Complexes of ambiphilic ligands: reactivity and catalytic applications

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Complexes of ambiphilic ligands: reactivity and catalytic applications

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Abstract

Since the mid 2000's, the incorporation of Lewis acid moieties in ligands for transition metals has been studied extensively. So-called ambiphilic ligands were shown to possess rich and unusual coordination properties and special focus was given to the coordination of Lewis acids as σ-acceptor ligands (concept of Z-type ligands). Recent studies have demonstrated that the presence of Lewis acids at or nearby transition metals can also strongly impact their reactivity. These results are surveyed in this review. The stoichiometric transformations and catalytic applications of complexes deriving from ambiphilic ligands are presented. The different roles the Lewis acid can play are discussed.

Introduction

The structure, properties and applications of coordination complexes are known to strongly depend on the ligands bound to the metal. This has continuously motivated synthetic chemists to design and develop various ligand frameworks. In particular, polyfunctional ligands incorporating weakly coordinating and chemically / redox active functional groups (hemilabile and non-innocent ligands) have attracted considerable attention and led to spectacular achievements. Over the last decade, systems combining electron donor and acceptor groups, so-called ambiphilic ligands, have also spurred much interest and their study represents a very active field in main-group chemistry.

For a long time, Lewis acids (typically Al and B-based compounds) were mostly associated with coordination complexes to act as external activators, co-catalysts or additives. This situation has changed dramatically and since the 2000's, the incorporation of Lewis acid moieties within ligands has been studied extensively. Phosphine-boranes and related ambiphilic ligands have been shown to possess rich and unusual coordination properties. As depicted in Chart 1, four coordination modes can be distinguished, according to the way the Lewis acid moiety enters (or not) the coordination sphere of the transition metal. Among them, special attention has been devoted to the coordination of Lewis acids to transition metals as σ-acceptor ligands. Accordingly, Z-type ligands have been progressively moved from an exotic, sometimes contentious notion, to a relatively well-established, general and promising concept.[1]

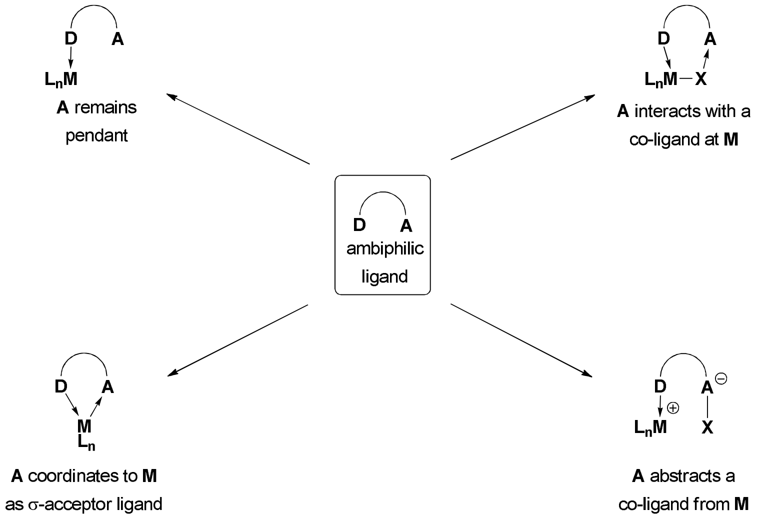


Chart 1. Schematic representation of the four coordination modes of ambiphilic ligands (D = electron donor and A = electron acceptor, Lewis acid).

Good knowledge has been progressively acquired on the factors controlling the coordination properties of ambiphilic ligands and on the way the properties of transition metal complexes can be influenced by ambiphilic ligands. These structural aspects have been summarized in several recent reviews[1,2] and are not discussed again here. Instead, this tutorial review is focused on the reactivity of complexes deriving from ambiphilic ligands. As shown by a series of recent seminal contributions, the presence of a Lewis acid moiety in the first coordination sphere of transition metals opens new reactivity paths, both at the stoichiometric and catalytic level. These contributions are discussed hereafter, with special emphasis on the role and influence of the Lewis acid moiety. The manuscript is organized following the denticity of the ambiphilic ligands, from bidentate donor-acceptor (DA) systems, to tridentate (D_2A) and tetradentate (D_3A) ligands (the various ligands discussed in the review are displayed in Chart 2). The number of donor buttresses does not strictly impose the way Lewis acids participate in the reactivity of transition metal complexes, but it is often the key parameter to control the position and behavior of the Lewis acid. The review covers complexes of phosphine-boranes and related ambiphilic ligands, as well as metallaboratrane complexes deriving from poly(methimazolyl) and poly(azaindolyl) hydrido borates.

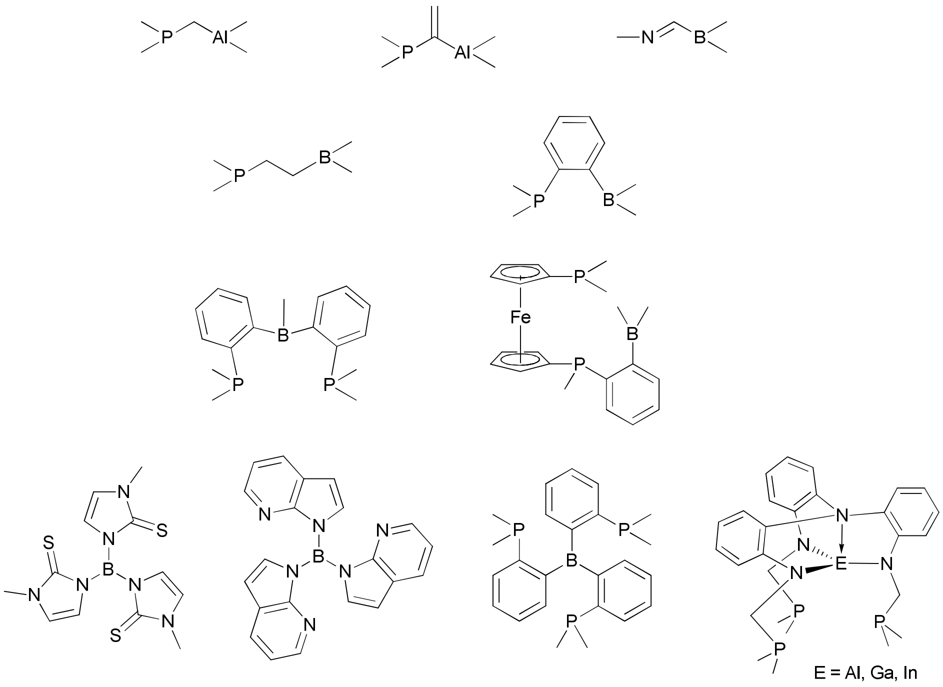
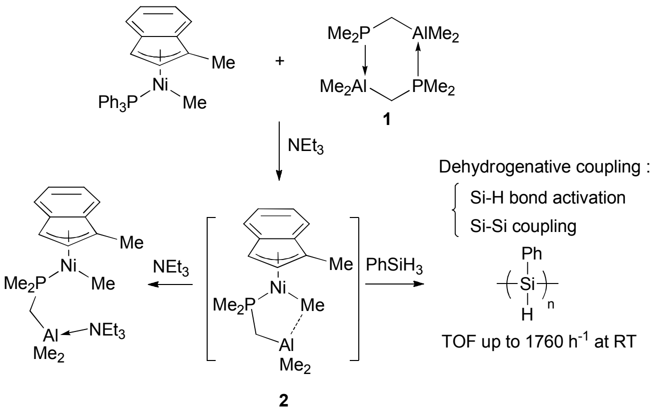


Chart 2. Structure of the ambiphilic ligands whose complexes are discussed in this review.

Complexes of bidentate ambiphilic ligands

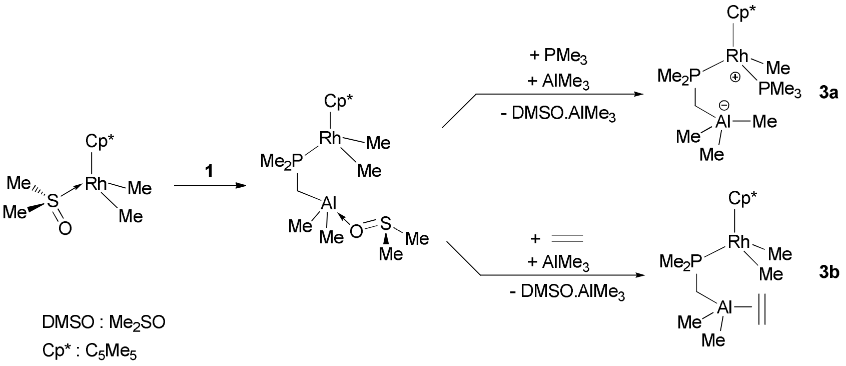
Dissociation of Ni/Rh–Me and Au–Cl bonds with PCAl ligands

The first evidence for a positive effect of an ambiphilic ligand on catalytic activity was reported in 2004 by Fontaine and Zargarian.[3] To improve the Ni-catalyzed dehydrogenative coupling of $PhSiH_3$ and assess the role of the methylaluminoxane MAO co-catalyst, the combination of P,Al compound $(Me_2PCH_2AlMe_2)_2$ **1** with [(1-Me-indenyl)Ni(PPh_3)Me] was used as alternative catalytic system. This resulted in a 50-fold increase of the turn-over frequency, and further rate enhancement was observed upon addition of Lewis bases (such as NEt_3), which split the P,Al dimer and facilitate the displacement of PPh_3 at Ni (Scheme 1). With the P,Al ligand, the Lewis acid moiety was supposed to be ideally positioned to interact with the Me group at Ni. The key active species **2** could not be characterized per se, but its Lewis pair adduct Al←NEt_3 adduct was authenticated by NMR.



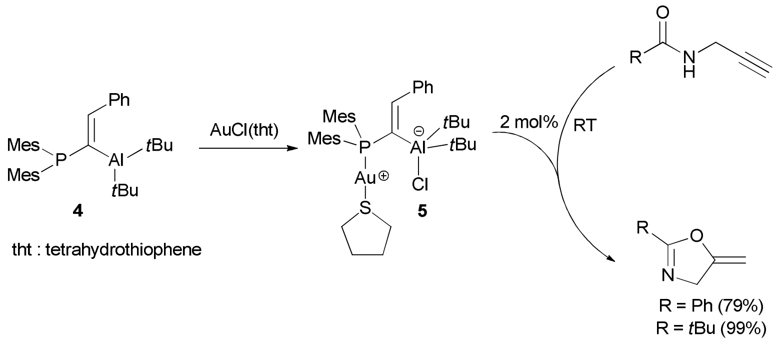
Scheme 1. Key P,Al Ni complex **2** proposed to account for the dehydrogenative coupling of $PhSiH_3$.

Subsequently, Fontaine studied $[(Cp^*)RhMe_2]$ complexes (Scheme 2)[4] and demonstrated by spin saturation transfer NMR experiments the ability of the P,Al ligand to reversibly abstract a methyl group at the metal. This requires the addition of $AlMe_3$ (to scavenge DMSO, Me_2SO, which otherwise remains bound to the Al center of the P,Al ligand) and results in a zwitterionic complex, whose PMe_3 and ethylene adducts **3a,b** have been characterized by NMR (Scheme 2).



Scheme 2 Coordination of the P,Al ligand **1** to Rh and abstraction of a methyl group at Rh.

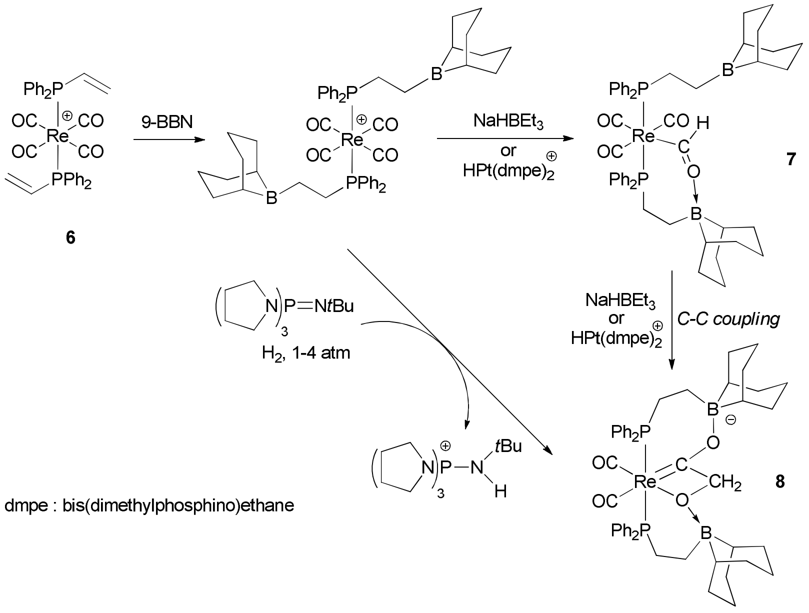
The stability and versatile reactivity of the geminal P,Al compound **4** towards small molecules[5] prompted us to explore its coordination properties.[6] Bridging P→M–Cl→Al coordination was observed with Rh and Pd fragments, while chloride abstraction systematically occurred with Au chloride precursors.[6a] Most remarkable is the formation of the zwitterionic complex **5** upon reaction with AuCl(tht) (Scheme 3). Instead of ligand displacement, as typically observed with standard phosphines, the P,Al ligand formally inserted into the Au–Cl bond, the LA moiety acting as an internal chloride abstractor. This generates an electro-deficient metal center with a labile THT co-ligand. As such, ambiphilic ligands may offer an alternative to silver salts for the activation of gold(I) precatalysts, and this hypothesis was validated in a model reaction, namely the cycloisomerization of propargylamides into alkylidene oxazolines (Scheme 3).



Scheme 3. Formation of a zwitterionic Au complex **5** with a geminal P,Al ligand, and application to silver-free catalytic isomerization of propargylamides.

Hydride transfer to CO and C–C coupling at Re with a PC$_2$B ligand

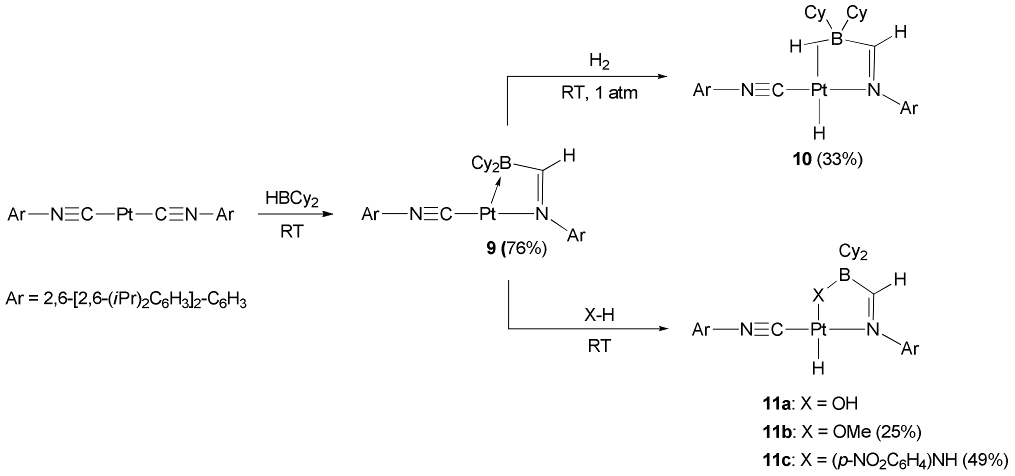
The known ability of Lewis acids to promote carbonyl insertion into M-H and M-Me bonds combined with the interest for homogeneous Fischer-Tropsch processes (formation of organic compounds from syngas H_2/CO) has stimulated investigations on reductive coupling of CO at Re with a P,B ligand.[7] Hydroboration of a bis vinyl-phosphine complex **6** with 9-BBN enabled to install two phosphine-boranes at the Re(CO)$_4$ fragment (Scheme 4). Reaction with boron or platinum hydrides induced hydride transfer and C–C coupling, resulting in an anionic Re carbene complex **8** stabilized by two strong O→B interactions.[8a] The role of the borane was investigated in detail.[8b] The first hydride transfer, leading to a B-stabilized formyl complex **7**, also occurred with external boranes, but the PCH$_2$CH$_2$B ligand proved to be critical for the second hydride transfer and C–C coupling steps. Interestingly, complex **8** could also be obtained *via* H_2 activation, using an FLP approach with a strong and sterically hindered phosphazene Lewis base.[8c]



Scheme 4. Reduction and coupling of CO assisted by a pendant borane at Re.

Addition reactions across Pt→B interactions with a NCB ligand

In 2014, Figueroa reported very interesting results on a Pt complex featuring an imine-borane ligand.[9] The N,B ligand was prepared in the coordination sphere of Pt, by reacting the bis isocyanide complex $(ArNC)_2Pt$ with Cy_2BH (Scheme 5). Formal 1,1-hydroboration of one ligand and migration of Pt from C to N resulted in the T-shaped complex **9**. ^{11}B NMR and XRD data indicate the presence of significant Pt→B interaction. This is a very rare case where a bidentate ambiphilic ligand fosters such a M→LA interaction,[10] and this is all the more remarkable that it results in a strained 4-membered ring with a small NPtB bite angle (105.6°). The reactivity of complex **9** was explored and a broad range of small molecules were found to be activated at room temperature. The Pt→B interaction is systematically eradicated, the metal center is formally oxidized to Pt(II) and the boron atom interacts with a fragment of the incoming molecule. Dihydrogen is activated irreversibly to give a hydride-borohydride Pt complex **10**. Polar X–H bonds are cleaved too, as substantiated with *p*-nitroaniline, water and methanol. The resulting complexes **11a-c** are stabilized by interaction of the X lone pair with B.



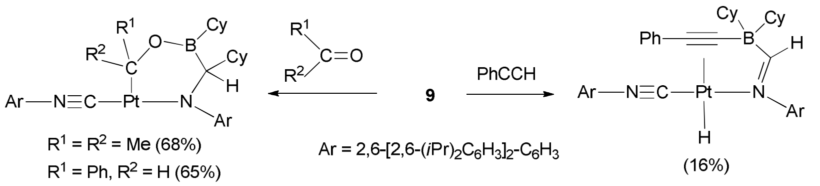
9 (76%)

10 (33%)

11a: X = OH
11b: X = OMe (25%)
11c: X = (*p*-NO$_2$C$_6$H$_4$)NH (49%)

Scheme 5. Synthesis of Pt complex **9** with a N,B ligand, activation of dihydrogen and X–H bonds.

Phenylacetylene is also readily activated, *via* 1,2 addition of the C–H bond to the Pt→B linkage (Scheme 6). The acetylide fragment is transferred to B and remains coordinated to Pt in a side-on fashion. Complex **9** also reacts with carbonyl compounds (acetone, benzaldehyde) (Scheme 6). The Pt center attacks the electrophilic carbon atom while the oxygen bonds to boron and promotes the migration of one Cy group from B to the adjacent imidoyl carbon atom.

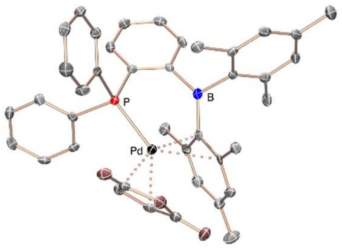


Scheme 6. Activations of C–H and C=O bonds across a Pt→B interaction.

Although the exact role that the boron center plays in these reactions is not known, it obviously facilitates the activation of the substrates and participates in the stabilization of the resulting products.

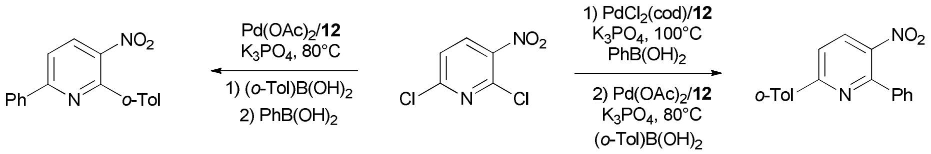
Boron enhancement effect in Pd-catalyzed C–C coupling and hydroboration with o-phenylene P,B ligands

Aryl and biaryl phosphines are ubiquitous and powerful ligands in TM-catalysis. The presence of a boryl moiety next to phosphorus can strongly affect catalytic behavior, as we observed with the iconic *o*-phenylene phosphine-borane **12**.[11] Introduction of an *o*-BMes$_2$ moiety on PPh$_3$ induced a decrease of both activity and regioselectivity in the Rh-catalyzed hydroformylation of 1-octene,[12] but significant improved the efficiency of the Pd-catalyzed Suzuki-Miyaura coupling of *p*-bromoanisole with PhB(OH)$_2$ (Scheme 7).[13a] A possible explanation for this catalytic enhancement can be found in the ability of the Mes rings at B to coordinate Pd,[14] as evidenced crystallographically in the Pd(0) complex **13** obtained by reacting **12** with Pd(nbd)(ma) (nbd = 2,5-norbornadiene, ma = maleic anhydride). The Pd / P,B system was then applied to the preparation of heterobiaryl compounds starting from chloro *N*-heterocycles,[13b] having in mind that the boron center may anchor these substrates by N→B interaction. The reaction worked very well with 2-, 3- and even 4-chloropyridines, as well as pyrimidine, pyrazine, quinolone and quinazoline substrates. Even 4-amino-2-chloropyridine featuring an unprotected amino group was efficiently coupled with PhB(OH)$_2$ under these conditions (Scheme 7).



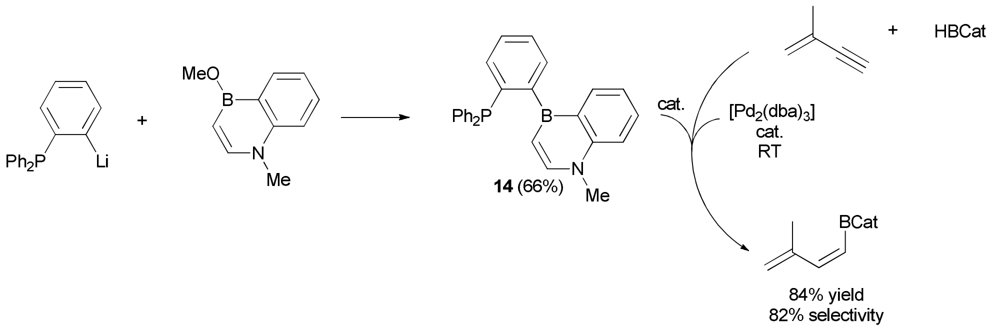
Scheme 7. Pd-catalyzed Suzuki-Miyaura cross-couplings with an *o*-phenylene P,B ligand **12**, molecular structure of **13**.

Interestingly, the phosphine-borane **12** displayed good selectivity in the coupling of 2,6-dichloro-3-nitropyridine as a model of unsymmetrical difunctional substrate (Scheme 8).[13b] This was exploited to perform two cross-couplings sequentially and thereby, unsymmetrical pyridines were readily prepared in good isolated yields (~60%).



Scheme 8. Pd-catalyzed sequential cross-coupling of a 2,6-dichloropyridine with an *o*-phenylene P,B ligand.

Another *o*-phenylene P,B ligand **14** was recently prepared by Liu and applied in Pd-catalyzed hydroboration.[15] A N,B analog of naphthalene (a monobenzofused 1,4 –azaborine) was synthesized and coupled with *o*-lithiated triphenyl phosphine (Scheme 9). In the presence of $Pd_2(dba)_3$, it promotes the *trans*-1,2-hydroboration of a model enyne (with small amounts of *cis*-1,2 and 1,4 hydroboration). Although the precise role of the azaborine moiety is not known, it improves activity and provides unique selectivity, compared with the corresponding *o*-naphthalenyl phosphine (42% overall yield, 71% of 1,4 hydroboration).

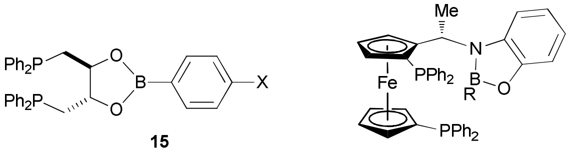


Scheme 9. Preparation of an *o*-substituted azaborine triphenylphosphine **14** and its application to the Pd-catalyzed hydroboration of an enyne.

Complexes of tridentate ambiphilic ligands

Substrate anchoring with boron-appended diphosphines

Kagan, Jacobsen and Landis envisioned early on the possibility to anchor substrates in the coordination sphere of transition metals by installing boron moieties on diphosphines.[16] Ligands of types **15** and **16** were prepared (Chart 3) and their Rh(I) complexes were evaluated in various catalytic transformations (hydrogenation of C=C and C=O bonds, hydrosilylation of carbonyl compounds, hydroformylation of alkenes). No significant enhancement of activity or selectivity was observed, but the ability of the pendant boron center to interact with the N atom of alkenamines was supported by NMR studies. Fine tuning of the ligand framework is probably necessary to ensure optimal interaction of the incoming substrate and induce noticeable catalytic effects.



15

X = H, Cl, CF_3

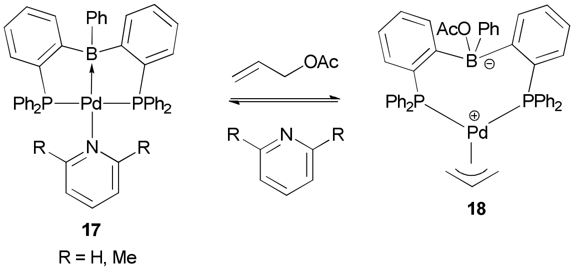
16

R = Me, Ph, *p*-C_6H_4Cl

Chart 3. Boron-appended diphosphines investigated for substrate anchoring.

Activation of C–O bonds with PBP ligands

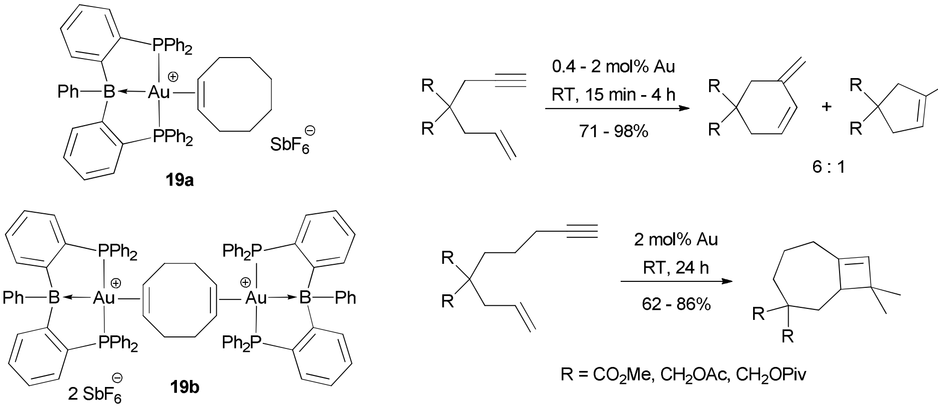
In 2011, Britovsek prepared a series of square-pyramidal Rh(I) complexes from the diphosphine-borane $[Ph_2P(o\text{-}C_6H_4)]_2BPh$.[17] The idea was to take advantage of the Lewis acid moiety to facilitate the activation and ultimately the carbonylation of methyl acetate (the most important industrial process to produce acetic anhydride). Unfortunately, all the tested complexes feature apparently too strong Rh→B interactions to be displaced by methyl acetate and no reaction occurred. In a quite related study, Tauchert recently prepared Pd(0) PBP complexes **17** and studied oxidative additions.[18] Phenyl bromide failed to react but allyl acetate was activated, affording the zwitterionic Pd allyl complex **18** with the acetate bound to boron (formal addition of the allyl–OAc bond across the Pd→B interaction). The latter reaction is reversible and requires an excess of allyl acetate (9-27 equiv.) (Scheme 10). It also proceeds with allyl benzoate and allyl trifluoroacetate, but not with allyl ethers. The zwitterionic complex **18** displayed good catalytic activity in the allyl substitution of allyl acetate with diethylamine. Comparison with the related Pd(0) complex **17** suggests that the Pd→B interaction does not assist the transformation but rather has an inhibiting effect in this case.



Scheme 10. Addition of allyl acetate across the Pd→B interaction of complexes **17**.

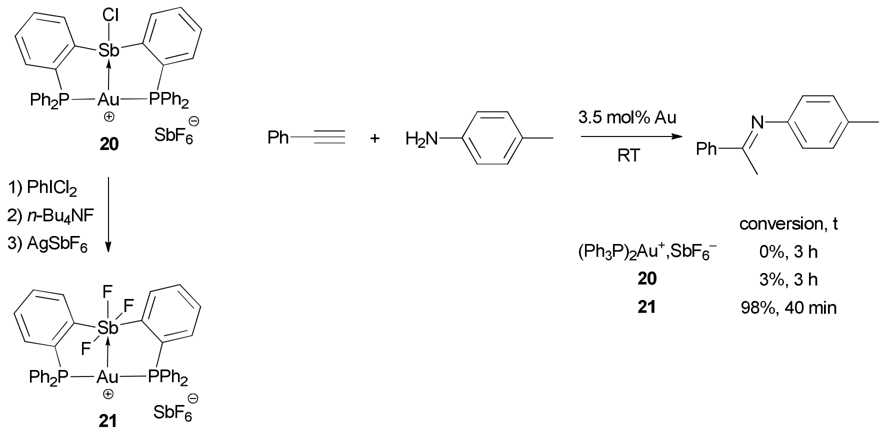
Lewis acid enhancement with PBP and PSbP ligands

The coordination of Lewis acids as σ-acceptor ligands induces a depletion of electron-density at transition metals.[1,2] This can be used to modulate Lewis acidity and catalytic activity, as shown recently for gold complexes of PBP and PSbP ligands. Using cod and coe co-ligands, Inagaki was able to isolate cationic gold(I) complexes of $[Ph_2P(o\text{-}C_6H_4)]_2BPh$.[19] Unprecedented activities and selectivities were observed in the cycloisomerization of enynes, allowing for the preparation of 5, 6 and 7-membered carbocycles (Scheme 11). The critical role of the Au^+→B interaction was supported by the inertness of the related diphosphine complex $[Au(PPh_3)_2]SbF_6$. However, it is surprising that only the dinuclear PBP gold complex **19b** is active (no reaction was observed with the related mononuclear complex **19a**).



Scheme 11. Cationic PBP gold(I) complexes and representative catalytic cycloisomerization reactions.

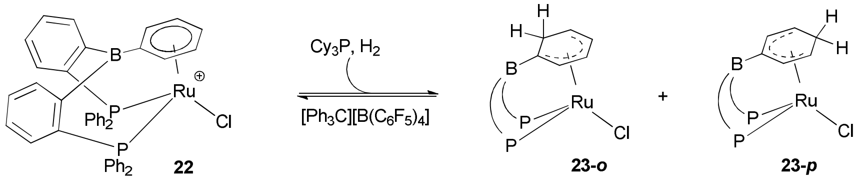
Gabbaï recently pushed forward the concept with redox non-innocent PSbP ligands (Scheme 12).[20] The cationic complexes **20** features a central chlorostilbine moiety which can be readily oxidized to give the trifluorostiborane complex **21**. The two Sb moieties behaves as σ-acceptor ligands with a distinctly stronger $Au^+ \rightarrow Sb$ interaction in the oxidized complex **21** (as visible from the shorter Au–Sb distance, 2.82 *vs* 2.93 Å). The depletion of electron density at gold was exploited to promote catalytic hydroamination. The reference complex $[(Ph_3P)_2Au^+,SbF_6^-]$ showed no activity towards the addition of *p*-toluidine to phenylacetylene, while a poor conversion was observed with **20** (3 % within 3 hours). Comparatively, complex **21** proved very active and complete conversion was achieved within only 40 minutes. The reaction shows some generality and imines were efficiently prepared with sterically hindered anilines [2,6-(iPr)$_2$-C_6H_3-NH_2], electro-deficient anilines (C_6F_5-NH_2), hydrazines (PhNH-NH_2) as well as aliphatic alkynes (nBuC≡CH).



Scheme 12. Cationic PSbP gold(I) complexes and catalytic hydroamination.

Another type of Lewis acid enhancement was observed by Stephan upon coordination of the PBP ligand $[Ph_2P(o\text{-}C_6H_4)]_2BPh$ to Ru(II).[21] The cationic complex **22** reacts with H_2 in the presence of $PMes_3$ (FLP-type activation) (Scheme 13). The η^6-coordinated Ph group at boron behaves as a C-centered Lewis acid (no reaction is observed with BPh_3 under similar conditions). This results in a mixture of neutral complexes **23-*o*** and **23-*p*** (both the *ortho* and *para* positions of the BPh moiety can fix the hydride), which can be converted back to the cationic complex **22** upon reaction with

$(Ph_3C^+)[B(C_6F_5)_4]^-$. Complex **22** can be used for catalytic hydrogenation of aldimines at room temperature under high pressure (102 atm).

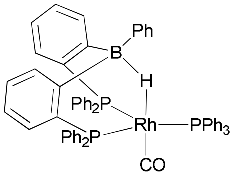


Scheme 13. C-based Lewis acid behavior of a PBP ligand, once coordinated to Ru.

Hydrogen transfer, hydrogenation and hydrosilylation with PBP ligands

The ability of borane ligands to fix reversibly hydrogen atoms has been recognized early on and this facet of ambiphilic ligands has stimulated much interest (see also the next section on tetradentate ligands).[22]

In 2012, Kameo and Nakazawa prepared Rh and Ir hydride complexes of $[Ph_2P(o\text{-}C_6H_4)]_2BPh$ and tested them in the catalytic transfer hydrogenation of ethyl phenyl ketone with *i*PrOH (Chart 4).[23] The Rh(I) complex **24** proved quite efficient (90% yield after 20 h at 70°C using 0.5 mol% cat). Only 29% yield is obtained with the related boron-free complex $Rh(H)(CO)(PPh_3)_3$ under the same conditions, and the addition of BPh_3 further decreases its activity. Apparently, the mode of coordination of the borane moiety plays an important role in this transformation. Significant catalytic enhancement is only observed for the Rh complex, which features a three-center two-electron Rh–H–B interaction. The related Ir complex **25**, which displays a direct Ir→B interaction, is only poorly active.



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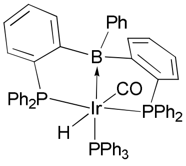
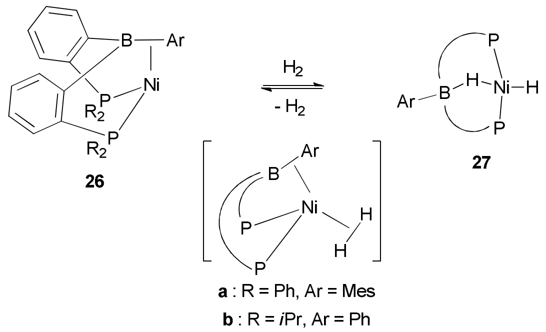


25

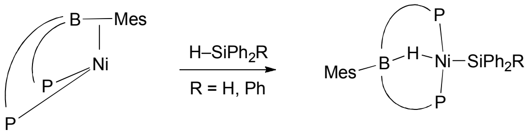
Chart 4. Rh(I) and Ir(I) hydride PBP complexes investigated in transfer hydrogenation.

Soon after, Peters reported spectacular results in the activation and transfer of H_2 with related Ni(0) PBP complexes.[24] Complex **26** was found to react rapidly and reversibly with H_2 under mild conditions (RT, 1 atm) to give the corresponding Ni(II) dihydride complex **27** (Scheme 14). The BMes group plays several important roles. It stabilizes the Ni(0) center by η^3-BCC coordination (without being too strongly bound),[25] and it interacts with one hydride of the ensuing Ni(II) complex (Ni-H-B bridging interaction). Remarkably, H_2 can be transferred back to olefins and complex **26a** is an efficient catalyst for the hydrogenation of styrene (complete conversion is achieved within 1 h at room temperature and 1 atm using 1 mol% cat).



Scheme 14. Reversible activation of H_2 involving cooperation between Ni and B.

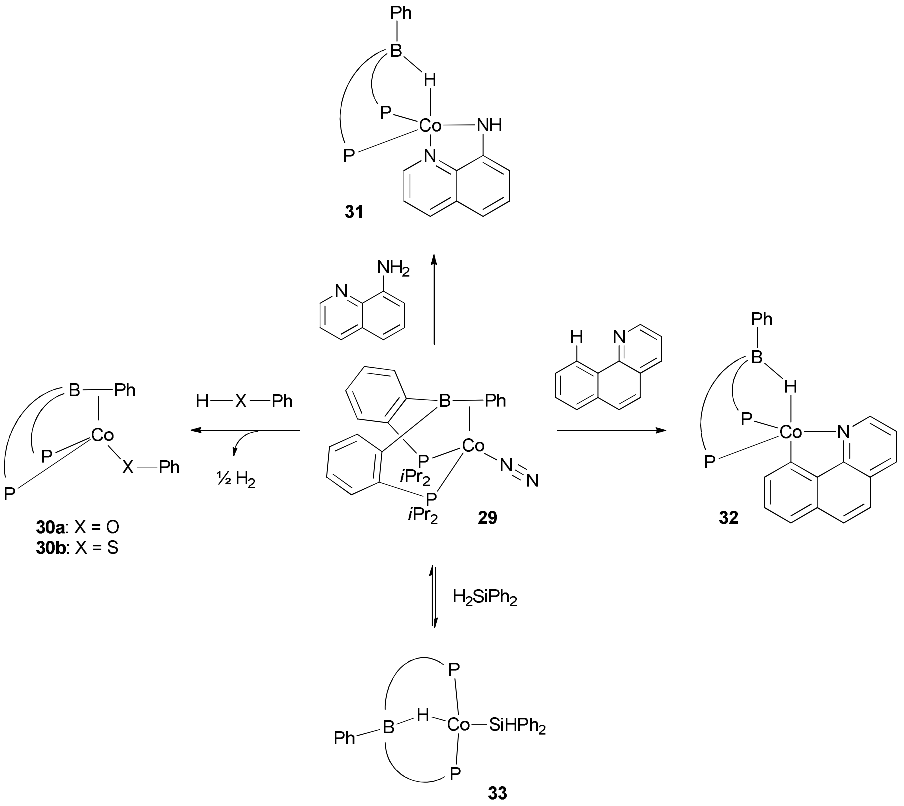
The reaction of complexes **26** with H_2 starts by side-on coordination of the H–H bond to Ni, as shown by ^{1}H NMR with the PBP ligand $[i\mathrm{Pr}_2\mathrm{P}(o\text{-}\mathrm{C}_6\mathrm{H}_4)]_2\mathrm{BPh}$ (in this case, activation of H_2 at Ni is quantitative but slow).[26] Active participation of boron in the activation of H_2 has been substantiated by DFT calculations.[26,27] This significantly lowers the activation barrier for the oxidative addition of H_2 and represents a new type of metal-ligand cooperation.[22b] Such bifunctional activation between electron-rich Ni(0) and Lewis acidic boron centers was then generalized to H–Si bonds.[28] Ni(II) hydride silyl complexes deriving from the reaction of **26a** with $PhSiH_3$ and Ph_2SiH_2 were isolated and the presence of stabilizing Ni–H–B interactions were unequivocally authenticated by XRD analyses (Scheme 15). As for H_2, the system is amenable to catalysis and complex **26a** was found to efficiently promote the hydrosilylation of *p*-substituted benzaldehydes at room temperature using 5 mol% cat.



26a **28a**

Scheme 15. Ni/B cooperative activation of silanes (the reaction is equilibrated for $HSiPh_3$).

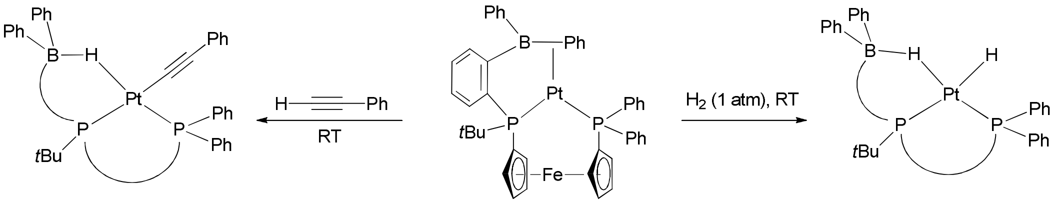
Recently, the approach was further extended to Co and Fe PBP complexes (Scheme 16).[29] Polar H–X bonds (X = O, S) were readily activated under mild conditions (eventually with release of H_2). Strong H–N and H–C bonds could also be activated using substrates with *N*-directing groups (8-aminoquinoline and benzoquinoline). The presence of Co/Fe–H–B bridging interactions in the resulting complexes **31** and **32** was established by X-ray diffraction and IR analyses. Moreover, the Co complex **29** mediates the activation of diphenylsilane (H–Si bond) in a reversible manner. The Co complex **29** and its Fe analog were evaluated in catalytic hydrosilylation. They outperform the Ni complex **24a** and proved efficient towards benzaldehydes, alkyl aldehydes as well as aryl and alkyl ketones under mild conditions (most reactions are complete within a few minutes to a few hours at room temperature with 1 equiv. of Ph_2SiH_2 and 1 mol% cat).



Scheme 16. Activation of H–E (E = O, S, N, C, Si) bonds by the Co PBP complex **29**.

Activation of H–H and H–C bonds with a Pt(0) PPB complex

Recently, Emslie further illustrated the concept of metal-Lewis acid cooperativity with an original PPB ligand (featuring a 1,1'-diphosphine-ferrocene core and a pendant borane moiety).[30] The ensuing Pt(0) complex **34** is stabilized by η^3-BPh coordination and rapidly reacts with H_2 to give a boron-stabilized Pt(II) dihydride complex (Scheme 17). In this case, the reaction is irreversible and neither olefins nor internal alkynes could be catalytically hydrogenated conclusively. However, an interesting C–H activation process was observed with phenylacetylene (the ensuing Pt(II) complex rapidly rearranged but its structure, including the Pt–H–B bridging interaction, was unambiguously authenticated by NMR). A related Pt(0) PPAl complex featuring strong Pt→Al interaction was then prepared.[31] It displays rich reactivity, but Al always remains coordinated to Pt.

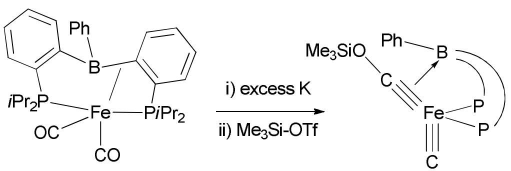


34

Scheme 17. Activation of H_2 and H–CCPh by a Pt PPB complex **34**.

Transformation of CO and N_2 with low-valent Fe complexes featuring PBP ligands

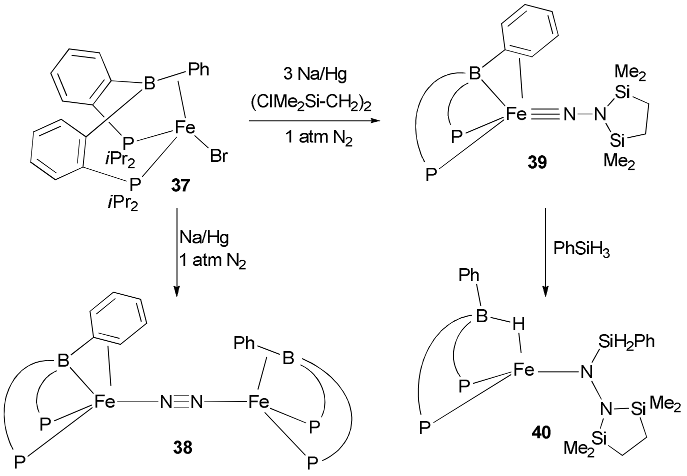
Low-valent iron complexes are also efficiently stabilized by PBP ligands, as shown and exploited by Peters. Neutral, mono and dianionic Fe complexes displaying either η^2-BC coordination or Fe→B interaction were isolated.[32] The O atoms of $(PBP)Fe(CO)_2$ can be functionalized by reduction with excess potassium followed by addition of trimethylsilyl triflate (Scheme 18). The resulting dicarbyne complex undergoes C–C coupling and releases $(Me_3SiO)CH=CH(OSiMe_3)$ under addition of H_2 (room temperature, 1 atm).



35 **36**

Scheme 18. Functionalization and coupling of CO at a Fe PBP complex.

Iron PBP complexes have also been investigated as nitrogenase models in the context of dinitrogen fixation and transformation.[33] The binuclear N_2-bridged complex **38** was prepared by reduction of the corresponding Fe(I) bromide **37** under N_2. Treatment of **37** with 3.1 equiv. of Na/Hg and 1.1 equiv. of $(ClSiMe_2CH_2)_2$ under N_2 induced double silylation of N_β (Scheme 19). The resulting amino-imido complex **39** readily reacts with $PhSiH_3$ to give a trisilyl-hydrazido hydride complex ($N\alpha$-functionalization). Upon activation of the Si–H bond, the BPh moiety shifts from η^2-CC coordination to Fe–H–B bridging interaction.

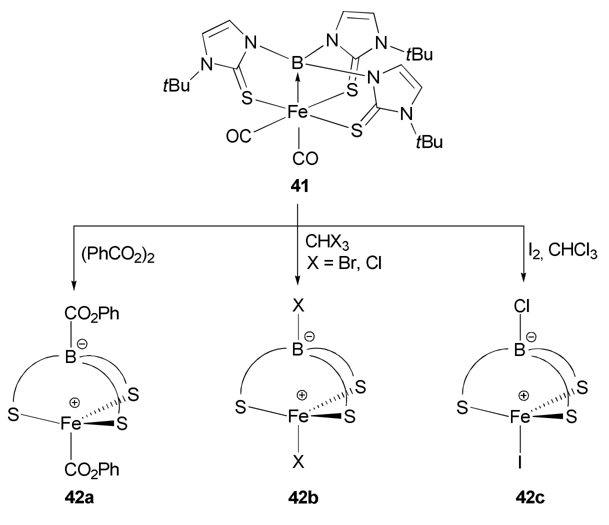


Scheme 19. Fixation and functionalization of N_2 at a Fe PBP complex.

Complexes of tetradentate ambiphilic ligands

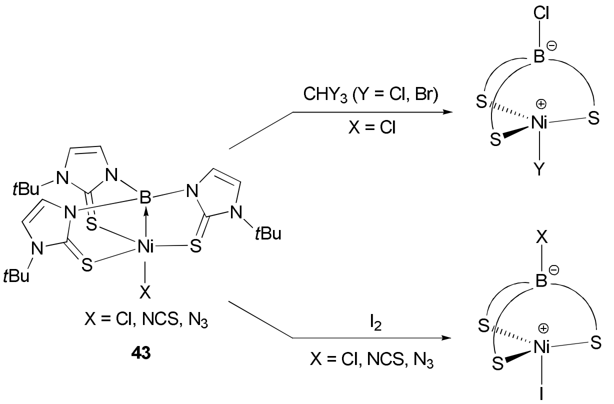
Oxidative additions to Fe and Pt cage complexes deriving from tri(methimazolyl)borane ligands (S_3B)

The first examples of 1,2-addition reactions across M→B interactions were reported by Parkin in 2006.[34] Dibenzoyl peroxide, chloroform and bromoform readily react with the ferraboratrane complex **41** to give the B-functionalized tris(methimazolyl)borate complexes **42a-c** (Scheme 20). A benzoyl fragment or an halogen atom is fixed at boron, which no longer interacts with Fe. Treatment of **41** with I_2 in $CHCl_3$ induces unsymmetric functionalization of the ferraboratrane, with selective introduction of I at Fe and Cl at B. It is possible that these reactions proceed *via* stepwise radical pathways rather simple concerted 1,2-additions across the Fe→B interaction.



Scheme 20. 1,2-Addition reactions across a Fe→B interaction.

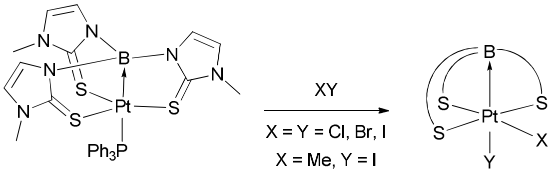
Soon after, the Ni(I) cage complexes **43** were reported to react with chloroform, bromoform and I_2 with cleavage of the Ni→B interaction, functionalization of boron and oxidation of Ni (Scheme 21).[35]



43

Scheme 21. Reactions of the Ni(I) cage complex **43** with cleavage of the Ni→B interaction.

In a related study, Hill explored the reaction of the Pt(0) cage complex **44** with X_2 (X = Cl, Br, I) and MeI.[36] In this case, oxidation addition to Pt occurred and the Pt→B interaction was retained. It is difficult to rationalize the difference observed between the Fe/Ni and Pt boratranes, but it is likely that the Lewis basicity of the metal and the strength of the M→B interaction come into play (Scheme 22).

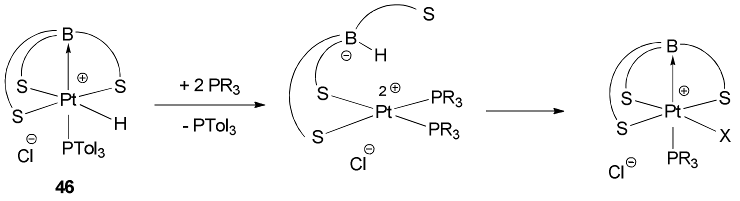


44 **45**

Scheme 22. Oxidative additions to a Pt(0) cage complex **44** with retention of Pt→B interaction.

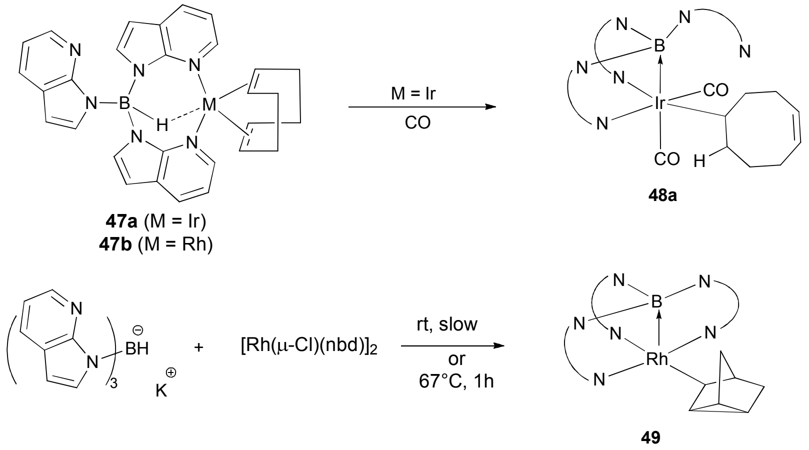
Hydride shuttling with tris(azolyl) complexes

As mentioned above, the ability of boron to fix and transfer H atoms to organic compounds (hydride shuttling) is a very appealing feature of ambiphilic ligands.[22a] This phenomenon was actually first authenticated with tetradentate ligands. As discussed hereafter, it has been thoroughly studied and developed up to catalytic applications. The first example of reversible transfer of H between boron and a transition metal was observed by Hill in 2008 with the Pt(II) boratrane **46** (derived from protonation of a complex of type **44**).[37] Displacement of $PTol_3$ (Tol = *o*-tolyl) with unhindered trialkylphosphines PR_3 (R = Me, Et) induces dissociation of one methimazolyl arm and hydride migration from Pt to boron (Scheme 23). Upon dissociation of PR_3, the B–H bond is slowly reactivated, with hydride migration from B to Pt, and formation of Pt→B interaction.



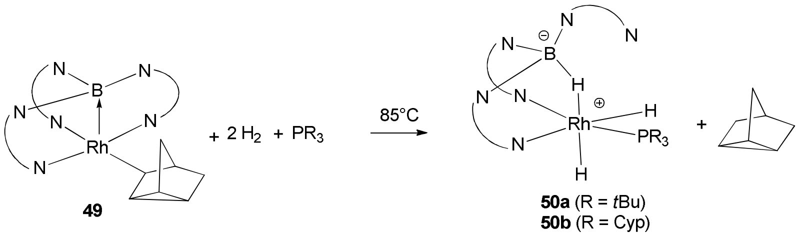
Scheme 23. Hydride migration between Pt and B upon coordination/dissociation of phosphines.

Soon after, Owen studied Rh and Ir tri(azaindolyl)borohydride complexes and observed hydride transfer from boron to an organic compound (a coordinated olefin).[38] The cod complexes **47a,b** (cod = 1,5-cyclooctadiene) display strong B–H–M interactions and one of the azaindolyl moiety is pendant. Under CO atmosphere, the Ir complex **47a** rapidly evolves into **48a**, in which Ir bears a cyclooctenyl group and is engaged into Ir→B interaction (Scheme 24).[39] The reaction probably involves hydride migration from B to Ir followed by insertion of one C=C bond of cod. The process was then generalized to a Rh nbd complex (nbd = 2,5-norbonadiene). The original rhodaboratrane **49** featuring a nortricyclyl group (due to C–C coupling) was isolated and structurally characterized. Hydride transfer from boron to the strained olefin is favored and occurs directly (without CO), albeit slowly at room temperature.



Scheme 24. Hydride migration from boron to cod/nbd in tri(azaindolyl) Rh/Ir complexes.

The reactivity of the rhodaboratrane complex **49** was explored and cooperation between Rh and B was observed in the activation of dihydrogen.[40] In the presence of bulky trialkylphosphines PR_3 (R = *t*Bu, Cyp) at 85°C and 2.5 atm, two molecules of H_2 are fixed to give tricyclo[2.2.1.0^{2,6}]heptane and Rh(III) trihydride complexes **50** stabilized by bridging B–H–Rh interactions (Scheme 25). This reaction offers a mean to recharge hydrogen at boron and opens the way to catalytic turnover.



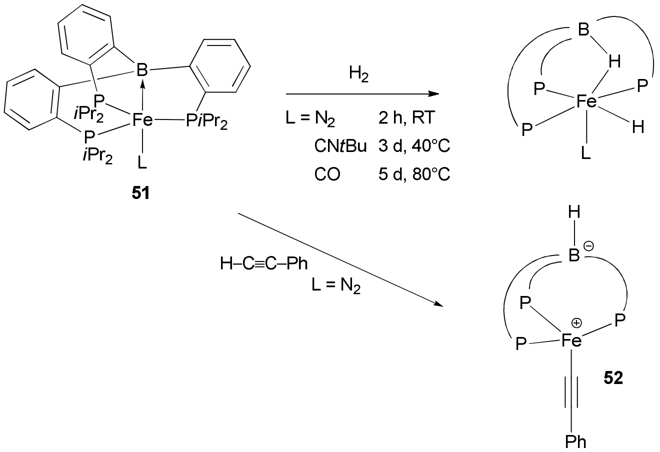
Scheme 25. Activation of H_2 by the rhodaboratrane complex **49**.

Catalytic applications of tri(azaindolyl)boron complexes

Some promising catalytic studies were reported in 2008 and 2011 by Owen on the tri(azaindolyl)boron complexes. First, transfer hydrogenation of acetophenone, benzophenone and cyclohexanone could be achieved with the Rh and Ir complexes **47a,b** at 83°C with *i*PrOH / KOH.[41] The presence of boron and the B–H–M bridges are compatible with this transformation, but apparently do not induce noticeable improvement compared to standard systems. The reaction of rhodaboratrane **49** with H_2 described above also spurred Owen to investigate its ability to catalytically hydrogenate alkenes.[40] Gratifyingly, styrene and cyclooctene could be efficiently converted into ethylbenzene and cyclooctane under relatively mild conditions (85°C, 2.5 atm, 18 h, 1 mol% cat).

Reaction of Fe P_3B complexes with H–H and H–C bonds, stoichiometric reactions and catalytic applications

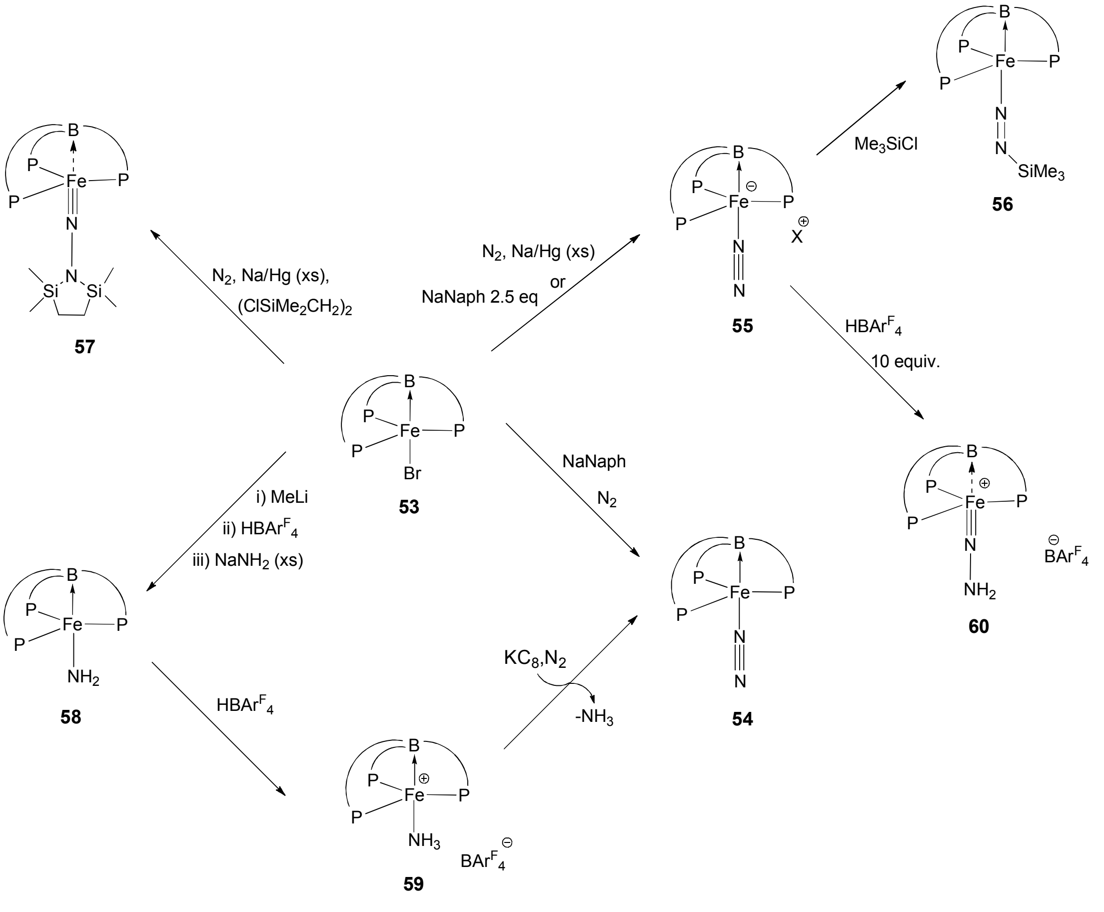
As an extension of his work on diphosphine-borane Ni complexes, Peters studied the reactivity of triphosphine-borane iron complexes and reported H–H as well as H–C activation across the Fe→B interaction (Scheme 26).[42] Dihydrogen reacts easily and reversibly with the end-on N_2 complex **51** (see below for N_2 fixation and transformation with Fe P_3B complexes). The Fe→B interaction is replaced for a Fe–H–B bridging interaction. The change of environment around Fe, from trigonal pyramidal to octahedral, gives the necessary flexibility to the cage structure. Similar reactions are observed with the CN*t*Bu and CO complexes, albeit under more forcing conditions (a few days at 40–80°C). The ability of boron to act as an hydride shuttle was supported by transfer reactions to organic substrates. In addition, the N_2 complex was shown to be a competent catalyst for the hydrogenation of ethylene (into ethane), styrene and phenyl acetylene (into ethylbenzene) at room temperature under 1 atm. It is noteworthy that the N_2 complex **51** reacts with phenylacetylene *via* reversible C–H bond activation (Scheme 26). According to XRD and IR data, the resulting complex adopts a trigonal pyramidal zwitterionic structure in this case. The arylacetylene moiety occupies the axial position while the H atom is bound to boron, without significant interaction to Fe.



Scheme 26. Activation of H_2 and H–CCPh across a Fe→B interaction.

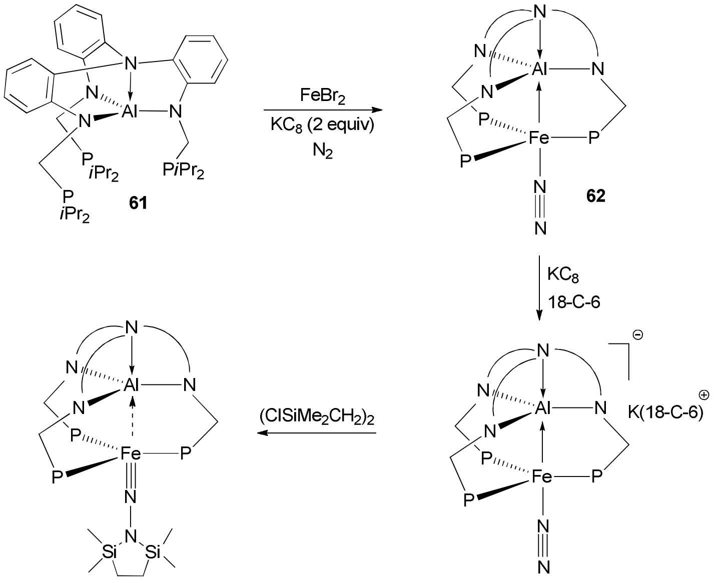
N_2 fixation and transformation with P_3B complexes

Encouraged by the results obtained with related PBP complexes, Peters investigated triphosphine-borane Fe complexes for N_2 activation and functionalization (Scheme 27). The neutral and monoanionic N_2 complexes **54** and **55** were prepared by controlled reduction of the Fe bromide precursor **53** under N_2 atmosphere.[43] The terminal nitrogen of **55** was readily silylated by Me_3SiCl to give the diazenido complex **56**. Reduction of **53** with excess Na/Hg in the presence of N_2 and $ClMe_2SiCH_2CH_2SiMe_2Cl$ afforded the corresponding disilylhydrazido complex **57** (as the result of bis N_β-functionalization).[44] A series of complexes relevant to $N_2 \rightarrow NH_3$ reduction were then isolated.[45] The parent amide species Fe–NH_2 **58** was prepared by a multi-step sequence and then subjected to a protonolysis / reduction sequence. Addition of $HBAr^F_4$ [Ar^F = 3,5-$(CF_3)_2$-C_6H_3] at low temperature gave the ammonia complex **59**. Treatment with KC_8 under N_2 atmosphere then induced the release of NH_3 and the formation of the neutral N_2 complex **54**. Very recently, addition of $HBAr^F_4$ to the anionic N_2 complex **55** at very low temperature enabled the characterization of the cationic hydrazido complex Fe≡N–NH_2 **60**. All together, these stoichiometric reactions provide evidence for most individual steps invoked in the distal pathway for $N_2 \rightarrow NH_3$ reduction. The anionic N_2 complex **55** was actually found to catalyse this transformation with turnover up to 7 at –78°C using excess of $HBAr^F_4$ and KC_8.[46] These results represent a major breakthrough in the study of Fe-mediated N_2 reduction. The key role of the P_3B ligand also deserves to be emphasized. It possess unique properties and in particular, the boron center shows unique ability to accommodate the various electronic environments involved at Fe. According to XRD and DFT calculations, most Fe P_3B complexes display Fe→B interactions, the distance of which varying from 2.22 Å (in complex **55**) to 2.77 Å in complex **60**. Moreover, the feasibility of $N_2 \rightarrow NH_3$ reduction was also demonstrated with the cobaltrane related to **55**, although with a slightly lower efficiency (2.4 equiv. of NH_3 per Co center).[47]



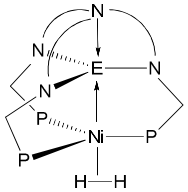
Scheme 27. Fixation and transformation of N_2 in the coordination sphere of a P_3B Fe complex.

Lu expanded the chemistry of P_3B Fe complexes to an original P_3Al ligand **61** derived from an aluminatrane. The ability of this tetradentate ligand to form cage complexes was illustrated by the preparation of several zerovalent complexes (Ni, Co, Fe), all featuring strong M→Al interactions (with a pentacoordinate, trigonal bipyramidal Al center).[48] In particular, the iron double-decker complex **62** was prepared upon reaction of with $FeBr_2$ in the presence of KC_8 and N_2 (Scheme 28). According to IR and XRD data, the N_2 molecule is end-on coordinated and labile (there exists a mononuclear / dinuclear equilibrium). Further reduction with KC_8 in the presence of 18-C-6 crown ether afforded the corresponding anionic complex, which was subsequently doubly silylated at N_β.[49] Herealso, the Lewis acid moiety was found to adapt its interaction to the Fe environment, the Fe•••Al distance varying from 2.57 to 2.82 Å.



Scheme 28. Fixation and transformation of N_2 in the coordination sphere of a P_3Al Fe complex.

Recently, aluminum was replaced for gallium or indium, and the corresponding Ni(0) complexes were thoroughly studied.[50] Most remarkable is the propensity of the Ni→Ga and Ni→In species to form side-on adducts **63a,b** with dihydrogen (Chart 5). Stronger $\sigma(H_2)\rightarrow Ni$ donation is observed in the indium complex **63b** (consistent with stronger Ni→E electron withdrawing with In than with Ga). Preliminary investigations in catalytic hydrogenation pointed out a noticeable influence of the Lewis acid moiety. The gallium complex **63a** gave the best results. It promotes styrene → ethylbenzene conversion under mild conditions (room temperature, 1 atm, 5 mol% cat). Complex **63a** is also efficient with 1-octene, 1-hexene, *cis*-cyclooctene, but not with more hindered olefins (diphenylethylene, *trans*-2-octene). The indium complex **63b** is less active and induces isomerization (into internal olefins) in parallel with hydrogenation.

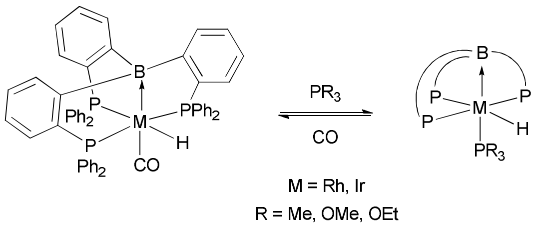


63a (E = Ga)
63b (E = In)

Chart 5. Side-on H_2 adducts of of a P_3Ga and P_3In Ni complexes.

Ligand dissociation / substitution in P_3B Rh / Ir complexes

During their study of Rh and Ir P_3B hydride complexes, Kameo and Nakazawa noticed an unusual tendency for dissociation and substitution of the ligand *trans* to boron.[51] Strong backdonation tends to prevent CO displacement in Rh(I) and Ir(I) complexes, but in the case of the rhoda and iridaboratranes, reversible exchange between CO and unhindered phosphines / phosphites was observed (Scheme 29).[52] This behavior has to do with the strong *trans* influence of Z-type ligands.[53]



Scheme 29. CO / PR_3 substitution reactions in Rh,Ir→B cage complexes.

Conclusions and perspectives

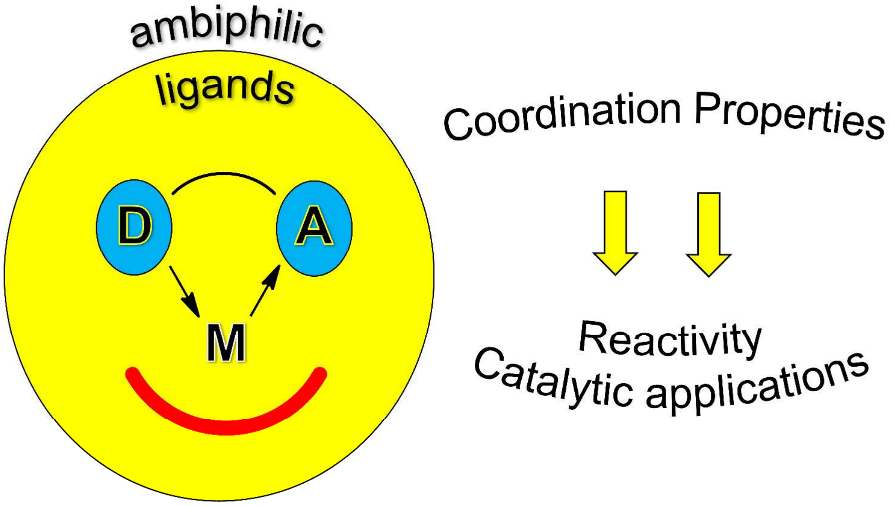
The recent studies discussed in this review clearly show that besides their versatile coordination properties, ambiphilic ligands possess rich and interesting reactivity. In most cases, the presence of the Lewis acid moiety at, or nearby, the metal has a strong impact and induces unique chemical behavior. So far, evidences for such Lewis acid-assisted reactivity mainly concern stoichiometric transformations, but ambiphilic ligands have also started to be successfully applied to catalytic reactions, and positive influence of the Lewis acid moiety has been sometimes established.

From these first results, at least four interesting directions of research corresponding to different roles of the Lewis acid moiety can be identified:

- Metal→Lewis acid interactions and M–X bond ionizations with Lewis acids can be used to generate electron-deficient complexes.
- Lewis acids can cooperate with transition metals to activate small molecules and transfer them to organic substrates. It is probably one of the most attractive facet of Metal→Lewis acid complexes. It represents a conceptually new approach of metal-ligand cooperation which can be potentially applied to a broad variety of strong σ-bonds (H–H, C–H, C–Cl, C–F…). It is noteworthy that in addition to the bond activation process, the Lewis acid moiety can also intervene in subsequent steps. For example, bridging M–H–LA / M–X–LA interactions may enable to release a vacant coordination site at the metal, facilitating the coordination and reaction of incoming substrates.
- σ-Acceptor ligands can stabilize complexes of different electronic and geometric environments (weak, adaptative Metal–Lewis acid interactions), as in the case of the triphosphine-borane Fe complexes successfully applied to the $N_2 \rightarrow NH_3$ reduction.
- Pendant Lewis acid moieties can act as anchors and activate / orientate incoming substrates in the coordination sphere of transition metals.

Of course, much remains to be done before ambiphilic ligands are eventually used widely in catalysis, but the field has progressed very rapidly and attracts interest of an ever-larger community. Future work will aim to understand and control the way the Lewis acid moiety of ambiphilic ligands participates in the reactivity of transition metal complexes. For sure, catalytic applications of ambiphilic ligands will also quickly progress.

TOC Graphic


ambiphilic
ligands
D
A
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Coordination Properties
Reactivity
Catalytic applications

Acknowledgments

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