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Coordination Chemistry of Neutral (L_n)–Z Amphoteric and Ambiphilic Ligands

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This review focuses on the coordination chemistry of neutral ambiphilic and amphoteric ligands. The various designs of molecules having both donor and acceptor moieties and the strategies to prevent self-aggregation and favour transition-metal coordination will be discussed.

Introduction

Catalysts play an important role in increasing the yield and the selectivity of syntheses and in reducing waste products of the chemical industry. While several homogeneous and heterogeneous synthetic catalysts have achieved remarkable efficiency, very few compare to enzymes in their activity. Indeed, these macromolecules have well-ordered three-dimensional assemblies with several active sites operating in synchronicity to give great specificity to many chemical reactions.[1] In order to mimic catalysts encountered in nature, chemists have been working on multifunctional molecules, which are compounds having more than one functional group where all sites have the possibility to work cooperatively. The possible molecular architectures are limitless and are only bound by chemists' imagination; however, one combination that has proven quite challenging to achieve is the presence of both Lewis acid and Lewis base sites within the same framework.[2–6] The increasing number of ambiphilic and amphoteric[7] molecules in the recent literature are an indication of the great potential of such molecules. They have been shown to act as catalysts,[2] as precursors to semiconductors,[3] as fluorescent and conductive materials,[4] as sensors,[5] as small-molecule activators[6] and finally as ligands for transition metals. Although all of these applications are worth discussing thoroughly, this microreview will focus on the coordination chemistry of ambiphilic and amphoteric ligands binding transition metals via neutral moieties.

Amphoteric and ambiphilic ligands can be described as molecules having donor groups (L and/or X) that can bind transition metals by using classical rules of coordination chemistry and at least one Lewis acid (Z). The Lewis acid

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can be available prior to coordination, but in order to avoid aggregation of the ambiphilic ligand, various preventive measures must be taken. Bulky substituents can be present on the molecule or the acidity can be reduced. Often, the Lewis acid moiety will be base-stabilized or made available by functionalization of an ancillary ligand.

The Lewis acid of an ambiphilic complex is usually reactive and may be involved in a number of interactions with its environment, depending on its acidity, on the nature of the transition metal and on the linker. Three different possibilities can occur: (1) The functional group Z has no or weak intramolecular bonding, and the empty orbital is available to interact with an incoming substrate (S) having basic functionalities (Figure 1a). Such cooperative behaviour, reminiscent of the working mode of enzymes, can help orienting an incoming molecule for a specific interaction with the active metal centre. (2) The Lewis acid (Z) can interact with a ligand (X) within the coordination sphere of the metal complex, as shown in Figure 1b, which will have the effect of weakening the M–X interaction and can ultimately lead to the formation of a zwitterionic species. While the interaction between Lewis acids and transition metals has been studied in great extent in many catalytic applications,[8] there is only a limited number of studies comparing the reactivity of cationic and zwitterionic complexes.[9] (3) If the metal centre is nucleophilic, the Lewis acid (Z) can interact directly with the transition metal (Figure 1c). The interaction between group XIII Lewis acids and transition metals has been reported in unsupported systems,[10] but most species are ill-characterized and their existence is doubtful.[11] It has been found that the presence of buttresses linking the Lewis acid site to the transition metal can enhance the stability of the interaction, allowing easier characterization and helping to investigate the properties of this novel bonding mode.

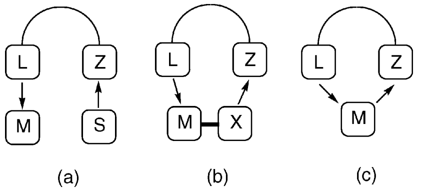


Figure 1. Coordination modes of an ambiphilic ligand (L = donor group, Z = Lewis acid) on a transition metal (M) where the Lewis acid interacts with (a) a substrate (S), (b) a ligand (X) or (c) the transition metal.

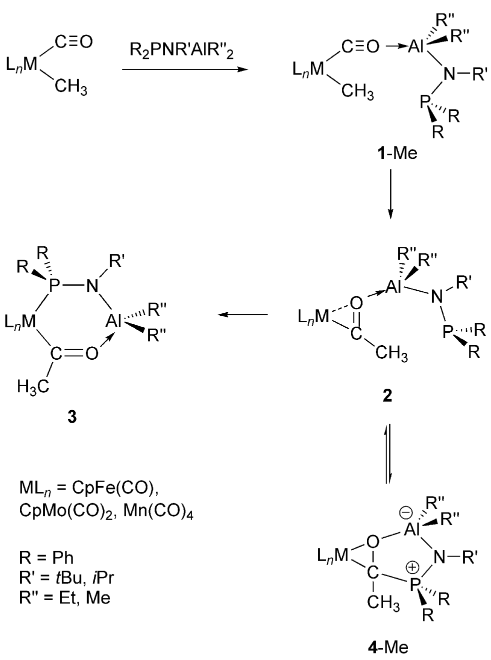
This review will describe the various synthetic routes available to coordinate ambiphilic ligands onto a metal centre, where donor groups are neutral L_n ligands. By limiting the scope of our review to these moieties, we have omitted a large array of ambiphilic ligands whose donor groups have an anionic character (X), even if they are related to the discussion that follows. However, we would like to acknowledge and cite some leading references on topics that have been put aside deliberately. These include principally, but not exclusively, the work on:·ferrocenylboranes (and other related compounds) and the study of the M–B interaction in these complexes;[12] group IV metallocenylboranes and the study of zwitterionic complexes in Ziegler–Natta polymerization;[13] the hydroboration of olefin-containing metallocenes;[14] the electrophilic attack of dienes and alkyl groups by Lewis acids;[15] boryls, borylenes and other metal-bonded boron species;[16] some bidentate Lewis acids;[17] multimetallic species containing bridging boronates.[18]

Coordination of Base-Free Amphoteric Ligands

Bulky Amphoteric Ligands

Several amphoteric molecules containing both group XIII and group XV moieties have been reported in the literature, but most of them exhibit strong intra- or intermolecular interactions limiting the availability of both Lewis basic and acid functionalities. The thermodynamic properties of these adducts are highly dependent on the nature of the substituents on both the Lewis acid and the Lewis base, but it is difficult to discern any trend on the stability of the adducts on the basis of the nature of the Lewis acid or the Lewis base.[19] The most common strategy for breaking up the aggregate relies on using bulky substituents on the donor group, on the Lewis acid group or on the linker. The steric hindrance will create “frustrated pairs,” a term introduced by Stephan,[6] which prevents self-aggregation, frees up both active sites and allows the coordination of the ligand to a transition metal. In all of the examples reported in this section where the donor–acceptor pairs bind transition metals without the aid of base-stabilization, some intra- or intermolecular interaction is present; however, the equilibrium between the aggregate and the free form shifts towards the latter species and drives the coordination to completion.

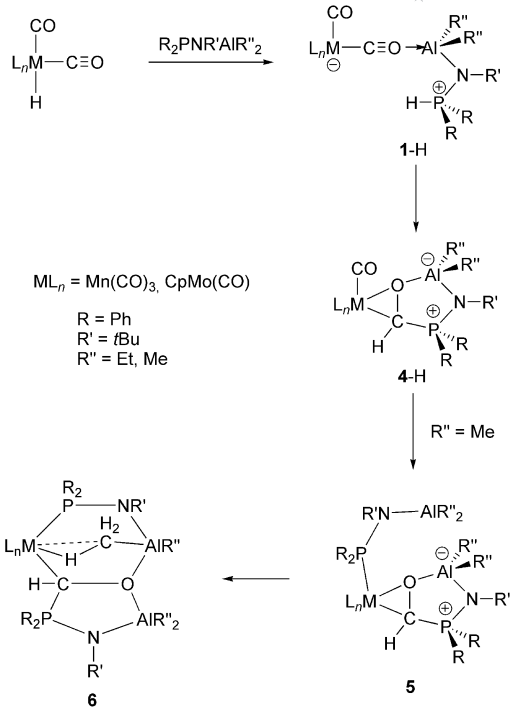
Labinger has observed that the coordination rate of an aluminoaminophosphane $R_2PNR'AlR''_2$ (R = Me, Ph; R′ = *i*Pr, *t*Bu; R′′ = Me, Et) is highly dependent on the dissociation rate of the aggregate and relies mainly on the steric bulk of the substituents.[20] According to the mechanistic evidence, the dissociation of the aggregate is imperative for the Lewis acid moiety to interact with a transition-metal–carbonyl species, such as $[CpFe(CO)_2Me]$, $[CpMo(CO)_3Me]$ and $[MeMn(CO)_5]$,[20–21] to yield adducts such as **1**-Me in Scheme 1. As it has been observed with the addition of various Lewis acids to carbonyl species,[22] the aluminium–oxygen adduct weakens the metal–ligand bond and makes the carbonyl moiety more electrophilic, leading to the 1,1 insertion to give η^2-acyl complex **2**. Once the acyl group is formed, the phosphane group of the amphoteric ligand will fill the free coordination site to form the six-membered metallacycle, **3**, which is the thermodynamic product, as observed by NMR spectroscopy. While it was not possible to characterize **3** by X-ray diffraction studies, the isolation and solid-state characterization of compound **4**-Me, the kinetic product, supports the hypothesis that the Lewis acid component of the ambiphilic ligand interacts initially with the carbonyl oxygen atom, since the chelated ligand can favour the nucleophilic attack of the phosphane on the acyl group, a reaction that does not occur in absence of a Lewis acid.



Scheme 1. Reaction of aluminoaminophosphanes with alkyl–carbonyl–metal species.

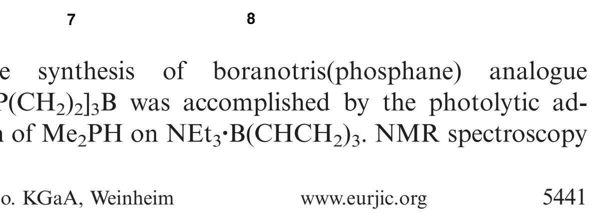
The reaction between the aluminoaminophosphane and $[HMn(CO)_5]$ did lead to the crystallization of **4**-H, which is analogous to **4**-Me (Scheme 2).[23–24] However, as can be expected, the kinetic studies were not consistent with an unfavoured 1,1 hydride insertion into a carbonyl ligand. It was proposed that the first step, a Lewis acid coordination onto the carbonyl ligand, can make the metal hydride acidic enough for deprotonation by a phosphane to occur and form **1**-H, which is supported by the presence of a P–H bond with a coupling constant of J_{P-H} = 500 Hz. Unfortunately, no hypothesis on the mechanism of formation of **4**-H, where an insertion of the P–H bond into the CO occurs, was proposed. While the ethylaluminophosphane species is stable, the methylaluminophosphane was shown to react further. The donor moiety of the ambiphilic ligand can displace one carbonyl group to form **5** first, before yielding complex **6**, where the Lewis acid interacts with the oxygen atom of the formyl intermediate. The characterization of **6** by X-ray crystallography confirmed the connectivity of this complex heterocycle, which includes one agostic interaction.

Bourissou synthesized a number of boranes having one or more bulky phosphanes in the *ortho* position of an aromatic spacer. Even in the presence of a rigid framework, the compounds $[o\text{-}(i\mathrm{Pr}_2\mathrm{P})\mathrm{C}_6\mathrm{H}_4]_2\mathrm{BPh}$ and $[o\text{-}(i\mathrm{Pr}_2\mathrm{P})\mathrm{C}_6\mathrm{H}_4]_3\mathrm{B}$ have phosphorus–boron intramolecular interactions in the solid state and in solution, as observed by low-temperature ^{31}P and ^{11}B NMR spectroscopy.[25] However, at ambient temperature, the open and closed forms are in rapid equilibrium, which allows the donor groups to bind transition-metal centres first.

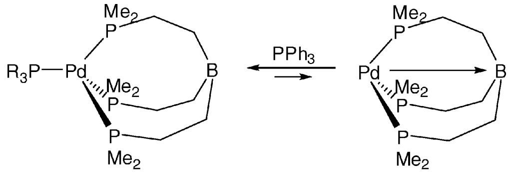


Scheme 2. Reaction of aluminoaminophosphanes with carbonyl–hydride–metal species.

When $[o\text{-}(i\mathrm{Pr}_2\mathrm{P})\mathrm{C}_6\mathrm{H}_4]_3\mathrm{B}$ reacts with $\mathrm{AuCl(SMe_2)}$ or $\mathrm{Pt}(\mathrm{P}t\mathrm{Bu}_3)_2$, ligand exchange occurs to yield complexes $[\{\kappa^4\text{-}[o\text{-}(i\mathrm{Pr}_2\mathrm{P})\mathrm{C}_6\mathrm{H}_4]_3\mathrm{B}\}\mathrm{AuCl}]$ (**7**) or $[\{\kappa^4\text{-}[o\text{-}(i\mathrm{Pr}_2\mathrm{P})\mathrm{C}_6\mathrm{H}_4]_3\mathrm{B}\}\mathrm{Pt}]$ (**8**), respectively, where the three phosphane moieties and the boron acceptor bind the metal centre with C_3 symmetry.[26] Complex **7** adopts a trigonal-bipyramidal geometry, where one of the axial positions is occupied by a boron atom. The short Au–B bond length of 2.318(8) Å, the pyramidalization of the boron (ΣB_α = 339.3°) and the upfield ^{11}B NMR chemical shift (δ = 27.7 ppm), as compared to the 60–80 ppm range usually observed for triarylboranes, are good indications of a Au→B dative interaction. Similar evidence is noted for **8**, which adopts trigonal-pyramidal geometry. However, the shorter M–B bond length [2.224(4) Å] and the upfield ^{11}B NMR chemical shift (δ = 18.2 ppm) are indicative of a stronger interaction with platinum than with gold. In both cases, the P–C–C–B plane is not perpendicular to the plane containing the transition metal and the phosphanes, which prevents C_{3v} symmetry.



The synthesis of boranotris(phosphane) analogue $[\mathrm{Me_2P(CH_2)_2}]_3\mathrm{B}$ was accomplished by the photolytic addition of $\mathrm{Me_2PH}$ on $\mathrm{NEt_3{\cdot}B(CHCH_2)_3}$. NMR spectroscopy indicates that both intra- and intermolecular interactions are observed between boron and phosphorus atoms. Addition of this ambiphilic ligand onto $Pd(PPh_3)_4$ leads primarily to complex **9**. No solid state characterization was possible, but a broad resonance for the PPh_3 signal in the $^{31}P\{^1H\}$ spectrum and computational data suggest that an equilibrium is established between complex **9** and the phosphane-free analogue $[\{\kappa^4\text{-}[Me_2P(CH_2)_2]_3B\}Pd]$ (Scheme 3).[27]



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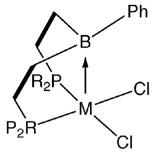
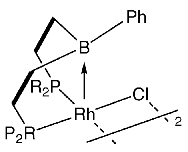
Scheme 3. Boranotriphosphane complexes of palladium.

A large variety of complexes containing the boranobis(phosphane) ligand $[o\text{-}(R_2P)C_6H_4]_2BPh$ (R = *i*Pr or Ph) were also reported by Bourissou. Ligand exchange from precursors $M(cod)Cl_2$ (M = Pt and Pd) and $[RhCl(nbd)]_2$ gave compounds **10**, **11**[28] and **12**,[29] respectively. As observed with boranotris(phosphane) complexes **7** and **8**, the phosphane buttresses of the amphoteric ligand can induce the formation of a M→B dative interaction. For the d^8 transition metals, close to perfect planarity is observed for the plane containing the transition metal and the donor ligands ($\Sigma Pt_\alpha = 360.3°$ for **10**, $\Sigma Pd_\alpha = 360.1°$ for **11** and $\Sigma Rh_\alpha = 359.8°$ for **12**). The platinum and rhodium complexes have a significant M→B interaction, as demonstrated structurally by the short distance between the atoms [Rh–B = 2.306(3) Å for **12** and Pt–B = 2.429(3) Å for **10**] and the pyramidalization of the boron atom ($\Sigma B_\alpha = 338.8°$ for **12** and 346.6° for **10**). The Rh→B interaction can even withstand the presence of dmap; by adding this Lewis base to complex **12** the isolation of **13** is observed, while the coordination of the Lewis acid on the metal centre is not affected. The σ-acid interaction is, however, much weaker with the palladium(II) species, as demonstrated notably by the fact that the summation of the angles around boron is close to planarity ($\Sigma B_\alpha = 354.9°$) and that the Pd–B distance is longer than the Pt–B distance in **10** by more than 0.2 Å. Quite surprisingly, the boranobis(phosphane) ligand can also adopt a *trans* geometry when coordinated to precursor $[Rh(\mu\text{-}Cl)(CO)_2]_2$, as observed in the solid-state structure of **14**.[28] The carbonyl stretching frequency in the latter complex at 2001.8 cm^{-1}, relative to 1966.7 cm^{-1} for *trans*-$[RhCl(CO)(iPr_2PPh)_2]$, is an indication that the M→B dative interaction withdraws significant electron density from the metal centre. Compound **15**, synthesized from precursor $AuCl(SMe_2)$, has a square-planar geometry, which is confirmed by the fact that the sum of the angles around Au is approximately 360° ($\Sigma Au_\alpha = 362.2°$ for R = *i*Pr and 364.2° for R = Ph).[30] In addition to the coordination of two phosphanes from the ambiphilic ligand to the metal centre, one Au→B dative interaction is observed [Au–B = 2.309(8) Å for R = *i*Pr and 2.335(5) Å for R = Ph]. A more detailed analysis on the nature of the M→B interaction in this complex will be discussed in a further section.



R = *i*Pr

M = Pt (**10**), Pd (**11**)



R = *i*Pr

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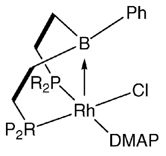
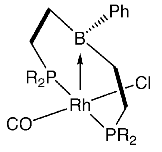


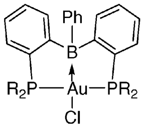
R = *i*Pr

13



R = *i*Pr

14



R = *i*Pr, Ph

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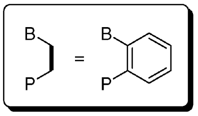
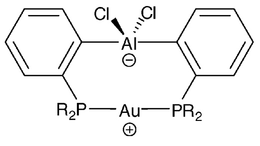


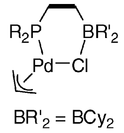
The coordination of aluminobis(phosphane) $[o\text{-}(iPr_2P)\text{-}C_6H_4]_2AlCl$, which has two P→Al interactions, to precursor $AuCl(SMe_2)$ is possible.[31] Isolation of **16** reveals that the ambiphilic aluminium ligand favours the ionization of the metal centre by chloride abstraction rather than coordination of the Lewis acid onto the metal centre itself, contrary to what was observed with the boron analogue. The distances between Au and the chlorides are over 3.04 Å, which is too long to be considered a bond. A more detailed analysis of **16** by DFT indicates that the ionization of the chloride by the Lewis acid is favoured over an Al–Au interaction by about 8 kcal/mol, which is the inverse tendency relative to that observed with boranes, where adducts are favoured by more than 10 kcal/mol. The greater Au–Cl bond strength and the weakness of the Au→Al dative interaction are the reasons.



R = *i*Pr

16

Boranomonophosphanes have been used to some extent in coordination chemistry. The synthesis of $[o\text{-}(iPr_2P)C_6H_4]\text{-}BR_2$ (R_2 = Cy_2 and Flu) has been reported by Bourissou, and spectroscopic evidence shows them to be monomeric in solution.[32] The coordination of these species on Pd^{II} and Au^{I} metal centres afforded **17** and **18**, respectively. In the former complex, the Lewis acid moiety interacts with the chloride, as indicated by the short B–Cl distance of 2.165(2) Å, but this interaction does not lead to ionization. With the more nucleophilic Au^{I}, instead of an interaction with a ligand within the coordination sphere, the boron atom has a close contact with the metal centre. As expected, the more electrophilic fluorenyl derivative, $[\{\kappa^2\text{-}[o\text{-}(iPr_2P)\text{-}C_6H_4]BFlu\}AuCl]$, possesses a shorter Au–B bond length [2.663(8) Å] than the bis(cyclohexyl) analogue, $[\{\kappa^2\text{-}[o\text{-}(iPr_2P)C_6H_4]BCy_2\}AuCl]$ (2.90 Å). The negligible pyramidalization at the boron atom ($\Sigma B_\alpha = 355.8°$) and the shorter Au–B bond length of **18** compared to those of boranotris(phosphane) and boranobis(phosphane) analogues **7** and **15**, respectively, are experimental evidence of a much weaker interaction when only one phosphane buttress is involved in the stabilization of the Au→B interaction. Nevertheless, DFT calculations confirm the presence of a Lewis adduct with gold(I).



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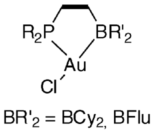

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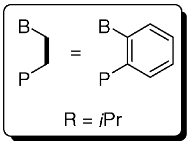
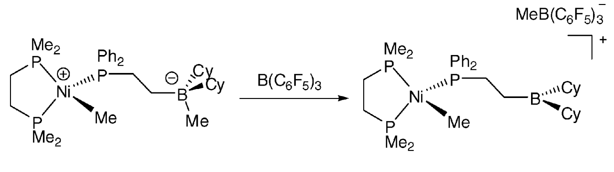


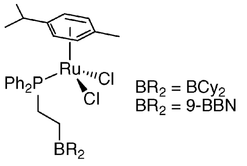
Aliphatic analogues $Ph_2P(CH_2)_2BR_2$ ($R_2 = Cy_2$ and bbn) were obtained by the hydroboration of vinyldiphenylphosphane with the corresponding hydroboranes, as reported in back-to-back communications by Tilley,[33] by Sabo-Etienne and Bourissou[34] and recently by Muhoro.[35] The solid-state characterization of the amphoteric ligand $Ph_2P(CH_2)_2B(bbn)$ shows the presence of a weak intermolecular Lewis adduct [P···B = 2.056(2) Å].[33] While the broadening resonances in the ^{11}B and ^{31}P NMR spectra at –80 °C are indicative of aggregation of the ambiphilic ligands in solution, it was also observed that the monomeric form is predominant at room temperature.[33–34] The addition of $Ph_2P(CH_2)_2BR_2$ to $(dmpe)NiMe_2$ leads to the formation of zwitterionic species **19**, which was characterized by X-ray diffraction studies (Scheme 4). The coordination of the phosphane moiety onto nickel and the abstraction of the alkyl group by the borane provide evidence for the ambiphilic behaviour of the ligand. The boron-bound methyl group on **19** seems to be more nucleophilic than the nickel-bound one, since the addition of $B(C_6F_5)_3$ leads to methyl exchange between the boranes to form cationic species **20**, without any evidence of subsequent interaction between the ambiphilic ligand and the metal complex.[33]



19 **20**

Scheme 4. Formation of ambiphilic complex **19** and its reactivity with $B(C_6F_5)_3$.

It is also possible to coordinate $Ph_2P(CH_2)_2BR_2$ by displacing the bridging chloride in the starting precursor [(*p*-cymene)$RuCl_2]_2$ to give ambiphilic complex **21**.[34] Whereas the borane moiety of this boranophosphane ligand can ionize the nickel centre to form **19**,[33] it is surprising that no boron–chloride interaction was observed with **21**, neither in solution, nor in the solid state, especially since the coordination of (2-picolyl)BCy_2 to the same ruthenium(II) precursor affords compound **22** in which a boron–chloride interaction is present, as observed by the short B–Cl distance [2.103(9) Å].[36] In order to induce ionization of **21**, silver salts were used (Scheme 5). When the Ag^I salt, with weakly coordinating anion BF_4^-, was added in acetonitrile, cationic compound **23** was observed; however, the more basic silver acetate induced B–C bond cleavage and the formation of four-membered metallacycle **24**, which can reform **21** upon addition of one equivalent of $ClBCy_2$.[34]



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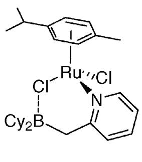

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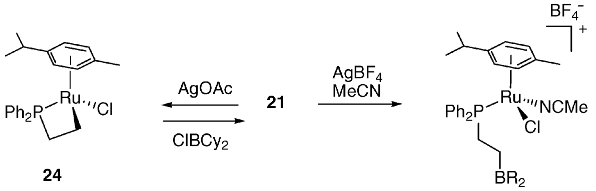
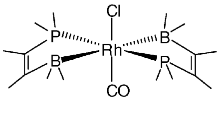


24 **23**

Scheme 5. Reactivity of complex **21**.

Grobe reported the synthesis of vinyl boranophosphane $Ph_2PC(Me)=C(Me)BMe_2$ and its reactions with [Rh(μ-Cl)$(CO)_2]_2$ and [Cp*Rh$(CO)_2$].[27] With the former starting material, compound **25** was isolated and characterized structurally. Notable are the Rh–B distances that average 2.955 Å, which is considerably longer than that observed in complex **12** [2.306(3) Å] with the ambiphilic boranobis(phosphane) ligand. With the cyclopentadienyl precursor, complexes **26** and **27** were reported, but they were only characterized by NMR spectroscopy. It is proposed, however, that, in the case of **26**, an interaction between the carbonyl ligand and the boron centre takes place.



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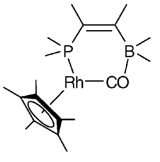

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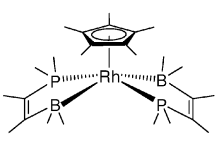

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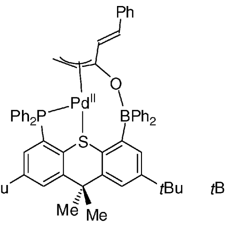
The synthesis of a boranophosphane amphoteric ligand with a thioxanthene framework was performed by Emslie.[37] The rigid structure helps preventing the formation of intra- and intermolecular Lewis adducts, without affecting the propensity of the ligand to coordinate transition metals. Upon addition of this ambiphilic ligand to [$Pd_2(dba)_3$], the complexation of the palladium to the two donor moieties occurs to form complex **28**, in which one of the dba ligands remains bound to the metal centre. Interestingly, the Lewis acid plays an important role in coordinating the ketone moiety of dba to yield a zwitterionic palladium(II) alkoxyboratoallyl complex, as confirmed by one short C–C bond and one elongated C=C bond in the palladium-bound benzylidene fragment.[37] This ambiphilic framework was also used to coordinate onto a Rh^I precursor, $[RhCl(CO)_2]_2$, to yield complex **29**.[38] In this square-planar complex, the ambiphilic ligand is P,S-coordinated, and the chloride ligand bridges the rhodium and boron atoms. Elegantly, the chloride can be displaced by the nucleophilic metal anion $K[CpFe(CO)_2]$ to form dimetallic species **30**.[38] DFT calculations and X-ray diffraction studies support the presence of a weak interaction between the boron and rhodium centres in the form of a boratabenzyl fragment [Rh–B = 2.62(2) Å], in which one of the aryl groups on the boron acts as a benzyl source.



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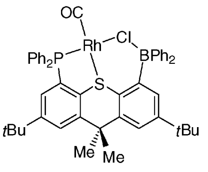

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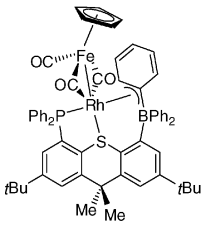

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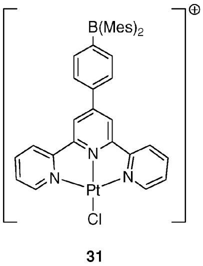
Some ambiphilic ligands having bulky Mes_2BR moieties and pyridine derivatives as donor groups have been synthesized recently in order to probe the photophysical properties of the ligands upon metal coordination. The mesityl substituents on boron are large enough to prevent aggregates from forming. Using a Suzuki–Miyaura coupling, Kitumara et al. have synthesized a terpyridine ligand bearing the triarylborane and have coordinated it on $Pt(cod)Cl_2$ to obtain **31**.[39] The latter compound exhibits an interesting electronic communication between the metal and the boron atoms. The enhanced emission of complex **31** relative to the analogue without the Lewis acid is probably due to a greater transition dipole moment. Using a similar synthetic strategy, Wang reported two new families of compounds having ambiphilic ligands exhibiting anion binding properties (complex **32**)[40] and enhanced metal-to-ligand-charge-transfer phosphorescence (complex **33**).[41]



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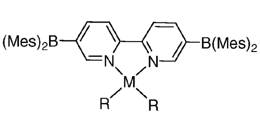
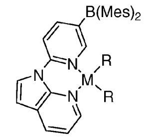


M = $[Cu]BF_4$, R = PPh_3
M = Pt, R = Ph, Me

32



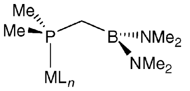
M = $[Cu]BF_4$, R = PPh_3
M = Pt, R = Ph, Cl

33

Weakly Lewis Acidic Ambiphilic Ligands

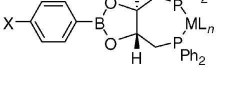
Most of the ambiphilic ligands reported in the former section have alkyl- or arylboranes without π-donating substituents (with the exception of Labinger's work). It is well known that the acidity on the boron and aluminium atoms will be greatly reduced by the presence of alkoxide or amido groups on the boron or aluminium atom. This is expected to have the effect of limiting the propensity of these ambiphilic ligands to aggregate and will favour the coordination of the basic moieties on the metal centre.

Using this type of strategy, Braunschweig reported the synthesis of a boranoaminophosphane, $Me_2PCH_2B(NMe_2)_2$, one of the few boranophosphanes that does not form Lewis acid–base adducts with itself.[42] The coordination of this ligand to $[Co(CO)_5(thf)]$, $[(MeC_5H_4)Mn(CO)_2(thf)]$ and $[Fe_2(CO)_9]$ gave compounds **34**, **35** and **36**, respectively. In these species, the chemical shift of the borane moieties was unaffected by coordination, and ^{11}B NMR chemical shifts remained close to those of the starting materials. Interestingly, it was possible to modify the nature of the Lewis acid by post-functionalization of the borane moiety. When MeOH, HCl or $LiAlH_4$ was added to iron complex **36**, the methoxyborane, chloroborane or hydroborane ambiphilic complex, respectively, was obtained. Complex **36** was even found to oxidatively add across the Si–H bond of triphenylsilane to give the silyl hydride iron(II) complex.



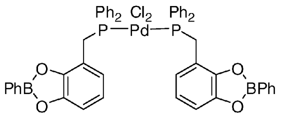
ML_n = $Cr(CO)_5$ (**34**),
$(MeC_5H_4)Mn(CO)_2$ (**35**), $Fe(CO)_4$ (**36**)

The weak acidity of boronic esters also allows the synthesis of ambiphilic boranophosphane ligands that do not aggregate. Two research groups reported back-to-back syntheses of an optically active phenylboronic ester bis(phosphane) analogous to the bis(phosphane) diop.[43,44] This ambiphilic ligand was coordinated to Rh^I by ligand exchange from $[(cod)RhCl]_2$[43,44] and to Pd^{II} by using $[PdCl_2L_2]$ [$L_2 = (CH_3CN)_2$ or cod][44] to yield complexes **37** to **39**. The binding constants between these complexes and alkeneamines were measured in order to probe for cooperative behaviour. The general hypothesis was that the amine would interact with the hard boronic ester, whereas the alkene would interact with the soft acid, which is the transition metal.[44] A cooperative behaviour between the Lewis acid and rhodium was observed for **37**, but no significant effect was observed with the palladium and platinum analogues. Attempts to perform the asymmetric catalytic hydrogenation of *N*-acetyldehydrophenylalanine and the hydrosilylation of ketones by using **37** as catalyst gave disappointing results, since this reaction yielded lower enantioselectivity and stereoselectivity than that with the Rh–diop complexes, which do not bear the acid part.[43] By a similar strategy, the synthesis of a *cis* and *trans* mixture of palladium complex **40**, containing a phosphanyl-substituted benzodioxaborol ambiphilic ligand, was published recently. The formation of the boronic ester functionality on the am-



ML_n = $[Rh(COD)]ClO_4$ (**37**)
X = H, Cl, CF_3

ML_n = $PdCl_2$ (**38**), $PtCl_2$ (**39**)
X = Cl, CF_3



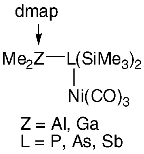
40

biphilic ligand, starting from the corresponding diol, is possible prior to or after phosphane coordination on palladium.[45]

Base-Stabilized Ambiphilic Ligands

In some instances, the bond strength of the aggregate is too strong to allow the coordination of either the Lewis acidic or the basic site of the ambiphilic ligand to a transition metal. One of the strategies used to overcome such a limitation is the addition of an external Lewis base to break down the aggregate and make available the donor group for metal coordination. By choosing a labile Lewis base or by trapping it once the ambiphilic ligand is bound to the transition metal, it is possible to take advantage of the Lewis acid for further reactivity.

For example, it is possible to bind dmap to the Lewis acid to prevent the aggregation of amphoteric species $Me_2ZL(SiMe_3)_2$ (Z = Al, Ga; L = P, As). In turn, the donor group of the ambiphilic ligand can be coordinated onto transition metals. Compounds **41**, **42** and **43** were synthesized by ligand exchange from $[Ni(CO)_4]$,[46,47] $[Fe_3(CO)_{12}]$[47] and $[Cr(CO)_5(NMe_3)]$,[47] respectively. In all these complexes, the ambiphilic ligand can be considered as a bulky phosphane. However, crystallographic and spectroscopic studies revealed the ligand to be weakly π-accepting, the nature of the Lewis acid playing only a marginal role in its electronic properties.



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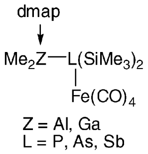

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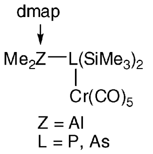

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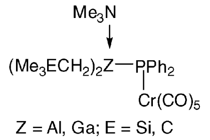
Beachley et al. reported in 1983 that the amphoteric ligand $Ph_2PAl(CH_2SiMe_3)_2$ reacted with $[Cr(CO)_5(NEt_3)]$, yielding $[Cr(CO)_5\{PPh_2Al(CH_2SiMe_3)_2{\cdot}NEt_3\}]$ (**44**), in which the displaced amine ligand stabilizes the Lewis acid.[48] However, this proved to be a limited strategy, since related starting materials, such as $[Cr(CO)_6]$, $[Cr(CO)_5(thf)]$ and $[Cr(CO)_5(CH_3CN)]$, either did not react with the aluminophosphane or decomposed in its presence. Only $Ph_2PAl(CH_2CMe_3)_2$ was found to exhibit the same behaviour as the original ambiphilic ligand.[49] The nitrogen–aluminium bond in these complexes was revealed to be impressively strong, since the addition of 3 equiv. of HBr led to the cleavage of the relatively weak Al–P bond to form $[Cr(CO)_5(PPh_2H)]$, while keeping intact the Al–N interaction to form Br_3AlNMe_3. $[Cr(CO)_5\{PPh_2Al(CH_2SiMe_3)_2{\cdot}NEt_3\}]$ was found to react over time with thf to yield $[Cr(CO)_5\{PPh_2(CH_2)_4OAl(CH_2SiMe_3)_2\}]$ (**45**), where one equivalent of thf is activated.[50] Interestingly, compound **45** and analogues $[Cr(CO)_5\{PPh_2(CH_2)_4OAl(R)_2\}]$ (R = CH_2SiMe_3, Me, Et and Br) can be synthesized independently from $[Cr(CO)_5(PPh_2K){\cdot}n(dioxane)]$ in the presence of $BrAlR_2$.



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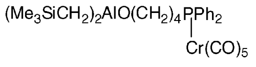

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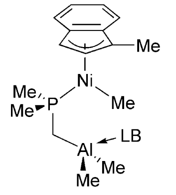
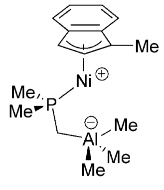
The ambiphilic ligand $(Me_2PCH_2AlMe_2)_2$, first reported by Karsch in 1985,[51] forms a six-membered ring dimer both in solution and in the solid state, as observed by NMR spectroscopy and X-ray diffraction studies. In the presence of a Lewis base (LB), it is possible, however, to break the cyclic dimer to form the monomeric $Me_2PCH_2AlMe_2{\cdot}LB$. If the Lewis base is not too nucleophilic, such as NEt_3 or thf, an equilibrium between the mono- and dimeric forms is established, and the Lewis acid moiety can be available once the phosphane is coordinated to a transition-metal centre. It was demonstrated spectroscopically that the addition of 4 equiv. of NEt_3 to a solution of $(Me_2PCH_2AlMe_2)_2$ and (1-MeInd)Ni(PPh_3)Me gave complex (1-MeInd)Ni($Me_2PCH_2AlMe_2{\cdot}NEt_3$)Me (**46**·$NEt_3$) by associative substitution of the less donating phosphane PPh_3.[52] Complex **46**·NEt_3 was found to be more than two orders of magnitude more active than [(1-MeInd)Ni(PPh_3)Me] in the dehydropolymerization of phenylsilane.[52,53] Substitution of the NEt_3 by more nucleophilic quinuclidine gives **46**·quinuclidine, where the highly donating amine binds the Lewis acid irreversibly. The resulting complex was found to be no more active than (1-MeInd)Ni(PMe_3)Me, where no ambiphilic ligand is present.[52] Although the exact role of the ambiphilic ligand is not known, it was proposed that the constrained geometry imposed by the tether was favouring the formation of zwitterionic species such as **47**, whereas the usual Lewis acids, such as $AlMe_3$, instead formed adducts in the style of **48**, in which the sites where the incoming substrates usually bind are occupied. Indeed, the addition of $AlMe_3$ to (1-MeInd)Ni(PMe_3)Me was found to inhibit phenylsilane dehydropolymerization.[52]



46·LB



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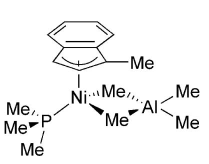

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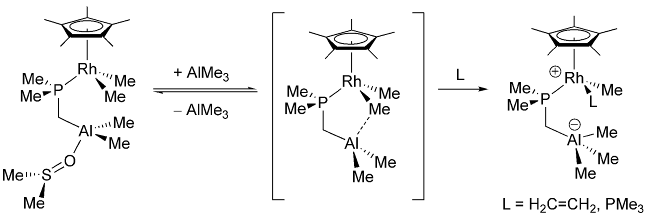
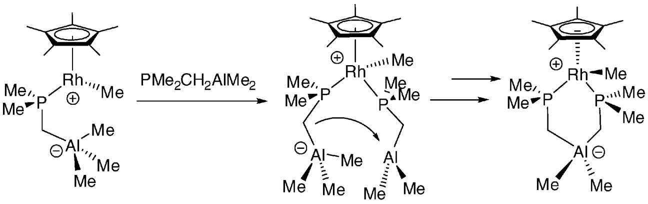
More information on the role of $Me_2PCH_2AlMe_2$ was obtained by examining the coordination chemistry of the ambiphilic ligand on rhodium(III) complexes. Using a strategy reminiscent of the first report by Beachley, the Lewis acid fragment of the dimeric species $(Me_2PCH_2AlMe_2)_2$ interacts first with the oxygen atom of the sulfoxide group on Cp*$RhMe_2$(dmso) to form adduct Cp*$RhMe_2$($Me_2PCH_2AlMe_2{\cdot}$dmso) (**49**), as confirmed by NMR spectroscopy.[54] In the latter complex, the dimethyl sulfoxide is tightly bound to the aluminium centre, and the reactivity observed resembles that of the analogous dimethyl complex Cp*Rh(PMe_3)Me_2. However, the addition of one equivalent of $AlMe_3$ gives a fast equilibrium between **49** and **50**, after the added $AlMe_3$ forms an adduct with dmso. Even at –80 °C, the exchange rates are too fast to characterize the base-free complex by NMR spectroscopy; however, circumstantial evidence gives a strong indication that ionization at the metal centre occurs. Indeed, upon addition of neutral ligands such as ethylene[55] or trimethylphosphane,[54] it is possible to trap zwitterionic species **51**, as shown in Scheme 6.



49 **50** **51**

Scheme 6. Trapping of zwitterionic species **51**.

While species **49** to **51** were only characterized by using various NMR spectroscopic experiments, two new structurally characterized complexes, **52** and **53**, give strong support to the proposition that the ambiphilic ligand ionizes the rhodium centre.[54] As shown in Scheme 7, the addition of one more equivalent of $Me_2PCH_2AlMe_2$ gave zwitterionic species **52**. It is presumed that an additional equivalent of the aluminophosphane ligand coordinates the zwitterionic metal centre, which promotes the attack of the methylene moiety of the aluminate on the free Lewis acid, leading to the elimination of one equivalent of $AlMe_3$ and to the formation of the metallacycle. Similarly, when species **50** is heated or kept for several days at room temperature, species **53** can be isolated (Scheme 8). In this case, however, the methylene group of the aluminate moieties attacks a zwitterionic complex in an intermolecular manner, leading to dimerization and to the formation of metallacycle **53**.



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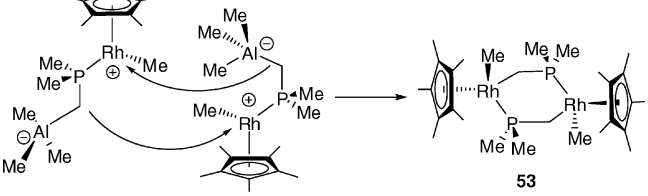
Scheme 7. Proposed mechanism for the formation of **52**.



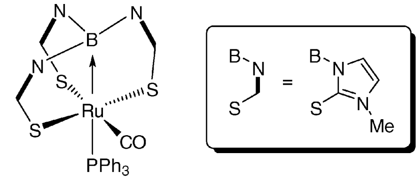
53

Scheme 8. Proposed mechanism for the formation of **53**.

Modification of Bound Moieties

B–H Activation on Hydrotris(methimazolyl)borate Ligands

The hydrotris(methimazolyl)borate ligand $[HB(mim^R)_3^-$ = Tm] is a soft and flexible analogue of the well-known hydrotris(pyrazolyl)borate ligand (Tp).[56] The Tm ligand cannot be considered an ambiphilic or an amphoteric ligand, since there is a tetravalent boronate moiety, which makes the Lewis acid unavailable for an interaction with the metal centre. However, in 1999, Hill reported an unusual reaction where a Tm ligand undergoes B–H activation to form a metallaboratrane complex, $[\{\kappa^4\text{-}B(mim^{Me})_3\}Ru(CO)(PPh_3)]$ (**54**).[57] In this ruthenium complex, which possesses a pseudo-octahedral geometry, the methimazolyl moieties bind the transition metal in a *mer* arrangement, and the trivalent boron interacts with the ruthenium atom *trans* to a phosphane. This was the first report of an unambiguous dative bond between a transition metal and trivalent boron; therefore, once bound and activated, $B(mt)_3$ fits the description of an amphoteric and ambiphilic neutral ligand.



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Since this early report, metalloboratrane complexes having this common ligand have been reported for all members of the Fe, Co and Ni triads, as enumerated in Table 1. The possible geometries for metallaboratranes are illustrated in Figure 2. Most complexes (**55**–**61**, **63**–**66**, **68**–**77**, **82**, **90**–**95**) adopt a pseudooctahedral geometry with a κ^4-tris(methimazolyl)borane (κ^4-oct), but few species (**78**–**81**)[65,68] can have the σ-acid ligand linked by two mim buttresses, as a κ^3-bis(methimazolyl)borane framework (κ^3-oct). A trigonal-bipyramidal geometry (κ^4-pyr) was observed with Co (**62**),[62] Ni (**83**–**86**),[69–70] Pd (**87**)[71] and Pt (**89**)[72–73] complexes that can be described as having a d^9 and d^{10} electronic configuration if the borane interaction is considered to be dative. However, this supposition has led to some debate (vide infra). Each palladium centre in complex **88** possess a four-coordinate geometry (μ-κ,κ^3), in which two mim moieties of one ligand bind in a highly distorted *trans* fashion (S^1–Pd–S^2 = 154.71°), and the boron atom from the same tris(methimazolyl)borane and one mim from another ligand are orthogonal (S^3–Pd–B 178.38°). The Pd–S^3 bond from the lone fragment of the ligand bridging the two metallic fragments is significantly longer than the other Pd–S bonds from the chelating $\{\kappa^3\text{-}B,S,S'\text{-}B(mim^{Me})_3\}$ fragment (Pd–S^3 is 2.576 Å compared to an average of 2.341 Å for Pd–S^1 and Pd–S^2).

In complex **67**, one tris(methimazolyl)borane ligand is involved in what is a formal μ-κ^2 S,S′,κ^4 coordination, in which two of the sulfur atoms bridge two rhodium centres,

Table 1. Various metallaboratranes with a Tm framework.

Species	Geometry	Linker	M	L_{trans}	L_{cis}	R	M–B [Å]	δ(^{11}B NMR) [ppm]
55[58]	κ^4-oct	mim$^{t\text{Bu}}$	Fe	CO	CO		2.108(6)	20.3
54[57,59]	κ^4-oct	mim$^{\text{Me}}$	Ru	PPh_3	CO		2.161(5)	17.1
56[60]	κ^4-oct	mim$^{\text{Me}}$	Ru	CO	CO		N.A.	N.A.
57[60]	κ^4-oct	mim$^{\text{Me}}$	Ru	CN*t*Bu	CO		2.176(7)	14.6
58[60]	κ^4-oct	mim$^{\text{Me}}$	Ru	CNXyl	CO		N.A.	N.A.
59[60]	κ^4-oct	mim$^{\text{Me}}$	Ru	CNMes	CO		2.146(4)	N.A.
60[60]	κ^4-oct	mim$^{\text{Me}}$	Ru	PPh_3	CS		2.154(5)	N.A.
61[61]	κ^4-oct	mim$^{\text{Me}}$	Os	PPh_3	CO		2.171(8)	12.4
62[62]	κ^4-pyr	mim$^{t\text{Bu}}$	Co[a]	PPh_3			2.132(4)	N.A.
63[63]	κ^4-oct	taz	Rh	PPh_3	CO		2.155(5)	–7.5
64[64]	κ^4-oct	mim$^{\text{Me}}$	Rh	Cl	PPh_3		2.132(6); 2.122(7)[b]	1.7
65[65]	κ^4-oct	mim$^{t\text{Bu}}$	Rh	Cl	PPh_3		2.095(3)	N.R.
66[66]	κ^4-oct	mim$^{\text{Me}}$	Rh[a][d]	cod	cod		N.A.	4.1[c]
67[66]	μ-κ^2 S,S′,κ^4	mim$^{\text{Me}}$	Rh[a][e]	κ^2 Tm	κ^2 Tm		2.098(6); 2.091(5)	N.A.
68[67]	κ^4-oct	mim$^{\text{Me}}$	Rh	PPh_3	H		N.A.	2.1
69[67]	κ^4-oct	mim$^{\text{Me}}$	Rh[a]	PPh_3	CN*t*Bu		2.155(7)	9.0
70[67]	κ^4-oct	mim$^{\text{Me}}$	Rh[a]	PPh_3	CNXyl		2.146(3)	8.8
71[67]	κ^4-oct	mim$^{\text{Me}}$	Rh[a]	CNXyl	PPh_3		N.A.	8.7
72[67]	κ^4-oct	mim$^{\text{Me}}$	Rh[a]	PPh_3	CNMes		2.146(3)	–9.1
73[67]	κ^4-oct	mim$^{\text{Me}}$	Rh[a]	CNMes	PPh_3		N.A.	–2.0
74[67]	κ^4-oct	mim$^{\text{Me}}$	Rh[a]	PMe_3	PMe_3		2.153(11); 2.148(10) [b]	9.5
75[67]	κ^4-oct	mim$^{\text{Me}}$	Rh[a]	PMe_3	PPh_3		N.A.	8.8
76[67]	κ^4-oct	mim$^{\text{Me}}$	Rh[a]	PPh_3	PPh_3		N.A.	N.A.
77[67]	κ^4-oct	mim$^{\text{Me}}$	Rh	S_2CNEt_2	S_2CNEt_2		N.A.	N.A.
78[68]	κ^3-oct	mim$^{\text{Me}}$	Ir	PPh_3	CO; H	mim$^{\text{Me}}$	N.A.	3.2
79[68]	κ^3-oct	mim$^{\text{Me}}$	Ir	PPh_3	CO; H	H	2.210(5)	–4.5
80[65]	κ^3-oct	mim$^{t\text{Bu}}$	Ir	PPh_3	CO; H	mim$^{t\text{Bu}}$	2.179(4)	N.A.
81[65]	κ^3-oct	mim$^{\text{Ph}}$	Ir	PPh_3	CO; H	mim$^{\text{Ph}}$	2.186(3)	N.A.
82[65]	κ^4-oct	mim$^{t\text{Bu}}$	Ir	Cl	PPh_3		2.15(2); 2.18(2)[b]	
83[69–70]	κ^4-pyr	mim$^{t\text{Bu}}$	Ni	Cl			2.108(6); 2.110(6)	
84[70]	κ^4-pyr	mim$^{t\text{Bu}}$	Ni	N_3			2.092(5)	
85[70]	κ^4-pyr	mim$^{t\text{Bu}}$	Ni	NCS			2.079(13)	
86[70]	κ^4-pyr	mim$^{t\text{Bu}}$	Ni	OAc			2.112(3)	
87[71]	κ^4-pyr	mim$^{t\text{Bu}}$	Pd	PMe_3			2.050(8)	N.A.
88[71]	μ-κ,κ^3	mim$^{t\text{Bu}}$	Pd[e]				2.073(4)	N.A.
89[72–73]	κ^4-pyr	mim$^{\text{Me}}$	Pt	PPh_3			N.A.	1.5
90[72–73]	κ^4-oct	mim$^{\text{Me}}$	Pt[a]	PPh_3	H		2.157(4)	1.6
91[74]	κ^4-oct	mim$^{\text{Me}}$	Pt[a]	PR_3 (R = Me, Et, Tol)	H		N.A.	N.A.
92[73]	κ^4-oct	mim$^{\text{Me}}$	Pt	Cl	Cl		N.A.	0.4
93[73]	κ^4-oct	mim$^{\text{Me}}$	Pt	Br	Br		N.A.	2.1
94[73]	κ^4-oct	mim$^{\text{Me}}$	Pt	I	I		2.119(4)	5.1
95[73]	κ^4-oct	mim$^{\text{Me}}$	Pt	I	Me		2.119(4)	4.2

[a] Cationic complex. [b] Two independent molecules. [c] At –80 °C. [d] In equilibrium with trigonal-bipyramidal geometry. [e] Dimetallic species.

in addition to its usual κ^4 coordination. All of the Rh–S distances, including the bridging one, are in the same range [2.2867(15) Å to 2.3693(17) Å], with the exception of the Rh–S distances involving the two mim moieties that are *trans* to boron that are significantly longer (average 2.646 Å), indicating that the M→B interaction exerts a strong trans influence (vide infra).

The general mechanism for the formation of metallolboratranes, as initially proposed by Hill,[59] is shown in Scheme 9. Step A involves a transmetallation reaction between a hydrotris(methimazolyl)borate salt (TmM′; M′ = Li, Na, K or Tl) and a metal halide precursor containing one alkyl or hydride moiety to form an [{κ^2-*S,S′*-HB(mim)$_3$}ML$_n$(R)] intermediate. It is important to note, however, that, in some instances, the R group is introduced after the addition of the Tm ligand. As seen in step B, the dissociation of a ligand is necessary to open a coordination site, induce the formation of a B–H agostic interaction and form the intermediate [{κ^3-*H,S,S′*-HB(mim)$_3$}ML$_{n-1}$(R)]. This species has been observed in a few instances, notably when a hydride is present, such as with [{κ^3-*H,S,S′*-HB(mim$^{\text{Me}}$)$_3$}Ru(PPh$_3$)(CO)(H)],[59] since the elimination of H_2, rather than an alkane, is thermodynamically unfavoured. Finally, as observed in step C, B–H activation takes place, followed by the elimination of RH and the coordination of the additional mim moiety to give a metallaboratrane.[75] In some instances, notably during the formation of species where the M–H bond is quite strong and where no R group is present, such as in iridium complexes **78** to **81**, the reductive elimination does not occur and a *mer*-κ^3-*B,S,S′*-coordination mode is observed, in which the additional substituent on the boron atom does not interact with the metal centre.[65,68] Recently, Hill observed for the first time the reverse reaction of step C, where a B–H bond

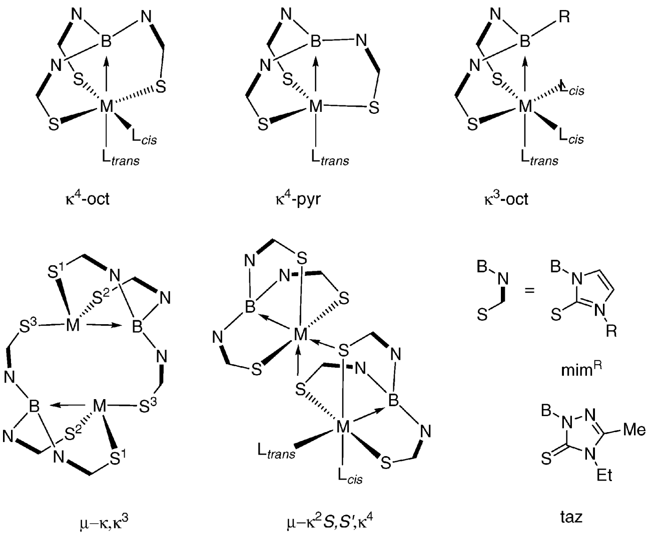
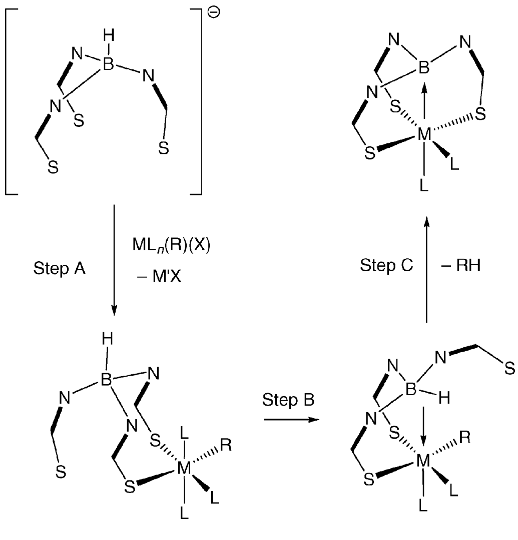
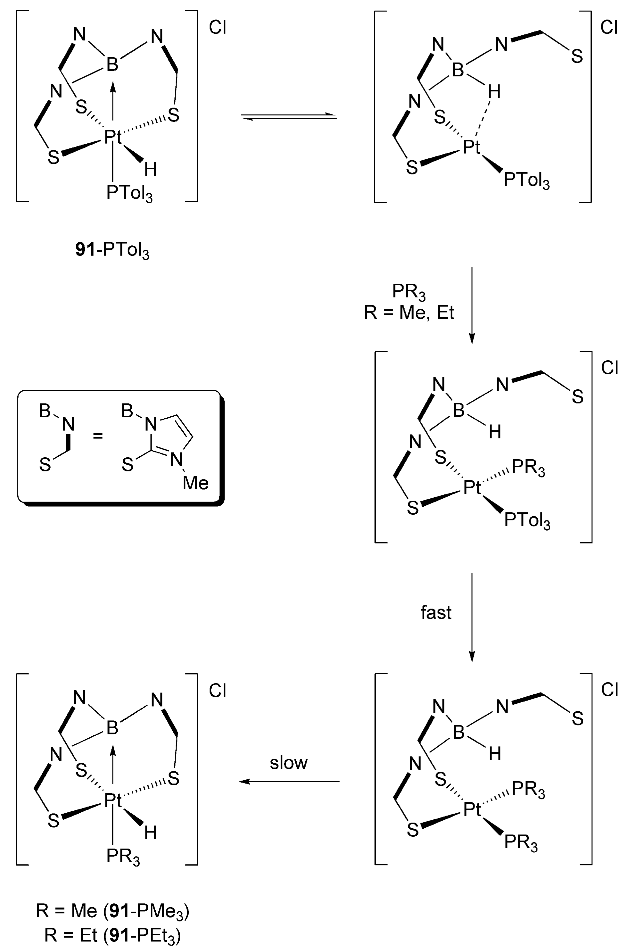


Figure 2. Coordination modes of metallaboratranes.

is formed from a metalloboratrane (Scheme 10).[74] Indeed, metalloboratrane $[\{\kappa^4\text{-B(mim}^{\text{Me}})_3\}\text{Pt(H)(P(tol)}_3)]\text{Cl}$ [**91**-P(tol)_3] with κ4-oct geometry, gave, in the presence of PMe_3 or PEt_3, square-planar complex $[\{\kappa^2\text{-}S,S'\text{-HB(mim}^{\text{Me}})_3\}\text{Pt(PR}_3)_2]$ (R = Me or Et), in which the labile P(tol)_3 is substituted for a more basic phosphane and a new B–H bond that does not interact with the metal centre is formed. The dissociation of PR_3 in this complex does not occur readily, and the formation of **91**-PMe_3 and **91**-PEt_3 is very slow. This result is in agreement with the assumption that one labile ligand needs to leave the coordination sphere in order to allow for a B–H agostic interaction to take place, which is necessary for the B–H addition to happen.



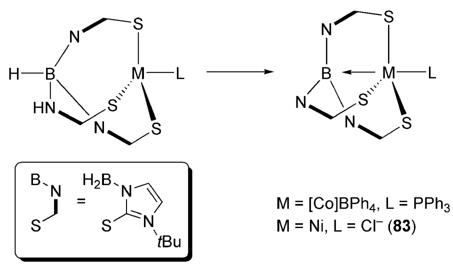
Scheme 9. General mechanism for the formation of metallaboratranes.



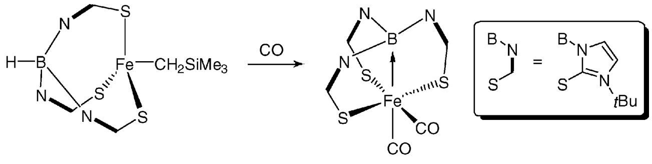
Scheme 10. Formation of a B–H bond from a metallaboratrane.

Some alternative syntheses that do not rely on the general mechanism described above were also performed, notably for the 3d transition metals. In some instances, the reduction mechanism does not necessitate the elimination of an alkane, such as in the formation of $[\{\kappa^4\text{-B(mt}^{t\text{Bu}})_3\}\text{Co(PPh}_3)](\text{BPh}_4)$ (**62**)[62] and $[\{\kappa^4\text{-B(mt}^{t\text{Bu}})_3\}\text{NiCl}]$ (**83**) (Scheme 11).[69] Indeed, in both cases, the complexes are made from a formal one-electron reduction of the respective hydrotris(methimazolyl)borate starting materials.[75] The B–H addition does not take place from bulky alkyl $[(\text{Tm}^{t\text{Bu}})\text{Fe(CH}_2\text{SiMe}_3)]$, since the iron atom is much less nucleophilic relative to its heavier analogues. As an alternative route to form the metallaboratrane, the addition of CO was done via a 1,1 insertion to form an acyl intermediate, which induced the elimination of the aldehyde $\text{Me}_3\text{SiCH}_2\text{C(O)H}$ and the formation of $[\{\kappa^4\text{-B(mt}^{t\text{Bu}})_3\}\text{Fe(CO)}_2]$ (**55**) (Scheme 12).[58] It was also possible to synthesize complex $[\{\kappa^4\text{-B(taz)}_3\}\text{Rh(CO)(PPh}_3)]$ (**63**), where taz (Figure 2) stands for thioxotriazolyl, from the two-electron oxidation of $[\{\text{HB(taz)}_3\}\text{Rh(PPh}_3)(\text{CO})]$ by using $[\text{Cp}_2\text{Fe}](\text{PF}_6)$ as oxidant.[63] Such a reaction suggests that the borane dative bond would rather act as a dianion (BR_3^{2-}) once coordinated to a transition metal, a feature that has been argued in the characterization of the M→B interaction (to be discussed in a further section).

In several cases, modification of the coordination sphere in which a $\kappa^4\text{-B(mt)}_3$ ligand is present is possible without breaking the M→B interaction. Nickel complexes **84**, **85** and **86** have been synthesized by a metathesis reaction with **83** by using the Na, K and Tl salts, respectively.[70] The li-



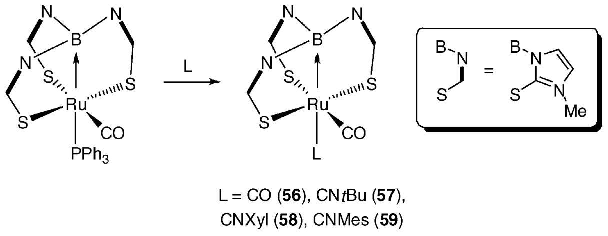
Scheme 11. Formation scheme for **62** and **83**.



55

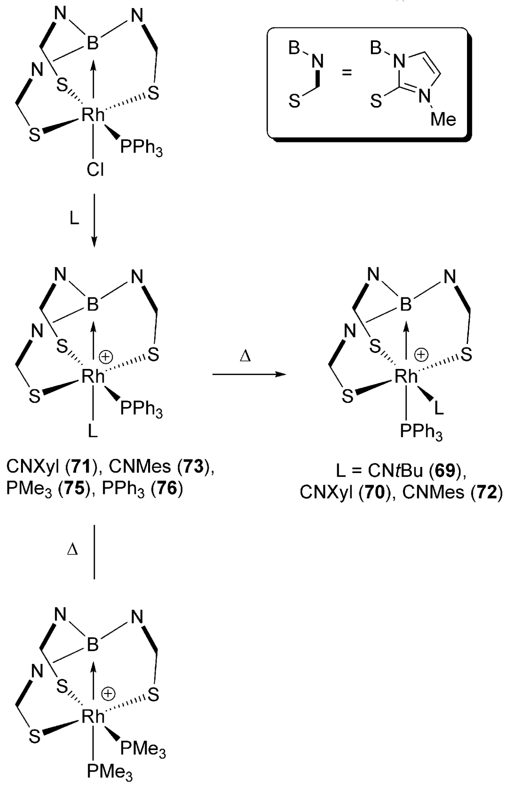
Scheme 12. Formation of **55** by elimination of $Me_3SiCH_2C(O)H$.

gand *trans* to boron was found to be quite labile in κ^4-oct metallaboratranes, which can be useful for ligand substitutions. As such, complex [{κ^4-B(mim^{Me})$_3$}Ru(CO)(PPh$_3$)] (**54**) was found to be a good starting material for a variety of complexes having π-acceptor ligands instead of the phosphane, such as in complexes **56** to **59** (Scheme 13).[60] The chloride, which is *trans* to boron in complex [{κ^4-B-(mim^{Me})$_3$}Rh(Cl)(PPh$_3$)] (**64**), readily leaves the coordination sphere in the presence of isonitriles and phosphanes to form complexes **69** to **76** (Scheme 14).[67] It is interesting to note that a fast isomerization takes place in the latter complexes to accommodate the less sterically demanding group in the *cis* position relative to boron.



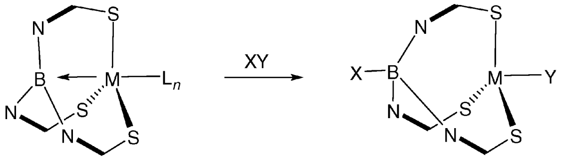
Scheme 13. Formation of **56**–**59** by substitution of PPh_3.

Parkin and Hill have probed the reactivity of metallaboratranes, which has been found to be quite dependent on the nucleophilicity of the metal centre. Metallaboratranes with first-row metals which are weakly basic, such as [{κ^4-B(mt^{tBu})$_3$}Fe(CO)$_2$] (**55**)[58] and [{κ^4-B(mt^{tBu})$_3$}NiCl] (**83**),[70] undergo 1,2 additions of several reagents, such as trihalomethane and organic peroxides, across the M→B bond to yield functionalized complexes of general formula [{XTm^R}MY], where the more electronegative substituent binds the boron atom (Scheme 15).[70] Indeed, it has been found that the driving force is the strong B–X bond when X is an electronegative group. When the transition metal is more nucleophilic, such as in [{κ^4-B(mt^{tBu})$_3$}Pt(PPh$_3$)] (**89**), the addition of halogens (X_2), such as chlorine, bromine and iodine, results in an oxidative addition at the metal centre to yield complexes [{κ^4-B(mim^{Me})$_3$}Pt(X)$_2$] (**92**, **93** and **94**, respectively).[73] The same strategy was used to form the first metallaboratrane with an alkyl substituent, [{κ^4-B(mim^{Me})$_3$}Pt(Me)(*I*)] (**95**), which is made by adding MeI to **89**.



74

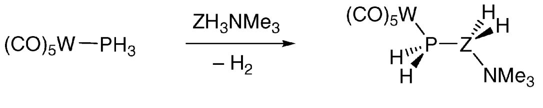
Scheme 14. Formation of **69**–**76** by substitution of a Cl ligand followed by isomerization.



Scheme 15. 1,2 addition across a M→B bond.

Miscellaneous Complexes

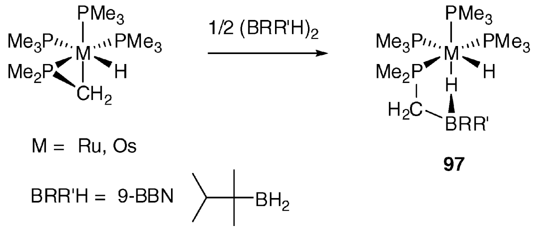
Some alternative strategies have been used to synthesize ambiphilic complexes by modification of bound moieties. Scheer et al. have synthesized complexes W(CO)$_5$-[PH$_2$ZH$_2$·NMe$_3$] (Z = Al or Ga) (**96**) by a dehydrogenative pathway starting with W(CO)$_5$(PH$_3$) and ZH$_3$·NMe$_3$ (Scheme 16).[76] The stabilization of both the Lewis acid by the amine and the phosphane by the transition metal is necessary for this reaction to be thermodynamically favoured, since the formation of the metal-free ambiphilic ligand is not feasible by using similar routes.



96

Scheme 16. Formation scheme for **96**.

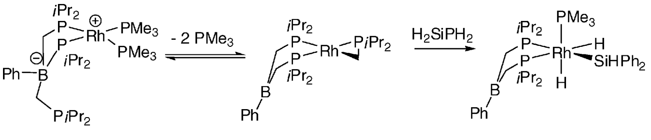
In a 1995 report, Baker and Marder et al. demonstrated that the addition of secondary boranes to ruthenium and osmium complexes having an alkylphosphane moiety (η^2-CH_2PMe_2) gave phosphane hydridoborate complexes **97** (Scheme 17).[77] These species can be better represented as having phosphaneborane ligands in which a strong bridging interaction with a hydride is present. While the free borane was never observed, a hydride exchange process, which probably requires the presence of a rollover mechanism with inversion at the boron centre, is evident.



97

Scheme 17. Formation scheme for **97**.

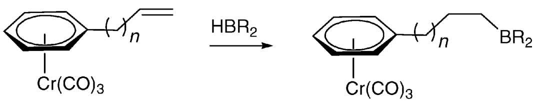
During their work on tripodal phosphane ligand $[PhB(CH_2PiPr_2)_3]^-$, Tilley et al. observed the presence of an unusual B–C bond activation on the rhodium complex $[\{\kappa^2-PhB(CH_2PiPr_2)_3\}Rh(PMe_3)_2]$, reminiscent of the B–H bond activation for the formation of metallaboratranes from Tm-containing complexes, to yield complex **98** (Scheme 18).[78] Contrary to boranobis(phosphane) ligands reported by Bourissou that also have two phosphane moieties bound on the rhodium atom,[29–31] complex **98** does not exhibit a M→B interaction. However, in the presence of diphenylsilane, complex **99**, where the free borane is unaffected, is formed (at least two equivalents of diphenylsilane must be added to **98**).[78]



98 **99**

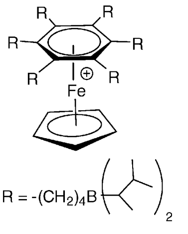
Scheme 18. Formation scheme for **98**.

Similar to the work done on olefin-containing cyclopentadienyl ligands, notably by Piers and Erker,[14] the hydroboration of olefin-containing arene complexes is possible. Green and Wagner reported the hydroboration of a variety of chromium carbonyl species having an arene with an olefinic side-arm to yield ambiphilic species **100** (Scheme 19).[79] However, because of the nature of the boranes that were used, such as catecholborane, 9-bbn and $HBBr_2{\cdot}SMe_2$, the boron side-arms are only weakly acidic, and no interactions at all are observed with either the metal centre or the carbonyl ligands. A similar strategy has been used for the synthesis of complexes **101**[80] and **102**,[81] whereas complex **103** was obtained by the coordination of the areneborane on $Cr(CO)_6$.[82]



100

Scheme 19. Formation of **100** by hydroboration, where *n* = 1 or 2 and $HBR_2 = HB(1,2\text{-}O_2C_6H_4)$ (catecholborane), HBC_8H_{14} (bbn) or $HBBr_2{\cdot}SMe_2$.



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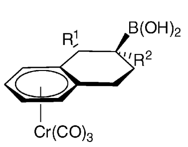

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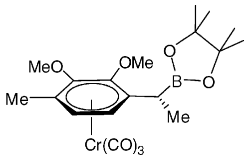

103

Electronic Configuration of Complexes with M→B Interactions

The synthesis of the metallaboratrane framework, first by Hill and Parkin using hydrotris(methimazolyl)borate metallic precursors, then by Bourissou using phosphanylboranes, has allowed the rational synthesis of species with a genuine M→B interaction. It was the first unambiguous report of an interaction between a transition metal and a neutral trivalent boron species in the literature,[11] whereas some analogues with aluminium are known.[10] It is clear that the bonding involves the transfer of a lone pair on the transition metal into an empty orbital on the boron atom. However, little was known about the nature of the molecular orbitals in this interaction, on the directing influence of the Lewis acid on other bound ligands and on the formal oxidation state of the metal sharing an electron pair with the Lewis acid. On the one hand, the interaction may be regarded as being purely dative, the electrons in the M→B bond remaining mainly on the transition metal while its oxidation state is unaffected. On the other hand, according to Green's covalent bond classification, a net two-electron transfer occurs, which would cause the boron to be a metal-stabilized dianion, BR_3^{2-}.[83]

The computational work on the hypothetical species $[\{\kappa^4-HB(mim^H)_3\}Ir(PH_3)Cl]$ did show that the iridium, the borane and the chloride *trans* to it mix in a set of three frontier molecular orbitals, which are reproduced in Figure 3.[65] The lowest-energy metallaboratrane molecular orbital corresponds to a totally bonding interaction of the Cl p_z, Ir d_{z^2} and B p_z orbitals. This orbital, mainly localized in the Ir–B bond, is lower in energy relative to the Ir–Cl σ bond. The orbital that is second-most-stable in energy is a

B–Ir–Cl nonbonding orbital with a significant mixing between both the Ir d_{z^2} and p_z orbitals and the B p_z orbital. This nonbonding orbital now lies lower in energy relative to the t_{2g} orbitals of the octahedral transition metal. The final orbital is an antibonding interaction between the z-oriented orbitals of the three atoms. According to Parkin, since the nonbonding orbital lies lower in energy than the t_{2g} orbital of the transition metal, two of the electrons from the fundamental state of the metal fragment should be located in it. Therefore, the metal in the complex should have a d^{n-2} electronic configuration relative to the borane-free complex. Experimental results that support this viewpoint are numerous. First, the formation of the metallaboratrane involves an oxidative addition of a B–H bond or the two-electron oxidation of a Tm-bound precursor, which normally also implies the oxidation of the transition metal. Furthermore, the geometry of the resulting complexes are often those characteristic of the d^{n-2} complexes; for example, complex [{κ^3-(*o*-(iPr$_2$P)$_2$C$_6$H$_4$)BPh}AuCl] (**15**) made by Bourissou[30] is square-planar, a coordination mode typical of Au^{III}, while iridium and rhodium metallaboratranes are pseudo-octahedral, as observed in most d^6 complexes.

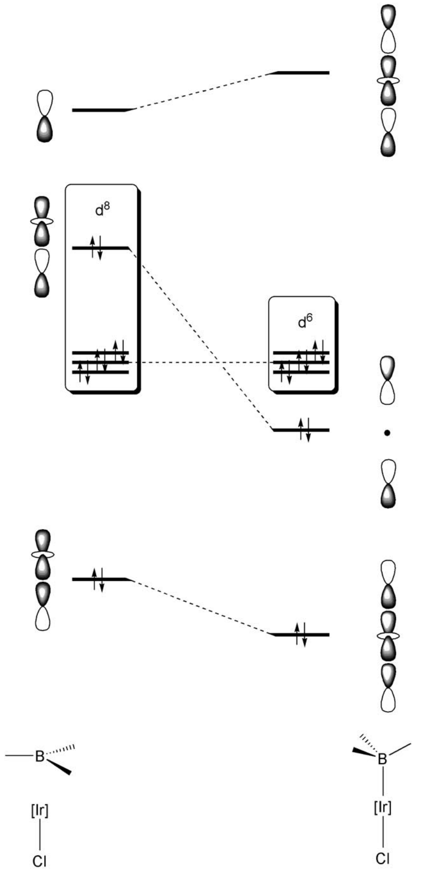

Figure 3. Orbital diagram for the coordination of a borane to an Ir^I moiety, as adapted from Parkin et al.[65]

Nevertheless, strong computational and experimental evidence indicates that the M–B bond may not influence the oxidation state of the transition metal, although the geometry and the molecular orbital scheme would dictate so. In complex [{κ^3-(*o*-(iPr$_2$P)C$_6$H$_4$)$_2$BPh}RhCl(dmap)] (**13**), 79.3 % of the contribution in the bonding comes from the Rh d_{z^2} orbital while only 17.1 % comes from a delocalization tail on the vacant boron orbital, according to natural localized molecular orbitals.[29] Furthermore, the computed natural electronic configuration of gold in complex [{κ^3-(*o*-(iPr$_2$P)C$_6$H$_4$)BPh}AuCl] (**15**) is [Xe]6s^{1}5d^{10}, which is indicative of an Au^I complex.[30] Both these results are strong indications that most of the electron density remains on the metal centre and therefore metallaboratranes should still be considered to have a d^n electronic configuration. One of the strongest experimental pieces of evidence for such a statement was also observed by Bourissou, whose group performed a ^{197}Au Mössbauer spectroscopic analysis of complex **15**.[30] Indeed, the isomer-shift-to-quadrupole-splitting ratio obtained is comparable to that reported for gold(I) phosphane complexes, strongly suggesting that these species should be considered to have a d^{10} electronic configuration instead of d^8, although its square-planar geometry is more typical of Au^{III}.

On a final note, it was found that the dative Lewis acid interaction has an important *trans* effect in metallaboratrane complexes with the κ^4-B(mim)$_3$ ligand. The ligands *trans* to the boron atom are quite labile and are prone to ligand substitution.[67] This is probably due to the nature of the orbitals involved in the B–M–X interaction (Figure 3), where there is a bonding combination between the metal and the boron atom, while the interaction between the *trans* ligand and the metal centre is antibonding in character.[65] It is also observed that the weakest π-acceptor will preferably bind the metal *trans* to the boron atom, a factor that is likely due to the strong π-basicity of the methimazolyl moieties. Indeed, π-acceptors will be favourably placed in the position *cis* to the boron atom, since they would share the same interaxial molecular orbitals as all three mim moieties, which are strong π-donors.[67]

Conclusions

In the past ten years, a surge in the synthesis of ambiphilic molecules has been observed. These bifunctional compounds have been shown to have an impact in several fields, including coordination chemistry. Much of the work on amphoteric ligands in the 1990s was conducted with metallocenes, mainly with titanocene- and zirconocene-based ambiphilic cyclopentadienyl ligands and on borylferrocenes. However, the discovery of metallaboratranes by Hill demonstrated that neutral and dative ligands could provide rich coordination chemistry in ambiphilic settings, where novel reactivity and unusual bonding modes could be observed. The work of Bourissou et al. and several other research groups, including ours, demonstrated that the synthesis and coordination of ambiphilic ligands was not limited to molecules having weak Lewis acids or bulky substituents and that aggregation was a problem that could be overcome with an appropriate synthetic design. Indeed, because of the addition of a stabilizing Lewis base onto the acceptor fragment and coordination of a transition metal to the donor moiety, the complexation of the ambiphilic ligand became thermodynamically favoured over the formation of the aggregate. By tuning the various equilibria taking place with the ambiphilic complexes containing an internal Lewis acid, interesting reactivity and structural properties, which are not seen in analogous bimolecular systems, can be observed.

Among the advantages of ambiphilic ligands, two are of major importance. First, the donor buttresses help in stabilizing M→Z interactions, which are otherwise difficult to observe. Metalloboratranes are a good example, since these complexes were the first structurally characterized species with a direct M→B interaction, opening a new field of organometallic chemistry, which is the study of multidentate ligands containing an acceptor fragment. The second obvious advantage is the formation of zwitterionic species, which may help modulate the reactivity of complexes relevant to catalysis. Indeed, in many cases, the Lewis acids can interact with one ligand in the coordination sphere and ionize the metal centre, as observed in our work with $Me_2P\text{-}CH_2AlMe_2$. With the appropriate Lewis acid, this abstraction can be reversible, which could trigger an open/close mechanism and increase the reactivity and selectivity of catalytic systems. When the wrong or no substrate is present, the catalyst would be on “close” mode and be stable for a long time in solution, but with the right substrate, the “open” mode would be activated and catalysis would begin.

The research on ambiphilic ligands is still in its infancy and much remains to be done, including further studies of the reactivity of these ambiphilic complexes. Among the challenges that need to be addressed, we can include the rational synthesis of ambiphilic ligands that would serve as spectator or ancillary ligands with σ-acid character. Also, while most of the work has been done on boron compounds, which tend to be very stable, the synthesis of ambiphilic ligands with other, more reactive, group XIII Lewis acids may prove worthy of consideration.

Abbreviations: bbn: borabicyclo[3.3.1]nonane; cod: *cis,cis*-1,5-cyclooctadiene; Cy: cyclohexyl; dba: dibenzylideneacetone; DFT: Density functional theory; diop: 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphanyl)butane; dmap: 4-(dimethylamino)pyridine; dmpe: 1,2-bis(dimethylphosphane)ethane; dmso: dimethyl sulfoxide; Flu: fluorenyl; L: generalized 2-electron donor ligand; M: transition metal; 1-Me-Ind: 1-methyl-indenyl; Mes: mesityl; mim^R: 2-mercapto-1-(R)imidazolyl; nbd: 2-norbornene; bicyclo[2.2.1]hept-2-ene; oct: octahedral; pyr: pyramidal-trigonal; S: substrate; taz: thioxotriazolyl; Tm: hydrotris(methimazolyl)borate; Tp: hydrotris(pyrazolyl)borate; X: generalized 1-electron anionic ligand; Z: generalized 2-electron acceptor ligand.

Note Added in Revision (received: September 18, 2008): The addition of $NaHBEt_3$ or $[HPt(dmpe)_2]^+$ to phosphanylborane complex *trans*-$[(Ph_2P(CH_2)_2B(C_8H_{14}))_2Re(CO)_4][BF_4]$ induces the reduction of one rhenium-bound carbon monoxide to a boroxymethyl group and its migration into another carbon monoxide, as recently reported by Bercaw and Labinger.[84]

Acknowledgments

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