Insights into the Formation of Borabenzene Adducts
via Ligand Exchange Reactions and TMSCl Elimination from Boracyclohexadiene Precursors

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This is the peer reviewed version of the following article: [Insights into the Formation of Borabenzene Adducts via Ligand Exchange Reactions and TMSCl Elimination from Boracyclohexadiene Precursors, Organometallics 2014, 33, 3596–3606], which has been published in final form at [10.1021/om500524].
Table of Contents Graphic

No Reaction

[Diagram showing chemical reactions involving boron and Lewis structures.]
Abstract The bonding properties of borabenzene with various neutral Lewis bases have been investigated. 1-Chloro-4-iso-propyl-2-trimethylsilyl-2,4-boracyclohexadiene reacts with a number of Lewis bases – notably pyridine, PMe₃, PCy₃ and PPh₃ – to afford 4-iso-propylborabenzene-base adducts. These adducts can undergo ligand exchange to afford new borabenzene complexes. The scope and mechanism of the reaction, as well as the steric and electronic properties of different adducts were studied experimentally and computationally.
Introduction

Both the electron donating properties and the steric hindrance of a Lewis base can play a major role in the stability of a Lewis adduct.\(^1\) On one hand work has been done to minimize the binding interactions of Lewis adducts in order to exploit the Lewis character of each individual component. It is notably the case in the now popular “Frustrated Lewis Pairs”\(^2\) that can activate small molecules, such as hydrogen\(^3\) and carbon dioxide,\(^4\) and in the design of ambiphilic molecules,\(^5\) notably as ligands for transition metals\(^6\) and for ion sensing.\(^7\) On the other hand some research has been aiming at increasing the strength of these interactions in order to stabilize very reactive Lewis acid sites from further transformations. Such strategy has been recently devised in the work of Braunschweig to stabilize the borolyl anion (Figure 1A),\(^8\) of Piers to synthesize stable boraanthracene adducts (Figure 1B),\(^9\) and of Bertrand to generate the highly reactive borylene fragment.\(^10\)

![Figure 1. Carbene stabilized borolyl anion (A), boraanthracene adduct (B), phenylboratabenzene (C), and borabenzene-pyridine adduct (D).](image)

Even when generated by flash thermolysis and condensed at 10 K in an argon matrix, the base-free borabenzene moiety has never been isolated or observed.\(^11\) Base-free borabenzene has been calculated to possess a stable aromatic ring but the low lying σ* orbital on boron requires stabilization
by a Lewis base.\textsuperscript{12} Although the boratabenzene moiety, the anionic equivalent of borabenzene, was first reported by Herberich in 1970 (Figure 1C),\textsuperscript{13} the pyridine-borabenzene adduct, the first stable neutral borabenzene, was only reported in 1985 (Figure 1D).\textsuperscript{14} In 1996, an elegant general synthetic route for the generation of neutral borabenzene derivatives was designed by Fu where the aromatization of trimethylsilyl substituted chloroboracyclohexadiene derivatives is initiated by the addition of a Lewis base L which induces the elimination of SiMe\textsubscript{3}Cl (Scheme 1).\textsuperscript{15} The aromatization, however, relies heavily on the capacity of the Lewis base to isomerize the 2,5-boracyclohexadiene precursor to the 2,4-boracyclohexadiene and to form a strong enough bond with boron to stabilize the aromatic product. In such regard, it was observed that the phospholyl complex CpFe(3,4-Me\textsubscript{2}C\textsubscript{5}H\textsubscript{2}P) failed to react with the boracyclohexadiene precursor to generate a borabenzene adduct because of the lack of nucleophilicity at the phosphorous atom.\textsuperscript{16}

Scheme 1. General synthesis of neutral borabenzene adducts.

In the past years, there have been a large number of reports on the properties of boratabenzene derivatives, notably as ligand for transition metals.\textsuperscript{17} There are, however, only a limited number of transition metal adducts with neutral borabenzene analogues as ligands,\textsuperscript{18} and although several boraaromatic adducts have been synthesized by Piers for their optoelectronic properties,\textsuperscript{19} a limited
number of studies have been reported on the reactivity of the neutral fragment.\textsuperscript{14,20} It was observed that although the boron atom is formally electronically saturated in the borabenzene adduct, the Lewis acidic character remains prevalent in borabenzene complexes. The coplanarity between the borabenzene plane and the conjugated system of the acrolein in (3-(dimethylamino)acrolein-borabenzene)Cr(CO)$_3$ complex suggests that the borabenzene acts as a $\pi$-acceptor ligand.\textsuperscript{18b} However, the $\pi$-acidity of the metal-free borabenzene adducts has never been clearly determined.

It has been demonstrated on several occasions that the addition of anionic nucleophiles on borabenzene-PMe$_3$ cleanly generates the boratabenzene analogues by an associative pathway, and that other routes, such as the formation of a borabenzene intermediate, were unlikely.\textsuperscript{20e} We reported that the reverse reaction, the generation of pyridine and trimethylphosphine borabenzene species from an anionic chloroboratabenzene, was also possible, presumably through an associative pathway.\textsuperscript{21} Although it has been reported that (CO)$_3$Cr(THF-borabenzene) could undergo substitution reactions at boron with neutral Lewis bases, to our knowledge no such reaction has been carried out on the metal-free borabenzene species. It was even reported by Fu that the addition of $d_9$-PMe$_3$ to borabenzene-PMe$_3$ in THF at 20°C did not yield ligand exchange.\textsuperscript{20e}

Following our interest in the generation of novel coordination modes for bora(ta)benzene derivatives and in the generation of $Z$-type ligands for transition metals, we decided to evaluate the possibility of synthesizing $\kappa^B$-borabenzene complexes. One possible route for making such complex is by substitution reaction between a neutral borabenzene adduct and a nucleophilic metal centre, to generate the metal-$\kappa^B$-boratabenzene species and the free Lewis base. In order to correctly probe the choice of borabenzene adduct to use for such a reaction, we report herein our study on the formation of neutral borabenzene adducts from the 1-chloro-2-trimethylsilyl-3,5-boracycloexadiene and the possibility to generate novel borabenzene adducts from ligand exchange reactions on a large array of borabenzene adducts.
Results and discussion

Synthesis and characterization of borabenzene adducts.

The synthesis of borabenzene adducts 4-iPr-C₆H₄B-L (2-L, L = PMe₃, pyridine (Py), lutidine (Lu), PCy₃, PPh₃, 1,3-dimesityl-imidazol-2-ylidene (IMes)) was carried out by aromatization of the boracyclohexadiene precursor (1) induced by the coordination of the corresponding Lewis bases L and driven by the release of TMSCl (see Scheme 1, R = i-Pr). As expected, ¹H NMR spectra of species 2-L exhibit two resonances at low field, confirming the aromatic character of the borabenzene adducts. All ¹³C resonances for the borabenzene derivatives are in the expected range for this class of molecules. Interestingly, the ¹¹B chemical shift of neutral borabenzene adducts is highly dependent on the nature of the Lewis base ligand. Indeed, whereas 2-Lu and 2-Py both have resonances at 32.7 ppm, the carbene and phosphine adducts of borabenzene were found to have ¹¹B resonances in the 17 – 22 ppm range. Therefore, little correlation between the bond strength and the ¹¹B chemical shift was observed. In the case of the phosphine adducts, the ¹¹B NMR peaks are present as doublets whereas in the ³¹P spectra the resonances appear as broad quadruplets. In both ¹¹B and ³¹P NMR spectra, coupling constants of 97 and 110 Hz were measured for 2-PPh₃ and 2-PMe₃, respectively, whereas no coupling constant was observed with 2-PCy₃.

Addition of weaker Lewis bases (acetone, tetrahydrofuran, acetonitrile) to 1 did not afford any of the aromatized products and left the starting material unreacted. Interestingly, the reaction of 1 with excess diisopropylamine leads to the consumption of the boracyclohexadiene without the elimination of TMSCl. Indeed, NMR spectroscopy experiments showed complete disappearance of the signals associated with 1 and consumption of amine twelve hours after the addition of two equivalents HNiPr₂. By ¹H NMR spectroscopy, 3a shows the presence of two doublets at δ = 6.87 and 6.51 (J = 12.3 Hz). Also present are two other signals at δ = 6.10 and 2.38 that were found to belong to adjacent protons according to COSY experiments. The SiMe₃ was still present as a singlet at 0.97 ppm. These results are
consistent with the presence of a 2-SiMe₃-3,5-boracyclohexadiene framework as shown in Scheme 2.²²

The observation of four diastereotopic resonances for the methyl groups of the two iPr substituents of the amido, both by ¹H and ¹³C NMR spectroscopy, indicates that no rotation occurs around the B-N bond which suggests a double bond character. These findings are consistent with the formation of 1-diisopropylamido-2-trimethylsilyl-3,5-boracyclohexadiene (3a), which is reminiscent of the previously reported 1-(dimethylamino)-3-methylene-1,2,3,6-tetrahydroborinines.²³ This assignment was further supported by ¹¹B NMR spectroscopy which showed a ~10 ppm upfield shift of the signal from 1, consistent with the substitution of a chlorine atom at boron with an amido group. Similar reactivity was observed with H₂NᵗBu (Scheme 2). In the latter case, only one regioisomer was observed for 3b. Although there is no structural evidence for it, one would suspect the tBu group to be further away from the bulky SiMe₃ substituent for steric reasons (see Experimental Section). As reported by our group recently in the generation of mesityl boratabenzene species, the first step in the generation of borabenzene and boratabenzene adducts is the nucleophilic attack on boron.²² The strong π-donation of the electron lone pair on nitrogen to the empty p orbital on boron makes 3 a very stable conjugated-base. Therefore, the elimination of the acidic proton in Int3 to generate the HCl salt of the corresponding amine is a strong driving force for the generation of derivatives of 3 rather than forming SiMe₃Cl and the expected borabenzene adduct.
Scheme 2. Reactivity of 1 with secondary amines generating derivatives 3 (3a: $R^1 = R^2 = i$Pr; 3b: $R^1 = H, R^2 = t$Bu).

Single crystals were obtained for products 2-PMe₃, 2-PCy₃, and 2-IMes. The ORTEP representations are shown in Figures 2 to 4, respectively, and the important structural data are in Table 1. Species 2-PCy₃ exhibits a disordered borabenene moiety that was easily resolved, but which is nevertheless affecting the precision of the atomic coordinates and of the structural data. The P-B bond lengths in 2-PMe₃ and 2-PCy₃ are of 1.905(3) Å and 1.917(17) Å, respectively, which are in the expected range for phosphine-borabenene species. The C<sub>carbene</sub>-B distance in 2-IMes of 1.570(5) Å is comparable to the B-C bond lengths observed by Herberich in 1-(1,3,4,5-tetramethylimidazol-2-ylidene)-3,5-dimethylborabenene (1.596 Å)²⁰f and by Piers in a IMes-boranthracene adduct (1.607 Å).³⁹b The torsion angle of 25.5° between the plane of the borabenene ring and the imidazolyl moiety of the carbene does not suggest any electronic communication. The B-C bond and C-C bond lengths in the structurally characterized species are unremarkable.
Figure 2 - ORTEP drawing of 2-PMe₃, with anisotropic atomic displacement ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Figure 3 - ORTEP drawing of 2-PCy₃, with anisotropic atomic displacement ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity.
Figure 4 - ORTEP drawing of 2-PCy₃, with anisotropic atomic displacement ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected structural data for 2-L.

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<tr>
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<th>2-PCy₃</th>
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<td></td>
<td></td>
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<tr>
<td>B-L</td>
<td>1.917(17)</td>
<td>1.905(3)</td>
<td>1.570(5)</td>
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<td>1.484(4)</td>
<td>1.482(5)</td>
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<td>124.6(10)</td>
<td>122.1(2)</td>
<td>122.2(3)</td>
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DFT study on borabenzene adducts.

In order to better quantify the stabilizing ability of neutral Lewis pairs, a quantum chemical study was done on the binding energies of 49 neutral Lewis bases to base-free borabenzene (Step b, Scheme 3) in the gas phase using DFT methods and the B3LYP hybrid functional. Hess’ law suggests that the thermodynamic values given in Table 2 will be an indication of the overall trend observed in borabenzene adducts stability even in the absence of the base-free borabenzene species in solution. For simplicity, unsubstituted borabenzene adducts were modeled instead of the iPr analogues synthesized and will be referred to as $2'-L$. In all cases, as expected, the association of Lewis bases to base-free borabenzene proved to be exothermic and exogenic. However, the formation of base-free borabenzene via aromatization of precursor 1 with the elimination of SiMe$_3$Cl was found to be endothermic by 18.2 kcal.mol$^{-1}$ (Step a, Scheme 3). Therefore, a ligand has to stabilize the borabenzene by at least 18 kcal.mol$^{-1}$ in order for the overall process to be thermodynamically favorable. Otherwise, the reverse reaction – the addition of SiMe$_3$Cl on the borabenzene – is expected to be thermodynamically favored.\(^{25}\)

<table>
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<th>L-B-C$_5$</th>
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<td>$\Delta H$</td>
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<td>120.8(2)</td>
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<tr>
<td>$\Delta G$</td>
<td>114.9(12)</td>
<td>117.0(3)</td>
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\(^{24}\)Hess’ law suggests that the thermodynamic values given in Table 2 will be an indication of the overall trend observed in borabenzene adducts stability even in the absence of the base-free borabenzene species in solution.

\(^{25}\)Otherwise, the reverse reaction – the addition of SiMe$_3$Cl on the borabenzene – is expected to be thermodynamically favored.
Scheme 3. Formation of borabenzene adducts as modeled using DFT.

Table 2. Gas phase binding energies of selected Lewis bases (Ligand) with borabenzene at the B3LYP Level of Theory at 298 K using TZVP as a basis set for all atoms.

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<tr>
<th>Ligand</th>
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<th>$\Delta G^\ddagger$ kcal/mol</th>
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<th>$\Delta H^\ddagger$ kcal/mol</th>
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<td>-7.7</td>
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<td>-20.6</td>
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<td>NEt$_2$H</td>
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<td>-31.2</td>
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$^a$Energy of the transition state corresponding to the rotation of the carbonyl ligand bound to borabenzene.

As can be visualized in Figure 5, a direct trend was observed between the Tolman’s electronic parameter of the phosphines modeled and the binding energies for the various phosphine-borabenzene analogues, suggesting that the σ-donating capability of the Lewis pair plays an important role in the
overall stability of the borabenzene adduct.\textsuperscript{26} Indeed, strongly donating PCy\textsubscript{3} and P(i-Pr)\textsubscript{3} give respectively $\Delta G^\circ$ values of -30.9 and -28.1 kcal.mol\textsuperscript{-1}, but electron deficient phosphines such as P(OPh)\textsubscript{3} and PF\textsubscript{3} have binding energies under -20 kcal.mol\textsuperscript{-1}. The steric hindrance of phosphines also seems to play a key role in their binding ability with borabenzene. Indeed, the three species having stronger binding energies than the trend observed are the ones with the smallest cone angles (PMe\textsubscript{3}, P(OMe)\textsubscript{3}, and PF\textsubscript{3}), whereas P(t-Bu)\textsubscript{3} and P(o-tolyl)\textsubscript{3}, the two most encumbered phosphines with Tolman’s cone angles superior to 180°, clearly do not show the trend expected based on the electronic contribution. In both cases, the binding energies are lower than the expected trend by 7-8 kcal.mol\textsuperscript{-1}.

**Figure 5.** Diagram of the bonding energy of phosphine-borabenzene adducts (kcal.mol\textsuperscript{-1}) as determined by DFT methods in function of the Tolman electronic parameters calculated from Ni(CO)\textsubscript{3}L complexes.\textsuperscript{1a}

The steric influence of the amines seems to be much more important factor in the $\Delta G^\circ$ of formation of borabenzene adducts than in the case of phosphines. Although NMe\textsubscript{3}, NEt\textsubscript{3} and NiPr\textsubscript{3} have similar
Lewis basicities,\textsuperscript{1c} there is a very significant difference in affinity between the various adducts formed between the borabenzene and the tertiary amines. Indeed, the smallest amine NMe$_3$ possesses the highest affinity for borabenzene at -26.9 kcal.mol$^{-1}$, which is about 7 kcal.mol$^{-1}$ more favorable than NEt$_3$ (-19.7 kcal.mol$^{-1}$), which in turn is more favorable than NiPr$_3$ by 12 kcal.mol$^{-1}$ (-7.7 kcal.mol$^{-1}$). The same trend can be observed with secondary amines. As for the primary amines, the formation of adducts, even with tBuNH$_2$, is highly exergonic with energies close to -30 kcal.mol$^{-1}$. N-heterocyclic carbenes (NHCs) prove to be the strongest neutral donor, giving binding energies of -50.4 kcal.mol$^{-1}$ in the case of IMes and of -55.9 kcal.mol$^{-1}$ with the less hindered N-methyl containing carbene (IMe). The latter result is not surprising since NHCs are known to stabilize Lewis acid orbitals on boron, notably in the generation of highly reactive fragments such as the borolyl anion and boraanthracene.\textsuperscript{8,9}

It is well documented that boratabenzene species possess $\pi$-accepting capabilities by the presence of an electrophilic $p_z$ orbital on boron, notably evidenced by the planarization of the nitrogen atom on amidoboratabenzene species.\textsuperscript{17} $\eta^6$-Borabenzenene transition metal complexes also exhibit some level of $\pi$-acidity as shown by the coplanarity between the borabenzene plane and the conjugated system of the boron coordinated 3-(dimethylamino)acrolein in a chromium(0) borabenzene complex.\textsuperscript{18b}

However, to our knowledge there is no report on the $\pi$-acidity of metal-free borabenzene adducts. In that regard, we computationally investigated $\pi$-basic ketones and aldehydes as neutral ligands for borabenzene. We found that they do not bind significantly borabenzene and are in the low end of stability of borabenzene adducts with $\Delta G^\circ$ values for MeC(O)Me, PhC(O)Ph, and MeC(O)Ph respectively of -19.1, -19.4, and -22.0 kcal.mol$^{-1}$. The optimized geometry of these species shows coplanarity between the aromatic borabenzene ring and the carbonyl moiety, suggesting some level of $\pi$-donation from the ketones to borabenzene. Modeling of an antiplanar structure for 2’-acetone and 2’-formaldehyde showed that the a free energy gain of respectively 1.1 and 9.3 kcal.mol$^{-1}$ was associated with coplanarization of the borabenzene and ligand fragments. This energy value is representative of the
amount of π-bond character but will include, especially in the case of acetone, a steric hindrance component. Therefore, it appears that B-O π-bond is highly dependent on the steric factors. Nevertheless, the strength of the π-bond is significantly less important than that observed in amido-borane species which are in the range of 30 kcal.mol\(^{-1}\).\(^2^7\)

We also modelled adducts of borabenzene and π-accepting ligands. These ligands were found to bind borabenzene more strongly than their Lewis basicity would suggest. The ΔG° values for the CO, CNMe, CN\(^t\)Bu, CNPh, and CN(C\(_5\)H\(_{11}\)) adducts were found to be respectively -29.1, -38.1, -38.6, -38.8, and -38.4 kcal.mol\(^{-1}\). These results reveal that the borabenzene ring behaves more as a π-donor than a π-acceptor. This latter property is further shown by the geometry of the HOMO of the borabenzene adducts of π-acceptor ligands (Figure 6). This molecular orbital is strongly delocalized between the aromatic cycle and the antibonding π orbital of CO and CNMe. Therefore, these numeric data suggest that the borabenzene ring is a better π-donor than a π-acceptor. However, one should note that the values given in Table 2 do not take into account the possible rearrangements for borabenzene adducts, that are numerous, as demonstrated by the formation 3 in presence of secondary amines or the lack of experimental evidence for the generation of the CO adduct.
Figure 6. Representation of the highest occupied molecular orbital of $2'\text{-CO}$ (MO = 27) and $2'\text{-CNMe}$ (MO = 31) corresponding to the back donation of the $\pi$-system of the borabenzene ring to the $\pi^*$ orbitals of the ligand.

**Experimental validation of the thermodynamic stability of borabenzene adducts**

It was previously demonstrated that the addition of anionic nucleophiles on borabenzene-PMe$_3$ adducts could lead to a large array of boratabenzene species.\textsuperscript{20c} However, no report of substitution of a neutral Lewis base on a metal-free borabenzene adduct was ever reported. In order to test the possibility of such reaction to occur, series of reactions were carried out where neutral Lewis bases (IMes, Pyridine (Py), PCy$_3$, 2,6-lutidine (Lu), and PPh$_3$) were added to species $2\text{-L}$ ($L = \text{IMes, Py, PCy}_3$, Lu, PMe$_3$, and PPh$_3$) and heated in benzene-$d_6$ at 80°C for three days or until equilibrium was reached (Scheme 4), with the results displayed in Table 3.

**Table 3.** Outcome of the addition of various Lewis bases to species $2\text{-L}$. In benzene-$d_6$ at 80 °C for three days. X = reaction does not take place; O = complete substitution occurs; Eq. = Equilibrium has been reached.

<table>
<thead>
<tr>
<th></th>
<th>IMes</th>
<th>Py</th>
<th>PCy$_3$</th>
<th>Lutidine</th>
<th>PPh$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{-IMes}$</td>
<td>-</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>$2\text{-Py}$</td>
<td>O</td>
<td>-</td>
<td>Eq.</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>$2\text{-PMe}_3$</td>
<td>O</td>
<td>Eq.</td>
<td>Eq.</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>$2\text{-PCy}_3$</td>
<td>X</td>
<td>Eq.</td>
<td>-</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>$2\text{-Lu}$</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
<td>X</td>
</tr>
<tr>
<td>$2\text{-PPh}_3$</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>X</td>
<td>-</td>
</tr>
</tbody>
</table>
Scheme 4. Exchange reaction of borabenzene adducts.

As can be expected from the DFT results, species 2-IMes with a very strong carbene-boron interaction does not undergo any exchange reaction with any other ligand. On the other hand, the addition of IMes to 2-PMe₃, 2-Py, and 2-PPh₃ leads to the formation of 2-IMes, which is again explained by the stability of the N-heterocyclic carbene adduct. However, 2-PCy₃ and 2-Lu do not undergo exchange reaction with IMes. The later result suggests that the steric environment around boron is playing an important factor in the substitution reactions. This result is supported by the evidence that 2-Lu does not undergo substitution reaction with any of the ligands that were used, or that the addition of 2,6-lutidine to any borabenzene adduct does not form new adducts. As can be seen on the DFT model of 2-Lu (Figure 7B), the boron pₓ orbital is shielded on both sides by the methyl groups of the 2,6-lutidine which should prevent an associative substitution at the boron atom, especially when compared with 2-PMe₃ where the pₓ orbital on boron is much more prominent (Figure 7).
Figure 7. Representation of the molecular orbital of (A) 2’-PMe3 (LUMO; MO = 42) and (B) 2’-Lu (LUMO + 5; MO = 55) putting in evidence the p\textsubscript{z} orbital on boron.

2-PPh\textsubscript{3}, which according to the DFT results is the weakest of the synthesized borabenzene adduct with a ligand-borabenzene bond strength of 24 kcal.mol\textsuperscript{-1}, undergoes complete substitution with PMe\textsubscript{3}, pyridine and IMes. 2-PPh\textsubscript{3} proved to be an excellent precursor for substitution reaction. Indeed, although borabenzene-NEt\textsubscript{3} and borabenzene-PMe\textsubscript{3} have both been used as starting reagents for accessing novel bora- and boratabenzene species and are useful by the fact that NEt\textsubscript{3} and PMe\textsubscript{3} are volatile side-products, borabenzene-PPh\textsubscript{3} proves to be easier to isolate and more stable in solution than borabenzene-NEt\textsubscript{3}. Furthermore, PPh\textsubscript{3} is significantly less expensive and easier to handle than PMe\textsubscript{3}. Interestingly, the addition of the Lewis bases L (L=PMe\textsubscript{3}, Py, PCy\textsubscript{3}) to species 2-L’ (L’ ≠ L = Py, PMe\textsubscript{3}, PCy\textsubscript{3}) leads to an equilibrium between 2-L and 2-L’. A series of experiments was conducted in which various combinations of L and 2-L’ in different ratios and concentrations were combined in benzene-\textit{d}\textsubscript{6}
with hexamethylbenzene as an internal standard and allowed to reach equilibrium. The equilibrium constants were then calculated as the average of three equilibrium reactions and were used to calculate the difference in Gibbs’ free energy between the studied systems (Table 4). The experimental results are in agreement with computations that indicated very small energy gap between those three adducts. PCy$_3$ is unsurprisingly found to form the strongest bond with borabenzene as the strongest donor of the studied ligands. The positive $\Delta G^\circ$ of 0.5 kcal.mol$^{-1}$ found in the case of the substitution of trimethylphosphine by pyridine is opposed to the calculated energy gap of -2.9 kcal.mol$^{-1}$ but remains in the error margin of the computational method.

**Table 4**- Determination of $\Delta G^\circ$ between the various borabenzene adducts according to the equilibrium constants and the DFT calculations (B3LYP-TZVP). L and L’ are represented in Scheme 4.

<table>
<thead>
<tr>
<th>Ligands</th>
<th>$\Delta G^\circ$ (DFT) (kcal.mol$^{-1}$)</th>
<th>$\Delta G^\circ$ (Experimental) (kcal.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L = PMe$_3$, L’ = Pyridine</td>
<td>-2.7</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>L = PMe$_3$, L’ = PCy$_3$</td>
<td>-0.7</td>
<td>-0.6 ± 0.1</td>
</tr>
<tr>
<td>L = Pyridine, L’ = PCy$_3$</td>
<td>-2.0</td>
<td>-1.0 ± 0.2</td>
</tr>
</tbody>
</table>

**DFT study on the ligand exchange reaction**

Our observations indicate that the exchange of the Lewis bases at boron is possible with borabenzene adducts. As expected, the NHC-boratabenzene adducts reveal to be the most thermodynamically favoured borabenzene species that can be obtained. Towards the lower end of thermodynamic stability, other than the NEt$_3$ which has been made on several occasions and proved to be quite labile, we can include the triphenylphosphine analogue, which undergoes full conversion to the PCy$_3$, pyridine, PMe$_3$, and IMes borabenzene adducts. However, these species tend to degrade slowly over time in solution, as we observed with the NEt$_3$ adduct. Once the bond energy gets closer to 30
kcal.mol\(^{-1}\), as it is observed with the PCy\(_3\), pyridine and PMe\(_3\) adducts, the compounds get stable in solution for a prolonged period of time.

The absence of any exchange reaction when lutidine is added to a Lewis base-borabenzene adduct, or when a Lewis base is added to a borabenzene-lutidine adduct, suggests that an associative process is taking place at the boron atom. However, A DFT model of the transition state for a direct exchange reaction between borabenzene-pyridine and PMe\(_3\) goes against such proposal since the activation barriers of 28.9 (enthalpy) and 40.4 (Gibbs free energy) kcal.mol\(^{-1}\), respectively, are too important for such process to occur, even at 70 °C. Fu did mention in a previous report that the exchange of borabenzene-PMe\(_3\) with borabenzene-PMe\(_3\)-d\(_9\) did not occur in THF at room temperature.\(^{20c}\) Our attempts to study the kinetics of this reaction are in accordance with the observations of Fu, since the rate of the reaction was highly dependent on the purity of the sample studied and the rates were highly irreproducible. In the case of the exchange reaction using 2-PMe\(_3\) and pyridine to generate 2-Py at 70 °C, the reaction with freshly sublimed starting material was very slow, whereas a sample that had been left in a freezer in a glove-box for two weeks underwent exchange reactions much more rapidly.

Therefore, it is highly likely that this exchange can be catalyzed by the presence of trace amount of some electrophile (notably some H\(^+\) or B-containing species) in solution that could arise from thermal degradation of the borabenzene adducts when heated at 70 °C. Nevertheless, the observations made above suggest that it is still highly dependent on the steric hindrance around the boron atom. The most likely process for such exchange reaction would be the generation of borenium species that are generated readily in the presence of H\(^+\), as previously reported by Piers, which would make the boron atom much more electrophilic and would reduce the energy of the transition state (Figure 8).\(^{20c}\)
Figure 8. Possible pathways for the ligand substitution reaction on borabenzene.

Calculations were performed at the DFT level using the B3PW91 hybrid functional to investigate the possibility for the borenium ligand exchange pathway. The borenium $2^{++}$-Py was modeled and used as a starting point for the exchange reaction. Its formation energy from $2$-Py could not be calculated since the electrophilic impurity reacting with $2$-$L$ in our reaction conditions is unknown. However, this borenium cation has been reported by Piers as the product of the reaction of $2$-$L$ with HCl and thallium tetrapherfluorophenylborate.$^{20c}$
A stable tetracoordinated borenium structure (IM1) was found as the product of the association of PMe₃ on 2⁺-Py. This stable intermediate is reminiscent of [C₅H₅B(Py)₂]⁺[B(C₆F₅)₄]⁻ also reported by Piers.²⁵ Unsurprisingly, IM1 is thermodynamically favoured, as the borenium fragment is then stabilized by two Lewis bases. Either pyridine or PMe₃ can easily dissociate from IM1 to give the corresponding monocoordinated borenium complex. The highest energy barrier found for the ligand exchange reaction of 2⁺-Py with PMe₃ to give 2⁺-PMe₃ and free pyridine is 15.1 kcal.mol⁻¹, which is consistent with a reaction that occurs rapidly at room temperature. The reaction pathway is illustrated in Figure 9.

![Reaction pathway diagram](image)

**Figure 9.** Reaction pathway for the ligand exchange between 2-Py and PMe₃ to generate 2-PMe₃ and pyridine.

These results indicate that ligand exchange on borenium derivatives of borabenzene should be easy and proceed through an associative pathway. The rate of reaction is thus expected to be highly dependent on the steric properties of the ligands involved and their ability to form a tetracoordinated intermediate. Borenium complexes of bulky ligands, such as 2,6-lutidine, that completely protect the boron atom of
the borenium are expected to be inert in regards to ligand substitution. Unfortunately, the thermodynamics of the relation between borenium derivatives $2^{+}$-L and borabenzene complexes $2$-L remain unknown. The main factors governing the rate of the overall ligand substitution on neutral borabenzene adducts through a borenium pathway have to include the nature and concentration of the catalytic electrophile.

In order to experimentally verify this mechanistic hypothesis, 1-triphenylphosphine-4-H-borabenzene was reacted with an equivalent of PCy$_3$ in deuterated benzene in presence of 10 mol% of triphenylphosphonium bromide. A control experiment without the acidic phosphonium was conducted at the same time in similar conditions. Within 15 minutes, we observed complete conversion of borabenzene triphenylphosphine in the acid catalyzed reaction by $^1$H and $^{31}$P NMR (see Supporting Information). The control experiment did not show any conversion in these conditions. These findings give strong support to the idea that ligand exchange at borabenzene is an acid catalyzed process involving protonation of the aromatic cycle and formation of a borenium intermediate.

**Conclusion**

The borabenzene fragment has found applications in a large array of fields, from catalysis to material sciences. In that regard, the nature of the substituent on boron can play a large role in the activity and properties of the molecules of interest. While it is widely known that the borabenzene is kinetically reactive, we have quantified in this report, by computational and experimental results, the stability of the borabenzene adducts according to the nature of the substituents, and demonstrated that trace impurities can greatly enhance exchange reactions. We have also demonstrated that the neutral borabenzene fragment mostly acts as a $\pi$-donor rather than a $\pi$-acceptor, because of the availability of electron density from the aromatic ring. These results should be helpful in the design of more stable and durable boron heterocycles.
Experimental Section

General Procedures. All manipulations were conducted under a nitrogen atmosphere using standard Schlenk and glovebox techniques. Reactions were carried out either in a sealed J-Young NMR tube, in which case NMR conversions are indicated, or in standard flame dried Schlenk glassware. Dry deoxygenated solvents were employed for all manipulations. All solvents were distilled from Na/benzophenone. Benzene-d₆ and toluene-d₈ were purified by vacuum distillation from Na/K alloy. 1-chloro,2-TMS,4-Pr,2-5-boracyclohexadiene¹⁹ (1), 1-pyridine-4-(isopropyl)borabenzene (2-Py)²⁰c, and 1-tricyclohexylphosphine-4-(isopropyl)borabenzene (2-PCy₃)²⁰, were prepared and characterized according to literature procedures. NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (¹H), 100.580 MHz (¹³C), 161.923 MHz (³¹P), Bruker Advance NMR 400 MHz spectrometer at 128.336 MHz (¹¹B), or on a Bruker NMR AC-300 at 300MHz (¹H), 75.435 MHz (¹³C), 121.442 MHz (³¹P). ¹H NMR and ¹³C{¹H} NMR chemical shifts are referenced to residual solvent signals in deuterated solvent. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), overlapping (ov.) or broad (br). Chemical shifts are reported in ppm. Peak assignment was confirmed using COSY (¹H) and gHSQC (¹³C) 2D NMR experiments. Coupling constants are reported in Hz. HRMS characterization was performed with an Agilent Technologies 6210 LC Time of Flight Mass Spectrometer. Products in toluene solutions were introduced to the nebulizer by direct injection. Neutral borabenzene adducts were characterized using APPI ionization in positive mode.
Synthesis of Borabenzene Adducts

1-trimethylphosphine-4-(isopropyl)borabenzene (2-PMe3)

Trimethylphosphine (0.23 mL, 168 mg, 2.21 mmol) was added dropwise at room temperature to 1 (500.3 mg, 2.21 mmol) in hexane (25 mL). The presence of a white precipitate was observed immediately and the mixture was stirred for 2 hours. Removal of the volatiles in vacuo and subsequent washing with hexane yielded 212.4 mg of a white solid (yield =50%). 1H NMR (benzene-d6) \( \delta \): 7.91 (br, 2H, \( H^2 \)), 7.23 (dd, \( J = 8.7, 10.3 \) Hz, 2H, \( H^1 \)), 3.20 (sept., \( ^3J_{H-H} = 6.9 \) Hz, 1H, CH(CH3)2), 1.53 (d, \( ^3J_{H-H} = 6.9 \) Hz, 6H, -CH(CH3)2), 0.65 (d, \( ^2J_{H-P} = 10.8 \) Hz, 9H, PMe3). 13C{1H} NMR (C6D6) \( \delta \): 140.0 (s, C3), 132.0 (d, \( ^1J_{C-P} = 41.8 \) Hz, PMe3).

31P{1H} NMR (C6D6) \( \delta \): -23.2 (q, \( ^1J_{P-B} = 110 \) Hz). 11B NMR (C6D6) \( \delta \): 19.8 (d, \( ^1J_{B-P} = 110 \) Hz). DI-MSTOF (APPI, m/e): [M + H]+ 195.1714 (calc: 195.0691).

1-triphenylphosphine-4-(isopropyl)borabenzene (2-PPh3)

A saturated solution of triphenylphosphine (526.6 mg, 2.02 mmol) in hexane was added dropwise at room temperature to 1 (455 mg, 2.02 mmol). The presence of a white precipitate was observed immediately and the mixture was stirred for 1 hour. Removal of the volatiles in vacuo and subsequent washing with hexane yielded 347.2 mg of a white solid (yield =45%). 1H NMR (C6D6) \( \delta \): 7.98 (dd, \( ^3J_{H-H} = 10.3, ^4J_{P-H} = 4.7 \) Hz, 2H, \( H^1 \)), 7.58 (m, 6H, PPh3), 7.46 (dd, \( ^3J_{H-H} = 10.3, ^3J_{P-H} = 7.8 \) Hz, 2H, \( H^1 \)), 6.98 (m, 3H, PPh3), 6.90 (m, 6H, PPh3), 3.21 (sept., \( ^3J_{H-H} = 6.9 \) Hz, 1H, CH(CH3)2), 1.53 (d, \( ^3J_{H-H} = 6.9 \) Hz, 6H, -
CH(CH₃)₂. ¹³C{¹H} NMR (CD₂Cl₂) δ: 140.4 (s, C³), 134.6 (d, J_C-P = 10.3 Hz, PPh₃), 132.5 (d, J_C-P = 17.3 , C⁵), 131.6 (d, J_C-P = 2.4 Hz, PPh₃), 131.5 (d, J_C-P = 3.0 Hz, PPh₃), 128.5 (br, C¹), 36.2 (s, C⁴), 25.7 (s, C⁵). ³¹P{¹H} NMR (CD₂Cl₂) δ: 8.2 (br). ¹¹B NMR (CD₂Cl₂) δ: 18.8 (d, J_B-P 96.7). DI-MSTOF (APPI, m/e): [M + H - Pr⁺]: 339.2670 (calc: 339.1468).

1-(2,6-lutidine)-4-(isopropyl)borabenzone (2-Lu)

2,6-lutidine (0.30 mL, 272 mg, 2.54 mmol) was added dropwise at room temperature to a saturated hexane solution of 1 (575.8 mg, 2.54 mmol). The reaction mixture was stirred for 3 hours and all volatiles were removed in vacuo. The resulting bright yellow solid was washed with hexane to yield 342.7 mg of a white solid (yield = 60%). ¹H NMR (CD₂Cl₂) δ: 8.00 (d, J_H-H = 10.2 Hz, 2H, H²), 6.47-6.52 (m, 1H, lut(p-H)), 6.49 (d, J_H-H = 10.2 Hz, 2H, H¹), 6.11 (d, J_H-H = 7.7 Hz, 2H, lut(m-H)), 3.29 (sept., J_H-H = 7 Hz, 1H, CH(CH₃)₂), 2.22 (s, 6H, lut(CH₃)), 1.62 (d, J_H-H = 7 Hz, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (CD₂Cl₂) δ: 156.9 (s, lut(o-C)), 139.0 (s, lut(p-C)), 133.9 (s, C²), 123.5 (s, lut(m-C)), 116.9 (br, C¹), 35.9 (s, C⁴), 26.3 (s, C⁵), 26.0 (s, lut(CH₃)), not located (C³). ¹¹B NMR (CD₂Cl₂) δ: 32.7 (s). DI-MSTOF (APPI, m/e): (M⁺): 225.1435 (calc: 225.1689).

1-(1,3-dimesitylimidazolin-2-ylidene)-4-(isopropyl)borabenzone (2-IMes)

A saturated solution of 1,3-dimesitylimidazoline-2-ylidene (310.2.9 mg, 1.01 mmol) in hexane was added dropwise at room temperature to 1 (231.3 mg, 1.01 mmol). The yellow reaction mixture was stirred for 2 hours. Removal of the volatiles in vacuo and several washings in hexane yielded 212.4 mg of a pale solid. ¹H NMR (CD₂Cl₂) δ: 7.51 (d, J_H-H = 10.5 Hz, 2H, H²), 6.68 (s, 4 H, Mes(m-H)), 6.53 (d, J_H-H = 10.5 Hz, 2H, H¹), 5.92 (s, 2 H, Im(CH)), 2.91 (sept., J_H-H = 6.9 Hz, 1H, CH(CH₃)₂), 2.08 (s, 6H, Mes(p-CH₃)), 1.96 (s, 12H, Mes(o-CH₃)), 1.26 (d, J_H-H = 6.9 Hz, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (CD₂Cl₂) δ: 146.1 (s, Mes(ipso)), 139.3 (s, Mes(p-C)), 135.5 (s, C³), 135.0 (s, Mes(o-C)), 131.9 (s, C²), 129.8 (s, Mes(m-C)), 121.3 (s, Im), 35.9 (s, C⁴), 25.6 (s, C⁵), 21.1 (s, Mes(p-CH₃)), 17.9 (s, Mes(o-
not located ($C^3$ and carbene). $^{11}$B NMR ($C_6D_6$) δ: 21.0 (s). DI-MSTOF (APPI, m/e): ($M^+$): 422.2892 (calc: 422.2893).

1-di(iso-propyl)amido-2-trimethylsilyl-4-isopropyl-3,5-boracyclohexadiene (3a)

To a solution of 1 (8.6 mg, 0.04 mmol) in 0.5 mL of $C_6D_6$ was added di(iso-propyl)amine (55 µL, 0.2 mmol) by syringe. A white precipitate was immediately formed. The reaction mixture was kept at room temperature for 16 hours and analyzed by NMR spectroscopy. The assignment was confirmed based on COSY experiments and with comparison to similar compounds.\textsuperscript{16}

$^1$H NMR ($C_6D_6$) δ: 6.87 (d, $^3J_{H-H}$ = 12.3 Hz, 1H, $H^5$), 6.51 (d, $^3J_{H-H}$ = 12.3 Hz, 1H, $H^6$), 6.10 (s, 1H, $H^3$), 3.74 (br s., 1H, N(CHMe$_2$)$_2$), 3.21 (br s., 1H, N(CHMe$_2$)$_2$), 2.38 (br. ov. s., 1H, CHMe$_2$), 2.38 (br. ov. s., 1H, $H^1$), 1.31 (br. s., 3H, N(CHMe$_2$)$_2$), 1.28 (br. s., 3H, N(CHMe$_2$)$_2$), 1.10 (br, 6H, CHMe$_2$), 1.01 (br, 3H, N(CHMe$_2$)$_2$), 0.91 (br, 3H, N(CHMe$_2$)$_2$), 0.10 (s, 9H, TMS); signals for excess di(iso-propyl)amine are present at δ: 2.78 and 0.94. $^{13}$C{$^1$H} NMR ($C_6D_6$) δ: 143.3 (s, $C^5$), 138.8 (s, $C^4$), 131.6 (br, $C^6$), 129.8 (s, $C^3$), 48.8 (s, N(CHMe$_2$)$_2$), 44.9 (s, N(CHMe$_2$)$_2$), 34.5 (s, CHMe$_2$), 25.5 (s, CHMe$_2$ or N(CHMe$_2$)$_2$), 24.8 (s, CHMe$_2$ or N(CHMe$_2$)$_2$), 23.0 (s, CHMe$_2$ or N(CHMe$_2$)$_2$), 22.8 (s, CHMe$_2$ or N(CHMe$_2$)$_2$), 22.7 (s, CHMe$_2$ or N(CHMe$_2$)$_2$), 21.2 (s, CHMe$_2$ or N(CHMe$_2$)$_2$), 0.0 (s, TMS); signals for excess di(iso-propyl)amine are present at δ: 45.3 and 23.7. $^{11}$B NMR ($C_6D_6$) δ: 41.2 (s).
1-tert-butyramido-2-trimethylsilyl-4-isopropyl-3,5-boracyclohexadiene (3b)

To a solution of 1 (8.7 mg, 0.04 mmol) in 0.5 mL of C₆D₆ was added tert-butylamine (20 µL, 0.2 mmol) by syringe. A white precipitate was immediately formed. The reaction mixture was kept at room temperature for 24 hours and analyzed by NMR spectroscopy.

^1^H NMR (C₆D₆) δ: 7.00 (d, ^3^J_H-H = 12.3 Hz, 1H, H^5^), 6.48 (d, ^3^J_H-H = 12.3 Hz, 1H, H^6^), 6.07 (d, ^3^J_H-H = 4.9 Hz, 1H, H^3^), 3.44 (br, 1H, NH), 2.40 (sept, ^3^J_H-H = 6.9 Hz, 1H, CHMe₂), 1.80 (d, ^3^J_H-H = 5.4 Hz, 1H, H^1^), 1.09 (m, 6H, CHMe₂), 0.66 (s, 9H, NCMe₃), 0.04 (s, 9H, TMS); signals for excess tert-butylamine are present at δ 1.20 (s) and 0.98 (s). ^1^C{^1^H} NMR (C₆D₆) δ: 146.4 (s, C^5^), 139.5 (s, C^4^), 130.2 (s, C^3^), 129.2 (br, C^6^), 50.0 (s, N(CMe₃)), 35.5 (br, C^2^), 34.7 (s, CHMe₂), 22.9 (s, CHMe₂ or N(CMe₃)), 23.0 (s, CHMe₂ or N(CMe₃)), -1.3 (s, TMS). ^1^B NMR (C₆D₆) δ: 40.9 (s).

b. General Procedure for Ligand Exchange

Qualitative ligand exchange reactions were performed at the NMR scale with 2-L (L = 2,6-lutidine, pyridine, PMe₃, PCy₃, PPh₃, IMes). In these experiments, a molar equivalent of L’ (L’ = 2,6-lutidine, pyridine, PMe₃, PCy₃, PPh₃, IMes) was added to a C₆D₆ solution of 2-L. The reaction mixtures were heated to 60°C overnight. NMR analysis was then used to verify if the exchange reaction occurred. Reaction mixtures that did not undergo reaction were heated 80 °C for up to five more days to make sure no exchange occurred.

Quantitative analysis of the exchange reaction was done for L = pyridine, PMe₃, PCy₃ and L’ = pyridine, PMe₃, PCy₃. These reactions were done at the NMR scale in C₆D₆ with hexamethylbenzene (HMB) as an internal standard. 4.2 mol.L⁻¹ solutions of (2-L + HMB) and L’ were prepared. These solutions were mixed in air-tight NMR tubes in 1:2, 1:1, and 2:1 ratios. The reaction mixtures were
heated to 80°C for 72 hours and the equilibrium constants were measured by NMR spectroscopy. Gibb’s free energy variation for these systems was calculated as the average of the measurements taken for the 1:2, 1:1, and 2:1 mixtures.

c. Acid catalyzed ligand exchange reaction

Two C₆D₆ (ca. 0.4 mL) solutions of 2-PPh₃ (4.4 mg, 0.012 mmol) and tricyclohexylphosphine (3.3 mg, 0.012 mmol) were prepared. To one of them was added 0.4 mg (0.001 mmol) of triphenylphosphonium bromide. The solutions thus prepared were introduced into J-Young NMR tubes and analyzed by NMR spectroscopy after 15 minutes.

Computational details

The density functional theory calculations were carried out with the B3LYP/B3PW91 hybrid functional as implemented in the G03 program. B3LYP is Becke’s three parameter functionals (B3) with the non-local correlation provided by the LYP expression and VWN functional III for local correlation. The TZVP basis set was used for all atoms. The tight geometry optimizations were performed without symmetry constraints and with the use of the modified GDIIS algorithm. Vibrational analyses were performed to confirm the optimized stationary points as true minima on the potential energy surface or as transition states, and to obtain the zero-point energy, thermodynamic data and orbital analysis. The free Gibbs energies, G, were calculated for T = 298.15 K. For every transition state, the reaction path in both directions was followed using the intrinsic reaction coordinate (IRC).

Acknowledgment. We are grateful to NSERC (Canada), CFI (Canada), CCVC (Québec), and C3V (Université Laval) for financial support; M.-A.L. and G. B.-C. are grateful to NSERC and FQRNT for
scholarships. Prof T. Woo and S. Goreskky are acknowledged for the training of M.-A. L and G. B.-C. and their help with DFT calculations. We also acknowledge Prof A. Hill for his insightful input.

**Supporting Information Available.** Spectroscopic data for all compounds. Cartesian coordinates for numerical models. This material is available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).
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