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A comparative study of frustration in Al/P and B/P-based intramolecular frustrated Lewis pairs

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Intramolecular frustrated Lewis pairs (IFLPs) have emerged as versatile systems for small molecule activation, with their reactivity critically influenced by the nature of the bridging unit and the intrinsic properties of the Lewis acid and base. In this work, we present a comparative computational analysis of AlP- and BP-based IFLPs featuring a series of structurally analogous linkers. Using H₂ activation as a unified metric, we evaluate the degree of frustration encoded within each system by examining transition state energetics, adduct stability, and electronic structure features. Our findings reveal that while AlP-IFLPs often exhibit masked behavior due to partial Al-P interactions, their BP counterparts remain classical FLPs with greater spatial separation. The geminal-bridged AlP_{Gem} system exhibits the most favorable energetic profile, whereas rigid systems like AlP_{Nap} incur substantial strain. This study underscores the role of both electronic and geometric parameters in dictating FLP behavior and provides valuable insights for the rational design of future IFLPs with enhanced reactivity and tunability.

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Introduction

Since the pioneering work by Stephan and co-workers in 2006 on the metal-free activation of dihydrogen using sterically encumbered Lewis acid-base pairs, the concept of Frustrated Lewis Pairs (FLPs) has emerged as a powerful platform for small molecule activation and catalysis.¹ In conventional Lewis acid-base adducts, the acid and base form a stable dative bond. However, in FLPs, such bonding is hindered by steric or geometric constraints, resulting in reactive acid-base pairs that can activate otherwise inert substrates.^{2–13} FLPs are generally classified into three types: intermolecular, intramolecular, and masked (or hidden) FLPs.¹⁴ Intermolecular FLPs involve separate Lewis acid and base moieties, typically with bulky substituents to prevent adduct formation. In contrast, intramolecular FLPs (IFLPs) tether both the acid and base within a single molecule *via* a linker, offering improved control over the proximity and orientation of the reactive sites. Masked FLPs appear as classical Lewis adducts in the solid state but dissociate in solution or under strain, exhibiting FLP-like reactivity under specific conditions.¹⁴

Since their discovery, FLPs have demonstrated a wide range of reactivities, particularly in the activation of small molecules such as H₂, CO₂, N₂O, and olefins.^{2,15,16} Their applications span metal-free hydrogenation, carbon capture and utilization, C–F

and C–H bond activation, and even polymerization catalysis.^{17–19} Most commonly, boron-based Lewis acids like B(C₆F₅)₃ are employed due to their well-defined synthesis and tunable Lewis acidity. The reactivity of FLPs has been significantly modulated through variations in substituents, the nature of the bridging unit, and by electronic tuning—notably *via* aromatic and anti-aromatic modifications to the acidic or basic sites.^{20–28} To expand the chemical space of FLPs and explore new avenues for reactivity, alternative Lewis acid/base combinations have been investigated. In this context, replacing boron with aluminum as the Lewis acidic component presents a particularly appealing strategy.²⁹ Aluminum, being more acidic than boron, offers the potential for enhanced reactivity, but also presents synthetic and stability challenges.³⁰ Recent studies have demonstrated that Al-based FLPs can successfully activate a wide range of substrates including H₂, CO₂, C=O, and C=C bonds.^{29,31–33} For example, the intermolecular system Al(C₆F₅)₃ combined with bulky phosphines such as Mes₃P or *o*-Tol₃P was found to reversibly activate H₂ and CO₂, and also engage in olefin hydrogenation and C–F bond activation.^{29,33,34} The Al/P FLPs have been shown to catalyze the hydrogenation of ethylene and cyclohexene,^{32,34} while another study demonstrated the use of Al FLPs in CO₂ reduction to methanol using HBpin as the reductant.³⁵ Moreover, Uhl and co-workers have reported a geminal Al-P FLP based on a *t*-butyl-substituted aluminum and diphenylphosphine, capable of activating a range of small molecules such as isocyanates, CO₂, and organic azides.^{36–38}

It is worth noting, however, that despite their higher intrinsic Lewis acidity, Al-based IFLPs have been comparatively less investigated than BP analogues, largely due to experimental

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challenges. The strong oxophilicity and moisture sensitivity of aluminum complicate synthesis and handling, while the preparation of intramolecular Al-P linkages often requires specific synthetic routes such as aluminum–tin exchange. These technical and stability-related difficulties, along with the greater synthetic accessibility of boron precursors, have collectively slowed the broader experimental development of AlP IFLPs. Although various intermolecular Al based FLPs have been extensively studied, examples of intramolecular Al/P FLPs (Al-P IFLPs) remain comparatively limited. A few recent reports have detailed the synthesis and reactivity of Al-P IFLPs with rigid tethers like *ortho*-phenylene or biphenylene, which play a pivotal role in tuning the spatial proximity and interaction of the acid–base sites.^{39–41} Such rigid systems can enforce strain that enhances reactivity by favorably preorganizing the reactive centers and lowering activation barriers through enthalpic and entropic contributions. For instance, xanthenes- and biphenylene-linked Al-P systems have shown reactivity toward CO₂ and other polar substrates, demonstrating that carefully chosen linkers can modulate the degree of frustration and the resulting chemical behavior.⁴² Despite these advances, a systematic comparison of Al-P and B-P IFLPs, particularly regarding how the bridging unit affects their reactivity and activation capability, remains lacking. Notably, B-P IFLPs have been more widely investigated across a variety of linkers and substitution patterns, whereas their Al-based counterparts are still in their early stages of exploration. This study aims to fill this gap by providing a comparative analysis of Al-P and B-P intramolecular FLPs, focusing on structurally analogous bridging units that have previously been explored in B-P systems. By studying these systems side by side, we aim to identify trends in reactivity and to understand how the intrinsic Lewis acidity of the central atom (Al vs. B) and the choice of linker affect the degree of frustration and bond activation potential.

To this end, a set of representative bridging motifs, commonly used in B/P-FLPs, have been adapted and systematically studied in their Al/P analogues (Fig. 1), enabling direct comparisons and a deeper understanding of structure–activity (*i.e.*, frustration) relationships. The frustration of these FLPs

has been evaluated by comparing their calculated H₂ splitting energies. Density functional theory (DFT) calculations, along with detailed orbital analyses, have been carried out to gain insight into how the bridging unit, electronic structure, and intrinsic Lewis acidity collectively influence the behavior of these FLP systems.

Computational details

The geometries of the considered IFLPs, transition states (TSs) and adducts (ADs) formed in the reaction of H₂ with the considered IFLPs were fully optimized employing M062X functional with 6-311++G** basis set.^{43,44} This level of theory was chosen because M06-2X has been extensively benchmarked and shown to provide accurate thermochemistry, kinetics, and noncovalent interaction energies for main-group systems, including frustrated Lewis pairs and H₂ activation processes.^{45–50} The inclusion of diffuse functions in the 6-311++G** basis set is essential for correctly describing the anionic character that develops at the phosphide site during H₂ activation, representing the elongated and polarized H–H bond in transition states, and capturing long-range frustrated interactions between the spatially separated acid–base centers.^{45–50} No symmetrical or geometrical constraints were imposed during the optimization. The SMD⁵¹ implicit solvent model was applied using toluene ($\epsilon = 2.3741$) with the default parameters in Gaussian 16, consistent with previous computational studies on H₂ activation by FLPs.^{45–50} The harmonic frequency calculations were carried out on the same level of theory to depict the nature of the stationary points as local minima and as first order saddle point. The transition states were confirmed by the presence of single imaginary frequency in the direction of bond alterations. The intrinsic reaction coordinate (IRC) analysis has been carried out to confirm the TSs as the structures connecting the product with the reactants. The fully optimized structures were then used to study the energetics of the reaction at 1 atm pressure and 298.15 K. The calculations have been performed using Gaussian 16 software.⁵² The energetic results were systematically compared. Further to gain insights to the frustration and catalytic behaviour of the IFLPs, NBO have been carried out.⁵³ The second order perturbation analysis from the NBO is employed to derive the orbital charge transfer analysis. The natural bond orbitals were plotted at 0.02 a.u. iso value. To assess the interaction between the acidic and basic site the quantum theory of atoms in molecule (QTAIM)^{54–56} analysis was carried out using Multiwfn software.⁵⁷

To understand the origin of the activation barriers and to dissect the energetic contributions involved in the H₂ activation by the investigated IFLPs, the Activation Strain Model (ASM),⁵⁸ also referred to as the Distortion–Interaction Model, was employed. In this model, the activation energy (ΔE^\ddagger) for the transition state is decomposed into two principal components: strain (or distortion) energy (ΔE_{strain}) and interaction energy (ΔE_{int}). The total activation energy is expressed as:

$$\Delta E^\ddagger = \Delta E_{\text{strain}} + \Delta E_{\text{int}}$$

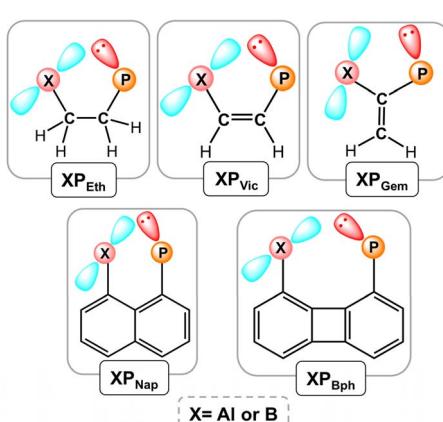


Fig. 1 AlP and BP based IFLPs considered in the present work.



where, E_{strain} corresponds to the energy required to deform the individual fragments—namely, the FLP and H_2 —from their optimized geometries in the isolated state to the geometries they adopt in the transition state. The ΔE_{int} is the stabilizing energy gained from the electronic interaction between the deformed fragments at the transition state geometry. The strain energy for a fragment was calculated as:

$$\Delta E_{\text{strain}} (\text{FLP}) = E_{\text{FL}}^{\text{TS-geom}} - E_{\text{FLP}}^{\text{opt}}$$

$$\Delta E_{\text{strain}} (\text{H}_2) = E_{\text{H}_2}^{\text{TS-geom}} - E_{\text{H}_2}^{\text{opt}}$$

where $E^{\text{TS-geom}}$ denotes the single-point energy of the fragment in the geometry it adopts within the transition state, and E^{opt} is the energy of the fully optimized fragment in its equilibrium structure.

The total strain energy is the sum of the individual strain energies:

$$\Delta E_{\text{strain}}^{\text{total}} = \Delta E_{\text{strain}} (\text{FLP}) + \Delta E_{\text{strain}} (\text{H}_2)$$

The interaction energy (ΔE_{int}) was then computed as:

$$\Delta E_{\text{int}} = E_{\text{TS}} - E_{\text{FLP}}^{\text{TS-geom}} - E_{\text{H}_2}^{\text{TS-geom}}$$

where E_{TS} is the total electronic energy of the full transition state complex. This decomposition allows for a quantitative

analysis of the balance between geometric distortion and favourable orbital interaction in determining the activation barrier.

Results

In the present study, the activation energy for H_2 splitting has been employed as a uniform metric to assess and compare the degree of frustration across the investigated intramolecular frustrated Lewis pairs (IFLPs). This approach facilitates a consistent comparison of the impact of structural immobilization induced by various bridging units. Accordingly, the relative Gibbs free energies (ΔG) of the transition states (TS-XP_{Abr}; X = Al or P, and Abr = Eth, Vic, Gem, Nap, and Bph), along with the free energies of the corresponding adducts formed upon H_2 activation, are presented in Fig. 2.

From Fig. 2, it is evident that the H_2 activation barrier for the ethyl-bridged AlP system (TS-AlP_{Eth}) is 31.4 kcal mol⁻¹. This value remains essentially unchanged upon replacing the ethyl bridge with a vinyl group, as seen in TS-AlP_{Vic}. The free energy of the adduct in AlP_{Eth} (AD-AlP_{Eth}) is calculated to be 24.9 kcal mol⁻¹, whereas the corresponding adduct in AlP_{Vic} (AD-AlP_{Vic}) has a slightly higher ΔG of 25.5 kcal mol⁻¹, suggesting a marginal destabilization induced by the vinyl bridge.

In contrast, the BP analogue BP_{Eth} exhibits a higher H_2 activation barrier of 34.1 kcal mol⁻¹, while the ΔG of its adduct (AD-BP_{Eth}) remains comparable to that of AD-AlP_{Eth}. Interestingly, upon changing the bridging unit from ethyl to vinyl in the

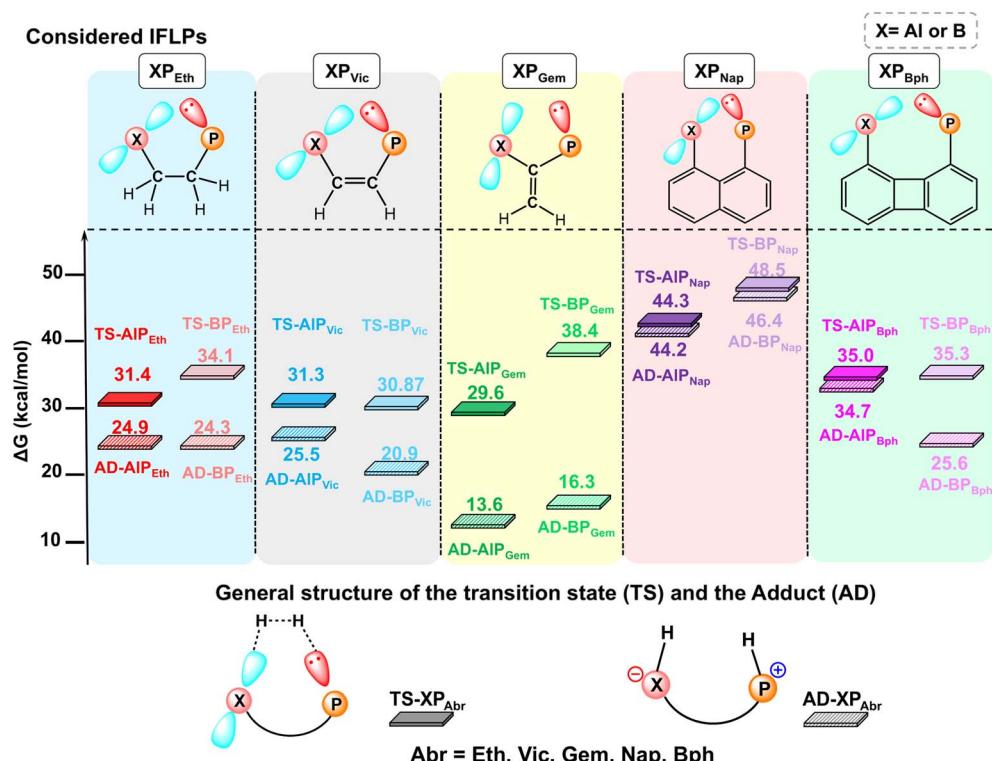


Fig. 2 Relative free energy of the transition state (TS-XP_{Abr}, X = Al/B and Abr = Eth, Vic, Gem, Nap, Bph) and the adduct (AD-XP_{Abr}) found in the reaction of H_2 with considered IFLPs along with their general structures.



BP system, both the transition state (TS-BP_{Vic}) and adduct (AD-BP_{Vic}) energies decrease by approximately 4 kcal mol⁻¹ (see Fig. 2). This trend is notably different from the AlP system, where a similar structural modification yields negligible change. These observations underscore that identical modifications exert distinct effects in AlP-*versus* BP-based IFLPs. Moreover, incorporation of a naphthyl bridging unit leads to the highest H₂ activation barriers and adduct ΔG values among all systems examined. Specifically, both AlP_{Nap} and BP_{Nap} show transition states and adducts with ΔG values exceeding 44 kcal mol⁻¹. In contrast, replacing the naphthyl bridge with a biphenylene unit reduces the activation energy to approximately 35 kcal mol⁻¹ in both AlP_{Bph} and BP_{Bph} systems, reflecting a significant energetic improvement. Among all IFLPs studied, the geminal-bridged system AlP_{Gem} exhibits the most favorable energetics, with the lowest ΔG values for both the transition state (29.6 kcal mol⁻¹) and the adduct (13.6 kcal mol⁻¹). Conversely, its BP analogue BP_{Gem} shows a much higher transition state energy of 38.4 kcal mol⁻¹ which is second only to the naphthyl-bridged cases, while the adduct energy (16.3 kcal mol⁻¹) remains relatively low. Overall, these

free energy profiles highlight the critical role of structural immobilization in tuning the degree of frustration in IFLPs. Moreover, they clearly demonstrate that AlP- and BP-based IFLPs exhibit distinct energetic trends in response to the same bridging unit modifications. These findings underscore the importance of further investigating the structural and electronic factors governing the reactivity of AlP *versus* BP-based systems.

Accordingly, a detailed analysis of the electronic structures of the studied IFLPs, along with the geometries of their respective transition states and H₂-activation adducts, has been undertaken to rationalize these observations. The optimized geometries of AlP_{Eth} and AlP_{Vic}, along with their corresponding natural bond orbital (NBO) plots and electron density contour plots, are presented in Fig. 3a and b, respectively. The fully labeled optimized geometries of the transition states (TS) and the respective adducts formed upon reaction with H₂ are also depicted in Fig. 3, along with key geometrical parameters. From the geometries shown in Fig. 3a and b, the Al-P bond distances in AlP_{Eth} and AlP_{Vic} are found to be 2.61 Å and 2.58 Å, respectively. Quantum Theory of Atoms in Molecules (QTAIM) analysis

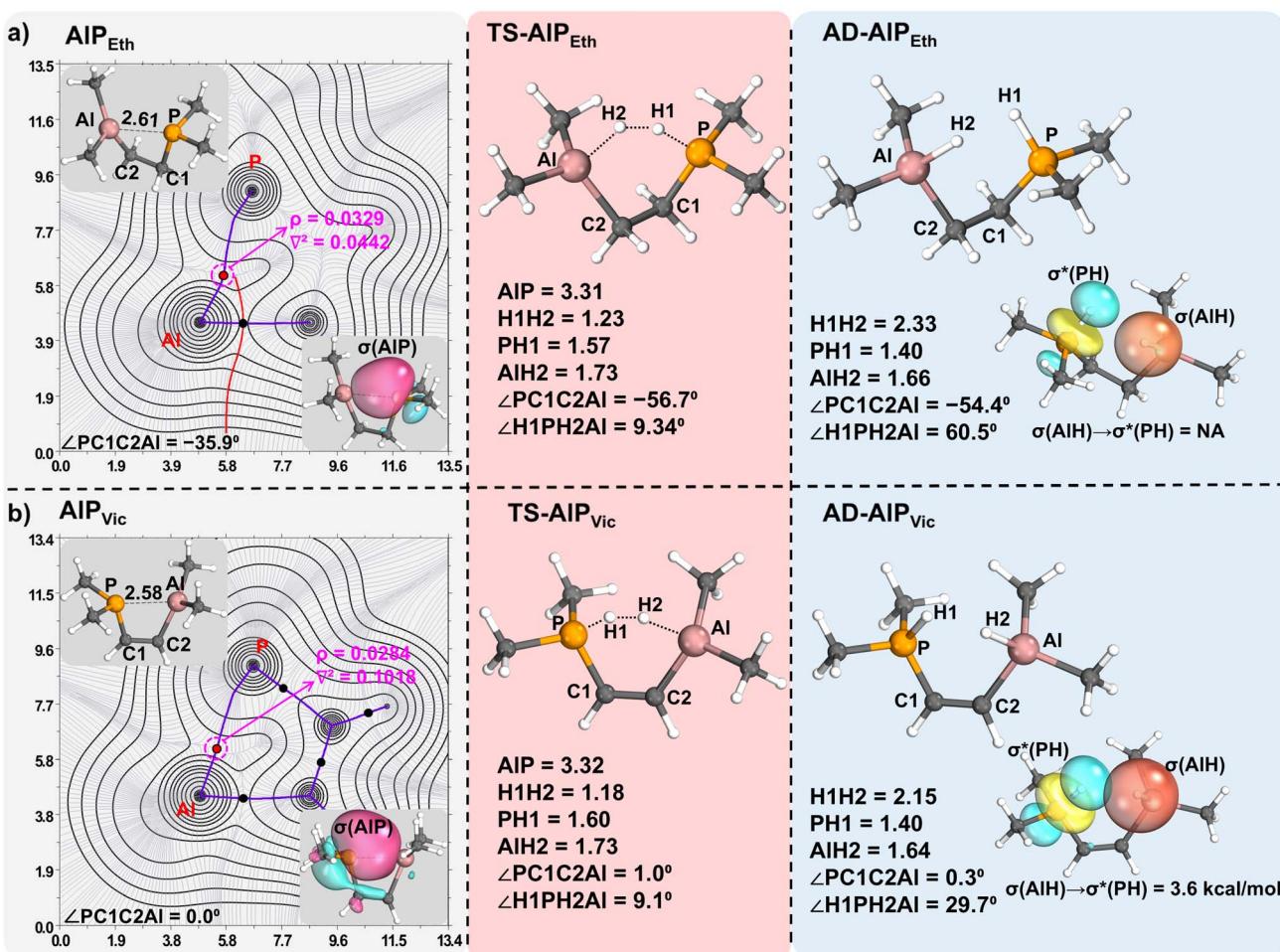


Fig. 3 Optimized geometries of (a) AlP_{Eth} and (b) AlP_{Vic} with electron density contour and natural bond orbital plots along with respective optimized geometries of the transition states and the adducts formed in the reaction of the IFLPs with H₂. (All the distances are given in the angstrom, the contours are plotted at 0.001 a.u. iso value and the electron densities at the bond critical points are in a.u.).

reveals the presence of a bond critical point (BCP) between the Al and P atoms in both molecules, with electron density (ρ) values of 0.0329 a.u. for AlP_{Eth} and 0.0284 a.u. for AlP_{Vic} . The presence of a BCP indicates a significant interaction between the Al and P centres, which is further corroborated by the existence of a σ -bonding orbital between them, as identified in the NBO analysis.

The short Al-P distances, presence of a BCP, and the σ -type bonding interaction collectively suggest that both AlP_{Eth} and AlP_{Vic} exist in the form of masked FLPs. Accordingly, during the reaction with H_2 , the Al-P bond is expected to elongate to accommodate the incoming dihydrogen molecule. Additionally, analysis of the optimized geometries shows that the dihedral angle $\angle \text{P-C1-C2-Al}$ is -35.9° in AlP_{Eth} and 0.0° in AlP_{Vic} , suggesting that the C1-C2 bond in AlP_{Eth} allows rotational flexibility, while such rotation is restricted in AlP_{Vic} . This distinction becomes more apparent in the transition state structures. In $\text{TS-AlP}_{\text{Eth}}$, the Al-P distance increases to 3.31 Å, reflecting the elongation required to interact with the H_2 molecule. A similar elongation is observed in $\text{TS-AlP}_{\text{Vic}}$, as shown in Fig. 3b. The H1-H2, P-H1, and Al-H2 bond distances in $\text{TS-AlP}_{\text{Eth}}$ are 1.23 Å, 1.57 Å, and 1.73 Å, respectively, and the dihedral angle $\angle \text{H1-P-Al-H2}$ is 9.34° , all of which closely match the corresponding values in $\text{TS-AlP}_{\text{Vic}}$. However, the dihedral angle $\angle \text{P-C1-C2-Al}$ changes significantly in $\text{TS-AlP}_{\text{Eth}}$ it is -56.7° , while in $\text{TS-AlP}_{\text{Vic}}$ it remains nearly unchanged at 1.0° . This indicates that AlP_{Eth} allows rotational adjustment about the C1-C2 bond during reaction, thereby relieving strain, whereas such flexibility is absent in AlP_{Vic} due to the rigidity of the vinyl bridging unit. The geometric similarities between the two transition states suggest comparable energetic profiles. To investigate this further, strain and interaction energies were calculated. The strain energy developed in AlP_{Vic} upon reaching the transition state was found to be 21.15 kcal mol $^{-1}$, while in AlP_{Eth} it was 18.95 kcal mol $^{-1}$. The slightly higher strain in AlP_{Vic} can be attributed to its restricted rotational freedom, as indicated by the minimal change in the $\angle \text{P-C1-C2-Al}$ angle. Conversely, the strain energy within the H_2 molecule at the transition state was 38.39 kcal mol $^{-1}$ for $\text{TS-AlP}_{\text{Vic}}$ and 44.25 kcal mol $^{-1}$ for $\text{TS-AlP}_{\text{Eth}}$. Consequently, the total strain energy for $\text{TS-AlP}_{\text{Vic}}$ is 59.54 kcal mol $^{-1}$, slightly lower than 63.20 kcal mol $^{-1}$ for $\text{TS-AlP}_{\text{Eth}}$. The interaction energies between H_2 and the FLPs in their respective transition states were also evaluated. In $\text{TS-AlP}_{\text{Vic}}$, the interaction energy was -37.33 kcal mol $^{-1}$, which is lower than that of $\text{TS-AlP}_{\text{Eth}}$ (-40.92 kcal mol $^{-1}$). The reduced interaction energy in AlP_{Vic} may be due to limited access to the reactive site, resulting from the rigid vinyl bridge. This lower interaction energy offsets the lower strain energy in $\text{TS-AlP}_{\text{Vic}}$, while in $\text{TS-AlP}_{\text{Eth}}$, the higher strain is compensated by stronger interaction with H_2 . Overall, these opposing effects result in comparable transition state energies for both systems.

Further, in the adduct structure $\text{AD-AlP}_{\text{Eth}}$, the H1-H2 distance was found to be 2.23 Å, which is slightly longer than the corresponding distance in $\text{AD-AlP}_{\text{Vic}}$ (see Fig. 3). The dihedral angles $\angle \text{P-C1-C2-Al}$ and $\angle \text{H1-P-Al-H2}$ were calculated to be -54.4° and 60.5° , respectively, in $\text{AD-AlP}_{\text{Eth}}$, whereas in $\text{AD-AlP}_{\text{Vic}}$ these values were 0.3° and 29.7° . This difference in

dihedral angles further supports the observation that AlP_{Eth} undergoes structural relaxation *via* rotation around the C1-C2 bond, which facilitates a more open geometry. As a result, the newly formed P-H1 and Al-H2 bonds in $\text{AD-AlP}_{\text{Eth}}$ are spatially oriented away from each other, suggesting minimal interaction between them. In contrast, the restricted rotation in $\text{AD-AlP}_{\text{Vic}}$ appears to maintain the proximity of these bonds, possibly allowing intramolecular interaction between the hydrogen atoms. This inference is supported by the NBO analysis of $\text{AD-AlP}_{\text{Vic}}$, which reveals an orbital charge transfer (OCT) from the bonding orbital $\sigma(\text{Al-H2})$ to the antibonding orbital $\sigma^*(\text{P-H1})$ with an associated stabilization energy of 3.6 kcal mol $^{-1}$ which is absent in the case of $\text{AD-AlP}_{\text{Eth}}$ (see Fig. 3). This OCT supports the geometric observations made in the adduct structures. Although small, this interaction contributes to weakening of the P-H1 bond in $\text{AD-AlP}_{\text{Vic}}$, thereby destabilizing the adduct and resulting in a slightly higher ΔG compared to $\text{AD-AlP}_{\text{Eth}}$.

Unlike the AlP-based IFLPs, the B-P distances in BP_{Eth} and BP_{Vic} were found to be significantly longer, measuring 3.44 Å and 3.21 Å, respectively (see Fig. S1). Notably, no bond critical point (BCP) or σ -bonding orbital was identified between the B and P atoms in either system, as shown in Fig. S1 in the SI. Instead of a direct $\sigma(\text{B-P})$ bond, a lone pair orbital at P ($\text{lp}(\text{P})$) and an empty p orbital at B ($\text{p}(\text{B})$) were observed, along with an orbital charge transfer (OCT) from $\text{lp}(\text{P})$ to $\text{p}(\text{B})$. The corresponding OCT energies were calculated to be 1.59 kcal mol $^{-1}$ for BP_{Eth} and 4.55 kcal mol $^{-1}$ for BP_{Vic} . The higher OCT value in BP_{Vic} is likely due to its more rigid structure, which brings the B and P centres closer together, as evidenced by the small dihedral angle $\angle \text{P-C1-C2-B}$ of 0.6° in BP_{Vic} compared to the more relaxed geometry in BP_{Eth} (see Fig. S1). These geometrical and electronic features indicate that BP_{Eth} and BP_{Vic} behave as classical, unmasked FLPs, in contrast to the masked nature of the AlP IFLPs. This fundamental difference in bonding and flexibility between B-P and Al-P systems may contribute to their distinct energetic profiles, even under structurally analogous conditions. In the case of the transition state of BP_{Eth} (*i.e.*, $\text{TS-BP}_{\text{Eth}}$), rather than an increase in B-P distance, as observed for AlP_{Eth} , the distance decreases from 3.44 Å in BP_{Eth} to 3.07 Å in $\text{TS-BP}_{\text{Eth}}$. Additionally, the dihedral angle $\angle \text{P-C1-C2-B}$ becomes -51.4° , suggesting a significant structural distortion and strain buildup. The calculated strain energy in $\text{TS-BP}_{\text{Eth}}$ was 23.71 kcal mol $^{-1}$, which is higher than the corresponding value for $\text{TS-AlP}_{\text{Eth}}$. Moreover, the interaction energy between H_2 and BP_{Eth} in the transition state was calculated to be -36.69 kcal mol $^{-1}$, which is less favourable than that in $\text{TS-AlP}_{\text{Eth}}$, indicating a higher ΔG for the reaction pathway in the BP_{Eth} system. In contrast, in going from BP_{Vic} to $\text{TS-BP}_{\text{Vic}}$ involved only minor changes in structural parameters, resulting in minimal geometric distortion. The overall strain energy in $\text{TS-BP}_{\text{Vic}}$ was calculated to be 47.70 kcal mol $^{-1}$, which is lower than that observed for $\text{TS-BP}_{\text{Eth}}$ and contributes to a lower ΔG for $\text{TS-BP}_{\text{Vic}}$. Furthermore, as observed in the AlP-based systems, an OCT from $\sigma(\text{B-H2})$ to the antibonding orbital $\sigma^*(\text{P-H1})$ was absent in $\text{AD-BP}_{\text{Eth}}$, but present in $\text{AD-BP}_{\text{Vic}}$, providing an explanation for their relative stabilities (see Fig. S1).



As in the cases of AlP_{Eth} and AlP_{Vic} , the electron density contour plots of AlP_{Nap} and AlP_{Bph} , shown in Fig. 4, reveal the presence of a bond critical point (BCP) between the aluminum and phosphorus centres. Additionally, natural bond orbital (NBO) analysis confirms the presence of a $\sigma(\text{Al-P})$ bonding orbital in both systems (see Fig. S2 in the SI). These findings indicate that AlP_{Nap} and AlP_{Bph} , like the other AlP-based IFLPs investigated in this study, exhibit the characteristics of masked FLPs. A closer geometrical comparison (Fig. 4) reveals that in AlP_{Bph} , the P-C1 and Al-C2 bonds are bent inward toward one another. This geometry arises from intramolecular Al-P interaction, resulting in a strained structure, consistent with previous reports.^{39,41} During the formation of the transition state, elongation of the Al-P bond alleviates this strain.

In contrast, the initial structure of AlP_{Nap} is less strained; however, it exhibits the shortest Al-P bond distance *i.e.*, 2.49 Å, among all the AlP IFLPs studied. As a result, when H_2 approaches AlP_{Nap} to form the transition state (TS- AlP_{Nap}), significant distortion occurs in the molecule. In the optimized structure of TS- AlP_{Nap} , the Al-P bond length increases to 3.29 Å, and the dihedral angle $\angle \text{P-C1-C2-Al}$ changes from 0.0° in the parent molecule to -29.4° . By comparison, in TS- AlP_{Bph} , the Al-P bond length increases to 3.75 Å, and $\angle \text{P-C1-C2-Al}$ changes to only -13.5° , suggesting a comparatively lesser degree of distortion. The calculated strain energy in TS- AlP_{Nap} was found to be 80.87 kcal mol⁻¹, which is not only higher than that in TS- AlP_{Bph} (*i.e.*, 75.12 kcal mol⁻¹) but also the highest among all the AlP-based IFLPs studied. This corresponds to the highest Gibbs

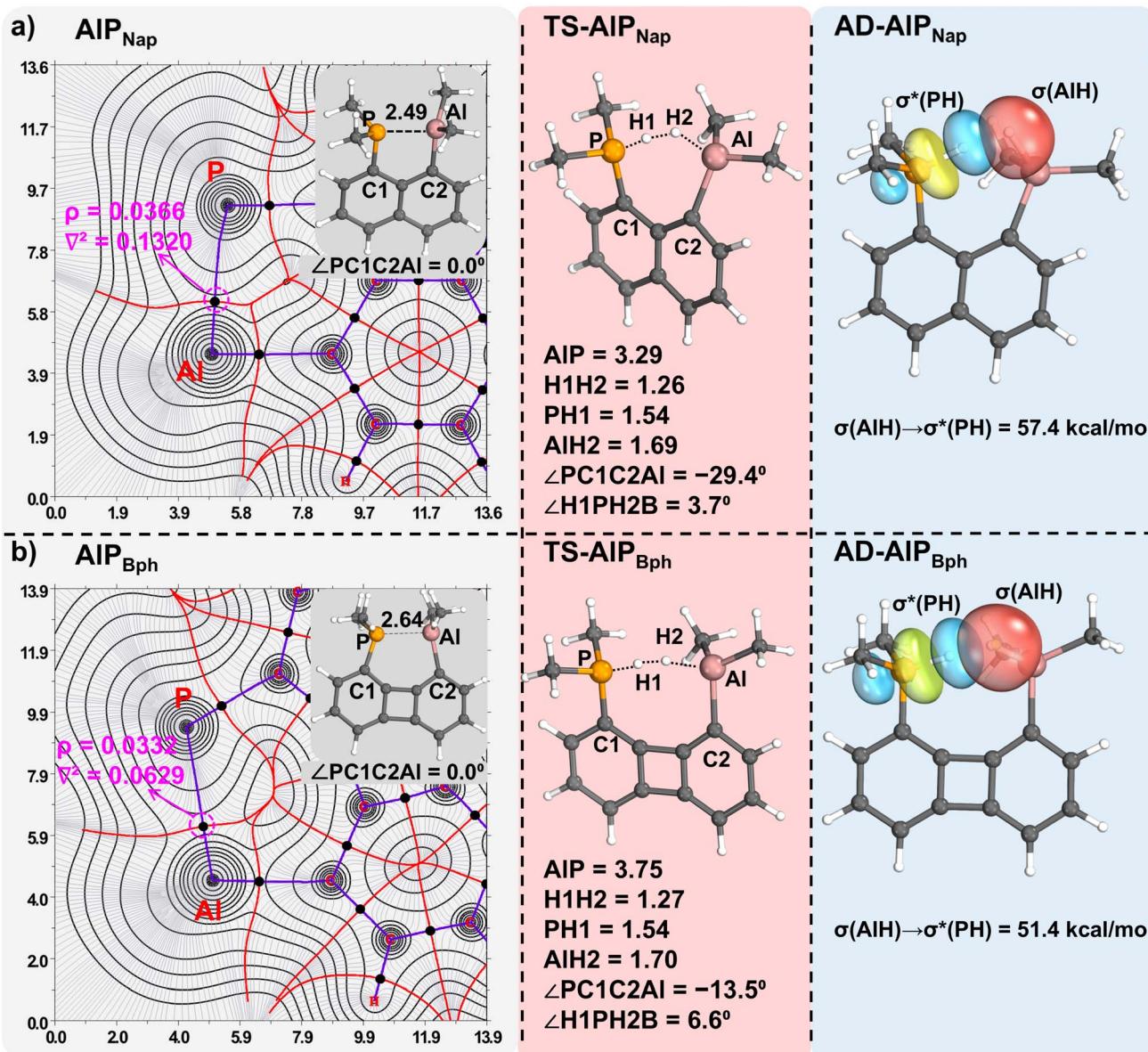


Fig. 4 Electron density contour plots and optimized geometries of (a) AlP_{Nap} and (b) AlP_{Bph} , along with their corresponding transition state structures and natural bond orbital (NBO) plots, highlighting key orbital charge transfer (OCT) interactions observed in the adducts. (All the distances are given in the angstrom, the contours are plotted at 0.001 a.u. iso value and the electron densities at the bond critical points are in a.u.).



free energy (ΔG) for H_2 activation in this series, underscoring the energetic cost of the pronounced distortion in AlP_{Nap} . Further structural insights can be drawn from the optimized geometries of the adducts $\text{AD-AlP}_{\text{Nap}}$ and $\text{AD-AlP}_{\text{Bph}}$, shown in Fig. S2. $\text{AD-AlP}_{\text{Nap}}$ appears to be more distorted than $\text{AD-AlP}_{\text{Bph}}$. The NBO analysis reveals strong orbital charge transfer (OCT) from the $\sigma(\text{Al}-\text{H}2)$ bonding orbital to the $\sigma^*(\text{P}-\text{H}1)$ antibonding orbital, with stabilization energies of $57.4 \text{ kcal mol}^{-1}$ for AlP_{Nap} and $51.4 \text{ kcal mol}^{-1}$ for AlP_{Bph} . These strong OCT interactions indicate significant electronic perturbation and rationalize the observed instability of both adducts. Similar, observation can also be made for the BP_{Nap} and B_{Bph} form the Fig. S3 and S4 in the SI.

Among all the IFLPs investigated in this study, the geminally bridged IFLPs represent a particularly interesting case. The optimized structure of AlP_{Gem} , along with the key natural bond orbitals (NBOs), is shown in Fig. 5a. The corresponding transition state (TS- AlP_{Gem}) and adduct (AD- AlP_{Gem}) geometries, including relevant bond lengths and angles, are provided in Fig. 5b and c, respectively. Additionally, the optimized geometries and NBO plots for the boron analogue (BP_{Gem}), including TS- BP_{Gem} and AD- BP_{Gem} , are presented in Fig. S5 of the SI. As illustrated in Fig. 5a, the optimized geometry of AlP_{Gem} shows an Al-P distance of 3.28 \AA , with the Al and P centres oriented away from each other, in contrast to the close proximity observed in other AlP-based IFLPs. NBO analysis reveals the

presence of a lone pair orbital on phosphorus ($\text{lp}(\text{P})$) and an empty p orbital on aluminum ($\text{p}(\text{Al})$), both aligned parallel to one another but perpendicular to the molecular plane. Notably, no orbital charge transfer (OCT) from $\text{lp}(\text{P})$ to $\text{p}(\text{Al})$ is observed. Instead, two distinct charge transfer interactions are present: $\pi(\text{C}1=\text{C}2) \rightarrow \text{p}(\text{Al})$ and $\text{lp}(\text{P}) \rightarrow \pi^*(\text{C}1=\text{C}2)$, with stabilization energies of $7.81 \text{ kcal mol}^{-1}$ and $6.10 \text{ kcal mol}^{-1}$, respectively (see Fig. 5a). These interactions are likely responsible for the unique structural arrangement of AlP_{Gem} . The parallel orientation of the electron-rich $\text{lp}(\text{P})$ and electron-deficient $\text{p}(\text{Al})$ orbitals provides spatially separated reactive sites, allowing for synergistic activation of the H_2 molecule. This structural feature plays a critical role in the reactivity of AlP_{Gem} .

In the transition state (TS- AlP_{Gem}), the Al-P distance shortens to 3.09 \AA , and the key geometrical parameters associated with H_2 activation—namely the $\text{H}1-\text{H}2$, $\text{P}-\text{H}1$, and $\text{Al}-\text{H}2$ bond lengths are 1.15 \AA , 1.60 \AA , and 1.77 \AA , respectively. The dihedral angle $\angle \text{H}1-\text{P}-\text{Al}-\text{H}2$ is calculated to be -3.9° . The total strain energy in TS- AlP_{Gem} is $54.49 \text{ kcal mol}^{-1}$, the lowest among all the transition states investigated in this study. This relatively low strain correlates with the lower relative energy of TS- AlP_{Gem} . In the resulting adduct (AD- AlP_{Gem}), the structural parameters of the TS- AlP_{Gem} changes to 2.70 \AA ($\text{H}1-\text{H}2$), 1.39 \AA ($\text{P}-\text{H}1$), 1.64 \AA ($\text{Al}-\text{H}1$), and -31.6° ($\angle \text{H}1-\text{P}-\text{Al}-\text{H}2$). The increased $\text{H}1-\text{H}2$ bond length and the substantial change in dihedral angle suggest that the $\text{Al}-\text{H}2$ and $\text{P}-\text{H}1$ bonds are spatially oriented away from each other, thereby minimizing intramolecular interaction. This spatial separation likely contributes to the enhanced stability of the adduct, as reflected in both its optimized geometry and electronic structure. A similar behaviour is observed in BP_{Gem} , which also features parallel $\text{lp}(\text{P})$ and $\text{p}(\text{B})$ orbitals. These arise from $\pi(\text{C}1=\text{C}2) \rightarrow \text{p}(\text{B})$ and $\text{lp}(\text{P}) \rightarrow \pi^*(\text{C}1=\text{C}2)$ orbital charge transfers, with associated stabilization energies of $21.11 \text{ kcal mol}^{-1}$ and $4.85 \text{ kcal mol}^{-1}$, respectively (see Fig. S5). The greater stabilization from $\pi(\text{C}1=\text{C}2) \rightarrow \text{p}(\text{B})$ charge transfer effectively occupies the $\text{p}(\text{B})$ orbital, reducing its availability for interaction with H_2 . As a result, BP_{Gem} exhibits a higher H_2 activation barrier, as evident from Fig. 2. This reduced reactivity is also reflected in the interaction energy between H_2 and BP_{Gem} in the transition state. The calculated interaction energy in TS- BP_{Gem} is $-28.74 \text{ kcal mol}^{-1}$, which is less favourable compared to $-33.03 \text{ kcal mol}^{-1}$ in TS- AlP_{Gem} . Consequently, BP_{Gem} displays a higher ΔG for the transition state than AlP_{Gem} . Further, the geometrical parameters obtained from the optimized structure of AD- BP_{Gem} (Fig. S6) support the observed order of Gibbs free energies (ΔG) of the adducts, consistent with the trends seen in AD- AlP_{Gem} . The structural features of AD- BP_{Gem} reflect reduced stabilization compared to AD- AlP_{Gem} , thereby explaining its relatively higher ΔG and lower thermodynamic stability.

Having examined each linker system individually, it is instructive to consolidate these findings and establish the underlying reasons for the divergent behavior of Al-P and B-P IFLPs.

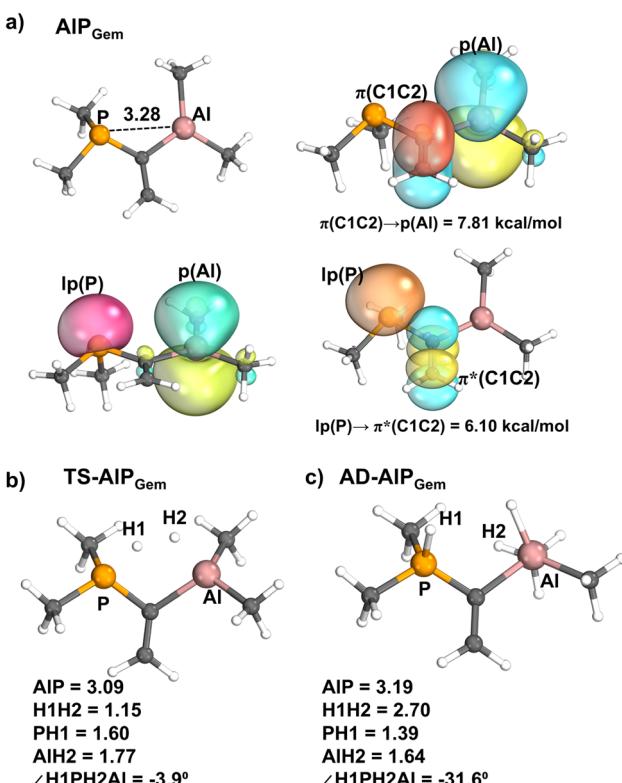


Fig. 5 (a) Optimized geometry of the AlP_{Gem} and NBO plots indicating important orbitals and OCTs, optimized geometry of (b) of TS- AlP_{Gem} and (c) AD- AlP_{Gem} along with important geometrical parameters. (All the distances are in \AA).



Discussion

A broader perspective can be drawn by integrating the observations across all linker types and directly contrasting the AlP and BP systems. The unifying conclusion from the structure analysis is that AlP IFLPs frequently exhibit masked behavior due to partial AlP bonding, while BP analogues consistently retain classical frustrated Lewis pair character. In AlP systems such as AlP_{Eth}, AlP_{Vic}, AlP_{Nap}, and AlP_{Bph}, the presence of a BCP and a σ (Al-P) orbital, as revealed by QTAIM and NBO analysis, confirms a tangible AlP bonding interaction. This interaction stabilizes the parent structures but reduces the extent of open frustration, necessitating AlP bond elongation during H₂ activation. In contrast, for BP analogues, BP_{Eth} and BP_{Vic}, no B-P bond was identified; instead, a donor-acceptor interaction between lp(P) and p(B) has been observed. This fundamental difference underscores the susceptibility of AlP systems towards strain and bond reorganization, while BP IFLPs remain dictated by the accessibility of the empty boron orbital and the geometric proximity enforced by the linker. The ethyl- and vinyl-bridged cases clearly illustrate this point. AlP_{Eth} and AlP_{Vic} exhibit similar activation barriers, despite differences in flexibility, because both must elongate a pre-existing Al-P bond during reaction. Their masked nature is reflected in comparable electronic structures and strain-interaction balances. On the other hand, BP_{Eth} and BP_{Vic} behave differently, BP_{Eth} has a higher barrier, while BP_{Vic} shows an approximately 4 kcal mol⁻¹ reduction, attributable to improved orbital overlap between lp(P) and p(B) in the more rigid framework. This divergent response to the same modification highlights the contrasting mechanistic origins of frustration. For AlP, masking by bond formation dominates and is only weakly influenced by ethyl *versus* vinyl flexibility, whereas for BP, the absence of bond masking makes the system more responsive to linker imposed preorganization.

The rigid aromatic linkers provide another interesting comparison. In AlP_{Nap}, the shortest Al-P bond distance (2.49 Å) among all AlP systems intensifies the masked character, resulting in the largest strain energy of 80.87 kcal mol⁻¹ at the transition state. This strain penalty translates directly into the highest energy barrier for H₂ activation. Conversely, AlP_{Bph}, though also strained, begins from a more bent geometry with an Al-P bond of 2.75 Å and requires less distortion, leading to a lower barrier. The BP analogues follow the same trend of BP_{Nap} being less favorable than BP_{Bph}, but the origin differs. For BP_{Nap} and BP_{Bph}, the key factor is not the breaking of a B-P bond, since none exists, but rather the geometric rigidity imposed by the aromatic backbone and its effect on aligning lp(P) and p(B). Thus, while both Al-P and B-P systems show reduced reactivity in naphthyl-linked cases, AlP systems are penalized by bond elongation and excessive distortion, whereas BP systems are destabilized by restricted flexibility and electronic delocalization.

The geminally bridged systems further emphasize the contrast. AlP_{Gem} emerges as the most reactive AlP system, with the lowest transition state energy (29.6 kcal mol⁻¹) and the most

stable adduct (13.6 kcal mol⁻¹). This favorable profile arises because the geminal bridge prevents effective overlap between lp(P) and p(Al), thereby suppressing masking and preserving true frustration. NBO analysis confirms the absence of lp(P) \rightarrow p(Al) charge transfer, with stabilization instead arising from $\pi(C=C) \rightarrow p(Al)$ and lp(P) $\rightarrow \pi^*(C=C)$ interactions. This arrangement aligns the reactive orbitals in parallel, providing spatially separated acid and base sites that synergistically activate H₂. In contrast, the BP analogue BP_{Gem} exhibits a much higher barrier (38.4 kcal mol⁻¹). The p(B) orbital is significantly stabilized by $\pi(C=C) \rightarrow p(B)$ charge transfer, reducing its availability to accept electron density during H₂ activation. As a result, BP_{Gem} shows weaker interaction energies with H₂ and a less stable adduct. The geminal case thus demonstrates how identical bridging units can optimize AlP systems by unmasking reactivity but hinder B-P systems by saturating the boron acceptor orbital.

Together, these comparisons establish that the same structural motif can exert fundamentally different effects depending on the nature of the Lewis acidic center. In AlP IFLPs, the masked character requires careful management of AlP interactions that is flexible linkers like ethyl or geminal arrangements reduce masking and yield lower barriers, while overly rigid linkers like naphthyl exacerbate distortion and raise barriers. In BP systems, the absence of masking means that linker effects are transmitted directly to orbital alignment and charge transfer, making rigid frameworks such as vinyl or biphenylene beneficial while naphthyl introduces excessive destabilization. Thus, linker flexibility stabilizes AlP systems but has limited impact on BP, whereas rigid preorganization is advantageous for BP but energetically costly for AlP. These findings complement prior literature that studied either AlP or BP systems in isolation.

From a design perspective, these results imply that AlP systems benefit from strategies that minimize AlP overlap, such as geminal bridges or flexible tethers, while BP systems are more effectively tuned through rigid linkers that promote orbital alignment without excessive strain. This distinction provides a rational basis for tailoring intramolecular FLPs toward specific applications. By identifying the contrasting roles of strain and orbital interactions in AlP *versus* BP systems, the present comparative framework extends beyond H₂ activation and can guide the design of element-specific FLPs for activation of other small molecules such as CO₂, olefins, and C-H or C-F bonds.

Conclusion

In this study, the activation of dihydrogen was employed as a diagnostic tool to assess and compare the degree of frustration in a series of structurally analogous AlP- and BP-based intramolecular frustrated Lewis pairs (IFLPs). Through detailed DFT investigations, the impact of various bridging units ranging from flexible (ethyl, vinyl) to rigid (naphthyl, biphenylene, geminal), on the geometric distortion, orbital interactions, and energetic profiles was systematically analyzed. The calculated Gibbs free energies for transition states and



adducts served as key metrics for quantifying the degree of frustration within each system. A fundamental difference in the electronic nature of Al-P and B-P pairs emerged. AlP-IFLPs generally exhibit masked character due to partial Al-P bonding, while BP-IFLPs behave as classical, unmasked FLPs with spatially separated acid-base centres. Despite structural similarities, these intrinsic differences led to distinct responses upon modification of the bridging unit. For example, the geminal-bridged AlP_{Gem} displayed the lowest transition-state energy, highlighting its optimal balance between structural preorganization and electronic separation. Conversely, systems like AlP_{Nap}, though preorganized, exhibited high strain penalties upon activation, leading to reduced reactivity. This comparative approach establishes H₂ activation not as an end goal, but as a measure of structural and electronic frustration in FLPs. The insights derived here provide a foundational framework for rational FLP design, emphasizing the importance of tuning not only the acid-base strength but also the spatial and electronic interplay enforced by the linker. Future work may extend this methodology to predict and tailor reactivity toward more challenging small molecules.

Conflicts of interest

The authors declare no competing financial interests.

Data availability

The data supports the findings is provided in the manuscript and the SI. Supplementary information: images of the optimized structure, NBO plots are given. The coordinates of the optimized structures are also provided. See DOI: <https://doi.org/10.1039/d5ra05892a>.

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