Supplementary Information

New insights into H_2 activation by intramolecular Frustrated Lewis Pairs based on aminoboranes: The local electrophilicity index of boron as a suitable indicator to tune the reversibility of the process

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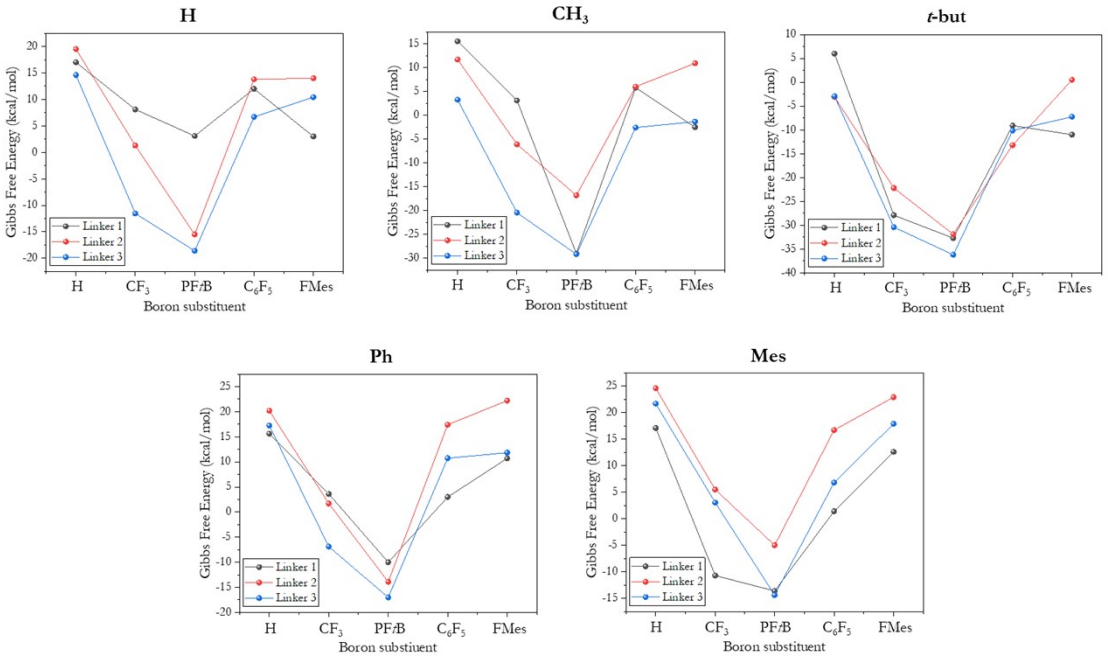


Figure S1. Gibbs free energy associated with the H_2 activation employing all the possible combinations of substituents and linkers.

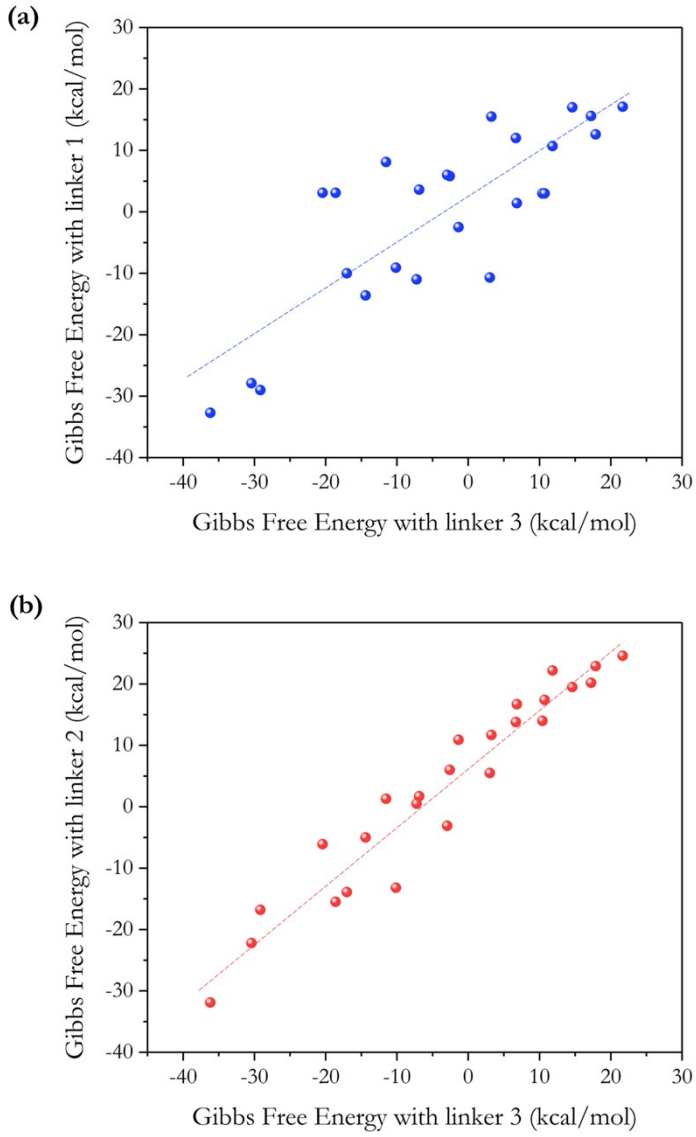


Figure S2. Gibbs free energy associated with the H_2 activation process employing all the possible combinations of substituents and linkers. The linear fitted functions are: $\Delta G_{linker\ 1} = 0.73\Delta G_{linker\ 3} + 2.1; R^2 = 0.67$ for linker 1 and $\Delta G_{linker\ 2} = 0.94\Delta G_{linker\ 3} + 6.4; R^2 = 0.93$ for linker 2.

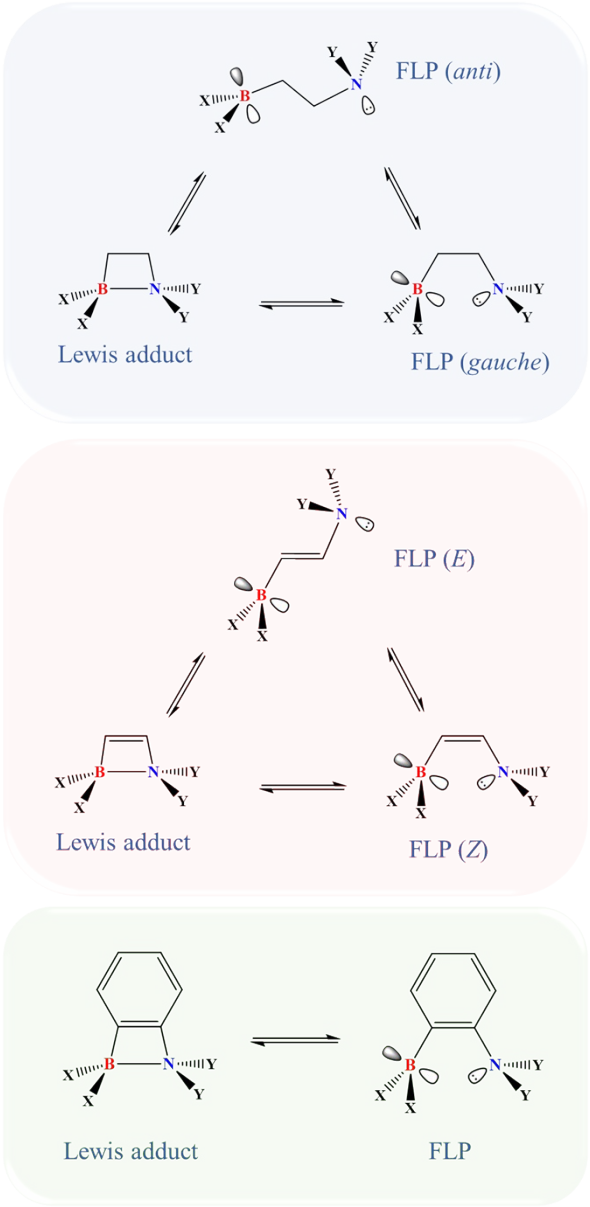


Figure S3. Conformational equilibrium of the aminoboranes for each linker.

Table S1. Gibbs free energy in kcal/mol (at 298 K) of the interconversion between the three different conformers. NF means no formed. The percentage from Boltzmann distribution is also shown.

LB center	LA center	FLP (*gauche* or *Z*)	*Anti* or *E*	Lewis adduct	FLP/*anti* or *E*/Lewis adduct
			Linker 1		
CH_3	**FMes**	0.0	1.9	12.0	**96/**4/0
Mes	**C_6F_5**	0.0	-5.9	-1.9	0/100/0
			Linker 2		
H	**CF_3**	0.0	-2.6	-2.2	**1/**66/33
***t*-but**	**H**	0.0	-7.7	-0.6	0/100/0
***t*-but**	**FMes**	0.0	-17.2	3.5	0/100/0
Ph	**CF_3**	0.0	-8.6	5.5	0/100/0
			Linker 3		
CH_3	**C_6F_5**	0.0	NF	-2.2	**2/**NF/98
CH_3	**FMes**	0.0	NF	16.6	**100/**NF/0
***t*-but**	**H**	0.0	NF	-3.2	**1/**NF/99

Table S2. Activation Gibbs free energy and overall Gibbs free energy change for the H_2 activation process employing CH_3 and Ph in nitrogen and all substituted studied in boron. Electrophilic and nucleophilic Fukui function condensed on boron and nitrogen. respectively. are shown for each system.

LB center	LA center	Linker 3						
		$\Delta G_{act.H_2}$	ΔG_{H_2}	f_B^+	f_N^-	ω	ω_B^+	ω_N^-
CH_3	**H**	12.4	3.3	0.193	0.398	1.22	0.235	0.486
	CF_3	12.1	-20.4	0.214	0.293	1.76	0.377	0.516
	PF*t*B	17.2	-29.2	0.358	0.306	1.92	0.687	0.588
	C_6F_5	18.7	-2.6	0.167	0.333	1.91	0.319	0.636
	FMes	25.5	-1.4	0.166	0.363	1.78	0.295	0.646
	SD						0.178	0.072
Ph	**H**	11.2	17.2	0.181	0.245	1.33	0.241	0.326
	CF_3	11.9	-6.9	0.230	0.237	1.96	0.451	0.465
	PF*t*B	20.4	-17.0	0.363	0.248	2.21	0.802	0.548
	C_6F_5	19.3	10.7	0.163	0.241	1.94	0.316	0.468
	FMes	26.9	11.8	0.166	0.236	1.95	0.324	0.460
	SD						0.223	0.080

SD: Standard Deviation

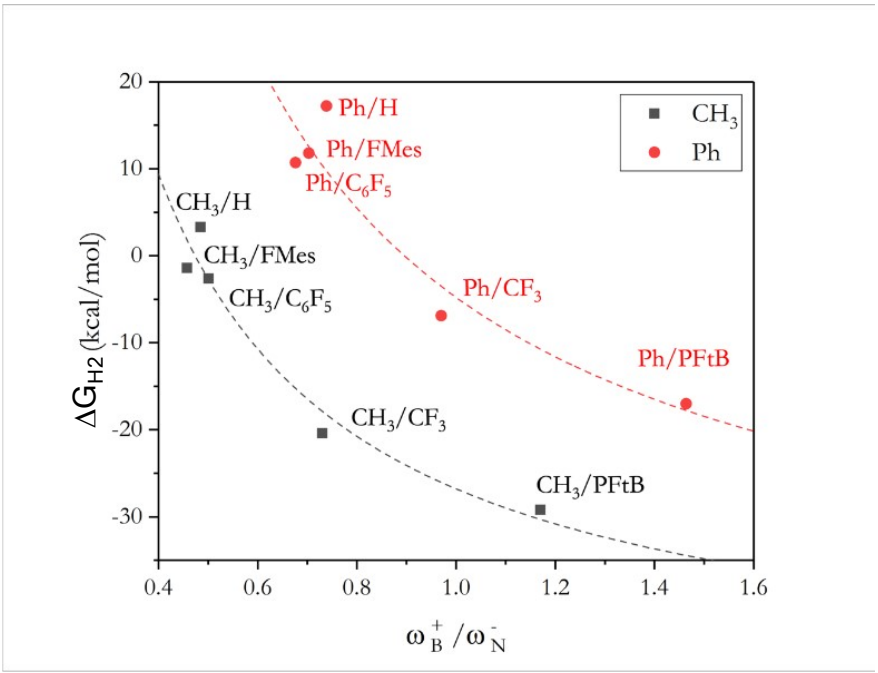
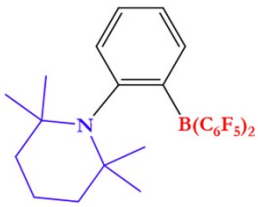
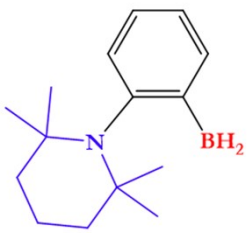


Figure S4. Relationship between ΔG_{H_2} and the ratio of philicities condensed to boron and nitrogen for CH_3 and Ph attached to nitrogen. The linear fit equations are: $\Delta G_{H_2} = 24.1\left(\frac{\omega_B^+}{\omega_N^-}\right)^{-1} - 50.9$ for CH_3 (R^2 = 0.95) and $\Delta G_{H_2} = 41.0\left(\frac{\omega_B^+}{\omega_N^-}\right)^{-1} - 45.8$ for Ph (R^2 = 0.89).

Table S3. Global electrophilicity, condensed-to-boron Fukui index, condensed-to-boron electrophilicity index, boron-nitrogen internuclear distance, predicted Gibbs free energy change from the relation ($\Delta G_{H_2} \leftrightarrow \omega_B^+$) shown in Fig. 7a, computed Gibbs free energy change of H_2 activation, and previous experimental data for two of the experimentally tested intramolecular FLPs showed in Fig. 5.

System	ω	f_B^+	ω_B^+	d_{B-N}	Predicted ΔG_{H_2}	Computed ΔG_{H_2}	Experimental data
	1.82	0.178	0.324	3.043	-10.5	-11.4	Non-reversible
	1.33	0.198	0.263	2.967	-0.3	-2.1	Reversible

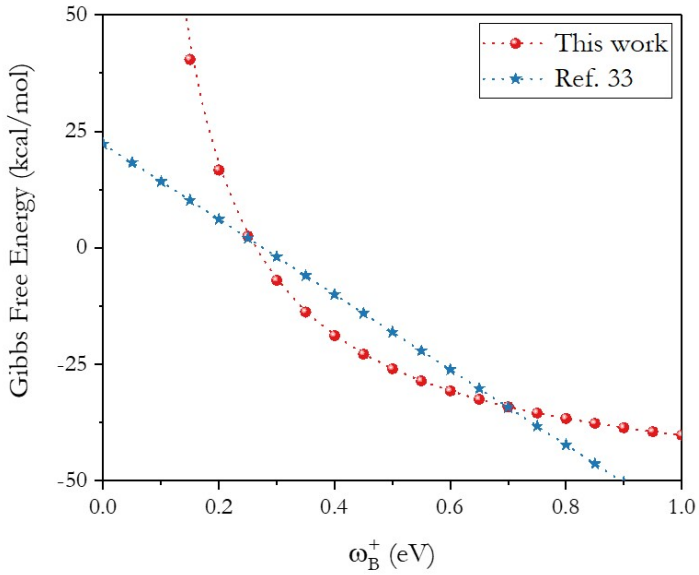


Figure S5. $\Delta G_{H_2} \leftrightarrow \omega_B$ relationship found in this work and in reference 33 ($\Delta G_{H_2} = -80.7\omega^{Def2-TZVP}_{B} + 22.3$).

Fig. S5 shows both fitting functions. where we can see that both are almost equivalent in the ω_B range of 0.22 to 0.75 eV. which is the range of values analyzed in the previous work (notice that a relationship between ω_B values at the corresponding level of theories of each case was found: $\omega^{6-311+G(d.p)}_{B} = 0.681\omega^{Def2-TZVP}_{B} + 0.048.$ and it was used to perform the comparison). At lower ω_B values. the function found in this work grows faster than the linear one. tending to infinity as ω_B tends to zero. while at larger ω_B values. the decay of is ΔG_{H_2} almost linear with a lower slope than the linear relationship. in addition. it depends on the electronic and steric nature of the substituents.