Computational Studies of [2+2] and [4+2] Pericyclic Reactions between Phosphinoboranes and Alkenes. Steric and Electronic Effects in Identifying a Reactive Phosphinoborane that Should Avoid Dimerization

Thomas M. Gilbert*,[1] and Steven M. Bachrach[2]

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115, and Department of Chemistry, 1 Trinity Place, Trinity University, San Antonio, Texas 78212

Received January 2, 2007

Computational studies of pericyclic reactions between phosphinoboranes X_2BPY_2 and alkenes/dienes were undertaken for comparison with organic analogues. Identification of a suitable phosphinoborane required examination of several differently substituted examples. The data show that $(F_3C)_2BP(CH_3)_2$ contains a nearly planar P atom (a requirement for multiple bonding), but it dimerizes without a barrier and so would be unsuitable experimentally. Increasing the size of the P-bound groups lowers the dimerization exothermicity, but an adequate barrier arises only for $(F_3C)_2BP(t\text{-Bu})_2$, **1**. This compound is predicted to undergo facile [2+2] cyclization with C_2H_2 and C_2H_4 and [4+2] cyclization with *cis*-C_4H_6 and *c*-C_5H_6, with barriers of <10 kcal mol^{-1} and exothermicities of >30 kcal mol^{-1}. It thus represents a candidate for synthesis and subsequent reactions. The reactivity provides insight into the nature of the B−P bond (whether double, single, or in between) in phosphinoboranes, but does not allow unambiguous classification.

Introduction

While a number of aminoboranes X_2BNY_2 have been reported, relatively few phosphinoborane homologues X_2BPY_2 have appeared.[3] In general, this reflects the propensity of the latter to oligomerize. Nonetheless, phosphinoboranes are of interest for comparisons with aminoboranes, because the latter are generally considered to contain BN double bonds, and one would like to know whether similar multiple bonding can occur for the heavier phosphorus. Structural[3,4] and computational[5] studies indicate that phosphinoboranes containing small peripheral substituents exhibit pyramidal phosphorus atoms and minimal (if any) BP multiple bonding.

However, Power and co-workers[3,6] have reported phosphinoboranes containing bulky substituents that display characteristics consistent with their containing BP double bonds: short B−P distances,[7] planar (or nearly so) phosphorus atoms, and hindered rotation around the B−P axis. The archetype is Mes_2BPMes_2 [Mes = mesityl(2,4,6-trimethylphenyl)], for which the B−P distance is 1.839(8) Å and the sum of the angles around phosphorus is 360°. It is generally agreed that these phosphinoboranes contain BP double bonds; the only disconcerting characteristics are the ^{31}P and ^{11}B NMR chemical shifts, which do not appear to reflect multiple versus single BP bonding as much as one would expect by comparison to alkanes/alkenes or phosphines/phosphaalkenes.[3]

Reactivity with substrates represents a potentially fascinating probe of the nature of the BP bonds in Power's phosphinoboranes. However, no such studies have appeared to our knowledge, presumably reflecting that the bulky substituents required to force the phosphorus atom planar while inhibiting dimerization also block attack by other reactants. Given this, it is obviously important to determine the boundaries: can one place substituents on the boron and phosphorus that are large enough to adequately inhibit phosphinoborane dimerization, but small enough to allow interaction of the BP core with smaller substrates? And can the substituents be electronically tuned to enhance the latter reactivity while controlling the former?

We previously found that reactivity studies, particularly cyclizations, of amino- and iminoboranes proved useful in examining the nature of the heteroatom multiple bonds.[8] Studies of iminoboranes in particular provided insight into the relationship between substituent steric bulk, dimerization energetics, and reactivity with small organic molecules. We wished to explore phosphinoborane reactivity to see if similar examinations were possible and also to compare the energetics of the homologues. A recent report that a phosphine−borane might function as a dihydrogen storage medium[9] further justified our interest in examining BP bond reactivity. Accordingly, we

---

* Corresponding author. E-mail: tgilbert@niu.edu.

[1] Northern Illinois University.

[2] Trinity University.

[3] (a) Power, P. P. *Chem. Rev.* **1998**, *99*, 3463−3503. (b) Paine, R. T.; Nöth, H. *Chem. Rev.* **1995**, *95*, 343−379. (c) Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 449−460.

[4] Hoic, D. A.; DiMare, M.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 7155−7156.

[5] (a) Vogel, U.; Hoemensch, P.; Schwan, K.-C.; Timoshkin, A. Y.; Scheer, M. *Chem.−Eur. J.* **2003**, *9*, 515−519. (b) Allen, T. L.; Scheiner, A. C.; Schaefer, H. F., III. *Inorg. Chem.* **1990**, *29*, 1930−1936. (c) Coolidge, M. B.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1704−1706.

[6] Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8426−8437.

[7] Paine and Nöth (ref 3b) suggest distance ranges of 1.90−2.00 Å for BP single bonds and 1.79−1.84 Å for BP double bonds.

[8] (a) Gilbert, T. M. *Organometallics* **1998**, *17*, 5513−5520. (b) Bissett, K. M.; Gilbert, T. M. *Organometallics* **2004**, *23*, 850−854. (c) Gilbert, T. M. *Organometallics* **2003**, *22*, 2298−2304. (d) Bissett, K. M.; Gilbert, T. M. *Organometallics* **2004**, *23*, 5048−5053.

[9] Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124−1126.

10.1021/om070002t CCC: $37.00

Table 1. Predicted Structural Parameters (MP2/6-31G(d), distances in Å, angles in deg) and Relative Energies (MP4(SDTQ)/6-31G(d)//MP2/6-31G(d), kcal/mol) of X_2BPY_2 Conformers

compound	structure	B−P	Σ angles around P	$\angle$B−PX$_2$[a]	E_{rel}
H_2BPH_2[b]	P_{pyr}	1.862	311.9	109.4	0.0
	P_{pl} (ts)[c]	1.785	360.0		4.8
F_2BPH_2	P_{pyr}	1.919	292.7	98.5	0.0
	P_{pl} (ts)	1.837	360.0		17.5
$(F_3C)_2BPH_2$	P_{pyr}	1.840	315.3	111.0	0.0
	P_{pl} (ts)	1.772	360.0		3.7
$H_2BP(CH_3)_2$	P_{pyr}	1.820	337.0	129.1	0.0
	P_{pl} (ts)	1.778	360.0		2.2
$H_2BP(CF_3)_2$	P_{pyr}	1.890	304.6	105.2	0.0
	P_{pl} (ts)	1.792	360.0		9.3
$(H_3C)_2BP(CH_3)_2$	P_{pyr}	1.881	321.0	115.6	0.0
	P_{pl} (ts)	1.802	360.0		5.9
$(F_3C)_2BP(CH_3)_2$	P_{pyr}	1.784	350.6	146.6	0.0
	P_{pl} (ts)	1.769	360.0		0.8
$(F_3C)_2BP(CH_2CH_3)_2$	P_{pyr}	1.790	347.5	141.0	
$(F_3C)_2BP[CH(CH_3)_2]_2$	P_{pyr}	1.787	350.9	148.3	
$(F_3C)_2BP[C(CH_3)_3]_2$	P_{pyr}	1.794	358.8	167.4	
		1.792[d]	360.0[d]	180.0[d]	

[a] $\angle$B−PX$_2$ is the angle between the B−P axis and the bisector of the angle formed by the P atom and the two non-B atoms attached to it. [b] 6-311+G(d,p) basis set. [c] Structures marked "P_{pl} (ts)" were constrained to maintain a planar geometry around P and confirmed as transition states for inversion by frequency analysis at the HF/6-31G(d) level. [d] BS1 basis set.

discuss here computational studies of several phosphinoboranes designed to identify one that would prove reactive toward small organic molecules, but containing substituents large enough to inhibit dimerization. The unknown, but seemingly preparable $(F_3C)_2BP(t\text{-}Bu)_2$, **1**, proved a successful candidate. We then focus on cyclization reactions between **1** and alkenes/dienes, showing that both [2+2] and [4+2] reactions should occur readily, making **1** a potent synthon for a vast range of molecules. Finally, we comment on what our results suggest regarding the nature of the BP bond in **1** and phosphinoboranes generally.

Computational Methods

All calculations were performed with the GAUSSIAN code.[10] Searches for a phosphinoborane suitable for cyclization studies (results in Table 1) involved fully optimizing candidates at the HF/6-31G(d) level using several different starting geometries to explore the potential surface and ensure that the lowest energy conformation was selected. Three or four of the lowest energy conformations were selected (in those cases where multiple stationary points were found), and their natures probed by analytical frequency analysis at this level. The stationary point structures that were minima were then reoptimized at the MP2/6-31G(d) level, and the lowest energy conformation was selected to appear in Table 1. Single-point MP4-(SDTQ)/6-31G(d) energies were then calculated to provide the most likely relative energies between conformations. The values in Table 1 were corrected using scaled[11] zero-point energies (ZPEs) from the frequency analysis.

Table 2. Energetics (kcal mol^{-1}) Using the MP2 and Various DFT Models (basis set BS1) for Pericyclic Reactions between $(F_3C)_2BP(t\text{-}Bu)_2$, 1, and Alkenes/Alkynes

	MP2	MPW1K	mPW1	PBE1	mPW	PBE
		[2+2] Cyclizations				
1 + **1**, ts		15.4	18.5	15.5	16.8	21.6
1 + **1**		−16.0	−9.4	−14.0	−7.6	−0.9
1 + C_2H_2, ts	2.2	3.4	5.1	3.2	4.6	7.4
1 + C_2H_2	−58.1	−62.9	−58.4	−60.4	−55.1	−52.5
1 + C_2H_4, ts	3.2	7.7	10.0	7.8	9.8	12.9
1 + C_2H_4	−47.5	−45.9	−41.0	−43.4	−37.6	−34.4
		[4+2] Cyclizations				
1 + *cis*-C_4H_6, ts		7.1	7.5	5.7	4.9	7.5
1 + *cis*-C_4H_6	−67.0	−60.4	−53.9	−56.9	−49.1	−45.0
1 + *c*-C_5H_6, ts		7.1	7.8	5.8	5.4	8.2
1 + *c*-C_5H_6	−45.7	−35.2	−29.2	−32.1	−25.1	−21.2

$(F_3C)_2BP(t\text{-}Bu)_2$, **1**, was selected as the phosphinoborane most suitable for cyclization computations, for reasons enumerated below. Initial searches for transition states and product phosphaboracycles derived from **1** employed either the HF/3-21G, HF/6-31+G(d), or B3LYP/3-21+G(d) models. The models were used sequentially, with the more sophisticated employed only to locate transition state stationary points when the less sophisticated led to separation or cyclization of the reacting molecules (i.e., the structure optimized away from the transition state). Frequency analysis at whichever level of the three provided a stationary point was used to determine its nature and to give ZPEs. The stationary point structures were then reoptimized using the models given in Table 2 and a mixed basis set (BS1) consisting of the 6-311+G(d) basis set on B, P, and C atoms, and on the H atoms of the organic reactant, and the 3-21G basis set on H atoms of the phosphinoborane *tert*-butyl groups. Because the transition state structures contain exceptionally long distances between atoms that ultimately bond, intrinsic reaction coordinate (IRC) calculations were used for the dimerization of **1**, and its reactions with C_2H_2 and *cis*-C_4H_6, to demonstrate that the transition states found connect reactants and products. Relative energies, corrected using scaled ZPEs[12] from the frequency analyses, appear in Table 2; structures appear in Figures 1−3.

The mPWPW91, mPW1PW91,[13] PBEPBE,[14] and PBE1PBE[15] density functional theory (DFT) models (hereafter abbreviated as mPW, mPW1, PBE, and PBE1, respectively) and the MP2[16] perturbation theory model were used as coded in Gaussian; the MPW1K DFT model was generated using IOp keywords.[17] The DFT models were selected to give a range of pure (mPW, PBE) and hybrid (mPW1, MPW1K, PBE1) approaches; the MP2 perturbation theory model served as a non-DFT check. Multiple models were used to provide a computational "error bar"[18] for the results, since several recent studies have shown that DFT results can vary wildly, even for structurally similar compounds.[19] The values in Table 2 bear this out; DFT barriers and reaction energies differ by up to 15 kcal mol^{-1} for the same reaction. Since DFT calculations are not independent measurements that can be related

---

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, A D.; Rabuck, K. D.; Raghavachari, K; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople. J. A. *Gaussian 98*, Revision A.11.4; Gaussian, Inc.: Pittsburgh, PA, 1998.

(11) (a) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513. (b) http://comp.chem.umn.edu/freq_scale.htm.

(12) (a) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513. (b) http://comp.chem.umn.edu/freq_scale.htm.

(13) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664−675. It should be noted that this functional was coded incorrectly into Gaussian 98, leading to a slight error. Commentary on this may be found on the World Wide Web at http://comp.chem.umn.edu/info/mpw1k.pdf.

(14) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(15) Perdew, J. P.; Burke, K.; Ernzerhof, M. *J. Chem. Phys.* **1996**, *105*, 9982−9985.

(16) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618−622.

(17) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936−2941.

(18) Check, C. E.; Gilbert, T. M. *J. Org. Chem*. **2005**, *70*, 9828−9834.

(19) (a) Grimme, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4460−4464. (b) Schreiner, P. R.; Fokin, A. A.; Pascal, R. A., Jr.; de Meijere, A. *Org. Lett.* **2006**, *8*, 3635−3638. (c) Wodrich, M. D.; Corminboeuf, C.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 3631−3634.

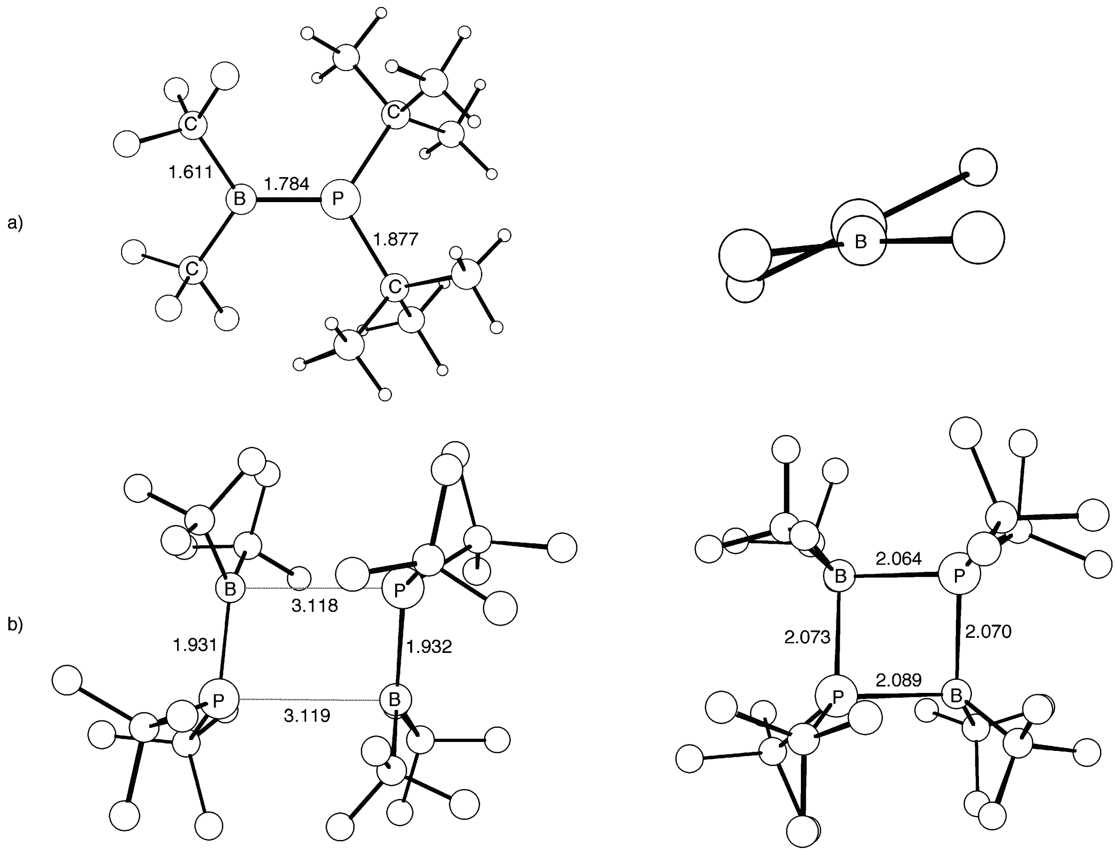

Figure 1. (a) Two views of the optimized (MPW1K/BS1; bond distances in Å) structure of $(F_3C)_2BP(t\text{-}Bu)_2$, **1**. (b) Optimized (MPW1K/BS1; bond distances in Å) structures of the transition state (left) and product (right) of dimerization of **1**.

statistically, but rather models with individual strengths and flaws,[20] it is inappropriate to average the results. The reader should keep in mind the existence of this range, in *all* papers reporting DFT results, including this one. The discussion below will focus on MPW1K results, since several published studies[8b,17,21] suggest MPW1K generally predicts barriers better than the other models studied here. As the reaction energies are uniformly exothermic across models, the barriers largely determine the efficacy of the reactions. Moreover, the MPW1K model gives results most consistent with the MP2 results.

The MP2 model is known to underestimate transition state barriers for pericyclic reactions, particularly [4+2] versions like the Diels−Alder reaction.[22] This appears to occur in the reactions between **1** and *cis*-butadiene/cyclopentadiene. We have been unable to locate stationary points for the transition states of these reactions using this model; moreover, single-point energies determined at the MPW1K geometries and geometries near them are uniformly lower than the sum of the reactant energies (i.e., the “barriers” are negative). Thus the barrier energies for these reactions do not appear in Table 2. We note that this supports the concept that the cyclizations are likely to occur readily at or below room temperature.

Cartesian coordinates at either MP2 or MPW1K levels of all molecules in Tables 1 and 2 are available as Supporting Information.

Results and Discussion

Identifying a $R_2BPR'_2$ Compound Suitable for Cyclization Studies. Criteria for a phosphinoborane that satisfies computational and experimental needs for probing multiple bonding by examining cyclization reactions include a planar (or nearly so) phosphorus atom and peripheral substituents sufficiently large to inhibit dimerization of the phosphinoborane, but small enough to allow attack by alkenes and dienes. The parent H_2BPH_2 meets neither of these. Allen and Fink calculated that its lowest energy conformer contains a pyramidal P atom[5b,23] and lies 5.9 kcal mol^{-1} below the conformer with planar phosphorus (a transition state). Its dimerization was predicted to be exothermic by 31.7 kcal mol^{-1}.[24] While the barrier to dimerization has not been reported, test scans of the potential energy surface for the process performed as a peripheral part of this work suggest that it is essentially barrierless. This is consistent with calculations giving the barrier for the dimerization of homologous H_2BNH_2 as 8−10 kcal mol^{-1};[8] the barrier for the phosphinoborane is expected to be substantially lower owing to the greater size of P versus N. At the other extreme, experimentally isolated $R_2BPR'_2$ compounds that contain planar P atoms neither dimerize nor undergo cyclizations with other substrates.[6]

---

(20) For instance, the MPW1K model generally predicts barriers accurately, but predicts too-exothermic reaction energies (see ref 17). Pure DFT models like MPW and PBE generally underestimate barriers (see ref 21).

(21) (a) Lingwood, M.; Hammond, J. R.; Hrovat, D. A.; Mayer, J. M.; Borden, W. T. *J. Chem. Theory Comput.* **2006**, *2*, 740−745. (b) Andersson, S.; Gruening, M. *J. Phys. Chem. A* **2004**, *108*, 7621−7636. (c) Zhao, Y.; Pu, J.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2004**, *6*, 673−676. (d) Guner, V.; Khuong, K. S.; Leach, A. G.; Lee, P. S.; Bartberger, M. D.; Houk, K. N. *J. Phys. Chem. A* **2003**, *107*, 11445−11459. (e) Ren, Y.; Wolk, J. L.; Hoz, S. *Int. J. Mass Spectrom.* **2002**, *221*, 59−65. (f) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2002**, *106*, 842−846. (g) Parthiban, S.; de Oliveira, G.; Martin, J. M. L. *J. Phys. Chem. A* **2001**, *105*, 895−904.

(22) (a) Wiest, O. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; Wiley: New York, 1998; Vol. 4, pp 3104−3114. (b) Wiest, O.; Montiel, D. C.; Houk, K. N. *J. Phys. Chem. A* **1997**, *101*, 8378−8388.

(23) Allen, T. L.; Fink, W. H. *Inorg. Chem.* **1992**, *31*, 1703−1705.

(24) Vogel, U.; Hoemensch, P.; Schwan, K.-C.; Timoshkin, A. Y.; Scheer, M. *Chem.−Eur. J.* **2003**, *9*, 515−519.

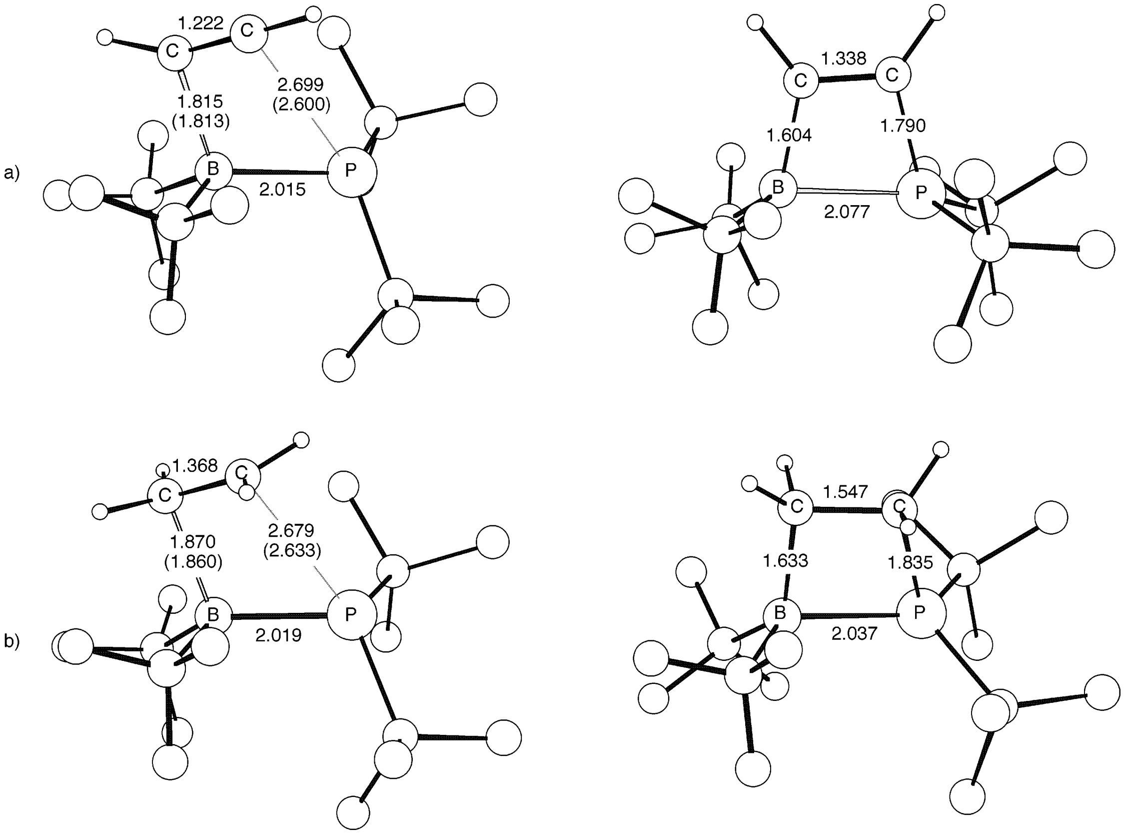

Figure 2. (a) Optimized (MPW1K/BS1, MP2/BS1 in parentheses; bond distances in Å) structures of the transition state (left) and product (right) of [2+2] cyclization between **1** and ethyne. (b) Optimized (MPW1K/BS1, MP2/BS1 in parentheses; bond distances in Å) structures of the transition state (left) and product (right) of [2+2] cyclization between **1** and ethene.

We thus chose to systematically examine the effect of substitution on the structure and dimerization characteristics of a series of phosphinoboranes. The results appear in Table 1. Several points suggest themselves. Qualitatively, multiple bonding should increase with the electron-attracting capacity of the R_2B moiety, which is enhanced by electron-withdrawing R groups. However, fluorine substituents on boron cause greater pyramidalization at phosphorus (compare F_2BPH_2 and H_2BPH_2), indicating that the π donor properties of F toward B outweigh its acceptor behavior.[25] Placing methyl groups on phosphorus has a substantial effect, increasing the planarity of this atom in $H_2BP(CH_3)_2$ by 20° over the parent phosphinoborane. Placing donor groups on boron [$(H_3C)_2BP(CH_3)_2$] or acceptor groups on phosphorus [$H_2BP(CF_3)_2$] has the expected deleterious effect, increasing the energy gap between pyramidal and planar conformers.

Unsurprisingly in view of the above, the "best case scenario" was $(F_3C)_2BP(CH_3)_2$, for which the planar/pyramidal energy gap is predicted to be 0.8 kcal mol^{-1} (Table 1). However, test calculations quickly showed that this compound was unlikely to prove experimentally suitable for cyclization reactions. Its dimerization appears barrierless (as determined by scans of the potential energy surface for decomposition of the diboradiphosphacyclobutane) and is exothermic by 81 kcal mol^{-1}. We therefore explored the effect of sequential substitution of methyl groups for hydrogens on the phosphorus-bound carbon atoms. Surprisingly, the PEt_2 and P(*i*-Pr)$_2$ moieties exhibited geometries around phosphorus very similar to those of the PMe_2 compound. Only the P(*t*-Bu)$_2$ compound combined a sufficiently planar geometry around the P atom with an adequate barrier to dimerization (Table 2) to merit studies of its cyclization behavior.

The predicted structure of $(F_3C)_2$BP(*t*-Bu)$_2$, **1**, appears in Figure 1a. The BP bond distance compares well with those seen experimentally for phosphinoboranes thought to contain BP double bonds, and other bond distances are typical. The only notable aspect other than the planar phosphorus atom is that the C_2B and PC_2 planes are canted at an angle of ca. 23°[26] rather than coincident (Figure 1a, right side). This lowers steric repulsions between the $(F_3C)_2B$ and P(*t*-Bu)$_2$ fragments, at a cost of some overlap of the B and P p-π orbitals. A natural bond order (NBO)[27] calculation (B3LYP/6-311++G(d,p) level) indicates that this cost is not excessive, in that the method predicts the presence of a BP π bond. The natural π bond is composed of 30% boron natural atomic orbitals and 70% phosphorus natural atomic orbitals, denoting its polarity but also the substantial transfer of electron density from P to B. For comparison, using the same model, the BP π bond for the planar transition state of H_2BPH_2 consists of 21 and 79% respectively of boron and phosphorus natural atomic orbitals.

Characterization of bond order from molecular orbital calculations is inherently artificial, since such characterization requires localization of delocalized electron density, and is typically model and basis set dependent. The point of examining

---

(25) We also examined phosphinoboranes with nitro groups on boron. These tended to distort so as to coordinate a nitro oxygen atom to the boron, in accord with the concept of hard Lewis acid boron preferring to bind to a hard Lewis base oxygen rather than the softer phosphorus π cloud.

(26) Determined as the average of the relevant torsion angles since the planes are slightly skewed because the geometry around the phosphorus atom is not perfectly planar.

(27) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, 2001.

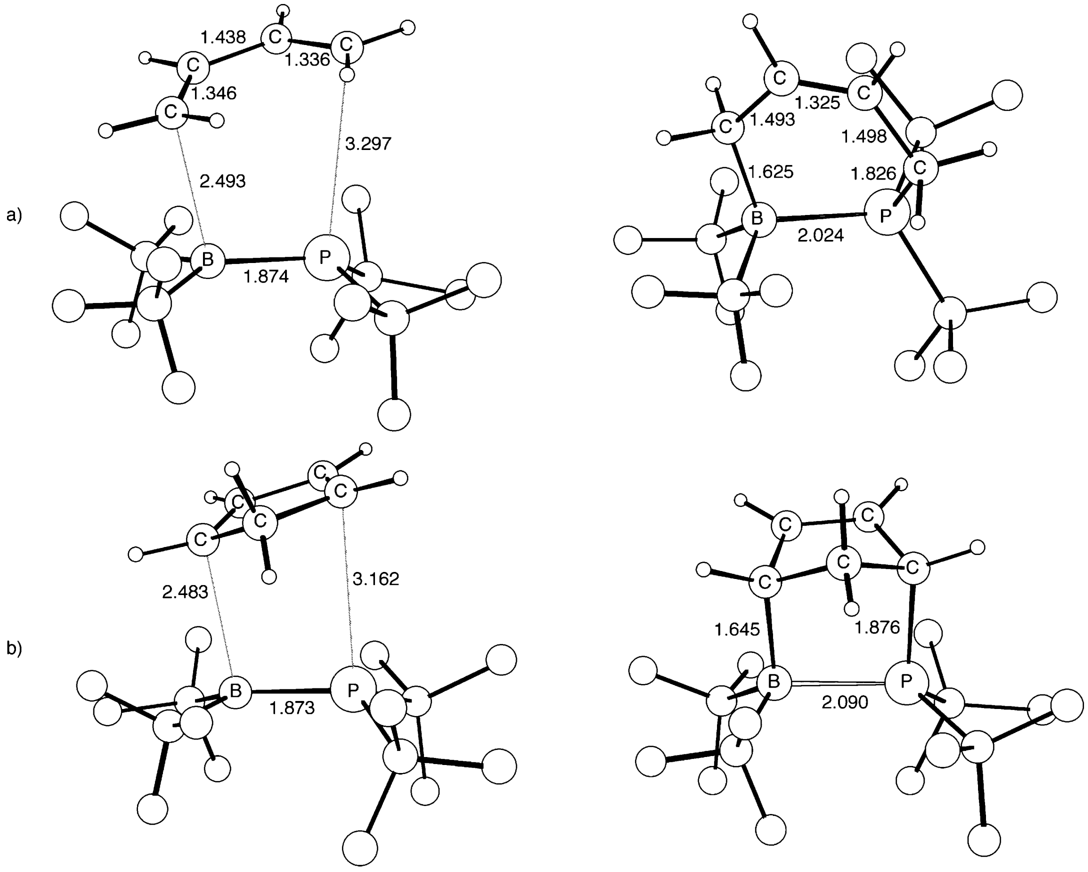

Figure 3. (a) Optimized (MPW1K/BS1; bond distances in Å) structures of the transition state (left) and product (right) of [4+2] cyclization between **1** and *cis*-butadiene. (b) Optimized (MPW1K/BS1; bond distances in Å) structures of the transition state (left) and product (right) of [4+2] cyclization between **1** and cyclopentadiene.

heteroatom “multiple-bond” reactivity is to avoid using theory/model-based means of characterizing multiple bonds. That said, it was of interest to examine how such methods described the B−P bonding in phosphinoborane **1**. The NBO program provides several approaches through the BNDIDX (bond index) and NRT (natural resonance theory) keywords. In general, these indicated bond orders near 2. For instance, the Wiberg method[28] gave a BP bond order of 1.70. For comparison, the BC and PC bond orders were predicted to be 0.90, suggesting that this approach underestimates bond orders of heteroatom bonds. NRT analysis[29] suggested a BP bond order of 1.93, of which 1.42 (74%) is the covalent contribution and 0.51 (26%) is the ionic contribution, with BC and PC bond orders of 0.99 and 0.95, respectively. Thus to the extent these approaches are trustworthy, they support the presence of a BP double bond in **1**.

To estimate the strength of the BP π bond in **1**, we optimized its conformer where the BC2 plane was constrained to bisect the CPC angle (Allen's C_s transition state).[23] This conformer exhibits a pyramidal phosphorus atom, denoting loss of P lone pair → B donation; frequency analysis characterizes it as a transition state for rotation around the BP axis. The MPW1K/BS1 energy of this conformer relative to **1** is 10.6 kcal mol^{-1}, approximating the π bond energy. This agrees with that predicted for H_2BPH_2 (9−10 kcal mol^{-1}),[23,30] but differs somewhat from those determined experimentally from NMR measurements of the barrier to rotation around the BP bond in several phosphinoboranes (17−22 kcal mol^{-1}).[6] It is possible the latter are larger owing to solvent effects; it seems worthy to examine this in future experimental and theoretical work.

The transition state and product of dimerization of **1** appear in Figure 1b, and their associated energetics in Table 2. Dimerization is clearly inhibited by the steric demands of the peripheral substituents, in that the reaction is only modestly exothermic and the barrier is substantial (compared to the other cyclizations). The slight asymmetry of the product reflects asymmetric steric repulsions resulting from asymmetric conformations of the methyl and trifluoromethyl groups, which are probably lost for realistic, room-temperature molecules where the substituents rotate more freely. The fairly long distances (3.118 Å) between the bond-forming boron and phosphorus atoms in the transition state point to this being fairly early along the reaction coordinate; however, the BP bond lengths of the reactants (1.932 Å) are in the range for BP single bonds and 0.15 Å longer than that in **1**, arguing that most of the multiple-bond character is lost upon reaching the transition state.

[2+2] Cyclizations between $(F_3C)_2BP(t\text{-}Bu)_2$ and C_2H_2/C_2H_4. Optimized structures of the reaction components for the title cyclizations appear in Figure 2; reaction energetics are given in Table 2. The heterocyclobutene and heterocyclobutane products show no unusual structural features given the differences in the hybridization of the carbon atoms. It is notable that the B−P distance in the former is 0.04 Å longer than that in the latter; this probably arises as a means for the heterocy-

---

[28] Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083−1096.

[29] (a) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593−609. (b) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 610−627. (c) Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628−646.

[30] Grant, D. J.; Dixon, D. A. *J. Phys. Chem. A* **2006**, *110*, 12955−12962, predict 9.2 kcal mol^{-1} at the CCSD(T)/CBS level.

cloalkene to release excess ring strain not present in the heterocycloalkane. As one sees in Table 2, the cyclizations are extremely exothermic, with formation of the heterocyclobutene more so.

The transition states are both highly asymmetric, to the point where it is questionable that any C−P interaction exists. Moreover, the difference in C−B bond lengths between transition states and products is only ca. 0.2 Å. This suggests that the reactions should be thought of as coordination of the Lewis basic sp or sp^2 carbon to the Lewis acidic boron (or alternatively, asymmetric coordination of the CC π cloud to the boron), followed by ring closure through C−P bond formation. Thus the model indicates that the process is concerted and asynchronous, thereby avoiding the symmetry-forbidden path.

This is borne out by the remarkably small barriers predicted. That for the reaction between **1** and ethyne suggests that cyclization would occur well below room temperature; cyclization with ethene would require slightly more heat. Most importantly, both cyclizations exhibit barriers approximately half that of dimerization, indicating that formation of the carbon-containing rings will be significantly preferred to formation of the diphosphadiborane ring. Thus we predict **1** will exhibit the desired reactivity characteristics.

It is instructive to compare the energetics of these cyclizations with those of aminoboranes. The transition state for [2+2] cyclization between $(F_3C)_2BNMe_2$ and C_2H_4 exhibits asymmetry similar to that above.[8b] However, the aminoborane reaction is predicted to be much less exothermic (-15.3 kcal mol^{-1}; G3-(MP2) level) and to have a far larger barrier (23.8 kcal mol^{-1}). The latter probably results from the greater size of phosphorus versus nitrogen, resulting in greater accessibility of the B−P core to the alkene. Experimentally, what happens when $(F_3C)_2BNMe_2$ is treated with ethene has not been reported. However, treatment of the aminoborane with 1-alkenes provides either acyclic B-alkylated amine−boranes or B-alkylated borane−imines through ene-type rearrangements.[31] Similar reactions between the aminoborane and 1-alkynes give a variety of products depending on specifics,[32] but all appear derived from ene rearrangement transition states, indicating that the barrier to [2+2] cyclization of $(F_3C)_2BNMe_2$ is sufficiently large to force the reactants down other pathways. By contrast, treatment of phosphinoborane **1** with 1-alkynes and 1-alkenes should give isolable heterocycles.

[4+2] Cyclizations between $(F_3C)_2BP(t\text{-}Bu)_2$ and *cis*-C_4H_6/*c*-C_5H_6. For purely organic systems, [2s+2s] cyclizations are symmetry forbidden, while [4s+2s] cyclizations are symmetry allowed. Computationally, this comparison appears in predicted barrier energies that are very large for the former and relatively small for the latter. Since the [2+2] cyclizations above show such small barriers, we considered the possibility that [4+2] cyclizations involving **1** might be barrierless. This was not borne out; in fact, the models predict quite similar energetics overall between the two types (Table 2).

Optimized structures of the reaction components appear in Figure 3. As above, the more strained ring system of the heterobicycloheptene shows a significantly longer B−P bond distance (2.090 vs 2.024 Å). The B−C and P−C distances are the longest of three molecules where the ring carbons are sp^3-hybridized, indicating sizable ring strain. This presumably accounts for why cyclization with cyclopentadiene is the least exothermic predicted.

As above, the transition states are both highly asymmetric, with short C−B and long C−P bond forming distances. Gauged by the B−P bond distance in these as compared to that in **1** (only ca. 0.09 Å longer), both [4+2] transition states lie very early along the reaction coordinate. Again it appears proper to view the process as initial coordination of basic diene electron density to the Lewis acidic boron, with subsequent ring formation as the molecule proceeds down the energy hill. It is interesting to note that the P−C bond-forming distance in the cyclopentadiene case is shorter than that in the butadiene case, although this probably reflects only the lack of conformational flexibility in the substrate.

Aminoborane $(F_3C)_2BNMe_2$ reacts with several dienes in a [4+2] fashion to form azaboracyclohexenes.[33] Intriguingly, despite the efficacy of ene-type reactions noted above, dienes that were also 1-alkenes gave only cyclization products. Computations supported this reactivity, in that cyclization showed a barrier (15.0 kcal mol^{-1}; B3LYP/6-31G(d) level) some 8 kcal mol^{-1} smaller than that for dimerization and presumably smaller than that for ene reactions.[8a] We predict here much smaller barriers for [4+2] cyclizations involving **1**, and so likely greater reactivity with a broader range of dienes. However, since the barriers for [2+2] cyclization are similar or lower, it is possible that the two reactions will compete. As a reviewer noted, all the cyclizations are so exothermic that retrocyclization is implausible (Table 2), so treatment of **1** with *cis*-butadiene, for example, might provide both the heterocyclobutane from [2+2] cyclization and the heterocyclohexene from [4+2] cyclization.

Conclusion

The models predict that phosphinoborane **1** should undergo [2+2] and [4+2] cyclizations easily at ambient temperature. This makes it a target for synthetic chemists interested in probing the reactivity of BP bonds. While preparing **1** may not prove trivial, owing to the difficulties associated with preparing $(F_3C)_2B{-}X$ precursors,[34] its reactivity should reward those who do so. If this proves impossible, similar phosphinoboranes such as $(F_5C_6)_2BP(t\text{-}Bu)_2$ might prove easier to handle and as reactive. Using the perfluorophenyl substituent proved valuable in iminoborane chemistry.[35]

Structurally, **1** should have the characteristics one associates with a BP double bond. It seems, though, that examining the reactivity characteristics of **1** does not allow classification of the bond order, since it should undergo symmetry-forbidden [2+2] and symmetry-allowed [4+2] cyclizations equally well. Both types show considerable asymmetry in their transition states, apparently a result of the sizable Lewis acidity of the trifluoromethyl-substituted boron. This acidity presents a qualitative means for characterizing the bond order: the boron's acidity attracts the phosphorus lone pair in isolated **1**, increasing the BP bond order, but this effect is sufficiently weak that Lewis bases like alkenes and alkynes easily displace the P lone pair in the cyclizations. Overall, though, the problem may prove insoluble: any phosphinoborane reactive enough to allow study of BP bonding through reactivity may contain a BP bond too polar (a boron too acidic) to allow this.

---

(31) Bürger, H.; Hagen, T.; Pawelke, G. *J. Organomet. Chem.* **1993**, *456*, 19−24.

(32) Bürger, H.; Hagen, T.; Pawelke, G. *Main Group Met. Chem.* **1995**, *18*, 235−241.

(33) Ansorge, A.; Brauer, D. J.; Bürger, H.; Dörrenbach, F.; Hagen, T.; Pawelke, G.; Weuter, W. *J. Organomet. Chem.* **1990**, *396*, 253−267.

(34) Pawelke, G.; Bürger, H. *Appl. Organomet. Chem.* **1996**, *10*, 147−174.

(35) Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123−170.

Nonetheless, we encourage synthetic chemists to prepare **1** or similar phosphinoboranes, since they should exhibit a wealth of cyclization chemistry. We plan to expand on these reactivity patterns in future computational work.

Acknowledgment. The NIU Computational Chemistry Laboratory was created using funds from U.S. Department of Education Grant P116Z020095 and is supported in part by the taxpayers of the State of Illinois. We thank the GridChem portion of the TeraGrid consortium (www.gridchem.org) for an allocation of computing time.

Supporting Information Available: Optimized Cartesian coordinates (various models) of all molecules in Tables 1 and 2, with absolute energies. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070002T