Mono-boratabenzene and -phospholyl zirconocene(IV) derivatives: towards mixed heterocycles zirconocene complexes

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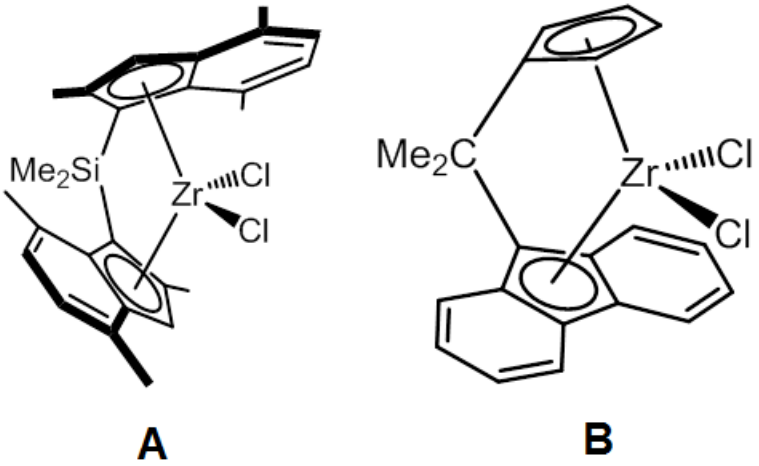
Abstract

In hopes of extending the existing knowledge on the chemistry of phospholyl and boratabenzene complexes of zirconium, which have shown potential notably as polymerization catalysts, this study aims at exploring the synthesis of mono boratabenzene and mono phospholyl zirconium complexes and at studying their reactivity towards the formation of mixed (boratabenzene)(phospholyl)zirconium complexes. Several derivatives of (η^5-phospholyl)$Zr(NMe_2)_xCl_{3-x}$ and (η^6-boratabenzene-NMe_2)$Zr(NMe_2)_xCl_{3-x}$ were synthesized and used as precursors for the formation of mixed (boratabenzene)(phospholyl)zirconium complexes.

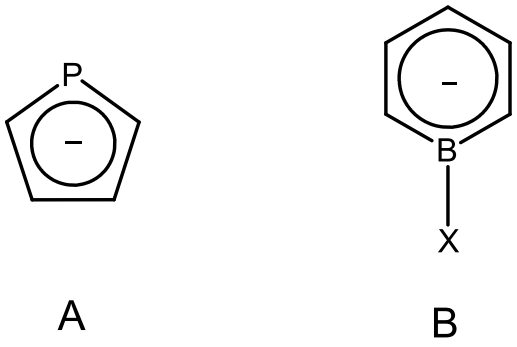
Introduction

Zirconocene derivatives are of considerable interest in a wide variety of transformations, including notably the polymerization of alkenes, [1] the catalytic homologation of silanes and germanes [2], and the functionalization of molecular nitrogen [3-5]. Not surprisingly, a great number of derivatives have been synthesized and the factors influencing their catalytic activity, especially in polymerization reactions, were probed extensively [6-9]. A distinct feature of this type of precatalysts is that their activity and the nature of the polymers formed can vary greatly depending on the steric and electronic properties of the ancillary ligands [6, 7, 9], which in most cases can be conveniently functionalized to one's needs. Striking examples of this role, shown in Scheme 1, include a highly congested *ansa*-(bis)indenyl zirconocene (Scheme 1A) which displays impressive activities for ethylene polymerization despite its steric congestion [10]. The latter system is also selective for the formation of isotactic polypropylene [11], while *ansa*-(cyclopentadienyl)(fluorenyl)zirconocene systems (Scheme 1B) favor the formation of syndiotactic polypropylene [12]. Such change of selectivity and activity upon Cp or Cp-like ligand modifications can also be observed in many synthetically useful reactions, such as hydrozirconation [13], carboalumination [14] and alkene and alkyne coupling [15].



Scheme 1: Typical examples of *ansa*-(bis)indenyl zirconocene (A) and *ansa*-(cyclopentadienyl)(fluorenyl) zirconocene derivatives (B) as selective polymerization pre-catalysts for syndio- and isotactic polypropylene, respectively.

In hopes of expanding the search for novel reactivities of cyclopentadienyl metal derivatives, the synthesis of heteroaromatic analogues has been devised. Two of the most common analogues are the phospholyl [16-36] and boratabenzene moieties, [37-66] each of which having a well-studied coordination chemistry. Most importantly, group IV complexes of the phospholyl [67-72] and boratabenzene [73-77] ligands (Scheme 2) have shown promising activities in olefin oligo- and polymerization [78-87]. Since these ligands appear to be amongst the most attractive heterocyclic Cp analogs for this type of catalysis, it would be worthwhile to study the synthesis of zirconium complexes comprising *both* phospholyl and boratabenzene ligands. These complexes might display reactivities quite different from the ones observed for both families of compounds (bis-phospholyl and bis-boratabenzene zirconium complexes) and would further increase their tunability.



Scheme 2: Simple phospholyl, **Pp** (A) and boratabenzene, **X-Bb** (B) ligands.

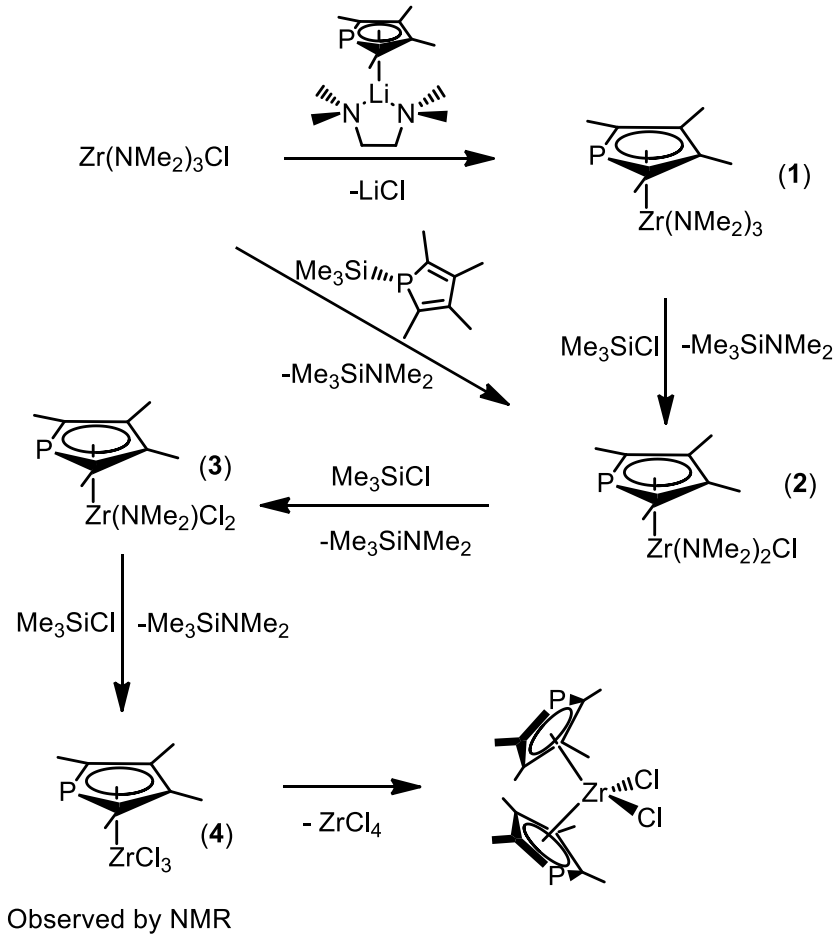
However, the selective synthesis of zirconocene complexes featuring mixed cyclopentadienyl analogues is rarely trivial and the simple sequential addition of A and B ligands (in this work, phospholyl- and boratabenzene- based ligands) is likely to yield a mixture containing mostly A_2ZrCl_2 and B_2ZrCl_2, rather than $ABZrCl_2$. Furthermore, the application of synthetic methodologies well known for mixed all-carbon zirconocene complexes to the synthesis of mixed heteroaromatic ligands is not necessarily straightforward, since the heterocyclic analogues are often less nucleophilic and have lower aromaticities because of the presence of the heteroelements. The most promising strategy to achieve such goal is to target stable derivatives of the $AZrX_3$ and $BZrX_3$ types to which can subsequently be coordinated a B- and an A-ring, respectively. However, the synthesis of such precursors is also challenging, as illustrated by the fact that the very useful precursor $CpZrCl_3$ can only be made efficiently by photolytically initiated chlorination of Cp_2ZrCl_2 [88].

While mono boratabenzene zirconium complexes have already been studied [38, 89, 90], it was interesting to notice that no synthesis has been reported for monophospholyl zirconium complexes. Hence we sought to extend the existing methodologies to make various derivatives of monoboratabenzene zirconium compounds while developing alternative strategies to obtain monophospholyl complexes. Herein, we report the synthesis and observation of the first monophospholyl zirconium complex, $(C_4Me_4P)ZrCl_3$ as well as of several boratabenzene analogues and their reactivity towards the formation of $(C_4Me_4P)(Me_2N\text{-}BC_5H_5)ZrX_2$ mixed compounds.

Synthesis of monophospholyl zirconium complexes.

To the best of our knowledge, no example of $PpZrX_3$ (Pp = phospholyl; X = anionic ligand) species was ever reported. Indeed, attempts made by our group indicated that even an excess of $ZrCl_4$ reacts quickly with phospholyl lithium derivatives to yield Pp_2ZrCl_2 complexes [71]. The preparation of $PpZrX_3$ complexes was thus of particular interest.

Two important strategies have been devised in order to generate Zr-E bonds (E = heteroatom or heterocycle). It was shown that the protonolysis of a zirconium-amido moiety by an E-H molecule could release the corresponding secondary amine and lead to the formation of a Zr-E interaction [91-93]. Since phosphole-H derivatives tend to dimerize through a Diels-Alder pathway [94], the latter method can only be useful for sterically demanding phospholyl ligands [95]. Another route is the use of $E\text{-}SiMe_3$ reagents in the presence of zirconium halides, which takes advantage of the elimination of the stable $SiMe_3Cl$ species as a driving force. These methods yield $EZrX_3$ compounds in cases where E is particularly sterically demanding [96]. It has been shown that phospholyl-$SiMe_3$ [20] or phospholyl-$SnMe_3$ [72] compounds could lead to phospholyl-metal complexes, including $PpTiCl_3$ complexes [70, 95], but no report could be found on the successful use of the method to make monophospholyl zirconium complexes. Hence a different method had to be designed. Scheme 3 illustrates our most successful attempts at making monophospholyl zirconium species using the 2,3,4,5-tetramethylphospholyl ligand (**Pp***) [71], a phospholyl analogue of the ubiquitous pentamethylcyclopentadienyl ligand (Cp*****).



Scheme 3: Synthesis or detection of the first η^5-mono phospholyl zirconocenes.

$Zr(NMe_2)_3Cl$ [97, 98] proved to be a useful synthon for the generation of monophospholyl zirconium complexes. The reaction of Pp*Li·TMEDA [18] with $Zr(NMe_2)_3Cl$ cleanly yielded $Pp^*Zr(NMe_2)_3$ (**1**). The ratio of the ^1H NMR signals at 1.89 and 2.21 ppm for the phospholyl-bonded methyl groups integrating for 6H each relative to the dimethylamido methyl groups at 2.94 ppm (18H) and the absence of a complex coupling pattern, as seen for the previously reported bis(2,3,4,5-tetramethylphospholyl) zirconocene, ($Pp^*_2ZrCl_2$) [71], are consistent with the expected structure. In addition, the $^{31}P\{^1H\}$ NMR signal for the Pp* moiety (δ 89.9) is in the range expected for zirconium-bonded phospholyl compounds (cf. 87 ppm for $Pp^*_2ZrCl_2$) [71].

1-trimethylsilyl-2,3,4,5-tetramethylphosphole, (TMS-Pp*), a compound previously reported [20], proved to be a useful starting material. Prepared in good yields from Pp*Li and $SiMe_3Cl$, the resulting colorless oil was reacted with $Zr(NMe_2)_3Cl$, conveniently yielding $Pp^*Zr(NMe_2)_2Cl$ (**2**) instead of the $SiMe_3Cl$ elimination product **1**. ^1H NMR signals again did not show the complex coupling pattern expected for a bis(phospholyl)zirconium species and the ratio of the Pp* integrations (1.98 and 2.07 ppm integrating for 6H each) against the NMe_2 signal (2.92 ppm, 12H) indicated the $Pp^*Zr(NMe_2)_2Cl$ composition. The ^{31}P NMR signal for the phospholyl (97.2 ppm) is at lower field compared to **1**, in agreement with the replacement of a dimethylamido ligand with the more electron withdrawing and less π-donating chlorido ligand. In contrast to the more soluble **1**, compound **2** could be recrystallized from a pentane solution, yielding yellow crystals of X-ray diffraction quality.

Compound **2** crystallizes in the triclinic $P\bar{1}$ space group with Z = 4. The asymmetric unit contains two crystallographically independent molecules, one of which is shown in Figure 1. Intramolecular short contact distances between Zr and one of the amino methyl groups were found (2.813 and 2.848 Å), suggesting the possibility of a weak agostic interaction, which would be in agreement with the electron-deficient nature of the chlorido substituted compound. The sum of the angles around N(1) and N(2) is 360°, within the experimental error, indicating that the amido groups adopt a sp^2-type arrangement, expected for a π-basic amido moiety donating electrons to a formally electron-poor metal center. Nevertheless, the Zr-N-C angles in these amido group deviate significantly from the expected 120° (C(10)-N(1)-Zr(1) and C(12)-N(2)-Zr(1) of 129.7(3) and 141.0(3)°, respectively) indicating a kinking of the Me-N-Me group towards the metal center, which might be caused by the weak agostic interactions observed. Mono phospholyl titanium complexes are known [95], but to our knowledge **2** represents the first example of an η^5-monophospholyl zirconium complex.

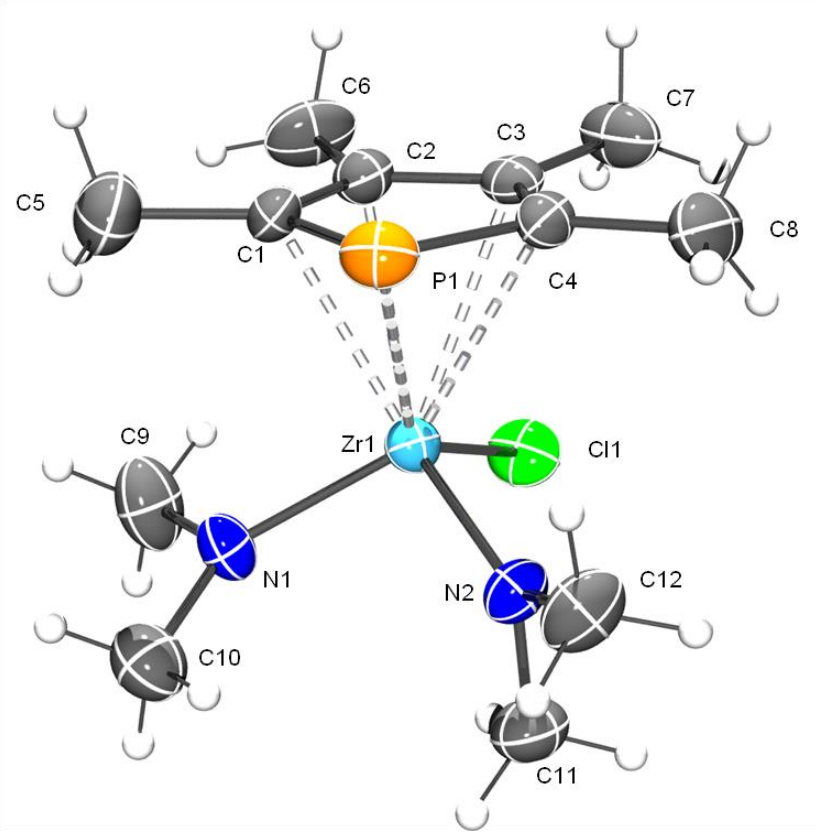


Figure 1: ORTEP plot of one of the two molecules in the asymmetric unit of **2** with ellipsoids at the 50% probability level. Hydrogen positions are idealized and hydrogen atoms are drawn as spheres of arbitrary radius. Selected bond distances (Å): Zr(1)-N(1) 2.021(4), Zr(1)-N(2) 2.006(4), Zr(1)-Cl(1) 2.4383(13), Zr(1)-P(1) 2.7346(14), Zr(1)-C(1) 2.558(5), Zr(1)-C(2) 2.579(5), Zr(1)-C(3) 2.631(4), Zr(1)-C(4) 2.656(4), Zr(1)-C(11) 2.848(6), N(2)-C(11) 1.459(7), N(2)-C(12) 1.469(5), N(1)-C(9) 1.453(6), N(1)-C(10) 1.451(6). Selected bond angles (°): N(1)-Zr(1)-Cl(1) 101.97(11), N(2)-Zr(1)-Cl(1) 108.22(11), N(1)-Zr(1)-N(2) 101.38(15), C(10)-N(1)-C(9) 110.6(4), C(10)-N(1)-Zr(1) 129.7(3), C(9)-N(1)-Zr(1) 119.6(3) , C(11)-N(2)-Zr(1) 109.6(3), C(12)-N(2)-Zr(1) 141.0(3), C(11)-N(2)-C(12) 109.4(4) .

The addition of $SiMe_3Cl$ to **2** allowed the identification of $Pp^*Zr(NMe_2)Cl_2$ (**3**) by NMR spectroscopy. The ^{31}P NMR signal (107.8 ppm) follows the trend observed for **1** and **2** and is at even lower field. The ^{1}H NMR spectrum displays two signals for the phospholyl moiety (1.93 and 2.07 ppm, integrating for 6H each) and one signal for the dimethylamido ligand at 3.06 ppm (6H). The simple coupling pattern observed is

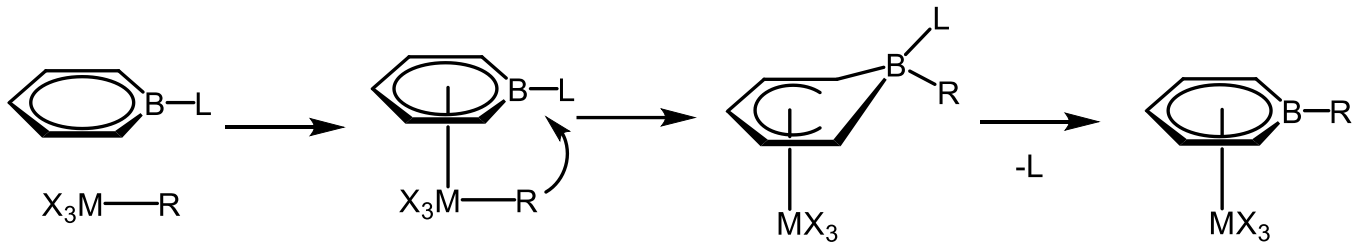
consistent with a monophospholyl species. The compound is relatively stable in solution, although some ligand exchange was suggested by the detection of a small amount of $Pp^*_2ZrCl_2$ by NMR. When **1** reacts with an excess of $SiMe_3Cl$ at 50 °C, the disappearance of the NMe_2 resonance and the appearance of a new species can be followed by ^1H NMR. The new species displays two broad ^1H NMR signals (1.80 and 2.16 ppm, each integrating for 6H each), consistent with a new mono phospholyl complex, which is in all likelihood Pp^*ZrCl_3 (**4**). The new species also displays a broad ^{31}P NMR resonance (138.6 ppm) at much lower field than **1-3**. The formation of **4** was accompanied by the formation of large amounts of $Pp^*_2ZrCl_2$, indicating its instability in solution. The broadness of the ^1H and ^{31}P NMR signals attributed to **4** likely indicates the presence of **4** as a polymeric material, $[Pp^*ZrCl_3]_n$, This is in line with the observation that $(Bb)ZrCl_3$ is a polymeric material which readily decomposes to $(Bb)_2ZrCl_2$ and $ZrCl_4$ [90]. The short lifetime of **4** in solution illustrates the highly favorable formation of the $Pp^*_2ZrX_2$ complexes in the absence of good π-donating ligands.

Synthesis of $BbZrX_3$ derivatives.

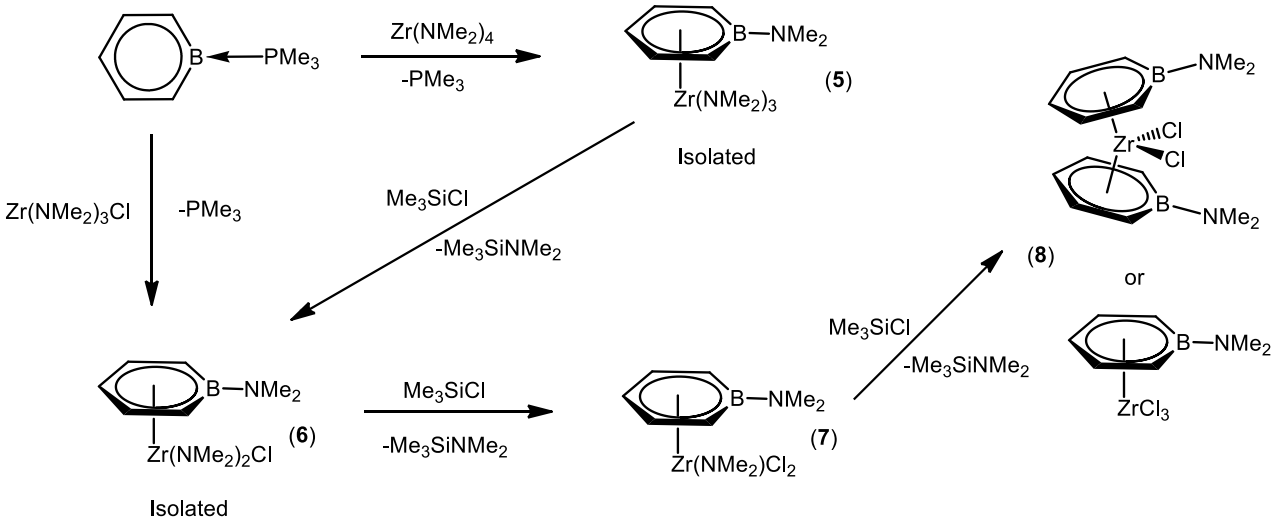
The boratabenzene (**Bb**) moiety has also been coordinated to most transition metals [73]. It usually adopts an η^6-coordination mode, although in some instances, notably in the presence of π-donating ligands or bulky ligands on the boron atom, the boron centre can be farther from the metal centre than the carbon atoms and will formally be in an η^5-coordination mode [80, 90]. Although more coordination modes are possible for the boratabenzene ligand, they remain relatively rare [63].

Zirconium complexes bearing two NMe_2-Bb ligands have been shown to be active in the polymerization of ethylene [80]. The synthesis of mono-boratabenzene species $(NMe_2\text{-}Bb)Zr(NMe_2)_3$ has been reported by Bazan [89], from the reaction of $Zr(NMe_2)_4$ with the PMe_3-borabenzene adduct (Bb-PMe_3) [99]. The mechanistic pathway involves the migration of the amido group to the boron atom and the elimination of PMe_3. During the process, the borabenzene ring changes from an L_3-type ligand to an L_2X-type ligand (Scheme 4). We thus set out to prepare Me_2N-boratabenzene derivatives of zirconium using a similar

approach (Scheme 5) bearing chlorides moieties on the zirconium atom which could be used as precursors to generate the desired mixed boratabenzene-phospholyl zirconium species.



Scheme 4: Postulated mechanism of coordination-intramolecular nucleophilic substitution for the synthesis of $(NMe_2\text{-Bb})Zr(NMe_2)_3$ [89].



Scheme 5: Boratabenzene-NMe_2 zirconium complexes (BbZr) synthesized or observed in this study.

In qualitative agreement with Bazan's postulated coordination-intramolecular nucleophilic substitution (Scheme 4), a rough picture of the importance of steric hindrance could be drawn from the various synthesis attempts. Indeed, the reaction with $Zr(NMe_2)_4$ was reported to proceed for over a day at 70 °C [89], while the reaction with $Zr(NMe_2)_3Cl$ was complete in 90 minutes under similar conditions. Reaction times with a *para*-functionalised borabenzene analogue are even longer (see Supporting Information). No reaction

with the very hindered Bb-PCy_3 was observed. These observations are in agreement with a recent report by our group where it was demonstrated that the substitution mechanism probably occurs through electrophilic activation of the borabenzene moiety at the *ortho* position, generating a boronium intermediate, followed by the delivery of the donating group to the boron atom [100]. The same report concluded that the bulkier groups at the boron atom would not undergo ligand exchange reactions.

Unfortunately, all of the BbZr complexes studied were highly oxygen- and moisture-sensitive oils that were not amenable to crystallization and could not be characterized by other methods than NMR spectroscopy. (NMe_2-Bb)Zr(NMe_2)$_3$ (**5**) has previously been reported [89] and the new compounds reported herein were easily identified based on comparisons with NMR data reported for **5**. Two different pathways have been explored to generate the (NMe_2-Bb)Zr(NMe_2)$_2$Cl derivative, **6**. First, the addition of Zr(NMe_3)$_3$Cl to a Bb-PMe_3 adduct generated the expected product. Also, the addition of Me_3SiCl to species **5** generated **6**, similarly to what was observed with the phospholyl derivatives. We found that the first approach was the most practical, as it did not require the isolation of **5**, which was more tedious to isolate than Zr(NMe_2)$_3$Cl. Compound **6** possesses very similar spectroscopic properties to species **5**, with NMe_2 resonances at 2.75 (6H) and 2.84 ppm (12H) and aromatic multiplets at 5.77 (overlapping, 3H) and 6.96 (2H) ppm in ^{1}H NMR. The only important difference was the integration of the NMe_2 resonances, which were in a 2:1 ratio (Zr-NMe_2: B-NMe_2) rather than in a 3:1 ratio for **5**.

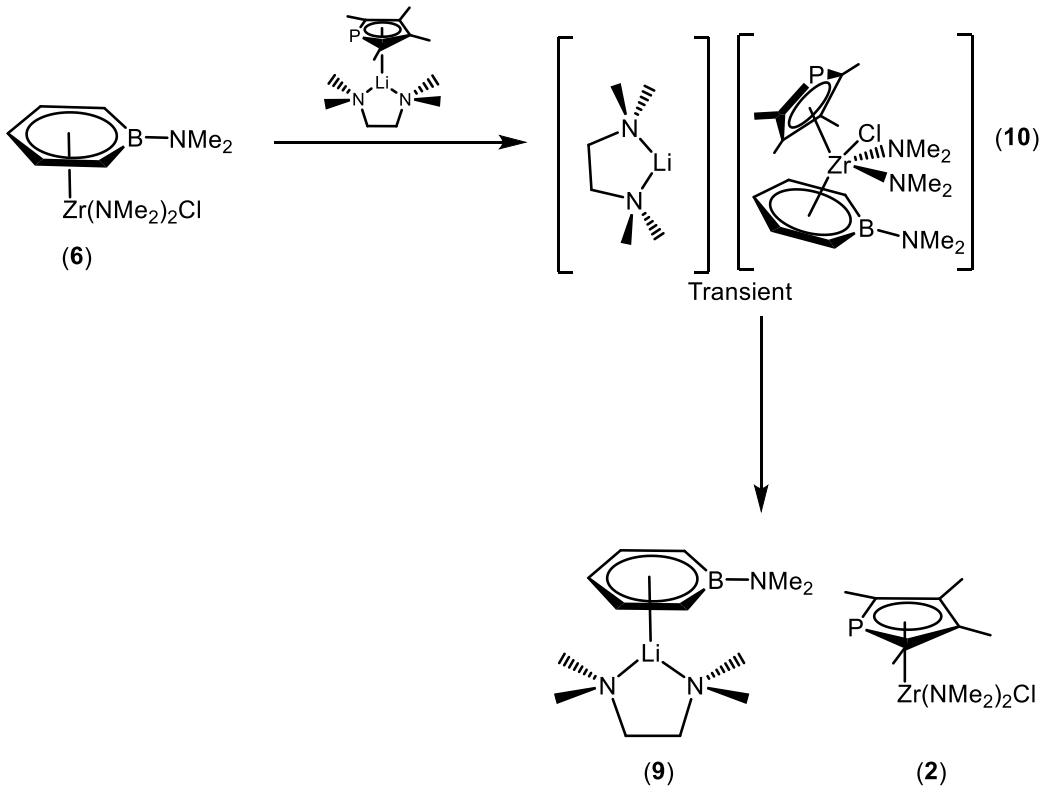
The replacement of the zirconium bounded amido moieties on **6** could be done by direct addition of Me_3SiCl, generating species (NMe_2-Bb)Zr(NMe_2)Cl_2 (**7**) and "(NMe_2-Bb)$ZrCl_3$" (**8**) when one and two equivalents of the silyl reagent were added, respectively. In both cases, the difficulty in isolating the species limited their characterization, but the integration of the resonances (1:1 for the Zr-NMe_2:B-NMe_2 ratios) strongly suggested the (NMe_2-Bb)Zr(NMe_2)Cl_2 structure (**7**), at least ruling out the generation of a possible bis-boratabenzene species (NMe_2-Bb)$_2$Zr(NMe_2)Cl. In the case of the generation of **8**, two products were observed by ^{1}H NMR spectroscopy. Unfortunately, no clear trend from the NMR shifts of the aromatic protons can be used as an aid to the conclusive identification of **8**. Moreover, ^{13}C and especially ^{11}B have

been uninformative. One of the sets of resonances for the boratabenzene moieties (5.57, 5.80 and 7.06 ppm), closely resembles that observed for (N*i*Pr$_2$-Bb)$_2$ZrCl$_2$ (5.70, 5.84, 7.14 ppm)[80] while the other product displayed a set of ^{1}H resonances at lower field (6.16, 6.39 and 7.33 ppm) which could be tentatively assigned to **8**. However, the instability of the reaction mixture made impossible the isolation of these species in the solid state for a conclusive assignment. In all the cases, ^{1}H NMR aromatic signals and NMe$_2$ signals within the range expected for boratabenzene adducts, thus confirming the integrity of the boratabenzene ligand moiety throughout the reactions studied.

Attempts to generate a mixed complex

In order to generate the desired mixed heterocyclic product (NMe$_2$-Bb)(Pp*)Zr(NMe$_2$)$_2$, one equivalent of Pp*Li·TMEDA was added to compound **6** in a deuterated benzene solution. A transient species with ^{1}H NMR signals at 1.70 (6H), 2.23 (6H), 2.81 (6H), 2.93 (12H), 5.31(1H), 5.89 (2H) and 6.88 (2H) ppm and a ^{31}P{^{1}H} NMR signal at 79.7 ppm was identified right after the addition. Letting the reaction run for 9 hours did show that the latter species was transient since the major end products identified by ^{1}H and ^{31}P NMR spectroscopy were **2**, (Pp*)Zr(NMe$_2$)$_2$Cl, and (NMe$_2$-Bb)LiTMEDA (**9**) (See Figure S22-25). It is very likely that the transient species observed is that of an 18-electron species, [(Pp*)(Bb-NMe$_2$)Zr(NMe$_2$)$_2$Cl]$^-$ (**10**) which ultimately eliminates **9** to form **2.** The lability of boratabenzene ligands has been reported before [101]. It is known that this heterocyclic moiety is one of the most stable aromatic rings, notably in the presence of π-donor groups on the boron atom. Indeed, it was shown to be more stable than cyclopentadienyl systems [102]. In order to verify whether the removal of the NMe$_2$-Bb is a general process, a functionalized derivative of **5**, (1-NMe$_2$-4-*i*PrBb)Zr(NMe$_2$)$_3$ (**5a**), was reacted with Pp*LiTMEDA in conditions similar to those described above (see supporting information). It was shown that species **1** and (1-NMe$_2$-4-*i*PrBb)Li·TMEDA (**9a**) were formed cleanly. Similarly, several other reactions were performed on similar functionalized derivatives of **5-7**. In all the cases, poor conversion rates

and/or the formation of **1**, **2** or $Pp^*_2ZrCl_2$ as the only identifiable products were observed, once more demonstrating the ease of ligand exchange in these systems.



Scheme 6: Major products identified in the reaction mixture of **6** with Pp*LiTMeDA.

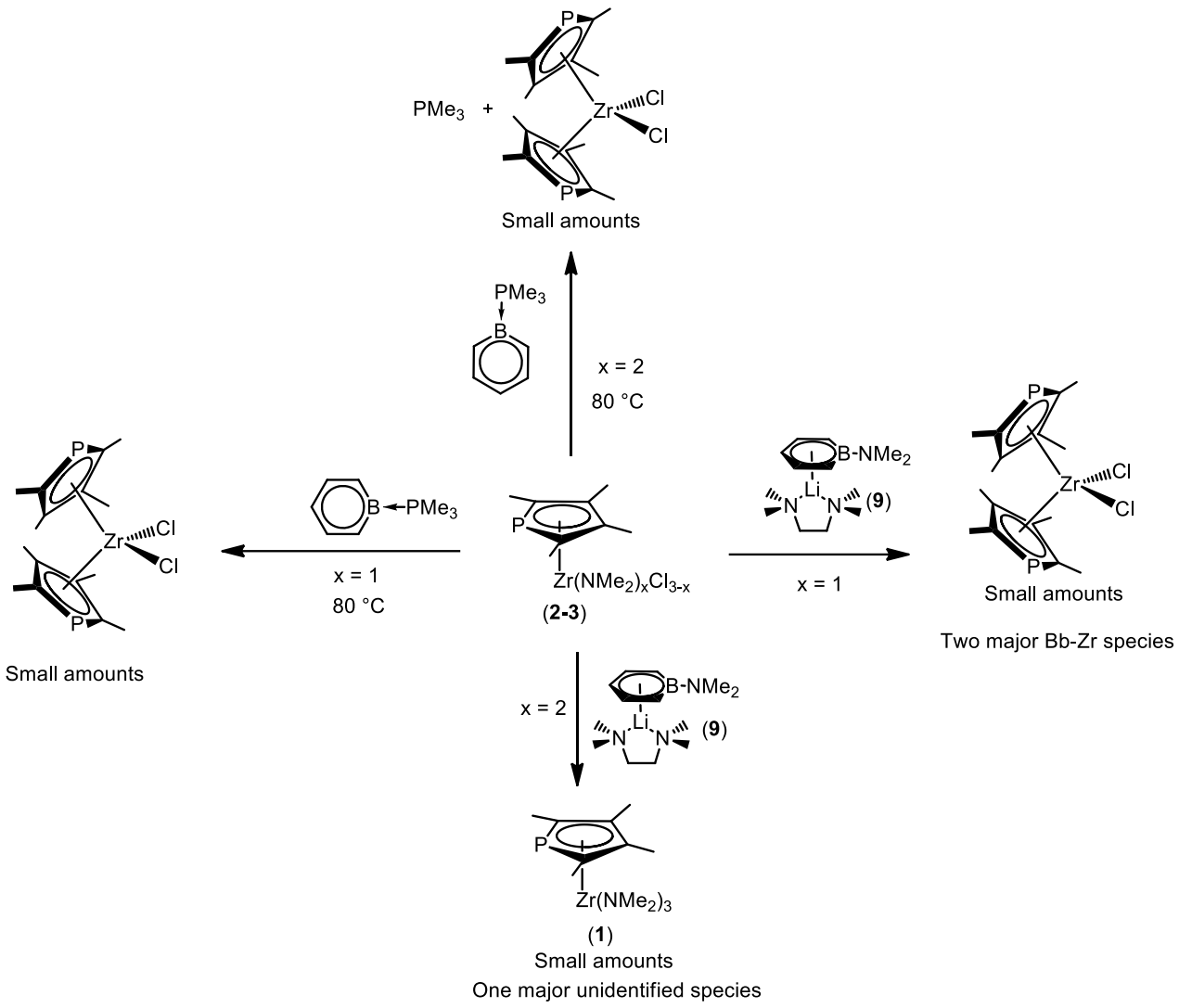
In a similar fashion to our work with (NMe_2-Bb)Zr derivatives, Pp*Zr derivatives were reacted with **9** (Scheme 7). Within a few hours, the reaction of **2** with **9** allowed the observation of two $^{31}P\{^1H\}$ resonances NMR at 83.7 ppm and 89.9 ppm, the latter one corresponding to **1**.

When **9** was reacted with **3** instead, at least four unidentified ^{31}P NMR resonances (including one at 83.7 ppm) were observed in addition to $Pp^*_2ZrCl_2$. The ^1H NMR spectrum, although complex in the Pp* region, strongly suggests the presence of two major (Bb-NMe_2)Zr species in an approximate 1:1 ratio. The major ^{31}P and ^1H NMR signals are consistent with the presence of either a transient intermediate similar to **10**

(which has a ^{31}P NMR resonance at 79.7 ppm) or, most likely, with the presence of a PpBbZr species, since the composition of the mixture does not evolve significantly in time. Unfortunately, the complexity of the mixture does not allow a definitive interpretation of the reaction.

When **3** was reacted with Bb-PMe_3 at 80 °C in deuterated benzene for several days, the complete consumption of the Bb-PMe_3 starting material could be observed by NMR, with $Pp^*_2ZrCl_2$ as the major reaction product and the only identifiable one in the mixture. Two sets of aromatic resonances consistent with boratabenzene moieties could be observed by ^1H NMR, but no conclusive assignments could be made.

Several more reactions based on this method were performed, all of which lead to poor conversion rates and to PMe_3, $Pp^*_2ZrCl_2$ and Pp*Zr species as the only identifiable products. Therefore, it seems that the possibility of generating the desired compounds is plagued with rearrangement reactions. Indeed, the lability of the boratabenzene moiety which is stable as an anionic species and the stability of the phospholyl zirconium complexes tend to disfavour the mixed heterocyclic species.



Scheme 7: Products observed in reaction mixtures of PpZr derivatives **2-3** with Bb-PMe_3 or **9**.

Conclusion. In the course of this study, we successfully prepared and characterized the first η^5 mono phospholyl zirconium compounds. Apart from **1**, all of the species observed exhibited some degree of instability in solution with respect to ligand exchange. In general, the more stable complexes were the ones having the highest number of amido groups coordinated to zirconium, whereas the presence of chlorido ligands decreased the stability toward ligand scrambling. We also successfully synthesized and identified several mixed chlorido/dimethylamido derivatives of (NMe_2-Bb)Zr complexes. The evidence strongly

suggests that a mixed complex was obtained at least as a transient species, [($PpMe_4$)(Bb-NMe_2)Zr(NMe_2)-$_2$Cl]$^-$(**10**). Given the number of unknown ^{31}P signals observed, Pp*BbZr mixed species were likely present in the complex reaction mixtures obtained throughout this work, with several experiments strongly suggesting the formation of such species. Unfortunately, the complexity of the mixtures made conclusive assignments by ^{1}H NMR very difficult. Moreover, the mixtures were generally viscous, moisture and air sensitive oils which made their purification impractical. In any case, our results indicate that the mixed species are unlikely to be robust compounds, thus severely limiting their application. Indeed, the reactivity of our precursors exhibit a strong tendency to form Pp*Zr complexes and (Bb-NMe_2)Li (**9**). Moreover, the complexes are prone to ligand scrambling. However, the complexes synthesized and isolated in this study could be useful intermediates to generate other mixed species, which will hopefully exhibit a greater stability with respect to ligand exchange.

Experimental section. Syntheses were performed using standard drybox and Schlenk techniques. Solvents were distilled over sodium/benzophenone and stored over 3 Å molecular sieves. Deuterated benzene was dried over Na/K. NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^{1}H), 100.580 MHz (^{13}C), 161.923 MHz (^{31}P), or on Bruker NMR AC-300 at 300MHz (^{1}H), 75.435 MHz (^{13}C), 121.442 MHz (^{31}P). ^{1}H and ^{13}C NMR spectra were referenced internally to the (residual) solvent signals of deuterated solvents. ^{11}B and ^{31}P NMR spectra were referenced externally to $BF_3{\cdot}Et_2O$ and to H_3PO_4, respectively. All spectra were recorded in benzene-d_6 solutions unless otherwise mentioned. 1-chloro-2-(trimethylsilyl)-boracyclohexa-2,5-diene[99], borabenzene-PMe_3 (Bb-PMe_3)[99], $Zr(NMe_2)_4$[92], $ZrNMe_3Cl$[98], bis(cyclopentadienyl)zircona(2,3,4,5)-tetramethylcyclopentadiene[104], 1-phenyl-2,3,4,5-tetramethylphosphole[71], 2,3,4,5-tetramethylphospholyl lithium TMEDA[18], bis(2,3,4,5-tetramethylphospholyl)zirconium dichloride[71] and (NMe_2-boratabenzene)Zr(NMe_2)$_3$ (**5**) [89] were synthesized according to literature methods. Borabenzene-PCy_3[100] was prepared as for borabenzene-PMe_3[99] and reacted with amido zirconium compounds in the same way as described for **5**

and **6**. All compounds synthesized proved to be highly air and water sensitive and no reliable elemental analyses could be obtained.

Synthesis 1-(trimethylsilyl)-2,3,4,5-tetramethylphosphole (TMS-Pp*). 1-phenyl-2,3,4,5-tetramethylphosphole (959 mg; 4.43 mmol) was reacted with lithium (123 mg; 17.7 mmol) in THF for 2h, upon which time TMSCl (1.90 g; 17.0 mmol) was added. An exothermic reaction ensued while a white precipitate formed. After 10 min, the solvent was evaporated under vacuum and diethyl ether was added to the resulting beige suspension. The solution was filtered and evaporated under vacuum. The resulting brown oil was distilled under vacuum (1-10 mtorr) at 51 °C, yielding a colorless liquid (592 mg; 63% yield). ^{1}H NMR : δ 2.04 (d, *J*=10 Hz, 6H), 1.85 (s, 6H), 0.03 (d, *J*=4Hz, 9H); ^{31}P{^{1}H} NMR : δ -32.7.

Synthesis of (2,3,4,5-tetramethylphospholyl)tris(dimethylamido)zirconium (1). $Zr(NMe_2)_3Cl$ (30.5 mg; 118 μmol) and Pp*Li TMEDA (30.9 mg; 118 μmol) were dissolved in toluene, yielding a yellow solution, which was stirred for one hour. The resulting white suspension was evaporated to dryness under vacuum and extracted with pentane. The extract was evaporated to dryness under vacuum, yielding a yellow powder (26 mg, 60% yield). ^{1}H NMR: δ 2.94 (s, 18H), 2.21 (d, *J* = 9 Hz, 6H), 1.89 (s, 6H); ^{13}C{^{1}H} NMR : δ 143.2 (d, *J*=47 Hz), 134.5 (d, *J*=5 Hz), 44.3, 15.3 (d, *J*=25 Hz), 14.0; ^{31}P{^{1}H} NMR : δ 89.9.

Synthesis of (2,3,4,5-tetramethylphospholyl)bis(dimethylamido)zirconium chloride (2). A solution of TMS-Pp* (393 mg; 1.85 mmol) in toluene (10 mL) was added to a solution of $Zr(NMe_2)_3Cl$ (482 mg; 1.86 mmol) (10 mL). The mixture was stirred for 24h, after which time the solvent was evaporated to dryness under vacuum. The compound was extracted with pentane and the extract was evaporated to dryness under vacuum, yielding a crystalline yellow solid (402 mg; 62% yield). ^{1}H NMR: δ 2.92 (s, 12H), 2.07 (d, *J* = 10 Hz, 6H), 1.98 (s, 6H); ^{13}C{^{1}H} NMR: δ 144.2 (d, *J*=51 Hz), 138.0 (d, *J*=5 Hz), 43.8 (d, *J*=2 Hz), 15.1 (d, *J*= 24 Hz), 14.4; ^{31}P{^{1}H} NMR: δ 97.2.

NMe_2-Cl reactions of 1 (Observation of 3 and 4). *Formation of (2,3,4,5-tetramethylphospholyl)(dimethylamido)zirconium dichloride* (**3**). TMSCl (5 μL ; 40 μmol) was added to a solution of **1** (7.0 mg;

20 μmol) in C_6D_6. The solution was heated to 84 °C for 75 minutes. The solution then contained **3** with small amounts of $Pp^*_2ZrCl_2$. ^{1}H NMR: δ 3.06 (s, 6H), 2.07 (d, *J*=9 Hz, 6H), 1.93 (s, 6H);^{13}C{^{1}H} NMR: δ 148.1 (d, *J*=51 Hz), 141.8 (d, *J*=5 Hz), 45.3 (d, *J*=5Hz), 16.4 (d, *J*=23.4 Hz), 14.9 (s); ^{31}P{^{1}H} NMR : δ 107.8.

Formation of (2,3,4,5-tetramethylphospholyl)zirconium trichloride (**4**). TMSCl (6.4 μL; 51 μmol) was added to a solution of **1** (3.6 mg; 10 μmol) in C_6D_6. The solution was heated to 50 °C for an hour and left at room temperature for 14 days. The solution then contained **4** with large amounts of $Pp^*_2ZrCl_2$. ^{1}H NMR: δ 2.16 (d, *J*=10 Hz, 6H), 1.80 (s, 6H); ^{31}P{^{1}H} NMR: δ 138.6 (bs).

Synthesis of (1-dimethylamidoboratabenzene)tris(dimethylamido)zirconium chloride (6). $Zr(NMe_2)_3Cl$ (201 mg; 0.776 mmol) and Bb-PMe_3 (118 mg; 0.776 mmol) were placed inside a Schlenk tube. Toluene (5-10 mL) was added and the yellow solution was heated to 80 °C for 90 min. The solvent was removed under vacuum and the resulting oil was washed once with pentane at -80 °C. The remainder of the product was extracted in pentane at room temperature, yielding 134 mg (51%) of reasonably pure material. ^{1}H NMR: δ 6.96 (dd, *J*= 11 Hz, 8Hz, 2H), 5.77 (two overlapping m, 3H), 2.84 (s, 12H), 2.75 (s, 6H); ^{11}B NMR: δ 31.6. ^{13}C{^{1}H} NMR: δ 138.4, 114.7 (bs), 101.9, 43.6, 38.5.

Cl-NMe_2 substitution reactions of 6 (Observation of 7 and 8). *Formation of (1-dimethylamidoboratabenzene)(dimethylamido) zirconium dichloride* (**7**). TMSCl (13μL; ≈100 μmol) was added to a C_6D_6 solution of **6** (27 mg ; 81μmol). The solution was heated to 80 °C for 1h, after which time the major new NMR signals were assigned to 7. ^{1}H NMR: δ 6.93 (dd, *J*=12 Hz, 7 Hz, 2H), 5.85 (dd, 12 Hz, 2 Hz, 2H), 5.78 (tt; *J*= 7 Hz, 2 Hz, 1H), 2.87(s, 6H), 2.64 (s, 6H); ^{11}B NMR: δ 31.4. ^{13}C{^{1}H} NMR: δ 139.9, 117.9 (bs), 104.1, 44.3, 38.3.

1-dimethylamidoboratabenzene zirconium trichloride* (8) *and/or bis(1-dimethylamidoboratabenzene) zirconium dichloride ($(NMe_2$-Bb$)_2ZrCl_2$). To the previous solution containing **7**, TMSCl was added in large

excess (70 μL) and the resulting mixture was heated to 80 °C for 10 minutes, yielding a red suspension. Two sets of major signals were found in the ^{1}H NMR spectrum along with signals for unreacted **7**.

*Compound **1**, likely (NMe$_2$-Bb)$_2$ZrCl$_2$.* ^{1}H NMR: δ 7.05 (dd, *J*=11 Hz, 7 Hz, 2H), 5.88 (tt, overlapping with compound 2, *J*=7 Hz, 2 Hz, 1H), 2.64 (s, 6H) 5.57 (dd, *J*=11 Hz, 2 Hz, 2H).

Compound 2, likely **8**. ^{1}H NMR: δ 7.33 (dd, *J*= 12 Hz, 7 Hz, 2H), 6.40 (dd, *J*=11.1 Hz , 1.38 Hz, 2H), 6.16 (tt, *J*= 7 Hz, 2 Hz, 1H), 2.72 (s, B-NMe$_2$, 6H).

Synthesis of 1-dimethylamido-boratabenzene lithium·TMEDA (9) [105]. Bb-PMe$_3$ (151 mg; 0.993 mmol) and LiNMe$_2$ (50.7 mg; 0.993 mmol) were dissolved in THF (5 mL). The solution was stirred for 6 hours. A slight vacuum was applied to remove the PMe$_3$ that was produced. The solution was filtered, yielding a brown solution, which was concentrated *in vacuo*. TMEDA (0.25 mL ; 1.5 mmol) was added, and the solution was concentrated further *in vacuo*, then later evaporated to dryness. The solid was extracted with pentane and a greyish solid crystallized from the solution at -80 °C. The solid contained significant amounts of leftover Bb-PMe$_3$ (26 mol %), but could still be used in screening reactions. ^{1}H NMR: δ 7.52 (dd, *J*= 9Hz, 6Hz, 2H), 6.22 (dd, *J*=11Hz, 1Hz, 2H), 5.94 (tt, *J*=7 Hz, 1Hz, 1H), 3.09 (s, 6H), 1.63 (s, 12H), 1.40 (s, 4H); ^{11}B NMR: δ 11.8; ^{13}C{^{1}H} NMR: δ 134.3, 110.3 (bs, barely visible), 99.3, 55.6, 45.0, 39.6.

Reactivity studies. The complex mixtures resulting from the tentative syntheses of mixed complexes made the exhaustive analysis of the ^{1}H NMR highly impractical, if not impossible. Herein we list only the known products observed (both in ^{31}P and ^{1}H NMR) and the unidentified ^{31}P signals in the interest of concision.

6+ Pp*Li TMEDA (Detection of 10). A suspension of Pp*Li TMEDA (2.5 mg; 10 μmol) in C_6D_6 was added to a solution of **6** (3.6 mg; 11 μmol) in benzene-d$_6$. The solution was immediately analyzed by NMR spectroscopy, which allowed to identify a transient intermediate species before **2** and **9** became the major reaction products. ^{1}H NMR: δ 6.88 (dd, *J*= 9Hz, 6Hz, 2H), 5.89 (d, *J*=11 Hz, 2H), 5.31 (bt, *J*=8 Hz, 1H), 2.93 (s, 12H), 2.81 (s, 6H), 2.23 (d, *J*=10Hz, 6H), (2.09 and 2.36 broad features : most likely TMEDA),1.70 (s, 6H); ^{31}P{^{1}H} NMR: δ 79.7.

2+ Bb-PMe$_3$. 2 (5.7 mg; 16 μmol) and Bb-PMe$_3$ (2.4 mg; 16 μmol) were dissolved in C_6D_6. The solution was heated to 80 °C for 14h. Small amounts of conversion occurred. Pp*$_2$ZrCl$_2$ and small amounts of PMe$_3$ were detected by NMR. Unidentified signals : $^{31}P\{^1H\}$ NMR: δ 83.7, 73.5.

3+ Bb-PMe$_3$. Bb-PMe$_3$ (1.2 mg; 8.0 μmol) was added to a solution of **3** generated *in situ* (maximum 9.0 μmol) in C_6D_6. The solution was heated to 80 °C for 3 days, after which time all of the Bb-PMe$_3$ starting material was consumed. Pp*$_2$ZrCl$_2$ was detected as the major product. The ^1H NMR signal attributed to the PMe$_3$ moiety (0.88 ppm, broad multiplet) suggested a very different chemical environment for the ligand. Unidentified signals : $^{31}P\{^1H\}$ NMR: δ 104 (bs), 100.1 (bs), 85.0.

2+ 9. A sample of **9** (4.7 mg ; max 19 μmol) containing some Bb-PMe$_3$ was dissolved in C_6D_6 along with **2**(6.8 mg; 19 μmol). After two days at room temperature, the starting materials and small amounts of **1** were identified in solution. After five days at room temperature, the reaction mixture contained a major unidentified ^{31}P NMR signal at 83.8 ppm as well as **1** and **2.** Unidentified signals: $^{31}P\{^1H\}$ NMR: δ 92.8, 83.8, 78.0.

3+ 9. 9 (4.2 mg ; max 18 μmol) containing Bb-PMe$_3$ was added to **3** generated *in situ* (max. 19.4 μmol) in C_6D_6. Pp*$_2$ZrCl$_2$ was detected in the products by ^{31}P NMR. Unidentified signals : $^{31}P\{^1H\}$ NMR: δ 96.3, 84.9, 83.7, 73.6 (major).

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Appendix A: Supplementary material

CCDC for **2** (1037962) contains the supplementary crystallographic data for this article. It can be obtained free of charge from the Cambridge Crystallographic Data centre at http://www.ccdc.cam.ac.uk/data_request/cif.

Appendix B: Supplementary Information

Experimental details and discussion of the results related to the functionalized boratabenzene derivatives **5a-8a**, crystallographic reports and copies of the relevant spectra can be found in the Supplementary Information.

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