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On the Nucleophilicity of Boryllithium Compounds. A Theoretical Study

Paula Jaramillo,*,[†] Patricia Pérez,*,[‡] and Patricio Fuentealba[§]

Departamento de Física Geral, Instituto de Física, Universidade de São Paulo, cidade universitaria. S.P. Brasil, Facultad de Ecología y Recursos Naturales, Departamento de Ciencias Químicas, Laboratorio de Química Teórica, Universidad Andres Bello, Republica 275, Santiago, Chile, and Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653-Santiago, Santiago, Chile

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Boron compounds are widely used in synthetic chemistry. The synthesis of the compounds is relatively easy, presenting thermodynamic stability and synthetic versatility. Almost all of them show electrophilic reactivity. Recently, some boryllithium species have been reported as a base or a nucleophile in reaction with organic electrophiles in S_N2 reactions. In the present work, the proton affinity (PA) of boryllithium compounds was calculated. These values can be useful as theoretical reference values and to provide valuable complementary information for the interpretation and discussion of the basicity of these compounds. The proton affinity was calculated using a theoretical method based on density functional theory and high-level theoretical methods through MP2 and G2MP2 levels of theory. In addition, some global and local reactivity indexes based on density functional theory (DFT) on boryllithium compounds were studied. In order to compare and discuss the chemical reactivity of these compounds, some analogues and electrophilic boron compounds were also studied. Our results showed a local and global nucleophilic reactivity of the boryllithium molecules in agreement with the experimental reactivity. The boryllithium compounds revealed to be strong bases in comparison to other analogue compounds studied in this work.

I. Introduction

Boron compounds have been used as electrophiles for many years.[1] The chemistry of boron is generally characterized by its electronic deficiency. It is known that trivalent compounds of boron behave as electrophilic molecules. The boron atom has only three electrons in its valence shell and behaves as an electron acceptor.[2] Trihalide boron species are known to be strong Lewis acids. The Lewis acidity of boron has been shown to be controlled by the localizability of the unoccupied reactive orbital and the polarizability of the boron center.[3] On the other hand, the formation of an additional bond to boron generates an anionic tetravalent species having tetrahedral structure and behaving as nucleophilic ions.[4] Other molecules where the boron shows an electrophilic character are organoboron compounds such as organoboric acids and esters that are widely used in transmetalation reactions.[5] In general, the boron compounds have a large application in synthetic chemistry, but few reactions exist in which boron behaves as a nucleophile (electron donor). Theoretical predictions have shown that lithioborane compounds could be nucleophilic reagents due to the partial negative charge of the boryl anion moiety.[6] There are few cases in which the boron atom serves as a nucleophile.[7] In transition-metal-catalyzed additions of $(RO)_2B{-}B(OR)_2$ to groups C=C and C=O with double bonds (diboration), one boron atom is transferred as a nucleophile and the other one as an electrophile. The dimer compounds $(Me_2N)_2B{-}B(NMe_2)_2$, in which the B−B bond is present, have many applications in reactions catalyzed by transitions metals. However, it has not been possible to isolate the anion $(R_2N)_2B^-$.[7] In 2006, Nozaki et al.[8] reported the synthesis and spectroscopic characterization of a boron compound, lithium boryl, where the boron center has a nucleophilic character. Boryllithium showed to be reactive with a variety of electrophiles, demonstrating that this compound behaves as a base or a nucleophile.[8] Recently, Segawa et al.[9] showed in boryllithium compounds that the boron−lithium bond is polarized where the boron atom is anionic in comparison with structures of hydroborane and free boryl anions. In this work,[9] the HOMO orbital of boryllithium was theoretically studied and compared with its hydroborane analogue. In the first one, the HOMO presented a lone pair character on the boron atom, while in the second one, the HOMO corresponded to the π orbital of the boron-atom-containing five-membered heterocycle.[9] The NPA analysis showed positive charge with higher reactivity of on boron atom. On the other hand, the stability of nucleophilic carbenes of group IIIa (B, Al, Ga, In) was studied theoretically,[10] showing in these compounds a high electron affinity. Other computational studies[11] showed the reactivity of carbenes of boron, aluminum, and gallium. They predicted the thermodynamic stability of these species and their high reactivity toward electrophiles due to the availability of the lone pair and the high energy of the HOMO orbital.[11]

The aim of this paper is to study the basicity of the boryllithium compounds through the proton affinity (PA)[12] calculated in the gas phase using the B3LYP functional, and for comparison, we also used high-level theoretical methods such as MP2 and G2MP2.[13] These can provide more reliable information on the basicity of these compounds and yield accurate values. Since in the literature there are no theoretical studies showing the basicity and nucleophilic reactivity using descriptors based in DFT,[14] different descriptors of reactivity were calculated in these species (see Chart 1). Global descriptors such as the electrophilicity index,[15] nucleophilicity index,[16] and

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* To whom correspondence should be addressed. E-mail: paulajg@if.usp.br or paujaramillo@gmail.com. Address: Rua do matão, travessa R, 187. CEP 05508-090 Cidade universitaria, São Paulo, Brasil (P.J.).

[†] Universidade de Sao Paulo.

[‡] Universidad Andres Bello.

[§] Universidad de Chile.

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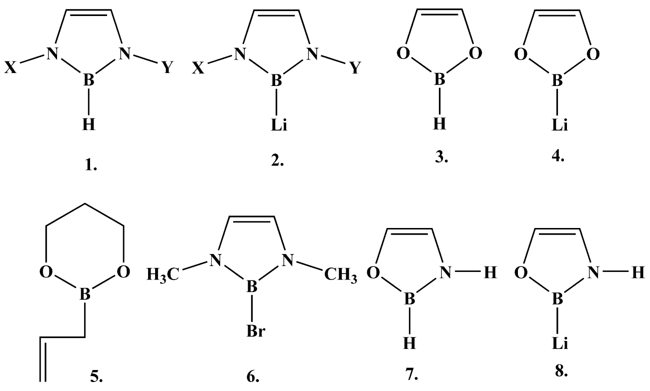
CHART 1: Boron Compounds Used in the Reactivity Study



electrodonating power (EDP)[17] and local descriptors such as the Fukui function,[18] philicity concept,[19] and local nucleophilicity,[20] previously applied in several compounds,[21] will be studied. In order to compare the nucleophilic behavior of boryllithium compounds, the classic boron electrophilic compounds[2,3] such as BH_3, BCl_3, BF_3, $BFCl_2$, and BF_2Cl were included. The NBO[22] analysis was used to obtain the charges on the boron and lithium atom.

II. Theoretical Background and Computational Details

The reactivity of molecules has been studied from the theoretical point of view based on the framework of DFT[23] and basic chemical concepts such as chemical potential,[23] hardness,[23] electrophilicity,[15] and others;[16,17] these global reactivity descriptors have been used to describe the reactivity in several chemical families, providing information about the nature of the molecular system, and for comparison between experimental measures such as kinetics constants,[16b,24] proton affinity,[25] polarizability, and electronegativity.[26]

The electrophilicity index (ω) was proposed by Parr et al.[15] as

$$\omega = \frac{\mu^2}{2\eta} \tag{1}$$

where μ is the electronic chemical potential[23] and η is the chemical hardness.[23] Both quantities may be approached in terms of the one-electron energies of the frontier molecular orbitals HOMO and LUMO, ε_H and ε_L, as $\mu \approx (\varepsilon_H + \varepsilon_L)/2$ and $\eta \approx (\varepsilon_L - \varepsilon_H)$, respectively. The ω index measures the energy stabilization when an optimal electronic charge transfer from the environment to the system ocurrs.[15]

Recently, a nucleophilicity index was proposed by Jaramillo et al.[16a,b] This index depends not only on the nucleophilic system but also on the electrophilic species. It can be written as[16a]

$$\omega^- = \frac{1}{2}\frac{(\mu_a - \mu_b)^2}{(\eta_a + \eta_b)^2}\eta_a \tag{2}$$

where a represents the nucleophile and b represents the electrophile. The electrodonating power, EDP,[17] is another index proposed in the literature to sense the nucleophilic character of species. This index is a measure of the propensity of a system to donate charge.[17] The quantification of the electrodonating power[17] is written in terms of the ionization potential, I, and the electronaffinity, A, by

$$\mathrm{EDP} \equiv \frac{(\mu^-)^2}{2\eta^-} \approx \frac{(3I + A)^2}{16(I - A)} \tag{3}$$

The identification of the reactive centers (nucleophilic or electrophilic) has been explored with the Fukui function.[27] This index has been used to form other new local descriptors such as the local electrophilicity and local nucleophilicity normally called the philicity,[19] dual descriptor,[28] local hardness,[29] and local softness.[30] The Fukui function is defined as[27]

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{v(\vec{r})} = \left(\frac{\delta \mu}{\delta v(\vec{r})}\right)_N \tag{4}$$

The condensed value at site k of the Fukui function (f_k^α) can be obtained from the operational formulation for the Fukui function by using the coefficients ($c_{i\alpha}$) of the frontier molecular orbitals (α: HOMO or LUMO) and the overlap matrix ($S_{\nu\mu}$)[18a]

$$f_k^\alpha = \sum_{\mu \in k} f_\mu^\alpha \tag{5}$$

where

$$f_\mu^\alpha = |c_{\mu\alpha}|^2 + c_{\mu\alpha}\sum_{\nu \neq \mu} c_{\nu\alpha} S_{\mu\nu} \tag{6}$$

The generalized concept of philicity was proposed by Chattaraj,[19] encompassing electrophilic, nucleophilic, and radical reactions. Therefore, there are three different types of local philicity indexes.[19] The philicity at a site k is given by the nucleophilic Fukui function f_k^-[27] and the global electrophilicity index ω[15] through

$$\omega_k^- = \omega f_k^- \tag{7}$$

Considering a local extension for the global EDP, we obtain the following equation for the selectivity

$$(\mathrm{EDP})_k = \frac{(\mu^-)^2}{2\eta^-} f_k^- = (\mathrm{EDP}) f_k^- \tag{8}$$

Following the suggestion of Contreras et al.,[20a] very recently, Politzer's idea[31] of using the ionization potential as a measure of nucleophilicity has been applied.[16c,32] A global nucleophilicity index, N, based on the latter idea and using the Koopmans theorem can be calculated by[16c,32]

$$N = E_{\mathrm{HOMO(Nu)}} - E_{\mathrm{HOMO(TCE)}} \tag{9}$$

Note that this index is referred to as tetracyanoethylene (TCE) taken as reference because it represents the lowest HOMO energy in a large series of molecules already investigated in the context of polar DA cycloadditions.[32] It is worth mentioning that the last nucleophilicity index can be very useful to predict the nucleophilic character, and it is very easy to calculate depending only on the quality of HOMO orbital.[32] The condensed to atom nucleophilicity index using the last empirical equation and the nucleophilic Fukui function has been applied in a substituted aromatic system[20b]

$$N_k = Nf_k^- \tag{10}$$

On the other hand, the intrinsic (gas-phase) basicity can be probed and quantified by the proton affinity (PA),[12] which is defined as the negative of the enthalpy change (ΔH) associated with the following reaction

$$B(g) + H^+(g) \rightarrow BH^+(g) \tag{11}$$

The PA of a base B can be calculated by

$$PA(B) = -\Delta H_f^0 = \Delta H_f^0(B) + \Delta H_f^0(H^+) - \Delta H_f^0(BH^+) \tag{12}$$

and may be approximated by

$$PA(B) = -\Delta H_f^0 \cong \Delta E = E(B) - E(BH^+) \tag{13}$$

where E(B) and E(BH$^+$) correspond to the total energies of the B, boryllithium compounds, and the conjugated acid, BH$^+$, respectively. ΔE is the energy change of the reaction in eq 11 and may be associated with the PA of the boryllithium compounds.

Geometries of the boryllithium compounds and the others shown in Chart 1 were optimized at the B3LYP level of theory and with the 6-31G(d,p) basis set using the Gaussian 03[33] package of programs. Single-point calculations were performed for all boryllithium compounds and protonated species at B3LYP and second-order Moller−Plesset (MP2) perturbation theory using 6-31G(d,p) and 6-311++g(d,p) basis sets, respectively. The G2MP2[13] method was also used to calculate the PAs.

The HOMO and LUMO energies at the B3LYP/6-31G(d,p) level of theory were used to calculate the μ, η, ω, ω^-, EDP, philicity, and N for all systems shown in Chart 1 and the classical boron compounds, within the frozen orbital approximation. The electronic properties of the electrophilic partner, 1-chlorobutane (*n*BuCl), as the electrophile (electrophile used in experimental reactions with boryllithium compounds)[8] were used to obtain the nucleophilicity index values via eq 2. Charges were obtained from NBO (natural bond orbitals)[22] analysis implemented in Gaussian03.[33]

III. Results and Discussion

TABLE 1: Proton Affinity (PA) Values Calculated at MP2/6-311++G(d,p) and G2MP2 Theory for Boron Compounds

molecule	PA[a]		
X−Y	B3LYP/6-31G(d,p)	MP2/6-311++G(d,p)	G2MP2
1H−H	199.7	189.7	183.4
2H−H	258.6	294.9	285.8
1H−Me	206.8	198.0	192.1
2H−Me	260.7	297.4	288.0
1Me−Me	213.3	205.7	200.3
2Me−Me	262.7	299.9	290.1
1H−Ph	210.8	200.0	192.5[b]
2H−Ph	258.3	255.2	246.1[b]
1Ph−Ph	219.0	208.7	201.0[b]
2Ph−Ph	259.8	257.1	247.8[b]
3	152.0	143.4	137.1
4	232.1	262.8	250.8
5	187.0	180.7	173.8[b]
6	182.8	179.4	172.6[b]
7	177.6	168.1	161.9
8	246.2	289.8	281.9

[a] All values are given in kcal/mol. [b] These values were calculated using the relation PA(G2MP2) = −1.47 + 0.97PA(MP2).

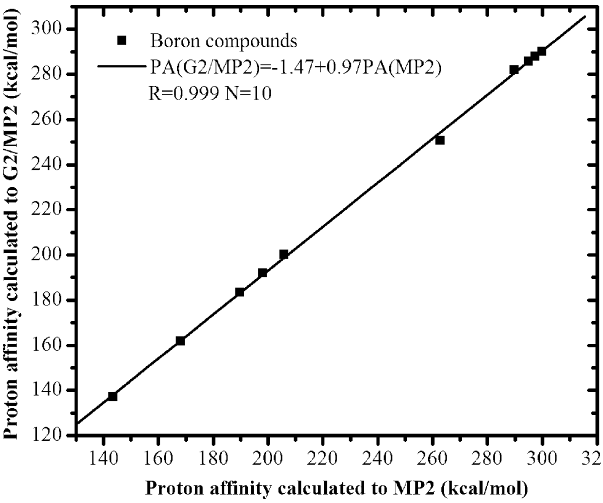


Figure 1. Linear regression between the PA obtained at MP2 and G2MP2 levels of theory.

The basicity of boryllithium species was evaluated by their PA values. Lectures of energy at the G2MP2 level of theory were made on geometry optimization calculations at MP2/6-311++G(d,p). In Table 1, the PA values for 16 boron compounds (see Chart 1) calculated at three levels of theory, B3LYP/6-31G(d,p), MP2/6-311++G(d,p), and G2MP2, are depicted. At all levels of theory, it may be seen that the molecules containing a B−Li bond (2H−H, 2H−Me, 2Me−Me, 2H−Ph, 2Ph−Ph, 4, and 8) present a higher proton affinity than other boron compounds with B−H, B−R, and B−Br bonds (compare these PA values with those of 1H−H, 1H−Me, 1Me−Me, 1H−Ph, 1Ph−Ph 3, 5, 6, and 7). Our results show that the boryllithium compounds behave as strong bases or superbases.[34] The PA values for six compounds of our series cannot be calculated through G2MP2 calculations because of computational limitations. Hence, a linear regression between G2MP2 and MP2 values of the proton affinity has been performed for only 10 molecules (1H−H, 2H−H, 1H−Me, 2H−Me, 1Me−Me, 2Me−Me, 3, 4, 7, and 8). The linear relationship is PA(G2MP2) = −1.47 + 0.97 PA(MP2), with a very good regression coefficient (R = 0.999). Figure 1 depicts this trend. With this equation, it has been possible to predict the PA values at the G2MP2 level for molecules of higher size, such as 1H−Ph, 2H−Ph, 1Ph−Ph, 2Ph−Ph, 5, and 6. If we compare the third and fourth columns of Table 1 for all compounds, the MP2 energies overestimate the proton affinity values between 12 and 5.4 kcal/mol. The values calculated at the B3LYP level do not present any good correlation with the most exact one of the G2MP2 model. Nevertheless, the observed trend is the same using the three methodologies; the molecules with a B−Li bond are stronger bases than those without the presence of lithium. The basic behavior of the boryllithium compounds follows the trend 4 < 8 < 2H−H < 2H−Me < 2Me−Me. The higher PA values are obtained for methylated heterocycles. This trend has been attributed to inductive and polarization stabilization effects due to the presence of a methyl

TABLE 2: Global and Local Reactivity Indexes for Boron Compounds Calculated at B3LYP/6-31g(d)

molecule X−Y	HOMO (eV)	LUMO (eV)	μ (eV)	η (eV)	ω^- (eV)	ω (eV)	f_k^-	f_k^+	$\omega_k^- = \omega f_k^-$ (eV)	EDP (eV)	local EDP (eV)	N (eV)	N_k
1H−H	−5.129	1.844	−1.642	6.973	0.053	0.19	0.176	0.004	0.034	1.644	0.290	4.0	0.704
2H−H	−4.249	−1.127	−2.688	3.122	0.009	1.16	0.170	0.069	0.197	3.852	0.655	4.9	0.833
1H−Me	−5.068	1.683	−1.692	6.751	0.050	0.21	0.184	0.034	0.039	1.692	0.312	4.1	0.754
2H−Me	−4.242	−1.136	−2.689	3.106	0.009	1.16	0.176	0.067	0.205	3.867	0.682	4.9	0.862
1Me−Me	−5.015	1.568	−1.724	6.582	0.048	0.23	0.191	0.003	0.043	1.725	0.330	4.1	0.783
2Me−Me	−4.237	−1.144	−2.691	3.093	0.009	1.17	0.182	0.066	0.213	3.879	0.706	4.9	0.892
1H−Ph	−5.232	0.014	−2.609	5.246	0.012	0.65	0.165	0.099	0.107	2.930	0.483	3.9	0.644
2H−Ph	−4.473	−1.063	−2.768	3.409	0.007	1.12	0.158	0.054	0.178	3.845	0.608	4.7	0.743
1Ph−Ph	−5.333	−0.244	−2.789	5.090	0.008	0.76	0.171	0.188	0.130	3.240	0.553	3.8	0.650
2Ph−Ph	−4.604	−1.130	−2.867	3.475	0.006	1.18	0.157	0.048	0.186	4.016	0.632	4.5	0.707
3	−6.635	0.707	−2.958	7.353	0.005	0.60	0.107	0.003	0.064	3.129	0.335	2.5	0.268
4	−5.093	−1.224	−3.164	3.588	0.002	1.30	0.516	0.458	0.670	4.418	2.280	4.0	2.064
5	−6.317	0.980	−2.667	7.302	0.012	0.49	0.045	0.143	0.022	2.764	0.123	2.8	0.126
6	−5.230	1.279	−1.978	6.504	0.036	0.30	0.141	0.004	0.042	1.997	0.281	3.9	0.550
7	−5.815	1.197	−2.308	7.013	0.023	0.38	0.144	0.215	0.055	2.352	0.338	3.3	0.475
8	−4.734	−1.170	−2.950	3.568	0.005	1.22	0.493	0.059	0.601	4.137	2.040	4.4	2.169
*n*BuCl[a]	−7.867	0.762	−3.559	8.616		0.74		0.430	0.316			1.3	
TCE[b]	−9.116												
									$\omega^* f^+$ (eV)	EAP (eV)	local EAP (eV)		
BH_3	−9.551	−1.796	−5.660	7.755		2.08	0.451	0.992	2.059	1.800	1.786		
BCl_3	−8.789	−1.877	−5.333	6.911		2.05	0.000	0.748	1.535	1.873	1.401		
BF_3	−9.034	−1.061	−5.034	7.973		1.59	0.006	0.771	1.229	1.164	0.898		
$BFCl_2$	−9.360	−0.109	−4.735	9.251		1.21	0.016	0.786	0.950	0.631	0.496		
BF_2Cl	−11.265	0.980	−5.143	12.245		1.08	0.000	0.799	0.864	0.354	0.283		

[a] *n*BuCl is 1-chlorobutane. [b] TCE is tetracyanoethylene.

group (Me) directly bonded to the nitrogen atom that acts as an electron donor for the boron atom.[9] This fact leads to enhance the proton affinity in these compounds (2H−Me and 2Me−Me) in comparison with 2H−Ph and 2Ph−Ph that show the lowest proton affinity in the boryllithium set. Note that the reported G2MP2 proton affinity values varie between 246.2 and 290.1 kcal/mol, corresponding to values of strong bases similar to imines, diimines,[34] guanidines,[35] and so forth. It is worth mentioning that the PA values obtained at the G2MP2 level of theory are a valuable tool to be used with a predictive character for these species.

In Table 2 are shown all of the calculated electronic properties, μ, η, ω^-, ω, the philicity ($\omega_k^- = \omega f_k^-$), EDP (eq 3), $(EDP)_k$ (eq 7), the global nucleophilicity index, N, via eq 8, and the local nucleophilicity, N_k (eq 9) for the boron compounds. The electronic chemical potential, μ, and the global hardness, η, were calculated to obtain the global electrophilicity, ω, via eq 1. The general trend is that boryllithium compounds like 2H−H, 2H−Me, 2Me−Me, 2H−Ph, 2Ph−Ph, 4, and 8 are soft molecules (see Table 2, column 5) compared with those having a B−X (X = H, halogen, alkyl) bond. The global hardness for the BX_3 molecules (where X = H, halogen) is higher than that for the boryllithium compounds, and the η values are very similar to those for the 1H−H, 1H−Me, 1Me−Me, 1H−Ph, 1Ph−Ph 3, 5, 6, and 7 compounds.

The nucleophilicity[16] values (ω^- in Table 2, column 6) obtained for all molecules are not able to show the observed nucleophilic character[8,9] in molecules containing a B−Li bond (2H−H, 2H−Me, 2Me−Me, 2H−Ph, 2Ph−Ph, 4, and 8); even the ω^- values are smaller than those for the compounds having a B−H bond.

On the other hand, it may be seen that the electrophilicity index[16] in Lewis acids[2] (BH_3, BCl_3, BF_3, $BFCl_2$, BF_2Cl) is, in general, higher than those for the cyclic boron compounds (see Figure 2). The local reactivity of these compounds can be also sensed by the philicity index ($\omega_k^- = \omega f_k^-$) through the condensed nucleophilic Fukui function at the boron atom (f_B^-),[27] which is also shown in Table 2 (column 8). The f_B^- values by themselves do not show a nucleophilic behavior of the boron compounds. Conversely, the f_B^+ (Fukui function for nucleophilic attack) values are higher only for the classical BX_3 compounds, stressing their local acid Lewis behavior. However, the nucleophilic reactivity on boryllithium compounds[8,9] can be observed by the philicity values (Table 2, column 10), which display high values compared with those for compounds without the lithium atom. Figure 3 shows clearly this trend. All molecules containing the B−Li bond (2H−H, 2H−Me, 2Me−Me, 2H−Ph, 2Ph−Ph, 4, and 8) are locally more nucleophilic at the boron atom than those molecules containing B−H, B−R, or B−Br bonds. Some substituents (X−Y) in the boron systems of the group 1 and 2 (2Me−Me, 2H−Ph, 2Ph−Ph) show steric effects, but it seems that this does not affect the local reactivity on the boron atom. Molecule 6 is a precursor of the molecule 2Ph−Ph.[8] The first one presents a lower local nucleophilic character (philicity =

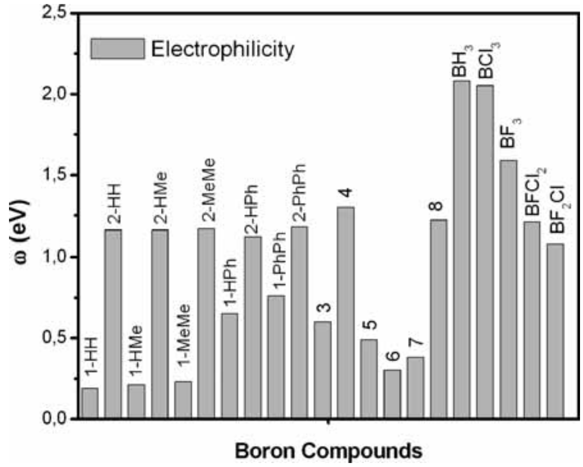


Figure 2. Electrophilicity[15] values for all systems studied here (see Chart 1 and the text for details).

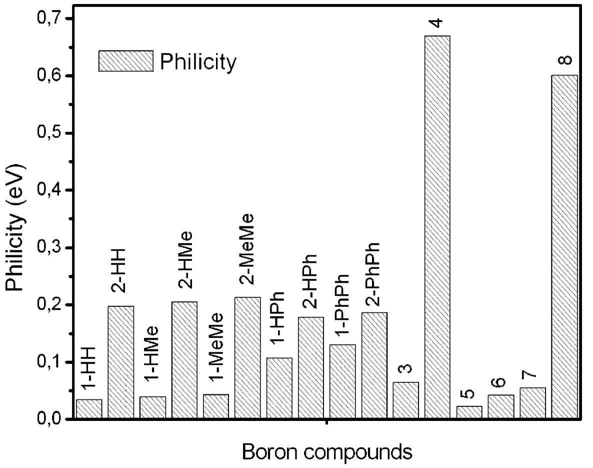


Figure 3. Philicity[19] values for all systems studied here (see Chart 1 and the text for details).

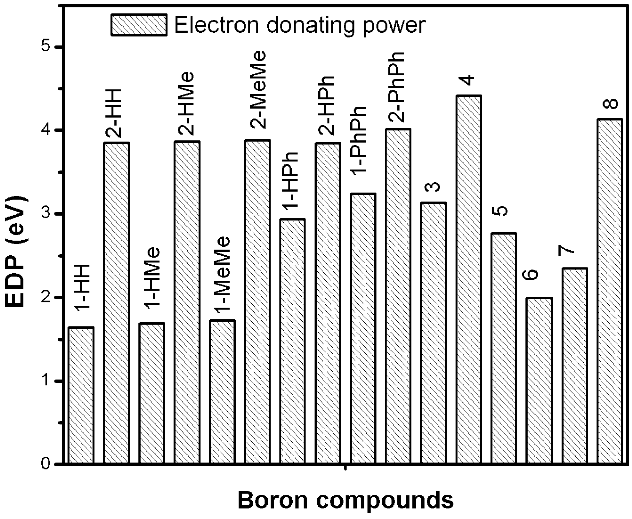


Figure 4. Electrodonating power (EDP)[17] for all systems studied here (see Chart 1 and the text for details).

0.042 eV) than the second one (philicity = 0.186 eV). It has been reported that boryllithium (2Ph−Ph) experimentally reacts with several electrophiles[8] to give the substituted products. Our theoretical results are in agreement with the experimental nucleophilic character on the boron atom.[8] Molecule 5 also shows a lower local reactivity (philicity = 0.022 eV) compared with that of boryllithium molecules. Molecule 5 reacts with aldehydes; thus, the experimental character of the boron atom in allylboron compounds is electrophilic,[36] in agreement with our results.

The electrodonating power, EDP (eq 3 and column 11 in Table 2), shows more clearly the global nucleophilic character of the boryllithium compounds. The comparative nucleophilic character using EDP in this series is shown in Figure 4. From Table 2 (column 12), it may be seen that the local electrodonating power on the boron atom also shows the same trend found for the global EDP. On the other hand, the calculated values for the global and local electroaccepting power[17] for the traditional BX_3 Lewis acids (Table 1, column 11) show their electrophilic character, in contrast to boryllithium compounds. This trend is in agreement with theoretical reports,[37] where it was shown that BCl_3 is a stronger Lewis acid than BF_3.

The global nucleophilicity index evaluated from eq 8 seems to be a better descriptor to sense this property, in agreement with the experimental data.[8,9] Note, for instance, that all compounds containing a B−Li bond (2H−H, 2H−Me, 2Me−Me, 2H−Ph, 2Ph−Ph, 4, and 8) present a higher nucleophilic reactivity in comparison with other compounds containing a B−H bond. Compounds 2H−H, 2H−Me, and 2Me−Me show a value of $N = 4.9$ eV compared with those no boron−lithium compounds ranging from 2.8 to 4.1 eV (see column 13 in Table 2). On the other hand, the traditional boron compounds such as BH_3, $BFCl_2$, and BF_2Cl show negative values (not shown here) because their HOMOs are lower than the reference system TCE, and consequently, this reference cannot be applied to account for their reactivity pattern. The local nucleophilicity index[32] calculated through the nucleophilic Fukui functions at the boron atom, f_{B}^{-}, characterizes the most nucleophilic site. From Table 2 (last column), it may be seen that this index shows a very good local behavior at the boron atom. The highest values of N_{k} correspond to the boryllithium compounds (2H−H, 2H−Me, 2Me−Me, 2H−Ph, 2Ph−Ph, 4, and 8).

TABLE 3: NBO Charges on Boron and Lithium Atoms at B3LYP/6-31g(d)

molecule X−Y	B	Li
1H−H	0.611	
2H−H	0.104	0.541
1H−Me	0.621	
2H−Me	0.123	0.545
1Me−Me	0.630	
2Me−Me	0.143	0.547
1H−Ph	0.639	
2H−Ph	0.143	0.617
1Ph−Ph	0.664	
2Ph−Ph	0.115	0.655
3	0.888	
4	0.289	0.641
5	1.171	
6	0.714	
7	0.758	
8	0.206	0.591

Another method used to sense the nucleophilic character in these boryllithium compounds was to study the charges on B and Li atoms in the context of natural bond orbitals (NBO).[22] The values are shown in Table 3. It may be observed that the electronic charge at the boron atom is greater in organoboron compounds containing B−H, B−R, and B−Br bonds than that in the boryllithium compounds. Boryllithium compounds show a decrease of the positive charge on the boron atom related to those boryl compounds having no lithium atom (see Figure 5). Hence, the boryllithium compounds show a more nucleophilic character in the presence of the lithium atom. The compound 5

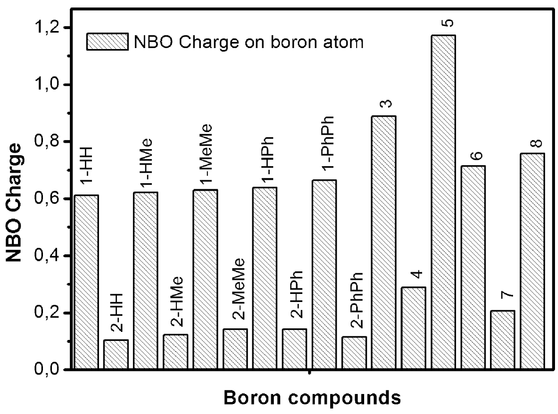


Figure 5. NBO[22] charge on the boron atom for all systems studied here (see Chart 1 and the text for details).

presenting a B−R bond shows the highest positive charge in the series. This fact could help to estimate the electrophilicity of the boron center of the allylboron molecule[36] for compound 5. The synthesis and electrophilic reactivity of this species has been widely studied.[36b]

In summary, the nucleophilic reactivity in compounds containing a B−Li bond[8,9,38] compared with those having B−H, B−Br, and B−R bond can be predicted using calculated proton affinities and also using global and local reactivity indexes based in DFT such as philicity, EDP, and *N*. Our results are in agreement with the experimental trend in synthesized boryllithium compound (2Ph−Ph). However, this compound does not show the highest reactivity in this series. Some compounds substituted with H and CH_3 have a more nucleophilic character than the synthesized compound. Some analogues such as 4 and 8 also showed a high nucleophilic reactivity. The PA values for all boryllithium species showed that they behave as strong bases or superbases.

IV. Conclusions and Perspectives

The calculated proton affinity showed an important result; the boryllithium compounds have a strong base behavior in comparison with other bases reported in the literature. The nucleophilic character of a boryllithium series of molecules and other similar compounds (not containing lithium) was studied using different descriptors based on the chemical reactivity density functional theory such as electrophilicity, nucleophilicity, philicity, and global and local electrodonating power. These boryllithium compounds do not show an electrophilic behavior as the traditional BX_3 ($X = H$, halogen) Lewis acids. It seems to be that the presence of the N and O atoms in the vicinity of the boron atom gives a local nucleophilic reactivity when the compounds contain the B−Li bond. Our results showed that a local and global nucleophilic reactivity in the boryllithium species is in agreement with the experimental nucleophilic character of these compounds. As a result, the philicity index, global and local electrodonating power, global and local nucleophilicity indexes (N and N_k, respectively), and NBO charges on the boron atom showed a systematic nucleophilic trend of these compounds in comparison with the analogues compounds containing B−H, B−R, and B−Br bonds. Therefore, it has been possible to predict the reactivity of analogue compounds of boryllithium which can be used by experimentalist for synthesis of analogue compounds.

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