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Distinct π-Bonding Capability between Phosphinidene and Phosphonium Ion: A Computational Study†

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The heavy dipnictenes (RE═ER, where E = P, As, Sb, and Bi with the substituent R) have essentially planar geometry and appreciable strength in π-bonding, unlike related heavier main group 14 analogues of alkenes as concluded recently by Power. This work demonstrated that the protonated pnictenes behave more like the heavy carbene for their weak π-bonding character from the computational study with the B3LYP/6-311++G** method. For example, although both phosphinidene (HP) and the phosphonium ion (H_2P^+) are isoelectronic to silylenes, the π-bonding tendency of the former is rather strong and it forms a planar adduct with both the stable carbene and stable silylene ($(HCNH)_2E$, where E = C and Si). In contrast, the latter forms trans-bent adducts with the two species. These results can be interpreted in terms of the Carter−Goddard−Malrieu−Trinquier (CGMT) model, and the fact that the value of ΔE_{ST} [E(triplet) − E(singlet)] of the HP fragment increases significantly after protonation. All other heavy pnictenes resemble the phosphinidene. In contrast, nitrene (HN) and nitrenium (H_2N^+) have a ground triplet state, thus both have strong π-bonding character similar to that of carbene.

Introduction

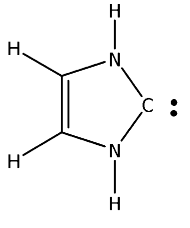
The development of the chemistry of multiple bonded systems involving elements in higher periods is generally regarded as a renaissance of main group chemistry.[1−15] In particular, the low-coordination chemistry of the group 15 elements has been extensively developed in the past decade owing to the use of sterically demanding substituents.[16−18] Among the many stable multiple bond systems which have been successfully characterized, compounds with π-bonds to phosphorus were among the first stable species to be synthesized.[19−23] For the heavier dipnictenes, there are five structurally characterized molecules with As═As double bonds[24−29] and three with Sb═Sb double bonds.[24,30] Through the elegant studies performed by Tokitoh et al.[30] and Power et al.,[24] kinetically stabilized molecules bearing a Bi═Bi double bond, dibismuthenes, have been synthesized and fully characterized. The bonding of these heavy dipnictenes related to that of heavy alkenes is conceivable through the isolobal relations.

Some interesting comments made by Power et al.[24] have stimulated the direction of the present study. They pointed out that the stable dipnictene compounds, unlike related heavy main group 14 analogues of alkenes, bear considerable structural similarity to their lighter, congeneric dimines, diphosphenes, and diarenes. They generally exhibit a planar, trans geometry with E═E bonds shorter by 6−7% than the corresponding single bonds. The π-bonding is quite appreciable in strength even in the fifth and sixth periods. The only notable structural difference is the reduction in the bond angle ∠CEE (in CEEC array) from 113.6(2)° with E = N to 100.5(2)° with E = Bi.

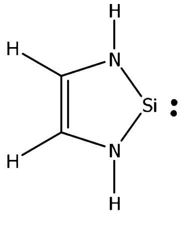
The focus of this study concerns the change in such π-bonding character of the pnictenes after protonation. The number of studies is relatively small on this type of cationic tricoordinate tetravalent species.[31−37] We will focus on the phosphonium ion R_2P^+ for some available information from previous studies. Phosphonium has a unique position in that its π-bonding character is qualitatively representative for the heavier analogues, but in great contrast with the lighter nitrenium ion (R_2N^+).

From previous studies on doubly bonded P═C and P═Si compounds,[38−40] we note that some examples which illustrate that phosphindene (RP) and phosphonium (R_2P^+) have important difference in π-bonding capability. Scholler[38] et al. showed the planar structure for $HPCH_2$ and $HPSiH_2$ from MCSCF calculation. Frison and Sevin[39] reported that the adduct between the stable carbene $(HCNH)_2C$: and PH is planar from B3LYP/6-31G* calculation. Arduengo et al.[40] found that there is some twist from planar structure in the adduct between the imidazol-2-ylidene and alkyl-or aryl-substituted phosphindene. The corresponding PC bond length is about 4% shorter than that of the P−C single bond from the X-ray structure determination. In contrast, Pietschnig[41] showed that the adduct between diamino silylene and phosphonium (R_2P^+, where R = NH_2) adopts a pyramidal geometry at phosphorus.

We would like to compare the simplest models, HP and H_2P^+, in their π-bonding capability with the same bonding partners. We will examine the geometries of their adducts with either stable carbene **(A)** or stable silylene **(B)**. According to the CGMT model,[42,43] the value of $\Sigma\Delta E_{ST}$ of the two bonding fragments dictates the existence of nonclassical distortion for



(A)



(B)

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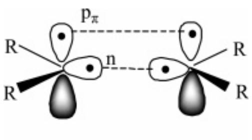
the adduct. Therefore **A** and **B**, with large ΔE_{ST}, 83.42 and 60.19 kcal/mol, respectively, can provide some stringent tests for their bonding partners. We also consider other carbenoid moieties CH_2, SiH_2, NH, and NH_2^+ for comparison.

The ΔE_{ST} for a carbenoid moiety AR_2 here is the quantity of E(triplet) $-E$(singlet), the promotion energy from the ground singlet state with the lone pair n^2 to the triplet state with the configuration $n^1p_\pi^1$, the correct valence state for double bond formation **(C)**.



(C)

Methodology

The geometries of all the stationary points were fully optimized at the B3LYP/6-311++G** level of theory. They were confirmed to be real minima by frequency analysis. We considered the stable structures for the adducts between stable carbene **(A)** or silyene **(B)**, and the carbenoid $AH_n = CH_2$, SiH_2, NH, NH_2^+, PH, and PH_2^+. Therefore, we adopted similar methodology and systems similar to those of Frison and Sevin.[39] When we considered some properties for the whole group, we switched to the LANL2DZdp basis set[44~47] which includes the relativistic effective core potentials using the double-ζ (DZ) basis sets augmented by a set of d-type polarization functions. The DZ basis set for the hydrogen element was augmented by a set of p-type polarization functions (p exponent 0.356). The d exponents used for N, P, As, Sb, and Bi are 0.736, 0.364, 0.286, 0.207, and 0.192, respectively. Therefore, all the B3LYP calculations are denoted by B3LYP/LANL2DZdp. These results were also compared with the QCISD/LANL2DZdp method. The Gaussian 98 was used for this work.[47]

Results and Discussion

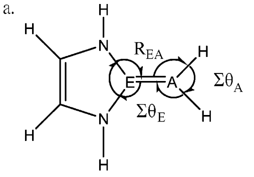
1. Adducts between Stable Carbene or Silylene with Carbenoids. In Table 1, relevant structural parameters extracted from the optimized structures (B3LYP/6-311++G**) of the adducts between stable carbene **(A)** or stable silyene **(B)** and the carbenoid $AH_n = CH_2$, SiH_2, NH, NH_2^+, PH, and PH_2^+ are reported. It is interesting to note the four adducts, **A** = SiH_2, **A** = PH_2^+, **B** = SiH_2 and **B** = PH_2^+, with the results shown in bold have local pyramidal structures at Si or P with $\Sigma\theta_A$ (A = Si or P) much small than 360°. The corresponding E sites (C or Si in five-membered ring) are essentially planar with $\Sigma\theta_E$ near 360°. These distorted adducts also have the values of $\Sigma\Delta E_{ST}$ much greater than the other planar adducts. Such distortions are anticipated from the CGMT[42,43] model. The bond distance of C−P in the distorted adduct **A** = PH_2^+ is 0.16 Å longer than that in the planar adduct **A** = PH. Also the Si−P distance in the distorted **B** = PH_2^+ is 0.10 Å longer than that in the planar **B** = PH. It indicates that the double bond character in the planar neutral adducts are reduced substantially in the distorted cationic adducts.

The distortion of the AH_n fragment is also indicted by the bending angle α_A, the angle between the plane containing the five-membered ring and the plane containing the AH_2 fragment. For the case of HN and HP, a dummy hydrogen atom (denote as (H)) is added without electronic contribution such that the NH(H) and PH(H) fragments have a local C_{2v} symmetry. Therefore, the definition of the bending angle α_A is feasible.

TABLE 1: B3LYP/6-311++G Results for the Adducts between Stable Carbene (A) or Silylene (B) and Carbenoid AH_n = CH_2, SiH_2, NH, NH_2^+, PH, and PH_2^+**

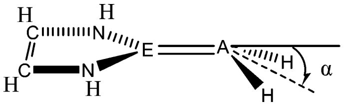
adducts	R_{EA}[a]	$\Sigma\theta_E$[a]	$\Sigma\theta_A$[a]	α_A[b]	$\Sigma\ \Delta E_{ST}$[c]
A=CH_2	1.352	360.0	360.0	1.6	71.26
A=SiH_2	1.926	358.8	285.3	104.4	103.60
A=NH	1.284	360.0	360.0	0.0	33.04
A=NH_2^+	1.285	360.0	360.0	0.3	50.45
A=PH	1.698	360.0	360.0	0.0	51.35
A=PH_2^+	1.858	360.0	283.7	83.4	99.32
B=CH_2	1.698	360.0	360.0	0.1	48.03
B=SiH_2	2.331	354.0	275.6	109.4	80.37
B=NH	1.589	360.0	360.0	0.0	9.81
B=NH_2^+	1.641	360.0	360.0	0.0	27.22
B=PH	2.098	360.0	360.0	0.0	28.12
B=PH_2^+	2.196	357.8	286.0	97.1	76.09

a.



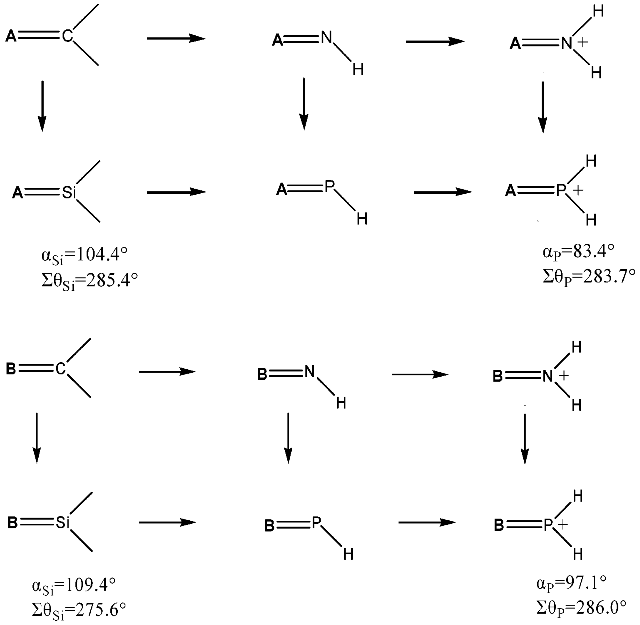
E=C or Si, R_{EA} in Å; $\Sigma\ \theta_E$ and $\Sigma\ \theta_A$ in degree.

[b] Bending angle (in degrees) between the plane containing the 5-membered ring and the plane containing AH_2 fragment. A dummy hydrogen atom (denoted as (H)) is assigned without electronic contribution for the NH and PH such that the NH(H) and PH(H) have a local C_{2V} planar geometry, and thus the definition of α_A is feasible.



[c] The sum of E(triplet) − E(singlet) for the two fragments in the adduct in kcal/mol.

SCHEME 1: Nonplanarity at the A Site in AH_n Are Described by α_A and $\Sigma\theta_A$ for the Adducts between Stable Carbene (A) or Silylene (B) with AH_n (from Table 1)[a]



[a] α_A and $\Sigma\theta_A$ are not shown for the planar sites.

The key information of Table 1 can be depicted in Scheme 1, where the four distorted adducts associated with SiH_2 or PH_2^+ are indicated with the values of α_A and $\Sigma\theta_A$. The corresponding E sites are planar. All the other adducts are essentially planar at both A and E sites.

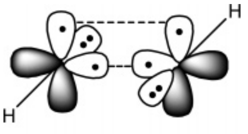
TABLE 2: B3LYP/LANL2DZdp Results of *E*(Singlet), *E*(Triplet) in Atomic Unit, and ΔE_{ST} (*E*(Triplet) − *E*(Singlet)) in kcal/mol for the Carbenoid Moieties AH_n of Group 14 and 15 Elements

carbenoid	*E*(singlet)	*E*(triplet)	ΔE_{ST}(kcal/mol)[a]
NH	−55.1551	−55.2361	−50.83 (−49.58)[b] [−50.37][c]
PH	−6.9914	−7.0442	−33.14 (−33.53) [−32.07]
AsH	−6.6276	−6.6769	−30.96 (−31.84) [−29.84]
SbH	−5.9240	−5.9674	−27.24 (−28.59)
BiH	−5.9733	−6.0148	−26.03 (−27.95)
NH_2^+	−55.4253	−55.4767	−32.23 (−32.70) [−32.97]
PH_2^+	−7.3058	−7.2821	14.87 (13.87) [15.90]
AsH_2^+	−6.9461	−6.9127	21.01 (19.49) [23.73]
SbH_2^+	−6.2536	−6.2126	25.69 (24.07)
BiH_2^+	−6.3076	−6.2501	36.10 (34.66)
CH_2	−39.1416	−39.1604	−11.77 (−11.49) [−12.16]
SiH_2	−5.0141	−4.9884	16.18 (15.78) [20.18]
GeH_2	−4.9181	−4.8810	23.26 (22.27) [26.51]
SnH_2	−4.5332	−4.4917	26.03 (24.63)
PbH_2	−4.6298	−4.5715	36.61 (35.51)

[a] The third-order Douglas−Kroll relativistic coupled-cluster results (DK3-CCSDTQ/TZ) from ref 50 are −29.4 kcal/mol (NH_2^+), +17.4 (PH_2^+), +21.6 (AsH_2^+), −10.0 (CH_2), and +20.3 (SiH_2). [b] Values in parentheses are the QCISD/LANL2DZdp results. [c] Values in brackets are the B3LYP/6-311++G** results.

2. *π*-Bonding Trend of Pnictenes and Carbene Analogues. There is a simple parameter, ΔE_{ST}, that correlates well with the *π*-bond capability for the carbenoid moieties according to the CGMT model. From Table 2, it is interesting to note that the value ΔE_{ST} decreases in magnitude smoothly for the pnictenes AH of the group 15 elements. Besides the B3LYP/LANL2DZdp results, the QCISD/LANL2DZdp results are also presented for comparison. The two sets of ΔE_{ST} values are virtually identical. The B3LYP/6-311++G** results for Sb, Bi, Sn, and Pb are missing because the basis sets are unavailable for these elements in the Gaussian Program. The pattern of ΔE_{ST} for the pnictenes AH is useful to interpret Power' s comments mentioned in the introduction that the heavy dipnictenes bear considerable similarity both in structure and *π*-bonding character to the lighter dipnictenes.

The pnictene AH has two open-shell p orbitals with ground triplet state (with negative ΔE_{ST}), the correct valence state ready to form a stable double bond. In the dipnictene HAAH, the HA fragment has to bond in the side way **(D)**, and this results in a small bond angle −HAA near 90° as observed for heavy dipnictene such as RBiBiR.[24] After protonation, the AH_2^+ is isolobal to carbene with a stable lone pair n^2, thus a significant $n \rightarrow p_\pi$ promotion is required for double bond formation, especially for the heavy AH_2^+.



(D)

It is also interesting to examine the ΔE_{ST} for the protonated species AH_2^+ in comparison with those of the carbene analogues of group 14 elements. This information is useful to interpret their *π*-bonding behaviors discussed previously. The original difference of ΔE_{ST} by B3LYP/LANL2DZdp between PH and NH is 17.69 kcal/mol. After protonation, this energy difference increases significantly to the value of 47.10 kcal/mol between PH_2^+ and NH_2^+. This gap stands out among the group 15 elements. This situation resembles the occurrence of the largest ΔE_{ST} gap between SiH_2 and CH_2 for the group 14 elements. Therefore, the smooth pattern of the strong *π*-bonding character in the pnicetenes series breaks down after protonation. A fault appears between the first two members. The ΔE_{ST} of all the heavy AH_2^+ switch the sign from those of AH. They are expected to have a rather weak *π*-bonding character. The distinction in *π*-bonding capability between PH_2^+ and NH_2^+ therefore resembles that between SiH_2 and CH_2. Interestingly, the nitrenium (NH_2^+) has a persistent *π*-bonding tendency with a negative ΔE_{ST} = −32.23 kcal/mol compared with −50.83 kcal/mol for NH. Therefore, both of these resemble carbene. The discussion here can be summarized diagramatically in (**E**).

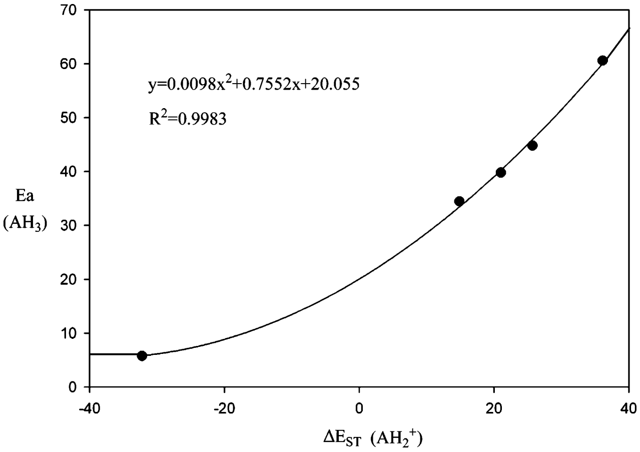


Figure 1. The correlation between ΔE_{ST} of AH_2^+ from Table 2 and inversion Barriers E_a of AH_3 for the group 15 elements at the B3LYP/LANL2DZdp level. Our calculated E_a values for the AH_3 are 5.79, 34.46, 39.78, 44.80, and 60.60 kcal/mol.

$$\begin{tikzcd}
PH \arrow[r, leftrightarrow] \arrow[d, "H^+"] & CH_2 & & NH \arrow[r, leftrightarrow] \arrow[d, "H^+"] & CH_2 \\
PH_2^+ \arrow[r, leftrightarrow] & SiH_2 & & NH_2^+ \arrow[ur, leftrightarrow] &
\end{tikzcd}$$

(E)

The double arrow between the two AH_n means their similarity in the *π*-bonding capability, as indicated qualitatively by the structural information in Table 1 or the magnitudes of ΔE_{ST} values in Table 2.

Finally, the important gap of ΔE_{ST} between NH_2^+ and PH_2^+ is useful to interpret a significant increase in the inversion barrier between NH_3 and PH_3.[51] The ΔE_{ST} is related to the orbital energy gap between p_π and the nonbonding orbital n for a carbene-like fragment. During the inversion process for AH_3, it also involves n-to-p_π two-electron promotion ($n^2 \rightarrow p_\pi^2$). Therefore, reasonable correlation between the ΔE_{ST} of AH_2^+ from Table 2 and our calculated inversion barrier E_a of AH_3 is anticipated as shown in Figure 1. It is interesting to see that the gap between nitrogen and phosphorus in both quantities are more noticeable than elsewhere between the heavier compounds.

Conclusion

Although both phosphinidene and phosphonium ion are isoelectronic to silylene, the *π*-bonding tendency of the former is rather strong, forming planar adducts with both the stable carbene and stable silylene. In contrast, the latter forms trans-bent adducts with the two species. Therefore, they are actually analogous to the carbene and silylene, respectively, in the *π*-bonding capability. These results can be interpreted in terms of CGMT model and the fact that the value of ΔE_{ST} of the HP fragment increases significantly after protonation ($\Delta\Delta E_{ST}$ = 48.01 kcal/mol). The former has two open-shell p orbitals, ready to form a stable double bond. The latter has a stable lone pair, thus a significant promotion energy is required for the double bond formation. The other heavier pnictenes behave similarly to phosphinidene. In contrast, nitrene (NH) and nitrenium (NH_2^+) have ΔE_{ST} values of −50.83 and −32.23 kcal/mol, respectively. Therefore both are analogous to carbene in π-bonding capability, unlike the conspicuous distinction between HP and H_2P^+. Finally, the notable gap in ΔE_{ST} between NH_2^+ and PH_2^+ of 47.10 kcal/mol in the AH_2^+ series is useful for interpreting a significant jump in the inversion barriers between NH_3 and PH_3 for the AH_3 series.

Our comment that the phosphinidene is analogous to carbene in π-bonding capability in fact is one aspect of the diagonal relation in the periodic table between these two elements. It has been generally accepted in the organophosphorus community (e.g., ref 23). We underline here the switch of π-bonding character after protonation from the diagonal phosphorus−carbon analogy to the neighboring phosphorus−silicon analogy.

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