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"Frustration" of Orbital Interactions in Lewis Base/Lewis Acid Adducts: A Computational Study of H_2 Uptake by Phosphanylboranes $R_2P{=}BR'_2$

Jonas Nyhlén[a] and Timofei Privalov*[a]

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The reaction of molecular hydrogen with phosphanylboranes $R_2P{=}BR'_2$ (**1**) is systematically studied by means of density functional theory calculations and second order Møller-Plesset perturbation theory. The potential energy barriers and the exothermicity of H_2 uptake are reported for a series of phosphanylboranes with different electron-donating and -withdrawing groups bound to phosphorus and boron. Systematic molecular orbital analysis reveals that the "frustration" between boron and phosphorus can be increased by modifying the substituents, and thus, atomic orbital interactions could be exploited in order to increase the reactivity of **1**. Additionally, we found a correlation between the potential energy barrier for H_2 uptake and the energy of the HOMO of the P=B complex, which could be relevant for the prediction of the properties of candidate compounds for H_2 activation and therefore useful for the development of such systems.

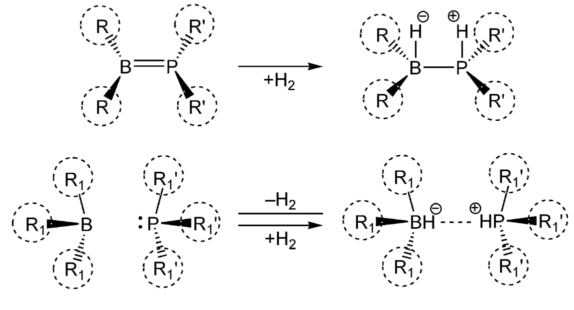
Introduction

Accurate prediction of how chemical reactions take place is one of the central goals of theoretical chemistry. Wavefunction and density functional methods have emerged as important tools for theoretical modelling of complex chemical transformations.[1,2] Recently, the unprecedented reactivity of novel main group species, referred to as "frustrated Lewis pairs" (FLPs),[3–6] led to a substantial effort to rationalize the experimentally observed reactivity by means of theory.[7–10] Efficient activation of molecular hydrogen[3a–3c,4,5,11] and catalysis of H_2 additions under relatively mild reaction conditions[3d–3f,5] are examples of novel metal-free chemistry of FLPs.

Uptake of H_2 by main group species is a process that relates to the development of efficient hydrogen storage methodologies for environmentally benign energy sources. Molecular hydrogen in its gaseous form is difficult and unpractical to store and transport with current technology. New hydrogen storage methodologies and materials are required to achieve the storing of hydrogen in a lightweight, compact, and practical fashion without the use of high pressure-, cryogenic-, or metal hydride approaches.[12]

The reaction of molecular hydrogen with phosphanylboranes $R_2P{=}BR'_2$ (**1**) is one of the discoveries made by Stephan's group.[13] The P=B bond in **1** undergoes H_2 addition, which affords $R_2HP\text{-}BHR'_2$ (**1′**).

The interaction of molecular hydrogen with a dative P=B bond of **1** is intriguing; on the one hand, complex **1** activates molecular hydrogen, a reaction that according to the current FLP framework requires "unquenched" Lewis acid and Lewis base fragments (Scheme 1).[14] On the other hand, electron-rich and electron-deficient fragments in **1** do not exhibit the same level of steric hindrance as those in FLPs and are therefore not precluded from forming a classic Lewis base/Lewis acid adduct. Thus, **1** demonstrates reactivity that is characteristic of a typical FLP, but its geometry shows no obvious signs of "frustration" between donor and acceptor.



Scheme 1. Activation of H_2 by phosphane/borane combinations with different degrees of steric hindrance.

The balance between a Lewis acid and a Lewis base, which could be adjusted with the right combination of electron-donating and -withdrawing groups (EDG and EWG, respectively), is the apparent key for controlling the chemistry of Stephan's main-group systems, in general, and the uptake of H_2, in particular.[4] For instance, it has recently been reported that subtle changes in the design of borane- and phosphorus-bound ligands dramatically improves the

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[a] Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University,
10691 Stockholm, Sweden
E-mail: priti@organ.su.se
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performance of B- and P-containing FLPs towards the reversible activation of molecular hydrogen.[15] This emphasizes the need for accurate and systematic theoretical studies of EDG-/EWG-induced effects in main group systems that are known to activate molecular hydrogen.

Among several novel main group species known to activate H_2, phosphane/borane combinations exhibit tunable reactivity and are, in general, able to reversibly activate and release H_2 under mild conditions.[16] In view of Equation (1), computational screening of H_2 uptake by a series of FLP-like and B–P bonded phosphane/borane-based species is therefore highly desirable for the determination of key factors that control reactivity. Such theoretical studies of FLP-like phosphane/borane combinations are complicated by the fact that: (i) the size of a molecular model of a typical FLP makes it rather unpractical to conduct the computational screening of H_2 uptake by an accurate non-DFT method, for instance MP2, and (ii) DFT methods, which are well suited for the purpose with regard to the size of a typical molecular model, have a common weakness in describing medium-range dispersive interactions that significantly contribute to the overall binding energies.[17]

$$R_2P{=}BR'_2 + H_2 \rightleftharpoons R_2HP\text{-}BHR'_2 \qquad (1)$$
$$R = t\text{Bu, Cy} \qquad R' = C_6F_5$$

A complete molecular model describing Equation (1) is much less affected by dispersive interactions between phosphane/borane-bound groups; it is also relatively small and computationally affordable, not only for DFT but also for MP2 methods. For these reasons, and since, to the best of our knowledge, no systematic theoretical studies of EDG-/EWG-induced effects for Equation (1) have appeared and only the uptake of H_2 by $(t\text{Bu})_2P{=}B(C_6F_5)_2$ has been addressed so far,[9,13] we decided to perform a systematic quantum chemical investigation of Equation (1) for a series of phosphanylboranes with the objective to disclose key electronic structure effects that control the reactivity. The reported results here are based on DFT and MP2 computations. The latter serves as a computational benchmark for the DFT calculations.

Results and Discussion

Since the reactivity of $(C_6F_5)_2B{=}P(t\text{Bu})_2$, herein referred to as **A**, has been experimentally validated,[13] the potential energy barrier of H_2 uptake by **A** will serve as a reference point. In order to limit the model/theory-dependence of our study, we consciously focus on the potential energy and disregard thermochemical corrections and solvent effects.[18]

DFT- and MP2-Based Screening of H_2 Uptake by $R_2P{=}BR'_2$

The DFT-computed heat of formation (ΔE), potential energy barriers ($\Delta E^‡$), $\Delta E_L^‡ = \Delta E^‡ - \Delta E$ of the direct and reverse processes, as well as the bond lengths between boron and phosphorus in **1** and **1′** are reported in Table 1. Key geometrical parameters of all computed transition states and the MO energies of the reacting species are available in the Supporting Information.

Table 1. Summary of B3LYP-computed BP bond lengths in $R_2P{=}BR'_2$ (**1**) and $R_2HP\text{-}BHR'_2$ (**1′**), potential energy barriers ($\Delta E^‡$), and the exothermicity (ΔE) of H_2 uptake by **1** according to Equation (1); $\Delta E_L^‡ = \Delta E^‡ - \Delta E$. The experimentally studied complex **A** is in bold.

Entry	R′	R	B=P [Å]	B-P [Å]	$\Delta E^‡/\Delta E_L^‡$ [kcal/mol]	ΔE [kcal/mol]
1	CF_3	H	1.81	1.98	11.6/44.7	–33.1
2	CF_3	Me	1.80	1.97	17.0/57.6	–40.6
3	CF_3	Et	1.78	1.98	18.6/57.9	–39.3
4	CF_3	*i*Pr	1.79	1.99	25.3/66.2	–40.9
5	CF_3	*t*Bu	1.80	2.01	20.5/64.8	–44.3
6	CF_3	Pr	1.78	1.98	18.6/58.1	–39.5
7	C_6F_5	Me	1.85	1.98	24.7/53.2	–28.5
8	C_6F_5	*i*Pr	1.83	2.00	26.4/51.9	–25.5
9	$\mathbf{C_6F_5}$	***t*Bu**	**1.84**	**2.05**	**28.8/58.5**	**–30.8**
10	Me	Me	1.90	1.99	25.8/41.5	–15.7
11	Me	*i*Pr	1.88	2.01	31.0/46.3	–15.2
12	Me	*t*Bu	1.91	2.06	27.5/47.6	–19.1
13	Ph	*i*Pr	1.91	2.03	28.6/46.2	–17.6
14	Ph	Me	1.90	2.00	26.9/45.4	–18.4
15	Ph	*t*Bu	1.89	2.06	28.8/51.9	–23.1

Recent computational screening of potential candidates for H_2 storage emphasized the importance of affordable methods that are able to consistently describe both activation energies and heats of formation at the same level of accuracy.[7e] We therefore performed MP2 calculations for Entries 1, 2, 3, 6, 10, 11, and 15 from Table 1 in order to validate the B3LYP results (Table 2). As expected, the potential energy barriers calculated with B3LYP are different with respect to those calculated with MP2. However, the discrepancy is rather systematic and therefore a relative comparison of the model compounds could be made. It is also reassuring that B3LYP reproduces MP2-computed geometries quite well.[7e,19]

Table 2. Summary of MP2-computed BP bond lengths in $R_2P{=}BR'_2$ (**1**) and $R_2HP\text{-}BHR'_2$ (**1′**), potential energy barriers ($\Delta E^‡$), and the exothermicity (ΔE) of the H_2 uptake by **1** according to Equation (1).

Entry from Table 1	B=P [Å]	B–P [Å]	$\Delta E^‡$ [kcal/mol]	ΔE [kcal/mol]	Energy difference in calculation methods for $\Delta E^‡/\Delta E$ ("B3LYP – MP2") [kcal/mol]
1	1.86	2.01	18.3	–28.8	–6.7/–4.3
2	1.79	1.98	24.5	–41.3	–7.5/1.3
3	1.79	1.98	24.9	–38.5	–6.2/–0.8
6	1.80	1.97	28.3	–37.0	–9.7/–2.6
10	1.89	2.01	31.0	–13.5	–5.1/–2.2
11	1.87	1.98	36.4	–12.7	–5.4/–2.5
15	1.85	2.06	33.1	20.1	–4.4/–3.1

The previously reported complex **A** (Entry 9, Table 1) has a relatively high potential energy barrier for H_2 uptake in comparison with some of the other tested compounds.

Substitution of C_6F_5 by CF_3 seems to be beneficial; we found the potential energy barriers to be lower in all cases in which this substitution was made; thus, stronger electron-withdrawing groups on boron increase the Lewis acidity and consequently lower the barrier for H_2 uptake.

It is noteworthy that while the geometry around boron remains planar through the series of the tested compounds, the geometry around phosphorus changes quite considerably. The planarity of the geometry around phosphorus appears to have a significant effect on the activity towards H_2 uptake. The sum of all bond angles around phosphorus changes from 326° for $(CF_3)_2B{=}PH_2$ to 349° for $(CF_3)_2B{=}PMe_2$ and reaches almost 360° for $(CF_3)_2B{=}P(i\text{Pr})_2$; in the latter case, almost perfect planarity is observed. The activity of **1** with different P-bound groups is as follows: H > Me > *i*Pr. The lowest barrier for H_2 uptake is observed for the complex with the most pyramidal-type geometry around phosphorus, while the complex with the most planar geometry around the P atom and an in-plane arrangement of the P and B ligands has the highest barrier.

Electronic Structure to Reactivity Relationships

Complexes with distinctively pyramidal geometry around phosphorus, such as $(CF_3)_2B{=}P(H)_2$ (Figure 1 A), are characterized by HOMOs that clearly show signs of “frustration” between interacting P- and B-based p orbitals; only a small portion of the electron density is attracted to boron whereas the dominating lobe of the asymmetrical π orbital is centered on phosphorus. In the case of $(CF_3)_2B{=}P(Me)_2$, the geometry around phosphorus is more planar and the shape of the HOMO shows a more pronounced shift of electron density towards boron (Figure 1 B). Because of the direct bonding between the boron and phosphorus atoms, planarity strengthens the interaction between the P- and B-based p orbitals, which affords a classical Lewis acid/Lewis base complex in terms of both geometrical and electronic structures. The shape of the HOMO is nearly π-like in the case of unhindered overlap between the p orbitals; this is particularity evident for $(CF_3)_2B{=}P(i\text{Pr})_2$ (Figure 1 C).

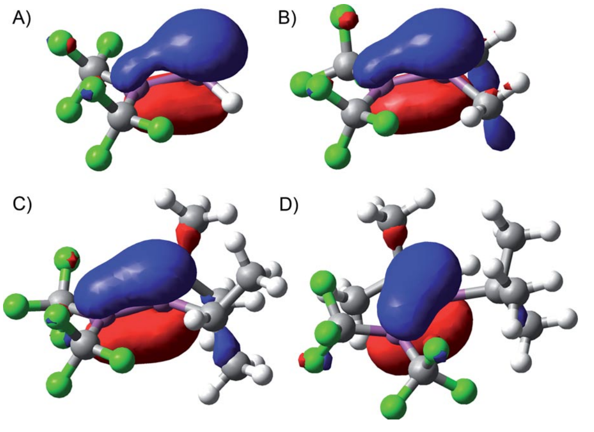


Figure 1. Electron density maps of the HOMOs for Entries 1, 2, 4, and 5 from Table 1, (A)–(D), respectively.

However, pyramidalization around phosphorus is not the only way to “frustrate” orbital overlap. Though the geometry around phosphorus is planar for both $(CF_3)_2B{=}P(i\text{Pr})_2$ and $(CF_3)_2B{=}P(t\text{Bu})_2$ (Figure 1 C and D), the H_2 uptake barrier is lower for the latter since the R_2B and PR_2 planes in $(CF_3)_2B{=}P(t\text{Bu})_2$ are twisted at an angle of approximately 21°, which “frustrates” the overlap between the B- and P-based p orbitals. Though the overall shape of the HOMO is very π-like, the upper lobe and the lower lobe are inclined with respect to the B=P bond in the case of $(CF_3)_2B{=}P(t\text{Bu})_2$. This clearly indicates that the angle between the normal vectors of the B- and P-based p orbitals is a key parameter that controls the reactivity of **1** (Figure 2). Furthermore, comparison of the MOs of the H_2-uptake transition states and those of the reacting species, as well as potential energy scans of H_2 activation by **1**, firmly indicates that the interaction between H_2 and B=P occurs through the boron atom.[9,13] The overlap between the $\sigma^*(H_2)$ orbital and the HOMO depends on the orientation and the positioning of molecular hydrogen with respect to boron and phosphorus. The degree of the asymmetry of the boron-based part of the HOMO appears to be important for the overlap between the HOMO and the antisymmetric $\sigma^*(H_2)$ orbital (Figure 2). We therefore suggest that symmetry selection rules that govern MO interactions are the reason for H–H bond cleavage in the vicinity of the boron atom. The HOMO becomes significantly more symmetric in the case of the “unfrustrated” interaction between B- and P-based p orbitals; this reduces the reactivity because of the diminishing orbital overlap between the $\sigma^*(H_2)$ orbital and a nearly symmetrical HOMO. It can be noted that the shape of the LUMO is rather insensitive to induction effects of different B- and P-based groups in **1**.

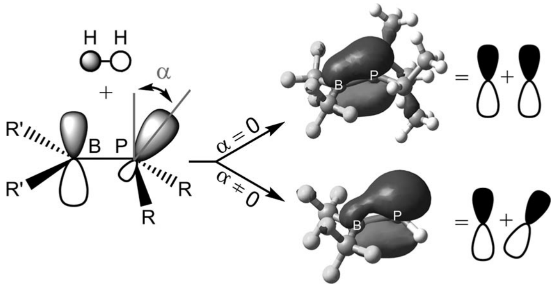


Figure 2. Schematic representation of the “frustration” of the overlap of the B- and P-based p orbitals in **1** as a result of the pyramidality around the P center and/or the twisting of the R_2B and PR_2 planes; *α* is the angle between the normal vectors of B- and P-based p orbitals.

The shape and the energy of the HOMO, as well as the potential energy barrier of Equation (1), appear to depend on donor–acceptor interactions between phosphorus and boron. It is therefore plausible that there might be a correlation between the energy of the HOMO and the potential energy barrier for H_2 uptake ($\Delta E^{\ddagger}$). A plot of $\Delta E^{\ddagger}$ vs. the energy of the HOMO based on B3LYP and MP2 computations supports this hypothesis (Figure 3).[20] A lower potential energy barrier corresponds to a more stable HOMO

(Figure 3), which in its turn is characterized by a more asymmetric π-like shape (Figure 1). This is apparent in the case of electron-withdrawing groups on boron and electron-donating groups on phosphorus.

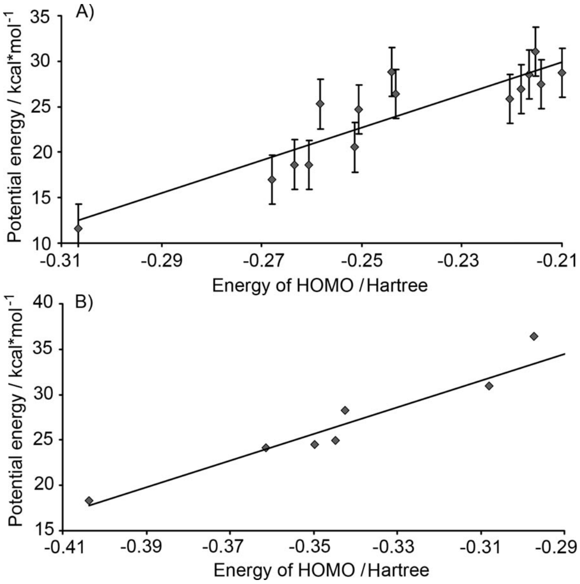
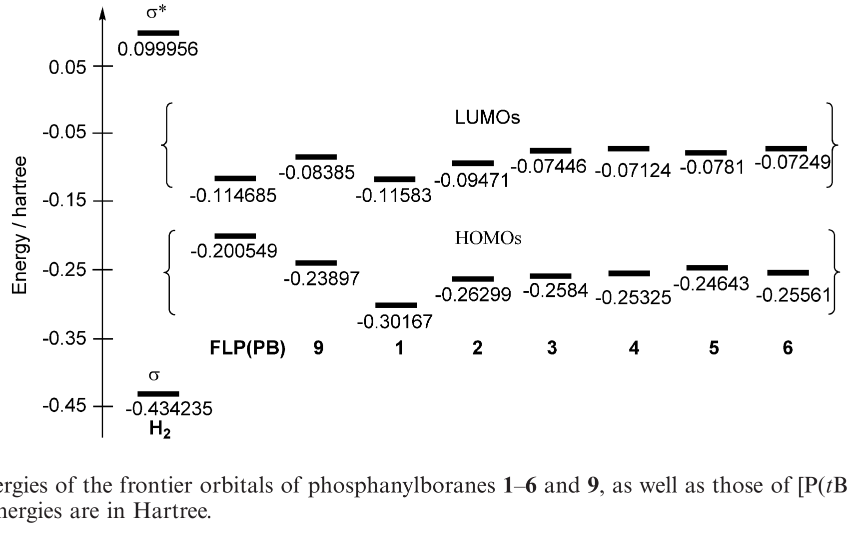


Figure 3. The potential energy barrier for H_2 uptake ($\Delta E^{\ddagger}$) vs. the electronic energy of HOMO of **1**; B3LYP and MP2 calculations (A) and (B), respectively. The R^2 values are 0.795 and 0.922, respectively. Vertical error bars for the B3LYP calculations are derived with respect to the MP2 benchmark.

The computational results are also consistent with the simplified description of phosphanylboranes **1** in terms of Lewis structures (resonant forms) with vastly different activity towards the cleavage of the H_2 bond. The formal Lewis structure that complies with the octet rule is thought to contain a BP double bond, whereas the other contains a BP single bond between electron-deficient boron and phosphorus, with an electron lone pair on the latter. The Lewis acidity of boron and the basic character of phosphorus both increase with the increase in the weight of the formal Lewis structure with a single BP bond; the potential energy barrier of H–H cleavage decreases accordingly. In terms of frontier orbital interactions, the difference between the two Lewis structures of **1** can be seen in the shape of the HOMO, which is, in general, highly symmetric for the structure containing a BP double bond and highly asymmetric for the other as illustrated in Figure 2. Strong B-based asymmetry of the HOMO of a formal Lewis structure of **1** with a BP single bond lifts the selection rule, which would otherwise prohibit interaction between the HOMO and the antisymmetric $\sigma^*(H_2)$ orbital. This correlates with the expected changes in the electronic energies of the frontier orbitals of the tested phosphanylboranes (Scheme 2, see also the complete MO data in the Supporting Information). By placing electron-donating groups on boron, the Lewis acidity of boron is largely "quenched" and, consequently, the potential energy barrier to cleave the H–H bond increases. In spite of the acceptable R^2 value of the linear regression in Figure 3 (0.795 and 0.922 at the B3LYP and MP2 level, respectively), it seems that the reaction in Equation (1) is not completely MO-controlled.

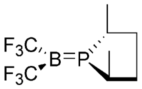
Computational Identification of B=P Compounds Suitable for Active Uptake of H_2

On the basis of the potential energy barriers (Table 1), $(CF_3)_2B{=}P(Me)_2$ should be significantly more reactive than reference complex **A**. However, the practical significance of the former is limited since it lacks steric hindrance, which could prevent dimerization and cyclization. Therefore, a series of phosphanylboranes with different groups on the phosphorus atom was tested in an attempt to find a candidate that has a low potential energy barrier for H_2 uptake and is bulky enough to hinder dimerization.[21] A promising candidate, **B**, is shown in Scheme 3. The sum of all angles around phosphorus deviates from 360° by ca. 20°, which indicates a pyramidal geometry (Figure 4). B3LYP-computed potential energy barriers for the uptake of H_2 by **B** is 18.4 kcal/mol.[22] This model complex appears to exhibit



Scheme 2. Electronic energies of the frontier orbitals of phosphanylboranes **1**–**6** and **9**, as well as those of $[P(tBu)_3][B(C_6F_5)_3]$, labeled as FLP(BP), and H_2. All energies are in Hartree.

a significant improvement in reactivity relative to complex **A**, and the methyl groups are thought to be able to hinder dimerization.



Scheme 3. The proposed phosphanylboranes **B** suitable for H_2 uptake.

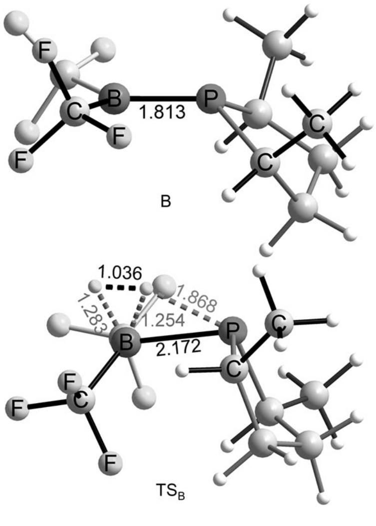


Figure 4. Optimized geometry of model complex **B** and the corresponding transition states TS_B for H_2 uptake. All distances are in Å.

Conclusions

We have demonstrated that though the structure of the $R_2P{=}BR'_2$ species resembles a classical Lewis base/Lewis acid adduct its electronic structure could be "frustrated". Theoretically, it is possible to increase the "frustration" between the phosphorus and boron-based p orbitals, and thus to decrease the barrier for H_2 cleavage. The key is to control the geometry around the phosphorus atom in order to hinder the deactivation of donor–acceptor interactions within the BP core. This can be achieved, for instance, by a pyramidal geometry around phosphorus and/or by the twisting of the C_2B and PC_2 planes.

Symmetry selection rules for the interaction between antisymmetrical and symmetrical MOs appear to be important for the reaction. It is the pronounced asymmetry of the HOMO in the vicinity of the boron center that allows the symmetry-suppressed interaction to take place.

With regard to the plausible derivatives of Stephan's complex, we predict that species with CF_3 groups on boron should, in general, be more reactive than species with boron-bound C_6F_5 groups. Furthermore, the computational screening of a series of phosphanylboranes with different phosphorus-bound ligands singled out one plausible candidate for which we predict a lower barrier for H_2 uptake than that for the original complex developed by Stephan. We therefore believe that reactivity of phosphanylboranes containing a BP double bond could be improved by a balanced choice of electron-withdrawing and -donating groups.

Computational Details

All calculations are performed with the Jaguar 4.0 quantum chemistry package.[23] Our approach is somewhat similar to the previously reported procedure[24] with respect to finding low-energy conformers. Validation of the computational methods is provided in the Supporting Information.

DFT Calculations

We initially performed a conformational search with the B3LYP[25,26] functional by using the split-valence double-zeta basis set, 6-31+G*,[27,28] augmented with diffuse and polarization functions, and the molecular model system formally in the gas phase. Since we are interested in raw potential energy barriers, no solvent effects were considered in the present study. The geometries of the conformers with the lowest energy were then reoptimized by using B3LYP with the 6-31+G* basis set; all degrees of freedom were optimized. All transition states were found at the B3LYP/6-31+G* level of theory by using the quadratic synchronous transit (QST) method, as implemented in the Jaguar computational package, and were characterized by one single imaginary vibrational frequency along the proper reaction coordinate. Intrinsic reaction coordinate scans were performed to verify that all reported transition states indeed "connect" appropriate intermediates along the reaction coordinate, which is defined by the Hessian at the corresponding transition-state structure. The BP86 density functional was used as an independent DFT check within the same computational procedure as described for the B3LYP and at the same level of theory. All recomputed results were found to be in agreement with the results obtained at the B3LYP level. No appreciable basis set dependence of the relative reactivity, i.e. relative potential energy barriers, was found.

MP2 Calculations

The MP2 method[29] was employed according to the same procedure (vide supra) at the 6-31+G* level and as implemented in Jaguar. Conformation studies singled out low energy candidates; those were reoptimized at the same level of theory and a lowest energy conformer accepted for the reporting. All MP2-computed transition states were searched for independently from the DFT-based results. All transition-state structures were characterized by one single imaginary vibrational frequency along the proper reaction coordinate.

Supporting Information (see footnote on the first page of this article): *XYZ* data for all relevant complexes, gas phase and solvent reference energies, and a frequency analysis of the transition states are presented.

Acknowledgments

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[18] See ref.[7e] for the effect of thermochemical corrections on the potential energy barriers and heat of formation in a related system.

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[20] Results have been validated with other B3LYP density functionals as well.

[21] We considered species with the following phosphorus-bound ligands: functionalized phenyl rings, functionalized five- and six-membered cyclic alkenes and alkanes, and functionalized biphenyl moieties. In all cases, the potential energy barrier for H_2 uptake is predicted to be in the range 19–21 kcal/mol.

[22] The MP2 result for **B** is 23.0 kcal/mol.

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