JOC Article

G3(MP2) Ring Strain in Bicyclic Phosphorus Heterocycles and Their Hydrocarbon Analogues

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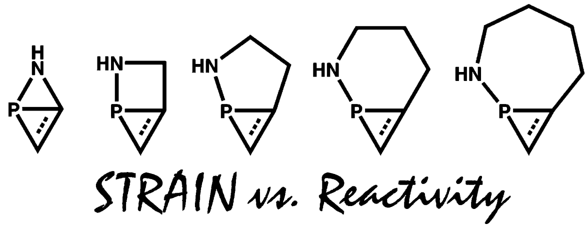

The ring strain present in 2-aza-1-phosphabicyclo[*n*.1.0]alka(e)nes ($n = 1{-}5$) is calculated at the G3(MP2) level using homodesmotic reactions. The influence of cyclopropa(e)nation and heteroatom substitution is analyzed by a comparison with the corresponding bicyclic hydrocarbons and separate ring systems. It is shown that the strain caused by fusion with a cyclopropane is the sum of the separate rings, whereas the strain resulting from fusion with cyclopropene leads to strain energies much larger than the sum of rings, as a result of the inverted nature of the bridgehead carbon. In all ring structures but one, cyclohexane, substitution by nitrogen and phosphorus is favorable and the effect is most pronounced for the most condensed structures. The calculated strain energies correlate very well with the experimental stability and reactivity of the bicyclic iron-amino phosphirane and phosphirene complexes.

Introduction

Phosphorus-containing rings are undergoing a rejuvenation with the recent discoveries of stable 2,4-diphosphacyclobutane-1,3-diyls,[1,2] their diboradiphospha analogues,[3] and *P*-heterocyclic carbenes.[4] Addition of electrophilic phosphinidenes to unsaturated bonds[5] is a powerful method to obtain such small rings as in 2,3-dihydrophosphasiletes,[6] phospha[3]radialanes,[7] and 7-phosphatriangulane.[8]

Strain is often invoked to explain the stability and/or reactivity of these ring structures. Using homodesmotic reactions[9] accurate theoretical estimates can be obtained for strain energies that compare well to experimentally determined values. Significant efforts have been devoted to obtain strain energies for three- and four-membered (un)saturated heterocyclic rings, but relatively little is known about bicyclic structures.[10−14] In our continuing quest for novel systems we now present ring strain

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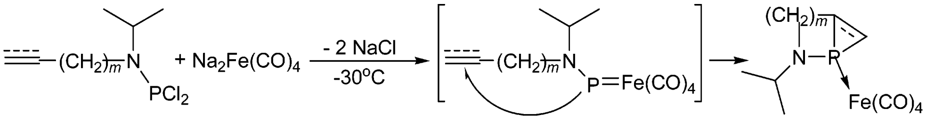
10.1021/jo0513010 CCC: $30.25

SCHEME 1. Intramolecular Phosphinidene Addition Leading to 2-Aza-1-phosphabicyclo[*n*.1.0]alkanes 4 (*n* = 3−5) and 2-Aza-1-phosphabicyclo[*n*.1.0]alkenes 5 (*n* = 4, 5) at −30°C (*m* = *n* − 1)

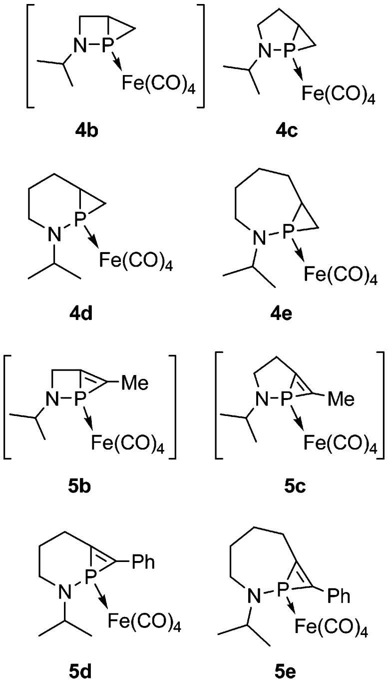


1 **2** **3** **4-5**

energies for phospha[*n*.1.0]bicycloalka(e)nes and the corresponding hydrocarbons.

Recently, we reported a homologous series of bicyclic iron-amino phosphirane (**4**) and phosphirene (**5**) $\mathrm{Fe(CO)_4}$ complexes that were synthesized by the intramolecular addition of transient phosphinidene complex $[\mathrm{R}^i\mathrm{PrNP{=}Fe(CO)_4}]$ (**3**) to unsaturated bonds (Scheme 1).[15] The in situ generation of phosphinidene complex **3** by the anionic reaction of a dichlorophosphane (**1**) with Collman's reagent (**2**)[16] is one of the few methods to gain access to these highly reactive phosphorus complexes.[17] The series shown in Chart 1 displays a remarkable diversity in stabilities. Compounds **4d** and **5e** are crystalline, **4c** is a distillable oil, **4e** and **5d** are unstable oils, and **4b** and **5b,c** could not be isolated or observed. Given the ease of retroaddition of the simpler monocyclic phosphirane $\mathrm{Fe(CO)_4}$ complexes,[18] the stability of **4c,d** and **5e** is surprising, but their ability to undergo retroaddition to regenerate the transient phosphinidene complex could be shown by reacting them with alkynes, thus revealing dynamic behavior. The reactivity toward phenylacetylene, giving $\mathrm{Fe(CO)_4}$-complexed phosphirenes, differs markedly, with phosphirane **4d** reacting about 30 times faster than the smaller **4c** (k_{obs} 2.9×10^{-4} $\mathrm{s^{-1}}$ vs 9.7×10^{-6} $\mathrm{s^{-1}}$) and much faster than phosphirene **5e** (k_{obs} of 5.2×10^{-7} $\mathrm{s^{-1}}$). Nevertheless, the formation of bicyclic **4** and **5** is surprising as *inter*molecular cycloaddition might be a viable alternative that could lead to oligomeric or polymeric materials.

CHART 1. Bicyclic Phosphiranes and Phosphirenes[a]



[a] Compounds in brackets could not be isolated.

We report on the high-level ring strain energies of these 2-aza-1-phosphabicyclo-[*n*.1.0]alkanes and -alkenes (*n* = 1−5), simplified by removing the metal group and the amino substituent from **4** and **5**, which are then denoted with capital letters. The heterocyclic bicyclo[1.1.0]butane (**4A**) and -butene (**5A**) are part of this study aimed to quantify the strain effect of ring fusion on the three-membered heterocycles and to rationalize the experimentally observed stability/reactivity of **4** and **5**. Whereas ring strain reflects the energy released by breaking up the cyclic system into strain-free components, we presume that it also relates to the reactivity of bicyclic structures. Specifically, although the addition of $[^i\mathrm{PrNPFe(CO)_4}]$ to ethylene is estimated to be exothermic by 9.4 kcal/mol, the reaction has a barrier of only 6.2 kcal/mol (BP88/TZP).[18] It is then reasonable to assume that the rate of retroaddition of **4** and **5** relates to the magnitude of their ring strain energies. A larger ring strain destabilizes the heterocycle with respect to the phosphinidene and would imply an easier release of the phosphinidene moiety.

Computational Details

All calculations were performed using the GAUSSIAN 98 suite of programs.[19] Structures were optimized with density functional theory using Becke's three-parameter hybrid exchange functional[20] and the Lee et al. correlation functional[21] (B3LYP) and verified as minima by frequency calculations. All strain energies were determined by calculating the G3(MP2)[22] enthalpy at 298.15 K for the homodesmotic reaction[9] involving

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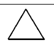
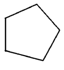
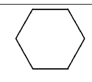
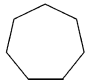
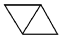
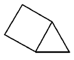
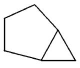
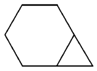
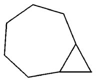
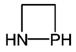
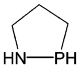
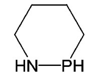
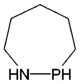
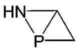
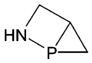
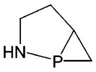
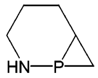
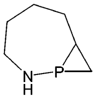
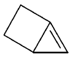
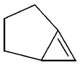
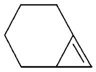
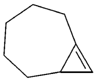
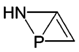
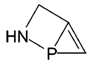
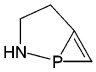
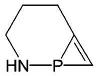
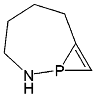
TABLE 1. G3(MP2) Strain Energies (in kcal/mol) for Bicyclo[*n*.1.0]alkanes, Bicyclo[*n*.1.0]alkenes, and Monocycles

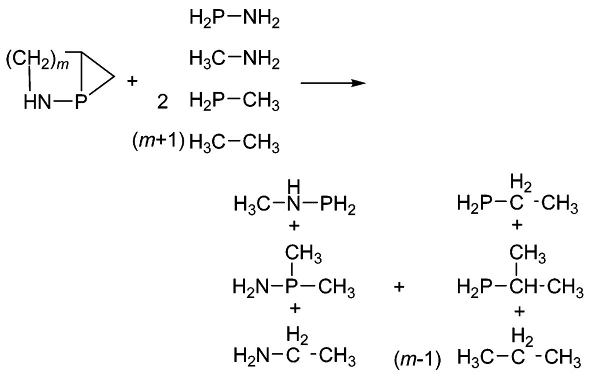
					
	8A	**8B**	**8C**	**8D**	**8E**
SE	28.4[b]	26.7	6.5	chair: 0.6 boat: 6.8	6.7
					
	6A	**6B**	**6C**	**6D**	**6E**
SE	68.1[c]	56.7	32.7	32.2	31.6
ESE	11.3	1.6	-2.2	3.2	-3.5
					
	9A	**9B**	**9C**	**9D**	**9E**
SE	26.5[b]	23.1	5.1	1.1	5.2
SSE	-1.9	-3.6	-1.5	0.5	-1.5
					
	4A	**4B**	**4C**	**4D**	**4E**
SE	57.7	45.5	27.0	28.0	30.8
ESE	9.8	0.9	0.6	5.5	4.2
SSE	-10.4	-11.2	-5.7	-4.2	-2.6[d]
					
	7A	**7B**	**7C**	**7D**	**7E**
SE	101.3	114.0	75.9	62.6	58.2
ESE	16.9	31.3	13.4	6.0	-4.5
OS	33.2	57.3	43.2	30.4	26.6
					
	5A	**5B**	**5C**	**5D**	**5E**
SE	92.3	91.1	58.1	46.0	39.6
ESE	26.8	29.0	14.1	6.0	-4.6
OS	34.6	45.6	31.1	18.0	8.8
SSE	-9.0	-22.9	-17.8	-16.6	-18.6

[a] ESE is excess strain energy, OS is olefinic strain, and SSE is substitution strain energy. [b] Reference 12. [c] Reference 10. [d] Note 35.

the ring structure. Structural parameters of the calculated compounds refer to geometries optimized at the MP2(full)/6-31G(*) level, generated as part of the G3(MP2) calculation.

Results and Discussion

The G3(MP2) ring strain energies of the [*n*.1.0]bicyclic structures **4A**−**E** and **5A**−**E** are calculated using homodesmotic[9] equations (eqs 1 and 2) where $m = n - 1$. The strain energies of the corresponding hydrocarbons, the bicyclo[*n*.1.0]alkanes **6** and the bicyclo[*n*.1.0]alkenes **7**, are calculated in the same manner. Finally, for proper evaluation, we include the strain energies for the monocyclic hydrocarbons **8** and the heterocyclic rings **9** with a ring size of 3 to 7. The molecular graphs and energies are summarized in Table 1. This table also lists the excess strain energy (ESE),[14] which is the difference between the strain energy of a polycyclic compound and that of its separate composite rings, and the olefinic strain (OS),[23] which is the difference in strain energy between the unsaturated and saturated analogue. In this table is further listed the substitution strain energy (SSE), which we define as the difference in strain energy between the heterosubstituted system and its hydrocarbon analogue. As expected, the calculated strain energies (SE) of **6A**−**E**, **7B** and **8A**−**E** agree well with earlier reported computational and experimental data.[24,25] The MP2(full)/6-31G* optimized structures for **4A**−**E**, **5A**−**E**, **6A**−**E**, and **7A**−**E** are shown in Table 2.



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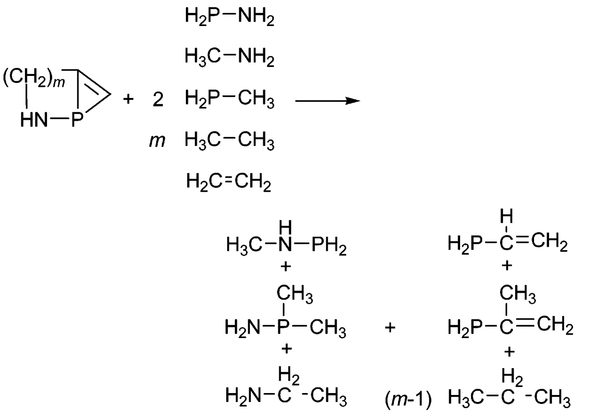

(2)

The influence of cyclopropanation will be discussed first for the saturated hydrocarbons by comparing the strain

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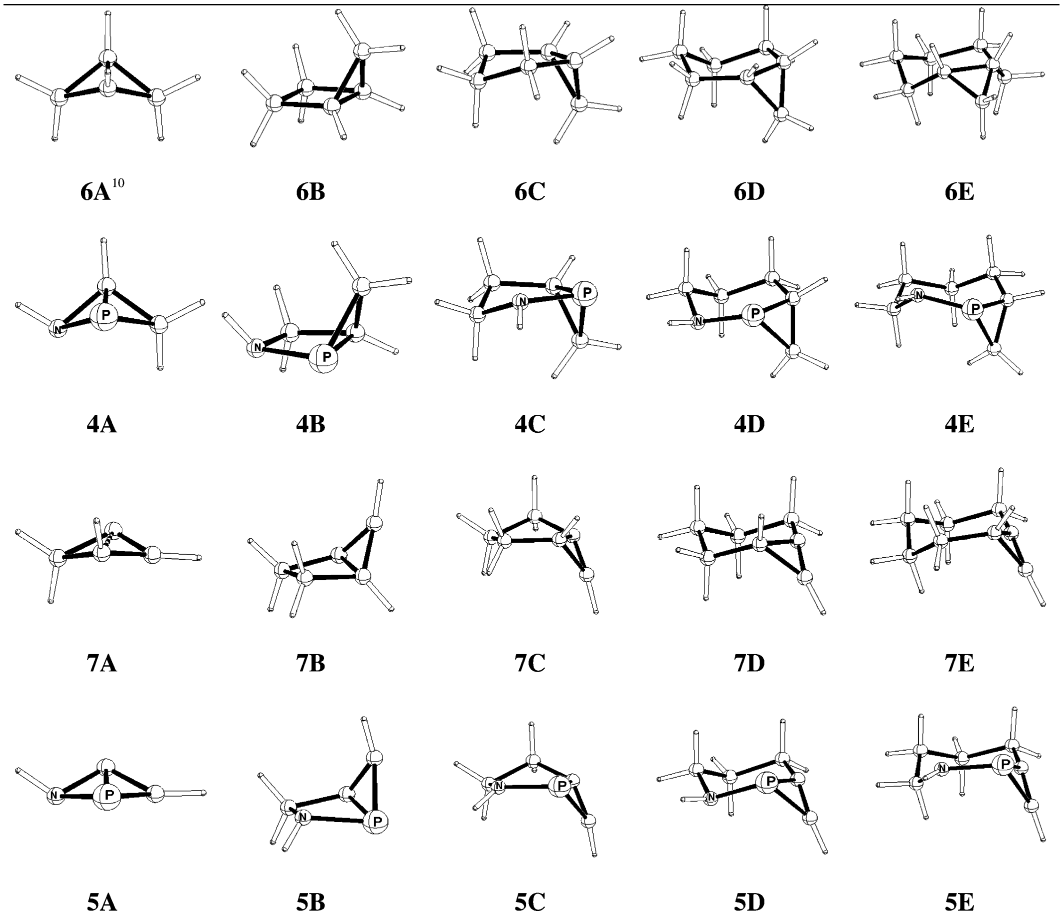
TABLE 2. MP2(full)/6-31G* Optimized Structures for Phosphiranes 4, Phosphirenes 5, and Their All-Carbon Analogues



energies of the cycloalkanes **8** with those of the bicyclic structures **6**, followed by an evaluation in the same manner of the effect of replacing a CH_2CH unit for an isovalent NHP unit in the heterobicyclic structures **4**. A similar procedure will be followed in the second section to delineate the strain in the unsaturated structures **5**. These analyses will be balanced against available experimental data.

Saturated Bicyclic Structures. Hydrocarbons. The strain energies of the cycloalkanes **8** show the established features.[24] The chair conformation of cyclohexane **8D** is virtually strain-free (0.6 kcal/mol) and 6.8 kcal/mol more stable than the boat form. The puckered five- and seven-membered rings are equally strained by, respectively, 6.5 and 6.7 kcal/mol, and this is also the case for cyclopropane **8A** (28.4 kcal/mol) and cyclobutane **8B** (26.7 kcal/mol). Cyclopropane has more angle-strain than cyclobutane[10,26] as a result of its more strained carbon atoms[27] but also has more σ-delocalization[28,29] and less eclipsing interactions.

Spiroannulating two rings usually increases the strain over that of the two separate rings, which is expressed in the excess strain energy (ESE). This additional strain is caused by the introduction of a second small valence angle for the spiro atom, which cannot be compensated for by rehybridization.[10] Cyclopropanating the cycloalkanes (series **6**) forces *two* atoms to have smaller valence angles but also reduces the eclipsing interaction for the larger rings and rehybridization is still possible. As a result, only bicyclo[1.1.0]butane **6A** has a large ESE of 11.6 kcal/mol, which results from angle-strain and additional 1,3-nonbonded interactions.[14a] These effects are far less pronounced in the larger bicyclo[2.1.0]pentane (**6B**, ESE 1.6 kcal/mol). Bicyclo[3.1.0]cyclohexane (**6C**) has even a *negative* ESE of 2.2 kcal/mol, because two of the eclipsing hydrogens in the cyclopentane ring are removed upon fusion with the cyclopropane ring. This effect also underlies the negative ESE of bicyclo[5.1.0]-octane **6E**. Cyclopropanating cyclohexane leads to a positive ESE of 3.2 kcal/mol (**6D**), because fusion causes the cyclohexane ring to adopt a half-boat conformation.

Heterobicyclic Structures. The increase in angle strain that results on nitrogen substitution is balanced by the decrease in strain resulting from phosphorus substitution, because this latter element is able to

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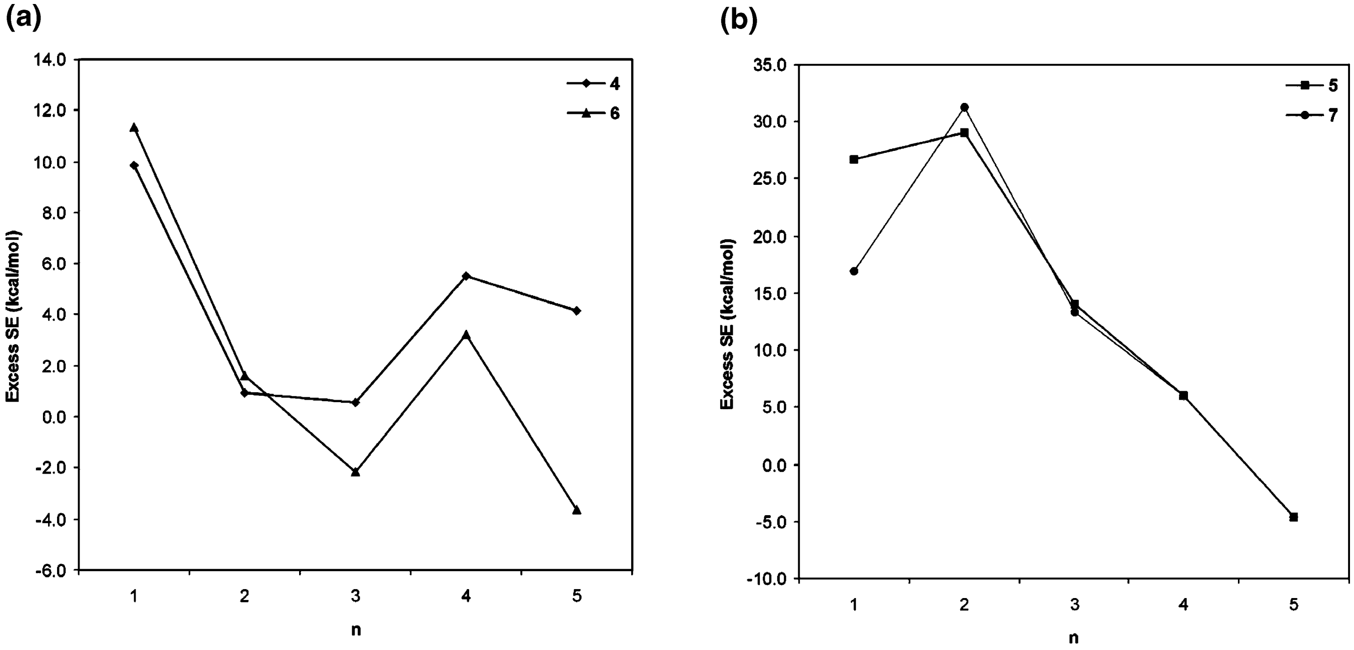

FIGURE 1. Excess strain energy (in kcal/mol) for (a) the 2-aza-1-phosphabicyclo[*n*.1.0]alkanes (**4**) and their hydrocarbons analogues (**6**) and (b) the 2-aza-1-phosphabicyclo[*n*.1.0]alkenes **5** and their hydrocarbon analogous **7**.

accommodate much smaller angles than carbon. Moreover, the number of (possibly) eclipsing hydrogens is reduced. Consequently, N,P-substitution of the cycloalkanes is seen to result in small negative substitution strain energy (SSE) values that show the 2-aza-1-phosphacycloalkanes **9** to be slightly less strained than their hydrocarbon analogues. The exception is cyclohexane, for which the heterocyclic ring is slightly more strained (+0.5 kcal/mol) as a result of the adjustment of the ideal bond angles and the absence of eclipsing hydrogens in cyclohexane.

Both effects, the cyclopropanation and the N,P-substitution, are present in the 2-aza-1-phospha-bicycloalkanes **4A**−**E**. Figure 1a graphically displays the relationship of the excess strain energy with ring size for both bicyclic systems **4** and **6**. Electronegative elements adjacent to a three-membered ring, in the present case nitrogen, reduce the surface density and therefore diminish σ-delocalization,[10] which explains why **4C**−**E** have larger ESE[30] values than their hydrocarbon analogues **6C**−**E**. These ESE values for the smallest heterobicyclic rings **4A,B**, however, are smaller than those for the corresponding hydrocarbons **6A,B**, because the smaller bond angles are better accommodated by the bridgehead phosphorus, which is corroborated by the smaller SSE values on increasing the ring size. This favorable influence of a bridgehead phosphorus can be illustrated by comparing bicyclo[1.1.0]butane **4A** (SE 57.7 kcal/mol) with the even more strained 2-aza-bicyclo[1.1.0]butane **10** (SE 74.9 kcal/mol, not displayed) where only the phosphorus atom is replaced for a carbon.[10] Specifically, the sizable ESE of **4A** almost doubles in **10** (9.8 vs 18.3 kcal/mol, respectively) and likewise the large negative SSE for **4A** becomes a positive one in **10** (−10.4 vs +6.8 kcal/mol, respectively).

Thus, the least strained structure of the series is the five-membered ring containing bicyclo[3.1.0]hexane **4C** (27.0 kcal/mol), although the one-carbon-larger bicyclo[4.1.0]heptane **4D** is only 1.0 kcal/mol more strained despite its larger ESE (Δ 4.9 kcal/mol), while the difference with bicyclo[4.1.0]octane **4E** is more (ΔSE 3.8 kcal/mol). Interestingly, the ESE for this structure is 7.7 kcal/mol larger than that for hydrocarbon **6E**. The opposite trend in strain energies is seen for the corresponding hydrocarbons of which the largest one (**6E**) is the least strained. Thus, N,P-substitution reverses the ring strain order of the hydrocarbons from **6C** > **6D** > **6E** to **4C** < **4D** < **4E** for the heterobicyclic structures.

Comparison with Experimental Data. The calculated SE values of bicyclic phosphiranes **4B**−**E** correlate exceptionally well with the reported experimental data[15] for phosphiranes **4**. The most strained heterocyclic compound **4b** could indeed not be synthesized, and that of **4a** was not even attempted. Both larger bicyclic systems **4c** and **4d** have been isolated as stable compounds, being apparently the least strained ones, which is in accordance with the calculations on the simpler models. The difference in reaction rates of these systems concurs with the calculation of the 2-aza-1-phosphabicyclo[4.1.0]hexane frame (**4c**) as the least strained of the two, as the larger bicyclo[4.1.0]heptane **4d** reacts 30 times faster with phenylacetylene than bicyclo[3.1.0]hexane **4c** does. The slightly more strained **4e** (SE = 30.8 kcal/mol) has been isolated but does not survive purification procedures. Apparently, this molecule is more strained, which again is in accordance with the calculated strain energies.

Unsaturated Bicyclic Structures. This section starts again with an evaluation of the hydrocarbons before discussing the N,P-containing unsaturated bicyclic structures.

Hydrocarbons. Fusion of a cycloalkane with a cyclopropene instead of a cyclopropane ring is expected to introduce considerably more strain, and this is confirmed by the calculated strain energies, excess strain energies,[31]

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[30] From ref 10: SE = 21.4 kcal/mol for the parent phosphirane.

SCHEME 2. Resonance Stabilization of (a) Bicyclo[1.1.0]butene 7A and (b) Heterobicyclic 5A

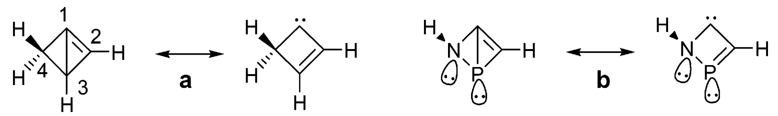

TABLE 3. Strain Energies (kcal/mol) and Bond Angles (deg) around the Bridgehead Olefinic Carbon (e.g., ∠C3−C1−C4, Scheme 2a)

		7				5			
compd	n ring	SE	OS	Σ angles	angle	SE	OS	Σ angles	angle
A	1	101.3	33.2	200.3	52.2	92.3	34.6	217.7	58.2
B	2	114.0	57.3	292.0	95.2	91.1	45.6	291.4	96.2
C	3	75.9	43.2	320.9	114.5	58.1	31.1	327.4	115.6
D	4	62.6	30.4	347.4	129.2	46.0	18.0	346.2	131.4
E	5	58.2	26.6	357.0	139.8	39.6	8.8	356.9	141.7
cyclopropene		56.0	27.6	360.0	150.0	39.0	17.6	360.0	146.0[36]

and olefinic strains of the bicyclo[n.1.0]alkenes **7** (n = 1−5) that are listed in Table 1. This, of course, is due to the unsaturated bridgehead carbon that has "inverted" sp^2 character[32] with limited rehybridization options.

The smallest member of the series, bicyclo[1.1.0]butene **7A**, has an expectedly large strain energy of 101.3 kcal/mol, which is nevertheless a surprisingly 12.7 kcal/mol less than that for the larger bicyclo[2.1.0]-pentene **7B**. This difference is even more pronounced in the olefinic strain, which for **7A** is much smaller than that for **7B** (33.2 vs 57.3 kcal/mol) and more comparable to that of the parent three-membered cyclopropene (27.6 kcal/mol). Bicyclo[1.1.0]butene is clearly stabilized, which is also reflected by the short C2−C3 bond (1.436 Å), the elongated C1−C3 distance (1.788 Å), and the large puckering angle (145°) for the bicyclic frame, all of which point to a strong contribution of the vinyl carbene mesomeric form (see Scheme 2a). This stabilization reflects the established electron delocalization that underlies the relationship between cyclopropenes and vinyl carbenes.[33]

Bicyclo[2.1.0]pentene **7B** is a more conventional bicyclic structure with normal C=C (1.324 Å) and transannular C−C bond lengths (1.502 Å). Yet the olefinic bridgehead carbon is significantly pyramidalized (Σ angles 292.0°) and the olefinic bond is therefore twisted, which is the origin of the large olefinic strain (57.3 kcal/mol). The next larger member of the series, bicyclo-[3.1.0]hexene **7C**, is expected to be less strained, and this is indeed the case (SE 75.9 kcal/mol), even though the olefinic strain (43.2 kcal/mol) remains substantially larger than for cyclopropene. On further enlarging of the aliphatic ring, the strain reduces still more but to a smaller degree as illustrated by the OS value, which for bicyclo[4.1.0]heptene **7D** (SE 62.6 kcal/mol) is only 2.8 kcal/mol more than for cyclopropene (27.6 kcal/mol) and even 1.0 kcal/mol less for bicyclo[5.1.0]octene (SE 58.2 kcal/mol). These data comply with experimental data in the literature that report compound **7d** to react already at −90 °C, whereas **7e** is persistent for several hours at room temperature.[34] In summary, the strain of the bicyclo[n.1.0]alkenes relates to the olefin strain and thus to the pyramidalization of the bridgehead olefinic carbon, which is linked to the olefinic angle of the larger ring (Table 3).

Heterobicyclic Structures. With the bridgehead phosphorus and its neighboring nitrogen present in the bicyclic frame, as in **5**, the strain for each member is less than that of the all-hydrocarbon homologue (**7**), as expected (see above), but the excess strain energies (ESE) are remarkably similar for both systems (Table 1), as graphically displayed in Figure 1b. This strongly suggests that bond-angle strain is also the determining factor for the heterobicyclic structures and hence the olefinic strain and thus the pyramidalization of the olefin carbon (Table 3). We discuss specific aspects.

The smallest member, 2-aza-1-phospha-bicyclo-[1.1.0]-butene **5A** (n = 1), is deformed, like **7A**, to reduce its otherwise excessive strain energy. Electron delocalization is evident from the elongated C=C (1.421 vs ca. 1.31 Å for **5C**−**E**) and transannular C−P bonds (2.088 vs 1.82 Å for **5C**−**E**) and the shortened peripheral C−P bond (1.804 Å) that suggests double bond character. These features are indicative of the mesomeric contribution of carbene phospha-alkene form (Scheme 2b). Compared to the OS of 1*H*-phosphirene (17.6 kcal/mol),[12] that of **5A** is large (34.6 kcal/mol), yet much smaller than that of the larger bicyclic phosphirene **5B** (45.6 kcal/mol), which underscores the stabilization that results from electron delocalization. Whereas these structures have similar strain energies, bicyclic phosphirene **5B** (SE 91.1 kcal/mol) is more condensed than **5A** (SE 92.3 kcal/mol) as a result of the stronger interaction between the phosphorus atom and the pyramidal bridgehead olefinic carbon (1.791 Å). Because of its condensed nature, bicyclo[2.1.0]pentene **5B** gains the most by N,P-substitution (SSE −22.9 kcal/mol) of the series. Yet also the high strain in this structure can be released in part, like **4A**, by cleaving the relative weak P−C bond (2.672 Å) to give

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(31) The strain energy of the bicyclic systems **7** and **5A**−**E** cannot be compared directly to cyclopropene and 1*H*-phosphirene, respectively, and the corresponding cycloalkane **8**, because the latter lacks the sp^2 carbon present in the fused system. Therefore, calculation of excess strain based on these structures can only serve as an indication.

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(35) The lowest-energy conformations of **6E** and **4E** are different. To obtain a "proper" SSE, the same conformers were compared. For **6E** this conformer is 1.8 kcal/mol less stable than the one that is displayed and used for calculating the SE and ESE values. See Supporting Information for details.

(36) Based on the ideal CPC phosphirene angle of 44°, cf. Mathey, F. *Chem. Rev.* **1990**, *90*, 997−1025.

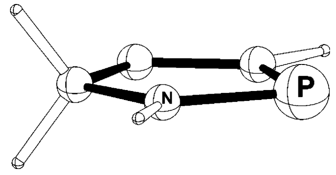
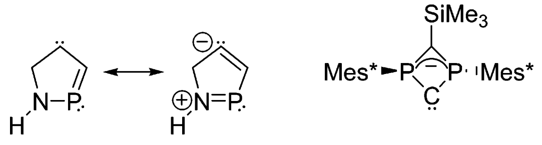


FIGURE 2. Planar isomer **5B′** of 2-aza-1-phosphabicyclo-[1.1.0]butene.

SCHEME 3. Planar Isomer 5B′ of 2-Aza-1-phosphabicyclo[1.1.0]butene and 11



5B' **11**

the 23.2 kcal/mol more stable planar isomer **5B′** (SE 67.9 kcal/mol, Figure 2), thereby indicating that the bicyclic structure is not likely to be observed experimentally. Resonance stabilization of **5B′** is suggested by the elongated C=C bond (1.394 Å), the shortened P−C bond (1.751 Å), and the planar nitrogen. Structure **5B′** is then best described as a hybrid of a phospha-alkene carbene and a mesomeric azaphosphole carbene that shows similarities with the recently developed carbenes by Bertrand[4] and Niecke's 1,3-diphosphacyclobutane-2,4-diyl-2-ylidenide **11**[1c] (Scheme 3). A similar planar structure for **5A** is not feasible and represents, in fact, the transition (E_a = 11.9 kcal/mol) for inversion of the puckered form.

Enlarging the cycloalkane ring reduces its bridgehead CCP-angle and consequently the strain energy (Table 3). 2-Aza-1-phospha-bicyclo[1.1.0]hexene **5C** is a large 33.0 kcal/mol less strained than **5B** and even 12.1 kcal/mol more for the next larger homologue **5D** that has a phosphirene fused to a six-membered ring. The SE for the next larger bicyclic **5E** is still further reduced (by 6.4 kcal/mol) to become virtually the same as 1*H*-phosphirene itself.[12] This significant decrease in SE for this series of structures **5C** > **5D** > **5E** contrast that of the saturated series **4C** < **4D** < **4E** and reflects the energetic cost of "inverting" an sp^2 hybridized carbon or in other words twisting an olefinic carbon (Table 3). This behavior mimics that of the all-hydrocarbon series **7** as underlined by the similar N,P-substitution effect (SSE values, Table 1).

Comparison with Experimental Data. The calculated ring strain energies of the bicyclic phosphirenes **5C**−**E** are in excellent agreement with the reported experimental data.[15] Assuming that high SE values reduce the structural accessibility and viability, it is clear why the smallest phosphirene complexes **5b**,**c** could not be synthesized. It is equally clear that of the two compounds that could be obtained, **5e** is more stable than **5d** and indeed the latter could not be obtained in pure form. That **5e** reacts slowly with phenylacetylene is also in line with expectations, considering that **5E** is more strained than 1*H*-phosphirene, indicating a slight preference for intermolecular cycloaddition.

Conclusions

G3(MP2) calculations show the ring strain energies (SE) of the bicyclo[*n*.1.0]alkanes (**6**) with $n = 2-5$ to be similar to that of the sum of the separate rings, and this is also the case on replacing $CHCH_2$ for the isovalent PNH unit (**4**). Of course, the heterobicyclic structures are strained less than the hydrocarbons, as reflected in negative substituent strain energy (SSE) values, which become smaller on enlarging one of the rings. The bridgehead phosphorus atom accommodates small valence angles better than carbon, which is quite evident in the much more strained bicyclo[1.1.0]butanes **4A** and **6A**.

The strain energies for the unsaturated series of bicyclo[*n*.1.0]alkenes are larger than the sum of the separate rings, both for the hydrocarbons **7** and the heterocyclic structures **5** except for the largest member with $n = 5$. On enlarging one of the rings the strain energy decreases monotonically. The smaller members are extremely strained as a result of the "inverted" nature of the bridgehead carbon that causes twisting of the C=C bond. For both bicyclo[1.1.0]butene structures **7A** and **5A** this brings about a weakening of the transannular bond to enable stabilization by a vinyl carbene resonance structure. This also occurs in the dihetero analogue of bicyclo[2.1.0]pentene (**5B**) to give a 23 kcal/mol more favorable monocyclic form that is likewise stabilized by a vinyl carbene resonance form.

The calculated strain energies for the model 1-aza-1-phospha-bicyclo[*n*.1.0]alkanes and -alkenes correlated exceptionally well with the reported experimental data on the $Fe(CO)_4$-complexed derivates, not only with respect to the isolated compounds but also with respect to their observed reactivities.

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Supporting Information Available: Calculated energies and *x*,*y*,*z*-coordinates of the species discussed. This material is available free of charge via the Internet at http://pubs.acs.org.

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