J. Am. Chem. Soc. **1991**, *113*, 1899–1906 1899

Conclusion

We have used ab initio molecular orbital theory at the HF/3-21G* level to study the structures and relative energies of the complexes formed by the chelation bidentate binding of Mg(II) and Ca(II) ions to malonate. These calculations can be viewed as simple models for the interaction between these ions and the malonate side chain of Gla residues in coagulation zymogens. The calculations have several limitations: entropic effects are necessarily absent, and finite computer resources prevent us from fully solvating the complexes or using basis sets and correlation treatments capable of yielding quantitative accuracy. We believe that these limitations will not fundamentally affect our main conclusions, which are summarized below.

(1) We report optimized structures and relative energies for the parent complexes, their enol forms, and the deprotonated forms of these complexes. We also report the first ab initio calculations on the effect of hydration on the malonate–metal complexes. We include four water molecules to allow the metal ion to become hexacoordinated. Consideration of hydration is shown to be very important in the study of deprotonated reactions: we find the most acidic proton is from one of the coordinated water molecules, not from the methylene carbon of the malonate.

(2) Comparison of the relative energies of the keto, enol, and deprotonated structures with and without complexed metal ions suggests that the mechanism of electrophilic attack at C_γ on the malonate side chain of Gla occurs via the alkylation of the enol form. Furthermore, the metal ion complexed enol form is destabilized relative to the uncomplexed form. This appears to be consistent with the reductions in the observed rate of alkylation of the Gla containing proteins upon complexation with metal ions.

(3) On the basis of our calculations, we suggest that the experimental results showing reduced reactivity at most Gla sites are consistent with protection of only those sites in which the divalent metal ion is bound in a chelation bidentate orientation.

(4) Physiologically, there are critical differences between Ca(II) ion–malonate and Mg(II) ion–malonate complexes. Thus, the origin of the Ca(II) ion specificity in the coagulation cascade does not appear evident in the chelation bidentate binding of a single metal to malonate. Future work will consider the influence of waters of hydration on other possible metal ion–malonate modes of coordination.[41]

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Supplementary Material Available: Tables (I–IV) of the ab initio optimization results (4 pages). Ordering information is given on any current masthead page.

Nature of Bonding in Phosphazoylides. A Comparative Study of N_2H_4, NPH_4, and P_2H_4†

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Abstract: Structures, energies, and electronic properties of the ylides H_3NNH (**2**), H_3PPH (**5**), H_3PNH (**8**), and H_3NPH (**10**) of hydrazine (**1**), diphosphine (**4**), and aminophosphine (**7**) have been studied with ab initio molecular orbital theory by use of a split valence plus polarization basis set and incorporating electron correlation and zero-point energy corrections. The results show all ylides to be equilibrium structures. The Staudinger tautomer H_3PNH (**8**) is 29.7 kcal/mol less stable than aminophosphine H_2NPH_2 with a 50.0 kcal/mol barrier for hydrogen migration. The very short P–N bond of **8** is ascribed to result mainly from the large Coulombic interaction between the NH and PH_3 groups, augmented with a partial triple bond contribution that results from π and σ interactions. The properties of the H_3PPH ylide **5** are similar to the Staudinger complex **8** but less pronounced. The chemical bonding in these "hypervalent" molecules **5** and **8** is dominated by ionic bonding and conjugative stabilization with little if any d-orbital participation.

Phosphazo compounds have become widely applied synthons since their first synthesis by Staudinger and Meyer in 1919.[1] For six decades primary amines and amides have been synthesized by the Staudinger reaction,[2] which recently also has been used for polymerizations.[3] The applicability and varied reactivity of the key intermediates, the iminophosphoranes, are of experimental and theoretical interest. In this paper we describe the nature of bonding in the parent phosphazo compound.

The extensive literature and detailed understanding on the nature of P=C (alkylidenephosphoranes)[4] P=O bonding[5] contrasts the limited information on the iminophosphorane P=N bond. The Staudinger intermediate signifies the importance of the iminophosphorane $R_3P{=}NR$, which is isoelectronic with the well-studied Wittig reagent $R_3P{=}CR_2$ and phosphine oxide $R_3P{=}O$. The reactivity of the Wittig reaction is considered to result from zwitterionic (ylide) character. In analogy, this may also be an important resonance form for the iminophosphoranes.

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† Dedicated to Professor P. v. R. Schleyer, on the occasion of his 60th birthday.

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Little is known about the structural and electronic properties of phosphorus–nitrogen ylides. Most studies concerned with P–N bonding have focused on aminophosphines (R_2PNR_2) in relation to hydrazines (R_2NNR_2) and diphosphines (R_2PPR_2).[6] Recently, a theoretical study by Gonbeau et al.[7] focused on the electronic properties of the H_3PNH ylide, its tautomer H_2PNH_2, and their cations and anions. On the basis of Mulliken populations and a 4-31G* MO analysis the iminophosphorane was suggested to have a zwitterionic nature and partial triple P–N bonding. Earlier Kutzelnigg,[8] and later Schmidt and Gordon,[5b] arrived at similar conclusions for the isoelectronic H_3PO, which they presented as a resonance hybrid between singly and triply bound structures! In a thorough comparison of H_3NO with H_3PO, Kutzelnigg[8] has eloquently shown that the phosphorus d AOs contribute through back-bonding to the partial triple bonding in phosphine oxide, but according to Streitweiser et al.,[5a] who used integrated spatial electron populations, the dipolar structure $H_3P^+{-}O^-$ dominates with little contribution of the double-bond structure $H_3P{=}O$. A different view was expressed by Molina et al.[9] in their HF/6-31G* study, using localized orbitals. These authors gave three different representations for the three isoelectronic structures H_3PX (X = CH_2, NH, O). They assigned partial triple bond character to the phosphine oxide, i.e., $H_3P^+{\equiv}O^-$ (d_{PO} = 1.456 Å), represented the iminophosphorane as an ylide structure $H_3P^+{-}N^-H$ (d_{PN} = 1.543 Å), and argued that methylenephosphorane is better represented as $H_3P{=}CH_2$ (d_{PC} = 1.655 Å). However, it is unlikely that these isoelectronic species have such different descriptions since that would imply different valencies for the phosphorus atom. Also the remarkably small and similar bond rotation barriers for the PN bond in iminophosphorane H_3PNH of only 2 kcal/mol and the 1.0 kcal/mol for the PC bond (HF/6-31G*) in H_3PCH_2[9-12] are in contrast with the description of Molina et al.

Aside from the comparison with H_3PCH_2 and H_3PO, an important question is how the stability of the Staudinger complex H_3PNH compares with its conventional tautomer. The equilibrium $H_3P{=}NH \rightleftharpoons H_2P{-}NH_2$ has been studied experimentally.[13] Gonbeau et al.[7] reported an energetic preference of only 17 kcal/mol for the aminophosphine at HF/4-31G*. However, as we will show, higher levels of theory, which include electron correlation, are needed to describe the tautomers and their energy differences. To highlight the special properties of the Staudinger complex and to provide internal calibration, we make the necessary comparisons with the tautomeric structures of the analogous N_2H_4 and P_2H_4 systems.

Surprisingly, to our knowledge, no study has yet appeared on the other NPH_4 tautomeric form, the phosphinoammonium ylide $RPNH_3$, which contains a trivalent phosphorus and resembles a complex between PH and NH_3. Can such a complex exist? Several recent studies, mainly experimental, point in this direction. For example, the terminal phosphinidene complex, depicted by Mathey as $Ph{-}P{=}W(CO)_5$, can be generated in situ[14,15] and the $HPCr(CO)_5$ complex has been subject of theoretical studies.[16] Recently, a phosphinidene borate has been synthesized[17] and H_2PBH_2 has been studied theoretically.[18] Gonbeau et al.[7] have reported on the ionic phosphinidene complexes $HPNH_2^+$ and $HPNH_2^-$. However, most studies concerned with trivalent phosphorus have focussed on the π bond strength in species like $HP{=}CH_2$, $HP{=}NH$, $HP{=}PH$, $HP{=}O$, and $HP{=}S$.[4] Whereas we are unaware of a study on the PH_3PH tautomer of diphosphine ($H_2P{-}PH_2$), the phosphinophosphinidene tautomer ($H_2P{-}P$) of diphosphene ($HP{=}PH$) is predicted to be a kinetically stable species.[19] In a related study on the NPH_2 system, Trinquier[20] has reported on the isomeric phosphazenes ($HN{=}PH$), phosphinonitrenes ($H_2P{-}N$), and aminophosphinidene ($H_2N{-}P$). A $W(CO)_5$ complex of the latter has been generated experimentally.[21]

An important issue of the present study is the comparison of the two NPH_4 tautomers of aminophosphine. These have formally different valencies for the phosphorus atom. Reed and Schleyer addressed in a recent, landmark study[22] on 32-valence-electron species of the X_3AY type (like F_3PO) the issue of chemical bonding in hypervalent molecules. From the natural population and natural bond orbital analysis on HF/6-31G* optimized geometries they concluded that ionic bonding and negative hyperconjugation dominate over d-orbital participation. The latter has been the traditional model to interpret hypervalent molecules. We address this issue for the NPH_4 ylide tautomers and the corresponding isomers of hydrazine and diphosphine. The comparison between the XYH_4 (X = N, P) ylides enables an evaluation of the ionic nature, hyperconjugative interactions, and the importance of d AOs (or d-polarization functions) in the bonding of these compounds.

The strategy that we use in this paper is to investigate various properties of the molecules. These are the geometries, stabilities, binding energies, bonding properties, charges, molecular orbitals, and bond orders. Each of these topics is discussed separately since they reveal incidental aspects of the ylide structure(s) or the methodology, which sometimes are seemingly in conflict with each other. However, it is the culmination of the analyses that is of significance. Because polar compounds are typically sensitive to the theoretical level employed (as is the case in this study) our study is based on geometries optimized at correlated levels. For the analyses of the one-electron charge density distribution and atomic charges we use Bader's topological theory of atoms in molecules and MP2/6-31G* wave functions.

Computational Methods

Ab initio molecular orbital calculations[23] were performed with the GAUSSIAN 88 series of programs.[24] Geometries were optimized within the indicated symmetry constraints by using the standard split valence basis sets 3-21G,[25] the d-polarized 6-31G*,[26] and 6-31+G*,[27] which

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Table I. Total (−au) and Relative (kcal/mol) Energies of XYH_4 (X, Y = N, P) Isomers

structures		state	HF/3-21G//HF/3-21G			HF/6-31G*//HF/6-31G*			HF/6-31+G*//HF/6-31+G*	
			total	rel	NIMAG	total	rel	NIMAG	total	rel
1	C_2	^1A	110.550 00	0.0	(0)	111.169 39	0.0	(0)	111.176 04	0.0
2	C_s	$^1A'$	110.475 60	46.7	(0)	111.088 08	51.0	(0)	111.100 35	47.5
3	C_1	^1A	110.435 13	72.1	(1)	111.038 68	82.0	(1)		
4	C_2	^1A	680.276 69	0.0	(0)	683.751 98	0.0	(0)	683.753 07	0.0
5	C_s	$^1A'$	680.226 37	31.6	(0)	683.705 30	29.3	(0)	683.707 10	28.8
6	C_1	^1A	680.183 15	59.7	(1)	683.638 99	70.9	(1)		
7	C_s	$^1A'$	395.437 99	0.0	(0)	397.481 64	0.0	(0)	397.486 40	0.0
8	C_s	$^1A'$	395.323 26	72.0	(0)	397.427 31	34.1	(0)	397.432 57	33.8
9	C_1	^1A	395.238 83	125.0	(1)	397.314 59	104.8	(1)		
10	C_s	$^1A'$	395.423 92	8.8	(0)	397.431 16	31.7	(0)	397.435 67	31.8
11	C_1	^1A	395.339 26	62.0	(1)	397.360 67	75.9	(1)		

Table II. Total (−au) and Relative (kcal/mol) MP Energies of MP2/6-31G* Optimized XYH_4 (X, Y = N, P) Geometries

structure		MP2		MP3		MP4		
		total	rel	total	rel	total	rel	corr MP4[a]
1	C_2	111.497 88	0.0	111.515 74	0.0	111.527 52	0.0	0.0
2	C_s	111.423 27	46.8	111.434 36	51.1	111.447 59	50.2	49.4
3	C_1	111.386 18	70.1	111.394 87	75.9	111.411 78	72.6	68.4
4	C_2	683.976 78	0.0	683.988 73	0.0	684.000 71	0.0	0.0
5	C_s	683.935 36	26.0	683.944 66	27.7	683.957 35	27.2	27.6
6	C_1	683.872 86	65.2	683.881 52	67.3	683.896 90	65.1	63.2
7	C_s	397.762 55	0.0	397.771 52	0.0	397.783 53	0.0	0.0
8	C_s	397.715 52	29.5	397.718 08	33.5	397.734 06	31.0	29.7
9	C_1	397.628 92	83.9	397.628 31	89.9	397.650 30	83.6	79.7
10	C_s	397.712 26	31.6	397.722 95	30.5	397.734 87	30.5	32.3
11	C_1	397.663 92	61.9	397.669 92	63.8	397.685 72	61.4	58.8

[a] Corrected for zero point energies (ZPE), scaled by 0.95.

contains additional N and P diffuse functions. The (Hartree–Fock) optimized geometries were used to analytically compute the force constant matrices and vibrational harmonic frequencies. Minima are characterized by real frequencies only, while transition structures have one imaginary frequency. To obtain more reliable relative energies it is usually necessary to include the effects of electron correlation. These were estimated through (frozen core) full fourth-order Møller–Plesset perturbation theory[28] using MP2(Full)/6-31G* optimized geometries. The final relative energies are corrected for scaled[29] zero-point energy (ZPE) differences.

The bonding properties of all structures were investigated with Bader's topological electron density analysis, which is based on the theory of atoms in molecules.[30,31] The MP2/6-31G* geometries and wave functions were used to analyze the one-electron density distribution $\rho(\mathbf{r})$, its gradient vector field $\nabla\rho(\mathbf{r})$, and the Laplacian $\nabla^2\rho(\mathbf{r})$. The latter determines regions in space wherein electronic charge is concentrated ($\nabla^2\rho(\mathbf{r}) < 0$) or depleted ($\nabla^2\rho(\mathbf{r}) > 0$). Of particular interest are the (3, − 1) or "bond critical points" $\mathbf{r}_b$ which have a minimum value in $\rho(\mathbf{r})$ along the maximum electron density path connecting two nuclei. The spatial symmetry of a bond is described by the ellipticity ϵ of its bond critical point and is defined as $\epsilon = \lambda_1/\lambda_2 - 1$, where λ_1 and λ_2 are the two negative curvatures of the three eigenvalues of the Hessian matrix of $\rho(\mathbf{r})$. Finally, a bond is described as covalent or ionic (closed-shell interaction) if the local total energy density $H(\mathbf{r})$ at a critical point is negative or positive, respectively.[30d]

Results and Discussion

The N_2H_4, NPH_4, and P_2H_4 structures of this study are displayed in Figure 1.[32] Their total and relative energies at the 3-21G, 6-31G*, and 6-31+G* levels are given in Table I, which also lists the number of imaginary frequencies. Presented in Table II are the total and relative energies at the correlated MP levels for the MP2/6-31G* optimized structures. The last column in this table gives our final relative energies, which include scaled zero-point energy (ZPE) corrections. Unscaled MP2/6-31G* harmonic frequencies and ZPEs are given in Table III in the supplementary material. Throughout the discussion MP2/6-31G* geometrical parameters and MP4/6-31G* + ZPE energies are used unless noted otherwise.

Geometries and Energies. N_2H_4 System. The hydrazine molecule H_2NNH_2 (**1**), the iminoammonium H_3NNH (**2**), and the transition structure **3** have been studied previously by Pople et al.[33] We report the geometries and energies of these species to facilitate the discussion. The hydrazine geometry (C_2 symmetry) is somewhat dependent on the level of theory employed. As expected, its 3-21G N–N bond contracts (0.038 Å) when d-polarization functions are included (6-31G*) and relaxes slightly (0.025 Å) with the inclusion of electron correlation effects. At the MP2/6-31G* level the N–N bond is 1.438 Å, which compares well with the experimental value of 1.447 Å.[34]

It is evident from Figure 1 that (a) the geometry of the iminoammonium ylide H_3NNH (2) is more sensitive to the level of theory than hydrazine is and (b) the N–N bond of this ylide **2** is nearly of the same length as that of **1** at the correlated level. At MP2/6-31G* its bond length is 1.456 Å, which is only 0.018 Å longer than the hydrazine N–N bond. This implies essentially

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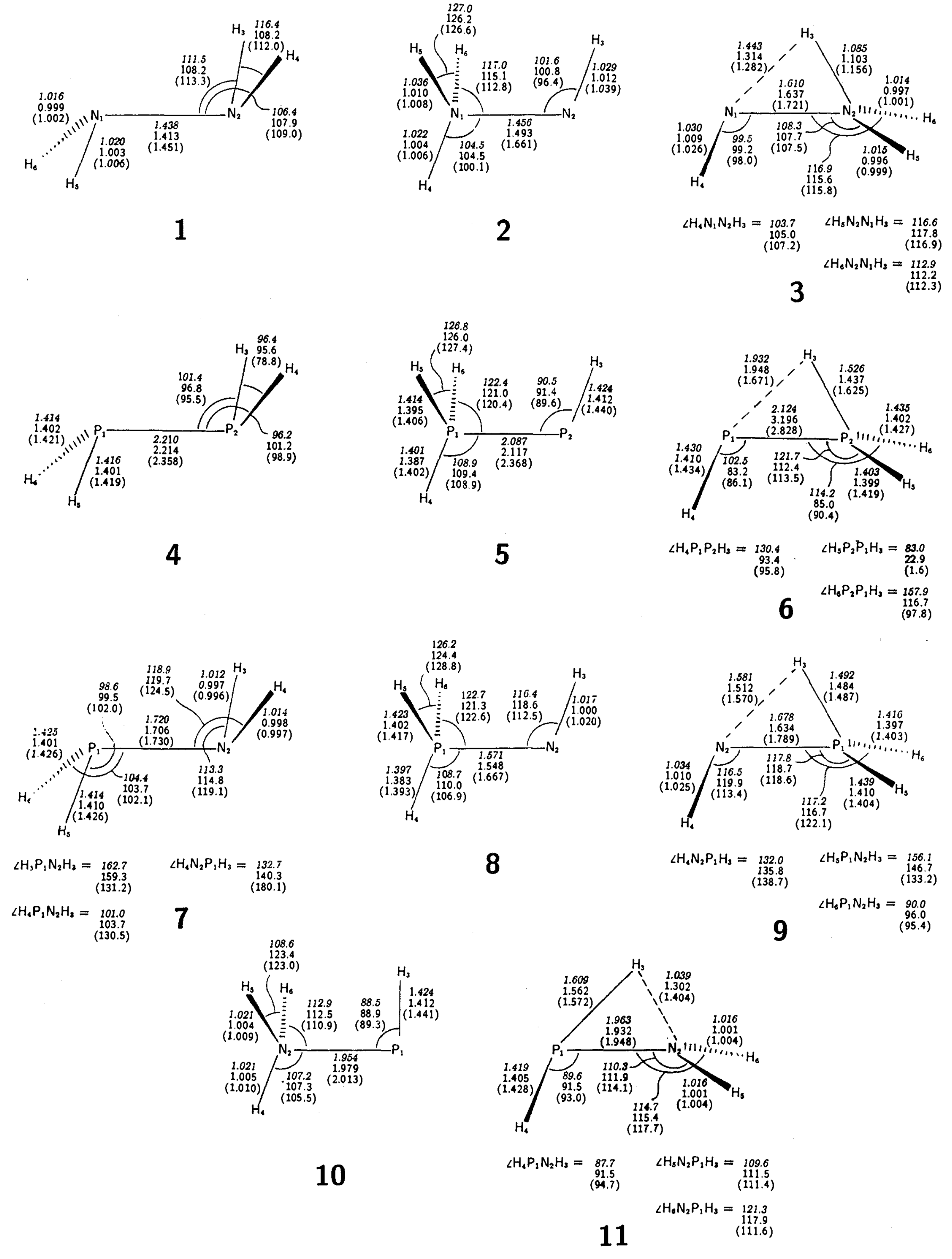

Figure 1. Optimized structures for the ylides, their conventional isomers, and their transitions for H transfer. Top (italic) values are at MP2/6-31G*, middle values are at HF/6-31G*, and bottom values (in parentheses) are the geometrical parameters at HF/3-21G.

single N–N bonding between the nitrene and ammonia "fragments" of **2**, possibly enhanced by electrostatic interactions.

Although ylide **2** is 49.4 kcal/mol less stable than hydrazine at MP4/6-31G* + ZPE it has significant kinetic stability. The barrier for rearrangement (via **3**, C_1 symmetry) amounts to 19 kcal/mol (same level) and is rather insensitive to the level of theory employed.

P_2H_4 System. The trends observed for the N_2H_4 system are also found for the second-row analogue P_2H_4, but the effects of electron correlation on the geometry optimization are less pronounced. Diphosphine **4** has a P–P bond length of 2.210 Å at MP2/6-31G*,[35] which compares well with the experimental value of 2.219 Å.[34]

However, in contrast to H_3NNH the H_3PPH ylide tautomer, phosphinophosphorane **5**, has a 0.123 Å shorter P–P bond (i.e., 2.087 Å, same level) than diphosphine **4**. Its PP bond is of similar length as the calculated[19] P=P double bond of 2.064 and 2.055 Å (TCSCF) in *trans*- and *cis*-diphosphene (P_2H_2), respectively, and the experimental[36] value of 2.034 Å for a derivative. Thus, the short PP bond length of **5** suggests P=P multiple bond character.

As expected, the energy difference between the P_2H_4 tautomers is smaller than for the N_2H_4 species and amounts to 27.6 kcal/mol (MP4/6-31G* + ZPE). The kinetic stability of H_3PPH is much larger than that of its first-row analogue, with a barrier of 35.6 kcal/mol for rearrangement via **6** to H_2PPH_2.

Yates et al.[37] have made similar geometrical and energetic observations in a comprehensive study on carbon ylides. They also found (a) that the energetic differences between the ylides and their conventional isomers is smaller for second-row systems and (b) that the associated barriers for rearrangement are larger.

NPH_4 System. The most stable NPH_4 isomer is aminophosphine H_2NPH_2 (**7**). Its C_1 symmetry structure has a N–P bond length of 1.720 Å at MP2/6-31G*,[38] which compares well with the experimental value of 1.71 Å for bis(diphenyl)isopropylamine.[39,40]

The Staudinger tautomer H_3PNH (**8**) distinguishes itself from the ylides H_3NNH (**2**) and H_3PPH (**5**) discussed above. The iminophosphorane **8** has a NP bond length of only 1.571 Å at MP2/6-31G*, which is 0.149 Å (!) shorter than that of its conventional isomer H_2NPH_2. This very short bond length suggests a NP multiple bond.[41] As noted, Gonbeau et al.[7] attributed the short N–P bond of H_3PNH to a partial triple bond; however, their analysis was in part based on a shorter HF/4-31G* bond length of 1.532 Å. Figure 1 illustrates that the bond length of H_3PNH ylide **8** is strongly dependent on the theoretical level.[42] Yates et al.[37] have noted even larger effects for carbon ylides and, as is the case here, found several second-row carbon ylides to have shorter CX bonds than their conventional isomers. The PN bond length of H_3PNH can be compared with the 1.619 (1.556) Å (MCSCF, HF/3-21G(d)) calculated N=P bond of *trans*-phosphazene NPH_2[4b] and the experimental value of 1.544 Å for a sterically congested derivative.[43] These N=P double bond lengths are of the same magnitude as the N—P bond length of **8**!

Table IV. MP4/6-31G* Binding Energies (kcal/mol)[a]

2 → NH_3 + NH	54.9
5 → PH_3 + PH	53.8
8 → PH_3 + NH	109.8
10 → NH_3 + NH	42.1
1 → $NH^{\bullet}_2$ + $NH^{\bullet}_2$	78.2
4 → $PH^{\bullet}_2$ + $PH^{\bullet}_2$	48.0
7 → $NH^{\bullet}_2$ + $PH^{\bullet}_2$	83.1

[a] Corrected for ZPE.

In contrast to H_3PNH (**8**), the tautomeric phosphinoammonium ylide H_3NPH (**10**) has a much longer N–P bond length of 1.954 Å (MP2/6-31G*), which shows little basis set and level dependence. At the correlated level the Δd_{NP} differences of **10** with the single PN bonded **7** is 0.234 Å and that with **8** is 0.383 Å. These large fluctuations in N–P bond lengths for the NPH_4 system are somewhat unexpected, also because Trinquier[20] reports much smaller variations in a (DZ + d(P)) study on the related singlet NPH_2 system, i.e., N—P bond lengths of 1.559 Å for *trans*-phosphazene (HP=NH), 1.515 Å for phosphinonitrene (H_2P—N), and 1.637 Å for aminophosphinidene (P—NH_2).

Despite the large variation in NP bond lengths, H_3PNH (**8**) and H_3NPH (**10**) are of nearly equal stability. The energy difference with the global minimum H_2NPH_2 (**7**) is 29.7 for **8** and 32.3 kcal/mol for **10** (MP4/6-31G* + ZPE). These relative energies differ significantly from those obtained with lower levels of theory (see Table I and ΔE(**7**–**8**) = 17 kcal/mol at HF/4-31G*[7]). Both ylide structures lie in sizable potential energy wells. However, the barrier for rearrangement to the global minimum **7** is much larger for the Staudinger species H_3PNH (50.0 kcal/mol via **9**, C_1 symmetry) than it is for H_3NPH (26.5 kcal/mol via **11**, C_1 symmetry).

Binding Energies. The stabilities of the ylide structures can be evaluated by determining the binding energies between the fragments XH_3 and YH. These MP4/6-31G* energies, corrected for zero-point energy contributions, are listed in Table IV. Interestingly, the H_3NNH ylide **2** and the H_3PPH ylide **5** have rather similar binding energies, while, of course, the homolytic bond dissociation energies for hydrazine and diphosphine differ substantially. This lends support to multiple bond character between the phosphorus atoms in H_3PPH (**5**).

The Staudinger complex H_3PNH has, in comparison to the other ylides, an overwhelmingly high binding energy, which is about twice that of either H_3NNH or H_3PPH. In sharp contrast, the phosphinoammonium ylide H_3NPH has a much more modest binding energy. These different energies are a reflection of the different stabilities of the separate fragments, but the strong stabilization in the iminophosphorane H_3PNH is evident and again suggests multiple NP bonding.

Bond Properties. To investigate in more detail the bonding characteristics of the phosphazoylide **8**, we resort to Bader's topological electron density analysis. The MP2/6-31G* critical point data for **1**–**11** are listed in Table V.

First we compare the conventional structures hydrazine **1**, diphosphine **4**, and aminophosphine **7**, which serve as reference molecules. The ellipticity ϵ of 0.00, the very negative Laplacian, and the negative energy density H for the N–N bond critical point (r_{b1}) are supportive of a strong covalent N–N σ bond for the C_2 structure **1**. The lower values of ρ, the Laplacian, and H for the P–P bond critical point in diphosphine illustrate that the covalent P–P σ bond is weaker. Its small ellipticity of 0.019 suggests some P–P π participation. As expected, the covalent N–P bond of aminophosphine is polarized ($\nabla^2\rho(r_{b1}) > 0$, $H < 0$) and has an electron density at r_{b1}, which is in between that of hydrazine and diphosphine.

The bond properties of the ylides differ significantly from those of their conventional isomers. Whereas iminoammonium ylide (**2**) and hydrazine have similar N–N bond distances (Δd_{NN} = 0.018 Å), the less negative value for the Laplacian of H_3NNH indicates a polarized N–N bond. The difference between the H_2PPH_2 and H_3PPH structures is even more pronounced than for the N_2H_4 isomers. Whereas diphosphine and H_3PPH have

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(35) A distance of 2.205 Å at HF/3-21G(d) is reported in ref 4b.

(36) Cowley, A. H. *Polyhedron* **1984**, *3*, 389, and references cited.

(37) Yates, B. F., Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2250.

(38) Slightly shorter N–P bond lengths for **7** of 1.66 and 1.68 Å have been reported by: Barthelat, M.; Mathis, R.; Mathis, F. *J. Mol. Struct.* **1981**, *85*, 351, and ref 20, respectively.

(39) Keat, R.; Manojlivic-Muir, L.; Muir, K. W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2192.

(40) Gonbeau at al.[7] reported a N–P bond distance for H_2NPH_2 (**7**) of 1.685 Å at essentially 4-31G* (Monstergauss 80) and Schmidt et al.[4ba] reported a value of 1.701 Å at 3-21G(d).

(41) The virtually 90° valence angle for XPH with the larger XNH angles for **2** (101.6°) and **8** (116.4°) follows expectations as outlined by Kutzelnigg.[8] The XNH angle in **2** being larger than in **8**, despite the NN bond being shorter than the NP bond, may also suggest an increased "Pauli" ("Fermi") repulsion. This supports a partial multiple bond between N and P in **8**.

(42) Inclusion of a set of diffuse functions at the SCF level has little effect, (d_{NP} = 1.550 Å at HF/6-31+G*).

(43) Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 687.

Table V. Bond Critical Point Data for XYH_4 (X, Y = N, P) Species at MP2/6-31G*[a]

struct	bond X-Y	d_X	d_Y	λ_1	λ_2	λ_3	ϵ	ρ(r)	$\nabla^2\rho$(r)	H(r)
1	N_1-N_2	0.718	0.720	-0.623	-0.621	0.721	0.002	2.028	-12.594	-1.874
	N_1-H_5	0.756	0.264	-1.197	-1.138	0.751	0.051	2.216	-38.158	-3.080
	N_1-H_6	0.761	0.255	-1.238	-1.178	0.787	0.051	2.232	-39.261	-3.130
2	N_1-N_2	0.821	0.635	-0.498	-0.380	0.695	0.312[b]	1.782	-4.418	-1.624
	N_2-H_3	0.747	0.283	-1.103	-1.019	0.687	0.083	2.146	-34.576	-2.891
	N_1-H_4	0.779	0.243	-1.269	-1.264	0.859	0.004	2.216	-40.332	-3.133
	N_1-H_5	0.776	0.260	-1.166	-1.157	0.768	0.008	2.145	-37.466	-2.971
3	N_1-H_2	0.738	0.873	-0.339	-0.257	0.587	0.319	1.283	-0.215	-0.886
	N_2-H_3	0.845	0.240	-0.940	-0.867	0.786	0.084	1.666	-24.618	-2.147
	N_1-H_4	0.755	0.275	-1.129	-1.051	0.704	0.074	2.148	-35.545	-2.930
	N_2-H_5	0.773	0.241	-1.266	-1.238	0.867	0.022	2.200	-39.456	-3.085
	N_2-H_6	0.769	0.246	-1.238	-1.211	0.835	0.022	2.192	-38.905	-3.063
4	P_1-P_2	1.105	1.105	-0.130	-0.128	0.095	0.019	0.789	-3.917	-0.426
	P_1-H_5	0.698	0.718	-0.220	-0.197	0.260	0.116	1.079	-3.766	-1.108
	P_1-H_6	0.698	0.717	-0.223	-0.196	0.264	0.134	1.084	-3.734	-1.116
5	P_1-P_2	1.321	0.768	-0.117	-0.058	0.104	1.006[b]	0.821	-1.714	-0.695
	P_2-H_3	0.710	0.714	-0.206	-0.163	0.219	0.267	1.031	-3.594	-1.034
	P_1-H_4	0.686	0.715	-0.245	-0.242	0.312	0.011	1.143	-4.214	-1.208
	P_1-H_5	0.693	0.722	-0.240	-0.235	0.270	0.021	1.126	-4.923	-1.194
6	P_1-P_2	0.980	1.150	-0.135	-0.114	0.007	0.186	0.841	-4.210	-0.538
	P_2-H_3	0.958	0.571	-0.198	-0.162	0.176	0.219	0.853	-4.435	-0.525
	P_1-H_4	0.713	0.717	-0.207	-0.193	0.190	0.073	1.053	-5.045	-1.075
	P_2-H_5	0.722	0.714	-0.222	-0.203	0.141	0.092	1.064	-6.854	-1.097
	P_2-H_6	0.688	0.714	-0.246	-0.206	0.308	0.196	1.122	-3.459	-1.170
7	P_1-N_2	0.657	1.064	-0.210	-0.206	0.857	0.019	1.028	10.629	-0.758
	N_2-H_3	0.762	0.251	-1.206	-1.157	0.787	0.043	2.186	-37.986	-3.043
	N_2-H_4	0.761	0.253	-1.192	-1.147	0.778	0.040	2.176	-37.616	-3.018
	P_1-H_5	0.692	0.722	-0.245	-0.204	0.292	0.199	1.103	-3.781	-1.149
	P_1-H_6	0.698	0.728	-0.233	-0.197	0.265	0.187	1.078	-3.986	-1.115
8	P_1-N_2	0.618	0.955	-0.311	-0.264	1.466	0.176[b]	1.363	21.477	-1.093
	N_2-H_3	0.761	0.257	-1.117	-1.106	0.744	0.010	2.110	-35.666	-2.905
	P_1-H_4	0.678	0.719	-0.276	-0.256	0.370	0.079	1.169	-3.888	-1.249
	P_1-H_5	0.691	0.733	-0.250	-0.238	0.289	0.049	1.119	-4.785	-1.191
9	P_1-N_2	0.648	1.035	-0.222	-0.211	0.909	0.052	1.142	11.463	-0.928
	P_1-H_3	0.947	0.550	-0.211	-0.165	0.180	0.280	0.881	-4.728	-0.560
	P_1-H_5	0.716	0.723	-0.235	-0.211	0.160	0.114	1.077	-6.867	-1.128
	P_1-H_6	0.691	0.725	-0.243	-0.216	0.294	0.127	1.112	-3.968	-1.168
	N_2-H_4	0.767	0.267	-1.081	-1.075	0.173	0.006	2.079	-34.750	-2.827
10	P_1-N_2	0.768	1.190	-0.079	-0.036	0.236	1.162	0.594	2.927	-0.364
	P_1-H_3	0.703	0.720	-0.231	-0.149	0.256	0.553	1.035	-2.983	-1.033
	N_2-H_4	0.778	0.243	-1.229	-1.213	0.830	0.013	2.173	-38.864	-3.044
	N_2-H_5	0.777	0.244	-1.231	-1.216	0.831	0.013	2.179	-38.943	-3.053
11	P_1-N_2	0.794	1.171	-0.101	-0.033	0.163	2.103	0.674	0.694	-0.465
	P_1-H_3	1.051	0.561	-0.151	-0.092	0.216	0.650	0.678	-0.652	-0.307
	P_1-H_4	0.701	0.718	-0.229	-0.168	0.254	0.359	1.065	-3.453	-1.085
	N_2-H_5	0.770	0.246	-1.211	-1.177	0.814	0.029	2.162	-37.920	-3.007
	N_2-H_6	0.770	0.247	-1.200	-1.169	0.811	0.027	2.149	-37.548	-2.981

[a] d_X (d_Y) is the distance from the critical point to atom X (Y); the eigenvalues λ_i are in e·a_0^{-5}; the electron density ρ(r) is in e·Å^{-3}; the Laplacian $\nabla^2\rho$(r) is in e·Å^{-5}; the local total energy density H(r) is in hartree·Å^{-3}. [b] The direction of this ellipticity ϵ is perpendicular to the $H_4P_1N_2H_3$ plane.

similar $\rho(r_{b1})$ values, the PP bond in the ylide is shorter and stronger ($\Delta H(r_{b1})$ = 0.269 hartree Å^{-3}). Its ellipticity ϵ of 1.01 is of a magnitude that is common to double bonds (!) and very much larger than the corresponding N–N ellipticity of 0.312 for the H_3NNH ylide.[44]

The bond properties of the two ylide tautomers H_3PNH (**8**) and H_3NPH (**10**) are very different from each other as well as from those of H_3NNH and H_3PPH. The Staudinger complex **8** has the shortest and most polarized NP bond (($\nabla^2\rho(r_{b1})$) $\gg$ 0) with the highest electron ($\rho(r_{b1})$) and energy density ($H(r_{b1})$), whereas the smallest ρ, H, and $\nabla^2\rho(r_{b1})$ values are found for the long NP bond in the H_3PNH tautomer. The bond ellipticities for the two structures are also very different. The small ϵ value of 0.18 excludes double bonding for the short NP distance in the Staudinger complex and rather supports single or partial triple bonding.[44]

Charges. Due to the different electronegativities for nitrogen and phosphorus, the concentration of charge between these two heavy elements varies significantly, as is evident from the Laplacians of the ylide structures, which are displayed in Figure 2. The differences between the H_3PNH (**8**) and H_3NPH (**10**) tautomers are particularly illustrative. Because nitrogen is less capable of accommodating positive charge than phosphorus, the NP bond in H_3PNH is both more polarized and stronger than in H_3NPH, which is essentially of reversed polarity (umpolung). This is supported by the computed atomic charges, which were obtained from integration of the MP2/6-31G* electron density in the atomic basins of molecules, as defined in Bader's electron density analysis, that are listed in Table VI for **2**, **5**, **8**, and **10**.

In all ylide structures the nitrogen has a negative charge while the phosphorus is positive. The magnitude of these atomic charges varies significantly.[45] The special character of H_3PNH is

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[44] The large ϵ values for the H_3NNH (**2**) and H_3NPH (**10**) ylides of 0.31 and 1.17, respectively, may suggest the relative importance of the two lone pairs on the polarization of the total electron density at the N–N and N–P bond critical points; see: Slee, T. S. *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1988.

[45] The Bader integrated net atomic charges for **8** differ significantly in magnitude from the Mulliken charges reported by Gonbeau et al.,[7] but they show similar trends. The Bader charges are obtained from quantum mechanically well defined atomic boundaries that inherently account for local electronegativities, which are not accounted for in the Mulliken analysis. The charges from integration of the charge density over the atomic basins are generally high even if the integration of the spatial (projected) electron density is used as in Streitweiser's model (see, e.g., ref 5a for H_3PO and the discussion in ref 9a). The method illustrates the importance of electrostatic interactions in neutral molecules (including hydrocarbons)[46] and hydrogen-bonded systems,[47] where the polarizing forces are much weaker than in the ylides discussed here. Our observation is that the integrated MP2/6-31G* atomic charges tend to be smaller than those obtained with the HF wave function.

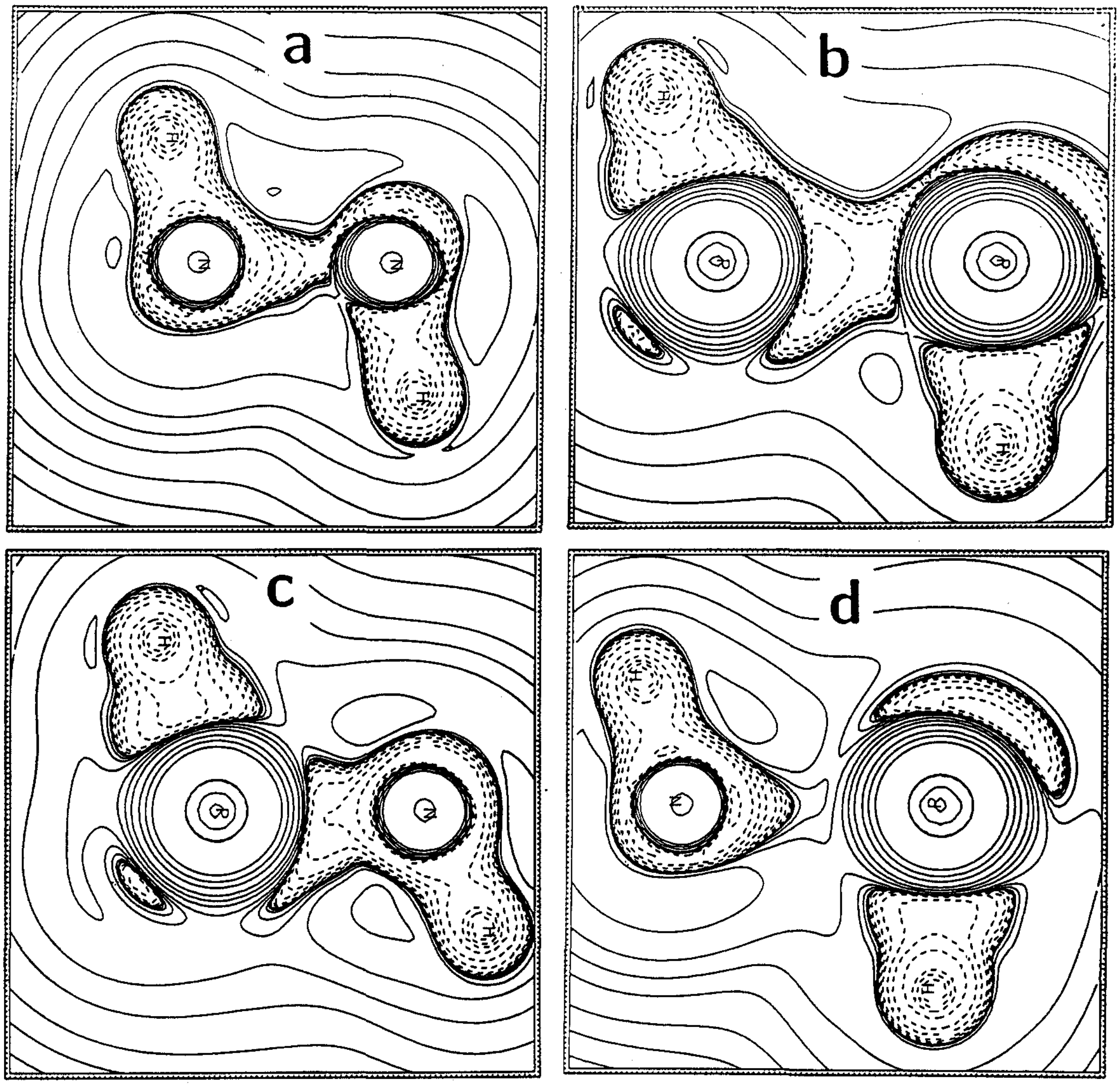

Figure 2. Display of the contour map of the Laplacian concentration of the charge density $\nabla^2\rho$ in the plane of X, Y, and the two transiod hydrogens of the H_3X–YH ylide structures (a) **2**, (b) **5**, (c) **8**, and (d) **10** at the MP2/6-31G* level of approximation. Dashed lines denote negative values and indicate regions where electronic charge is concentrated.

highlighted in the comparison with the H_3NNH (**2**) and H_3PPH (**5**) ylide structures. The group charge of 0.466e in **2** for the two NH_3 and NH fragments (with a positive value for the ammonium group) indicates transfer of charge between the two entities. However, both nitrogens in **2** have nearly the same net atomic charge. In the case of H_3PPH there is less net transfer of charge between its constituents, (i.e., the PH_3 and PH group charges are only 0.069e), leading to smaller polarization as indicated by the Laplacian of r_{b1}. But in **5** there is a strong Coulombic component to the PP bond, as indicated by the large difference in net atomic charge between the heavy atoms.

The tightly bound Staudinger structure H_3PNH (**8**) has by far the strongest polar character. Its PH_3 and NH fragment charges are 1.332e! This value is of a magnitude similar to that reported by Streitweiser et al.[5] for phosphine oxide and emphasizes the very important ionic contribution to the PN bonding in **8**. This is also evident from the large difference in net atomic P and N charges.

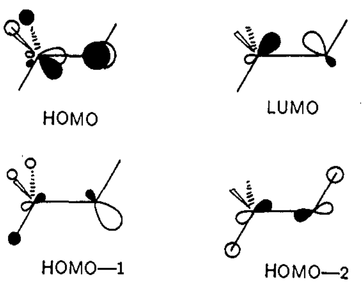

Figure 3. MOs for structure **8**.

As expected, the polarity is reversed for the more loosely bound H_3NPH isomer **10**, which has not only smaller charges of 0.166e on the NH_3 and PH groups, but also a significantly smaller difference in heavy atom charges than in H_3PNH.

Molecular Orbitals. Evaluation of the molecular orbitals of the ylide structures H_3NNH, H_3PPH, H_3PNH, and H_3NPH reveals important contributors to the bonding between the heavy elements. Figure 3 displays the LUMO and the three highest occupied MOs for **8**. The LUMO is a N–P σ^* orbital, the HOMO is essentially a nitrogen p orbital interacting in a π fashion with a strongly (d-)polarized phosphorus p orbital that has antibonding σ^* character with two of its H ligands. The HOMO-1 is a nitrogen (σ) lone pair with a small hyperconjugative interaction with the neighboring PH_3 group. The next occupied MO represents a

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(46) (a) Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61. (b) Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 3379. (c) Bader, R. F. W.; Gillespie, R. J.; MacDougall, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7329. (d) Bader, R. F. W.; Chang, C. *J. Phys. Chem.* **1989**, *93*, 2946. (e) MacDougall, P. J.; Scrobligen, G. J.; Bader, R. F. W. *Inorg. Chem.* **1989**, *28*, 763. (f) Bader, R. F. W.; Larouche, A.; Gatti, C.; Carroll, M. T.; MacDougall, P. J.; Wiberg, K. B. *J. Chem. Phys.* **1987**, *87*, 1142.

(47) (a) Cheeseman, J. R.; Carroll, M. T.; Bader, R. F. W. *Chem. Phys. Lett.* **1988**, *143*, 450. (b) Carroll, M. T.; Chang, W.; Bader, R. F. W. *Mol. Phys.* **1988**, *63*, 387.

Table VI. Atom Properties of XYH_4 (X, Y = N, P) Ylides[a]

struct	atom	charge	scaled energy
2	N_1	−0.730	54.892 71
	N_2	−0.737	54.653 00
	H_3	+0.270	0.511 53
	H_4	+0.440	0.434 99
	H_5	+0.378	0.461 98
	sum		111.416 19
			(111.423 27)
5	P_1	+1.545	340.160 43
	P_2	+0.370	340.511 34
	H_3	−0.439	0.730 84
	H_4	−0.488	0.784 41
	H_5	−0.494	0.786 93
	sum		683.760 88
			(683.935 36)
8	P_1	+2.961	339.596 17
	N_2	−1.729	55.182 01
	H_3	+0.396	0.439 44
	H_4	−0.541	0.826 51
	H_5	−0.544	0.813 56
	sum		397.671 25
			(397.715 52)
10	P_1	+0.335	340.607 92
	N_2	−1.168	54.988 83
	H_3	−0.500	0.767 74
	H_4	+0.448	0.423 13
	H_5	+0.443	0.427 39
	sum		397.642 40
			(397.712 26)

[a] The kinetic energies (hartrees) are corrected for the small virial defect found in the calculations by multiplying them by $-V/(T-1)$. The values in parentheses are the total energies found in the MP2/6-31G* calculations.

σ-conjugative interaction between the transoid P–H and N–H bonds. The orbital sequence is the same for all ylide structures, but subtle differences in particular orbitals do exist. These are discussed briefly.

While the PH_3 p orbital in the π HOMO of the Staudinger complex H_3PNH (**8**) is strongly polarized (equal p and d_{yz} contributions) toward the imino group, this is not the case with the phosphinidene group, i.e., H_3PPH (**5**). However, it is evident that both these structures have a π component to the bonding between the heavy elements, albeit of different strength. In the plane orthogonal to this π interaction both **5** and **8** have (a) similar negative hyperconjugation between the respective phosphino/imino lone pair and the cisoid P–H bond of the PH_3 group (HOMO-1) and (b) comparable σ conjugation between the corresponding P–H/N–H bond and the transoid phosphorane P–H bond (HOMO-2). In the case of the Staudinger complex, this leads to the conclusion of partial triple bonding between the phosphorus and nitrogen atoms. This interpretation is in line with the small ϵ value of 0.18 for r_{b1}. The extent of partial multiple bonding in **5** is less evident since its ϵ value is a large 1.19.[44a]

The higher ionic contribution to the P–H bonds (see Table VI) further supports the stronger bonding in ylide H_3PNH compared to H_3PPH. The difference in their P–H bonds may be interpreted to result from the participation of polarization functions on the phosphorus in H_3PNH that enhances the π overlap with the NH group while reducing the unfavorable overlap in the σ* PH orbital.

If there is indeed partial triple bonding in H_3PNH and possibly in H_3PPH, how does this compare with the H_3NNH (**2**) and H_3NPH (**10**) ylides, which contain a NH_3 group instead of a PH_3 group. On the basis of the relative ineptness of nitrogen to display hypervalency, we expect an absence of multiple bond character in **2** and **10**. This expectation is confirmed. There is no π character in the N–N and N–P bonds. The HOMO of **2** displays a pure nitrogen π lone pair without any overlap with the NH_3 group, and similarly, the HOMO-1 displays a pure nitrogen σ lone pair without any NH_3 hyperconjugation. The same applies to the phosphorus lone pairs of structure **10**. The σ-conjugative interaction in the HOMO-2 is evident in the N_2H_4 ylide but not in **10**. This leads to the expected conclusion that there is no partial multiple bonding in H_3NNH or in H_3NPH.

Bond Orders. Empirical bond orders can be obtained by assigning a bond order of 1 to $H_2X{-}YH_2$ and a value of 2 to $HX{=}YH$.[48] Using bond lengths as a criterion ($n = e^{a(l-b)}$, l is the bond length) leads to MP2/6-31G* bond orders of 0.99 (NN) for H_3NNH **2**, 1.67 (PP) for H_3PPH **5**, 2.54 (NP) for H_3PNH **8**, and 0.23 (NP) for H_3NPH **10**. However, as has been pointed out in the literature and as is evident from the present discussion, determination of bond orders based on the charge density in the bonding region (r_{b1}) may be more reliable. Using the two-point model $n(r_b) = e^{a[\rho(r)-b]}$ gives MP2/6-31G* bond orders of 0.84 for **2**, 1.11 for **5**, 2.58 for **8**, and 0.29 for **10**. There is good agreement between the sets except for the H_3PPH ylide **5**. The large bond order for the Staudinger complex **8** does suggest at least partial multiple bond character between the phosphorus and nitrogen atoms. However, the much smaller value for H_3PPH (whether 1.67 or 1.11 is used!) is surprising in light of the similarities discussed above for the phosphorane-carrying ylides. This underscores that caution is required in the quantitative use of the bond orders for highly polar (or "hypervalent") species, a conclusion that is in line with Reed and Schleyer's analysis.[22]

Conclusions. All XYH_4 ylides of this study, the iminoammonium **2**, the phosphinophosphorane **5**, the iminophosphorane **8**, and the phosphinoammonium **10** (a) are equilibrium structures with significant barriers for conversion to the thermodynamically favored conventional tautomers and (b) have strong binding energies with respect to the XH_3 and YH fragments.

The Staudinger tautomer **8** and the phosphinoammonium ylide **10** are of similar stability and have energy differences with aminophosphinidene **7** of 29.7 and 32.3 kcal/mol, respectively, but their corresponding barriers for hydrogen migration of 50.0 and 26.5 kcal/mol differ significantly. The energy difference between H_3NNH and hydrazine amounts to 49.4 (barrier 19.0) and 27.6 (barrier 35.6) kcal/mol for the corresponding P_2H_4 isomers.

In light of the large body of data on the experimentally known Staudinger compounds, the inescapable conclusion is that derivatives of the other ylides of this study should also be experimentally accessible.

The bonding properties vary significantly between the different ylide structures. The Staudinger species H_3PNH, with its very short N–P bond distance, is of a character similar to the Wittig reagent and phosphine oxide. Its geometrical parameters, binding energies, bond critical point data, integrated atomic charges, molecular orbitals, and bond orders all suggest the presence of partial triple bonding between the phosphorus and nitrogen atoms. However, the overriding effect is the large Coulombic interaction and consequently the very polar component to the N–P bond. The difference in electronegativities between the phosphorus and nitrogen enables maximization of this polarity in the Staudinger complex. A much smaller effect is present in the phosphinophosphorane **5**. It is evident that the chemical bonding in these "hypervalent" ylides H_3PPH and H_3PNH is dominated by ionic and conjugative stabilization with little if any d-orbital participation.

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Registry No. **2**, 72635-52-0; **5**, 132047-44-0; **8**, 25682-80-8; **10**, 58734-27-3.

Supplementary Material Available: MP2/6-31G* vibrational frequencies for XYH_4 (X, Y = N, P) isomers (Table III) (2 pages). Ordering information is given on any current masthead page.

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(48) The MP2(Full)/6-31G* optimized interatomic distances for the double-bonded systems N_2H_2, NPH_2, and P_2H_2 are for N–N 1.266 Å, for N–P 1.609 Å, and for P–P 2.043 Å. The charge densities at their bond critical points $\rho(r_b)$ are 3.028, 1.273, and 0.997 e·Å^{-3}, respectively.