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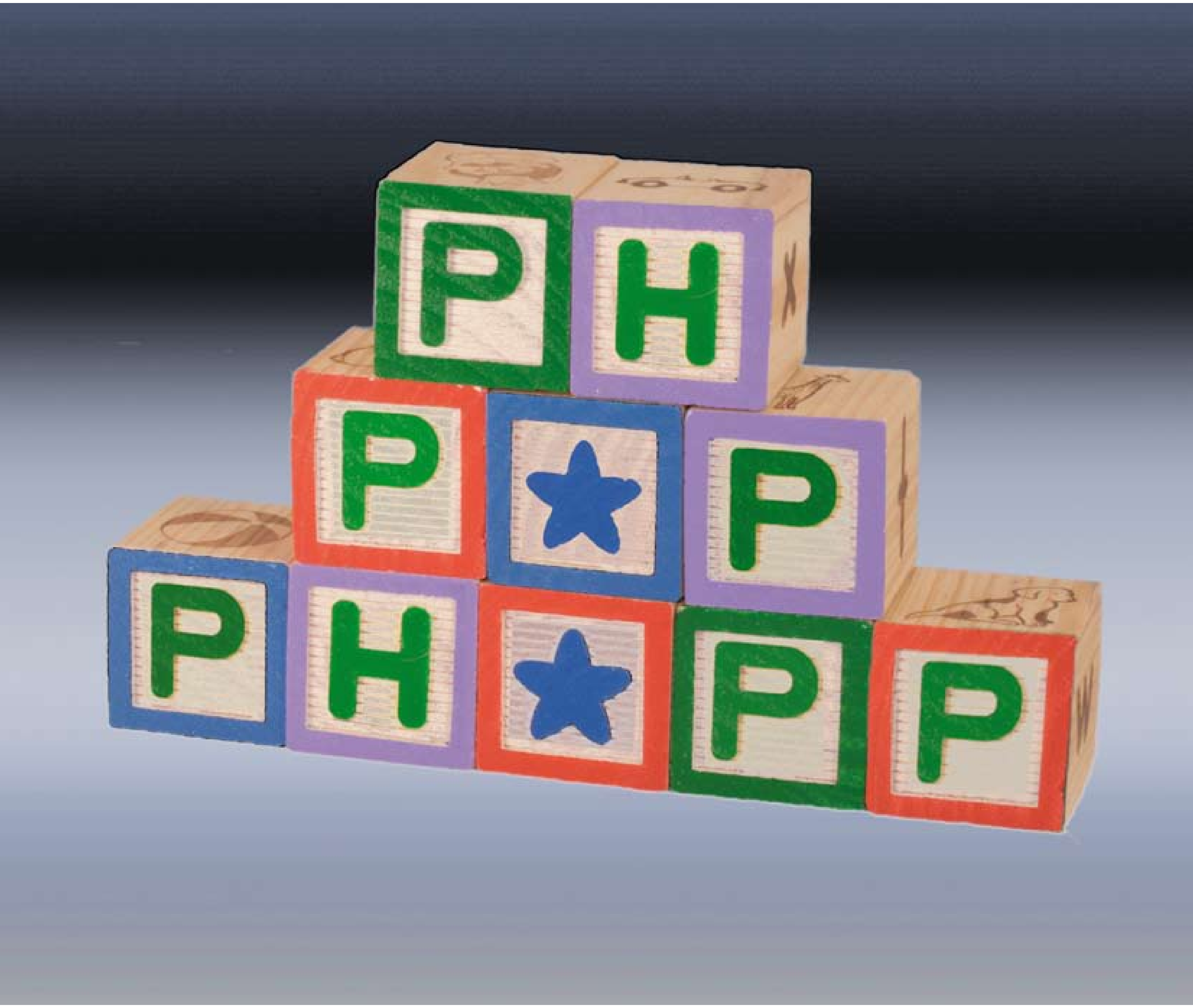

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Stoichiometric and catalytic activation of P–H and P–P bonds

Sharonna Greenberg and Douglas W. Stephan*

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The abilities of transition metal species to activate P–H and P–P bonds are emerging. Such investigations provide novel M–P species, as well as stoichiometric and catalytic routes to P(III) compounds. The application of organometallic approaches and methodologies to phosphorus chemistry is providing emerging, stoichiometric and catalytic routes to phosphorus compounds and materials. This *tutorial review* surveys recent advances, with a focus on the activation of P–H and P–P bonds. The isolation of novel M–P species provides insight, while stoichiometric and catalytic reactivity expands the arsenal of synthetic strategies leading to P(III) compounds.

1. Introduction

Organometallic chemistry is a comparatively young field, as its roots can be traced to key findings in the 1950s. Nonetheless, the power of transition metals in mediating both the stoichiometric and catalytic synthesis of organic compounds is now firmly established. From commodity materials to many fine chemicals, organometallic chemistry plays a key role in the production of a wide range of materials. In addition, a fundamental component of the synthetic arsenal of an organic chemist relies on the development of stoichiometric and catalytic organometallic methodologies.

Parallel to the progress in organic chemistry made possible by transition metals, a new field coined inorganometallic chemistry has emerged at the crossroads of main group and transition metal chemistry. This new field is driven by the desire to extend the principles of organometallic synthesis to explore compounds containing main group elements. Previously, we have reviewed developments in the synthesis and reactivity of complexes containing Zr–P single and double bonds, as well as substituent-free phosphorus atoms.[1] Early efforts to exploit transition metal–phosphorus chemistry to catalytically synthesize organophosphorus oligomers were also described in a 2000 review.[1] Since then, a number of researchers have continued to examine both the stoichiometric and catalytic reactivity of transition metal–phosphorus compounds, which is the focus of the present review. In particular, the transition metal-mediated P–H and P–P bond activation of P(III) species is described, and the future potential of such findings is considered.

2. Titanium and zirconium

The genesis of early metal phosphide chemistry began in the 1960s, although it was not until the work of Baker and co-workers[1] in the early 1980s that interest in such compounds became sustained. In the late 1990s, Harrod and co-workers[1] described the first stoichiometric and catalytic dehydrocoupling reactions of primary and secondary phosphines, using Cp_2TiMe_2 as a precatalyst.[1] These findings spurred interest in the potential utility of such P–H bond activations.

In more recent studies, we have described the dehydrocoupling of primary and secondary phosphines using a catalyst derived from the Ti(II)/Ti(IV) synthon $CpTi(NPtBu_3)(CH_2)_4$.[2] NMR studies of reactions involving $PhPH_2$ reveal the formation of $CpTi(NPtBu_3)(PPh)_3$, while the stoichiometric reaction of $CpTi(NPtBu_3)(CH_2)_4$ and $PhPH_2$ gives the dimeric species $[CpTi(NPtBu_3)(\mu\text{-}PHPh)]_2$ (Scheme 1).[2]

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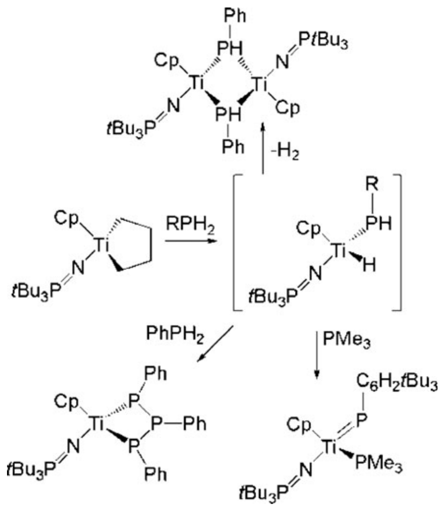
Doug Stephan earned a PhD at the University of Western Ontario, did postdoctoral work at Harvard and joined the faculty at Windsor in 1982. His research interests focus on transition metal and main group chemistry in catalysis. He has received awards, including a 2003 Humboldt Research Award and the 2004 Ciapetta Lectureship. In 2008, he began a Professorship and Canada Research Chair at Toronto.



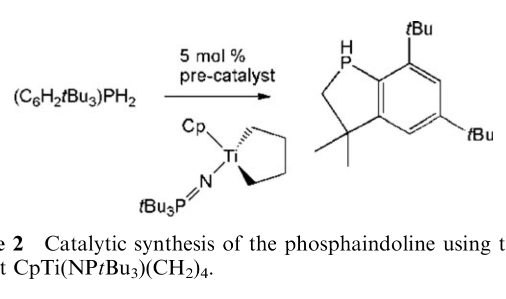
Scheme 1 The reactivity of $CpTi(NPtBu_3)(CH_2)_4$ with phosphines.

Mechanistically, these data imply that the Ti(II) synthon undergoes oxidative addition of the P–H bond to generate a transient phosphide hydride species, which eliminates H_2 to form either a Ti(III) dimer or a Ti(IV) phosphinidene. This latter species can also react with excess phosphine to effect P–P bond coupling. This proposition is supported by the isolation of $CpTi(NPtBu_3)(PMes^*)(PMe_3)$ ($Mes^* = 2,4,6\text{-}tBu_3C_6H_2$) (Scheme 1) *via* an analogous stoichiometric reaction with the more sterically hindered phosphine H_2PMes^* in the presence of PMe_3.[2] Under catalytic conditions, H_2PMes^* is converted cleanly to the phosphaindoline $C_6H_2tBu_2(Me_2CCH_2)PH$, affirming the role of the Ti-phosphinidene intermediate in C–H bond activation (Scheme 2).

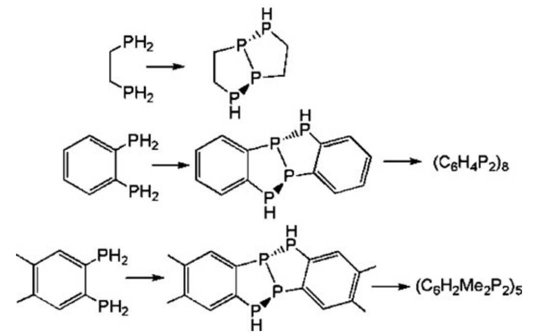
Catalytic dehydrocoupling of bisphosphines using the Ti catalysts $Cp'Ti(NPtBu_3)(CH_2)_4$ ($Cp' = Cp$ or $Cp' = Cp^*$) results in the dimeric, octameric or pentameric species $(C_2H_4P(PH))_2$, $(C_6H_4P(PH))_2$, $(C_6H_2Me_2P(PH))_2$, $(C_6H_4P_2)_8$ and $(C_6H_2Me_2P_2)_5$ (Scheme 3, Fig. 1).[2] Stoichiometric reactions afford the species $[Cp'Ti(NPtBu_3)(PH)_2C_6H_4]_n$ ($Cp' = Cp$, $n = 2$; $Cp' = Cp^*$, $n = 1$), where the sterically demanding Cp* ligand precludes dimerization (Scheme 4).[2]

While much of the initial work in Zr–P chemistry was based on halide metathesis, more recent efforts have exploited P–H bond activation as an avenue leading to Zr–P species. Various P–H bond activation routes towards Zr–P and Zr=P compounds have been previously reviewed.[1]

Driess and co-workers[3] reported the reaction of bisphosphido zirconocene $[Cp_2Zr(PHR)_2]$ ($R = Me_2(iPrMe_2C)Si)$) with $Zr(NEt_2)_4$, affording $[Cp_2Zr(\mu_2\text{-}PR)_2Zr(NEt_2)_2]$ in almost quantitative yield. Alternatively, P–H/Zr–N σ-bond metathesis is observed for the reaction between $Cp^*Zr(NEt_2)_3$ and $H_2PSiMe_2(CiPrMe_2)$ in a 1 : 3 molar ratio, giving the trisphosphide $Cp^*Zr(PHR)_3$ ($R = SiMe_2(CiPrMe_2)$). Prolonged heating of this species yields the cluster compound $[(Cp^*Zr)_2(RP\text{–}P\text{–}PR)_2]$ (Scheme 5), which is best described as a dimer of two butterfly-like ZrP_3 fragments.[3]



Scheme 2 Catalytic synthesis of the phosphaindoline using the precatalyst $CpTi(NPtBu_3)(CH_2)_4$.



Scheme 3 Phosphine oligomers prepared by catalytic dehydrocoupling.

The anionic zirconocene trihydride salts $[Cp^*_2Zr(\mu\text{-}H)_3Li]_3$ and $[Cp^*_2Zr(\mu\text{-}H)_3K(THF)_4]$ have been shown to catalyze the dehydrocoupling of primary phosphines RPH_2 (R = Ph, Cy, Mes ($2,4,6\text{-}Me_3C_6H_2$) or $C_{10}H_7$) to give cyclic oligomers $(RP)_n$, $n = 4$ or 5.[1,2] In stoichiometric reactions, species $[Cp^*_2Zr((PPh)_n)H][K(THF)_4]$ ($n = 2$ or 3) are observed spectroscopically, supporting a dehydrocoupling mechanism involving a sequential reaction of phosphine, affording P–P bond formation with the loss of H_2 (Scheme 6). In this fashion, these Zr-trihydride catalysts were employed to oligomerize $C_6H_4(PH_2)_2$ to the P_{16} macrocycle $(C_6H_4P_2)_8$ (Fig. 1(a)).

In very recent work, Waterman *et al.*[4,5] studied the catalytic dehydrocoupling of primary and secondary phosphines $RR'PH$ using the precatalyst $(N(CH_2CH_2NSiMe_3)_3)ZrMe$ to give exclusively diphosphines $(RR'P)_2$ ($R = H$, $R' = Ph$, Mes, $4\text{-}MeC_6H_4$, $2\text{-}EtC_6H_4$, Cy or tBu; $R = Ph$, $R' = Ph$ or Cy). Steric congestion inhibits this catalysis: the use of H_2PMes^* results in only very low yields of the diphosphine, despite longer reaction times. The resting state of the catalysts was shown to be primary phosphido complexes of the form $(N(CH_2CH_2NSiMe_3)_3)ZrPHR$ (Scheme 7), and kinetic data are consistent with an ordered transition state, in which the P–P bond-forming step proceeds *via* σ-bond metathesis. These Zr catalysts were shown to effect the heterodehydrocoupling

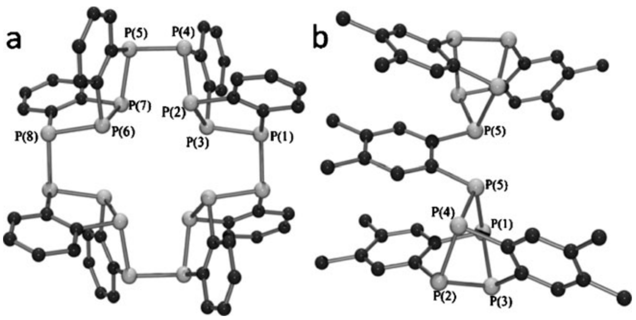
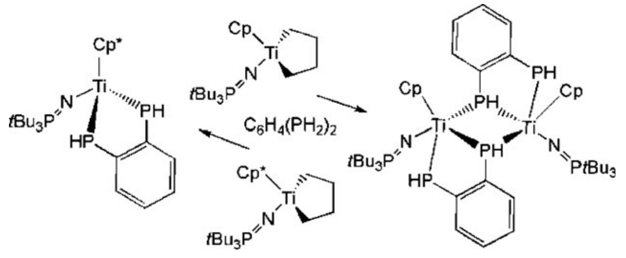
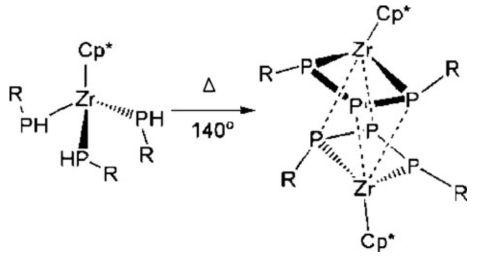


Fig. 1 Structures of the phosphine oligomers (a) $(C_6H_4P_2)_8$ and (b) $(C_6H_2Me_2P_2)_5$.



Scheme 4 Synthesis of $[Cp'Ti(NPtBu_3)(PH)_2C_6H_4]_n$ (Cp′ = Cp, n = 2; Cp′ = Cp*, n = 1).

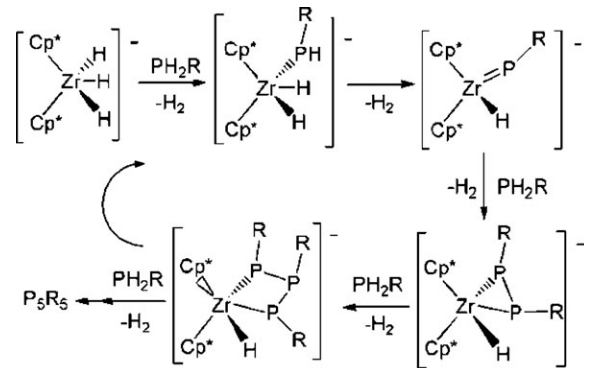


Scheme 5 Synthesis of $[(Cp^*Zr)_2(RP–P–PR)_2]$ (R = $SiMe_2$-(CiPrMe$_2$)).

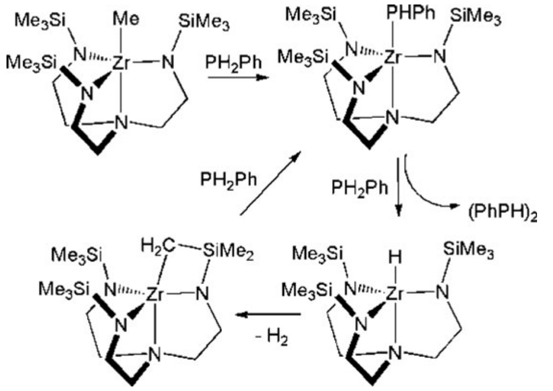
of primary phosphines with primary and secondary silanes and germanes.

3. Niobium and tantalum

Cummins and co-workers reported activation of the P–P bonds of P_4 by the niobaziridine hydride Nb(H)-(η^2-tBuHC=NAr)(N(Np)Ar)$_2$ (Np = CH_2tBu, Ar = 3,5-$C_6H_3Me_2$) to yield (μ_2:η^2,η^2-P_2)[Nb(N(Np)Ar)$_3$]$_2$.[6] Subsequent reduction using Na/Hg gives a terminal anionic phosphide [P≡Nb(N(Np)Ar)$_2$]$^-$ (Scheme 8). In contrast to neutral Mo and W terminal phosphide complexes, which are unreactive, the anionic niobium phosphide bears a nucleophilic phosphorus center that can readily react with pivaloyl chloride or 1-adamantoyl chloride to give, initially, four-membered NbP=C(R)O-metallacycles, which undergo a retro [2 + 2]-fragmentation, affording the oxo-niobium compounds O≡Nb(N(Np)Ar)$_3$ and the phosphaalkynes R–C≡P (R = tBu or 1-adamantyl). The corresponding reactions with $ClPR_2$ (R = tBu or Ph) yield the complexes η^2-R_2PPNb(N(Np)Ar)$_3$, heavier group 15 analogues of a 1,1-diazene. In a similar fashion, the use of Niecke's chloroiminophosphane, ClP=N(Mes), gives (η^2-(Mes)NPP)Nb(N(Np)Ar)$_3$ (Scheme 8).[7] Heating this complex to 65 °C in neat 1,3-cyclohexadiene generates (Mes)N=Nb(N(Np)Ar)$_3$ and permits the trapping of the P_2 unit as a double Diels–Alder adduct (Scheme 8).[7] This chemistry, which is directly analogous to that of an organic azide, afforded the first readily accessible route to diatomic P_2.

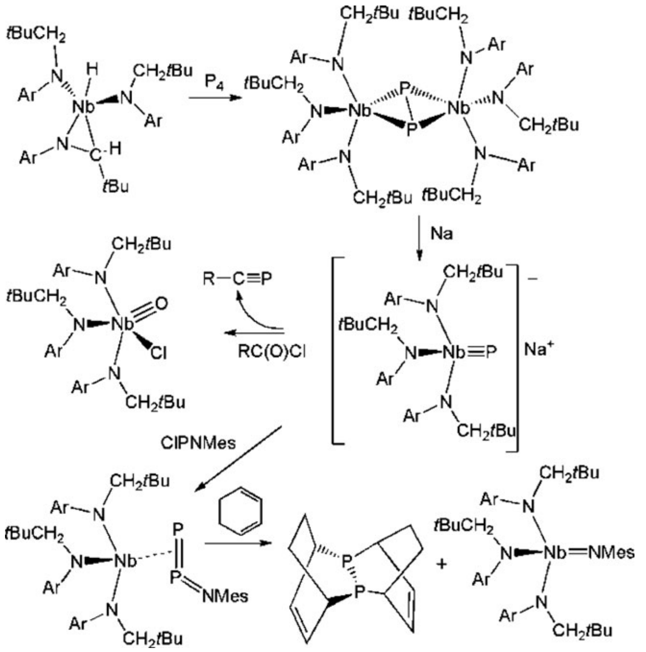


Scheme 6 Proposed partial mechanism of phosphine oligomerization using the precatalyst $[Cp^*{}_2Zr(\mu\text{-}H)_3K(THF)_4]$.

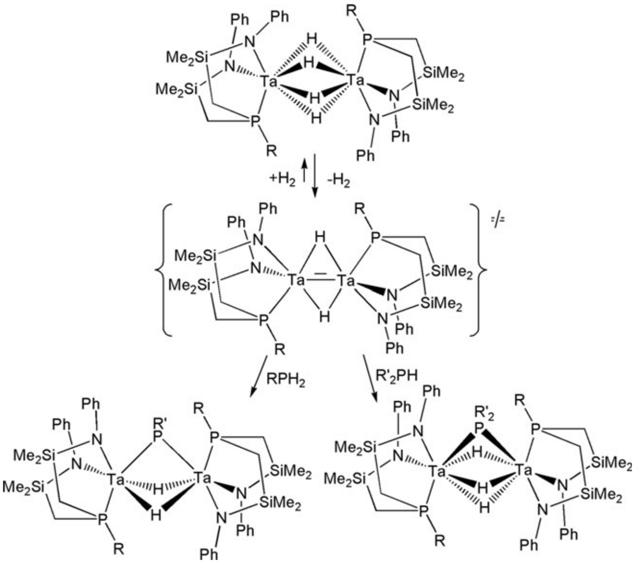


Scheme 7 Proposed mechanism for the dehydrocoupling of phosphines, using $(N(CH_2CH_2NSiMe_3)_3)ZrMe$ as a precursor.

Shaver and Fryzuk[8] have described P–H bond activation by ditantalum tetrahydride species $(RP(CH_2SiMe_2NPh)_2Ta)_2$-($\mu$-H)$_4$ (R = Ph or Cy) in reactions with secondary phosphines R'_2PH (R′ = Ph or Cy) to give the trihydrido phosphido compounds $(RP(CH_2SiMe_2NPh)_2Ta)_2(\mu\text{-}H)_3(PR'_2)$ with the loss of H_2 (Scheme 9).[8] Isotopic labelling studies indicate that these reactions proceed *via* the loss of D_2, generating a Ta=Ta species. Subsequent P–H addition across the metal–metal bond occurs, with the rate-determining step being D_2 elimination. Primary phosphines $R''PH_2$ (R″ = Cy or Ad) react in a



Scheme 8 Formation and reactivity of NbP_2 species.

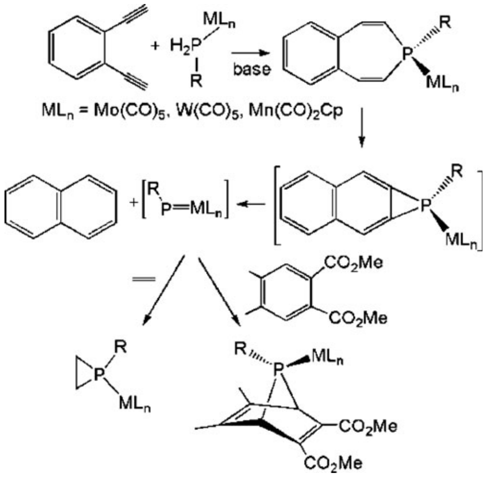


Scheme 9 Synthesis of $(RP(CH_2SiMe_2NPh)_2Ta)_2(\mu\text{-}H)_3(PR')$ R′ = Ph, Cy and $(RP(CH_2SiMe_2NPh)_2Ta)_2(\mu\text{-}H)_2(PR')$ R′ = Cy, Ad; R = Ph, Cy.

similar fashion to effect double P–H bond activation, affording the dihydrido phosphinidene-bridged complexes $(RP(CH_2SiMe_2NPh)_2Ta)_2(\mu\text{-}H)_2(PR'')$ (Scheme 9).[8] In these reactions, 1,2-elimination of H_2 follows P–H addition to the transient Ta=Ta bond. The corresponding reaction with $PhPH_2$ is complicated by protonation of the amido groups of the ancillary ligand.

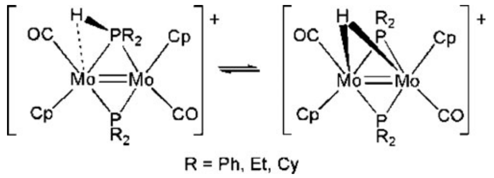
4. Manganese, chromium, molybdenum and tungsten

Complexes of benzophosphepines, $C_6H_4(C_2H_2)_2PR$, have been studied in detail by Lammertsma and co-workers.[9] Such species were synthesized by treating diethynylbenzene with a transition metal adduct (L_nM = $MnCp(CO)_2$, $Cr(CO)_5$, $Mo(CO)_5$ or $W(CO)_5$) of a primary phosphine (H_2PR; R = Ph, Me, *t*Bu or NEt_2) (Scheme 10).[10] These reactions proceed in the presence of a base *via* two sequential hydrophosphination steps; the initially formed *cis*-vinylphosphine intermediate undergoes a second hydrophosphination reaction to give the final product. These benzophosphepine species rearrange to unstable phosphanorcaradienes, followed by naphthalene elimination to give transition metal phosphinidenes. Kinetic and computational studies suggest that isomerization is the rate-determining step in the formation of these metal phosphinidenes. This synthetic route provides ready access to a broad range of transition metal phosphinidene complexes.



Scheme 10 Synthesis and reactivity of benzophosphepine complexes.

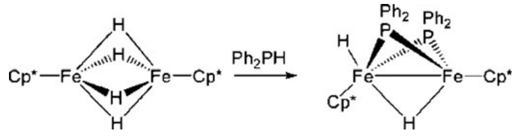
Thermal or photochemical P–H bond scission has been reported by Ruiz and co-workers in the formation of hydrido phosphido complexes $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PRR')(CO)_4]$ (M = Mo or W) from secondary phosphines and various metal precursors. The same group studied related agostic complexes of the type $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}\kappa^2\text{-}HPR_2)(CO)_2]BF_4$, accessed *via* $HBF_4{\cdot}OEt$ protonation of the dimeric species $[Mo_2Cp_2(\mu\text{-}PR_2)_2(CO)_2]$[11] bearing electron rich phosphides (R = Cy or Et).[12] The presence of an agostic interaction was inferred from the X-ray crystallographic data, as well as the NMR data.[12] The PH coupling constant in these cases was observed to be intermediate between that of a bridging phosphine ($\mu\text{-}PHR_2$), and a bridging phosphide and a bridging hydride ($\mu\text{-}PR_2$)(μ-H). These agostic complexes undergo intramolecular exchange of the hydride between the two phosphide units, and are in equilibrium with their hydride tautomers $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)_2(CO)_2]BF_4$ (Scheme 11). The agostic : hydride ratio depends on the phosphide substituent; for R = Cy, the equilibrium ratio was 10 : 1, while for R = Et, the ratio was 30 : 1.[12] For the mixed phosphide $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}PPh_2)(CO)_2]$, treatment with $HBF_4{\cdot}OEt$ resulted only in protonation at PCy_2, with a much smaller agostic : hydride tautomer ratio of 1 : 2. These agostic complexes provide models for the transition state of P–H bond activation. It is noteworthy that the analogous ditungsten derivatives, as well as the dimolybdenum derivative bearing less electron rich phosphides (R = Ph), behaved differently. These complexes are protonated by $HBF_4{\cdot}OEt_2$ at the metal, affording terminal metal hydride species. These species rearranged to bridging phosphide-hydride compounds, without evidence of any agostic interactions.



Scheme 11 Agostic hydride tautomers of $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)_2(CO)_2]BF_4$.

5. Iron and osmium

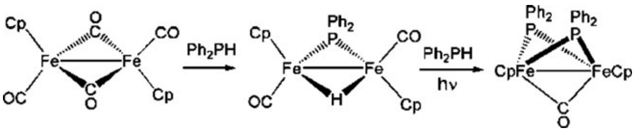
The diiron tetrahydride complex $(Cp^*Fe)_2(\mu\text{-}H)_4$ was reported by Ohki and Suzuki to effect C–H, Si–H and P–H bond activations.[13] Reaction with Ph_2PH affords the dinuclear bis-μ-phosphido complex $(Cp^*Fe)_2(H)(\mu\text{-}H)(\mu\text{-}PPh_2)_2$ (Scheme 12), which is stable below 0 °C. An X-ray diffraction study revealed two distinct hydrido ligands in the solid state, as one bridges the two Fe centers while the second occupies a terminal position.[13]



Scheme 12 Synthesis of $(Cp^*Fe)_2(H)(\mu\text{-}H)(\mu\text{-}PPh_2)_2$.

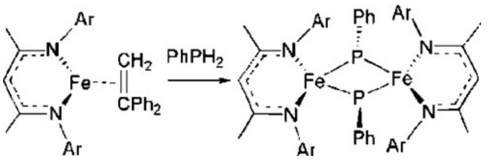
In solution, the two hydride ligands undergo rapid exchange, as evidenced by ^1H NMR spectroscopy.

Thermally induced P–H bond cleavage of $HPPh_2$ by dimeric $[Fe_2Cp_2(CO)_4]$ occurs to give almost exclusively *trans*-$[(Cp)(CO)Fe]_2(\mu\text{-}H)(\mu\text{-}PPh_2)$ (Scheme 13).[14] The *cis*-isomer is obtained by photochemical irradiation of the *trans*-isomer at low temperature under an atmosphere of CO.[15] A related photochemical reaction of *trans*-$[(Cp)(CO)Fe]_2(\mu\text{-}H)(\mu\text{-}PPh_2)$ in the presence of an additional equivalent of $HPPh_2$ yields $(CpFe)_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)$, with *cis*-$[(Cp)(CO)Fe]_2(\mu\text{-}H)(\mu\text{-}PPh_2)$ detected as an intermediate by IR spectroscopy.[14] This latter approach provides a general route to mixed bis-phosphide complexes.



Scheme 13 Synthesis and photochemical reaction of $[(Cp)(CO)Fe]_2(\mu\text{-}H)(\mu\text{-}PPh_2)$.

P–H bond activation *via* oxidative addition is evidenced in the reaction of Fe(I) complex $(NacNac)Fe(\eta^2\text{-}CH_2CPh_2)$ (NacNac = $HC(CMeN(2,6\text{-}iPr_2C_6H_2))_2$) with H_2PPh, which liberates 1,1-diphenylethylene and H_2, yielding the Fe(III) dimeric phosphinidene species $[(NacNac)Fe(\mu^2\text{-}PPh)]_2$ (Scheme 14).[16] The same species is prepared by the reaction of $(NacNac)Fe(\mu\text{-}Cl)_2Li(THF)_2$ with $HPPh_2$ and Na/K. X-Ray data revealed that both the Fe_2P_2 core and the P environments are planar.[16]

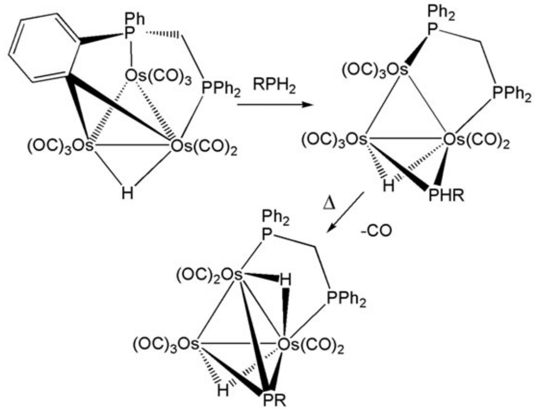


Scheme 14 Synthesis of $[(NacNac)Fe(\mu^2\text{-}PPh)]_2$.

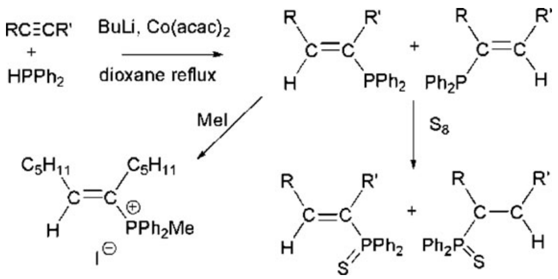
Kabir and co-workers[17] examined the addition of primary phosphines RPH_2 (R = Ph or Cy) to the unsaturated triosmium cluster $[(\mu\text{-}H)Os_3(CO)_8(Ph_2PCH_2P(Ph)C_6H_4)]$. At 25 °C, P–H bond activation occurs to give the species $[(\mu\text{-}H)Os_3(CO)_8(\mu\text{-}PRH)(\mu\text{-}dppm)]$ (dppm = $Ph_2PCH_2PPh_2$), in which a phosphide and a hydride bridge two Os centers. At higher temperatures (128 °C), the complex loses CO and forms the trinuclear cluster $[(\mu\text{-}H)_2Os_3(CO)_7(\mu_3\text{-}PR)(\mu\text{-}dppm)]$ (Scheme 15), capped by a phosphinidene ligand.

6. Cobalt and rhodium

Oshima and co-workers have described the $Co(acac)_2$ and butyllithium-catalyzed hydrophosphination of alkynes with $HPPh_2$ to generate exclusively *syn*-alkenylphosphines, which could be derivatized to phosphine-sulfides or phosphonium salts (Scheme 16).[18] Interestingly, a variety of other transition metal species failed to effect the hydrophosphination, although the role of Co in the catalytic cycle was not postulated. The yields were also maximized by refluxing in dioxane for 12 h.

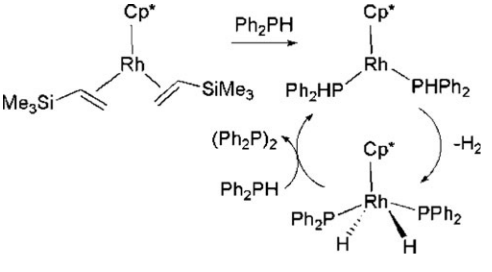


Scheme 15 Synthesis of $[(\mu\text{-}H)Os_3(CO)_8(\mu\text{-}PRH)(\mu\text{-}dppm)]$ and $[(\mu\text{-}H)_2Os_3(CO)_7(\mu_3\text{-}PR)(\mu\text{-}dppm)]$.



Scheme 16 The co-catalyzed hydrophosphination of alkynes.

Bohm and Brookhart[19] showed that the Rh compound $Cp^*Rh(H_2C{=}CHSiMe_3)_2$ catalyzes the homo-dehydrocoupling of various primary and secondary phosphines between 140 and 150 °C. The addition of the hydrogen acceptor 3,3-dimethyl-1-butene allowed the dehydrocoupling reaction to occur at lower temperatures (70 or 110 °C), although lower turnover rates were observed, presumably as a result of coordination of the olefin to Rh. The proposed catalytic cycle proceeds *via* coordination of the phosphine to Rh, followed by oxidative addition of P–H to Rh to give a bis-phosphide bis-hydride Rh(V) intermediate (Scheme 17). Reductive P–P coupling and concurrent loss of H_2 regenerates the catalytic species. The authors suggest that

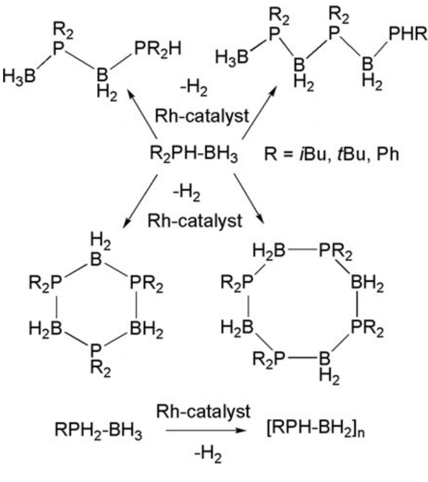


Scheme 17 Proposed mechanism for the dehydrocoupling of phosphines by a Rh catalyst derived from $Cp^*Rh(H_2C{=}CHSiMe_3)$.

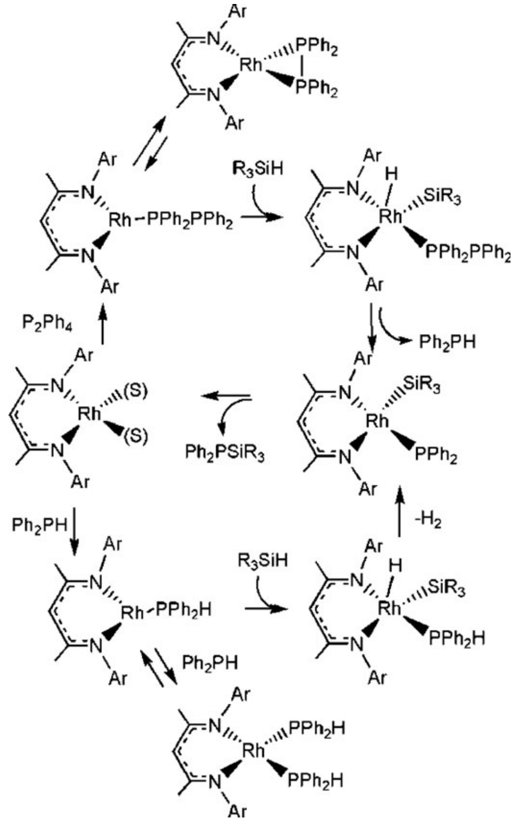
these reactions are insensitive to electronic factors, but that the different steric effects of secondary phosphines play a significant role, as sterically demanding phosphines (R = Mes, *t*Bu or Cy) do not undergo coupling.[18]

In a related study, Han and Tilley[20] examined [(dippe)Rh(η^3-CH_2Ph)] (dippe = $i Pr_2PCH_2CH_2P i Pr_2$) as a precatalyst for the homo- and hetero-dehydrocoupling of primary and secondary phosphines. Primary arylphosphines with single *ortho*-substituents are readily dehydrocoupled, whereas $MesPH_2$ or (2,4,6-$i Pr_3C_6H_2$)PH_2 require higher temperatures for appreciable conversion. The nature of the phosphine ancillary ligand on Rh is crucial, as neither monodentate PR_3 (R = Et, *t*Bu or Ph) nor bidentate $R_2PCH_2CH_2PR_2$ (R = Me or Ph) phosphine ligands yield active catalysts.[20] It is also noteworthy that the catalyst generated *in situ* from (cod)Rh(η^3-CH_2Ph) (cod = 1,5-cyclooctadiene) and chelating diphosphine dippe is catalytically active, while the related system derived from $[Rh(cod)Cl]_2$ is not. Stoichiometric reactions of [(dippe)Rh(η^3-CH_2Ph)] with $PhPH_2$ and Ph_2PH give [(dippe)Rh(H)(PHPh)(CH_2Ph)] and [(dippe)Rh($PHPh_2$)(PPh_2)], respectively. These species slowly transform into dimeric complexes $[(dippe)Rh(\mu\text{-}PRPh)]_2$ (R = H or Ph). Assessment of the catalytic activity of these isolated species supports the view that the dehydrocoupling catalyst is monomeric in nature.[20]

Manners and co-workers have pioneered the use of Rh catalysts to activate the P–H bonds of phosphine–borane adducts, effecting dehydrocoupling to give a variety of P–B products.[21–24] For example, heating $R_2PH–BH_3$ (R = *t*Bu, Ph or *p*-$CF_3C_6H_4$) to 90–120 °C using various Rh catalysts gives the linear dimers $R_2PH–BH_2R_2P–BH_3$ and cyclic trimers or tetramers $[R_2P–BH_2]_n$ (*n* = 3 or 4) (Scheme 18).[22,24] A series of elegant experiments confirmed that the dehydrocoupling of secondary phosphine–boranes proceeds by a homogeneous mechanism.[23] Primary phosphine–borane adducts such as $RPH_2–BH_3$ (R = Ph or *i*Bu) undergo Rh-catalyzed dehydrocoupling to give oligomers,[22] and at temperatures between 90 and 130 °C to give poly(phosphine–borane) polymers,[21] whereas (*p*-$CF_3C_6H_4$)$PH_2–BH_3$ could be polymerized at a lower temperature (60 °C).[24] In these cases, polymer molecular weights ranged from 80 000–160 000. It is noteworthy that in the absence of the Rh catalyst, thermally induced dehydrocoupling occurs very slowly, yielding only low molecular weight materials that possessed branched structures. Such phosphine–borane materials that are accessible by metal-catalyzed reactions have recently been reviewed.[25,26]



Scheme 18 The synthesis of phosphine–borane oligomers and polymers by Rh catalysts.

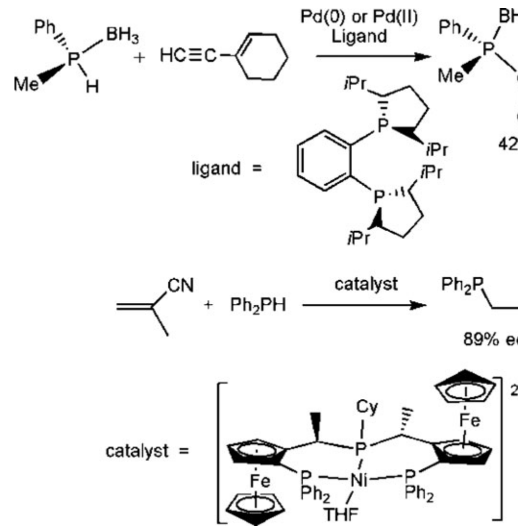


Scheme 19 Proposed mechanism of the hydrogenation of P–P bonds using precatalyst $[(NacNac)Rh(C_8H_{14})N_2]$.

We have probed the ability of Rh species to activate P–P bonds. The species $[(NacNac)Rh(C_8H_{14})N_2]$ is an effective precatalyst for the reactions of the diphosphine P_2Ph_4 with H_2 or silanes $R_2R'SiH$ to give Ph_2PH (Scheme 19) and/or silylphosphines Ph_2PSiR_2R', respectively.[27] The reactions of P_2Ph_4 with silanes R_3SiH were expected to generate equal amounts of Ph_2PH and Ph_2PSiR_3. However, only low concentrations of Ph_2PH are observed, suggesting that Ph_2PH is transformed into a silylphosphine with the loss of H_2. It is noteworthy that this Rh catalyst is not active for the dehydrocoupling of secondary phosphines, presumably due to the steric constraints of the bulky NacNac ancillary ligand. Stoichiometric reactions of the Rh precursor with P_2R_4 (R = Ph or Et) yield [(NacNac)Rh(η^2-P_2R_4)].[27] Interestingly, the Rh complex bearing the smaller and more basic P_2Et_4 ligand is catalytically inactive towards hydrogenation or hydrosilation, suggesting that partial dissociation of the diphosphine is required for subsequent P–P bond cleavage.

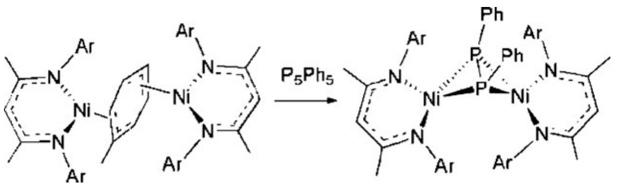
7. Nickel, palladium and platinum

Ni and Pd catalysts have been shown to catalyze the reaction of Ph_2PH with various styrene derivatives in high yields and selectivities, giving only the anti-Markovnikov product.[28] In a similar fashion, $PhMePH(BH_3)$ and a variety of chiral chelate Pd(0) complexes have been used to hydrophosphinate 1-ethynylcyclohexene to give chiral phosphine–borane adducts in enantiomeric excesses of up to 42% (Scheme 20).[29] The hydrophosphination of methacrylonitrile by bulky secondary phosphines is catalyzed by $[(CpFeC_5H_3(PPh_2)(CHMe))_2PCy]Ni(THF)][X]_2$ (X = ClO_4, BPh_4 or BF_4) to give high yields and enantiomeric excesses of 45–89% (Scheme 20).[30] X-Ray data for the $CH_2C(Me)CN$ adduct of the Ni catalyst revealed that the two axial faces of the complex are differentiated by the displacement of the $Ni(CH_2C(Me)CN)$ moiety from the three P atoms in the ligand, accounting for the stereoselectivity. The mechanism, supported by experimental and computational studies, involves the attack by phosphine on the pendant olefinic fragment of $CH_2C(Me)CN$ that is coordinated to the Ni-ligand cation through the CN moiety.[31]



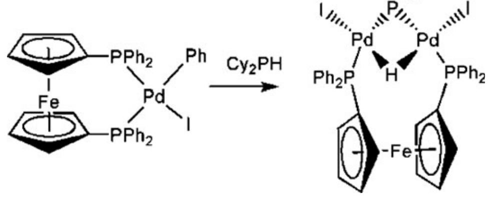
Scheme 20 Stereoselective hydrophosphination.

Stoichiometric P–P bond activation by the dimeric Ni(I) complex $[(NacNac)Ni]_2(\mu\text{-}\eta^3\text{-}\eta^3\text{-}C_6H_5Me)$ has been investigated. The reaction with P_5Ph_5 affords the formally Ni(II) dimeric species $[(NacNac)Ni]_2(\mu^4\text{-}P_2Ph_4)$ (Scheme 21).[16] While the mechanism of formation is not clear, formal oxidation of the Ni center is thought to occur by electron transfer, leading to P–P bond cleavage. This species exhibits a reversible reduction, generating the mixed-valent Ni(I)/Ni(II) species $[(NacNac)Ni]_2(\mu^4\text{-}P_2Ph_4)]^-$.[16] It is also noteworthy that while the Ni(I) species reacts with P–P bonds, reactions with primary and secondary phosphines do not result in P–H bond activation. Instead, these reactions lead only to Ni(I)-phosphine adducts (NacNac)Ni(PPhRH) (R = H or Ph).[15]



Scheme 21 The formation of $[(NacNac)Ni]_2(\mu^4\text{-}P_2Ph_4)$ by the activation of P_5Ph_5.

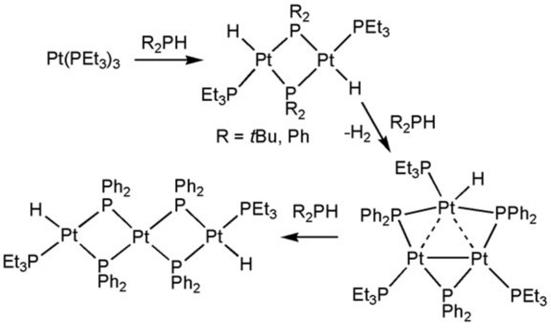
Stoichiometric P–H bond cleavage is effected by the reaction of the Pd-aryl complex [(dppf)Pd(Ph)(I)] (dppf = $Ph_2PC_5H_4FeC_5H_4PPh_2$) with R_2PH (R = Ph or Cy) to generate dinuclear complexes $[Pd_2(I)_2(\mu\text{-dppf})(\mu\text{-H})(\mu\text{-PR}_2)]$ (Scheme 22). In the case of R = Ph, this species is converted into $[Pd_2(I)_2(PHPh_2)_2(\mu\text{-PPh}_2)_2]$, with the loss of dppf and H_2.[32]



Scheme 22 Synthesis of $[Pd_2(I)_2(\mu\text{-dppf})(\mu\text{-H})(\mu\text{-PCy}_2)]$.

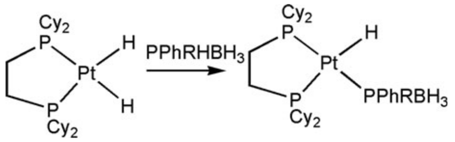
Glueck and co-workers[33] observed that Mes_2PH underwent P–H or P–C bond activation with Pt(0) species. For example, the reaction with Pt(dppe)(*trans*-stilbene) (dppe = $Ph_2PCH_2CH_2PPh_2$) generated $PtH(dppe)(PMes_2)$. This species was subsequently converted to Pt(Mes)(dppe)(PHMes). Mechanistic studies suggest a three-coordinate intermediate $Pt(dppe)(PHMes)_2$, which undergoes a reversible oxidative addition of the P–H bond or irreversible oxidative addition of the P–C bond of $PHMes_2$. The proposed intermediate was not observed under these reaction conditions.

The oxidative addition of tBu_2PH to $Pt(PEt_3)_3$ gives the *anti*-isomer of the dinuclear complex $[Pt_2(H)_2(PEt_3)_2(\mu\text{-H})(\mu\text{-P}t\text{Bu}_2)_2]$ (Scheme 23).[34] Related reactions of $Pt(PEt_3)_3$ and Ph_2PH result in an analogous dimeric compound, the trinuclear Pt cluster $[Pt_3(H)(\mu\text{-PPh}_2)_3(PEt_3)_3]$, which formally contains two Pt(I) and one Pt(II) center, or the linear trimeric product $[Pt_3(H)_2(\mu\text{-PPh}_2)_4(PEt_3)_2]$, in which the major isomer has an *anti*-structure. These reactions proceed *via* the oxidative addition of R_2PH to $Pt(PEt_3)_3$ by the loss of PEt_3, giving the transient intermediate Pt(II) complex $[Pt(H)(PR_2)(PEt_3)_2]$. Further loss of PEt_3 and dimerization yields the dinuclear product. The bulky *t*Bu substituents preclude further reaction, whereas for R = Ph, the diplatinum intermediate $[Pt_2(H)_2(PEt_3)_2(\mu\text{-H})(\mu\text{-PPh}_2)]$ can react further, with the loss of H_2 and PEt_3.



Scheme 23 Stoichiometric activation of P–H bonds by Pt reagents.

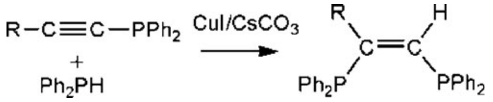
The P–H bonds in phosphines $PhPH_2$ and Ph_2PH, as well as phosphine–boranes $PhPH_2\text{–}BH_3$ and $Ph_2PH\text{–}BH_3$, are cleaved by their reaction with the Pt(II) dihydride *cis*-PtH_2(dcpe) (dcpe = $Cy_2PCH_2CH_2PCy_2$). The resulting products, *cis*-PtH(PPhR)(dcpe) and $PtH(PPhRBH_3)$(dcpe) (R = H or Ph), are formed with the concurrent loss of H_2 (Scheme 24).[35]



Scheme 24 The synthesis of $[PtH(PPhRBH_3)(dcpe)]$.

8. Copper

The hydrophosphination of 1-alkynylphosphines to give 1,2-diphosphino-1-alkenes, using CuI/Cs_2CO_3 as the catalyst, has been described (Scheme 25).[36] A variety of Cu salts were tested and shown to be less active towards hydrophosphination than CuI. Late transition metal compounds also displayed very low activities. Other bases tested were less effective, with the exception of nBuLi, which catalyzed the reaction in the absence of the Cu salt, although a mixture of *Z*- and *E*-isomers was obtained. The resulting 1,2-diphosphinoalkenes were hydrogenated to give chiral diphosphines.



Scheme 25 Cu-catalyzed hydrophosphination.

9. Summary and future prospects

The research reviewed herein demonstrates that the stoichiometric activation of P–H bonds can be effected *via* both σ-bond metathesis and oxidative addition reactions. Such avenues to hydrido-phosphido complexes provide the basis for the development of transition metal-based catalysis. Indeed, early and late transition metal species have proved useful as precatalysts for both P–H and P–P bond activation. Catalytic P–H bond activation, in conjunction with dehydrocoupling, provides easy access to a wide range of compounds containing P–E bonds (E = P, B, Si, Ge, *etc.*), while reactions with C–C multiple bonds allow the synthesis of new phosphines *via* hydrophosphination. The activation of P–P bonds is considerably less well studied, but should prove promising in the synthesis of new phosphorus-based derivatives. The burgeoning field of inorganometallic chemistry, highlighted herein with respect to transition metal–phosphorus compounds, has provided synthetic strategies towards phosphorous-containing small molecules, macrocycles, and even polymers.

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