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A Computational and Conceptual DFT Study on the Mechanism of Hydrogen Activation by Novel Frustrated Lewis Pairs

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Abstract

A computational and conceptual density functional theory (DFT) study on the mechanism of the molecular hydrogen activation by a set of three frustrated Lewis pairs (FLPs) was performed at the ωB97X-D/6-311G(d,p) level of theory. A reduced model and other two prototypes derived from experimental data, based on the donor nitrogen and acceptor boron atoms, were used. Analysis grounded on the energy results, geometries and the global electron density transfer at the TSs made it possible to obtain some interesting conclusions: i) despite the well-known very low reactivity of molecular hydrogen, the catalytic effectiveness of the three FLPs produces reactions with almost unappreciable activation energies; ii) the reactions, being exothermic, follow a one-step mechanism via polarised TSs; iii) there are neither substituent effects on the kinetics nor on the thermodynamics of these reactions; iv) the activation of molecular hydrogen seems to be attained when the N–B distance in the FLP derivatives is around 2.74 Å; and v) the proposed FLP model is consistent with the behaviour of the experimental prototypes. Finally, the ability of the three FLPs as efficient catalysts was evaluated studying the hydrogenation of acetylene to yield ethylene.

Introduction.

Formation of dative bonds between electron pair donors (D) and acceptors (A) constitute a central element of the known acid-base theory proposed by Lewis in 1923[1, 2] (see (a) in Scheme 1). However, in some cases, adduct formation might be precluded due to a steric hindrance of acidic and basic centres or by the strain caused by a tether giving rise to the so-called frustrated Lewis pairs (FLPs) (see (b) and (c) in Scheme 1).
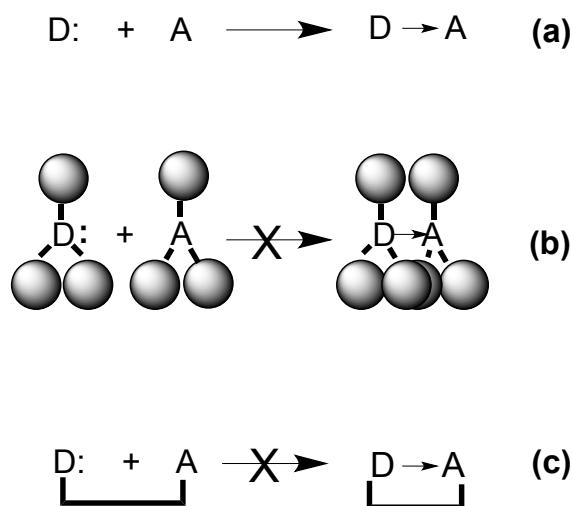
Scheme 1

The idea that a combination of Lewis acids and Lewis bases D/A sterically prevented has an intrinsic reactivity towards the activation of molecular hydrogen and other small molecules was initially addressed by Stephan's group.[3-5] Their strategy consisted of attaching both the Lewis acid-base fragments in the same molecule but quenching the interaction each other, and thereby avoids the formation of the traditional donor-acceptor adduct by steric factors and spatial arrangement within the molecule. From these studies it was shown that the presence of a transition metal (TM) to activate molecular hydrogen was not a requisite. Concomitantly, the FLP chemistry has progressed from stoichiometric reactions to TMs-free catalytic processes. Stephan *et al.*[3, 4, 6] reported that such reversible molecular hydrogen activation was possible using sterically encumbered borane and

phosphorous Lewis acid and base pairs, since they are able to heterolytically split the molecular hydrogen **1** (see Scheme 2). Thus, phosphane/borane (P/B) combinations, such as **I** reacts quickly and effectively with molecular hydrogen **1**, yielding the corresponding zwitterions: phosphonium cation/hydridoborate (also named as borohydride) anion pairs[7] (see **II** in Scheme 2).

The development of the frustrated Lewis pairs chemistry was preceded by some significant experimental facts. In 1942 Brown *et al.* have already identified the presence of steric strains as an important factor on the stability of the acid-base adducts using boron-containing compounds.[8, 9] Later on, notions about the presence of FLPs was anticipated by Piers using tris(pentafluorophenyl) borane, $B(C_6F_5)_3$, as catalyst in the hydrosilation of aromatic aldehydes, ketones and esters.[10] It was not until late 2006, when Stephan *et al.,*[3] reported the remarkable cooperative reactivity of the Lewis acid and Lewis base combination in the reversible TMs-free H_2 activation by the compound $(C_6H_2(CH_3)_3)_2P$-C_6F_4-$B(C_6F_5)_2$. Afterwards, the concept was extended to intermolecular FLPs using different combinations of bulky Lewis bases with the Lewis acid reagent $B(C_6F_5)_3$.[11, 12] Among other applications of Lewis acids such as $B(C_6F_5)_3$ and trityl cation $[CPh_3]^+$, the polymerization catalysis field is highlighted, in this sense, Cabrera *et al.* probed the formation of the donor-acceptor adducts between amines, pyridines and phosphines with the Lewis acid trityl borate $[CPh_3][B(C_6F_5)_4]$ as potential activators in ethylene polymerization.[13] Following in the exploration of the unusual P/B systems, Stephan *et al.* also demonstrated that sterically bulky N-heterocyclic carbenes (NHCs)[14-16] gave FLPs that activated H_2 yielding the respective zwitterions. At the same time, Erker's group reported the reversible activation of H_2 by the new intramolecular FLP $Mes_2PCH_2CH_2B(C_6F_5)_2$.[17] The concomitant extension using nitrogen bases in the H_2 activation by FLPs was a natural evolution.[18] The combination between 2,6 lutidine and $B(C_6F_5)_3$ deserves special mention because Geier and Stephan showed that employing the classical Lewis acid-base adduct, which is speculated to be

unreactive, two typical reactions to recognize FLPs can take place: the activation of H_2 and the tetrahydrofuran-ring opening forming a zwitterionic compound and piridinium salt, respectively.[18] This fact was explained on the basis of an equilibrium between the classical and FLP adducts determined by a competition of steric and acidity:basicity factors.

Based on these findings, these FLPs have been used as active TMs-free hydrogenation catalysts, opening the gate towards a new reactivity in TMs-free catalysis.[19-25]
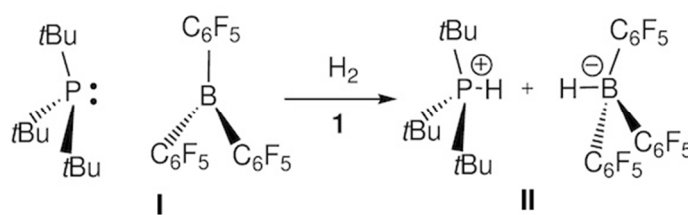
Scheme 2

After Stephan's studies, a great variety of inter- and intramolecular Lewis acids and bases containing phosphorus, nitrogen or carbon donors and boron or aluminium acceptors have been successfully employed to activate molecular hydrogen **1** and other species.[11, 26-29] A great deal of attention has been paid to the activation of small molecules, such as CO_2, CO, N_2O, NO and SO_2 by these FLPs[6, 11, 24, 26-28, 30-34] as well as the hydrogenation of olefins,[24] anilines,[35] NHC compounds,[36] alkynes,[37] imines,[23, 38] enones[39] and other molecules[38, 40, 41] under mild conditions. It is worth to mention that a common characteristic on the mechanisms for the reduction of imines to the respective amines[23, 38] is the protonation of the imine from the phosphonium (or ammonium) centre increasing the electrophilicity of the imine moiety, which is subsequently attacked by the borohydride. For the reduction of enones it is necessary to reduce the electrophilic character of the Lewis acids of the FLP.[39] On the other hand, hydrogenation of unpolarized olefins with fluorinated phosphines has been reported[42] to proceed via a transient carbocation, which reacts with the corresponding borohydride

yielding the respective hydrocarbon and regenerating FLP.

One of the most efficient way to incorporate the Lewis acid fragment (more electrophilic boron-containing fragments in FLPs) is by hydroboration using the "Piers borane", $HB(C_6F_5)_2$.[43-46] By this method, it is possible to access bifunctional phosphine-borane products connected by alkenes or alkynes. This strategy allows controlling the distance and features of the bridge between the acidic and basic fragments (FLPs). Some of the resulting FLPs have performed as useful catalysts for hydrogenation of olefins, imines, and activation of small molecules.[11, 17, 47-49]

Hydroboration with "Piers borane" is also a direct method for hydroborating, for example, enamines,[50] amidinates,[30] generating types of FLPs of novel structures able to activate H_2 and CO, CO_2 and imines. This method is becoming a powerful tool to directly incorporate the Lewis acid fragment in FLPs complex structures.[51, 52]

On the other hand, a very important aspect has been observed, this involves the formation of the four-membered rings from FLPs which is stabilized by classical Lewis acid-base interactions.[5, 53, 54] In this sense, *ansa*-aminoboranes, which contain an intramolecular N/B interaction, activate H_2 and subsequently hydrogenate imines and enamines.[55-58] Erker's experimental studies revealed that di(mesityl)cyclohexenyl-phosphine undergoes hydroboration using "Piers borane" to yield the cyclohexylene-anellated FLP. This P/B pairs breaks H_2 and adds to the C=O double bond of phenyl isocyanate.[59] Later on, the same experimental group prepared a series of enamines undergoes anti-Markovnikov hydroboration with "Piers borane" to give a series of related bridged intramolecular FLPs based on N/B system, which were active catalysts for the hydrogenation of enamines.[54] Recently, Erker *et al.* [60] have reported the 1,1-carboboration reaction modify a FLP to give a C3-bridged FLP, which cleaves dihydrogen. This new FLP also undergoes 1,1-carboboration to give a

P/B/P FLP and later reacting with nitric oxide (NO) by oxidation to yield a persistent FLPNO aminoxyl radical. [60]

From the theoretical point of view, the activation of molecular hydrogen **1** by FLPs has been mainly studied by Papai's[61-63] and Grimme's[64, 65] groups. Both groups agree about the formation of an encounter complex between the Lewis acid and base, but while Papai's group suggests an instantaneous electron transfer (ET) from the lone pair of the Lewis base to the $\sigma*$ orbital of molecular hydrogen **1** and from $\sigma*$ orbital of H_2 to the empty p orbital on the Lewis acid to finally produce the heterolytic cleavage of the H−H bond,[61-63] Grimme's group suggests that the electric field (EF) generated by the donor/acceptor atoms of the FLP polarises the molecular hydrogen **1**, causing its heterolytic split.[64-66]

To date, several experimental[67-74] and theoretical[61, 75-83] studies have tried to gain insight into the energies and mechanisms of the molecular hydrogen activation in order to predict the properties of Lewis acid-base pairs with desired TMs-free catalytic hydrogenation.

We present herein a theoretical study of the activation of molecular hydrogen **1** using a reduced FLP model **2**, and two intramolecular FLP prototypes derived from experimental data, **3**[84] and **4**, based on N/B as donor and acceptor atoms, to obtain a better description of the activation of small molecules (see Scheme 3), using density functional theory[85] (DFT). FLP model **2** was constructed in order to mimic the main electronic and structural features of FLP experimental prototype **3** (see later). Analysis of the reactivity indices of the reagents, activation and reaction energies as well as analysis of the global electron density transfer[86] (GEDT) enable a complete characterisation of the molecular hydrogen activation mechanism. Finally, the hydrogenation of acetylene **8** by the three FLPs is discussed in the light of the results of the hydrogen activation.

Computational Methods

All stationary points involved in the activation processes were optimised using the hybrid ωB97X-D[87] exchange-correlation functional, including long-range corrected and empirical atom-atom dispersion corrections, together with the standard 6-311G(d,p) basis set.[88] The optimisations were carried out using the Berny analytical gradient optimisation method.[89] The stationary points were characterised by frequency computations in order to verify that TSs have one and only one imaginary frequency. The IRC paths[90] were traced in order to check the energy profiles connecting each TS to the two associated minima of the proposed mechanism using the second order González-Schlegel integration method.[91] All studied reactions presented a one-step mechanism. IRC analyses of the corresponding TSs directly connect the reagents with the hydrogenated products. Bulk solvent effects of toluene were considered implicitly by performing single point energy calculations on the gas phase stationary structures using the polarisable continuum model (PCM) as developed by Tomasi's group[92] in the framework of self-consistent reaction field (SCRF).[93, 94] The corresponding thermodynamic quantities were obtained at 120ºC and 1atm to reproduce the experimental conditions (unpublished results). All computations were carried out with the Gaussian 09 suite of programs.[95]

The global electrophilicity index,[96] ω, is given by the following expression, $\omega = (\mu^2 / 2\eta)$, in terms of the electronic chemical potential[85] μ and the chemical hardness[85] η. Both quantities may be approached in terms of the one-electron energies of the frontier molecular orbital HOMO and LUMO, ε_H and ε_L, as $\mu \approx (\varepsilon_H + \varepsilon_L)$ and $\eta \approx (\varepsilon_L - \varepsilon_H)$, respectively.[85] The empirical (relative) nucleophilicity index,[97] N, based on the HOMO energies obtained within the Kohn-Sham scheme,[98] is defined as $N = E_{HOMO}(Nu) - E_{HOMO}(TCE)$, where tetracyanoethylene (TCE) is the reference, as it presents the lowest HOMO energy in a long series of molecules already investigated in the context of polar organic

reactions. This choice allows handling conveniently a nucleophilicity scale of positive values in polar organic reactions.[97]

Results and Discussion

The present study has been divided into three parts: i) first, an analysis of the DFT reactivity indices of the reagents involved in the molecular hydrogen activation by a set of three FLP models is carried out; ii) next, the activation and reaction energies, geometries and results from NBO analysis of the stationary points involved in the molecular hydrogen activation are discussed in order to establish the electronic nature and mechanism of this process; and iii) finally, the three hydrogenated FLPs are used as catalyst models for the hydrogenation of small molecules, *i.e.* reduction of acetylene. Energies, geometries and electronic reorganisation processes will be discussed.

i) Analysis of the DFT reactivity indices of reagents.

Studies devoted to organic reactions have shown that the analysis of the reactivity indices defined within the context of the conceptual[85, 99, 100] DFT is a powerful tool to understand the reactivity in chemical reactions. DFT reactivity indices, namely, electronic chemical potential, μ, hardness, η, electrophilicity, ω, and nucleophilicity, N, are given in Table 1 for molecular hydrogen **1**, and FLPs, **2**, **3** and **4**. Note that structures of **3** and **4** (see Scheme 3) are very similar with the exception that the *N*-pentafluorophenyl substituent in FLP **3** is replaced by a *N*-*p*-cyanophenyl substituent in FLP **4**. FLP model **2** was constructed mimicking the structure of FLP **3** containing a 2,6-dimethylbenzene group instead of the bulky 2,6-diisopropylbenzene ones bound to the donor nitrogen atom, and two strong electron-withdrawing CF_3 groups bound to the acceptor boron atom.

Additionally, the *N*-pentafluorophenyl substituent of structure **3** was replaced by an electron-withdrawing CF_3 group in FLP model **2**.
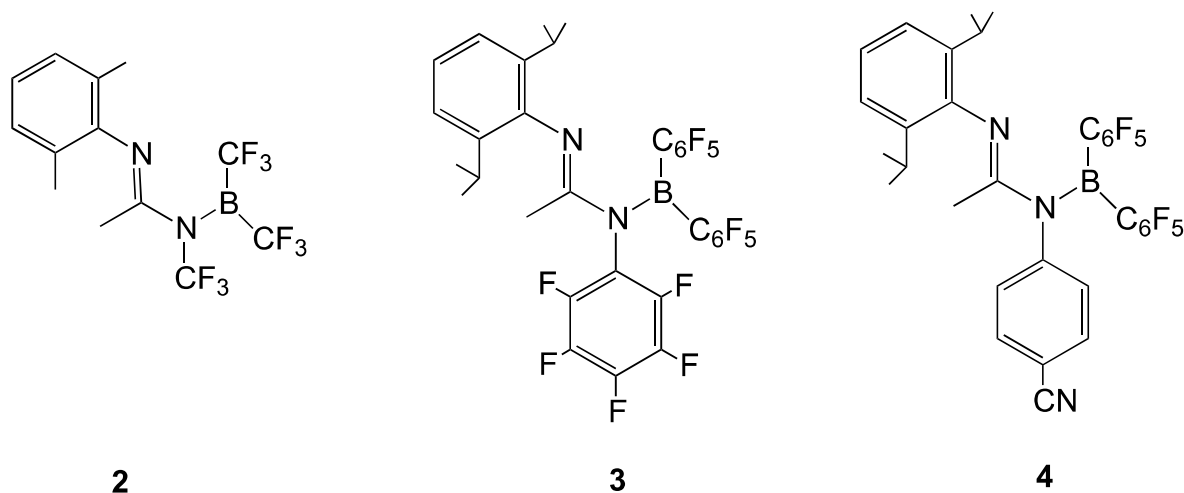
Scheme 3. FLP models **2**, **3** and **4**.

The electronic chemical potential μ of the three FLPs, −4.27 (**2**), −4.26 (**3**) and −4.33 (**4**) eV, is higher than that of the molecular hydrogen **1**, −5.10 eV, suggesting that the GEDT in the process of molecular hydrogen activation will take place from these FLPs towards **1**.

**Table 1.** Electronic chemical potential, μ, hardness, η, electrophilicity, ω, and nucleophilicity, *N*, indices of molecular hydrogen **1**, and FLPs **2**, **3**, and **4**, computed in toluene. Values are given in eV.

	μ	η	ω	*N*
1	-5.10	17.86	0.73	-2.63
2	-4.27	8.37	1.09	2.95
3	-4.26	8.08	1.13	3.10
4	-4.33	8.01	1.17	3.07

The electrophilicity ω indices of the reagents are: 0.73 (**1**), 1.09 (**2**), 1.13 (**3**) and 1.17 (**4**) eV. According the electrophilicity scale[101] molecular hydrogen **1** is considered a poor electrophile, while FLPs **2**, **3** and **4** can be classified as moderate electrophiles. On the other hand, the nucleophilicity N index of these reagents, -2.63 (**1**), 2.95 (**2**), 3.10 (**3**) and 3.07 (**4**) eV, indicates that molecular hydrogen **1** is then the poorest nucleophile, while the three FLPs are strong nucleophiles in agreement with the above chemical potential discussion. Note that the low electrophilic character of molecular hydrogen **1** is a consequence of its extreme hardness ($\eta = 17.86$ eV), which is consistent with its expected low reactivity at ground state.

*ii) Study of the activation of molecular hydrogen **1** by the FLP models **2**, **3** and **4**.*

The molecular hydrogen **1** activation by FLPs is modelled by the following process:

$$FLP + H_2 \rightarrow FLP - H_2. \qquad (1)$$
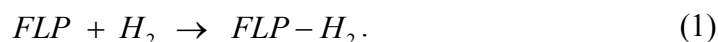
The corresponding activation and reaction energies calculated at ωB97X-D/6-311G(d,p) level of theory for FLP model **2**, and the prototypes from the experimental FLPs, **3** and **4**, are displayed in Table 2.

The activation energies associated with the activation of **1** by FLPs **2**, **3** and **4**, are 2.4 (**TS2/H$_2$**), 5.7 (**TS3/H$_2$**), and 6.8 (**TS4/H$_2$**) kcal/mol, while formation of the corresponding zwitterions FLPs (also called here as hydrogenated) are exothermic reactions by 40.2 (**5**), 27.0 (**6**) and 27.4 (**7**) kcal/mol. Compounds **5**, **6** and **7** are the respective hydrogenated FLPs (see Scheme 4). Accordingly to the energy barrier ($\Delta E^{\neq}$) data, the hydrogen activation process by these FLPs is feasible. Interestingly, the proposed FLP **2** is a suitable reduced model of the prototype derived from experimental FLPs **3** and **4** for the hydrogen activation process, although it attaches more strongly the

hydrogen atoms to the substrate than **3** and **4**, by about 13 kcal/mol, plausibly letting them less

available for subsequent steps. Some appealing conclusions can be obtained from these energy

results: i) these reactions have unappreciable activation energies; ii) these reactions are notably

exothermic; and iii) there is neither substituent effect on the kinetics nor on the thermodynamics of

these reactions. The three studied processes are energetically very similar.

Table 2. ωB97X-D/6-311G(d,p) relative electronic energies (ΔE, in kcal/mol), enthalpies (ΔH in kcal/mol), entropies (ΔS in cal/molK), and Gibbs free energies (ΔG in kcal/mol), computed at 120ºC and 1 atm in toluene for the reaction of molecular hydrogen **1** and models of FLPs **2**, **3** and **4**.

	2 + H$_2$	**3 + H$_2$**	**4 + H$_2$**
$\Delta E^{\neq}$	2.4	5.7	6.8
ΔE_{reac}	-40.2	-27.0	-27.4
$\Delta H^{\neq}$	3.6	6.6	7.5
ΔH_{reac}	-35.3	-21.8	-23.0
$\Delta S^{\neq}$	-33.4	-31.9	-29.9
ΔS_{reac}	-33.5	-33.8	-32.8
$\Delta G^{\neq}$	16.7	19.2	19.2
ΔG_{reac}	-22.1	-8.5	-10.1

In order to illustrate the Gibbs free energy profiles associated with the activation of molecular

hydrogen **1**, thermodynamic calculations in toluene at 120°C and 1 atm were performed to reproduce

the experimental hydrogenation process. The thermodynamic data are also presented in Table 2. A

comparison of the relative electronic energies and relative enthalpies shows similar results. Notice

that adding the thermal corrections to the electronic energies, which can be computed using the

harmonic-oscillator-rigid-rotor model plus k$_B$T term, lead to a slight increase of the activation

enthalpy of the three TSs, i.e. 3.6 (**TS2/H$_2$**), 6.6 (**TS3/H$_2$**) and 7.5 (**TS4/H$_2$**) kcal/mol, while the

reaction enthalpies decrease slightly with respect to the overall energy change by about 4-5 kcal/mol; the respective high exothermicity is kept along the reactions. Once the entropies are added to enthalpies, the activation Gibbs free energies increase between 16 and 20 kcal/mol due to the unfavourable activation entropies associated with these bimolecular reactions: 16.7 (**TS2/H$_2$**), 19.2 (**TS3/H$_2$**) and 19.2 (**TS4/H$_2$**) kcal/mol. In spite of this increase, the Gibbs free energy of the reactions remains exergonic for the formation of the hydrogenated FLP adducts by −22.1 (**5**), −8.5 (**6**) and − 10.1 (**7**) (see Scheme 4). Again, it is noteworthy that the proposed FLP model **2** displays very similar thermodynamic parameters to those obtained using experimental prototypes, FLPs **3** and **4**. Vankova *et al.* have also computed favourable Gibbs free energy of the reaction for the activation of molecular hydrogen **1** employing a series of phosphine/borane combinations used as FLPs.[102]

5	**6**	**7**
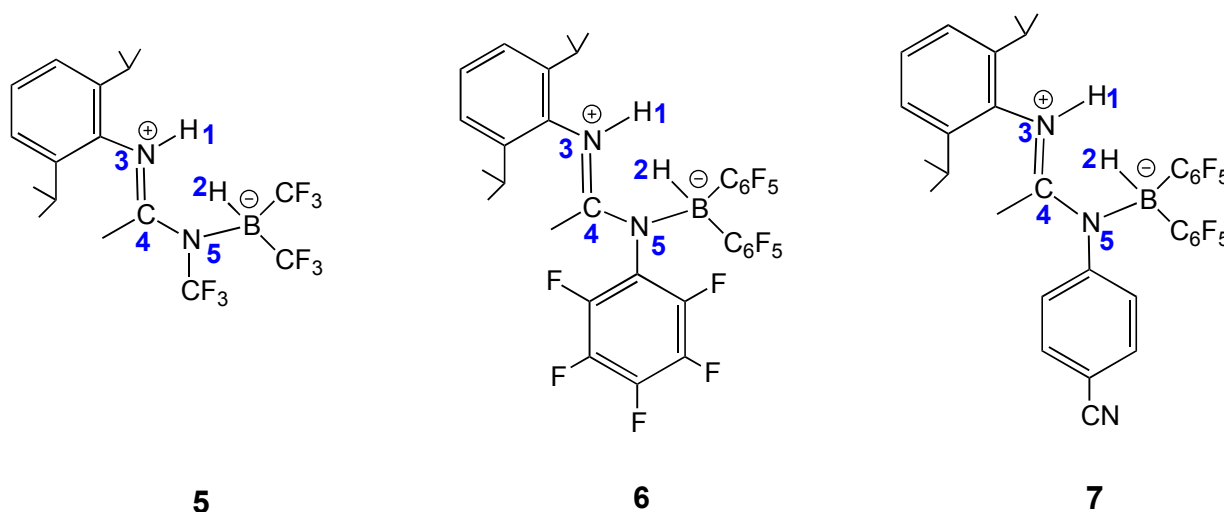
Scheme 4. Hydrogenated FLPs **5**, **6**[84] and **7**.[84]

It is noteworthy that the three FLPs systems can be found in two forms, the typical intramolecular FLPs, also called open-chain form that is in equilibrium with a four-membered ring through N→B interaction in agreement with other reports.[5, 53, 55] The former is expected to be reactive whereas the latter to be unreactive since the reactivity of the Lewis acidity of the B centre and Lewis

basicity of N centre is quenched by the formation of typical N→B interaction. Total electronic and thermodynamic quantities in toluene for all systems are quoted in Table S2 of the Supplementary Material. From these results, some interesting conclusions can be drawn, i) the three four-membered rings of the FLP models show more favourable entalphies than the open-chain structures by 29.8 kcal/mol for **2** and by 14.4 kcal/mol for **3** and by 15.7 kcal/mol for **4**, ii) the bulky 2,6-diisopropylbenzene present in FLPs **3** and **4** probably avoid a strong N→B interaction yielding a lower stabilization than that found in FLP **2** containing a 2,6-dimethylbenzene group, and iii) Gibbs free energies agree with the trend of the enthalpies found for the three systems, therefore the equilibrium mixture is displaced toward the four-membered rings, however, in a major degree in **2** than **3** and **4** systems.

The geometries of the TSs associated with the molecular hydrogen activation by FLP models **2**, **3** and **4** are given in Figure 1a-c. The lengths of the N – H1 and B – H2 single bond formation at the TSs are: 1.994 Å and 1.822 Å at **TS2/H$_2$**, 1.774 Å and 1.663 Å at **TS3/H$_2$** and 1.781 Å and 1.687 Å at **TS4/H2**, respectively. These distances indicate that they correspond to a slight asynchronous bond formation process. On the other hand, the lengths of the H1−H2 breaking bonds using the experimental prototypes **3** and **4** vary in a narrower range, i.e. 0.799 Å and 0.796 Å (for FLP model **2**, it is slightly shortened to 0.774 Å), the distance between the nitrogen and boron atoms is 2.738 Å at **TS3/H$_2$** and 2.745 Å at **TS4/H$_2$**. It is worth mentioning that the B–N distance in FLP model **2** is very close to that found at **TS3/H$_2$** and **TS4/H$_2$**, *i.e.* 2.710 Å; therefore, the geometry where the hydrogen activation occurs in the proposed FLP model **2** is quite similar to that observed in those experimental prototypes of FLPs **3** and **4**. It can be also noted that at the reagents (structures reported in the Supplementary Material), the B–N distances are longer than those found at the TSs, *i.e.* 2.972Å at **3**

and 3.045Å at **4** which are shorter than the sum of the nitrogen and boron van der Waals radii, 3.47 Å.[103] Evident geometrical changes occur when the system moves from reagents to the TSs: the B–N lengths decrease by 0.24 Å for **TS3/H$_2$** and by 0.30 Å for **TS4/H$_2$**, with respect to the reactants, while the H1−H2 lengths slightly increase by approximately 50 mÅ at both TSs. Finally, the TSs are relaxed towards to the hydrogenated FLP adducts, *i.e.* **5**, **6** and **7** (see Scheme 4), with the hydrogen atoms moving further apart from each other and binding to the N and B atoms of the FLPs. Note that the N−H1 lengths are longer than the B−H2 ones as a consequence of the H1−H2 bond polarisation (see later). For FLP model **2**, the corresponding distances at the TS are very similar to the ones derived from experimental data, while the N–B distance is reduced by 0.4 Å from the reactants to the TSs, the H1–H2 distance slightly decreases at the TS by 30 mÅ. Similar results in intermolecular FLPs were found by Papai *et al.* [61]
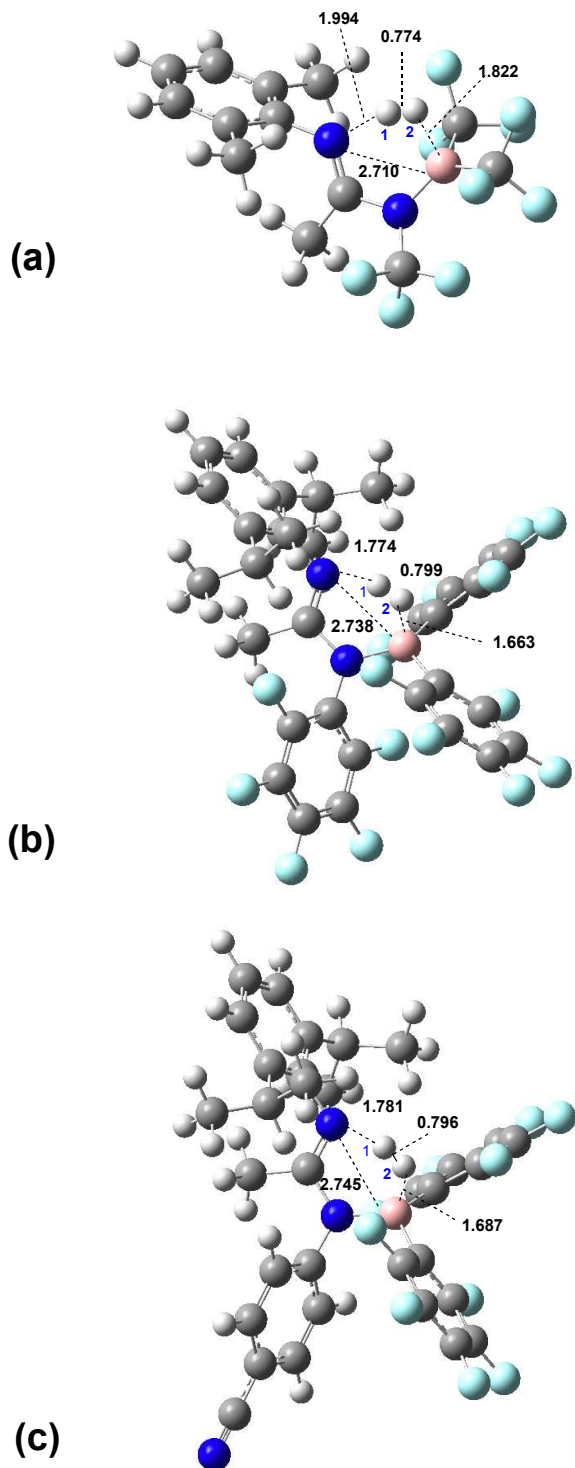
Figure 1. ωB97X-D/6-311G(d,p) gas phase optimised TS geometries involved in the hydrogen activation process using the three FLPs: (a) **TS2/H₂**, (b) **TS3/H₂** and (c) **TS4/H₂**. Grey: Carbon; Blue: Nitrogen; Pink: Boron; Cyanogen: Fluor, and White: Hydrogen atoms. Lengths are given in Angstroms.

The polar character of the hydrogen activation process was evaluated computing the GEDT at the TSs. The natural atomic charges at the gas phase of reagents and TSs (see Table 3) obtained through a natural population analysis (NPA) were shared between molecular hydrogen **1** and the FLP frameworks. The GEDT at these TSs is 0.18e at **TS2/H$_2$**, 0.24e at **TS3/H$_2$** and 0.21e at **TS4/H$_2$**. These relative values suggest that the hydrogen activation process has a polar character and the direction of electronic flow is from H2 toward FLPs. Concomitantly, it can clearly be seen that molecular hydrogen **1** is polarised when it is approaching to the FLPs: at the TSs, for both systems the H1 atom close to the donor N atom is positive whereas, the charge of H2 atom close to the acceptor B atom is almost null, or slightly negative, in consistency with the negative charge of the N atom and positive charge of the B atom (see Table 3). The N and B atoms at the TSs are also polarised comparing with the reactants. In the reagents, the H1 and H2 atoms are not charged; however, when they approach to the FLPs, they quickly begin to be polarised, mainly by the N and B atoms. The N and B atoms have acquired some charge from the reagents to reach the TSs, which are being prepared for the rupture of the molecular hydrogen **1**.

Finally, it is expected that in the presence of an olefin under reaction conditions, the polarised H1 and H2 atoms of the hydrogenated FLP adducts **5-7** (see Scheme 4) are prepared to produce the hydrogenation of small molecules such as acetylene **8**, which will be discussed later. Note that the pattern of charges shown by our FLP model **2** at the **TS2/H$_2$** is very similar to that found at **TS3/H$_2$** and **TS4/H$_2$**. The same type of polarisation of molecular hydrogen **1** induced by an intermolecular FLPs was found by Papai *et al.* using the frontier molecular orbital approximation.[62]

Some appealing conclusions can be derived from the activation of molecular hydrogen **1**: i) the N–B distance decreases from the reagents towards the TSs. In the latter, the N–B distance is very
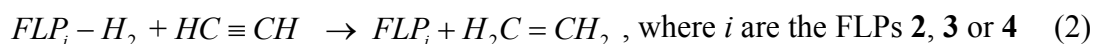
similar in the three FLPs studied here; ii) the N–B distance of around 2.74 Å can be considered

necessary to attain the activation of molecular hydrogen **1**; iii) at the TSs, molecular hydrogen **1** is

mainly polarised by the N and B atoms along the reactions. Note that neither strong effects of the

substituent in experimental prototypes of FLPs **3** and **4** are observed in the energies nor at the TS's

geometries; iv) the GEDT values indicate that the activation of the molecular hydrogen **1** is associated

to a polar process and, consequently, lower activation barriers are expected; and finally, v) FLP model

2 appears to be a very good representative model to reproduce the important geometrical parameters

necessary to induce the hydrogen activation.

Table 3. ωB97X-D/6-311G(d,p) GEDT and atomic charges (in e units) at the most important centres of the **TS2/H$_2$**, **TS3/H$_2$** and **TS4/H$_2$** obtained through natural population analysis (NPA). Charge values of the FLPs at reactants are given in parentheses.

	TS2/H$_2$	**TS3/H$_2$**	**TS4/H$_2$**
GEDT	0.18	0.24	0.21
q(H1)	0.15	0.22	0.23
q(H2)	0.03	0.02	-0.02
q(N)	-0.84 (-0.45)	-0.59 (-0.48)	-0.60 (-0.48)
q(B)	0.68 (0.71)	0.82 (1.00)	0.85 (0.95)

*3) Study of FLPs in the hydrogenation of acetylene **8**.*

Finally, as the three FLPs proved to be suitable to produce the molecular hydrogen activation,

they were tested as possible catalysts of small molecules, specifically in the hydrogenation of

acetylene **8**. The reduction of acetylene **8** to yield ethylene **9** is given by the following reaction (see

Scheme 5):

$$FLP_i - H_2 + HC \equiv CH \ \rightarrow \ FLP_i + H_2C = CH_2 \text{, where } i \text{ are the FLPs } \mathbf{2}, \mathbf{3} \text{ or } \mathbf{4} \quad (2)$$

Note that in reaction (2), the three selected FLPs operate as catalysts for the hydrogenation of

acetylene **8**. The corresponding reaction and activation energies are given in Table 5.
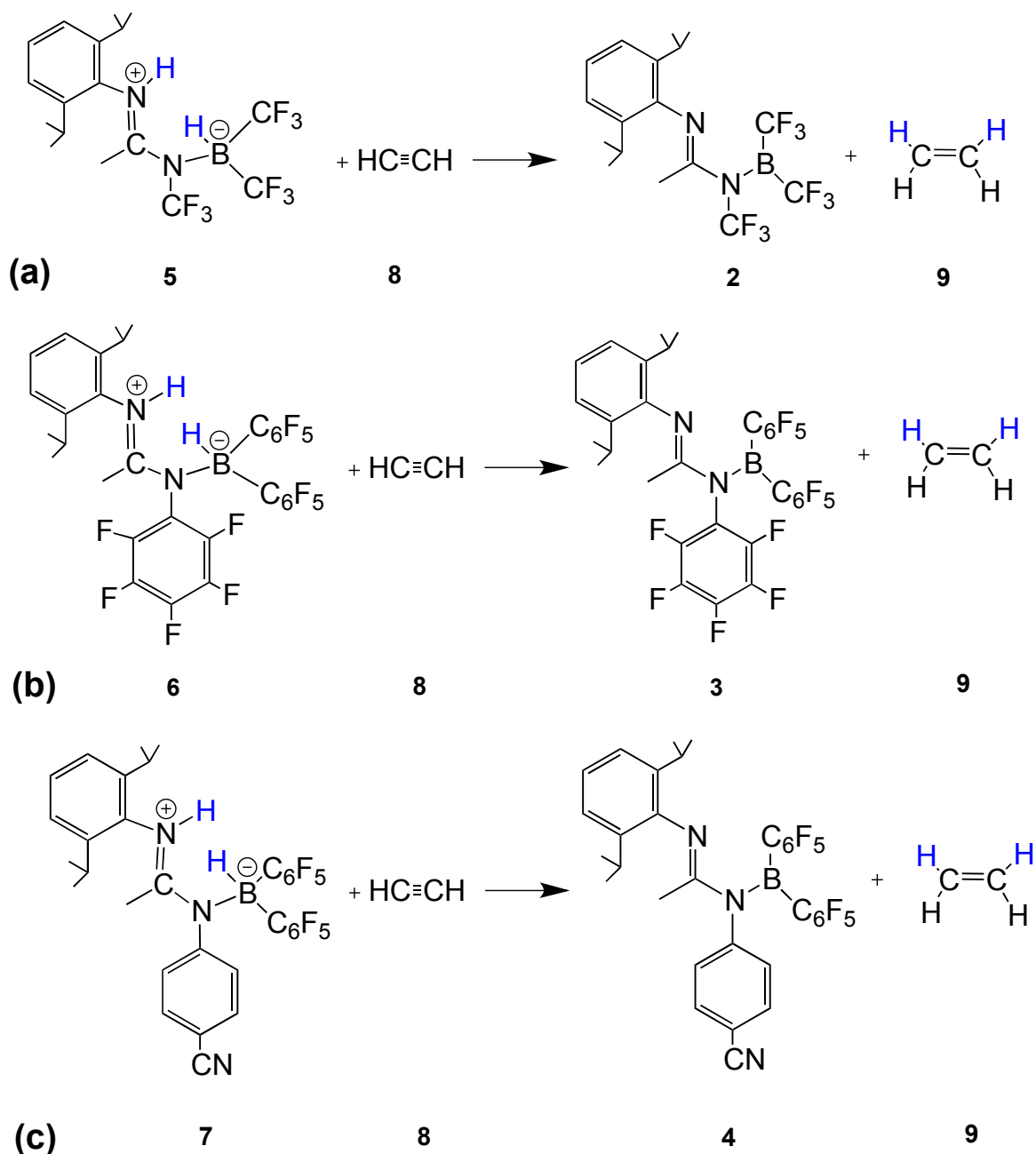
Scheme 5. Representation of hydrogenation of acetylene **8** by the three zwitterions to yield
the respective FLP models and ethylene **9**.

The activation energy associated with the hydrogenation of **8** by FLP-H$_2$, derived from FLP model **2** is (**TS2-H$_2$/8**) 35.3 kcal/mol, while for those derived from experimental data, FLPs **3** and **4**, these values are 30.8 (**TS3-H$_2$/8**), and 31.7 (**TS4-H$_2$/8**) kcal/mol. Formation of ethylene **9** and recovery of the FLPs **2**, **3** and **4** is relatively exothermic by 12.3, 25.4 and 25.1 kcal/mol, respectively. An analysis of the activation and reaction enthalpies shows that they slightly decrease in comparison to those obtained from the electronic energies: hydrogenation of acetylene **8** to yield ethylene **9** at 120ºC in toluene is achievable having activation enthalpies of 31.7 (**TS2-H$_2$/8**), 27.7 (**TS3-H$_2$/8**) and 29.7 (**TS4-H$_2$/8**) kcal/mol, and the formation of **9** remains an exothermic process by 11.0, 24.6 and 23.3 kcal/mol, respectively, in the three processes. Finally, the addition of entropy to enthalpy increases the activation Gibbs free energies to 47.2 (**TS2-H$_2$/8**), 43.3 (**TS3-H$_2$/8**) and 44.8 (**TS4-H$_2$/8**) kcal/mol. In spite of this, the process is still exergonic and favourable: −13.5, −27.2 and −25.5 kcal/mol for the corresponding isolated FLPs and ethylene **9** as products. From these energy results it can be concluded that: i) these reactions have achievable activation energies under the experimental conditions; ii) there are neither substituent effects on the kinetics nor on the thermodynamics of these reactions; iii) hydrogenation of acetylene **8** occurs through a one-step mechanism; and iv) FLPs **2**, **3** and **4** can be used as efficient catalysts in the hydrogenation of small molecules such as acetylene **8**. Note that FLP model **2** reproduces the thermodynamic data in good order when the corresponding values are compared to those of the ones from the experimental FLPs **3** and **4**, despite the fact that it predicts to be less favourable from kinetic and thermodynamic points of view than **3** and **4**. It is noteworthy that Papai *et al*. recently verified experimentally as well as theoretically a catalytic performance for the reduction of alkynes to cis-alkenes using an aminohydroborane as a FLP catalytically active.[104]

Table 5. ωB97X-D/6-311G(d,p) electronic energies (ΔE, in kcal/mol), enthalpies (ΔH in kcal/mol), entropies (ΔS in cal/molK), and Gibbs free energies (ΔG in kcal/mol), computed at 120ºC and 1 atm, in toluene for the hydrogenation of acetylene **8** to yield ethylene **9** according to reaction (2).

	TS2-H$_2$/8	**TS3-H$_2$/8**	**TS4-H$_2$/8**
$\Delta E^{\neq}$	35.3	30.8	31.7
ΔE_{reac}	-12.3	-25.4	-25.1
$\Delta H^{\neq}$	31.7	27.7	29.7
ΔH_{reac}	-11.0	-24.6	-23.3
$\Delta S^{\neq}$	-36.9	-39.7	-38.7
ΔS_{reac}	6.5	6.7	5.8
$\Delta G^{\neq}$	47.2	43.3	44.8
ΔG_{reac}	-13.5	-27.2	-25.5

In order to discuss the geometries of the TSs for the hydrogenation of acetylene **8** by FLP-H$_2$ derived from FLP models **2**, **3** and **4**, Figure 2 shows the most important parameters and the corresponding data are compiled in Table 6.

Table 6. Most important geometrical parameters (in Å) at the ωB97X-D/6-311G(d,p) level at the corresponding TSs for the hydrogenation of acetylene **8** using the hydrogenated FLPs **2**, **3** and **4**.

Parameter	**TS2-H$_2$/8**	**TS3-H$_2$/8**	**TS4-H$_2$/8**
d(H1-H2)	1.886	2.037	2.048
d(N-B)	2.851	2.920	2.919
d(N-H1)	1.280	1.125	1.125
d(B-H2)	1.285	1.337	1.344
d(H1-C1)	1.373	1.598	1.597
d(H2-C2)	1.479	1.346	1.331
d(C1-C2)	1.253	1.262	1.264

It may be clearly observed that the H1−H2 and N−B distances have been lengthened to 1.886 and 2.851 Å at **TS2-H$_2$/8**, 2.037 and 2.920 Å at **TS3-H$_2$/8**, 2.048 Å and 2.919 Å at **TS4-H$_2$/8**, respectively, agreeing with the larger size of these TSs. It is remarkable to mention that there is no great difference in the most important geometrical parameters of **TS3-H$_2$/8** and **TS4-H$_2$/8**. Clearly, these geometrical results are in agreement with the similitude of the thermodynamic quantities found for these systems and discussed in the paragraph above. On the other hand, the H1–C1 and H2–C2 distances show a slight asynchronicity in the formation of the two new C–H single bonds to yield ethylene **9** as product. Some differences in the geometrical parameters of **TS2-H$_2$/8** with those of **TS3-H$_2$/8** and **TS4-H$_2$/8** are found, and they may explain the slight differences in the activation of the processes. The great difference is based on the fact that FLP model **2** does not contain complete bulky and electronic properties that the experimental FLPs have. Therefore this feature remains in the second process of hydrogenation of acetylene **8**; even so FLP model **2** proves to be a very appropriate model of experimental prototype, FLP **3,** to discuss all the properties presented in this study.
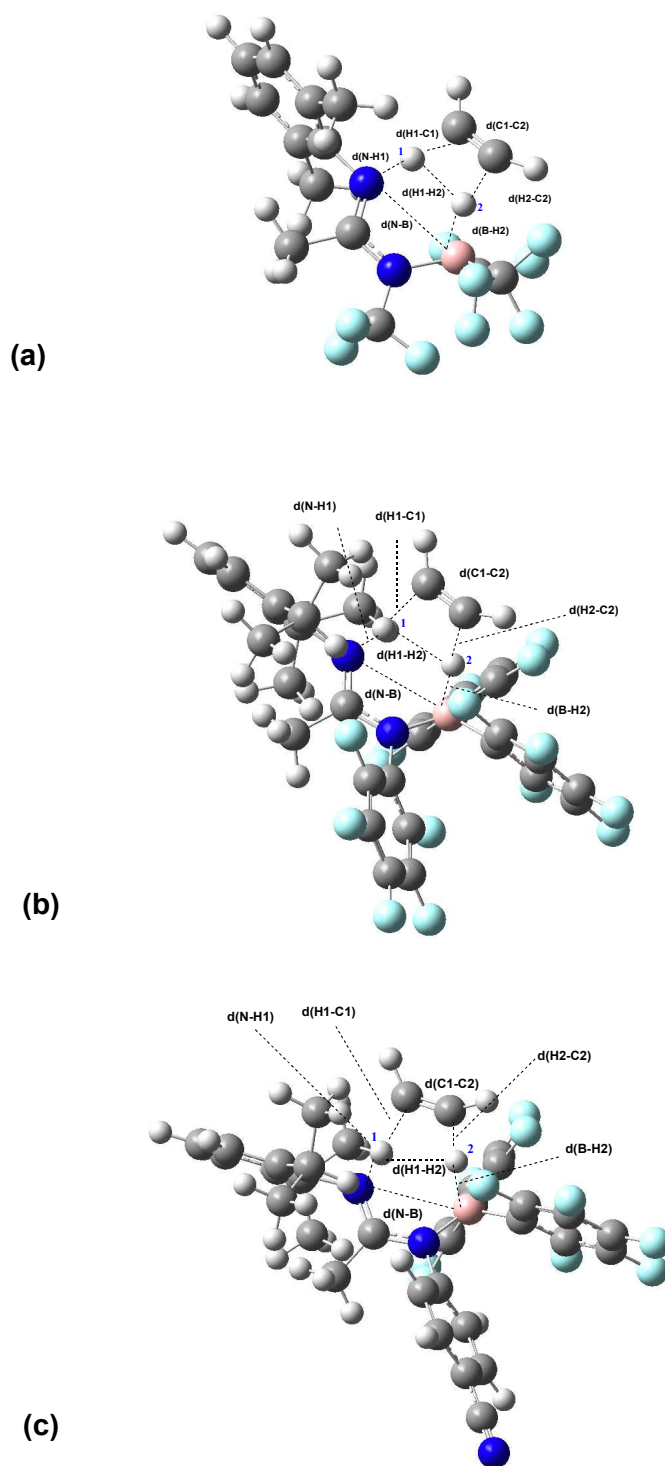
(a)

(b)

(c)

Figure 2. Most important parameters of the ωB97X-D/6-311G(d,p) gas phase optimized TSs involved in the hydrogenation of acetylene **8**: (a) **TS2-H₂/8** (b) **TS3-H₂/8** and (c) **TS4-H₂/8**. Grey: Carbon; Blue: Nitrogen; Pink: Boron; Cyanogen: Fluor, and White: Hydrogen atoms.

Finally, in order to test the polar character at the TSs for the hydrogenation of acetylene **8**, the GEDT and the atomic charges given by the natural population analysis (NPA) at the most important centres involved in this process have been calculated. The corresponding data are displayed in Table 7. Notice that within a ternary system composed by **1** + FLPs + **8**, the global electron density transfer was computed between **1** and FLP + **8** subsystems. The respective values of GEDT are: 0.39e at **TS2-H$_2$/8**, 0.42e at **TS3-H$_2$/8** and 0.42e at **TS4-H$_2$/8**, it can be deduced that the hydrogenation of acetylene **8** to yield ethylene **9** has a very high polar character for the three considered FLPs. The GEDT together with atomic charges also give information about the direction of the electronic flow as well as in which subsystem the electron density is accumulated or depleted. In this sense, the electron density is transferred from **1** towards the FLPs + HC≡CH framework, in accord with the fact that a reduction process takes place in the hydrogenation of olefins and alkynes. It may be also observed that molecular hydrogen **1** is strongly polarised at the three TSs. Note however that while the B atoms gain greater electron density in the three systems than those in the hydrogen activation, N atoms remain almost without changes in their electronic population, especially for **TS3-H$_2$/8** and **TS4-H$_2$/8** (compare q(N) values in Table 7 to those in Table 3).

Table 7. Atomic charges (in e units) at the most important centres of the **TS2-H$_2$/8**, **TS3-H$_2$/8** and **TS4-H$_2$/8** obtained through a natural population analysis (NPA) at ωB97X-D/6-311G(d,p) level.

	TS2-H$_2$/8	TS3-H$_2$/8	TS4-H$_2$/8
GEDT	0.39	0.42	0.42
q(H1)	0.38	0.43	0.43
q(H2)	0.01	-0.01	-0.01
q(N)	-0.57	-0.62	-0.63
q(B)	0.29	0.64	0.65

Concluding Remarks.

The mechanism of the molecular hydrogen activation by a set of three FLPs has been theoretically studied using DFT methods at the ωB97X-D/6-311G(d,p) level of theory. These reactions take place through a one-step mechanism via a polar and slightly synchronous TSs. From the analysis of energies, geometries and the GEDT, the following appealing conclusions can be drawn: i) in spite of the very low reactivity of molecular hydrogen **1**, the catalytic effectiveness of the three FLPs produces hydrogen activations, with almost unappreciable activation energies; ii) no substituent effects are observed in the FLPs **3** and **4**; iii) the observed TSs display a polar character; and iv) the proposed FLP model **2** appears to be appropriate to reproduce consistently the main electronic characteristics of FLP **3** derived from experimental data. Finally, the proposed FLP model **2** and those FLPs **3** and **4** can be regarded as useful and reasonable models of catalysts, specifically in hydrogenation processes of small molecules such as acetylene. According to our preliminary results, the hydrogen transfer from the three hydrogenated FLPs towards acetylene **8**, which is polar and slightly asynchronous, is thermodynamically feasible. Progress concerning this kind of non-metal based catalysis is currently being made at our laboratory.

Supplementary Material. ωB97X-D/6-311G(d,p) gas phase total energies (in a.u.), unique imaginary frequency (in cm^{-1}), and Cartesian coordinates of all structures involved in the activation of molecular hydrogen by the FLP models and for the hydrogenation of acetylene. Total energies (E, in au), enthalpies (H, in au), entropies (S, in cal/mol K) and Gibbs free energies (G, in au), computed at 120ºC and 1 atm in toluene are also reported.

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