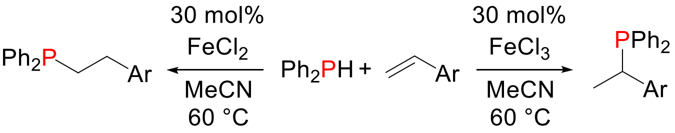
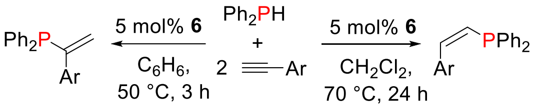
Figure 2. Hydrophosphination catalysts used by Webster and co-workers.

From where does the hypothesis that a well-defined metal–phosphido intermediate is important arise? Both iron and zirconium provide some insight into why a reasonably long-lived, if not metastable, metal–phosphido intermediate is important. Catalytic hydrophosphination is primarily an exploratory reaction in that few established processes use hydrophosphination and those that do are often radical based.[7] Thus, less abundant metals would only add complexity in the uptake of newly discovered processes, despite these providing key understanding of processes. For that reason, the use of our most abundant transition metals in exploratory catalysis is very attractive. Indeed, the challenge of scarce elements demands that more sustainable catalysts be used whenever possible as well. Iron has been intriguing as the best metal thus far to provide differential selectivity between Markovnikov and anti-Markovnikov products. This was accomplished initially with the simplest of iron precatalysts, arguably among the most simple precatalysts known, $FeCl_2$ and $FeCl_3$, where the former provides Markovnikov products while the latter affords anti-Markovnikov products, for the hydrophosphination of styrene substrates (Scheme 14).[72]



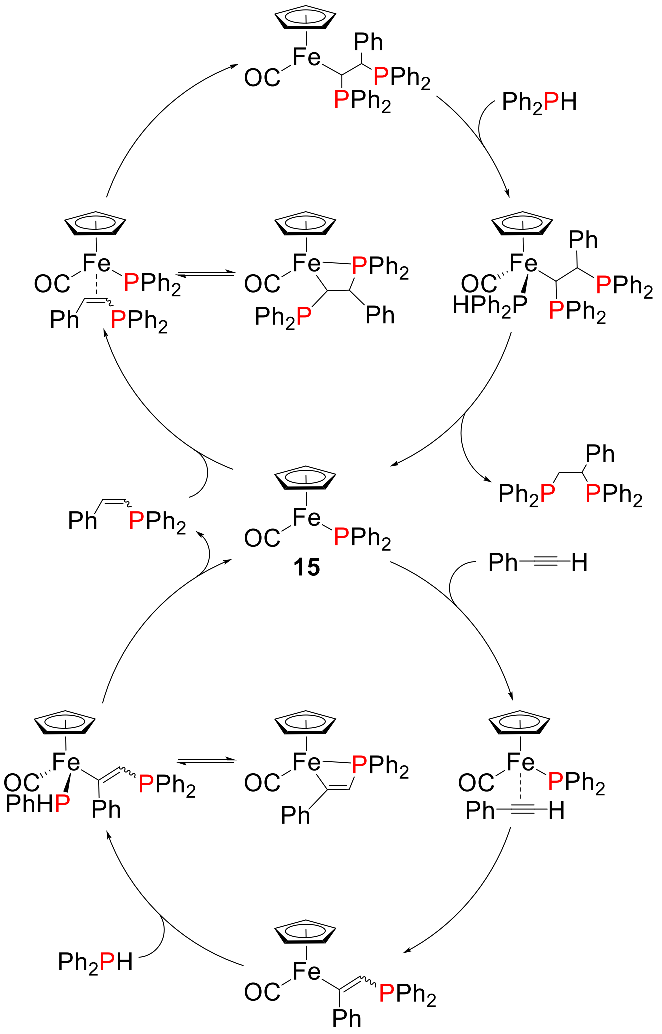
Scheme 14. Changes in selectivity between two simple iron catalysts.

Following this triumph by Gaumont, Webster identified that hydrophosphination of terminal alkynes using **6** (Figure 2, *right*) can differentiate between Markovnikov and anti-Markovnikov products based on solvent and other reaction conditions (Scheme 15).[73] That differential selectivity was successfully extended to intramolecular hydrophosphination, which allowed Webster and co-workers to prepare five- and six-membered phosphorus-containing heterocycles (Scheme 20).[74]



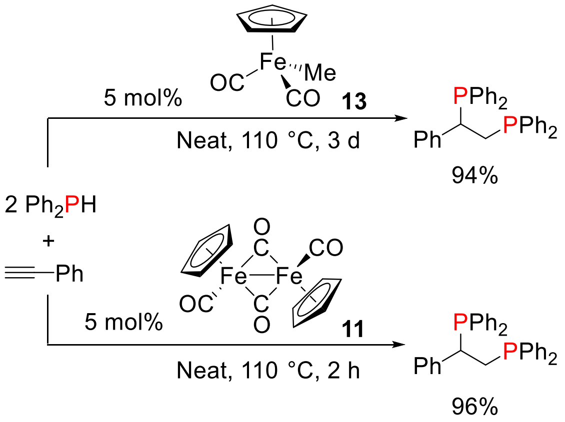
Scheme 15. Effect of reaction conditions on regiochemical outcomes in iron-catalysed hydrophosphination as reported by Webster.[73]

These successes set the stage for problems that illustrate where the relative stability of a phosphido intermediate appears to be important. Our exploration of iron compounds stemmed from the aim to generate low-valent phosphorus fragments from half-sandwich iron compounds. The in-road to hydrophosphination catalysis was somewhat accidental in that eliminating photocatalysis from the phosphinidene transfer reactivity. Irradiation did not enhance reactivity of $Cp(CO)_2FeMe$ (**13**) to phosphines in our hands, but light was known to activate **11** to a pair of 17-electron intermediates. This photoactivation was successful in activating the P–H bond of secondary phosphines, and this system provides modest turnovers for common substrates like Michael acceptors and styrene derivatives.[75] What was known is that the putative phosphido compound $Cp(CO)_2FePPh_2$ (**14**) is unstable.[76] Nakazawa had identified this during broader explorations of catalysis using piano-stool iron derivatives as well as the direct exploration of these and related compounds. That instability may be connected to relatively slow reactions times (i.e., low activity). In this particular instance, the working hypothesis is that decomposition of **14** is competitive with P–C bond formation. Interestingly, the instability of **14** does not lead to catalyst deactivation, and that fact at least explains the difference between modest activity and inactivity in this system.



Scheme 16. Mechanism for iron-catalysed hydrophosphination as reported by Nakazawa.[77]

While a deeper understanding of the complexities of hydrophosphination may arise from that example of modest iron catalysis, there was greater immediate gain as well that came from validating an excellent hypothesis in the literature. A tour de force in hydrophosphination applicability came from Nakazawa who initially reported **13** as a precatalyst for the double hydrophosphination of terminal alkynes.[77] This direct preparation of 1,2-diphosphinoethanes, privileged ligands in late transition-metal catalysis, was a noteworthy realization of what hydrophosphination can accomplish. Further work by Nakazawa demonstrated additional generality and applicability through a selective preparation of unsymmetrical derivatives as well.[78] This catalysis was challenging and therefore slow. Reactions of several days were required in the original report. Nakazawa reported that the proposed intermediate, $Cp(CO)FePPh_2$ (**15**), was also unstable due to a formal 16-electron configuration, which was subject to intramolecular phosphine coordination after the first insertion event that ultimately inhibited the progress of the reaction. The formally 18-electron phosphido compound, **14**, generated by photoactivation of **11** would be inert to such coordination with the final coordination site occupied by a carbonyl ligand. As such, this compound might exhibit improved relative rates of double hydrophosphination based on the mechanistic proposal by Nakazawa.[78] Indeed, **11** exhibits full conversion in about two-thirds of the time needed for **13** under photochemical conditions. Furthermore, cleavage of **11** can be achieved thermally, and the use of **11** under thermal conditions improves reaction times tremendously compared to **13** (Scheme 17). Despite some examination of double hydrophosphination by other catalysts, this remains an intriguing fast-track to established value-added products.



Scheme 17. Comparison between $Cp(CO)_2FeMe$ and $Cp_2(CO)_4Fe_2$ in the double hydrophosphination of terminal alkynes.[77, 79]

In sum, limited reactivity of a low-stability iron–phosphido derivative, the inability to even observe tin–phosphido compounds, and the complete inability to find evidence for a zirconium–phosphido informed the hypothesis that a threshold level of stability is necessary for productive hydrophosphination (and other P–E bond forming) catalysis. This suggested relationship is remarkably difficult to quantify, but it provides a good reason why many precatalysts with acid-labile alkyl or amido substituents demonstrate limited activity. Such thinking does yield a testable hypothesis: Isolation of phosphido derivatives and comparing these with non-phosphido (e.g., alkyl) precatalysts may show enhance reactivity by the former. This is more than an intellectual curiosity. A variety of well-designed systems with otherwise favourable properties do not provide conversions or activity that merit further study. If this hypothesis is borne out, these could become viable catalysts again.

As the exploration of hydrophosphination systems continued, an excellent example of success in the mid-transition metals was demonstrated by Rosenberg. On-going study of indenyl ruthenium derivatives has yielded excellent understanding of fundamental chemistry and reactivity of the Ru–P bond.[80] These derivatives have displayed modest activity as hydrophosphination catalysts; in a triumph of mechanistic analysis, Rosenberg and co-workers identified several pivotal features of the system with respect to its conjugate addition mechanism that allowed for a redesign of the ruthenium system that yielded an order of magnitude improvement in activity.[81] The success from this study shows the significant gains from tuning of the catalysis informed by thorough mechanistic study involving the metal–phosphido intermediate.

Zirconium gave more credence to the need for a terminal M–PR_2 compound in hydrophosphination catalysis. As will be described, the successes with triamidoamine-supported zirconium arose from the study of discrete phosphido derivatives. The story, however, starts with poor reactivity.

In the routine exploration of triamidoamine-supported zirconium compounds, a variety of $(N_3N)ZrER_n$ compounds were readily prepared that exhibited rich reactivity. Among the reactions observed, insertions into the Zr–P bond were facile, which suggested that these could be viable hydrophosphination catalyst. The misadventures associated with chasing this initial hypothesis have been described, but the punchline is that poor reactivity was observed.[82] What is now understood is that the pocket around the Zr–P bond is too sterically encumbered and the Zr–P bond is too strong which inhibits hydrophosphination. The results were limited activity and a poor substrate scope in the original investigation.[83] Exploration of tripodal frameworks included trisphenolatoamine-supported [O_3N = $N(CH_2C_6H_2(^tBu)_2O)_3^{3-}$] zirconium compounds, based on the report by Davidson (Figure 3).[84] These derivatives and related have found great success in ring-opening polymerizations, particularly in recent years. Simple alkyl derivatives of the form $(O_3N)Zr^tBu$ gave poor conversions of dehydrocoupling products and virtually no hydrophosphination products under conditions that mimicked prior successful hydrophosphination with triamidoamine-supported zirconium. That limited reactivity was coupled to a general inability to prepare or even observe a Zr–PR_2 compound. Unlike the tin chemistry, there was too little reactivity to muster a report, and those efforts at a phosphido failed to result in reliable 'competitive' chemistry like P–P coupling products.

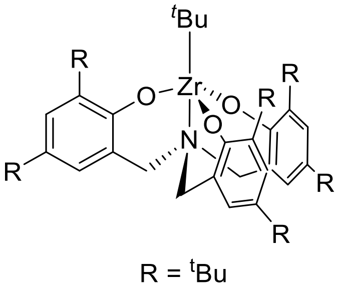
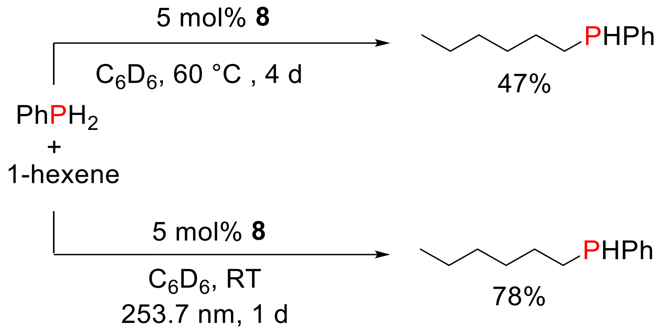


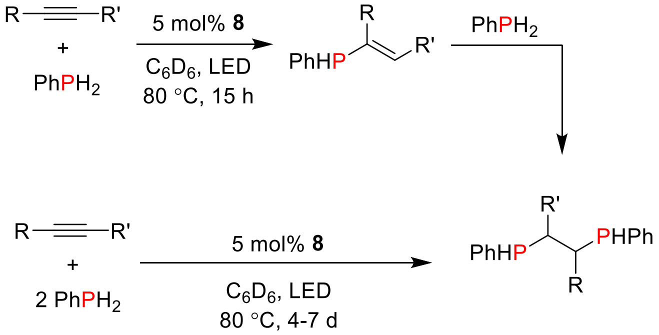
Figure 3. Triphenolate-supported zirconium compounds.

There are various ways in which greater activity has been achieved, and the remarkable efforts of several investigators follows the linear development (with several intellectual leaps) of catalysts across the metals. The recent emergent development, however, has been photocatalysis. For the prior description of $CpFe(CO)_2X$-based catalysis, light was important, but this was photoactivation of iron to a 17-electron intermediate. Recent developments, starting with zirconium, demonstrate that photocatalysis results in high activity for hydrophosphination, allowing for transformative substrate access, particularly with unactivated substrates. Several studies now support the notion that photocatalysis appears to be general. This generality has extended from triamidoamine-supported zirconium to other d^0 metals and now late metals, namely copper.

Our internal renaissance of $(N_3N)Zr$-based hydrophosphination catalysis started with the accidental discovery of successful hydrophosphination with RPH_2 substrates.[82, 85] That discovery highlighted the steric constraints of the triamidoamine framework in hydrophosphination. The discovery of photocatalysis was again fortuitous but squarely the result of researchers asking questions about unexpected results. As this has been described,[82] only a brief summary is needed. Under irradiation, triamidoamine-supported zirconium compounds exhibit dramatically enhanced catalytic activity in hydrophosphination.[82] Study of that reactivity indicates that a ligand-to-metal (LMCT) charge transfer band has adequate σ* character such that there is significant Zr–P bond elongation in the excited state.[86] Such elongation may allow for substate to coordinate within the more open binding area and/or promote insertion into a weaker bond. This is an unanswered aspect of the catalysis. The effects of irradiation are clear and pronounced. For the hydrophosphination of 1-hexene with $PhPH_2$, *decreasing* the reaction temperature and *decreasing* the reaction time by as much as 75% by irradiating *increased* yield by >50%, depending on the light source/intensity (Scheme 18).[86] Unactivated α-olefins became a viable substrate overnight, quite literally.



Scheme 18. Improvement in the catalytic hydrophosphination of 1-hexene under irradiation using **8**.[86]

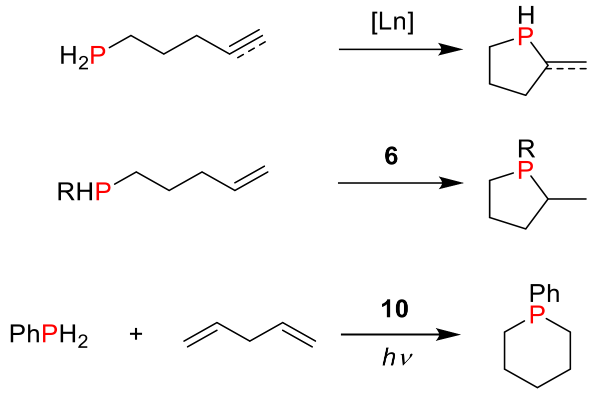


Scheme 19. Zirconium-catalysed double hydrophosphination of internal alkynes using $PhPH_2$.[6]

The ramifications of this increased reactivity were realized quickly. For example, the formation of 1,2-diphosphinoethanes could be achieved by a one-pot synthesis using internal alkyne with two equiv. of $PhPH_2$ for extended periods or by direct addition of one P–H bond across the isolable secondary vinyl phosphine product (Scheme 19).[6] Both unactivated and activated substrates showed similar TONs, indicating that electronics have minimal impact on catalyst efficiency. Attempts of double hydrophosphination of terminal alkynes provided little to no conversion (up to 5%), and this was unexpected. Previous reports had demonstrated that, while terminal alkynes are substrates in hydrophosphination with Ph_2PH with this catalyst, the reactivity is stymied by the high relative stability of a terminal alkynyl derivative of zirconium.[83] Extended reaction times in attempts with phenylacetylene yielded the *hydrogenation* product in 30% conversion rather than the double hydrophosphination product. The observation of 1,2-diphenyldiphosphine (20% conversion) indicated the source of hydrogen, and is somewhat surprising given the relatively poor activity of **8** in hydrogenation catalysis with H_2.[45] As an exception, ethylene was a successful substrate in this reaction with good conversions to bis(phenylphosphino)ethane in 18 h. There was some competitive C–H bond activation in this catalysis, but the reduced steric constraints of the substrate appeared to overcome substrate inhibition challenges. Indeed, the study reflected that steric considerations are the significant challenge in double hydrophosphination with zirconium.[6] Overall, this work is highly complementary of Nakazawa's original discovery and related late catalysts that have been active with terminal alkynes and secondary phosphine substrates. For both categories of catalyst, improvement in activity is needed for these to be practical in the routine synthesis of these highly value-added products.

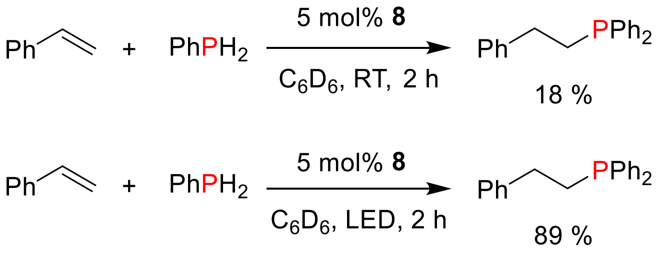
As noted, the enhanced activity imparted on triamidoamine-supported zirconium transformed unactivated alkynes from proof-of-concept type substrates to those that could be accessed under more routine circumstances. This observation extends to phosphine substrates as well, where other bulky primary phosphine substrates, such as $CyPH_2$ and $MesPH_2$, also showed improved catalytic activity, but the scope of phosphines in this catalysis is certainly an area for growth.[7]

Photocatalytic hydrophosphination allows for new reactivity as well in more direct synthesis of value-added products. For example, the direct preparation of a phosphorus heterocycle was undertaken by the reaction of 1,4-pentadiene and $PhPH_2$ under irradiation centred at 253.7 nm in the presence of **8**. The result is the phosphorinane product (Scheme 20, *bottom*) with trace vinyl phosphine, which is the product of hydrophosphination of one half of the diene.[86] The vinyl phosphines were the suspected intermediate and independent preparation of this molecule followed by subjecting it to catalytic conditions gave the same heterocycle. Conjugated dienes have received attention in hydrophosphination catalysis,[67] but unconjugated dienes are effectively a pair of unactivated alkenes.[67] Thus, ring-closing reactions are well known for hydrophosphination, harkening back to the turn of the century with more recent and more sustainable examples as well.[74, 87-89] What is unusual about the zirconium in the more developed examples by both Marks (Scheme 20, *top*) and Webster (Scheme 20, *middle*) is selectivity. Those reactions afford the five-membered ring versus the six-membered ring, which also appears to be a spontaneous product under irradiation. The underscore is that amplified activity has not only yielded unavailable substrates, but also new synthetic strategies; this tandem inter/intramolecular combination are now possibilities for hydrophosphination.



Scheme 20. Synthesis of five- and six-membered phosphine products via metal-catalysed hydrophosphination. [Ln] = $Cp^*_2LnCH(SiMe_3)_2$.[74, 86, 87]

Finally, this photocatalytic enhancement to hydrophosphination demonstrates that prior limitations can be overcome. A reinvestigation of triamidoamine-supported zirconium and secondary phosphine substrates under photocatalytic conditions demonstrated substantially improved activity (Scheme 21).[90] The two changes in this work as compared to the original investigation were that a general array of styrene derivatives, Michael acceptors, and alkynes were utilized in good conversions, and that unactivated alkenes were possible, albeit not practical substrates under these conditions. The improved activity that **8** demonstrated under photocatalytic conditions highlights the potential for irradiation of a well-defined metal–phosphido intermediate for hydrophosphination catalysis. However, a critical question remained, is this phenomenon general?



Scheme 21. Visible-light-enhanced hydrophosphination of alkenes with $PhPH_2$.[86]

Beyond any personal preferences, there are several features that make $(N_3N)ZrPRR'$ derivatives special.[82] The particular features in consideration include the somewhat unusual geometry of zirconium, highly ionic bonding, and absence of appreciable Zr–P π-bonding.[91] The degree to which other zirconium compounds (much less other metals) have these features is low, which would be problematic if they drive the productive photochemistry. For this reason, related zirconium compounds were first considered. In a pair of reports, Yuan and Yao reported a broad family of zirconium compounds with nitrogen and oxygen donors screened for hydrophosphination catalysis with both primary and secondary phosphines substrates.[92] The activity of the compounds varied but were within the norms of reasonably active catalysts of the day. Importantly, these derivatives varied by donor, geometry, and coordination number compared to triamidoamine-supported zirconium. In a recent study, precatalysts with the ligands O-2,4-$^tBu_2C_6H_2$-6-$CH_2(NCH_2CH_2NMe_2)CH_2$-2-MeO-3,5-$^tBu_2C_6H_2$ (Figure 4, *left*) and 1,4-bis(O-2,4-$^tBu_2$-6-CH_2)piperazine (Figure 4, *right*), chosen for their strong differences from (N_3N) and their variable activity in the original reports, were subjected to a comparison study of photocatalytic versus thermal hydrophosphination.[93] For both compounds, improvement in activity for all substrates tested was observed under photocatalytic conditions as comparted to control reactions that comparted favourably with the original literature reports. Computational analysis supports a similar mechanism for the increased activity in which the excited state demonstrates an elongation and weakening of the Zr–P bond.[67] This simple study eliminated a variety of factors in establishing the generality of photocatalytic hydrophosphination, which then needed to be tested in other metals. Further to the point of this section, it may be that these compounds would be even more active if high conversion to a phosphido derivative were realized, but none of the three studies isolated or demonstrated high conversion to such an intermediate.

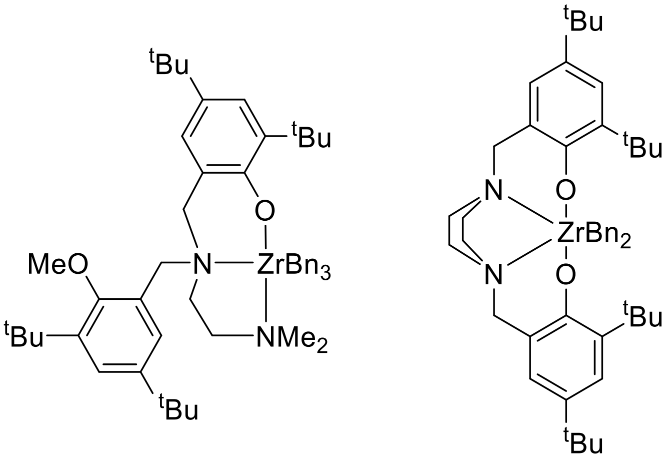


Figure 4. Further examples of light-enhanced hydrophosphination via zirconium compounds that were originally reported by Yuan and Yao.[93]

Photocatalytic hydrophosphination has been extended to group 8. The earlier catalysis with **11** under visible light irradiation is photoactivation, which was demonstrated with control experiments and even extended to the ruthenium congener (Figure 5).[75, 94] The photocatalytic conditions tested for these compounds did not enhance reactivity, and this can be rationalized to some extent. Both metals yield 18-electron, coordinatively saturated phosphido compounds of varying stability, $Cp(CO)_2MPR_2$. If photocatalysis requires a LMCT, then the metal may not have an appropriate orbital as an acceptor. Like most things that do not work well, there is less impetus to continue to study this system than move to others. Nevertheless, there may be fundamental understanding to be gained in this system.

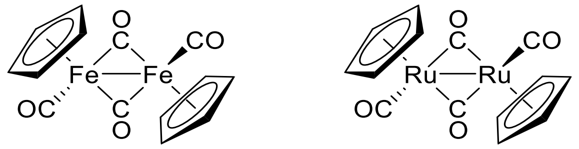


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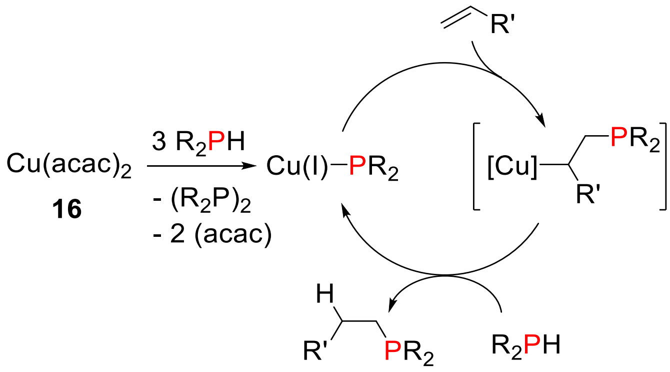
Figure 5. Iron and ruthenium precatalysts used by Waterman and co-workers.[75, 94]

Finally, the simplest photocatalyst has been found. Copper-catalysed hydrophosphination has been known for several years with a mix of simple precursors and more complex ligands.[67] A reinvestigation of simple copper salts, particularly Cu(acac)$_2$ (**16**), uncovered exceptional activity that both dwarfed prior reports with copper as well as the most broadly active catalysts in the literature.[95] The change here was irradiation, which was done with visible- and UV-centred sources. The result was a range of substrates, including unactivated alkenes, experiencing high conversions in short reaction times. The authors identified the key activation step as reduction to copper(I) (Scheme 22).



Scheme 22. Proposed catalytic cycle for copper-catalysed hydrophosphination via insertion.[95]

For the simplicity, availability, and ease-of-use of the catalyst, the photocatalytic conditions should be considered. The simplest of these is a commercial LED bulb in a desk lamp, but compact fluorescent, near-UV ‘blacklights’ have been used as well as more intense sources.[95] The supply of germicidal lamps has varied with the pandemic, but these are again available and provide high near-UV photon density. These are inexpensive “photoreactors” for this catalysis. Ambient light provides conversion, but *any* direct lighting will accelerate the catalysis. Copper also demonstrated high activity with Michael acceptors, where runs with these substrates were often complete before measurements could be taken.[95] Recent mechanistic study shows both a conjugate addition mechanism as well as an insertion-based mechanism for this system. What emerged from that work that is most germane here is a model monometallic copper–phosphido compound, noting polymetallic derivatives are precatalysts,[96] was used for study. In this instance, Liptrot’s compound, (NHC)CuPPh$_2$,[97] was both highly active for photocatalytic hydrophosphination and already structurally characterized.[98] Computational analysis of this compound showed that the LUMO has significant Cu–P anti-bonding character. Like zirconium, it was hypothesized that photoexcitation from the HOMO, which has high P lone pair character, weakens the Cu–P bond, facilitating insertion.

Overall, **16** is arguably the best exploratory hydrophosphination precatalyst, being convenient and highly active under simple photochemical conditions. However, the key discovery for the purpose of this Feature is that the activity of copper is enhanced by irradiation similar to the way in which zirconium compounds experienced enhanced reactivity. These observations point to a general phenomenon of photoactivation of the metal–phosphorus bond that may be extended beyond hydrophosphination catalysis to all pnictogens if not all π-basic ligands. Indeed, photocatalysis of this type has already been extended beyond the metal–phosphorus bond.

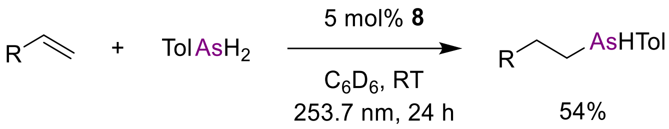
Metal–Arsenido Bonds

Hydroarsination

In moving down the pnictogens, metal–arsenic chemistry is a dark horse. There are far fewer studies than those with lighter congeners, but the reactivity is arguably more varied. In two instances, arsenic’s refusal to be a heavier version of phosphorus becomes clear, and its ability to borrow from the observed chemistry of both phosphorus and antimony suggest a deeper richness yet to be seen.

A handful of studies involving hydroarsination have been reported. These and the far more limited hydrostibination reports were recently reviewed,[7] and a recap of that list is not needed here. The interest in such transformations is less broad, and at the risk of overt speculation, the smaller number of organoarsines and organostibines used as ligands for transition metals may be a factor. The original triamidoamine-supported zirconium study of hydrophosphination also included investigation of hydroarsination for the same fundamental reason, a readily available Zr–As bond had become available. By the metrics of the time, the hydroarsination catalysis was more fruitful with zirconium than hydrophosphination was. These reactions of Ph$_2$AsH with simple unsaturated substrates gave modest turnovers with academic catalyst loading.[99]

The emergence of photocatalytic hydrophosphination begged the question for hydroarsination, and the easy-to-prepare derivative TolAsH$_2$ (Tol = *p*-tolyl) was screened as an analogue for PhPH$_2$.[86] The UV-vis spectrum of (N$_3$N)ZrAsHTol showed similar features and relative intensities to that of **12**. It was therefore unsurprising that hydroarsination reactions with TolAsH$_2$ and a variety of alkene substrates were accelerated under photocatalytic conditions with zirconium catalysts (Scheme 23). For example, styrene substrates were converted with greater relative rates under photocatalytic conditions than in control reactions under ambient light or in the dark. This is exactly the hypothesized behaviour: Photocatalysis enhances hydroarsination in the same way that hydrophosphination is enhanced.



Scheme 23 Zirconium-catalysed hydroarsination of alkenes using a primary arsine.[100]

From these preliminary results, it was theorized that the arsenido would engage in analogous chemistry to a phosphido, but the reactivity diverged with different substrates. In control reactions with Michael acceptors, there was substantial conversion in the dark but enhanced reactivity in the light.[86] These observations suggested that the zirconium–arsenido compounds may be engaging in behaviour unfamiliar to early M–PR$_2$ compounds, nucleophilic attack (i.e., conjugate addition). While an arsenido ligand should be more nucleophilic than an arsine,[101] the reactivity of arsines (and by extension the metal-arsenido) should be less nucleophilic than that of phosphido derivatives. However, arsenic has, unabashedly, engaged in reductive elimination from early metals.[102] Unanticipated reactivity should therefore be expected.

In that regard, arsenic has not disappointed. The earliest examples of a well-defined metal–arsenic bond in unique catalytic reactions were in the catalytic dehydrocoupling of arsines. Zirconium–arsenido derivatives were engaged in catalytic dehydrocoupling of Ph$_2$AsH to afford 1,2-tetraphenyldiarsine.[99] All evidence for this substrate was consistent with σ-bond metathesis[20] process that had been measured for phosphine substrates.[60] These data points were comfortably in-line with a reasonable conclusion, but were not consistent with the landscape of the reactivity.

Bulky primary arsines reacted differently and afforded diarsene products. Such products are unexplainable in a simple σ-bond metathesis scheme. Interestingly, reactivity that results in the dehydrogenation of E–E σ-bonds is exceptionally rare. Thus, this observation prompted greater investigation. The results of that work, with MesAsH$_2$ as a model system, supported the evolution of arsinidene fragments (e.g. "α-arsinidene elimination").[99] This kind of reactivity would not be documented for phosphorus for most of a decade.[103, 104] Indeed much of that chemistry is more reminiscent of heavier elements like antimony than phosphorus, displaying the flexibility that arsenic has to act as both a light and heavy main group element.[105] Though metal–stibinido chemistry is yet less developed than that of the arsenido , α-stibinidene elimination was documented first. This observation teases that greater study of antimony can potentially identify new reactivity for the lighter elements.

Outlook and Conclusions

There are three major themes that arise from this compilation of studies, beyond the gross conclusion that the M–E bond is important. First, as the Si–N bond formation demonstrates, mechanism matters a great deal. This is highlighted by how unpredictable new, high activity catalysts are. These catalysts continue to emerge, and the understanding of mechanistic features is a grounding point to develop trends and structure-function relationships that will lead to the next discoveries.

The idea that rigorous study of mechanism will drive new reactivity is easily echoed among the heavier pnictogens. Webster has demonstrated this well with desired reactivity of iron catalysis,[74] and this strategy has yield substantially greater activity with ruthenium catalysts by Rosenberg.[81] There are more examples of excellent chemistry among these elements, but the limitations of publication place constraints on the number of examples that can be included.

In this context, we have followed how the initial understanding of photocatalysis in hydrophosphination has become a general phenomenon and that it has significantly chipped at the largest underlying challenge in this catalysis, limited activity.

The second theme is more specific about M–E bonds, considering how their reactivity is intimately attached to their relative lifetime in solution. This still is very much an empirical This reactivity is correlated to the number of activated metal centres, which would provide a new feature in catalyst design and a potential tool in screening or refinement.

The final theme is about the need for increased predictability in the reactivity of these systems. Whether it is the counter examples of metal–silyl compounds driving Si–N coupling or a nucleophilic early metal–arsenido compound, the spaces in which the expected patterns are broken are places to learn and make new discoveries. The subtle corollary to predictability is that the heaviest pnictogen discussed herein, antimony, predates the same reactivity discovered for arsenic and then phosphorus. That pattern would suggest that more study of the heavier elements is likely to reveal unique chemistry that is exportable up the group.

None of these themes are truly unexpected but in cataloguing some of the work in this way, significant gaps are revealed. Some of these are related to latent challenges for various transformations, but there are some many open questions with regards to metal–pnictogen reactivity. Some of these questions would inform reactions that are under active interest and others are likely to fuel new reactivity with these elements.

Author Contributions

All authors jointly conceptualized this paper and wrote individual sections that were compiled and edited by M.B.R. and R.W. Additional proof reading was conducted by all authors.

Conflicts of Interest

There are no conflicts to declare.

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Rory Waterman is currently Professor of Chemistry at the University of Vermont (UVM). His research interests span synthetic and catalytic inorganic and organometallic chemistry with applications in materials and energy as well as issues in professional development and inclusion in the sciences. A life-long troublemaker, he enjoys running, hiking, and telling the occasional dad joke.

Notes and references

1. I. Manners, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1602-1621.
2. E. M. Leitao, T. Jurca and I. Manners, *Nat. Chem.*, 2013, **5**, 817-829.
3. J. H. Clark, *Green Chem.*, 1999, **1**, 1-8.
4. P. Anastas and N. Eghbali, *Chem. Soc. Rev.*, 2010, **39**, 301-312.
5. R. Waterman, *Chem. Soc. Rev.*, 2013, **42**, 5629-5641.
6. C. A. Bange and R. Waterman, *Chem. Eur. J.*, 2016, **22**, 12598-12605.
7. S. Lau, T. M. Hood and R. L. Webster, *ACS Catal.*, 2022, **12**, 10939-10949.
8. A. Falk Øgaard and E. Brod, *J. Agric. Food. Chem.*, 2016, **64**, 4821-4829.
9. J. C. Slootweg, *Angew. Chem. Int. Ed.*, 2018, **57**, 6386-6388.
10. K. Kuciński and G. Hreczycho, *ChemCatChem*, 2017, **9**, 1868-1885.
11. M. B. Reuter, K. Hageman and R. Waterman, *Chem. Eur. J.*, 2021, **27**, 3251-3261.
12. V. Verma, A. Koperniku, P. M. Edwards and L. L. Schafer, *Chem. Commun.*, 2022, **58**, 9174-9189.
13. K. Takaki, T. Kamata, Y. Miura, T. Shishido and K. Takehira, *J. Org. Chem.*, 1999, **64**, 3891-3895.
14. J. X. Wang, A. K. Dash, J. C. Berthet, M. Ephritikhine and M. S. Eisen, *J. Organomet. Chem.*, 2000, **610**, 49-57.
15. L. H. Sommer and J. D. Citron, *J. Org. Chem.*, 1967, **32**, 2470-2472.
16. C. Biran, Y. D. Blum, R. Glaser, D. S. Tse, K. A. Youngdahl and R. M. Laine, *J. Mol. Cat.*, 1988, **48**, 183-197.
17. D. Seyferth and G. H. Wiseman, *J. Am. Ceram. Soc.*, 1984, **67**, C-132-C-133.
18. F. Buch and S. Harder, *Organometallics*, 2007, **26**, 5132-5135.
19. J. F. Dunne, S. R. Neal, J. Engelkemier, A. Ellern and A. D. Sadow, *J. Am. Chem. Soc.*, 2011, **133**, 16782-16785.
20. R. Waterman, *Organometallics*, 2013, **32**, 7249-7263.
21. P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, 1985, **18**, 51-56.
22. M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 203-219.
23. M. Rauch, R. C. Roberts and G. Parkin, *Inorg. Chim. Acta*, 2019, **494**, 271-279.
24. M. S. Hill, D. J. Liptrot, D. J. MacDougall, M. F. Mahon and T. P. Robinson, *Chem. Sci.*, 2013, **4**, 4212-4222.
25. C. Bellini, J.-F. Carpentier, S. Tobisch and Y. Sarazin, *Angew. Chem. Int. Ed.*, 2015, **54**, 7679-7683.
26. D. Gasperini, A. K. King, N. T. Coles, M. F. Mahon and R. L. Webster, *ACS Catal.*, 2020, **10**, 6102-6112.
27. H. Q. Liu and J. F. Harrod, *Organometallics*, 1992, **11**, 822-827.
28. J. He, H. Q. Liu, J. F. Harrod and R. Hynes, *Organometallics*, 1994, **13**, 336-343.
29. A. F. Maddox, K. A. Erickson, J. M. Tanski and R. Waterman, *Chem. Commun.*, 2011, **47**, 11769-11771.
30. K. A. Erickson, M. P. Cibuzar, N. T. Mucha and R. Waterman, *Dalton Trans.*, 2018, **47**, 2138-2142.
31. M. B. Reuter, M. P. Cibuzar, J. Hammerton and R. Waterman, *Dalton Trans.*, 2020, **49**, 2972-2978.
32. S. Anga, Y. Sarazin, J.-F. Carpentier and T. K. Panda, *ChemCatChem*, 2016, **8**, 1373-1378.
33. N. V. Forosenko, I. V. Basalov, A. V. Cherkasov, G. K. Fukin, E. S. Shubina and A. A. Trifonov, *Dalton Trans.*, 2018, **47**, 12570-12581.
34. A. Baishya, T. Peddarao and S. Nembenna, *Dalton Trans.*, 2017, **46**, 5880-5887.
35. W. Xie, H. Hu and C. Cui, *Angew. Chem. Int. Ed.*, 2012, **51**, 11141-11144.
36. M. P. Cibuzar and R. Waterman, *Organometallics*, 2018, **37**, 4395-4401.
37. A. Pindwal, A. Ellern and A. D. Sadow, *Organometallics*, 2016, **35**, 1674-1683.
38. L. K. Allen, R. García-Rodríguez and D. S. Wright, *Dalton Trans.*, 2015, **44**, 12112-12118.
39. Z. Zhou, *Npj Comput. Mater.*, 2021, **7**, 209.
40. A. Staubitz, A. P. M. Robertson and I. Manners, *Chem. Rev.*, 2010, **110**, 4079-4124.
41. A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. Schmedt auf der Günne and I. Manners, *J. Am. Chem. Soc.*, 2010, **132**, 13332-13345.
42. A. L. Colebatch and A. S. Weller, *Chem. Eur. J.*, 2019, **25**, 1379-1390.
43. P. Xu and X. Xu, *Organometallics*, 2019, **38**, 3212-3217.
44. D. E. Ryan, K. A. Andrea, J. J. Race, T. M. Boyd, G. C. Lloyd-Jones and A. S. Weller, *ACS Catal.*, 2020, **10**, 7443-7448.
45. K. A. Erickson, J. P. W. Stelmach, N. T. Mucha and R. Waterman, *Organometallics*, 2015, **34**, 4693-4699.
46. T. M. Maier, S. Sandl, I. G. Shenderovich, A. Jacobi von Wangelin, J. J. Weigand and R. Wolf, *Chem. Eur. J.*, 2019, **25**, 238-245.
47. J. K. Pagano, J. P. W. Stelmach and R. Waterman, *Dalton Trans.*, 2015, **44**, 12074-12077.

48. T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18-29.
49. N. L. Dunn, M. Ha and A. T. Radosevich, *J. Am. Chem. Soc.*, 2012, **134**, 11330-11333.
50. M. R. Adams, C.-H. Tien, B. S. N. Huchenski, M. J. Ferguson and A. W. H. Speed, *Angew. Chem. Int. Ed.*, 2017, **56**, 6268-6271.
51. C. C. Chong, H. Hirao and R. Kinjo, *Angew. Chem. Int. Ed.*, 2014, **53**, 3342-3346.
52. M. A. Chacón-Terán, R. E. Rodríguez-Lugo, R. Wolf and V. R. Landaeta, *Eur. J. Inorg. Chem.*, 2019, **2019**, 4336-4344.
53. V. Naseri, R. J. Less, R. E. Mulvey, M. McPartlin and D. S. Wright, *Chem. Commun.*, 2010, **46**, 5000-5002.
54. K. A. Erickson, L. S. H. Dixon, D. S. Wright and R. Waterman, *Inorg. Chim. Acta*, 2014, **422**, 141-145.
55. K. A. Erickson, D. S. Wright and R. Waterman, *J. Organomet. Chem.*, 2014, **751**, 541-545.
56. S. J. Geier and D. W. Stephan, *Chem. Commun.*, 2010, **46**, 1026.
57. M. C. Fermin and D. W. Stephan, *J. Am. Chem. Soc.*, 1995, **117**, 12645-12646.
58. N. Etkin, M. C. Fermin and D. W. Stephan, *J. Am. Chem. Soc.*, 1997, **119**, 2954-2955.
59. J. D. Masuda, A. J. Hoskin, T. W. Graham, C. Beddie, M. C. Fermin, N. Etkin and D. W. Stephan, *Chem. Eur. J.*, 2006, **12**, 8696-8707.
60. R. Waterman, *Organometallics*, 2007, **26**, 2492-2494.
61. A. J. Roering, S. N. MacMillan, J. M. Tanski and R. Waterman, *Inorg. Chem.*, 2007, **46**, 6855-6857.
62. D. S. Glueck, in *C-X Bond Formation*, ed. A. Vigalok, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, ch. 4, pp. 65-100.
63. R. Dobrovetsky, K. Takeuchi and D. W. Stephan, *Chem. Commun.*, 2015, **51**, 2396-2398.
64. L. Wu, V. T. Annibale, H. Jiao, A. Brookfield, D. Collison and I. Manners, *Nat. Commun.*, 2019, **10**, 2786.
65. S. Molitor, J. Becker and V. H. Gessner, *J. Am. Chem. Soc.*, 2014, **136**, 15517-15520.
66. K. Oberdorf, A. Hanft, J. Ramler, I. Krummenacher, F. M. Bickelhaupt, J. Poater and C. Lichtenberg, *Angew. Chem. Int. Ed.*, 2021, **60**, 6441-6445.
67. B. T. Novas and R. Waterman, *ChemCatChem*, **n/a**, e202200988.
68. L. Rosenberg, *ACS Catal.*, 2013, **3**, 2845-2855.
69. J. P. W. Stelmach, C. A. Bange and R. Waterman, *Dalton Trans.*, 2016, **45**, 6204-6209.
70. A. N. Barrett, H. J. Sanderson, M. F. Mahon and R. L. Webster, *Chem. Commun.*, 2020, **56**, 13623-13626.
71. R. J. Schwamm, J. R. Fulton, M. P. Coles and C. M. Fitchett, *Dalton Trans.*, 2017, **46**, 2068-2071.
72. L. Routaboul, F. Toulgoat, J. Gatignol, J.-F. Lohier, B. Norah, O. Delacroix, C. Alayrac, M. Taillefer and A.-C. Gaumont, *Chem. Eur. J.*, 2013, **19**, 8760-8764.
73. A. K. King, K. J. Gallagher, M. F. Mahon and R. L. Webster, *Chem. Eur. J.*, 2017, **23**, 9039-9043.
74. M. Espinal-Viguri, A. K. King, J. P. Lowe, M. F. Mahon and R. L. Webster, *ACS Catal.*, 2016, **6**, 7892-7897.
75. J. K. Pagano, C. A. Bange, S. E. Farmiloe and R. Waterman, *Organometallics*, 2017, **36**, 3891-3895.
76. H. Nakazawa, Y. Ueda, K. Nakamura and K. Miyoshi, *Organometallics*, 1997, **16**, 1562-1566.
77. M. Kamitani, M. Itazaki, C. Tamiya and H. Nakazawa, *J. Am. Chem. Soc.*, 2012, **134**, 11932-11935.
78. M. Itazaki, S. Katsube, M. Kamitani and H. Nakazawa, *Chem. Commun.*, 2016, **52**, 3163-3166.
79. B. J. Ackley, J. K. Pagano and R. Waterman, *Chem. Commun.*, 2018, **54**, 2774-2776.
80. M.-A. M. Hoyle, D. A. Pantazis, H. M. Burton, R. McDonald and L. Rosenberg, *Organometallics*, 2011, **30**, 6458-6465.
81. R. G. Belli, J. Yang, E. N. Bahena, R. McDonald and L. Rosenberg, *ACS Catal.*, 2022, **12**, 5247-5262.
82. R. Waterman, *Acc. Chem. Res.*, 2019, **52**, 2361-2369.
83. A. J. Roering, S. E. Leshinski, S. M. Chan, T. Shalumova, S. N. MacMillan, J. M. Tanski and R. Waterman, *Organometallics*, 2010, **29**, 2557-2565.
84. M. G. Davidson, C. L. Doherty, A. L. Johnson and M. F. Mahon, *Chem. Commun.*, 2003, 1832-1833.
85. M. B. Ghebreab, C. A. Bange and R. Waterman, *J. Am. Chem. Soc.*, 2014, **136**, 9240-9243.
86. C. A. Bange, M. A. Conger, B. T. Novas, E. R. Young, M. D. Liptak and R. Waterman, *ACS Catal.*, 2018, **8**, 6230-6238.
87. M. R. Douglass and T. J. Marks, *J. Am. Chem. Soc.*, 2000, **122**, 1824-1825.
88. M. R. Douglass, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 2001, **123**, 10221-10238.
89. A. M. Kawaoka, M. R. Douglass and T. J. Marks, *Organometallics*, 2003, **22**, 4630-4632.
90. B. T. Novas, C. A. Bange and R. Waterman, *Eur. J. Inorg. Chem.*, 2019, **2019**, 1640-1643.
91. A. J. Roering, A. F. Maddox, L. T. Elrod, S. M. Chan, M. B. Ghebreab, K. L. Donovan, J. J. Davidson, R. P. Hughes, T. Shalumova, S. N. MacMillan, J. M. Tanski and R. Waterman, *Organometallics*, 2009, **28**, 573-581.
92. Y. Zhang, X. Wang, Y. Wang, D. Yuan and Y. Yao, *Dalton Trans.*, 2018, **47**, 9090-9095.
93. B. T. Novas, J. A. Morris, M. D. Liptak and R. Waterman, *Journal*, 2022, **2**, 77-87.
94. M. P. Cibuzar, S. G. Dannenberg and R. Waterman, *Isr. J. Chem.*, 2020, **60**, 446-451.
95. S. G. Dannenberg and R. Waterman, *Chem. Commun.*, 2020, **56**, 14219-14222.
96. S. G. Dannenberg and R. Waterman, *Molbank*, 2022, **2022**, M1334.
97. T. M. Horsley Downie, J. W. Hall, T. P. Collier Finn, D. J. Liptrot, J. P. Lowe, M. F. Mahon, C. L. McMullin and M. K. Whittlesey, *Chem. Commun.*, 2020, **56**, 13359-13362.
98. S. G. Dannenberg, D. M. Seth Jr., E. J. Finfer and R. Waterman, submitted.
99. A. J. Roering, J. J. Davidson, S. N. MacMillan, J. M. Tanski and R. Waterman, *Dalton Trans.*, 2008, 4488-4498.
100. C. A. Bange and R. Waterman, *Polyhedron*, 2018, **156**, 31-34.
101. D. S. Glueck, *Dalton Trans.*, 2008, 5276-5286.
102. L. T. Elrod, H. Boxwala, H. Haq, A. W. Zhao and R. Waterman, *Organometallics*, 2012, **31**, 5204-5207.
103. K. Pal, O. B. Hemming, B. M. Day, T. Pugh, D. J. Evans and R. A. Layfield, *Angew. Chem. Int. Ed.*, 2016, **55**, 1690-1693.
104. J. K. Pagano, B. J. Ackley and R. Waterman, *Chem. Eur. J.*, 2018, **24**, 2554-2557.
105. R. Waterman and T. D. Tilley, *Angew. Chem. Int. Ed.*, 2006, **45**, 2926-2929.