Concerted attack of frustrated Lewis acid–base pairs on olefinic double bonds: a theoretical study†

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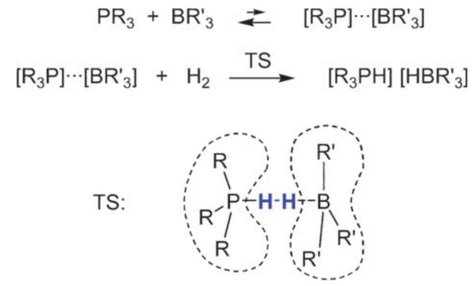
A computational approach reveals cooperative action of the preorganized acidic and basic centers of the frustrated $P(t\text{-}Bu)_3/B(C_6F_5)_3$ Lewis pair on olefinic bonds as the key to the observed regioselective addition reaction.

The concept of frustrated Lewis pairs has recently been introduced by Stephan and coworkers after their remarkable discovery that the phosphine borane compound, $R_2P–C_6F_4–BR'_2$ ($R = C_6H_2Me_3$ and $R' = C_6F_4$), can reversibly activate molecular hydrogen (H_2).[1] According to this concept,[2] steric congestion between bulky phosphine donors (PR_3) and Lewis acidic boranes (BR'_3) does not allow the formation of classical Lewis adducts ($R_3P–BR'_3$), which in turn opens a variety of new reaction channels. It has been shown by Stephan and coworkers that mixtures of frustrated phosphines and boranes can heterolytically cleave H_2 under very mild conditions,[3,4] and certain combinations can be used as hydrogenation catalysts for the reduction of imines, nitriles and aziridines by H_2.[5,6] Imines and aziridines can themselves act as the basic partner of a frustrated pair, rendering their BR'_3-catalyzed direct hydrogenation possible.[6,7]

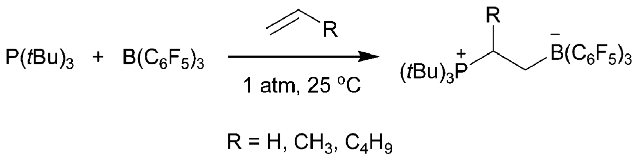
To gain a better mechanistic understanding of these reactions, we have recently undertaken a theoretical study for the reaction of the $P(t\text{-}Bu)_3/B(C_6F_5)_3$ pair with hydrogen.[8] The mechanistic picture emerging from our results involves the preassociation of the donor and acceptor molecules to a loosely bound $[R_3P]\cdots[BR'_3]$ adduct, which acts as a highly reactive species because (i) it represents an energetically strained structure that lowers the activation barrier, and (ii) the active donor–acceptor sites in $[R_3P]\cdots[BR'_3]$ are properly oriented for cooperative interaction with an H_2 molecule (see Scheme 1). We proposed that secondary interactions between the bulky R and R′ substituents play an essential role in these reactions as they allow the formation of frustrated adducts and provide important stabilization of the transition state (TS) as well. In our present work, we extend the applicability of this model to another family of mechanistically intriguing reactions, namely to the addition of frustrated PR_3/BR'_3 pairs to olefins.[9] We show that the preorganized sites of the frustrated adduct can easily give rise to the activation of an olefinic π bond as well.



Scheme 1 Mechanism proposed for H_2 activation by frustrated Lewis pairs.

Stephan and coworkers have recently reported that ethylene and other alkenes (propylene and 1-hexene) react readily with mixtures of $P(t\text{-}Bu)_3$ and $B(C_6F_5)_3$, yielding alkanediyl-linked zwitterionic phosphonium borates (Scheme 2).[9] Both NMR and X-ray crystallographic data indicated that $P(t\text{-}Bu)_3$ and $B(C_6F_5)_3$ add to opposite ends of the olefinic bond and, for substituted alkenes, the reaction is regioselective in that the secondary carbon center is attacked by $P(t\text{-}Bu)_3$. The authors suggested that these three-component reactions are initiated by activation of the olefin by the Lewis acidic borane, which is followed by phosphine addition. Nevertheless, no spectroscopic evidence of related binary adducts was found in experiments even at lower temperatures.[9]

On the basis of the model we put forward for H_2 activation,[8] one expects that the addition of the $P(t\text{-}Bu)_3/B(C_6F_5)_3$ pair to alkenes takes place in a single step *via* synergistic phosphine–olefin and borane–olefin interactions. Our present quantum chemical calculations[10] carried out for the $P(t\text{-}Bu)_3 + B(C_6F_5)_3 + C_2H_4$ system confirm this assumption as seen from the structure of the identified TS. Fig. 1 shows that the C_2H_4 molecule in the TS interacts simultaneously with the two active centers of the frustrated Lewis pair in an antarafacial manner. The concerted addition has an early TS, but the distorted structure of C_2H_4 implies a considerable degree of activation already at this stage of the reaction.[11] The population analysis indicates significant charge density redistribution in the TS relative to the reactants. The ethylene molecule undergoes charge polarization and electron transfer is observed corresponding to $(t\text{-}Bu)_3P \rightarrow \pi^*(C_2H_4)$ and $\pi(C_2H_4) \rightarrow B(C_6F_5)_3$ donations. These electronic effects are very similar to those



Scheme 2 Addition of frustrated $P(t\text{-}Bu)_3/B(C_6F_5)_3$ pair to olefins.

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† Electronic supplementary information (ESI) available: Detailed description of some parts of the work, Cartesian coordinates and computed energies of located stationary points. See DOI: 10.1039/b804662j

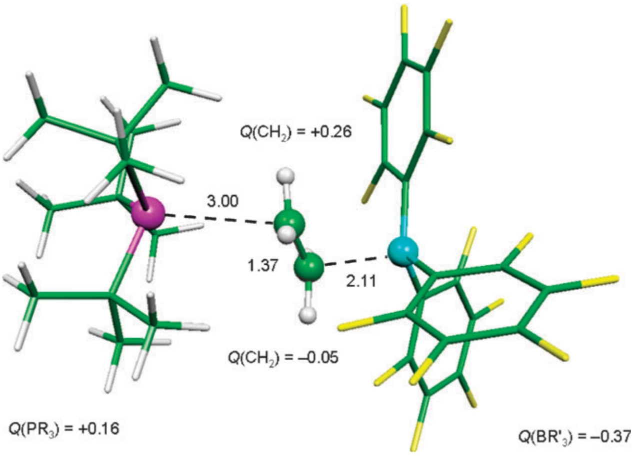
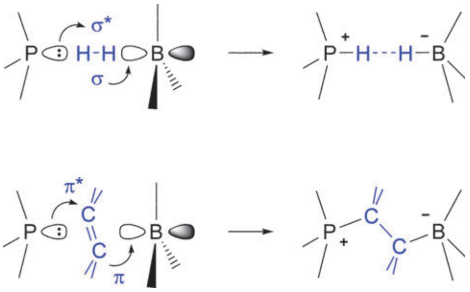


Fig. 1 Structure of the located TS. Bond distances are given in Å. Net charges (Q) were obtained from NBO analysis.

found for the heterolytic cleavage of H_2,[8] and underline the mechanistic analogy between the two reactions. The relative energy of the TS (+10.2 kcal mol^{-1} with respect to [(t-Bu)$_3$P]···[B(C_6F_5)$_3$] + C_2H_4) is also comparable to that of the hydrogenation reaction and is consistent with the observed reaction rate.[9]

Our calculations suggest that the present addition process has a slight asynchronous character in that the development of the P–C bond lags somewhat behind the formation of the B–C bond.[12] The calculated structure of the [(t-Bu)$_3$P–(CH_2)$_2$–B(C_6F_5)$_3$] product agrees well with the available X-ray data[9] and the charge separation in this zwitterionic species is confirmed by the large dipole moment (μ_{calc} = 18.7 D).[13] The relative stability of the addition product is predicted to be −50.1 kcal mol^{-1} with respect to the separated reactants, which points to highly exothermic and irreversible reaction.[14] On the reactant side of the TS, a weakly bound ternary complex is identified as an energy minimum, which corresponds to an open form of the [(t-Bu)$_3$P]···[B(C_6F_5)$_3$] frustrated adduct interacting with a C_2H_4 molecule.[13] This transient species lies 7.8 kcal mol^{-1} below the reactants and the stabilization arises partly from van der Waals and C–H···F contacts between the aryl groups of the phosphine–borane pair and also from weak borane–ethylene interactions. This latter interaction provides an additional contribution to the preorganization of reacting molecules to an arrangement favorable for cooperative interactions. The association energy for the (C_6F_5)$_3$B···C_2H_4 adduct is predicted to be −3.5 kcal mol^{-1}, which is slightly larger than that reported for the F_3B···C_2H_4 complex identified previously in matrix isolation studies,[15] but much smaller than the stabilization energy of the [(t-Bu)$_3$P]···[B(C_6F_5)$_3$] complex (−8.0 kcal mol^{-1}).[8,16] We find no indication of charge transfer between the two molecules in (C_6F_5)$_3$B···C_2H_4, therefore, contrary to the suggestion of Stephan and coworkers,[9] this weak association does not represent olefin activation. A stepwise mechanism involving either P–C or B–C covalent bond formation as the first step can also be excluded, because interaction of B(C_6F_5)$_3$ and C_2H_4 in the covalent bond region, as well as interactions between P(t-Bu)$_3$ and C_2H_4 at all distances are repulsive for chemically relevant geometric arrangements.[17]



Scheme 3 Cooperative electron donation in H–H and C–C bond activation reactions.

It is worth pointing out that the present addition reaction and the heterolytic cleavage of H_2 with the P(t-Bu)$_3$/B(C_6F_5)$_3$ pair can both be regarded as concerted Lewis acid–base reactions taking place between the amphoteric frustrated Lewis pair and the polarized centers of H_2 and C_2H_4. These reactions are initiated by cooperative electron donations that lead to weakening and ultimate cleavage of strong chemical bonds (see Scheme 3). The energy loss associated with the σ H–H and π C–C bond breaking processes is compensated and even exceeded through the formation of two new covalent bonds. Coexistence and cooperativity of free Lewis acidic and basic groups of necessary strength are ensured by the unique properties of frustrated pairs.

The Lewis concept can also account for the regioselectivity observed for the addition of P(t-Bu)$_3$/B(C_6F_5)$_3$ to alkyl-substituted olefins. Due to the excess electron density on the primary carbon of the olefinic bond, the terminal CH_2 group will preferentially act as a Lewis base in the concerted addition and react more favorably with borane.[18] Our calculations support this reasoning as we find that the TS corresponding to the experimentally observed product in the reaction with propylene lies 3.5 kcal mol^{-1} lower in energy than that identified for the reverse addition pathway.[19] These results are in qualitative agreement with the observed regioselectivity.[9] We also note that the antarafacial attack of the frustrated Lewis pair implies stereoselectivity for additions involving 1,2-disubstituted olefins (2-butene, for instance), which may serve to probe the proposed reaction mechanism.

In summary we have demonstrated that the frustrated adduct model developed for the heterolytic splitting of H_2 can also account for the reactivity of frustrated Lewis pairs in addition reactions with olefins. We found a close mechanistic analogy for these two types of activation process. In particular, we have shown that the cooperativity of the Lewis acid and base centers in the preorganized complex facilitates the heterolytic breaking of the π-bond and the B–C and P–C covalent bond formations in a regio- and stereoselective way. These observations may assist in exploiting the reactivity of frustrated Lewis pairs to further metal-free activation reactions.

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10. A combination of DFT and *ab initio* methods were used to characterize the structure and relative stability of species relevant to the title reaction. Details are provided in the ESI†. Briefly, the geometry optimizations were carried out at the B3LYP/6-31G(d) level, which were followed by single-point SCS-MP2/cc-pVTZ calculations for all located stationary points. Solvent effects have been assessed by employing the PCM model with chlorobenzene as the solvent. All energy values reported in this paper refer to solvent-corrected SCS-MP2/cc-pVTZ electronic energies. We note that omitting the solvent effects would not alter our conclusions. Great care was exercised in analyzing the B3LYP geometries and drawing conclusions from them, as in general B3LYP performs poorly for dispersion interactions. Nevertheless, for this small basis, partial error compensation can be expected due to the basis set superposition error See *e.g.* (*a*) P. Jurečka, J. Černý, P Hobza and D. R. Salahub, *J. Comput. Chem.*, 2007, **28**, 555; (*b*) S. Grimme, M. Steinmetz and M. Korth, *J. Org. Chem.*, 2007, **72**, 2118.
11. In the TS, the ethylene C–C bond is elongated by 0.04 Å with respect to free C_2H_4, and the molecule notably deviates from planarity as well.
12. The progress of the reaction has been monitored by the planarity of the olefinic unit defined as the angle between the C–C bond and the sum of the C–H vectors of a given C atom. For more details, see the ESI†.
13. For the structures of the two energy minima associated with the TS, see the ESI†.
14. Similar exothermicity and product dipole moment were calculated for the related hypothetical $PH(Mes)_2 + BH(C_6F_5)_2 + C_2H_4 \rightarrow (Mes)_2HP{-}(CH_2)_2{-}BH(C_6F_5)_2$ reaction in the ESI of ref. 4.
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16. The gas phase association energy was calculated to be −11.5 kcal mol^{-1} (see ref. 8).
17. For further details regarding the borane$\cdots C_2H_4$, and phosphine$\cdots C_2H_4$ interactions, see the ESI†.
18. The early nature of the located TS allows us to associate the reaction rate and regiochemistry with the electron distribution of the reactants. For a discussion of the polar nature of propylene and its relevance to regioselectivity, see: L. J. Sæthre, T. D. Thomas and S. Svensson, *J. Chem. Soc., Perkin Trans. 2*, 1997, 749.
19. Four different TS structures have been identified for the addition of $P(t\text{-Bu})_3/B(C_6F_5)_3$ to propylene corresponding to four possible CH_3 substitutions on C_2H_4 in the TS shown in Fig. 1. The relative energies of these TSs are: 0.0 and 1.8 kcal mol^{-1} for CH_3 at the P side; 3.5 and 9.6 kcal mol^{-1} for CH_3 at the B side. For details, see the ESI†.