RESEARCH PAPER

Design of Heterocyclic Ligand–Based Lewis Acid Frustrated Lewis Pairs and Their Application in H_2 Activation

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ABSTRACT

A new frustrated Lewis pair (FLP) has been designed by combining the heterocyclic ligand–based Lewis acid $B(C_3N_2F_3)_3$ with the sterically hindered Lewis base $P(tBu)_3$. The bulky substituents on both components prevent the formation of a classical Lewis acid–base adduct, preserving their intrinsic reactivity. Density functional theory (DFT) calculations reveal that this FLP can effectively activate molecular hydrogen without the need for a metal center. The cooperative action of the acid and base creates a highly polarized environment, where the electron-deficient boron centre interacts with one hydrogen atom while the electron-rich phosphorus donates electron density to the other. This dual interaction leads to the progressive weakening and heterolytic cleavage of the H–H bond. The design emphasizes the importance of steric and electronic tuning in FLPs, allowing the components to remain reactive yet unquenched. Such systems offer promising routes for metal-free hydrogen activation and other small-molecule transformations, highlighting their potential in sustainable catalysis.

Keywords: Heterocyclic ligands, Lewis acids, Frustrated Lewis pairs (FLPs), Hydrogen activation

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INTRODUCTION

Frustrated Lewis pairs (FLPs) have gained considerable attention as efficient metal-free systems for small-molecule activation and catalytic transformations [1]. Numerous studies have demonstrated that FLPs are capable of activating a wide variety of substrates, including molecular hydrogen [2], carbon dioxide [3], carbon monoxide [4], nitric oxide [5], nitrous oxide [6], sulfur dioxide [7], as well as unsaturated hydrocarbons such as alkenes [8] and alkynes [9]. In addition to these small molecules, FLPs have also been shown to activate E–H bonds (E = B, C, N, O, and Si), further highlighting their versatile reactivity [10].

Molecular hydrogen is of central importance in the context of sustainable energy technologies and industrial chemistry. It plays a crucial role in hydrogen storage, water-splitting processes, and serves as a key reagent in the synthesis of ammonia and methanol, hydrogenation reactions, and fossil-fuel processing [11]. Despite its widespread utility, the activation of H_2 remains challenging due to the strength of the H–H bond and the low polarizability of the molecule. Conventionally, hydrogen activation has been achieved through homolytic or heterolytic cleavage mediated by transition-metal complexes [12]. However, transition-metal-based catalysts are often expensive, scarce, and raise environmental concerns, which has driven

increasing interest in developing alternative metal-free strategies.

Early attempts to activate hydrogen using main-group compounds generally relied on harsh reaction conditions or hydrogen surrogates rather than molecular H_2 itself [13,14]. A major breakthrough was reported in 2006 when Stephan and co-workers demonstrated reversible, metal-free hydrogen activation under mild conditions using sterically encumbered phosphine–borane systems [15]. Subsequently, it was shown that stoichiometric combinations of strong Lewis acids such as $B(C_6F_5)_3$ with bulky phosphines, including tBu_3P and Mes_3P, could heterolytically cleave H_2 at ambient temperature and pressure to form stable ion pairs [16]. These findings led to the formulation of the frustrated Lewis pair concept, in which steric congestion prevents the formation of classical Lewis acid–base adducts. As a result, the inherent Lewis acidity and basicity of the individual components remain intact, enabling cooperative activation of H_2 and other small molecules, such as CO_2 [17].

Despite the rapid progress in FLP chemistry and the growing number of experimental and theoretical studies, the detailed mechanism of hydrogen activation by FLPs continues to be actively debated. In particular, previous investigations have suggested that H_2 activation proceeds through a cooperative electron-transfer mechanism involving donation from the Lewis base into the σ* orbital of H_2 and back-donation from the σ orbital of H_2 to the Lewis acid [18]. In the present work, we aim to provide a comprehensive mechanistic analysis of H_2 activation by a newly designed FLP system, with special emphasis on the electronic structure changes occurring along the reaction pathway.

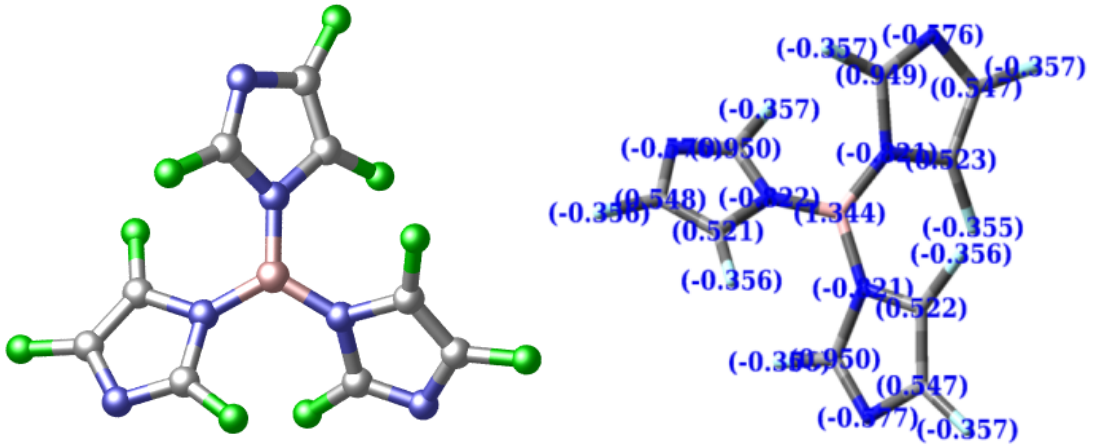
Computational details

All quantum chemical calculations were performed using the Gaussian 16 software package [19]. Geometry optimizations and vibrational frequency analyses were carried out within the framework of density functional theory employing the hybrid B3LYP exchange–correlation functional [20,21] in combination with the 6-31+G(d,p) basis set for all elements. Unless otherwise specified, all molecular structures were optimized in the gas phase. Harmonic frequency calculations were subsequently conducted at the same level of theory to confirm the nature of each stationary point on the potential energy surface, ensuring the absence of imaginary frequencies for true minima. These calculations also provided zero-point energy and thermal corrections. In addition, Natural Population Analysis (NPA) was performed to evaluate atomic charge distributions and to gain insight into charge transfer within the studied systems.

RESULTS AND DISCUSSION

A new intermolecular frustrated Lewis pair (FLP), $(C_3N_2F_3)_3B\cdots P(tBu)_3$, has been systematically designed and examined using theoretical methods. The Lewis acid component, $(C_3N_2F_3)_3B$, displays close structural similarity to the well-known Lewis acid $B(C_6F_5)_3$, which has been widely utilized in the development of FLP systems. Notably, substitution of the perfluorophenyl groups with heterocyclic five-membered aromatic $C_3N_2F_3$ ligands markedly increases the electron-withdrawing character of the surrounding ligand framework. Consequently, the boron center becomes more electron deficient, leading to an enhancement of its intrinsic Lewis acidity. This increased acidity is expected to promote stronger cooperative interactions with the Lewis base component and to facilitate more efficient activation of small molecules. Furthermore, the incorporation of heterocyclic ligands may offer additional electronic tunability, providing a useful strategy for the rational design of highly reactive FLP systems.

The optimized molecular structures of the newly proposed Lewis acid and the widely employed Lewis base $P(tBu)_3$ are depicted in Figure 1. To obtain a detailed understanding of the electronic characteristics of the individual fragments and their mutual interaction within the frustrated Lewis pair, Natural Population Analysis (NPA) was performed. The calculated atomic charge distributions offer quantitative insight into electron density polarization and the extent of charge redistribution between the Lewis acid and Lewis base components. While notable charge separation is observed within the individual fragments, the overall FLP system remains charge neutral, consistent with its intermolecular nature. Furthermore, the NPA results indicate enhanced electron deficiency at the boron center and significant electron density localization at the phosphorus atom, which together facilitate cooperative reactivity. The detailed NPA charge distributions for both the Lewis acid and the Lewis base are also shown in Figure 1, clearly illustrating the electronic features that underpin the frustrated character and the potential of the designed system for small-molecule activation.



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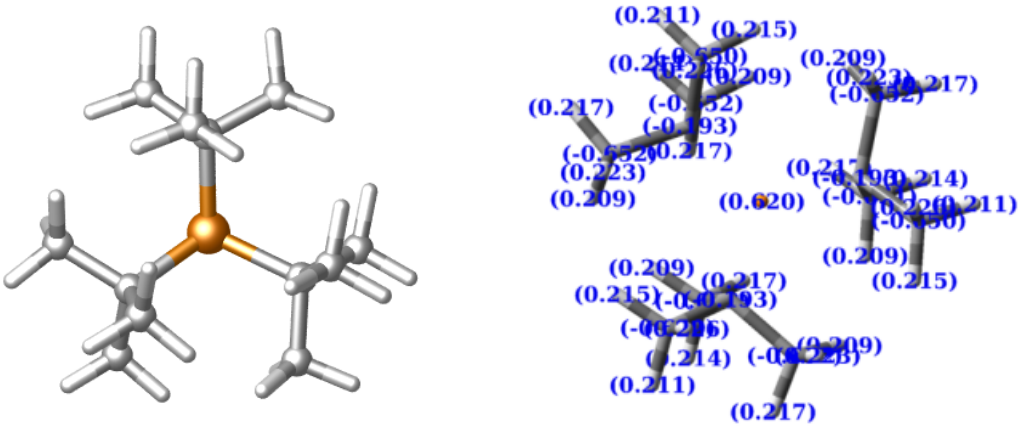
$B(C_3N_2F_3)_3$

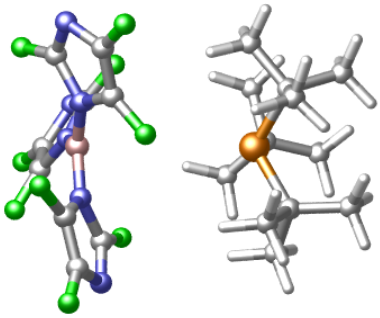


$P(C(CH_3)_3)_3$

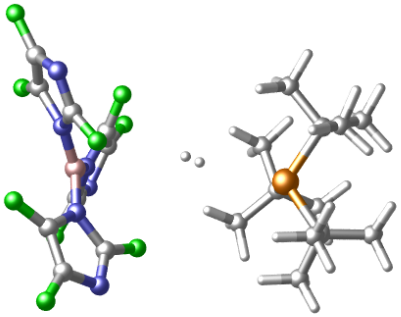
Figure 1. Optimized geometries and NBO charges of $B(C_3N_2F_3)_3$ and $P(C(CH_3)_3)_3$ molecules at B3LYP/6-31+G(d,p) level of theory.

Subsequently, the frustrated Lewis pair was assembled and its equilibrium structure was fully optimized, as illustrated in Figure 2. To evaluate the reactivity of the designed FLP toward molecular hydrogen, H_2 was introduced into the system and a complete reaction pathway was explored. Accordingly, the geometries of the reactant complex, transition state, and product complex associated with H_2 activation were optimized. The optimized structure of the FLP, $(C_3N_2F_3)_3B\cdots P(tBu)_3$, together with the ground-state geometries of the reactant complex, transition state (TS), and hydrogenated product complex, are presented in Figure 2.

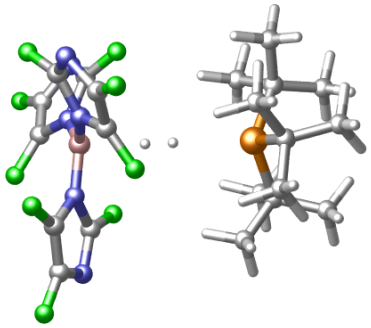
Inspection of the optimized structures indicates that hydrogen activation proceeds through a concerted, single-step mechanism in which the association of H_2 and its subsequent cleavage occur simultaneously through cooperative interactions with the Lewis acid and Lewis base sites. The overall reaction is exothermic, characterized by a negative reaction energy. The calculated activation energy barrier for the H_2 cleavage process is approximately 41 kcal mol^{-1}, indicating that the reaction is kinetically accessible under appropriate conditions.



$B(C_3N_2F_3)_3.P(^tBu)_3$

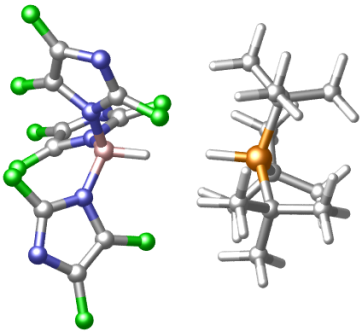


Reactant Complex(RC)



Transition State(TS) $B(C_3N_2F_3)_3H_2P(^tBu)_3$

$[B(C_3N_2F_3)_3H^-]\,[HP(^tBu)_3{}^+]$



Product Complex (PC)

Figure 2. Optimized geometry of $B(C_3N_2F_3)_3.P(^tBu)_3$ (Frustrated Lewis Pair(FLP)), RC, TS and PC at B3LYP/6-31+G(d, p) level of theory.

To elucidate the role of kinetic factors in FLP-mediated hydrogen activation, detailed mechanistic investigations were carried out by mapping the minimum energy reaction pathway for the bimolecular interaction between molecular hydrogen and the preorganized FLP complex. The calculated potential energy surface provides insight into the energetic feasibility of each elementary step involved in the activation process. Figure 3 presents the resulting energy profile for the studied system, where the gas-phase electronic energies (ΔE) are reported relative to the separated frustrated Lewis pair and an isolated H_2 molecule. In addition to the key stationary points along the reaction pathway, the relative energies of the isolated phosphine, borane, and hydrogen molecule are included for comparison. This comprehensive energy representation allows for a clear assessment of the energetic stabilization upon FLP formation and subsequent hydrogen activation. Moreover, analysis of the energy barriers and reaction energetics offers valuable information on the kinetic accessibility and thermodynamic favorability of the process.

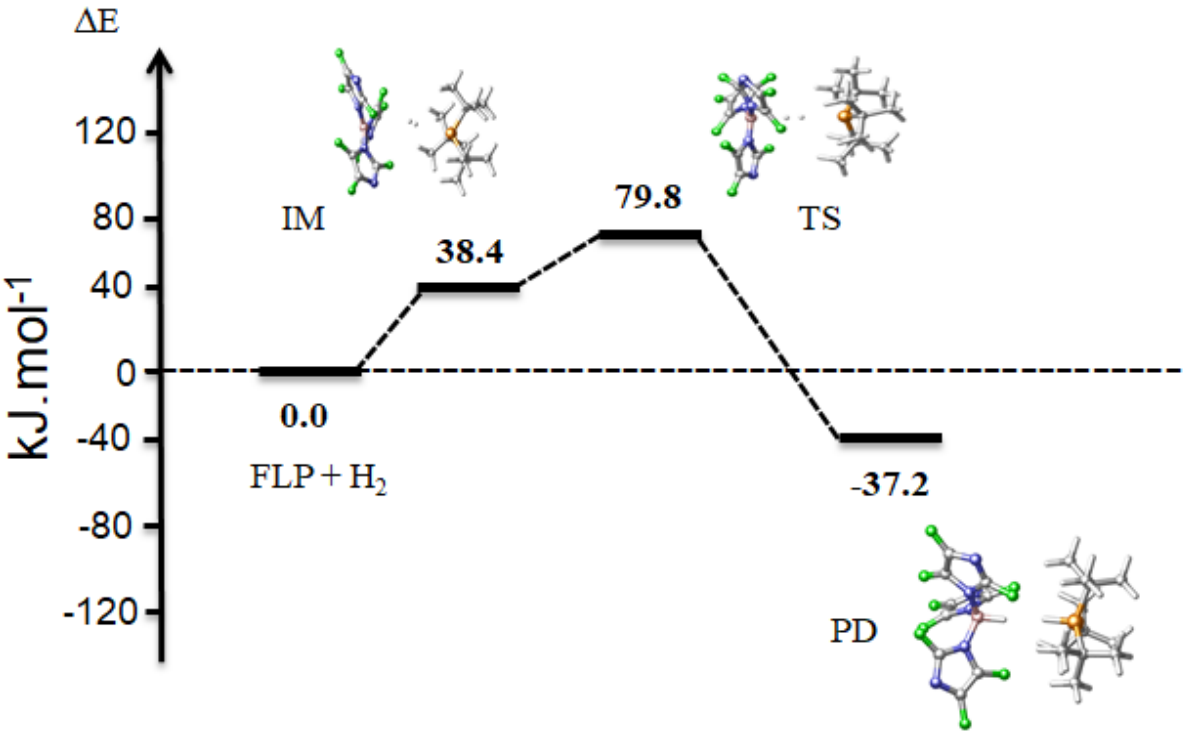


Figure 3. B3LYP/6-31+G(d, p) energy profiles of the hydrogen cleavage reaction with FLP $B(C_3N_2F_3)_3.P(^tBu)_3$. The calculated Δ*E* values are the gas-phase electronic energies. All energy values (in kJ mol^{-1}) are given relative to the total energy of the respective Lewis pair and an isolated H_2 molecule (FLP+H_2). Other notations used: IM for intermediate complex, TS for transition state, and PD for hydrogenated product.

CONCLUSIONS

In summary, a heterocyclic ligand–based frustrated Lewis pair has been successfully designed and theoretically investigated using density functional theory. The newly developed intermolecular FLP demonstrates a clear ability to activate molecular hydrogen without the involvement of transition metals, emphasizing the effectiveness of heterocyclic boron-containing Lewis acids in FLP chemistry. The incorporation of electron-withdrawing heterocyclic ligands enhances the electron deficiency at the boron center, thereby strengthening the Lewis acidity and promoting cooperative interaction with the bulky phosphine Lewis base.

The computational results indicate that hydrogen activation occurs through a cooperative interaction between the Lewis acid and Lewis base sites, resulting in efficient heterolytic cleavage of the H–H bond. The process is initiated by interaction of molecular hydrogen with the boron center of the Lewis acid, leading to polarization and weakening of the H–H bond. Subsequent transfer of hydrogen to the phosphorus center of the Lewis base completes the activation process, yielding a stabilized hydrogenated FLP complex.

Overall, the present findings highlight the crucial role of electronic tuning of the Lewis acid component in controlling FLP reactivity. The enhanced hydrogen activation capability observed for the designed system suggests that heterocyclic ligand modification provides a promising strategy for developing efficient metal-free systems for small-molecule activation. These results offer valuable insight for the rational design of next-generation frustrated Lewis pairs with improved reactivity and potential catalytic applications.

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