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# Coordination Chemistry of Neutral (L*n*)–Z Amphoteric

# and Ambiphilic Ligands

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# Coordination Chemistry of Neutral (L*n*)-Z Amphoteric and Ambiphilic Ligands

## Frédéric-Georges Fontaine*,[a] Josée Boudreau,[a] and Marie-Hélène Thibault[a]

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 Nature's catalysts, 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.[3-7] The increasing number of ambiphilic and amphoteric[2] molecules in the recent literature are an indication of the great potential of such molecules. They have been shown to act as catalysts,[3] as precursors to semiconductors,[4] as fluorescent and conductive materials,[5] as sensors,[6] as small-molecule activators,[7] 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.
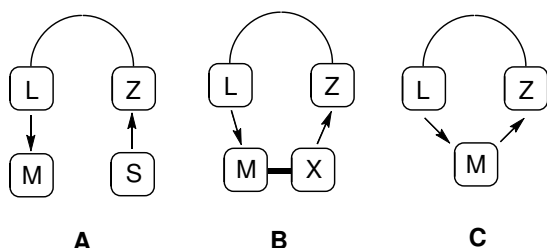


Figure 1. Coordination modes of an ambiphilic ligand (L = donor group, Z = Lewis acid) on a transition metal (M) where the Lewis acid interacts with A) a substrate (S), B) with a ligand (X), or C) with the transition metal.

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

A.    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 center.

B.    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]

C.    If the metal center 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.

This review will describe the various synthetic routes available to coordinate ambiphilic ligands onto a metal center, 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 with donor groups having 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]
- boryl, 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 based on 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,[7] 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 aluminoaminophosphine $R_2PNR'AlR''_2$ (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)$_2$Me], [CpMo(CO)$_3$Me], 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 aluminum-oxygen adduct weakens the metal-ligand bond and makes the carbonyl more electrophilic, leading to the 1,1 insertion to give $\eta^2$-acyl complex **2**. Once the acyl group is formed, the phosphine 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 is interacting initially with the carbonyl oxygen atom, since the chelated ligand can favour the

nucleophilic attack of the phosphine on the acyl group, a reaction that does not occur in absence of a Lewis acid.
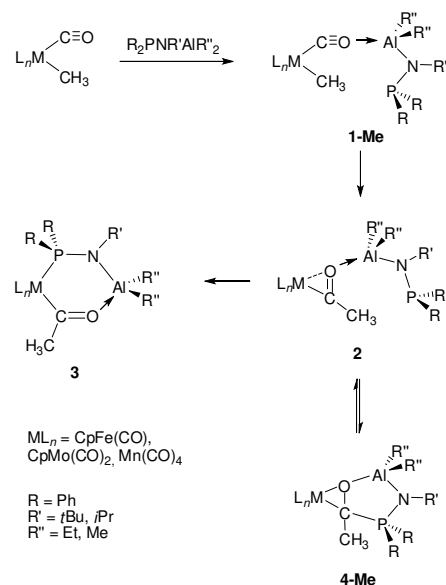


Scheme 1. Reaction of aluminoaminophosphines with alkyl carbonyl metal species.
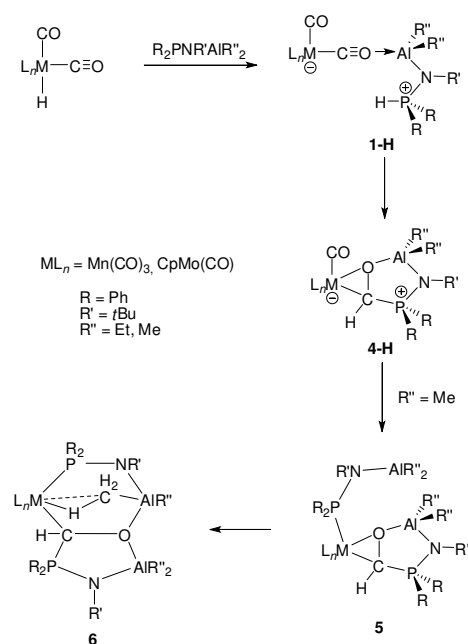


Scheme 2. Reaction of aluminoaminophosphines with carbonyl hydride metal species.

The reaction between the aluminoaminophosphine 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 unfavored 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 phosphine to occur and form **1-H**, which is supported by the presence of a P-H bond with the 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 ethylaluminophosphine species is stable, the methylaluminophosphine was shown to react further. The donor

moiety of the ambiphilic ligand can displace one carbonyl 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 phosphines in the *ortho* position of an aromatic spacer. Even in the presence of a rigid framework, the compounds [*o*-(*i*Pr$_2$P)C$_6$H$_4$]$_2$BPh and [*o*-(*i*Pr$_2$P)C$_6$H$_4$]$_3$B have phosphorous-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 centers first.

When [*o*-(*i*Pr$_2$P)C$_6$H$_4$]$_3$B reacts with AuCl(SMe$_2$) or Pt(P*t*Bu$_3$)$_2$, ligand exchange occurs to yield complexes [{κ$^4$-[*o*-(*i*Pr$_2$P)C$_6$H$_4$]$_3$B}AuCl] (**7**) and [{κ$^4$-[*o*-(*i*Pr$_2$P)C$_6$H$_4$]$_3$B}Pt] (**8**), respectively, where the three phosphine moieties and the boron acceptor bind the metal center 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 observed usually 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 phosphines, which prevents C$_{3v}$ symmetry.
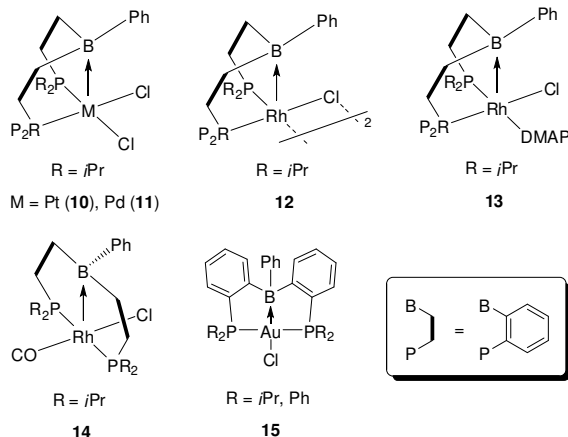


**7**          **8**
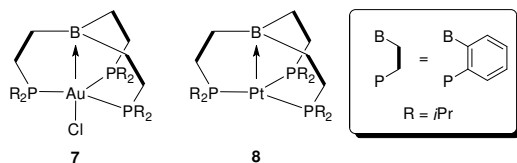
The synthesis of boranotrisphosphine analogue [Me$_2$P(CH$_2$)$_2$]$_3$B was accomplished by the photolytic addition of Me$_2$PH on NEt$_3$.B(CHCH$_2$)$_3$. NMR spectroscopy indicates that both intra- and intermolecular interactions are observed between boron and phosphorous atoms. Addition of this ambiphilic 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{$^1$H} spectrum and computational data suggest that an equilibrium is established between complex **9** and the phosphine-free analogue [{κ$^4$-[Me$_2$P(CH$_2$)$_2$]$_3$B}Pd] (Scheme 3).[27]



**9**
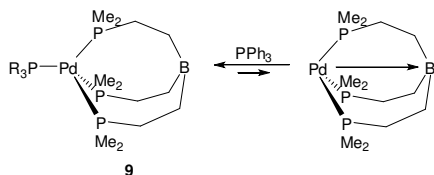
Scheme 3. Boranotriphosphine complexes of palladium.

A large variety of complexes containing the boranobisphosphine ligand [*o*-(R$_2$P)C$_6$H$_4$]$_2$BPh (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 boranotrisphosphine complexes **7** and **8**, the phosphine 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 (ΣPt$_α$ = 360.3° for **10**, ΣPd$_α$ = 360.1° for **11**, and ΣRh$_α$ = 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 (ΣB$_α$ = 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 center is not affected. The σ-acid interaction is, however, much weaker with the palladium(II) species, as demonstrated notably by the summation of the angles around boron being close to planarity (ΣB$_α$ = 354.9°) and the Pd-B distance being more than 0.2 Å longer than the Pt-B distance in **10**. Quite surprisingly, the boranobisphosphine ligand can also adopt a *trans* geometry when coordinated to precursor [Rh(μ-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)(*i*Pr$_2$PPh)$_2$], is an indication that the M→B dative interaction withdraws significant electron density from the metal center. 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° (ΣAu$_α$ = 362.2° for R = *i*Pr and 364.2° for R = Ph).[30] In addition to the coordination of two phosphines from the ambiphilic ligand to the metal center, 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          R = *i*Pr          R = *i*Pr
M = Pt (**10**), Pd (**11**)   **12**          **13**



R = *i*Pr          R = *i*Pr, Ph
**14**          **15**

The coordination of aluminobisphosphine [*o*-(*i*Pr$_2$P)C$_6$H$_4$]$_2$AlCl, which has two P→Al interactions, to precursor AuCl(SMe$_2$) is possible.[31] Isolation of **16** reveals that the ambiphilic aluminum ligand favours the ionization of the metal center by chloride abstraction rather than coordination of the Lewis acid onto the metal center 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 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.

4

**16**

R = iPr
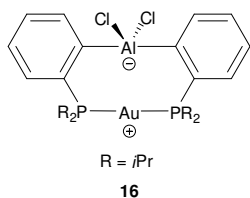
Boranomonophosphines have been used to some extent in coordination chemistry. The synthesis of [o-(iPr₂P)C₆H₄]BR₂ (R₂ = Cy₂ and Flu) has been reported by Bourissou and spectroscopic evidence shows them to be monomeric in solution.[32] The coordination of these species on both Pd(II) and Au(I) metal centers 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 does not lead to ionization. With the more nucleophilic Au(I), instead of an interaction with a ligand within the coordination sphere, the boron has a close contact with the metal center. As expected, the more electrophilic fluorenyl derivative [{κ²-[o-(iPr₂P)C₆H₄]BFlu}AuCl] possesses a shorter Au-B bond distance (2.663(8) Å) than the biscyclohexyl analogue [{κ²-[o-(iPr₂P)C₆H₄]BCy₂}AuCl] (2.90 Å). The negligible pyramidalization at the boron ($\Sigma B_\alpha$ =355.8°) and the shorter Au-B bond length of **18** compared to the boranotrisphosphine (**7**) and the boranobisphosphine (**13**) analogues are experimental evidence of a much weaker interaction when only one phosphine buttress is involved in the stabilization of the Au→B interaction. Nevertheless, DFT calculations confirm the presence of a Lewis adduct with gold(I).



**17**    **18**
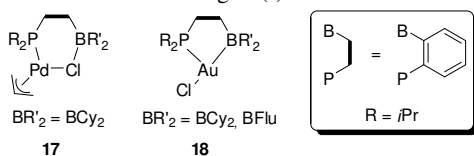
The aliphatic analogues Ph₂P(CH₂)₂BR₂ (R₂ = Cy₂ and BBN) were obtained by the hydroboration of vinyldiphenylphosphine with the corresponding hydroboranes, as reported in back-to-back communications by Tilley[33], by Sabo-Etienne and Bourissou,[34] and recently by Muhoro.[35] The solid-state characterization of the amphoteric ligand Ph₂P(CH₂)₂B(BBN) shows the presence of a weak intermolecular Lewis adduct (P---B = 2.056(2) Å).[33] While the broadening resonances in the ¹¹B and ³¹P 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 Ph₂P(CH₂)₂BR₂ to (dmpe)NiMe₂ leads to the formation of zwitterionic species **19**, which was characterized by X-ray diffraction studies (Scheme 4). The coordination of the phosphine moiety onto nickel and the abstraction of the alkyl group by the borane put in evidence 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(C₆F₅)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**
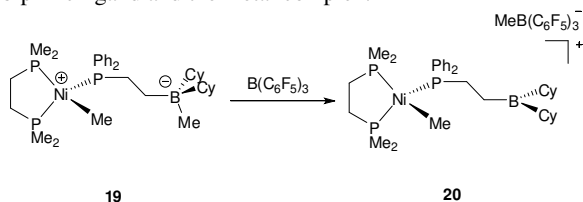
Scheme 4. Formation of ambiphilic complex **19** and its reactivity with B(C₆F₅)₃.

It is also possible to coordinate Ph₂P(CH₂)₂BR₂ by displacing the bridging chloride in the starting precursor [(p-cymene)RuCl₂]₂ to give ambiphilic complex **21**.[34] Whereas the borane of this boranophosphine ligand can ionize the nickel center 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)BCy₂ to the same ruthenium(II) precursor affords compound **22** where 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 BF₄⁻ was added in acetonitrile, the cationic compound **23** was observed; however, using the more basic silver acetate induces B-C cleavage



**21**    **22**



**24**    **23**
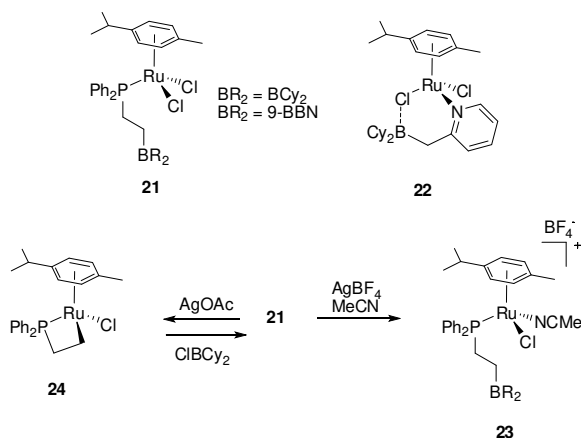
and the formation of four-membered metallacycle **24**, which can reform **21** upon addition of one equivalent of ClBCy₂.[34]
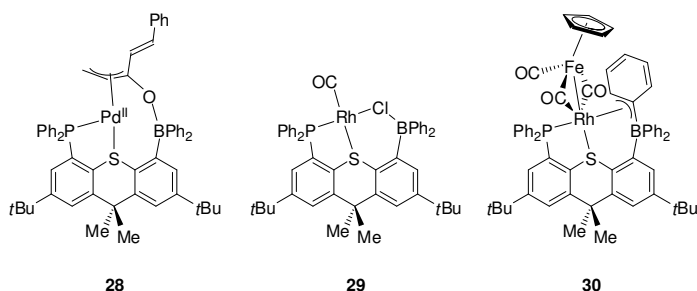
Scheme 5. Reactivity of complex **21**.

Grobe reported the synthesis of vinyl boranophosphine Ph₂PC(Me)=C(Me)BMe₂ 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 boranobisphosphine ligand. With the cyclopentadienyl precursor, complexes **26** and **27** were reported, but 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 center takes place.



**25**    **26**    **27**
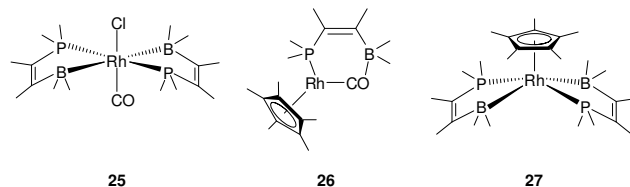
The synthesis of a boranophosphine amphoteric ligand with a thioxanthene framework was done by Emslie.[37] The rigid structure helps preventing the formation of intra- and intermolecular Lewis adducts, without affecting the ligand's propensity to coordinate transition metals. Upon addition of this ambiphilic ligand to [Pd₂(dba)₃], the complexation of the palladium to the two donor moieties occurs to form complex **28**, where one of the dba ligands remains bound to the metal center. 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, with the chloride bridging rhodium and boron atoms. Elegantly, the chloride can be displaced by the nucleophilic metal anion K[CpFe(CO)2] to form bimetallic species 30.[38] DFT calculations and X-ray diffraction studies support the presence of a weak interaction between the boron and rhodium centers in the



**28**   **29**   **30**

form of a boratabenzyl fragment (Rh-B = 2.62(2) Å), where one of the aryl groups on the boron acts as a benzyl source.
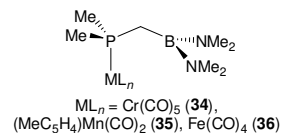
Some ambiphilic ligands having bulky Mes2BR moieties and pyridine derivatives as donor groups have been synthesized recently in order to probe the photophysical properties of the ligands upon metal coordination. The mesityl substituents on boron are large enough to prevent aggregates from forming. Using a Suzuki-Miyaura coupling, it has been possible for Kitumara *et al.* to synthesize a terpyridine ligand bearing the triarylborane and coordinate it on Pt(cod)Cl2 to yield 31.[39] The latter compound exhibits an interesting electronic communication between the metal and the boron. The enhanced emission of complex 31 compared 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 (32) [40] and enhanced metal-to-ligand charge-transfer phosphorescence (33).[41]



**31**   **32**   **33**

M = [Cu]BF4, R = PPh3
M = Pt, R = Ph, Me

M = [Cu]BF4, R = PPh3
M = Pt, R = Ph, Cl
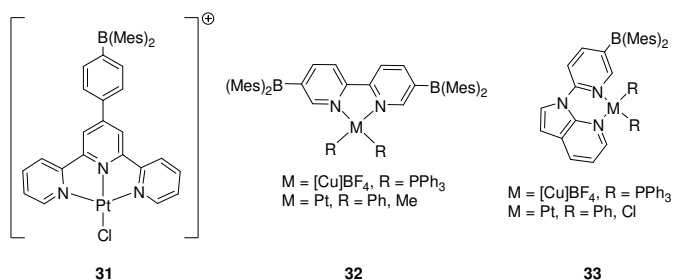
**Weakly Lewis acidic ambiphilic ligands**

Most of the ambiphilic ligands reported in the former section have alkyl- or arylboranes without π-donating substituents (with the exception Labinger's work). It is well known that the acidity on the boron and aluminium will be greatly reduced by the presence of alkoxide or amido groups on the boron or aluminium. 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 center.

Using this type of strategy, Braunschweig reported the synthesis of a boranoaminophosphine, Me2PCH2B(NMe2)2, one of the few boranophosphines that does not form Lewis acid-base adducts with itself.[42] The coordination of this ligand to [Co(CO)5(THF)], [(MeC5H4)Mn(CO)2(THF)], and [Fe2(CO)9], gave compounds 34,

35, and 36, respectively. In these species, the chemical shift of the borane moieties was unaffected by coordination, with ^{11}B NMR chemical shifts remaining 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 LiAlH4 was added to the iron complex 36, the methoxyborane, chloroborane, or hydroborane ambiphilic complexes were obtained respectively. 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**),
(MeC5H4)Mn(CO)2 (**35**), Fe(CO)4 (**36**)

The weak acidity of boronic esters also allows the synthesis of ambiphilic boranophosphine ligands that do not aggregate. Two research groups reported back-to-back syntheses of an optically active phenylboronic ester bisphosphine analogous to the bisphosphine DIOP.[43,44] This ambiphilic ligand was coordinated to Rh(I) by ligand exchange from [(cod)RhCl]2[43,44] and to Pd(II) using [PdCl2L2] (L2 = (CH3CN)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 analogs. Attempts to perform the asymmetric catalytic hydrogenation of N-acetyldehydrophenylalanine and the hydrosilylation of ketones using 37 as catalyst gave disappointing results, since this reaction yielded lower enantioselectivity and stereoselectivity than with the Rh-DIOP complexes, which do not bear the acid part.[43] Using 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 ambiphilic ligand, starting from the corresponding diol, is possible prior to or after phosphine coordination on palladium.[45]



ML_n = [Rh(COD)]ClO4 (**37**)
X = H, Cl, CF3

ML_n = PdCl2 (**38**), PtCl2 (**39**)
X = Cl, CF3

**40**
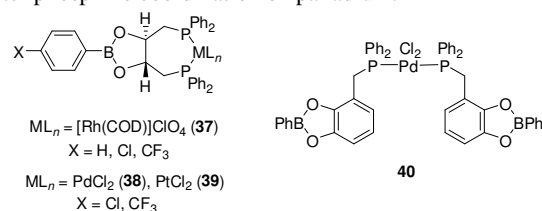
**Base-stabilized ambiphilic ligands**

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 Me2ZL(SiMe3)2 (Z = Al, Ga; L = P, As). In turn, the donor group of the ambiphilic ligand can be coordinated onto transition metals. Compounds 41 to

**43** were synthesized by ligand exchange from [Ni(CO)₄],[46,47] [Fe₃(CO)₁₂],[47] and [Cr(CO)₅(NMe₃)],[47] respectively. In all these complexes, the ambiphilic ligand can be considered as a bulky phosphine. However, crystallographic and spectroscopic studies revealed the ligand to be a weakly π-accepting, with the nature of the Lewis acid playing only a marginal role in its electronic properties.
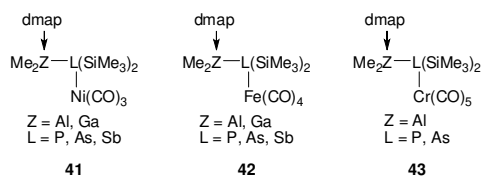


Beachley *et al.* reported in 1983 that the amphoteric ligand Ph₂PAl(CH₂SiMe₃)₂ reacted with [Cr(CO)₅(NEt₃)], yielding [Cr(CO)₅{PPh₂Al(CH₂SiMe₃)₂.NEt₃}] (**44**) where the displaced amine ligand stabilizes the Lewis acid.[48] However, this proved to be a limited strategy, since related starting materials, such as [Cr(CO)₆], [Cr(CO)₅(THF)], and [Cr(CO)₅(CH₃CN)], either did not react with the aluminophosphine or decomposed in its presence. Only Ph₂PAl(CH₂CMe₃)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(PPh₂H)], while keeping intact the Al-N interaction to form Br₃AlNMe₃. [Cr(CO)₅{PPh₂Al(CH₂SiMe₃)₂.NEt₃}] was found to react over time with THF to yield [Cr(CO)₅{PPh₂(CH₂)₄OAl(CH₂SiMe₃)₂}] (**45**), where one equivalent of THF is activated.[50] Interestingly, compound **45** and analogues [Cr(CO)₅{PPh₂(CH₂)₄OAl(R)₂}] (R = CH₂SiMe₃, Me, Et, and Br) can be synthesized independently from [Cr(CO)₅(PPh₂K).*n*dioxane] in the presence of BrAlR₂.
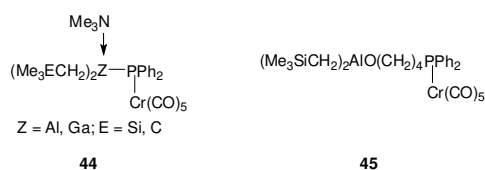


The ambiphilic ligand (Me₂PCH₂AlMe₂)₂, first reported by Karsch in 1985,[51] and forms a six-membered ring dimer both in solution and in the solid state, as observed by NMR spectroscopy and X-ray diffraction studies. In the presence of a Lewis base (LB), it is possible, however, to break the cyclic dimer to form the monomeric Me₂PCH₂AlMe₂.LB. If the Lewis base is not too nucleophilic, such as NEt₃ or THF, an equilibrium between the mono- and di-meric forms is established and the Lewis acid moiety can be available once the phosphine is coordinated to a transition metal center. It was demonstrated spectroscopically that the addition of 4 equiv of NEt₃ to a solution of (Me₂PCH₂AlMe₂)₂ and (1-MeInd)Ni(PPh₃)Me gave complex ((1-MeInd)Ni(Me₂PCH₂AlMe₂.NEt₃)Me (**46.NEt₃**) by associative substitution of the less donating phosphine PPh₃.[52] Complex **46.NEt₃** was found to be more than two orders of magnitude more active than [(1-MeInd)Ni(PPh₃)Me] in the dehydropolymerization of phenylsilane.[52,53] Substitution of the NEt₃ by more nucleophilic quinuclidine gives **46.quinuclidine**, where the highly donating amine binds irreversibly the Lewis acid. The resulting complex was found to be no more active than (1-MeInd)Ni(PMe₃)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 AlMe₃ instead formed adducts in the style of **48**, in which the sites where the incoming substrates usually bind are occupied. Indeed, the addition of AlMe₃ to (1-

MeInd)Ni(PMe₃)Me was found to inhibit phenylsilane dehydropolymerization.[52]
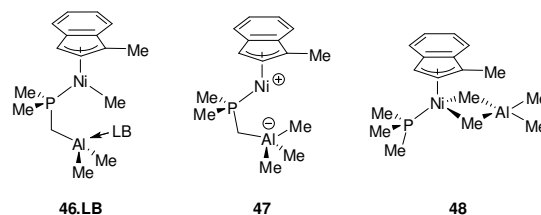


More information on the role of Me₂PCH₂AlMe₂ was obtained by examining the coordination chemistry of the ambiphilic ligand on rhodium(III) complexes. Using a strategy reminiscent of the first report by Beachley, the Lewis acid fragment of the dimeric species (Me₂PCH₂AlMe₂)₂ interacts first with the oxygen of the sulfoxide on Cp*RhMe₂(DMSO) to form the adduct Cp*RhMe₂(Me₂PCH₂AlMe₂.DMSO) (**49**), as confirmed by NMR spectroscopy.[54] In the latter complex, the dimethylsulfoxide is tightly bound to the aluminum center and the reactivity observed resembles that of the analogous dimethyl complex Cp*Rh(PMe₃)Me₂. However, the addition of one equivalent of AlMe₃ gives a fast equilibrium between **49** and **50**, after the added AlMe₃ forms an adduct with dmso. Even at -80 °C, the exchange rates are too fast to characterize by NMR spectroscopy the base-free complex; however, circumstantial evidence gives a strong indication that ionization at the metal center occurs. Indeed, upon addition of neutral ligands such as ethylene[55] or trimethylphosphine,[54] it is possible to trap zwitterionic species **51**, as shown in Scheme 6.
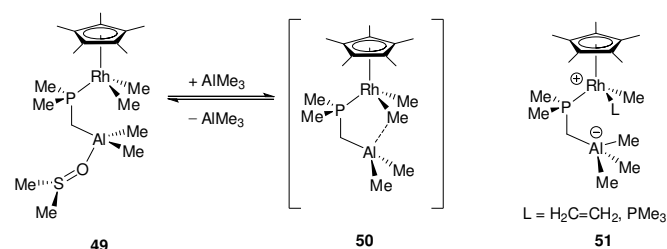


Scheme 6. Trapping of the zwitterionic intermediate **49**.

While species **49** to **51** were only characterized using various NMR experiments, two new structurally characterized complexes, **52** and **53**, gives strong support to the proposition that the ambiphilic ligand ionizes the rhodium center.[51] As shown in Scheme 7, the addition of one more equivalent of Me₂PCH₂AlMe₂ gave the zwitterionic species **52**. It is presumed that an additional equivalent of the aluminophosphine ligand coordinates the zwitterionic metal center, which promotes the attack of the methylene moiety of the aluminate on the free Lewis acid, leading to the elimination of one equivalent of AlMe₃ and to the formation of the metallacycle. Similarly, when species **50** is heated or left for several days at room temperature, species **53** can be isolated (Scheme 8). In this case, however, the methylene of the aluminate moieties attacks a zwitterionic complex in an intermolecular
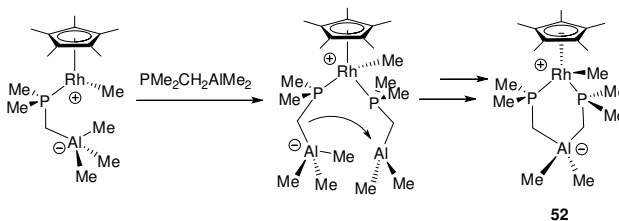
manner, leading to the dimerization and the formation of the metallacycle **53**.
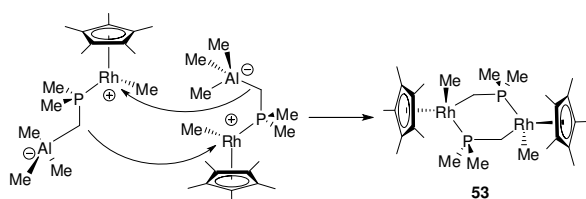


Scheme 7. Proposed mechanism for the formation of **52**.


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 center. However, in 1999 Hill reported an unusual reaction where a Tm ligand undergoes B-H activation to form a metallaboratrane complex [{κ$^4$-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, *trans* to a phosphine. It 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.
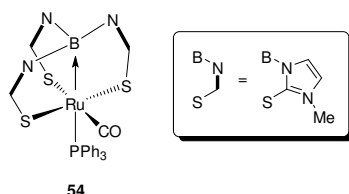


Since this early report, metalloboratrane complexes having this common ligand have been reported for all members of the Fe, Co, and Ni triads, as enumerated in Table 1. The possible geometries for metallaboratranes are illustrated in Figure 2. Most complexes (**55-61**; **63-66**; **68-77**; **82**; **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 center in complex **88** possess a four-coordinate geometry (**μ-κ,κ$^3$**) with two mim moieties of one ligand binding in a highly distorted *trans* fashion (S$^1$-Pd-S$^2$ = 154.71°) and with the boron from the same tris(methimazolyl)borane and one mim from another ligand being 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 {κ$^3$-*B,S,S'*- 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 the tris(methimazolyl)borane ligand is involved in what is a formal μ-κ$^2$ S,S',κ$^4$ coordination, where two of the sulphur atoms are bridging two rhodium centers 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 of 2.646 Å), indicating that the M→B interaction exert a strong trans influence (vide infra).
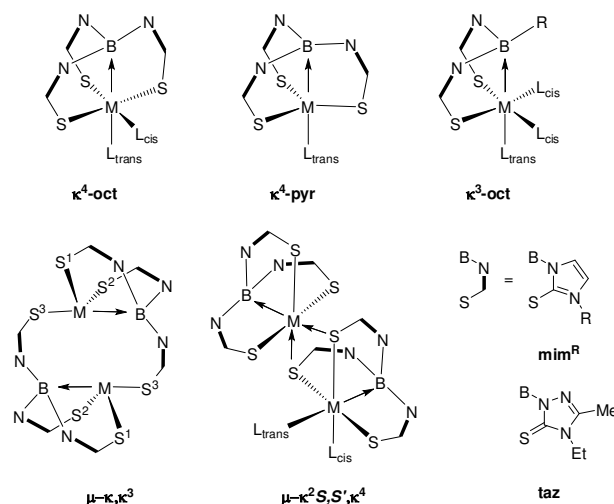


Figure 2. Coordination modes of metallaboratranes.


The general mechanism for the formation of metalloboratranes, as initially proposed by Hill, 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$^{Me}$)$_3$}Ru(PPh$_3$)(CO)(H)],[59] since the elimination of H$_2$, rather than an alkane, is thermodynamically unfavored. 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, where 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 is formed from a metalloboratrane (Scheme 10).[74] Indeed, metalloboratrane [{κ$^4$-B(mim$^{Me}$)$_3$}Pt(H)(P(tol)$_3$)]Cl (**91-P(tol)$_3$**), with κ$^4$-oct geometry, in presence of PMe$_3$ or PEt$_3$ gave square planar complex [{κ$^2$-*S,S'*-HB(mim$^{Me}$)$_3$}Pt(PR$_3$)$_2$] (R = Me or Et) where the labile P(tol)$_3$ is substituted for a more basic phosphine 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-PMe₃** and **91-PEt₃** 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.
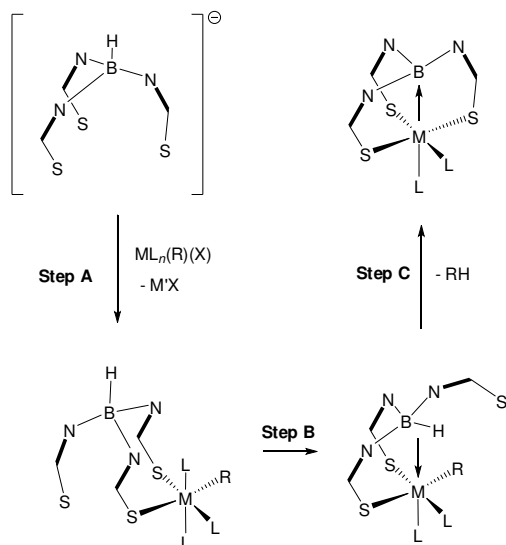


Scheme 9. General mechanism for the formation of metallaboratranes.
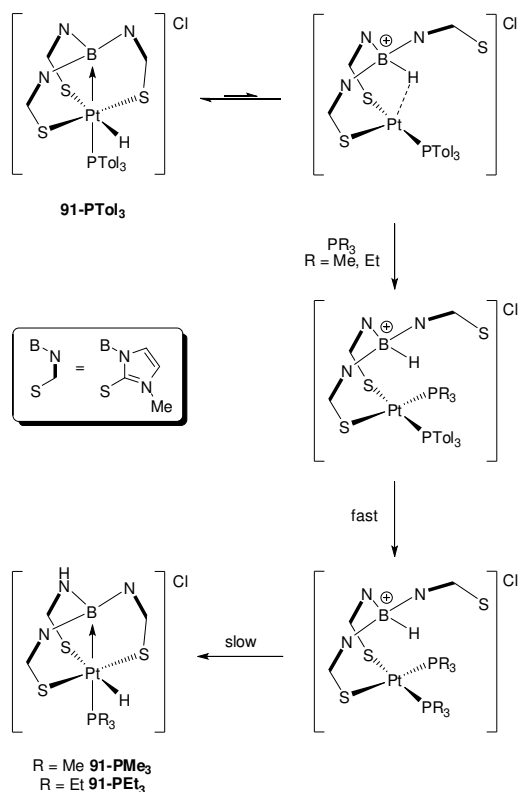


Scheme 10. Formation of a B-H bond from a metallaboratrane.

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 $[\{\kappa^4\text{-B}(mt^{tBu})_3\}Co(PPh_3)](BPh_4)$ (**62**)[62] and $[\{\kappa^4\text{-}B(mt^{tBu})_3\}NiCl]$ (**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 $[(Tm^{tBu})Fe(CH_2SiMe_3)]$, since the iron is much less nucleophilic compared to its heavier analogues. Instead, the addition of CO occurred presumably via a 1,1 insertion to form an acyl intermediate, which will induce the elimination of the aldehyde $Me_3SiCH_2C(O)H$ and the formation of $[\{\kappa^4\text{-B}(mt^{tBu})_3\}Fe(CO)_2]$ (**55**) (Scheme 12).[58] It was also possible to synthesize complex $[\{\kappa^4\text{-B}(taz)_3\}Rh(CO)(PPh_3)]$ (**63**), where taz (Figure 2) stands for thioxotriazolyl, from the two-electron oxidation of $[\{HB(taz)_3\}Rh(PPh_3)(CO)]$ using $[Cp_2Fe](PF_6)$ 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).
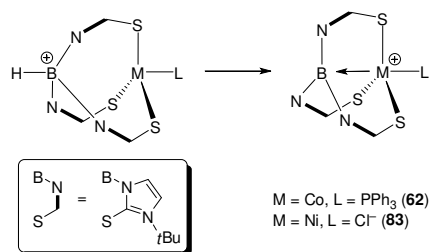


Scheme 11. Formation scheme for **62** and **83**.
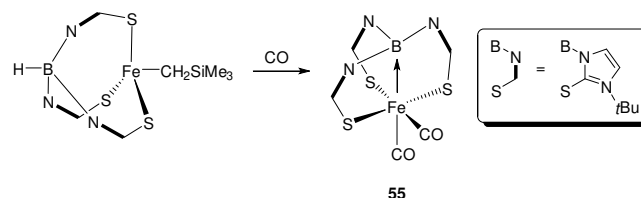


Scheme 12. Formation of **55** by elimination of $Me_3SiCH_2C(O)H$.

In several cases, modification of the coordination sphere where a $\kappa^4$-B(mt)₃ ligand is present is possible without breaking the M→B interaction. Nickel complexes **84** to **86** have been synthesized by a metathesis reaction with **83** using respectively the Na, K, and Tl salts.[70] The ligand *trans* to boron was found to be quite labile in $\kappa^4$-oct metallaboratranes, which can be useful for ligand substitutions. As such, complex $[\{\kappa^4\text{-B}(mim^{Me})_3\}Ru(CO)(PPh_3)]$ (**54**), was found to be a good starting material for a variety of complexes having π-acceptor ligands instead of the phosphine, such as in **56** to **59** (Scheme13).[60] The chloride, which is *trans* to boron in complex $[\{\kappa^4\text{-B}(mim^{Me})_3\}Rh(Cl)(PPh_3)]$ (**64**), readily leaves the coordination sphere in presence of isonitriles and phosphines to form complexes **69** to **76**(Scheme 14).[67] It is interesting to note that a fast isomerisation is taking place in the latter complexes to accommodate the less sterically demanding group in *cis* position relative to boron.

9

L = CO (**56**), CN*t*Bu (**57**),
CNXyl (**58**), CNMes (**59**)

**56-59** by substitution of PPh₃.
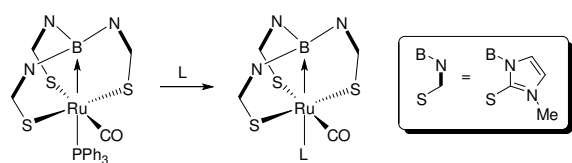
Scheme 13. Formation of
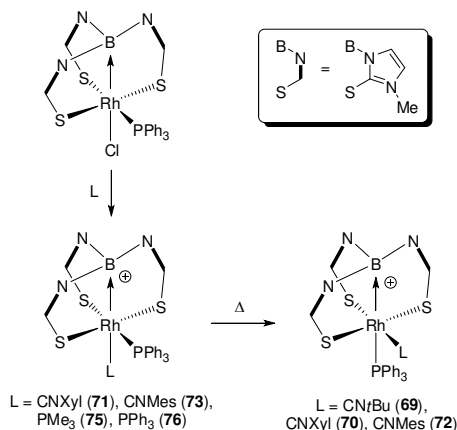


L = CNXyl (**71**), CNMes (**73**),
PMe₃ (**75**), PPh₃ (**76**)

L = CN*t*Bu (**69**),
CNXyl (**70**), CNMes (**72**)

**74**

Scheme 14. Formation of **69-76** by substitution of a Cl ligand followed by isomerisation.

Parkin and Hill have probed the reactivity of metallaboratranes, which has been found to be quite dependent on the nucleophilicity of the metal center. The metallaboratranes with first row metals which are weakly basic, such as $[\{\kappa^4\text{-}B(mt^{tBu})_3\}Fe(CO)_2]$ (**55**)[58] and $[\{\kappa^4\text{-}B(mt^{tBu})_3\}NiCl]$ (**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 (Scheme15).[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 $[\{\kappa^4\text{-}B(mt^{tBu})_3\}Pt(PPh_3)]$ (**89**), the addition of halogens (X₂), such as chlorine, bromine, and iodine, results in an oxidative addition at the metal center to yield complexes $[\{\kappa^4\text{-}B(mim^{Me})_3\}Pt(X)_2]$ (**92** to **94**, respectively).[73] The same strategy was used to form the first metallaboratrane with an alkyl substituent, $[\{\kappa^4\text{-}B(mim^{Me})_3\}Pt(Me)(I)]$ (**95**), which is made by adding MeI to **89**.

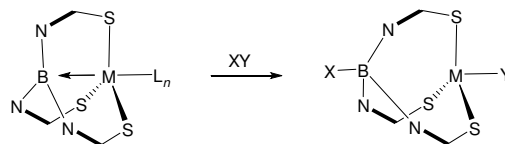Scheme 15. 1,2 addition across a M→B bond.



**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[PH₂EH₂.NMe₃] (Z = Al or Ga) (**96**) by a dehydrogenative pathway starting with W(CO)₅(PH₃) and AlH₃.NMe₃ (Scheme 16).[76] The stabilization of both the Lewis acid by the amine and the phosphine by the transition metal is necessary for this reaction to be thermodynamically favored, since the formation of the metal-free ambiphilic ligand is not feasible using similar routes.



Z = Al, Ga       **96**
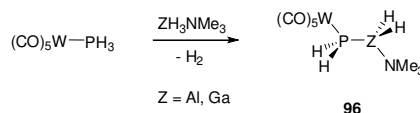
Scheme 16. Formation scheme for **96**.

In a 1995 report, Baker and Marder *et al.* demonstrated that the addition of secondary boranes to ruthenium and osmium complexes having an alkylphosphine moiety (η²-CH₂PMe₂) gave phosphine hydridoborate complexes **97** (Scheme 17).[77] These species can be better represented as having phosphineborane ligands where 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 center, is evident.



M = Ru, Os       **97**

BRR'H = 9-BBN
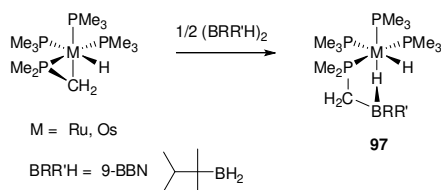
Scheme 17. Formation scheme for **97**.

During their work on tripodal phosphine ligand [PhB(CH₂P*i*Pr₂)₃]⁻, Tilley *et al.* observed the presence of an unusual B-C bond activation on the rhodium complex $[\{\kappa^2\text{-}PhB(CH_2P i Pr_2)_3\}Rh(PMe_3)_2]$, 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 boranobisphosphine ligands reported by Bourissou that also have two phosphane moieties bound on rhodium,[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]
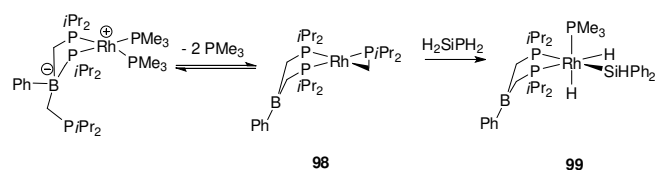


Scheme 18. Formation scheme for **98**.

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 $HBBr_2.SMe_2$, the boron side-arms are only weakly acidic and no interactions at all are observed with either the metal center or the carbonyl ligands. A similar strategy has been used for the synthesis of complex **101**[80] and **102**,[81] whereas complex **103** was obtained by the coordination of the areneborane on $Cr(CO)_6$.[82]



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



**101**
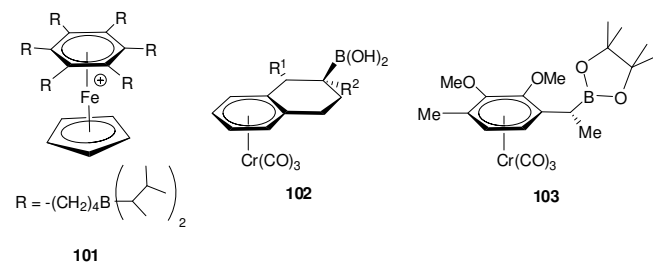
## Electronic configuration of complexes with M→B interactions

The synthesis of the metallaboratrane framework, first by Hill and Parkin using hydrotris(methimazolyl)borate metallic precursors, then by Bourissou using phosphinoboranes, 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 boron. 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 that is sharing an electron pair with the Lewis acid. On the one hand, the interaction may be regarded as being purely dative with 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 2-electron transfer occurs, which instead 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 $d_{z2}$, and B $d_z$ 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 non-bonding orbital with a significant mixing between both the Ir $d_{z2}$ and $p_z$ orbitals and the B $p_z$ orbital. This non-bonding orbital now lies lower in energy compared 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 [{$\kappa^3$-(o-(iPr_2P)_2C_6H_4)BPh}AuCl$] (**15**) made by Bourissou 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.
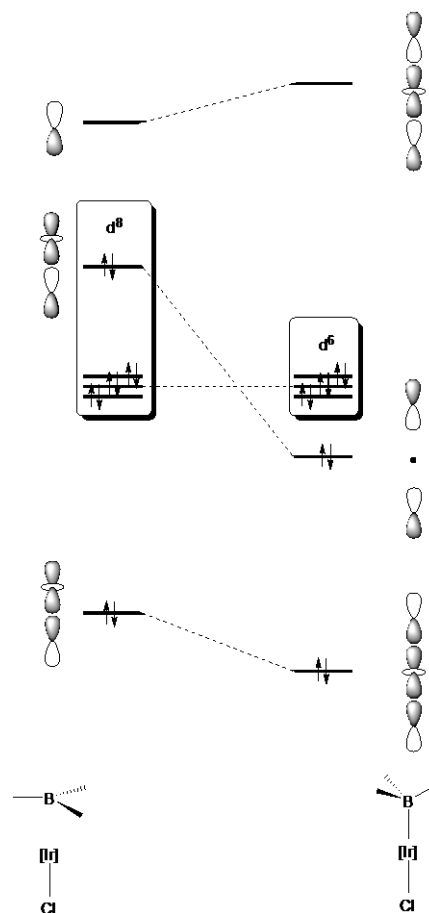
Figure 3. Orbital diagram for the coordination of a borane to an Ir(I) moiety, as adapted from Parkin *et al.*[65]

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 [{$\kappa^3$-(*o*-(*i*Pr$_2$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 [{$\kappa^3$-(*i*Pr$_2$P)C$_6$H$_4$)BPh}AuCl] (**15**) is [Xe]$6s^1 5d^{10}$, indicative of an Au(I) complex.[30] Both these results are strong indications that most of the electron density remains on the metal center 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 reported gold(I) phosphine 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 $\kappa^4$-B(mim)$_3$ ligand. The ligands *trans* to the boron 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, while the interaction between the *trans* ligand and the metal center is antibonding in character.[65] It is also observed that the weakest $\pi$-acceptor will preferably bind the metal *trans* to the boron atom, a factor that is likely due to the strong $\pi$-basicity of the methimazolyl moieties. Indeed, $\pi$-acceptors will be favourably placed in the position *cis* to boron, since they would share the same interaxial molecular orbitals as all three mim moieties, which are strong $\pi$-donors.[67]

### Note Added after Submission

The addition of NaHBEt$_3$ or [HPt(dmpe)$_2$]$^+$ to phosphinoborane complex *trans*-[(Ph$_2$P(CH$_2$)$_2$B(C$_8$H$_{14}$))$_2$Re(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. [87]

## Conclusion

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 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$_2$PCH$_2$AlMe$_2$. 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(diphenyl-phosphino)butane
dmap = 4-(dimethylamino)pyridine
dmpe = 1,2-bis(dimethylphosphine)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

## Acknowledgments

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[2] While "amphoteric" indicates that a molecule can act as an acid or a base, which is the case for the class of ligands reported here, "ambiphilic" put in evidence that these ligands can interact by two distinctive chemical functionalities. The two terms will be used indiscriminately throughout the document.

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[75] According to Green's bond classification,[79] the M→Z interaction is formally a -2 ligand, which is in agreement with the activation of the B-H bond which is oxidative in nature. However, as shown in one of the latter section of the document, experimental evidences are in favour of a M→B interaction being dative in nature with the transition metal keeping its original electronic configuration.

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Table 1. Various metallaboratranes with a Tm framework

| Species | Geometry | Linker | M | $L_{trans}$ | $L_{cis}$ | R | M-B (Å) | $^{11}$B NMR ($\delta$) |
|---|---|---|---|---|---|---|---|---|
| **55**[58] | $\kappa^4$-oct | mim$^{tBu}$ | Fe | CO | CO | | 2.108(6) | 20.3 |
| **54**[57,59] | $\kappa^4$-oct | mim$^{Me}$ | Ru | PPh$_3$ | CO | | 2.161(5) | 17.1 |
| **56**[60] | $\kappa^4$-oct | mim$^{Me}$ | Ru | CO | CO | | N.A. | N.A. |
| **57**[60] | $\kappa^4$-oct | mim$^{Me}$ | Ru | CN$t$Bu | CO | | 2.176(7) | 14.6 |
| **58**[60] | $\kappa^4$-oct | mim$^{Me}$ | Ru | CNXyl | CO | | N.A. | N.A. |
| **59**[60] | $\kappa^4$-oct | mim$^{Me}$ | Ru | CNMes | CO | | 2.146(4) | N.A. |
| **60**[60] | $\kappa^4$-oct | mim$^{Me}$ | Ru | PPh$_3$ | CS | | 2.154(5) | N.A. |
| **61**[61] | $\kappa^4$-oct | mim$^{Me}$ | Os | PPh$_3$ | CO | | 2.171(8) | 12.4 |
| **62**[62] | $\kappa^4$-pyr | mim$^{tBu}$ | Co[a] | PPh$_3$ | | | 2.132(4) | N.A. |
| **63**[63] | $\kappa^4$-oct | taz | Rh | PPh$_3$ | CO | | 2.155(5) | -7.5 |
| **64**[64] | $\kappa^4$-oct | mim$^{Me}$ | Rh | Cl | PPh$_3$ | | 2.132(6); 2.122(7) [b] | 1.7 |
| **65**[65] | $\kappa^4$-oct | mim$^{tBu}$ | Rh | Cl | PPh$_3$ | | 2.095(3) | N.R. |
| **66**[66] | $\kappa^4$-oct | mim$^{Me}$ | Rh[a][d] | cod | cod | | N.A. | 4.1[c] |
| **67**[66] | $\mu$-$\kappa^2$ S,S',$\kappa^4$ | mim$^{Me}$ | Rh[a][e] | $\kappa^2$ Tm | $\kappa^2$ Tm | | 2.098(6); 2.091(5) | N.A. |
| **68**[67] | $\kappa^4$-oct | mim$^{Me}$ | Rh | PPh$_3$ | H | | N.A. | 2.1 |
| **69**[67] | $\kappa^4$-oct | mim$^{Me}$ | Rh[a] | PPh$_3$ | CN$t$Bu | | 2.155(7) | 9.0 |
| **70**[67] | $\kappa^4$-oct | mim$^{Me}$ | Rh[a] | PPh$_3$ | CNXyl | | 2.146(3) | 8.8 |
| **71**[67] | $\kappa^4$-oct | mim$^{Me}$ | Rh[a] | CNXyl | PPh$_3$ | | N.A. | 8.7 |
| **72**[67] | $\kappa^4$-oct | mim$^{Me}$ | Rh[a] | PPh$_3$ | CNMes | | 2.146(3) | -9.1 |
| **73**[67] | $\kappa^4$-oct | mim$^{Me}$ | Rh[a] | CNMes | PPh$_3$ | | N.A. | -2.0 |
| **74**[67] | $\kappa^4$-oct | mim$^{Me}$ | Rh[a] | PMe$_3$ | PMe$_3$ | | 2.153(11); 2.148(10) [b] | 9.5 |
| **75**[67] | $\kappa^4$-oct | mim$^{Me}$ | Rh[a] | PMe$_3$ | PPh$_3$ | | N.A. | 8.8 |
| **76**[67] | $\kappa^4$-oct | mim$^{Me}$ | Rh[a] | PPh$_3$ | PPh$_3$ | | N.A. | N.A. |
| **77**[67] | $\kappa^4$-oct | mim$^{Me}$ | Rh | S$_2$CNEt$_2$ | S$_2$CNEt$_2$ | | N.A. | N.A. |
| **78**[68] | $\kappa^3$-oct | mim$^{Me}$ | Ir | PPh$_3$ | CO; H | mim$^{Me}$ | N.A. | 3.2 |
| **79**[68] | $\kappa^3$-oct | mim$^{Me}$ | Ir | PPh$_3$ | CO; H | H | 2.210(5) | -4.5 |
| **80**[65] | $\kappa^3$-oct | mim$^{tBu}$ | Ir | PPh$_3$ | CO; H | mim$^{tBu}$ | 2.179(4) | N.A. |
| **81**[65] | $\kappa^3$-oct | mim$^{Ph}$ | Ir | PPh$_3$ | CO; H | mim$^{Ph}$ | 2.186(3) | N.A. |
| **82**[65] | $\kappa^4$-oct | mim$^{tBu}$ | Ir | Cl | PPh$_3$ | | 2.15(2); 2.18(2)[b] | |
| **83**[69-70] | $\kappa^4$-pyr | mim$^{tBu}$ | Ni | Cl | | | 2.108(6); 2.110(6) | |
| **84**[70] | $\kappa^4$-pyr | mim$^{tBu}$ | Ni | N$_3$ | | | 2.092(5) | |
| **85**[70] | $\kappa^4$-pyr | mim$^{tBu}$ | Ni | NCS | | | 2.079(13) | |
| **86**[70] | $\kappa^4$-pyr | mim$^{tBu}$ | Ni | OAc | | | 2.112(3) | |
| **87**[71] | $\kappa^4$-pyr | mim$^{tBu}$ | Pd | PMe$_3$ | | | 2.050(8) | N.A. |
| **88**[71] | $\mu$-$\kappa,\kappa^3$ | mim$^{tBu}$ | Pd[e] | | | | 2.073(4) | N.A. |
| **89**[72-73] | $\kappa^4$-pyr | mim$^{Me}$ | Pt | PPh$_3$ | | | N.A. | 1.5 |
| **90**[72-73] | $\kappa^4$-oct | mim$^{Me}$ | Pt[a] | PPh$_3$ | H | | 2.157(4) | 1.6 |
| **91**[74] | $\kappa^4$-oct | mim$^{Me}$ | Pt[a] | PR$_3$ (R = Me, Et, Tol) | H | | N.A. | N.A. |
| **92**[73] | $\kappa^4$-oct | mim$^{Me}$ | Pt | Cl | Cl | | N.A. | 0.4 |
| **93**[73] | $\kappa^4$-oct | mim$^{Me}$ | Pt | Br | Br | | N.A. | 2.1 |
| **94**[73] | $\kappa^4$-oct | mim$^{Me}$ | Pt | I | I | | 2.119(4) | 5.1 |
| **95**[73] | $\kappa^4$-oct | mim$^{Me}$ | Pt | I | Me | | 2.119(4) | 4.2 |

[a] Cationic complex. [b] Two independent molecules. [c] At -80ºC. [d] In equilibrium with trigonal bipyramid geometry. [e] Dimetallic species**.**

((Author Portrait))

*Frédéric-Georges Fontaine (left in the picture) obtained his B.Sc. in chemistry at the Université de Montréal in 1998 and received his Ph.D. degree in 2002 at the same university, under the supervision of Davit Zargarian. In 2003, he went to work with T. Don Tilley at University of California, Berkeley as an NSERC post-doctoral fellow. In July 2004, he accepted a position as assistant professor at the Département de Chimie at Université Laval, in Quebec City. His main research interests are the synthesis and coordination chemistry of boron and aluminium ambiphilic ligands with a major emphasis on reactivity.*

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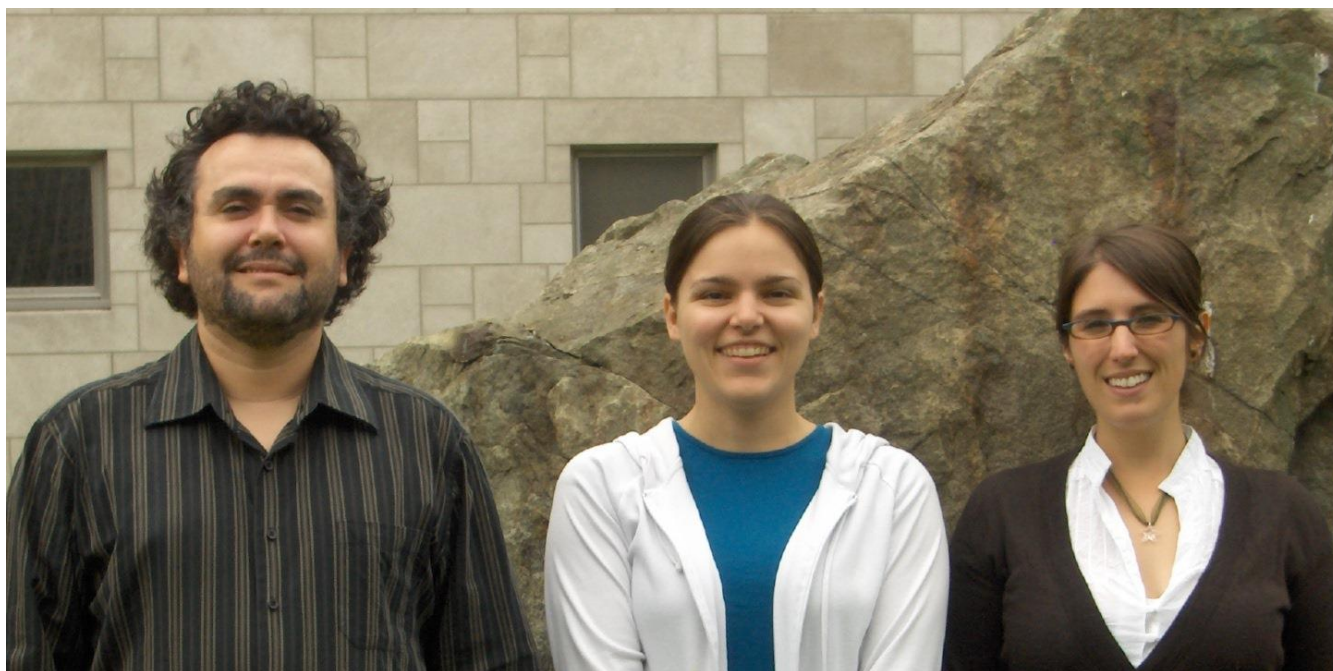
*and synthesis of aluminium ambiphilic ligands and their coordination to late transition metals.*

**Entry for the Table of Contents** (Please choose one layout)

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Ambiphilic and amphoteric molecules, which have both a donor and an acceptor group, display great potential in many applications. This microreview will focus on the coordination chemistry of a subclass of these molecules, where the donor groups can be represented as $L_n$ ligands. The various strategies to overcome aggregation and the reactivity and properties of these complexes will be discussed.

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**Frédéric-Georges Fontaine\*, Josée Boudreau, and Marie-Hélène Thibault**.

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

**Keywords:** (( Ambiphilic ligands / Amphoteric ligands / Bifunctional ligands / Lewis acids ))